COMPREHENSIVE COORDINATION CHEMISTRY

The Synthesis, Reactions, Properties & Applications of Coordination Compounds

Editor-in-Chief: Sir Geoffrey Wilkinson, FRS

Executive Editors: Robert D. Gillard & Jon A. McCleverty

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The Synthesis, Reactions, Properties & Applications of Coordination Compounds

Volume 5

Late Transition Elements

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Preface

Since the appearance of water on the Earth, aqua complex ions of metals must have existed. The subsequent appearance of life depended on, and may even have resulted from, interaction of metal ions with organic molecules. Attempts to use consciously and to understand the metal-binding properties of what are now recognized as electron-donating molecules or anions (ligands) date from the development of analytical procedures for metals by Berzelius and his contemporaries. Typically, by 1897, Ostwald could point out, in his 'Scientific Foundations of Analytical Chemistry', the high stability of cyanomercurate(II) species and that 'notwithstanding the extremely poisonous character of its constituents, it exerts no appreciable poison effect'. By the late 19th century there were numerous examples of the complexing of metal ions, and the synthesis of the great variety of metal complexes that could be isolated and crystallized was being rapidly developed by chemists such as S. M. Jørgensen in Copenhagen. Attempts to understand the 'residual affinity' of metal ions for other molecules and anions culminated in the theories of Alfred Werner, although it is salutary to remember that his views were by no means universally accepted until the mid-1920s. The progress in studies of metal complex chemistry was rapid, perhaps partly because of the utility and economic importance of metal chemistry, but also because of the intrinsic interest of many of the compounds and the intellectual challenge of the structural problems to be solved.

If we define a coordination compound as the product of association of a Brönsted base with a Lewis acid, then there is an infinite variety of complexing systems. In this treatise we have made an arbitrary distinction between coordination compounds and organometallic compounds that have metal–carbon bonds. This division roughly corresponds to the distinction — which most but not all chemists would acknowledge as a real one — between the cobalt(III) ions $[Co(NH_3)_6]^{3+}$ and $[Co(\eta^5\text{-}C_5H_5)_2]^+$. Any species where the number of metal–carbon bonds is at least half the coordination number of the metal is deemed to be 'organometallic' and is outside the scope of our coverage; such compounds have been treated in detail in the companion work, 'Comprehensive Organometallic Chemistry'. It is a measure of the arbitrariness and overlap between the two areas that several chapters in the present work are by authors who also contributed to the organometallic volumes.

We have attempted to give a contemporary overview of the whole field which we hope will provide not only a convenient source of information but also ideas for further advances on the solid research base that has come from so much dedicated effort in laboratories all over the world.

The first volume describes general aspects of the field from history, through nomenclature, to a discussion of the current position of mechanistic and related studies. The binding of ligands according to donor atoms is then considered (Volume 2) and the coordination chemistry of the elements is treated (Volumes 3, 4 and 5) in the common order based on the Periodic Table. The sequence of treatment of complexes of particular ligands for each metal follows the order given in the discussion of parent ligands. Volume 6 considers the applications and importance of coordination chemistry in several areas (from industrial catalysis to photography, from geochemistry to medicine). Volume 7 contains cumulative indexes which will render the mass of information in these volumes even more accessible to users.

The chapters have been written by industrial and academic research workers from many countries, all actively engaged in the relevant areas, and we are exceedingly grateful for the arduous efforts that have made this treatise possible. They have our most sincere thanks and appreciation.

We wish to pay tribute to the memories of Professor Martin Nelson and Dr Tony Stephenson who died after completion of their manuscripts, and we wish to convey our deepest sympathies to their families. We are grateful to their collaborators for finalizing their contributions for publication.

Because of ill health and other factors beyond the editors' control, the manuscripts for the chapters on Phosphorus Ligands and Technetium were not available in time for publication.

However, it is anticipated that the material for these chapters will appear in the journal *Polyhedron* in due course as Polyhedron Reports.

We should also like to acknowledge the way in which the staff at the publisher, particularly Dr Colin Drayton and his dedicated editorial team, have supported the editors and authors in our endeavour to produce a work which correctly portrays the relevance and achievements of modern coordination chemistry.

We hope that users of these volumes will find them as full of novel information and as great a stimulus to new work as we believe them to be.

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Nickel

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50.1 INTRODUCTION

Nickel metal was isolated in 1751 by A. F. Cronsted from some ores in the cobalt mines of Helsingland, Sweden. He proposed the name 'nickel' for the newly discovered metal from the mineral 'kupfernickel', described by U. Hiarne in 1694, which he demonstrated to contain the new element instead of copper as previously believed.[1] Nickel is widely distributed in the Earth's crust as sulfide, arsenide and silicate, with an estimated abundance of 0.016%.[2] Selected physical properties of elemental nickel are reported in Table 1. The metal is hard and brittle, possesses a face-centred cubic lattice and is ferromagnetic. Naturally occurring nickel exists as a mixture of five stable isotopes (Table 2). Nickel compounds have been found to occur with the metal in oxidation states ranging from −1 to +4.[5] However, comparatively very few compounds correspond to the lowest (−1) and to the higher (+3 and +4) oxidation states.

Table 1 Selected Physical Properties of Nickel[3]

Atomic number	28
Electronic configuration	$(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^8(4s)^2$
Atomic mass	58.71
Ionization energy ($kJ\ mol^{-1}$)	
first	743
second	1758
third	3400
Standard electrode potential (V)	
Ni^{2+}/Ni^0	−0.25
M.p. (°C)	1453
B.p. (°C)	2732

Table 2 Natural Isotopes of Nickel[4]

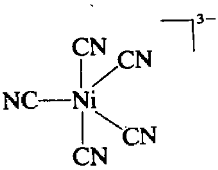
Isotope	*Abundance (%)*	*Atomic mass*
^{58}Ni	67.88	57.9353
^{60}Ni	26.23	59.9332
^{61}Ni	1.19	60.9310
^{62}Ni	3.66	61.9283
^{64}Ni	1.08	63.9280

Most of the nickel compounds in the solid state and almost all in aqueous solution contain the metal in the oxidation state +2, which, by consequence, can be considered the ordinary oxidation state for nickel in its compounds. The electronic structure and stereochemistry of nickel(II) were reviewed in 1968.[6] The most stable electronic configuration of the free Ni^{II} ion is $[Ar]3d^8$ which is also the ground state configuration in its complexes. The overwhelming majority of nickel(II) complexes have coordination numbers of four, five and six. Complexes with coordination numbers of three, seven and eight are still quite rare.

In almost all its six-coordinate complexes nickel(II) has a pseudooctahedral stereochemistry with a spin triplet as ground state (high-spin configuration). A typical example is the hexaaquanickel ion $[Ni(H_2O)_6]^{2+}$ which is characteristically bright green. The replacement of water molecules by ligands such as NH_3 or en, which have greater donor strength, shifts the absorption spectra to higher frequencies and the colour of the corresponding six-coordinate complexes $[Ni(NH_3)_6]^{2+}$ and $[Ni(en)_3]^{2+}$ becomes blue. The magnetic moments of octahedral complexes of nickel(II) usually lie between 2.9 and 3.3 BM and the temperature dependence of the magnetic susceptibilities follows a Curie–Weiss law.

Five-coordination is now quite common in nickel(II) complexes and many polydentate ligands such as polyamines, salicylaldimines, polyarsines and polyphosphines have been designed with the purpose of favouring this stereochemistry.[7,8] However, five-coordinate complexes with monodentate ligands ($[Ni(CN)_5]^{3-}$ and $[Ni(OAsMe)_5]^{2+}$) are also known.

The five-coordinate nickel(II) complexes have structures which are generally near to one of the two limiting geometries, namely the square pyramid (C_{4v} symmetry) and the trigonal bipyramid (D_{3h} symmetry). The electronic ground state of nickel(II) in five-coordinate complexes can be either a spin singlet (low-spin configuration, diamagnetic) or a spin triplet (high-spin configuration, with magnetic moments in the range 3.2–3.4 BM). For example, the square pyramidal complexes $[Ni(CN)_5]^{3-}$ (**1**) and $[Ni(OAsMe_3)_5]^{2+}$ (**2**) are low-spin and high-spin, respectively, and $[NiBr(Me_6tren)]^+$ (**3**) and $[NiBr(np_3)]^+$ (**4**) are trigonal bipyramidal high-spin and low-spin complexes, respectively. In general, low-spin complexes are formed by donor atoms such as C, P, As and S, which have low electronegativity, whereas high-spin complexes are formed by highly electronegative donors such as O and N.[9]



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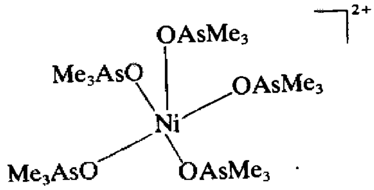

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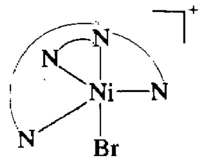

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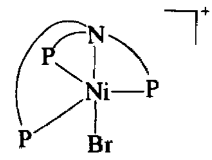

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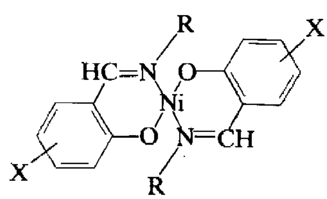
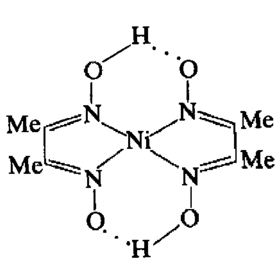
The majority of four-coordinate nickel(II) complexes are square planar and invariably diamagnetic, whereas pseudotetrahedral complexes, which are always paramagnetic, are relatively rare. Typical examples of pseudotetrahedral species are the tetrahalonickelates(II), $[NiX_4]^{2-}$. It is, in general, found that ligands with weaker donor strength favour a pseudotetrahedral structure, whereas ligands with a higher donor strength tend to produce square planar structures. The complexes $NiX_2(PR_3)_2$ are either square planar or pseudotetrahedral, depending on the coordinated halide. It must also be borne in mind that ligands which contain bulky substituents on the donor atoms may prevent a planar structure due to steric hindrance, and a distorted tetrahedral structure may become preferred.[10] As a matter of fact, in the bis(*N*-alkylsalicylaldiminato)nickel(II) complexes (**5**), the tetrahedral species are favoured by the increasing steric hindrance of the substituents in the donor atoms. Most of the aforementioned complexes give rise in solution to temperature-dependent equilibria between pseudotetrahedral and square planar species. Pseudotetrahedral nickel(II) complexes have spectral transitions in the visible region with a much greater intensity than octahedral complexes, owing to the lack of an inversion centre ($\varepsilon_M \approx 10^2$ compared to $\varepsilon_M < 10$).



(5)

Nickel(II) in tetrahedral symmetry has an orbitally degenerate ground state and the magnetic moments of tetrahedral complexes are expected to be substantially higher than those of six-coordinate complexes because of the larger orbital contribution. The magnetic moments are usually found to be in the range 3.3–4.0 BM at room temperature and tend to zero at very low temperatures.

Strong Ni–ligand interactions stabilize planar configurations in four-coordinate nickel(II) complexes, as shown by the shorter bond distances found in planar complexes. Planar complexes of nickel(II) are often red or yellow owing to an absorption ($\varepsilon_M < 100$) around 500 nm. Square planar complexes formed by monodentate ligands are not rare, $[Ni(CN)_4]^{2-}$ being a particularly well-known example. The majority of them are formed by either chelate ligands or tetradentate macrocyclic ligands. The red bis(dimethylglyoximato)nickel(II) (**6**) and bis(dipivaloylmethanato)nickel(II) (**7**) are examples of neutral bis-chelate planar complexes.



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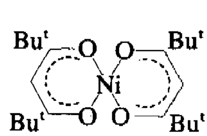

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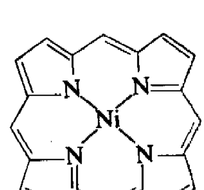


(8)

Porphyrin (**8**) and phthalocyanine complexes stabilize a square planar structure, probably as a result of extensive electron delocalization. Square planar complexes often give paramagnetic bis adducts with a *trans* octahedral geometry.

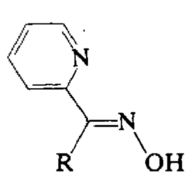
Amongst the compounds of nickel in low oxidation states (−1, 0, +1), the nickel(0) complexes are by far the most common and the most intensively studied[11] while nickel(−I) has been claimed to be formed only in a few organometallic complexes.[5,12] Besides the organic compounds of nickel(0) which contain only Ni—C, many nickel(0) complexes are formed by ligands containing P or As as donor atoms. Although the electronic states $^3D\,(3d^94s^1)$, $^3F\,(3d^84s^2)$ and $^1S\,(3d^{10})$ are energetically very close to each other in the free Ni atom, the reported nickel(0) complexes are all diamagnetic. This means that the ligands stabilize the $^1S\,(3d^{10})$ configuration relative to the other ones.

The nickel(0) complexes are, in general, unstable towards atmospheric oxygen and moisture. The $Ni(PR_3)_4$ complexes (R = halogens, alkyl, phenyl) are the first examples of nickel(0) complexes containing four phosphorus-donor atoms, and are all considered to have a pseudotetrahedral structure. The complex $Ni(np_3)$ is one of the very few examples of trigonal pyramidal geometry. Both monodentate and polydentate tertiary phosphines have been found to stabilize the coordination to nickel(0) of molecules such as CO_2, SO_2, N_2 and NO which otherwise give very unstable linkages with the metal. Some important examples are $[Ni(CO_2)(PCy_3)_2]$, $[\{Ni(PCy_3)_2\}_2N_2]$, $[Ni(SO_2)(triphos)]$ and $[Ni(NO)(np_3)]^+$.

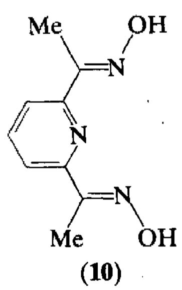
Nickel(I) complexes are comparatively much less numerous than the nickel(0) complexes, and in general are formed by the same types of ligand as those encountered in nickel(0) chemistry. Mononuclear nickel(I) complexes are paramagnetic (d^9 configuration with μ_{eff} in the range 1.7–2.4 BM) and, in general, are either four-coordinate pseudotetrahedral or five-coordinate trigonal bipyramidal as exemplified by $[NiBr(PPh_3)_3]$ and $[NiI(np_3)]$.

Ni^{III} and Ni^{IV} complexes are now well known, even though they are not very numerous.[12] The large majority of these complexes are formed by ligands with highly electronegative donor atoms such as F, O and N, but the earliest reports on complexes of nickel in higher oxidation states concern the five-coordinate $[NiBr_3(PEt_3)_2]$ and the six-coordinate $[NiCl_2(diars)_2]Cl$. All the reported nickel(III) complexes have a spin doublet ground state originating from the $[Ar]3d^7$ free ion configuration and are paramagnetic. Nickel(IV) complexes have a singlet ground state originating from $[Ar]3d^6$ and are diamagnetic.

Oxime-type ligands (**9**) and (**10**) have been found to stabilize authentic Ni^{III} and Ni^{IV} complexes, respectively, when the nickel(II) complexes are oxidized by $K_2S_2O_8$ in alkaline solution.



(**9**)



(**10**)

In recent years tetraaza macrocycles have been found to stabilize both Ni^{I} and Ni^{III} oxidation states in nickel complexes.

50.2 NICKEL(0)

50.2.1 Introduction

In this section we will review the most significant complexes of nickel(0). Many of these complexes are on the borderline between classical coordination chemistry and organometallic chemistry; they will be reviewed in general when the number of Ni—C bonds is less than or equal to the number of bonds from Ni to non-carbon atoms. However, complexes with classical ligands such as CN^- will be included. The chapter is divided into sections according to different classes of ligands. Within each section the synthesis of the complexes and their reactivity will be described in general terms first, followed by consideration of the structure and bonding and by comments on relevant physical properties.

50.2.2 The Stabilization of Low Oxidation States

A nickel complex, namely $Ni(CO)_4$, was the first reported (1890) coordination compound of a metal in a low oxidation state.[13] Today the number of the nickel(0) complexes is enormous and is still increasing.

It is generally accepted[11,14,15] that an important factor for the stabilization of low oxidation states in metal complexes is the transfer of electron density from the metal into suitable empty π^* orbitals of the donor atoms (the so-called π back-donation). This π bonding, arising from the transfer of ligand electrons into excited empty metal orbitals, is superimposed on the σ bonding. This π back-donation usually gives a significant contribution to the total energy of the complexes. The importance of this contribution increases when the energy difference between the filled metal *d* orbitals and the empty π^* orbitals on the ligands decreases, and it is therefore also very sensitive to the nature of the other coligand bound to the metal.

Low oxidation states are generally stabilized by ligands which have both σ donor (lone pairs) and π acceptor (either empty *d* orbitals or empty antibonding π^* orbitals) capability. Examples of common ligands with these characteristics are carbon monoxide, cyanide ion, alkyl and aryl isocyanides, tertiary phosphines and arsines, and alkyl or aryl phosphites.

Unsaturated organic molecules such as alkenes, alkynes, dienes, polyenes and arenes can also stabilize low oxidation states in metal complexes, being both σ donors (filled bonding π orbitals) and π acceptors (empty antibonding π^* orbitals). In these so-called π complexes, only π orbitals are involved in the metal-to-ligand bonds. This latter type of complex is beyond the scope of this chapter and only a few examples will be given.

Owing to the extensive sharing of valence electrons over the metal and donor atoms in complexes of metals in low oxidation states, the zero oxidation state has little, if any, physical significance, and may be used for classifying purposes only. Outstanding examples are the complexes with nitric oxide which may be considered as NO^+, NO^- or NO, and consequently different oxidation states may be assigned to the same complex.

Nickel complexes with η^3-bonded cyclotriphosphorus and cyclopropenyl fragments are discussed together in a separate Section (50.3). As a matter of fact the bonding mode of these ligands is the same in all of the complexes, irrespective of the different oxidation states which can be assigned to the nickel atom.

50.2.3 Cyano and Isocyano Complexes

Only a limited number of cyano and isocyano complexes and mixed carbonyl, nitrosyl and phosphine cyano complexes of nickel(0) have been described so far.[16]

$K_4Ni(CN)_4$ is a yellow solid which is extremely sensitive to oxygen and moisture. It can be prepared by reducing $K_2Ni(CN)_4$ in liquid NH_3 with an excess of potassium[17] and decomposes in water with H_2 evolution. CN^- ions can be easily replaced by ligands with greater π acceptor properties such as CO, NO and phosphines. Mixed carbonyl and nitrosyl cyano complexes have been prepared by direct reactions (equations 1 and 2).[18,19]

$$K_4Ni(CN)_4 + CO \xrightarrow{\text{liq. } NH_3} K_2[Ni(CN)_2(CO)_2] \quad (1)$$

$$K_4Ni_2(CN)_6 + NO \xrightarrow{\text{liq. } NH_3} K_2[Ni(CN)_3(NO)] \quad (2)$$

$$[Ni(CN)_4]^{2-} + NH_2OH + OH^- + \tfrac{1}{2}O_2 \longrightarrow [Ni(CN)_3NO]^{2-} + CN^- + 2H_2O \quad (3)$$

$$K_4Ni(CN)_4 \xrightarrow{\text{liq. } NH_3,\ R_3P} [Ni(R_3P)_4] + KCN \quad (4)$$

$$K_4Ni(CN)_4 \xrightarrow{\text{liq. } NH_3,\ \text{diphos}} [Ni(\text{diphos})_2] + KCN \quad \text{diphos} = Ph_2PCH_2CH_2PPh_2 \quad (5)$$

$$K_4Ni(CN)_4 \xrightarrow{\text{liq. } NH_3,\ \text{bipy}} [Ni(\text{bipy})_2] + KCN \quad (6)$$

$K_2[Ni(CN)_3NO]$ has also been reported, from the reaction of nickel(II) and hydroxylamine in alkaline solution (equation 3).[20,21]

Displacement reactions have been carried out in liquid ammonia (−33 °C) with R_3P, R_3As, R_3Sb, ditertiary phosphines, bipy and phen[22] leading to complete substitution of CN^- groups (equations 4–6).

Tetrakis(alkyl isocyanide) complexes of nickel(0), $Ni(CNR)_4$, and the mixed isocyanide complexes with phosphines and unsaturated molecules are strictly analogous to the corresponding carbonyl complexes.[23,24] They are generally more stable than $[Ni(CN)_4]^{4-}$. Mixed isocyanide complexes have been prepared by the reaction of $Ni(cod)_2$ and $CNBu^t$ followed by reaction with the appropriate phosphine or unsaturated molecules (alkenes, arylnitroso compounds, azo compounds, *etc.*) as outlined in equations (7) and (8).[25]

$$Ni(cod)_2 + 2CNBu^t \longrightarrow Ni(CNBu^t)_2{}^* + 2cod \qquad (7)$$

$$Ni(CNBu^t)_2 + 2Ph_3P \longrightarrow [Ni(CNBu^t)_2(Ph_3P)_2] \qquad (8)$$

By bubbling O_2 into a solution of $Ni(CNR)_4$ or $Ni(CNR)_2$ at temperatures below −20 °C, green compounds having the formula $[Ni(CNR)_2O_2]$ are formed (R = Cy, Bu^t).[26] It is reported that these compounds are very air-sensitive and thermally unstable: they may explode spontaneously when dried. The reactivity of the $[Ni(CNR)_2O_2]$ complexes has however been studied (equations 9–14).[27] In general, the oxygen atoms are transferred from the isocyanide complex to the different reactants with the formation of different oxo compounds such as oxoanions, peroxides and phosphine oxides. Reactions (9)–(14) (referred to as atom transfer reactions) all occur at low temperatures.

$$[Ni(CNBu^t)_2O_2] + Ph_3P\ (excess) \longrightarrow [Ni(CNBu^t)_2(Ph_3P)_2] + 2Ph_3PO \qquad (9)$$

$$[Ni(CNBu^t)_2O_2] \xrightarrow{N_2O_4,\ -30\,^{\circ}C} [Ni(NO_3)_2(CNBu^t)_2] \qquad (10)$$

$$[Ni(CNBu^t)_2O_2] \xrightarrow{NO,\ -20\,^{\circ}C} [Ni(CNBu^t)_3NO]NO_3 \qquad (11)$$

$$[Ni(CNBu^t)_2O_2] \xrightarrow{CO_2,\ below\ 0\,^{\circ}C} [Ni(CO_3)(CNBu^t)_2] \qquad (12)$$

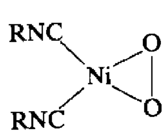
$$[Ni(CNBu^t)_2O_2] \xrightarrow{SO_2,\ -70\,^{\circ}C} [Ni(SO_4)(CNBu^t)_2] \qquad (13)$$

$$[Ni(CNBu^t)_2O_2] + 2PhCOCl \longrightarrow [NiCl_2(CNBu^t)_2] + PhC(=O)OC(=O)Ph \qquad (14)$$

The reaction with $(CF_3)_2CO$ leads to an explosive compound which undergoes transformation to the more stable compound $[(RNC)_2\overline{NiOC(CF_3)_2OC}(CF_3)_2$.[28]

The *t*-butyl isocyanide complexes of nickel(0) are used as starting materials for the synthesis of a number of complexes with unsaturated groups π bonded to the nickel atom in reactions similar to those given by dioxygen or diazo complexes (Sections 50.2.7.2 and 50.2.6.3).

The only X-ray crystal structure available is that of $[Ni(CNBu^t)_2O_2]$ (**11**).[29] In this complex nickel(0) has square planar coordination with oxygen bonded in the side-on mode.



(11)

Four-coordinate $[Ni(CN)_4]^{4-}$ or $Ni(CNR)_4$ molecules are usually assumed to have a pseudotetrahedral structure like $Ni(CO)_4$.

The coordinate nature of the CN^- or CNR groups is generally inferred by the low frequency shift of the CN band in the IR spectra as a consequence of π back-bonding interactions with the nickel atom. The $\nu(CN)$ band in $K_4Ni(CN)_4$ is at 1985 cm^{-1}, and at 2000 cm^{-1} in $[Ni(CNBu^t)_4]$. This frequency shifts to higher values, in the range 2025–2125 cm^{-1}, in phosphine-substituted complexes of the type $[Ni(CNBu^t)_2(R_3P)_2]$ (R_3P = Et_3P, Ph_3P, $PhMe_2P$, $P(OMe)_3$).[30]

* This is not a compound but a mixture of NiL_4 and Ni_4L_7 which has an approximate composition NiL_2.

50.2.4 Complexes with Phosphines, Arsines and Stibines

The most common nickel(0) complexes are those containing phosphorus, arsenic and antimony as donor atoms. Besides the Malatesta and Cenini book,[11] which specifically deals with metal(0) complexes, nickel(0) complexes have been summarized in books and review articles which report complexes with phosphine, arsine and stibine ligands.[31–37] Actually the nickel(0) complexes with these ligands amount to hundreds and the number of new complexes which are synthesized is increasing very rapidly, making nickel(0) phosphine chemistry a very extensive topic.

50.2.4.1 Synthesis

Several synthetic procedures have been developed for the preparation of complexes with phosphines, arsines and stibines, and the most convenient or historically important ones are summarized in Table 3. They can be grouped in three main types of reaction: the direct reactions of nickel with ligands, ligand replacement reactions and reduction reactions of nickel(II) complexes.

Direct reaction of elemental nickel with the ligands. This is the method which Quin used in 1957 to synthesize the first nickel(0) complex known after $Ni(CO)_4$, namely $[Ni(PCl_2Me)_4]$.[38] In this method pyrophoric nickel (obtained by thermal decomposition of $Ni(CO)_4$ or nickel(II) oxalate) is allowed to react with the appropriate phosphine at temperatures in the range 50–150 °C to yield the expected complex. A list of phosphines which react in this way with nickel is reported in Table 3 together with the stoichiometric formula of the reaction product. More recently NiL_4 complexes have been prepared by the reaction of nickel vapour with the fluorophosphines PF_3,[78] PHF_2,[45] PF_2NMe_2[46,47] and $(PF_2)_2NMe$.[46] The reaction of a 4:1 mixture of Me_2NPF_2 and $MeN(PF_2)_2$ with nickel vapour gives a mixture of $[Ni\{PF_2NMe_2\}_3\{(PF_2)_2NMe\}]$ and $[Ni_2\{PF_2NMe_2\}_2\{(PF_2)_2NMe\}_3]$.[30] The fluorine atoms of the $[Ni(PF_3)_4]$ complex have been found to react with alkyl(trimethylsilyl)amines and amides according to reactions (15)–(17).[79–81]

$$[Ni(PF_3)_4] \xrightarrow[\text{ether}]{NaN(SiMe_3)_2} [Ni(PF_3)_{4-n}PF_2N(SiMe_3)_2] \quad n = 1, 2 \qquad (15)$$

$$[Ni(PF_3)_4] \xrightarrow[\text{ether, r.t.}]{NHR(SiMe_3)} [Ni(PF_3)_{4-n}(PF_2NHR)_n] \quad n = 1, 2, 3;\ R = Me, Bu^n \qquad (16)$$

$$[Ni(PF_3)_4] \xrightarrow[\text{ether, 0 °C}]{LiNR(SiMe_3)} [Ni(PF_3)_{4-n}\{PF_2NR(SiMe_3)\}_n] \quad n = 1, 3, 4;\ R = Me, Et, Bu^n \qquad (17)$$

Ligand replacement reactions. The complete substitution of CO in $Ni(CO)_4$ by tertiary phosphines requires, in general, drastic reaction conditions (prolonged heating at $T > 100$ °C) and, possibly, high pressure of PR_3,[41,48] otherwise a mixture of $[Ni(CO)_x(PR_3)_y]$ ($x = 3, 2, 1; y = 4 - x$) compounds is formed. Similar reactions occur with arsines. Aromatic diphosphines $C_6H_4(PR_3)_2$[40] (R = Ph, Et) and phosphites[57–61] can more easily displace CO from the very stable $Ni(CO)_4$. $Ni(cod)_2$, $Ni(\pi\text{-}C_5H_5)_2$ and $K_4[Ni(CN)_4]$ are the most suitable starting products for ligand replacement reactions with phosphines and arsines. As an example, the reaction of $Ni(cod)_2$ with PH_3 occurs at −40 °C yielding the very thermally unstable (decomposes at −30 °C) pyrophoric liquid $Ni(PH_3)_4$.[49]

The tetrakis-phosphino and -arsino complexes reported in Table 3 have very different thermal and air stabilities. In general, complexes with alkyl-phosphines and -arsines are air-unstable or pyrophoric. The tetrakis(arylphosphino) complexes (but not the bis or tris derivatives) are moderately air- and heat-stable, and the tetrakis phosphites may be handled in the atmosphere. $Ni(PF_3)_4$ is a stable liquid compound, whereas $Ni(PCl_3)_4$ and $Ni(PBr_3)_4$ are solids and stable only in dry air.

Reduction reactions of nickel(II) compounds. The reduction of nickel(II) compounds to yield nickel(0) phosphine complexes has been carried out using a variety of reducing agents such as sodium amalgam, sodium sand, sodium borohydride, sodium naphthalenide and aluminum trialkyls. In some cases the phosphine ligand itself was found to act as the reducing agent.

The reduction of $NiCl_2(PPh_3)_2$ with sodium amalgam in C_6H_6 yields $Ni(PPh_3)_2$,[64] whereas

Table 3 Summary of Nickel Complexes with Phosphines, Arsines and Stibines, and their Methods of Synthesis

Complex	*Synthesis*	*Conditions*	*Ref.*
$Ni(PCl_2Me)_4$	Ni + L	81–104 °C	38
$Ni(EBr_2Me)_4$ E = P, As	Ni + L	Ether, −70 °C	39
Ni(P—P)$_2$	Ni + L	160 °C	40
P—P = $C_6H_4(PEt_2)_2$, $C_6H_4(PPh_2)_2$, $Ph_2P(CH_2)_2PPh_2$	Ni + 4L	70 atm, 100 °C	41
$Ni(PF_3)_4$	$Ni(PCl_3)_4 + SbF_3$		42
	$Ni(CO)_4 + 4PF_3$		43
$Ni\{PF(CF_3)_2\}_4$	Ni + L	60 °C	43, 44
$Ni(PHF_2)_4$	Metal vapour technique	−196 °C	45
$Ni(PF_2NMe_2)_4$	Metal vapour technique		46, 47
$Ni(PCl_3)_4$	$Ni(CO)_4$ + L	Refluxing PCl_3	48
$Ni(PBr_3)_4$	$Ni(PCl_3)_3$ + L		42
$Ni(PH_3)_4$	$Ni(cod)_2$ + L	Ether, −40 °C	49
$Ni(PR_3)_4$ R = *n*-alkyl	$Ni(cod)_2$ + L	*n*-Pentane, 0 °C	25, 50–53
$Ni(PMePh_2)_4$	$Ni(cod)_2$ + L	Hexane, r.t.	54
$Ni(AsMe_2Ph)_4$	$Ni(cod)_2$ + L	Ether, 0 °C	55
$Ni(PPh_3)_4$	$K_4Ni(CN)_4$ + L	Liq. NH_3, −33 °C	22
$Ni(AsPh_3)_4$	$K_4Ni(CN)_4$ + L	Liq. NH_3, −33 °C	22
$Ni(SbPh_3)_4$	$K_4Ni(CN)_4$ + L	Liq. NH_3, −33 °C	22
$Ni(SbR_3)_4$ R = Ph, tolyl, $MeOC_6H_4$	$Ni(cod)_2$ + L	Benzene	56
$Ni\{C_2H_4(EPh_2)_2\}_2$ E = P, As	$K_4Ni(CN)_4$ + L—L	Liq. NH_3, −33 °C	22
$Ni\{C_6H_4(AsPh_2)_2\}_2$	$Ni(cod)_2$ + L	Ether, 0 °C	55
$Ni\{C_2H_4(PPh_2)_2\}_2$	$Ni(CO)_4$ + L	Refluxing toluene	40
	$Ni(\pi\text{-}C_5H_5)_2$ + L		57
$Ni\{P(OR)_3\}_4$	$Ni(cod)_2$ + L	Benzene, pentane, 0 °C	50, 57–61
R = alkyl, aryl	$Ni(CO)_4$ + L	200 °C	
$Ni(PHPh_2)_4$	$NiBr_2 + PHPh_2$	EtOH, conc. HCl, r.t.	62, 63
$Ni(PPh_3)_3$	$NiCl_2$ + L + Zn	Refluxing acetonitrile	64
$Ni(PPh_3)_2$	NiL_2Cl_2 + NaHg	Benzene	65
$Ni\{C_2H_4(PPh_2)_2\}_2$	Ni(L—L)$_2(NO_3)_2$ + $NaBH_4$	Warm acetone or ethanol	66
$Ni\{C_2H_4(PMe_2)_2\}_2$	Ni(L—L)Br_2 + L—L + sodium naphthalenide	Tetrahydrofuran, r.t.	66
$Ni\{C_6H_4(PEt_2)_2\}_2$	Ni(L—L)$_2(NO_3)_2$ + $NaBH_4$	Warm acetone or ethanol	66
$Ni\{C_6H_4(AsMe_2)_2\}_2$	Ni(L—L)$_2Cl_2$ + $NaBH_4$	Warm acetone or ethanol	66
$Ni\{MeC(CH_2PPh_2)_3\}_2$	$Ni(NO_3)_2$ + triphos + $NaBH_4$	Warm acetone or ethanol	66
$Ni\{C_nH_{2n}(PPh_2)_2\}_2$ *n* = 3, 4	$Ni(acac)_2$ + L—L + Al(alkyl)$_3$	Benzene, ether, r.t.	67
$Ni\{P(OR)_3\}_4$ R = Me, Et	NiX_2 + L + R_3N	Cold acetonitrile, ethane	68, 69
$Ni\{P(OPh)_3\}_4$	$Ni(acac)_2$ + L + Et_3Al	Benzene, −25 °C	70
	$Ni(acac)_2$ + L + $NaBH_4$	Refluxing petrol	71
$Ni\{P(OR)_3\}_4$ R = C_6H_4Me	$Ni(NO_3)_2$ + L + $NaBH_4$	Refluxing petrol	71
$Ni\{P(OTol)_3\}_3$	$Ni(NO_3)_2$ + L + $NaBH_4$	Acetonitrile	72
$Ni\{P(OCH_2)_3CMe\}_4$	$NiL_6^{2+} + NaHCO_3$	Boiling water	73, 74
$Ni(PR_3)_4$ R = Et, Bu^n	NiL_2X_2 + Na	Toluene, heptane, r.t.	75, 76
$Ni(PCy_3)_3$	NiL_2X_2 + Na	Toluene, heptane, r.t.	75
$Ni(PR_3)_4$ R = OEt, Ph, Et	$NiCl_2 + PR_3$ + PhI	Refluxing petrol	77
$Ni(PR_3)_4$ R = Me, OEt, OMe, aryl	$NiCl_2 + PR_3$	Acetonitrile	73

reduction of $NiCl_2$ by zinc dust in refluxing MeCN in the presence of triphenylphosphine results in the $Ni(PPh_3)_3$ complex.[65] Both of these complexes are extremely air-unstable.

Other examples of three-coordinate nickel(0) complexes with phosphine ligands have been reported.[37] The reduction of $[NiX_2(PCy_3)_2]$ in toluene at room temperature with sodium sand gives either $Ni(PCy_3)_3$ or $[NiX(PCy_3)_2]$ depending on the reaction conditions.[75] With less bulky triphosphines PEt_3, PEt_2Ph and $P(Bu^n)_3$ the tetrakis complexes NiL_4 are obtained;[75,52,53] these dissociate to the tris adducts when stored at room temperature (equation 18).[75,51] This dissociation may explain the ready addition of N_2 to the $Ni(PR_3)_4$ complexes.

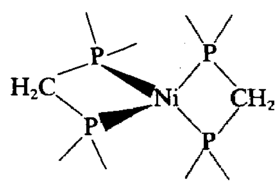
$$[Ni(PR_3)_4] \xrightarrow{r.t.} [Ni(PR_3)_3] + PR_3 \quad (18)$$
white violet

The borohydride reduction of nickel(II) compounds in protic solvents may result either in the formation of nickel(0) complexes[66,71] or in the formation of hydrido complexes of nickel(II). Two easily interconvertible isomers, $Ni(triphos)_2$, have been obtained in the reduction of $Ni(NO_3)_2$ in the presence of the ligand triphos, but their structures are not known with certainty.[66]

The ligand by itself acted as the reducing agent of Ni^{II} in several reactions, usually performed in ethanolic solution. In the case of trialkyl phosphito complexes, trialkylamine has been added to the reactants to neutralize the acidity which arises from the reduction reaction.[68,69]

50.2.4.2 Structural properties

The tetrahedral coordination of $Ni(PF_3)_4$ has been confirmed by two independent electron diffraction studies of the compound in the gaseous state,[82,83] giving the following molecular parameters: Ni—P = 210–211 pm, ∠PNiP = 109° (not refined). Tetrahedral coordination around nickel(0) has also been found in tetrakis(2-thienyldifluorophosphine)nickel, $Ni\{PF_2(C_4H_3S)\}_4$, in the solid state. Relevant molecular distances and angles are Ni—P 209 pm, ∠PNiP 106–111°.[84] The Ni—P bond distances found in these two complexes are noticeably shorter than those found in other pseudotetrahedral complexes of nickel(0) with phosphines which do not contain fluoro atoms. In bis{bis(dicyclohexylphosphino)-methane}nickel(0) (**12**) the Ni—P distances are in the range 219–222 pm.[85]



(**12**)

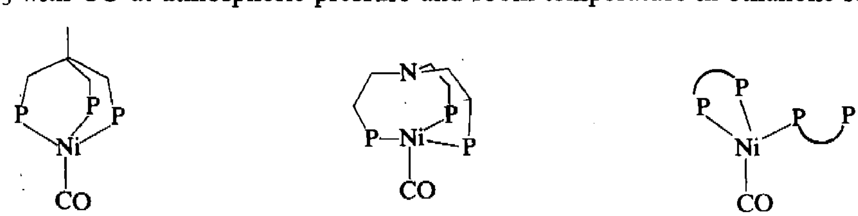
50.2.5 Carbonyl and Nitrosyl Complexes

50.2.5.1 Carbonyl complexes

A fairly large number of mixed carbonyl phosphine and arsine complexes have been reported so far. They are generally prepared by displacement of CO from $Ni(CO)_4$. Owing to the high stability of $Ni(CO)_4$, when it is reacted with phosphines and arsines at room temperature and atmospheric pressure, only a partial displacement of CO usually occurs. Most of the mixed phosphine (or arsine) carbonyl compounds have the general formula $[Ni(CO)_n(PR_3)_{4-n}]$ ($n = 3, 2$) and $[Ni(CO)_2(L—L)]$ (L—L is a diphosphine or diarsine). These complexes are colourless or yellow-orange solids or liquids. Many of them are thermally stable but decompose in air. The most relevant mixed carbonyl complexes with common phosphines are reported in Table 4.

Some of the mixed carbonyl phosphine complexes have been found to be efficient catalysts of oligomerization of alkanes.

The complex [Ni(CO)(triphos)] (**13**) has been obtained by the reaction of $[Ni(H_2O)_6]^{2+}$ and the ligand p_3 with CO at atmospheric pressure and room temperature in ethanolic solution.[98]



(**13**) (**14**) (**15**)

The reaction of $Ni(np_3)$ with CO in THF–ethanol solution yields the monocarbonyl

Table 4 Mixed Carbonyl Phosphine and Arsine Complexes

Complex		*M.p.* (°C)	*Ref.*
$[Ni(CO)_2(PR_3)_2]$	R = Me, Et, Bu^n	liq.	57, 59, 86–88
	R = Ph	206–209	
$[Ni(CO)_2(AsEt_3)_2]$		liq.	89
$[Ni(CO)_2(PPh_2Et)_2]$			90
$[Ni(CO)_2(PPhEt_2)_2]$			91
$[Ni(CO)_2(PPh_2CH_2CH_2SR)_2]$	R = Me, Et, Ph		91, 92
$[Ni(CO)_2\{C_6H_4(PR_2)_2\}]$	R = Me	123	40, 57
	R = Et	65	40, 57
	R = Ph	226	40, 57
$[Ni(CO)_2\{C_2H_4(PR_2)_2\}]$	R = Ph	139	40, 57
	R = Et	liq.	40, 57
	R = Me	71	93
$[Ni(CO)_2Ph_2PCH{=}CHPPh_2]$		156	94
$[Ni_2(CO)_4(Ph_2PC{\equiv}CPPh_2)_2]$		190	95
$[Ni(CO)_2\{CH_2(PPh_2)_2\}]$			96
$[Ni(CO)_2\{C_3H_6(PPh_2)_2\}]$			96
$[Ni(CO)_2\{C_6H_4(AsMe_2)_2\}]$			97
[Ni(CO)(P—P—P)]	P—P—P = $PhP(C_6H_4PEt_2)_2$	189–192	98
	P—P—P = $MeC(CH_2PPh_2)_3$	317	
$[Ni(CO)_2(PF_3)_2]$		liq.	99
$[Ni(CO)\{P(OPh)_3\}_3]$		98	100
$[Ni(CO)\{Ph_2P(CH_2)_4PPh_2\}_2]$			101
$[Ni(CO)_2L_2]$	L = PH_2CF_3, $PH(CF_3)_2$		102
$[Ni(CO)(np_3)]$	$np_3 = N(CH_2CH_2PPh_2)_3$		103

compound $[Ni(CO)(np_3)]$ (**14**).[103] The reaction of 1,4-bis(diphenylphosphino)butanenickel(0) with CO in hexane yields the monocarbonyl compound $[Ni(CO)(dppb)_2]$ (**15**).[101,104] This reacts with trialkyl phosphites with a displacement of one molecule of the diphosphine (equation 19).[105]

$$[Ni(CO)(dppb)_2] \xrightarrow{P(OR)_3} [Ni(CO)P(OR)_3(dppb)] \qquad (19)$$

The reaction of $[Ni\{C_nH_{2n}(PPh_2)_2\}_2]$ ($n = 2, 3$) with CO in benzene or CH_2Cl_2 at room temperature and pressure gives in general a mixture of $[Ni(CO)(P—P)_2]$ and $[Ni(CO)_2(P—P)]$ complexes.[101]

Relevant structural data for selected mixed phosphine carbonyl complexes are shown in Table 5. In all these complexes the nickel(0) atom is four-coordinate in a pseudotetrahedral geometry with the Ni—CO linkage essentially linear, the Ni—C—O angles being in the range 173–178°. In complex (**14**) the np_3 ligand bonds through the three phosphorus atoms and the nickel is in a pseudotetrahedral environment.[103]

Table 5 Some Molecular Parameters for Mixed Phosphine–Carbonyl Complexes

	Bond distances (pm)				*Bond angles* (°)			
Complex	*Ni—P*	*Ni—C*	*C—O*	*NiCO*	*PNiP*	*CNiC*	*PNiC*	*Ref.*
$[Ni(CO)_2(PPh_3)_2]$	222	176	114	178	117	113	109	106
$[Ni(CO)_2(PCy_3)_2]$	226	175	116	177	123	113	100–110	107
$[Ni(CO)_2\{C_3H_6(PHPh)_2\}]$	222	174	113	178	98	117	108–112	108
$[Ni(CO)(np_3)]$	222	174	118	173	106	—	111–115	103

$Ni(CO)_4$: Ni—C bond distances, 184 pm; C—O bond distances, 115 pm; [109] ν(CO) stretch, 2057 cm^{-1}

A number of MO calculations have been performed on carbonyl complexes, with methods ranging from *ab initio* to DVM–HFS. In any case it was found that both σ donation and π back-donation interactions are important in determining the geometrical structure and physical properties of these complexes. The *ab initio* calculations of Sakaki *et al.*[110] have shown that the strengthening of π back-donation is the driving force which stabilizes the pseudotetrahedral geometry *vs.* the square planar one in $[Ni(PR_3)_2(CO)_2]$ complexes.

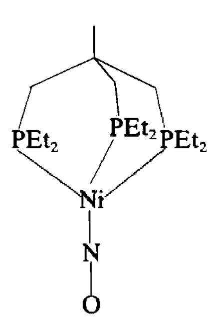
IR spectroscopy has been used to characterize the CO group bound to nickel(0). The ν(CO) stretching frequency shifts to lower frequency upon coordination as a consequence of π back-bonding interactions; it occurs at about 1900–1980 cm^{-1} in bis(carbonyl) derivatives and at about 1880 cm^{-1} in the $[Ni(np_3)(CO)]$ complex. Ziegler and Rauk have computed the contributions to the C—O force constants in $[Ni(CO)_3L]$-type complexes through DVM–HFS calculations.[111] They found that a relevant contribution to the force constant comes from steric interactions (including electrostatic and exchange energy) which oppose the contributions coming from π back-bonding interactions. This causes a smaller decrease of the force constant, as compared to those of the free CO molecule, upon coordination than that expected considering only the amount of charge transferred through σ and π interactions.

50.2.5.2 Nitrosyl complexes

Different oxidation numbers may be assigned to the metal in any nitrosyl complex depending on the different formalism adopted to represent the coordinated nitrosyl group, which may be considered as either a cationic NO^+ or an anionic NO^- species, as well as the neutral paramagnetic NO molecule. In the early papers, in the absence of X-ray structural characterizations, much effort was made to correlate the stretching frequency of the coordinated nitrosyl group to its coordination mode: linear or NO^+ type, and bent or NO^- type. The large number of structural determinations now available indicates (i) that between the truly 'bent' coordination (angles in the range 119–128°) and 'linear' coordination (angles in the range 167–180°), there are numerous examples of intermediate coordination (angles of about 150–165°); and (ii) that no simple correlation can be drawn between the ν(NO) stretch and the coordination mode of NO, the ν(NO) stretch also being influenced by the nature of the coligands and by the geometry of the molecule. According to the majority of the authors cited in this section, we consider that Ni—N—O angles greater than 150° are associated with coordination of the nitrosyl group as, in a formal sense, NO^+ and consequently the oxidation number of the nickel atom can be assigned.

A number of review articles dealing with nitrosyl complexes of nickel(0) have appeared.[112–116] Most of the nickel(0) nitrosyl complexes have been obtained as phosphine complexes using a great variety of synthetic procedures. The most important reactions leading to nitrosyl complexes are shown in Table 6. The complexes are, in general, sensitive to oxygen and moisture while in solution, and the preparations have mostly been carried out in a nitrogen atmosphere using anhydrous degassed solvents. Reactions also occurred between gaseous NO or $NOBF_4$ and complexes of nickel in low oxidation states; other reactions imply the reduction of the NO_2^- in the presence of nickel(II) compounds. The reduction of coordinated NO_2^- or NO_3^- by CO under very mild conditions, *i.e.* room temperature and low pressure of CO, should be noted (reaction 2).[118–120] The same reaction carried out at high temperature and pressure of CO yields the $[Ni(CO)_2(PR_3)_2]$ complex. The $[Ni(NO_3)(NO)(PR_3)_2]$ complex can be used as the parent complex to prepare numerous $[NiX(NO)(PR_3)_2]$ complexes (X = halides, NCS, NCO, N_3) by metathetic reactions with NaX.[132–134]

The nitrosyl compounds are, in general, intensely coloured, dark blue, purple or violet, and diamagnetic. The crystalline products are mostly stable and soluble in organic solvents. Some physical and chemical properties of the complexes whose X-ray structures have been determined are collected in Table 7. The complexes $[Ni(Et_6p_3)(NO)]BF_4$ **(16)** and $[Ni(np_3)NO]BPh_4$ **(17)** have essentially the same distorted tetrahedral structure,[121,127] the np_3 acting as a tridentate ligand. The bis-monophosphine nitrosyl complexes $[NiX(NO)(PR_3)_2]$ are all mononuclear,[133–135] while the monodiphosphine complex $[Ni(NO_2)(NO)(dppe)]_2$ **(18)** is dinuclear[136] with bridging diphosphine and monodentate O-bonded nitrito. A nearly symmetrical bridging iodide has been found in the anionic $[Ni_2I(3,5\text{-}Me_2pz)_2(NO)_2]^-$ **(19)**.[131]



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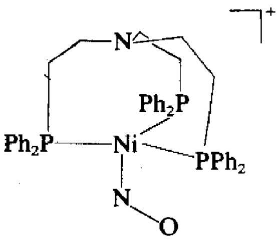

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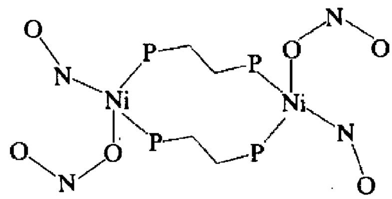

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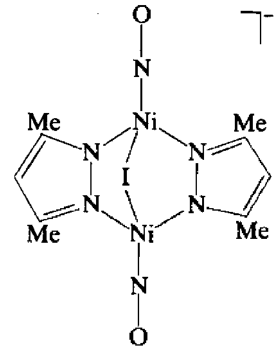


(19)

Table 6 Reaction Schemes for the Synthesis of Nitrosyl Complexes

		Ref.
(1)	$2NiX_2 + 2NO + Zn \longrightarrow 2[NiX(NO)] + ZnX_2$	115
	X = Br, I; ν(NO) 1859–1870	
(2)	$[NiX_2(PR_3)_2] + CO \xrightarrow[Me_2CO]{r.t., 1\ atm} [NiX(NO)(PR_3)_2] + CO_2$	118–120
	$X = NO_2, NO_3$; R = Me, Et; ν(NO) 1705–1750	
(3)	$NiX_2 + triphos + KNO_2 \xrightarrow{NaBF_4} [Ni(NO)(triphos)]BF_4$	121
	X = halides; triphos = p_3, Et_6p_3	
(4)	$[NiX_2(PPh_3)_2] + NaNO_2 + PPh_3 \xrightarrow[reflux]{THF} [NiX(NO)(PPh_3)_2] + NaX + Ph_3PO$	122
	$X = Cl, Br, NO_2, NO_3$	
(5)	$[Ni(CO)_2(PPh_3)_2] + NO \xrightarrow[r.t., NO_2]{CCl_4, hexane} [Ni(NO_2)(NO)(PPh_3)_2] + CO + N_2O$	123
(6)	$[Ni(CO)_2(PPh_3)_2] + NO \xrightarrow{C_6H_6} [Ni(NO)_2(PPh_3)_2]$	124
	ν(NO) 1745	
(7)	$[Ni(CO)_2(PPh_3)_2] + NOPF_6 + PR_3 \xrightarrow[C_6H_6, MeOH]{r.t.} [Ni(NO)(PR_3)_2]PF_6$	125
	$PR_3 = PPh_3, PMePh_2$	
(8)	$[NiCl_2(PPh_2Me)_2] + NaNO_2 + PPh_2Me + CO \xrightarrow[Me_2CO, H_2O, 56\ ^\circ C]{NaPF_6} [Ni(NO)(PPh_2Me)_2]PF_6$	125
	ν(NO) 1785–1790	
	$[Ni(Ph_2P(CH_2)_2SEt)_2]ClO_4 + NaNO_2 + CO \xrightarrow[MeOH, reflux]{NaBF_4} [Ni(NO)(Ph_2P(CH_2)_2SEt)_2]BF_4$	126
(9)	$[NiH_x(np_3)]BPh_4 + NO \xrightarrow[CH_2Cl_2]{r.t.} [Ni(NO)(np_3)]BPh_4$	127
(10)	$[Ni\{P(OCH_2)_3CMe\}_4] + NOBF_4 \xrightarrow{MeCN} [Ni\{P(OCH_2)_3CMe\}_3NO]BF_4$	128
(11)	$NiXNO + 2PR_3 \longrightarrow [NiX(NO)(PR_3)_2]$	120
	X = Cl, Br	
	$NiINO + 2EPh_3 \longrightarrow [NiI(NO)(EPh_3)_2]$	121
	E = As, Sb	
	$NiINO + PPh_3 \longrightarrow [NiI(NO)PPh_3]_2$	129
(12)	$NiINO + Na(3,5\text{-}Me_2Pz) \xrightarrow{THF} [Ni(3,5\text{-}Me_2Pz)NO]_2 + [Ni(3,5\text{-}Me_2Pz)]_2Ni$	130
(13)	$NiINO + Na(3,5\text{-}Me_2Pz) \xrightarrow{THF, Et_4N^+} [Ni_2(3,5\text{-}Me_2Pz)_2(NO)_2I]Et_4N$	131

Table 7 Some Structural Data for Nitrosyl Complexes

Compound[a]	*Synthetic procedure* (*Table 6*)	*ν(NO)* (cm^{-1}) *Nujol mull*	*Angle* (°) *Ni—N—O*	*Distance* (pm) *Ni—NO*	*Ni—N*[b]	*Coordination geometry*	*Ref.*
$[Ni(NCS)(NO)(PPh_3)_2]$	(4)		162	165	194	Td	133
$[Ni(N_3)(NO)(PPh_3)_2]$	(4)		153	169	202	Td	134
$[Ni(NO)_2(NO)(PMe_3)_2]$	(2)	1718	166	165	200	Td	135
$[Ni(NO_2)(NO)(dppe)_2]$	(2)	1750	153	166	—	Td	136
$[Ni\{P(OCH_2)_3CCH_3\}_3NO]BF_4$	(10)	1867	177	158	—	Td	131
$[Ni(Et_6p_3)(NO)]BF_4$	(3)	1750	180	163	—	Td	131
$[Ni(np_3)NO]BPh_4$	(8)	1755	168	159	—	Td	127
$[Ni(3,5\text{-}Me_2pz)NO]_2$	(12)	1800	179	161	187–192	TrPl	130
$[Ni_2I(3,5\text{-}Me_2pz)_2(NO)_2]Et_4N$	(13)	1752	171–174	164–165	196–199	Td	131

[a] All of the complexes are diamagnetic. A feeble paramagnetism in a few complexes may be due to paramagnetic impurities.
[b] Additional ligand containing nitrogen donor.

Pseudotetrahedral nickel nitrosyl complexes [NiLNO] have also been reported with the novel ligands {dimethyl(3,5-dimethyl-1-pyrazolyl)(2-thioethoxyethoxy)gallato}$^-$ and {dimethyl(3,5-dimethyl-1-pyrazolyl)(2-dimethylaminoethoxy)gallato}$^-$.[137,138]

50.2.6 Complexes with η^2-Coordinated Unsaturated Molecules

50.2.6.1 Complexes with alkenes and alkynes

A large number of nickel(0) phosphine complexes with η^2-bonded unsaturated organic molecules have been reported. Here we will review relevant examples of complexes with η^2-bonded molecules which contain a number of Ni—C bonds not exceeding the number of bonds from nickel to non-carbon atoms (usually phosphorus). The early examples (up to 1972) of complexes with alkenes have been extensively reviewed.[11]

General synthetic procedures. In general, the nickel(0) complexes with alkenes and either phosphines or arsines, although thermally stable, are air-sensitive, especially in solution, and their preparation must be carried out under nitrogen or argon using anhydrous and oxygen-free solvents. Relevant examples of alkene complexes together with their preparation schemes are reported in Table 8.

In complexes of the type $Ni(PR_3)_4$, the tertiary phosphines can be easily replaced by alkenes[2] with strongly electron-withdrawing substituents, which increase their π acceptor capability, according to reaction (20).

$$[Ni\{C_nH_{2n}(PPh_2)_2\}] + (CN)_2C{=}C(CN)_2 \longrightarrow [Ni\{C_nH_{2n}(PPh_2)_2\}\{(CN)_2C{=}C(CN)_2\}] \quad (20)$$

$$[Ni(PCy_3)_2] + MeCH{=}CHMe \longrightarrow [Ni(PCy_3)_2(MeCHCHMe)] \quad (21)$$

$$[Ni\{P(OR)_3\}_2] + C_5H_6 \longrightarrow [Ni\{P(OR)_3\}_2(C_5H_6)] \quad (22)$$

$R = o\text{-}C_6H_4Ph,\ C_5H_6$ = cyclopentadiene

Displacement reactions of phosphines by some 'non-activated' alkenes and alkynes have also been reported.[67]

Alkenes and related ligands readily add to coordinatively unsaturated complexes of the type $Ni(PR_3)_n$ ($n = 2, 3$) (equations 21 and 22).[139–143]

Reaction (21) occurs with cyclohexene and both *cis*- and *trans*-2-butene, without isomerization of the alkenes,[139] while the reduction of $Ni(acac)_2$ with $Al(alkyl)_3$ in the presence of PCy_3 and 2-butene (*cis* and *trans*) affords the complex bis(tricyclohexylphosphine)(1-butene)nickel(0).[140]

It is expected that alkenes can be substituted by other alkenes which are stronger π acids.

Table 8 Complexes with Phosphines (or Arsines) and Alkenes (or Alkynes) and their Methods of Synthesis

Complex	*Synthesis, conditions*	*Ref.*
$[Ni\{C_nH_{2n}(PPh_2)_2\}\{(CN)_2C{=}C(CN)_2\}]$	$Ni(P{-}P)_2 + (CN)_2C{=}C(CN)_2$, benzene	67
$n = 3, 4$	$[Ni(CO)(P{-}P)_2] + (CN)_2C{=}C(CN)_2$, CH_2Cl_2	105
$[Ni\{C_nH_{2n}(PPh_2)_2\}L]$ L = alkenes, dienes, alkynes	$Ni(P{-}P)_2 + L$, benzene	67
$[Ni(PCy_3)_2MeCH{=}CHMe]$	$NiL_2 + MeCH{=}CHMe$	139
	$NiL_2(N_2) + MeCH{=}CHMe$, toluene, −20 °C	140
$[Ni\{Cy_2P(CH_2)_2PCy_2\}ArH]$ ArH = benzene, naphthalene, anthracene	$NiL_2Cl + Li + ArH$, diglyme, 0 °C	141
$[Ni(PCy_3)_2(1,2\text{-}\eta^2\text{-anthracene})]$	$NiL_2 + C_4H_{10}$	142
$[Ni\{P(OR)_3\}_2C_5H_6]$ R = o-C_6H_4Ph	$NiL_2 + C_5H_6$, toluene, −20 °C	143
$[Ni(PPh_3)_2C_2F_4]$	$[Ni(CDT)C_2F_4] + PPh_3$	144
$[Ni(PPh_3)_3C_2F_4]$	$[Ni(PPh_3)_2C_2H_4] + C_2F_4$, xylene	145
$[Ni(PPh_3)_2L]$ L = CF_2CH_2, $CFHCH_2$, CF_3CFCF_2, cyclohexafluorobutene	$[Ni(PPh_3)_2C_2H_4] + L$	146
$[Ni(PPh_3)_2(CF_2CHFCHFCF_2)]$	$[Ni(PPh_3)_2C_2H_4] + CF_2CHF$, ether	146
$[Ni(PR_3)_2(CF_2)_4]$ $PR_3 = PEt_3$, PBu^n_3, PPh_2Me $(PR_3)_2 = Ph_2PCH_2CH_2PPh_2$	$[Ni(PR_3)_2(1,5\text{-cod})] + CF_2CF_2$, light petroleum, Carius tube, r.t.	147
	$Ni(PR_3)_4 + CF_2CF_2$, light petroleum, Carius tube, r.t. or 80 °C	55
$[Ni(p_3)(C_2F_4)]$	$Ni(CDT) + p_3 + CF_2CF_2$, toluene, ether, −78 °C	148, 149
$[Ni(as_3)(CF_2)_4]$	$Ni(as_3) + CF_2CF_2$, benzene, hexane, Carius tube, 60 °C	148
$[Ni(PR_3)_2C_2H_4]$ $PR_3 = PPh_3$, PEt_3, PCy_3	$Ni(acac)_2 + PR_3 + C_2H_4$	146, 150, 151
$[Ni\{P(O\text{-}o\text{-tolyl})_3\}_2(C_2H_4)]$	$Ni(acac)_2 + P(OR)_3 + AlEt_3$, toluene, −50 °C	152
$[Ni(PPh_3)_2(1,5\text{-cod})]$	$Ni(acac)_2 + PPh_3 + 1,5\text{-cod} + AlEt_3$	153
$[Ni(PPh_3)_2(CH_2{=}C{=}CH_2)]$	$Ni(PPh_3)_2Br_2 + C_3H_4 + NaHg$, MeCN	65
$[Ni(PPh_3)_2(PhCHCHPh)]$	$Ni(PPh_3)_2Cl_2 + Li + PhCHCHPh$, cooled THF	154
$[Ni(PPh_3)_2(CH_2CHCN)_2]$	$Ni(CH_2CHCN)_2 + PPh_3$	155
$[Ni(PPh_3)_2RC{\equiv}CR']$ R = R′ = Me, Ph R = Me, R′ = Ph	$[Ni(PPh_3)_2(C_2H_4)] + RC{\equiv}CR'$	150, 151
$[Ni(PR_3)_2(CH_2{=}C(R'')CO_2R''')]$ R′ = Et, Cy, Ph; R″ = Me, H R‴ = Me, Et	$Ni(1,5\text{-cod})_2 + PR_3$ + unsaturated ester, ether, hexane, r.t. or below 0 °C	162

Indeed, some fluoroalkene complexes have been obtained with metathetical reactions as exemplified by equations (23) and (24).[145,146]

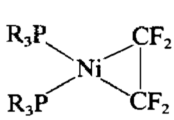
$$[Ni(PPh_3)_2(C_2H_4)] + C_2F_4 \longrightarrow \underset{(\mathbf{20})}{[Ni(PPh_3)_2(C_2F_4)]} + C_2H_4 \quad (23)$$

$$[Ni(PPh_3)_2(C_2H_4)] + CF_2CH_2 \longrightarrow [Ni(PPh_3)_2CF_2CH_2] + C_2H_4 \quad (24)$$

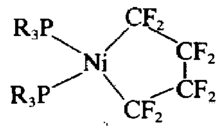
$$[Ni(PPh_3)_2CF_2{=}CF_2] \xrightarrow{C_2F_4} \underset{(\mathbf{21})}{[Ni(PPh_3)_2(CF_2)_4]} \quad (25)$$

The reaction of fluoroalkenes with nickel(0) phosphine and arsine complexes may also result in the dimerization of the fluoroalkene and in the formation, for example, of octafluoronickelacyclopentane complexes $[Ni(ER_3)_2(CF_2)_4]$ (E = P, As), which contain the nickel atom in the formal oxidation state +2.[147,55] A similar reaction also occurs when $[Ni(PPh_3)_2C_2F_4]$ reacts with an excess of C_2F_4 (equation 25). The reaction of an excess of C_2F_4 with Ni(CDT) and the tritertiary phosphine triphos in toluene gives, on the contrary, the complex $[Ni(triphos)CF_2{=}CF_2]$ which does not react further with an excess of C_2F_4.[148]

Complexes with a five-membered fluoroalkane ring are assumed to form through an intermediate state with two molecules of $CF_2{=}CF_2$ coordinated to the metal (**22b**). The addition of the second alkene molecule to the complex (**22a**) may be prevented by the coordination of the tridentate ligand p_3 in the place of two PPh_3 groups. In this case the

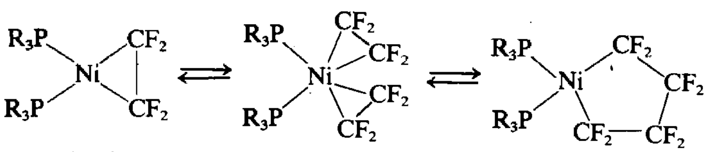


(20)



(21)

complex is five-coordinate and the access to the nickel of a bidentate ligand is blocked. Using the ligand as$_3$ instead of p$_3$ does not prevent the bonding of the second $CF_2{=}CF_2$ molecule since an $AsPh_2$ group of the as$_3$ ligand may be replaced by the alkene in the intermediate complex (**22b**).



(**22a**) (**22b**) (**22c**)

Nickel(0) complexes with two coordinated alkene molecules have also been isolated in the solid state. As an example the $[Ni(PR_3)(C_2H_4)_2]$ complexes have been obtained according to reaction (26).[157]

$$[Ni(PR_3)(CDT)] + C_2H_4 \xrightarrow{\text{ether, }-20\,^{\circ}C} [Ni(PR_3)(C_2H_4)_2] \quad (26)$$

$$PR_3 = PPh_3, PCy_3$$

All the reactions described so far are important for elucidating the mechanism of oligomerization of alkenes catalyzed by nickel(0) complexes.

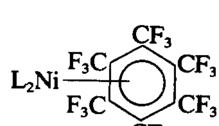
One of the most general methods for the synthesis of mixed complexes of nickel(0) with phosphines and alkenes is the reduction of nickel(II) salts in the presence of phosphines and alkenes. Aluminum trialkyls are the most widely employed reducing agents. The complex $[Ni(PPh_3)_2(C_2H_4)]$ has been prepared as a yellow crystalline compound in 90% yield according to equation (27).[146,150] The analogous complexes with PEt_3 and PCy_3 were prepared by similar reactions and the complex $[Ni(PEt_3)_2(C_2H_4)]$ has been obtained as a yellow oil.[141] The ethylene adduct has also been obtained in the absence of C_2H_4, although in a lower yield (about 75%),[150] the source of ethylene in this reaction being the decomposition of $AlEt_2(OEt)$ (equation 28).

$$Ni(acac)_2 + PPh_3 + C_2H_4 \xrightarrow[AlEt(OEt)_2]{\text{ether, }0\,^{\circ}C} [Ni(PPh_3)_2(C_2H_4)] \quad (27)$$

$$Ni(acac)_2 + PPh_3 \xrightarrow[C_6H_6,\ 20\,^{\circ}C]{AlEt_2(OEt)} [Ni(PPh_3)_2(C_2H_4)] \quad (28)$$

Sodium amalgam and elemental lithium have also been used as reducing agents in the preparation of $[Ni(PPh_3)_2(CH_2CCH_2)]$[65] and $[Ni(PPh_3)_2(PhCHCHPh)]$.[154]

In the $[Ni(PPh_3)_2(C_2H_4)]$ complex the ethylene molecule can be replaced by alkynes such as $MeC{\equiv}CMe$, $PhC{\equiv}CPh$ and $PhC{\equiv}CMe$.[150,151] The reaction of $CF_3C{\equiv}CCF_3$ with $[Ni(PPh_3)_2(C_2H_4)]$ or $[Ni(AsMe_2Ph)_4]$ affords the complex (**23**).[158] ^{19}F NMR spectra indicate that the $(CF_3)_6C_6$ molecule is symmetrically bonded with respect to the L_2Ni moiety.



(**23**) $L = PPh_2, AsMe_2Ph$

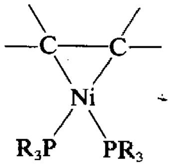
A number of X-ray crystal structures of nickel(0) complexes containing both alkenes and phosphines have been reported to date with the aim of gaining more information on the bonding in metal alkene complexes. Structural data for the most relevant nickel(0) phosphine alkene complexes are reported in Table 9.

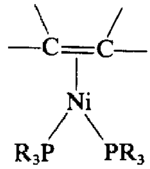
Table 9 Structural Data for some Nickel(0) Phosphine Alkene Mixed Complexes and Related Compounds

Complex	Bond distances (pm) Ni—P	Ni—C	C—C[b]	θ[a] (°)	Ref.
$[Ni(PPh_3)_2(C_2H_4)]$	215, 216	198, 200	143	5	159
	215, 216	192, 196	139	—	160, 161
$[Ni\{P(O\text{-}o\text{-}Tol)_3\}_2(CH_2CHCN)]$	210, 212	191, 202	146	3.9	162
$[Ni\{P(O\text{-}o\text{-}Tol)_3\}_2(CH_2CH_2)]$	209, 210	199, 204	146	6.6	162
$[Ni(PTol_3)_2(PhCHCHPh)]$	218, 219	201, 203	147	18.5	163
$[Ni\{Cy_2P(CH_2)_2PCy_2\}(Me_2CCMe_2)]$	215, 216	198	142	16.5	164
$[Ni(PPh_3)_2(CH_2C(CH_3)CO_2Et)]$	217, 219	198, 203	141	6.4	165
$[Ni(PPh_3)_2(PhCOCHCHCO_2Me)]$	217, 220	197, 199	142	8.5	166
$[Ni(PCy_3)_2(1,2\text{-}\eta^2\text{-anthracene})]$	223, 224	199, 206	142	22	142
$[Ni(p_3)(CF_2CF_2)]$	221, 226, 226	184, 188	137	—	149

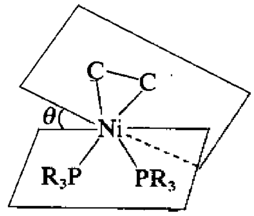
[a] Dihedral angle between the PNiP and CNiC planes (**24b**).
[b] Carbon atoms bonded to nickel.

In all the complexes shown in Table 9 (with one exception) the nickel atom is four-coordinated by two phosphorus atoms and by two carbon atoms in a distorted planar arrangement (**24a**). The plane containing the nickel and phosphorus atoms and the plane containing the nickel and the coordinated carbon atoms form a dihedral angle which varies between 4° and 27° (**24b**), depending on the coordinated alkene. In the $[Ni(p_3)(C_2F_4)_2]$ complex (**25**) the nickel atom is five-coordinated by three phosphorus atoms of the tridentate ligand and two carbon atoms of tetrafluoroethylene.[146]

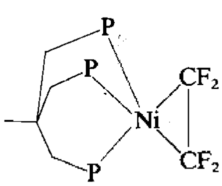




(24a)



(24b)



(25)

The C—C bond of the coordinated alkene is generally about 10 pm longer than the same bond in the free molecule (C=C in C_2H_4 is 134 pm long). The R_2C groups are not planar: the angles between the central C—C bond and the normals to the R_2C planes range between 27° in $[Ni\{C_2H_4(PCy_2)_2\}(Me_2CCMe_2)]$[164] and 62° in $[Ni(CNBu^t)_2\{(CN)_2CC(CN)_2\}]$.[178] Both the lengthening of the C=C bond and the loss of planarity of the $R_2C{=}C$ group indicate a weakening of its double bond character upon coordination. Ethylene and symmetrically substituted ethylenes are symmetrically bonded to the nickel atom, with a CNiC angle of about 41–43°.

Chemical and physical properties of metal alkene complexes have been rationalized on the basis of the Dewar–Chatt–Duncanson bonding model[167,168] and a number of semiempirical and *ab initio* MO calculations have been performed for a more quantitative description of the bonding.[169–177]

The main contributions to the binding energies have been found to be donative and back-donative interactions. The donative interaction is mainly due to the delocalization of an alkene orbital on to the vacant Ni sp^* orbital. This causes a decrease of electron density on the alkene and an increase in the Ni—C region. The back-donative interaction is mainly due to the bonding interaction between a filled d orbital on nickel and the empty π^* orbital of the alkene. This causes an accumulation of electron density in the Ni—C region and a decrease of charge density along the line of the C—C bond affecting the bond length and the internal geometry of the alkene. Recent *ab initio* calculations[176] on the model complex $[Ni(PH_3)_2(C_2H_4)]$ showed that the amount of transferred charge in the π back-donation is about five times larger than the donative one and the energy stabilization is about three times larger. The π back-bonding donation is increased by electron-withdrawing substituents on the alkenes which lower the π^* orbital. It has indeed been found that the complexes with C_2F_4 or $(CN)_2CC(CN)_2$[178] are more stable than those with C_2H_4. It has also been computed that substitution of PH_3 with NH_3, which is more basic, strengthens the π back-donative interaction, but no amine alkene complex has yet been described.

Variable temperature ^{1}H NMR studies of toluene solutions of $[Ni(PPh_3)_2(C_2H_4)]$ indicate that the complex is appreciably dissociated at room temperature according to equation (29).[179] If an excess of C_2H_4 is present in the solution of the complex, the equilibrium is also shifted to the left at room temperature, and a rapid exchange occurs between coordinated and free C_2H_4. The same equilibrium also occurs in complexes formed by other alkenes and phosphines.

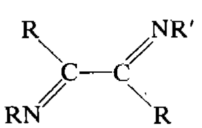
$$[Ni(PPh_2)_3(C_2H_4)] \rightleftharpoons [Ni(PPh_3)_2] + C_2H_4 \qquad (29)$$

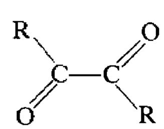
^{13}C NMR spectra of a series of alkene complexes with different phosphines show that the alkene carbon signals are shifted upfield on coordination.[152,180] The amount of this upfield shift is correlated to the degree of the π back-bonding interaction, and depends, in turn, on the σ basicity of the coordinated phosphines.[180]

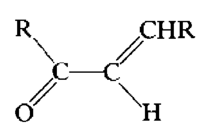
The ethylene molecule in $[Ni(PPh_3)_2(C_2H_4)]$ may be replaced by a variety of mono- and bi-dentate ligands by means of a direct metathetical reaction at room temperature in solvents such as Et_2O, C_6H_6 and THF. The complexes $[Ni(PPh_3)_2(bipy)]$,[181] $[Ni(PPh_3)_2(DIIM)]$ (DIIM = benzylbisphenylimine),[182] $Na[Ni(PPh_3)_3(EPh_3)]$ (E = Ge, Sn, Pb) and $Na_3[Ni(PPh_3)(EPh_3)_3]$ (E = Ge, Sn)[183] have been prepared following this procedure.

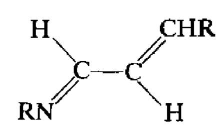
50.2.6.2 Complexes with 'heteroalkenes'

Aromatic and aliphatic aldehydes, ketones, imines and related compounds are usually bonded to a metal atom through lone pairs of the donor atom. When NiL_2 moieties have a high electron density on the metal atom, *e.g.* when L = phosphines, arsines, isocyanides, bipy and also Me_4en,[184] they are able to back-donate electrons to a π^* orbital of the heteroalkene, thus stabilizing their η^2-coordination mode. Numerous nickel(0) complexes $Ni(PR_3)_2L$ have indeed been prepared with monodentate and bidentate heteroalkenes of the types (**26**)–(**32**), by means of metathetic reactions starting from $Ni(CO)_4$, $Ni(cod)_2$ or $[Ni(PR_3)_2(C_2H_4)]$ in anhydrous conditions and under an inert atmosphere.[146,185–187] General schemes for the synthesis of nickel(0) complexes with η^2-coordinated heteroalkenes are shown in Table 10.


(**26**)


(**27**)


(**28**)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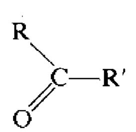
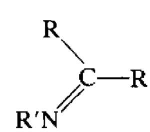
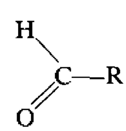

(**30**)


(**31**)


(**32**)

Analogous compounds which are assumed to contain imines, diazenes, ketones and nitroso compounds η^2-coordinated to the $Ni(CNBu^t)_2$ moiety have been also reported.[30]

The compounds $[NiL_2(heteroalkene)]$ are generally air-unstable and must be prepared and handled in rigorous anhydrous and air-free conditions. The complexes are always diamagnetic.

Tetrakis phosphino complexes of nickel(0) readily react with aliphatic and aromatic nitro compounds RNO_2 to afford the corresponding nitroso complexes of nickel(0) $[Ni(PR_3)_2(RNO)]$ and the phosphine oxide. Kinetic studies have been carried out to elucidate the mechanism of this oxygen transfer reaction. The reaction mechanism shown in equations (30)–(32) has been postulated.[193]

$$Ni(PEt_3)_4 \rightleftharpoons Ni(PEt_3)_3 + PEt_3 \qquad (30)$$

$$Ni(PEt_3)_3 + RNO_2 \longrightarrow Ni^I(PEt_3)_3^+RNO_2^- \qquad (31)$$

$$Ni^I(PEt_3)_3^+RNO_2^- \longrightarrow Ni(PEt_3)_2(RNO) + P(O)Et_3 \qquad (32)$$

Table 10 General Reactions for the Synthesis of Complexes with η^2-Coordinated 'Heteroalkenes'

	Ref.
$[Ni(PR_3)_2(C_2H_4)] + L^a \xrightarrow[r.t.]{THF/N_2} [Ni(PR_3)_2L] + C_2H_4$	185, 186
$Ni(cod)_2 + Me_4en + ArCHO \xrightarrow[r.t.]{THF/N_2} [Ni(Me_4en)(ArCHO)] + 2cod$	186
$[Ni(bipy)(cod)] + L \xrightarrow[r.t.]{THF/N_2} [Ni(bipy)L] + cod$	187
$Ni(cod)_2 + CNBu^t + L \xrightarrow[r.t.]{THF/N_2} [Ni(CNBu^t)_2L] + cod$	30
$[Ni(PPh_3)_2(C_2H_4)] + (CF_3)_2CO \xrightarrow[r.t.]{Et_2O} [Ni(PPh_3)_2\{(CF_3)_2CO\}] + C_2H_4$	146
$[Ni(PR_3)_2(C_2H_4)] + (Me_2N{=}CH_2)X \xrightarrow{THF/N_2} [NiX(PPh_3)(Me_2NCH_2)]$ R = Ph, Tol; X = Cl, Br, I, ClO_4	188
$Ni(CO)_4 + C_5H_{10}NCN \longrightarrow [Ni(CO)(C_5H_{10}NCN)]_3$ (**37**)	189
$Ni(cod)_2 + C_6H_4(OH)CHNMe \xrightarrow[r.t.]{toluene} [Ni\{C_6H_4(OH)CHNMe\}_2]$	190
$Ni(cod)_2 + Ph_2C{=}NLi \xrightarrow{Et_2O/-40\,°C} [Ni_2(Ph_2CNH)_2(Ph_2CNLi)_3(Et_2O)_2]$ (**38**)	191
$Ni(cod)_2 + Ph_2C{=}NH \xrightarrow{Et_2O/-40\,°C} [Ni(Ph_2CNH)_2]_3$ (**36**)	192
$Ni(PEt_3)_4 + RNO_2 \xrightarrow[<0\,°C]{butane} [Ni(PEt_3)_2(RNO)] + Et_3PO$	193
$Ni(CNBu^t)_4 + PhNO \xrightarrow[r.t.]{n\text{-hexane}} [Ni(CNBu^t)_2(PhNO)]$	194
$Ni(CNBu^t)_4 + PhNO$ (excess) $\xrightarrow[r.t.]{n\text{-hexane}} [Ni(CNBu^t)_2(PhNO_2)]$	194
$[NiCl_2(PMe_3)_2] + \{(Me_3Si)_2CH]_2P\}Na \xrightarrow[-20\,°C]{n\text{-hexane}} [Ni(PMe_3)_2\{(Me_3Si)_2C{=}PC(H)(SiMe_3)_2\}]$	195

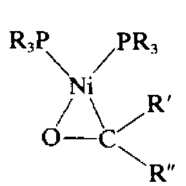
[a] L = a heteroalkene molecule.

The $[Ni(PEt_3)_2(Bu^tNO)]$ complex is extremely air-sensitive, melts below 0 °C and can be recovered from the reactants solution at −78 °C.

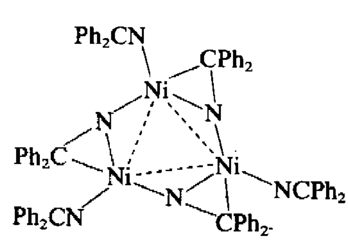
Aryl nitroso complexes can also be obtained by direct reaction of ArNO with $Ni(CNBu^t)_4$.[194]

A number of X-ray crystal structures of complexes with coordinated heteroalkenes have been reported, unambiguously confirming the η^2 coordination of the unsaturated molecules with one exception (*vide infra*). Structural features of the most relevant complexes are shown in Table 11. The inner coordination about the nickel(0) atom is nearly planar, as already found in alkene complexes. The η^2 coordination of the C=O group has been determined in the three complexes (**33**)–(**35**).

In complex (**33**) the C=O group is symmetrically bonded to the metal atom, while in (**34**) and (**35**) the Ni—C and Ni—O distances are significantly different. The R′R″C=O groups are not planar in the complexes (**33**) and (**34**), the phenyl and trifluoromethyl groups being bent away from the metal (48° and 63°, respectively), as is also usually found in substituted η^2 alkenes. The lengthening of the C=O groups upon coordination is about 10 pm in complexes (**33**), (**34**) and (**35**) and can be revealed by the low frequency shift of the ν(C=O) stretch (from 1718 cm^{-1} to less than 1500 cm^{-1} in complex **35**).



(**33**) R = Ph, R′ = R″ = CF_3
(**34**) R = Et, R′ = R″ = Ph
(**35**) R = Cy, R′ = H, R″ = Ph



(**36**)

Table 11 Molecular Parameters for some η^2-'Heteroalkene' Complexes

Complex		Bond distances (pm) Ni—C (π)	Ni—O (π)	Ni—P (trans to C)	Ni—P (trans to O)	C—O	θ[a] (°)	Ref.
$[Ni(PPh_3)_2\{(CF_3)_2CO\}]$	(**33**)	189	187	225	218	132	6.9	196
$[Ni(PEt_3)_2(Ph_2CO)]$	(**34**)	197	185	219	214	134	3.3	51
$[Ni(PCy_3)_2(PhCHO)]$	(**35**)	198	187	224	217	133		197
		Ni—C (π)	Ni—N (π)	Ni—D[b]	Ni—D[c]	C—N		
$[Ni(Ph_2CNH)_2]_3$	(**36**)	196	191	196 (N)	187 (N)	142		192
$[Ni_2(Ph_2CNH)_2(Ph_2CNLi)_3(Et_2O)_2]$	(**38**)	197	192	196 (N)	189 (N)	141		191
$[Ni(CO)(C_5H_{10}NCN)]_3$	(**37**)	199	199	175 (N)	175 (C)	113		189
$[Ni(PPh_3)(PhCN)]_4$	(**39**)	185	191	190 (N)	214 (P)	126		198
$[NiCl(PPh_3)(Me_2NCH_2)]$	(**40**)	188	192	221 (Cl)	214 (P)	139		188
$[Ni\{Ph(O)CHNMe\}\{Ph(OH)\text{-}(CHNHMe)\}]$	(**41**)	198	187	186 (N)	193 (O)	143	4.4	190
$[Ni(CNBu^t)_2\{Bu^tNCC(CN)_2\}]$	(**43**)	186	184	188 (C)	182 (C)	124		199

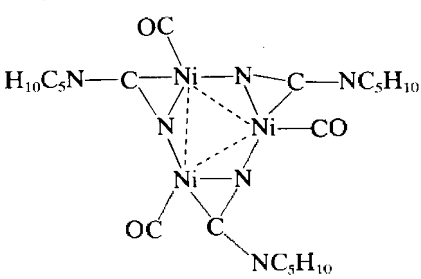
[a] Dihedral angle of (**24c**). It represents a measure of the twist of the unsaturated coordinated groups towards the planar arrangement of the donor atoms.
[b] Bridging or terminal σ-donor atom.
[c] Terminal donor atom.

The reaction between $Ni(cod)_2$ and iminobenzophenone has been carried out as outlined in equation (33).[192] The bis-imino complex (**36**) is trinuclear in the solid state containing bridging, terminal, 'end-on' and 'side-on' coordinated imino groups.

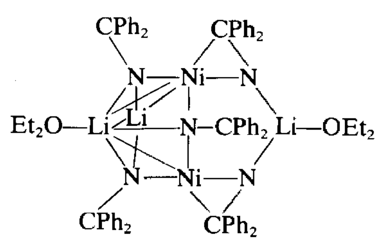
$$Ni(cod)_2 + Ph_2C{=}NH \xrightarrow{Et_2O/-40\,^\circ C} [Ni(Ph_2CNH)_2]_3 + cod$$
$$Ni(cod)_2 + Ph_2C{=}NH \xrightarrow[+bipy]{Et_2O/-40\,^\circ C} [Ni(bipy)(Ph_2CNH)] + cod \qquad (33)$$

A similar trinuclear structure has also been found in the carbonyl(piperidine-*N*-carbonitrile)nickel(0) complex (**37**).[189]

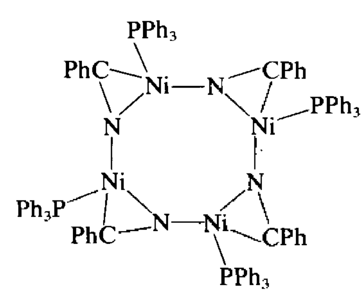
The reaction of $Ni(cod)_2$ with lithium imidobenzophenone under the same conditions as that with iminobenzophenone yields a compound with a very complicated structure (**38**)[191] containing bridging σ- and π-bonded RCN groups which interact with both lithium and nickel atoms.



(**37**)



(**38**)



(**39**)

The reaction of $Ni(cod)_2$ with Ph_3P and benzonitrile affords different compounds according to equations (34) and (35).[198,200] In the complex (**39**), which is tetrameric, each PhCN group bridges two nickel atoms. The eight-membered NiN ring has a boat conformation. The C—N bond distance (126 pm) is longer than that of a triple bond (116 pm) and the ν(CN) stretch at 1750 cm^{-1} is typical of a C=N group. The NCC(Ph) angle is 131°.[198]

$Ni(PCy_3)_2$ reacts in toluene with alkanenitriles R(Ph)CHCN (R = H, Me) according to equation (36).[201]

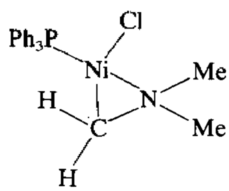
$$Ni(cod)_2 + 3PPh_3 + PhCN \xrightarrow{toluene/hexane} [Ni(PPh_3)_3(PhCN)] \qquad (34)$$

$$Ni(cod)_2 + PPh_3 \xrightarrow{toluene} [Ni(cod)(PPh_3)] + cod \xrightarrow[toluene]{PhCN} \underset{(\mathbf{39})}{[Ni(PPh_3)(PhCN)]} + cod \qquad (35)$$

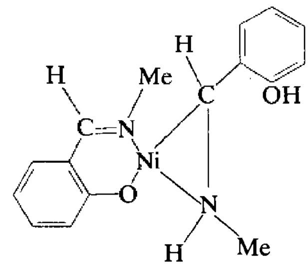
$$Ni(PCy_3)_2 + PhCH_2CN \rightleftharpoons Ni(PCy_3)_2(\sigma\text{-}PhCH_2CN) \rightleftharpoons Ni(PCy_3)(\pi\text{-}PhCH_2CN) + PCy_3 \qquad (36)$$

^1H NMR and IR spectra are employed to distinguish between the two coordination modes of RPhCHCN molecules. In the end-on coordination of RPhCHCN $\nu(CN)$ is at lower frequencies than in the edge-on coordination and the α protons are markedly deshielded when the molecule is edge-on coordinated.

In complex (**40**) the dimethylmethyleneiminium cation, isoelectronic with $H_2C{=}CMe_2$, is η^2-bound to the $NiClPPh_3$ moiety.[199] Short *trans* bonds (σ-type) are generally found in the $[NiL_2(heteroalkene)]$ complexes, as for the alkene complexes.



(**40**)

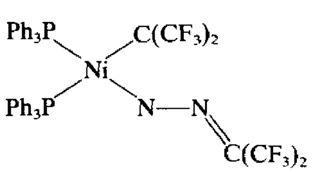


(**41**)

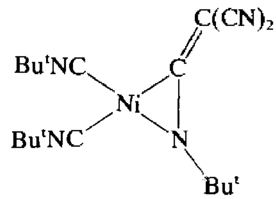
In the (N-methylsalicylaldiminato)(N-methylsalicylaldiminium)nickel(0) complex (**41**)[190] the OH proton of one ligand molecule has been transferred to the nitrogen atom of the other ligand molecule and the nickel(0) is σ-coordinated to one N-methylsalicylaldiminato anion and π-coordinated to the azomethine group of the protonated ligand molecule. The Ni—O bond distances are longer than the Ni—N ones and the C—N bond distance of the π-bonded group is the longest found, rather close to a single C—N bond length.

Bis(trifluoromethyl)diazomethane, $(CF_3)_2CNN$, reacts at room temperature with $[Ni(PPh_3)_2(C_2H_4)]$ to yield a complex which has been assigned the structure (**42**).[202] Complex (**43**) has been obtained by reaction (37).[199] The N=C=C group in complex (**43**) is severely distorted from linearity upon coordination.

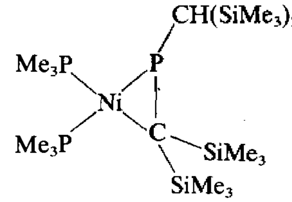
Phosphaalkene ($RP{=}CR'_2$) complexes, whose structures are similar to that of complex (**44**), have recently been reported.[195,203]



(**42**)



(**43**)



(**44**)

$$Ni(CNBu^t)_4 + N_2C(CN)_2 \xrightarrow[-78\,^\circ C]{Et_2O} \underset{\text{purple}}{[Ni\{N_2C(CN)_2\}(CNBu^t)_3]} \xrightarrow[-N_2]{-10\,^\circ C} [Ni(CNBu^t)_2\{Bu^tN{=}C{=}C(CN)_2\}] \quad (37)$$

50.2.6.3 Diazene (RN=NR), diazenato (RN=N) and tetraazadiene complexes and related compounds

The first diazene complexes of nickel(0), namely $[Ni(CNBu^t)_2(PhNNPh)]$ and $[Ni(PR_3)_2(PhNNPh)]$ ($PR_3 = PMe_3$, PBu_3, PPh_3) were simultaneously prepared by Otsuka and co-workers[204,205] and Klein and Nixon[154] according to equations (38)–(40).

$$Ni(CNBu^t)_2 + PhN{=}NPh \xrightarrow[r.t.]{ether/N_2} [Ni(CNBu^t)_2(PhNNPh)] \quad (38)$$

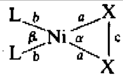
$$[NiCl_2(PR_3)_2] + PhN{=}NPh + Li \xrightarrow{THF} [Ni(PR_3)_2(PhNNPh)] + LiCl \quad (39)$$

$$R = Me, Bu, Ph$$

$$Ni(PPh_3)_4 + PhN{=}NPh \longrightarrow [Ni(PPh_3)_2(PhNNPh)] + PPh_3 \quad (40)$$

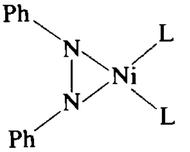
Table 12 Some Molecular Parameters for Diazene, Diazenato and Related Complexes

Compound		*IR bands* $\nu(CN)$ (cm^{-1})	*Bond distances*[a] (pm) *a*	*b*	*c*	*Bond angles*[a] (°) α	β	*Ref.*
$[Ni(CNBu^t)_2(PhNNPh)]$	(**45**)	2168, 2140	190 (N)	184 (C)	139 (N)	42.8	101.8	206
$[Ni(PTol_3)_2(PhNNPh)]$	(**46**)	—	193 (N)	220 (P)	137 (N)	41.6	107.4	208
$[Ni(CNBu^t)_2DAF]^b$	(**48**)	2180, 2158	187, 183 (N)	184 (C)	125 (N)	39.2	100.4	209
$[Ni(CNBu^t)_2KIM]^c$	(**49**)	2180, 2160	186, 184 (N)	188, 182 (C)	125 (CN)	39.5	105.4	199

[a] 

[b] DAF = diazofluorene.
[c] KIM = $Me_3CN{=}C{=}C(CN)_2$

The orange-red $[Ni(CNBu^t)_2(PhNNPh)]$ and the dark red $[Ni(PR_3)_2(PhNNPh)]$ complexes are diamagnetic and extremely air-sensitive compounds. The structural features of the most relevant diazene complexes are shown in Table 12 together with the IR stretching frequencies. The X-ray crystal structures of the complexes $[Ni(CNBu^t)_2(PhNNPh)]$ (**45**)[206,207] and $[Ni(PTol_3)_2(PhNNPh)]$ (**46**),[208] prepared according to reaction (38) with PR_3 in place of RNC, showed that the nickel atom is nearly square planar and is bonded to two nearly equidistant nitrogen atoms and two carbon or phosphorus atoms. The —N=N— group is symmetrically coordinated to the L_2Ni moieties and the N—N distances (137–139 pm) are significantly longer than the N=N double bond (124–126 pm). INDO calculations ascribed the observed lengthening of the N—N bond to σ donation and π back-donation effects.[169]



(**45**) L = $CNBu^t$
(**46**) L = $(p\text{-tolyl})_3P$

The visible absorption bands of a series of azobenzene complexes are reported in Table 13. It has been noted that the visible band shifts to higher energy on increasing the σ basicity of the coligand L.[208]

Table 13 Visible Absorption Bands of Various Azobenzene Species[208]

	λ_{max} (nm)
$[NiL_2(PhN{=}NPh)]$	
L = PPh_3	526
L = $P(C_6H_4Me)_3$	523
L = PPh_2Et	505
L = $PPhEt_2$	500
L = PMe_3	489
L = PBu_3	482
L = $CNBu^t$	465
PhN=NPh	440

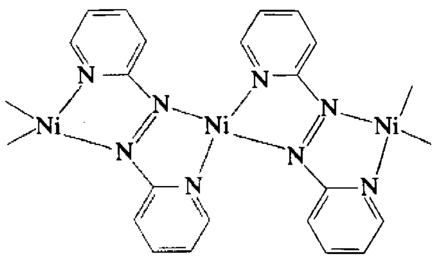
Together with azobenzene, other diaryldiazenes have also been found to form complexes with nickel(0) and PEt_3. All the complexes are air-unstable and have been prepared in rigorous anhydrous and oxygen-free conditions according to equation (41).[210]

$$Ni(cod)_2 + RN{=}NR + PEt_3 \xrightarrow[\text{r.t.}]{\text{hexane}} [Ni(PEt_3)_2RN{=}NR] \quad (41)$$

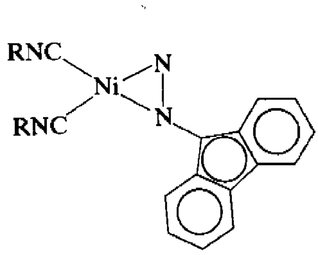
R = p-MeC_6H_4, p-FC_6H_4, p-$EtOC_6H_4$, p-$Me_2NC_6H_4$, 3,5-$Me_2C_6H_3$, p-$H_2NC_6H_4$

On increasing the electron-donor ability of the substituents on the phenyl rings the stability of the $NiL_2(RNNR)$ complexes is going to decrease. With the 2,2′-azapyridine a complex has been reported for nickel(0) for which a polymeric structure (**47**) has been suggested.[210]

Aryldiazenato complexes of nickel(0) have been prepared using reaction (38) at −78 °C with the neutral azo molecules tetrachlorodiazocyclopentadiene ($N_2C_5Cl_4$) and diazofluorene ($N_2C_{13}H_8$) in the place of azobenzene.[209,211]



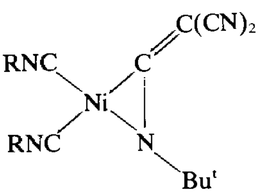
(47)



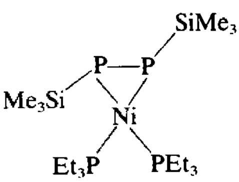
(48)

The X-ray crystal structure of the diazofluorene complex (**48**) showed that the two Ni—N bond distances are slightly, but significantly, different. Relevant bond distances and angles are reported in Table 12 (the shorter Ni—N bond distance in Table 12 refers to the N atom bonded to the aryl residue). The N—N bond distance is 12 pm shorter than that observed in the free ligand and is comparable with an N═N double bond.

The ketenimine complex [Ni(CNBu^t)$_2$(Bu^{t}N═C(CN)$_2$)] (**49**) has been prepared by reaction of Ni(CNBu^t)$_4$ and diazocyanomethane, $N_2C(CN)_2$.[199]



(49)



(50)

The reaction of LiP(SiMe$_3$)$_2$ with NiCl$_2$(PEt$_3$)$_2$ affords two air-sensitive compounds, namely [Ni(PEt$_3$)$_2$(PSiMe$_3$)$_2$] (**50**) and [Ni$_2$(PEt$_3$)$_2${P(SiMe$_3$)$_2$}$_2$].[212] The inner coordination of the nickel atom in complex (**50**) is nearly planar, with the Me$_3$SiPPSiMe$_3$ fragment symmetrically bonded to the nickel atom (Ni—P, 225 pm (av)). Actually the P—P bond distance is significantly shorter than that of a single P—P bond (222 pm) which might induce one to depict the bonding mode within the three-membered P$_2$Ni ring as the η^2-bonding of the hypothetical Me$_3$SiP═PSiMe$_3$ molecule.

The ν(CN) stretching frequencies of the diazo complexes are shown in Table 12. They are as high as that observed in the Bu^{t}NC group bonded to Ni^{II} and reflect the importance of π back-donation effects.

To date, the tetraazadiene species RN═N—N═NR have not been isolated as free molecules, but they have been found coordinated to a metal centre when aryl azides are reacted with nickel(0) complexes (equations 42 and 43).[213–215]

$$\mathrm{Ni(cod)_2 + ArN_3\ (excess)} \xrightarrow[-30\,^\circ\mathrm{C}]{\text{toluene}} \mathrm{[Ni(Ar_2N_4)_2] + cod + N_2} \quad (42)$$

$$\mathrm{Ar = 4\text{-}MeC_6H_4,\ 4\text{-}MeOC_6H_4,\ 3,5\text{-}Me_2C_6H_3}$$

$$\mathrm{Ni(cod)_2 + C_6F_5N_3\ (excess)} \xrightarrow[-35\,^\circ\mathrm{C}]{\mathrm{Et_2O}} \mathrm{[Ni(cod)\{(C_6F_5)_2N_4\}] + cod + N_2} \quad (43)$$

$$\downarrow \mathrm{PPh_3}$$

$$\mathrm{[Ni\{(C_6F_5)_2N_4\}(PPh_3)_2]}$$

$$\mathrm{Ni(Ar_2N_4)_2 + CNBu^t\ (excess)} \xrightarrow[\text{reflux}]{\text{toluene}} \mathrm{[Ni(Ar_2N_4)(CNBu^t)_2]} \quad (44)$$

$$\mathrm{Ni(cod)_2 + Ni(Ar_2N_4)_2} \xrightarrow[60\,^\circ\mathrm{C}]{\mathrm{CNBu^t}} \mathrm{[Ni(Ar_2N_4)(CNBu^t)_2]}$$

One molecule of tetraazadiene in the complex $Ni(Ar_2N_4)_2$ can be replaced by $CNBu^t$ groups (equation 44).[214,216,217] The structure of the complex $[Ni\{(3,5\text{-}Me_2C_6H_3)_2N_4\}_2]$ is pseudo-tetrahedral with the two planar Ar_2N_4 ligands orthogonal to each other. The N—N bond distances in the chelate rings are nearly equal with a mean value of 132 pm.[214]

50.2.6.4 Complexes with CO_2, CS_2 and related ligands

CO_2 is the most abundant source of carbon in the world, and the coordination chemistry of CO_2 has relevance in the field of environmental chemistry and in the search for alternative energy sources. The coordination chemistry of this potentially very important ligand is currently under investigation.

It is generally accepted that CO_2 is somewhat unreactive towards transition metal complexes and that the metal CO_2 linkage is favoured by a nucleophilic metal centre such as a tertiary phosphine metal(0) moiety.

The coordination chemistry of CO_2 has been reviewed in recent years[218–221] and we will report here only the most significant complexes.

The first authentic nickel(0) complex with coordinated CO_2 was prepared by following the rather simple procedures outlined in equations (45) and (46).[222] Oxygen and moisture are rigorously excluded from the reactant solutions, and CO_2 is bubbled at room temperature and atmospheric pressure. The analogous complexes with PEt_3 and PBu^n_3 were obtained following a similar procedure (equation 47).[223]

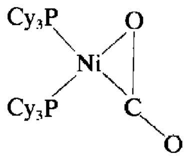
$$[\{Ni(PCy_3)_2\}_2N_2] + CO_2 \xrightarrow[\text{r.t.}]{\text{toluene, }Et_2O} [Ni(PCy_3)_2(CO_2)]\cdot 0.75C_7H_8 \quad (45)$$

$$[NiBr_2(PCy_3)_2] + CO_2 \xrightarrow[\text{r.t.}]{\text{toluene, Na}} [Ni(PCy_3)_2(CO_2)]\cdot 0.75C_7H_8 \quad (46)$$

$$Ni(PR_3)_4 + CO_2 \xrightarrow[-30\text{ to }-70\,^{\circ}C]{\text{toluene}} [Ni(PR_3)_2CO_2] \quad (47)$$

From a reaction analogous to reaction (45) a yellow complex, analyzed as $[\{Ni(PCy_3)_2\}_2CO_2]$, has also been obtained.[139] The complexes of formula $[Ni(PR_3)_2CO_2]$ are yellow to red-orange and are diamagnetic. They are moderately air-stable (decomposing in a few hours in the atmosphere) and easily lose CO_2 when treated in the solid state with I_2 or $P(OR)_3$ and when argon is bubbled into solutions of them.

Structural features of the most relevant complexes with CO_2 are shown in Table 14. The X-ray crystal structure of $[Ni(PCy_3)_2CO_2]$ (**51**) showed that CO_2 coordinates in an η^2 mode.[222] The coordinated CO_2 molecule is no longer linear and the C—O bond distance in the η^2-coordinated molecule is about 10 pm longer than that in the free molecule (116 pm), as already found for other η^2-bonded molecules.



(51)

Recent *ab initio* MO calculations showed that the main contributions to the Ni—CO bonding energies come from electrostatic and back-donative interactions between filled *d* orbitals on nickel and an empty π^* orbital on CO_2, while donative interaction gives a small contribution to the total energy. It has been also computed that back-bonding stabilizes the side-on coordination mode whereas electrostatic interaction favours the end-on coordination mode, and it has been concluded that when a metal has a considerable positive charge, as in $[Cu(PH_3)_2]^+$, the end-on coordination mode is preferred. A decrease in the OCO angle stabilizes the π^* orbital, thus favouring π back-bonding. The coordinated CO_2 molecule has been computed to have an OCO angle of 139°.[225]

Several attempts have been made to prepare CS_2 analogues of $[Ni(PR_3)_2CO_2]$

Table 14 Molecular Parameters for CO_2 and CS_2 Complexes

Complex	*IR bands* (cm^{-1}) $\nu(C{=}X)$ (*Nujol mull*)	*Bond distances* (pm)		*Bond angles* (°)		*Ref.*
$[Ni(PCy_3)_2CO_2]$	1740br, vs	Ni—C	184	O—C—O	133	222
	1698w	Ni—O	199	O—Ni—C	37	
		C—O (π)	122			
		C—O	117			
$[Ni(PPh_3)CS_2]_2$	1122s	Ni—C	181	S—C—S	137	224
		Ni—S (π)	216	S—Ni—C	47.5	
		Ni—S (σ-bridge)	215			
		C—S (π)	163			
		C—S (σ-bridge)	168			

complexes.[219,220] Deep red compounds having the elemental formula $Ni(PR_3)CS_2$ have been prepared according to reactions (48)–(51).[219,226,227]

$$[Ni(PPh_3)_2(CO)_2] \xrightarrow[\text{reflux}]{CS_2} [Ni(PPh_3)(CS_2)] + CO_2 \quad (48)$$

$$[Ni(cod)_2] + PR_3 + CS_2 \xrightarrow[\text{r.t.}]{\text{THF}} [Ni(PR_3)(CS_2)] + cod \quad (49)$$

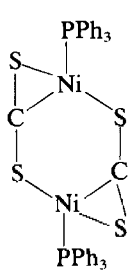
$$R = Ph, Tol, Cy$$

$$[Ni(PPh_3)_2(C_2H_4)] + CS_2 \longrightarrow [Ni(PPh_3)(CS_2)] + C_2H_4 \quad (50)$$

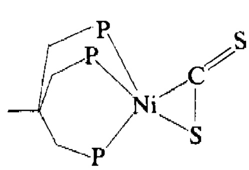
$$[Ni(PPh_3)_2(C_3Ph_3)]BPh_4 + CS_2 \xrightarrow{CH_2Cl_2} [Ni(PPh_3)(CS_2)] \quad (51)$$

(52)

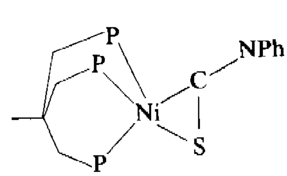
The X-ray crystal structure of complex $Ni(PPh_3)(CS_2)$ (**52**) (Table 14) has shown that it is a dinuclear complex, where each CS_2 group is η^2-bonded to a nickel atom and σ-bonded to the other nickel atom through the second sulfur atom. The inner coordination around the nickel atom is nearly planar.[224] The C—S π-bond distances are significantly shorter than the C—S σ-bond ones, and the $(NiCS)_2$ six-membered ring is substantially planar. The complex $[Ni(p_3)CS_2]$ has been prepared as outlined in equation (52).[228]



(52)



(53)



(54)

$$[Ni(p_3)_2] + CS_2 \xrightarrow[\text{r.t.}]{\text{EtOH}} [Ni(p_3)(CS_2)] + p_3 \quad (52)$$

(53)

$$[Ni(p_3)(CS_2)] + PhNCS \xrightarrow[\text{r.t.}]{CH_2Cl_2} [Ni(p_3)(PhNCS)]\cdot 0.5CH_2Cl_2 + CS_2 \quad (53)$$

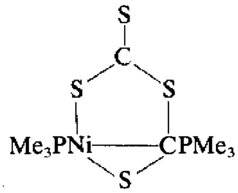
(54)

The reaction of complex (**53**) with PhNCS affords the analogous complex (**54**; equation 53) whose X-ray structure has been determined.[229] In these cases the two heteroallenes PhNCS and CS_2 behave similarly towards the $Ni(p_3)$ moiety.

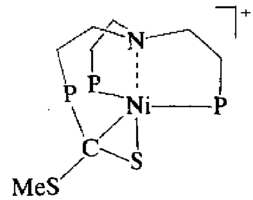
CS_2 has also been found to react with tertiary phosphine bound to nickel(0) and to afford phosphoniodithiocarboxylato linkages (equations 54 and 55, structures **55**[226] and **56**[230]).

$$\mathrm{Ni(cod)_2 + 2PR_3 + 2CS_2 \longrightarrow [Ni(PR_3)\{SC(S)SC(PR_3)S\}]} \quad R = Me, Et \tag{54}$$

$$\mathrm{Ni(np_3) + MeOSO_2F \xrightarrow[NaBPh_4]{CS_2} [NiPhPCH_2CH_2N(CH_2CH_2PPh_2)_2(CS_2Me)]BF_4} \tag{55}$$

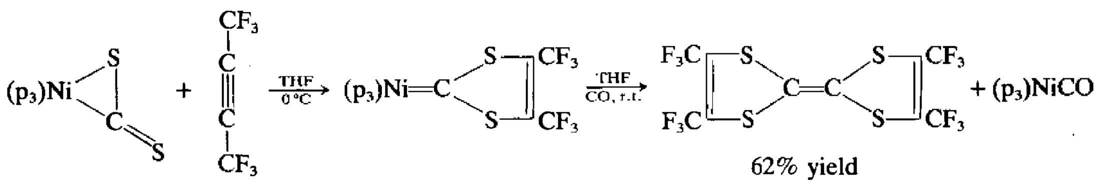


(55)



(56)

$[Ni(p_3)(CS_2)]$ has been found to react with hexafluorobut-2-yne and subsequently with CO giving tetrakis(trifluoromethyl)tetrathiafulvalene.[231] The reaction route is shown in Scheme 1.



Scheme 1

50.2.7 Complexes with Dinitrogen and Dioxygen

50.2.7.1 Complexes with dinitrogen

Nickel complexes with dinitrogen are quite rare.[232–234] The knowledge of the structure and bonding of dinitrogen in transition metal complexes may however be of fundamental importance for the understanding of the mechanism of biological fixation of nitrogen and for the general problem of the reduction of elemental dinitrogen under milder conditions than those needed in the Haber–Bosch process for the synthesis of ammonia.

The first nickel(0) complex containing coordinated dinitrogen, $[\{Ni(PCy_3)_2\}_2N_2]$, was prepared by Jolly and Jonas in 1968, as an unstable dark-red compound (equation 56).[235]

The same complex can be prepared using other different procedures involving either the reduction of Ni^{II} compounds or the reaction of gaseous N_2 with coordinatively unsaturated nickel(0) complexes (equations 57 and 58).[75,139] The formation of dinitrogen adducts of the type $[Ni(PR_3)_3N_2]$ ($R = Et$,[52] Bu^n [75]) has been claimed to occur in solutions of $Ni(PR_3)_3$ complexes saturated with N_2 (equation 59) on the basis of IR ($\nu(N_2)$ stretch assigned at $2074\ cm^{-1}$) and ^{31}P NMR spectra.[228] The dinitrogen molecule in these complexes is labile and can easily be replaced by ligands such as phosphines, CO and alkenes.

$$\mathrm{Ni(acac)_2 + 4PCy_3 + AlMe_3 \xrightarrow[-20/+20\,^\circ C]{toluene/N_2} [\{Ni(PCy_3)_2\}_2N_2]} \quad 40\%\ \text{yield} \tag{56}$$

$$\mathrm{[NiBr_2(PCy_3)_2] + Na\ (sand) \xrightarrow[20\,^\circ C]{toluene/N_2} [\{Ni(PCy_3)_2\}_2N_2]} \quad 50\%\ \text{yield} \tag{57}$$

$$\mathrm{[Ni(PCy_3)_2(C_2H_4)] + PCy_3 \xrightarrow[100\,^\circ C]{toluene/Ar} Ni(PCy_3)_3 \xrightarrow{toluene/N_2} [\{Ni(PCy_3)_2\}_2N_2]} \quad 34\%\ \text{yield} \tag{58}$$

$$\mathrm{Ni(PR_3)_3 \underset{Ar}{\overset{N_2}{\rightleftharpoons}} [Ni(PR_3)_3N_2]} \quad R_3 = Et_3, Bu^n_3, Et_2Ph \tag{59}$$

Relevant bond distances and angles of dinitrogen complexes whose X-ray structure has been determined are shown in Table 15. The complex $[\{Ni(PCy_3)_2\}_2N_2]$ (Figure 1) is dimeric, with the N_2 molecule coordinated end-on to the two nickel atoms. Each nickel atom is surrounded by four cyclohexyl groups of the phosphine ligands which give some steric protection.[227] IR, ^{31}P and ^{1}H NMR spectra indicate that in toluene solutions of this complex the equilibrium shown in equation (60) operates.[236]

Table 15 Molecular Parameters for Dinitrogen and Dioxygen Complexes

	IR bands (cm^{-1}) $\nu(N_2)$ *(benzene soln)*	*Bond distances*[a] (pm) *N—N*	*Ni—N*	*Ni—P*	*Bond angles*[b] (°) *NiNN*	*Ref.*
$[\{Ni(PCy_3)_2\}_2N_2]$	2028	112	178	218	178	139
	$\nu(O_2)$ *(Nujol mull)*	*O—O*	*Ni—O*	*Ni—C*	*ONiO*	
$[Ni(CNBu^t)_2O_2]$	895	145	181	184	47	29

[a] Bond distances (pm) in free molecules: N_2, 109.8; O_2, 121.
[b] The framework of the two P—Ni—P groups forms a dihedral angle of 105°.

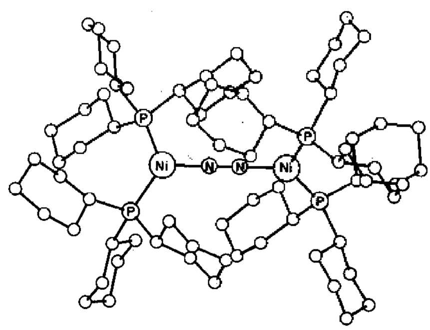


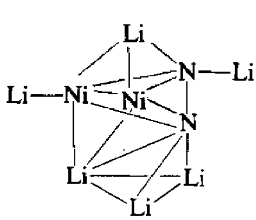
Figure 1 The complex $[\{Ni(PCy_3)_2\}_2N_2]$

$$[\{Ni(PCy_3)_2\}_2N_2] \rightleftharpoons [Ni(PCy_3)N_2] + PCy_3 \quad (60)$$

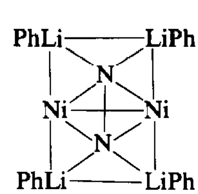
Unusual and complicated dinitrogen complexes have been reported to be formed by reactions (61)[237,238] and (62).[239] In both complexes (**57**) and (**58**) the N_2 molecules are bound in a side-on mode to nickel atoms. The N—N bond distances (135 pm and 136 pm, respectively) are the longest ones found in any complex with coordinated dinitrogen.

$$2Ni(CDT) + 6PhLi \xrightarrow[0\,°C]{Et_2O/N_2} \underset{(\mathbf{57})}{[\{Ni(PhLi)_3\}_2N_2{\cdot}2H_2O]_2} \quad (61)$$

$$Ni(CDT) + (NaPh)_{3.36}{\cdot}(LiPh){\cdot}0.6Et_2O \xrightarrow[-78\ to\ 0\,°C]{Et_2O/N_2} \underset{(\mathbf{58})}{[Ph(NaOEt_2)_2(Ph_2Ni)_2(N_2)NaLi_6(OEt)_4OEt_2]_2} \quad (62)$$



(**57**) Ni—N, 193–194 pm
N—N, 135 pm

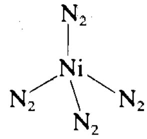


(**58**) Ni—N, 275 pm
N—N, 136 pm

Part of the inner coordination showing reciprocal interactions of Li, Ni and N in complexes (**57**) and (**58**)

A special technique which has yielded highly unstable and simple dinitrogen complexes trapped in low-temperature solids (N_2 or Ar) is the metal atom cocondensation technique in low-temperature matrices. By the cocondensation of nickel atoms and N_2 at 4.2–10 K the binary compounds $Ni(N_2)_n$ ($n = 1$–4) result, whose structure has been inferred from IR and

Raman spectra.[240,241] $Ni(N_2)_4$ (**59**) has been assigned a regular tetrahedral geometry in Ar matrix and a slightly distorted tetrahedral geometry in N_2 matrix, with end-on-bonded dinitrogen.[241]



(**59**)

In the presence of a mixture of N_2 and O_2 the species $Ni(N_2)_n(O_2)$ ($n = 1, 2$) were identified.[242] It has been proposed that O_2 is coordinated to nickel in a side-on mode, while the dinitrogen is coordinated end-on.

In cocondensation experiments of nickel atoms in various CO/N_2 matrices, mixed carbonyl–dinitrogen species $Ni(CO)_x(N_2)_{4-x}$ ($x = 1$–3) were observed.[243] The $Ni(CO)_3(N_2)$[244,245] species was also generated by the UV photolysis of $Ni(CO)_4$ in N_2-doped liquid Kr, and the decay kinetics were studied.[246] The Ni—N_2 dissociation energy was estimated to be about 42 kJ mol^{-1}.

Recent *ab initio* MO calculations on the complex $[Ni(N_2)(O_2)]$ showed that the end-on and side-on geometries have similar total energies, with the end-on configuration stabilized mainly by σ donation.[247]

The existence of side-on dinitrogen bonded to nickel in the structures (**57**) and (**58**) has recently been explained within the EH formalism in terms of π back-bonding interactions.[248]

50.2.7.2 Complexes with dioxygen

Nickel complexes containing coordinated dioxygen are rarer than those with dinitrogen.[249–252] Interest in the coordination chemistry of molecular oxygen comes from the importance of understanding the biological mechanism of oxygen transport and oxidase function, as well as in the industrial field of homogeneous catalysis of oxidation reactions.

The first reported nickel complexes with coordinated dioxygen were prepared according to equations (63), (64)[253] and (65)[26,254–256]

$$[Ni(PR_3)_2(C_2H_4)] \xrightarrow[-78\,°C]{Et_2O/O_2} [Ni(PR_3)_2O_2] \quad (63)$$

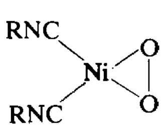
$$R = Ph, Cy$$

$$Ni(PPh_3)_4 \xrightarrow[-78\,°C]{Et_2O/O_2} [Ni(PPh_3)_2O_2] \quad (64)$$

$$Ni(CNBu^t)_4 \xrightarrow[-20\,°C]{Et_2O/O_2} [Ni(CNBu^t)_2O_2] \quad (65)$$

(**60**)

The complexes $[Ni(PR_3)_2O_2]$ are generally air-unstable and decompose in solution at temperatures greater than −30 °C. Only complex (**60**) has been obtained, as a pale green crystalline product with considerable thermal stability. It is diamagnetic. The nickel atom is in a planar environment of two carbon and two oxygen atoms, the dioxygen being coordinated in the side-on mode with an O—O distance as large as 145 pm.



(**60**)

INDO calculations on these complexes[257] gave a net stabilization of the planar geometry over the tetrahedral one. The nickel–dioxygen bond was formed primarily through the donation and back-donation of electrons using the π_u and π_g^* oxygen orbitals parallel to the molecular plane.

A number of reactions which demonstrate the reactivity of the coordinated O_2 molecule have been carried out starting from complex (**60**). The reaction of (**60**) with Bu^tNC, PPh_3 and CO results in transfer of oxygen to the added ligand molecule (equations 66–68).[26,27] These reactions occur by cleavage of the O—O bond. When the reactant is electrophilic, reaction (69) occurs.[26]

$$(\mathbf{60}) + 4CNBu^t \xrightarrow[\text{r.t.}]{\text{toluene}} Ni(CNBu^t)_4 + 2Bu^tNCO \qquad (66)$$

$$(\mathbf{60}) + 4PPh_3 \xrightarrow[\text{r.t.}]{\text{toluene}} [Ni(CNBu^t)_2(PPh_3)_2] + 2PPh_3O \qquad (67)$$

$$(\mathbf{60}) + 4CO \xrightarrow[-30\,^{\circ}C]{\text{PhCl}} [Ni(CO)_2(CNBu^t)_2] + 2CO_2 \qquad (68)$$

$$(\mathbf{60}) + (CN)_2C{=}C(CN)_2 \longrightarrow [Ni(CNBu^t)_2\{(CN)_2C{=}C(CN)_2\}] + O_2 \qquad (69)$$

Another series of oxygen transfer reactions involves neutral molecules such as N_2O_4, NO, CO_2 and SO_2, with formation of anionic species coordinated to nickel(II) (equations 70–73).[27]

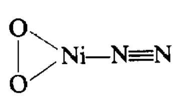
$$(\mathbf{60}) + N_2O_4 \xrightarrow[-30\,^{\circ}C]{CH_2Cl_2} [Ni(ONO_2)_2(CNBu^t)_2] \qquad (70)$$

$$(\mathbf{60}) + NO + CNBu^t \xrightarrow[-30\,^{\circ}C]{CH_2Cl_2} [Ni(NO)(CNBu^t)_3]NO_3 \qquad (71)$$

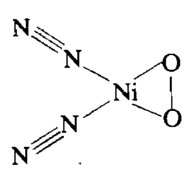
$$(\mathbf{60}) + CO_2 + CNBu^t \xrightarrow[-30\,^{\circ}C]{\text{toluene}} [Ni(OCO_2)(CNBu^t)_2] + Bu^tNCO \qquad (72)$$

$$(\mathbf{60}) + SO_2 \xrightarrow[-20\,^{\circ}C]{n\text{-hexane}} [Ni(O_2SO_2)(CNBu^t)_2] \qquad (73)$$

Cocondensation reactions of nickel atoms with oxygen or oxygen–argon mixtures at 4.2–10 K afforded dioxygen complexes of the type $Ni(O_2)$ and $Ni(O_2)_2$ containing side-on-coordinated dioxygen.[258] When a mixture of O_2, N_2 and Ar at 6–10 K is employed, the products of cocondensation are the species $Ni(O_2)(N_2)_n$ ($n = 1, 2$) (**61**, **62**) containing end-on-coordinated nitrogen and side-on-coordinated oxygen.[242]



(**61**)



(**62**)

50.2.8 Miscellaneous Complexes of Nickel(0)

50.2.8.1 Complexes with sulfur dioxide

SO_2, as a ligand, exhibits amphoteric nature, behaving as either a Lewis base or a Lewis acid and correspondingly giving rise to η^1-planar or η^1-pyramidal (or bent) coordination modes.[259,260]

The reduction of $[NiBr(np_3)]^+$ with BH_4^- in the presence of SO_2 (equation 74) results in the formation of the complex $[Ni(np_3)(SO_2)]$ (**63**)[261] which contains SO_2 coordinated in a bent mode. With the p_3 ligand the same reaction occurs without reducing agents, since the triphosphine itself can reduce nickel(II) (equation 75).

$$[NiBr(np_3)]^+ + BH_4^- + SO_2 \xrightarrow[\text{r.t.}]{\text{EtOH, THF}} [Ni(np_3)(SO_2)] \qquad (74)$$

$$Ni(H_2O)_6(BF_4)_2 + p_3 + SO_2 \xrightarrow[0\,^{\circ}C\text{ to r.t.}]{\text{EtOH, acetone}} [Ni(p_3)(SO_2)] \qquad (75)$$

SO_2 complexes with PPh_3 have been also described.[262] They have been prepared using reactions (76) and (77). A complex of formula $[Ni(CNBu^t)_3(SO_2)]$ has been prepared according to reaction (78).[257] It reacts with dioxygen to give the sulfato nickel(II) complexes according to reaction (79).

$$[Ni(CO)_2(PPh_3)_2] + SO_2 \xrightarrow[\text{r.t.}]{\text{benzene/heptane}} [Ni(PPh_3)_2(SO_2)_2] \tag{76}$$

$$Ni(PPh_3)_4 + PPh_3\ (\text{excess}) + SO_2 \xrightarrow{\text{benzene/heptane}} [Ni(PPh_3)_3(SO_2)] \tag{77}$$

$$Ni(CNBu^t)_4 + SO_2 \xrightarrow[-20\text{ to }0\,^\circ C]{\text{hexane}} [Ni(CNBu^t)_3(SO_2)] + CNBu^t \tag{78}$$

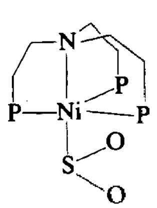
$$[Ni(CNBu^t)_3(SO_2)] + O_2 \xrightarrow[-60\text{ to }-20\,^\circ C]{\text{toluene}} [Ni(SO_4)_2(CNBu^t)_2] + CNBu^t \tag{79}$$

The nickel(0) complexes with coordinated SO_2 are, in general, air-unstable, diamagnetic compounds.

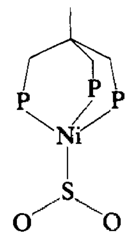
Relevant structural features of the SO_2 complexes are collected in Table 16 together with the IR absorption frequency of SO_2. In complex (**63**) the nickel atom is in a distorted trigonal bipyramidal environment,[250] with a bent coordinated SO_2 molecule, while in $[Ni(p_3)(SO_2)]$ (**64**) SO_2 is coplanar with nickel which achieves a distorted pseudotetrahedral structure.[228]

Table 16 Molecular Parameters for SO_2 Complexes of Nickel(0)

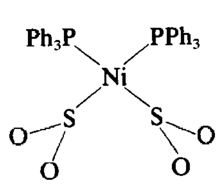
Complex	*IR bands* (cm^{-1}) $\nu(SO_2)$ (*Nujol mull*)	*Bond distances* (pm) *Ni—S*	*Ni—P*	*Ni—N*	*S—O*	*Bond angles* (°) *O—S—O*	*Ni—S—O*	*Ref.*
$[Ni(np_3)SO_2]$	1115, 1005	234	225	232	131	112	106	250
$[Ni(p_3)SO_2]$	1190, 1055, 1045	201	220	—	137	109	125	252
$[Ni(PPh_3)_3SO_2]$	1205, 1055	204	223	—	145	113	—	251
$[Ni(PPh_3)_2(SO_2)_2]$	1288, 1278, 1120, 1113	207	224	—	132, 142	112, 119	—	251
$[Ni(CNBu^t)_3(SO_2)]$	1208, 1060	211	—	—	147	110	123	246



(**63**)



(**64**)



(**65**)

A nearly planar coordination mode has also been found for the PPh_3 complexes (**65**).[259] Some general considerations on the binding mode of the SO_2 molecule have been published.[261,228]

50.2.8.2 Complexes with coordinated P_4, P_4S_3 and P_4Se_3

By reducing hydrated nickel(II) nitrate with $NaBH_4$, in the presence of the tetradentate tripodal ligand np_3 (equation 80), the complex $[Ni(np_3)]$ (**66**) has been obtained.[263] Complex (**66**) undergoes oxidative reaction with $HClO_4$ or HBF_4 to afford the nickel(II) hydrido complex $[NiH(np_3)]^+$.[264] It also reacts with CO to give the carbonyl derivative[263] and with white phosphorus to give the complex $[Ni(np_3)(\eta^1\text{-}P_4)]$ (**67**) containing the *η^1-tetrahedro*-tetraphosphorus (equations 81–84).[265]

$$Ni(H_2O)_6(NO_3)_2 + np_3 \xrightarrow[\text{acetone/EtOH, 50 °C}]{\text{NaBH}_4\text{ excess}} [Ni(np_3)] \quad (80)$$

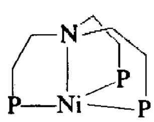
$$[Ni(np_3)] \xrightarrow{\text{THF/EtOH + HClO}_4} [NiH_x(np_3)]ClO_4 \quad (81)$$

$$[Ni(np_3)] \xrightarrow[\text{r.t.}]{\text{THF/EtOH + CO}} [Ni(CO)(np_3)] \quad (82)$$

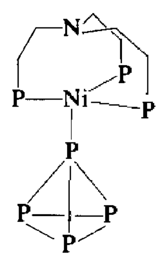
$$[Ni(np_3)] \xrightarrow[\text{0 °C}]{\text{THF + P}_4} [Ni(np_3)(\eta^1\text{-}P_4)] \quad (83)$$

$$[Ni(np_3)] \xrightarrow[\text{40 °C}]{\text{C}_6\text{H}_6\text{/THF + P}_4\text{X}_3} [Ni(np_3)(\eta^1\text{-}P_4X_3)] \quad (84)$$

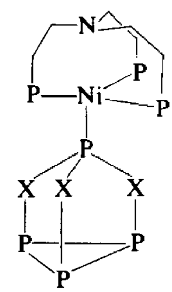
X = S, Se



(**66**)



(**67**)



(**68**) X = S, Se

The coordination of nickel in complex (**67**) is nearly regular tetrahedral with the coordinated tetraphosphorus molecule having a slightly elongated pyramidal geometry (P_{basal}—P_{basal}, 209 pm; P_{basal}—P_{apical}, 220 pm) with respect to the regular tetrahedral geometry of the free P_4 molecule (P—P, 221 pm).[266]

In the complexes $[Ni(np_3)(\eta^1\text{-}P_4X_3)]$ (X = S, Se) (**68**)[266] the intact molecules P_4S_3 and P_4Se_3 are bound to the nickel through the apical phosphorus atoms.[266,267]

Complexes (**67**) and (**68**) are only slightly sensitive to aerial oxidation in the solid state, and are insoluble in common organic solvents.

50.2.9 Some Examples of Oxidative Addition Reactions to Nickel(0) Complexes

In this section we will briefly report some examples of oxidative addition reactions to nickel(0) compounds which yield nickel(I) and nickel(II) compounds.

Some complexes of nickel(0) with phosphines have been found to react with several Brönsted acids in non-aqueous solvents and under an inert atmosphere to give hydrido complexes of nickel(I) and nickel(II) (equations 85–87).[264,268,269]

$$[Ni(np_3)] + HClO_4 \xrightarrow[\text{r.t.}]{\text{THF, EtOH}} [NiH_x(np_3)ClO_4] \quad (85)$$

$x = 1$

$$[Ni(PCy_3)_2] + HX \xrightarrow[\text{r.t.}]{\text{toluene, Et}_2\text{O}} [NiH(X)(PCy_3)_2] \quad (86)$$

HX = HCl, $MeCO_2H$, PhOH

$$[Ni\{C_2H_4(PPh_2)_2\}_2] + AlCl_3 + HCl \xrightarrow[\text{r.t.}]{\text{toluene}} [NiH\{C_2H_4(PPh_2)_2\}_2]AlClO_4 \quad (87)$$

$$NiL_n + RX \longrightarrow NiX(R)L_2 \quad (88)$$

R = alkyl, aryl, acyl
X = halide or pseudohalide
L = phosphine ligand

Phosphino complexes of nickel(0) such as $Ni(PPh_3)_4$, $Ni(PEt_3)_3$ and $Ni(PCy_3)_2$ have been found to react easily at room temperature with PhX (X = Cl, I), MeI, EtBr and other organohalogens or pseudohalogens affording nickel(II) compounds (equation 88).[139,270–272]

Similar reactions occur with organonitrile compounds such as PhCN,[273] while the reaction of PhCOCl with $Ni(PPh_3)_4$ gives the compound $[NiCl(Ph)(PPh_3)_2]$ with spontaneous evolution of CO.[270,271] The oxidative addition of a variety of *para*-substituted aryl halides to $Ni(PEt_3)_3$ solutions affords the diamagnetic $[NiX(aryl)(PEt_3)_2]$ and paramagnetic $[NiX(PEt_3)_2]$ derivatives in variable amounts which depend on the reaction conditions.[272] The oxidation of $[Ni(bipy)(PPh_3)_2]$ by alkyl or aryl iodides or bromides yields nickel(I) complexes of the type $[NiX(bipy)(PPh_3)]$.[274]

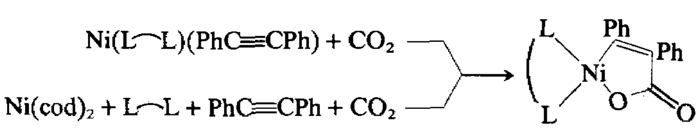
The reaction of $Ni(P—P)_2$ and PhCN (equation 89) is reversible, the reductive elimination of PhCN being easily induced by refluxing [Ni(CN)(Ph)(P—P)] in the presence of the diphosphine.[275]

$$Ni(P—P)_2 + PhCN \underset{-PhCN}{\overset{-P—P}{\rightleftharpoons}} [Ni(CN)(Ph)(P—P)] \qquad (89)$$

$$P—P = (Et_2P)_2(CH_2)_4$$

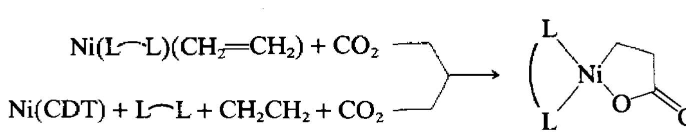
The kinetics of the oxidative addition of nitriles to $Ni(P—P)_2$ have been studied. The organocyano nickel(II) complexes presumably have a dinuclear structure with *trans* planar coordination for the nickel atom.[276] Some of the $[Ni(CN)(R)(PR_3)_2]$ compounds (R = alkyl, aryl) are unstable and therefore cannot be isolated in the solid state. Their decomposition in solution promotes the formation of alkanes, alkenes, diphenyl, *etc.*[277]

Carbon dioxide reacts either with alkene and alkyne complexes of nickel(0) or with free alkenes and alkynes in the presence of nickel(0) complexes, giving five-membered cyclic nickel(II) complexes (equations 90 and 91).[278]



(90)

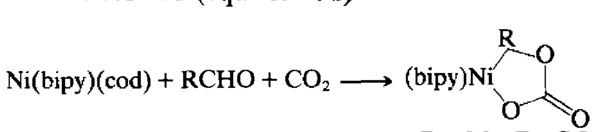
L⌒L = Me_4en, bipy, $Cy_2PCH_2CH_2PCy_2$



(91)

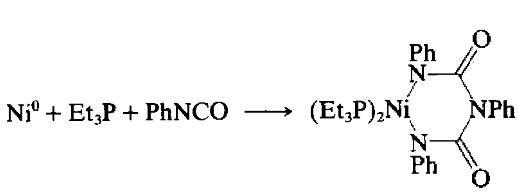
The same reactions have also been carried out with 1,3-dienes and cyclic nickelacarboxylates have been obtained.[279]

The reactions of CO_2 with aliphatic aldehydes in the presence of Ni(bipy)(cod) have been studied. As the result of oxidative coupling of CO_2 and RCHO on the Ni(bipy) moiety, five-membered metallacycles are formed (equation 92).[280,281]

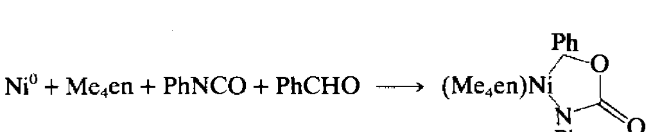


(92)

R = Me, Et, C_6H_{13}



(93)



(94)

Head–tail linkage of PhNCO occurs in the presence of Ni(L) to give five- or six-membered nickelacycles, depending on whether L is Me_4en or $2Et_3P$.[282] Similar reactions carried out in the presence of aldehydes afford the condensation of PhNCO with PhCHO to give oxazanickelacyclopentanones (equations 93 and 94).[283]

50.3 COMPLEXES WITH η^3-BONDED SPECIES

In this section we will briefly review some complexes of nickel with η^3-coordinated fragments or molecules. In this case the assignment of an oxidation number to the nickel atom in a formal sense may be questionable, owing to the extensive rearrangement of the electronic distribution in the molecule with respect to the starting species.

Structural features of the most relevant complexes are shown in Tables 17 and 18.

Table 17 Structural Data for some Complexes Containing the C_3Ph_3 Fragment Coordinated to the Nickel Atom

	Bond distances[a] (pm)							
Complex	*Ni—C¹*	*Ni—C²*	*Ni—C³*	*Ni—P (av)*	*C¹—C³*	*C¹—C²*	*C²—C³*	*Ref.*
$[Ni(C_3Ph_3)(PPh_3)_2]PF_6$	190	201	206	224	142	144	133	285
$[Ni(C_3Ph_3)(p_3)]ClO_4$	204	204	201	231	141	142	140	286
$[Ni(C_3Ph_3)pp_2pO]BPh_4$	205	195	200	228	138	138	139	286
				Ni—N (av)				
$[Ni(C_3Ph_3)py_2Cl]$	190	197	196	202	142	143	141	287
				Ni—C (C_5H_5)				
$[Ni(C_3Ph_3)(C_5H_5)]$	195	196	197	210	142	143	144	288

[a] The indices refer to formula (**69**).

Table 18 Molecular Data for Complexes Containing the η^3-P_3 Fragment

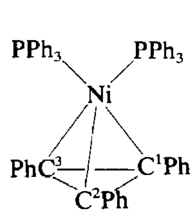
			Bond distances (av) (pm)			
Complex	*VEN*	μ_{eff} (BM)	*Ni—P (P_3)*	*Ni—P (η^3-P_3)*	*P—P*	*Ref.*
$[Ni_2(p_3)_2(\eta^3\text{-}P_3)](BPh_4)_2$	33	2.00	225	235	216	292
$[Ni,Co(p_3)_2(\eta^3\text{-}P_3)](BPh_4)_2$	32	3.14	224	233	216	292
$[Ni,Rh(p_3)_2(\eta^3\text{-}P_3)](BF_4)_2$[a]	32	1.50	221–234	231–256	215–231	295
$[Ni(p_3)(\eta^3\text{-}P_3)](BF_4)$	18	Diamagnetic	224	231	212	297

[a] For the highly distorted Ni,Rh complex, the range of values is given.

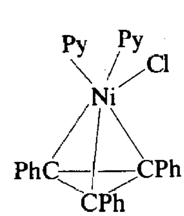
Complexes containing a coordinated cyclopropenyl fragment have been prepared using different synthetic procedures (always in an inert atmosphere) using the cyclopropenylium ion $(C_3Ph_3)ClO_4$ as starting reagent (equation 95).[284]

$$[Ni(C_2H_4)(PPh_3)] + (C_3Ph_3)ClO_4 \xrightarrow[C_6H_6,\ MeOH]{(Bu^n_4N)PF_6} [Ni(C_3Ph_3)(PPh_3)_2]PF_6 \qquad (95)$$

(**69**) 75% yield



(**69**)



(**70**)

Complex (**69**) is diamagnetic. Nickel is coordinated to two phosphorus atoms of the phosphines and to three carbon atoms of the C_3Ph_3 fragment which acts as a trihapto ligand.

The C_3Ph_3 fragment has been found to coordinate to nickel in an unsymmetrical fashion. It has an isosceles shape with the two carbon atoms at the base, which are linked together at a shorter bond distance, linked to the nickel at a longer distance than the apical carbon atom (Table 17). The NiP_2 plane is nearly perpendicular to the plane of the C_3 triangle.

Reactions of $[Ni(C_3Ph_3)(CO)Cl]$[289] with a variety of ligands (equations 96 and 97) led to neutral complexes containing the η^3-bonded fragment C_3Ph_3 and coordinated halide,[287,290] as shown by the structure of complex $[NiCl(C_3Ph_3)py_2]$ (**70**).[287]

$$[NiCl(C_3Ph_3)CO] \xrightarrow[\text{r.t.}]{2L,\ CH_2Cl_2} [NiCl(C_3Ph_3)L_2] \qquad (96)$$

$$L = THF, PR_3, P(OR)_3; L_2 = bipy$$

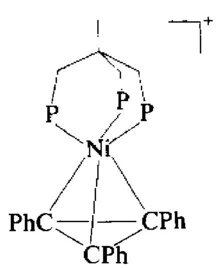
$$[NiCl(C_3Ph_3)CO] \xrightarrow{py} [NiCl(C_3Ph_3)py_2] \qquad (97)$$

By the metathetical reaction of complex (**69**) with some tridentate phosphine or arsine ligands, a number of complexes of the type $[Ni(C_3Ph_3)L]Y$ ($Y = ClO_4$, BPh_4, L = triphosphine, triarsine) have been obtained (equation 98).[286]

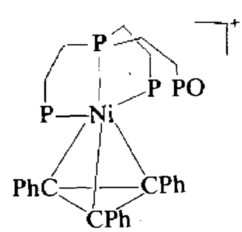
$$[Ni(C_3Ph_3)(PPh_3)]ClO_4 + L \xrightarrow[\text{r.t.}]{THF,\ Bu^tOH} [Ni(C_3Ph_3)L]ClO_4 \qquad (98)$$

$$L = Mep_3, p_3, ppp, pnp, as_3$$

In the complex $[Ni(C_3Ph_3)p_3]ClO_4$ (**71**), the nickel atom is coordinated to the three phosphorus atoms of the tridentate ligand and to the three carbon atoms of the C_3Ph_3 fragment. In contrast to complex (**69**), complex (**71**) contains a symmetrically bonded C_3Ph_3 fragment. The same coordination mode of C_3Ph_3 in all complexes obtained by equation (98) has been inferred from ^{13}C NMR studies.



(**71**)



(**72**)

Solutions of the complex $[Ni(C_3Ph_3)(pp_3)]BPh_4$, which is obtained by the method of equation (98), undergo aerial oxidation to give the complex $[Ni(C_3Ph_3)(pp_2pO)]BPh_4$ (**72**).[291] The nickel atoms in both complexes (**71**) and (**72**) are similarly coordinated to three phosphorus atoms. In complex (**72**) one arm of the original pp_3 ligand is not involved in coordination and has undergone oxidation. The coordination mode of $[C_3Ph_3]^+$ has been analyzed by Sacconi and co-workers,[285] within the framework of the EH model, in Ni, Pd and Pt complexes to provide a rationale for the observed geometrical distortions. The main interactions stabilizing the η^3-coordination mode in nickel complexes are both π donation from a full π orbital of the cyclopropenium cation to the LUMO of the NiL_2 fragment, and π back-donation from full $3d$ orbitals of NiL_2 to a π^* orbital of cyclopropenium as shown in Figure 2. This last interaction occurs between the b_1 and e'' orbitals and was found to be the most important one.

Hydrated nickel(II) salts in the presence of the ligand p_3 react with both white phosphorus and yellow arsenic, breaking up the structure of the tetraatomic P_4 and As_4 molecules to form triatomic *cyclo*-triphosphorus and *cyclo*-triarsenic species. These fragments act as trihapto ligands yielding double sandwich complexes (equation 99).[292] The compounds are air-stable both in the solid state and in solution. Upon reduction with $NaBH_4$ the complexes of equation

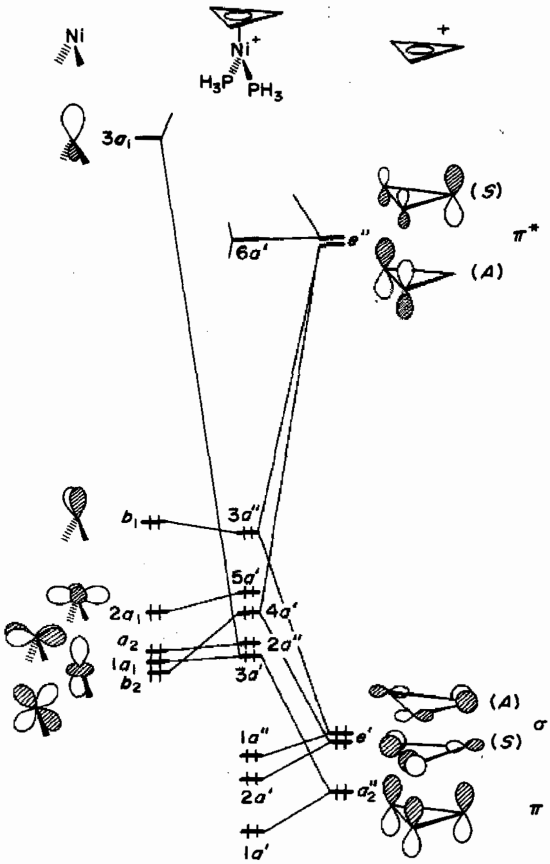


Figure 2 Orbital interaction diagram for the model complex $[Ni(C_3H_3)(PH_3)_2]^+$ (reproduced by permission of the American Chemical Society from ref. 285)

(99) give the diamagnetic monocation species $[Ni_2(p_3)(\eta^3\text{-}E_3)]BF_4$, whereas upon electrochemical oxidation at the anode they give the unstable triply charged cations.[293]

$$Ni(H_2O)_6(BF_4)_2 + E_4 + p_3 \xrightarrow[\text{r.t.}]{\text{THF, Et}_2\text{O}} [Ni_2(p_3)_2(\eta^3\text{-}E_3)](BF_4)_2 \qquad (99)$$

$$E = P, As$$

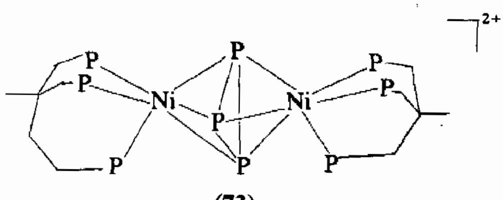
$$[Co(p_3)(\eta^3\text{-}P_3)] + Ni(H_2O)_6(BF_4)_2 + L \xrightarrow[\text{NaBPh}_4\text{, r.t.}]{\text{CH}_2\text{Cl}_2\text{, EtOH}} [Ni,Co(p_3)(L)(\eta^3\text{-}P_3)](BPh_4)_2 \qquad (100)$$

$$L = p_3, Etp_3$$

$$[Rh(p_3)(\eta^3\text{-}P_3)] + Ni(H_2O)_6(BF_4)_2 + p_3 \xrightarrow[\text{r.t.}]{\text{THF, EtOH}} [Ni,Rh(p_3)_2(\eta^3\text{-}P_3)](BF_4)_2 \qquad (101)$$

Mixed double sandwich complexes have been prepared by the general methods of equations (100)[292,294] and (101).[295]

A typical structure of these so called triple-decker sandwich complexes is that of the complex $[(p_3)Ni\{\mu\text{-}(\eta^3\text{-}P_3)\}Ni(p_3)](BPh_4)_2\cdot 2.5Me_2CO$ (**73**). In each complex the trihapto P_3 (or trihapto As_3) groups form a bridge between the two $Ni(p_3)$ residues.[292] Each nickel atom is thus six-coordinated by three phosphorus atoms from the ligand p_3 and by three phosphorus atoms from the *cyclo*-P_3 (or arsenic atoms from the *cyclo*-As_3), which acts as a three-electron-donor ligand.



(**73**)

Spectral and magnetic properties, structural features and bonding modes of these complexes have been critically discussed in a recent review.[296] It is interesting to note that the average P—P bond length in the trihapto P_3 group is only slightly less than the distances found in the tetrahedral P_4 molecule.

The mononuclear species $[Ni(p_3)(\eta^3\text{-}P_3)]^+$, which could not be obtained by the reaction of a nickel(II) salt with P_4, was obtained by the reaction outlined in equation (102) through the cleavage of the P_4S_3 cage molecule.[297]

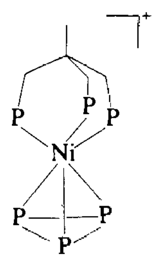
$$Ni(H_2O)_6(BF_4)_2 + p_3 + P_4S_3 \xrightarrow[\text{reflux}]{\text{THF, EtOH}} \underset{(74)}{[Ni(p_3)(\eta^3\text{-}P_3)]BF_4} \qquad (102)$$

$$Ni(H_2O)_6(BF_4)_2 + p_3 + As_4S_3 \xrightarrow[\text{r.t.}]{\text{THF, EtOH}} [Ni_2(p_3)_2(\eta^3\text{-}As_3)](BF_4)_2 \qquad (103)$$

$$Ni(H_2O)_6(BF_4)_2 + p_3 + As_4S_3 \xrightarrow[\text{reflux}]{\text{THF, EtOH}} [Ni_2(p_3)_2(\eta^3\text{-}As_3)]BF_4 \qquad (104)$$

When the As_4S_3 cage is used as the starting material, two compounds with different charges are obtained depending on the experimental conditions (equations 103 and 104).[298]

The nickel atom in complex (**74**) is six-coordinated in a distorted octahedral environment similar to that existing in the dinuclear complex (**73**) (Table 18).



(**74**)

The two complexes $[Ni_2(p_3)_2(\eta^3\text{-}As_3)](BF_4)_n$ ($n = 1, 2$) are identical to those obtained by the direct reaction with yellow arsenic (equation 99), and by reduction of the dication with $NaBH_4$.

50.4 NICKEL(I)

50.4.1 Introduction

Nickel(I) complexes are far less numerous than those of nickel(0). Like nickel(0) complexes, nickel(I) complexes are generally obtained with ligands having π-acceptor capability. Most complexes of nickel(I) which have been isolated as solids contain tertiary phosphines (or arsines) as ligands and are sufficiently stable in the absence of air to allow them to be studied with several physicochemical techniques.

A number of nickel(I) complexes were prepared *in situ* by electrochemical reduction of the corresponding nickel(II) complexes, mainly with macrocyclic tetraaza ligands and dithiolenes.

The external electronic configuration of Ni^I in its complexes is $3d^9$. Mononuclear complexes are all paramagnetic with a magnetic moment μ_{eff} in the range 1.7–2.4 BM. The electronic structure of several complexes has been studied by means of EPR spectroscopy. The EPR spectra can be interpreted using an $S = \frac{1}{2}$ spin Hamiltonian with g values in the range 2.0–2.45, the deviations of g from 2.0023 being due to spin–orbit coupling mixing of excited states into the ground level. Spin Hamiltonian parameters for selected nickel(I) complexes are shown in Table 19. The spin–lattice relaxation time is generally sufficiently long to give observable spectra at room temperature,[299] but in the case of pseudotetrahedral $[Ni(p_3)X]$ complexes (X = Cl, Br, I) the spectra were observed only at temperatures lower than 30 K.[300] This was accounted for by ligand field calculations, which put the energy levels deriving from the splitting of the tetrahedral ^2E ground state close in energy, shortening the spin–lattice relaxation time.

Table 19 Spin Hamiltonian Parameters for some Nickel(I) Complexes

Compound	*Chromophore*[a]	g_1[b]	g_2[b]	g_3[b]	*Ref.*
[(Cu,Ni)Cl(p$_3$)]	NiP_3Cl	2.344	2.124	2.040	300
[(Cu,Ni)Br(p$_3$)]	NiP_3Br	2.391	2.102	2.006	300
[NiCl(p$_3$)]	NiP_3Cl	2.14	2.12	2.24	300
[NiBr(p$_3$)]	NiP_3Br	2.12	2.16	2.24	300
[NiI(p$_3$)]	NiP_3I	1.99	2.10	2.38	300
[NiCl(np$_3$)]	$NiNP_3Cl$	2.210		2.001	301
[NiBr(np$_3$)]	$NiNP_3Br$	2.184		2.004	301
[NiI(np$_3$)]	$NiNP_3I$	2.151		2.004	301
[(Cu,Ni)Cl(PPh$_3$)$_2$]	NiP_2Cl	2.111	2.167	2.446	302
[(Cu,Ni)Br(PPh$_3$)$_2$]	NiP_2Br	2.112	2.209	2.435	302

[a] Metal and nearest-neighbour atoms.
[b] 1, 2 and 3 refer to *x*, *y* and *z* in single crystal spectra. When two values are reported, the first is the perpendicular component.

In a series of trigonal bipyramidal five-coordinate complexes of formula [Ni(np$_3$)X] (X = Cl, Br, I) having C_3 site symmetry, the *g* value pattern is $g_\perp > g_\parallel \approx 2.0023$. This pattern is indicative of a d_{z^2} ground state and the observed small deviations of *g* from 2.0023 were rationalized using simple MO calculations.[301]

In all the reported dinuclear complexes, the Ni^I ions are strongly coupled together to give $S = 0$ singlet ground states.

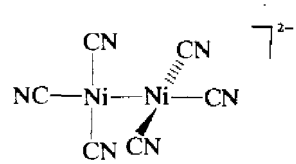
Most of the nickel(I) complexes are four-coordinate, either tetrahedral (phosphine and arsine complexes) or square planar (macrocyclic and dithiolene complexes), but five-coordinate complexes are also easily formed in the presence of tetradentate tripodal ligands.

A few three-coordinate nickel(I) complexes are also known.

A review dealing with nickel(I) complexes has appeared.[303]

50.4.2 Cyano Complexes

The earliest reported nickel(I) complex is the bright red compound of stoichiometry K_2NiCN_3[304] which was later obtained in a pure form by the reduction of $K_2Ni(CN)_4$ either in liquid ammonia with potassium or in aqueous solution with sodium amalgam.[305] The electrochemical reduction of $[Ni(CN)_4]^{2-}$ was also carried out and afforded the same nickel compound as the chemical reduction. The K_2NiCN_3 complex is dinuclear and diamagnetic on account of the short Ni—Ni linkage (232 pm) joining the two planar $Ni(CN)_3$ units which are twisted relative to each other by about 82° (**75**).[306]



(75)

The $[Ni_2(CN)_6]^{4-}$ anion absorbs both CO and NO. In the latter case a nitrosyl complex of nickel(0) results, namely $K_2[Ni(CN)_3NO]$.[307] The formulation of the carbonyl compound is dubious.[308]

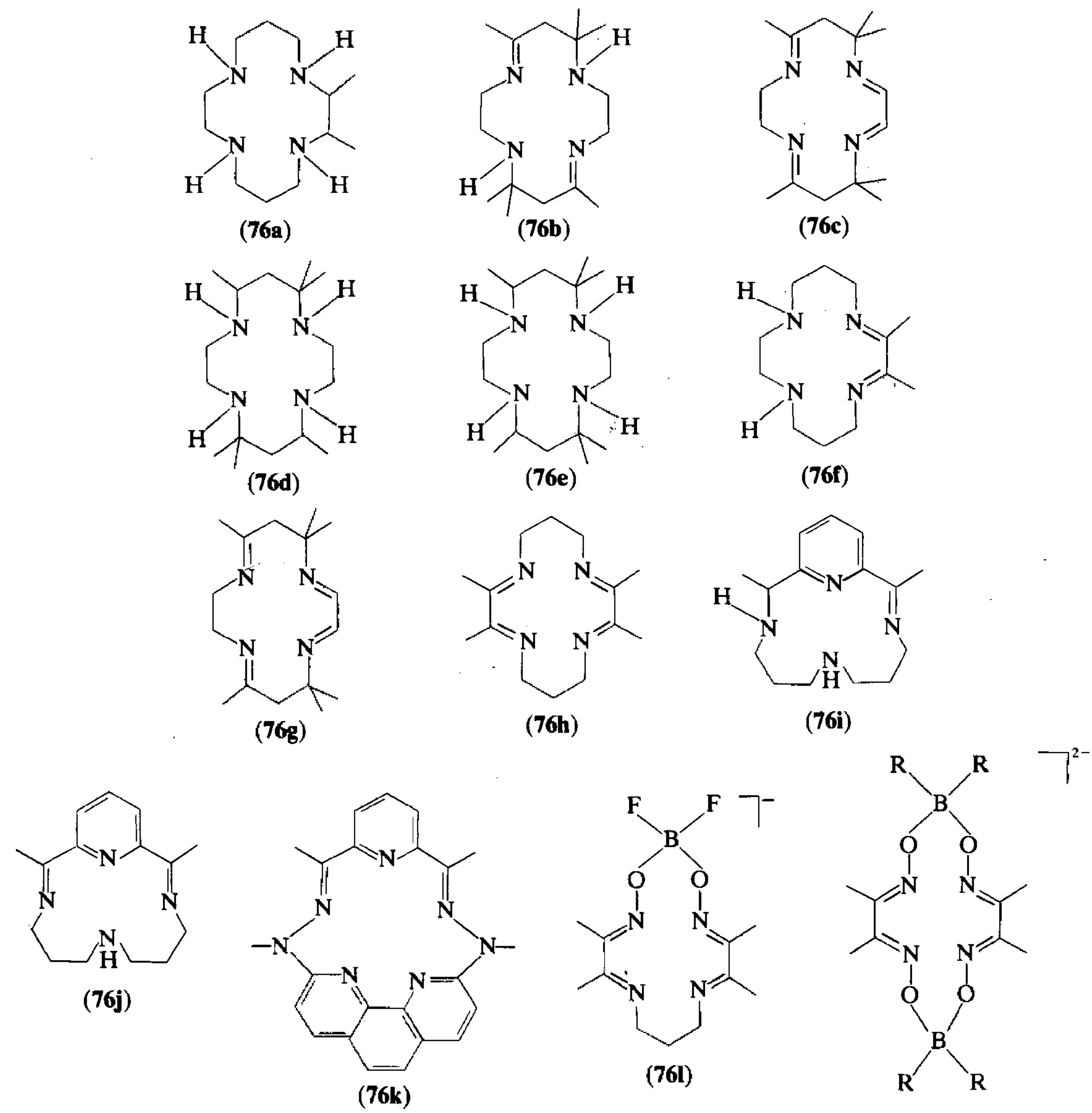
A paramagnetic (1.78 BM), extremely reactive compound formulated as $K_3Ni(CN)_4$ has been obtained by reducing $K_2Ni(CN)_4$ with hydrazine in strong alkaline solution.[309]

50.4.3 Complexes with Nitrogen Donors

The electrochemical reduction of an acetonitrile solution of $[Ni(bipy)_3]^{2+}$ affords a solution of $[Ni(bipy)_3]^+$ and neutral $[Ni(bipy)_3]$. EPR data in solution ($\langle g \rangle = 2.136$) are consistent with a nickel(I) complex formulation.[310] An $[Ni(bipy)_3]^-$ species has been also produced which can be better described as a ligand-stabilized anion ($\langle g \rangle = 2.007$) with nickel in the formal oxidation state 0.

Mixed ligand complexes of the type $[NiX(bipy)(PPh_3)]$ (X = halides, $\mu_{eff} = 2.1$ BM) have been reported.[311]

Some nickel(II) complexes with tetraaza macrocycles exhibit remarkable inertness towards dissociation. This property has allowed the stabilization of the metal in an unusual oxidation state by reducing (or oxidizing) the corresponding nickel(II) complexes. Most of the nickel(I) complexes with macrocyclic ligands have been prepared in solution by electrochemical means, but in some cases the compounds were also isolated in the solid state. The most widely used macrocycles are shown in Scheme 2. Selected electrochemical and ESR data are reported in Table 20. The square planar complexes $[NiL]ClO_4$ (L = **76b**, **76c**) have been isolated as black crystalline compounds in aprotic media by the reduction of the corresponding nickel(II) complexes with sodium amalgam (equation 105). These nickel(I) complexes are stable in the absence of air and moisture.[312] Similar reactions occur with ligands (**76d**) and (**76e**). All the aforementioned complexes were also obtained by means of electrochemical reduction of the corresponding nickel(II) complexes in MeCN solutions. Polarographic behaviour of these macrocyclic nickel complexes indicates that the reduction products are authentic nickel(I) complexes which, moreover, are stable towards further reduction to nickel(0) complexes.



Scheme 2

Table 20 Electrochemical and ESR Data for some Reduced Nickel Complexes with Macrocyles

Macrocycle	*Reduction potential for NiL^{2+}/NiL^{+} in MeCN vs. Ag/Ag^{+} (0.1 M); 0.1 M $Bu^n_4NBF_4$* (V)	*ESR data in frozen MeCN (77 K)* $g_{\parallel}$	$g_{\perp}$
(76a)	−1.73	2.261	2.060 Ni(I)
(76d)	−1.57	2.266	2.055 Ni(I)
(76b)	−1.57	2.226	2.055 Ni(I)
(76f)	−1.16	2.004[a]	(ligand radical)
(76i)	−1.25	2.005[a]	(ligand radical)
(76j)	−0.96	2.003[a]	(ligand radical)
(76g)	−0.76	2.003[a]	(ligand radical)
(76h)	−0.82	1.999[a]	(ligand radical)

[a] Isotropic signal.

$$[NiL](ClO_4)_2 + Na/Hg \xrightarrow[r.t.]{MeCN} [NiL]ClO_4 \quad L = \mathbf{(76b)}, \mathbf{(76c)}, \mathbf{(76d)}, \mathbf{(76e)} \qquad (105)$$

Busch and co-workers studied numerous synthetic macrocyclic complexes by means of EPR and electrochemical techniques.[313] Nickel(II) complexes with a variety of tetraaza macrocycles were found to undergo reversible one-electron electrochemical reduction. Depending on the ligand, the species produced are either nickel(II)-stabilized anionic ligand radicals (ligands **76f–76j**, which possess conjugated α-diimine groups) or authentic nickel(I) species (saturated or unsaturated non-conjugated macrocycles), as clearly shown by the g values reported in Table 20. The electrochemical behaviour of the nickel macrocyclic compounds is affected by a variety of factors, mainly the degree of unsaturation and the size of the macrocyclic ligand. An increase in the size of the macrocycle makes the reduction of nickel(II) easier, on account of the greater size of nickel(I) which is more easily accommodated in the larger cavity of the macrocycle. Ligand unsaturation also favours the reduced species which are stable under the action of relatively low potential (Table 20).

Nickel(II) complexes with the ligands **(76b)** and **(76d)** have been reduced in aqueous solution by solvated electrons with the aid of the pulse radiolysis technique.[314] The decay kinetics and the behaviour of these complexes as bases and as reducing agents have also been studied.

Methyl substituents on the nitrogen donor atoms of **(76d)** greatly enhance the stability of the corresponding nickel(I) complexes in water solution ($t_{1/2}(NiL)^{+} > 100$ h),[315] as compared with the nickel(I) complex with the unmethylated ligand **(76d)**, which decomposes even in THF solution.

Electrochemical reduction of the nickel(II) complexes $[Ni(L)R_2]^{2+}$ (L = **76k**; R = pyridine, 4-aminopyridine, imidazole, 2-methylimidazole, H_2O) in the presence of either CO or $P(OMe)_3$ produces nickel(I) species which may have either a pentagonal bipyramidal or a pentagonal pyramidal geometry.[316] Nickel complexes with the ligand **(76b)**, **(76c)** and **(76d)** also coordinate CO in solution to give five-coordinate carbonyl complexes of nickel(I) as deduced from their ERP spectra. Even the reduced complexes which may be formulated as nickel(II) complexes of mononegative radical macrocycles **(76g)**, **(76h)**, **(76l)** and **(76m)** bind CO in solution giving five-coordinate square pyramidal carbonyl complexes of nickel(I). In the latter case it is assumed that an electron migration occurs from a ligand orbital to the metal orbital upon coordination of CO.[317]

50.4.4 Complexes with Phosphines and Arsines

Selected nickel(I) complexes with phosphines and arsines, together with relevant properties and synthetic routes, are reported in Table 21. In general, these nickel(I) complexes are air-unstable, especially when dissolved in solution; consequently their preparation and handling require the exclusion of oxygen and, often, of moisture. The synthetic routes which afford nickel(I) complexes are strictly dependent on the nature of the phosphines and arsines and are not of general application, except in the case of some tripodal ligands. Most of the nickel(I)

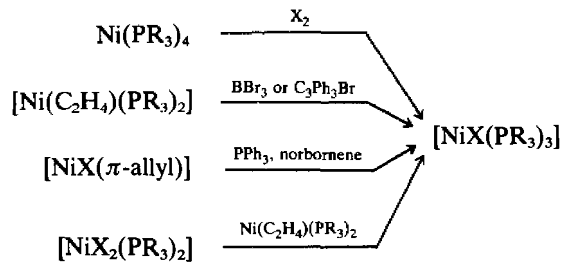
Table 21 Summary of Synthetic Procedures and Properties of Nickel(I) Complexes with Phosphines and Arsines

	Synthetic procedure	*Remarks*	*Ref.*
$[NiX(PPh_3)_3]$	$Ni(PPh_3)_4 + X_2$; benzene, 80–90% yield $Ni(PPh_3)_4 + NiX_2(PPh_3)_2$; Et_2O, 100% yield	$\mu_{eff} = 2.2$ BM for $NiCl(PPh_3)_3$ X = Cl, Br, I	318
$[NiBr(PPh_3)_3]$	$[Ni(C_2H_4)(PPh_3)_2] + BBr_3 + Et_2O$; Carius tube, r.t.		319
$[NiX(PPh_3)_3$	$[NiX(\pi\text{-allyl})] + PPh_3$ + norbornene; C_6H_6, Et_2O, r.t.	$\mu_{eff} = 1.9$–2.0 BM X = Cl, Br, I	320
$[Ni(BH_4)(PPh_3)_3]$	$Ni(H_2O)_6Cl_2 + PPh_3 + NaBH_4$; EtOH	Diamagnetic, presumably dinuclear	321
$[NiBr(PPh_3)_3]$	$[Ni(C_2H_4)(PPh_3)_2] + C_3Ph_3Br$	Tetrahedral structure (**77**); Ni—P 232 pm, Ni—Br 244 pm (average values for the independent molecules in the cell)	322
$[Ni_2(PPh_3)_6](PF_6)_2$	$[Ni(BH_4)(PPh_3)_3] + NaPF_6$; EtOH	Diamagnetic, supposedly dinuclear	323
$[Ni(PPh_3)_4]PF_6$	$[Ni_2(PPh_3)_6](PF_6)_2 + PPh_3$; THF	$\mu = 2.31$, tetrahedral structure	323
$[NiX(PPh_2Me)_3]$	Electrochemical reduction	X = Br, I; NMR studies	324
$[NiBr(PPh_3)_2]$	$[Ni(C_2H_4)(PPh_2)_2] + [NiBr_2(PPh_3)_2]$; Et_2O, 100% yield		318
$[NiX(PCy_3)_2]$	$[NiX_2(PCy_3)_2]$ + Na sand; toluene, pentane, r.t., 50% yield	X = Cl, Br; $\mu_{eff} = 2.1$–2.2 BM; supposedly dimeric with halide bridges and planar geometry	325
$[Ni(BPh_2)(PPh_3)_2]$	$[Ni(C_2H_4)(PPh_3)_2] + BPh_2Br$; Et_2O, r.t.	$\frac{1}{2}Et_2O$ solvated; supposedly dimeric with BPh_2^- bridges; diamagnetic	319
$[Ni\{N(SiMe_3)_2\}(PR_3)_2]$	$[NiCl_2(PPh_3)_2] + LiN(SiMe_3)_2$; benzene	$PR_3 = PPh_3$, PEt_3, PMe_2Ph, $PMePh_2$, PEt_2Ph, $PEtPh_2$; $(PR_3)_2 = Ph_2P(CH_2)_2PPh_2$; trigonal planar structure as in (**85**), Ni—P 221, 222 pm, Ni—N 188 pm, PNiP 107°, PNiN 122°, 130°	326
$[Ni(PCy_2)(PCy_2Ph)]$	$[NiCl_2(PCy_2Ph)_2]$ + Na sand, toluene, r.t.	$\mu_{eff} = 1.9$ (r.t.)–1.36 BM (75 K); supposedly dimeric with phosphido bridges	327
$[Ni(PCy_2)(CO)_2]$	$[Ni(PCy_2)(PCy_2Ph)]$ + CO; *n*-pentane, r.t.	$\mu_{eff} = 0.46$ BM (r.t.)	327
$[Ni\{P(SiMe_3)_2\}(PMe_3)]_2$	$NiCl_2(PMe_3)_2 + LiP(SiMe_3)_2$; 263–268 K	Dinuclear structure (**84**); trigonal planar coordination, Ni—Ni 238 pm; diamagnetic	328

$[Ni(PMe_3)_4]BPh_4$	$[Ni(Me)(PMe_3)_4]^+$; recryst. from THF	$\mu_{eff} = 2.40$ BM; tetrahedral structure (**78**)	329
$[Ni(CN)(P—P)_{1.5}]$	$[Ni(CN)_2(P—P)_{1.5}] + NaBH_4$; EtOH	$\mu_{eff} = 2.0–2.3$ BM; supposedly dinuclear; P—P = $Ph_2P(CH_2)_nPPh_2$, $n = 3, 4$	330
$[Ni(H)(P—P)]$	$[NiCl_2(P—P)] + Na(HBMe_3)$; toluene r.t., 75% yield	P—P = $Ph_2P(CH_2)_nPPh_2$, $n = 2, 3, 4$; supposedly dimeric with bridging hydrides; diamagnetic	331
$[Ni(H)(Cy_2P(CH_2)_3PCy_2)]_2$	$[NiCl_2(P—P)] + Na(HBMe_3)$; toluene, r.t., 75% yield	Dinuclear structure (**86**) with bridging hydrides; diamagnetic; the two P_2Ni planes are twisted relative to each other	332
$[NiXp_3]$	$NiX_2 + p_3 + NaBH_4$; CH_2Cl_2, EtOH, r.t.	X = Cl, Br, I; $\mu_{eff} = 1.93–1.98$ BM; tetrahedral structure Ni—I 255 pm, Ni—P 222 pm (av) (**79**)	333, 334
$[Ni(SH)p_3]$	$[p_3Ni(S_2CNEt_2)]BPh_4 + NaBH_4$; EtOH, acetone, 40% yield	Tetrahedral structure (**79**); $\mu_{eff} = 2.11$ BM	335, 336
$[NiXas_3]$	$NiX_2 + as_3 + NaBH_4$; Bu^tOH, Et_2O	X = Br, I; $\mu_{eff} = 2.11–2.20$ BM	337
$[NiL]ClO_4$	$[Ni(C_2H_4)(PPh_3)_2] + (C_3Ph_3)ClO_4 + L$; MeOH, THF, 50 °C	L = np_3, pp_3; trigonal pyramidal structure (**80**)	338
$[Ni(np_3)]ClO_4$	$[Ni(H_2O)_6](ClO_4)_2 + np_3$; acetone, boiling, 70% yield		338
$[NiX(np_3)]$	$NiX_2 + np_3 + NaBH_4$; CH_2Cl_2, EtOH, r.t.	X = Cl, Br, I, CN, NCS; $\mu_{eff} = 1.72–1.94$ BM; trigonal bipyramidal structure, quite similar to that of (**82**)	339, 340
$[Ni(CO)(np_3)]BF_4$	$[NiH_x(np_3)]BF_4 + CO$, $x < 1$; CH_2Cl_2	$\mu_{eff} = 1.79$ BM	339, 340
$[NiX(np_3)]$	$[Ninp_3] + RX$; C_6H_6/THF	RX = MeI, EtCl, PrCl, PhCl, PhBr, PhI	341
$[NiX(nas)_3]$	$NiX_2 + nas_3$; CH_2Cl_2/EtOH + $NaBH_4$, r.t.	X = Cl, Br, I, NCS, NO_3; $\mu_{eff} = 2.03–2.23$ BM; air-stable in solid state	340, 342
		X = I, trigonal bipyramidal structure (**82**), Ni—I 286 pm, Ni—As 235.5 pm (av)	
$[Ni_2X(nas_3)_2]BPh_4$	$[NiX(nas_3)]BPh_4 + BPh_4^- + NaBH_4$, EtOH + CH_2Cl_2 + THF, r.t.	X = Br, I; $\mu_{eff} < 1$ BM, antiferromagnetic; dinuclear structure (**83**)	343
$[Ni(nas_3)Ph_3P]ClO_4$	$[C_3Ph_3]ClO_4 + Ni(C_2H_4)(PPh_3)_2 + nas_3$; MeOH + THF (1:1), 50 °C, N_2, 65% yield	Air-unstable; $\mu_{eff} = 2.01$ BM; trigonal bipyramidal structure, Ni—N 258 pm, Ni—P 235 pm, Ni—As 241 pm (av) (**81**)	338

complexes with the polydentate ligands p_3, as_3, np_3 and nas_3 were easily obtained by the reduction with $NaBH_4$ of nickel(II) salts in the presence of the appropriate ligand.

The early reports on nickel(I) and phosphine donors deal with the monotertiary phosphine PPh_3, and it is remarkable that such a variety of different routes afforded the same complexes (equation 106). Structural features of selected complexes are reported in Table 22. All of the complexes of the type $[NiX(PPh_3)_3]$ are mononuclear species with magnetic moment values corresponding to an unpaired electron and possess a pseudotetrahedral structure like $[NiBr(PPh_3)_3]$ (**77**)[322] where the bond angles deviate from the tetrahedral value by less than 1.5°. Larger deviations have been observed in the complex $[Ni(PMe_3)_4]BPh_4$ (**78**).

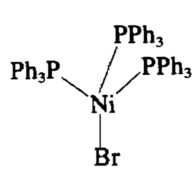


(106)

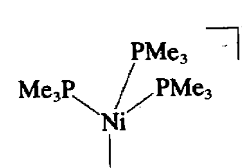
Table 22 Molecular Parameters for some Nickel(I) Complexes with Tertiary Phosphines and Arsines

Complex	Bond distances[a] (pm) Ni—Y	Ni—L	Ni—X	Bond angles[a] (°) Y—Ni—Y	Y—Ni—X		Ref.
$[NiBr(PPh_3)_3]$	232		244 (Br)	108	111 (Br)		322
$[Ni\{N(SiMe_3)_2\}(PPh_3)_2]$	221	188 (N)		107	126 (N)		326
$[Ni\{P(SiMe_3)_2\}(PMe_3)]_2$	213	238 (Ni)	219 (phosphido)	119	66 (NiPNi)		328
$[Ni(PMe_3)_4](BPh_4)$	222			105–120			329
$[Ni(H)(Cy_2P(CH_2)_3PCy_2)]_2$	213	244 (Ni)	156 (H)	103	93 (H)		332
$[NiI(p_3)]$	222		255 (I)	94	123 (I)		334
$[Ni(SH)(p_3)]$	225		217 (S)	92	124 (S)		335
$[Ni(pp_3)]ClO_4$	222 (P_{bas})	216 (P_{apic})		120 ($P_{bas}NiP_{bas}$)	88 ($P_{ap}NiP_{bas}$)		338
$[NiI(np_3)]$	227	226 (N)	302 (I)	119	96 (I)	176 (N—Ni—I)	340
$[NiI(nas_3)]$	236	247 (N)	286 (I)	118	98 (I)	176 (N—Ni—I)	340
$[Ni_2I(nas_3)]BPh$	235	231 (N)	299 (I)	119	95 (I)	178 (N—Ni—I)	343
$[Ni(nas_3)(PPh_3)]ClO_4$	241	258 (N)	235 (P_{bas})	117	101 (P)	179 (N—Ni—P)	338

[a] Y = P or As as appropriate.



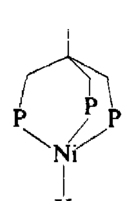
(**77**)



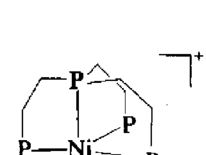
(**78**)

The $[Ni(PMe_3)_4]BPh_4$ complex has been unexpectedly obtained through a reductive elimination reaction, by the simple recrystallization in THF of the five-coordinate nickel(II) complex $[Ni(Me)(PMe_3)_4]BPh_4$.[329]

A pseudotetrahedral geometry is imposed by the steric requirements of the tridentate ligand in the complexes $[NiIp_3]$[333,334] and $[NiSHp_3]$ (**79**).[335,336]



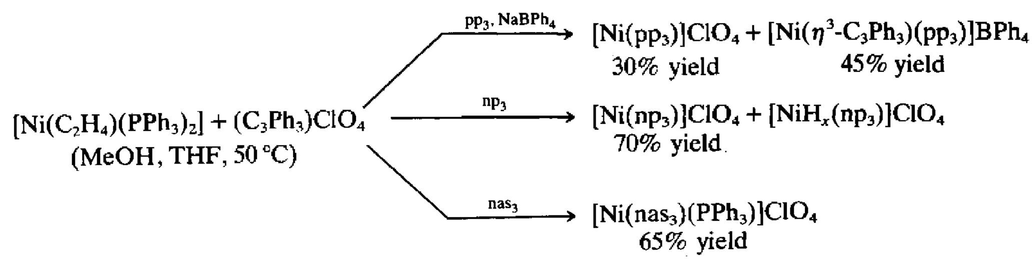
(**79**) X = I, SH



(**80**)

The geometry of the complex $[Ni(pp_3)]ClO_4$ (**80**) approaches trigonal pyramidal with the nickel atom nearly in the basal plane.

Similar structures are assumed for the analogous complexes $[Ni(np_3)]ClO_4$[338] and $[Ni(nas_3)]BF_4$.[342] The formation reactions of complexes $[NiL]ClO_4$ ($L = np_3, pp_3$) (Table 22) are not straightforward and deserve some comment. It was suggested that the $(C_3Ph_3)^+$ ion replaces C_2H_4 in the starting complex either giving the intermediate species $[Ni(C_3Ph_3)(PPh_3)_2]^+$ or oxidizing nickel(0) to nickel(I). Thus in the presence of the ligand pp_3 both the complexes (**80**) and $[Ni(C_3Ph_3)(pp_3)]^+$ are formed (equation 107).[338] In the same way, in the presence of the np_3 ligand, the formation of $[Ni(np_3)]ClO_4$ is accompanied by traces of the nickel(II) hydrido complex $[NiH_x(np_3)]ClO_4$. Finally, the analogous reaction with nas_3 ligands affords a different complex, namely $[Ni(nas_3)(PPh_3)]ClO_4$ (**81**)[338] whose structure is distorted trigonal bipyramidal with a significant lengthening of the Ni—N and Ni—P axial bonds (Table 22). A lengthening of the axial bond distances was also found in the complexes $[NiI(nas_3)]$ (**82**)[340,342] and $[Ni_2I(nas_3)_2]BPh_4$ (**83**).[343] The dinuclear complex (**83**) has been obtained by the reduction at room temperature of the monomeric nickel(II) complex $[NiI(nas_3)]^+$ with the stoichiometric amount of $NaBH_4$. When more forcing reaction conditions were employed (excess of $NaBH_4$ and boiling temperature), the mononuclear complex (**82**) resulted.



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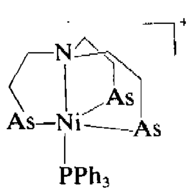
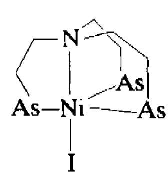
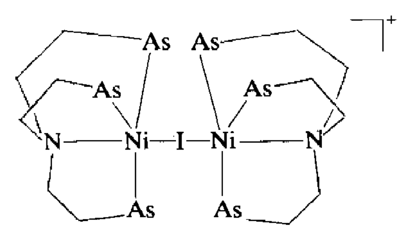


(**81**)



(**82**)



(**83**)

In complex (**83**) there is a linear bridge through the iodine atom connecting the two nickel atoms, which have trigonal bipyramidal geometry. The magnetic moments of both the iodo and bromo derivatives ($\mu_B < 1.0$ BM at room temperature) indicate strong antiferromagnetic interaction between the two nickel atoms.[343]

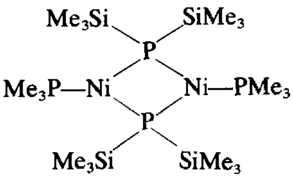
When nickel(II) salts containing a coordinating anion (halide and pseudohalide) are reacted with $NaBH_4$ in the presence of np_3, trigonal bipyramidal nickel(I) complexes of the type $[NiXnp_3]$, in which the coordinating anion occupies the axial position,[339,340] are obtained. When nickel(II) salts with poorly coordinating anions are used, non-stoichiometric hydrido complexes of nickel(II) are obtained (equations 108 and 109).

$$NiX_2 + np_3 + BH_4^- \longrightarrow [NiX(np_3)] \quad X = \text{halides} \tag{108}$$

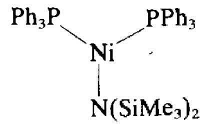
$$Ni(H_2O)_6(BF_4)_2 + np_3 + BH_4^- \longrightarrow [NiH_x(np_3)]BF_4 \quad x < 1 \tag{109}$$

The reaction of $LiP(SiMe_3)_2$ with $NiCl_2(PR_3)_2$ affords an unstable intermediate, $[Ni\{P(SiMe_3)_2\}_2(PR_3)_2]$, which decomposes at temperatures in the range 263–268 K yielding the complex $[NiP(SiMe_3)_2(PMe_3)]_2$ (**84**) and $[NiP(SiMe_3)_2]$.[328] Complexes (**84**) and $[NiN(SiMe_3)_2(PPh_3)_2]$ (**85**) have been found to be three-coordinate with a trigonal planar coordination. Complex (**84**) has a dinuclear structure with bridging phosphido groups. A similar structure has been assumed for the dicyclohexylphosphido complex

$[Ni(PCy_2)(PCy_2Ph)]_2$ which was obtained by reducing the nickel(II) complex $[NiCl_2(PCy_2Ph)_2]$ with sodium sand.[327]



(84)



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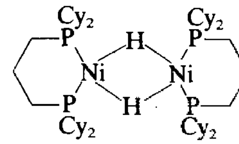
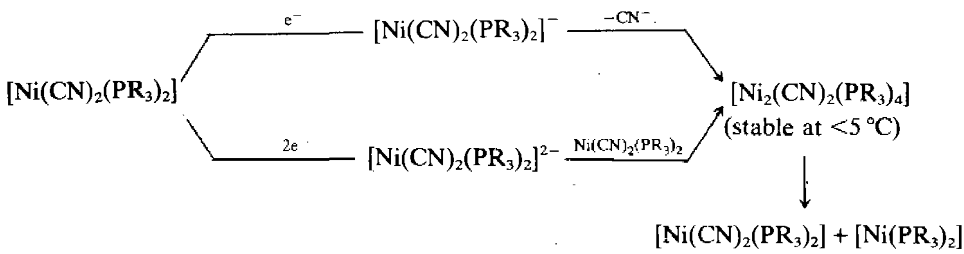


(86)

Finally, a dinuclear structure with two hydrogen bridges has been found in the diamagnetic complex [NiH(P—P)] (**86**) (P—P = $Cy_2P(CH_2)_3PCy_2$).[332] The two PNiP planes connected through the hydrogen atoms form a dihedral angle of 63.5°. The same structure is supposed to occur in analogous hydrido complexes with other diphosphines.[331]

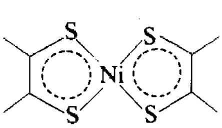
The reduction of planar *trans*-$[Ni(CN)_2(PR_3)_2]$ ($PR_3 = PEt_3$, $PEtPh_2$, PEt_2Ph, PBu^t_3, PPr_3) complexes has been investigated by cyclic voltammetry and controlled potential electrolysis techniques in MeCN solutions.[344] The $[Ni(CN)_2(PR_3)_2]$ complexes were found to undergo electrochemical reduction to unstable nickel(I) and nickel(0) complexes which decay to more stable nickel(I) dimeric complexes (equation 110). Some of the latter compounds undergo a third cathodic process leading to nickel(0) species. Differences in the reduction potentials of the couples $[Ni(CN)_2(PR_3)_2]/[Ni(CN)_2(PR_3)_2]^-$ (in the range −2.06 to −1.38 V *vs.* SCE) have been rationalized assuming that a greater π-acceptor capability of the phosphines corresponds to an easier reduction of nickel(II) to nickel(I). Electrochemical behaviour of MeCN solutions of $Ni(ClO_4)_2$ in the presence of either tertiary phosphines or phosphites was studied. It was found that nickel(I) species are stabilized towards disproportionation reactions in the presence of phosphines, whereas the opposite occurs with phosphites.[345]



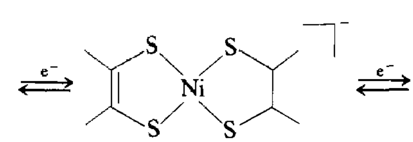
(110)

50.4.5 Complexes with Dithiolenes, Dithiocarbamates and Related Ligands

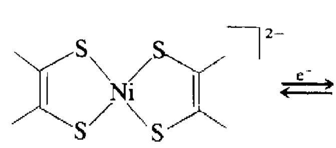
The electron transfer properties of nickel 1,2-dithiolenes $Ni(R_2C_2S_2)^{n-}$ have been extensively studied in recent years, but there is still much controversy concerning the nature of the bonding in these complexes. On the basis of a simple VB model neutral and binegative species (**87**) may be assumed to contain the metal in the oxidation state +2, mononegative species may contain either nickel(II) or nickel(III), and trinegative species are assumed to contain nickel(I).



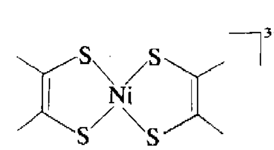
(87a)



(87b)



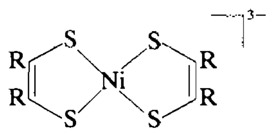
(87c)



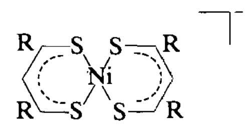
(87d)

The square planar [bis(maleonitriledithiolato)nickel(I)] trianion (**88**; R = CN) was produced in MeCN solution by the electrochemical reduction of the corresponding dianion at rather high negative potential (-1.8 V *vs.* SCE).[346,347] The reduction is accompanied by a colour change of the solution from orange to green. The solution is extremely air-sensitive (but otherwise stable) and reverts to the dianion upon exposure to traces of air. Frozen solution EPR spectra have been interpreted with a rhombic g tensor with $g_1 = 2.205$, $g_2 = 2.081$, $g_3 = 2.061$.[348] The complex (**88**; R = Me) is unstable even in the absence of air.

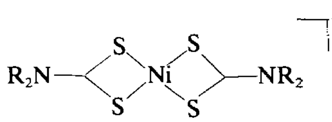
Square planar 1,3-dithioketonato complexes $Ni(R_2C_3S_2)_2$ are reminiscent of the 1,2-dithiolene complexes and their electrochemical behaviour is comparable. The neutral complexes have been found to undergo a one-electron reduction to the unstable monoanions $[Ni(R_2C_3S_2)_2]^-$ (**89**) in the range -0.9 to -1.1 V *vs.* SCE in MeCN or DMF at a Pt electrode.[349] There is also some controversy as to whether the reduction of these complexes is metal- or ligand-based.[349,350]



(**88**) R = CN, Me



(**89**) R = H, Me



(**90**) R = alkyl, aryl

A number of nickel(II) dithiocarbamates $[Ni(R_2NCS_2)_2]$ (**90**; R = alkyl, benzyl, phenyl) were found to undergo one-electron reduction at a Pt electrode at quite negative potentials (-1.2 to -1.5 V *vs.* Ag/AgCl electrode) giving formally nickel(I) species which are moderately stable in acetone solution.[351,352] The effect of the substituents R on the redox couple has been investigated.[351] The reduction mechanism of some of the aforementioned complexes (R = alkyl) was studied in DMSO at the mercury electrode. It was supposed that the reduction is essentially metal-centred in nature and involves dissociation products which are more easily reduced than the starting $Ni(R_2NCS_2)_2$.[353] The one-electron reduction of the mixed complex $[Ni(R_2NCS_2)(P—P)]PF_6$ ($P—P = Ph_2PCH_2CH_2PPh_2$) in various solvents results in the initial formation of an unstable neutral complex of nickel(I), $[Ni(R_2NCS_2)(P—P)]$, which disproportionates to the $[Ni(R_2NCS_2)_2]$ and $[Ni(P—P)_2]$ complexes.[352] The mechanism of the disproportionation reaction is assumed to be similar to that of $[Ni(CN)_2(PPh_3)_2]$ (equation 110).

50.4.6 Miscellaneous Complexes

The reduction of nickel(II) salts with $NaBH_4$ was studied in the presence of several ligands. With ligands such as en, no appreciable reduction occurs, whereas with NH_3 reduction to the metal takes place. In the same way the reduction of $[NiL_3]^{2+}$ (L = bipy, phen) in water or ethanol affords compounds of stoichiometry $[NiXL_2]$ and $[NiXL]$ ($X = BH_4$, PF_6, BPh_4) with magnetic moments indicative of one unpaired electron (1.95–2.38 BM). The complexes with formula $[NiXL_2]$ were assigned either square planar or five-coordinate structure whereas a tetrahedral geometry was assigned to the complex $[NiBH_4(phen)]$.[354]

Nickel(I) complexes with ligands such as en, CN^-, L-alaninate, succinimide anion, $C_3H_5NO_2$, methyl and ethyl xanthogenate, $C_2H_3OS_2^-$ and $C_3H_5OS_2^-$ are produced by the reduction of the corresponding nickel(II) complexes by means of γ irradiation.[355] EPR data suggest that the paramagnetic centre produced by γ irradiation is metal-centred.

50.5 NICKEL(II)

50.5.1 Electronic Spectra and Spectromagnetic Properties of Nickel(II) Complexes

50.5.1.1 Introduction

The large variety of coordination environments and geometries achieved by nickel(II) in its complexes makes this ion one of the most extensively studied among transition metal ions. The electronic structure of nickel(II) complexes has been investigated using optical spectroscopic (optical absorption, MCD) and magnetic (magnetization, magnetic susceptibility, EPR, NMR) techniques and several reviews have already appeared.[356–360] The purpose of this section is to present a general account of the electronic structure of nickel(II) complexes, as well as that of reviewing their spectral and magnetic properties.

In the first part we will describe the electronic energy levels of nickel(II) complexes in the most common stereochemistries and the appearance of the electronic spectra. High-spin complexes will be considered first.

In the second part we will review the properties connected with the nature of the ground state, such as magnetic susceptibility and magnetization, EPR and NMR of paramagnetic complexes.

In the last part we will give explicit references to those complexes which have been studied by several techniques, paying special attention to systems for which single crystal data are available.

50.5.1.2 Energy levels and electronic spectra

The description of the electronic energy levels and of their dependence on the structure and geometry is the starting point for the understanding of the spectral and magnetic properties of nickel(II) complexes. The basic theory for the interpretation of these properties is already known.[361] Much of the work already done on this subject has been based on a ligand field description of the energy levels and we will adopt this picture throughout this section. The ligand field model we refer to is the Angular Overlap Model (AOM) of the ligand field[362] which has been successfully applied in the last few years to describe electronic and magnetic properties of low symmetry chromophores.[363] In the AOM the antibonding effects of the ligand on the metal d orbital energies are parameterized using the e'_λ ($\lambda = \sigma, \pi, \delta$) parameters which are related to the metal–ligand σ, π and δ interactions which are familiar to all chemists. It is customary to use as parameters $e_\sigma = e'_\sigma - e'_\delta$ and $e_\pi = e'_\pi - e'_\delta$. In general, correlation exists between the AOM parameters and the usual crystal field parameters. For example in cubic complexes

$$10Dq = \gamma(3e_\sigma - 4e_\pi)$$

$\gamma = 1$ for octahedral and $-4/9$ for tetrahedral complexes.

General relationships between AOM and crystal field parameters are shown in Table 23. Using the AOM one can easily compute the electronic energy levels, inclusive of spin–orbit coupling, without any symmetry assumption or perturbation procedure, and it is also easy to account for the different chemical natures of the ligands and for differences in bond distances. It is also possible to handle anisotropic π interactions, which can be expected to occur with pyridine or pyridine N-oxide ligands.[366,367] General review articles on the AOM and its applications have already appeared.[364,368–371]

Table 23 General Relationship Between Angular Overlap Model and Ligand Field Parameters

$I_2 = (7/2)C_p = e_\sigma + e_\pi$
$I_4 = 6Dq = (9/5)e_\sigma - (12/5)e_\pi$
$C_p = (2/7)I_2 = (2/7)e_\sigma + (2/7)e_\pi$
$Dq = (1/6)I_4 = (3/10)e_\sigma - (4/10)e_\pi$
$e_\sigma = (4/7)I_2 + (5/21)I_4 = 2C_p + (10/7)Dq$
$e_\pi = (3/7)I_2 - (5/21)I_4 = (3/2)C_p - (10/7)Dq$

The symbols are defined in refs. 364 and 365.

Nickel(II) is a $3d^8$ ion. From this configuration the Russell–Saunders terms ^3F, ^3P, ^1G, ^1D and ^1S arise whose relative energies are expressed in terms of the Racah parameters B and C in Table 24. The ground state of the gaseous ion is ^3F; $B = 1084\,cm^{-1}$ and $C = 4831\,cm^{-1}$. For nickel(II) complexes both triplet (high-spin) and singlet (low-spin) states are known as ground state, depending on the relative value of the interelectronic repulsion and crystal field stabilization energy which in turn depend on the covalency of the metal–ligand bonds, the nature of the ligands and the stereochemistry of the complex. When the interelectronic repulsion P overcomes the crystal field stabilization energy Δ, a low-spin state occurs; when $\Delta > P$ the high-spin configuration is stabilized. In intermediate situations when $\Delta \approx P$ the ground state is expected to depend on external conditions such as pressure or temperature giving rise to spin equilibria. Six-coordinate complexes are generally high-spin, unless one or more ligands are at a larger distance. Five-coordinate complexes can be both high-spin and

Table 24 Energies of Terms of d^8 Configuration as a Function of the Racah Parameters

Term	*Energy*[a]
^3F	0
^3P	$15B$
^1G	$12B+2C$
^1D	$5B+2C$
^1S	$22B+7C$

[a] B and C are defined in ref. 361.

low-spin. Four-coordinate complexes are high-spin in a tetrahedral or pseudotetrahedral environment and low-spin in square planar geometry. In Figure 3 the energies of the electronic levels in various coordination geometries are shown. The purpose of Figure 3 is to give a qualitative picture of the energy levels in each stereochemistry, the exact order of the energy levels depending on the actual value of the AOM parameters. The ground state of trigonal bipyramidal and tetrahedral complexes is orbitally degenerate, $^3E'$ and $^3T_1$ respectively, while in all the other stereochemistries the ground state is orbitally non-degenerate. In any case low-spin complexes possess an orbitally non-degenerate ground state.

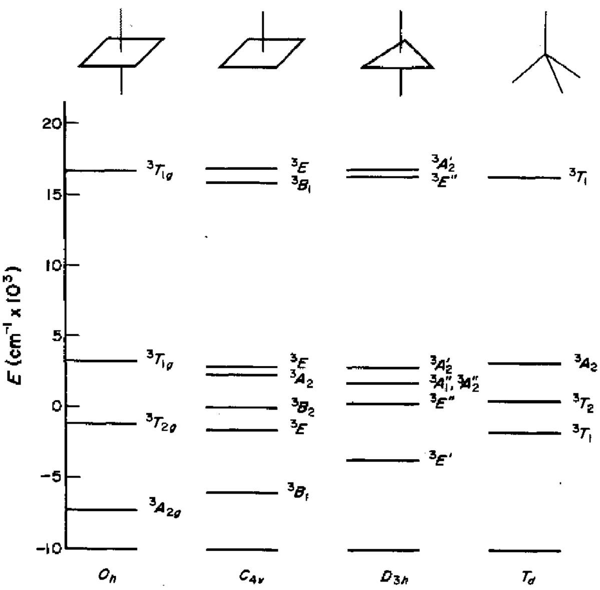


Figure 3 Energies of the triplet levels in various geometries

Energy levels for a regular octahedral NiA_6 chromophore are shown in Figure 4. Figure 4a shows the effect of increasing the e_σ parameters for the A ligands in strict O_h symmetry. The e_σ values lie in the range which can in principle be found for nickel(II) complexes.

In Figure 4b the effect of varying the e_π/e_σ ratio is shown. Positive e_π/e_σ values correspond to an antibonding effect on the metal orbitals and represent the effect of a π-donor ligand, while negative e_π/e_σ values represent the effect of π-acceptor ligands. Both σ- and π-bonding interactions largely affect the energy of the singlet and triplet levels. Here and in all the following figures only triplet levels and singlet levels lying below $20\,000\ \text{cm}^{-1}$, which in principle can be relevant to the interpretation of the electronic spectra, will be shown.

The effect of trigonal distortion is shown in Figure 4c where ξ is the angle between three of the A ligands and the C_3 axis. Perfect octahedral geometry corresponds to $\xi = 55°$. Lower values give trigonally elongated complexes, while for larger values a trigonal compression of the octahedron occurs. The main effect of this distortion is to remove the degeneracy of the excited T_{1g} and T_{2g} energy levels, also changing the nature of the low-lying split level from A_2 to

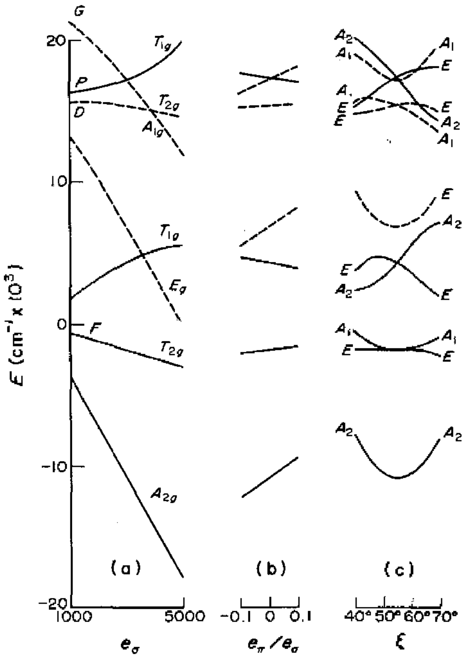


Figure 4 Energy level diagram for an octahedral NiA_6 chromophore. Full lines refer to triplet states, broken lines to singlet states. The free ion parentage is shown on the left side. (a) The effect of varying e_σ ($e_\pi = 0\ cm^{-1}$); (b) the effect of varying e_π/e_σ ($e_\sigma = 3000\ cm^{-1}$); (c) the effect of varying ξ (see text; $e_\sigma = 3000\ cm^{-1}$, $e_\pi = 0\ cm^{-1}$)

E and from E to A_2, for T_{1g} (F) and T_{1g} (P) respectively, on passing from a trigonal elongation to a trigonal compression of the octahedron. Other distortions towards a trigonal prismatic configuration have been found to affect the electronic energies greatly and have been considered elsewhere.[372]

The energy levels of tetragonally distorted NiA_2B_4 chromophores are shown in Figure 5. The energy levels are mainly affected by the e_σ^A/e_σ^B ratio (Figure 5a). In tetragonally compressed chromophores ($e_\sigma^A/e_\sigma^B > 1$) the ${}^3T_{2g}$ (O_h) level is split in such a sense that ${}^3B_{2g}$ (D_{4h}) lies lower than ${}^3E_g$ (D_{4h}) while the sense of the splitting is reversed for tetragonally elongated chromophores. Analogous considerations hold for the ${}^3T_{1g}$ (O_h) energy levels.

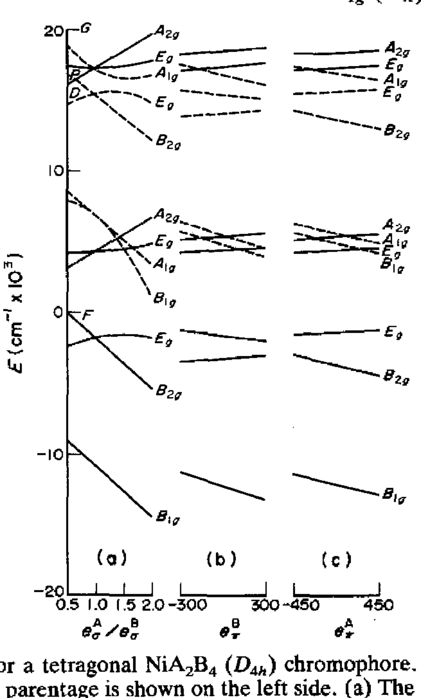


Figure 5 Energy level diagram for a tetragonal NiA_2B_4 (D_{4h}) chromophore. Full lines refer to triplet states, broken lines to singlet states. The free ion parentage is shown on the left side. (a) The effect of varying e_σ^A/e_σ^B ($e_\sigma^B = 3000\ cm^{-1}$; $e_\pi^A = e_\pi^B = 0\ cm^{-1}$); (b) the effect of varying e_π^B ($e_\sigma^A = 4500\ cm^{-1}$; $e_\pi^A/e_\sigma^A = 0.05$; $e_\sigma^B = 3000\ cm^{-1}$); (c) the effect of varying e_π^A ($e_\sigma^B = 3000\ cm^{-1}$; $e_\pi^B/e_\sigma^B = 0.05$; $e_\sigma^A = 4500\ cm^{-1}$)

The electronic spectra of octahedral nickel(II) complexes are formed by three main spin-allowed bands. They can be assigned in O_h symmetry to $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}$ and $^3A_{2g} \rightarrow {}^3T_{1g}$ (P). Less intense spin-forbidden bands attributable to transitions to ^1D and ^1G states can also be observed. The first spin-allowed transition is usually in the range 5000–12 000 cm^{-1}. The $^3A_{2g} \rightarrow {}^3T_{1g}$ band is in the range 12 000–19 000 cm^{-1} and has often been found to be split into two components as a consequence of the spin–orbit coupling of ^1E (D) with $^3T_{1g}$. The third band is to the P manifold and ranges between 20 000 and 29 000 cm^{-1}. In tetragonal complexes the splitting of the energy levels increases the number of observable transitions. Six spin-allowed transitions may be anticipated and in practice at least five are observed; in addition some spin-forbidden bands may appear. The transitions to the doubly degenerate ^3E_g (D_{4h}) levels are usually the most intense features.[373] The molar extinction coefficients of the transitions are generally very close to 10, the highest energy bands being more intense. The electronic spectra of some pseudooctahedral nickel(II) complexes are shown in Figure 6.

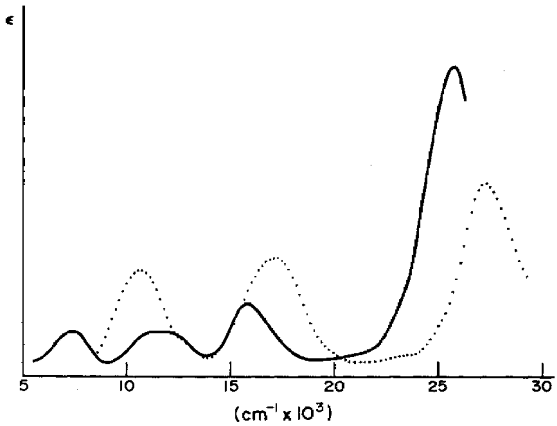


Figure 6 Electronic spectra of $Ni(pyrazole)_6(NO_3)_2$ (full line) and $Ni(pyrazole)_4Br_2$ (dotted line) after ref. 475

The energy levels of five-coordinate NiA_5 chromophores are shown in Figure 7. Square pyramidal complexes possess an orbitally non-degenerate ground level, $^3B_1$ in C_{4v} symmetry, the next excited state being a ^3E level. The ^4P levels are not greatly affected by both e_σ and e_π variations (Figures 7a and 7b). The e_σ parameter strongly influences the energy of the ground $^3B_1$ level and the energies of the ^1D levels which are coming near to the ground state as e_σ increases. π interactions produce smaller variations in the energy levels as already observed for six-coordinate complexes. In Figure 8 the energy levels of an NiB_4A complex are shown.

The electronic spectra of square pyramidal chromophores are characterized by a band in the near IR region from 4000 to 9000 cm^{-1} ($^3B_1 \rightarrow {}^3E$) with molar extinction coefficient ε_M near 10–20, a more intense transition at 12 000–18 000 cm^{-1} ($^3B_1 \rightarrow {}^3E$, $\varepsilon_M \approx 20$–100) with a shoulder on the low frequency side due to $^3B_1 \rightarrow {}^3B_2$ transitions, a weak band at 17 000–25 000 cm^{-1} ($^3B_1 \rightarrow {}^3A_2$ (P)) and the most intense transition at 19 000–29 000 cm^{-1} ($^3B_1 \rightarrow {}^3E$ (P), $\varepsilon_M \approx 100$–800).

In Figures 7c and 7d the effect of varying e_π/e_σ and e_σ parameters for NiA_5 trigonal bipyramidal (D_{3h}) complexes is shown. The ground state is an orbitally degenerate $^3E'$ state. Analogously to the square pyramidal case the energy levels are more sensitive to σ than to π effects and the splitting of the ^3P state is less than that of the ^3F state. The $^1A_1'$ level is largely stabilized by increasing e_σ. The effect of changing the symmetry from D_{3h} to C_{3v} by allowing the angle between the axial and equatorial ligands to be different from 90° has been considered elsewhere[374] and the main effect is that of removing the accidental degeneracy of the A_1'' and A_2'' levels. This splitting can be observed and used as a test of deviation of the complexes from D_{3h} symmetry.

The electronic spectra of trigonal bipyramidal high-spin complexes are characterized by four bands. The first band is in the near IR region ranging from 5000 to 8000 cm^{-1} ($^3E' \rightarrow {}^3E''$, $\varepsilon_M \approx 10$–30), the second one is in the range 8000–14 000 cm^{-1} ($^3E' \rightarrow {}^3A_1'' + {}^3A_2''$, $\varepsilon_M \approx 10$–20), the third band is at 17 000–22 000 cm^{-1} ($^3E' \rightarrow {}^3A_2''$, $\varepsilon_M \approx 20$–30) and the fourth band is the most intense one ($\varepsilon_M \approx 50$–200), with a shoulder in the low frequency part. This band corresponds to transitions from the ^3F to the ^3P manifold ($^3E''$ and $^3A_2'$). Examples of electronic

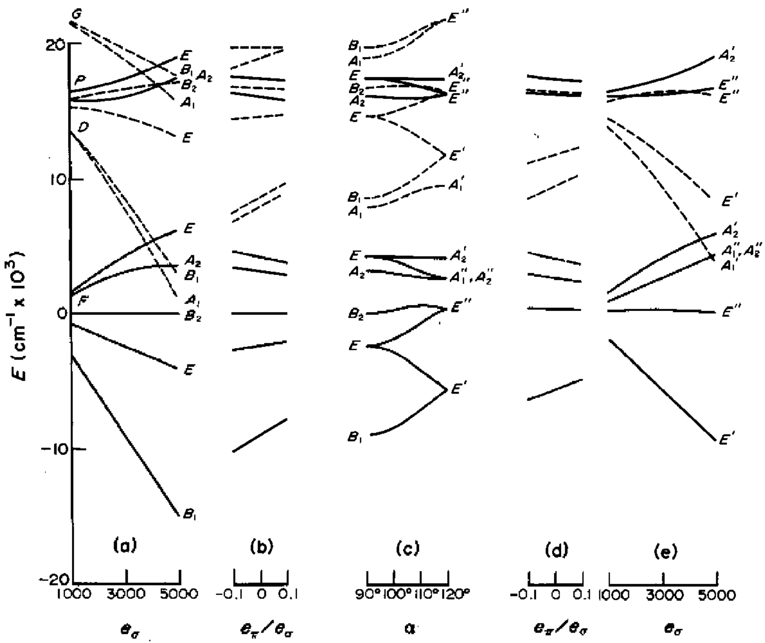


Figure 7 Energy level diagram for an NiA_5 chromophore. Full lines refer to triplet states, broken lines to singlet states. The free ion parentage is shown on the left side. Square pyramidal geometry (C_{4v}): (a) the effect of varying e_σ; (b) the effect of varying e_π/e_σ ($e_\sigma = 3000\,\mathrm{cm}^{-1}$). Geometry intermediate between square pyramidal and trigonal bipyramidal (C_{2v}): (c) the effect of varying α (see text): $\alpha = 90°$ corresponds to C_{4v} symmetry, $\alpha = 120°$ to D_{3h} symmetry ($e_\sigma = 3000\,\mathrm{cm}^{-1}$; $e_\pi = 0\,\mathrm{cm}^{-1}$). Trigonal bipyramidal geometry (D_{3h}): (d) the effect of varying e_π/e_σ ($e_\sigma = 3000\,\mathrm{cm}^{-1}$); (e) the effect of varying e_σ ($e_\pi = 0\,\mathrm{cm}^{-1}$)

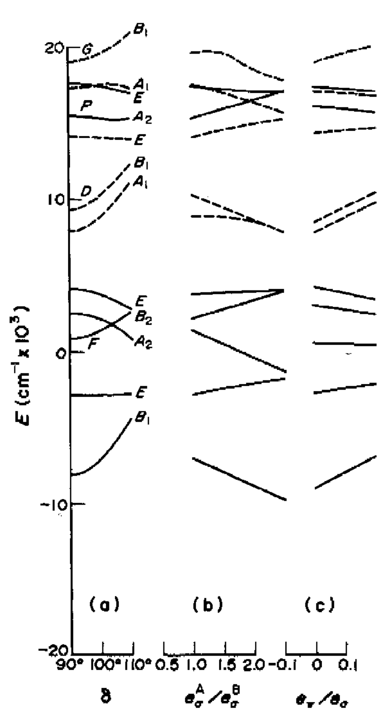


Figure 8 Energy level diagram for an NiB_4A chromophore (C_{4v}). Full lines refer to triplet states, broken lines to singlet states. The free ion parentage is shown on the left side. (a) The effect of varying δ, the angle A—Ni—B ($e_\sigma^A = 1500\,\mathrm{cm}^{-1}$; $e_\sigma^B = 3000\,\mathrm{cm}^{-1}$; $e_\pi^A = e_\pi^B = 0\,\mathrm{cm}^{-1}$; (b) the effect of varying e_σ^A/e_σ^B ($e_\sigma^B = 3000\,\mathrm{cm}^{-1}$; $e_\pi^A = e_\pi^B = 0\,\mathrm{cm}^{-1}$; $\delta = 100°$); (c) the effect of varying e_π/e_σ ($e_\sigma^A = e_\sigma^B = 3000\,\mathrm{cm}^{-1}$; $\delta = 100°$)

spectra of nickel(II) complexes with approximate square pyramidal and trigonal bipyramidal stereochemistries are shown in Figure 9.

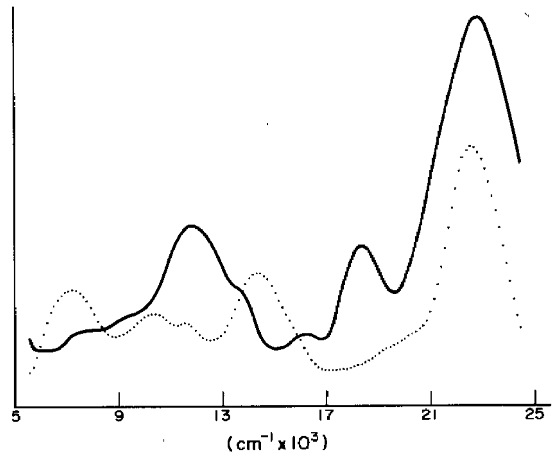


Figure 9 Electronic spectra of a square pyramidal ($[Ni(MePh_2AsO)_4(ClO_4)](ClO_4)$; full line) and a trigonal bipyramidal ($[Ni(Me_6tren)Br]Br$; dotted line) complex (after ref. 360)

Figure 7c illustrates the energy levels of complexes with geometries intermediate between square pyramidal and trigonal bipyramidal. The geometrical variation is achieved by changing one of the A—Ni—A angles α from 90° to 120° preserving overall C_{2v} symmetry of the chromophore. The main effect of this distortion is to remove the degeneracy of the E levels causing an increase of the total number of bands and in particular the appearance of three bands in the near IR region due to transition to the split component of the E' and E'' state of D_{3h} symmetry, which have often been observed.

The electronic energy levels of tetrahedral NiA_4 complexes are shown in Figures 10a and 10b. The largest effects on the energy levels are caused by the variations in the e_σ parameter. The ^3P levels are almost unaffected by both σ and π interactions. Two main distortions from T_d symmetry are considered in Figures 10c and 10d. In Figure 10c the effect is shown of varying the angle α between two ligands and the S_4 axis, preserving overall D_{2d} symmetry. π interactions have a much smaller influence on the energy levels. The largest splittings are observed for the $^3T_1$ and $^3T_2$ levels of the ^3F manifold and the ground state can be orbitally degenerate or not depending on whether the complex is compressed or elongated. In Figure 10d the effect of varying the angle β between two ligands and the C_3 axis of the tetrahedron while preserving C_{3v} symmetry is shown. Also in this case π interactions have a smaller influence on the energy levels. The largest splitting is observed for $^3T_1$ (F) levels and also in this case the nature of the ground state is influenced by the sign of the distortion.

The electronic spectra of pseudotetrahedral nickel(II) complexes are characterized by three main bands. The first one ($^3T_1 \rightarrow {}^3T_2$, $\varepsilon_M \approx 10$–50) falls in the near IR region from 4000 to 7000 cm^{-1}; the second one is in the range 7000–11 000 cm^{-1} ($^3T_1 \rightarrow {}^3A_2$, $\varepsilon_M \approx 100$–$200$); and the third band is assigned to the transitions to the ^3P manifold and lies between 15 000 and 20 000 cm^{-1} ($\varepsilon_M \approx 200$–$500$). Low-symmetry components of the ligand field can modify this assignment (Figure 10) and transitions within the ground $^3T_1$ manifold become observable in the IR region.

Typical spectra of pseudotetrahedral nickel(II) complexes are shown in Figure 11.

50.5.1.3 Spectral and magnetic properties related to the ground states

A number of physical observables, such as magnetic susceptibility and EPR spectra, are largely determined by the nature of the ground state, the excited states playing only a minor role.

Tetrahedral and trigonal bipyramidal complexes have orbitally degenerate ground states while octahedral and square pyramidal complexes possess orbitally non-degenerate ground

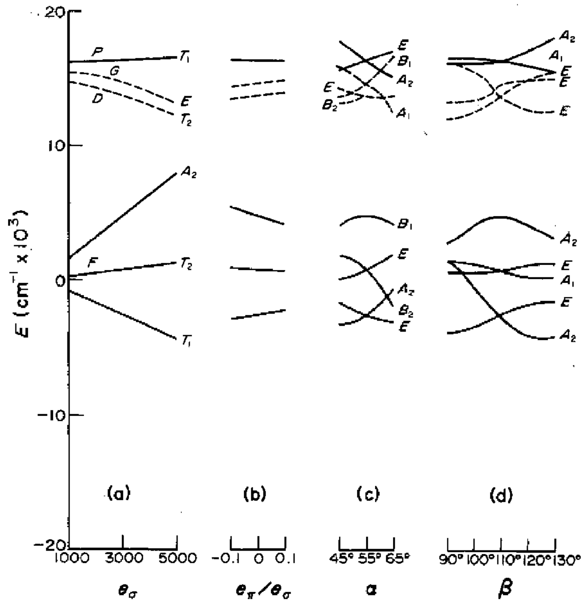


Figure 10 Energy level diagram for an NiA_4 pseudotetrahedral chromophore. Full lines refer to triplet states, broken lines to singlet states. The free ion parentage is shown on the left side. (a) The effect of varying e_σ ($e_\pi = 0\,cm^{-1}$); (b) the effect of varying e_π/e_σ ($e_\sigma = 3000\,cm^{-1}$); (c) the effect of varying the α angle (see text; $e_\sigma = 3000\,cm^{-1}$; $e_\pi = 0\,cm^{-1}$); (d) the effect of varying the β angle (see text; $e_\sigma = 3000\,cm^{-1}$; $e_\pi = 0\,cm^{-1}$)

states. When the ground state is orbitally non-degenerate, spin–orbit coupling removes the three-fold spin degeneracy causing a zero field splitting of the ground manifold as shown in Figure 12.

In general this zero field splitting is large enough ($5–50\,cm^{-1}$) to prevent any direct observation of the transitions between the ground levels which are in principle observable through EPR spectroscopy, so that magnetic susceptibility measurements remain the most widely employed technique to investigate the magnetic properties of high-spin nickel(II) complexes. When the ground state is orbitally degenerate, both spin–orbit coupling and low-symmetry components of the ligand field are effective in removing any degeneracy. In this case more complicated situations occur. In general no EPR spectra can be observed for these complexes and the measured magnetic susceptibilities are very anisotropic and largely temperature dependent.

(i) *Magnetic susceptibility*

The theory of the magnetic susceptibility of nickel(II) complexes is well established and several review articles have already appeared.[375–379] A quantity of interest in studying the magnetic properties of nickel(II) complexes is the effective magnetic moment $\mu = (8\chi T)^{1/2}$.

The magnetic moments usually observed at room temperature for nickel(II) complexes are shown in Table 25. The spin-only value of μ for a d^8 ion is 2.83 BM; larger values are generally observed due to orbital contributions derived from the mixing into the ground state of low-lying excited states under the spin orbit operator, or directly, because the ground state is orbitally degenerate. It is apparent from Table 25 that the value of the room temperature magnetic moment cannot be used to distinguish between tetrahedral and five-coordinate complexes.

The largest magnetic moments are observed for tetrahedral and trigonal bipyramidal complexes which possess orbitally degenerate states. Large orbital contributions are also expected for square pyramidal complexes which have an E level lying near to the ground state.

The computed variation of μ as a function of e_σ and e_π/e_σ for octahedral NiA_6 complexes is shown in Figures 13a and 13b. The explicit formalism for these calculation has been described elsewhere.[380] The magnetic moments are more sensitive to variations in e_σ than in e_π. An increase in e_σ results in a decrease in μ.

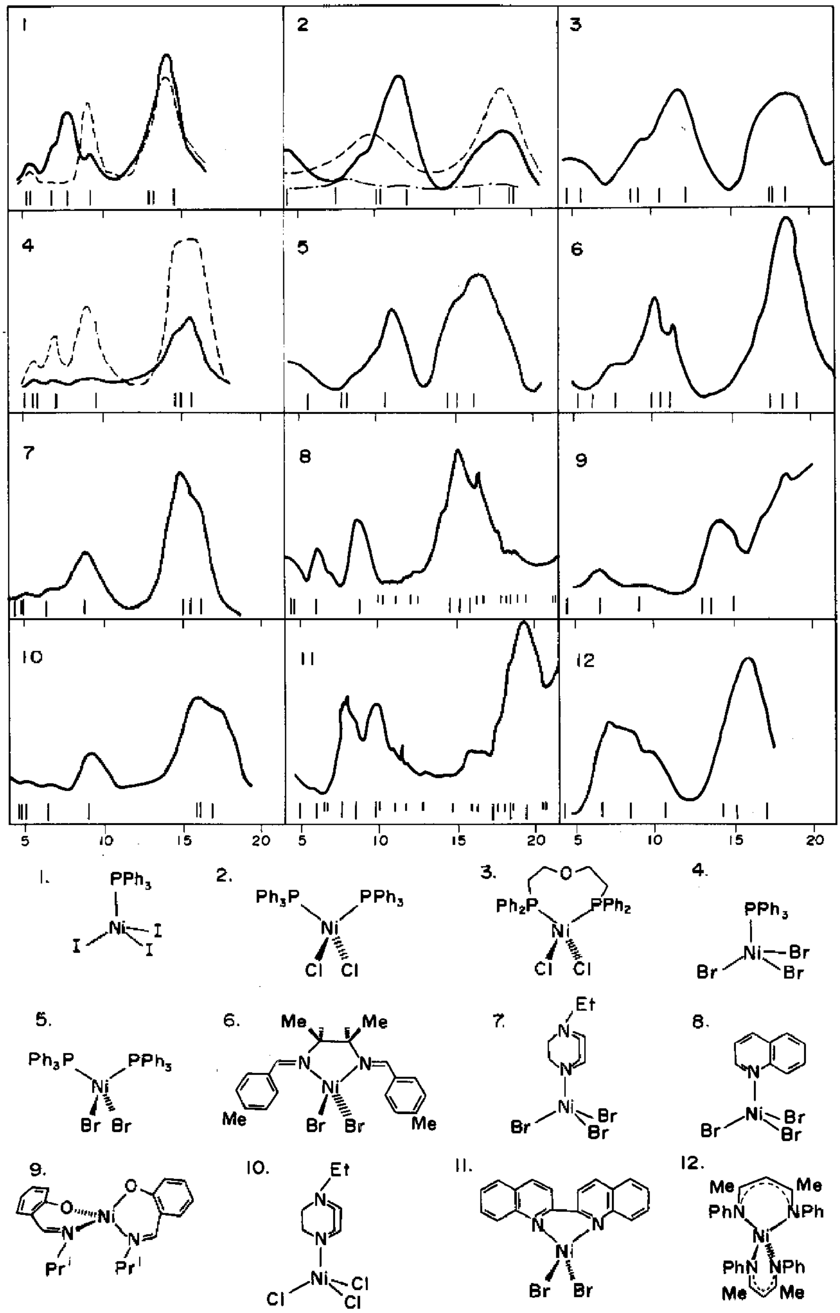


Figure 11 Electronic spectra of pseudotetrahedral nickel(II) complexes (reproduced from ref. 542)

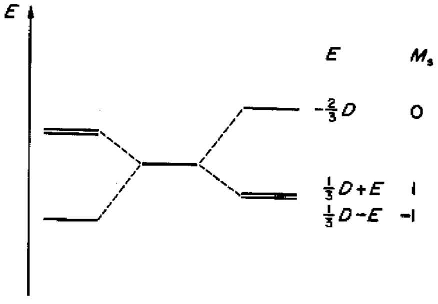


Figure 12 Zero field splitting of an orbitally non-degenerate triplet ground state. D and E are related to the zero field splitting tensor by $D = 3/2D_{zz}$ and $E = \frac{1}{2}(D_{xx} - D_{yy})$. The states are labelled according to the z components of the spin operator on the right

Table 25 Typical Values of the Effective Magnetic Moment at Room Temperature of Nickel(II) Complexes in Various Coordination Environments

Coordination	μ_{eff} (BM)
Octahedral	2.9–3.3
Trigonal bipyramidal	3.2–3.8
Square pyramidal	3.2–3.4
Tetrahedral	3.2–4.0
Square planar	Diamagnetic

Since the ground state in O_h symmetry is $^3A_{2g}$ and the next excited state $^3T_{2g}$ is generally well separated in energy (>7000 cm^{-1}), no large temperature dependence of the magnetic moment is anticipated (Figures 13a and 13b) and anisotropic effects are also of minor importance unless very low temperatures (<4 K) are reached. At temperatures below 4 K the differences in thermal populations of the levels of the ground manifold due to the zero field splitting become important and larger anisotropies are observed.[376] The effects on the magnetic moments of varying the angle ξ between the trigonal axis of the octahedron and the bond direction is shown in Figure 13c. The most dramatic effect is on the 5 K magnetic moment which shows a maximum at ~45°. This is due to a change of the sign of the zero field splitting induced by the distortion from O_h symmetry.

The calculated magnetic moments of tetragonal NiA_2B_4 complexes are shown in Figure 14. The magnetic moments are almost insensitive to both σ and π interactions. Owing to the splitting of the excited $^3T_{2g}$ state of O_h symmetry a larger variation of μ with temperature than in the octahedral case is computed.

In Figure 15 the magnetic moments computed for five-coordinate chromophores are shown. Owing to the degenerate nature of the ground state for trigonal bipyramidal complexes, the computed magnetic moments are larger than those of the square pyramidal complexes. σ and π

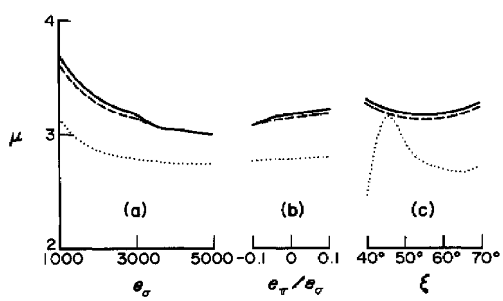


Figure 13 Computed magnetic moments for an octahedral NiA_6 chromophore. Full lines refer to 305 K, broken lines to 155 K, and dotted lines to 5 K. (a) The effect of varying e_σ ($e_\pi = 0$ cm^{-1}); (b) the effect of varying e_π/e_σ ($e_\sigma = 3000$ cm^{-1}); (c) the effect of varying ξ (see text; $e_\sigma = 3000$ cm^{-1}, $e_\pi = 0$ cm^{-1})

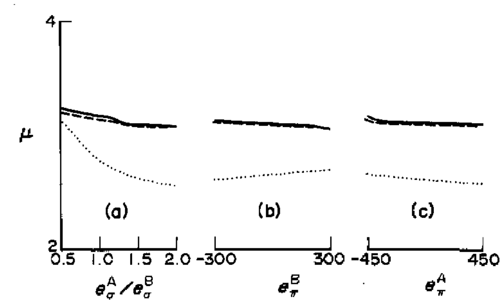


Figure 14 Computed magnetic moments for an NiA_2B_4 chromophore. Full lines refer to 305 K, broken lines to 155 K, and dotted lines to 5 K. (a) The effect of varying e_σ^A/e_σ^B ($e_\sigma^B = 3000$ cm^{-1}; $e_\pi^A = e_\pi^B = 0$ cm^{-1}); (b) the effect of varying e_π^B ($e_\sigma^A = 4500$ cm^{-1}; $e_\pi^A/e_\sigma^A = 0.05$; $e_\sigma^B = 3000$ cm^{-1}); (c) the effect of varying e_π^A ($e_\sigma^B = 3000$ cm^{-1}; $e_\pi^B/e_\sigma^B = 0.05$; $e_\sigma^A = 4500$ cm^{-1})

interactions do not greatly affect the magnetic moments, for both square pyramidal and trigonal bipyramidal complexes. The magnetic moment computed for complexes with geometries intermediate between square pyramidal and trigonal bipyramidal is shown in Figure 15c.

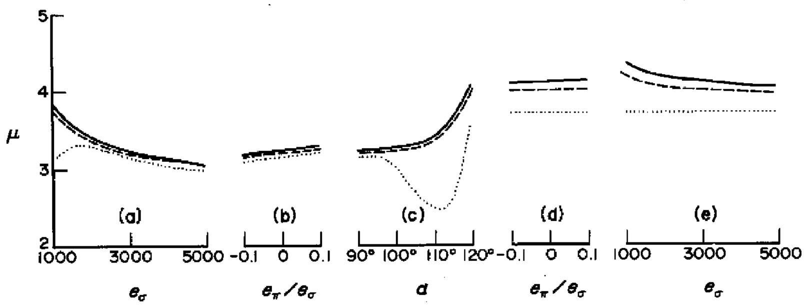


Figure 15 Computed magnetic moments for an NiA_5 chromophore. Full lines refer to 305 K, broken lines to 155 K, and dotted lines to 5 K. (a) The effect of varying e_σ; (b) the effect of varying e_π/e_σ ($e_\sigma = 3000\ cm^{-1}$); geometry intermediate between square pyramidal and trigonal bipyramidal (C_{2v}): (c) the effect of varying α (see text): $\alpha = 90°$ corresponds to C_{4v} symmetry, $\alpha = 120°$ to D_{3h} symmetry ($e_\sigma = 3000\ cm^{-1}$; $e_\pi = 0\ cm^{-1}$); trigonal bipyramidal geometry (D_{3h}): (d) the effect of varying e_π/e_σ ($e_\sigma = 3000\ cm^{-1}$); (e) the effect of varying e_σ ($e_\pi = 0\ cm^{-1}$)

Complexes with geometries near to the trigonal bipyramidal limit show the largest variation of μ with temperature. For these complexes the simple ligand field theory generally fails to reproduce the experimentally observed magnetic moments which are lower than the computed ones. An explanation which has been suggested will be discussed in Section 50.5.1.4.iii.

The magnetic moments computed for NiB_4A complexes are shown in Figure 16.

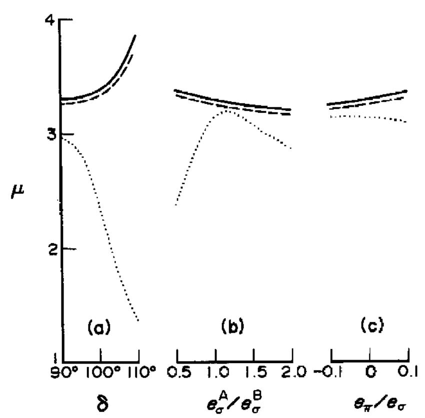


Figure 16 Computed magnetic moments for an NiB_4A chromophore. Full lines refer to 305 K, broken lines to 155 K, and dotted lines to 5 K. (a) The effect of varying δ, the angle A—Ni—B ($e_\sigma^A = 1500\ cm^{-1}$; $e_\sigma^B = 3000\ cm^{-1}$; $e_\pi^A = e_\pi^B = 0\ cm^{-1}$); (b) the effect of varying e_σ^A/e_σ^B ($e_\sigma^B = 3000\ cm^{-1}$; $e_\pi^A = e_\pi^B = 0\ cm^{-1}$; $\delta = 100°$); (c) the effect of varying e_π/e_σ ($e_\sigma^A = e_\sigma^B = 3000\ cm^{-1}$; $\delta = 100°$)

The magnetic moments computed for tetrahedral complexes NiA_4 are shown in Figure 17. Since the ground state is $^3T_1$, the room temperature magnetic moment is larger (>4) than for octahedral and five-coordinate chromophores. Spin–orbit coupling splits the ground $^3T_1$ term into three states of multiplicity 0, 3 and 5 with the 0 state lying lower. At low temperatures only the 0 state is populated and μ becomes zero, giving a large temperature dependence of the magnetic moments. The dependence of μ on e_σ and e_π (Figures 17a and 17b) is not large. The effects of tetragonal and trigonal distortions are considered in Figures 17c and 17d respectively.

(ii) EPR spectra

The EPR spectra of nickel(II) complexes can be interpreted using an $S = 1$ spin Hamiltonian. Since nickel(II) is not a Kramers ion the zero field splitting can be large enough to lift all the three-fold spin degeneracy of the ground state and give no observable ESR signal. The spectra

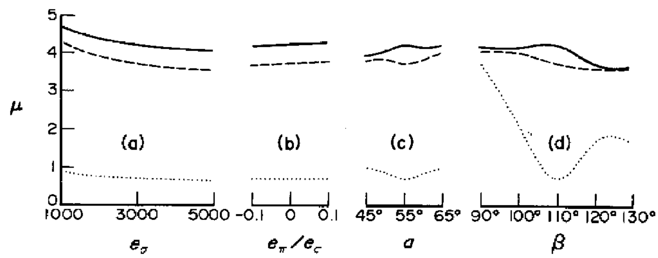


Figure 17 Computed magnetic moments for a pseudotetrahedral NiA_4 chromophore. Full lines refer to 305 K, broken lines to 155 K, and dotted lines to 5 K. (a) The effect of varying e_σ ($e_\pi = 0\ cm^{-1}$); (b) the effect of varying e_π/e_σ ($e_\sigma = 3000\ cm^{-1}$); (c) the effect of varying the α angle (see text; $e_\sigma = 3000\ cm^{-1}$; $e_\pi = 0\ cm^{-1}$); (d) the effect of varying the β angle (see text; $e_\sigma = 3000\ cm^{-1}$; $e_\pi = 0\ cm^{-1}$)

have often been recorded for octahedral complexes. They have generally been interpreted with a nearly isotropic g tensor with principal values in the range 2.0–2.4. Spin Hamiltonian parameters for selected nickel(II) complexes are shown in Table 26. More details on the EPR spectra of nickel(II) can be found in ref. 395.

Table 26 Spin Hamiltonian Parameters for some Nickel(II) Complexes

Compound	*Chromophore*[a]	g_1[b]	g_2[b]	g_3[b]	D[c]	E/D	*Ref.*
$NiSiF_6 \cdot 6H_2O$	NiO_6		2.25		−0.51	0	381
$(Zn,Ni)SiF_6 \cdot 6H_2O$	NiO_6		2.26		−0.64	0	382
$Ni(BrO_3)_2 \cdot 6H_2O$	NiO_6		2.29		−1.97	0	383
$NiSO_4 \cdot 6H_2O$	NiO_6		2.25		4.85	0.01	384
$(Fe,Ni)SiF_6 \cdot 6H_2O$	NiO_6		2.255		−3.05	0.056	385
$Cs(Mg,Ni)Cl_3$	$NiCl_6$	2.241		2.257	2.000	0	386
$Cs(Mg,Ni)Br_3$	$NiBr_6$	2.23		2.23	1.70	0	386
$Cs(Mg,Ni)I_3$	NiI_6	2.16		2.16	1.03	0	386
$Cs(Cd,Ni)Br_3$	$NiBr_6$	2.22		2.22	1.28	0	387
$Cs(Cd,Ni)Cl_3$	$NiCl_6$	2.29		2.28	0.905	0	388
$RbNiCl_3$	$NiCl_6$		2.23				389
$RbNiBr_3$	$NiBr_6$		2.22				389
$Ni(im)_6(NO_3)_2$	NiN_6		2.185		0.882	0	390
$Ni(1\text{-Meim})_6(ClO_4)_2$	NiN_6		2.180		0.820	0.004	391
$Ni(MeCN)_6SbCl_6$	NiN_6		2.190		0.260	0.10	391
$Ni(MeCN)_6InBr_4$	NiN_6		2.198		0.270	0.17	391
$Ni(MeCN)_6(ClO_4)_2$	NiN_6		2.195		0.380	0.047	391
$Ni(5\text{-Mepz})_6(ClO_4)_2$	NiN_6		2.178		0.400	0.00	391
$Ni(4\text{-Mepz})_6(ClO_4)_2$	NiN_6		2.190		0.510	0.333	391
$Ni(4\text{-Clpz})_6(ClO_4)_2$	NiN_6		2.180		0.26	0.00	391
$Ni(pz)_6(NO_3)_2$	NiN_6		2.19		0.07	0.001	391
$(Zn,Ni)(NH_3)_6NO_3$	NiN_6		2.17		0.606		392
$(Cd,Ni)(NH_3)_6Cl_2$	NiN_6		2.18		0.265		393
$(Cd,Ni)(NH_3)_6Br_2$	NiN_6		2.17		0.30		393
$(Zn,Ni)(NH_3)_6Cl_2$	NiN_6		2.16		0.30		393
$(Zn,Ni)(NH_3)_6Br_2$	NiN_6		2.18		0.30		393
$Ni(dbsc)_2(py)_2$	$NiSe_4N_2$		2.087		0.0043		394

[a] Metal and nearest-neighbour atoms.
[b] Subscripts 1, 2 and 3 refer to x, y and z. When two values are reported, the first is the perpendicular component.
[c] Values in cm^{-1}.
Abbreviations: im = imidazole; 1-Meim = 1-methylimidazole; 5-Mepz = 5-methylpyrazole; 4-Mepz = 4-methylpyrazole; 4-Clpz = 4-chloropyrazole; pz = pyrazole; dbsc = di-*n*-butyldiselenocarbamate.

(*iii*) *NMR spectra*

In principle, measurement of the nuclear magnetic resonance of paramagnetic molecules allows measurement of the delocalized spin density over the ligand and gives information on the MO nature of the ground state.[396] Nickel(II) complexes have been particularly studied by this technique because: (1) the electron relaxation time and/or the characteristic exchange time are favourable; (2) in most cases, especially in octahedral complexes, the pseudocontact shift, which originates from magnetic anisotropy effects, can be neglected in comparison to the Fermi contact shift due to the coupling of the nuclear spin with the unpaired spin density on the nucleus.[397–402] While no theoretical approach has been found to be valid to account completely for the spin delocalization in nickel(II) complexes, several trends have however been justified within a valence bond formalism. The contact shift for hydrogen nuclei is correlated to the unpaired electron density on the atom to which the hydrogen is bonded. In the absence of pseudocontact shift contributions the observed shift should represent the mechanism of spin delocalization. When the delocalization mechanism is occurring through σ orbitals, the contact shifts for protons in a ligand are negative (low field shift) and attenuate on increasing the number of atoms between the resonating proton and nickel(II). In a π-delocalization mechanism the protons are alternatively displaced at high and low field (positive and negative contract shifts). This very simple picture cannot account for the observed spin distributions in low symmetry chromophores, where a distinction between σ and π orbitals is no longer possible.[397,403–408]

A number of adducts of bis(acetylacetonato)nickel(II) have been studied by ^1H and ^{13}C NMR spectroscopy.[397,399,407–422] In several cases, always when aromatic bases are involved, the shifts of both protons and carbons cannot be accounted for by σ- and π-delocalization mechanisms. Similar results have been found for non-aromatic amines such as piperidine derivatives, showing that in these complexes there are also alternating ^{13}C contact shifts which have been accounted for by inclusion of spin polarization in the mechanism of electron spin transfer through the carbon skeleton with INDO–MO calculations.[412]

References to NMR studies of selected examples of pseudooctahedral complexes are given in Table 27.

Table 27 Selected References for NMR Spectra of Six-coordinate Nickel(II) Complexes

Ligand	*Ref.*
Pyridine and derivatives	423–430
Imidazole and derivatives	431
Phenanthroline	432, 433
Water	434, 435

Since the ground state of tetrahedral complexes is orbitally degenerate ($^3T_1$), it can be expected that the shifts observed in ^1H NMR spectra of pseudotetrahedral complexes are due to both contact and pseudocontact contributions. Kurland and McGarvey[436] have derived the equations for calculating contact and pseudocontact terms in complexes with nearly orbitally degenerate ground states. Calculations of NMR shifts in pseudotetrahedral complexes are reported in ref. 437. Selected examples of pseudotetrahedral complexes whose NMR spectra have been studied are reported in Table 28 and ref. 455.

Table 28 Selected References for NMR Spectra of Pseudotetrahedral Nickel(II) Complexes

Ligand	*Ref.*
Aminotroponeiminates	438–443
Salicylaldehyde imines	444–446
Benzaldehyde imines	447
Benzaldehyde ketoamines	448
Pyrrole-2-aldimines	449
Dihalobisphosphines	450–453
Nickelocenes	454

An important contribution to the nuclear spin relaxation time in paramagnetic nickel(II) complexes comes from the dipole–dipole interaction with the unpaired electron spin. The relaxation rate for this process is proportional to the inverse sixth power of the distance between spins and can be used to provide geometrical data.[456]

Table 29 Magnetic and Spectral Parameters for some Six-coordinate Nickel(II) Complexes[a]

Complex	Donor set	Conditions[b]	T_{2g} (ε_M)	^1E	T_{1g} (ε_M)	T_{1g} (P) (ε_M)	Ref.	μ_{eff} (BM)	Ref.	g_1	g_2	g_3	D[c]	λ_c	Ref.
$[Ni(H_2O)_6]^{2+}$	O_6	S	8500	15 400	13 500	25 300	460	3.24	461						
$Ni(OMPA)_3(ClO_4)_2$	O_6	C	7200–7250 (2.8–5.3)	14 700	12 300–12 500 (8.5–2.6)	23 500–23 600 (4.6–23.4)	462	3.26	463						
$[Ni(PNO)_6]^{2+}$	O_6	S	7936 (11.0)	12 986	14 184 (13.7)	25 733	464	3.14–3.32	465		2.33	2.26	3.16	0	466
										2.33		2.32	4.34	0	467
												2.28	5	0	468
$Ni(acac)_6(ClO_4)_2$	O_6	P	8600	14 900	13 600	25 300	469								
$Ni(DMSO)_6(ClO_4)_2$	O_6	S	7728 (3.5)		12 970 (3.6)	24 038 (10.1)	470								
$Ni(TMSO)_6(ClO_4)_2$	O_6	S	7752 (3.7)		12 987 (3.8)	24 010 (10.8)	470								
$[Ni(O_4C_2)_3]^{4-}$	O_6	S	8900	13 500	15 500	25 900	471								
$Ni(3\text{-}Mepz)_6(ClO_4)_2$	N_6	P	11 100	13 300	18 100	28 400	472	3.06	472						
$Ni(py)_6^{2+}$	N_6	P	9700	13 100	16 000	26 300	473								
$Ni(bipy)_3Br_2\cdot 6H_2O$	N_6	C	12 740	11 400	18 870		474								
$Ni(pz)_6(NO_3)_2$	N_6	C	10 650	13 500	17 100	27 500	475								
$Ni(en)_3(NO_3)_2$	N_6	C	11 330	12 700	18 520–18 600	29 750	476	2.82	477						
$Ni(im)_6(NO_3)_2$	N_6	C	10 150–10 300	13 098	17 600	28 150	473								
$Ni(den)_2Cl_2\cdot H_2O$	N_6	C	11 200–11 600–11 600		18 100–18 300–18 600	28 700–28 700–28 900	478								
$[Ni(amp)_3]^{2+}$	N_6	S	11 300	12 700	18 800		471								
$Ni(N_2H_4)_3Cl_2$	N_6	P	11 600	18 500		29 200	479								
$Ni(MeCN)_6(ClO_4)_2$	N_6	S	10 400 (5.5)	13 900	17 200 (4.6)	27 200 (6.3)	480	3.15	480						
$Ni(NH_3)_6(ClO_4)_2$	N_6	P	11 050	13 333	18 018	28 570	481								
$Ni(NH_3)_6Cl_2$	N_6							3.04	482						
$[NiP(py)_3](ClO_4)_2$	N_6	S	12 600 (4.9)	11 500 (4.0)	19 000 (6.4)		372	3.06	372						
$[Ni\{(py)_3tren\}](ClO_4)_2$	N_6	S	12 550 (7.7)	11 630 (7.9)	18 300 (12)		372	3.12	372						
$CsNiI_3$	I_6	P	6500	8000	11 000		483	3.6	483						
$CsNiCl_3$	Cl_6							3.41	484						
$CsNiBr_3$	Br_6							3.42	485						
$CsNiF_3$	F_6							3.6	486						
$Ni(py)_4(N_3)_2$	N_4N_2	P	9900	12 420	16 260		481								
$Ni(py)_4Cl_2$	N_4Cl_2	P	9040–11 730		16 820–14 930	25 960–24 900	487								
$Ni(py)_4Br_2$	N_4Br_2	P	8430–11 490		16 390–14 080	26 030	487								
$Ni(py)_4I_2$	N_4I_2	P	7905–11 834		16 393–13 158		481								
$Ni(pz)_4Cl_2$	N_4Cl_2	C	8000–10 950		16 400–13 100	26 500	475								
$Ni(pz)_4Br_2$	N_4Br_2	C	7240–10 900		15 900–12 000	25 800	475								
$Ni(5\text{-}Mepz)_4Cl_2$	N_4Cl_2	C	8560–11 400		16 710–13 680	26 460	488	3.16	472						
$Ni(5\text{-}Mepz)_4Br_2$	N_4Br_2	C	7650–11 500		16 200–12 220	25 980–24 170	488	3.09	472						

$Ni(5\text{-}Mepz)_4I_2$	N_4I_2	P	6529–10 759		15 364–10 850	25 416–23 446	489	3.15	472			
$Ni(4\text{-}vpy)_4(NCS)_2$	N_4N_2	P		12 850	17 400	10 400	490	3.18	490			
$Ni(anil)_4(ClO_4)_2$	N_4O_2	P	8300–11 300	12 500	16 300–14 300	24 500	491					
$Ni(anil)_4Cl_2$	N_4Cl_2	P	7900		13 700	23 300	491					
$Ni(anil)_4Br_2$	N_4Br_2	P	8200–9300	11 400	14 400	24 000	491					
$Ni(anil)_4I_2$	N_4I_2	P	7600–10 700	10 300	14 900	19 100	491					
$Ni(N_2H_4)_2SO_4$	N_4O_2	P	11 700		18 500	29 000	479					
$Ni(3\text{-}Etpy)_2Cl_2$	N_4Cl_2	P		11 630	13 420	23 580	492	3.37	492			
$Ni(N,N'\text{-}Et_2en)_2(NCS)_2$	N_4N_2	C	11 310–13 050		18 115–16 650	28 460	372					
$Ni(N,N'\text{-}Et_2en)_2Cl_2$	N_4Cl_2	C	8600–11 915	12 630	17 285–14 670	27 365	372					
trans-$[Ni(py)_4(H_2O)_2]I_2$	N_4O_2	C	9750–11 780	13 160	17 390–15 760	28 000	473					
trans-$[Ni(im)_4(H_2O)_2]Br_2$	N_4O_2	C	9340–11 830	13 990	17 510–14 815	28 300	473					
trans-$[Ni(py)_4(NH_2SO_3)_2]$	N_4O_2	P	8970–12 290		17 420–15 380	28 040	493					
trans-$[Ni(N,N'\text{-}Me_2en)_2(CCl_3CO_2)]$	N_4O_2	C	10 205–10 100–12 305	13 125–13 255	16 160–17 830–18 220	28 900	494					
trans-$[Ni(N,N\text{-}Me_2en)_2(CCl_3CO_2)]$	N_4O_2	C	8515–9955–12 010	13 055	15 625–17 542–17 687	27 640–28 345	494					
$Ni(N,N\text{-}Et_2en)_2(NCS)_2$	N_6	C	9140–10 420–12 120		15 770–18 350–18 350	28 310	495					
$Ni(NH_3)_4(NO_2)_2$	N_4O_2	P	11 500		16 000	28 000 sh	496	3.10	496	2.18	10.4	496
$Ni(en)_2(NCS)_2$	N_4O_2	C	9600–12 000	13 200	17 900–16 000	28 300–27 700	497					
$Ni(dtco)_2Cl_2$	S_4Cl_2	P	8260–9050		14 050–18 750	26 800	498	3.04	498			
$Ni(tu)_4Cl_2$	S_4Cl_2	C	7500–9300	10 500	13 500–12 300	23 300–22 200	499	3.19	500		0.8	500
$Ni(etu)_6(ClO_4)_2$	S_6	P	8000		13 500	19 100	501	3.24	501			
$Ni(detu)_6(ClO_4)_2$	S_6	P	8060		13 700	20 000	501	3.17	501			
$Ni(IMP)\cdot 7H_2O$	O_5N	P	8390		13 950	25 800	502	3.13	502			
$[Ni(pyDPT)Cl]Cl$	N_5Cl	S	10 950		22 900	27 870	503	3.9	503			
$Ni(py)_2(H_2O)_2(O_2CMe)_2$	O_4N_2	C	9260–10 360	14 490	16 800		504					
$Ni(DL\text{-}His)_2\cdot H_2O$	N_4O_2	C	10 600–11 400	12 800	16 500–18 800–19 000	27 300–28 900–29 600	505					
$Ni(NH_3)_2Cl_2$	Cl_4N_2	P	7800–8030		13 300–14 600	23 530–25 680	506					
$Ni(py)_2Cl_2$	Cl_4N_2	P	8580		13 400–14 360	23 850–24 650	506					
$NiCl_2(Me_6nas_3)$	As_3NCl_2	P	8500–9500		16 800	25 000	507	3.06	507			

[a] The energies of the electronic transitions are labelled according to the parent symmetry of the excited states. P refers to the free ion term which contributes mostly to the indicated state.
[b] The conditions under which the electronic spectra were obtained: S, solution; P, diffuse reflectance; C, single crystal.
[c] D and λ are the zero field splitting parameters: $D = \frac{3}{2}D_{zz}$, $\lambda = \frac{1}{2}(D_{xx} - D_{yy})/D$.

Abbreviations: OMPA = octamethylpyrophosphoramide; PNO = pyridine *N*-oxide; amp = 2-aminomethylpyridine; 4-vpy = 4-vinylpyridine; anil = aniline; 3-Etpy = 3-ethylpyridine; N,N'-Et_2en = 1,2-bis(ethylamino)ethane; N,N'-Me_2en = 1,2-bis(methylamino)ethane; N,N-Me_2en = 1-(dimethylamino)-2-aminoethane; N,N-Et_2en = 1-(diethylamino)-2-aminoethane; dtco = 1,5-dithiacyclooctane; tu = thiourea; etu = ethylthiourea; detu = N,N'-diethylthiourea; IMP = inosine-5′-monophosphate; DL-His = DL-histidine; Me_6nas_3 = tris(2-dimethylarsinoethyl)amine; pyDPT = $HN[CH_2CH_2NCH(C_5H_5N)]_2$; $P(py)_3$ = tris-2-pyridylphosphine; $(py)_3tren$ = 3,3′,3″-tris(pyridine-2-carboxaldimino)nitrilotriethane; den = bis(2-aminoethyl)amine.

Kowalewski analyzed the validity of the point dipole approximation in a series of complexes and found that the effective distance from the ligand nucleus to the unpaired spin agreed well with the internuclear distance for ^1H nuclei. Large deviations from the point dipole approximation have been found for the ligand nuclei directly bound to the metal.[457–459]

50.5.1.4 Survey of experimental results

In this section spectral and magnetic data on selected nickel(II) complexes are presented. The purpose of this section is that of showing some of the most relevant spectromagnetic studies on nickel(II) complexes. Particular emphasis will be given to work where a correlation between the properties and the electronic structure of nickel(II) complexes has been investigated. Much information is to be found in the tables, albeit without any detailed comment.

(i) *Six-coordinate complexes*

In Table 29 spectroscopic properties of selected six-coordinate nickel(II) complexes are shown.

Hydrated salts of hexaaqua ions have been studied for a long time. In Figure 18 the visible and MCD spectra[508] of some nickel(II) complexes are shown. In the case of $Ni(H_2O)_6(BrO_3)_2$ both *B* and *C* terms have been found to contribute to the MCD spectrum, the spectrum at 4.2 K being dominated by the *C* terms. This study supports the view that the ^1E_g state is interacting *via* spin–orbit coupling with the $^3T_{1g}$ giving the characteristic double-peaked 13 000 cm^{-1} band ('red band') of the absorption spectrum.

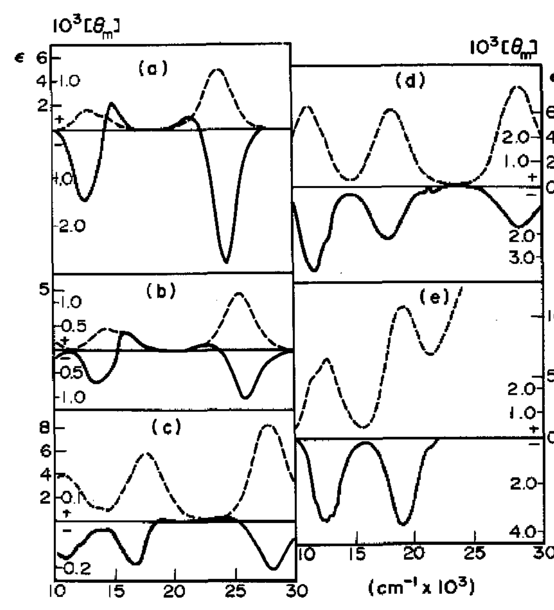


Figure 18 The absorption (dashed line) and magnetic circular dichroism (full line) spectra of (a) $[Ni(DMSO)_6]^{2+}$ in DMSO, (b) $[Ni(H_2O)_6]^{2+}$ in water, (c) $[Ni(NH_3)_6]^{2+}$ in water, with excess of ammonia present, (d) $[Ni(en)_3]^{2+}$ in water, and (e) $[Ni(bipy)_3]^{2+}$ in water (reproduced after ref. 508b)

An analogous interpretation has been given for the splitting of the red band in other octahedral complexes.[481,509,510]

The magnetic properties of octahedral nickel(II) complexes are dominated by the zero field splitting of the ground $^3A_{2g}$ state which, neglecting the rhombic components, is split into a doublet and a singlet whose energy separation is called *D* (Figure 12). The sign of *D* determines whether the doublet ($D<0$) or the singlet ($D>0$) lies lowest. The parameter *D* is usually found to be less than 10 cm^{-1}. The sign of *D* can be determined by measuring the anisotropy of the magnetic susceptibility, $\chi_\perp > \chi_\parallel$ leading to positive D values. Both signs of D have been found; it is positive, for example, in $Ni(H_2O)_6(NO_3)_2$,[511] $Ni(H_2O)_6SnCl_6$,[511,512] $Ni(PNO)_6X_2$ ($X = ClO_4$, BrO_3, BF_4)[466–468] and $Ni(tu)_4Cl_2$,[500] and negative in $NiCl_2{\cdot}4H_2O$,[513] $NiZrF_6{\cdot}6H_2O$,[512] $Ni(H_2O)_6(ClO_4)_2$,[514] $Ni(H_2O)_6Br_2$[515] and $Ni(en)_3(NO_3)_2$.[516] The zero field splitting of the ground state has important consequences on the magnetic behaviour of octahedral nickel complexes at very low temperatures. When D is negative, at low temperature only the low-lying doublet will be populated and long range magnetic ordering can occur, as in an effective $S = \frac{1}{2}$ ion.[515,517] When D is positive the singlet level lies lowest but long range order can occur, induced by the magnetic field (subcritical interactions).[467,511]

The AOM has been used to rationalize the electronic structure of six-coordinate nickel(II) complexes.[518] Particular attention was devoted to the rationalization of the magnetic properties of $Ni(PNO)_6(BF_4)_2$. In this complex Ni^{II} possesses S_6 site symmetry and the oxygens occupy almost exactly the positions expected in O_h symmetry. However, this complex shows quite large magnetic anisotropy[519] which can be rationalized using an anisotropic π interaction between the metal and the pyridine *N*-oxide ligands. The sign of the magnetic anisotropy determines the sign of the zero field splitting ($D \approx 3$–$4\ cm^{-1}$) which in turn fixes the sign of the π anisotropy requiring $e_{\pi x} < e_{\pi y}$, where y and x refer to the directions perpendicular and parallel respectively to the Ni—O—N plane.

Bertini *et al.*[497] and Lever *et al.*[495] measured the electronic spectra of a series of tetragonal nickel(II) ammine complexes and found a relationship between the Ni—N distance and the e_σ parameter, e_σ decreasing when the Ni—N distance increases.

The electronic and magnetic structure of $Ni(NH_3)_4(NO_2)_2$ has been investigated using spectromagnetic techniques,[496] as well as by determination of electron density by X-ray diffraction[520] and of spin density by polarized neutron diffraction.[521] The magnetic susceptibility follows a Curie–Weiss equation with $\theta = -5.5$ K between 10 and 300 K. Below 10 K zero field splitting effects become important and a value of D of $10.4\ cm^{-1}$ has been estimated. Both charge density and spin density show that the nitrito groups and ammonia molecules are σ-bonded to the nickel atom and that the nitrito group is a stronger σ donor. π bonding effects were found to be negligible. Non-zero spin densities were measured on two of the three ammonia hydrogen atoms and on the oxygen atoms of the nitrito groups.

(*ii*) *Tetrahedral complexes*

In Table 30 spectroscopic properties of selected pseudotetrahedral nickel(II) complexes are shown.

The magnetic properties of pseudotetrahedral complexes have been extensively studied since their magnetic moments show a sharp variation with temperature below 80 K. A typical example is the $NiCl_4^{2-}$ ion whose magnetic moment varies from 1.0 to 3.5 BM in the temperature range 4.2–80 K.[523,546,547]

The electronic structure of pseudotetrahedral nickel(II) complexes has been widely studied by Gerloch *et al.* using mainly the AOM to fit electronic transitions and anisotropic magnetic susceptibility. The sign of the anisotropy of the magnetic susceptibility has been related to the nature of the tetragonal distortion, being $\mu_\perp < \mu_\parallel$ for compressed ones[548] reflecting the change in the nature of the ground state (Figure 10).

The nature of the Ni^{II}—P bond in pseudotetrahedral phosphine complexes has received much attention. With the AOM Gerloch *et al.* showed that phosphine bonds are characterized by a large σ basicity and large π acidity corresponding to a back-donation of electrons from the nickel to the phosphorus atom in both mono and bis phosphine complexes.[549,550]

(*iii*) *Five-coordinate Complexes*

In Tables 31–33 spectroscopic properties of selected five-coordinate nickel(II) complexes are shown.

Many ligand field calculations have been performed on five-coordinate nickel(II) complexes to assign the electronic transitions,[518,573–577] but no systematic application of these calculations has been reported. The suggested assignment of the electronic transitions is shown in Tables 31–33.

Table 30 Magnetic Moments and Spectral Parameters for some Pseudotetrahedral Nickel(II) Complexes[a]

Complex	*Donor set*	*Conditions*[b]	T_1 (ε_M)	T_2 (ε_M)	A_2 (ε_M)	^1D (ε_M)	T_1 (*P*) (ε_M)	^1G (ε_M)	*Ref.*	μ_{eff} (BM)	*Ref.*
$(Et_4N)_2NiCl_4$	Cl_4	C		4000–4500	7270	12 100	14 700		522	3.9	523
$NiBr_4^{2-}$	Br_4	S			7070	10 580	13 260–14 230	18 350–21 510	524	3.80	525
NiI_4^{2-}	I_4	S			7030 (47)		11 350–12 120 (369–396)	13 720–14 900 (65)	524	3.44	526
Ni^{2+} in ZnO	O_4	C		4300	8400	8800–13 500	15 300–17 300		527		
$Ni(PhN{=}C(Me)CH_2C(Me){=}NPh)_2$	N_4	S		7250–8500 (63–56)	10 000 (38)		15 870 (500)		402	3.10	402
$Ni(MMPM)_2$	N_4	S			6050 (24)		13 500–14 600 (345–337)		528	3.42	528
$Ni(MBrPM)_2$	N_4	S			6450 (27)		12 310–13 590 (645, 496)		528	3.55	528
$Ni(DPMT2)_2$	N_4	S			7300 (24)	12 300sh	13 000–14 200 (361, 338)		529		
$[NiPPh_3Br_3][Ph_4As]$	PBr_3	C	5800	7100	9500		14 700–15 600		530	3.42	531
$[NiPPh_3I_3][Ph_4As]$	PI_3	C	7100	5600–7800	9400		13 400–14 800		530	3.36	531
$(Ni,Zn)(dabc)Cl_3$	NCl_3	C		5100–6410	8700		15 000–16 200		532	3.66	533
$Ni(quin)Br_3$	NBr_3	C	4760	6150	8550	10 500–12 350	13 500–17 000	18 700–21 800	534	3.84	534
$Ni(dabc)Br_3$	NBr_3	P		5100–6400	8700		15 000–16 200		533	3.59	533
$Ni(pop)Cl_2$	P_2Cl_2	P	4900	8100–9350	11 700		18 200		535	3.26	535
$(Ph_3P)_2NiCl_2$	P_2Cl_2	C	4800	8000–10 200	11 200	10 800	17 000–18 100		536, 537	3.41	538
$Ni(PCyp_3)_2Cl_2$	P_2Cl_2	S			11 900 (109)		19 450 (255)		452	3.15	452
$(Ph_3P)_2NiBr_2$	P_2Br_2	P	4000	8800–10 900	14 900		16 800		537	3.27	538
$Ni(pop)Br_2$	P_2Br_2	S	5000 (36)	8800	11 500 (200)		17 400 (147)		535	3.23	535
$Ni(PCyp_3)_2Br_2$	P_2Br_2	S			11 840 (228)		11 770 (208)		452	3.16	452
$Ni(pop)I_2$	P_2I_2	S	5000		10 900 (565)		15 400		535		
$NispCl_2$	N_2Cl_2	P	5000	7200–9000	12 000		16 500–20 500		539	3.69	539
$Ni(lut)_2Cl_2$	N_2Cl_2	S			12 050		18 083 (109)		540	3.61	540
$Ni(B_2bn)Br_2$	N_2Br_2	S		7550–10 150(25–84) 11 230 (60)	11 430 (60)		15 500–18 630 (183)		541		
$Ni(lut)_2Br_2$	N_2Br_2	S			11 560		17 480 (134)		540	3.54	540
$Ni(biquin)Br_2$	N_2Br_2	P	4500	7700	9800		19 250		542		
$Ni(sal\text{-}N\text{-}Pr^i)_2$	N_2O_2	P			6200	12 000	14 280–17 500	19 000–22 400	523	3.23	543
$Ni(Ph_3PO)_2Cl_2$	O_2Cl_2	P			14 300		16 300		544	3.7	544
$Ni(Ph_3AsO)_2Cl_2$	O_2Cl_2	S	7812 (15)		12 270 (6.5)		15 000–16 5000 (77–79)		545	3.95	545
$Ni(Ph_3AsO)_2Br_2$	O_2Br_2	S	7690 (27)		11 760 (6)		14 600–15 900 (164–184)		545	3.96	545
$Ni(Ph_3PO)_2Br_2$	O_2Br_2	S			13 300		15 500 (101)		544	3.98	544
$Ni(Ph_3PO)_2I_2$	O_2I_2	S	7067 (18.2)		13 700		15 100 (137)	22 700 (470)	544	3.84	544

[a] The energies of the electronic transitions are labelled according to the parent symmetry of the excited states. P refers to the free ion term which contributes mostly to the indicated state.
[b] The conditions under which the electronic spectra were obtained: S, solution; P, diffuse reflectance; C, single crystal.
Abbreviations: quin = quinoline; pop = oxydiethylenebis(diphenylphosphine); lut = lutidine; biquin = 2,2′-biquinoline; sal-*N*-Pr^i = *N*-isopropylsalicylideneiminate; dabc = *N*-ethyl-1,4-diazabicyclo[2.2.2]octonium; MMPM = 3,3′,5,5′-tetramethyldipyrromethene-4,4′-dicarboxylate; MBrPM = 5′-bromo-3,4′,5-trimethyldipyrromethene-4,4′-dicarboxylate; DPMT2 = 3,3′,5-trimethyldipyrromethene; $PCyp_3$ = tricyclopropylphosphine; sp = (−)-spartein; B_2bn = 2,3-bis(benzololimino)butane.

Table 31 Magnetic Moments and Spectral Parameters for some High-spin Five-coordinate Nickel(II) Complexes with Nearly Trigonal Bipyramidal Geometry[a]

Complex	*Donor set*	*Conditions*[b]	E'' (ε_M)	A_1 (ε_M)	A_2 (ε_M)	E'' (P) (ε_M)	A_2 (P) (ε_M)	^1D		μ_{eff} (BM)	*Ref.*
[Ni(Me_6tren)NCS]NCS	N_5	C	7700	13 200	13 200	16 200	21 000	24 600		3.3	551
[Ni(Me_6tren)Br]Br	N_4Br	P	7100 (28)	10 500 (21)	11 400 (18)	14 500 (34)	20 000sh	23 000 (71)		3.42	552
[Ni(Me_6tren)Cl]Cl	N_4Cl	P	7100 (26)	10 700 (22)	11 500 (19)	14 600 (30)	20 000sh	23 300 (172)		3.42	552
[Ni(Me_6tren)I]I	N_4I	P	7200	10 400	10 400	13 800		24 300		3.40	552
[Ni(Me_6tren)NO_3]NO_3	N_4O	P	9300	11 400	12 300	15 600		24 600		3.28	552
Ni(Et_4den)Cl_2	N_3Cl_2	S		10 000 (20)		12 500 (20)	18 900 (55)	22 150 (80)		3.40	553
Ni(Me_5den)Cl_2	N_3Cl_2	P	5000	9600	12 700	15 700	18 900	21 700		3.38	554
Ni(Et_4den)Br_2	N_3Br_2	S		10 100 (15)		12 700 (15)	18 300 (185)	21 650 (90)			553
Ni(Et_4den)I_2	N_3I_2	S		10 500 (8)			17 400 (150)				553
[Ni(dabc)Cl_3]Cl	N_2Cl_3	P	5500			10 700	17 700	20 400		3.73	555
Ni(sal-*N*-Me)$_2$	N_2O_3	P	7300	14 400						3.2	556
Ni(dabc)(H_2O)Br_3	$NOBr_3$	P	5500			10 500		20 000	16 400	3.69	557
Ni(dabc)(H_2O)Cl_3	$NOCl_3$	P	5000	800	8000	10 800	18 000	20 700	16 000	3.69	557

[a] The energies of the electronic transitions are labelled according to the parent symmetry of the excited states. P refers to the free ion term which contributes mostly to the indicated state.

[b] The conditions under which spectra were obtained: S, solution; P, diffuse reflectance; C, single crystal.

Abbreviations: Et_4den = bis(diethylaminoethyl)amine; sal-*N*-Me = *N*-methylsalicycaldiminato.

Table 32 Magnetic Moments and Spectral Parameters for some High-spin Five-coordinate Nickel(II) Complexes with Nearly Square Pyramidal Geometry[a]

Complex	*Donor set*	*Conditions*[b]	$E\ (\varepsilon_M)$	$A_2\ (\varepsilon_M)$	$B_2(\varepsilon_M)$	$E\ (\varepsilon_M)$	$A_2\ (\varepsilon_M)$	$E\ (\varepsilon_M)$	^1D	μ_{eff} (BM)	*Ref.*
$[Ni(Me_3AsO)_5](NO_3)_2$	O_5	P		8700	11 300	13 500	17 150	19 100	22 100		558
$[Ni(Me_3PO)_5](ClO_4)_2$	O_5	P		8300	10 800	13 950	17 300	19 400	22 200		558
$[Ni(Ph_3AsO)_4ClO_4]ClO_4$	O_5	P	9400	12 300	13 900	16 800	19 800	23 600			559
$[Ni(Ph_3PO)_4ClO_4]ClO_4$	O_5	P	8000	11 700	14 100	17 100	20 000	23 200			559
$[Ni(MePh_2PO)_4ClO_4]ClO_4$	O_5	P	7400	11 700	13 800	16 500	18 700	23 000			559
$[Ni(MePh_2AsO)_4NO_3]NO_3$	O_5	C	5500	8200	9300	11 900	19 000	22 900	10 500–21 000	3.39	560
$Ni(N_3As)(NCS)_2$	N_5	P	6300	11 300	12 200	14 900	24 400	28 600		3.37	561
$Ni(N_3P)(NCS)_2$	N_5	S	6200 (19)	11 300sh	12 100sh	14 800 (36)		21 900 (640)		3.34	561
$[Ni(tpen)](ClO_4)_2$	N_5	S	7385 (12.5)	11 870 (6.9)	13 630 (5.9)	17 510 (47.8)				3.14	562
$[Ni_2Cl_8](dabc)_2$	Cl_5	P	7140	9600	11 900	15 300	17 200	19 200		3.35	563
$[Ni(2\text{-}Meim)_4Cl]Cl$	N_4Cl	P	5500	10 550	11 500	15 150	23 000	26 000	12 560–21 700		518
$[Ni(tet)Cl]Cl$	N_4Cl	P	5600	10 600	11 400	16 200	21 500	25 500		3.2	564
$[Ni(2\text{-}Meim)_4Br]Br$	N_4Br	C	5150	10 300	11 600	15 300	22 800	24 800	12 400–27 700		518
$[Ni(tet)Br]Br$	N_4Br	P	5200	10 000		16 200	19 000	25 300		3.0	564
$Ni(5\text{-}Cl\text{-}SalNEt_2)_2$	N_3O_2	P	7700	9900	12 600	16 500				3.19	566
$Ni(Pr^i\text{-}dpt)_2quin$	S_4N	S		13 300 (120)			21 740 (337)				567
$[Ni(N_3P)Cl]BPh_4$	N_3PCl	P	7700	10 000	11 400	15 400	23 200	26 300		3.24	561
$Ni(triphos)SO_4$	P_3O_2	P	9800			14 200	18 800	26 300		3.01	568
$Ni(dacoda)H_2O$	N_2O_3	S		12 300 (21.4)	13 100 (25.2)	15 800 (28)		26 400 (86.5)		3.30	569

[a] The energies of the electronic transitions are labelled according to the parent symmetry of the excited states.
[b] The conditions under which the electronic spectra were obtained: S, solution; P, diffuse reflectance; C, single crystal.
Abbreviations: N_3As = bis(diethylaminoethane)(diphenylarsinoethane)amine; N_3P = bis(diethylaminoethane)(diphenylphosphinoethane)amine; tpen = *N,N,N'*-tris[2-(2'-pyridyl)ethyl]ethylenediamine; tet = *N,N'*-di(3-aminopropyl)piperazine; 5-Cl-SalNEt_2 = *N,N*-diethyl-5-chlorosalicylideneiminate; Pr^idpt = diisopropylethyldithiophosphate; dacoda = 1,5-diazacyclooctane-*N,N'*-diacetate.

Table 33 Magnetic Moments and Spectral Parameters for some High-spin Five-coordinate Nickel(II) Complexes with Geometry Intermediate between a Trigonal Bipyramid and a Square Pyramid[a]

Complex	*Donor set*	*Conditions*[b]	$A_1\ (E')$	$B_1\ (E')$	$A_2\ (E'')$	$B_2\ (E'')$	$B_1\ (A_2)$	$A_2\ (A_1'')$	$B_2\ (A_2)$	$A_2\ (P)$	$B_1\ (P)$	$B_2\ (P)$	μ_{eff} (BM)	*Ref.*
$Ni(mpt)_2(Me_2phen)$	S_3N_2	C		6400	7400		9700	11 700	14 500	23 800	19 800	23 100		570
Ni(sal-MeDPT)	N_3O_2	C		5000	10 000	8400	16 800	12 000	16 800				3.3	571
$[Ni_2(dbhe)_2(ClO_4)_2]$	N_3O_2	C			9000	7000	12 000	11 300	15 200	24 000	21 200			572

[a] The energies of the electronic transitions are labelled according to the parent symmetry of the excited states. **P** refers to the free ion term which contributes mostly to the indicated states.
[b] The conditions under which the electronic spectra were obtained: C, single crystal.
Abbreviations: mpt = dimethylphosphorodithioato; Me_2phen = 2,9-dimethylphenanthroline; sal-MeDPT = bis(3-salicylaldiminatopropyl)methylamine; dbhe = *N,N*-bis[2-(diethylamino)ethyl][(2-hydroxyethyl)amino-O].

Gerloch *et al.* measured the anisotropic susceptibility of the complexes $(Ph_2MeAsO)_4NiNO_3^+$ and bis(5-chloro-*N*-*p*-diethylaminoethylsalicylideneiminato)-nickel(II).[560,566] The nickel(II) in the first complex has C_{4v} site symmetry and the sign of the magnetic anisotropy is $\mu_\perp > \mu_\parallel$. In the second complex, nickel(II) has no such high symmetry, and although the chromophore is not largely distorted from C_{4v}, the magnetic tensor is far from that expected in C_{4v} symmetry, showing that low-symmetry components of the ligand field play an important role in determining the magnetic properties of five-coordinate complexes.

The magnetic moment of trigonal bipyramidal nickel(II) complexes is smaller, at room temperature, than that expected for a $^3E'$ ground state. This fact has been attributed either to an admixture of an excited orbital doublet into the ground state[578,579] or to Jahn–Teller effects.[551] The temperature variation of the magnetic susceptibility of $[NiBr(Me_6tren)]Br$ and $[NiNCS(Me_6tren)]SCN \cdot H_2O$, measured in the range 4.2–280 K, was recently measured and fitted using an AO model[580] with high anisotropic orbital reduction factors ($k_x = 0.93$, $k_y = 0.93$, $k_z = 0.34$ and $k_x = 0.90$, $k_y = 0.94$ and $k_z = 0.50$ for the Br and SCN derivatives respectively). These highly anisotropic k values lead the authors to conclude that the Ham effect, which yields a large vibronic quenching of the z component of the orbital angular momentum, is responsible for the low magnetic moments of high-spin trigonal bipyramidal nickel(II) complexes.

50.5.1.5 Low-spin complexes

Low-spin nickel(II) complexes exist in five-coordinate (either trigonal bipyramidal or square pyramidal) and in square planar geometries. The low-spin state is favoured with respect to the high-spin state by ligands containing donor atoms with high e_σ and e_π values and large nephelauxetic effects such as P, S, As, *etc.* The nephelauxetic effect, which is related to the delocalization of the metal electrons over the ligand's nuclei and to the covalency of the metal–ligand bond, reduces the separation between the free ion terms while the stronger e_σ and e_π interactions increase the crystal field stabilization energy.

The influence of these effects on the nature of the ground state in nickel(II) complexes has been investigated by several authors.[581–587]

Sacconi found a useful correlation between the spin state of five-coordinate complexes and the sum of the electronegativities and the nucleophilic reactivity constant of the donor groups.[582]

Low-spin complexes have a ^1A ground state and are all diamagnetic. The spectroscopic technique most widely used to investigate their electronic structures is electronic absorption spectroscopy. In the following subsections we will consider some applications of this spectroscopic technique.

(*i*) *Five-coordinate complexes*

In the limit of a regular trigonal bipyramidal geometry (D_{3h} symmetry) the ^1D levels split into $^1A_1$, $^1E'$ and $^1E''$ levels, as shown in Figures 7d and 7e, and two electronic transitions, $^1A_1 \rightarrow {}^1E'$ and $^1A_1 \rightarrow {}^1E''$, are anticipated which can be further split on going to low symmetry chromophores where the degeneracy of the E levels is removed (see Figure 7c). The intensity of these transitions is generally fairly high ($\varepsilon_M \approx 1000$–$4000$) due to the appreciable ligand character of the metal–ligand bond which causes these *d–d* transitions to become more dipolar-allowed. In the two band spectrum the low energy transition usually has higher intensity than the higher energy one since the $^1A_1 \rightarrow {}^1E''$ transition is forbidden in D_{3h} symmetry. Typical examples of spectra are shown in Figure 19. In Table 34 spectral data for selected examples of low-spin five-coordinate complexes are shown.

The splitting of the ^1D term for square pyramidal complexes in the limit of C_{4v} symmetry is shown in Figures 7a and 7b. In this symmetry three electronic transitions are anticipated, namely $^1A_1 \rightarrow {}^1B_1$, $^1A_1 \rightarrow {}^1E$ and $^1A_1 \rightarrow {}^1A_2$, with a stronger $^1A_1 \rightarrow {}^1E$ band which is allowed in C_{4v} symmetry. The three 'C_{4v}' bands lie in the ranges 15 000–18 000, 21 000–24 000 and 27 000–29 000 cm^{-1}. Typical examples of spectra are shown in Figure 20. Spectroscopic data for selected examples of low-spin five-coordinate square pyramidal complexes are shown in Table 35.

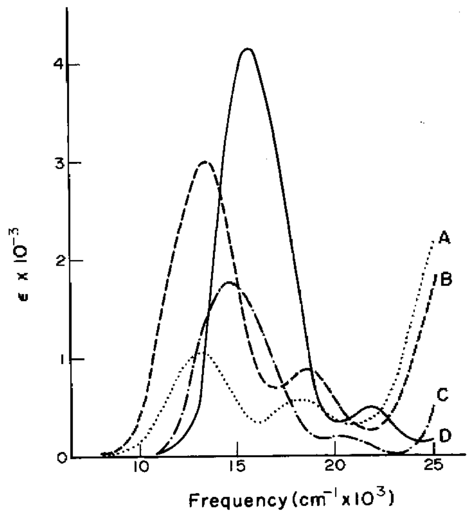


Figure 19 Electronic spectra of (A) $[NiBr(tan)]^+$, (B) $[NiBr(tpn)]^+$, (C) $[NiBr(tsep)]^+$, (D) $|NiBr(qas)|^+$ (reproduced after ref. 360)

Table 34 Spectral Parameters for some Low-spin Five-coordinate Nickel(II) Complexes with Nearly Trigonal Bipyramidal Geometry[a]

Complex	*Donor set*	*Conditions*[b]	$^1E'$ (ε_M)	$^1E''$ (ε_M)	*Ref.*
$Ni(PMe_3)_3Br_2$	P_3Br_2	S	14 100–17 200 (600–800)	22 200 (170)	588, 589
$Ni(PMe_3)_3Cl_2$	P_3Cl_2	P	15 100–17 200	23 200	589
$Ni(PMe_3)_3I_2$	P_3I_2	P	13 700–16 700	23 800	589
$[Ni(Sbta)Cl]BPh_4$	As_2Sb_2Cl	S	18 350 (2620)	23 950 (220)	590
$[Ni(Sbta)Br]BPh_4$	As_2Sb_2Br	S	18 000 (2150)	23 500 (65)	590
$[Ni(Sbta)NCS]NCS$	As_2Sb_2N	S	19 400 (3150)	24 250 (605)	590
$[Ni(tap)Cl]ClO_4$	As_3PCl	S	15 900sh	17 900 (2300)	591
$[Ni(taa)Cl]ClO_4$	As_4Cl	S	14 600sh	16 600 (1950)	591
$[Ni(qas)Cl]ClO_4$	As_4Cl	S	16 200 (4470)	21 800 (330)	592
$[Ni(tsp)Cl]ClO_4$	PS_3Cl	S	15 390 (1260)	20 960 (303)	593
$[Ni(tpn)X]X$ (X = Cl, Br, I)	NP_3X	S	13 200, 13 900 (2800–3100)	18 200, 20 000 (800–1450)	594
$[Ni(tan)Br]BPh_4$	NAs_3Br	S	12 650 (1000)	17 100 (600)	594
$[Ni(tan)I]BPh_4$	NAs_3I	S	13 150 (2620)	18 100 (1400)	594

[a] The energies of the electronic transitions are labelled according to the parent symmetry of the excited states.
[b] The conditions under which the electronic spectra were obtained: S, solution; P, diffuse reflectance.
Abbreviations: Sbta = tris(*o*-dimethylarsinophenyl)stibine; tap = tris(3-dimethylarsinopropyl)phosphine; taa = tris(3-dimethylarsinopropyl)arsine; qas = tris(*o*-diphenylarsinophenyl)arsine; tsp = tris(*o*-methylthiophenyl)phosphine; tpn = tris(diphenylphosphinoethyl)amine; tan = tris(diphenylarsinoethyl)amine; $tsep_2$ = tris(*o*-methylselinophenyl)phosphine.

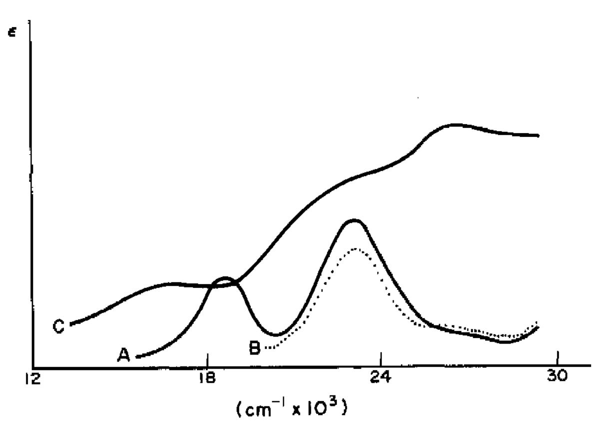


Figure 20 Electronic spectra of (A) $[Ni(diars)(triars)]^{2+}$, (B) $[Ni(diars)_2]^{2+}$, (C) $[Ni(dsp)(sp)](ClO_4)_2$ (after refs. 595 and 596)

Table 35 Spectral Parameters for some Low-spin Five-coordinate Nickel(II) Complexes with Nearly Square Pyramidal Geometry[a]

Complex	*Donor set*	*Conditions*[b]	$^1B_1$ (ε_M)	^1E (ε_M)	$^1A_2$ (ε_M)	*Ref.*
$[Ni(diars)(triars)]ClO_4$	As_5	S	18 620 (1150)	23 365 (2380)	26 850sh	595
$[Ni(diars)_2Cl]Cl$	As_4Cl	S	18 030sh	22 080 (1530)	26 285 (190)	595
$[Ni(dsp)(sp)](ClO_4)_2$	S_3P_2	S	16 000 (200)	21 000 (750)	26 000 (5500)	596
$[Ni(tas)Br_2]$	Br_2As_3	S	14 930 (348)	19 230sh	21 980 (951)	597
$[Ni(dap)(CN)_2]$	C_2As_3	P	18 740		26 360	597
$[Ni(dpp)Cl_2]$	P_3Cl_2	P	18 700		23 800	598, 599

[a] The energies of the electronic transitions are labelled according to the parent symmetry of the excited states.
[b] Indicates the conditions under which the electronic spectra were obtained: S, solution; P, diffuse reflectance.
Abbreviations: diars = *o*-phenylenebidimethylarsine; triars = bis(*o*-dimethylarsinophenyl)methylarsine; dsp = bis(*o*-methylthiophenyl)methylarsine; tas = bis(3-dimethylarsinopropyl)methylarsine; dap = bis(3-dimethylarsinopropyl)-phenylphosphine; dpp = bis(2-diphenylphosphinoethyl)phenylphosphine; sp = diphenyl(*o*-methylthiophenyl)phosphine.

(ii) Square planar complexes

In a regular square planar environment (D_{4h} symmetry), three spin-allowed transitions corresponding to $^1A_{1g}\rightarrow{}^1B_{2g}$, $^1A_{1g}\rightarrow{}^1E_g$ and $^1A_{1g}\rightarrow{}^1B_{1g}$ are expected with low intensity ($\varepsilon_M\approx 50$–200) due to the presence of the inversion centre. Generally the *d–d* spectra are not very well resolved and are obscured by charge transfer transitions; much ambiguity still remains in the assignment of the electronic transitions which are very sensitive to low symmetry effects and π interactions. On passing to low symmetry chromophores the E_g state is split and two transitions can in principle be observed. In D_{2h} symmetry ^1E_g splits into $^1B_{2g}$ and $^1B_{3g}$; the splitting of this doublet state can be expressed as $E = E(^1B_{2g}) - E(^1B_{3g}) = 4\cos\alpha\, e_{\pi c}$ where α is 90° in D_{4h} complexes and $e_{\pi c}$ is the x component of the π interaction.[600]

Spectroscopic data for selected examples of square planar complexes are shown in Table 36.

Table 36 Spectral Parameters for some Square Planar Nickel(II) Complexes[a]

Complex	*Donor set*	*Conditions*[b]	$^1B_{2g}$ (ε_M)	^1E_g (ε_M)	$^1B_{1g}$ (ε_M)	*Ref.*
$Ni(daco)_2(ClO_4)_2\cdot 2H_2O$	N_4	C	23 480	24 540	22 370	601
$Ni(EMG)_2$	N_4	C	20 200	24 700–26 000	31 000	602
$Ni(CN)_4^{2-}$	N_4	C	31 100	31 650		603
$Ni(dpm)_2$	O_4	C	16 000	20 000	18 500	604
$Ni(Et_2dtp)_2$	S_4	C	14 900	17 200	19 200	605
$Ni(Et_2dtc)_2$	S_4	C	15 900	17 000–19 000	21 000	606, 607
$Ni(taa)_2$	S_2O_2	C	15 870	15 870	19 450	608
$Ni(dtp)_2$	S_4	P	19 100	14 500	26 100	609
$Ni(dtc)_2$	S_4	P	21 200	15 800		609
Ni(bdt)	S_4	S	11 600sh			610
Ni(ptt)	S_4	S	13 800 (225)	17 400 (2300)		610
$Ni(OEtsacsac)_2$	S_4	S	14 700 (101)	17 500 (385)		611
$Ni(sacsac)_2$	S_4	S	14 890 (330)			612

[a] The energies of the electronic transitions are labelled according to the parent symmetry of the excited states.
[b] The conditions under which the electronic spectra were obtained: S, solution; P, diffuse reflectance; C, single crystal.
Abbreviations: daco = 1,5-diazacyclooctane; EMG = ethylmethylglyoximate; dpm = dipivaloylmethane; Et_2dtp = diethyldithiophosphate; Et_2dtc = *N,N*-diethyldithiocarbamate; dtp = dithiophosphate; dtc = dithiocarbamate; bdt = ethylene-1,2-dithiolato; ptt = propene-3-thione-1-thiolato; OEtsacsac = *O*-ethylthioacetate; sacsac = dithioacetylacetonato; taa = monothioacetylacetonato.

Spectra of four-coordinate complexes which show four bands attributed to *d–d* transitions have been recorded at low temperature. An example is shown in Figure 21.

In $Ni(taa)_2$ absorption maxima at 19 000–25 000 cm^{-1} have been attributed to charge transfer transitions.[608]

The tetracyanonickelate(II) ion is the most extensively studied square planar complex of nickel(II). The electronic spectrum is characterized by *d–d* bands at 31 000–32 000 cm^{-1} ($\varepsilon_M\approx 500$–800) and charge transfer bands ($\varepsilon_M\approx 6000$–15 000) at 33 000–37 000 cm^{-1}. In Figure 22 the electronic and MCD spectra of $K_2Ni(CN)_4$ are shown. In the MCD spectrum of the low energy band (*d–d*), since *C* terms are zero because the ground state is $^1A_{1g}$, the presence of the

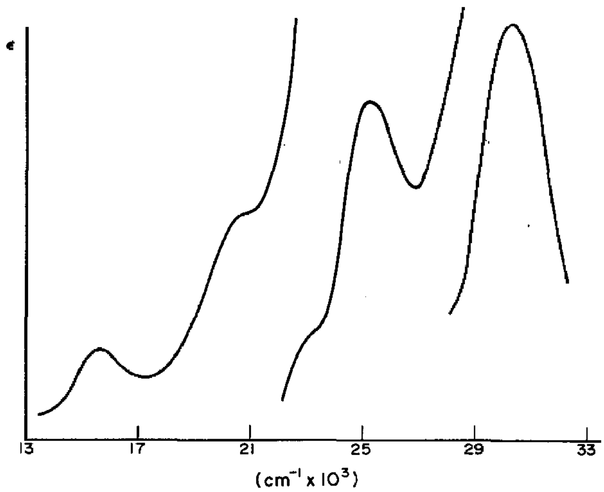


Figure 21 Electronic spectra of $Ni(Et_2dtc)_2$

A term (which changes sign at the absorption maximum) is evident, thus confirming that this band arises from a transition to a degenerate E_g state.[613] Several MO calculations[583,613–615] have been performed to clarify the nature of the charge transfer transitions, the low energy ones being due to a $4p_z$-stabilized π^* CN orbital. MCD spectra of $Ni(dtp)_2$ and $Ni(dtc)_2$ also showed that in these complexes the low energy transition is to a ^1E state.[616,617] The electronic spectra of square planar nickel(II) complexes with sulfur ligands have been extensively studied by Gray and co-workers.[618–620]

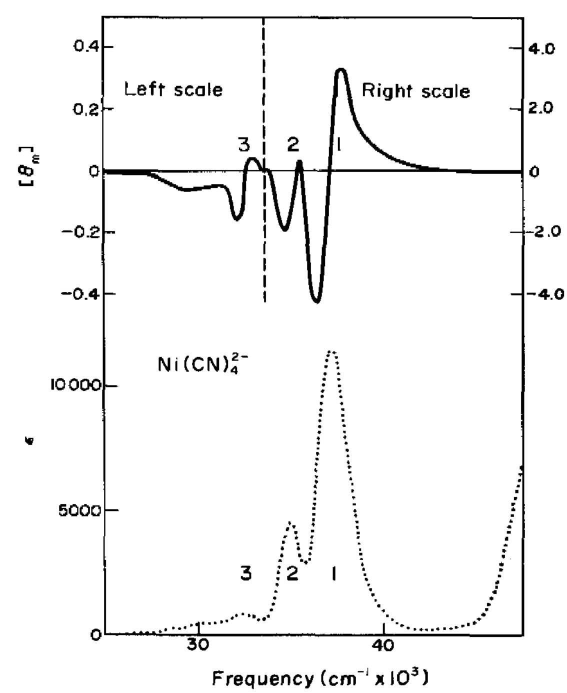
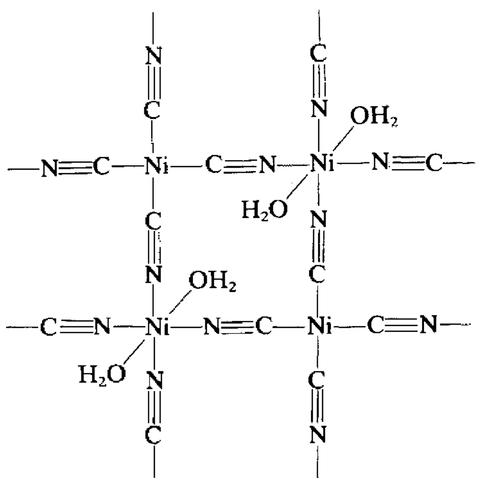


Figure 22 Absorption spectrum and MCD of $Ni(CN)_4^{2-}$ in H_2O. $[\theta_M]$ is the molar ellipticity (defined as in natural optical activity in degrees deciliter decimeter^{-1} mole^{-1}) per gauss in the direction of the light beam. ε is the molar extinction coefficient. The numbering of the bands is indicated (reproduced after ref. 613)

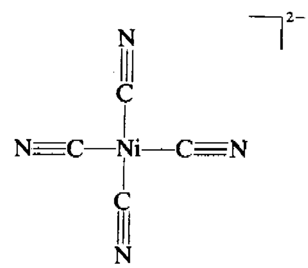
50.5.2 Cyano Complexes[621–624]

A grey-blue compound of stoichiometry $Ni(CN)_2{\cdot}1.5H_2O$ is formed by the reaction of $NiSO_4$ and KCN in stoichiometric ratio in boiling water. In this polymeric compound the bridging CN groups are C-bonded in square planar $Ni(CN)_4$ units and N-bonded in octahedral $Ni(NC)_4(OH_2)_2$ units (**91**).[625] The magnetic moment (about 2.3 BM) accounts for the existence of both diamagnetic and paramagnetic nickel(II) in a 1:1 ratio. Numerous hydrates $Ni(CN)_2{\cdot}xH_2O$, of uncertain structure, have been prepared and may be converted by heating in the diamagnetic anhydrous $Ni(CN)_2$.[626]

Hydrated $Ni(CN)_2$ dissolves in aqueous KCN and the yellow diamagnetic potassium tetracyanonickelate(II) $K_2Ni(CN)_4$ (**92**) crystallizes upon evaporating the solvent (equation 111).



(91)



(92)

$$Ni(CN)_2{\cdot}xH_2O + 2KCN \xrightarrow{H_2O} K_2[Ni(CN)_4]{\cdot}H_2O \xrightarrow{105\,°C} K_2[Ni(CN)_4] \qquad (111)$$

The $[Ni(CN)_4]^{2-}$ anion is one of the most stable nickel(II) complexes and an overall formation constant as high as about 10^{30} has been determined.[627,628] The structure of the complex is square planar with the nickel(II) bound to carbon atoms of cyanides and with linear Ni—C—N linkages (Table 37).[629,630] The planar $[Ni(CN)_4]^{2-}$ units are stacked in columns in the crystal lattice with Ni—Ni interlayer distances as short as 330 pm. C-bonded CN^- is a strong field donor and the electronic spectrum of $[Ni(CN)_4]^{2-}$ shows two weak *d–d* bands at 444 and 328 nm.

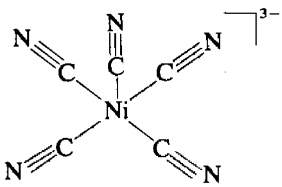
Table 37 Some Properties of the Diamagnetic $[Ni(CN)_4]^{2-}$ and $[Ni(CN)_5]^{3-}$ Complexes

Complex	*Colour*	*ν(CN) stretch (Nujol mull)* (cm^{-1})	*Ni—C bond distance* (pm)	*Ref.*
$Ba[Ni(CN)_4]$	Yellow	2123s, 2143s	186	629
$[Cr(tmd)_3][Ni(CN)_5]{\cdot}2H_2O$	Red	2070m, 2100s 2113w, 2126w	186–190[a] 214[b]	632
$[Cr(en)_3][Ni(CN)_5]{\cdot}1.5H_2O$	Red		183–199[c] 184–187[a,d] 217[b,d]	633

[a] Basal CN. [b] Apical CN. [c] Distorted trigonal bipyramidal species. [d] Square pyramidal species.

The yellow $[Ni(CN)_4]^{2-}$ adds a fifth cyanide in concentrated KCN solution (equation 112). Crystalline salts containing the pentacyanonickelate(II) anion can be obtained using large tripositive countercations. For example, by reacting an aqueous solution of $Cr(tmd)_3Cl_3$ (tmd = 1,3-diaminopropane) with an aqueous solution of KCN and $K_2Ni(CN)_4$, the red crystalline $[Cr(tmd)_3][Ni(CN)_5]{\cdot}2H_2O$ separates after the resulting cooled solution is allowed to stand for several hours.[631] Using similar synthetic procedures $[Cr(en)_3][Ni(CN)_5]{\cdot}1.5H_2O$ and $[Cr(NH_3)_6][Ni(CN)_5]{\cdot}2H_2O$ have also been prepared.[631,632] The diamagnetic $[Ni(CN)_5]^{3-}$ ion (**93**) contained in the tmd complex and in $[Cr(NH_3)_6][Ni(CN)_5]$ has an almost regular square pyramidal geometry, whereas in the complex $[Cr(en)_3][Ni(CN)_5]{\cdot}1.5H_2O$ both square pyramidal and distorted trigonal bipyramidal $[Ni(CN)_5]^{3-}$ anions have been found.[633] The dehydration of the latter complex results in the transformation of the trigonal bipyramidal species into the square pyramidal one.

$$\underset{\text{yellow}}{[Ni(CN)_4]^{2-}} + CN^- \longrightarrow \underset{\text{red}}{[Ni(CN)_5]^{3-}};\ \Delta H = -13\,\text{kJ mol}^{-1},\quad K_{eq} = 0.28\ (298\ \text{K}) \tag{112}$$



(93)

The reaction of nickel cyanide with aqueous ammonia affords compounds of the type $Ni(CN)_2{\cdot}NH_3{\cdot}xH_2O$. The structure of the complex where $x = 0.25$ closely resembles that of $Ni(CN)_2{\cdot}1.5H_2O$ with four-coordinate $Ni(CN)_4$ units and six-coordinate $Ni(NC)_4(NH_3)_2$ units.[634]

Clathrates of the type $Ni(CN)_2NH_3{\cdot}$solv (solv = benzene, aniline, *etc.*) have also been reported. In general, the host molecules are arranged perpendicularly to the layers of nickel cyanide.[635]

A large number of complexes containing coordinated cyano groups and neutral ligands such as amines, phosphines and arsines have been reported. Relevant examples of such compounds according to the different ligands will be given in the appropriate section.

50.5.3 Complexes with Nitrogen-donor Ligands

50.5.3.1 Complexes with ammonia and monodentate amines

Ammonia complexes can be prepared by addition of ammonia solutions to aqueous solutions of nickel(II) salts.[636] Monodentate primary and secondary alkylamines require anhydrous reaction conditions and tertiary amines have only a very slight tendency to form complexes.[637,638] Few examples of nickel(II) complexes with Me_3N and Et_3N have been reported.[639,640]

Hexakis adducts $[Ni(NH_3)_6]X_2$ with a great many anions have been reported, their stability in the solid state depending on the nature of X^-.[641] The average Ni—N bond length in $[Ni(NH_3)_6](NO_3)_2$ is 215 pm.[642] On increasing the number and the size of the alkyl substituents on NH_3 the number of coordinated amines decreases together with the relative stability of the complexes. Primary amines still form six-coordinate complexes[638,643] while secondary amines give complexes of formula $[NiX_2(Me_2NH)_n]$ (X = halides, $n = 3, 4$), $[NiX_2(Et_2NH)_2]$[639] and $[Ni(CN)_2(Et_2NH)]$.[644]

Tetrakis adducts of ammonia, $[NiX_2(NH_3)_4]$ (X = NCS,[645] NO_2[646]), have been reported with tetragonal octahedral geometry and Ni—N(NH_3) bond lengths in the range 215–210 pm.

Other complexes are listed in Table 38 together with the relevant references.

Table 38 Selected Complexes with Ammonia and Monodentate Amines

Complex	*Donor set*	*Coordination geometry or number*	*Ref.*
$[Ni\{(CH_2)_2NH\}_6]X_2$ (X = Br, I, NO_3)	N_6	Oh	647–649
$[Ni(NH_2OH)_6]X_2$ (X = Cl, Br, ClO_4)	N_6	Oh	650
$[Ni(NH_2OH)_6]SO_4^*$	N_6	Oh	651
$[Ni(NCS)_2(pip)_4]$	N_6	Oh	652
$[Ni(NCO)_2(pip)_3]$	N_5	5	652
$[Ni(NCS)_2(Me_2pip)_2]$	N_4	SqPl	652
$[Ni(X)_3\{(CH_2)_6N_2H\}]$ (X = halogens)	X_3N	Td	653
$[Ni(X)_3\{(CH_2)_6N_2H\}]^*$ (X = Cl, Br)	X_3N_2	TBPy	654, 655
$[Ni\{(CH_2)_6N_4\}_2X_2]$ (X = Cl, Br, I)	X_2N_2	—	656
$[Ni(NCS)_2(NH_3)_3]^*$	N_5	—	657

* Structures determined by X-ray analysis. Abbreviations: pip = piperidine; Me_2pip = 2,6-dimethylpiperidine; $(CH_2)_2NH$ = ethyleneimine (aziridine); $(CH_2)_6N_4$ = hexamethylenetetramine; $(CH_2)_6N_2H^+$ = dabconium ion.

50.5.3.2 Complexes with diamines

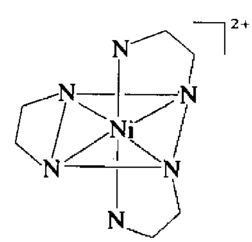
Aliphatic diamines, unsubstituted and either *N*- or *C*-substituted, give rise to a series of complexes whose stoichiometry and coordination geometry depend upon the length of the aliphatic chain, the size and the position of the substituents and the nature of the counteranions.

While complexes with primary diamines can be easily obtained in aqueous solution, the synthesis of complexes with substituted diamines must be carried out under anhydrous conditions.

1,2-Diaminoethane (en), $H_2NCH_2CH_2NH_2$, forms tris- and bis-chelate complexes. The tris-chelate $[Ni(en)_3]^{2+}$ cation (**94**) has been known since 1899.[658] It is considerably more stable than the six-coordinate complexes formed with monodentate amines as shown in Table 39 where the stability constants of some six-coordinate complexes are reported.

Table 39 Stepwise Stability Constants of some Six-coordinate Nickel(II) Amino Complexes in Aqueous Solution[659]

	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$	$\log K_5$	$\log K_6$
NH_3	2.36	1.90	1.55	1.23	0.85	0.42
py	1.78	1.05	0.31			
en	7.66	6.40	4.55			
bipy	6.80	6.46	5.20			
phen	8.8	8.3	7.7			



(**94**)

Structure (**94**) has been determined in several solid complexes (Ni—N bond lengths in the range 210–220 pm[661–665]) as well as in aqueous solution.[660] Each chelate ring is puckered and, consequently, chiral (λ and δ configurations). Moreover two enantiomeric configurations (known as Δ and Λ) of the three chelate rings around the metal occur.[665] Selected examples of bis-chelate complexes are reported in Table 40. The complexes can be either six-coordinate or square planar with average Ni—N bond distances of 209 pm and 192 pm, respectively. Square planar complexes are generally formed with anions with weak donor properties such as ClO_4^-, BPh_4^-, AgI_2^- and $AgBr_2^-$.[674,675] The six-coordinate complexes can be monomeric, generally with distorted *trans* octahedral geometries, dimeric or polymeric, generally with distorted *cis* octahedral geometries.

Complexes with 1,3-propanediamine (tmd) are less stable in water than those of en; only complexes of the type $Ni(tmd)_3(ClO_4)_2$ and $Ni(tmd)_2py_2(ClO_4)_2$ have been isolated in the solid state.[682,683]

1,4-Butanediamine and longer chain diamines do not form chelates in aqueous solution. These diamines form polymeric compounds in ethanol solution acting as bridges between two nickel atoms.

Selected nickel(II) complexes with *C*-substituted diamines are listed in Table 41. In solution the square planar coordination is favoured,[700] while both square planar and six-coordinate complexes have been isolated in the solid state. Complexes with 1,2-diphenyl-1,2-diaminoethane (stilbendiamine, stien) and 1-phenyl-1,2-diaminoethane have been widely studied.[701–706] Using $Cl_2CHCO_2^-$ as counterion, two complexes have been obtained with the former ligand, one blue, monoclinic, $P2_1/c$ ($\mu_{eff} = 3.16$ BM), the other yellow-green, triclinic,

Table 40 Selected Complexes with 1,2-Diaminoethane (en)

Complex	*Donor set*	*Comments*	*Ref.*
$[Ni(en)_2(H_2O)_2](ClO_4)_2$	N_4O_2	*trans* Oh	666
$[Ni(en)_2(H_2O)_2](BPh_4)_2$	N_4O_2	*cis* Oh	666
$[Ni(NCS)_2(en)_2]$*	N_6	*trans* Oh	667, 668
$[Ni(BF_4)(en)_2(H_2O)]BF_4$*	FN_4O	*cis* Oh; coordinated BF_4^-	669
$[Ni(NO_2)_2(en)_2]$*	N_6	*trans* Oh; N-bonded NO_2^-	670
$[Ni(NO_2)(en)_2]ClO_4$*	ON_5	Polynuclear *trans* Oh Bridging (O,N)NO_2^-	671, 672
$[Ni(NO_2)(en)_2]_2(BPh_4)_2$*	N_4O_2	Dinuclear *cis* Oh; bridging tridentate NO_2^- and terminal NO_2^-	673
$[Ni(en)(H_2O)_4](NO_3)_2$*	O_4N_2	*cis* Oh	674
$[Ni(en)_2][AgX_2]_2$*	N_4	SqPl	675
$[NiCl(en)_2]_2Cl_2$*	Cl_2N_4	Dinuclear *cis* Oh; bridging Cl^-	676–679
$[Ni(NCS)_2(en)_2]_2I_2$*	N_5S	Dinuclear *cis* Oh; bridging NCS^-	680
$[Ni_2(C_2O_4)_2(en)_4](NO_3)_2$*	N_4O_2	Dinuclear *cis* Oh; bridging $(CO_4^{2-})_2$	681

* Structures determined by X-ray analysis.

$P\bar{1}$ ($\mu_{eff} = 2.58$ BM). The monoclinic crystals contain the six-coordinate $[Ni(m\text{-stien})_2(H_2O)_2](Cl_2CHCO_2)_2\cdot 2H_2O$ while the triclinic form contains two inequivalent complexes, one square planar, $[Ni(m\text{-stien})_2](Cl_2CHCO_2)_2$, the other six-coordinate, $[Ni(m\text{-stien})_2(Cl_2CHCO_2)_2]$.

Selected nickel(II) complexes with *N*-substituted diamines are also shown in Table 41. It is usually found that as the number and size of the substituents increase, the number of the coordinated diamines decreases, as does the stability of the complexes which are, in general, sensitive to moisture. The complexes are soluble in dry solvents without dissociation or decomposition. Pseudotetrahedral coordination is stabilized by increasing the steric hindrance on the donor atoms. In the series of tetrasubstituted diamines the pseudotetrahedral species are stabilized in the order $Me_4en < Me_4pn < Me_4tmd$ and NCS < Cl < Br < I (Table 41).[696]

The formation in solution of nickel complexes with *N*-substituted ethylenediamines has been studied over a long period by many authors.[707] Solutions of nickel(II) complexes with *N*-substituted diamines often exhibit equilibria between pseudotetrahedral and pseudo-octahedral species. These equilibria are displaced towards the pseudotetrahedral species when the temperature increases.[696] Complexes $Ni(N,N\text{-}Et_2en)_2X_2$[691] with poorly coordinating anions are thermochromic. This behaviour has been investigated by means of calorimetric and NMR studies.[708,709]

50.5.3.3 Complexes with polydentate amines

Numerous nickel(II) complexes with a variety of polydentate amines have been described. Selected examples of such complexes are collected in Table 42. In general, solid complexes have been easily obtained by direct synthesis from nickel salts and the appropriate ligand using H_2O, MeOH, EtOH or butanol as reaction medium. Most of the complexes with the fully *N*-alkyl-substituted ligands are conveniently prepared under anhydrous conditions.

Stability constant measurements showed that complexes of den (**95**) having five-membered chelate rings are more stable than the corresponding complexes of dpt (**96**) involving six-membered chelate rings.[715,749] In both the $[NiL_2]^{2+}$ cations the den and dpt ligands coordinate in a *meridional* configuration, *i.e.* the two ligands in each complex lie in orthogonal planes. In the dpt complex, however, the Ni—N (secondary amine) bond length is about 17 pm longer than that in the den complex and the bond angles in the dpt rings are significantly larger than those observed in the den rings and larger than 109.5°, in agreement with a lower stability of the dpt complex.

The tetradentate ligand tren usually forms 1:1 six-coordinate complexes with two additional ligands in *cis* positions[750] as in the complex $[Ni(NCS)_2(tren)]$,[724] as well as dinuclear complexes of general formula $[NiX(tren)]_2(BPh_4)_2$ where two X groups are bridging the $Ni(tren)^{2+}$ moieties.[725–728] A common feature of both N_3^- and NCO^- complexes is the marked asymmetry

Table 41 Selected Complexes with *C*-Substituted and *N*-Susbstituted Diamines

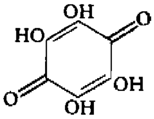
Complex	*Ligand (L) and counteranions*	μ_{eff} (*r.t.*) (BM)	*Donor set*	*Coordination geometry*	*Ref.*
$[NiL_2]X_n$	1,2-Diaminopropane, 2,3-diaminobutane; $n = 1$, $X = ZnCl_4^{2-}$; $n = 2$, $X = CuI_2^-$, ClO_4^-	—	N_4	SqPl	684–686
$[NiL_2](CCl_3CO_2)_2$	2,3-Dimethyl-2,3-diaminobutane	—	N_4	SqPl*	687
$[Ni(L)_2(H_2O)_2]Y_2{\cdot}2H_2O$	*meso*-1,2-Diphenyl-1,2-diaminoethane; $Y = Cl_2CHCO_2$	3.16	N_4O_2	Oh*	688, 689
$[Ni(L)_2(Cl_2CHCO_2)_2]$	As above	2.58	N_4	SqPl*	688, 689
$[Ni(L)_2(Cl_2CHCO_2)_2]$	As above		N_4O_2	Oh*	688, 689
$[NiL_3](ClO_4)_2$	L = *N*-Meen, *N*-Eten, *N,N'*-Me_2en, *N,N'*-Et_2en	3.20–3.32	N_6	Oh	690
$[NiL_2]X_2$	L = *N,N*-Me_2en, *N,N*-Et_2en; X = ClO_4, BF_4, BPh_4, NO_3, I	—	N_4	SqPl	691
$[NiX_2L_2]$	L = *N,N*-Me_2en, *N,N*-Et_2en; X = Cl, Br, NCS*, NO_2, $MeCO_2$	3.20–3.30	N_4X_2	Oh	691–694
$[NiX_2L_2]$	L = *N,N,N'*-Me_3en; X = Cl, Br, I	3.22–3.32	N_4X_2	Oh	695
$[NiX_2L]$	L = *N,N,N'*-Me_3en; X = Cl, Br	3.07–3.14	N_2X_4	Oh[a]	695
	L = *N,N,N'*-Et_3en, *N,N,N'*-Me_3tmd; X = Cl	3.29–3.32	N_2Cl_4	Oh[a]	695
$[NiX_2L]$	L = *N,N,N',N'*-Me_4en, *N,N,N',N'*-Me_4pn; X = Cl, NCS, NO_3	3.20–3.45	N_2Cl_4	Oh[a]	696
			N_4S_2	Oh[a]	
			N_2O_4	Oh[b]	
$[NiX_2L]$	L = *N,N,N'*-Et_3en, *N,N,N'*-Me_3tmd, *N,N,N',N'*-Me_4en, *N,N,N',N'*-Me_4pn; X = Br, I	3.24–3.40	N_2X_2	Td	696
$[NiX_2L]$	L = *N,N,N',N'*-Me_4tmd; X = Cl, Br, I	3.32–3.37	N_2X_2	Td	696
$[NiY_2L]$*	L = *N,N,N',N'*-Me_4en; Y = $PhCHNO_2$	—	N_2O_4	Oh	697
	L = *N,N,N',N'*-Me_4en; Y = $S_2P(OEt)_2$	—	N_2S_4	Oh	698
$[Ni_2(CF_3CO_2)_4(H_2O)L_2]$*	L = *N,N,N',N'*-Me_4en	—	N_2O_4	Oh	699

* Structures determined by X-ray analysis.
[a] Polymeric structures with bridging halides or thiocyanate.
[b] Bidentate (*O,O'*)-nitrate.
Abbreviations: tmd = 1,3-diaminopropane; pn = 1,2-diaminopropane.

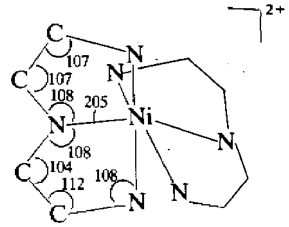
Table 42 Complexes with Tri-, Tetra- and Penta-dentate Amines

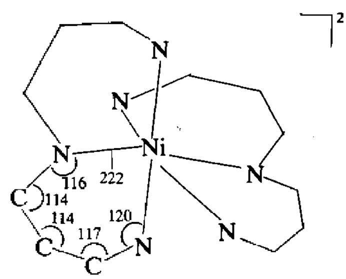
Complex	*Donor set*	*Coordination geometry or number*	*Ref.*
$[Ni(den)_2]X_2$ X = Cl, ClO_4, NO_3	N_6	Oh	710, 711, 713, 714
$[Ni(den)_2]Cl_2·2H_2O$*	N_6	Oh	715
$[NiX_2den]$ X = NO_3, Cl, ClO_4	N_3X_3	Dinuclear Oh	710–714
$[Ni(dpt)_2]ClO_4$*	N_6	Oh	715
$[Ni(dpt)L]X_2$ L = en, tmd; X = Cl, Br, I, ClO_4	N_5	SqPy	716
$[Ni(Me_3den)_2]X_2$ X = I, ClO_4	N_6	Oh	717
$[NiX_2(Me_3den)]$ X = Cl, Br, NCS	N_3X_3	Dinuclear Oh	717
$[NiX_2(Me_3dpt)]$ X = Cl, Br, I, NCS, NO_3	N_3X_2	5	717
$[NiX_2(Medpt)]$ X = Cl, Br, I	N_3X_2	5	718
$[NiX(Et_4den)]X$ X = Cl, Br, I	N_3X	SqPl	719
$[Ni(NCS)_2(Et_4den)]$	N_5S	Dinuclear Oh	720
$[Ni(NO_2)(Et_4den)]BPh_4$	N_4	SqPl	721
$[Ni(NCX)(Et_4den)]BPh_4$ X = O, S, Se		5, 6, 4	722
$[NiX_2(Me_5den)]$ X = Cl, Br, I	N_3X_2	5	723
$[Ni(NCS)_2(tren)]$*	N_6	*cis* Oh	724
$[\{Ni(NCO)(tren)\}_2](BPh_4)_2$*	N_5O	*cis* Oh, dinuclear, NCO bridging	725
$[\{Ni(N_3)(tren)\}_2](BPh_4)_2$*	N_6	*cis* Oh, dinuclear, N_3 bridging	726
$[\{Ni(NCBH_3)(tren)\}_2](BPh_4)_2$*	N_5H	*cis* Oh, dinuclear, BH_3CN bridging	727
$[Ni_2(C_6H_2O_6)(tren)_2](BPh_4)_2$[a]*	N_4O_2	*cis* Oh, dinuclear, $C_6H_2O_6^{2-}$ bridging	728
$[Ni_3(CN)_4(tren)_2](ClO_4)_2$	$N_6 + C_4$	*cis* Oh + SqPl, $Ni(CN)_4$ bridging	729
$[NiX(Me_6tren)]X$ X = Cl, Br*, I*, NCS*, NO_3, ClO_4	N_4X	TBPy, high-spin	730–733
$[NiX(Et_6tren)]X$ X = Cl, Br, I, NCS	N_4X	TBPy, high-spin	734
$[NiX(Me_6tpt)]X$ X = Cl, Br, I	N_4X	TBPy ↔ Td, high-spin	735–737
$[Ni(2,2,2\text{-tet})](ClO_4)_2$*	N_4	SqPl	738
$[Ni(NCS)_2(2,2,2\text{-tet})]$*	N_6	Distorted *cis* Oh	739
$[Ni(2,3,2\text{-tet})]X_2$ X = halides, ClO_4	N_4	SqPl	740–744
$[Ni(3,2,3\text{-tet})]X_2$ X = halides, ClO_4	N_4	SqPl	740–744
$[Ni(appi)]X_2$ X = I, ClO_4, NO_3	N_4	SqPl	745, 746
$[NiX(appi)]X$ X = Cl, Br	N_4X	SqPy	745, 746
$[NiX(tetren)]X$ X = halides	N_5X	Oh	747
$[Ni(Me_7tetren)](ClO_4)_2$	N_5	5	748

* Structures determined by X-ray analysis.
[a] $C_6H_2O_6^{2-}$ is the dianion of chloroanilic acid,



Ligand abbreviations and formulas:
$H_2N(CH_2)_2NH(CH_2)_2NH_2$, den (1,5-diamino-3-azapentane)
$H_2N(CH_2)_3NH(CH_2)_3NH_2$, dpt (1,7-diamino-4-azaheptane)

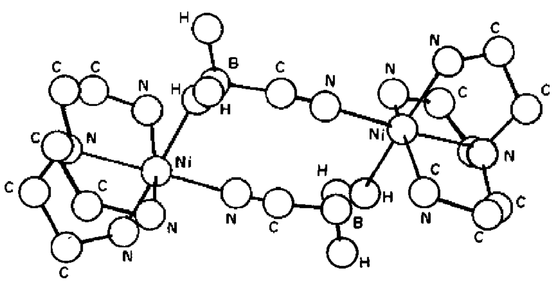


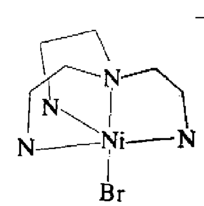


(95) (96)

Distances are in pm, angles in degrees

of the bridges joining the two nickel atoms (Section 50.5.3.9). In the cyanotrihydroborato complex (**97**) the nickel atom is coordinated to the nitrogen and to a hydrogen atom of the BH_3CN^- anion (Ni—N (BH_3CN) 201 pm; Ni—H (BH_3CN) 214 pm).[727]





(**97**) (reproduced from ref. 727 by permission of the American Chemical Society) (**98**)

An increase of the bulkiness of the donor groups, with respect to tren, as in the ligand Me_6tren, reduces the coordination number from six to five and a number of high-spin five-coordinate [NiX(Me_6tren)]X complexes have been obtained.[730–733] The complexes are in a trigonal bipyramidal coordination with C_3 site symmetry (**98**).[731,732] The trigonal bipyramidal coordination is retained in the complexes dissolved in solution.

From electronic spectra it is inferred that the trigonal bipyramidal geometry of [NiX(Me_6tpt)]X is distorted towards a tetrahedron. In this distorted geometry the steric constraints resulting from the presence of six-membered chelate rings are, at least in part, relieved.[735–737]

Table 42 (*footnote continued*)

$RR'N(CH_2)_nN(R'')(CH_2)_nNRR'$, $n = 2$, R = H, R′ = R″ = Me Me_3den
$n = 3$, R = H, R′ = R″ = Me Me_3dpt
$n = 3$, R = R′ = H, R″ = Me Medpt
$n = 2$, R = R′ = Et, R″ = H Et_4den
$n = 2$, R = R′ = R″ = Me Me_5den

$N(CH_2CH_2NR_2)_3$ R = H tren (tris(2-aminoethyl)amine, 1,5-diamino-3-(2-aminoethyl)-3-azapentane)
R = Me Me_6tren (tris(2-dimethylaminoethyl)amine, 1,5-bis(dimethylamino)-3-(2-dimethylaminoethyl)-3-azapentane)
R = Et Et_6tren (tris(2-diethylaminoethyl)amine, 1,5-bis(diethylamino)-3-(2-diethylaminoethyl)-3-azapentane)

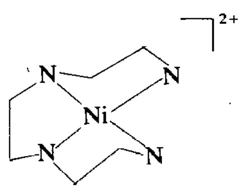
$N(CH_2CH_2CH_2NR_2)_3$, R = H tpt (tris(3-aminopropyl)amine, 1,7-diamino-4-(3-aminopropyl)-4-azaheptane)
R = Me Me_6tpt (tris(3-dimethylaminopropyl)amine, 1,7-bis(dimethylamino-4-(3-dimethylaminopropyl)-4-azaheptane)

$H_2N(CH_2)_nNH(CH_2)_mNH(CH_2)_nNH_2$, $n = m = 2$ trien or 2,2,2-tet (1,8-diamine-3,6-diazaoctane, triethylenetetramine)
$n = 2, m = 3$ 2,3,2-tet (1,9-diamine-3,7-diazanonane))
$n = 3, m = 2$ 3,2,3-tet (1,10-diamine-4,7-diazadecane)

$H_2N(CH_2)_3N(CH_2CH_2)_2N(CH_2)_3NH_2$, appi (*N,N′*-bis(3-aminopropyl)piperazine)

$R_2N(CH_2)_2N(R)(CH_2)_2N(R)(CH_2)_2N(R)(CH_2)_2NR$, R = H tetren (1,11-diamino-3,6,9-triazaundecane)
R = Me Me_7tetren (1,11-tetramethyldiamino-3,6,9-trimethyltriazaundecane)

The direct reaction of hydrated $Ni(ClO_4)_2$ with the open-chain tetradentate ligand 2,2,2-tet in water yields the complex $[Ni_2(2,2,2\text{-tet})_3](ClO_4)_4$. This complex, when reacted with an equimolar amount of hydrated $Ni(ClO_4)_2$, gives the orange square planar complex $[Ni(2,2,2\text{-tet})](ClO_4)_2$ (**99**)[686,738] which is reported to explode if subjected to pressure or heat. A thermal equilibrium between blue paramagnetic species of the type $[Ni(2,2,2\text{-tet})(solv)_2]^{2+}$ and yellow diamagnetic species exists in coordinating solvents.[739–741,751] In the distorted square planar $[Ni(2,2,2\text{-tet})]^{2+}$ cation, the central ring formed by the secondary amine nitrogens is in the eclipsed *cis* form whereas the chelate ring formed by the primary and secondary amine nitrogens is in the *gauche* conformation. The bond angles (100–115°) and distances (182–193 pm) within the chelate rings indicate a considerable strain in the ligand when it coordinates in a plane.[103] This strain is released when the ligand adopts a non-planar configuration, as occurs in the *cis* octahedral $[Ni(NCS)_2(2,2,2\text{-tet})]$ complex.[739] The hexamethylated 2,2,2-tet behaves similarly to 2,2,2-tet.[752]



(**99**)

The introduction of a trimethylenic chain connecting the two secondary amine nitrogens reduces the steric constraints of the ligand 2,3,2-tet, which adopts a planar conformation. As a matter of fact the stability constant of the yellow planar $[Ni(2,3,2\text{-tet})]^{2+}$ complex is *ca.* 10^2 times larger than that of the analogous $[Ni(2,2,2\text{-tet})]^{2+}$ complex. The ligand 3,2,3-tet behaves similarly to 2,3,2-tet since both ligands prefer planar and *trans* octahedral configurations.

Other examples of nickel(II) complexes with neutral ligands containing amine nitrogens are reported in Table 43.

50.5.3.4 Complexes with N-heterocyclic ligands

(*i*) *Complexes with pyridine, substituted pyridines and related ligands*

A considerable number of nickel(II) complexes with pyridine and substituted pyridines have been reported so far. Selected examples are reported in Table 44.

The most common stoichiometries found in nickel(II) pyridine and substituted pyridine complexes are NiX_2L_4 and NiX_2L_2 where X is a mononegative ion and L is pyridine or a substituted pyridine. Complexes of formula $Nipy_6X_2$ have been found to correspond to either $[NiX_2py_4]\cdot 2py$ (X = NCS, NCO)[818] or $[Ni(NO_3)_2py_3]\cdot 3py$.[819]

The tetrakis complexes are easily obtained by the addition of an excess of the appropriate pyridine, in absolute ethanol or methanol, to a solution in the same solvent of the anhydrous nickel salt.[147] The bis adducts are prepared by using stoichiometric amounts of the anhydrous reactants[783] or by heating the corresponding tetrakis complexes at temperatures in the range 80–110 °C.[784,820] Thermal decomposition of the bis and tetrakis adducts leads to the mono adducts. Using hydrated nickel salts as starting material may cause the formation of complexes with coordinated water molecules.

In the NiX_2L_4 complexes the nickel(II) ion is generally six-coordinate in a *trans* octahedral N_4X_2 geometry with average Ni—N (equatorial) bond distances in the range 208–213 pm. Square planar complexes can be obtained when X is a weakly coordinating anion such as ClO_4^- and BF_4^- and depending on the nature of the pyridine ligand. For example, ClO_4^- is coordinated to nickel in the complex $[Ni(OClO_3)_2(3,5\text{-lut})_4]$[798] while it is uncoordinated in $[Ni(3,4\text{-lut})_4](ClO_4)$.[797] The average Ni—N bond lengths in the square planar complexes are about 190 pm. Most of the NiX_2L_4 complexes in solutions of non-coordinating solvents give rise to an equilibrium between octahedral and tetrahedral species when X = halides, and between octahedral and square planar species when X = ClO_4, BF_4.

The structures of the bis adducts NiX_2L_2 are critically dependent upon the steric hindrance of

Table 43 Miscellaneous Amino Complexes

Complex	Ligand	Donor set	Comments	Ref.
$[Ni(daco)_2](ClO_4)_2\cdot 2H_2O$*	1,5-Diazacyclooctane	N_4	SqPl; does not easily form six-coordinate adducts	753, 754
$[Ni(dach)_2]X_2$ X = Cl, Br, NO_3, ClO_4	1,4-Diazacycloheptane	N_4	As above	755
$[Ni(typh)_2](ClO_4)_2$*	5,6,11,12-Tetrahydro-2,8-dimethylphenhomazine	N_4	As above	756
$[NiLX_2]$, $[NiClL]ClO_4$, $[Ni_2L_3(ClO_4)_4]$ X = NCS	Various triazacycloalkanes with different sizes of aliphatic chains	N_3X_2, N_3Cl_2	Six- or five-coordinate	757
$[NiL_2]X_2$ X = ClO_4*, Cl	*cis,cis*-1,3,5-Triaminocyclohexane, 1,1,1-tris(aminomethyl)ethane	N_6	Oh	758–761
$[NiL_2]X_2$ X = halogens, ClO_4^-	1,3-Diaminocyclohexane	N_4	SqPl	762
	1,2-Diaminocyclohexane	N_4	SqPl	763
	1,2-Dicyano-1,2-diaminocyclohexane	N_4	SqPl	764
$[NiCl_2(N_2H_4)_n]$ n = 2, 3	Hydrazine	N_4Cl_2	Polymeric with hydrazine bridging two nickel atoms	765
$[NiX_2(N_2H_4)_2]\cdot nH_2O$ X = $\frac{1}{2}SO_4$, NO_3, $MeCO_2$, NCS		N_4X_2	As above	766
$[Ni(N_2H_4)_6]X_2$ X = mononegative ion		N_6	Oh	767–769
$[NiCl_2(MeNHNH_2)_2]$	1-Methylhydrazine	N_4Cl_2	Polymeric	770
$[NiL_3](ClO_4)_2$	2-Pyridylhydrazine	N_6	Oh	771
$[NiL_6]X_2$ X = ClO_4, NO_3	Aniline and substituted anilines	N_6	Oh	772–775
$[NiX_2L_4]$ X = Cl_3CO_2*	As above	N_4X_2	Oh	772–775
$[NiX_2L_2]$ X = Cl_3CO_2*	As above	N_4X_2	Polymeric	772–775
$[NiL_4]Cl_2\cdot 2L$*	1,2-Diaminobenzene	N_6	Oh; two chelate, two monodentate and two uncoordinated ligand molecules	776–778
NiL_nX_2 n = 1, 2, 3	1,3-Diaminobenzene, 1,4-diaminobenzene		Polymeric	779
$[NiX_2(H_2O)_2L]$ X = Cl, Br	*N,N,N′,N′*-Tetramethyl-1,2-diaminobenzene	$N_2O_2X_2$	Oh	780
$[Ni(NO_3)_2L]$	*N,N,N′,N′*-Tetramethyl-1,2-diaminobenzene	N_2O_4	Oh	781

* Structures determined by X-ray analysis.

Table 44 Selected Complexes with Pyridine and Substituted Pyridines

Complex	Ligand (L)	X	Coordination geometry Solid	Coordination geometry Solution	Ref.
NiX_2L_4	py	Cl*, Br*, NCS*, NCO	Oh	Oh	782–787
		I*	Oh	Oh ⇌ Td	788
	3-pic	Cl, Br, I	Oh	Oh ⇌ Td	783, 789
		ClO_4, BF_4	Oh, SqPl	Oh ⇌ SqPl	783
	4-pic	Cl, Br	Oh	Oh ⇌ Td	783
		I	Oh	Td	783
		NO_3, NCS*	Oh	Oh	783, 790–792
		ClO_4*, BF_4, PF_6*	SqPl	Oh ⇌ SqPl	790, 793, 794
	3,4-lut	Cl, Br	Oh	Oh ⇌ SqPl	795
		I	SqPl	Td	795, 796
		ClO_4*	SqPl		797
	3,5-lut	Cl, Br	Oh	Oh ⇌ Td	795
		I	Oh	Td	795
		NCS, NO_3	Oh	Oh	795
		ClO_4*, BF_4	Oh	SqPl	795, 798
NiX_2L_3	py, 3-pic	NO_3	Oh	Oh	782, 783
NiX_2L_2	py	Cl, Br, NCS	Oh	Oh	799, 796, 790, 800
		$(EtO)_2PS_2$*	*trans* Oh		801
		MeCOS*	*cis* Oh		802
		Me_3SiCH_2*	SqPl		803
	2-pic	Cl, Br	Td	Td	783, 789, 799, 804
		I	SqPl	Td	783, 804
		$PhCO_2$*, CF_3CO_2	*cis* Oh		805, 806
	3-pic	Cl	Oh	Oh	783, 789, 804
		Br	Oh	Td	783, 789, 804
		I	Td	Td	782, 783, 796, 804
	4-pic	Cl, Br	Oh	Td	783, 804
		I	Td	Td	783, 796, 804
		acac*	*trans* Oh		805
	2,3-lut, 2,4-lut	Cl, Br	Td	Td	807
		I	Oh	Td	807
		NO_3	Oh	Oh	807
	2,5-lut	Cl, Br, I	SqPl	Td	807
		NO_3	Oh	Oh	807
	2,6-lut, 2,3,6-Me_3py	Cl, Br, I, NCS	SqPl	Insoluble	808
	qui, qui^i	Cl	Oh, Td	Decomposes	790, 809
		Br	Td	Decomposes	790, 809
		I	SqPl	Decomposes	809
		$PhCO_2$*	*trans* Oh		806
NiX_2L	py	Cl, Br	Oh	Td	804
	2-pic, 3-pic	Cl, Br	Oh		804
$[Ni(H_2O)_2(3\text{-pic})_4](PF_6)_2\cdot 2(3\text{-pic})$*			*trans* Oh		810
$[NiBr_3L](NBu_4)$*	L = py, qui		Td		811, 812
$[NiX_2(H_2O)_2py_2]$*	$MeCO_2$, NO_3		*trans* Oh		813, 814
$[Ni(NCS)_2(H_2O)_2qui_2]$*			*trans* Oh		815
$[Ni_2(C_2O_4)_2py_6(NO_2)_2]$*			Oh dinuclear		816
$[Ni(Et_2PS_2)_2qui]$*			SqPy		817

* Structures determined by X-ray analysis.
Abbreviations: 2-pic, 3-pic, 4-pic = 2-methylpyridine, *etc.*; 2,3-lut, 2,4-lut, 2,5-lut, 2,6-lut, 3,4-lut, 3,5-lut = 2,3-dimethylpyridine, *etc.*; qui = quinoline; qui^i = isoquinoline.

the pyridine ligands and upon the coordinating properties of the anions. The bis adducts of pyridine and less hindered substituted pyridines are usually six-coordinate with a polymeric structure and bridging halides, whereas the complexes with 2-substituted pyridines or complexes with X = I are usually four-coordinate, either square planar or pseudotetrahedral (Ni—N about 203 pm in the latter complexes). Most of the bis adducts of substituted pyridines in solution in non-coordinating solvents are pseudotetrahedral. In the presence of anions which may act as chelate donors (acetylacetonate, benzoate, acetate, dithiophosphate, *etc.*), the NiX_2L_2 complexes are six-coordinate with either a *cis* or a *trans* configuration.[805,806]

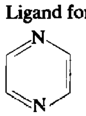
The $NiCl_2py_4$ complex reacts with trimethylsilylmethylmagnesium chloride in the presence of an excess of pyridine forming the air-unstable square planar complex $[Ni(Me_3SiCH_2)_2py_2]$ from which the pyridine molecules are displaced by phosphines, 2,2′-bipyridyl, 1,10-phenanthroline and *N,N,N′,N′*-tetramethylethylenediamine.[803]

Several complexes with ligands related to the pyridine ring have been reported and the most relevant ones are listed in Table 45.

Table 45 Nickel(II) Complexes with Ligands Related to Pyridine

Complex	*Ligand (L)*	*Donor set*	*Comments*	*Ref.*
NiX_2L_2 X = Cl, Br, I	Pyrazine (**I**)	N_2X_2, N_4X_2	Polynuclear SqPl or Oh	821, 822
NiX_2L X = Br, I	2,5- or 2,6-dimethylpyrazine	N_2X_2	Linear chain, SqPl, bridging pyrazine	821, 823
NiX_2L X = Cl, Br, I	Quinoxaline or substituted quinoxaline (**II**)	N_2X_2, N_2X_4	SqPl or Oh; bridging ligand and halides	824
$NiL_n(ClO_4)_2$ n = 3, 4	1,8-Naphthyridine and methyl derivatives (**III**)	N_{2n}	Oh (n = 3), eight-coordinate (n = 4)	825, 826
$NiL_2(NO_3)_2$	As above	N_4O_2	Oh	827
$NiL_2X(BPh_4)$ X = Cl, Br	As above	N_4X_2	Polymeric, Oh	828
$[NiL_2X]_2(BPh_4)$ X = Cl, Br* (**100**)	As above	N_4X	Dimeric, SqPy with bridging ligand	828
Ni_2L_4	Deprotonated 7-azaindole (**IV**)	N_4	Dimeric, SqPl with bridging ligand	829
NiX_2L X = halogen	1,2-dipyridylethylene	N_2X_4	Polymeric, Oh	830
$NiL_3(ClO_4)_2$	2,2′-Azopyridine	N_6	Oh, chelate ligand	831
$NiL_2(NCS)_2$	2,2′-Azopyridine	N_6	Oh, chelate ligand	831
NiX_2L X = Cl, Br	3,3′-Azopyridine, 4,4′-Azopyridine	N_2X_4	Polymeric, Oh, bridging ligands	832

* Structures determined by X-ray analysis.
Ligand formulae: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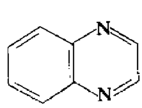
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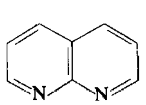
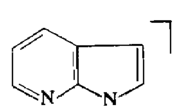

(III)


(IV)

The ligand 1,8-naphthyridine and the methyl derivatives yield different nickel complexes according to the reaction conditions as shown in Scheme 3. All the synthetic procedures have been carried out in anhydrous conditions. The complexes $NiL_3(ClO_4)_2$, $NiL_2(NO_3)_2$ and NiL_2XBPh_4[825–828] have been reported to be six-coordinate with the ligand presumably acting as chelate, while the complex $NiL_4(ClO_4)_2$ is assumed to be eight-coordinate due to the bidentate nature of the ligand and on the basis of the isomorphism with the analogous cobalt complex which has been shown to possess dodecahedral geometry. The X-ray crystal structure of the complex $[\{NiBrL_2\}_2](BPh_4)$ showed that it contains the dinuclear cation $[Ni_2L_4Br_2]^+$ (**100**) with the naphthyridine molecules acting as exobidentate ligands.[828] The nitrogen atoms of the naphthyridine ligand are bound to nickel with an average bond distance of 210.5 pm and the nickel–nickel distance is 242 pm. The magnetic properties and EPR spectra were interpreted assuming a large ferromagnetic coupling between the nickel atoms which can be assigned a formal oxidation number 1.5.[833]

Deprotonated 1,3-diphenyltriazene, $PhNNNPh^-$, gives a dinuclear complex $[Ni_2L_4]$ which has been found to possess a dinuclear structure with bridging triazenato ligands reminiscent of (**100**).[834,835]

$$Ni(ClO_4)_2 + nL \xrightarrow[EtOH]{r.t.} NiL_n(ClO_4)_2 \quad \text{(refs. 825, 826)}$$
$$n = 3, 4$$

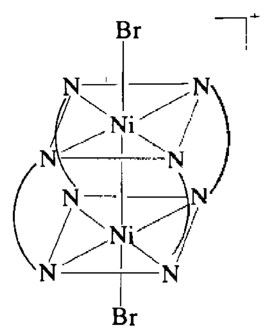
$$Ni(NO_3)_2 + L\ (excess) \xrightarrow[EtOH]{r.t.} NiL_2(NO_3)_2 \quad \text{(ref. 827)}$$

$$NiX_2 + 2L + NaBPh_4 \xrightarrow[EtOH]{r.t.} NiL_2XBPh_4 + NaX \quad \text{(ref. 828)}$$
pale green

$$NiX_2 + 2L + NaBPh_4 \xrightarrow[Bu^tOH]{boil} [NiL_2X]_2BPh_4 + \text{products} \quad \text{(ref. 828)}$$
black

$$NiX_2 + 2L + NaPF_6 \xrightarrow[Bu^tOH]{NaBH_4} [NiL_2X]_2PF_6 + \text{products} \quad \text{(ref. 828)}$$

Scheme 3 Some reactions of the naphthyridine ligand (L) and nickel(II) salts



(**100**) N⌒N = 1,8-naphthyridine

(*ii*) *Complexes with bipyridyl, phenanthroline and related ligands*

Review articles covering different aspects of the coordinating properties of 1,10-phenanthroline (phen) and 2,2′-bipyridyl (bipy) are available.[836–838] Selected examples of nickel(II) complexes with phen and bipy are collected in Table 46.

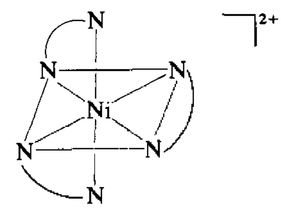
Table 46 Some Representative Complexes with bipy and phen whose Structures have been Determined by X-ray Analysis

Complex	*Coordination geometry*	*Bond distances (av) Ni—N* (pm)	*Ref.*
$[Ni(bipy)_3]_2Cl_2(C_6H_4O_6)$	Oh	211	842
$[Ni(bipy)_3]SO_4\cdot 7.5H_2O$	Oh	209	843
$[Ni(phen)_3]_3[Co(C_2O_4)_3]_2$	Oh	211	844
$[Ni(phen)_3][Mn(CO)_5]_2$	Oh	209	845
$[Ni(2,9\text{-}Me_2phen)Cl_2]_2$ (**102**)	SqPy dinuclear	204	846
$[Ni(2,9\text{-}Me_2phen)Br_2]_2$ (**102**)	SqPy dinuclear	203	846
$[Ni(2,9\text{-}Me_2phen)I_2]$ (**103**)	Td	200	847
$[Ni(dtp)_2(bipy)]$	Oh	206	848
$[Ni(dtp)_2(2,9\text{-}Me_2phen)]$	Distorted five-coordinate	203	817

Abbreviations: dtp = dimethyldithiophosphate; $C_6H_4O_6$ = tartrate anion.

The strong chelating ability of phen and bipy, due to the extended π system, makes the tris chelates $[NiL_3]^{2+}$ easy to obtain from the direct combination of a nickel salt with the appropriate ligand in aqueous solution.[839,840] The stability constants of the complexes in aqueous solution (20 °C, 0.1 M $NaNO_3$)[841] are reported in Table 39.

The tris chelates are enantiomeric and the racemic mixture can be conveniently resolved into the optical isomers by reaction with the optically active tartrate by virtue of the different solubility properties of the two enantiomers.[840] The enantiomers of $[Ni(phen)_3]^{2+}$ are more stable than those of $[Ni(bipy)_3]^{2+}$. In the tris-chelate complexes (**101**) the nickel atom is in a pseudooctahedral environment of six nitrogen atoms.



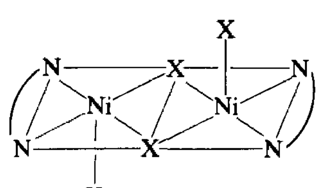
(**101**) N⌒N = bipy, phen

The coordinated phenanthroline ligand is almost planar while the two pyridyl groups in coordinated bipyridyl are twisted with respect to each other (less than 10°) as a consequence of steric repulsion between non-bonded atoms. Mixed complexes of the type $[Ni(bipy)(phen)_2]^{2+}$ and $[Ni(bipy)_2(phen)]^{2+}$ have been also reported.[849]

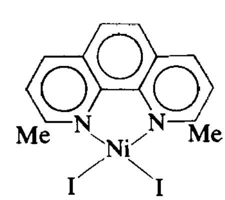
Besides the very stable tris chelates, numerous bis chelates with both bipy and phen have been reported.[850,851] Most of them have general formulas $[NiX_2(N—N)_2]$, $[Ni(N—N)_2(H_2O)_2]X_2$ and $[NiX(N—N)_2(H_2O)]X$ (X = halides, pseudohalides, ClO_4, NO_2; N—N = phen, bipy).[850] All of the complexes are six-coordinate with a *cis* structure.

By the stepwise thermal decomposition of the tris chelate, mono adducts of the type $[NiX_2(N—N)]$ (X = halides, NCS) were obtained.[852–854] These complexes are polynuclear six-coordinate with bridging anions. In the thiocyanato derivative the nickel atoms are ferromagnetically coupled.

In general, substituents in 2,9-positions of phen and 6,6′-positions of bipy prevent the formation of tris-chelate complexes due to the steric hindrance of the ligands and consequently the mono- and bis-chelate complexes become preferred. The two complexes $[NiX_2(N—N)]$ (**102**; X = Cl, Br) formed by 2,9-dimethyl-1,10-phenanthroline have been found to be square pyramidal dinuclear with both bridging and terminal halides,[848] while the iodo derivative $[NiI_2(N—N)]$ (**103**) is monomeric and pseudotetrahedral.[847]



(**102**) N⌒N = 2,9-Me₂phen



(**103**)

Complexes with ligands related to bipy have also been reported. Selected examples are shown in Table 47.

Bis adducts of terpyridyl, $[Ni(terpy)_2]X_2$, can be obtained in ethanol solutions. The mono adducts can be obtained by thermal decomposition of the corresponding bis adducts or by the reaction of excess nickel salt with the ligand in water–methanol solutions. The $[Ni(terpy)_2]X_2$ complexes (X = Cl, Br) are six-coordinate[863] whereas the mono adducts $NiLX_2$ are five-coordinate when X = Cl or Br[864,865] and polynuclear six-coordinate when X = NCS.[866] In the last complex the nickel atoms are ferromagnetically coupled.

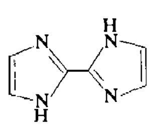
(iii) *Complexes with pyrazoles, imidazoles and related ligands*

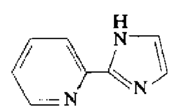
Selected nickel(II) complexes with imidazole, pyrazole and related ligands are shown in Table 48.

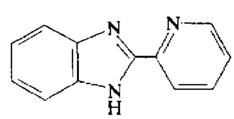
Table 47 Selected Nickel(II) Complexes with Ligands Related to phen and bipy

Complex	*Ligand (L)*	*Donor set*	*Comments*	*Ref.*
NiX_2L_2 X = halogens, NO_3	4,4'-Bipyridine	N_4X_2	Polymeric bridging ligand	855–857
$[NiL_3]X_2$ X = halogens, NO_3, ClO_4	2,2'-Biimidazole (I) 2-(2'-Pyridyl)imidazole (II) 2-(2'-Pyridyl)benzimidazole (III)	N_6	Oh, tris chelate	858–860
$[NiL_2(H_2O)_2](NO_3)_2$*	2,2'-Biimidazole	N_4O_2	*trans* Oh	861
$K_2[Ni(CN)_2L]$	4,4',5,5'-Tetracyano-2,2'-bi-imidazolate		SqPl	862
$[NiL_2]X_2$ X = Cl, Br	terpy	N_6	Oh	863
$[NiX_2L]$ X = Cl, Br	terpy	N_3X_2	Five-coordinate	864, 865
$[NiL(NCS)_2]$	terpy	N_3N_3	Oh, polynuclear	866

* Structure determined by X-ray analysis.


(I)


(II)


(III)

Hexakis imidazole and pyrazole complexes of nickel(II) can be easily obtained by the direct reaction of the hydrated nickel(II) salt with the appropriate ligand using ethanol as solvent and stoichiometric amounts of the reactants.[898,899] Analogous complexes can be obtained with pyrazoles and imidazoles having substituents in positions not adjacent to the donor site.

The effects of the substituents near the donor site is to reduce the number of coordinated ligand molecules from six to four or less. Tetrakis complexes with substituted pyrazoles and imidazoles are prepared using a large excess of the ligands, and, in the cases of 1,2-dimethylimidazole and 3,5-dimethylpyrazole derivatives, anhydrous reactants. Most of the mono and bis adducts may be conveniently prepared under anhydrous conditions and with the nickel salt in excess.

In the hexakis imidazole[871–875,900] and pyrazole[888,889] complexes the nickel atom is octahedrally coordinated by six nitrogen atoms (average Ni—N distances 213 pm) with the ligands coordinated through the 'pyridine-type' nitrogen. The imine nitrogens can be involved in hydrogen bonding with the anions and determine the reciprocal inclination of the ligand rings. The fact that both pyrazole and imidazole ligands can form hexakis complexes with nickel(II), contrary to pyridine which forms tetrakis complexes, has been attributed to the different π-acceptor properties and to the smaller R—N—C angle (about 107°) of pyrazole and imidazole as compared with that of pyridine (about 120°).[869,898]

The tetrakis complexes NiL_4X_2 can be octahedral or square planar according to the steric hindrance of the ligands and to the coordinating ability of the anions, as found for the analogous complexes with pyridine. In the *trans* octahedral complex $[NiBr_2(pz)_4]$[891] the pyrazole rings are nearly orthogonal to the NiN_4 basal plane while in the analogous pyridine complex the ligand rings make an angle of about 45°. This is probably due to the formation of NH · · · Br hydrogen bonds which stabilize the orthogonal orientation of the pyrazole rings.

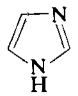
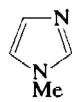
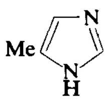
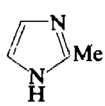
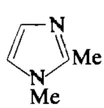
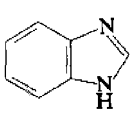
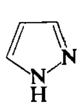
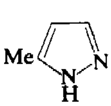
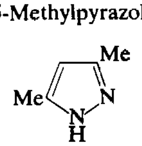
The coordination chemistry of the nickel complexes of benzimidazole is very complicated, critically depending on the exact reaction conditions.[883–885]

Most of the bis adducts NiX_2L_2 (L = substituted imidazoles and pyrazoles) have pseudotetrahedral coordination, but some of the chloride and thiocyanato complexes can be six-coordinate in a polymeric structure.

Thiazole, C_3H_3NS, and substituted thiazoles coordinate through the nitrogen atom in nickel complexes as imidazole does.[901–903]

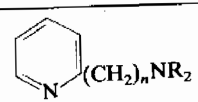
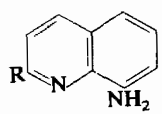
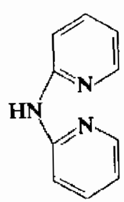
The neutral complexes $Ni(C_3H_3N_2)_2$ are obtained by the reaction of hydrated nickel(II) chloride and pyrazole, or imidazole, in an aqueous ammonia solution. These insoluble complexes contain uninegative 'exobidentate' pyrazolates or imidazolates which act as bridges between two metals (**104**).[899,904,905] Two additional ligands such as NH_3, H_2O or py may be

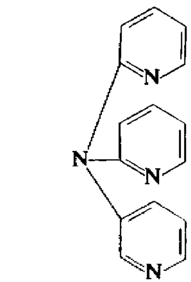
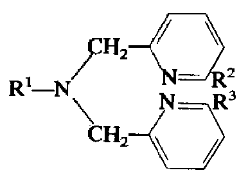
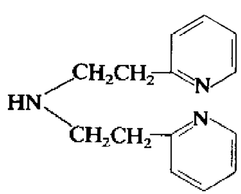
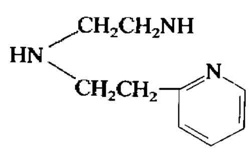
Table 48 Selected Complexes with some Imidazoles and Pyrazoles

Ligand	NiL_nX_2	*Coordination geometry*	*Ref.*
	$n = 6$; X = Cl^*, Br, I, NO_3^*, BF_4^*, ClO_4^*	Oh	867–873
	$n = 4$; X = Cl, Br, I	Oh	868, 870, 874
	X = Br, I	SqPl	868, 870
	$n = 2$; X = Cl, Br	Oh	874
Imidazole	X = I	Td	874
	$n = 1$; X = Cl, Br	Oh	868
	X = I	Td	874
	$n = 6$; X = Cl, Br, I, NO_3	Oh	875
	$n = 4$; X = Cl	Oh	875
	$n = 2$; X = Cl, Br, I	Td	875
	$n = 1$; X = Cl, Br	Oh	875
1-Methylimidazole			
	$n = 6$; X = Cl, Br, I, NCS, NO_3, ClO_4	Oh	876
	$n = 4$; X = Cl, Br, I, NCS	Oh	876
5-Methylimidazole			
	$n = 4$; X = Cl, Br^*	a	877, 878
	X = I	SqPl	877
	X = NO_2^*	Oh	879
	$n = 2$; X = Br, I	Td	877, 878
2-Methylimidazole	X = Cl	Oh	877
	$n = 1$; X = Cl	—	877
	$n = 4$; X = Cl, Br, I	SqPl	880
	X = NO_3^*	Oh	880
	$n = 2$; X = Cl, Br, I	Td	880
1,2-Dimethylimidazole			
	$n = 4$; X = Cl^*, Br	Oh	881, 882
	X = I, ClO_4	SqPl	883, 884
	$n = 2$; X = Cl, Br	Oh	885
Benzimidazole			
	$n = 6$; X = ClO_4, BF_4	Oh	869, 886–888
	X = NO_3^*	Oh	889
	$n = 4$; X = Cl^*, Br^*	Oh	886, 887, 890–892
	$n = 2$; X = Cl, Br	Oh	892, 893
Pyrazole			
	$n = 6$; X = ClO_4, BF_4	Oh	894
	$n = 4$; X = Cl, Br, I, NO_3, NCS	Oh	881, 892, 894, 895
	$n = 2$; X = Cl, Br, I, NO_3	Oh	882
5-Methylpyrazole			
	$n = 4$; X = Br, I, NO_3	Uncertain	896, 897
	X = ClO_4, BF_4	SqPl	896, 897
	$n = 2$; X = Cl, NCS	Oh	896
	X = Br, I	Td	896
3,5-Dimethylpyrazole			

* Structures determined by X-ray analysis.
a The two bromide ions are located in *trans* positions at different distances, 293 and 375 pm, from the nickel atom.

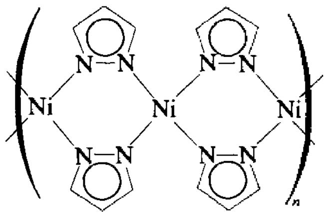
Table 49 Selected Complexes with Aminopyridines

Ligand		*Complex*	*Donor set*	*Coordination geometry or number*	*Ref.*
	$n = 1$, R = H	$Ni(amp)_3(BF_4)_2$*	N_6	Oh	917
		$Ni(amp)_3Cl_2$	N_6	Oh	918
	$n = 2$, R = H	$Ni(aep)_2X$	N_4X_2	Oh	919
		X = halides, NO_3, ClO_4			
	$n = 1$, R = Me	$Ni(dmamp)_3(ClO_4)_2$	N_6	Oh	920
		$Ni(dmamp)_2X_2$	N_4X_2	Oh	920
		X = Cl, Br, I, NCS			
		$Ni(dmamp)X_2$	N_2X_3	5; dimeric	920, 921
		X = Cl, Br			
		$Ni(dmamp)I_2$	N_2I_2	Td	921
	$n = 1$, R = Et	$Ni(deamp)_2Br_2$	N_4Br_2	Oh	920
		$Ni(deamp)_2I_2$	N_4I	5; mononuclear	920
		$Ni(deamp)Cl_2$	N_2Cl_3	5; dimeric	921
		$Ni(deamp)X_2$	N_2X_2	Td	920, 921
		X = Br, I			
	$n = 2$, R = Me	$Ni(dmaep)Cl_2$	N_2Cl_3	5; dimeric	922
		$Ni(dmaep)X_2$	N_2X_2	Td	922
		X = Br, I			
	$n = 2$, R = Et	$Ni(deaep)X_2$	N_2X_2	Td	922, 923
		X = Cl, Br, I			
	R = H amq	$Ni(amq)_nCl_2 \cdot xH_2O$	N_6, N_4O_2, N_2O_4	Oh	924
	R = Me meamq	$n = 1, 2, 3$; $x = 1, 2$			
		$Ni(meamq)_nX_2 \cdot xH_2O$	$N_2O_2X_2$, N_4O_2	Oh	925
		$n = 1, 2$; $x = 1, 2$; X = halogens			
		$[Ni(meamq)_2NO_3]NO_3$*	N_4O_2	*cis* Oh	926
		$[Ni(bpa)_3](ClO_4)_2$	N_6	Oh	927, 928
		$[Ni(bpa)_2X_2]$	N_4X_2	Oh	927, 928
		X = halides, NCS			
		$[Ni(bpa)X_2]$	N_2X_2	Td	927, 928
		X = Br, I			

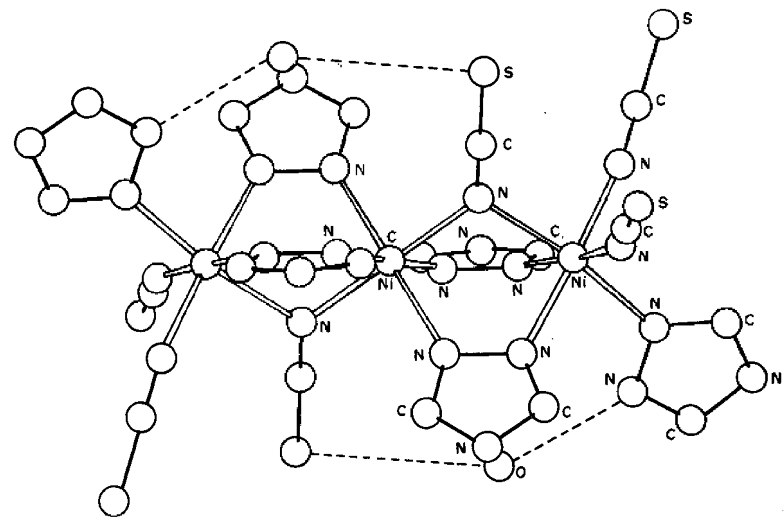
		$[Ni(tpa)_2](ClO_4)_2$	N_6	Oh	929
	$R^1 = R^2 = R^3 = H$ $R^1 = Me, R^2 = R^3 = H$ $R^1 = H, R^2 = R^3 = Me$ $R^1 = R^2 = R^3 = Me$	$[NiL_2]X_2$ X = halides	N_6	Oh	930–932
		NiX_2L X = halides	N_3X_2	TBPy	932, 933*
		NiX_2L X = halides	N_3X_2	Five-coordinate	934
		$Ni(NCS)_2L$		Oh, dinuclear	934
		NiX_2L X = halides, NCS, NO_3	N_3X_3	Oh, polynuclear	935
		NiX_2L_2 X = I, ClO_4	N_6	Oh	935

* Structures determined by X-ray analysis.

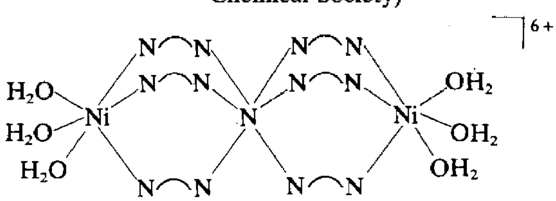
introduced in axial positions of the square planar complexes and six-coordinate complexes result.



(104)



(105) (reproduced from ref. 907 by permission of the American Chemical Society)



(106) N⌒N = 1,2,4-triazole

Other nitrogen heterocycles having two or more coordination sites in the rings can coordinate nickel(II) as exobidentate ligands.[904,906] For example, the two complexes $Ni_3(NCS)_6(LH)_6(H_2O)_2$ (LH = 3,5-dimethyl-1,2-4-triazole and the 3,5-diethyl analogue) contain the trinuclear unit (**105**) with both triazole and thiocyanate bridges. There are small ferromagnetic exchange interactions within the trimer.[907] Another trinuclear complex is $[Ni_3(LH)_6(H_2O)_6](NO_3)_6{\cdot}2H_2O$ (**106**) (LH = 1,2,4-triazole).[908] In this complex the neighbouring nickel atoms are bridged by three triazole molecules. A dinuclear structure has been found in the complexes $Ni_2L_2(H_2O)_4$ (X = halogens) with 1,4-dihydrazinophthalazine.[909]

A number of nickel complexes with substituted and unsubstituted tetrazoles[910–913] and with pyrazole- and imidazole-derived ligands have also been reported recently.[914–916]

50.5.3.5 Complexes with polydentate aminopyridines and related ligands

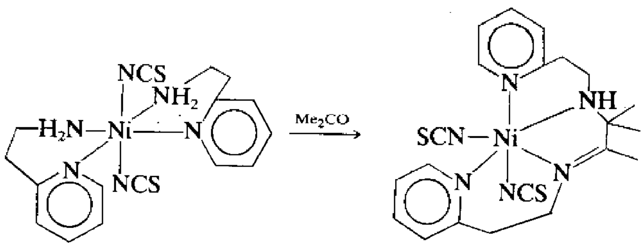
Selected examples of nickel(II) complexes with bidentate aminopyridines and related ligands are shown in Table 49.

The nickel complexes with 2-aminopyridines bear some similarity to complexes of the corresponding aliphatic diamines (Section 50.5.3.2). Most of the complexes are easily obtained by the direct reaction of nickel(II) salts with the appropriate amount of the diamine in ethanol solution. Complexes with *N*-substituted aminopyridines are preferably synthesized under anhydrous conditions.

The unsubstituted 2-aminomethylpyridine (amp) forms six-coordinate tris chelates of the type $[Ni(amp)_3]X_2$[917] with stability close to that of en complexes (en, $\log k_1 = 7.7$; amp, $\log k_1 = 7.1$).[936] The 2-(2′-aminoethyl)pyridine (aep) gives at most bis chelates of the type $[Ni(aep)_2X_2]$ (X = halides, NO_3, ClO_4).[919] The stability of these complexes is significantly lower than that of 1,3-propanediamine analogues (aep, $\log k_1 = 5.1$; tmd, $\log k_1 = 6.18$).[936]

N-Alkyl-substituted aminopyridines give 1:3, 1:2 and 1:1 complexes, depending on the bulkiness of the substituents, the length of the aliphatic chain and the reaction conditions. The formation of pseudotetrahedral structures is favoured by the increasing length of the connecting chain. The influence of the substituents of the pyridine ring on the structural properties of the nickel complexes has also been studied.[937]

$Ni(NCS)_2(aep)_2$ dissolves in acetone at room temperature after a period of weeks giving a blue product containing a quadridentate ligand formed by the condensation of two molecules of aep with two molecules of acetone (Scheme 4).[938]

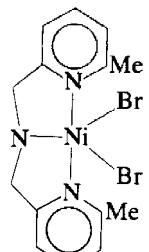


Scheme 4

Several six-coordinate complexes of stoichiometry $NiL_nCl_2{\cdot}xH_2O$ ($n = 1, 2, 3$; $x = 1, 2$) were prepared with the 8-aminoquinoline by the reaction of stoichiometric amounts of hydrated $NiCl_2$ and the ligand.

The bis(2-pyridyl)amine, although potentially a terdentate ligand, coordinates to nickel(II) as a bidentate ligand through the pyridine nitrogens giving complexes with one, two or three coordinated ligand molecules.[927,928] Analogously, the tris(2-pyridyl)amine[929] and tris(2-pyridyl)carbinol[939] act as facial tridentate ligands.

The X-ray crystal structure[933] of dibromo[1,3-di(6-methyl-2-pyridine)-2-azapropane]-nickel(II) (**107**) has shown that in this complex the nickel(II) is five-coordinate in an approximate trigonal bipyramidal geometry with the bromine atoms lying in the basal plane (average Ni—N and Ni—Br distances 203 pm and 248 pm, respectively).



(107)

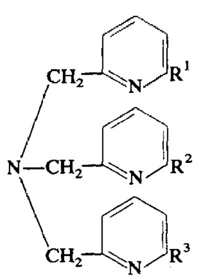
The ligands tris(2-pyridylmethyl)amine (tpma), tris(3,5-dimethyl-1-pyrazolylmethyl)amine (metpyma) and tris(3,5-dimethyl-1-pyrazolylethyl)amine (metpyea) are examples of tetradentate tripod-shaped ligands containing three heterocyclic nitrogen donors connected to an apical tertiary nitrogn donor by aliphatic chains. Selected nickel(II) complexes with these ligands are reported in Table 50.

Six-coordination is favoured, in general, by less bulky ligands while five-coordination is favoured by sterically hindered ligands and by increasing the size of the chelate ring. However, the ligand metpyma acting as tetradentate gives six-coordinate nickel(II) complexes in spite of the bulkiness of the heterocyclic groups. The complexes are dimeric with bridging halides (**108**). The intramolecular exchange interaction between adjacent nickel atoms is ferromagnetic.[940] The increased size of the chelate ring in the ligand metpyea as compared with the ligand metpyma stabilizes five-coordination in nickel complexes. The yellow complex $[NiBr(metpyea)]BPh_4{\cdot}EtOH$ transforms into a green isomer on dissolving in acetone or by grinding in the solid state. The yellow isomer has a structure close to a trigonal bipyramid, whereas the green isomer approaches a square pyramid.[941]

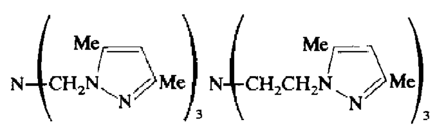
Table 50 Selected Complexes with Tetra- and Penta-dentate Ligands Containing Heterocyclic Nitrogen Donors

Complex		Coordination number: Solid state	Coordination number: Solution	Ref.
$[Ni(tpma)_2]ClO_4$		6	6	932
$[NiX_2(tpma)]$	X = Cl, Br	6	6	932
$[NiX_2(dmetpma)]$	X = Cl, Br	6	6 + 5	932
$[NiI(dmetpma)]I$		5	5	932
$[NiX_2(tmetpma)]$	X = Cl, Br	5	5	932
$[NiX(tmetpma)]Y$	X = Cl, Br, I, NCS; Y = Br, I, ClO_4	5	5	932
$[NiX(tmetpma)]ClO_4$	X = NO_3, ClO_4	6	6	932
$[Ni(NCS)_2(tmetpma)]$		6	6	932
$[Ni_2X_2(metpyma)_2](BPh_4)_2$	X = Cl, Br	6	6	940
$[NiX(metpyea)]BPh_4$	X = Cl, Br, NCS	5	5	941*
$[Ni(H_2O)(metpyea)]X_2$	X = ClO_4, BF_4	5	5	941
$[NiX_2L]$	X = Cl, Br, I, NCS, NO_3; L = bpdex, bpep	6	6	942
$Ni(bpdex)(H_2O)_2](ClO_4)_2$		6	6	942
$[Ni_2Cl_2L_2](ClO_4)_2$	L = bpdex, bpep	6	6	942
$[Ni(bpdo)](ClO_4)_2$		4	4, 6	943
$[Ni(tpen)](ClO_4)_2$ **(109)**	X = halogens	5	5	944

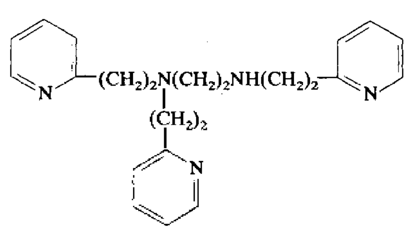
* Structures determined by X-ray analysis.
Ligand formulae and abbreviations:



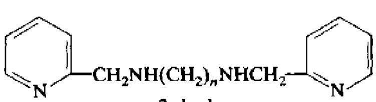
$R^1 = R^2 = R^3 = H$ tpma
$R^1 = H, R^2 = R^3 = Me$ dmetpma
$R^1 = R^2 = R^3 = Me$ tmetpma



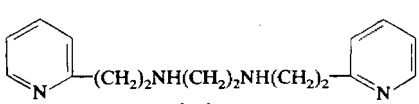
metpyma metpyea



tpen

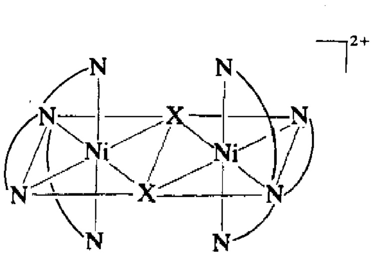


$n = 2$, bpdex
$n = 3$, bpep

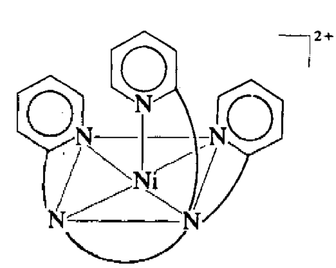


bpdo

The quadridentate linear-shaped ligands 1,6-bis(2′-pyridyl)-2,5-diazahexane (bpdex), 1,7-bis(2′-pyridyl)-2,6-diazaheptane (bpdep) and 1,8-bis(2′-pyridyl)-3,6-diazaoctane (bpdo) differ from each other in the length of the aliphatic chain inserted between the terminal pyridyl groups and the aliphatic amino groups. By virtue of their great flexibility these so-called 'facultative'[945] ligands may coordinate in a planar or non-planar arrangement of the four nitrogen donors. Actually, *cis* octahedral nickel(II) complexes have been reported both in the solid state and in solution with the ligands bpdep[942] while $Ni(bpdo)(ClO_4)_2$ is square planar.[943]

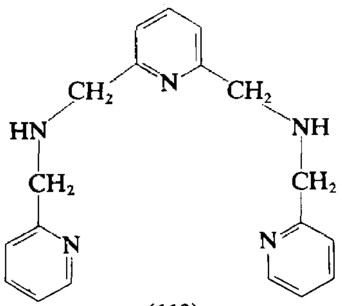


(108)

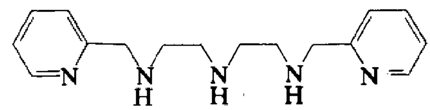


(109)

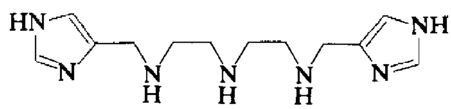
Thermodynamic investigations of the complexation of nickel(II) with the pentadentate ligands (**110**)–(**112**) having either pyridyl or imidazolyl terminal groups have been carried out.[946,947] The complexes are in general more stable than those of the linear ligands containing peripheral primary amines.



(**110**)



(**111**)



(**112**)

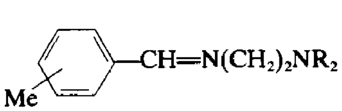
50.5.3.6 Complexes with Schiff base ligands

(*i*) *Synthesis and structural properties of the complexes*

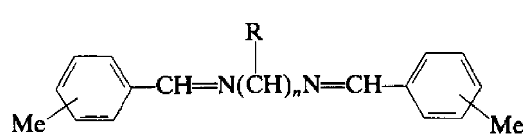
The ligands derived from diacetyl bis(hydrazone) and diacetyldiimine RN=C(Me)C(Me)=NR (R = NH_2, butane-2,3-dione bis(hydrazone); R = Me, butane-2,3-dione diimine), 2-pyridinal hydrazone and 2-pyridinalimine (C_6H_4N)CH=NR (R = Me, CH_2Ph, Bu^t, NH_2, NHMe, Me_2N, NHPh, NPh_2) contain the N=C—C=N dimethine structural unit which forms strong chelate rings and gives nickel(II) complexes whose stability is comparable with that of bipy and phen complexes. This remarkable stability may be correlated to the formation of highly conjugated chelate rings.

The reaction of nickel(II) salts with the appropriate ligands, usually in ethanol or water–ethanol mixture, produces bis and tris chelates of formulas NiX_2L_2 and NiL_3X_2 (X = Cl, I, BF_4).[948–953] The complexes generally have an octahedral geometry with effective magnetic moments in the range 2.90–3.26 BM at room temperature. In the case of phenyl-substituted pyridinalhydrazones the steric demand of the ligand prevents the formation of tris-chelate complexes.

The nickel halide complexes of Schiff bases (**113**) and (**114**) obtained from benzaldehyde and a number of diamines have the formula NiX_2L (X = Cl, Br, I) with pseudotetrahedral structure in the solid state and in solution as well.[954]



(**113**)

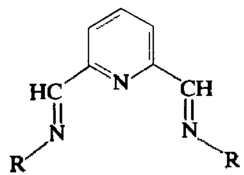
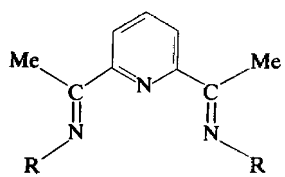
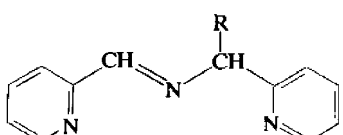
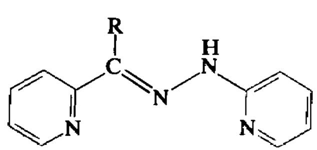


(**114**)

The bis-hydrazones and bis-imines derived from 2,6-pyridinedialdehyde and 2,6-diacetylpyridine contain the trimethine unit N=CC=N—CC=N which acts as tridentate with donor properties similar to those of terpyridyl. These ligands are coplanar and therefore should coordinate along an edge. Most of the complexes have been prepared in water or water–ethanol mixture by the direct reaction of nickel salts with the appropriate ligands.[949,951,955,956] According to the experimental procedures and to the different ligands, mono and bis chelates have been prepared. Selected examples of nickel(II) complexes with these ligands are reported in Table 51. The bis-chelate complexes are six-coordinate with the ligands acting as strong tridentate donors. The substitution of alkyl and aryl groups for hydrogen in the amine nitrogens decreases the donor strength of the ligands and favours the five-coordination. These five-coordinate complexes are considerably more stable than those obtained with linear aliphatic amines such as Me_5den (Table 42).

Other examples of nickel complexes with homologous tridentate ligands containing sp^2 nitrogen donors are reported in Table 51. Some cationic bis chelates $[NiL_2]^{2+}$ are changed to

Table 51 Selected Complexes Formed by Tridentate Schiff Bases

Ligand (L)	*Complex*	*Coordination number*	*Ref.*
 R = Me pdai; R = NH_2 pdah	$[Ni(pdai)_2]I_2 \cdot H_2O$	6	951
	$[Ni(pdah)_2]I_2$	6	949
	$[Ni(dapiR_2)X_2]$		
	R = Me, Et, Pr^n, Pr^i, Bu^s, Cy; X = Cl, Br	5	956
	R = Bu^s, Cy, Ph*; X = NO_3*, NCS	6	956, 957
	$[Ni(daphR)_2]X_2$		
	R = NH_2; X = Cl, I	6	955
	R = NHMe; X = I, ClO_4	6	955
	R = NMe_2; X = ClO_4	6	955
	R = NHPh; X = ClO_4	6	955
	$[Ni(daphR)Cl_2]$		
	R = NHMe, NHPh	5	955
	R = NMe_2	5	955
 R = alkyl	$NiL_2(ClO_4)_2$	6	958
	NiL'_2 (L′ = deprotonated ligand)	6	958
	$NiLX_2$		
	X = Cl, NCS	6	959, 960
	X = Br, I	5	959, 960
 R = alkyl	$NiL_2(ClO_4)_2$	6	959
	NiL'_2 (L′ = deprotonated ligand)	6	959

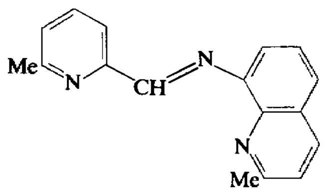
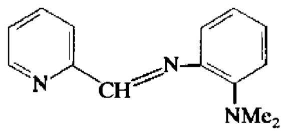
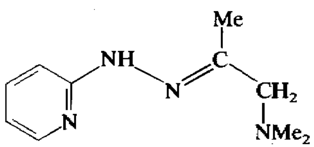
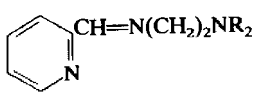
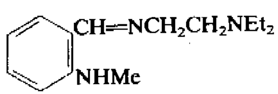
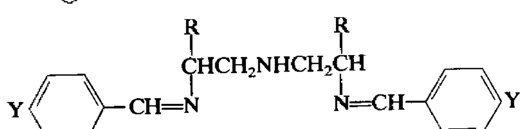
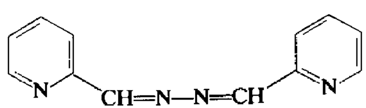
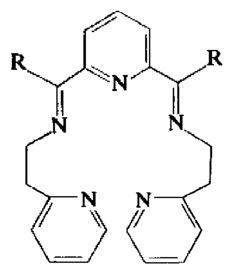
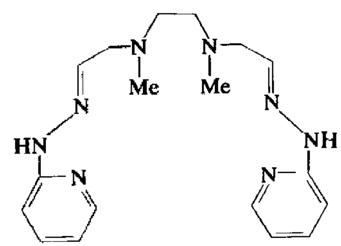
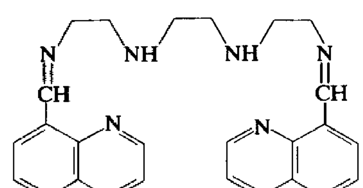
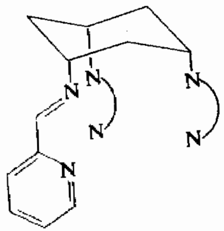
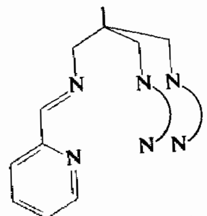
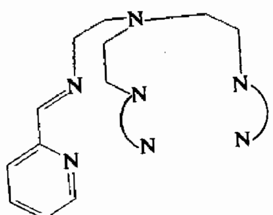
	NiX_2L $X = Cl, Br, I, NO_3$	5	961
	NiX_2L $X = Cl, Br$	5	962
	$NiL_2(ClO_4)_2$ NiL'_2 (L' = deprotonated ligand)	6 6	963 963
	NiX_2L $R = Me, Et; X = Br, I$ $Ni(NO_3)_2L$	5 6	964 964
	NiX_2L $X = Cl, Br, I$ $X = NO_3, NCS$	5 6	965 965
	NiX_2L $X = Cl, Br$ $Y = H, Me, OMe$	5	966
	NiL_2X_2 $X = I, ClO_4, BF_4$ $Ni_2L_3X_4$ $X = I, ClO_4, BF_4$	6 6	967, 968 967, 968

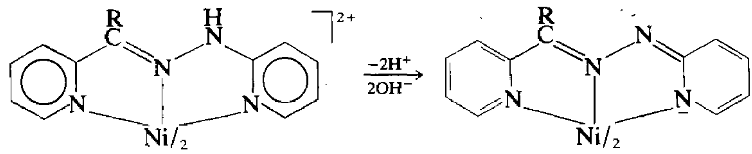
Table 52 Selected Nickel(II) Complexes with Tetra-, Penta-, and Hexa-dentate Schiff Base Ligands

Complex	Ligand (L)	Donor set	Comments	Ref.
$NiLX_2$ X = Cl, Br, I, ClO_4	Butane-2,3-dione bis(2′-pyridylhydrazone)	N_4	SqPl	969
NiL′*	As above	N_4	SqPl; obtained by deprotonation of $NiLX_2$ with ammonia	969, 970
$Ni_2L'_2$	As above	N_4	SqPl; dinuclear	971
$NiLX_2$ X = Br, I, NO_3	 2,6-Pyridinedialbis{2-(2′-pyridyl)ethylimine}	N_5X	Oh	972
X = NCS		N_4X_2	Oh; ligand acting as tetradentate	
$[NiL](ClO_4)_2$	 5,8-Dimethyl-1,12-di(2′-pyridyl)-1,2,5,8,11,12-hexaazadodeca-2,10-diene	N_6	Oh	963
NiL′		N_6	Oh; obtained by deprotonation of NiL^{2+} with NaOH	963
$[NiL]I_2·3H_2O$	 1,12-Di(8′-quinolyl)-2,5,8,11-tetraazadodeca-1,11-diene	N_6	Oh	973
$[NiL](BF_4)$*	Fluoroboratotris(2-carboxaldimino-6-pyridyl)phosphine	N_6	Trigonal prismatic	974, 975

$[NiL](ClO_4)_2$*	 *cis,cis*-1,3,5-Tris(2-carboxaldiminopyridine)cyclohexane **(117)**[a]	N_6	Trigonal prismatic	976, 977
$[NiL](ClO_4)_2$*	 1,1,1-Tris(2-carboxaldiminomethylpyridine)ethane **(118)**[a]	N_6	Trigonal prismatic	978
$[NiL](PF_6)_2$	 Tris{1-(2-pyridyl)-2-azabuten-4-yl}amine **(119)**[a]	N_6	Trigonal prismatic	979–981

* Structure determined by X-ray analysis.
[a] For reasons of clarity only one chelate ring structure is correctly depicted in **(117)**–**(119)**.

neutral complexes $[NiL'_2]$ upon addition in ethanol solution of NaOH which causes the deprotonation of the coordinated ligands as outlined in Scheme 5.[958]



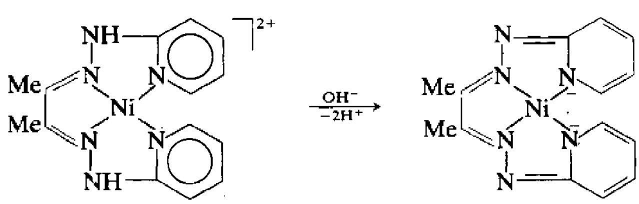
Scheme 5

The easy deprotonation of the charged complexes and the marked stability of the neutral complexes (most of them can be sublimed unchanged) can be ascribed to the formation of a conjugated system involving the whole molecular framework. In the neutral complexes containing such types of deprotonated ligands subnormal magnetic moments have usually been found.

Selected examples of tetra-, penta- and hexa-dentate Schiff base ligands and of the corresponding nickel(II) complexes are reported in Table 52.

When the ligand butane-2,3-dione bis(2'-pyridylhydrazone) is allowed to react with nickel(II) salts in ethanol–water mixture, the diamagnetic square planar complexes $[NiL]X_2$ (**115**; X = Cl, Br, I, ClO_4) (Scheme 6) are formed with the hydrazone molecule acting as a planar quadridentate ligand.[969] In aqueous ammonia solution deprotonation of the ligand occurs and the neutral square planar diamagnetic [NiL'] complexes (**116**) can be extracted from the reactant mixture with benzene (Scheme 6). In the neutral square planar complex the two Ni—N (pyridine) bond distances average 194 pm whereas the Ni—N (imine) bond distances average 183 pm[970] which are amongst the shortest Ni—N bond distances ever found.

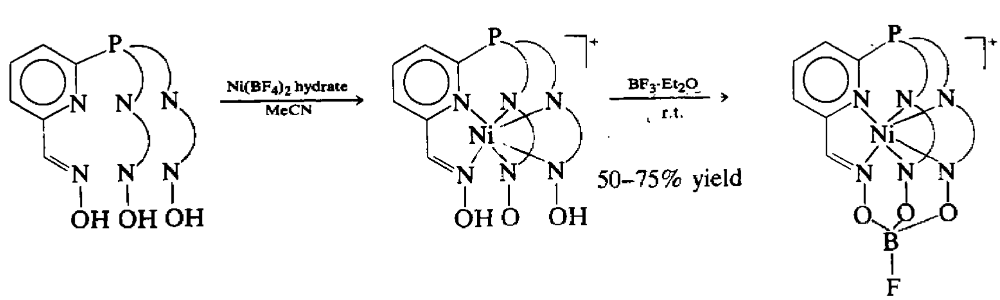
Other examples of complexes derived from deprotonated ligands are reported in Section 50.5.3.7.i.



(**115**) (**116**)

Scheme 6

A number of hexadentate ligands containing three pyridyl-2-aldimine groups have been designed to stabilize a six-coordinate trigonal prismatic geometry instead of the more common octahedral geometry. Relevant spectroscopic and structural parameters for these complexes are shown in Table 53. The complexes have been synthesized according to Schemes 7 and 8. The ligands obtained from the reactions of Scheme 8 (**117–119**) are reported in Table 52.



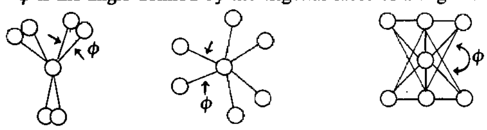
(**120**)

Scheme 7

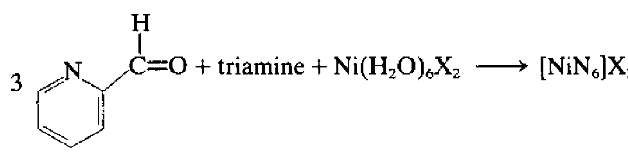
Table 53 Complexes with Hexadentate N_6 Ligands with Structures Between a Nearly Regular Trigonal Prism and an Octahedron

Complex	μ_{eff} (*r.t.*) (BM)	λ_{max} (ε_M) (cm^{-1})	ϕ[a]	*Ref.*
$[NiL](BF_4)$ L = (**120**)	3.11	9380 (28), 11 000 (27), 20 500sh, 22 280sh (80)	1.6°	974, 975
$[NiL](ClO_4)_2$ L = (**117**)	3.10	11 100 (25), 12 200 (25), 19 200 (40)	32°	976, 977
$[NiL](ClO_4)_2$ L = (**118**)	3.04	11 200 (21), 12 400 (28), 20 000 (69), 27 000sh (412)	36°	977, 978
$[NiL](PF_6)_2$ L = (**119**)	2.98	11 100 (5.0), 12 500 (6.4), 18 200 (11.6)	51°	979, 980

[a] ϕ is the angle defined by the trigonal faces of a trigonal prism with respect to the ideal eclipsed orientation.



<1.6° 32–36° 51°



triamine = *cis,cis*-cyclohexane-1,3,5-triamine,
1,1,1-tris(2-aminoethyl)ethane,
2,2,2-tris(2-aminoethyl)amine

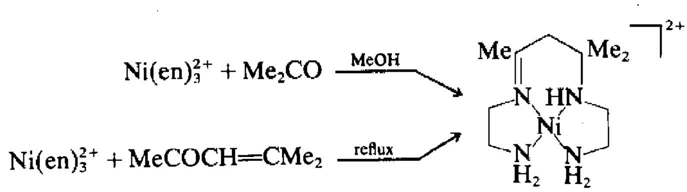
Scheme 8

The geometry of the complex (**120**) of Scheme 7 for which Busch coined the term 'clato-chelate'[976] is a nearly regular trigonal prism. The mean Ni—N distances are 204 pm and the twist angle between the trigonal faces of the prism is 1.6°. In a perfect trigonal prism $\phi = 0°$, and in an octahedron $\phi = 60°$ (Table 53).

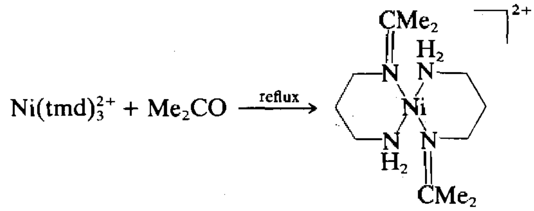
The structures of the complexes with the ligands (**117**) and (**118**) are almost halfway between octahedral and trigonal prismatic geometry ($\phi = 32°$ and 36° respectively).[976–978] The complex with ligand (**119**) is nearly regular octahedral ($\phi = 51°$) (Table 53).[979–981]

(*ii*) *Reaction of coordinated ligands and the formation of nickel complexes with amine–imine-containing ligands*

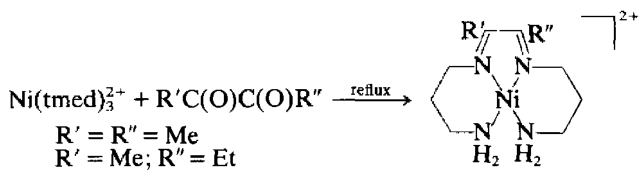
Twenty years ago Curtis and co-workers found that $[Ni(en)_3]^{2+}$ reacts with acetone under very mild conditions and new nickel complexes are formed which have a square planar geometry and contain tetraaza macrocyclic ligands (Section 50.5.9).[982–984] Starting from this pioneering work, it has been well established that this condensation reaction is a general one and the reaction of various carbonyl compounds with amines coordinated to nickel(II) is, in general, an easy synthetic route which affords polydentate amine–imine ligands which are otherwise either inaccessible or obtainable in a low yield through tedious and time-consuming procedures. Some examples of such condensation reactions are reported in equations (113)–(119).



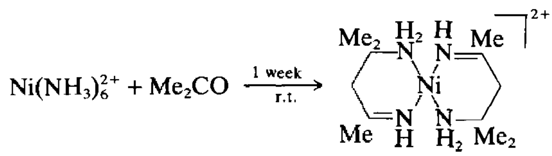
(113)[985,986]
(114)[986]



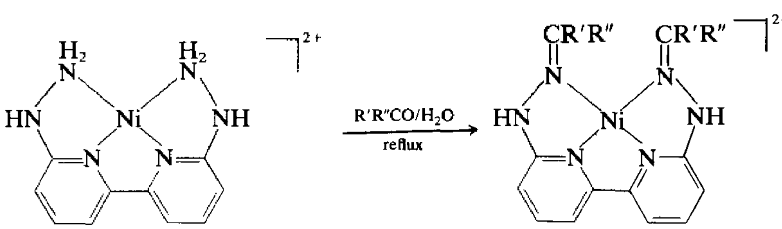
(115)[682]



(116)[987]

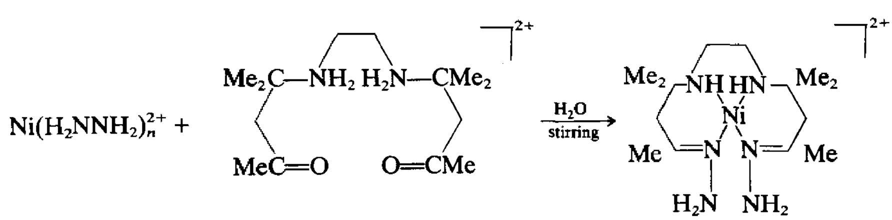


(117)[988–990]



(118)[991,992]

Caution: the starting $NiL(ClO_4)_2$ complex detonates on heating!
R′ = Me, Et, Pr^n; Me, Et, Et, Pr^n
R″ = H, H, H; Me, Me, Et, Me



(119)[992]

Reactions analogous to that described in equation (113) are given by various aldehydes and hydroxyketones.[985,986]

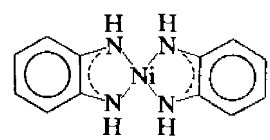
Most of the nickel complexes prepared according to reactions (113)–(119) have the general formula $[NiL]X_2$ or $[NiL_2]X_2$ ($X = ClO_4$, $\frac{1}{2}ZnCl_4$) and are square planar. The complexes obtained from reaction (118) as dihydrate, $NiL(H_2O)_2(ClO_4)_2$, are six-coordinate *cis* octahedral.

50.5.3.7 Four-coordinate neutral complexes with anionic ligands derived from deprotonated amines, imines, oximes and related ligands

(*i*) *Complexes with deprotonated amines, imines and β-aminoimines*

The general method of preparation of neutral complexes of the types $Ni(N—N)_2$ and $Ni(N_4)$ (N—N and N_4 stand for monoanionic bidentate and dianionic tetradentate ligands, respectively, having nitrogen donors) is the direct reaction of a nickel(II) salt and the appropriate ligand in alkaline solution (aqueous ammonia, ethanolic pyridine or tertiary amines). In some cases, however, special procedures have been employed which will be briefly reported

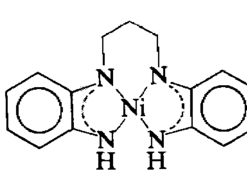
The preparation of the deep blue complex bis(*o*-phenylenediiminato)nickel(II) (**121**) by the reaction of nickel(II) and 1,2-diaminobenzene (*o*-phenylenediamine) in concentrated aqueous ammonia in the presence of air was reported as early as 1927.[993] The complex is square planar with the nickel atom four-coordinated by the nitrogen atoms at distances in the range 183–184 pm,[994] which are amongst the shortest Ni—N bond distances so far found. Distances in the chelate and benzene rings seem to indicate that the electrons are substantially delocalized throughout the entire molecule and the assignment of a definite oxidation number to the nickel atom may be questionable. Polarographic studies in non-aqueous solvents have shown that the neutral complex $Ni(C_6H_6N_2)_2$ can add electrons to give a series of new complexes (equation 120).[995] The complexes $[Ni(C_6H_6N_2)_2]I$ ($\mu_{eff} = 1.18$ BM) and $[Ni(C_6H_6N_2)_2]I_2$ (diamagnetic) were isolated in the solid state, by oxidation of the neutral complex with I_2. The two extreme complexes of equation (120), namely the dinegative and dipositive species, may be formulated as compounds of nickel(II) coordinated to the dianion of *o*-phenylenediamine and to the neutral benzoquinonediimine respectively. On this basis the neutral complex may be considered in a formal way a nickel(II) complex of the partially oxidized monoanion ligand $[C_6H_4(NH)_2]^-$ instead of the nickel(IV) complex of the dianion $[C_6H_4(NH)_2]^{2-}$



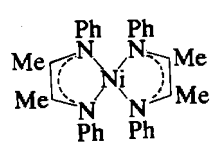
(**121**)

$$[Ni(C_6H_6N_2)_2]^{2-} \underset{e^-}{\overset{-e^-}{\rightleftharpoons}} [Ni(C_6H_6N_2)_2]^- \underset{e^-}{\overset{-e^-}{\rightleftharpoons}} [Ni(C_6H_6N_2)_2] \underset{e^-}{\overset{-e^-}{\rightleftharpoons}} [Ni(C_6H_6N_2)_2]^+ \underset{e^-}{\overset{-e^-}{\rightleftharpoons}} [Ni(C_6H_6N_2)_2]^{2+} \quad (120)$$

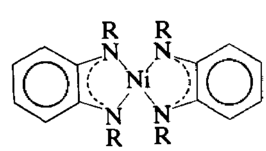
The complexes (**122**)[996] and (**123**)[995] have structural and electrochemical properties strictly correlatable to those of complex (**121**). Complex (**123**) is extremely air-unstable and has been prepared in the form of black crystals by the reaction of $Ni(CO)_4$ and the diacetylbisanildiimine in benzene/*n*-pentane mixture under an inert atmosphere.



(**122**)



(**123**)

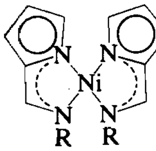


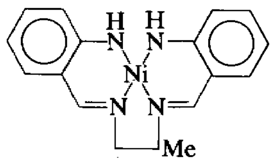
(**124**)

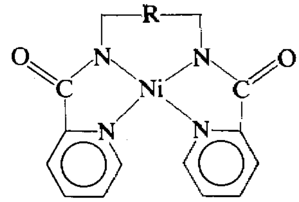
Bis(aminotroponeiminato)nickel(II) complexes (**124**) give rise to square planar ⇌ pseudotetrahedral equilibria in solution.[997–1000] The amount of the paramagnetic pseudotetrahedral species increases as the size of the substituents R becomes greater.

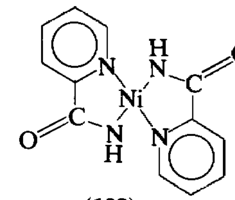
Bis(pyrrole-2-aldiminato)nickel(II) complexes (**125**) are diamagnetic in the solid state when R = H, Pr, Pr^i and Et, and paramagnetic pseudotetrahedral when R = Bu^t.[1001–1003] In solution there exists an equilibrium between square planar and tetrahedral species when R = Pr^i, Bu^s and Bu^t. Such equilibria were also investigated for complexes of the type (**126**) obtained from the condensation reaction in basic media of *o*-aminobenzaldehyde and a number of diamines in the presence of nickel(II).[1004–1007] Square planar complexes (**127**)[1008,1009] and (**128**)[1010] were obtained with deprotonated pyridinecarboxamide ligands. In these complexes the Ni—N (amide) bond distance (184–187 pm) is shorter than the Ni—N (pyridine) distance (192–195 pm).

The *β*-aminoimine (**129**) and formazyl (**130**) molecules are, in a formal way, the nitrogen analogues of the *β*-diketones. However, the neutral complexes formed by the deprotonated monoanionic ligands are mononuclear in contrast to the oligomeric structures formed by most of the *β*-diketonates. Owing to their sensitivity to moisture, the *β*-aminoiminato complexes must be prepared under rigorous anhydrous conditions. For example, the complexes with

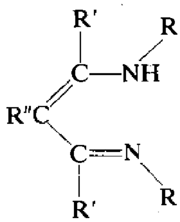

(125)

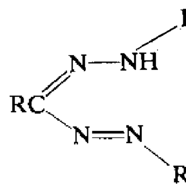

(126)

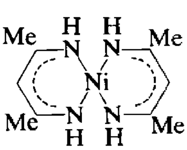

(127)

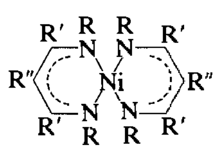

(128)

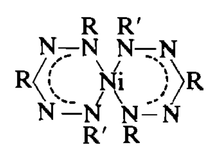
ligand (**129**), where R = aryl, R′ = Me, were prepared by the reaction of $[NiBr_4](Et_4N)_2$ with a mixture of the ligand and *n*-butyllithium in THF at −78 °C under nitrogen atmosphere.[1011] Complex (**131**) is square planar and all the other complexes of type (**132**) are pseudotetrahedral (μ_{eff} in the range 3.06–3.17 BM[1011–1016]). In the bis-formazan nickel complex (**133**) the NiN_4 chromophore is square planar. The two adjacent R and R′ groups reduce their steric crowding by distorting the molecule towards a stepped structure.[1017,1018]


(129)


(130)


(131)


(132)


(133)

(*ii*) *Complexes with deprotonated α,β-dionedioximato and related ligands*

Nickel(II) complexes with deprotonated α,β-dionedioximes have been widely studied.[1019] Selected examples of such complexes are reported in Table 54.

The complexes with unsubstituted and either alkyl- or aryl-substituted glyoximes have been prepared by the reaction of nickel(II) salts with the appropriate ligand in aqueous or ethanolic solution or an aqueous–ethanolic mixture. In most cases, the reaction is promoted by addition of ammonia as base and/or refluxing temperature.

The complexes are always square planar with general formulas NiL_2. In the crystal structure the NiL_2 molecules generally stack one over the other to give rise to a polydimensional structure which renders the complexes highly insoluble. There are two main structural motives adopted by these complexes. The first is exemplified by $Ni(DMG)_2$ (DMG = 1,2-dimethylglyoximato, Table 54). In this complex the planar units stack in columns with the Ni—Ni vector parallel to the stacking axis (MOM = metal over metal structure).[1020,1021] The repeating unit is generally formed by two molecules, the successive unit being rotated by approximately 45°. In this type of structure large channels exist which can contain solvent molecules or oxidants such as halogens. $Ni(DMG)_2$ is a weak semiconductor along the stacking axis with conductivity about 10^{-10} S cm^{-1}, and activation energy −0.6 eV.[1034]

The second structural motif is exemplified by $Ni(bqd)_2$ (bqd = 1,2-benzoquinonedioximato) (Figure 23). The planar molecules (Table 54) are in a slipped-stacked (SS) arrangement which makes the Ni—Ni directions inclined with respect to the stacking axis. In this type of complex the Ni—Ni distances are longer, the packing is also more efficient and no channels are present. The complexes with SS structure are generally insulators.

$Ni(DMG)_2$ reacts with BF_3 etherate to substitute the hydrogen atoms of oxime groups by BF_2 moieties forming a macrocyclic complex. Two such molecules are held together in the

Table 54 Selected Nickel(II) Complexes with Oxime Ligands

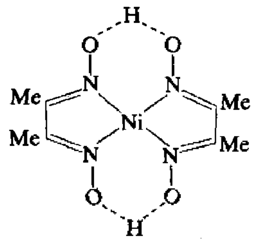
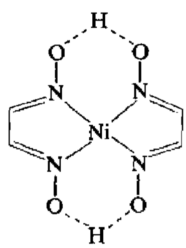
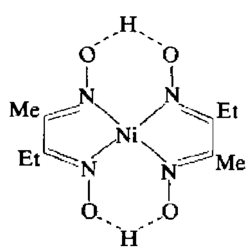
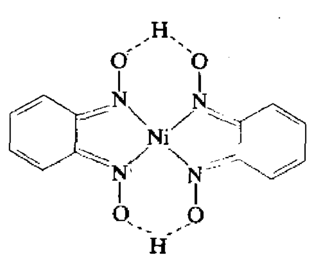
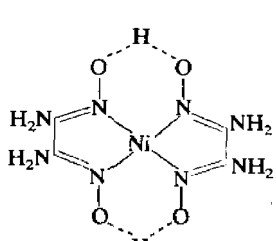
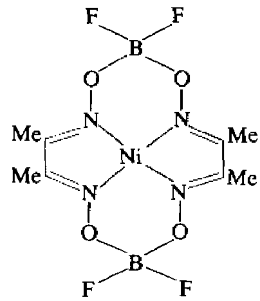
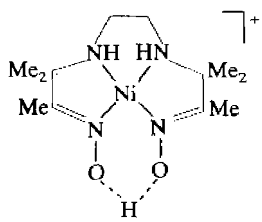
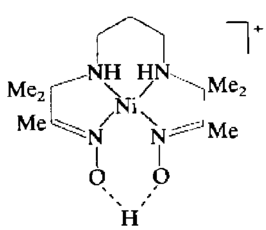
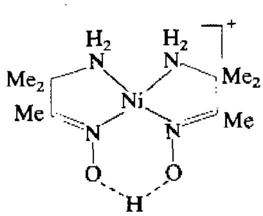
Complex	*Structural description and bond distances*[a] (*av*) (pm)		*Ref.*
 Bis(dimethylglyoximato)nickel(II)	Ni—N O—O Ni—Ni MOM	185 240 324	1020, 1021
 Bis(glyoximato)nickel(II)	Ni—N O—O Ni—Ni SS	187 245 420	1022, 1023
 Bis(methylethylglyoximato)nickel(II)	Ni—N O—O Ni—Ni SS	186 245 475	1024, 1025
 Bis(1,2-benzoquinone dioximato)nickel(II)	Ni—N O—O Ni—Ni SS	186 248 386	1026
 Bis{(oxamido)oximato}nickel(II)	Ni—N (ox) Ni—N (am) Ni—Ni O—O SS	186 304 498 249	1027

Table 54 (*continued*)

Complex	Structural description and bond distances[a] (av) (pm)		Ref.
 Bis(difluoroborondimethylglyoximato)nickel(II)	Ni—N Ni—N Ni—Ni Two molecules are linked together	187 321 465	1028
 2,2′-(1,2-Diaminoethane)bis(2-methyl-3-butanone oximato)nickel(II) perchlorate	Ni—N (am) Ni—N (ox) O—O	188 184 248	1029, 1030
 2,2′-(1,3-Diaminopropane)bis(2-methyl-3-butanone oximato)nickel(II) nitrate	Ni—N (am) Ni—N (ox) O—O	194 188 241	1031, 1032
 Bis(2-amino-2-methyl-3-butanone oximato)-nickel(II) chloride monohydrate	Ni—N (am) Ni—N (ox) O—O	191 188 242	1033

[a] Ni—Ni distance refers to intermolecular metal–metal interaction; N (am) and N (ox) mean amine and oxime nitrogen respectively; MOM = metal over metal structure; SS = slipped-stacked structure.

crystal giving rise to dimeric repeating units.[1028] The complex reacts with mono- and bi-dentate neutral ligands forming 1:1 and 1:2 adducts.[1035–1038]

Partial oxidation by halogens of the nickel(II) bis-dioximato complexes generally increases the electrical conductivity as shown in Table 55.[1039] The largest conductivity has been measured for the oxidation product of $Ni(DPhG)_2$ (DPhG = 1,2-diphenylglyoximato) with I_2 and Br_2.[1044–1047] The complexes have formulas $Ni(DPhG)_2I$ and $Ni(DPhG)_2Br$, respectively. The

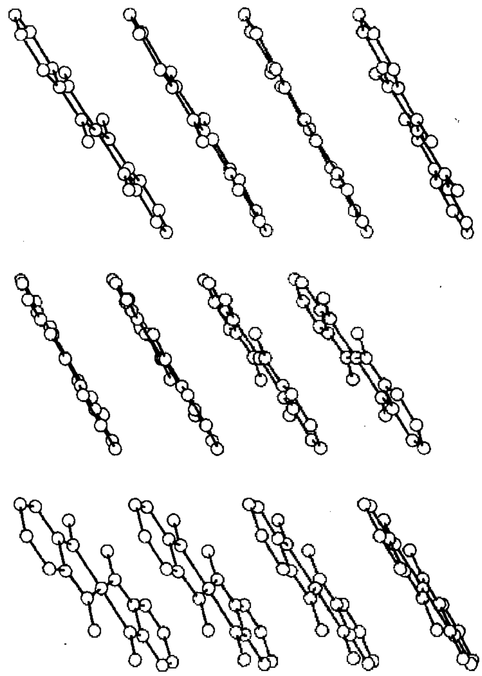


Figure 23 Packing diagram of $Ni(bqd)_2$ (reproduced from ref. 1039 by permission of Springer-Verlag)

crystal structure of $Ni(DPhG)_2I$ consists of $Ni(DPhG)_2$ columns arranged in the MOM structure with I_5^- ions in the channels. The MOM arrangement of planar units has also been found in the other oxidized complexes.[1048]

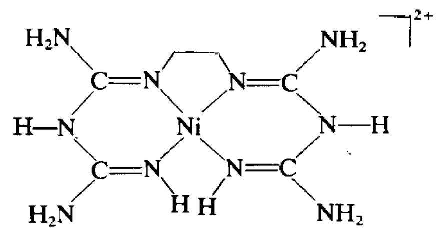
Table 55 Some Properties of Partially Oxidized Complexes with Oxime Ligands

Complex[a]	*Structural description and bond distances* (pm)		Conductivity ($S\ cm^{-1}$)	*Ref.*
$Ni(DPhG)_2I$	Ni—Ni	322	10^{-3}	1040
	Ni—N	187		
	I_5^-; MOM			
$Ni(bqd)_2I_{0.018}$	Ni—Ni	318	10^{-9}	1041
	Ni—N	186, 194		
	MOM		10^{-6}–10^{-7}	1041–1043
$Ni(bqd)_2I_{0.52}\cdot 0.32PhMe$	Ni—Ni	315		
	Ni—N	190		
	I_3^-; MOM			

[a] The ligands are defined in the text.

Other nickel(II) complexes with oxime ligands are reported in refs. 1035–1038 and 1049–1056.

The complex ethylenebis(biguanide)nickel(II) dichloride monohydrate (**134**)[1057] closely resembles the complexes reported in Table 54 in that an extensive delocalization of the electrons occurs over the entire molecular framework as indicated by the planar arrangement of the chelate rings and by the CN distances intermediate between a single and a double bond. The high exothermicity of complex formation ($\Delta H_f^\circ = -101.2\ kJ\ mol^{-1}$)[1058] has been explained in terms of this electron delocalization. The Ni—N bond distances in the above square planar complex are in the range 186–187 pm.[1058,1059] A similar complex with the ligand containing a trimethylene chain has been also reported.[1060]



(134)

50.5.3.8 Complexes with polypyrazolylborate and related ligands

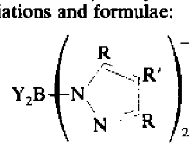
The mononegative polypyrazolylborate ligands (Table 56, **135–137**) form stable neutral complexes of the type [NiL_2] with nickel(II). The complexes are square planar or octahedral according to whether the ligand L is bi- or tri-dentate.[1061] [NiL_2] complexes are easily prepared in water or DMF–water mixture by metathetical reactions of the potassium salts of the appropriate ligand with a nickel(II) salt, in the stoichiometric ratio.[1062] The complexes are insoluble in water and sparingly soluble in polar solvents such as alcohols and acetone. They are soluble in $CHCl_3$, CH_2Cl_2, benzene and aromatic hydrocarbons. The complexes are stable enough to be sublimed unchanged *in vacuo*.

Selected nickel(II) complexes with polypyrazolylborate and related ligands are reported in Table 56.

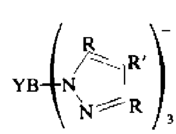
Table 56 Selected Complexes with Polypyrazolylborates and Related Ligands

Complex	*Donor set*	*Comments*	*Ref.*
[$Ni(H_2Bpz_2)_2$]* (**139**)	N_4	SqPl	1063, 1064
[$Ni(Et_2Bpz_2)_2$]*	N_4	SqPl	1063, 1065
[$Ni(Ph_2Bpz_2)_2$]*	N_4	SqPl	1063, 1066
[$Ni(H_2Bpz(Me_2pz)$] (**140**)	N_4	SqPl; geometrical and optical isomers	1067
[$Ni(HBpz_3)_2$] (**141**)	N_6	Oh	1063
[$Ni(Bpz_4)_2$]	N_6	Oh	1063
[Et_4N][$Ni(H_2Bpz_2)_3$]	N_6	Oh	1068
[$Ni(Me_2Gapz_2)_2$]*	N_4	SqPl	1069, 1070
[$Ni(MeGapz_3)_2$]*	N_6	Oh	1071
[$Ni(CHpz_3)_2$]($NO_3)_2$	N_6	Oh	1072
[$Ni_2F_2L_4$]($ClO_4)_2$* $L = H_2C(Me_2pz)_2$	N_4F_2	Oh; bridging F	1073
[$Ni_2Cl_4L_2$]* $L = H_2C(Me_2pz)_2$	N_2Cl_3	SqPy, bridging Cl	1074

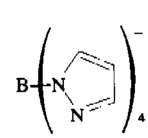
* Structures determined by X-ray analysis.
Ligand abbreviations and formulae:



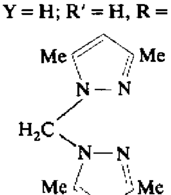
(**135**) Y = H; R = R′ = H; H_2Bpz_2
Y = Et; R = R′ = H; Et_2Bpz_2
Y = Ph; R = R′ = H; Ph_2Bpz_2
Y = H; R′ = H, R = Me; $H_2B(Me_2pz)_2$



(**136**) Y = H; R = R′ = H; $HBpz_3$



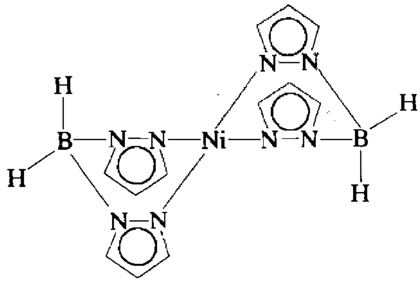
(**137**) Bpz_4



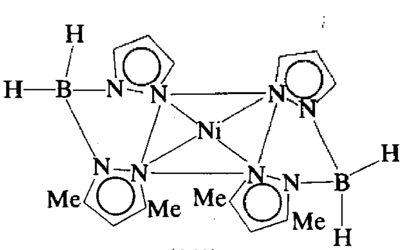
(**138**) $H_2C(Me_2pz)_2$

$H_2Bpz(Me_2pz)$ = dihydro-(1-pyrazolyl)(3,5-dimethyl-1-pyrazolyl)borate;
Me_2Gapz_2 = dimethylbis(1-pyrazolyl)gallate;
$CHpz_3$ = tris(1-pyrazolyl)methane.

The complexes with each of the polypyrazolylborate ligands have substantially the same properties irrespective of the number and type of the substituents in the pyrazole rings as well as on the boron atom.[1075] The bis-chelate complexes formed by all the bidentate ligands are square planar, as found in the structures of the three complexes $[Ni(H_2Bpz_2)_2]$ (**139**),[1064] $[Ni(Et_2Bpz_2)_2]$[1065] and $[Ni(Ph_2Bpz_2)_2]$.[1066] In these complexes each six-membered ring formed by Ni, the four N atoms and B is in a boat configuration, whereas the whole molecule is in a pseudochair conformation. The latter conformation reduces the non-bonding interactions between pyrazole hydrogens in the 3-positions. The Ni—N bond distances in these square planar complexes are in the range 188–189 pm as compared with the analogous distances of 209–210 pm in the six-coordinate complexes (*vide infra*).[1076] The presence of substituents in the 3-positions of the pyrazole rings and on the boron atoms imparts some steric protection to the metal in the axial position and the coordination of two more additional ligands to form six-coordinate complexes is unfavourable or not possible at all. The bis chelate with the unsymmetrical ligand dihydro(1-pyrazolyl)(3,5-dimethyl-1-pyrazolyl)borate has been found to exist in both geometrical and optical isomers.[1067] The enantiomers arise from the *cis* form of the complex (**140**). The reaction of $Et_4N(H_2Bpz_2)$ with hydrated $NiCl_2$ in ethanol at room temperature affords the 1:3 complex $Et_4N[Ni(H_2Bpz_2)_3]$[1068] which is indefinitely stable in the solid state. The same tris chelate occurs in either acetone or acetonitrile solution of the solid complex.[1068,1077]

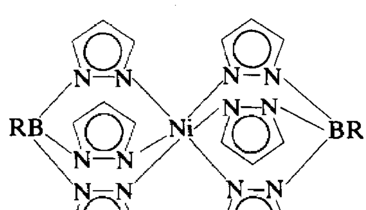


(**139**)

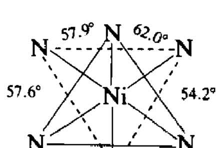


(**140**)

The $[NiL_2]$ complexes with both tridentate ligands (**136**) and (**137**) are six-coordinate, each ligand molecule in the complexes occupying the three facial positions of an octahedron (**141**).[1063,1075,1076] The two tridentate ligands are mutually staggered as indicated in (**142**) where the distortion from D_{3d} symmetry is indicated by the angles which deviate to a greater or lesser extent from the ideal value of 60°.[1076]



(**141**)



(**142**)

The poly(1-pyrazolyl)alkanes are isoelectronic and isosteric with the poly(1-pyrazolyl)borates, but are neutral. Consequently they may give nickel complexes which have no counterpart amongst the polypyrazolyborate complexes.[1072] For example, dinuclear fluoro- and chloro-bridged complexes $[Ni_2F_2L_4](ClO_4)_2$[1073] and $[Ni_2Cl_4L_2]$[1074] have been prepared with the ligand bis(3,5-dimethyl-1-pyrazolyl)methane (Table 56, **138**). The former complex is octahedral with the two nickel atoms antiferromagnetically coupled, whereas the latter contains ferromagnetically coupled five-coordinate nickel atoms.

50.5.3.9 Isocyanato, isothiocyanato, isoselenocyanato and related ligand complexes

The NCO^-, NCS^- and $NCSe^-$ ions can coordinate through N and O, S or Se atoms.[1078,1079] In the nickel(II) complexes terminal NCX^- ligands are invariably N-coordinated. Selected examples of nickel(II) complexes with NCO, NCS and NCSe are reported in Table 57.

Table 57 Selected Nickel(II) Complexes with Cyanate, Isothiocyanate and Isoselenocyanate Anions

Complex	Geometry of the chromophore		IR spectra (cm^{-1}) CN	CX[a]	Ref.
$(Et_4N)_2[Ni(NCO)_4]$	NiN_4	Td	2196s, br	1330m	1080, 1081
$(Et_4N)_4[Ni(NCS)_6]$	NiN_6	Oh	2112sh 2103s	828vw	1082
$(Ph_4As)_2[Ni(NCS)_4]$	NiN_4S_2	Oh	2141m 2096s 2079s	853w 813w 809w 790w	1082
$(Ph_4As)_2[Ni(NCS)_4]$	NiN_4	Td	2051s	830w	
$M[Ni(NCS)_3]\cdot xH_2O$	NiN_3S_3	Oh			1083
$Hg[Ni(NCS)_4(H_2O)_2]$	NiN_4O_2	Oh			1082, 1089, 1085
$(Me_4N)_4[Ni(NCSe)_6]$	NiN_6	Oh	2096s	606w	1086
$(cat^{2+})[Ni(NCSe)_4]$[b]	NiN_4Se_2	Oh	2145m 2092vs 2075s	653w	1086

[a] X = O, S, Se.
[b] cat^{2+} is $[p\text{-xylylenebis(triphenylphosphonium)}]^{2+}$.

The isothiocyanato complexes are the best known and the most numerous, and the compound $Na_4Ni(NCS)_6\cdot 8H_2O$ was reported as early as 1901.[1084] Anhydrous compounds have usually been prepared in non-aqueous solvents (ethanol, acetone, nitromethane) and crystallized using bulky cations. For example, the $(R_4N)_4[Ni(NCS)_6]$ (R = Me, Et) compounds can be obtained by the metathetical reaction in ethanol of nickel thiocyanate and $(R_4N)NCS$.[1082] The isoselenocyanato complexes have been prepared similarly.[1080,1087] The reaction of $(Ph_4As)NCS$ and nickel thiocyanate in 1:2 molar ratio in acetone yields the olive-green $(Ph_4As)_2Ni(NCS)_4$ which can be converted into a blue isomer upon heating at 155 °C.[1082]

The olive-green $(Ph_4As)_2[Ni(NCS)_4]$ and the yellow $(cat)^{2+}Ni(NCSe)_4$ are six-coordinate and contain both terminal and bridging NCX^- anions. The blue isomer of the former complex contains the tetrahedral $[Ni(NCS)_4]^{2-}$ anion. Tetrahedral species $[Ni(NCS)_4]^{2-}$ are easily obtained in solution by dissolving hydrated $Ni(NO_3)_2$ and an excess of KNCS in acetone.

The tetraisocyanatonickelate(II) has been obtained according to equation (121).[1088]

$$4AgNCO + NiBr_4^{2-} + 2Et_4N^+ \xrightarrow{Me_2CO} (Et_4N)_2[Ni(NCO)_4] + 4AgBr \qquad (121)$$

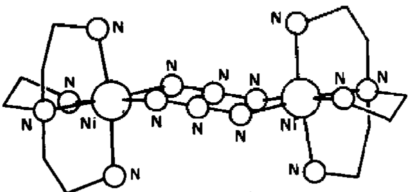
IR spectra of isocyanato and isothiocyanato complexes of nickel(II) have been widely studied.[1080–1082,1086,1087]

The complexes $HgNi(NCS)_4$, $HgNi(NCSe)_4$ and $HgNi(NCS)_2(NCSe)_2$ are supposed to contain six-coordinate nickel(II) in a polynuclear structure.[1082,1089] All of the complexes with the general formula $HgNi(NCX)_4$ behave as Lewis acids towards a number of bases such as alcohols, pyridine and substituted pyridines, PPh_3, bipy, phen, DMSO, *etc.*, giving in most cases polynuclear species.[1084,1089]

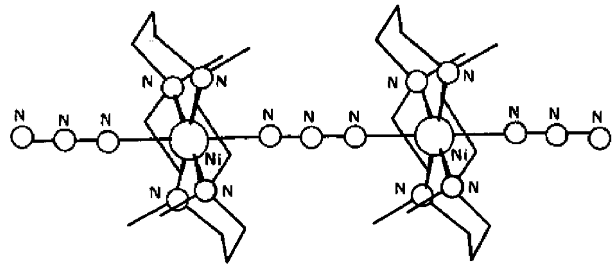
Organomercury thiocyanates and selenocyanates HgNCXL′ react with $Ni(NCS)_2L_4$ (L = py, 4-aminopyridine, aniline) affording complexes having the stoichiometry $Hg_2Ni(NCX)_4$-$L_2L'_2$.[1091–1093]

Isothiocyanato complexes have been prepared with nearly all of the known neutral ligands, whereas the same complexes with NCO^- and $NCSe^-$ are far less numerous. Relevant examples of isothiocyanato complexes are reported in the appropriate section according to the coligand. As an example of mixed-ligand cyanato complexes the dinuclear $[Ni_2(NCO)_2(tren)_2](BPh_4)_2$[1094] can be given because the NCO^- groups are bridging in the end-to-end position in contrast to the more common single atom bridging mode found, for example, in $[Ni(NCO)_2L_2]_2$ (L = 3- or 4-cyanopyridine).[1095] Finally, the structure of the *trans* octahedral $Ni(NCSe)_2(DMF)_4$ has been reported with the isoselenocyanato N-bonded at a distance of 205 pm.[1096]

Nickel azido complexes are less numerous than those with thiocyanate and only few compounds have been structurally characterized.[1097] The six-coordinate complex $K_4[Ni(N_3)_6]\cdot 2H_2O$ has been prepared from an aqueous solution of $Ni(N_3)_2$ and an excess of KN_3 (1:20 molar ratio).[1098] Two significant examples of mixed-ligand azido complexes are the dinuclear $[Ni_2(N_3)_2(tren)_2](BPh_4)_2$[726] and $[Ni_2(N_3)_3(Me_4cyclam)]I$[1099] (see also Section 50.5.9). The former complex contains two end-to-end coordinated bridging azido groups (**143**), whereas in the latter complex a single bridging azido group exists, and two additional azides are terminal (**144**). The $Ni(N_3)_2Ni$ ring in complex (**143**) is planar and asymmetric as indicated by the different Ni—N (azide) bond distances (220 and 207 pm) and Ni—N—N angles (135° and 123°) for each nickel atom. $[Ni(N_3)_2(diphos)]$ (diphos = $Ph_2PCH_2CH_2PPh_2$) is reported to react with $NOBF_4$ in CH_2Cl_2 to give the dinuclear complex $[Ni_2(N_3)_2(diphos)_2](BF_4)_2$ which is assumed to contain the azido group bridging with a single atom.[1100] This complex in turn reacts with NO (5 atm, 20 °C) in CH_2Cl_2 giving the mononuclear $[Ni(NCO)_2(diphos)]$.



(**143**)



(**144**)

50.5.3.10 Organonitrile complexes

Numerous nickel(II) adducts with organonitriles RCN (R = alkyl, aryl) having the general formula $Ni(RCN)_nY_2$ (n = 2, 3, 4, 6) have been prepared using different procedures (equations 122–126).[1101,1102] In general, strictly anhydrous conditions must be employed in order to avoid the displacement of RCN molecules by water. The use of large counteranions with low coordinating ability favours the formation of hexakis adducts. These compounds are hygroscopic and must be handled in a dry atmosphere.

$$Ni(ClO_4)_2{\cdot}6H_2O \xrightarrow[P_2O_5]{MeCN/Et_2O} [Ni(MeCN)_6](ClO_4)_2 \xrightarrow[vacuum]{65\,°C} [Ni(OClO_3)_2(MeCN)_4]$$

$$\xrightarrow[vacuum]{75\,°C} [Ni(OO'ClO_2)_2(MeCN)_2] \quad (122)^{1103}$$

$$Ni + 2NOBF_4 \xrightarrow{MeCN} [Ni(MeCN)_6](BF_4)_2{\cdot}0.5MeCN + 2NO \quad (123)^{1104}$$

$$Ni + 3Br_2 \xrightarrow{MeCN} [Ni(MeCN)_6](Br_3)_2 \quad (124)^{1104}$$

$$NiCl_2 + 2SbCl_5 \xrightarrow{RCN} [Ni(RCN)_6](SbCl_6)_2 \quad (125)^{1105-1107}$$

$$NiCl_2 + 2MCl_3 \xrightarrow{MeCN} [Ni(MeCN)_6](MCl_4)_2 \quad (126)^{1108}$$

M = Al, Fe, Ga, *etc.*

All of the organonitrile adducts of nickel(II) contain nickel(II) coordinated to six nitrogen atoms of the RCN molecules, as exemplified by the structure of $[Ni(MeCN)_6]^{2+}$ cation where the MeCN donor is coordinated in a nearly linear array (Ni—N—C angles average 172°) with Ni—N distances in the range 203–212 pm.[1109]

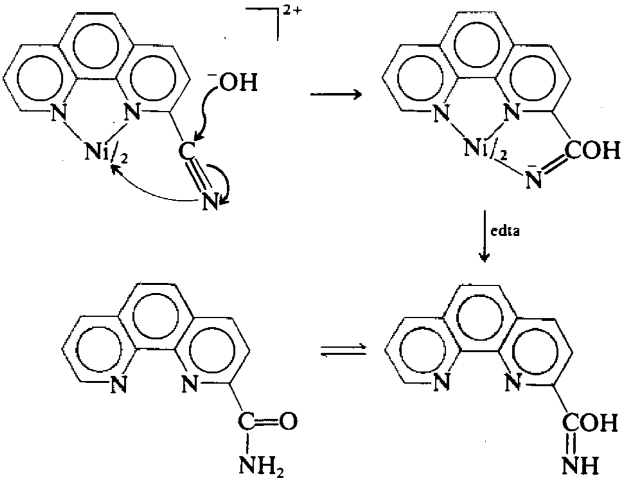
Coordinated nitrile groups undergo a number of reactions and some of those involving nickel(II) are reported here. The neutral pentachlorophenylnickel(II) complex is converted to the cationic complex with coordinated organonitriles according to equation (127).[1110] The latter complex reacts in turn with MeOH in the presence of triethylamine giving a complex where the nitrile has been converted to the corresponding imidate coordinated to the metal through the nitrogen atom (equation 128).

$$[Ni(C_6Cl_5)Cl(R_3P)_2] \xrightarrow[C_6H_6]{AgClO_4,\ R'CN} [Ni(C_6Cl_5)(R_3P)_2(R'CN)]^+ \quad (127)$$

$R_3P = MePh_2P, Me_2PhP$; R' = Me, Ph, CH_2Ph

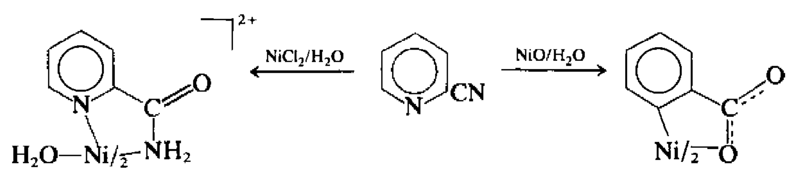
$$[Ni(C_6Cl_5)(R_3P)_2(R'CN)]^+ \xrightarrow[Et_3N]{MeOH} [Ni(C_6Cl_5)(R_3P)_2(NH{=}C(R')OMe]^+ \quad (128)$$

Nickel(II) compounds catalyze the hydration of organonitriles in basic and neutral media. For example, 2-cyano-1,10-phenanthroline is converted to the corresponding carboxamide by means of nucleophilic attack of OH^- on the nitrile carbon atom. The suggested mechanism is outlined in Scheme 9.[1111] The same mechanism holds for the hydration reaction of 2-cyano-8-hydroxyquinoline (8-hydroxyquinoline-2-carbonitrile).[1112] The hydrolysis of 2-cyanopyridine (2-pyridinecarbonitrile) is promoted by either nickel chloride or oxide in neutral solution, simply by refluxing the mixture in water. Nickel chelates of both pyridine-2-carboxamide and pyridine-2-carboxylate anion result (Scheme 10).[1113] These chelates also have catalytic activity and the free amide is formed. Other nickel complexes of the types $Ni(en)(H_2O)_4SO_4{\cdot}H_2O$, $Ni(en)_3Cl_2{\cdot}H_2O$ and $Ni(bipy)(H_2O)_4SO_4{\cdot}2H_2O$ have been found to exhibit catalytic activity towards the hydration reaction of organonitriles.[1114]



Scheme 9

(a)



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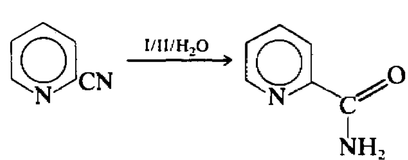
(b)



Scheme 10

Phthalonitrile, $C_6H_4(CN)_2$, has been found to cyclize in an MeOH solution of $NiSO_4$ at the cathode of an electrochemical cell to give the nickel phthalocyaninato complex.[1115,1116]

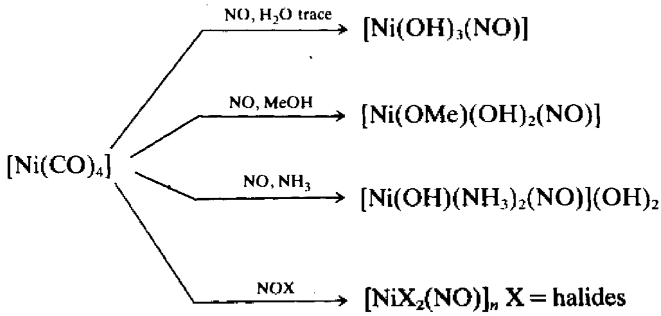
50.5.3.11 Nitrosyl complexes of (formally) nickel(II)

The nitrosyl complexes of nickel(II) are scarce and less studied than those of nickel(0) (see Section 50.2.5.2) even though they have been known for nearly a century. Selected examples of nitrosyl nickel(II) complexes are reported in Table 58. As early as 1891 it was reported by Berthelot[1117] that $Ni(CO)_4$ reacts with gaseous NO giving a blue compound which was later characterized as a pseudotetrahedral complex of nickel(II) having the formula $[Ni(OH)_3(NO)]$.[1118] This compound is paramagnetic and is formed only if traces of water are present in the reactants. Using a methanolic solution of $Ni(CO)_4$ a methoxo derivative is formed.

Table 58 Selected Nitrosyl Complexes of Nickel(II)

Complex	μ_{eff} (BM)	$\nu(NO)$ (cm^{-1})	*Geometry*	*Ref.*
$[Ni(OH)_3(NO)]$	2.97	1828	Td	1117, 1118
$[Ni(OMe)(OH)_2(NO)]$	—	1820	Td	1118
$[Ni(OH)(NH_3)_2(NO)](OH)_2$	—	1780	Td	1119
$[NiCl_2(NO)]_n$	3.70	1835, 1870	Polynuclear	1120
$[NiBr_2(NO)]_n$	3.20	1830, 1865	Polynuclear	1120

Other nitrosyl complexes are reported in Scheme 11.[1120]



Scheme 11

The purple, crystalline $K_2[Ni(CN)_3(NO)]$ has been prepared by the reaction of $NH_2OH{\cdot}HCl$ with K_2NiCN_4.[1121] This compound is assumed to form by displacement of CN^- by NO^- and thus the nickel atom is in the 2+ valence state. The anion $[Ni(CN)_3(NO)]^{2-}$ has been found to form using different reaction routes (equations 129 and 130).[1122]

$$Ni(CN)_4^{2-} + N_2O_3^{2-} \longrightarrow [Ni(CN)_3(NO)]^{2-} + NO_2^- + CN^- \qquad (129)$$

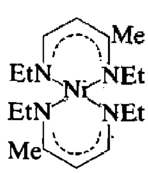
$$Ni(CN)_4^{2-} + 2NH_4OH \xrightarrow{OH^-} [Ni(CN)_3(NO)]^{2-} + NH_3 + CN^- + H_2O \qquad (130)$$

50.5.3.12 Dialkylamides and disilylamides

In contrast to the extensive coordination chemistry of Ni—C (alkyl) complexes, examples of nickel complexes containing Ni—N (dialkylamide) σ bonds are lacking.[1123]

The general reaction which affords transition metal dialkylamido complexes (equation 131) failed for nickel(II), and in the case of $LiNEt_2$ led to a diiminato complex (**145**).

$$MCl_n + nLiNR_2 \longrightarrow M(NR_2)_n + nLiCl \qquad (131)$$



(**145**)

On the other hand, when $LiN(SiMe_3)_2$ is employed, reaction (131) has been successful in preparing the nickel(II) disilylamide $[Ni\{N(SiMe)_2\}_2]$.[1124] This unusually unstable complex is assumed to contain two-coordinate nickel(II). By reacting $NiCl_2(PPh_3)_2$ with $LiN(SiMe_3)_2$ the three-coordinate nickel(I) complex $[Ni\{N(SiMe_3)_2\}(PPh_3)_2]$ has been obtained.[1125] The same reaction carried out with the lithium salt of 2,5-dimethylpyrrole in place of $LiN(SiMe_3)_2$ gave the diamagnetic nickel(II) complex $[Ni(NC_6H_8)_2(PPh_3)]$.[1123] The reactions of dialkylnickel(II), NiR_2L_2 (R = Me, Et; L = ½bipy, ½dpe, PEt_3), with compounds having acidic NH groups (succinimide, phthalimide, diacetamide, imidazole) gave the corresponding monoalkylnickel(II) complexes $NiR(NR'R'')L_2$.[1126]

50.5.4 Complexes with Ligands Containing Phosphorus, Arsenic and Antimony as Donor Atoms

50.5.4.1 Introduction

The number of nickel(II) complexes with mono-, bi- and poly-dentate ligands containing tertiary phosphines as a donor group is very large and increases day by day while complexes with tertiary arsines are less numerous and those with stibines are rarer still. The number of nickel(II) complexes with mixed donor ligands containing N, O and S donor atoms besides P or As is also very large.

The subject matter of the following sections has been divided according to the denticity of the ligands (mono-, bi-, tri-, and linear tetra-dentate, tripod-like ligands) and according to the nature of the donor atoms, phosphine and arsine complexes being reviewed before those containing mixed donor ligands.

50.5.4.2 Complexes with monodentate tertiary phosphines, arsines and stibines[1127–1131]

(i) Halo and pseudohalo compounds

Hundreds of nickel(II) complexes with monodentate phosphines have been reported. Selected complexes are reported in Table 59 together with some of their physicochemical properties. A selection of structural data is shown in Table 60.

Nickel(II) complexes containing up to four molecules of trialkylphosphines have been prepared by the direct reaction of a nickel(II) salt with the appropriate phosphine in either aprotic or protic solvents. Anaerobic conditions have sometimes been employed in order to avoid oxidation of unstable phosphines whereas dimethoxypropane has occasionally been employed as a dehydrating agent when using hydrated nickel(II) salts.

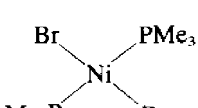
The complexes $[NiX_3PBu^t_3](PHBu^t_3)$ were obtained by the reaction of NiX_2 (X = Cl, Br, I) with PBu^t_3 in ethanol or *n*-butanol, under N_2.[1189]

Triphenylphosphine, because of its lower donor strength, reacts less easily than trialkylphosphines, and complexes with a maximum of two molecules of the phosphines were obtained. $NiX_2(PPh_3)_2$ were prepared by reacting hydrated nickel(II) salts and the phosphine in glacial acetic acid or in boiling butanol.[1155,1159,1160] Analogous complexes with mixed alkyl- and aryl-phosphines were also prepared.[1143,1144,1161–1170] In some cases two structural isomers were obtained.[1161,1164] For example, the reaction of $NiBr_2$ with PPh_2R (R = Et, Pr^n, Pr^i, Bu^s, Bu^n) in polar solvents affords green paramagnetic compounds. Their recrystallization at low temperature (−78 °C) in apolar or weakly polar solvents affords brown diamagnetic compounds which slowly isomerize into the paramagnetic species at room temperature.[1163]

Trihalo complexes containing a single coordinated triphenyl- or trialkyl-phosphine $[NiX_3(PR_3)]^-$ have a pseudotetrahedal structure and their electronic and magnetic properties have been studied in detail.[1155–1158,1174–1176]

Dihalobis(tertiary phosphine)nickel(II), $[NiX_2(PR_3)_2]$, may be either square planar or pseudotetrahedral species depending on the steric and electronic properties of the phosphine and, in a few cases, on the nature of the halide.

Trialkylphosphines, in general, give square planar complexes. A *trans* planar structure (**146**) has been found in most complexes which have been crystallographically investigated.[1136,1138,1177] A *cis* planar structure was found, for example, in $[NiCl_2(PC_{11}H_{13})_2]$ (**147**).[1188]



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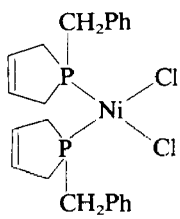

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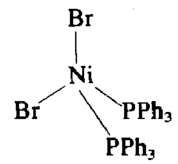


(148)

Complexes with triphenylphosphine are assumed to be pseudotetrahedral on account of their

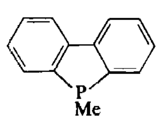
Table 59 Selected Complexes with Monodentate Phosphines, Arsines and Stibines

Complex	μ_{eff} *(r.t.)* (BM)	*Donor set*	*Coordination geometry or number*	*Remarks*	*Ref.*
$NiX_2(PMe_3)_2$	0–1.3	P_2X_2	SqPl	X = halides, CN, NCS, NO_2; air-sensitive	1132–1136
$NiX_2(PR_3)_2$		P_2X_2	SqPl	X = halides, CN, $\frac{1}{2}SO_4$; R = Et, Pr^n, Bu^n	1137–1141
$Ni(NO_3)_2(PEt_3)_2$	3.1	P_2O_2	Td		1137
$NiX_2(PR_3)_2$	Diamagnetic	P_2X_2	SqPl	X = halides, NCS; R = cyclohexyl; X = I, one diamagnetic and one paramagnetic isomer	1142, 1143
	3.15–3.16	P_2X_2	Td	X = Cl, Br; R = cyclopropyl; prepared under N_2	1144
$NiX_2(PMe_3)_3$	Diamagnetic	P_3X_2	5	X = halides, CN, NCS; air-stable	1133, 1135, 1145–1150
	0.3–0.7			X = NO_2	
$[NiX(PMe_3)_3]ClO_4$	Diamagnetic	P_3X	SqPl	X = Cl, Br	1133
$[NiX(PMe_3)_4]BF_4$	0.48–0.91	P_4X	TBPy	X = halides; prepared in an inert atmosphere	1148, 1151
$[NiX(PHEt_2)_n]BPh_4$	Diamagnetic Diamagnetic	P_3X P_4X	SqPl 5	X = Cl, Br, I; $n = 3$ $n = 4$	1152
$[NiX_2(PHEt_2)_3]$	Diamagnetic	P_3X_2	5	X = Cl, Br, I	1152
$[NiX_2(DMe_3)_3]$	0.36–1.61	D_3X_2	5	X = Br, I; D = As, Sb; prepared under N_2; stable when solid	1153, 1154
$[NiX_3(PPh_3)]AB_4$	3.46–3.68	PX_3	Td	X = Br, I; AB_4 = NEt_4, NBu^n_4, $AsPh_4$; prepared in hot n-butanol	1155–1158
$[NiX_2(PPh_3)_2]$	3.28–3.41	P_2X_2	Td	X = halides, NO_3	1155, 1159, 1160
	Diamagnetic	P_2X_2	SqPl	X = NCS	1159
$[NiX_2(PPh_2R)_2]$	3.14–3.30	P_2X_2	Td	X = Br, I; R = cyclohexyl, cyclopropyl	1143, 1144
$[NiX_2(PPhR_2)_2]$	Diamagnetic	P_2X_2	SqPl	X = halides, NCS; R = cyclohexyl, cyclopropyl	1143, 1144
$[NiX_2(PBu^t_nPh_{3-n})_2]$	Diamagnetic	P_2X_2 P_2X_2	SqPl Td	X = halides; $n = 2$ X = halides; $n = 1$	1161
$[NiX_2\{P(CH_2Ph)_3\}_2]$	Diamagnetic	P_2X_2	SqPl	X = halides, NCS	1162
$[NiX_2\{P(CH_2Ph)_2Ph\}_2]$	Diamagnetic	P_2X_2	SqPl	X = halides, NCS	1162
$[NiX_2\{P(CH_2Ph)Ph_2\}_2]$	Diamagnetic or 2.61–3.23	P_2X_2	SqPl/Td	X = halides; two structural isomers for each compound	1162
$[NiCl_2(PPh_2R)_2]$	Diamagnetic	P_2X_2	SqPl	R = Me, Et, Pr^n, Pr^i, Bu^i	1163
$[NiX_2(PPh_2R)_2]$	3.0–3.3	P_2X_2	Td	X = Br, I; R = Me, Et, Bu^t X = I; R = Pr^i, Bu^n, Pr^n, Bu^i	1163, 1164
$[NiBr_2(PPh_2R)_2]$	Diamagnetic 3.0	P_2X_2 P_2X_2	SqPl Td	R = Et, Pr^n, Pr^i, Bu^n, Bu^s; two structural isomers of each compound; the planar isomers isomerize to Td ones at room temp.	1163
$[NiX_2(PHPh_2)_3]$	0–1.48	P_3X_2	TBPy	X = Cl, Br, I	1165
$[Ni(CN)_2(PPh_2R)_3]$	Diamagnetic	P_3C_2	TBPy	R = Me, Et	1166
$[NiX_2(PPhF_2)_3]$	Diamagnetic	P_3X_2	5	X = Br, I; prepared by oxidation of NiL_4 with X_2	1167
$[NiX_2(PFBu^t_2)_2]$	Diamagnetic	P_2X_2	SqPl	X = Cl, Br, I; prepared by direct synthesis in benzene	1168, 1169
$[NiBr_2(PPh_2R)_2]$	Diamagnetic 3.6	P_2Br_2 P_2Br_2	SqPl Td	R = o-ClC_6H_4 R = o-$MeOC_6H_4$	1170
$[NiBr_2\{P(CH_2SiMe_3)_3\}_2]$		P_2Br_2	SqPl		1171
$[NiX_2(CO)(PR_3)_2]$	0–0.5	P_2X_2C	5	PR_3 = PMe_3, PEt_3, PPh_3, PPh_2Me, $PPhMe_2$; unstable in the air	1172, 1173
$[NiX(CO)(PMe_3)_3]BF_4$		P_2XC	5	Stable enough in CO atmosphere	1173

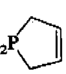
Table 60 Structural Data for Selected Monodentate Phosphine Complexes

Complex	*Bond distances* (pm) Ni—X	Ni—P	*Structure*	*Ref.*
$[NiBr_3(PBu^t_3)](PHBu^t_2)$	238[a]	248	Td	1174
$[NiBr_3(PPh_3)]AsPh_4$	237[a]	232	Td	1175
$[NiI_3(PPh_3)]AsPh_4$	254[a]	228	Td	1176
$[NiBr_2(PMe_3)_2]$ (**146**)	228	221	*trans* SqPl	1136
$[NiBr_2(PEt_3)_2]$	230	226	*trans* SqPl	1138
$[NiBr_2(PMe_2Ph)_2]$	230	225	*trans* SqPl	1177
$[NiBr_2\{PPh_2(CH_2Ph)\}_2]$	231	226	*trans* SqPl	1178
$[NiBr_2\{PPh_2(CH_2Ph)\}_2]$	236	232	Td	1178
$[Ni(NCS)_2(PPh_2Me)_2]$	180	224	SqPl	1179
$[NiBr_2(PPh_3)_2]$ (**148**)	234	233	Td	1180
$[NiBr_2(PMe_3)_3]$[b] (**149**)	250[a]	220[a]	TBPy	1150
$[NiI_2(PHPh_2)_3]$	249, 280	218[a]	TBPy	1181
$[Ni(CN)_2(PPhMe_2)_3]$ (**150**)	185[a]	223[a]	TBPy	1182
$[NiBr(PMe_3)_4]BF_4$ (**151**)	252	225–229	TBPy	1151
$[Ni(CN)_2\{PPh_2(CH_2OH)\}_3]\cdot\frac{1}{2}C_6H_6$	186	224,[a] 240	SqPy	1183
$[Ni(CN)_2\{PPh_2(CH_2OH)\}_2]$	186	221	SqPl	1183
$[NiCl_2\{P(CH_2CH_2CN)_3\}_2]$	240[c]	243	Oh	1184
$[Ni(NCS)_4\{P(CH_2CH_2CN)_3\}_2][NiL_2]$[d] (**152**)	207	243	Oh	1185a
$[Ni(NCS)_2\{PCH_2CH_2CN)_3\}_2]$[e]	183	224	SqPl	1185b
$[Ni(CN)_2\{PC_{13}H_{11}\}_3]$[f]	184	218 (bas), 232 (ax)	SqPy	1187
$[NiBr_2(PFBu^t_2)_2]$	229	223	SqPl	1169
$[NiCl_2(PC_{11}H_{13})_2]$[g]	221	215	*cis* SqPl	1188

[a] Average values.
[b] Two independent molecules in the unit cell.
[c] Ni—N bond distances, 209 pm.
[d] L = diacetone alcohol.
[e] Three conformational isomers were obtained.
[f] $PC_{13}H_{11}$ = 9-methyl-9-phosphafluorene,



[g] $PC_{11}H_{13}$ = 1-benzyl-Δ^3-phospholene, PhCH$_2$P



paramagnetism and this structure was found in the two complexes $[NiCl_2(PPh_3)_2]$[1190] and $[NiBr_2(PPh_3)_2]$ (**148**).[1180] Essentially the same structure is retained by the complexes in solution.

Complexes with mixed alkyl and phenyl phosphines may be either square planar or tetrahedral depending on the nature of the anion and the number of the phenyl groups which are attached to the phosphorus atom.[1162] Planar $\rightleftharpoons$ tetrahedral equilibria often exist in solution. In general, the amount of tetrahedral species in solution decreases in the order $PPh_3 > PPh_2R > PPhR_2 > PR_3$ for a given halide (R = alkyl), and I > Br > Cl > NCS for a given phosphine. The tetrahedral species are also favoured by polar solvents.[1143]

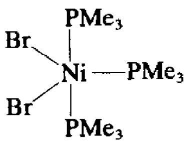
Complexes of the type $[NiX_2(PMe_3)_3]$ are diamagnetic five-coordinate both in the solid state and in solutions containing excess phosphine to prevent the formation of planar species. Five-coordinate species are also favoured by low temperature. The equilibria represented in equations (132) and (133) were studied by means of electronic, ^{31}P and ^{1}H NMR spectroscopy.[1151,1152,1191]

$$NiX_2(PR_3)_3 + PR_3 \rightleftharpoons [NiX(PR_3)_4]^+ + X^- \quad (132)$$

$$[NiX(PR_3)_3]^+ + PR_3 \rightleftharpoons [NiX(PR_3)_4]^+ \quad (133)$$

$$PR_3 = PMe_3, PHEt_2$$

In the two complexes $[NiBr_2(PMe_3)_3]$[1150] (**149**) and $[NiI_2(PHPh_2)_3]$[1181] the halides lie in the equatorial plane of a trigonal bipyramid, while in $[Ni(CN)_2(PPhMe_2)_3]$[1182] (**150**) the cyanide ions occupy the axial positions. A distorted trigonal bipyramidal structure has also been found in the complex $[NiBr(PMe_3)_4]BF_4$ (**151**).[1151]



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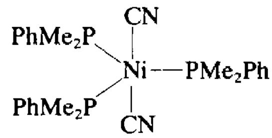

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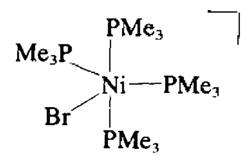


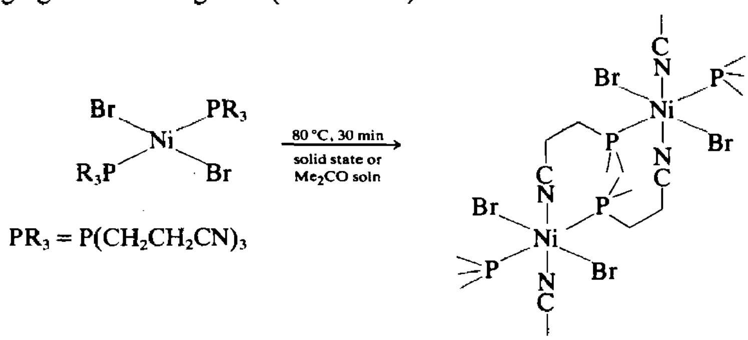
(151)

The stability of the five-coordinate $[NiX_2(DMe_3)_3]$ (D = As, Sb) in the solid state decreases in the order I > Br > Cl and no chloride complex was isolated in the solid state.

The complex $[Ni(CN)_2\{PPh_2(CH_2OH)\}_3]\cdot\frac{1}{2}C_6H_6$ which has been obtained according to equation (134) is square pyramidal with the ligand acting as monodentate through the phosphorus atoms. Owing to the long Ni—P(ap) bond distance, the five-coordinate complex easily dissociates into the four-coordinate square planar complex $[Ni(CN)_2\{PPh_2(CH_2OH)\}_2]$.[1183]

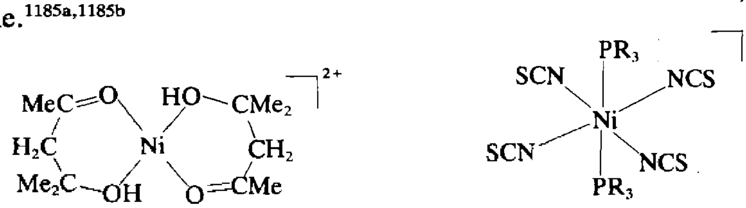
$$Na_2Ni(CN)_4\cdot 3H_2O + PPh_2(CH_2OH) + HCHO \xrightarrow[50\,^\circ C]{H_2O} [Ni(CN)_2\{PPh_2(CH_2OH)\}_3] \qquad (134)$$

The tris(2-cyanoethyl)phosphine can act either as a monodentate phosphorus donor ligand or as a bidentate mixed donor ligand. The red square planar $[NiX_2L_2]$ complexes (X = Cl, Br) transform in the solid state into blue six-coordinate isomers which have a polymeric structure involving bridging bidentate ligands (Scheme 12).[1178,1184,1192]



Scheme 12

During a preparation of the complex $[Ni(NCS)_2\{P(CH_2CH_2CN)_3\}_2]$ in acetone solution, a yellow-orange compound was obtained which was characterized as $[Ni(C_6H_{12}O_2)_2][Ni(NCS)_4\{P(CH_2CH_2CN)_3\}_2]$ (**152**) ($C_6H_{12}O_2$ = 4-hydroxy-4-methyl-2-pentanone; 'diacetone alcohol'). This reaction, which involves an aldol condensation of two acetone molecules, was found to be not reproducible.[1185a,1185b]



(152)

Nickel(II) complexes with cyclic phosphines are not numerous and, in general, resemble those of monotertiary phosphines. Some examples are reported in ref. 1186.

(*ii*) *Organometallic compounds*

A few representative examples of simple organometallic compounds of nickel(II) including carbonyl and hydrido compounds are reported here. A more complete listing of such types of compound is given in 'Comprehensive Organometallic Chemistry' (vol. 6, p. 37) and references therein. Selected structural data for organometallic nickel(II) complexes with monodentate phosphines are reported in Table 61.

Hydrido complexes with various tertiary phosphines have been prepared using different synthetic routes under anaerobic conditions (equations 135–138).[1204–1215] In the

Table 61 Some Structural Data for Selected Organometallic Complexes with Monodentate Phosphines

Complex	Bond distances (pm) Ni—C	Ni—P	Ni—X	Structure	Ref.
$[Ni(acac)(Me)(PCy_3)]$ (**155**)	194	216	189[a]	SqPl	1193
$[Ni(acac)(Et)(PPh_3)]$	197	214	191	SqPl	1194
$[Ni(acac)(PhC{=}CPhMe)PPh_3]$	190	218	192[a]	SqPl	1195
$[NiBr(C_6F_5)(PMePh_2)_2]$ (**156**)	188	222	232	SqPl	1196
$[Ni(C_6F_5)_2(PMePh_2)_2]$	194	221[a]		*trans* SqPl	1197
$[Ni(C_6F_5)(C_6Cl_5)(PMePh_2)_2]$	191,[b] 198[c]	223[a]		*trans* SqPl	1198
$[Ni(Me)(PMe_3)_4]BPh_4$	203	226 (eq),[a] 221 (ax)		TBPy	1199
$[Ni(C{\equiv}CPh)_2(PEt_3)_2]$ (**157**)	188	222		*trans* SqPl	1200
$[NiCl(CH_2SiMe_3)(PMe_3)_2]$[d]	194, 196	220,[a] 221[a]	225, 226	*trans* SqPl	1201
$[NiCl(COCH_2SiMe_3)(PMe_3)_2]$	178	220[a]	229	*trans* SqPl	1201
$[NiCl(COMe)(PMe_3)_2]$	184	220	226	*trans* SqPl	1202
$[NiCl_2(CO)(PMe_3)_2]$ (**154**)	173	221[a]	230	TBPy	1172
$[NiI_2(CO)(PMe_3)_2]$	173	222	260	TBPy	1173
$[Ni(BH_4)(H)(PCy_3)_2]$ (**153**)		219	148, 176,[e] 173[e]		1203

[a] Average values.
[b] Ni—C_6Cl_5.
[c] Ni—C_6F_5.
[d] Two crystallographically independent molecules.
[e] Ni—H (BH_4) distances.

$[NiCl(H)(PCy_3)_2]$ complex the chloride may be replaced by alkenes, alkynes, pyridine, pyrazole and imidazole giving complexes of the type $[Ni(H)L(PCy_3)_2]Y$ ($Y = BPh_4$, BF_4).[1216,1217]

$$NiCl_2(PCy_3)_2 + NaBH_4 \xrightarrow[\text{r.t.}]{\text{THF/EtOH}} [NiCl(H)(PCy_3)_2] \tag{135}$$

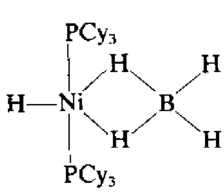
$$Ni(acac)_2 + PPh_3 + Et_2AlBr \xrightarrow[-20\,^{\circ}C]{Et_2O} [NiBr(H)(PPh_3)_3] + NiBr_2(PPh_3)_2 \tag{136}$$

$$Ni(PCy_3)_3 + HCl \xrightarrow{\text{EtOH}} [NiCl(H)(PCy_3)_2] \tag{137}$$

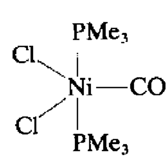
$$Ni(PR_3)_4 + HCN \xrightarrow{\text{EtOH}} [Ni(CN)(H)(PR_3)_3] \tag{138}$$

$$PR_3 = PPh_3,\ P(alkyl)_3,\ P(Oalk)_3$$

The hydrido complexes are diamagnetic, and are square planar or five-coordinate. Their stability, in general, increases with the number of coordinated phosphines. In the complex $[Ni(BH_4)(H)(PCy_3)_2]$ (**153**) the nickel atom is coordinated in the equatorial positions by two hydrogens of the borohydride and by one hydride anion.



(**153**)



(**154**)

The reaction of CO under normal conditions of temperature and pressure with solutions of $[NiX_2(PR_3)_n]$ ($n = 2$, 3) and $[NiX(PMe_3)_4]BF_4$ affords carbonyl complexes of formulas $[NiX_2(CO)(PR_3)_2]$ (**154**) and $[NiX(CO)(PMe_3)_3]BF_4$.[1173] The former neutral complexes are stable in the solid state and in solution under CO atmosphere. Amongst the cationic complexes only $[NiBr(CO)(PMe_3)_3]BF_4$ is stable.

Simple alkyl and aryl derivatives of nickel(II) with monodentate phosphines are, in general, too unstable to be isolated in the solid state as pure compounds. However, it has been found that a considerable stabilization occurs when the carbon σ-bonded to nickel(II) is part of either an alkynic group, a fluorinated or chlorinated group, or an *ortho*-substituted phenyl group.

Stable aryl compounds of nickel(II) were first reported by Chatt and Shaw with the use of

Grignard reagents (equations 139 and 140).[1218] Ethynyl complexes were also prepared according to equation (141).[1218]

$$NiBr_2(PR'_3)_2 + RMgBr \xrightarrow[-10/-40\,^{\circ}C]{Et_2O} [NiBr(R)(PR'_3)_2] \quad (139)$$

$$NiBr_2(PR'_3)_2 + 2RMgBr \xrightarrow[-10/-40\,^{\circ}C]{Et_2O} [NiR_2(PR'_3)_2] \quad (140)$$

PR′ = trialkyl, triaryl, mixed alkyl and aryl phosphines

$$NiBr_2(PR'_3)_2 + 2NaC{\equiv}CR \xrightarrow{liq.\ NH_3} [Ni(C{\equiv}CR)_2(PR'_3)_2] \quad (141)$$

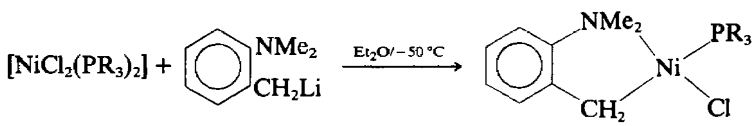
R′ = Et, Ph; R = H, Me, Ph

Following the aforementioned pioneering work, many other organometallic complexes of nickel(II) were prepared using different synthetic procedures. Complexes containing one molecule of tertiary phosphine were prepared using methods similar to that reported in equations (142) and (143) and Scheme 13.[1193–1195,1219–1223] All of these diamagnetic compounds have the square planar structure exemplified by (**155**).[1193]

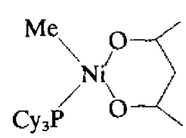
$$Ni(acac)_2 + AlR_3 + PCy_3 \xrightarrow[-10\,^{\circ}C]{Et_2O} [Ni(acac)R(PCy_3)] \quad (142)$$

R = Me, Et

$$Ni(acac)(Me)(PPh_3) + PhC{\equiv}CPh \xrightarrow[r.t.]{toluene} [Ni(acac)(PhC{=}CPhMe)(PPh_3)] \quad (143)$$



Scheme 13



(**155**)

The stability of the alkyl and aryl derivatives increases with the number of phosphines bound to nickel(II). The bis-phosphine derivatives can be prepared according to equations (144)–(146) and using organomagnesium halides or organolithium compounds.[1224–1231] A tetrakis phosphine complex was obtained similarly (equation 147).

$$NiX_2(PR_3)_2 + C_6F_5MgBr \xrightarrow[-15\,^{\circ}C]{Et_2O} [NiX(C_6F_5)(PR_3)_2] \quad (144)$$

$$NiX_2(PR_3)_2 + C_6Cl_5Li \xrightarrow[-78\,^{\circ}C]{Et_2O} [NiX(C_6Cl_5)(PR_3)_2] \quad (145)$$

$$NiX(C_6F_5)(PR_3)_2 + C_6F_5Li \longrightarrow [Ni(C_6F_5)_2(PR_3)_2] \quad (146)$$

X = Cl, Br; $PR_3 = PPh_2Me, PMe_2Ph$
X = Cl, Br, I; $PR_3 = PPh_3$

$$[NiBr(PMe_3)_4]BPh_4 + LiMe \xrightarrow[-70\,^{\circ}C]{Et_2O,\ THF} [Ni(Me)(PMe_3)_4]BPh_4 \quad (147)$$

Oxidative addition reactions to nickel(0) complexes are another well-developed synthetic method which affords mono and bis alkyl and aryl compounds (equation 148).[1232–1239] The oxidative addition of *α′*,*α′*-dichloro-*p*-xylene to $[Ni(C_2H_4)(PPh_3)_2]$ gives the dinuclear nickel(II) complex $[(PPh_3)_2ClNi(CH_2C_6H_4CH_2)NiCl(PPh_3)_2]$.[1240]

Specific synthetic procedures which are not of general application are summarized in equations (149)–(153).[1241–1244]

Cationic complexes of the type $[Ni(C_6Cl_5)L(PR_3)]^+$ (L = neutral ligand) were prepared according to equations (154) and (155).[1245,1246]

$$Ni(PR_3)_4 + arylCl \xrightarrow[r.t.]{toluene} [NiCl(aryl)(PR_3)_2] \quad R = Et, Ph \tag{148}$$

$$NiCl_2(PEt_3)_2 + 2HC{\equiv}CPh \xrightarrow{NaOMe} [Ni(C{\equiv}CPh)_2(PEt_3)_2] \tag{149}$$

$$Ni(C_2H_4)(PPh_3)_2 + FClC{=}CF_2 \xrightarrow[r.t.]{Et_2O} [NiCl(C_2F_3)(PPh_2)_2] \tag{150}$$

$$NiBr(PEt_3)_2 + Cd(CF_3)(glyme) \xrightarrow[r.t.]{CH_2Cl_2} [NiBr(CF_3)(PEt_3)_2] \quad glyme = (MeOCH_2)_2 \tag{151}$$

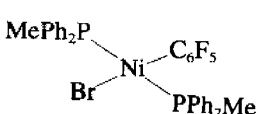
$$Ni(MeCO_2)_2 + PBu^t_2(C_6H_4OH) \xrightarrow[boil]{EtOH} [Ni\{PBu^t_2(C_6H_4O)\}_2] \tag{152}$$

$$NiCl(C_6Cl_5)(PMe_2Ph)_2 + HC{\equiv}CH \xrightarrow[NEt_3]{AgClO_4} [Ni(C{\equiv}CH)(C_6Cl_5)(PMe_2Ph)_2] \tag{153}$$

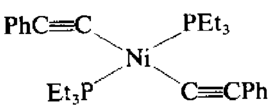
$$NiCl(C_6Cl_5)(PR_3)_2 + AgClO_4 \xrightarrow[MeCN]{L} [Ni(C_6Cl_5)L(PR_3)_2]ClO_4 \quad L = \text{neutral monodentate ligand} \tag{154}$$

$$Ni(C_6Cl_5)(R'CN)(PR_3)_2ClO_4 + Et_3N \xrightarrow[0\,^\circ C]{MeOH} [Ni(C_6Cl_5)\{NH{=}C(R')OMe\}(PR_3)_2]ClO_4 \quad R' = Me, Ph, CH_2Ph \tag{155}$$

The organometallic complexes of nickel(II) of general formula $[NiX(R)(PR'_3)_2]$ and $[NiR_2(PR'_3)_2]$ are invariably diamagnetic square planar compounds like (**156**)[1196] and (**157**).[1200] The cationic complex $[Ni(Me)(PMe_3)_4]BPh_4$, on the other hand, is five-coordinate.[1199]



(**156**)



(**157**)

CO reacts under normal conditions of pressure and temperature with some nickel(II) organometallic compounds and an insertion reaction into the original Ni—C σ bond results (equations 156–158).[1201,1236,1247–1249] A different example of an insertion reaction of CO is reported in equation (159).[1250]

An insertion reaction of 2-butyne into an Ni—C (aryl) σ bond is shown in equation (160).[1251]

$$NiX(Me)(PMe_3)_2 + CO \longrightarrow [NiX(MeCO)(PMe_3)_2] \quad X = Cl, Br, I \tag{156}$$

$$NiCl(Ph)(PEt_3)_2 + CO \longrightarrow [NiCl(PhCO)(PEt_3)_2] \tag{157}$$

$$Ni(C_6Cl_5)(C_6H_4X)(PMe_2Ph)_2 + CO \longrightarrow [Ni(C_6Cl_5)\{C(O)C_6H_4X\}(PMe_2Ph)_2] \tag{158}$$

$$Ni(C_6Cl_5)(ClO_4)(PPhMe_2) \xrightarrow[C_6H_6,\ 5\,^\circ C]{CO} [Ni(C_6Cl_5)(CO)(PPhMe_2)]ClO_4 \xrightarrow[MeOH,\ 0\,^\circ C]{NEt_3,\ CO} [Ni(MeCO_2)(C_6Cl_5)(PPhMe_2)_2] \tag{159}$$

$$NiBr(Ph)(PPh_3)_2 + MeC{\equiv}CMe \xrightarrow[r.t.]{MeOH} [NiBr(MeC{=}CMePh)(PPh_3)_2] \tag{160}$$

50.5.4.3 Complexes with alkyl and aryl phosphites as ligands

Alkylphosphito complexes of nickel(II) in general are easily prepared by the direct reaction of hydrated nickel(II) salts with the appropriate ligand in common organic solvents such as acetone or ethanol. In the case of phenylphosphito complexes, 2,2′-dimethoxypropane was sometimes employed as a dehydrating agent. Some representative complexes are shown in Tables 62 and 63.

Table 62 Selected Phosphito Complexes

Complex	Donor set	Coordination geometry	Remarks[a]	Ref.
$[Ni(CN)_2\{P(OR)_3\}_3]$	P_3C_2	TBPy	R = Me, Ph; prepared in acetone	1252
$[Ni(CN)_2\{PPh(OR)_2\}_3]$	P_3C_2	TBPy	R = Me, Et; prepared in refluxing MeOH or EtOH under N_2; decomposed in the air	1253
$[Ni(CN)_2(PPh_2OR)_2]$	P_2C_2	SqPl	R = Et, Pr^n; prepared in 1-propanol, under N_2	1254
$[Ni(PR_3)_5](ClO_4)_2$	P_5	TBPy	$PR_3 = PMe_2(OMe)$, $PMe(OMe)_2$, $P(OMe)_3$; prepared in acetone with 2,2-dimethoxypropane	1255
$[Ni(PR_3)_6](ClO_4)_2$[b]	P_6	Uncertain	From $Ni(DMSO)_6(ClO_4)_2 + PR_3$ in acetone	1256
$[Ni(PR_3)_5](BF_4)_2$	P_5	TBPy	$PR_3 = P(OMe)_3$, $P(OCH_2)_3CMe$,[b] $P(OCH)_3(CH_2)_3$,[c] $P(OCH_2)_3CEt$; in MeOH or EtOH	1257
$[Ni\{P(OR)_3\}_4]X_2$	P_4	SqPl	X = Br, NCS; R = Et–octyl; prepared *in situ*	1258

[a] All of the complexes are diamagnetic.

[b] PR_3 =

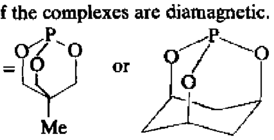
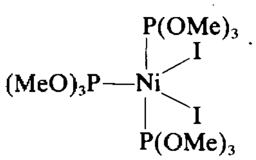
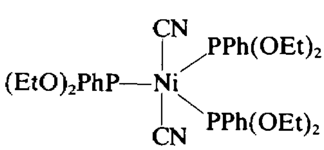


Table 63 Some Structural Data for Selected Phosphito Complexes

Complex	Bond distances (pm) Ni—P	Ni—X	Geometry	Ref.
$[NiI_2\{P(OMe)_3\}_3]$ (**158**)	218 (ax), 217 (eq)	266	TBPy	1259
$[Ni(CN)_2\{PPh(OEt)_2\}_3]$ (**159**)	220–229	188 (av)	Distorted TBPy	1260
$[NiBr\{P(OMe)_3\}_4]BF_4$	218 (ax), 219, 224 (eq)	246	Distorted TBPy	1261
$[Ni\{P(OCH)_3(CH_2)_3\}_5](ClO_4)_2$	214 (ax), 216, 221 (eq)	—	TBPy	1262

Complexes of the type $[NiX_2\{P(OR)_3\}_3]$ are obtained with coordinating anions. When X = CN and R = Me, Ph, the complexes easily lose one molecule of the ligand under vacuum yielding the bis complexes $[NiX_2\{P(OR)_3\}_2]$. Complexes with up to six molecules of the phosphite ligand were obtained with salts of poorly coordinating anions. The complexes are moderately air-stable and are decomposed only after prolonged exposure to air. All of the complexes are diamagnetic. $[NiI_2\{P(OMe)_3\}_3]$ has a trigonal bipyramidal structure with the two iodine atoms in the equatorial positions (**158**).[1259] In contrast a *trans* coordination of the cyanide ions was found in the complex $[Ni(CN)_2\{PPh(OEt)_2\}_3]$[1260] (**159**) which has a structure intermediate between trigonal bipyramidal and square pyramidal. The hexakis complexes $[Ni\{P(OCH_2)_3CR\}_6](ClO_4)_2$ (R = Me, Et) and $[Ni\{P(OCH)_3(CH_2)_3\}_6](ClO_4)_2$ (Table 62) are diamagnetic and this finding contrasts with the assumed distorted octahedral geometry.[1256] The aforementioned complexes are reported to be easily reduced to the corresponding nickel(0) complexes $[NiL_4]$.


(**158**)


(**159**)

The nickel(0) complexes $[Ni\{P(OR)_3\}_4]$ (R = Me, Et, Ph) react in organic solvents with strong acids such as HCl, H_2SO_4 and CF_3CO_2H giving hydrido complexes $[Ni(H)\{P(OR)_3\}_4]^+$ as inferred from their ^1H NMR signals (14.3–14.5 p.p.m. upfield from TMS).[1263] From the reactions with the acids HBF_4 and HPF_6 the complexes $[Ni(H)\{P(OCH_2)_3CMe\}_4]Y$ were isolated in the solid state.[1264]

50.5.4.4 Complexes with bidentate tertiary phosphines, arsines and stibines[1265,1266]

A large number of nickel(II) complexes with bidentate tertiary phosphines and arsines have been prepared and characterized since the initial reports on *o*-phenylenebisdimethylarsine and 1,2-bisdiphenylphosphinoethane (Table 64; **XVIII**, **III**) by Chatt and Mann,[1267] and Wymore and Bailar[1268] respectively. The most common diphosphines, diarsines, distibines and mixed donor ligands are collected in Table 64 and selected nickel(II) complexes are reported in Table 65.

Table 64 Bidentate Ligands Cited in Section 50.5.4.4; Structures, Formulas and Abbreviations Used in Table 65

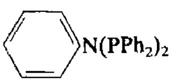
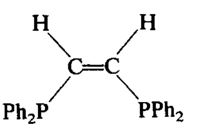
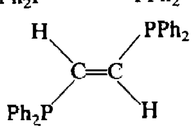
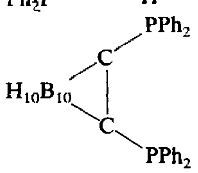
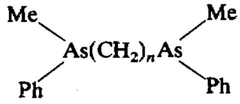
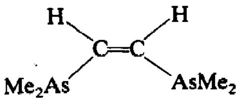
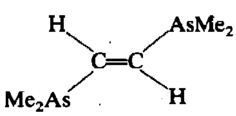
Structural scheme			*Formula*	*Abbreviation*
R_2PPR_2	R = Me, Et, Ph R = Cy		R_2PPR_2	
$R_2PCH_2PR_2$	R = Me R = Ph	 **(I)**	$R_2PCH_2PR_2$	
			$PhN(PPh_2)_2$	
$R_2PCH_2CH_2PR_2$	R = Me R = Et R = Ph	 **(II)** **(III)**	$R_2PC_2H_4PR_2$	 tep dpe
		**(IV)**	*cis*-$Ph_2PC_2H_2PPh_2$	
		**(V)**	*trans*-$Ph_2PC_2H_2PPh_2$	
			$(CPPh_2)_2B_{10}H_{10}$	
$Ph_2P(CH_2)_nPPh_2$	$n = 3$ $n = 4$ $n = 5$ $n = 8$	**(VI)** **(VII)** **(VIII)** **(IX)**	$Ph_2PC_3H_6PPh_2$ $Ph_2PC_4H_8PPh_2$ $Ph_2PC_5H_{10}PPh_2$ $Ph_2PC_8H_{16}PPh_2$	
$Cy_2P(CH_2)_nPCy_2$	$n = 3, 4, 5$	**(X)**	$Cy_2P(CH_2)_nPCy_2$	
$Ph_2PCH_2CH_2OCH_2CH_2PPh_2$		**(XI)**	$(Ph_2PC_2H_4)_2O$	bdpo
$Ph_2P(CH_2)_2O(CH_2)_2O(CH_2)_2PPh_2$		**(XII)**	$(Ph_2PC_2H_4OCH_2)_2$	
$Ph_2As(CH_2)_nAsPh_2$	$n = 2$ $n = 4$	**(XIII)**	$Ph_2As(CH_2)_nAsPh_2$	
	$n = 2$ $n = 3$	**(XIV)**	$MePhAsC_2H_4AsPhMe$ $MePhAsC_3H_6AsPhMe$	
		**(XV)**	*cis*-$Me_2AsC_2H_2AsMe_2$	
		**(XVI)**	*trans*-$Me_2AsC_2H_2AsMe_2$	

Table 64 (*continued*)

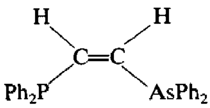
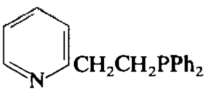
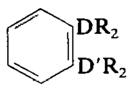
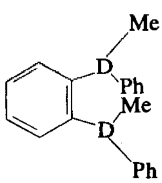
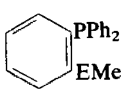
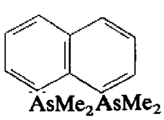
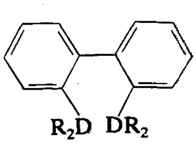
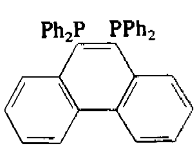
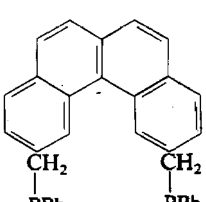
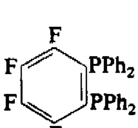
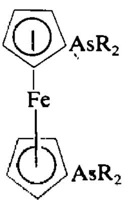
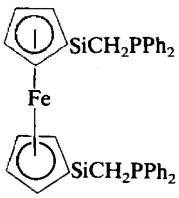
Structural scheme			*Formula*	*Abbreviation*
$Me_2SbCH_2CH_2CH_2SbMe_2$			$Me_2SbC_3H_6SbMe_2$	
$Ph_2PCH_2CH_2AsPh_2$			$Ph_2PC_2H_4AsPh_2$	
			$Ph_2PC_2H_2AsPh_2$	
$R_2PCH_2CH_2SR'$	R = R' = Et R = Ph; R' = Me, Et, Ph		$Et_2PC_2H_4SEt$ $Ph_2PC_2H_4SR'$	
			$pyC_2H_4PPh_2$	
	D = D' = P; R = Me, Et D = D' = As; R = Me D = D' = Sb; R = Me D = P; D' = As; R = Me, Ph D = Sb; D' = P, As; R = Ph D = Sb; D' = As; R = Me	**(XVII)** **(XVIII)**	$R_2PC_6H_4PR_2$ $Me_2AsC_6H_4AsMe_2$ $Me_2SbC_6H_4SbMe_2$ $R_2PC_6H_4AsR_2$ $Ph_2SbC_6H_4D'Ph_2$ $Me_2SbC_6H_4AsMe_2$	 diars
	D = P, As		$MePhDC_6H_4DPhMe$	
	E = S E = Se		$Ph_2PC_6H_4SMe$ $Ph_2PC_6H_4SeMe$	SP SeP
		**(XIX)**	$(C_5H_3AsMe_2)_2$	
	$DR_2 = AsMe_2$ $DR_2 = PEt_2$		$(C_6H_4AsMe_2)_2$ $(C_6H_4PEt_2)_2$	
		**(XX)**	$(C_7H_4PPh_2)_2$	
		**(XXI)**	$(C_{10}H_7PPh_2)_2$	
			$Ph_2PC_6F_4PPh_2$	

Table 64 (*continued*)

Structural scheme		*Formula*	*Abbreviation*
	R = Me	(**XXII**)	fdma
	R = Ph	(**XXIII**)	fdpa
		(**XXIV**)	

Most of the complexes have the general formulas [NiX_2(D—D)$_2$], [NiX_2(D—D)], [NiX(D—D)$_2$]Y or [Ni(D—D)$_2$]X_2 (X = halides, pseudohalides, NO_3; Y = ClO_4, BF_4, PF_6, BPh_4; D—D = bidentate ligand). In general, these complexes were prepared by the reaction of nickel(II) salts (hydrated or anhydrous) with the appropriate bidentate ligand in common organic solvents. In some cases the reactions were carried out under an N_2 atmosphere to prevent oxidation of the ligands. Hereafter we will give some examples of particular synthetic routes designed to obtain specific compounds.

The complexes [NiX(tep)$_2$]BPh_4 were prepared by mixing appropriate sodium or potassium halides with the [Ni(tep)$_2$](BPh_4)$_2$ derivatives. 2:1 complexes with the ligand dpe were prepared by reaction of the free ligand and the 1:1 complex in aqueous ethanol solution,[1276,1277] by reaction of hydrated Ni(NO_3)$_2$ with the ligand dpe[1278] or by reaction of Ni(dpe)$_2$ with a solution of $HClO_4$ in aqueous ethanol.[1286] The 1:1 complexes were readily prepared by reacting nickel(II) salts with dpe.[1276]

The nickel(II) complexes with the ligand diars (**XVIII**) were first reported by Nyholm. The NiX_2(diars)$_2$ complexes were prepared from the reactants in hot ethanol.[1318] The 1:1 complexes were originally prepared by oxidation of the nickel(0) carbonyl complex with gaseous hydrogen halides under anaerobic conditions (equation 161).[1283] Other complexes with diars were subsequently prepared according to equations (162)–(164).[1319–1321]

$$\mathrm{Ni(CO)_2(diars) + HX \xrightarrow[-CO,\,-H_2]{C_6H_6,\,H_2} [NiX_2(diars)]} \quad (161)$$

$$\mathrm{Ni(diars)_2(ClO_4)_2 + 2MX \xrightarrow{acetone} [NiX(diars)_2]X + 2MClO_4} \quad (162)$$

$$\mathrm{MX = NaI, LiBr, (AsPh_3Me)Cl}$$

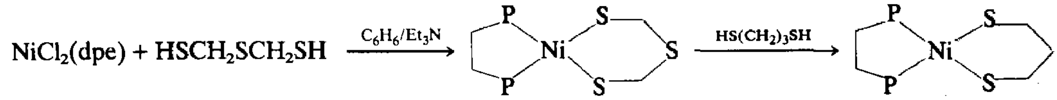
$$\mathrm{NiX_2 + Ni(ClO_4)_2\ hydrate + diars \xrightarrow{EtOH} [NiX(diars)_2]ClO_4} \quad (163)$$

$$\mathrm{Ni(diars)_2(ClO_4)_2 + (CN)_2C{=}C(CN)_2 \xrightarrow{EtOH} [Ni(CN)(diars)_2]ClO_4} \quad (164)$$

$$\mathrm{Ni(CO)_2\{(Et_2P)_2C_6H_4\} + X_2 \xrightarrow[-CO]{C_6H_6} [NiX_2\{(Et_2P)_2C_6H_4\}]} \quad (165)$$

The oxidation of a nickel(0) carbonyl compound with halogens was employed by Chatt and Hart to prepare nickel(II) complexes with the diphosphine ligand (**XVII**; R = Et; equation 165);[1311] 2:1 complexes were subsequently prepared by the direct synthesis of the reactants in acetone.[1287]

The complexes Ni(EH)$_2$(dpe) (E = S, Se) were prepared by the metathetical reaction of the bischloride compound with NaSH and NaSeH, respectively, in ethanol, under N_2.[1288] The analogous complex with the chelating dianion 2-thio-1,3-propanedithiolate was obtained as outlined in Scheme 14.[1289]



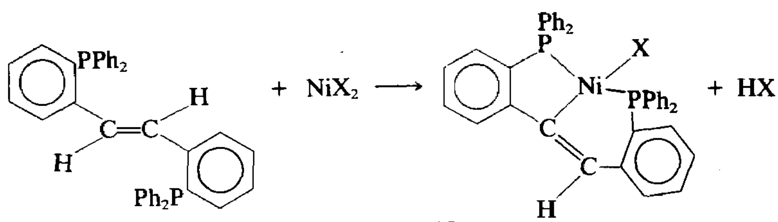
Scheme 14

The reaction under N_2 of tetracyanoethylene (TCE) with the five-coordinate complexes $[NiX(As—As)_2]ClO_4$ (As—As = **XIV**) affords either $[NiX(As—As)(TCE)]ClO_4$ or $[Ni(As—As)_2(TCE)_2]X(ClO_4)$.[1302] The reaction in ethanol of nickel(II) halides or thiocyanate with the isomeric mixture of *cis*- and *trans*-$Me_2AsC_2H_2AsMe_2$ (**XV, XVI**) affords the insoluble compounds $NiX_2(As—As)$ (X = Cl, NCS) and $NiBr_2(As—As)_2$ which are supposed to be polynuclear six-coordinate with bridging *trans*-diarsine. UV irradiation of an ethanolic solution of nickel(II) with the isomeric mixture of the same ligand, on the other hand, gives diamagnetic complexes of general formula $NiX_2(As—As)_2$ (X = Br, I, NCS) which contain the ligand in the *cis* form.[1303]

An interesting reaction occurs between C_2N_2 and a nickel(II) carbonyl compound (equation 166).[1333]

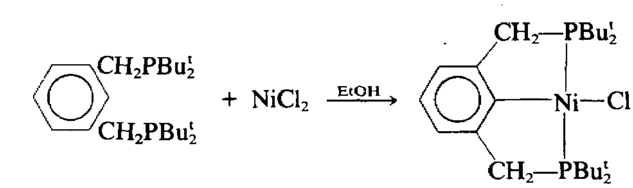
$$Ni(CO)_2(Ph_2PC_4H_8PPh_2) + C_2N_2 \xrightarrow[r.t.]{CH_2Cl_2} [Ni(CN)_2(Ph_2PC_4H_8PPh_2)]_2 + CO \qquad (166)$$

The *trans*-stilbene ligand *o*-$Ph_2PC_6H_4CH{=}CHC_6H_4PPh_2$-*o* reacts with nickel(II) halides to give red air-stable nickel(II) complexes according to Scheme 15.[1334]



Scheme 15

The bulky diphosphine $C_6H_4(CH_2PBu^t_2)_2$ reacts with an ethanolic solution of hydrated nickel(II) chloride at room temperature according to Scheme 16.[1335]



Scheme 16

In spite of the large number of complexes with diphosphines and diarsines, only a few crystal structures have been determined. Structural data for selected complexes are reported in Table 66.

On account of their diamagnetism and spectral properties the $[NiX_2(dpe)_2]$ complexes have a substantial square planar structure in the solid state, possibly with two weakly interacting anions in axial positions, as found in $NiI_2(diars)_2$ (*vide infra*). In solution either five-coordinate or square planar species are formed.[1277,1283,1347] The ligand tep (**II**) easily forms diamagnetic five-coordinate complexes $[NiX(tep)_2]Y$ in the solid state and in solution as well.[1276,1281,1282] The structure of $[NiI(tep)_2]I$ is essentially square pyramidal.[1281]

All of the 1:1 complexes $NiX_2\{R_2P(CH_2)_nPR_2\}$ are planar when R = cyclohexyl (ligand **X**), independent of the length of the chain and of the anion X. When R = phenyl, the complexes are *cis* square planar if $n = 1$, 2 or 3 (ligands **I, III, VI**). In the case of the ligand where $n = 3$ square planar and pseudotetrahedral species are in equilibrium.[1277] The effect of a further lengthening of the chain between the two phosphorus donors is to favour increasingly the pseudotetrahedral species, and when $n = 4$, 5 or 8 (ligands **VII, VIII, IX**) the complexes are tetrahedral in the solid state and in solution. The introduction of one or two ether oxygen atoms into the carbon backbone (ligands **XI, XII**) does not vary substantially the coordinating

Table 65 Selected Complexes With Ditertiary Phosphines and Arsines

Complex[a]	$\mu_{eff}(r.t.)$[b] (BM)	*Donor set*	*Coordination geometry or number*	*Remarks*	*Ref.*
$NiX_2(R_2PPR_2)$	D	P_2X_2	SqPl	X = halides; R = Me, Et, Cy; monodentate phosphine	1269–1272
$(NiX_2)_2(Me_2PPMe_2)_3$	D	P_2X_2	SqPl	X = halides	1270
$NiCl_2(Me_2PCH_2PMe_2)_2$	D	P_2Cl_2	SqPl	Monodentate phosphine	1273
$NiX_2(Ph_2PCH_2PPh_2)$	D	P_2X_2	SqPl	X = halides	1274
$[NiX_2(Ph_2PCH_2PPh_2)]_2$	D	P_2X_3	5	X = I, NCS; dinuclear; bridging anions	1274
$[NiX(Ph_2PCH_2PPh_2)_2]Y$	D	P_4X	5	X = halides, NCS, NO_2; Y = BPh_4, ClO_4	1275
$NiX_2(Ph_2PCH_2PPh_2)_2$	D	P_2X_2	SqPl	X = Cl, Br, I, NCS; prepared under N_2; monodentate phosphine	1274, 1276, 1277
		P_4	SqPl	X = NO_3, ClO_4, BF_4; prepared under N_2; bidentate phosphine; low and variable μ_{eff}	1278
$NiX_2\{PhN(PPh_2)_2\}$	D	P_2X_2	SqPl	X = halides, NCS	1279
$[NiX\{PhN(PPh_2)_2\}_2]ClO_4$	D	P_4X	SqPy	X = halides, NCS	1279
$NiX_2(Me_2PC_2H_4PMe_2)$			SqPl	Low and variable μ_{eff}; X = Cl, Br, I	1276
$NiX_2(Me_2PC_2H_4PMe_2)_2$	D			Substantially square planar; X = Br, I, NO_3	1276, 1280
$NiX_2(Et_2PC_2H_4PEt_2)$	D	P_2X_2	SqPl	Prepared under N_2; X = halides, NCS, CN	1281
$NiX_2(Et_2PC_2H_4PEt_2)_2$	D	P_4	SqPl	Prepared under N_2; X = ClO_4, PF_6	1282
	D	P_4I	SqPy	X = I	1276,1281
$[NiX(Et_2PC_2H_4PEt_2)_2]BPh_4$	D	P_4X	SqPy	Prepared under N_2; X = halides, NCS	1281
$[NiX_2(Ph_2PC_2H_4PPh_2)]$	D	P_2X_2	SqPl	X = halides, NCS, CN	1141, 1276, 1277, 1283–1286
$[Ni(Ph_2PC_2H_4PPh_2)_2]X_2$	D			SqPl in the solid state; X = Br, I, NO_3, ClO_4	1276, 1277, 1280, 1283, 1286, 1287
$NiX_2(Ph_2PC_2H_2PPh_2)$	D	P_2X_2	SqPl	Ligand (**IV**); X = halides, NCS, SH; $\frac{1}{2}$ dithiolates (Scheme 14)	1284, 1288, 1289
$[NiX(Ph_2PC_2H_2PPh_2)_2]BPh_4$	D	P_4X	SqPy	Ligand (**IV**); X = ClO_4, NO_3	1284
$[Ni(Ph_2PC_2H_2PPh_2)_2]X_2$	1.50–1.67			Ligand (**IV**); structure uncertain; μ_{eff} is temperature independent; X = ClO_4, NO_3	1290

$[Ni(Ph_2PC_2H_2PPh_2)X_2]$	3.03–3.16	P_2X_2	Td	Ligand (**V**); X = halides	1291
	D	P_2X_2	SqPl	X = NCS, CN	1291
$NiCl_2(Ph_2PCH{=}CRPR'_2)_2$	D	P_2Cl_2	SqPl	R = Ph, Bu^t; $PR'_2 = PPh_2$; R = CF_3, PR'_2 = PEtPh	1292
$[NiI\{(Ph_2PC)_2B_{10}H_{10}\}_2]I$	D	P_4I	TBPy		1293
$[NiX_2(Ph_2PC_3H_6PPh_2)]$	D	P_2X_2	SqPl	X = halides, NCS	1277, 1294, 1295
$[Ni(CN)_2(Ph_2PC_3H_6PPh_2)_{1.5}]$	D	P_3C_2	5		1285
$[NiX_2\{Ph_2P(CH_2)_nPPh_2\}]$	3.24–3.30	P_2Br_2	Td	n = 4, 5; X = Br, I	1296
	D	P_2N_2	SqPl	n = 4, 5; X = NCS	
$[NiX_2\{(Ph_2PC_2H_4)_2O\}]$	3.23–3.26	P_2X_2	Td	Bidentate ligand (**XI**); X = halides	1296
$[NiBr_2(Cy_2PC_5H_{10}PCy_2)]$	D	P_2Br_2	SqPl	*trans* structure	1297
$[NiX_2(Ph_2PC_8H_{16}PPh_2)]$	3.11–3.24	P_2X_2	Td	X = Br, I	1298
	D	P_2X_2	SqPl	X = NCS	
$NiX_2\{Ph_2As(CH_2)_nAsPh_2\}$	D	As_2X_2	SqPl	X = Br, I; n = 2	1299
	3.17	As_2I_2	Td	X = I; n = 4	
$[NiI(Ph_2AsC_2H_4AsPh_2)]I$	D	As_4I	SqPy		1300
$[NiX_2MePhAs(C_2H_2)_4AsMePh]$	D	As_2X_2	SqPl	X = halides	1301
$[NiX\{MePhAs(CH_2)_2AsMePh\}_2]ClO_4$	D	As_4X	5	X = halides, NCS	1301, 1302
$[NiX_2\{MePhAsC_3H_6AsMePh\}]$	3.25–3.20		6	X = Cl, Br; polynuclear in the solid state and SqPl in solution; X = I, supposed Td	1301
	D	As_2X_2	SqPl	X = NCS	
$[Ni(Me_2AsC_2H_2AsMe_2)_2]Y_2$	D	As_4	SqPl	Ligand (**XV**); prepared under N_2; Y = BF_4, PF_6	1303
$[NiX(Me_2AsC_2H_2AsMe_2)_2]Y$	D	As_4X	SqPy	As above; X = Cl, Br; Y = PF_6, BPh_4	1303, 1304
$[NiX_2(Me_2AsC_2H_2AsMe_2)_n]$	3.2–3.3		6	Ligand (**XVI**); polynuclear; X = Cl, NCS; n = 1	1303
	3.1		6	X = Br; n = 2; polynuclear; bridging diarsine	
$[NiX(Me_2SbC_3H_6SbMe_2)_2]ClO_4$	D	Sb_4X	5	X = halides	1305
$[NiX_2(Ph_2AsRPPh_2)]$	D	$PAsX_2$	SqPl	X = halides, NCS; R = C_2H_4, C_2H_2	1306, 1307
$[NiX(Ph_2AsRPPh_2)_2]BPh_4$	D	As_2P_2X	SqPy	X = Cl; R = C_2H_4 X = halides, NCS; R = C_2H_4	1306, 1307

Table 65 (*continued*)

Complex[a]	$\mu_{eff}(r.t.)^b$ (BM)	*Donor set*	*Coordination geometry or number*	*Remarks*	*Ref.*
$[Ni(Ph_2AsRPPh_2)_2](ClO_4)_2$	D	As_2P_2	SqPl	$R = C_2H_4$, C_2H_2	1306, 1307
$[NiX(Et_2PC_2H_4SEt)_2]ClO_4$	D	P_2S_2X	SqPy	X = halides	1308
$NiX_2(Et_2PC_2H_4SEt)_2$	D	P_2S_2, P_2N_2	SqPl	$X = ClO_4$, NCS; monodentate ligand in the NCS complex	1308
	2.96		Oh	X = NCS	
$[Ni(CN)(Ph_2PC_2H_4SR)_2]ClO_4$	D	P_2S_2C	5	R = Me, Et, Ph	1309
$[Ni(CN)_2(Ph_2PC_2H_4SR)_2]$	D	P_2C_2	SqPl	R = Et, Ph; monodentate ligands	1309
	D	P_2SC_2	5	R = Me; mono- and bi-dentate ligands	1309
$[NiX_2(pyC_2H_4PPh_2)]$	3.29, 3.33	PNX_2	Td	X = Cl, Br	1310
	D	PN_3	SqPl	X = NCS	
$[Ni(pyC_2H_4PPh_2)_2]X_2$	D		SqPl	X = I, CN	1309, 1310
$[NiX_2(Et_2PC_6H_4PEt_2)]$	D	P_2X_2	SqPl	X = halides, NCS $Ni(CO)_2$ + ligand + X_2/C_6H_6	1311
$[Ni(Et_2PC_6H_4PEt_2)_2]Y_2$	D	P_4	SqPl	Y = Br, NO_3, ClO_4 NiX_2 + ligand/acetone	1287, 1311
$[NiX_2(Ph_2PC_6F_4PPh_2)]$	D	P_2X_2	SqPl	X = halides, NCS	1312
$[Ni(Me_2PC_6H_4DMe_2)_2](ClO_4)_2$	D	P_4, P_2As_2	SqPl	D = P, As	1313–1315
$[NiX(Me_2PC_6H_4DMe_2)_2]Y$	D			X = halides, NCS, NO_3; $Y = ClO_4$; D = P, As; structure uncertain in the solid state	1314, 1315
$[NiX_2(Ph_2PC_6H_4AsPh_2)]$	D	$PAsX_2$	SqPl	X = halides, NCS; NiX_2 hydrate + ligand/Bu^nOH/C_6H_6	1316
$[NiX(Ph_2PC_6H_4AsPh_2)_2]ClO_4$	D	P_2As_2X	5	$Ni(NO_3)_2$ hydrate + NaX + $Ni(ClO_4)_2$ hydrate + ligand/Bu^nOH/C_6H_6; X = halides, NCS, NO_2	1316
$[Ni(NCS)_2(Ph_2PC_6H_4AsPh_2)_2]$	3.18	$P_2As_2N_2$	Oh	$Ni(NCS)_2$ + ligand/EtOH/CH_2Cl_2	1316
$[NiCl_2(Ph_2PC_6H_4SMe)]$	D	$PSCl_2$	SqPl	Prepared by dissolving $NiCl_2L_2$ in CH_2Cl_2	1317
$[NiBr(Ph_2PC_2H_4SMe)_2]ClO_4$	D	P_2S_2Br	5	Prepared using equimolar amounts of $NiBr_2$ and $NiClO_4$ in excess of ligand	1317
$[NiCl_2(Ph_2PC_6H_4SMe)_2]$	3.15	$P_2S_2Cl_2$	Oh	$NiCl_2$ + LiCl + L/EtOH	1317
$[NiX(Me_2AsC_6H_4AsMe_2)_2]Y$	D		5	$Y = X = ClO_4$; X = halides, NCS, ClO_4; NiX_2 hydrate + ligand/EtOH; $NiL_2(ClO_4)_2$ + LiX	1318–1321
$[NiX_2(Me_2AsC_6H_4AsMe_2)]$	D	As_2X_2	SqPl	X = halides; $Ni(CO)_2L$ + HX	1283

$[Ni(PhMeDC_6H_4DMePh)_2](PF_6)_2$	D	P_4, As_4	SqPl	D = P, As; Ni(acetate) hydrate $+NH_4PF_6$ + ligand	1322
$[NiCl(PhMeDC_6H_4DMePh)_2]Y$	D	P_4Cl, As_4Cl	SqPy	$NiCl_2$ hydrate + ligand/EtOH; D = P, As; Y = Cl, PF_6	1322
$[NiX(Ph_2SbC_6H_4PPh_2)_2]ClO_4$	D	Sb_2P_2X	5	X = halides, NCS; $NiX_2 + Ni(ClO_4)_2$ hydrate + ligand	1323
$[NiI(Ph_2SbC_6H_4AsPh_2)_2]_2NiI_4$		Sb_2As_2I	5	NiI_2 + ligand/Bu^nOH/CH_2Cl_2	1323
$[NiX(Me_2AsC_6H_4SbMe_2)_2]Y$	D	As_2Sb_2X	SqPy	X = halides, NCS; Y = X = BPh_4	1324
$[NiCl(Me_2SbC_6H_4DMe_2)_2]Cl$	D	Sb_4Cl, Sb_2As_2Cl	5	D = As, Sb	1325
$[NiX_2\{(C_6H_4PEt_2)_2\}]$	0.5–2.80			X = halides; structure uncertain in the solid state; SqPl ⇌ Td equilibrium in solution	1326
	D	P_2X_2	4	X = NCS	
$[NiX_2\{(C_6H_4AsMe_2)_2\}_2]$	3.2–3.6	As_4X_2	Oh	X = halides, NCS; five-coordinate in solution	1327
$[NiX\{(C_6H_4AsMe_2)_2\}_2]ClO_4$	D	As_4X	TBPy	X = halides	1327
$[Ni\{(C_6H_4AsMe_2)_2\}_2](ClO_4)_2$	D	As_4	SqPl		1327
$NiX_2(C_7H_4PPh_2)_2$	D	P_2X_2, P_4	SqPl	X = halides, NCS, ClO_4; ligand (**XX**)	1307
$[Ni(NO_3)\{(C_7H_4PPh_2)\}_2]BPh_4$	D	P_4O	5		1307
$[NiX_2\{(C_5H_3AsMe_2)_2\}]$	D	As_2X_2	SqPl	X = halides, NCS; ligand (**XIX**)	1328
$[NiX_2\{(C_{10}H_7PPh_2)_2\}]$	D	P_2X_2	SqPl	X = halides, NCS; ligand (**XXI**)	1329
$NiBr_2(fdma)_2$	3.06	As_4Br_2	Oh	Ligand (**XXII**)	1330
$NiI_2(fdpa)$	3.37	As_2I_2	Td	Ligand (**XXIII**)	1330
$NiI_2(CO)(fdma)$	D	As_2Cl_2	TBPy		1331
NiX_2L	1.36–1.93			X = Cl, Br; L = (**XXIV**); structure uncertain in the solid state; SqPl ⇌ Td equilibrium in solution	1332

[a] The structural formulas of the ligands and their abbreviations are given in Table 64.
[b] D = diamagnetic.

Table 66 Selected Complexes with Bidentate Phosphines and Arsines

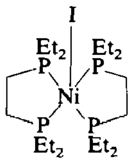
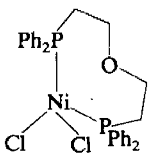
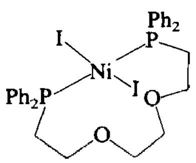
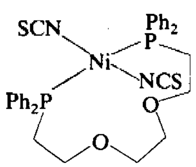
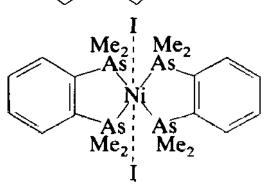
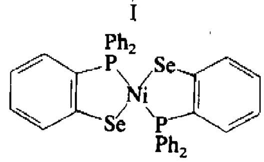
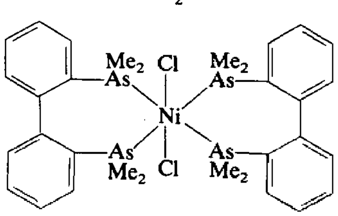
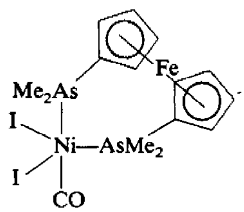
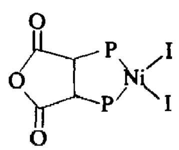
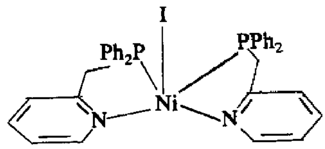
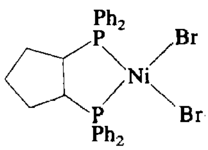
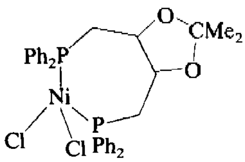
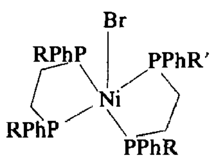
Complex	Structure	Bond distances (pm) Ni—P/As	Ni—X	Other	Ref.
	SqPy	222 (av)	280 (av)		1281
	Td	232 (av)	222 (av)	*Ni···O* 364	1336
	SqPl	224 (av) (distorted; P—Ni—P, 162°; I—Ni—I, 144°)	250 (av)	*Ni···O* 320, 316	1337
	SqPl	224 (av) (P—Ni—P, 176°; N—Ni—N, 170°)	183 (av)	*Ni···O* 306, 320	1338
	4 + 2	229 (av)	322		1339
	SqPl	218		*Ni—Se* 228	1340
	Oh	251 (av)	238 (av)		1341
	TBPy	232 (av)	262 (av)	*Ni—C* 182	1331
	SqPl	217	250		1342
	SqPy	217 (av)	305	*Ni—N* 196 (av)	1343

Table 66 *(continued)*

Complex	Structure	Bond distances (pm) Ni—P/As	Ni—X	Other	Ref.
	SqPl	217 (av)	234 (av)		1344
	Td	230	220		1345
 R = CH_2CO_2H R′ = CH_2CO_2	SqPy	232 (av)	259 (av)		1346

behaviour of the ligands with respect to that of the corresponding ligands (**VIII**) and (**IX**) in that the oxygen atoms remain uncoordinated (Table 66).[1336–1338]

The pioneering work of Nyholm and co-workers on nickel(II) complexes with the ligand diars (**XVIII**) indicated five-coordination for the diamagnetic complexes $[NiX_2(diars)_2]$ in solution.[1318,1319] Additional evidence for five-coordination in solution was provided by thermodynamic investigations.[1320] However, the structural investigation of $NiI_2(diars)_2$ showed that the molecule is tetragonally elongated with two weakly bonded iodine atoms.[1339] All of the $NiX_2(diars)_2$ complexes are assumed to possess substantially the same structure as the bis iodide in the solid state.

50.5.4.5 Complexes with tri- and tetra-dentate open-chain ligands containing tertiary phosphines and arsines, and with mixed-donor ligands[1348,1349]

(*i*) *Complexes with tridentate ligands*

Tridentate ligands of the linear type having donor sets P_3, As_3 or P_xAs_{3-x}, where the donor atoms are connected by *o*-phenylene, ethylene or trimethylene chains, were found to form stable complexes with nickel(II) salts.[1350] Listings of the most common ligands and nickel(II) complexes are given in Tables 67 and 68, respectively.

Most of the complexes have general formulas $[NiX_2L]$ and $[NiXL]Y$ where X is a coordinating anion and Y a weakly coordinating anion. Few complexes with the formula $[NiL_2]Y_2$ were also reported. The complexes in general were easily prepared by mixing equimolar amounts of the reactants in common organic solvents, generally alcohols at refluxing temperatures. Most of the $[NiX_2L]$ complexes (X = halide, pseudohalide) which were obtained with the ligands reported in Table 67 are diamagnetic and five-coordinate, irrespective of the substituents on the donor atoms and of the nature of the connecting chains. The complex $[NiBr_2(tas)]$ (**160**)[1356] has a distorted square pyramidal structure with an apical elongation of the bromide atom. An analogous structure was also found in $[Ni(CN)_2(dap)]H_2O$ (**161**).[1357]

The behaviour of the NiX_2L complexes in solution depends on the ligand L. In general it is found that in weakly polar and non-coordinating solvents the complexes are five-coordinate. The complexes with the ligands ptas (**XXV**) and pdap (**XXVI**) are decomposed in most organic solvents such as MeCN, $MeNO_2$, $PhNO_2$,[1361] as are ttas complexes in protic solvents.[1360] The

Table 67 Tridentate Ligands Containing P, As and Mixed Donor Groups, with their Abbreviations

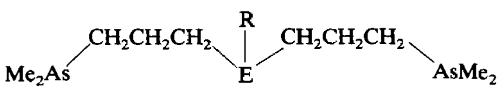
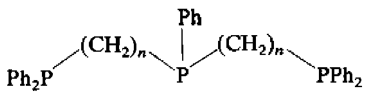
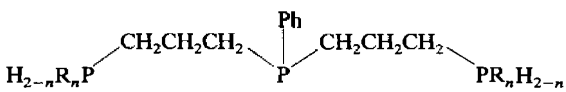
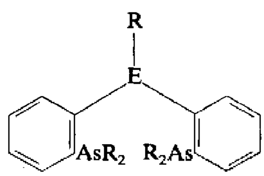
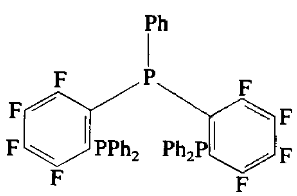
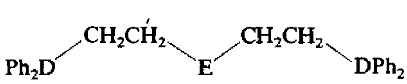
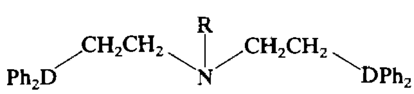
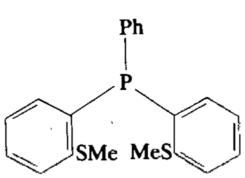
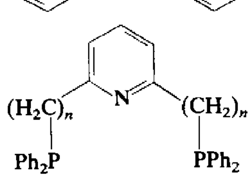
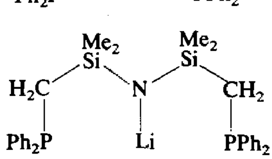
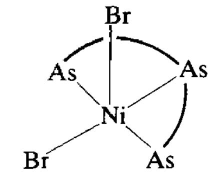
Structure		*Fomula*	*Abbreviation*
	ER = AsMe ER = PPh ER = AsPh ER = $AsCH_2CH_2Cl$		tas dap bdpa triars
	$n = 2$ $n = 3$		etp ttp
	R = Me, Ph $n = 0, 1, 2$	$RP(C_3H_6PHR)_2$	
	E = As; R = Ph E = P; R = Ph E = As; R = Me	**(XXV)** **(XXVI)**	ptas pdap ttas
			ftp
	E = O; D = As E = S; D = As E = O; D = P E = S; D = P	**(XXVIII)** **(XXIX)** **(XXX)**	bdao bdas bdpo bdps
	R = H; D = As R = H, Me, Ph, Cy; D = P	**(XXXI)** **(XXXII)**	bdaa R-bda
			dsp
	$n = 2$ $n = 1$	**(XXXIII)**	bdppe bdppm
		**(XXXIV)**	Li{[5,5]-PNP}

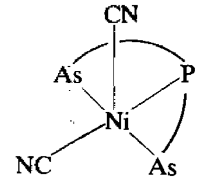
Table 68 Selected Complexes with Tridentate Ligands

Complex[a]	$\mu_{eff}(r.t.)$[b] (BM)	Donor set	Coordination number or geometry	Remarks[c]	Ref.
$[NiX_2L]$	D	P_3X_2	SqPy	X = halides, NCS, CN; L = etp, ttp	1351, 1352
$[NiXL]BPh_4$	D	P_3X	SqPl	X = halides, NCS, CN; L = etp, ttp	1351–1353
$[NiR(etp)]BPh_4$* **(164)**	D	P_3C, P_3O	SqPl	R = Me, Ph, CH_2Ph, $MeSO_2^*$, $PhSO_2$, $PhCH_2SO_2$; Ni—P, 211–220; Ni—O, 194	1354
$[NiX_2\{RP(C_3H_6PHR)_2\}]$	D	P_3X_2	SqPy	X = Cl, Br; R = Me, Ph	1355
$[NiX_2L]$* **(160)**	D	As_3X_2	SqPy	X = halides, NCS, CN; L = tas*; Ni—As (av), 226; Ni—Br, 237, 269 X = Br, I; L = triars	1350, 1356, 1357 1358
$[NiX_2(dap)]$* **(161)**	D	As_2PX_2	SqPy	X = halides, NCS, CN*; Ni—P, 218; Ni—As, 226; Ni—C, 186, 219	1357
$[NiX(dap)]Y$	D	As_2PX	SqPl	X = Cl; Y = ClO_4; X = Y = NO_3	1357
$[NiX_2(bdpa)]$	D	As_3X_2	SqPy	X = Cl, Br, I	1359
$[NiX_2(ttas)]$	D	As_3X_2	SqPy	X = Br, I	1360
$[NiX_2(ttas)]$	2.23, 2.84			X = NCS, Cl; presumably $[Ni(ttas)_2][NiX_4]$	1360
$[NiX_2L]$	D	As_3X_2, As_2PX_2	SqPy	X = Br, I; L = ptas, pdap	1361
$[NiX_2(ftp)]$	D	P_3X_2	SqPy	X = Cl, Br, I	1312
$[Ni(das)(ttas)](ClO_4)_2$* **(163)**	D	As_5	SqPy	Ni—As (ap), 239; Ni—As (eq), 226–232	1318, 1362, 1363
$[Ni_2(H_2O)L_3](ClO_4)_2$	D		5	L = tas, dap, ptas, pdap, bdpa; supposed dinuclear; bridging ligand	1357, 1359, 1361
$[NiI_2L]$	D	As_2NI_2, As_2SI_2	SqPy	L = bdaa, bdas; supposed dinuclear;	1299
$[NiBr_2(bdaa)]$	2.25			SqPl + Oh species	1299
$[NiBr_2(bdas)_2]$	3.12		Oh	Five-coordinate in solution	1299
$[NiX_2(bdpo)]$	3.23–3.26	P_2X_2	Td	Bidentate ligand	1296
$[NiI_2(bdao)]$	3.19	As_2I_2	Td	Bidentate ligand	1299
$[NiX(bdps)]Y$	D	P_2SX	SqPl	X = halides, Y = ClO_4, BPh_4	1364
$[NiX(bdps)]_2[NiX_4]$	3.79–3.91		SqPl + Td	X = Cl, Br; μ_{eff} refers to Td NiX_4^{2-} species	1365
$[NiX_2(R\text{-}bda)]$* **(165)**	D	NP_2X_2	SqPy	R = H, Me; X = Br*, I; Ni—P, 217; Ni—Br, 233, 270	1365, 1366
$[NiX(R\text{-}bda)]BPh_4$	D	NP_2X	SqPl	X = halides; R = Cy	1365
$[NiX_2(dsp)]$* **(166)**	D	S_2PX_2	SqPy	X = halides; Ni—P, 212; Ni—S, 219, 279; Ni—I, 251, 257	1317, 1367
$[Ni(dsp)_2](ClO_4)_2$	D		5	One bidentate and one tridentate ligand	1317
$[Ni(dsp)L](ClO_4)_2$	D		SqPy	L = $MeE(C_6H_4)PPh_2$; E = S, Se; $Me_2As(C_6H_4)PPh_2$	1317
$[NiCl_2(bdppe)]$	3.16	NP_2Cl_2	TBPy	1.30 BM at 99 K	1368
$[NiX_2(bdppe)]$	D	NP_2X_2	TBPy	X = Br, I; SqPl in polar solvents	1368
$[Ni(NCS)_2(bdppe)]$	D	N_2P_2	SqPl	Bidentate ligand	1368
$[NiX(bdppe)]ClO_4$	D	NP_2X	SqPl	X = Cl, Br	1368
$[NiX_2(bdppm)]$	D	NP_2X_2	SqPy	X = halides; SqPl in solution;	1369
$[Ni(NCS)_2(bdppm)]$	2.50			supposed SqPl + Oh species	1369–1371
$[NiX(bdppm)]ClO_4$	D	NP_2X	SqPl	X = halides	1369
$[Ni(bdppm)_2](ClO_4)_2$	D	NP_4	5	One bidentate and one tridentate ligand	1369, 1371
$[NiCl\{[5,5]\text{-}PNP\}]$	D	NP_2Cl	SqPl	Anionic ligand	1372

* Structures determined by X-ray analysis.
[a] The structural formulas of the ligands and their abbreviations are given in Table 67.
[b] D = diamagnetic.
[c] Bond distances are given in pm.



(160) Ni—Br_{ap} 237 pm
Ni—Br_{bas} 269
Ni—As 226 (av)

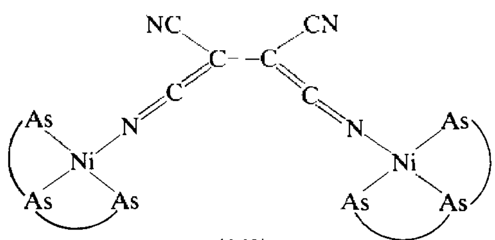


(161) Ni—CN_{ap} 219 pm
Ni—CN_{bas} 186
Ni—As 226
Ni—P 218

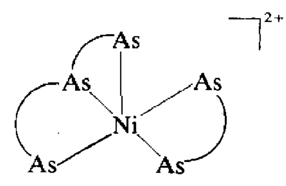
five-coordinate [NiX_2(etp)] complexes become square planar in MeCN solution[1351] and the complexes NiX_2(ttp) become $[NiX(ttp)MeCN]^+$ (still five-coordinate) in acetonitrile solution.[1352]

$[Ni_2(H_2O)(bdpa)_3](ClO_4)_4$ reacts with tetracyanoethylene yielding the diamagnetic complex **(162)** which contains the dianion TCE^{2-} bridging two nickel atoms.[1302]

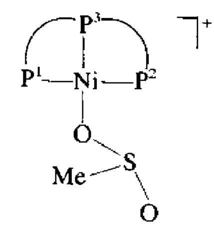
The reaction of diars **(XVIII)** with hydrated $Ni(ClO_4)_2$ in boiling diethylene glycol affords the mixed ligand complex $[Ni(diars)(ttas)](ClO_4)_2$ **(163)**,[1363] originally formulated as $Ni(diars)_2(ClO_4)_2$.[1318,1362]



(162)



(163) Ni—As_{ap} 239 pm
Ni—As_{bas} 229 (av)



(164) Ni—P^1 220 pm
Ni—P^2 221
Ni—P^3 211
Ni—O 194

The diamagnetic air-stable organometallic compounds [NiR(etp)]PF_6 (R = alkyl, aryl) were prepared by the reaction of the appropriate Grignard reagent with the corresponding halo complexes under nitrogen in THF–ether solution.[1354] These complexes contain a nickel–carbon σ bond and are square planar both in the solid state and in solution in non-polar solvents. They dissolve in liquid SO_2 which inserts into the Ni—C bond giving a sulfinate group bonded to nickel through an oxygen atom **(164)** (equation 167).

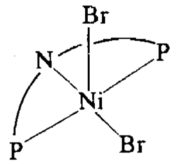
$$[NiR(etp)]PF_6 + SO_2 \xrightarrow{-78\,^\circ C} [Ni(SO_2R)(etp)]PF_6 \qquad (167)$$

The mixed-donor or 'hybrid' ligands which are collected in Table 67 contain N, O or S as well as P and As as donor atoms. Their complexes with nickel(II) are numerous. They have general formulas [NiX_2L] and [NiXL]Y. Selected complexes are reported in Table 68. Nickel(II) complexes with hybrid ligands exhibit a great variety of coordination geometries as exemplified, for example, by the four-, five- and six-coordination found in the complexes with the ligands bdao, bdas, bdpo and bdaa **(XXVIII)**–**(XXXI)**.

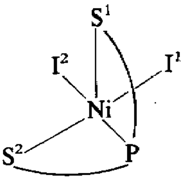
The coordination geometry of the complexes with the ligands with an NP_2 donor set (ligands **XXXI**, **XXXII**) is strictly dependent on the nature of the substituents on the nitrogen donor. The [NiX_2(R-bda)] complexes are low-spin five-coordinate when R = H or Me and square planar when R = Cy. All of the complexes become square planar, $[NiX(R\text{-}bda)]^+$, in solution.[1365] The structure of the complex [$NiBr_2$(H-bda)] **(165)** is typical of low-spin square pyramidal nickel(II) complexes, with the apical Ni—Br distance longer than the basal one and the nickel atom substantially in the basal plane.[1299]

The square pyramidal geometry of the [NiX_2(dsp)] complexes[1317] was confirmed by the X-ray structure of the [NiI_2(dsp)] derivative **(166)**[1367] in which both halogens are in the basal plane.

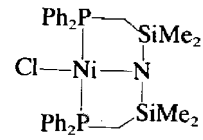
The square planar $[NiX(bdppm)]^+$ complex was found to react with CO at room temperature and atmospheric pressure in EtOH—H_2O solution according to equation (168). The nickel(0) carbonyl complex containing the protonated ligand Hbdppm reacts in turn with acids with evolution of H_2 (equation 169). Thus the complex $[NiX(bdppm)]^+$ acts as an effective homogeneous catalyst of the water-gas reaction.[1373]



(165) Ni—Br_{ap} 270 pm
Ni—Br_{bas} 233
Ni—P 217 (av)
Ni—N 201



(166) Ni—S^1 279 pm
Ni—S^2 219
Ni—I^1 251
Ni—I^2 257
Ni—P 212



(167)

$$[NiX(bdppm)]^+ + 3CO + H_2O \longrightarrow [Ni(CO)_2(Hbdppm)]^+ + CO_2 + X^- + H^+ \quad (168)$$

$$[Ni(CO)_2[Hbdppm)]^+ + H^+ + X^- \xrightarrow{t>40\,^\circ C} [NiX(bdppm)]^+ + H_2 + 2CO \quad (169)$$

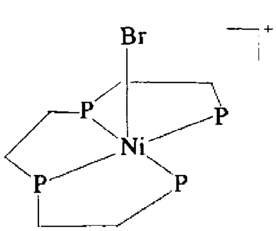
The reaction of the ligand **(XXXIV)** with $NiCl_2(PR_3)_2$ (R = Me, Ph) in THF at 0 °C produces the diamagnetic square planar complex **(167)**.[1372] The ^1H NMR spectrum of the complex at −80 °C suggests the formation of a tetrahedral isomer.

(ii) *Complexes with tetradentate ligands*[1349,1374]

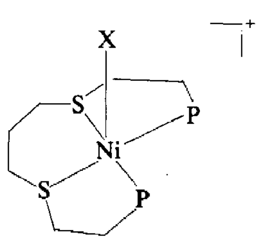
Listings of open-chain tetradentate ligands and of their complexes with nickel(II) are given in Table 69. The complexes were generally prepared by refluxing solutions of the reactants in common organic solvents, *e.g.* alcohols, acetone, dichloromethane, or their mixtures, sometimes under nitrogen atmosphere in order to prevent possible decomposition of unstable ligands. The complexes are stable and can be handled in the air.

All of the complexes structurally characterized have either a square planar or a square pyramidal structure with a planar arrangement of the four donor atoms. Complexes having general formulas $[NiL]Y_2$ and [NiXL]Y (L = quadridentate ligand; X = coordinated anion; Y = uncoordinated anion) are invariably low-spin as one can easily predict on the basis of the high nucleophilicity of the donor atoms.[1389]

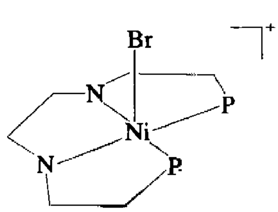
Actually a square pyramidal structure has been found in the complex [NiBrL]Br **(168)** which has been prepared with the tetraphosphine ligand Me_4p_4[1377] and in the complexes $[NiXL]BPh_4$ **(169)** with the mixed-donor ligand 2,3,2-p_2s_2.[1382,1383]



(168) Ni—Br 269 pm
Ni—P 208–227



(169) Ni—Br 264 pm
Ni—P 220 (av)
Ni—S 223 (av)
Ni—I 265 pm
Ni—P 222 (av)
Ni—S 225 (av)



(170) Ni—Br 281 pm
Ni—P 221 (av)
Ni—N 200 (av)

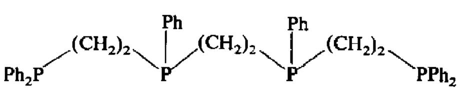
The p_2n_2 ligand containing two phosphorus and two nitrogen donors is reported to form square planar, square pyramidal diamagnetic, and octahedral paramagnetic complexes.[1385] Irrespective of the coordination number, the ligand arranges itself with the four donors in a plane as found in the five-coordinate $[NiBr(p_2n_2)]Br$ complex **(170)**.[1386] Square planar and pseudooctahedral complexes are also formed by the analogous ligand with terminal tertiary arsines.[1387]

A common feature of the aforementioned square pyramidal structures is the elongation of

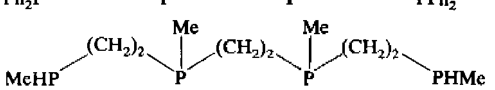
Table 69 Selected Complexes with Open-chain Tetradentate Ligands

Complex	μ_{eff}(r.t.)[a] (BM)	Donor set	Coordination number or geometry	Remarks[b]	Ref.
$[Ni(p_4)]Y_2$	D	P_4	SqPl	Y = Cl, PF_6	1375
$[NiX(p_4)]BPh_4$	D	P_4X	SqPy	X = halides, NCS	1376
$[NiBr(Me_4p_4)]Br$* (**168**)	D	P_4X	SqPy	Ni—P, 208–227; Ni—Br, 269	1377
$[NiX(3,2,3\text{-tetars})]ClO_4$	D	As_4X	SqPy	X = halides, NCS	1378
$[Ni(3,3,3\text{-}p_2s_2)](ClO_4)_2$	D	P_2S_2	SqPl		1379
$[NiX(3,3,3\text{-}p_2s_2)]ClO_4$	D	P_2S_2X	TBPy	X = halides, NCS	1379
$[Ni(3,3,3\text{-}as_2s_2)](ClO_4)_2$	D	As_2S_2	SqPl		1380
$[NiX(3,3,3\text{-}as_2s_2)]Y$	D	As_2S_2X	TBPy	X = Br, I; Y = ClO_4; X = Cl; Y = BPh_4	1380
$[NiX_2(3,3,3\text{-}as_2s_2)]$	3.0–3.1	$As_2S_2X_2$	Oh	X = Cl, Br, NCS	1380
$[Ni(2,3,2\text{-}p_2s_2)](ClO_4)_2$*	D	P_2S_2	SqPl	Ni—P (av), 219; Ni—S (av), 222	1381
$[NiX(2,3,2\text{-}p_2s_2)]BPh_4$* (**169**)	D	P_2S_2X	SqPy	X = Br, I; Ni—P (av), 221; Ni—S (av), 224; Ni—Br, 264; Ni—I, 265	1382, 1383
$[Ni(2,3,2\text{-}s_2p_2)]$	D	P_2S_2	SqPl	*meso* and *rac* diastereoisomers; Ni—P (av), 213; Ni—S (av), 219	1384
$[NiBr(p_2n_2)]Br\cdot 0.5EtOH$* (**170**)	D	P_2N_2Br	SqPy	Ni—P (av), 221; Ni—N (av), 200; Ni—Br, 281	1385, 1386
$[Ni(p_2n_2)]Y_2$	D	P_2N_2	SqPl	Y = ClO_4, BPh_4, PF_6, Br, I	1385
$[Ni(NCS)_2(n_2p_2)]$	3.12	P_2N_4	Oh		
$[Ni(as_2n_2)]Y_2$	D	As_2N_2	SqPl	Y = ClO_4, BPh_4, BF_4	1387
$[NiX_2(as_2n_2)]$	3.07–3.35	$As_2N_2X_2$	Oh	X = Br, I, NCS	1387
$[NiCl(3,3,3\text{-}n_2p_2)]PF_6$*	D	P_2N_2Cl	SqPy	Ni—P (av), 217; Ni—N (av), 202; Ni—Cl, 270.	1388

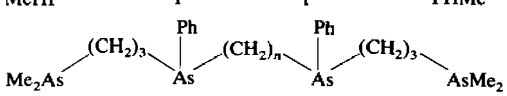
* Structures determined by X-ray analysis.
[a] D = diamagnetic.
[b] Bond distances are given in pm.
Ligand formulas and abbreviations:



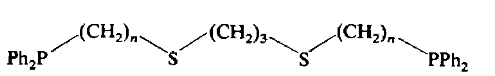
p_4



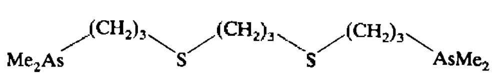
Me_4p_4



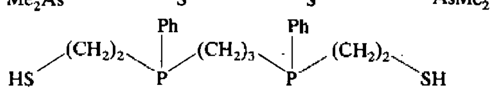
$n = 3$, 3,3,3-tetars
$n = 2$, 3,2,3-tetars



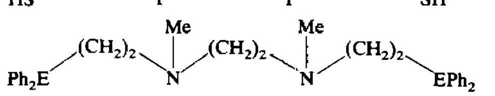
$n = 3$, 3,3,3-p_2s_2
$n = 2$, 2,3,2-p_2s_2



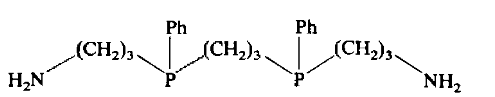
3,3,3-as_2s_2



2,3,2-$H_2s_2p_2$



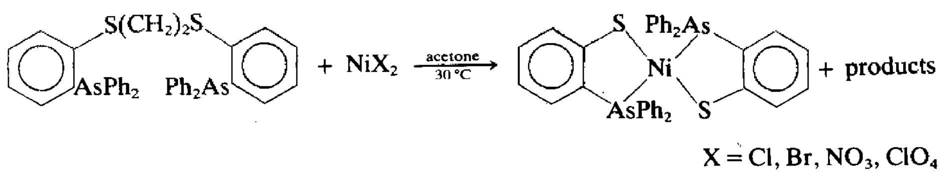
E = P, p_2n_2
E = As, as_2n_2



3,3,3-n_2p_2

the apical nickel–ligand distance. This elongation is usually attributed to the stereochemical activity of the d_{z^2} orbital which contains two electrons in diamagnetic nickel(II) and points at the apical ligand. This effect is supposed to be increasingly important as the electronegativity of the apical donor increases.[1390]

The 1,2-bis(*o*-diphenylarsinophenylthio)ethane ligand in acetone solution was found to be unreactive towards nickel(II) salts at temperatures lower than 30 °C. However, when the temperature is raised to 30 °C the reaction depicted in Scheme 17 occurs.[1391]



Scheme 17

50.5.4.6 Complexes with tri- and tetra-dentate tripodal ligands

This subject has been extensively reviewed recently,[1348,1392–1394] and therefore this section will include only the main aspects of the coordination chemistry of these peculiar ligands towards nickel(II). A list of the tripodal ligands which give complexes with nickel(II) is reported in Table 70.

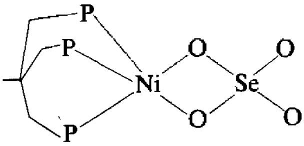
The ligands can be divided in two main groups: those which are potentially tridentate having three basal PR_2 or AsR_2 groups each attached to the same carbon atom through a methylene or an ethylene group, and the potentially tetradentate ligands where the three basal donors are connected to an apical donor by means of *o*-phenylene, trimethylene or ethylene chains. These latter ligands usually occupy four coordination positions around nickel(II) leaving room for only one additional donor, charged or uncharged, thus giving rise to five-coordinate structures. The tridentate ligands generally occupy a face of the coordination polyhedron of nickel(II) which exhibits both electronic and steric unsaturation. The coligands are thus favoured to occupy more than one coordination position and binuclear complexes with bridging monodentate coligands may result.

(*i*) *Structural properties of the complexes*

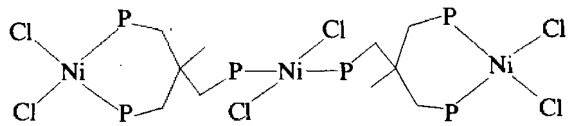
Selected nickel(II) complexes with potentially tridentate phosphines and arsines are shown in Table 71. They were generally prepared by the direct reaction of various nickel(II) salts with the appropriate ligand in common organic solvents. Sometimes triethylorthoformate was used as a dehydrating agent.[1396] The complexes with the ligands triphos (**XXXV**) and atriphos (**XXXVIII**) have the general formula NiX_2L (X = halides, NCS, CN, $\frac{1}{2}SO_4$, $\frac{1}{2}SeO_4$).[1395–1397] Those prepared with the two ligands etriphos (**XXXVI**) and etp_3 (**XXXIX**) have the formula $Ni_3X_6L_2 \cdot xCHCl_3$.[1398,1399] Starting from either anhydrous nickel(II) halides or hydrated salts with poorly coordinating anions and the ligand Me_6as_3 (**XXXVIII**), the 1:2 complexes $Ni(Me_6as_3)_2X_2$ were obtained.[1400]

The geometries of the first reported diamagnetic nickel(II) complexes of the triphos ligand are uncertain, but the sulfato and selenato derivatives are paramagnetic and exhibit a highly distorted square pyramidal geometry with the anion acting as bidentate (**171**).[1397]

Either increasing the length of the connecting chain (triphos becomes etp_3) or replacing the phenyl substituents by ethyl ones (triphos becomes etriphos) produces diamagnetic trinuclear complexes where the ligand is bound to two metal centres, $[Ni_3Cl_6(etriphos)_2] \cdot 2CHCl_3$ (**172**),[1398] or to three metal centres, $[Ni_3Cl_6(etp_3)_2] \cdot 0.7CHCl_3$ (**173**).[1399] The coordination of nickel(II) in both complexes is square planar.



(**171**) Ni—P 223 pm (av)
Ni—O 200 (av)



(**172**) Ni—P (bridging) 225 pm
Ni—Cl (bridging) 217
Ni—P (terminal) 216 (av)
Ni—Cl (terminal) 220 (av)

The tripod-like geometry of the tetradentate ligands containing the rigid *o*-phenylene connecting chains is such that nickel complexes with trigonal bipyramidal geometry are invariably formed. Ligands containing the more flexible ethylene or trimethylene chains also

Table 70 Tri- and Tetra-dentate Tripodal Ligands Cited in Section 50.5.4.6; Structures, Formulas and Abbreviations Used in Table 71

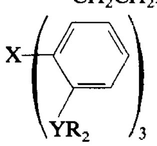
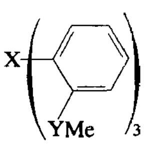
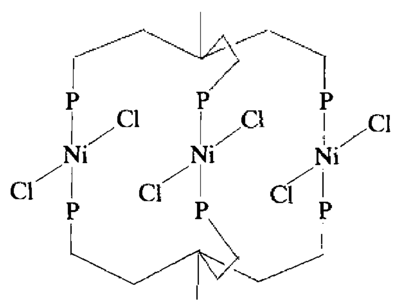
Ligand			*Abbreviation*
CH_2ER_2 $MeC—CH_2ER_2$ CH_2ER_2	$ER_2 = PPh_2$	**(XXXV)**	triphos (p_3)
	$ER_2 = PEt_2$	**(XXXVI)**	etriphos (Et_6p_3)
	$ER_2 = AsMe_2$	**(XXXVII)**	Me_6as_3
CH_2PPh_2 $MeC—CH_2PPh_2$ $CH_2CH_2PPh_2$		**(XXXVIII)**	atriphos (ap_3)
$CH_2CH_2PPh_2$ $MeC—CH_2CH_2PPh_2$ $CH_2CH_2PPh_2$		**(XXXIX)**	etp_3
	X = Y = P; R = Ph	**(XL)**	QP
	X = Y = As; R = Ph	**(XLI)**	QAs
	X = Y = As; R = Me	**(XLII)**	Qas
	X = As; $YR_2 = PPh_2$	**(XLIII)**	ASTP
	X = Sb; $YR_2 = PPh_2$	**(XLIV)**	SBTP
	X = P; $YR_2 = AsPh_2$	**(XLV)**	PTAS
	X = Sb; $YR_2 = AsPh_2$	**(XLVI)**	SBTAS
	X = Sb; $YR_2 = AsMe_2$	**(XLVII)**	Sbtas
	X = Bi; $YR_2 = AsMe_2$	**(XLVIII)**	Bitas
	X = P; Y = S	**(IL)**	Pts (TSP)
	X = P; Y = Se	**(L)**	Ptse (TSeP)
$C_6H_4AsPh_2$ $As—C_6H_4AsPh_2$ C_6H_4SMe		**(LI)**	As_3S
$CH_2CH_2CH_2YMe_2$ $X—CH_2CH_2CH_2YMe_2$ $CH_2CH_2CH_2YMe_2$	X = Y = As	**(LII)**	qas
	X = P; Y = As	**(LIII)**	tap
	X = Sb; Y = As	**(LIV)**	tasb
$(CH_2CH_2CH_2AsMe_2)_{3-n}$ As $(CH_2CH_2CH{=}CH_2)_n$	$n = 1$		tasol
	$n = 2$		dasdol
	$n = 3$		astol
$CH_2CH_2PR_2$ $P—CH_2CH_2PR_2$ $CH_2CH_2PR_2$	R = Ph		pp_3
	$R = CH_2CMe_3$		pp_3-neo
$CH_2CH_2YR_2$ $N—CH_2CH_2YR_2$ $CH_2CH_2YR_2$	$YR_2 = PPh_2$	**(LV)**	np_3
	$YR_2 = AsPh_2$	**(LVI)**	nas_3
	$YR_2 = PMe_2$	**(LVII)**	$Menp_3$
	$YR_2 = AsMe_2$	**(LVIII)**	$Menas_3$
	$YR_2 = PEt_2$	**(LIX)**	$Etnp_3$
	$YR_2 = PCy_2$	**(LX)**	$Cynp_3$
CH_2CH_2X $N—CH_2CH_2Y$ CH_2CH_2Z	X = Y = PPh_2; Z = NEt_2	**(LXI)**	n_2p_2
	X = Y = $AsPh_2$; Z = NEt_2	**(LXII)**	n_2as_2
	X = Y = NEt_2; Z = PPh_2	**(LXIII)**	n_3p
	X = Y = NEt_2; Z = $AsPh_2$	**(LXIV)**	n_3as
	X = Y = $AsPh_2$; Z = OMe	**(LXV)**	$noas_2$
	X = CH_2OMe; Y = Z = PPh_2	**(LXVI)**	n-op_2
	X = OMe; Y = Z = PPh_2	**(LXVII)**	nop_2

Table 71 Selected Complexes with Tridentate Tripodal Ligands

Complex[a]	μ_{eff}(r.t.)[b] (BM)	Donor set	Coordination number or geometry	Remarks	Ref.
$[Ni(CN)_2(triphos)]$	D	P_3C_2	5		1395, 1396
$[NiX_2(triphos)]$	D	P_2X_2	SqPl	X = Cl, Br, NCS; supposed bidentate ligand	1395
$[Ni(ZO_4)(triphos)]$* (**171**)	3.01, 3.12	P_3O_2	SqPy	Z = S, Se*; bidentate anion	1397
$[NiCl_2(atriphos)]$	D	P_2Cl_2	SqPl	Bidentate ligand	1398
$[Ni_3X_6L_2]\cdot xCHCl_3$* (**172, 173**)	D	P_2X_2	SqPl	L = etriphos; X = Cl* L = etp_3; X = Cl*, Br, I	1398, 1399
$[NiX_2(Me_6as_3)_2]$	3.02–3.22	As_4X_2	Oh	X = Cl, Br, I; bidentate ligand	1400
$[Ni(Me_6as_3)_2]Y_2$	D	As_5	SqPy	Y = ClO_4, BF_4, BPh_4; one bidentate and one tridentate ligand	1400
$[Ni(NCS)_2(Me_6as_3)]$	D	As_2N_2	SqPl	Bidentate ligand	1400

* Structures determined by X-ray analysis.
[a] The structural formulas of the ligands and their abbreviations are given in Table 70.
[b] D = diamagnetic.



(**173**) Ni—P 223 pm (av)
Ni—Cl 216 (av)

form complexes with square pyramidal geometry. On the other hand the 'soft' phosphorus and arsenic donors stabilize the low-spin state. Selected nickel(II) complexes are shown in Table 72.

The complexes were generally prepared by the direct reaction of nickel salts (halides and, in general, salts of coordinating anions) and the appropriate ligand in the common organic solvents. The reactions were often carried out in the presence of ClO_4^-, PF_6^- or BPh_4^- which give less soluble compounds. Most of the complexes have the general formulas [NiX(L)]X and [NiX(L)]Y (X = coordinating anion; Y = weak or non-coordinating anion; L = tripodal ligand).

The nickel(II) complexes with the ligands QP (**XL**), QAS (**XLI**) and Qas (**XLII**), where tertiary phosphines and arsines are connected by *o*-phenylene chains, were first reported by Venanzi and co-workers.[1401–1403] These complexes are stable and diamagnetic, and are assumed to possess an essentially trigonal bipyramidal geometry. Complexes with the mixed donor ligands (**XLIII**)–(**XLVI**) behave similarly.[1405] The complexes with the ligand SBTAS (**XLVI**) were prepared starting from $NiCl_2(PPh_3)_2$ under a nitrogen atmosphere.

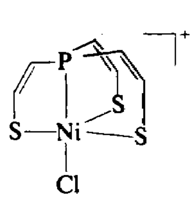
McAuliffe and co-workers and Dyer and Meek studied nickel(II) complexes with ligands containing methylated arsines Sbtas (**XLVII**), Bitas (**XLVIII**) and either thiomethyl or selenomethyl groups Pts (**IL**) and Ptse (**L**).[1406–1410] The two ligands Pts and Ptse give complexes with different stoichiometry and coordination geometry.

The only structures which were determined by X-ray analysis are those of $[NiCl(Pts)]ClO_4$ (**174**)[1409] and of $[NiBr(As_3S)]ClO_4$ (**175**).[141] The former complex has an almost regular trigonal bipyramidal structure, whereas the latter is more distorted because of the different donors in the equatorial plane of the ligand As_3S (**LI**). The short Ni—L_{apical} bond distances (211 pm, and 222 pm, respectively) were attributed both to steric factors (rigid *o*-phenylene chains) and electronic factors inherent in the trigonal bipyramidal low-spin d^8 configuration which makes the d_{z^2} orbital empty.

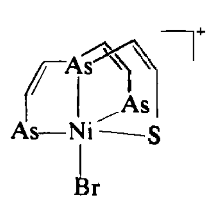
Table 72 Selected Complexes with Tetradentate Tripodal Ligands

Complex[a]	μ_{eff} (r.t.)[b] (BM)	Donor set	Coordination number or geometry	Remarks	Ref.
$[NiX(QP)]BPh_4$	D	P_4X	TBPy	X = Cl, Br, I	1401–1403
$[NiX(L)]Y$	D	As_4X	TBPy	L = QAs, Qas; X = halides, NCS, CN, NO_3, NO_2, N_3; Y = Br, I, ClO_4, BF_4, BPh_4	1402–1405
$[NiX(L)]BPh_4$	D	$As(Sb)P_3X$	TBPy	X = halides; L = ASTP, SBTP	1403
$[NiX(L)]BPh_4$	D	$P(Sb)As_3X$	TBPy	X = halides; L = PTAS, SBTAS	1403
$[NiX(Sbtas)]Y$	D	$SbAs_3X$	TBPy	X = Y = halides, NCS, NO_3; Y = BPh_4	1406
$[Ni(Sbtas)_2]Y_2$	D	Sb_2As_3	5	Y = ClO_4, BPh_4	1406
$[NiX(Bitas)]BPh_4$	D	$BiAs_3X$	SqPy	X = halides	1407
$[Ni_2(Bitas)_3](ClO_4)_4$	D	As_5, $BiAs_4$	5	Dinuclear, bridging ligand	1407
$[NiX(Pts)]ClO_4$* (**174**)	D	PS_3X	TBPy	X = halides, NCS	1408, 1409
$[NiL(Pts)](ClO_4)_2$	D	PS_3L	TBPy	L = neutral monodentate ligands	1408
$[NiX(Ptse)]ClO_4$	D	PSe_3X	TBPy	X = halides, NCS	1410
$[NiL_2](ClO_4)_2$	D			L = Pts, Ptse; structures uncertain	1408, 1410
$[NiBr_2(Pts)]$	3.2	$PSBr_2$	Td	Bidentate ligand	1408
$[NiBr(As_3S)]ClO_4$* (**175**)	D	As_3SBr	TBPy		1411
$[NiX(tap)]Y$* (**176**)	D	PAs_3X	TBPy	X = halides, NO_2, CN*, NCS, SEt; Y = BPh_4, ClO_4	1412, 1413
$[NiX_2(tap)]$	D	PAs_3X_2	6	X = Br, I	1412
$[NiX(qas)]ClO_4$	D	As_4X	TBPy	X = halides, CN	1414
$[NiX(tasb)]BPh_4$	D	$SbAs_3X$	TBPy	X = halides, CN, NCS, NO_3	1415
$[NiX(tasol)]Y$	D	As_3CX	5	X = Y = Cl, Br; Y = ClO_4; assumed η^2-bonded alkene	1416
$[NiCl(pp_3)]PF_6$	D	P_4Cl	TBPy		1375
$[NiCl(pp_3\text{-neo})]PF_6$	D	P_3X	4	Tridentate ligand	1417
$[NiX(np_3)]Y$* (**177**)	D	NP_3X	TBPy	X = Y = Cl, Br, I* X = Cl*, Br, I; Y = BPh_4, PF_6	1418–1420
$[NiX(nas_3)]BPh_4$	D	NAs_3X	TBPy	X = Br, I	1399
$[NiX(Cynp_3)_3)]BPh_4$	D	NP_2X	SqPl	X = halides, NCS; tridentate ligand	1421
$[Ni_3(Menp_3)_4]Y_6$	D	NP_4	TBPy	$Y_6 = (BF_4)_6$; $Br_3(BPh_4)_3$; trinuclear	1422
$[NiCl(Etnp_3)]BPh_4$	D	NP_3X	TBPy		1423
$[Ni_3Cl_4(Etnp_3)_2](BPh_4)_2$* (**178**)	D	NP_2Cl, P_2Cl_2	SqPl	Trinuclear	1423
$[NiX_2(Menas_3)]$	3.03–3.06	NAs_3X_2	Oh	X = Cl, Br; mononuclear X = I, NCS; polynuclear	1424
$[NiX(n_2p_2)]Y$* (**180**)	D	N_2P_2X	5	X = halides, NCS; Y = BPh_4 X = Y = I*	1425, 1426
$[NiI(L)]BPh_4$	D		SqPl	L = n_2as_2, $noas_2$; tridentate ligands	1425, 1427
$[NiX(n_3p)]BPh_4$	3.24–3.29	N_3PX	TBPy	X = Cl, Br	1425, 1428
	D	N_2PX	SqPl	X = Cl, Br*, I, CN	
$[NiX(n_3as)]BPh_4$* (**179**)	D	N_3X	SqPl	X = Cl, Br, NCS*; tridentate ligand	1425–1429
$[NiI(n_3as)]BPh_4$	3.25	N_3AsI	5		1425
$[Ni(NCS)_2L]$	3.34–3.37	N_5	SqPy	L = n_3as*, n_3p; tridentate ligand	1425, 1430
	3.24	N_4As_2	Oh	L = n_2as_2	
$[NiX(nop_2)]BPh_4$* (**181**)	D	NP_2X	SqPl	X = Cl, Br, I*, NCS; weak coordination of ether oxygen	1431, 1432
$[NiX(n\text{-}op_2)]BPh_4$	D	NP_2X	SqPl	X = halides	1431

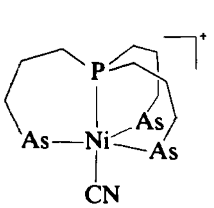
* Structures determined by X-ray analysis.
[a] The structural formulas of the ligands and their abbreviations are given in Table 70.
[b] D = diamagnetic.



(**174**) Ni—P 211 pm



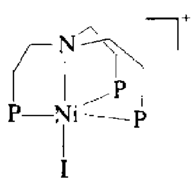
(**175**) Ni—As 222 pm



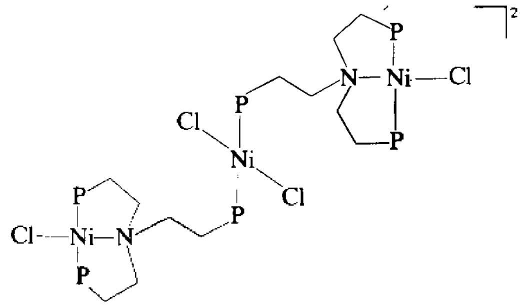
(**176**) Ni—P 221 pm

Meek and co-workers reported nickel complexes with the ligands qas (**LII**), tap (**LIII**) and tasb (**LIV**) where the terminal $AsMe_2$ groups are joined to the apical donor (As, P, Sb) by trimethylene chains.[1412,1414,1415] Most of the complexes have the usual formula [NiXL]Y, and are invariably diamagnetic with an essentially trigonal bipyramidal geometry as found in the $[Ni(CN)(tap)]ClO_4$ derivative **(176)**.[1413] Both the displacement of the nickel towards the apical phosphorus and the longer Ni—P bond distance are consequences of the longer trimethylene chains and their flexibility as compared to the rigid *o*-phenylene linkages in the complexes **(174)** and **(175)**.

The ligands np_3, nas_3, $Menp_3$, $Menas_3$, $Etnp_3$ and $Cynp_3$ **(LV–LX)** have the common characteristic of an apical nitrogen donor linked to basal phosphines and arsines through ethylene chains. The reaction of these ligands with nickel(II) halides in the presence of BPh_4^- or PF_6^- affords diamagnetic complexes of general formula [NiX(L)]Y (L = np_3, nas_3, $Etnp_3$, $Cynp_3$).[1299,1418,1423] With the exception of complexes with the ligand $Cynp_3$, which are square planar with the ligand acting as tridentate,[1421] these complexes have an essentially trigonal bipyramidal geometry as exemplified by that of the two complexes $[NiCl(np_3)]PF_6$[1419] and $[NiI(np_3)]I$ **(177)**.[1420]



(177) Ni—P 222 pm
Ni—N 213



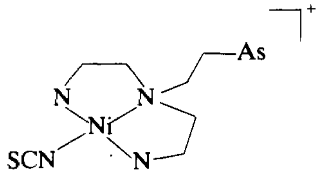
(178)

The $Etnp_3$ ligand also gives a trinuclear complex $[Ni_3Cl_4(Etnp_3)_2](BPh_4)_2$ **(178)**.[1423] The $Menp_3$ ligand also invariably gives trinuclear complexes $[Ni_3(Menp_3)_4]Y_6$.[1422] The $Menas_3$ ligand gives paramagnetic six-coordinate complexes with formula $[NiX_2(Menas_3)]$.[1424]

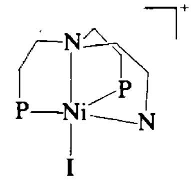
From the previous examples we reported, we may conclude that the ligands np_3 and nas_3 with phenyl substituents on the basal donors invariably form mononuclear complexes with trigonal bipyramidal geometry. In contrast, when the basal phenyl substituents are replaced by less bulky methyl or ethyl groups, the resulting ligands tend to form polynuclear complexes in which the tripod ligand is bound to two or three metal centres.

Reaction of the five-coordinate $[NiX(np_3)]X$ complexes with MX_2 salts (M = Fe, Co, Ni, Zn) affords mixed complexes $NiM(np_3)X_4$ containing a square planar $NiNP_2X$ chromophore and a tetrahedral MPX_3 chromophore.[1433]

Numerous 'hybrid ligands' **(LXI–LXVII)** were investigated together with nickel(II). Most of the complexes have the same general formula [NiXL]Y as with np_3 and nas_3 ligands; however, the properties of the complexes with hybrid ligands are often different from those of the corresponding complexes with np_3 and nas_3. $[NiX(L)]BPh_4$ complexes are diamagnetic square planar when L = n_2as_2,[1425,1427] n_3p[1425,1428] and n_3as,[1425,1429] which act as tridentate ligands **(179)**, and five-coordinate high-spin with n_3p[1425] and low-spin with n_2p_2 **(180)**.[1425,1426] In summary, the tripodal ligands which contain more than one 'hard' atom in the donor set are not always tetralegate in their diamagnetic complexes of nickel(II), and permit high-spin configurations in five-coordinate complexes, both trigonal bipyramidal and square pyramidal.



(179)



(180)

(*ii*) *Reactions involving nickel(II) and the tripodal ligands*

When one starts with nickel(II) salts of poorly coordinating anions such as hydrated $Ni(BF_4)_2$ and $Ni(ClO_4)_2$, and with the tripodal tetradentate ligands with phenyl substituents on the donor atoms, a complex fragment NiL^{2+} is initially formed in solution. This centre is highly reactive and may react with solvent molecules, water molecules from aqua cations, and with the species which are added to the reaction mixture. At the end of the reaction the ML^{2+} fragment is incorporated in the final products (Tables 73 and 74).

Table 73 Aqua, Hydroxo, Hydrido, Thio, Mercapto and Methylthio Complexes with Tripodal Ligands

Complex	μ_{eff} *(r.t.)*[a] (BM)	*Donor set*	*Coordination number or geometry*	*Remarks*	*Ref.*
$[Ni(H_2O)(QP)](BPh_4)\cdot THF$	D	P_4O	TBPy		1434
$[NiOH(L)]Y$	D	P_4O	TBPy	L = pp_3, QP; Y = BF_4, BPh_4	1434
$[NiH_x(np_3)]BF_4$* **(182)**	0.88–2.08	NP_3H	TBPy	x = 0.83–0.04	1435
$[NiH(pp_3)]Y$	D	P_4H	TBPy	Y = I, NO_3, BF_4, BPh_4	1436
$[Ni_2S(triphos)_2](BPh_4)_2$* **(183)**	D	P_3S	Td	Solvate = 1.6 DMF; dinuclear; bridging sulfur atom	1437
$[Ni_2(S_2)(triphos)_2]ClO_4$* **(184)**	2.04	P_3S_2	5	Dinuclear; bridging η^2-S_2 group; mixed valence nickel	1438
$[Ni(RS)(L)]BPh_4$* **(185)**	D	P_4S, NP_3S	TBPy	R = H*, Me; L = np_3, pp_3*	1439
$[Ni(RS)(n_2p_2H)]Y_2$* **(186)**	D	NP_2S	SqPl	R = H*, Me; Y = BF_4*, BPh_4	1440

* Structures determined by X-ray analysis.
[a] D = diamagnetic.

The hydrated $Ni(BF_4)_2$ reacts in different ways with pp_3, QP and np_3 ligands, according to the exact reaction conditions (Scheme 18). In the second reaction of Scheme 18, which also occurs with the ligand pp_3, the ligands presumably behave as base towards the weak acid H_2O, forming the hydroxide anion. These aqua and hydroxo complexes are diamagnetic with trigonal bipyramidal geometry.[1434]

$$Ni(H_2O)_6^{2+} + QP + 2Y^- \xrightarrow{\text{THF, reflux, 20 min}} [Ni(H_2O)(QP)]Y_2 + 5H_2O$$

$$Ni(H_2O)_6^{2+} + QP + 2Y^- \xrightarrow{\text{EtOH, reflux, 3 h}} [Ni(OH)(QP)]Y + 5H_2O + Y^-$$

$$Y = BF_4, BPh_4$$

Scheme 18

The reaction of the aqua cation of nickel(II) with np_3 is quite different from those with pp_3 and QP, and the reaction products critically depend on the nature of the solvent, the anion Y^- and the exact reaction conditions (Scheme 19).[1435] In ethanol solution both reduction and hydrogenation reactions occur (see also Section 50.2.9). These non-stoichiometric hydrides are made up from paramagnetic nickel(I) species $[Ni(np_3)]^+$ and diamagnetic hydridonickel(II) species $[NiH(np_3)]^+$ **(182)**. An IR band at $595\ cm^{-1}$ is indicative of the presence of hydrogen bound to nickel(II). Pure hydrido complexes of nickel(II) are air-sensitive compounds which are easily obtained in different ways with both pp_3 and np_3 ligands (equations 170 and 171).[1435,1436] The formation of non-stoichiometric hydrido complexes in the absence of specific hydrogenating agents is peculiar to the ligand np_3 and is favoured by ethanol as solvent and by the absence of coordinating anions.

$$Ni(H_2O)_6^{2+} + np_3 + Y^- \xrightarrow{\text{EtOH}} [NiH_x(np_3)]Y \quad x < 0.25,\ Y = BF_4, ClO_4$$

$$Ni(H_2O)_6^{2+} + np_3 + Y^- \xrightarrow{\text{EtOH, } BH_4^-} [NiH_x(np_3)]Y \quad x > 0.25,\ Y = NO_3, BF_4, ClO_4$$

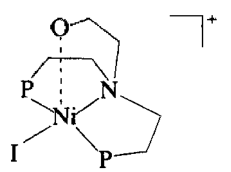
$$Ni(H_2O)_6^{2+} + np_3 + Y^- \xrightarrow{\text{Me}_2\text{CO}} [Ni(np_3)]Y \quad Y = BF_4$$

Scheme 19

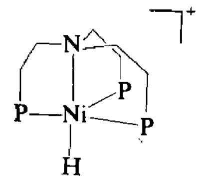
$$Ni(H_2O)_6Y_2 + pp_3 \xrightarrow{BH_4^-} [NiH(pp_3)]Y \qquad Y = I, NO_3, BF_4, ClO_4 \tag{170}$$

$$Ni(np_3) + HClO_4 \longrightarrow [NiH(np_3)]ClO_4 \tag{171}$$

By the action of H_2S or MeSH on solutions of nickel(II) and np_3, pp_3 or triphos, either mononuclear or binuclear complexes are formed which contain coordinated sulfur atoms. With



(181) Ni—O 262 pm
Ni—I 247
Ni—N 198
Ni—P 220 (av)



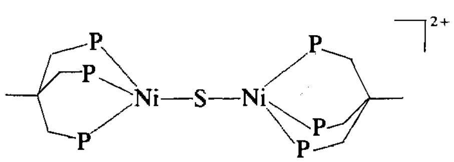
(182)

triphos two different compounds are formed according to the reaction conditions (Scheme 20). In both reactions of Scheme 20 the ligand triphos (in excess of the stoichiometric ratio) is assumed to behave as a proton acceptor from H_2S. Both the complexes (**183**)[1437] and (**184**)[1438] have unusual structural and electronic properties. The former complex is diamagnetic, has a distorted tetrahedral geometry and a linear Ni—S—Ni bridge with shorter distances than expected for a single bond. In complex (**184**), which has an unpaired electron, the two Ni(triphos) fragments are held together by a disulfur moiety which is coplanar with the two nickel atoms. The S—S distance, 221 pm, suggests a single bond between the two sulfur atoms.

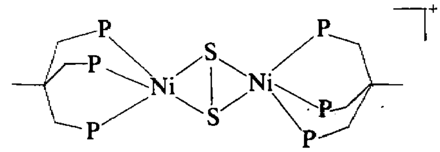
$$Ni(H_2O)_6^{2+} + \text{triphos} + H_2S \xrightarrow[\text{r.t., 5 min}]{\text{DMF/Bu}^n\text{OH, BPh}_4^-} [Ni_2S(\text{triphos})_2](BPh_4)_2\cdot 1.6\text{DMF}$$

$$Ni(H_2O)_6^{2+} + \text{triphos} + H_2S \xrightarrow[40\,^\circ\text{C}/0.5\text{ h}]{\text{DMF/Bu}^n\text{OH, ClO}_4^-} [Ni_2S_2(\text{triphos})_2]ClO_4$$

Scheme 20

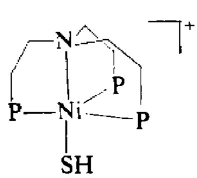


(183) Ni—S 203 pm
Ni—P 224 (av)
Ni—S—Ni 180°
P—Ni—P 92.4° (av)
P—Ni—S 123.5° (av)



(184) Ni—S 222 pm (av)
Ni—P 224 (av)
S—S 221
P—Ni—P 93° (av)
Ni—S—Ni 120°
S—Ni—S 59.5°

The formation of SR^- anions (as well as of OH^- in the hydroxo complexes) in the presence of phosphine ligands presumably results in the formation of protonated phosphine species. This hypothesis seems to be confirmed by the isolation of the complexes $[Ni(SR)(n_2p_2H)](BF_4)_2$ (R = H, Me) which were obtained starting from the hybrid ligand n_2p_2 (**LXI**) and either H_2S or MeSH. In these square planar complexes (**186**) one nitrogen atom of the ligand n_2p_2 is protonated and consequently uncoordinated to nickel(II).[1440]



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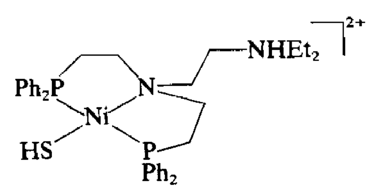


(186)

On the basis of complexes which were found to contain sulfur donors one can draw the conclusion that the coordination of SR^-, S^{2-} and S_2^{2-} species to nickel(II) in complexes with triphos, pp_3 and np_3 is possible only in coordination sites unoccupied by phosphine donors which are able to form strong covalent bonds as sulfur does. Moreover, the phenyl groups on the phosphorus atoms surround the sulfur atoms, preventing their non-bonded electron pairs from forming bonds with nickel atoms and forming polynuclear sulfides.

The reaction in methanol or ethanol of SO_2 with hydrated $Ni(BF_4)_2$ in the presence of either

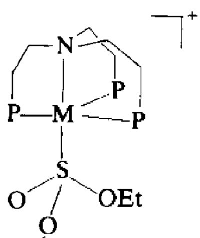
pp_3 or np_3 results in the formation of alkylsulfito complexes (equation 172).[1441] In these diamagnetic complexes the alkylsulfito groups are S-bonded to nickel(II) (**187**). Analogous complexes with the *p*-toluenesulfinato ligand $MeC_6H_4SO_2^-$ bound to nickel through the sulfur atom were prepared with np_3 and pp_3.[1442]

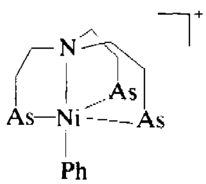
$NiCl_2$ in boiling butanol with nas_3 and $NaBPh_4$ gives the aryl complex $[Ni(Ph)(nas_3)]BPh_4$ (**188**).[1443] The phenyl group bound to nickel(II) comes from the decomposition of BPh_4^- according to reaction (173). The same reaction occurs with both QAs and $Menas_3$.

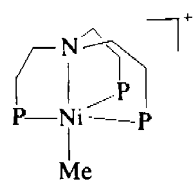
$$Ni(H_2O)_6^{2+} + np_3 + SO_2 \xrightarrow{ROH} [Ni\{SO_2(OR)\}(np_3)]^+ \quad R = Me, Et \qquad (172)$$

$$NiCl_2 + L + 2NaBPh_4 \longrightarrow [Ni(C_6H_5)(L)]BPh_4 + BPh_3 + 2NaCl \quad L = nas_3, Menas_3, QAs \qquad (173)$$

$$[NiX(L)]^+ + MgXR \longrightarrow [NiR(L)]^+ + MgX_2 \quad R = Me, Et, CH_2C_6H_5, \; L = np_3, pp_3, nas_3 \qquad (174)$$


(**187**)


(**188**)


(**189**)

Grignard reagents replace halides from the $[NiX(L)]^+$ derivatives by σ-bonded alkyl and aryl groups (equation 174), giving a series of diamagnetic organometallic complexes of nickel(II) (**189**) (Table 74).[1444]

Table 74 Some Organometallic Complexes of Nickel(II) with Tripodal Ligands

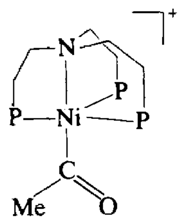
Complex	*Donor set*	*Coordination geometry*	*Remarks*	*Ref.*
$[Ni\{SO_2(OR)\}L]Y\cdot solv$* (**187**)	NP_3S, PP_3S	TBPy	R = Me, Et*; L = np_3*; solv. = $\frac{1}{2}MeOH$, $\frac{1}{2}H_2O$; Y = BF_4; L = pp_3; Y = BPh_4	1441
$[Ni(p\text{-}tolSO_2)L]BPh_4$	NP_3S, PP_3S	TBPy	L = np_3, pp_3; *p*-$tolSO_2$ = *p*-Me-$C_6H_4SO_2$	1442
$[Ni(Ph)L]BPh_4$* (**188**)	NAs_3C, As_4C	TBPy	L = nas_3, $Menas_3$, QAs	1443
$[NiR(L)]BPh_4$* (**189**)	NP_3C, NAs_3C, P_4C	TBPy	R = Me*, Et, CH_2Ph; L = np_3*, pp_3, nas_3	1444
$[Ni(COR)(L)]BPh_4\cdot xTHF$* (**190**)	NP_3C, NAs_3C	TBPy	R = Me*, Et, CH_2Ph; L = np_3*, nas_3;	1445

* Structures determined by X-ray analysis.
All of the complexes are diamagnetic.

The greater stability of these organometallic complexes, as compared with that of analogous complexes with monodentate phosphines, is attributed to the steric effects of the tripodal ligands which surround the metal atom with their phenyl groups on the basal donor atoms, thus imparting a degree of kinetic inertness to the compounds.

The reaction of CO with some of the preceding organometallic compounds is rapid at room temperature and pressure and insertion of CO into the Ni—C bond results (equation 175).[1445] In the case of the np_3 ligand the first product isolated is a solid solution of the acyl derivative of nickel(II), $[Ni(COR)(np_3)]^+$, and a carbonyl complex of nickel(I), $[Ni(CO)(np_3)]^+$, in a 1:1 ratio. When this solid solution is dissolved in THF and EtOH, the pure acyl derivative (**190**) resulted. The acetyl derivative spontaneously loses CO on exposure to air restoring the original methyl derivative.

$$[Ni(R)(nas)_3]^+ + CO \longrightarrow [Ni(COR)(nas_3)]^+ \quad R = Me, Et, CH_2C_6H_5 \qquad (175)$$



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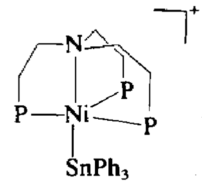


(191)

Complexes $[NiX(L)]^+$ (L = np$_3$, pp$_3$) also react with $LiSnPh_3$ giving complexes containing a nickel–tin σ bond (**191**).[1446]

50.5.5 Complexes with Oxygen-donor Ligands

50.5.5.1 Complexes with water, alcohols and related ligands

Aqueous solutions of nickel(II) salts in the absence of strong coordinating species are usually green because of the $[Ni(H_2O)_6]^{2+}$ cation.[1447] The number of coordinated water molecules in the inner-shell complex is now well ascertained in the temperature range −30 to 30 °C by means of electronic and both ^{17}O and ^1H NMR spectra.[1448–1451] The most recent value of the coordination number is 5.85 ± 0.2.[1451] Neutron diffraction studies of $NiCl_2$ in D_2O solution led to estimates of the Ni—O bond distance within the $[Ni(D_2O)_6]^{2+}$ cation in the range 195–220 pm.[1452] A second hydration sphere of about 15 water molecules has also been proposed.

The kinetics of the exchange reaction in aqueous solution (equation 176) have been investigated by some authors[1451,1453–1456] and values of the rate constants in the range $3.15–4.1 \times 10^4\ s^{-1}$ were reported.

$$Ni(H_2O)_6^{2+} + H_2O^* \longrightarrow Ni(H_2O)_5H_2O^* + H_2O \qquad (176)$$

A number of simple salts, as for example $Ni(NO_3)_2 \cdot 6H_2O$, $NiSO_4 \cdot nH_2O$ ($n = 6, 7$) and $Ni(ClO_4)_2 \cdot 6H_2O$, contain the hexaaqua cation $[Ni(H_2O)_6]^{2+}$, but $NiX_2 \cdot 6H_2O$ (X = Cl, Br) complexes contain the species $[NiX_2(H_2O)_4]$ and lattice water molecules.[1457,1458] Selected hexahydrated nickel(II) salts are shown in Table 75. In all of these compounds the nickel atom is octahedrally coordinated by six water molecules which, in turn, are involved in hydrogen bonding with the various anions which complete the salt.

Table 75 Some Structural Parameters of the $Ni(OH_2)_6^{2+}$ Cation in a Number of Hydrated Salts

Compound	*Bond distance* (pm) *Ni—O*	*Bond angle* (°) *O—Ni—O*	*Ref.*
$[Ni(H_2O)_6][UO_2(MeCO_2)_3]_2$	204–207	86.9–93.1	1459
$[Ni(H_2O)_6](NH_4)_2(SO_4)_2$	204–208	88.5–90.4	1460
$[Ni(H_2O)_6]SO_4$	202–204	—	1461
$[Ni(H_2O)_6]SO_3$	204–208	87.6–94.2	1462
$[Ni(H_2O)_6](NO_3)_2$	202–209	85.8–93.2	1463
$[Ni(H_2O)_6]S_2O_6$	204 (av)	91.0–91.6	1464
$[Ni(H_2O)_6]SeO_4$	204–208	87.0–96.7	1465
$[Ni(D_2O)_6]SO_4$[a]	202–210	88.5–93.3	1466
$[Ni(H_2O)_6]SiF_6$	205 (av)	90.5 (av)	1467

[a] Neutron diffraction analysis.

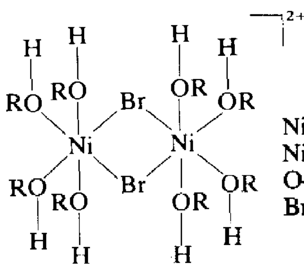
The hydrolysis of $[Ni(H_2O)_6]^{2+}$ has been studied by some authors. It has been found that polynuclear species are formed in alkaline solution, the main product being the tetranuclear cation $[Ni_4(OH)_4]^{4+}$.[1468–1471] A few solid compounds which contain nickel(II) linked only to hydroxide ions were reported, namely $M_2[Ni(OH)_6]$ (M = Ba, Sr) and $Na_2[Ni(OH)_4]$.[1472–1474]

The chemistry of oxo compounds of nickel(II) is very limited if the simple oxide NiO and the mixed-metal oxide Ba_3NiO_4 are excluded.[1475–1477] Dioxygen complexes of nickel(II) are not cited in a recent review article.[1478]

A number of alcohol adducts of nickel(II) of the type $[Ni(ROH)_6]X_2$ have been reported with a variety of simple alcohols.[1479–1481] The $Ni(ROH)_6(ClO_4)_2$ (R = Me, Et) complexes were prepared by dehydrating with dimethoxypropane $Ni(ClO_4)_2 \cdot 6H_2O$ dissolved in the appropriate alcohol. These complexes are reported to be extremely hygroscopic and must be handled in a dry atmosphere.

Tetrakisethanol complexes $NiX_2(EtOH)_4$ (X = Cl, Br) can be prepared by the dehydration with triethyl orthoformate of $NiX_2 \cdot 2H_2O$ in refluxing ethanol.[1482] Mono adducts of the type $NiCl_2(ROH)$ with a variety of primary alcohols (R = Me, Et, Bu^n, $n\text{-}C_6H_{13}$, $n\text{-}C_8H_{17}$) have been prepared by dissolving the anhydrous $NiCl_2$ in the appropriate alcohol.[1483] The analogous complexes with secondary and tertiary alcohols were prepared by dissolving $NiCl_2 \cdot MeOH$ in the appropriate alcohol. These compounds are, in general, deliquescent in saturated alcohol vapour and hygroscopic.

All of the complexes are six-coordinate high-spin. The complex $[NiBr(EtOH)_4]_2Br_2$ (**192**) has been found to be dinuclear.[1484]



(**192**)

Nickel(II) alkoxides have recently been reviewed[1485,1486] and we will report here a few examples of these complexes.

Alkoxides of nickel(II) are conveniently prepared according to equation (177) in anhydrous conditions.[1487,1488] All of these compounds are insoluble in the common organic solvents. Complexes with primary alkoxides are green and six-coordinated; complexes with secondary and tertiary alkoxides are tetrahedral with colours ranging from blue to violet. All of the complexes decompose at about 90–100 °C. The complexes with secondary and tertiary alkoxides undergo alcoholysis reactions when dissolved in primary alcohols. An interesting insertion reaction occurs when nickel alkoxide reacts with some isocyanates (equation 178).[1489]

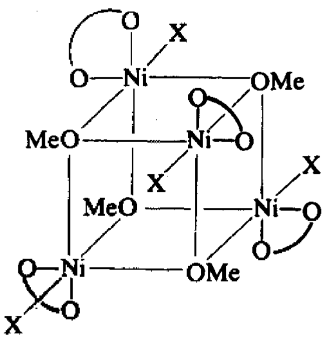
$$NiCl_2 + 2LiOR \xrightarrow{\text{dioxane}} Ni(OR)_2 + 2LiCl \qquad (177)$$
$$R = Me, Et, Pr^n, Pr^i, Bu^t, t\text{-}C_5H_{11}, t\text{-}C_6H_{13}$$

$$Ni(OR)_2 + nR'NCO \longrightarrow Ni(OR)_{2-n}\{N(R')CO_2R\}_n \qquad (178)$$
$$R = Me, Pr^i; R' = Ph, \text{naphthyl}$$

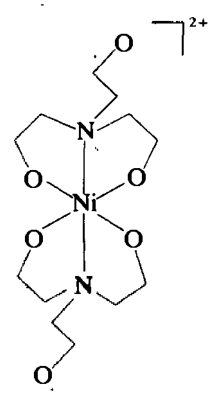
Mixed-ligand complexes of the type Ni(OR)L (L = deprotonated ancillary ligand) are formed when 1-amino-2-ethanol, β-diketones or carboxylic acids are reacted with bis-alkoxo complexes.[1490–1492]

KOH reacts with a boiling solution in MeOH of nickel(II) acetylacetonate giving the tetranuclear complex $[Ni_4(OMe)_4(acac)_4(MeOH)_4]$.[1493] In this compound, the four nickel atoms and the four methoxy oxygen atoms occupy the alternate corners of a distorted cube.[1494] Each oxygen of the methoxy groups bridges three nickel atoms which complete their six-coordination with an MeOH molecule and bidentate acetylacetonate (**193**). An analogous structure has been found in the tetramer $[Ni_4(OMe)_4(OC_6H_4CHO)_4(EtOH)_4]$.[1496]

A number of nickel(II) alkoxyhalides of the types Ni(OMe)X, $Ni_3(OMe)_5X$, $Ni_3(OMe)_4X_2$ (X = halides) and $Ni(OMe)Cl \cdot MeOH$ were prepared by reacting either NaOMe or LiOMe with anhydrous nickel halides in methanol.[1495] The structures of these complexes which exhibit ferromagnetic behaviour are thought to involve cubane-type clusters. Other complexes with miscellaneous ligands containing the OH function are collected in Table 76.



(193) O⌒O = acac; R = Me
O⌒O = salicylaldehydate; R = Et
X = −ROH



(194)

Table 76 Selected Nickel(II) Complexes with Ligands Containing the OH Function

Complex	*Ligand (L)*	*Remarks*	*Ref.*
NiX_2L_2	Triethanolamine	Oh; X = halides, NO_3* (**194**)	1497, 1498
NiX_2L	Triethanolamine	Oh; X = halides, NO_3	1497
$NiL_2(ClO_4)_2$	2-Amino-2-(hydroxymethyl)-1,3-propanediolo	Oh $[NiL]^{2+}$ and $[Ni(L^-)]^+$ species in solution	1499
$NiL_2(ClO_4)_2$*	4-Hydroxy-4-methylpentan-2-one (diacetone alcohol)	SqPl; ligand formed by the condensation of two molecules of acetone	1500
$NiL_2{\cdot}2H_2O$	Salicylaldehydate	Oh	1501, 1502
$NiL_2{\cdot}nH_2O$	Various 2-methoxyphenolates	Oh; $n = 0, 2, 3, 4$	1503
NiL_2py_2*	2-Methoxy-4-nitrophenolate	*trans* Oh; chelate ligand	1504
NiL_2B_2	Various 2-alkoxyphenolates	Oh; B = py, H_2O, $\frac{1}{2}$ tmd	1505
$NiL_2EtOH{\cdot}H_2O$	Various nitrosophenolates	Oh	1506
$NiL_4(ClO_4)_2{\cdot}H_2O$	8-Quinolinol *N*-oxide	Oh; monodentate ligand through OH group	1507

* Structures determined by X-ray analysis.

50.5.5.2 Complexes with ketones, aldehydes, ethers and related ligands

Monodentate ketones, aldehydes, ethers and esters are weakly coordinating ligands towards nickel(II) and in general the complexes can only be prepared using anhydrous reagents and solvents and with large counteranions.

A convenient and quite general synthetic route which allows the synthesis of hexasolvates of a number of ketones, esters, aldehydes, ethers and nitro compounds has been developed by Driessen and co-workers.[1507–1513] Most of the ketone (acetone, butanone, acetophenone, chloroacetone) and ester (methyl formate, ethyl acetate, diethyl malonate) complexes were prepared by stirring anhydrous $NiCl_2$ with either $FeCl_3$, $InCl_3$ or $SbSl_5$ with the appropriate ligand as solvent. In some cases a nitromethane solution of the ligand was employed (equations 179 and 180). The aldehyde (acetaldehyde, propionaldehyde, benzaldehyde and substituted benzaldehydes) and ether (tetrahydrofuran and dimethoxyethane) hexasolvates are conveniently prepared through a metathetical reaction of the appropriate aldehyde or ether with $Ni(MeNO_2)_6(SbCl_6)_2$[1512] in nitromethane solution. The synthesis of aldehyde adducts was carried out at low temperature (5 °C) in order to minimize polymerization of aldehydes. Solid compounds decomposed in a few days even if stored at 0 °C.[1514–1517]

$$NiCl_2 + 2InCl_3 \xrightarrow{Me_2CO} [Ni(MeCOMe)_6](InCl_4)_2 \quad (179)$$

$$NiCl_2 + 2SbCl_5 + 6MeCO_2Et \xrightarrow{NO_2Me} [Ni(MeCO_2Et)_6](SbCl_6)_2 \quad (180)$$

In general, all of the hexasolvates decompose rapidly when in contact with moisture. The formula and some spectroscopic properties of a number of representative complexes are reported in Table 77. All the complexes have been assigned a six-coordinate structure on the basis of electronic and IR spectra. The coordination of nickel(II) to the carbonyl oxygen is invariably indicated by the lowering of the CO stretching frequency compared with the frequency of the free ligand.

Table 77 Complexes with Ketones, Aldehydes and Ethers. Carbonyl Stretching Frequencies of Free and Coordinated Ligands. Ligand Field Parameters of the Complexes

Ligand	Complex	*ν(CO)* (cm^{-1}) (*Nujol mull*) Free ligand	Complex	*Ligand field parameters* (cm^{-1}) D_q	B'	Ref.
Acetone	$NiL_6(InCl_4)_2$	1718	1677	860	900	1508
Butanone	$NiL_6(InCl_4)_2$	1713	1655	820	890	1509
Phenylethanone	$NiL_6(InCl_4)_2$	1685	1621	810	840	1509
1-Chloro-2-propanone	$NiL_6(InCl_4)_2$	1730	1674	840	900	1509
Ethanal (acetaldehyde)	$NiL_6(InCl_4)_2$	1728	1670	945	890	1512
Propanal (propionaldehyde)	$NiL_6(InCl_4)_2$	1731	1672	940	900	1512
Benzaldehyde	$NiL_6(InCl_4)_2$	1701	1622	920	870	1512
Tetrahydrofuran	$NiL_6(SbCl_6)_2$	—	—	840	895	1514
Dimethoxyethane	$NiL_3(SbCl_6)_2$	—	—	860	895	1515
Methyl formate	$NiL_6(FeCl_4)_2$	1736	1641	880	915	1511
Ethyl acetate	$NiL_6(SbCl_6)_2$	1740	1652	800	910	1511
Ethyl malonate	$NiL_3(SbCl_6)_2$	1726	1682	910	900	1511

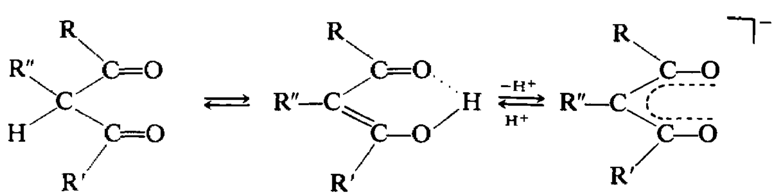
Other examples of nickel(II) complexes with coordinated acetone molecules[1518–1521] and ethers such as dimethoxyethane[1522,1523] and 1,3- and 1,4-dioxane[1524–1528] have been reported.

50.5.5.3 Complexes with β-diketones, tropolonates, catecholates, quinones and related ligands

(*i*) *Complexes with β-diketones*

Some articles review the coordination chemistry of β-diketones[1529,1530] and, specifically, isomerism[1531] and Lewis acid behaviour of the complexes.[1532] Amongst the carbon-bonded β-diketone complexes, those of nickel(II) have not been reported.[1533]

β-Diketones, by virtue of their keto–enol tautomerism (Scheme 21), are weak acids and in most cases bind nickel(II) in the deprotonated enol form, acting as uninegative chelating ligands.



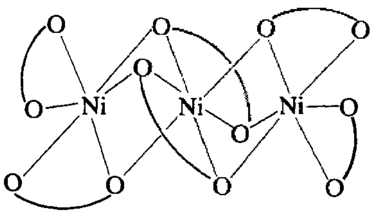
Keto ⇌ enol tautomerism

Scheme 21

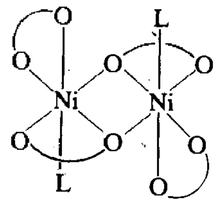
For a summary of the general methods of synthesis of β-diketonato complexes see ref. 1534. The archetype of β-diketones is acetylacetone (2,4-pentanedione; Scheme 21: R = R′ = Me; R″ = H). Nickel complexes with this ligand are very numerous and are the ones studied in most detail.

By the reaction of concentrated solutions of nickel acetate and Hacac in an ethanol–water mixture the bis-aqua adduct $[Ni(acac)_2(H_2O)_2]$ is obtained. An improved synthesis of the same compound has been devised starting from NiO(OH) which was reduced with Hacac at room temperature.[1549] The green anhydrous $Ni(acac)_2$ derivative is obtained by azeotropic distillation with toluene of the aqua complex or by its sublimation *in vacuo*.

Whereas $Ni(acac)_2(H_2O)_2$ has a mononuclear *trans* octahedral structure,[1536] the complex $Ni(acac)_2$ has been found to possess a trinuclear structure (**195**) in which NiO_6 octahedra share faces *via* bridging acac groups.[1534] A reddish brown compound having the same stoichiometry has been extracted from a solution of $Ni(acac)_2$ in CS_2. It is assumed that the former compound contains both square planar and octahedral species in a 1:3 ratio.[1550]



(195) O⌒O = acac



(196) O⌒O = acac; L = piperidine, isopropanol
O⌒O = tropolonate; L = H_2O

The trinuclear structure of $[Ni(acac)_2]_3$ persists in solutions of non-donor solvents even at elevated temperatures, but is broken down by coordinating solvents, such as H_2O, py, alcohols, and in general by the Lewis bases which give mono and bis adducts.[1551,1552]

Kinetic and thermodynamic studies on the nickel(II)/Hacac system have been carried out in water solution[1553–1555] and ^1H NMR studies have been carried out on the adducts of $Ni(acac)_2$ with a variety of Lewis bases.[1556–1559]

Ionic 1:3 complexes $[Ni(acac)_3](NBu^t_4)$[1560,1561] and $Ag[Ni(acac)_3]\cdot 2AgNO_3\cdot H_2O$[1562] have been synthesized. The structure of the six-coordinate anion $[Ni(acac)_3]^-$ has been determined in the former compound.

$Ni(acac)_2$ reacts with a variety of monodentate donors giving mono and bis adducts $Ni(acac)_2B_n$ ($n = 1, 2$; B = H_2O, primary and secondary amines, pyridine and substituted pyridines, pyridine *N*-oxide, alcohols, dioxane, substituted benzaldehydes).[1558,1563–1570] Details of the structures of some complexes are reported in Table 78. The chelate ring of the coordinated *β*-diketones is nearly planar, and, in the mononuclear complexes, the Ni—O bond distances (as well as the C—O and C—C bond distances within the chelate ring) are substantially similar. Two different dinuclear structures have been found in the two complexes $Ni_2(acac)_4B$ [B = py **(197)**,[1540,1571,1530] Ph_3AsO **(198)**[1542,1572]].

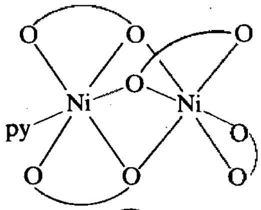
Table 78 Average Bond Distances within the Chelate Ring in Six-coordinate Complexes and in Square Planar Complexes with *β*-Diketones

Complex	Coordination geometry	Average bond distances (pm) Ni—O	C—O	C—C	Ref.
$[Ni(acac)_2]_3$ **(195)**	Oh	212 (bridging) 201 (terminal)	133	155	1535
$Ni(acac)_2(H_2O)_2$	*trans* Oh	202	127	141	1536
$Ni(acac)_2(py)_2$	*trans* Oh	202	124	140	1537
$Ni(acac)_2(4\text{-pic})_2$	*trans* Oh	202	128	138	1538
$Ni(acac)_2(PNO)_2$	*cis* Oh	202	128	137	1539
$Ni_2(acac)_4(pip)_2$ **(196)**	Oh dinuclear	212 (bridging) 204 (terminal)	—	—	1540
$Ni_2(acac)_4(Pr^iOH)_2$ **(196)**	Oh dinuclear	209 (bridging) 200 (terminal)	127	139	1541
$Ni_2(acac)_4py$ **(197)**	Oh dinuclear	207 (bridging) 200 (terminal)	—	—	1540
$Ni_2(acac)_4(Ph_3AsO)$ **(198)**	Oh dinuclear	208 (bridging) 198 (terminal)	127	137	1542
$[Ni(Hacac)_2Br_2]$	*trans* Oh	205	119	152	1543, 1544
$[Ni(Hacac)_2(H_2O)_2](ClO_4)_2$	*trans* Oh	203	121	151	1545
$Ni(acac)(Me)(PCy_3)$	SqPl	189	129	138	1546
$Ni(acac)(Et)(PPh_3)$	SqPl	191	129	138	1547
$Ni(DPM)_2$ **(199)**	SqPl	184	131	139	1548

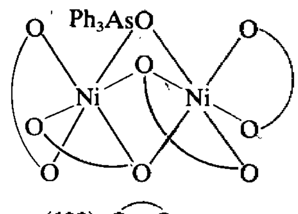
Abbreviations: 4-pic, 4-methylpyridine; PNO, pyridine *N*-oxide; pip, piperidine; Ph_3AsO, triphenylarsine oxide; DPM, 2,2,6,6-tetramethylheptane-3,5-dione.

$Ni(acac)_2$ does not react with PPh_3 in the absence of Et_2AlCl. With Et_2AlCl, on the other hand, the compound $Ni(acac)_2PPh_3$ is obtained, presumably through an unstable intermediate containing a nickel–ethyl linkage.[1570]

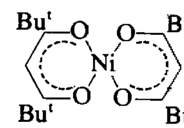
The IR spectra of free *β*-diketones show two intense bands below 2000 cm^{-1} which are attributable to the ν(C⎓O) and to the ν(C⎓C) stretch of the chelate ring in the enol form. Upon coordination these bands are shifted 100 cm^{-1} towards lower frequencies. Although the



(197) O⌒O = acac



(198) O⌒O = acac



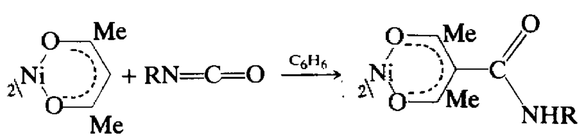
(199)

assignment of the two intense bands is a matter of debate, comparison with ^{18}O-labelled β-diketonato Cr^{III} complexes[1573] leads to assignment of the higher energy band found in the nickel complexes (*ca.* 1530–1590 cm^{-1}) as the ν(C⎓O) stretch, and the lower energy band (1460–1540 cm^{-1}) as the ν(C⎓C) stretch.

A few examples of complexes with acetylacetone in the neutral keto form have been reported.[1543–1545,1574] The complexes can generally be obtained by reacting HBr or $HClO_4$ with $Ni(acac)_2$ in anhydrous conditions using nitroethane, CH_2Cl_2 or acetic acid as solvent.

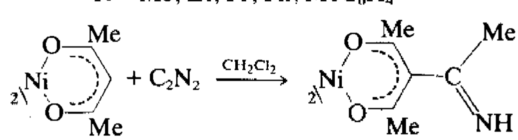
In the two octahedral complexes $[Ni(Hacac)_2Br_2]$[1543,1544] and $[Ni(Hacac)_2(H_2O)_2](ClO_4)_2$[1545] the neutral chelate ring is in a boat-folded configuration. The IR spectrum of $Ni(Hacac)_2Br_2$ shows a very strong C=O stretching absorption at 1693 cm^{-1}.

The methine hydrogens within the chelate ring of the $[Ni(acac)_2]_3$ complex were found to be reactive towards electrophiles. For example, alkyl and aryl isocyanates react with $Ni(acac)_2$ in C_6H_6 at refluxing temperature according to equation 181.[1575] The complexes are paramagnetic and presumably oligomeric. An insertion reaction also occurs with cyanogen (equation 182) to give a diamagnetic square planar complex.[1576]



(181)

R = Me, Et, Pr, Ph, MeC_6H_4



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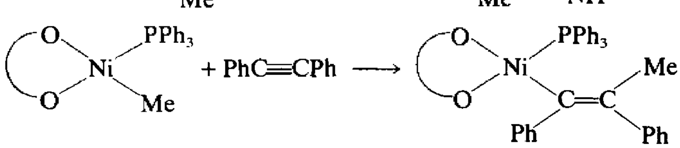
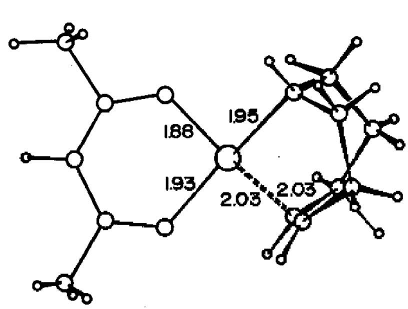


(183)

Recently, stable organometallic compounds derived from $Ni(acac)_2$ have been described. The square planar compounds $[Ni(acac)(PR_3)L]$ (R = Ph, Cy; L = Me, Et) were obtained by reacting $Ni(acac)_2$ and PR_3 in ether at $-20\,^{\circ}C$ with either diethyl- or dimethyl-aluminum monoethoxide.[1546,1547,1577] $[Ni(acac)(Me)PPh_3]$ reacts with diphenylacetylene at room temperature, according to equation (183).[1578]

The square planar complex Ni(Hacac)(cod) (**200**) is obtained from the reaction of $Ni(cod)_2$ with Hacac.[1579] The nickel atom is in a formal oxidation state +2 and is linked to the two oxygen atoms of acac, σ-bonded to a carbon atom and π-bonded to the residual double bond of the cyclooctenyl group.



(**200**) (reproduced from ref. 1579 with permission of the Royal Society of Chemistry)

β-Diketonates other than acetylacetonate also form complexes[1532] of formula Ni(β-diketonate)$_2$. By analogy to [Ni(acac)$_2$]$_3$, the paramagnetic complexes are assigned an oligomeric (presumably trinuclear) structure. In the case of bulky β-diketones (as for example 2,2,6,6-tetramethylheptane-3,5-dione or dipivaloylmethane, DPM, and either 3-alkyl- or 3-phenylpentane-2,4-dione) the steric hindrance of the substituents in the chelate ring may prevent the molecular association and stabilizes diamagnetic mononuclear square planar complexes (**199**; Table 78).[1548] Dibenzoylmethane gives both diamagnetic and paramagnetic isomers. Ni(β-diketonate)$_2$ complexes containing long-chain alkyl groups in the chelate rings (Scheme 21; R = R′ = *n*-heptyl, *n*-nonyl) show transition from a solid purple diamagnetic monomer to a liquid green paramagnetic oligomer at 17 (*n*-heptyl) and 42 °C (*n*-nonyl).[1580]

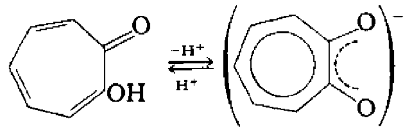
Both mononuclear and polynuclear Ni(β-diketonate)$_2$ complexes react with Lewis bases as Ni(acac)$_2$ complexes do, and their adducts have been investigated.[1563,1565,1569,1581–1584]

Metal complexes with fluoro-β-diketones have been comprehensively reviewed.[1585] The introduction of electron-withdrawing groups in the chelate ring increases the Lewis acidity strength of the ML$_2$ complexes, and consequently the bis adducts of the fluoro-β-diketonato complexes are more stable than the corresponding complexes with β-diketones. As an example of a nickel complex with 1,1,1-trifluoroacetylacetone which does not have a counterpart in the nickel acetylacetonate complexes we can mention the hexanuclear complex $Ni_6L_{10}(OH)_2(H_2O)_2$.[1586]

Some papers deal with specific aspects of the Ni(β-diketonate)$_2$ chemistry, as, for example, mass spectra,[1587,1588] CD spectra of adducts with amino acids and amino alcohols,[1589,1590] and photochemical reduction.[1591]

Finally, we must mention a number of reports concerning bis chelates, either mononuclear square planar or trinuclear octahedral, with anionic ligands which bear some resemblance to β-diketones, namely acetophenone,[1592] α-nitroketones,[1593,1594] hydroxymethylenecamphor and related ligands.[1595–1597]

Tropolone and its mononegative anion tropolonate roughly resemble β-diketonates when acting as chelate ligands (Scheme 22). However, the nickel(II) complexes with tropolonate are scarce. In general, very insoluble compounds are obtained. The structure of the complexes $Ni_2L_4(H_2O)_2$ (**196**); L = tropolonate anion)[1598] resembles that of $Ni_2(acac)_4(pip)_2$[1540] with both bridging and terminal chelate ligands.

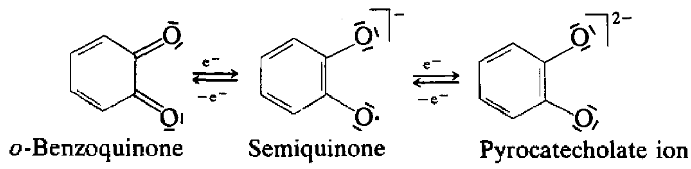


Scheme 22

A neutral complex NiL$_2$ has been reported with L = 5-isopropyltropolonate.[1599] The complex is paramagnetic in dilute solution as indicated by NMR measurements.

(*ii*) *Complexes with quinones, semiquinones and pyrocatechols*

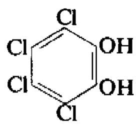
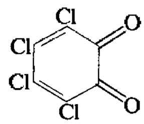
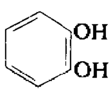
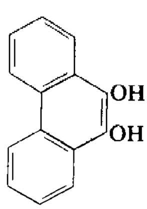
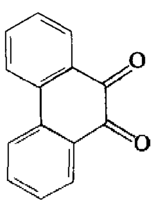
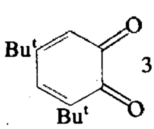
The redox properties of the quinone–pyrocatecholate system are shown in Scheme 23. If the species NiL_2^{2+}, NiL$_2$ and NiL_2^{2-} are taken into account, they can be assumed to contain nickel(II) ion and coordinated neutral benzoquinone, mononegative semiquinone and dinegative pyrocatecholate, respectively.



Scheme 23

Owing to the reactivity of 1,2-benzoquinone and pyrocatechol towards polymerization and oxidation, the most detailed and reliable investigations concern the chloro, alkyl and aryl derivatives of the ligands. Selected examples of nickel(II) complexes with quinone–pyrocatecholate ligands are shown in Table 79.

Table 79 Nickel(II) Complexes with Quinone–Pyrocathecol-derived Ligands

Ligand		*Formula*	μ_{eff} (*r.t.*) (BM)	*Ref.*
	Tetrachloropyrocatechol	$[Ni(C_6Cl_4O_2)_2](NPr^n_4)_2$	0	1600
		$[Ni(C_6Cl_4O_2)_2](NPr^n_4)_2$	3.80	1600
	Tetrachloro-*o*-benzoquinone	$[Ni(C_6Cl_4O_2)_2]$	3.49	1600
	Catechol	$[Ni(C_6H_4O_2)_2](NPr^n_4)_2$	0	1600
		$[Ni(C_6H_4O_2)_2]$	2.70	1600
	Phenanthrene-9,10-diol	$[Ni(C_{14}H_8O_2)_2](NPr^n_4)_2$	0	1600
	Phenanthrenequinone	$[Ni(C_{14}H_8O_2)_2]$		1601
		$[Ni_4(C_{14}H_8O_2)_8]$	3.16	1602
		$[Ni(C_{14}H_8O_2)_2py_2]\cdot py$	4.20	1601, 1602
		$[Ni(C_{14}H_8O_2)_2Br_2]$	3.22	1603
	3,5-Di-*t*-butyl-*o*-quinone	$[Ni\{Bu^t_2C_6H_2O_2\}_2]$	3.92	1600
		$[Ni\{Bu^t_2C_6H_2O_2\}_2(bipy)]$	4.30	1602
		$[Ni_4\{Bu^t_2C_6H_2O_2\}_8]$	4.35	1602

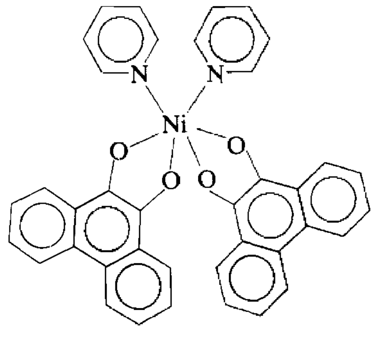
$Ni(phenanthrenequinone)_2Br_2$ is the only complex which seems to contain the neutral ligand coordinated to nickel(II).[1603] The complex has been synthesized by reacting $NiBr_2$ and the quinone in methanol–acetic acid solution.

Complexes of general formula $NiL_2(NPr^n_4)_2$ have been obtained by the reaction in ethanol–water mixture of the diol ligand and nickel(II) acetate in alkaline media (tetra-*n*-propylammonium hydroxide or ammonia).[1600]

The neutral complexes NiL_2 or NiL_2B_2 (B = py or $\frac{1}{2}$bipy) have been conveniently synthesized by reacting the quinone ligand and $Ni(CO)_4$ in apolar solvents (*n*-pentane, *n*-hexane, benzene).[1600,1601] The use of anaerobic conditions gives the best results. In one case, that of $Ni(C_6H_4O_2)_2$, the complex was obtained by the peroxodisulfate oxidation of an aqueous solution of nickel(II) acetate and pyrocatechol.

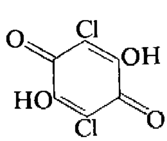
By reacting together $Ni(C_6Cl_4O_2)_2^{2+}$ and $Ni(C_6Cl_4O_2)_2$ in CH_2Cl_2 solution the $Ni(C_6Cl_4O_2)_2^+$ cation is isolated, which seems to contain the ligand in an apparently intermediate oxidation state.[1600]

The neutral complex $NiL_2py_2\cdot py$ (**201**; L = 9,10-phenanthrenequinone in the mononegative semiquinone form) has a *cis* octahedral structure.[1602] The magnetic moment of the complex (4.20 BM) has been attributed to the sum of one $S = 1$ and two $S = \frac{1}{2}$ non-interacting spin systems which allowed the description of the complex as a nickel(II)–semiquinone system. The same holds for other neutral complexes of the types NiL_2 and $NiL_2(bipy)$, as confirmed by IR evidence. For example, the $\nu(CO)$ vibration of the free phenanthrenequinone at 1675 cm^{-1} is shifted upon coordination to 1440 cm^{-1} in the NiL_2 complex. These data can be compared with the 50 cm^{-1} shift of $\nu(CO)$ found in the NiL_2Br_2 derivative (L = neutral phenanthrenequinone; μ_{eff} = 3.22 BM) with respect to the free ligand molecule. The structure of the paramagnetic NiL_2 complexes is presumably polynuclear with bridging ligands and six-coordinate nickel(II) ions. The NiL_2^{2-} complexes are diamagnetic and square planar with the nickel(II) ions coondinated to the ligand in the form of a dinegative catecholate ion.



(201) Ni—O (av) 206 pm
Ni—N (av) 208 pm

A homologous series of nickel(II) complexes with the general formula $Ni_2L(tren)_2(BPh_4)_2$ has been prepared with the dianionic ligands L which arise from the deprotonation of the neutral molecules **(202)**–**(207)**.[1604–1606] All of these complexes are assumed to exhibit the same dinuclear structure **(208)** as found in the complex with L = chloroanilate **(202)**.[1604]



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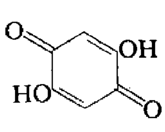

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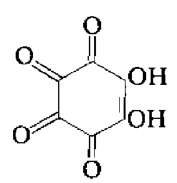

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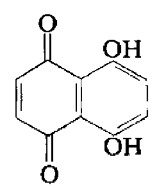

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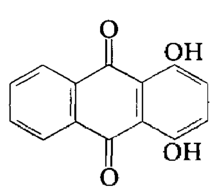

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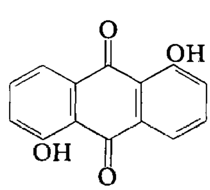

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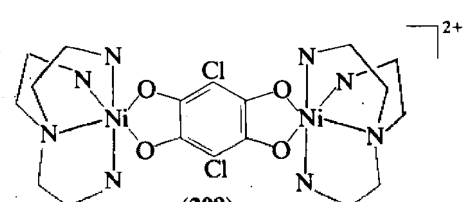


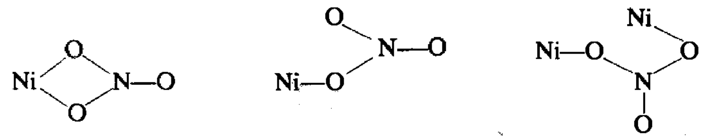
(208)

Other complexes of nickel with a number of chelate ligands of the quinone series are given in refs. 1605–1608.

50.5.5.4 Complexes with oxoanions as ligands

(i) Nitrato and nitrito complexes

Extensive reviews dealing with the various aspects of nitrate ion coordination are available.[1609–1611] Nickel(II) complexes containing coordinated nitrate groups are very numerous; with the exception of the tetranitrate $(R_4As)_2[Ni(NO_3)_4]$ and anhydrous $Ni(NO_3)_3$, they contain a variety of ancillary ligands. The bonding modes of the nitrato group found in nickel(II) complexes are summarized in Figure 24. Selected examples of nickel(II) complexes with coordinated NO_3 groups are reported in Table 80.



(I) Chelating (II) Monodentate (III) Bridging

Figure 24 Bonding modes of nitrate in nickel(II) complexes

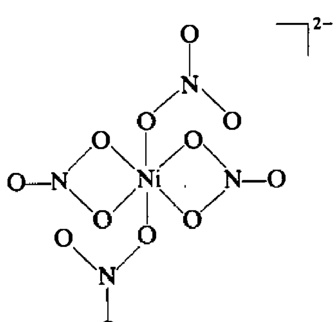
Table 80 Nickel(II) Complexes Containing Coordinated NO_3^-

Complex[a]	*Coordination geometry or number*	*Bonding mode of* NO_3^-	*Ref.*
$(Ph_4As)_2[Ni(NO_3)_4]$* (**209**)	Oh	Monodentate + chelating	1613
$[Ni(NO_3)_2(H_2O)_4]$* (**210**)	Oh	Monodentate	1614
$[Ni(NO_3)_2(H_2O)_2]$*	Oh	Bridging	1615
$[Ni(NO_3)_2(H_2O)_2py_2]$*	Oh	Monodentate	1616
$[Ni(NO_3)(OS_2N_2cpd)]NO_3$*	Oh	Monodentate	1617
$[Ni(NO_3)_2(Me_4pda)]$* (**211**)	Oh	Chelating	1618
$[Ni(NO_3)_2(tmim)_2]$*	Oh	Chelating	1619
$[Ni(NO_3)_2(dapa)]$* (**212**)	Oh	Monodentate + chelating	1620
$[Ni(NO_3)(aquin)]NO_3$*	Oh	Chelating	1621
$[Ni(NO_3)(atsc)_2]NO_3$*	Oh	Chelating	1622
$[Ni(NO_3)_2(en)_2]$	Oh	Monodentate	1623
$[Ni(NO_3)(en)_2]ClO_4$	Oh	Chelating	1623
$[Ni(NO_3)_2(2\text{-pic})_2]$	Oh	Chelating	1624
$[Ni(NO_3)_2(quin)_2]$	Oh	Chelating	1624
$[Ni(NO_3)_2(Me_4tmd)]$	Oh	Chelating	1625
$[Ni(NO_3)_2(Me_4en)]$	Oh	Chelating	1625
$[Ni(NO_3)(Me_6tren)]NO_3$	TBPy	Monodentate	1626
$[Ni(NO_3)_2(PEt_3)_2]$	Oh	Chelating	1627
$[Ni(NO_3)(QP)]ClO_4$	SqPy	Monodentate	1628
$[Ni(NO_3)_2(Ph_3PO)_2]$	Oh	Chelating	1629
$[Ni(NO_3)_2(PNO)_2]$	Oh	Chelating	1630
$[Ni(NO_3)_2(2\text{-PICNO})_2]$	5	Monodentate + chelating	1631
$[Ni(NO_3)(2\text{-PICNO})_4]NO_3$	5	Monodentate + ionic	1631
$[Ni(NO_3)_2(dpye)_2]$	Oh	Chelating	1632
$[Ni(NO_3)_2(4,4'\text{-bipy})_2]$	Oh	Monodentate	1633

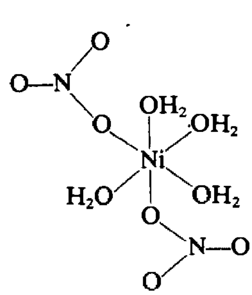
* Structures determined by X-ray analysis.
[a] All of the complexes are high-spin, except the diamagnetic $[Ni(NO_3)QP]ClO_4$ derivative.
Abbreviations: OS_2N_2cpd, 1-oxa-7,10-diaza-4,13-dithiacyclopentadecane; Me_4pda, *N,N,N',N'*-tetramethyl-*o*-phenylenediamine; tmim, 2-methylthio-3-methylimidazole; dapa, 2,6-diacetylpyridinebis(anilimine); aquin, 8-amino-2-methylquinoline; atsc, acetone thiosemicarbazone; 2-PICNO, 2-methylpyridine *N*-oxide; dpye, 1,2-dipyridylethylene; Me_4tmd, 1,3-bis(dimethylamino)propane.

The $(MePh_3As)_2[Ni(NO_3)_4]$ complex has been prepared by means of the metathetical reaction (184) in anhydrous MeCN solution.[1612] The structure of the $[Ni(NO_3)_4]^{2-}$ anion (**209**) consists of NiO_6 octahedra formed by two bidentate and two monodentate nitrato groups.[1613] The anhydrous $Ni(NO_3)_2$ can be prepared by dehydrating the hydrated salt with N_2O_5 in HNO_3 solution.[1634]

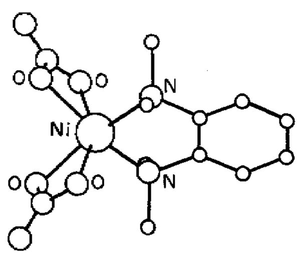
$$NiCl_2 + 2Ph_3MeAsI + 4AgNO_3 \xrightarrow{MeCN} (Ph_3MeAs)_2[Ni(NO_3)_4] + 4AgX \qquad (184)$$



(**209**)



(**210**)



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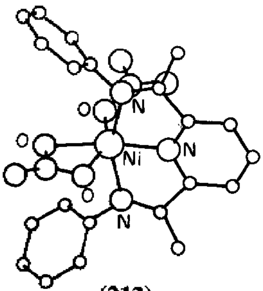


(212)

Special techniques are needed in order to obtain the aquanitrato complexes $[Ni(NO_3)_2(H_2O)_n]$. The tetrahydrate **(210)** is prepared by dehydration of the hexahydrate with liquid N_2O_4,[1614,1635] while the dihydrate is prepared by reacting anhydrous $NiCl_2$ with HNO_3.[1636] In the latter complex the six-coordination is achieved through bridging (type III) nitrato groups.[1615]

Mixed-ligand nitrato complexes are generally prepared by reacting hydrated nickel(II) nitrate with the appropriate ligand in common organic solvents. The majority of the complexes whose molecular structures have been determined by X-ray analysis contain NO_3 groups coordinated as chelate (type I) in a nearly symmetrical fashion. In all of these complexes the NO_3 group is planar with inequivalent N—O bonds and O—N—O angles. Owing to the short 'bite' of the NO_3^- ligand acting as chelate, the O—Ni—O angle is reduced to about 60° and the bidentate NO_2 group can be viewed as occupying only one coordination site.

In Table 81 the fundamental IR absorption bands of some representative nitrato complexes and of ionic nitrate are reported.

Table 81 Infrared Absorption Frequencies of the Nitrate Group in Nickel(II) Complexes

Complex	*Bonding mode of NO_3^-*	*IR absorption frequencies*[a] ν_2 (cm^{-1})	ν_3 (cm^{-1})	ν_4 (cm^{-1})	*Ref.*
$[Ni(NO_3)_2(H_2O)_4]$	Monodentate	815	1320, 1495s	760	1635
$[Ni(en)_3](NO_3)_2$	Ionic	823	1368 vs	704	1623
$[Ni(NO_3)_2(en)_2]$	Monodentate	818	1305, 1420s	708, 728	1623
$[Ni(NO_3)(en)_2]ClO_4$	Chelating	809	1290, 1476s	695, 746	1623
$[Ni(NO_3)_2(Me_4en)]$	Chelating	808	1540, 1510 1280, 1260s		1625

[a] Nujol mull.

The coordination chemistry of nitrite ion has recently been very extensively reviewed.[1637] The bonding modes of nitrite ion found in nickel(II) complexes are summarized in Figure 25 and selected nickel(II) complexes containing coordinated nitrite ions are shown in Table 82.

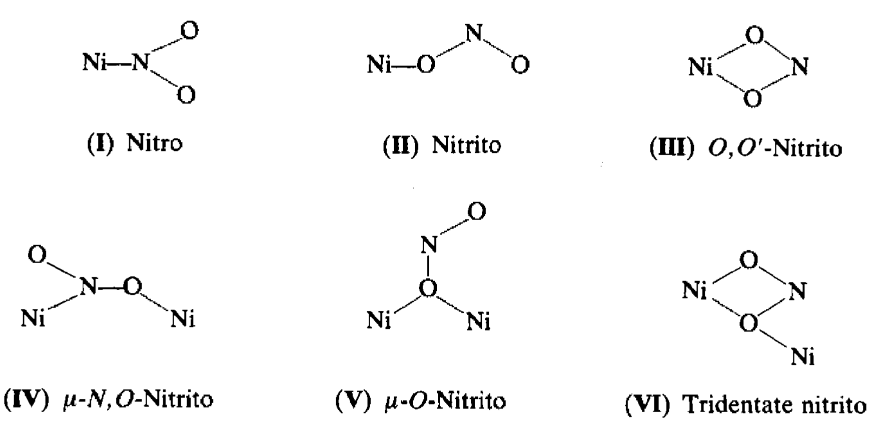


Figure 25 Bonding modes of nitrite in nickel(II) complexes

Table 82 Structural Data for Representative Nickel(II) Complexes Containing Coordinated Nitrite

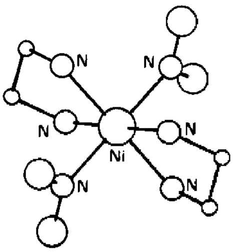
Complex	*Bond distance* (pm) *Ni—L*[a]	*N—O*	*Bond angle* (°) *O—N—O*	*Remarks*	*Ref.*
$K_2Ba[Ni(NO_2)_6]$	208	125	117	Monodentate nitro groups	1638
$K_2Pb[Ni(NO_2)_6]$	208	124	117	Monodentate nitro groups	1639
$K_2Sr[Ni(NO_2)_6]$	208	125	116	Monodentate nitro groups	1640
$[Ni(NO_2)_2(NH_3)_4]$	215	124	117	*trans* monodentate nitro groups	1641
$[Ni(NO_2)_2(en)_2]$ (**213**)	213	124	117	*trans* monodentate nitro groups	1642
$[Ni(NO_2)_2(N,N'\text{-}Me_2en)_2]\cdot H_2O$	212	124	117	*trans* monodentate nitro groups	1642
$[Ni(NO_2)(H_2O)(N,N\text{-}Me_2en)_2]ClO_4$	212	122	116	*cis* monodentate nitro group	1643
$[Ni(ONO)_2(N,N\text{-}Me_2en)_2]$ (**214**)	211	129, 122	115	*trans* monodentate nitrito groups	1642
$[Ni(ONO)_2(py)_4]\cdot 2py$[b]	205	105, 126	123	*trans* monodentate nitrito groups	1644
$[Ni(ONO)_2(4\text{-pic})_4]$[b]	209	119, 122	114	*trans* monodentate nitrito groups	1644
$[Ni(ONO)_2(2\text{-Meim})_4]$[b]	205	111, 117	123	*trans* monodentate nitrito groups	1645
	228	124, 126	117		
$[Ni(O_2N)(m\text{-stien})_2]Cl$	214	125	110	Chelating *O,O'*-nitrito group	1646
$[Ni(O_2N)_2(Me_4en)]$ (**215**)	207, 214	126	112	Chelating *O,O'*-nitrito group	1647, 16
	206, 211	126	112		
$[Ni(O_2N)_2(quin)_2]$	210, 214	125	113	Chelating *O,O'*-nitrito group	1649
	207, 212	128, 125	112		
$[Ni(O_2N)(N,N'\text{-}Et_2en)_2]BF_4$	210, 212	126	112	Chelating *O,O'*-nitrito group	1650
$[Ni(O_2N)(2\text{-Meim})_4]NO_3\cdot 0.5MeOH$	215, 218	127, 125	111	Chelating *O,O'*-nitrito group	1645
$[Ni(O_2N)(bipy)_2]NO_3$	213, 211	124, 126	114	Chelating *O,O'*-nitrito group	1651
$[Ni(NO_2)(en)_2]ClO_4$	218 (O), 217 (N)	125, 122	112	Bridging *O,N*-nitrito group; polynuclear structure	1648,16

[a] Bond distances from the nickel atom to either the N or an O atom of NO_2^-. Average values are usually given. When two values are given they refer non-equivalent bonds.
[b] Disordered NO_2^- groups.
Abbreviations: *N,N'*-Me$_2$en, 1,2-bis(methylamino)ethane; *N,N*-Me$_2$en, *N,N*-dimethyl(ethane-1,2-diamine); *m*-stien, 1,2-diphenylethane-1,2-di *N,N'*-Et$_2$en, 1,2-bis(ethylamino)ethane; 2-Meim, 2-methylimidazole.

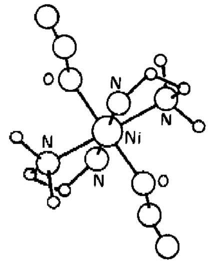
The reaction of a concentrated aqueous solution of $NiBr_2$ with a saturated aqueous solution of KNO_2 in excess of the stoichiometric ratio affords the orange-brown hexanitronickelate(II) $K_4Ni(NO_2)_6\cdot H_2O$.[1653] The structure of the $Ni(NO_2)_6^{4-}$ anion which is also present in the compounds $K_2M[Ni(NO_2)_6]$ (M = Ba, Sr, Pb)[1638,1639,1653] is octahedral with the six NO_2^- anions N-bonded to nickel.[1638–1640] The anhydrous $K_4Ni(NO_2)_4(ONO)_2$ complex, obtained by heating the monohydrate at 100 °C for several hours, contains both nitro and nitrito groups bound to nickel.[1653] The pentanitritonickelate $Cs_3[Ni(NO_2)_5]$ was obtained by the reaction in water of $Ni(NO_2)_2$ and $CsNO_2$ in 1:3 molar ratio and the trinitritonickelate $Me_4N[Ni(NO_2)_3]$ was obtained in the presence of a large excess of $(Me_4N)NO_2$.

Far more numerous are the complexes of nickel(II) which contain a variety of either aliphatic or aromatic amines and coordinated nitrite (Table 82). Most of these complexes are prepared by the reaction of the amine in methanolic solution with a methanolic solution of nickel nitrite prepared metathetically from hydrated nickel nitrate and sodium nitrite.[1654–1659]

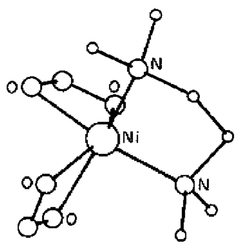
All of the complexes are six-coordinate high-spin. A *trans* octahedral structure has been found, for example, in the two complexes $[Ni(NO_2)_2(NH_3)_4]$[1641] and $[Ni(NO_2)_2(en)_2]$ (**213**).[1642] This type of coordination is usually found in complexes where the ancillary ligands do not exert much interligand repulsion. On the other hand, when some steric repulsion is present in the amine ligands O-bonded nitrito coordination usually occurs, as exemplified by the complex $[Ni(ONO)_2(N,N\text{-}Me_2en)_2]$ (**214**).[1642]



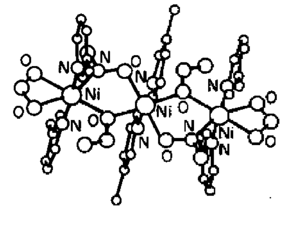
(**213**)



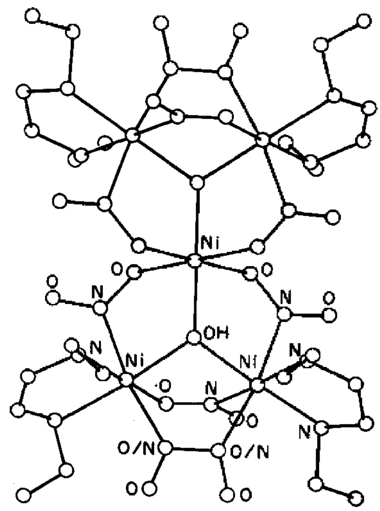
(**214**)



(**215**)



(**216**)

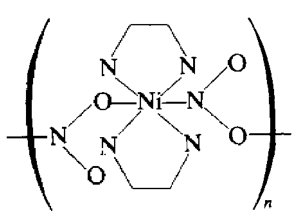


(217) (reproduced from ref. 1662 by permission from *Australian Journal of Chemistry*)

Type III chelating nitrito groups were unequivocally ascertained in a number of nickel complexes, for example $[Ni(O_2N)_2(Me_4en)]$ **(215)**.[1645–1651,1660] The coordination of the chelate NO_2^- groups is approximately symmetrical in the latter complex. Bridging N,O- and O-nitrito groups give rise to oligomers of the type $[Ni_2(NO_2)_4(4pic)_4]{\cdot}2C_6H_6$, $[Ni_3(NO_2)_6(3pic)_6]{\cdot}C_6H_6$ **(216)**,[1661] $[Ni_5(NO_2)_8(OH)_2(diamine)_4]$ **(217)** (diamine = en, *N*-Meen, *N*-Eten, *N,N'*-Et_2en, *N,N'*-Me_2en, *N,N*-Me_2en).[1662]

A chain polynuclear structure with O,N-bridging groups was found in the series of complexes $[Ni(NO_2)(en)_2]Y$ **(218)** ($Y = ClO_4$, BF_4, I_3)[1648,1652,1663] and strong antiferromagnetic intrachain coupling was measured in the two complexes with $Y = ClO_4$ and I_3.[1652]

The type VI tridentate bonding mode of nitrite has been found so far only in the complex $[Ni_2(NO_2)_2(en)_4](BPh_4)_2$ **(219)**.[1664]



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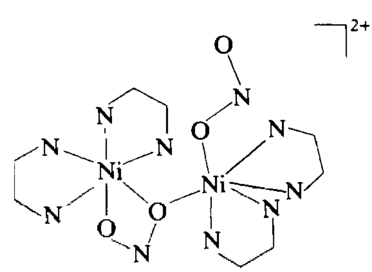


(219)

For details of the electronic specta of nickel complexes containing coordinated NO_2 groups see refs. 1643–1646, 1655, 1656 and 1665–1670. In the absence of X-ray crystal structure determinations, IR and, to a lesser extent, electronic spectroscopies were employed to infer the coordination mode of nitrite in its nickel complexes. It has often been found that the nickel complexes containing N-bonded nitrite, whether monodentate or bridging, are pink, yellow or red, while those containing nitrito groups, either monodentate or chelating, are blue or blue-green. In Table 83 the absorption frequencies of the nitrite ligand in some representative complexes are reported and compared with the free anion.

The six-coordinate nickel(II) complex $[Ni(N_2O_3)_3]_3[Co(NH_3)_6]_4{\cdot}3H_2O$ contains the trioxodinitrato ion $N_2O_3^{2-}$ coordinated as chelate. The complex is thermally and photochemically unstable. It was prepared under N_2 at 0 °C from $NiCl_2{\cdot}6H_2O$, $Co(NH_3)_6Cl_3$ and $Na_2N_2O_3$ in aqueous solution.[1675]

Table 83 IR Absorption Frequencies of NO_2^- Coordinated in Different Ways

Compound	Coordination mode	IR absorption frequencies ν_{as} (cm^{-1})	ν_s (cm^{-1})	$\delta(NO_2)$ (cm^{-1})	Ref.
$NaNO_2$	Ionic	1250	1335	830	1671
$K_2CaNi(NO_2)_6$	N-bonded	1355	1325	834	1672
$[Ni(NO_2)_2(NH_3)_4]$	N-bonded	1357	1303	—	1673
$[Ni(NO_2)_2(en)_2]$	N-bonded	1368	1302	—	1673
$[Ni(ONO)_2(N,N\text{-}Me_2en)_2]$	O-bonded	1387	1130	817	1655
$[Ni(ONO)_2py_4]$	O-bonded	1393	1114	825	1655, 1669
$[Ni(O_2N)_2(Me_4en)]$	Chelating	1200[a]	1289[a]	863	1637, 1660
$(Me_4N)[Ni(NO_2)_3]$	N,O-bridging	1435	1202	852	1653
$[Ni_3(NO_2)_6(3\text{-pic})_6]\cdot C_6H_6$ (**216**)	O-bridging	1460	1019	—	1674

[a] This assignment seems more plausible for the majority of the authors (see ref. 1637). ν_{as} and ν_s are reversed in ref. 1660.

(ii) *Perchlorato, sulfato, selenato and anionic organophosphorus complexes*

Even if the ClO_4^- ion is commonly believed to experience a scarce tendency to act as a ligand, nonetheless coordination of perchlorate as a monodentate ligand through an oxygen atom has been proposed in a number of nickel complexes containing alkylamines,[1676] pyridine and substituted pyridines,[1677–1680] arylamines such as aniline and substituted anilines,[1681] phosphine and arsine oxides[1682,1683] (Table 84).

Table 84 Infrared Absorption Frequencies of some Perchlorato Complexes

Complex	IR absorption frequencies (Nujol mull) (cm^{-1})	Ref.
$[Ni(H_2O)_6](ClO_4)_2$	1190–1030sb,[c] 930w[c]	1684
$[Ni(ClO_4)_2(H_2O)_2]$	1135s, 1035s, 937m	1684
$[Ni(ClO_4)(Ph_3PO)_4]ClO_4$[a]	1090sb	1682
$[Ni(ClO_4)(Ph_3AsO)_4]ClO_4$[a]	1090sb	1682
$[Ni(ClO_4)(Ph_2MePO)_4]ClO_4$	1139s, 1088s,[c] 1035m	1683
$[Ni(ClO_4)(Ph_2MeAsO)_4]ClO_4$	1137s, 1092s,[c] 1045m	1683
$[Ni(ClO_4)_2(N,N'\text{-}Me_2en)_2]$	1122s, 1040s, 940s	1676
$[Ni(ClO_4)_2(N,N,N'\text{-}Me_3tmd)_2]$[b]	1170s, 1125s, 1038s, 925s, 635, 623, 617m	1676
$[Ni(ClO_4)_2(MeCN)_2]$[b]	1195, 1106, 1000s, 950m, 920m	1685
$[Ni(ClO_4)_2(MeCN)_4]$	1135s, 1012s, 945s, 912s	1685
$[Ni(ClO_4)_2(py)_4]$	1130s, 1030s, 932s, 628m, 614m	1677, 1678
$[Ni(ClO_4)_2(anil)_4]$	1129s, 1009s, 900s, 633m, 613m	1681

[a] Supposed coordinated monodentate ClO_4^-.
[b] Supposed chelate ClO_4^-.
[c] Band associated with ionic ClO_4^-.

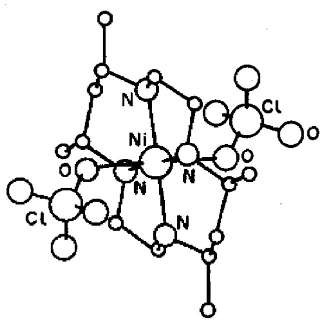
Most of the complexes were conveniently prepared by the reaction in ethanol of the appropriate ligand with hydrated nickel perchlorate which had sometimes been dehydrated previously by stirring it with an excess of 2,2-dimethoxypropane or triethyl orthoformate. It must be remembered that transition metal perchlorate complexes with amines are potentially hazardous and can explode even under mild conditions. Safety precautions must be used in preparations! $Ni(ClO_4)_2(H_2O)_2$ has been prepared by carefully heating the hexahydrate under vacuum at about 100 °C.[1684]

The two complexes $[Ni(ClO_4)_2(Me_4Cyclam)]$[1686] ($Me_4$Cyclam is 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradecane) (**220**) and $[Ni(ClO_4)_2(Me_2py)_4]$[1687] (Me_2py is 3,5-dimethylpyridine) (**221**) are *trans* octahedral with the perchlorate groups strongly bonded as monodentate in the axial positions.

In the absence of X-ray structural determinations, IR spectroscopy has been extensively used to determine the nature, either ionic or coordinated, of the perchlorato groups.

Actually, most of the nickel complexes which are assumed to contain coordinated ClO_4^- show two very strong and well-resolved peaks between 1000 and 1200 cm^{-1} and a strong band around 900 cm^{-1} (Table 84). In some cases the splitting of the medium band near 600 cm^{-1} has also been found.

There are few reports on nickel(II) coordinated to sulfate and selenate species.[1688]



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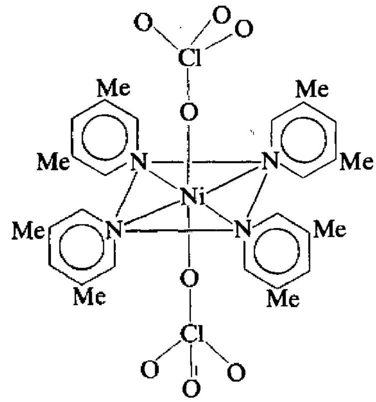
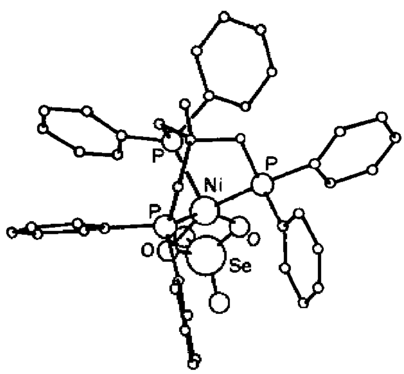


(221)

(221)	Ni—O	219 pm
	Cl—O	124–145 pm
	O—Cl—O	102–109°

$[Ni(SO_4)(triphos)]$ and $[Ni(SeO_4)(triphos)]$ (**222**) were obtained by the reaction of the hydrated nickel salts with the ligand triphos in MeOH–EtOH mixture (see Section 50.5.4.6.i). The SeO_4^{2-} group is symmetrically bonded as a chelate in the five-coordinate high-spin nickel(II) complex, and the same is assumed to occur in the sulfato complex.[1689] Distortions from T_d symmetry in the SeO_4 group are large and irregular and may be caused by the large size of the selenium atom.



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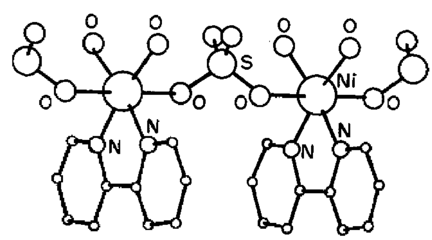
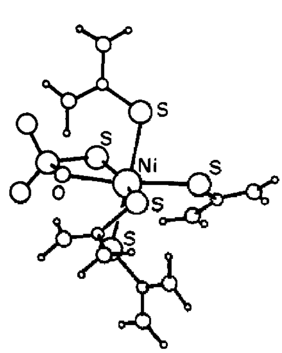


(223)

$[Ni(SO_4)(bipy)(H_2O)_2]$ (**223**) has a chain structure with a bridging sulfato group in the axial position of a distorted octahedron.[1690] The sulfato group is nearly regular. Bridging sulfato groups are assumed to occur in the polynuclear complex $[Ni(SO_4)(Ph_3PO)_2]$ whereas terminal bidentate sulfato groups are assigned to the dinuclear complex $Ni(SO_4)L_2$ with bridging 2,6-lutidine N-oxide.[1691]

A thiosulfate group coordinated as a chelate has been found in the complex $[Ni(S_2O_3)(thiourea)_4]H_2O$ (**224**).[1692] Actually, the Ni—$S(S_2O_3)$ bond distance is significantly longer than the Ni—S bonds usually found in six-coordinate nickel(II) and consequently the nickel coordination can be viewed as an intermediate one between octahedral and square pyramidal.



(224)

Hydrogen sulfite and alkyl sulfite groups are reported to coordinate through the sulfur atom in some diamagnetic nickel(II) complexes with tripod-like ligands (see also Section 50.5.4.6.ii). The hydrogen sulfite anion, HSO_3^-, is presumably coordinated through the oxygen atom in $Ni(HSO_3)_2L_2$ (L = benzene-1,2-diamine), which is unstable and decomposes in hot water with evolution of SO_2.[1693]

Sodium sulfinate $Na(RSO_2)$ (R = Ph, MeC_6H_4) reacts with hydrated nickel(II) salts giving $Ni(RSO_2)_2(H_2O)_2$ with chelating sulfinato groups ($\nu(SO_2)$, 972, 949 cm^{-1}).[1694] The latter compound further reacts with pyridine affording the bis adduct $Ni(RSO_2)_2py_2$.[1695] The sulfinato complex $[Ni(RSO_2)_2(bipy)_2]$ (R = MeC_6H_4) has been obtained as two isomers which involve linkage isomerism between either O- or S-bonded unidentate sulfinate anions.[1696] In the case of S-bonded sulfinato, $\nu_{as}(SO_2)$ stretch occurs at 1219 and 1204 cm^{-1} and $\nu_s(SO_2)$ stretch at 1035 and 1013 cm^{-1}. In the case of O-bonded sulfinato the corresponding frequencies are at 1055 $[\nu_{as}(SO_2)]$ and 958 and 943 cm^{-1} $[\nu_s(SO_2)]$.

In the benzeneseleninato complexes $[Ni(XC_6H_4SeO_2)_2(H_2O)_2]$ (X = H, *p*-Cl, *p*-Me, *p*-NO_2) two strong IR frequencies in the range 680–790 cm^{-1} were assigned to the two ν(SeO) stretch vibrations of the $RSeO_2^-$ groups acting as O,O′ chelate.[1697] In the corresponding complexes with bipy and phen as coligands $[Ni(XC_6H_4SeO_2)_2L_2]$ a strong ν(SeO) IR absorption in the range 815–890 cm^{-1} is assumed to be indicative of a monodentate O-bonded $RSeO_2^-$ group.[1698]

With methanesulfonate ligands, a number of nickel(II) complexes of the types $Ni(MeSO_3)_2$,[1699] $Ni(CF_3SO_3)_2$[1700] and $Ni(RSO_3)_2py_4$[1701,1702] (R = Me, CF_3) have been reported.

Nickel(II) complexes containing coordinated phosphates, phosphites and diphosphates have been little studied in the solid state even though oxoanions of phosphorus are well known to cordinate nickel(II) in solution. Examples of compounds characterized in the solid state are $Ni_3(PO_4)_2{\cdot}8H_2O$,[1703,1704] $Ni(O_2PCl_2)_2{\cdot}2POCl_3$,[1705] $Ni(H_2PO_2)_2{\cdot}6H_2O$[1706] and $Ni(H_2PO_2)_2py_2$.[1706]

More numerous by far are the nickel complexes with organophosphorus oxoanions such as phosphate and phosphite esters $(RO)_2PO_2^-$ and $(RO)_2PO^-$, phosphonates $(RO)R'PO_2^-$, phosphinates $R_2PO_2^-$ and phosphinites R_2PO^-.[1707]

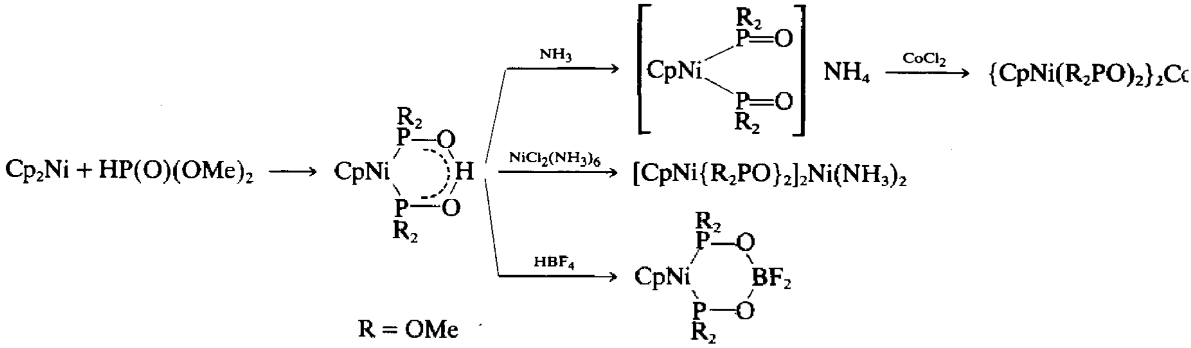
The reaction of trimethyl phosphate, $(MeO)_3PO$, with $NiBr_2$ results in the neutral bis-dimethoxyphosphato complex by elimination of one methyl group from the neutral phosphoric esters (equation 185).[1708] But when nickel halides are reacted at higher temperatures with the neutral diisopropylmethylphosphonate, an alkyl elimination and a phosphato condensation occur (equation 186).[1709]

$$NiBr_2 + 2(MeO)_3PO \xrightarrow{60\,^{\circ}C} Ni\{(MeO)_2PO_2\}_2 + 2MeBr \qquad (185)$$

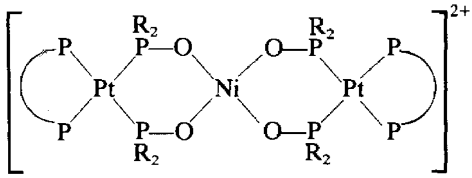
$$NiX_2 + (Pr^iO)_2(Me)PO \xrightarrow{180\,^{\circ}C} Ni_2\{(Pr^iO)(Me)PO_2\}_2\{O_2P(Me)OP(Me)O_2\} + \text{products} \qquad (186)$$

Neutral nickel phosphinates $NiL_2{\cdot}nH_2O$ (L = $Ph_2PO_2^-$, $PhHPO_2^-$, $Ph_2P(S)O^-$; n = 0, 4) are assigned a pseudotetrahedral structure with bridging ligands.[1710] The analogous bis-dioctylphosphinatonickel(II), $Ni\{(C_8H_{17})_2PO_2\}_2$, is a yellow six-coordinate complex with a cross-linked polymeric structure achieved by means of bridging phosphinato groups.[1711] The β-ketophosphonato anion $\{(EtO)_2P(O)CHC(O)CH_2NMe_2\}^-$ gives the polynuclear compound $[Ni_7L_6(OH)_6]X_2$ (X = NO_3, ClO_4).[1712]

An interesting series of reactions were carried out starting from bis (cyclopentadienyl)nickel and secondary phosphite esters (Scheme 24).[1713] Finally, the mixed-ligand complex $[Pt\{(MeO)_2PO\}_2diphos]$ can act by itself as a ligand towards nickel perchlorate giving the mixed metal oligomer (**225**).[1714]



Scheme 24



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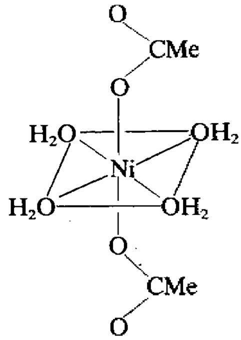
50.5.5.5 Complexes with carboxylates and related ligands

Nickel(II) complexes with simple carboxylate anions have been well known for a long time,[1715] and nickel(II) acetate tetrahydrate is one of the most thoroughly studied compounds. Selected examples of nickel(II) complexes with carboxylate anions are shown in Table 85. The carboxylato complexes are high-spin octahedral with few exceptions.

$Ni(O_2CMe)_2{\cdot}4H_2O$ (**226**) may be prepared by reacting acetic acid with an aqueous suspension of nickel carbonate. It is octahedral ($\mu_{eff} = 3.30$ BM at room temperature) with two *trans*-coordinated monodentate acetate groups.[1716–1718] The same structure occurs in $[Ni(O_2CCH_2Cl)_2(OH_2)_4]{\cdot}2H_2O$.[1743] Other investigations on nickel acetate tetrahydrate consider its electron density distribution[1744] and the complex formation reaction in aqueous solution. This latter investigation has been carried out by means of a variety of techniques, including potentiometric titrations,[1745] ^{13}C NMR spectroscopy[1746] and chemical relaxation methods.[1747] It has been generally concluded that the species $Ni(O_2CMe)^+$ is appreciably formed in aqueous solution.



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Acetic acid by itself acts as a monodentate neutral ligand in the hexakis complex $[Ni(HOCOMe)_6](BF_4)_2$.[1718,1748] The Ni—O bond distances are similar to those observed in the acetate complex indicating that $MeCO_2H$ is as strong a donor as its conjugate base. The hexakis acetic acid complex dissolves in $MeNO_2$ without appreciable dissociation.

$Ni(O_2CH){\cdot}2H_2O$ is reported to be polynuclear with formate bridges.[1749] The complex formation reaction with formate in aqueous solution has been studied.[1750] $Ni(O_2CPh)_2{\cdot}3H_2O$ is assumed to contain two different types of benzoates, chelate and ionic.[1751] In the *o*-, *m*- and *p*-halo-substituted benzoato complexes $Ni(O_2CC_6H_4X)_2{\cdot}nH_2O$, the degree of hydration is singularly dependent on substituent position.[1719,1752]

By the direct reaction of anhydrous nickel acetate with a large excess of the appropriate base, which sometimes acts as the reaction medium, $Ni(O_2CMe)_2L_2$ (L = pyridine, 2-picoline, quinoline,[1753] piperidine, piperazine[1754]) complexes are obtained. On the other hand, the reaction of hydrated nickel acetate with pyridine affords $Ni(O_2CMe)_2(H_2O)_2(py)_2$.[1753] Numerous other mixed-ligand complexes of the type $Ni(O_2CR)_2nL$ (R = Ph, CF_3, CCl_3, CH_xCl_{3-x}; L = pyridine and substituted pyridines, pyridine *N*-oxide and related monodentate ligands; $n = 1, 2, 4$) have been prepared using slightly different synthetic procedures.[1753,1755–1766]

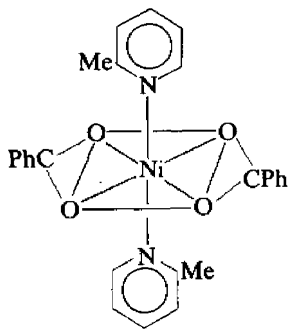
The complexes $Ni(O_2CR)_2L{\cdot}xH_2O$ (R = C_6F_5, *p*-$MeOC_6F_4$, *p*-$EtOC_6F_4$; L = bipy, phen; $x = 1, 2$) where found to decompose in boiling toluene yielding the corresponding organonickel(II) compounds.[1759]

The bis adducts $Ni(O_2CR)_2L_2$ (L = monodentate ligand) may be either mononuclear with chelate carboxylate (**227**) or di- or poly-nuclear with bidentate bridging carboxylate (**228**). The tetrakis adducts $Ni(O_2CR)_2L_4$ (L = monodentate ligand) are assumed to possess structures analogous to that of the tetraaquaacetate (**226**). A structure analogous to (**229**) occurs in the

Table 85 Selected Carboxylato and Thiocarboxylato Complexes whose Structures were Determined by X-Ray Analysis

Complex	Coordination geometry	Remarks	Selected bond distances (pm) Ni—O (carboxylate)	Ni—X	Ref.
$Ni(OCOMe)_2(OH_2)_4$	*trans* Oh	Monodentate $MeCO_2^-$ (**226**)	207	204–208 (OH_2)	1716–1718
$Ni(HOCOMe)_6(BF_4)_2$	Oh	Monodentate $MeCO_2H$	204–207		1718
$Ni(OCOR)_2(OH_2)_4$	*trans* Oh	R = *m*-ClC_6H_4; monodentate RCO_2^-	205	206–210 (OH_2)	1719
$Ni(OCOMe)_2(OH_2)_2py_2$	*trans* Oh	Monodentate $MeCO_2^-$	205	210 (OH_2), 210 (N)	1720
$Ni(OOCPh)_2(2\text{-pic})_2$	*trans* Oh	Chelating $PhCO_2^-$ (**227**)	210–213	207–209 (N)	1721
$Ni(OOCPh)_2(quin)_2$	*trans* Oh	Chelating $PhCO_2^-$	208–210	208 (N)	1721
$Ni(OCOR)_2(tmd)_2$	*trans* Oh	R = *m*-MeC_6H_4, *p*-MeC_6H_4, *m*-$NO_2C_6H_4$, *p*-$NO_2C_6H_4$, Ph; monodentate RCO_2^-	212–216	211–212 (N)	1722, 1723
$Ni(OCOCHCl_2)(m\text{-stien})_2$	*trans* Oh	Monodentate RCO_2^-	208	204–207 (N)	1724
$Ni(OOCMe)(tet\text{-}b)ClO_4$	*cis* Oh	tet-b = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, racemic isomer; chelating $MeCO_2^-$ and folded macrocycle	210–211	209–216 (N)	1725
$Ni_2(OOCR)_4(Me_4en)_2(H_2O)$	Oh	R = Me, CF_3, CH_2Cl, $CHCl_2$, 2-ClC_6H_4, 3-ClC_6H_4 (**228**); bridging and terminal RCO_2^-	205–207 (bridging) 210–211 (terminal)	215 (OH_2)	1726–1730
$Ni_2(OOCCMe_3)_4L_2$	SqPy	L = 2-methylquinoline (**229**); bridging RCO_2^-		275 (Ni)	1731
$Ni_4(OOCMe)_2(OMe)_4(TMB)_4(BPh_4)_2$	Oh	TMB = (**230**); bridging $MeCO_2^-$ and OMe^-; cubane cluster structure (**232**)	203–205	206–207 (OMe) 206–208 (C)	1732
$Ni(OOCR)_2(OH_2)_2$	*trans* Oh	R = CH_2OMe; chelating methoxyacetate	205	199 (methoxy) 207 (OH_2)	1733
$Ni(OSCMe)_2L_2$	*cis* Oh	L = py, 2-pic, 4-pic; chelating $MeCSO^-$	210–215	244–248 (S) 204–208 (N)	1734–1736
$Ni_2(OSCPh)_4(EtOH)$	SqPl + SqPy	Dinuclear; bidentate bridging $PhCSO^-$ (**233**)	201–206	222–223 (S) 250 (Ni)	1737, 1738
$Ni(OCOR)_2(OH_2)_4$	*trans* Oh	R = *o*-$HOCOC_6H_4$; monodentate RCO_2^-	204	206–210 (OH_2)	1739
$Ni_2(O_4C_2)(en)_4(NO_3)_2$	Oh	Bridging bidentate $C_2O_4^{2-}$ (**234**)	209–210	209–211 (N)	1740
$Ni_2(O_4C_2)(ONO)_2py_6$	Oh	Bridging bidentate $C_2O_4^{2-}$ and monodentate O-bonded NO_2^-	207	208 (ONO) 211–214 (N)	1741
$Ni(dacoda)H_2O\cdot 2H_2O$	SqPy	dacoda = 1,5-diazacyclooctane *N,N'*-diacetate	198, 200	203 (N) 201 (OH_2)	1742

complex $Ni_2(O_2CPh)_4L_2$ (L = quinoline)[1767] and in other complexes with various carboxylates and bases.[1757,1758]



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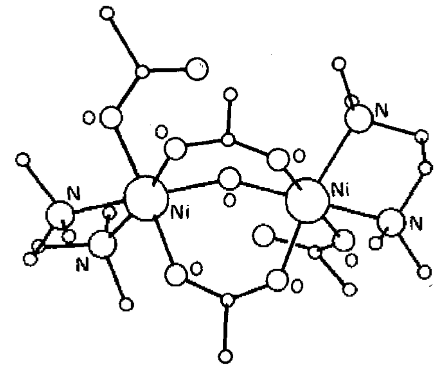

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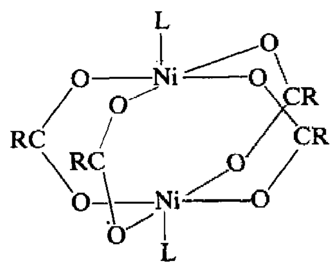
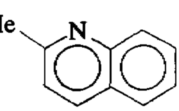
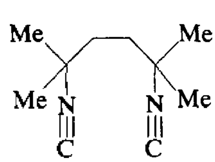


(229) R = CMe_3, L =



The ligands TMB (230) and DMB (231) both react with $Ni(O_2CMe)_2{\cdot}4H_2O$ in MeOH giving the complex cations $[Ni_4(OMe)_4(O_2CMe)_2L_4]^{2+}$ (L = TMB, DMB) which were isolated as the tetraphenylborate salts.[1732] The structure of these complexes is of cubane-type (232). Each nickel atom is in a distorted octahedral environment including two *cis* isocyanide groups, three methoxide oxygens and one acetate oxygen. The effective magnetic moment decreases from 2.88 BM at 286 K to 0.47 BM at 4.2 K, indicating that an overall antiferromagnetic exchange interaction is operative.

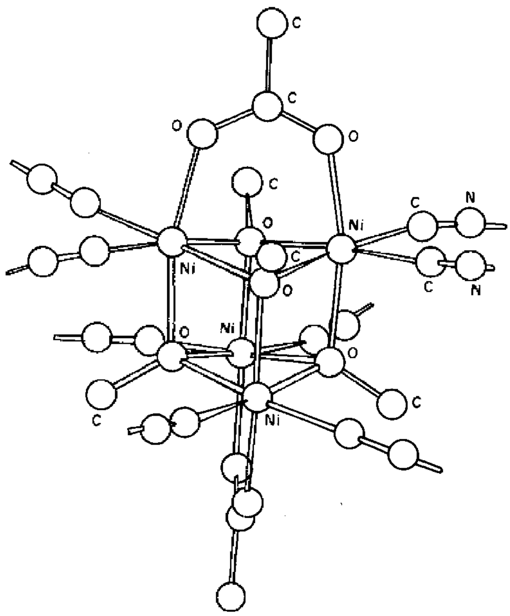


(230) TMB

(231) DMB

The reaction of hydrated $NiCl_2$ with thioacetic, thiopropionic or thiobenzoic acids in ethanolic solution made basic by NaOH results in the formation of compounds of general formula $Ni(OSCR)_2{\cdot}\frac{1}{2}EtOH$ (233). In these dinuclear complexes one nickel atom is in a square planar environment of four sulfur atoms whereas the other is coordinated by five oxygens in a square pyramidal geometry and is high-spin.[1737,1738] This dinuclear structure is broken up by reaction with a large excess of heterocyclic bases from which mononuclear complexes $Ni(OSCR)_2L_2$ with chelating thiocarboxylates result.[1734–1736]

A number of nickel complexes with a variety of deprotonated dicarboxylic acids, including maleic acid, and benzenedicarboxylic acids were reported.[1739,1768–1770] 1,5-Diazacyclooctane-*N,N'*-diacetate (dacoda) barium salt reacts with $NiSO_4{\cdot}6H_2O$ in water giving the blue-green complex $[Ni(dacoda)H_2O]{\cdot}2H_2O$.[1742,1771] This complex is square pyramidal and converts into a square planar derivative upon heating *in vacuo*. The complex $[Ni(dacoma)(H_2O)_2]ClO_4$ (dacoma = 1,5-diazacyclooctane-*N*-monoacetate) is also square pyramidal high-spin.[1772]



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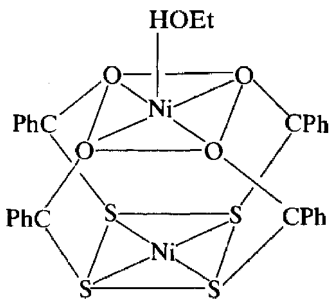
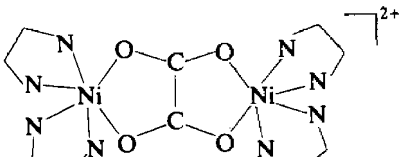


(233)

The coordination of oxalate dianion to nickel(II) has been studied in aqueous solution.[1773,1774] A number of oxalato complexes including the simple $K_2[Ni(O_4C_2)_2(OH_2)_2]\cdot 4H_2O$[1775–1777] salt were also studied in the solid state.[1778,1779]

Mixed-ligand complexes having general formulas $Ni(O_4C_2)_{0.5}$(L—L)$_2$$ClO_4$ (L—L = en, tmd), $Ni(O_4C_2)_{0.5}$(L—L—L)$(OH_2)ClO_4$ (L—L—L = dien, dpt), $Ni(O_4C_2)_{0.5}$(tet-b)ClO_4 and $Ni(O_4C_2)$(tet-a)$\cdot 3H_2O$ (tet = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; a = *meso* isomer; b = *racemic* isomer) were prepared by the reaction of a concentrated solution of sodium oxalate with an aqueous solution of the appropriate nickel(II) amine complex.[1780,1781] In the dinuclear complex $[Ni_2(O_4C_2)(en)_4](NO_3)_2$ (**234**)[1740,1741] the bridging oxalato group is planar and symmetrically bonded to the two nickel atoms. The same structure occurs in the complex $Ni_2(O_4C_2)(ONO)_2(py)_6$ which was obtained as a by-product in a very low yield when a pyridine solution of methanenitrosolic acid and nickel(II) were allowed to stand for several months.[1741]

The aromatic dianions croconate $C_5O_5^{2-}$ (**235**) and squarate $C_4O_4^{2-}$ (**236**) are the conjugate bases of dihydroxycyclopentenetrione and dihydroxycyclobutenedione respectively. The reaction of nickel(II) chloride and potassium croconate in aqueous solution gives a mixture of green compounds from which, on boiling, the pseudotetrahedral polynuclear complex $Ni(C_5O_5)\cdot 3H_2O$ (**237**) was isolated.[1782] $Ni(C_4O_4)\cdot 2H_2O$ (**238**) was prepared in a similar way.[1783,1784] In the latter complex the nickel atom is coordinated to four oxygen atoms from four different squarate anions which, in turn, bridge four different nickel atoms in a plane.[1785] The dihydrate is transformed into the anhydrous complex upon heating *in vacuo* at 210–260 °C.[1786] In aqueous solution the nickel squarate complex is less stable than the nickel oxalate complex.[1787]



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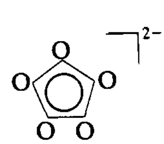

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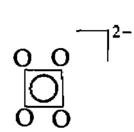

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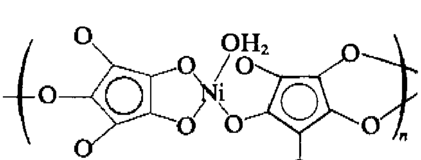

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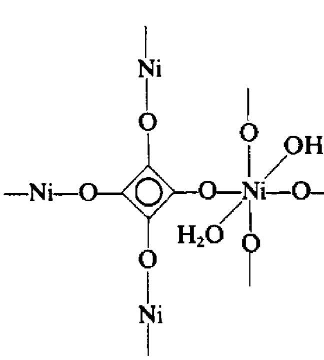

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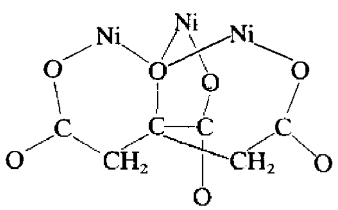
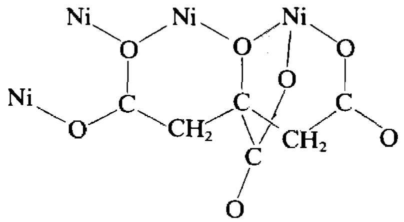
In the chain polynuclear complex $Ni(O_4C_4)(Im)_2(H_2O)_2$ (Im = imidazole) only two oxygen atoms of the bridging squarate are directly coordinated to nickel(II).[1788]

Complex formation of nickel(II) with a variety of hydroxy acids has been investigated. It has been reported that in aqueous solution in the pH range 6–7.2 at 25 °C, a 1:1 neutral complex is formed between nickel(II) and the salicylato monoanion, $HOC_6H_4CO_2^-$ ($K_{eq} = 1.4 \times 10^{-6}$), or its 5-substituted analogue, with the further release of a proton.[1789,1790] The effects of substituents on the stability constants of nickel complexes with various 4- and 5-substituted salicylic acids were also studied.[1791,1792]

A number of six-coordinate nickel(II) complexes with other hydroxy acids, including gluconic, mandelic and tartaric acids, were reported.[1793–1797,1799] The X-ray crystal structure of the complex $\{(Me_4N)_5[Ni_4(C_6H_4O_7)_3(OH)(H_2O)]\cdot 18H_2O\}_2$ has been determined.[1798] This very complicated structure can be described as consisting of two clusters of composition $[Ni_4L_3(OH)(H_2O)]^{5-}$ containing a tripyl bridging hydroxide ion and the tetraionized citrate ions which bridge either three or four nickel atoms (**239**, **240**).



(**239**)



(**240**)

50.5.5.6 Complexes with organo-phosphorus and -arsenic oxides, amine oxides, amides, sulfoxides and related ligands

(*i*) *Complexes with monodentate ligands*

Numerous nickel(II) complexes with a variety of phosphine and arsine oxides have been reported, but only a few X-ray crystal structures have been determined. In some cases the structures assigned to the complexes are not completely certain.[1800] A selection of nickel(II) complexes is reported in Table 86.

The complexes can be readily obtained by reacting the appropriate ligand and the nickel(II) salt in acetone or ethanol, sometimes in the presence of dehydrating agents. Most of the complexes are sensitive to atmospheric moisture and are preferably handled in a dry box. Special procedures are employed to obtain tetrakis complexes with tri-*n*-butylphosphine oxide (Bu^n_3PO) and the bis adducts with triphenylarsine oxide (Ph_3AsO) and triphenylphosphine oxide (Ph_3PO). The $Ni(Bu^n_3PO)_4(ClO_4)_2$ must be prepared in rigorously anhydrous conditions using triethyl orthoformate as reaction medium,[1806] whereas the $NiX_2(Ph_3AsO)_2$ and $NiX_2(Ph_3PO)_2$ derivatives are obtained by leaving ethanol solutions of the reactants in a desiccator over conc. H_2SO_4 for several days.[1808,1809] A different method for the preparation of the latter complexes consists of the oxidation of the corresponding $Ni(PPh_3)_2X_2$ complexes with 30% H_2O_2 solution.[1819]

Most of the complexes reported with phosphine and arsine oxide have general formulas $NiL_4(ClO_4)_2$ and $NiL_5(ClO_4)_2$ and are assigned a five-coordinate high-spin structure. In all of the complexes, evidence for oxygen bonding of the oxo ligands is given by the lowering of the ν(PO) and ν(AsO) stretching frequencies in the complexes with respect to the free ligands. The structure of the cation $[Ni(Me_3AsO)_5]^{2+}$ (**241**) can be described as a square pyramid with axial and equatorial Ni—O bond lengths of 194 and 200 pm, respectively.

The NiL_4X_2 complexes (L = Ph_3PO, Ph_3AsO; X = ClO_4, BF_4) have been obtained either as five-coordinate or as tetrahedral species.[1682,1802] The interconversion from the five-coordinate to the four-coordinate isomers can be performed in the solid state by heating.[1682]

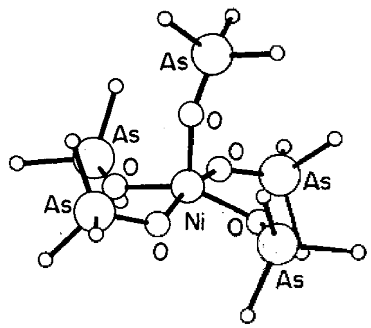
The bis complexes $[NiX_2L_2]$ (L = Ph_3PO, Ph_3AsO,[1807,1808] Me_3PO, Me_3AsO;[1809] X = halides) are pseudotetrahedral in the case of the bulky triphenyl-substituted ligands and polynuclear six-coordinated in the case of the trimethyl-substituted ligands.

Nickel(II) complexes with hexamethylphosphoramide, $(Me_2N)_3PO$ (HMPA), have been better characterized than those with other amino-substituted phosphine oxides (Table 86).

Table 86 Selected Complexes with Monodentate Organo-phosphorus and -arsenic Oxides

Complex	Coordination geometry	μ_{eff} (r.t.) (BM)	IR data (cm^{-1}) (Nujol mull) $\nu(PO)$, $\nu(AsO)$	IR data (cm^{-1}) $\nu(ClO_4)$	Remarks	Ref.
$Ni(Ph_3PO)_4(ClO_4)_2$[a]	SqPy	3.51	1143s	1090s	Coordinated $OClO_3^-$ or bridging ligand	1682, 1683, 1801
$Ni(Ph_3AsO)_4(ClO_4)_2$[a]	SqPy	3.51	863s	1090s	As above	1682, 1683
$NiL_4(ClO_4)_2$[b]	Td	3.97, 3.88	—	—	L = Ph_3PO, Ph_3AsO	1682
$NiL_4(BF_4)_2$	Td	HS	—	—	L = Ph_3PO	1802
$Ni(Ph_2MePO)_4(ClO_4)_2$	SqPy	HS	1139s	1139s 1088s 1035m[c]	One coordinated $OClO_3^-$	1683
$Ni(Ph_2MeAsO)_4(ClO_4)_2$	SqPy	HS	854s	1137s[c] 1092s 1045s[c]	As above	1683, 1803
$Ni(Me_3PO)_5(ClO_4)_2$	SqPy	HS	1141s 1132s	—		1804
$Ni(Me_3AsO)_5(ClO_4)_2$ (**241**)	SqPy	3.62	866s	—	Structure determined by X-ray analysis	1804, 1805
$Ni(Me_3AsO)_4XY$	SqPy	3.56	833–866s		X = ClO_4; Y = ClO_4, BPh_4 X = NO_3; Y = BPh_4; coordinated monodentate X	1804
$Ni(Bu^n_3PO)_4(ClO_4)_2$	Td	3.68	1126s	1092s[c]		1806
$Ni(Ph_3AsO)_2X_2$	Td	3.96	—	—	X = Cl, Br, NCS	1807
$Ni(Ph_3PO)_2X_2$	Td	3.7–4.0	1151–1160s	—	X = Cl, Br, I	1808
$Ni(Me_3PO)_2X_2$	Oh	—	1065–1133	—	Polynuclear	1809
$Ni(Me_3AsO)_2X_2$	Oh	3.29–3.44	846–861s	—	Polynuclear	1809
$Ni(HMPA)_4(ClO_4)_2$	Td	4.02	1193			1810–1812
$Ni(HMPA)_2X_2$	Td	3.98–4.03	1188–1193		X = halides	1810
$Ni(HMPA)_2X_2$	Oh	3.47	1198		X = NO_2, NO_3; coordinated as chelate	1810, 1813
$Ni\{(MeO)_3PO\}_5(ClO_4)_2$	5	HS	1236	1077s,[c] 621m[c]		1814
$Ni\{(MeO)_3PO\}_5(H_2O)(ClO_4)_2$	Oh	3.07	1236	1077[c]		1815
$Ni\{(Bu^nO)_3PO\}_4(H_2O)(ClO_4)_2$	Oh	3.05	1240	1108s,[c] 917s	Monodentate $OClO_3^-$	1816
$Ni\{(Bu^iO)_3PO\}_4(H_2O)_2(ClO_4)_2$	Oh	3.23	1235	1100s[c]		1816
$Ni\{(MeO)_2MePO\}_4(ClO_4)_2$	5	HS	1211	1100,[c] 621[c]	Polynuclear	1814
$Ni\{(Pr^iO)_2MePO\}_4(ClO_4)_2$	5	3.16	1197	1088,[c] 1121	Monodentate $OClO_3^-$	1814, 1817
$Ni\{(Pr^iO)_2MePO\}(CN)_2$	4 + 6	2.36 (av)	1212	—	Bridging CN^-; 1:1 SqPl and *trans* Oh Ni^{II}	1818
$Ni\{(Bu^nO)_2BuPO\}_4(H_2O)_2(ClO_4)_2$	Oh	3.17	1199	1085[c]		1816

[a] Yellow isomer. [b] Blue isomer. [c] Bands associated with ionic ClO_4^-.
Frequencies of the free ligands (cm^{-1}): Ph_3PO, 1195; Ph_3AsO, 880; Ph_2MePO, 1171; Ph_2MeAsO, 875; Me_3PO, 1166; Me_3AsO, 870; Bu^n_3PO, 1175.



(241)

Complexes of formula $Ni(HMPA)_4(ClO_4)_2$[1810,1811] are assigned a pseudotetrahedral structure in the solid state and in $MeNO_2$ solution.[1812]

The bis adducts $Ni(HMPA)_2X_2$ are pseudotetrahedral when X = halides[1810] and octahedral when $X = NO_2$, NO_3.[1810,1813] The complexes $Ni(HMPA)_2(NCX)_2$ (X = S, Se) are presumably five-coordinate.[1820,1821] When small amounts of water are progressively added to solutions of anhydrous $Ni(ClO_4)_2$ and HMPA, electronic and NMR spectra indicate the formation of complexes of the type $[Ni(HMPA)_2(OH_2)_4]^{2+}$.[1822]

Neutral phosphates $(RO)_3PO$, phosphonates $(RO)_2R'PO$ and phosphinates $(RO)R'_2PO$ are well known as extracting agents for metal ions.[1823] The isolation of their metal complexes as crystalline compounds is, in general, more difficult than the preparation of complexes with other substituted phosphoryl compounds. It is often essential to reflux solutions of the reactants with dehydrating agents such as triethyl orthoformate or 2,2′-dimethoxypropane. In some cases the neutral phosphoryl ligands or triethyl orthoformate by themselves act as the reaction media in the synthesis of the nickel(II) complexes.

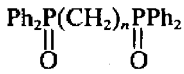
Selected nickel(II) complexes with various monodentate phosphoryl esters are reported in Table 86. It is generally found that the NiL_4^{2+} and NiL_5^{2+} species are converted to the hydrated species $NiL_4(OH_2)_2^{2+}$ on exposure to aerial moisture.

(*ii*) *Complexes with bidentate ligands*

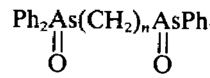
Some bidentate ligands which have been studied in conjunction with nickel(II) are reported in **(242)**–**(249)**.

Complexes with ditertiary phosphine and arsine oxides have been less extensively studied compared with those of the monodentate phosphine and arsine oxides. The complexes with ligands **(242)** and **(243)** were prepared, in general, by the direct reaction of the appropriate ligand and the nickel salt in hot ethanol or *n*-butanol. Starting from anhydrous nickel halides complexes of general formulas $[Ni(MDPPO)_3][NiX_4]$, $[Ni(EDPPO)_3][NiX_4]$ and $[NiX_2(TDPPO)]$ (X = Cl, Br, I) were obtained.[1824,1825] If hydrated $Ni(ClO_4)_2$ is employed, the complexes $[NiL_2(H_2O)_2](ClO_4)_2$ (L = EDPPO, BDPPO, BDPAsO), $[Ni(EDPAsO)_2](ClO_4)_2$[1826,1827] and $[Ni(MDPAsO)_3](ClO_4)_2$[1828] are obtained. The cationic $[NiL_3]^{2+}$ and $[NiL_2(H_2O)_2]^{2+}$ complexes are six-coordinate, whereas $[Ni(EDPAsO)_2](ClO_4)_2$ is five-coordinate. The $[NiX_2(TDPPO)]$ complexes are pseudotetrahedral ($\mu_{eff} = 3.68$–3.76 BM). On account of their very low solubility in the common organic solvents and on account of the low stability of eight-membered chelate rings which would be present if the TDPPO ligand acts as a chelate, it was suggested that the $NiX_2(TDPPO)$ complexes are polynuclear in the solid state with bridging ligands.[1829] On the other hand the bidentate ligands with methylene or ethylene connecting chains act as chelate in six-coordinate complexes. In this context we may note that monodentate phosphine and arsine oxides in no case give rise to hexakis complexes irrespective of the bulkiness of the substituents on phosphorus and arsenic atoms, and the five-coordinate species are the preferred ones.

The bidentate phosphoramide ligands **(244)** act as chelate ligands in complexes of the general formula $NiL_3(ClO_4)_2$ (L = NIPA, OMOPA, OMPA) which are invariably pseudooctahedral. IR absorptions in the range 1162–1203 cm^{-1} are assigned as the ν(PO) stretching frequencies.[1828–1833] The complexes $Ni(NIPA)SO_4$, $Ni(NIPA)_2I_2$[1834] and $Ni(NIPA)_nX_2$ (X = halides, NCS, NO_3; n = 1–3) were also reported.[1832] Tris-chelate complexes $NiL_3(ClO_4)_2$

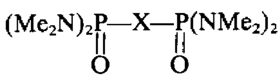


(242) $n = 1$, MDPPO
$n = 2$, EDPPO
$n = 3$, TDPPO
$n = 4$, BDPPO

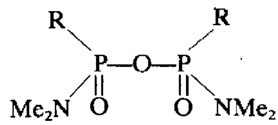


(243) $n = 1$, MDPAsO
$n = 2$, EDPAsO
$n = 3$, BDPAsO

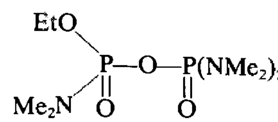
strictly analogous to those reported with the ligands **(244)** were also obtained with the ligands **(245)**[1835] and **(246)**.[1836]



(244) X = NMe, NIPA
X = O, OMOPA
X = CH_2, OMPA

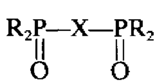


(245) R = Me, Et, Pr^i

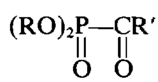


(246)

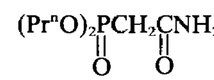
Bidentate ligands of type **(247)** give tris chelates $NiL_3(ClO_4)_2$ when an excess of the ligand is reacted with the nickel salt and an appropriate dehydrating agent.[1837,1838] Carbonyl phosphonates of the types **(248)** and **(249)** are also found to act as chelate in the complexes $Ni(L^1)_3(ClO_4)_2{\cdot}xH_2O$[1839] and $Ni(L^3)_3(ClO_4)_2$,[1840] whereas one monodentate and one chelate ligand molecule are supposed to exist in the complex $[Ni(L^2)_2(OH_2)_2OClO_3]ClO_4$.[1841]



(247) X = O, R = Me, Et, Ph
X = CH_2, R = Bu^n, OPr



(248) R = Et, R′ = Me, L^1
R = Et, R′ = benzoyl, L^2



(249) L^3

(iii) Complexes with aromatic and aliphatic amine oxides

A very large number of nickel(II) complexes with a variety of aromatic *N*-oxides are known.[1842,1843] A selection of the most representative aromatic *N*-oxides are reported in Table 87 together with their more significant nickel(II) complexes.

In general, nickel(II) complexes can be obtained by the direct reaction of nickel salts with the appropriate ligand. Since most of the complexes are decomposed by water, non-aqueous solvents are used and dehydrating agents are employed with hydrated nickel salts.

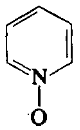
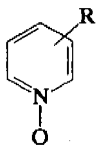
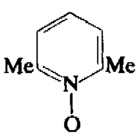
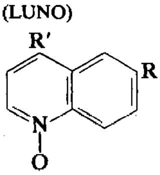
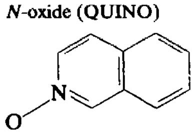
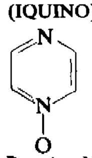
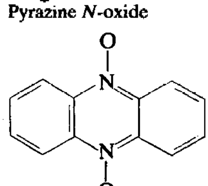
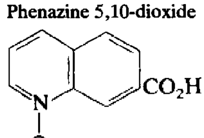
Nickel complexes with different stoichiometries are obtained with pyridine *N*-oxide ligands depending on the substituents in the aromatic ring, the nature of the nickel salts and the experimental conditions. In general, if salts of poorly coordinating anions are used, hexakis complexes $[NiL_6]X_2$ are produced, whereas complexes with a metal-to-ligand ratio less than 1:6 are formed if nickel salts of potentially coordinating anions are used.

Steric effects of the substituents on the aromatic ring influence the geometry of the complexes, as shown by the series of the nitrato complexes $Ni(NO_3)_2L_n$ prepared with various methyl-substituted pyridine *N*-oxides.[1631] All of the reported five- and six-coordinate complexes are high-spin. The coordination of the ligands through the oxygen atom of the amine oxide is invariably indicated by the ν(NO) stretching mode which is shifted towards lower frequencies upon coordination ($\Delta\nu$(NO) about 10–40 cm^{-1}).

In the $[Ni(PNO)_6]^{2+}$ cation the nickel atom is in a nearly regular octahedral environment.[1848,1849] The Ni—O bond distances (206 pm) are nearly equal and the Ni—O—N bond angles are non-linear (119°) as expected for the electronic distribution of the oxygen atom. Other complexes with a variety of aromatic *N*-oxides have been reported[1866–1873] which will not be mentioned here.

Mono *N*-oxides[1874,1875] and *N,N′*-dioxides[1876–1878] of 2,2′-bipyridyl and *o*-phenanthroline are reported to give 1:3 complexes of general formula $[NiL_3](ClO_4)_2$ where the ligands behave as chelates. All the complexes are six-coordinate. NMR data for the $[NiL_3]^{2+}$ (L = 2,2′-bipyridyl *N,N′*-dioxide) cation were interpreted by assuming a staggered configuration for the chelate ligand involving an angle of 67° between the planes of the two aromatic rings.[1877]

Table 87 Selected Complexes with some Aromatic *N*-Oxides

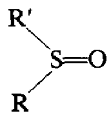
Ligand	Complex	Coordination geometry or number	$\nu(NO)$ (cm^{-1})	Remarks[a]	Ref.
	NiL_6X_2	Oh	1218–1220	X = Br, I, ClO_4	1844–1847
	NiL_6X_2	Oh		X = BF_4, BrO_3; structures determined by X-ray analysis	1848, 1849
	$NiCl_2L$	4	1200	Presumably dinuclear pseudotetrahedral	1850
Pyridine *N*-oxide	$Ni(O_2NO)_2L$	Oh		Chelate NO_3	1630
(PNO)	$Ni(NCS)_2L_3(H_2O)$	Oh	1220		1851
	NiL_6X_2	Oh	1201–1230	R = 4-Me, 4-Cl, 4-NO_2, 4-OMe, 2-Me; X = ClO_4, BF_4	1852, 1853
	$NiL_6(ClO_4)_2$	Oh		R = 2-, 3-, 4-CN	1854
	NiL_6X_2	Oh	1201–1208	R = 2-Et; X = ClO_4, NO_3	1855
	$[Ni(ONO_2)L_5]NO_3$	Oh	1251	R = 3-Me; monodentate and ionic nitrate	1631
R = 2-Me, picoline	NiL_4X_2	Oh	1205–1210	R = 2-Me; X = ClO_4, NO_3	1855
N-oxide (PICNO); R = 2-Et, 2-EtPNO	$[Ni(ONO_2)(O_2NO)L_2]$	5	1208	R = 2-Me; monodentate and chelate NO_3	1631
	$[Ni(ONO_2)L_4]NO_3$	5	1210	R = 2-Me; monodentate and ionic NO_3	1631
	$[Ni(O_2NO)_2L_2]$	Oh	1207–1262	R = 3-Me, 4-Me; chelate nitrate	1631
	$NiCl_2L\cdot 2H_2O$	6	1189–1195	R = 2-Me, 2-Et; polynuclear	1855
	$NiL_4(ClO_4)_2$	SqPl	1191	Diamagnetic; ionic perchlorate	1856
	$[Ni(ONO_2)(O_2NO)L_2]$	5	1194	Monodentate and bidentate nitrate	1857
	$Ni_2(NCS)_4L_4$	6	1207	Dinuclear with bridging and terminal thiocyanate	1857
	$Ni_2L_8(ClO_4)_3BPh_4$	SqPl	1197, 1218	Violet isomer, diamagnetic	1858
		5	1183, 1212	Green isomer (μ_{eff} = 2.86 BM)	
Lutidine *N*-oxide (LUNO)	$Ni(SO_4)L_2$	5	1207	Presumably dinuclear with bridging and terminal L	1859
	$NiL_6(ClO_4)_2$	Oh	1170–1300	R = H, Me, OMe, Cl, NO_2; R′ = H	1860
	$NiL_6(ClO_4)_2\cdot 4H_2O$	Oh	1213–1302	R′ = H, Me, OMe, Cl, NO_2; R = H	1861
Unsubstituted and substituted quinoline *N*-oxide (QUINO)	$Ni(NO_3)_2L_3\cdot 0.5H_2O$	Oh	1209	R = R′ = H	1855
	$NiL_6X_2\cdot nH_2O$	Oh	1160	X = NO_3, n = 0.5; X = ClO_4, n = 0	1855, 1861
Isoquinoline *N*-oxide (IQUINO)	$NiLCl_2\cdot 0.5H_2O$	6	1160	Polynuclear	1855, 1861
 Pyrazine *N*-oxide	NiL_3Cl_2	6	1309, 1322, 1332	Presumably dinuclear with bidentate bridging and terminal N-bonded ligands	1862
	$Ni_4Cl_8L(H_2O)_4$	Td	1257, 1270	Presumably tetranuclear	1863
	$[NiL_2(OH_2)_4](ClO_4)_2\cdot 2H_2O$	Oh	1331	Monodentate ligand	1864
Phenazine 5,10-dioxide	$[Ni(OClO_3)L_3(OH_2)_2]ClO_4$	Oh	1284, 1278, 1293	Monodentate ligand	1864
 Picolinic acid *N*-oxide	$NiL_2(H_2O)_2$	Oh	1232, 1272	Deprotonated ligand acting as chelate	1865

[a] All the complexes are paramagnetic, unless otherwise indicated.

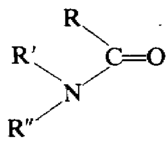
Different coordinating capacity is expected for aliphatic amine oxides with respect to the aromatic amine oxides. The Me_3NO[1878] and Et_3NO[1879] ligands give rise to tetrahedral nickel(II) complexes of the type $[NiL_4](ClO_4)_2$ and $[NiX_2L_2]$ ($L = Me_3NO$, X = halides).[1879] The ν(NO) stretching frequency undergoes very little change upon coordination. A six-coordinate complex $NiL_3(ClO_4)_2$ is reported with the bidentate ligand $H_2NCH_2CH_2N(O)Me_2$ which acts as chelate.[1880]

(*iv*) *Complexes with sulfoxides and amides*

Dimethyl sulfoxide (DMSO) and *N,N*-dimethylformamide (DMF) are widely used as reaction media and as solvents for solid substances. They are the precursors of many sulfoxides (**250**) and amides (**251**) which are reported to form a variety of complexes with nickel(II).[1881,1882]

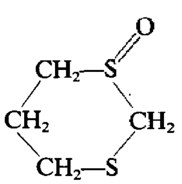


(**250**) R = R′ = Me
DMSO

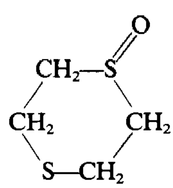


(**251**) R = H, R′ = R″ = Me
DMF

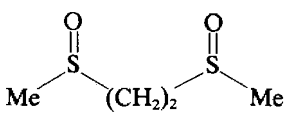
$[Ni(DMSO)_6](ClO_4)_2$ can be prepared by the reaction of anhydrous $Ni(ClO_4)_2$ with an excess of DMSO.[1846] The ligand coordinates to the metal though the oxygen atom as indicated by the ν(SO) stretching mode which is shifted to lower frequencies upon coordination (ν(SO) stretching at about 1000 cm^{-1}). An analogous complex with dimethyl selenoxide was also reported.[1883] Hexakis complexes, $NiL_6(ClO_4)_2$, have been reported with a variety of aromatic and aliphatic substituted sulfoxides, including tetramethylene sulfoxide,[1846,1884] dialkyl and methylphenyl sulfoxide,[1885,1886] diphenyl sulfoxide,[1887] dibenzyl sulfoxide,[1520] and 1,3- and 1,4-dithiane monosulfoxides (**252**, **253**).[1888–1890] The inductive effects of the substituents can greatly increase the donor strength of the substituted sulfoxides over that of DMSO. The bidentate ligand 2,5-dithiahexane 2,5-dioxide (**254**) has been reported to act as a bidentate ligand in the tris chelate $NiL_3(ClO_4)_2$.[1891]



(**252**)



(**253**)



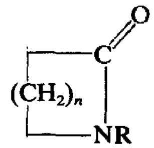
(**254**)

When nickel salts of coordinating anions are used, for example $Ni(NCS)_2$ and $Ni(NO_3)_2$, complexes with a number of coordinated monodentate ligand molecules less than six are obtained.[1888,1889,1892] Assignment of IR spectra of the $Ni(DMSO)_6^{2+}$ cation using ^{18}O isotope shifts has been reported.[1893]

SO_2 reacts with nickel sulfite in DMSO solution affording the compound $Ni(DMSO)_6S_2O_7$ containing disulfate anion. This compound is thermally unstable and decomposes to anhydrous nickel disulfate and nickel sulfate.[1894]

Numerous nickel(II) complexes having the general formula $NiL_6(ClO_4)_2$ have been characterized in the solid state with a variety of amides. Except for complexes of DMF,[1895] most of the hexakis complexes with primary alkyl amides (**251**; R = alkyl, R′ = R″ = H),[1896] acetamide (**251**; R = Me, R′ = R″ = H) and *N*-substituted acetamides,[1895–1897] benzamides (**251**; R = Ph, 4-$OMeC_6H_4$, 4-MeC_6H_4, 4-ClC_6H_4, 4-$NO_2C_6H_4$; R′ = R″ = H)[1898] and acetanilides (**251**; R = Me; R′ = H; R″ = Ph, 4-MeC_6H_4, 4-$OMeC_6H_4$, 4-ClC_6H_4, 4-$NO_2C_6H_4$)[1899] were prepared under anhydrous conditions using triethyl orthoformate as reaction medium and a large excess of the appropriate amide. In a similar way the analogous complexes with lactams (**255**) were obtained.[1900]

Complexes with a molar ratio of 1:4 were also reported, usually in conjunction with thiocyanate anion.[1901,1902]



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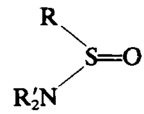
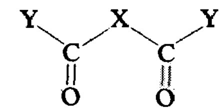


(256)



(257) X = NH; Y = NH_2, Me
X = CH_2; Y = NMe_2

It has invariably been found that in all of the amide complexes of nickel(II) the ligands coordinate through the oxygen atom, as inferred from IR evidence (ν(CO) stretching in the range 1630–1650 cm^{-1}) and confirmed by the structural determination of the two complexes $[Ni(DMF)_4(NCSe)_2]$[1901] and $[Ni(acetamide)_4(H_2O)_2]Cl_2$.[1903] All of the reported complexes are six-coordinate and high-spin. NMR studies on nickel(II) complexes with a variety of amides were carried out.[1904]

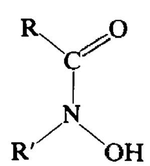
Alkanesulfinamides (**256**) are structurally similar to the carboxylic amides and, similarly, $NiL_6(ClO_4)_2$ complexes were obtained.[1905]

A few nickel(II) complexes were also reported with potentially chelating amides and imides (**257**). Two types of complex, namely $Ni(C_2H_5O_2N_3)_2X_2$ (X = Cl, Br) and $K_2[Ni(C_2H_3O_2N_3)_2]\cdot 2H_2O$ were obtained with biuret (**257**; X = NH; Y = NH_2) in neutral and alkaline solution respectively. In the former complex, paramagnetic and six-coordinate, biuret acts as a neutral chelating ligand through oxygen atoms, whereas in the latter complex, diamagnetic and planar, each dianion $HNC(O)NHC(O)NH^{2-}$ is coordinated through the two deprotonated amide nitrogens.[1906,1907]

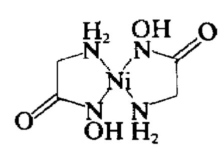
Tris chelates $Ni(L—L)_3(ClO_4)_2$ were reported with diacetamide (**257**; X = NH; Y = Me)[1908] and *N,N,N',N'*-tetramethylmalondiamide (**257**; X = CH_2; Y = NMe_2).[1909]

50.5.5.7 Complexes with deprotonated hydroxamic acids and related ligands

A few hydroxamato complexes of nickel(II) have been studied in detail.[1910,1911] The complexes were obtained, in general, by the reaction of nickel(II) acetate hydrate with the appropriate hydroxamic acid in aqueous solution. NiL_2 and $NiL_2\cdot H_2O$ complexes (HL = **258**; R = Me, Et, Ph; R' = H, Me, Ph) are paramagnetic six-coordinate and are assigned a polynuclear structure with the ligands acting as chelate through the oxygen atoms.[1912]



(258)

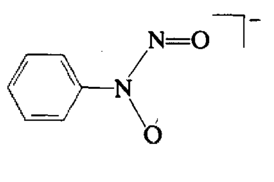


(259)

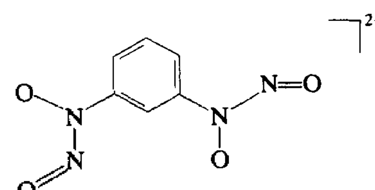
On the other hand, in the diamagnetic complex bis(glycinohydroxamato)nickel(II) the metal atom is coordinated to the nitrogen atoms of the ligand in a square planar environment (**259**).[1913] This complex is one of the few examples of N-coordinated hydroxamate.

Amongst the nickel complexes with ligands related to hydroxamic acid,[1910] we can mention the square planar complex with methylthiohydroxamate, MeC(S)NH(O).[1914,1915]

The thermal properties of the nickel complexes obtained with the cupferron ligand (**260**), NiL_2, and with dicupferron (**261**), $NiL\cdot H_2O$, were investigated.[1916,1917]



(260)



(261)

The complexes with *N*-hydroxypyrazolyl *N'*-oxide and *N,N'*-dihydroxybipyrazolyl *N,N'*-dioxide were also reported.[1918,1919]

50.5.6 Nickel(II) Complexes with Sulfur-, Selenium- and Tellurium-containing Ligands

50.5.6.1 Introduction

Nickel(II) complexes with ligands having sulfur donor atoms are still not as numerous as those with ligands having oxygen or nitrogen as donors. However, in recent years there has been growing interest in the field of metal complexes with sulfur-containing ligands and nickel(II) complexes are increasingly synthesized and characterized. Nickel(II) complexes with selenium and tellurium as donors still remain rare.

Until now the coordination chemistry of nickel(II) complexes with sulfur donors has been dominated by the dithiocarbamate and phosphorodithioate complexes since they are generally easy to prepare, and a wide range of substituents can be introduced in these ligands. Recently, complexes with simple ligands such as S^{2-}, S_2^{2-}, HS^- and RS^- have also been characterized and investigated.

Nickel(II) complexes with either bidentate mononegative ligands, such as dithiocarbamates, phosphorodithioates and thiocarboxylates, or monodentate neutral and anionic ligands are generally square planar. Nickel(II) complexes with Se and Te donors are strictly similar to those with S donors.

A number of review articles dealing with various aspects of the coordination chemistry of transition metals (including nickel) with sulfur, selenium and tellurium as donors are available even though some of them are not up to date. Apart from that of Livingstone, which covers all types of metal complexes with sulfur, selenium and tellurium donor ligands,[1920] most of the review articles are devoted to structural aspects of the coordination chemistry of specific ligands, namely thio-β-diketonates,[1921–1924] dithiolenes,[1923,1925,1926] dithiolates,[1923,1925–1927] thioethers[1928,1929] and simple sulfur atoms.[1930] Multinuclear complexes have also been reviewed,[1931] as well as some aspects of the reactions involving metal–sulfur bonds.[1932,1933] Jorgensen reported on the spectra of square planar complexes with sulfur donors.[1934]

In the following section we will report on the most recent developments of nickel–sulfur (as well as selenium and tellurium) coordination chemistry, but selected examples of the first reported complexes with classical sulfur-containing ligands which have been extensively reported in the aforementioned article reviews will be also included.

50.5.6.2 Complexes with ligands derived from hydrogen sulfide and thiols

Nickel(II) complexes with either HS^- or S^{2-} as ligands are quite rare because the action of H_2S or sulfides on solutions of nickel(II), even in the presence of strong coligands, in most cases gives insoluble binary sulfide polymers. It has been generally found, however, that tertiary phosphines can stabilize the nickel–sulfur bonds in mononuclear or oligonuclear soluble complexes. Consequently, most of the thio and mercapto complexes of nickel(II) are obtained by the reaction of H_2S, NaSH or polysulfides with nickel complexes having tertiary phosphines as coligands or with nickel(II) in the presence of phosphines (equations 187–193). The reactions are usually carried out under an inert atmosphere.[1935–1938] (see also Section 50.5.4.6.ii).

$$\mathrm{Ni(cpd)(PBu^n_3)_2Cl + SH^- \xrightarrow{H_2O} Ni(cpd)(SH)(PBu^n_3)} \tag{187}$$

$$\mathrm{NiCl_2(diphos) + 2SH^- \xrightarrow{EtOH/C_6H_6} \underset{\textbf{(262)}\ \text{also with SeH}^-}{Ni(SH)_2(diphos)}} \tag{188}$$

$$\mathrm{Ni(H_2O)_6^{2+} + triphos + H_2S \xrightarrow[r.t.]{DMF,\ BuOH} [Ni_2(\mu\text{-}S)(triphos)_2]^{2+}} \tag{189}$$

$$\mathrm{Ni(H_2O)_6^{2+} + triphos + H_2S \xrightarrow[40\,^\circ C]{DMF,\ BuOH} [Ni_2(\mu\text{-}S)_2(triphos)_2]^{+}}$$

$$\mathrm{Ni(H_2O)_6^{2+} + L + H_2S \longrightarrow [Ni(SH)L]^+} \tag{190}$$

$L = np_3$, pp_3; also with SeH^- and SMe^-

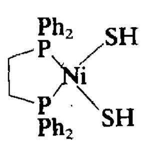
$$Ni(H_2O)_6^{2+} + PEt_3 + H_2S \xrightarrow{EtOH} [Ni_3(\mu_3\text{-}S)_2(PEt_3)_6]^{2+} \quad \textbf{(263)} \text{ also with } H_2Se \tag{191}$$

$$Ni(H_2O)_6^{2+} + PEt_3 + H_2S \xrightarrow{EtOH} [Ni_9(\mu_4\text{-}S)_3(\mu_3\text{-}S)_6(PEt_3)_6]^{2+} \quad \textbf{(264)} \tag{192}$$

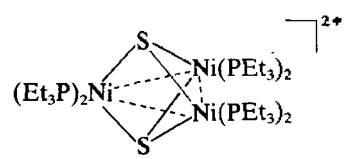
$$Ni(C_2H_4)(PPh_3)_2 + PEt_3 + H_2S \xrightarrow{THF/N_2} [Ni_3(\mu_3\text{-}S)_2(SH)(PEt_3)_5]^{+} \quad \textbf{(265)} \tag{193}$$

All of the complexes obtained from reactions (187)–(193) are diamagnetic. They are generally air-stable when solid, but decompose when dissolved in organic solvents.

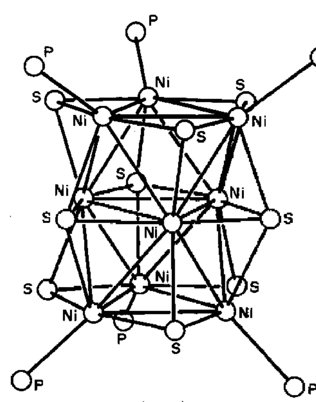
The Ni_3S_2 fragments in the two complexes **(263)** and **(265)** have a trigonal bipyramidal geometry with the two S atoms in the apical positions and the three nickel atoms in the equatorial plane, as found in other organometallic compounds which contain the same Ni_3S_2 unit.[1939] The formation of the enneanuclear complex **(264)**, on the contrary, is exceptional and no other complex of this stoichiometry was isolated with analogous tertiary phosphines, with selenium, or with metals other than nickel. It is not possible to assign any definite oxidation number to nickel in complex **(264)**. The lack of two electrons with respect to the situation of nine nickel(II) ions was reported to be essential for the existence of complex **(264)** because the oxidation is spontaneous and its reduction invariably leads to the decomposition of the cluster compound.[1937]



(262)



(263) Ni—S (av) 215 pm
Ni—Ni (av) 291 pm
S—S 270 pm



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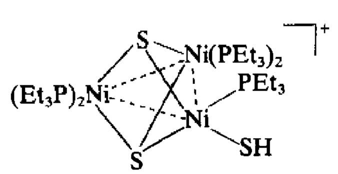
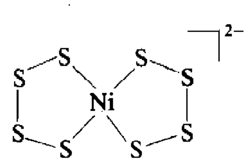


(265) Ni—S (av) 219 pm
Ni—Ni (av) 293 pm
S—S 280 pm



(266) Ni—S 218 pm

The reaction of ammonium polysulfide with nickel(II) acetate in MeOH solution gave the black diamagnetic square planar complex $[Ni(S_4)_2](NEt_4)_2$ **(266)** which contains the S_4^{2-} anion as the unique ligand.[1940]

Organosulfur compounds such as alkene- and arine-thiols apparently stabilize nickel–sulfur bonds as indicated by the complexes which were reported to have mercaptans as unique ligands. The tetrahedral tetrakis adduct with benzenethiolate, $(Ph_4P)_2[Ni(SPh)_4]$ (**267**; μ_{eff} =

3.20 BM),[1941,1942] has been obtained according to equation (194). The synthesis requires strictly oxygen-free conditions, but the solid compound is relatively stable in the air.

$$(Ph_4P)_2Ni(S_2O_2C_4)_2 + KSPh \xrightarrow{MeCN} (Ph_4P)_2Ni(SPh)_2(S_2O_2C_4) \xrightarrow{KSPh} (Ph_4P)_2[Ni(SPh)_4] \quad (194)$$

$S_2O_2C_4^{2-}$ = dithiosquarate; $(Ph_4P)_2[Ni(SPh)_4]$ = **(267)**

$$Mo(cpd)_2(SMe)_2 + NiCl_2 \xrightarrow{EtOH/N_2} [(cpd)_2Mo(MeS)_2Ni(SMe)_2Mo(cpd)_2]Cl_2 \quad (195)$$

(268)

$$SnMe_2(SEt)_2 + NiCl_2 \xrightarrow{EtOH} [Ni(SEt_2)_2]_6 \quad (196)$$

(269)

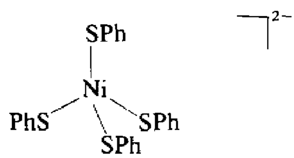
$$Ni(CO)_4 + R_2S_2 \xrightarrow{C_6H_6} Ni(SR)_2 \quad (197)$$

R = Me, Et, Ph

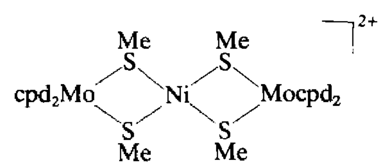
$$NiCl_2{\cdot}6H_2O + NH_{3(aq)} + HSC_5H_9NMe \xrightarrow[4\,^{\circ}C]{H_2O} [Ni(SC_5H_9NMe)_2]_4 \quad (198)$$

(270)

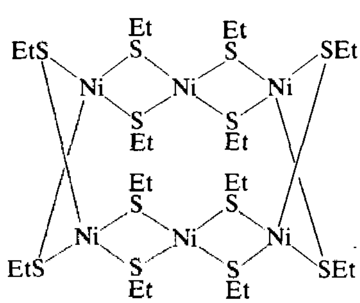
A number of complexes with coordinated thiolates have been prepared using different synthetic routes (equations 195–198).[1943–1946] In these oligomeric complexes the SR^- groups usually form μ_2 bridges and square planar NiS_4 units **(268–270)**.[1947]



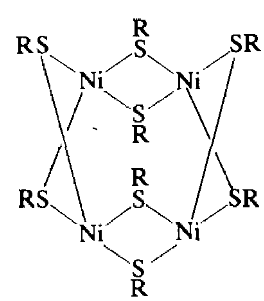
(267) Ni—S (av) 229 pm
S—Ni—S (av) 92°



(268) Ni—S (av) 219 pm



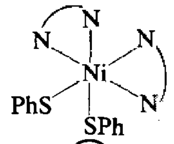
(269) Ni—S (av) 220 pm
Ni—Ni (av) 292 pm



(270) Ni—S (av) 220 pm
Ni—Ni (av) 292 pm

The complex **(269)** is hexameric in the solid state and in solution, and the same structure presumably occurs in the complexes $Ni(SR)_2$ obtained from reaction (197). In the cyclic hexamer the six nickel atoms form a regular hexagon with twelve symmetrically bridging SEt^- groups which are situated above and below the plane of the nickel atoms.[1944] A corresponding cyclic tetramer has been obtained with *N*-methylpiperidine-4-thiolate anion, $SC_5H_9NMe_2^-$.[1946] Also in the complex $[Ni(SC_5H_9NMe)_2]_4$ **(270)** the nickel atoms lie in a plane.

Mixed ligand complexes containing coordinated mercaptans were obtained in a number of ways (equations 190, 199–203).[1935,1948,1949] The complex $Ni(SPh)_2(bipy)_2$ **(271)** is *cis* octahedral with room temperature magnetic moment $\mu_{eff} = 3.03$ BM.[1950] The Ni—S bond distance is 244 pm, significantly larger than those observed in both square planar and tetrahedral complexes.



(271) N⌒N = bipy
Ni—S 244 pm

$$\mathrm{Ni(cpd)(PBu^n_3)_2^+ + SR^- \xrightarrow{H_2O} Ni(cpd)(SR)(PBu^n_3)} \quad R = Et, Ph \tag{199}$$

$$\mathrm{Mo(cod)_2(SMe)_2 + NiCl_2(dmpe) \xrightarrow[heat]{THF} (cod)_2Mo(SMe)_2Ni(dmpe)} \tag{200}$$
$\mathrm{dmpe = Me_2PCH_2CH_2PMe_2}$

$$\mathrm{NiCl_2(Et_3P)_2 + PhSNa \xrightarrow{C_6H_6/EtOH} Ni(SPh)_2(Et_3P)_2} \tag{201}$$

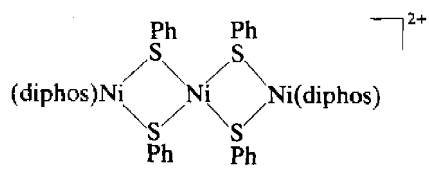
$$\mathrm{Ni(CO)_2(diphos) + PhSSPh \xrightarrow[reflux]{C_6H_6/hexane} Ni(SPh)_2(diphos)} \tag{202}$$

$$\mathrm{Ni(cpd)_2 + RSSR + 2L \xrightarrow{toluene/N_2} Ni(SR)_2L_2} \tag{203}$$
$\mathrm{R = Ph}, p\text{-}\mathrm{ClC_6H_4}, p\text{-}\mathrm{NO_2C_6H_4}$; L = bipy; R = Ph; $\mathrm{L = Et_3P}$

When simple nickel(II) salts are treated with thiols, in most cases stable thiolate-bridged polymers are formed. In a number of cases, treating these polymers with either tertiary phosphines or isocyanides gave mononuclear mixed-ligand complexes (equation 204).[1951] These mononuclear complexes, due to the presence of terminal thiolates which possess lone pairs, can further react with nickel(II) and give trinuclear complexes (equation 205).[1952]

$$\mathrm{[Ni(SPh)_2]_n} + m\mathrm{L} \xrightarrow[reflux]{CH_2Cl_2} \mathrm{Ni(SPh)_2L_2} \tag{204}$$
$\mathrm{L = PPhMe_2}$, $\frac{1}{2}$diphos, $\mathrm{C_6H_{11}CN}$

$$\mathrm{Ni(SPh)_2(diphos) + Ni(H_2O)_6^{2+} \xrightarrow{CH_2Cl_2/MeCN}} \tag{205}$$



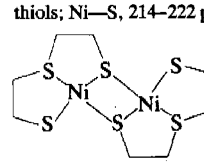
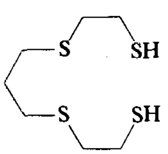
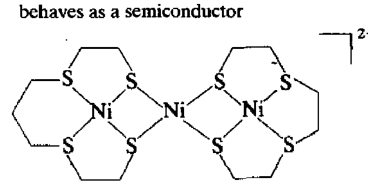
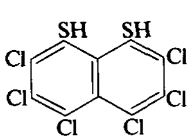
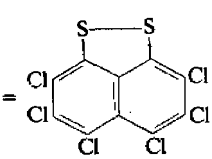
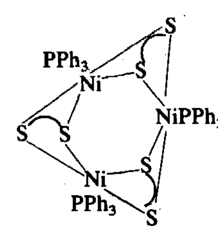
The nickel(II) complexes with bidentate dithiols, starting from those with 1,2-ethanedithiol, are well documented but they still remain far less numerous than those with 1,2-dithiolenes (Section 50.5.6.5.i). In Table 88 selected nickel(II) complexes with some dithiols and related ligands are reported together with synthetic and structural properties.

50.5.6.3 Complexes with thioethers and related ligands

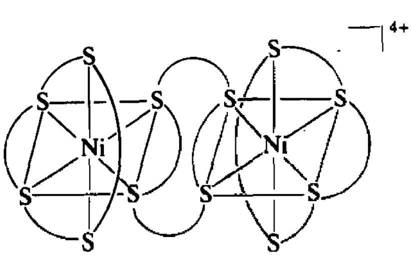
Thioethers have scarce σ donor and even lesser π back-donation capacity and by consequence monodentate thioethers are relatively poor ligands towards nickel(II). No nickel complex with monodentate thioethers has been reported so far to the best of our knowledge. The coordination capability of thioethers is substantially enhanced by chelation so that several nickel(II) complexes with polydentate thioether ligands have been reported. Contrary to the nickel(II) complexes with sulfide and mercaptide, six-coordination and high-spin configuration are common features of nickel(II) complexes with polydentate thioethers. These complexes are, in general, easily obtained by the direct synthesis of the appropriate ligands with nickel(II) salts, often in anhydrous conditions. Selected nickel(II) complexes with representative thioether ligands and their structural and synthetic properties are shown in Table 89.

The tetrathia macrocycles containing up to 13-membered chelate rings are too small to encircle the nickel(II) atom in a square-planar chelation like tetraaza macrocycles do, and give rise to dinuclear complexes. In contrast, a planar chelation was found with the 14-membered macrocycle 1,4,8,11-[S_4]-14-ane.[1967]

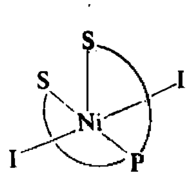
Table 88 Synthetic and Structural Properties of Selected Nickel(II) Complexes with Dithiols and Related Ligands

Ligand	*Complex*[a]	*Preparation*	*Remarks*	*Ref.*
CH_2—CH_2 SH SH (H_2edt)	$Ni_2(edt)_3^{2-}$, $Ni(edt)_2^{2-}$	$NiCl_2$, H_2edt in NH_3 buffer	Stable species prepared in air-free solution	1953
CH_2—CH_2—CH_2 SH SH OH (H_2dmp)	$[Ni_2(dmp)_3(OH)]^{3-}$, $Ni(dmp)_2^{2-}$	As above	Prepared in solution; coordination through S atoms of the ligand	1954
CH_2—CH_2 SH SH (H_2edt)	$[Ni(edt)(PPh_3)]_2$	$Ni(PPh_3)_4 + H_2edt$, CH_2Cl_2/hexane	Unstable compound; assumed dinuclear SqPl structure	1955
	Ni(edt)(diphos)	$NiCl_2{\cdot}6H_2O$ + diphos + H_2edt, H_2O/EtOH; $[Ni(edt)]_n$ + diphos	SqPl, mononuclear	1951, 1955
	$Ni(edt)(PMe_2Ph)$	$[Ni(edt)]_n + PMe_2Ph$	SqPl, mononuclear	
$HS(CH_2)_2S(CH_2)_2SH$ (H_2dmes)	$Ni_2(dmes)_2$	$NiSO_4 + H_2dmes$ in NH_3 buffer, H_2O/acetone solution	Dinuclear structure; the molecule is folded about the bridging thiols; Ni—S, 214–222 pm 	1956
 (H_2ttn)	$[Ni_3(ttn)_2](BF_4)_2$	$Ni(BF_4)_2{\cdot}6H_2O + H_2ttn$ in ethanol	SqPl coordination of nickel(II); $[Ni_3(ttn)_2](TCNQ)_2$ behaves as a semiconductor 	1951, 1952
 H_2L	$Ni_3L_3(PPh_3)_3$	$Ni(cod)_2$ + L′ + PPh_3; C_6H_6/hexane/N_2 L′ = 	 Ni—S in the range 225–234 pm S—S (intraligand), 305 pm S—S (interligand), 321 pm Ni—Ni (av) 264 pm	1957

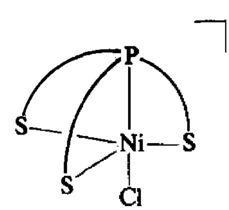
[a] All of the complexes are diamagnetic.



(272)



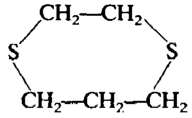
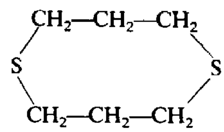
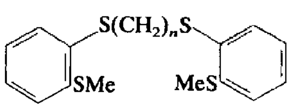
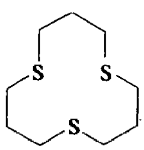
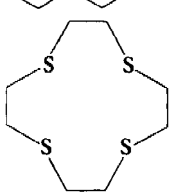
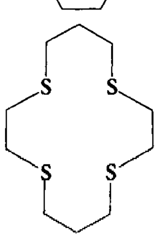
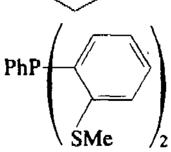
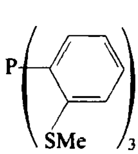
(273) Ni—S (ap) 279 pm
Ni—S (eq) 219 pm



(274) Ni—S (av) 227 pm

The rigid tripodal shape of the $P(C_6H_4SMe)_3$ ligand allows trigonal coordination. Moreover, the high nucleophilicity of the donor atoms strongly favours low-spin configurations. Actually, the

Table 89 Synthetic and Structural Properties of Selected Nickel(II) Complexes with Thioether Ligands

Ligand	*Complex*	*Preparation*	*Remarks*	*Ref.*
$MeSCH_2CH_2SMe$ $EtSCH_2CH_2SEt$ $Pr^iSeCH_2CH_2SePr^i$	NiL_2X_2	Direct synthesis in EtOH	Six-coordinate; X = halides, NCS; chelate ligands	1958–1960
 (dtch)	$NiL_2(BF_4)_2$	$Ni(EtOH)_6(BF_4)_2$ + dtco (dtch); $MeNO_2$, anhydrous conditions	L = dtch, dtco; SqPl; diamagnetic	1961
 (dtco)	NiL_2I_2 $NiLI_2$	Direct synthesis As above	L = dtch, Oh; L = dtco, SqPl L = dtco, Td	
	$Ni(dtco)_2Cl_2$	$NiCl_2$ + dtco; EtOH, anhydrous conditions	Oh; polynuclear with bridging bidentate ligands; Ni—S (av), 249 pm	1961, 1962
$MeS(CH_2)_nS(CH_2)_mS(CH_2)_nSMe$	$NiLX_2$	NiX_2·aq in boiling BuOH, L in CH_2Cl_2	$n = m = 2$; X = Cl, Br, I $n = 2$, $m = 3$; X = Br, I $n = 3$, $m = 2$; $n = m = 3$; X = I Oh; μ_{eff} = 2.9–3.24 BM; tetradentate ligand	1963
$MeSe(CH_2)_2Se(CH_2)_3Se(CH_2)_2SeMe$	$NiL_{1/2}I_2$	$NiI_2·6H_2O$ + hot BuOH + ligand	Oh; polynuclear with $NiSe_2I_4$ chromophore; μ_{eff} = 2.98 BM	1964
	$NiLX_2$	NiX_2·aq in boiling BuOH, L in CH_2Cl_2	X = halides; n = 2, 3; Oh; μ_{eff} = 2.9–3.23 BM; tetradentate ligand	1965
	$[NiL_2](BF_4)_2$	$Ni(MeCO_2H)_6(BF_4)_2$ + L in $MeNO_2$	Oh; μ_{eff} = 3.19 BM	1966
	$[Ni_2L_3](BF_4)_4$	As above	Oh; μ_{eff} = 3.06 BM; proposed dinuclear structure (**272**)	1966
	$[NiL](BF_4)_2$	As above	SqPl; diamagnetic; Ni—S, 218 pm (av)	1966, 1967
	$[NiLX_2]$	$(NiL)(BF_4)_2$ + NaX; $MeNO_2$, anhydrous conditions	X = halides, NCS; *trans* Oh; μ_{eff} = 3.04–3.18 BM	
	$[NiLX_2]$ $[NiL_2](ClO_4)_2$	Direct synthesis in acetone	X = halides; diamagnetic; SqPy structure (**273**); Ni—S (eq), 219 pm (av); Ni—S (ap), 279 pm	1968, 1969
	$[NiLX]ClO_4$	$Ni(ClO_4)_2·6H_2O$ + NiX_2 + L, hot BuOH	X = halides, NCS; diamagnetic; TBPy structure (**274**); Ni—S (av), 227 pm	1970, 1971
			Analogous complexes with $P(C_6H_4SeMe)_3$	1972
	$[NiLB](ClO_4)_2$	Direct synthesis in hot BuOh	B = neutral ligand such as PR_3, diphos, thiourea; five- and six-coordinate complexes	1970

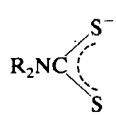
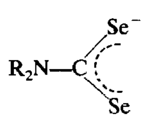
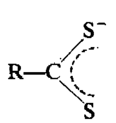
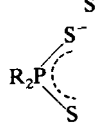
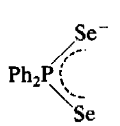
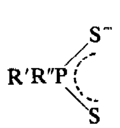
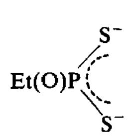
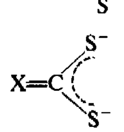
majority of the complexes formed by the aforementioned ligand are diamagnetic with a trigonal bipyramidal geometry, but paramagnetic six-coordinate complexes were also obtained.[1970]

50.5.6.4 Complexes with four-membered chelate rings

(*i*) *Complexes with dithiocarbamates, xanthates and related RCSS⁻ mononegative chelating ligands*

Substituted dithioformate anions as ligands $R'C(S)S^-$ are usually called dithiocarbamates ($R' = R_2N$), alkyl and aryl dithiocarbonates or xanthates ($R' = RO$), alkyl and aryl trithiocarbonates or thioxanthates ($R' = RS$). Dithioacid anions (R' = alkyl, aryl) have been rarely used as ligands of nickel(II) because of their instability. Structural properties of selected nickel(II) complexes with substituted dithioformate, dithiolene and related ligands are shown in Table 90.

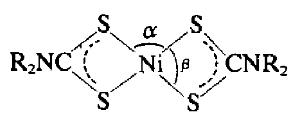
Table 90 Structural Properties of Selected Complexes with Dithioformates, Phosphorodithioates, 1,1-Dithiolenes and Related Ligands

Ligand		*Complex*	*Coordination geometry*	*Bond distances*[a] (pm) *Ni—S(Se)*	*C(P)—S(Se)*	*Ref.*
	R = H	NiL_2	SqPl	221	169	1973
	R = Et	NiL_2	SqPl	220	171	1974
	R = Et	NiL_2	SqPl	232	186	1975
	R = Bu^n	NiL_2	SqPl	231	186	1976
	R = $OC_6H_4Bu^t$	NiL_2	SqPl	222	169	1977
	R = OBu^i	$[NiL_3]^-$	Oh	243	167	1978
	R = Ph	$[NiL_2]_3$	SqPl[b]	222	170	1979
	R = $PhCH_2$	$[NiL_2]_2$	SqPl[b]	222	164, 172	1980
	R = OEt	NiL_2	SqPl	224	199	1981
	R = OEt	NiL_2py_2	*trans* Oh	250	199	1982
	R = Et	NiL_2	SqPl	223	221	1983
		NiL_2	SqPl	235	217	1984
	$R' = OPr^i$; $R'' = Et$	NiL_2	SqPl	212–226	190, 203	1985
	$R' = Me$, $R'' = NMe_2$	NiL_2	SqPl	222	199	1986
		$[NiL_2]^{2-}$	SqPl	222	203	1987
	X = $CC(OOEt)_2$	$[NiL_2]^{2-}$	SqPl	219	174	1988
	X = S	$[NiL_2]^{2-}$	SqPl	220	170	1989

[a] Average values.
[b] Additional intermolecular Ni—S interactions occur between either three or two SqPl molecules.

Dithiocarbamates of nickel(II) have been well known for a long time[1990] and numerous complexes having the general formula $Ni(RR'NCS_2)_2$ have been synthesized and characterized with unsubstituted ($R = R' = H$),[1991] *N*-substituted ($R = H$, $R' = Me$, Pr^i, Ph, tolyl) and *N,N*-disubstituted ($R = R' = Me$, Et, Pr^n, Pr^i, Bu^n, Bu^i; $R = Ph$, $R' = Me$, Et, *etc.*)[1992–1996] dithiocarbamates. A number of analogous diselenocarbamate complexes were also reported.[1997,1998]

The complexes have been generally prepared by direct reaction of a nickel(II) salt with an alkali metal or ammonium salt of the appropriate dithioacid in aqueous solution where the $Ni(S_2CNR_2)_2$ derivatives are quite insoluble. The complexes are dark coloured, often black, in the solid state and red or brownish in dilute solutions of organic solvents. All of the bis chelates are square planar as observed in the X-ray crystal structure of $Ni(RR'NCS_2)_2$: $RR'N =$ H_2N,[1973] MeNH,[1999] Pr^iNH,[2000] Et_2N,[1974] Pr^n_2N,[2001] Pr^i_2N,[2002] Bu^i_2N,[2003] MePhN,[2004] $O(CH_2CH_2)_2N$,[2005] $(C_3H_5)_2N$ (C_3H_5 = allyl),[2006] $\overline{CH_2CH_2CH_2CH_2N}$.[2007] These complexes are strictly planar (**275**) with the metal forming a four-membered chelate ring with the CS_2 moieties. The Ni—S bond distances are in the range 220–221 pm, and α and β angles average 100° and 80°, respectively. The two C—S bond distances in each ligand molecule are equal within experimental error and in the range 169–171 pm.



(**275**)

Complexes with formula $Ni(L^+)_2Cl_4$ were reported with the cationic ligand $[(Et_2N(H)CH_2CH_2)_2NCS_2]^+$.[2008]

Most of the complexes with the ligand R_2NNHCS_2 are square planar.[2009]

The square planar bis(dialkyldithiocarbamato)nickel(II) derivatives generally do not form adducts with monodentate Lewis bases. The first complex of this type, $NiL_2(4pic)_2$, was reported only recently.[2010]

Electronic,[1991,2011–2013] NMR,[2014,2015] IR and resonance Raman[1991,2016,2017] and, recently, UV photoelectron spectra of $Ni(R_2NCS_2)_2$ complexes were investigated.[2018]

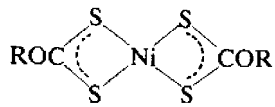
Standard enthalpies of formation of bis(dithiocarbamato)nickel(II) complexes were also reported[2019] and the results indicate that Ni—O and Ni—S bond energies in square planar nickel complexes are approximately the same from a thermochemical point of view. The electron-transfer properties of various dithiocarbamato and diselenocarbamato complexes were investigated by voltammetric techniques.[2020,2021] The observed processes were found to be irreversible.

Xanthate complexes of nickel(II) were prepared with a number of alkyl and aryl substituents[2022–2025] along with a few thioxanthate derivatives[2026,2027] which are, in general, less stable than xanthate complexes. Xanthate and thioxanthate complexes can be conveniently prepared by direct synthesis in aqueous solution of nickel acetate with alkali metal salts of the appropriate ligand. The $Ni(S_2COR)_2$ derivatives are lightly soluble in water and closely resemble the dithiocarbamate complexes. All of these complexes are square planar (**276**).[1977,2028] The $Ni(Se_2COEt)_2$ derivative was also reported.[2029]

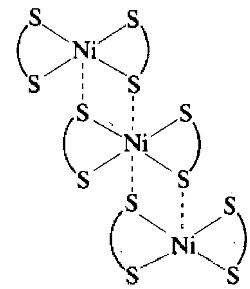
Solutions of $Ni(S_2COR)_2$ react with KS_2COR affording the tris chelates which may be obtained as crystalline compounds upon addition of large cations such as Me_4N^+ or $Bu^n_4N^+$.[1991] The complexes with the ligands where $R = Bu^n$,[2030] Bu^i [1978] and cyclohexyl[2031] have a pseudooctahedral structure with an NiS_6 chromophore. Six-coordinate adducts of the type $Ni(S_2COR)_2B_2$ (B = py, ½bipy, phen) are stable in the solid state and in solution.[1991,2032,2033] The tris chelates and the bis adducts are high-spin.

Dithiocarboxylate complexes $Ni(S_2CR)_2$ ($R = Ph$, CH_2Ph) have been prepared by the reaction of a nickel(II) salt with NaS_2CR in water–EtOH mixture.[2034] They are diamagnetic and contain essentially four-coordinate nickel(II). An association occurs in the bis(dithiobenzoato)nickel(II) derivative between three closely parallel molecules (**277**) through short Ni—S linkages (intermolecular Ni—S bond distances in the range 277–311 pm).[1979] An association between pairs of square planar complexes also occurs in the $Ni(S_2CBu^t)_2$ derivatives.[2035] The complexes $Ni(S_2CR)_2$ ($R = Me$, CH_2Ph) are dinuclear with the ligands acting as bridging groups between two nickel atoms (**278**).[1980]

Six-coordinate bis adducts $Ni(S_2CR)_2py_2$ ($R = Ph$, CH_2Ph) were also reported.[2036] Finally, the



(276)



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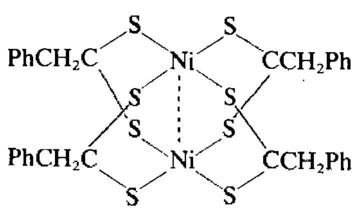
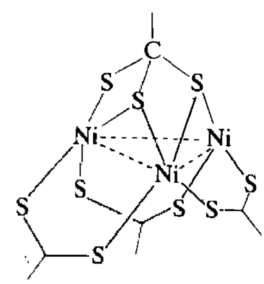


(278)

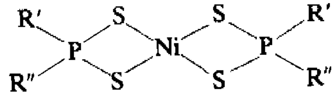


(279)

$Ni(S_2CR)_2$ ($R = -\overline{C\text{-}B_{10}H_{10}-C}Ph$) complexes and their five-coordinate adducts can be mentioned.[2037] The reaction of bis(dithioacetato)nickel(II) with CS_2/ethanol afforded a trinuclear complex (**279**) which contains three $MeCS_2^-$ bridges and a μ_3-trithioorthoacetato group $MeCS_3^{3-}$, presumably formed by the reaction of $MeCS_2^-$ with CS_2.[2038]

(*ii*) *Complexes with phosphorodithioate ligands*

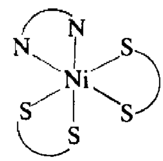
Numerous complexes of nickel(II) with phosphorodithioate ligands (also called dithiophosphates; **280**; R′ = R″ = *O*-alkyl, *O*-aryl) and dithiophosphinates (**280**; R′ = R″ = alkyl, aryl) have been reported to date. A few dithiophosphonato complexes (**280**; R′ = alkyl, R″ = *O*-alkyl) were also reported. The bis(dialkyldithiophosphato)nickel(II) complexes were obtained as purple diamagnetic compounds by means of the direct synthesis between the appropriate dithioacid $(RO)_2P(S)SH$ and a nickel(II) salt, often the acetate hydrate. The dithioacid can be conveniently prepared *in situ*, by reacting P_4S_{10} with the appropriate alcohol which sometimes acts by itself as reaction medium. Structural properties of selected nickel(II) complexes are reported in Table 90.



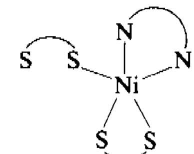
(280)

Complexes having the general formula $[Ni\{S_2P(OR)_2\}_2]$ (R = Me, Et, Pr^n, Pr^i, Bu^n, cyclohexyl, CH_2CH_2Cl, CH_2CH_2Ph, *etc.*)[2039–2044] are invariably square planar with the ligands acting as chelate and forming four-membered chelate rings with nickel, as found in the molecular structures of the complexes with the ligands where R = Me[2045] or Et,[1981] and R_2 = 1,1′-dinaphthyl-2,2′-diyl.[2046] The same holds for the $[Ni\{Se_2P(OEt)_2\}_2]$ derivative.[2047] The IR spectra of the aforementioned complexes were recently investigated.[2048]

The purple diamagnetic square planar complexes $[Ni\{S_2P(OR)_2\}_2]$ readily add either monodentate or bidentate bases such as py and substituted pyridines,[2040,2049] bipy, phen[2040,2050] and *N*-substituted en[2051] to form green paramagnetic derivatives which possess either a *cis* octahedral structure, $[Ni\{S_2P(OR)_2\}_2bipy]$,[2052] $[Ni\{S_2P(OEt)_2\}_2phen]$,[2053] $[Ni\{S_2P(OEt)_2\}_2\text{-}tmed]$[2054] (**281**) or a *trans* octahedral structure, $[Ni\{S_2P(OEt)_2\}_2py_2]$.[1982] The complex $[Ni\{S_2P(OMe)_2\}_2dmphen]$ (dmphen is 2,9-dimethyl-1,10-phenanthroline) (**282**), however, is high-spin five-coordinate ($\mu_{eff} = 3.2$ BM) with one chelating and one monodentate dithiophosphate ligand.[2055] The mechanism of the substitution reaction[2056] and the electronic spectrum[2057] of the latter five-coordinate complex were investigated. The reaction of tertiary phosphines with $Ni\{S_2P(OR)_2\}_2$ complexes gives different derivatives depending on the nature of the phosphine. Either paramagnetic, $[Ni\{S_2P(OR)_2\}_2PPh_3]$, or diamagnetic, $[Ni\{S_2P(OR)_2\}_2PR_3]$ ($PR_3 = PBu_3$, PCy_3, PMe_2Ph, $PMePh_2$), five-coordinate complexes were reported with monodentate phosphines.[2058,2059]

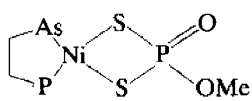


(**281**) N⌒N = bipy, phen, tmed; S⌒S = $S_2P(OR)_2$



(**282**) N⌒N = 2,9-Me_2phen; S⌒S = $S_2P(OMe)_2$

1-Diphenylarsino-2-diphenylphosphinoethane (dpae) reacts with $[Ni\{S_2P(OMe)_2\}_2]$ according to equation (206).[2060] This type of elimination reaction also occurs with diphos but remains uncommon for nickel(II).

$Ni\{S_2P(OMe)_2\}_2$ + dpae ⟶  + $MeS(S)P(OMe)_2$ (206)

Bis(dialkyldithiophosphinato)nickel(II) complexes were prepared by the direct synthesis of an alkali metal or ammonium salt of the dithiophosphinic acid and a nickel salt in aqueous solution.[2039,2061–2063] $Ni(S_2AsR_2)_2$ and $Ni(Se_2PR_2)_2$ complexes were prepared in a similar way.[2064–2066] All of these complexes are square planar like their dithiophosphate analogues. X-Ray crystal structures of the complexes $Ni(S_2PR_2)_2$, with R = Me,[2067] Et, Ph,[1983] R_2 = Me/Et,[2068] R_2 = Me/2-thienyl,[2069] and $Ni(Se_2PPh_2)_2$[1984] have been reported (Table 90).

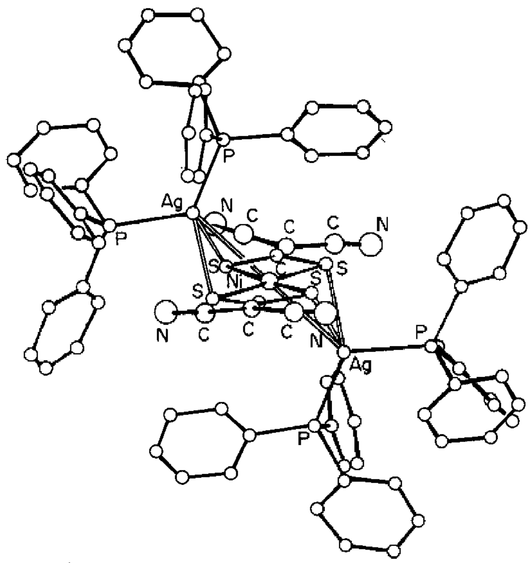
Either five- or six-coordinate adducts have been obtained with a number of nitrogen donors.[2070–2073]

Polynuclear square planar complexes were prepared with the bifunctional dithiophosphinate ligand $[S_2P(R)(CH_2)_nP(R)S_2]^{2-}$ (n = 4–10).[2074]

(*iii*) *Structural properties and reactivity of complexes with 1,1-substituted ethylene-2,2-dithiolates and related binegative and mononegative ligands*

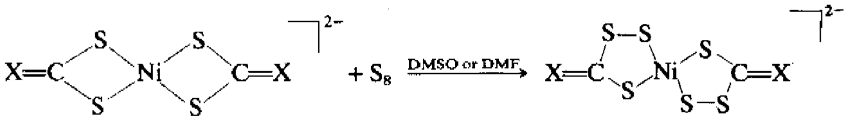
The preparation of $(cat)_2(NiL_2)$ complexes (cat is a large monopositive cation and L is a 1,1-disubstituted ethylene-2,2-dithiolate dianion) is generally accomplished using the sodium or potassium salt of the ligand and a nickel(II) salt in water–ethanol solution. The addition of a large cation readily affords crystalline compounds which may be of different colours, ranging from yellow-green to blue-violet. A number of complexes were synthesized in this way with various ligands of the type $R'R''CCS_2^{2-}$ where R′ = R″ = CN;[2075,2076] R′ = H, R″ = Ph; R′ = CN, R″ = COPh;[2077] and R′ = R″ = CO_2Et.[1988] All of the complexes $(cat)_2[Ni(S_2CCR'R'')_2]^{2-}$ are square planar. X-Ray crystal structures were determined for the complexes with R′ = R″ = CO_2Et[1988] (Table 90) and R′ = R″ = CN.[2078] In the latter, $[Ag(PPh_3)_2][Ni(S_2CC(CN)_2)_2]$, an interaction occurs between the NiS_4 moiety and the $Ag(PPh_3)_2^+$ cations which are located above and below the NiS_4 plane (**283**). Other structural characterizations refer to the complex $(Ph_4As)_2[Ni(CS_3)_2]$ (Table 90),[1989] $(Et_4N)_2[Ni(S_2CC_5H_4)_2]$ ($S_2CC_5H_4^{2-}$ = cyclopentadienedithiocarboxylato dianion),[2079] $(Bu_4N)_2[Ni\{SeSCC(CN)_2\}_2]$[2080] and $(Ph_4As)_2[Ni\{S_2CN(CN)\}_2]$ ($S_2CN(CN)^{2-}$ = *N*-cyanodithiocarbimato dianion).[2081] In the case of the complex with the trithiocarbonate ligand, CS_3^{2-}, the use of Ph_4As^+ or $Ni(NH_3)_6^{2+}$ as countercations was found to be decisive in obtaining solid compounds.[2076,2082]

A few complexes formed by the tetrathiomolybdate and tetrathiotungstate dianions MS_4^{2-} (M = Mo, W) as ligands have been synthesized. They have the general formula $(cat)_2[Ni(MS_4)_2]$ (cat = Et_4N, Ph_4As; M = Mo, W).[2083–2088]



(283)

The complexes $(R_4P)_2[Ni(CS_3)_2]$, $(R_4P)_2[Ni(S_2CCHNO_2)_2]$ and $(R_4P)_2[Ni(S_2CC(CN)COPh)_2]$ undergo sulfur addition to the ligands which are converted to perthio derivatives still coordinated to nickel(II) (equation 207).[2077] An analogous sulfur addition is promoted by the iodine oxidation of the parent 1,1′-dithiolate complexes. On the other hand, by means of the solid state reaction (208) only the violet mixed-ligand complex $Ni(S_3CPh)(S_2CPh)$ was obtained.[2025] Similar complexes were presumably obtained by the oxidation of the parent complexes $Ni(S_2CPh)_2$ and $Ni(S_2CNHPh)_2$ with ammonium polysulfide.[2089]



(207)

X = S, $CHNO_2$, C(CN)COPh

$$RCO_2H + P_2S_5 + Et_4NCl{\cdot}H_2O \xrightarrow[NiCl_2{\cdot}6H_2O]{\text{melting}} Ni(S_3CR)(S_2CR) \qquad (208)$$

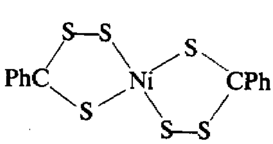
R = Ph, Bu^t, p-MeC_6H_4

$$Zn(S_3CR)_2 + NiCl_2{\cdot}6H_2O \xrightarrow{CS_2/EtOH} Ni(S_3CR)_2 + ZnCl_2 \qquad (209)$$

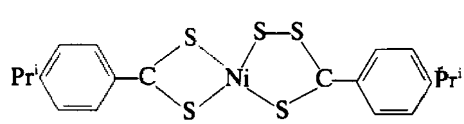
R = Ph, p-MeC_6H_4, Bu^t

The bis(perthioacid) complexes are conveniently and surely obtained as dark green or dark red compounds by means of the metathetical reaction (209).[2090–2092]

All of these 'sulfur-rich' derivatives are square planar complexes of nickel(II) as found in the X-ray crystal structures of $[Ni(S_3CPh)_2]$ (**284**)[2093] and $[Ni(S_3CR)(S_2CR)]$ (**285**).[2094]



(284)

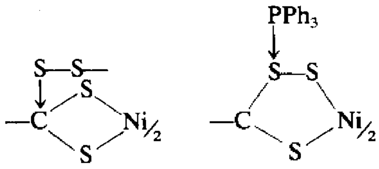


(285)

We may mention here the recently reported black compound $Ni(S_3N)_2$ formed by the $SNSS^-$ thio analogue of the peroxynitrite anion.[2095,2096]

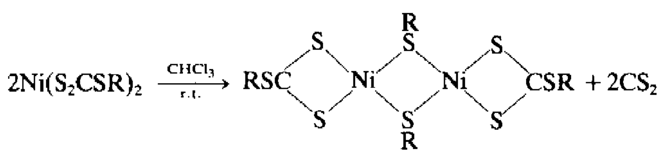
By heating solutions of $[Ni(S_3CR)_2]$ and $[Ni(S_3CR)(S_2CR)]$ with an excess of PPh_3 it was possible to recover the parent bis(dithio) complexes and Ph_3PS.[2025,2090] It has been suggested that in the oxidative formation of the perthio derivatives the sulfur attack initially occurs at the

CS_2 carbon of the parent ligand (**286**) and that the removal of the sulfur atom from the disulfide moiety by means of PPh_3 involves the sulfur atom adjacent to the carbon atom.



(**286**)

A reaction typical of the thioxanthate derivatives is the CS_2 elimination in very mild conditions with the formation of stable dimeric species with mercapto bridges (equation 210).[2097–2100] Conversely, reaction (211) represents CS_2 insertion into [(cpd)Ni(SEt)PBu_3] to produce an ethylthioxanthate complex[2100] where the ethylthioxanthate anion acts like the S_2COEt^- anion in the complex [(cpd)Ni(S_2COEt)Ph_3].[2101] Insertion reactions have also been reported to occur with PhNCS.[2102]



(210)

R = Et, Bu^t, CH_2Ph

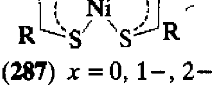
$$\text{(cpd)Ni(SEt)(PBu}_3\text{)} \xrightarrow[\text{r.t.}]{CS_2} \text{(cpd)Ni\{SC(S)SEt\}(PBu}_3\text{)} \quad (211)$$

A number of nickel(II) complexes containing η^2-bonded deprotonated dithioacids have recently been synthesized in the presence of triphos as ancillary ligand. It was found that $NaBH_4$ reacts with these complexes affording different compounds depending on the nature of the dithioacid (Scheme 25a).[2103] Nucleophiles such as PEt_3 and $NHEt_2$ have also been found to attack the carbon atom of the η^2-coordinated S_2CSMe group (Scheme 25b).[2104] The mixed-ligand complexes with η^2-coordinated trithiocarbonate, [Ni(CS_3)L] (L = triphos, diphos), have been prepared. The complex with triphos, because of the nucleophilicity of the uncoordinated sulfur atom, has been found to react with various metal–ligand moieties affording both mono- and hetero-metal complexes (Scheme 25c).[2105,2106] The same complex also reacts with dimethylacetylenedicarboxylate as outlined in Scheme 25d.[2107]

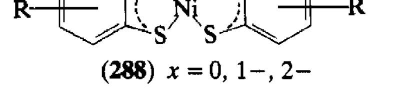
50.5.6.5 Complexes with five- and six-membered chelate rings

(*i*) *Complexes with 1,2-dithiolene ligands*

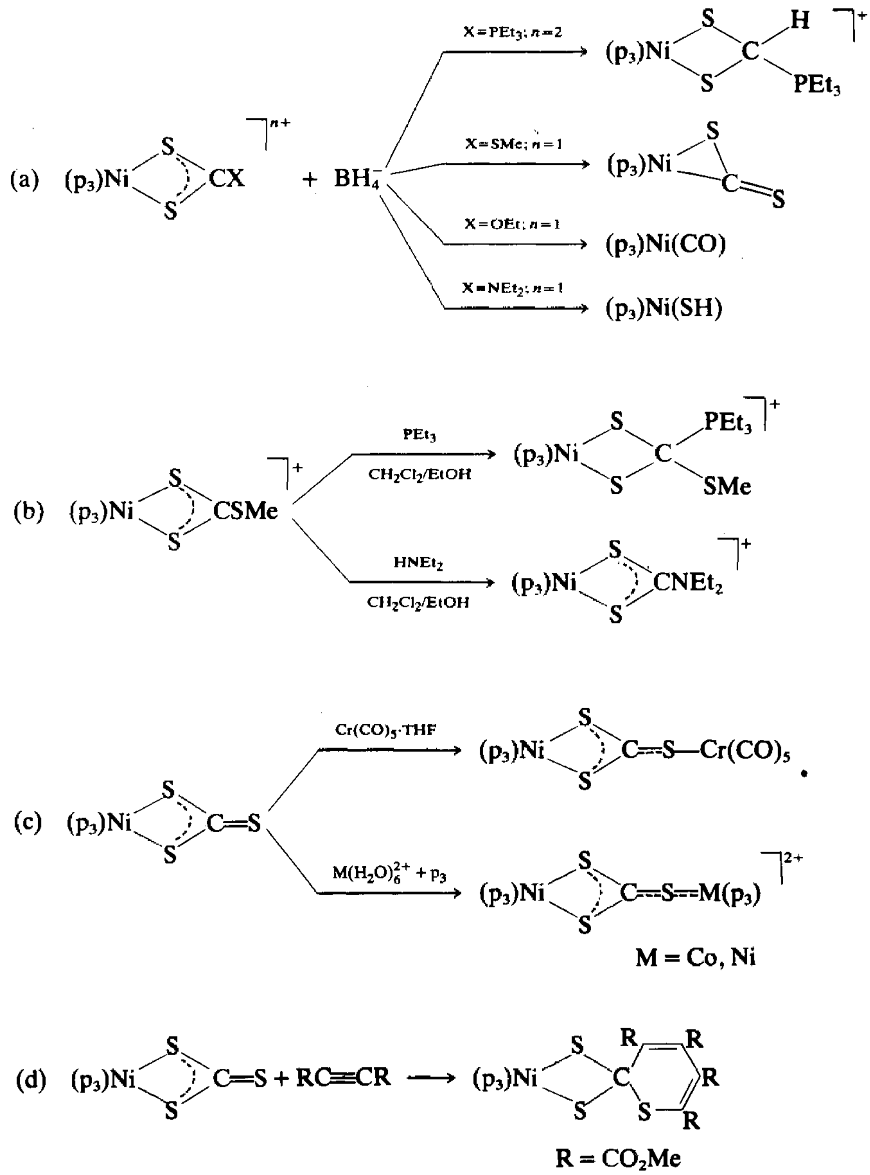
The chemistry of bis(1,2-dithiolene) complexes of nickel has stimulated considerable investigations over the past 20 years, owing to the peculiar and unusual electronic and electrochemical properties which the complexes exhibit both in the solid state and in solution. A number of articles cover the early reports up to 1970[1923,1925,1927,2108] on nickel complexes having general formulas (**287**) and (**288**). The formulas of representative complexes together with the synthetic routes and some physicochemical properties are summarized in Table 91.



(**287**) $x = 0, 1-, 2-$



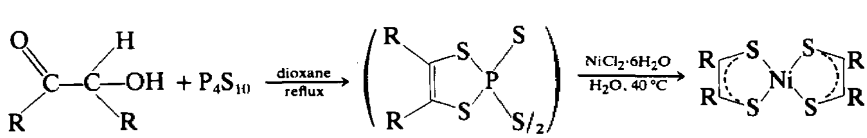
(**288**) $x = 0, 1-, 2-$



p_3 = 1,1,1-tris(diphenylphosphinomethyl)ethane

Scheme 25

The first general synthesis of neutral complexes $Ni(S_2C_2R_2)_2$ is given in equation (212).[2109] Mixed-ligand phosphino complexes were also prepared according to equations (213) and (214).[2116]



(212)

R = alkyl, aryl, CF_3

$$Ni(CO)_2(PPh_3)_2 + (CF_3)_2C_2S_2 \xrightarrow{CH_2Cl_2} Ni\{S_2C_2(CF_3)_2\}(PPh_3)_2 \tag{213}$$

$$NiBr_2(PPh_3)_2 + Na_2S_2C_2(CN)_2 \xrightarrow{acetone} Ni\{S_2C_2(CN)_2\}(PPh_3)_2 \tag{214}$$

$$[Ni(S_2C_2R_2)_2] \underset{-e^-}{\overset{e^-}{\rightleftharpoons}} [Ni(S_2C_2R_2)_2]^- \underset{-e^-}{\overset{e^-}{\rightleftharpoons}} [Ni(S_2C_2R_2)_2]^{2-} \tag{215}$$

Table 91 Synthetic Procedures and Properties of the Complexes $(cat)_x[Ni(S_2C_2R_2)_2]$ ($x = 0, 1, 2$)

Complex	*Method of preparation*	*Remarks*[a]	*Ref.*
$[Ni(S_2C_2R_2)_2]$	See equation (212)	R = Me, Et, Pr^n, Ph, CF_3; insoluble in water and slightly soluble in organic solvents	2109
$[Ni\{S_2C_2(CF_3)_2\}_2]$ (A)	$Ni(CO)_4 + S_2C_2(CF_3)_2$;[b] pentane	$\mu_{eff} = 1.85$ BM	2110
$(Et_4N)[Ni\{S_2C_2(CF_3)_2\}_2]$ (B)	(A) + Et_4NBr; acetone		2110
$(Et_4N)_2[Ni\{S_2C_2(CF_3)_2\}_2]$	(B) + p-$C_6H_4(NH_2)_2 + Et_4NBr$; DMSO, EtOH	Oxidized to the monoanion by I_2	2110
$(Ph_4As)_2[Ni\{S_2C_2(CF_3)_2\}_2]$	$NiBr_2(PPh_3)_2 + S_2C_2(CF_3)_2$[b] + $H_2NNH_2 + Ph_4AsCl$; benzene	The mononegative complex was prepared analogously, without hydrazine reduction	2111
$(Et_4N)[Ni(S_2C_2Ph_2)_2]$	$Ni(S_2C_2R_2) + Et_4NBr$	$\mu_{eff} = 1.82$ BM	2110
$[Et_4N)_2[Ni\{S_2C_2(CN)_2\}_2]$ (C)	$Na_2S_2C_2(CN)_2 + NiCl_2 + Et_4Br$; H_2O–MeOH		2112
$(Et_4N)[Ni\{S_2C_2(CN)_2\}_2]$	Oxidation of (C) with I_2 in DMSO, EtOH	Reduced to the dianion by basic solvents; $\mu_{eff} = 1.02$ BM	2110
$[Ni(S_2C_2H_2)_2]$	$Na_2S_2C_2H_2$[c] + Ni^{2+}; EtOH	Obtained in low yield; soluble in organic solvents	2113
$(Bu_4N)[NiS_2C_6H_4)_2]$	$K_2S_2C_6H_4$[d] + $NiCl_2 \cdot 6H_2O + Bu_4NBr$; EtOH	$\mu_{eff} = 1.83$ BM	2114
$(R_4N)[Ni(S_2C_6R'_2R''_2)_2]$	As above	R' = R'' = Me, Cl; R' = H, R'' = Me $\mu_{eff} = 1.82$–1.83 BM	2114
$(Bu_4N)[Ni(S_2C_2R_2)(S_2C_2R'_2)]$	$(Bu_4N)_2Ni(S_2C_2R_2)_2 + Ni(S_2C_2R'_2)_2$; acetone, reflux	R = CN, R' = Ph	2115
$(Et_4N)_2[Ni(S_2C_2R_2)(S_2C_2R'_2)]$.	$Ni(S_2C_2R_2)(PPh_3)_2 + (CF_3)_2C_2S_2$ + $H_2NNH_2 + Et_4NBr$	R = CN, R' = CF_3	2115

[a] All of the complexes are assumed to be SqPl and are diamagnetic unless otherwise stated.

[b] Bis(difluoromethyl)dithiene, S—CCF$_3$ | || S—CCF$_3$

[c] Sodium salt of the *cis*-dimercaptoethylene dianion.

[d] Prepared *in situ* from benzene-1,2-dithiol and potassium.

Structural data for selected complexes of formula $[Ni(S_2C_2R_2)_2]^{x-}$ ($x = 0, 1, 2$) are reported in Table 92.

All of the complexes are invariably square planar. They are members of homologous series of complexes which are related to each other through reversible one-electron-transfer reactions (equation 215). The oxidation and reduction steps may be easily accomplished both chemically and electrochemically, the structures of the complexes remaining substantially unchanged. As occurs for the complexes with quinones (Section 50.5.5.3.ii) and diimines (Section 50.5.3.7.i), the valence electrons are substantially delocalized in the entire chelate rings and the assignment of any oxidation number for both the metal and the ligand may be questionable. Recent studies on bis(1,2-dithiolene) complexes of nickel(II) concern the electronic structure of the neutral complexes,[2127] the electrochemical reduction of nickel(II) complexes to give the true nickel(I) complexes $[Ni(S_2C_2Ph_2)(diphos)]^-$,[2128] $[Ni\{S_2C_2(CN)_2\}(Ph_2N_2C_2Me)]^-$[2129] and $[Ni\{S_2C_2(CN)_2\}_2]^{3-}$.[2130] The photooxidation of $[Ni\{S_2C_2(CN)_2\}_2]^{2-}$ has also been investigated.[2131]

The neutral $[Ni(S_2C_2R_2)_2]$ complexes (R = CN, CF_3) are oxidizing agents and tend to interact with aromatic molecules forming 1:1 complexes which are usually referred to as donor–acceptor (DA) complexes. In these DA complexes the organic molecule is the donor and the nickel complex is the acceptor. The DA complex of $Ni\{S_2C_2(CF_3)_2\}_2$ with perylene (**289**) has been found to consist of stacks of alternating organic and complex neutral molecules (Figure 26).[2118] Other 1:1 DA complexes have been obtained by reacting equimolar amounts of $Ni\{S_2C_2(CF_3)_2\}_2$ with phenothiazine (**290**; X = S), phenoxazine (**290**; X = O),[2120] tetrathiafulvalene (**291**; ttf)[2132,2133] and cycloheptatriene.[2119] The same 1:1 DA complexes or strictly analogous complexes have also been obtained starting from the ionic species of the donor molecules (equations 216 and 217).[2119,2134] Most of the complexes consist of pairs of radical ions

Table 92 Some Structural Data for the $[Ni(S_2C_2R_2)_2]^{x-}$ Complexes ($x = 0, 1, 2$)

Complex	*Average bond distances (chelate ring) (pm)* Ni—S	C—S	C—C	*Bond angle (chelate ring) (°)* S—Ni—S	*Remarks*	*Ref.*
$Ni(S_2C_2Ph_2)_2$	210	171	137	89.8		2117
$Ni\{S_2C_2(CF_3)_2\}_2$	212	171	138	90.4	1:1 DA complex with neutral perylene (Figure 26)	2118
$[Ni\{S_2C_2(CF_3)_2\}_2]^-$	214	170	140	91.4	1:1 DA complex with $C_7H_7^+$ cation ($\mu_{eff} = 1.81$ BM)	2119
$[Ni\{S_2C_2(CF_3)_2\}_2]^-$	213	173	136	89.5	1:1 DA complex with radical monocation phenothiazine (**290**; X = S)	2120
$[Ni\{S_2C_2(CN)_2\}_2]^{2-}$	217	175	133	91.5	As Me_4N^+ salt	2121
$[Ni\{S_2C_2(CN)_2\}_2]^{2-}$	217	173	136	92.2	As Bu_4N^+ salt	2122
$[Ni\{S_2C_2(CN)_2\}_2]^{2-}$	218	174	139	88.1	As $(PPh_3)_2Ag^+$ salt	2078
$[Ni\{S_2C_2(CN)_2\}_2]^-$	214	171	136	92.4	As $MePh_3P^+$ salt	2123
$[Ni\{S_2C_2(CN)_2\}_2]^-$	215	172	137	92.5	As Et_4N^+ salt	2122
$[Ni\{S_2C_2(CN)_2\}_2]^{2-}$	217	174	135	92.0	As $EtNC_5H_4CO_2Me^+$ salt	2124
$[Ni\{S_2C_2(CN)_2\}_2]^{2-}$	217	173	136	92.0	As 2:1 DA complex with *N*-methylphenazinium cation (**290**; X = NMe)	2125
$[Ni\{S_2C_2(CN)_2\}_2]^{2-}$	218	173	138	92.1	As 2:1 DA complex with radical monocation 1,4-bis(dimethylamino)benzene	2126

in which one electron has been transferred from the organic molecule to the neutral nickel complex. These complexes give rise to different alternating stacking arrays of the ions in the crystal and hence different electric properties. DA complexes can often be semiconductors along the stacking axis.

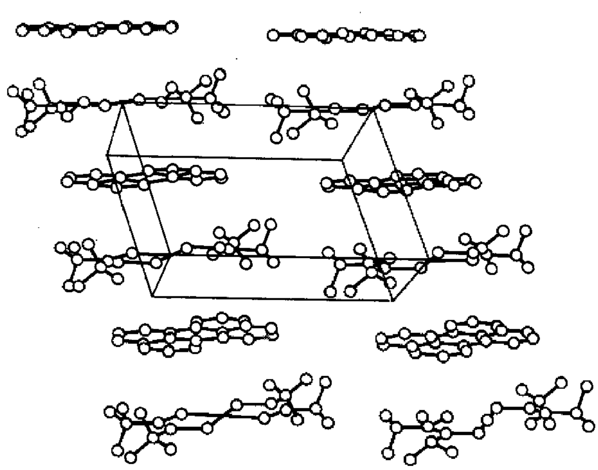
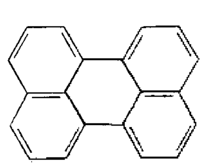
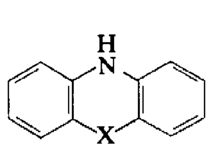


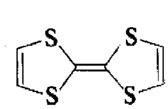
Figure 26 Molecular packing of the perylene–nickel thiete, $Ni\{S_2C_2(CF_3)_2\}_2$, complex (reproduced from ref. 2118 by permission of the American Chemical Society)



(**289**)



(**290**) X = O, S



(**291**)

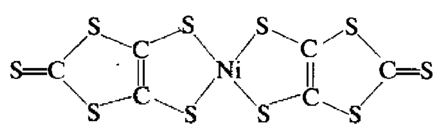
$$(C_7H_7^+)(ClO_4^-) + [Ni\{S_2C_2(CF_3)_2\}_2] \longrightarrow (C_7H_7)[Ni\{S_2C_2(CF_3)_2\}_2] \quad (216)$$

$$(ttf^{2+})2Cl^- + Na_2[Ni\{S_2C_2(CN)_2\}_2] \longrightarrow (ttf)[Ni\{S_2C_2(CN)_2\}_2] + 2NaCl \quad (217)$$

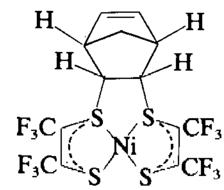
2:1 DA complexes have been obtained starting from either neutral species or ionic compounds. A few examples are $(ttf)_2[Ni(S_2C_2H_2)_2]$,[2132] $(nmp)_2[Ni\{S_2C_2(CN)_2\}_2]$ (nmp is *N*-methylphenazinium cation; **290**; X = NMe)[2125] and $(tmdp)_2[Ni\{S_2C_2(CN)_2\}_2]$[2126] (tmdp is the radical monocation 1,4-bis(dimethylamino)benzene) and their structures have been determined. The simple ionic complexes $(R'_4N)[Ni(S_2C_2R_2)_2]$ (R = Ph, CN; R' = alkyl) are several orders of magnitude more conducting than the corresponding neutral and dianionic complexes.[2122,2135,2136]

The complex $[Ni(dmit)_2](But_4N)_{0.29}$ (**292**) (dmit = 4,5-dimercapto-1,3-dithiole-2-thione anion) has been obtained by the oxidation of the monoanionic complex with bromine. The conductivity of this compound is $10\ S\ cm^{-1}$ at 300 K.

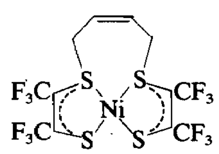
The sulfur atoms coordinated to nickel in complexes $Ni(S_2C_2R_2)_2^{2-}$ possess nucleophilic character and may react with alkylating agents, R'X, giving neutral diamagnetic complexes of the type $[Ni(R'S_2C_2R_2)_2]$ which are remarkably stable and resistant to electron-transfer reactions.[2137,2138] The completely *S*-methylated complexes are unstable and decompose giving the free $Me_2S_2C_2(CN)_2$ species.[2139]



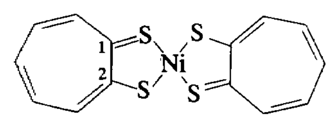
(**292**)



(**293**)



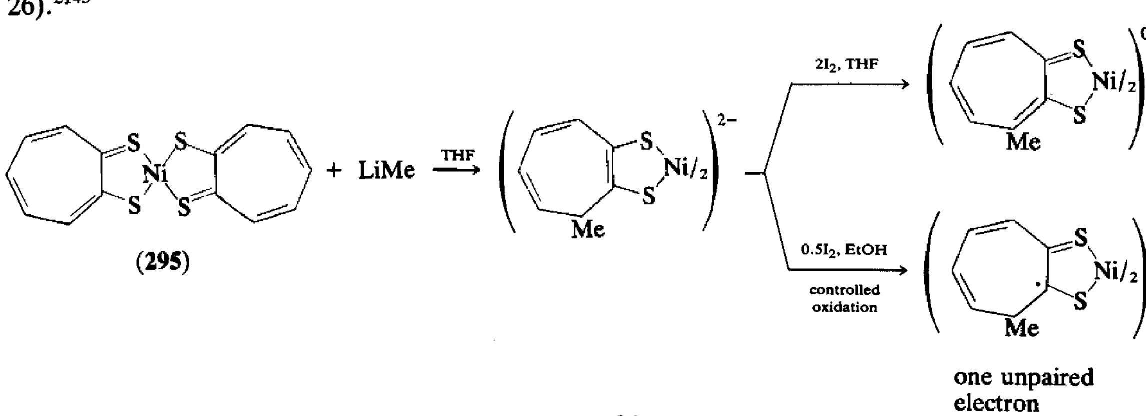
(**294**)



(**295**) Ni—S 215 pm
C—S 172 pm
C^1—C^2 143 pm

The reaction of $[Ni\{S_2C_2(CF_3)_2\}_2]$ with various organic substrates has been investigated. With either norbornadiene or 2,3-dimethylbutadiene the complexes (**293**) and (**294**) were obtained.[2140,2141]

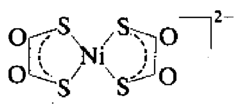
A square planar bis-chelate complex with dithiotropolonate monoanion has been isolated in the solid state (**295**).[2142] This complex does not exhibit the electrochemical properties of the bis(1,2-dithiolene) complexes and undergoes ring alkylation and oxidation reactions (Scheme 26).[2143]



Scheme 26

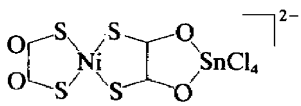
(*ii*) *Complexes with dithiooxalate and related dianionic ligands*

The nickel chelate with dithiooxalate anion ($S_2C_2O_2^{2-}$, dto) is much more stable than that with the oxygen analogue. $K_2Ni(dto)_2$ has been obtained in two polymorphic forms. A dark-red one has been obtained from concentrated, hot aqueous solutions of $NiSO_4$ and $K_2S_2C_2O_2$.[2144] When the red form is heated in a dilute solution of $K_2Cr_2O_7$, black crystals having the same composition as the starting complex are obtained.[2145] Both forms of $K_2Ni(dto)_2$ are diamagnetic and contain the square planar dianion $Ni(dto)_2^{2-}$ (**296**). In the black form these anions are stacked in columns, with intermolecular Ni—Ni distances of 419 pm. Linear stacking of the anions is absent in the red form.[2145,2146] Resonance Raman[2147] and electronic spectra of $K_2Ni(dto)_2$ were studied.[2148]

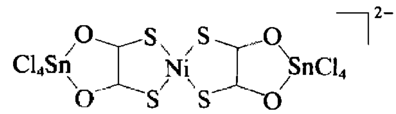


(**296**)

	Bond distances (pm) Black isomer	Red isomer
Ni—S	218	218
C—S	171	175
C—C	154	154



(**297**)

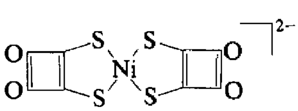


(**298**)

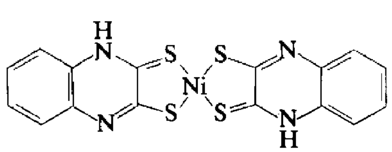
$SnCl_4$ gives 1:1 (**297**) and 2:1 (**298**) adducts with $Ni(dto)_2^{2-}$ and their structures were determined by X-ray analysis.[2146] Unlike the parent $K_2Ni(dto)_2$ complex, the heterometal complexes (**297**) and (**298**) undergo reversible electrochemical reductions which are mainly ligand-based.[2149]

The two compounds $ZnNi(dto)_2(H_2O)_{2.08}$ and $MnNi(dto)_2(H_2O)_{7.5}$ were synthesized from aqueous solutions of the metal(II) sulfate and $K_2Ni(dto)_2$.[2150] They consist of infinite parallel chains in which each nickel atom is coordinated by four sulfur atoms.

The bis(dithiosquarate) complex $K_2[Ni(S_2C_4O_2)_2]\cdot 2H_2O$ (**299**) has been obtained from aqueous solutions of $K_2S_2C_4O_2\cdot H_2O$ and $NiCl_2\cdot 6H_2O$. The complex is mononuclear, square planar and does not undergo reversible redox reactions.[2151]



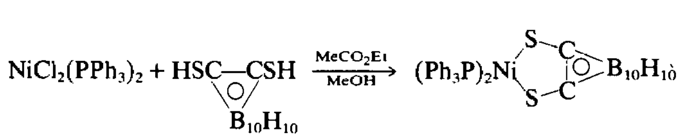
(**299**)



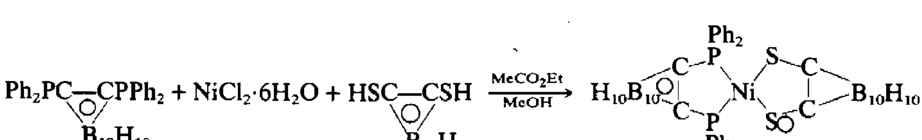
(**300**)

A stacked structure probably occurs in the complex formulated as $K_2Ni_{25}(S_4C_4)_{26}\cdot xH_2O$ ($x \approx 8$) which has a room temperature electrical conductivity of 5×10^{-4} S cm^{-1} (compressed powders).[2152]

1,2-Bis(mercapto)-*o*-carborane provides a potentially chelating dianionic ligand comparable with the aforementioned ligands. However, diamagnetic square planar complexes are stabilized by the presence of phosphines as ancillary ligands (equations 218 and 219).[2153]



(218)



brown

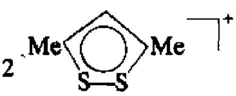
(219)

Quinoxaline-2,3-dithiol (H_2qdto) acts as a monoanionic and a dianionic chelate respectively in the two complexes $Ni(Hqdto)_2\cdot 2DMF$ (**300**) and $(Et_4N)_2[Ni(qdto)_2]\cdot 2H_2O$.[2154,2155]

(*iii*) *Complexes with thio-β-diketones and related ligands*

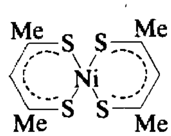
The violet bis(dithioacetylacetonato)nickel(II), $Ni(S_2acac)_2$ (**301**), has been prepared according to equation (220).[2156] In an analogous way, using H_2Se, the corresponding $Ni(Se_2acac)_2$ was prepared.[2157] $Ni(S_2acac)_2$ is diamagnetic, mononuclear and square planar,[2158] in marked contrast with $Ni(acac)_2$ which is trinuclear octahedral (see Section 50.5.5.3.i). A number of violet-green square planar complexes with some substituted dithio-β-diketonates have also been reported.[2159,2160]

$$\text{Hacac} + NiCl_2{\cdot}6H_2O + H_2S \xrightarrow{\text{EtOH/HCl}} Ni(S_2acac)_2 \qquad (220)$$

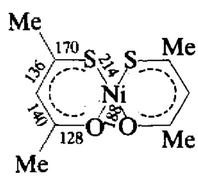
$$Ni(S_2acac)_2 + 2Cl_2 \longrightarrow 2$$  $$+ NiCl_4^{2-} \qquad (221)$$

Electrochemical investigations on $Ni(S_2acac)_2$ led to the conclusion that the neutral complex undergoes two successive reversible one-electron reductions in aprotic solutions leading to mono- and di-anionic species. These reductions are assumed to be mainly ligand-based in character, and the reduced species are less stable than those given by 1,2-dithiolenes.[2161,2162] Halogenation of $Ni(S_2acac)_2$ produces a dithiolium salt of tetrahalonickelate(II) (equation 221).[2163,2164] Like the 1,2-dithiolene complexes, $Ni(S_2acac)_2$ does not interact with Lewis bases and the complex remains unchanged even in pyridine solution.

The X-ray crystal structure of the square planar complex $Ni(S_2acac)Cl(PEt_3)_2$ has been determined.[2165]



(**301**)



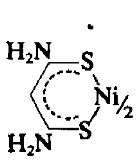
(**302**)

Monothio-β-diketones react with hydrated $Ni(MeCO_2)_2$ in refluxing MeOH giving brown diamagnetic compounds which, like the dithio analogues, are insoluble in water and readily soluble in most common organic solvents.[2160,2166,2167] All these complexes have essentially the same square planar coordination geometry as found in the archetypal monothioacetylacetonato complex (**302**).[2168] A mixed-ligand monothio- and dithio-acetylacetonato complex, $Ni(S_2acac)(Sacac)$, has also been reported.[2169,2170]

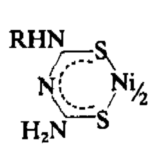
Resonance Raman and IR spectra for both $Ni(S_2acac)_2$ and $Ni(Sacac)_2$ were studied[2171,2172] and the band at about 700 cm^{-1} was assigned as the ν(C⩦S) stretch.

In contrast to $Ni(S_2acac)_2$, adducts of $Ni(Sacac)_2$ with py, substituted pyridines, phen, bipy and terpy have been reported.[2173,2174] They are paramagnetic ($\mu_{eff} = 3.05$–3.33 BM) six-coordinate species with either a *cis* or a *trans* octahedral coordination geometry, according to the nature of the ancillary ligands.

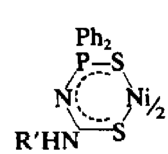
Other systems which give planar complexes of nickel(II) containing six-membered chelate rings are the dithiomalonamidate (**303**),[2175] substituted and unsubstituted dithiobiuretato (**304**)[2176–2178] and substituted thioureates (**305**; R′ = Me, Ph,[2179–2181] *p*-$MeOC_6H_4$[2182]). Some complexes which were obtained in the solid state ($\mu_{eff} = 1.3$–2.4 BM)[2183] have been assumed to contain both tetrahedral and square planar species. With the ligand imidotetramethyldithiophosphinate, an olive-green tetrahedral complex was obtained (**306**).[2184] The corresponding purple bis(imidotetraphenyldiiminodiphosphinato)nickel(II) complex is square planar.



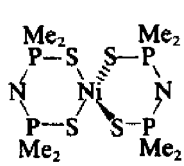
(**303**)



(**304**)



(**305**)



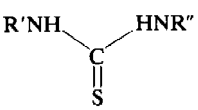
(**306**)

50.5.6.6 Complexes with thiourea and related neutral ligands

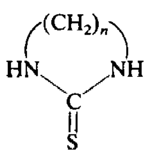
Nickel(II) complexes with thiourea (tu) (Table 93; **307**; R′ = R″ = H) and either *N*- or *N,N′*-substituted thioureas are very numerous and have in most cases been known for a long time.[1920]

The complexes have been prepared by the direct reaction of a nickel(II) salt with the appropriate ligand in suitable solvents, usually an alcohol. In some cases anhydrous conditions are required to obtain analytically pure products and, in general, to improve the synthetic route. Selected complexes are reported in Table 93. Thiourea and ligands derived from substituted thiourea coordinate to nickel through the sulfur atom. The Ni—S bond distances are in the range 220–230 pm in four-coordinate complexes and in the range 245–255 pm in six-coordinate ones. Polynuclear pseudooctahedral complexes of general formula $Ni(NCS)_2L_2$ possess either NCS bridges or sulfur bridges of thiourea molecules shared between two nickel atoms.

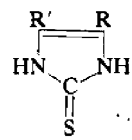
Table 93 Selected Nickel(II) Complexes with Thiourea, Substituted Thioureas and Related Neutral Monodentate Ligands



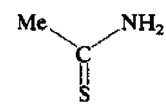
(**307**) R′ = R″ = H
Thiourea



(**308**) $n = 2$
Imidazolidine-2-thione



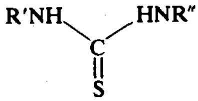
(**309**) R = R′ = H
4-Imidazoline-2-thione



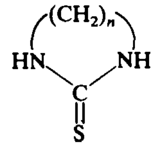
(**310**)
Thioacetamide

Complex		*Ligand*	*Remarks*	*Ref.*
Square planar diamagnetic complexes				
NiL_4X_2	(**307**)	R′ = R″ = Me; X = Br		2185
	(**307**)	R′ = R″ = Et; X = Br, I		2186
	(**308**)	$n = 2$; X = NO_3, ClO_4, I	Possibly a weak axial interaction in the iodo derivative	2187, 2188
	(**309**)	R = H, R′ = Me; X = ClO_4	Ni—S, 221, 224 pm	2189
	(**309**)	R = H, R′ = Me; X = Br, I, ClO_4, NO_3, BF_4		2190, 2191
	(**310**)	X = Br	Ni—S, 222 pm; two *trans* Ni—Br at 360 pm	2192
Complexes with intermediate magnetism and coordination				
NiL_4X_2	(**307**)	R′ = R″ = Et; X = Cl	μ_{eff} = 1.33 (300 K), 2.17 (370 K) BM	2188
	(**307**)	R′ = R″ = allyl; X = halides	μ_{eff} = 0–0.7 BM	2193
	(**307**)	R′ = R″ = Bu; X = halides	μ_{eff} = 0.7–2.5 BM	2193
	(**307**)	R′ = allyl, R″ = Et; X = halides	μ_{eff} = 0–0.7 BM	2193
Pseudotetrahedral complexes				
NiX_2L_2	(**307**)	R′ = H, R″ = 1-naphthyl; X = Br, I		2188
	(**307**)	R′ = R″ = Ph; X = Br	Ni—S, 229 pm	2194
	(**307**)	R′ = R″ = Ph; X = Cl		2193
Pseudoctahedral complexes				
NiL_6X_2	(**307**)	R′ = R″ = H; X = Br, ClO_4, NO_3		2195, 2196
	(**307**)	R′ = R″ = H; X = Br	Ni—S, 251 pm	2197
	(**307**)	R′ = R″ = Et, Bu, Ph, Cy, allyl; X = ClO_4	Dissociate in solution	2198, 2199
	(**307**)	R′ = R″ = Pr^i; X = ClO_4	Ni—S, 248 pm	2200
	(**308**)	$n = 2$; X = ClO_4		2188

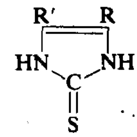
Table 93 (*continued*)



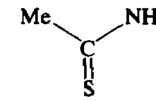
(307) R′ = R″ = H
Thiourea



(308) $n = 2$
Imidazolidine-2-thione



(309) R = R′ = H
4-Imidazoline-2-thione



(310)
Thioacetamide

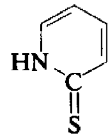
Complex		*Ligand*	*Remarks*	*Ref.*
NiX_2L_4	**(307)**	R′ = R″ = H; X = Cl, Br		2195
	(307)	R′ = R″ = H; 2X = S_2O_3	Ni—S, 243 pm; *cis* Oh	2201
	(307)	R′ = R″ = H; X = Cl	Ni—S, 246 pm; *trans* Oh	2202
	(307)	R′ = R″ = Et; X = NCS	Ni—S, 253 pm; *trans* Oh	2203
	(308)	$n = 2$; X = Cl, Br	$\mu_{eff} = 3.28–3.33$ BM	2188
	(308)	$n = 2$; X = Cl	Ni—S, 244–249 pm; *trans* Oh	2204
	(308)	$n = 3$; X = Cl	Ni—S, 248 pm; *trans* Oh	2205
	(309)	R = H, R′ = Me; X = Cl, NCS	$\mu_{eff} = 3.26–3.29$ BM	2191
	(309)	R = R′ = Me; X = NCS, NO_3, ClO_4, BF_4	$\mu_{eff} = 3.18–3.34$ BM	2191
	(309)	R = R′ = H; X = halides	$\mu_{eff} = 2.76–3.42$ BM	2191
	(310)	X = Cl	Ni—S, 246 pm; *trans* Oh	2206
NiX_2L_2	**(307)**	R′ = R″ = H; X = NCS	Polynuclear with tu bridges; Ni—S 253, 256 pm	2207
	(307)	R′ = H, R″ = Me, Et, Ph; X = NCS	As above	2208
	(307)	R′ = R″ = Cy; X = NCS	Polynuclear bridging NCS	2208
	(308)	$n = 2$; X = NCS	As above; Ni—S, 251 pm	2209
	(310)	X = NCS	Ni—S, 245 pm; *trans* Oh; bridging NCS	2210

Besides the fully paramagnetic *trans* octahedral NiX_2L_4 complexes and the fully diamagnetic square planar NiL_4X_2 ones, a number of complexes with the same stoichiometry have been reported to have magnetic moment values ranging from 0.6 to 2.5 BM at room temperature. The true structures of these complexes still remain uncertain.

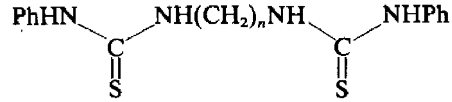
Nickel(II) complexes with thioacetamide (**310**) are similar to the corresponding ones with thiourea and were synthesized in a similar way.

Pseudotetrahedral complexes were reported with the ligand *N*-methylthiopyrrolidinone (**311**).[2211] The 2-mercaptopyridine (**312**)[2212] coordinates in the thione form in the pseudotetrahedral NiX_2L_2 complexes and in the square planar NiL_4X_2 complexes (X = halides; L = **312**).

(311)



(312)



(313)

A number of complexes with bidentate polymethylene bis(phenylthiourea) (**313**) have been reported with various stereochemistries and stoichiometries.[2213,2214]

50.5.6.7 Complexes with phosphine and arsine sulfides

Unlike the tertiary phosphine and arsine oxides which form a variety of nickel complexes with peculiar properties, tertiary arsine sulfides and, particularly, tertiary phosphine sulfides appear to have weak donor properties towards nickel(II). As a consequence, complexes with R_3AsS and R_3PS must be prepared under strictly anhydrous conditions using dehydrated nickel salts and solvents, often under N_2 atmosphere. A few complexes have been reported having the following stoichiometries: $NiL_4(ClO_4)_2$ (L = Me_3AsS,[2215] $(Me_2N)_3PS$[2216]), NiX_2L_2 (X = Cl, Br, L = Me_3AsS;[2215] X = Br, L_2 = $Ph_2As(S)CH_2CH_2As(S)Ph_2$;[2217] X = Br, I, L = $Ph_2P(S)CH_2P(S)Ph_2$[2218]) and $NiL_2(ClO_4)_2$ (L = $Me_2As(S)CH_2CH_2CH_2As(S)Me_2$[2219]). All of the complexes are paramagnetic (μ_{eff} in the range 3.27–3.58 BM) and are assigned a pseudo-tetrahedral coordination geometry in the solid state. Most of the complexes are solvolyzed in organic solvents.

50.5.7 Complexes with Halides

In anhydrous NiX_2 (X = halides), the nickel atom is octahedrally coordinated by six halogen atoms. Their relevant properties and synthetic procedures are reported in Table 94.[2220,2221]

Table 94 Some Properties of Nickel(II) Dihalides

Compound	*Colour*	μ_{eff} *(r.t.)* (BM)	*Preparation*	*Coordination geometry*
NiF_2	Yellow	2.85	N + F_2, 350 °C	Oh
$NiCl_2$	Yellow	3.32	Ni + Cl_2, EtOH; r.t.; dehydration of $NiCl_2{\cdot}6H_2O$ with $SOCl_2$	Oh
$NiBr_2$	Yellow	3.0	Ni + Br_2; ether; r.t.; dehydration of $NiBr_2{\cdot}6H_2O$ at 140 °C	Oh
NiI_2	Black	3.25	NaI + $NiCl_2$, EtOH; dehydration of $NiI_2{\cdot}6H_2O$	Oh

The tetrahalonickelate(II), R_2NiX_4, can be readily prepared from the appropriate nickel(II) halide (not necessarily anhydrous) and the halides of large cations such as Et_4N^+, Bu_4N^+, $MePh_3As^+$ and $MePh_3P^+$ in hot ethanol.[2222-2225] Other large cations which were found to stabilize the NiX_4^{2-} species are the dithiolium monocation,[2226] and the dabconium dication.[2227] With the anilinium cation (LH) the six-coordinate complexes $(LH)_2NiX_4{\cdot}6H_2O$ (X = Cl, Br) have been reported.[2228] The complexes are in general hygroscopic and are extensively solvolyzed when dissolved in H_2O, alcohols and DMF. They are soluble in NO_2Et, $CHCl_3$ and CH_2Cl_2 without substantial decomposition. Other relevant properties of tetrahalonickelates(II) are reported in Table 95. The NiX_4^{2-} anions have a tetrahedral coordination geometry revealed by X-ray analysis of the compounds $(Me_4N)_2NiCl_4$,[2235] and $(MePh_3As)_2NiCl_4$[2236] (Table 96). The former complex exhibits a somewhat flattened pseudotetrahedral structure, whereas the latter has a regular tetrahedral geometry. Spectral and magnetic properties of tetrahalonickelate(II) are discussed in detail in Section 50.5.1. The spectra of NiX_4^{2-} species have been investigated in the far-IR region,[2240,2241] and the ν(Ni—X) stretching frequencies have been assigned as follows:[2240] ν(Ni—Cl), 289 cm^{-1}; ν(Ni—Br), 224 cm^{-1}, 231sh cm^{-1}; ν(Ni—I), 189 cm^{-1}.

Unlike the other NiX_4^{2-} species, the NiF_4^{2-} anion is six-coordinate. The M_2NiF_4 compounds (M = K, Rb, NH_4, Tl, $\frac{1}{2}$ Ba) have antiferromagnetic behaviour with μ_{eff} at room temperature in the range 2.2–2.6 BM.[2229]

Trihalonickelates(II) $MNiX_3$ (M = alkali metal; X = F, Cl, Br) have been obtained in general by reacting NiX_2 and MX in 1:1 molar ratio in the melt or in MeOH. Me_4NNiCl_3, on the other hand, has been prepared from Me_4NCl, $NiCl_2$ and Ph_3P in hot butanol.[2223] These complexes contain octahedrally coordinated nickel(II) as found in NH_4NiBr_3,[2232] $RbNiF_3$[2230] and $CsNiCl_3$. The structures of these compounds consist of infinite parallel chains of octahedra sharing faces (Figure 27).[2242] An antiferromagnetic interaction occurs between the nickel atoms through halide atoms. Moreover, $CsNiI_3$ has been found to behave as an intrinsic semiconductor.

Ba_2NiF_6 has been prepared in the melt from BaF_2 and NiF_2 in 2:1 molar ratio. It contains distorted NiF_6^{4-} octahedra.[2237]

The temperature-dependent equilibrium

$$[NiCl_6]^{4-}\ (O_h) \rightleftharpoons [NiCl_4]^{2-}\ (T_d) + 2Cl^-$$

Table 95 Some Properties of Ionic Halonickelate(II) Complexes

Complex	*Colour*	*R/M*	μ_{eff} *(r.t.)*	*Remarks*	*Ref.*
R_2NiCl_4	Blue	$MePh_3As$, Et_4N, $MePh_3P$ $\frac{1}{2}[Ni(DMSO)_6]^{2+}$	3.87–3.89	Td; hygroscopic; R = $MePh_3P$; m.p. = 198 °C	2222–2225
R_2NiBr_4	Blue	Et_4N, Ph_4P	3.79–3.88	Td; deliquescent	2222, 2224
R_2NiI_4	Dark-red	$MePh_3As$, Bu_4N	3.47, 3.49	Td; hygroscopic; R = Bu_4N; m.p. = 115 °C	2222, 2224
M_2NiF_4		K, Rb, NH_4, Tl^I	2.23–2.60	Oh; polynuclear	2229
$MNiF_3$		Na, K, Rb, NH_4	2.05–2.63	Oh; polynuclear	2229, 2230
$RNiCl_3$	Buff-pink	Me_4N	3.20	Oh; polynuclear	2231
$RNiBr_3$	Red-brown	Me_4N, NH_4		Oh; polynuclear	2232
$RNiBr_3PPh_3$	Blue-green	Et_4N	3.68	Td; m.p. = 266 °C	2233
$RNiI_3PPh_3$	Dark red	Bu_4N, Ph_4As	3.46	Td; m.p. = 132 °C	2223, 2233, 2234

Table 96 Bond Distances and Angles in some Halo Complexes of Nickel(II)

Complex	*Coordination geometry*	*Ni—X* (pm)	*X—Ni—X* (°)	*Ref.*
$(Me_4N)_2NiCl_4$	Td, distorted	226, 228	107.8, 114.4	2235
$(MePh_3As)_2NiCl_4$	Td	227	109.5	2236
Ba_2NiF_6	Oh, distorted	197–203		2237
$(Me_4N)NiBr_3$	Oh, polynuclear	245, 267		2232
$(AsPh_4)NiI_3(PPh_3)$	Td, distorted	255	110–119	2238
$(Bu_4N)NiBr_3(qui)^a$	Td, distorted	238	113 (av)	2239

[a] qui = quinoline.

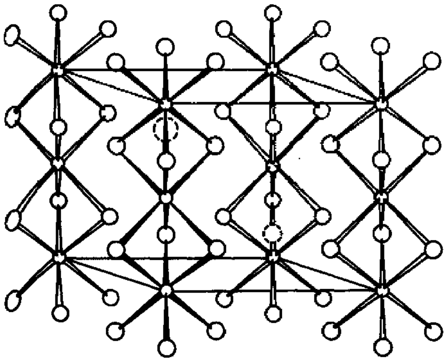


Figure 27 Schematic representation of the octahedral coordination of nickel in $CsNiCl_3$ (reproduced with permission from ref. 2242)

has been found to occur when $NiCl_2$ is dissolved in a concentrated (up to 8 M) aqueous solution of $MgCl_2$.[2243]

The mixed-ligand complexes $RNiX_3B$ (B = PPh_3, py and substituted pyridines) have been prepared in general by the reaction of RX and NiX_2 in the presence of the Lewis base B in hot butanol.[2223,2233,2234,2238,2239,2244] These complexes have a distorted tetrahedral structure[2238,2239] and their spectral and electronic properties have been investigated in detail.[2245]

50.5.8 Nickel Complexes with Open-chain Ligands Containing Mixed Donor Atoms

Nickel(II) complexes with ligands containing mixed donor atoms, in general N, O and S, are innumerable. In the present section we will mention complexes which are the archetypes or are suitable for the description of the properties of all complexes of the same type. Nickel complexes with hybrid polydentate ligands containing either P or As have been discussed in Section 50.5.4.

50.5.8.1 Complexes with Schiff bases

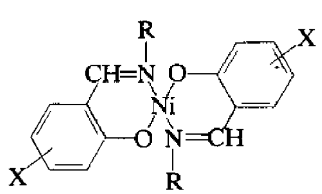
(i) Complexes with Schiff bases derived from salicylaldehyde and related aldehydes with various amines

The Schiff bases have contributed to a large extent to the development of the coordination chemistry of nickel(II), particularly those obtained by the condensation of salicylaldehyde with various mono- and poly-dentate amines. A large number of nickel(II) complexes have been synthesized with these ligands exhibiting all of the possible coordination geometries, spin states and spectromagnetic properties. The early complexes of nickel(II) with different salicylaldimines have been covered extensively in a number of review articles.[2246–2252]

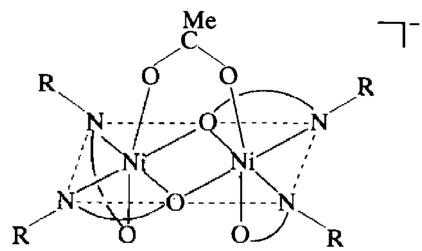
Most nickel(II) complexes with the various Schiff bases derived from salicylaldehyde and different amines have usually been easily prepared by three general methods: (i) the reaction of a nickel(II) salt, usually hydrated nickel(II) acetate, with the preformed Schiff base using water, EtOH, MeOH or their mixtures as reaction medium; (ii) the condensation reaction of bis(salicylaldehydato)nickel(II) with the appropriate amine in refluxing EtOH or H_2O/EtOH mixture; (iii) the template reaction of the aldehyde with the appropriate amine in the presence of a nickel salt. In Table 97 the formulas, synthetic methods and some physicochemical properties for a number of nickel(II) salicylaldiminato complexes are reported. Examples of dinuclear complexes formed with Schiff bases are specifically reported in Section 50.5.8.5.

The complexes obtained with bidentate salicylaldimines (**I**; Table 97) were extensively investigated about 20 years ago, particularly by Holm and co-workers and Sacconi and co-workers. It was definitely established that these complexes may exhibit a variety of coordination properties both in the solid state and in solution depending on the substituents R and X. When R = *n*-alkyl, aryl, cyclopentyl and cyclohexyl, the complexes are diamagnetic square planar in the solid state and become partially paramagnetic when dissolved in poorly coordinating solvents such as C_6H_6 and $CHCl_3$. Molecular association accounts for the observed paramagnetism in solution at room temperature, whereas a square planar ⇌ tetrahedral equilibrium accounts for the increasing paramagnetism in high-boiling solutions or in the melts, when the paramagnetism increases with temperature.[2246,2247,2249,2253–2255] Paramagnetic bis adducts are formed in pyridine solutions. The complexes where R = α-branched alkyl group, such as Pr^i, Bu^s and Bu^t, are paramagnetic and pseudotetrahedral in the solid state and undergo a conformational equilibrium in solution involving tetrahedral and square planar species.

The structures of some square planar and tetrahedral complexes (**314**) have been definitely ascertained by means of X-ray analysis.[2259–2266] Ni—N and Ni—O bond distances in these four-coordinate complexes are in the range 190–200 and 184–190 pm respectively, and do not differ substantially on going from one complex to another. The structures of two dinuclear complexes were reported to contain both bridging and terminal salicylaldimines (**315**).[2269,2270]



(314)



(315) O N—R = *N*-phenylsalicylaldiminate

Spectromagnetic properties of some tetrahedral complexes have been investigated in detail.[2330–2332]

The neutral complexes, NiL_2, prepared with deprotonated potentially tridentate ligands, may be square planar, five-coordinate or octahedral according to whether the ligands are trilegate or bilegate. Complexes obtained with ligand (**II**; Table 97) where RR′ = Et_2 are paramagnetic square pyramidal for X = 3-Cl, 5-Cl and 3,4-benzo. In these complexes one ligand molecule is trilegate and the other is bilegate (**316**).[2276,2277] In non-coordinating solvents four-, five- and six-coordinate species are in equilibrium. The Schiff bases formed by salicylaldehyde and *N*,*N*-disubstituted propane-1,3-diamine give either square planar or octahedral complexes. The latter have a *trans* structure (**317**).[2280–2282]

Table 97 Nickel(II) Complexes with Bi- and Poly-dentate Schiff Base Ligands Derived from Salicylaldehyde or Related Aldehydes and Various Amines

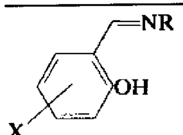
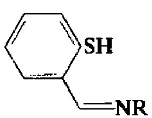
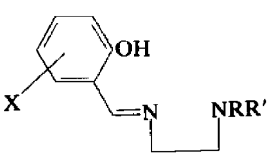
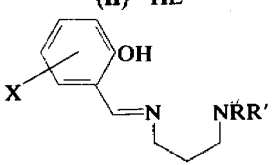
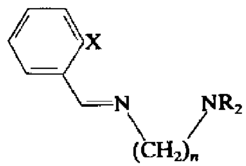
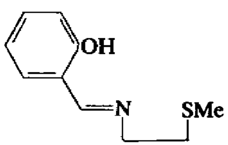
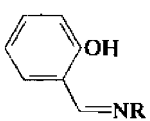
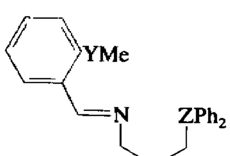
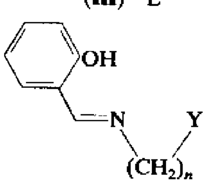
Schiff base	*Substituents*	*Preparation*[a]	*Formula*	*Remarks* (μ_{eff} *in BM*)	*Ref.*
 (I) HL	R = *n*-alkyl, Ph, 2-MeC_6H_4, cyclo-C_5H_9, cyclo-C_6H_{11}	$Ni(sal)_2 \cdot 2H_2O$ + amine; EtOH/reflux	NiL_2	SqPl	2246, 2247, 2249, 2253–2256
	R = Pr^i, Bu^s, Bu^t	As above	NiL_2	Td; μ_{eff} = 3.29–3.34	2255, 2257, 2258
	R = 3-, 4-substituted Ph	As above	NiL_2	Oh polynuclear; μ_{eff} = 3.33–3.39	2258
	R = Me, allyl, cyclohexyl, 2,6-diisopropylphenyl, *n*-heptyl	As above	NiL_2*	SqPl	2259–2264
	R = Pr^i; X = H, OMe		NiL_2*	Td	2265, 2266
	R = 4-ClPh, 4-BrPh; X = 3-OMe	As above	NiL_2	Two paramagntic isomers; five- and six-coordinate polynuclear	2267
	R = 9-fluorenyl	$Ni(sal)_2 \cdot 2H_2O$ + 9-aminofluorene	NiL_2	SqPl	2268
	R = Ph	Ni(sal-*N*-Ph)$_2$ + $MeCO_2^-$ + piperidine	[Ni_2L_4(ac)]pipH* (**315**)		2269
	R = *p*-$OMeC_6H_4$; X = 5-NO_2		[$Ni_2L_4(H_2O)$]$\cdot 2H_2O$*		2270
 HL	R = *n*-alkyl, aryl	Ligand + $Ni(OAc)_2 \cdot 4H_2O$/EtOH	NiL_2	SqPl	2271–2273
	R = Bu^t	As above	NiL_2	Td; μ_{eff} 3.15	2271, 2274
 (II) HL	R = H, R′ = *n*-alkyl	$Ni(sal)_2 \cdot 2H_2O$ + amine; EtOH/reflux	NiL_2	Oh; μ_{eff} = 2.8–3.3	2275
	R = H, R′ = aryl; R = R′ = Et	As above	NiL_2	Oh or SqPl, depending on X	2275, 2276
	NRR′ = NMe_2, pyrrolidine	As above	NiL_2	Oh; μ_{eff} = 3.30–3.34	2276
	X = 3-Cl, 5-Cl, 3,4-benzo; R = R′ = Et	As above	NiL_2 (**316**)*	SqPy; μ_{eff} = 3.30	2276–2278
	X = H, 5-Cl, 5-Br; R = R′ = Et		NiL(catechol)*	Five-coordinate dinuclear; μ_{eff} = 3.2–3.3	2279
 HL	R = H, R′ = *n*-alkyl	$Ni(sal)_2 \cdot 2H_2O$ + amine; EtOH/reflux	NiL_2 (**317**)*	Oh; μ_{eff} = 3.1–3.2	2280–2282
	R = R′ = Me; RR′ = $(CH_2)_4$	As above	NiL_2	SqPl	2280
	R = H, Me, Et; R′ = Et, Ph; RR′ = $(CH_2)_5$	As above	NiL_2	SqPl or Oh (depending on X)	2280

Table 97 (*continued*)

Schiff base	*Substituents*	*Preparation*[a]	*Formula*	*Remarks* (μ_{eff} *in BM*)	*Ref.*
 L	X = OMe; $n = 2$; $R_2 = Et_2$	Preformed ligand + NiX_2/BuOH	NiX_2L	Td; $\mu_{eff} = 3.3–3.5$; bidentate ligand	2282
	X = OMe; $n = 3$; $R_2 = Et_2$	As above	NiX_2L	Five-coordinate; $\mu_{eff} = 3.4$	2283, 2284
	X = SMe; $n = 2$; $R_2 = Et_2$	As above	NiX_2L	Five-coordinate; $\mu_{eff} = 3.3$	2285
	X = NHMe; $n = 2$; $R_2 = Et_2$	As above	NiX_2L	Five-coordinate; $\mu_{eff} = 3.1–3.3$	2286
	X = SH; $n = 2$; $R_2 = Et_2$ (HL)	Preformed ligand + NiI_2/BuOH	NiIL	SqPl	2285
 HL		$Ni(sal)_2 \cdot 2H_2O + H_2NCH_2CH_2SMe$	NiL_2	Oh	2287
 HL	R = $CH(Me)CH_2OMe$, $CH(Et)CH_2OMe$	$Ni(sal)_2 \cdot 2H_2O$ + amino ether; CH_2Cl_2	NiL_2	Oh; $\mu_{eff} = 3.2–3.3$	2288
	R = CH_2CH_2OMe, $CH_2CH_2CH_2OMe$	As above	NiL_2	SqPl	2288
 (III) L	Y = NH, O, S; Z = P, As	Preformed ligand + NiX_2/BuOH	NiX_2L	Five-coordinate; $\mu_{eff} = 3.1–3.4$	2289
	Y = NH, S; Z = P	As above	NiI_2L	SqPl	2289
 (IV) HL	Y = PPh_2, $AsPh_2$; $n = 2$ Y = $AsPh_2$; $n = 3$		NiL_2	SqPl; bidentate ligand	2290
	Y = PEt_2; $n = 2$		NiL_2	Oh; $\mu_{eff} = 3.0$; bidentate ligand	2290

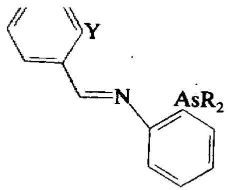
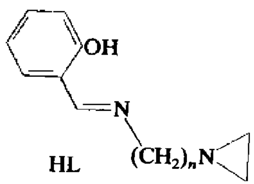
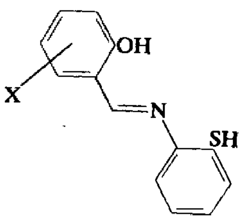
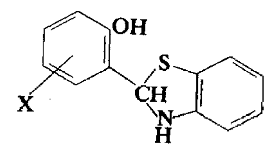
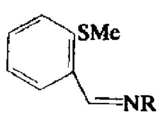
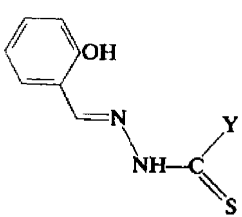
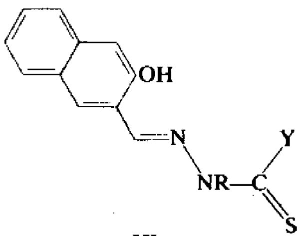
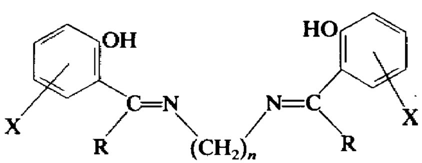
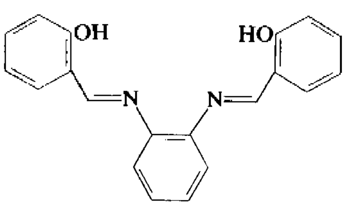
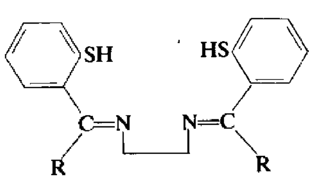
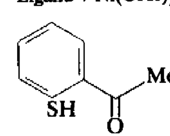
	Y = OH (HL)	Ligand + NiX_2/EtOH	$NiL_2 \cdot xH_2O$	Oh; $\mu_{eff} = 3.24$	2291
			$NiXL \cdot xH_2O$	Oh; $\mu_{eff} = 3.17$	
	Y = NHMe, NMe_2, NEt_2 (L)	As above	NiX_2L	Five-coordinate; X = halides; $\mu_{eff} = 3.0$–3.3	2292
				Oh; X = NO_3, NCS; $\mu_{eff} = 3.1$–3.3	2292
	Y = SMe, SEt	As above	NiX_2L	Five-coordinate; X = halides; $\mu_{eff} = 3.1$–3.4	2293
				Oh; X = NCS; $\mu_{eff} = 3.1$	
		$Ni(sal)_2 \cdot 2H_2O$ + amine /BuOH	NiL_2Y_2	Oh; Y = ClO_4, BPh_4; $\mu_{eff} = 3.2$–3.3	2293
 HL	$n = 2, 3$	$Ni(OAc)_2 \cdot 4H_2O$ + sal + amine	NiL_2	Oh; $\mu_{eff} = 3.1$–3.2	2294
 H_2L		 + Ni $(OAc)_2 \cdot 4H_2O$ + base/EtOH	NiLB	SqPl; base = py, H_2O, NH_3, DMSO	2295, 2296
 L	R = $O\text{-}CH_3SC_6H_4$	Ligand + NiX_2 hydrate/BuOH	NiX_2L	Oh, polynuclear; $\mu_{eff} = 3.0$–3.1	2297
	Y = NH_2 (H_2L)	Preformed ligand + NiX_2/EtOH	NiLB	SqPl; B = H_2O, py, NH_3	2298
	Y = SMe (HL)		NiLX	SqPl; X = halides	2299

Table 97 (*continued*)

Schiff base	*Substituents*	*Preparation*[a]	*Formula*	*Remarks* (μ_{eff} *in BM*)	*Ref.*
 HL	R = H; Y = NH_2 R = Me; Y = SMe		NiLX	SqPl; X = Cl, NCS, NO_3	2300, 2301
 (V) H_2L	R = H; X = H; n = 2–5	Preformed ligand + $Ni(OAc)_2 \cdot 4H_2O$/EtOH	NiL (**319**)*	SqPl	2302, 2303
	n = 6-12	As above	NiL	μ_{eff} = 0–3.0	2304
	R = Ph; X = 5-Cl; n = 2–12	As above	NiL	μ_{eff} = 0–2.1	2305
	n = 3–12		$NiLpy_2$	Oh; μ_{eff} = 3.0–3.4	2305
	R = H; X = 5,6-benzo; n = 2		NiL*	SqPl	2306
 (VI) H_2L		As above	NiL	SqPl	2307
 (VII) H_2L	R = H	Ligand + $Ni(OAc)_2 \cdot 4H_2O$/EtOH	NiL	SqPl	2271
	R = Me	 + Ni^{II} ethanolate; EtOH/N_2	NiL	SqPl	2308

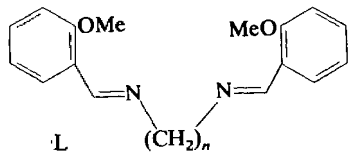
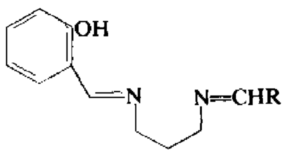
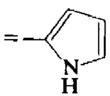
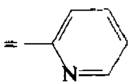
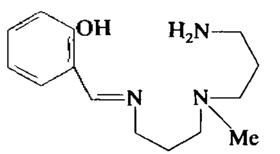
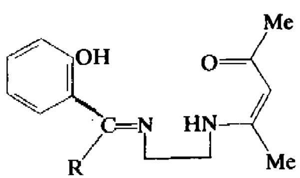
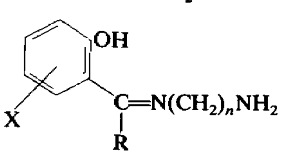
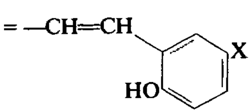
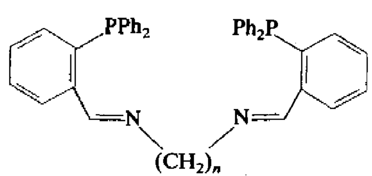
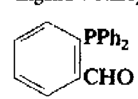
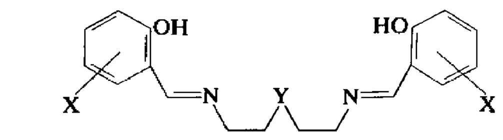
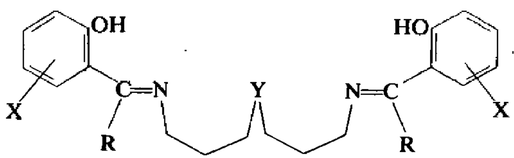
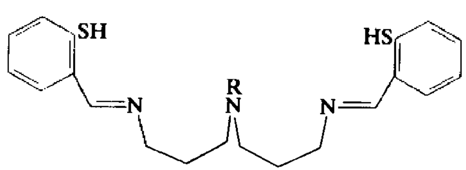
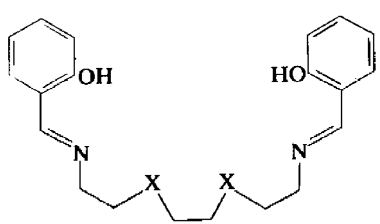
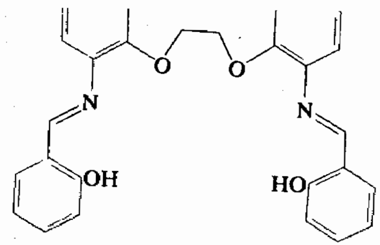
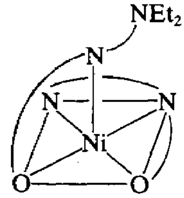
 L	$n = 2, 3$	Ligand + NiX_2/BuOH/reflux	NiX_2L	Td; $\mu_{eff} = 3.35–3.44$; bidentate ligand	2283
	H_2L; R = 	Schiff base + $CHOC_4H_3NH$ + Et_3N + $Ni(NO_3)_2 \cdot xH_2O$/EtOH	NiL	SqPl	2309
	HL; R = 	As above but with $CHOC_5H_4N$	$NiLNO_3$	SqPl	2309
 HL			$NiLNO_3$*	Oh	2310
 H_2L	R = H, Me	$Ni(OAc)_2 \cdot 4H_2O$ + ligand/MeOH	NiL	SqPl	2311, 2312
 H_2L	R =  X = H, Me, Cl; $n = 2, 3$	Ligand + $NiCl_5$hydrate + $MeCO_2Na$/EtOH	NiL	SqPl; dinuclear	2313
			NiL	Td; polynuclear $\mu_{eff} = 4.4–4.5$	
 L	$n = 2$	Ligand + $NiBr_2$ hydrate/EtOH; CH_2Cl_2	[NiBrL]Br	Five-coordinate	2314
	$n = 3$	 + amine + $Ni(BF_4)_2$ hydrate/EtOH	$[NiL](BF_4)_2$	SqPl	

Table 97 *(continued)*

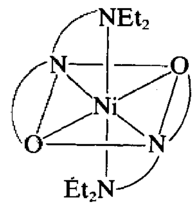
Schiff base	*Substituents*	*Preparation*[a]	*Formula*	*Remarks* (μ_{eff} *in BM*)	*Ref.*
 **(VIII)** H_2L	Y = S, NH	Ligand + $Ni(OAc)_2 \cdot 4H_2O$/EtOH	NiL	$\mu_{eff} = 1.1$–1.2	2315, 2316
	Y = S; X = H, 5-Cl, 5-Br, 5-Me, 3,5-Cl_2, 3,5-Br_2	As above/MeOH	$[NiL]H_2O$	Oh; polynuclear; $\mu_{eff} = 2.8, 2.9$	2317
			$[NiL(H_2O)]$	Oh; $\mu_{eff} = 3.1$–3.2	2317
 **(IX)** H_2L	Y = NH, S; R = Ph; X = 5-Cl, 5-Me	Ligand + $Ni(OAc)_2 \cdot 4H_2O$ + piperidine/MeOH	NiL* **(320)**	TBPy; $\mu_{eff} = 3.3$–3.5	2318–2320
		NiL + base	NiLB*	Oh; B = py and substituted py; $\mu_{eff} = 2.9$–3.3	2318–2320
	R = X = H; Y = NH, NMe		NiL	TBPy*	2321, 2322
	R = H; Y = NH; X = 3-Cl, 5-Cl, 3-Me, 5-Me	$Ni(sal)_2 \cdot 2H_2O$ + amine	NiL	Five-coordinate; $\mu_{eff} = 3.3, 3.4$	2323
	R = Ph; Y = NH; X = 5-Cl, 5-Me		$NiLH_2O$*	Oh	2324
	R = Me, Et; X = 4-Me, 4-MeO, H; Y = NH	As above	NiL*	Five-coordinate; $\mu_{eff} = 3.3$	2325
 **(X)** H_2L	R = H, Me, Et	Ligand + $Ni(OAc)_2 \cdot 4H_2O$/MeOH	NiL	Five-coordinate; $\mu_{eff} = 3.3$	2271
 H_2L	X = NH	$Ni(sal)_2 \cdot 2H_2O$ + amine; H_2O	$NiL \cdot 6H_2O$*	Oh; $\mu_{eff} = 2.88$; hexadentate ligand	2326, 2327
	X = S	Ligand + $Ni(OAc)_2 \cdot 4H_2O$; MeOH	NiL	Oh; $\mu_{eff} = 3.0$	2328

	As above/DMF, H_2O	NiL	Five-coordinate; $\mu_{eff} = 2.86$	2329

* Structure determined by X-ray analysis.
[a] $Ni(sal)_2 \cdot 2H_2O$ is bis(salicylaldehydato)nickel(II) dihydrate.



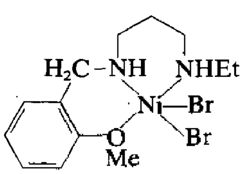
(316)



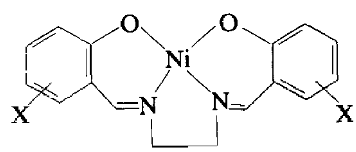
(317)

Mixed-ligand complexes having the same coordination geometry as **(316)** were easily obtained in solution by mixing equimolar amounts of the square planar bis(*N*-alkylsalicylaldiminato)nickel(II) **(314)** compounds with complex **(316)** in $CHCl_3$. Magnetic, optical and ^{1}H NMR measurements indicate that the equilibrium is shifted to the right.[2333]

Amongst the complexes of general formula NiX_2L formed by neutral Schiff bases, complex **(318)** has been fortuitously obtained by refluxing the parent complex in *n*-butanol, through the hydrogenation of the azomethine group and loss of one ethyl group.[2284]



(318)



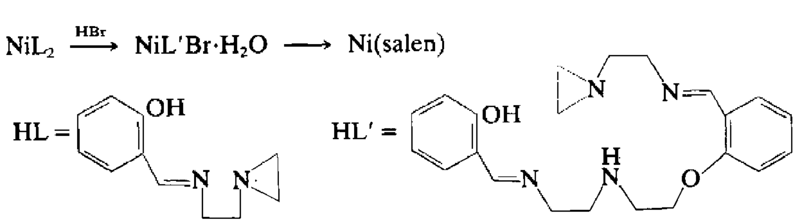
(319)

Tridentate Schiff bases containing a peripheral donor atom of low electronegativity (P, As) form high-spin five-coordinate complexes $[NiX_2L]$ with the neutral ligands (**III**; Table 97)[2289] and square planar complexes $[NiL_2]$ with the deprotonated ligands (**IV**) which are bilegate.[2290]

Tetradentate ligands of types (**V**)–(**VII**) strongly favour the formation of square planar nickel complexes of general formula $[NiL_2]$. Most of them remain essentially diamagnetic, even in pyridine solution. The square planar structure of complexes **(319)** has also been ascertained by means of X-ray analysis.[2303,2306] Complexes formed by ligands containing long polymethylene connecting chains ($n = 6$–12) have feeble and variable paramagnetism. Their structure is essentially square planar.[2304,2305]

Most of the complexes [NiL] given by the potentially pentadentate ligands (**IX**) and (**X**) (Table 97) are five-coordinate high-spin and possess an essentially trigonal bipyramidal structure **(320)**.[2320–2322] In contrast with the aforementioned complexes, those formed by the ligands (**VIII**) which possess the less flexible ethylene bridging chain are essentially square planar.[2315,2316]

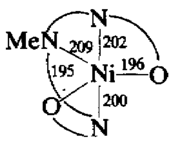
An intermediate product was identified and characterized in the reaction outlined in Scheme 27. X-Ray analysis has shown that this intermediate product contains a hexadentate monoanionic ligand formed through the reaction of a phenol group with an aziridine group once coordinated to nickel(II).[2334,2335]



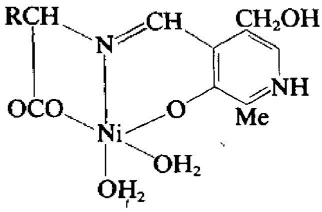
Scheme 27

Several nickel(II) complexes have been reported with Schiff bases derived from the condensation of salicylaldehyde and various amino acids. The structures of the complexes were investigated by means of electronic and ^{1}H NMR spectra as well as X-ray crystallography.[2336–2341] Recently the X-ray structure of complex **(321)**, prepared by the reaction of pyridoxal·HCl, *o*-phospho-DL-threonine and $Ni(NO_3)_2 \cdot 6H_2O$ at pH 5, has been reported.[2341]

Nickel(II) complexes are particularly suitable for investigation by means of ^{1}H NMR spectroscopy. Numerous studies have been carried out on Schiff base complexes.[2333,2342–2347]



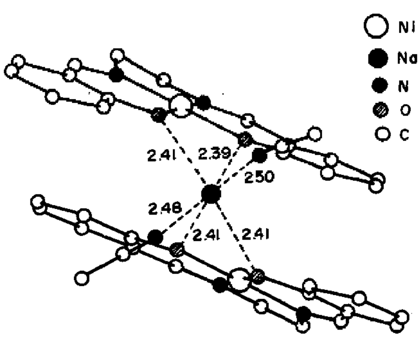
(320)



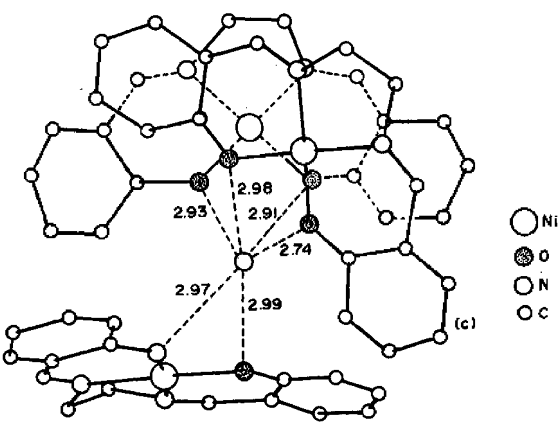
(321) R = CH(Me)OPO$_3$

(ii) Salicylideneiminato nickel(II) complexes as ligands

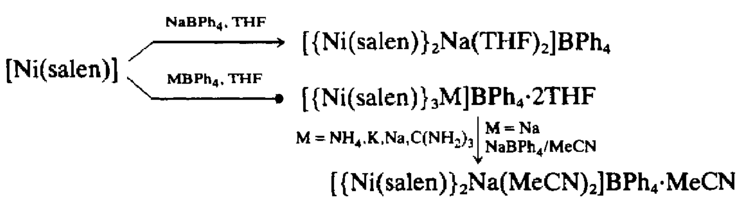
N,N'-Ethylenebis(salicylideneiminato)nickel(II), [Ni(salen)] **(319)**, behaves as a bidentate ligand through its oxygen atoms towards a variety of transition and non-transition metals, affording interesting and unusual di- and tri-nuclear heterometal complexes.[2348–2352] For example, [Ni(salen)] reacts with several alkali metal and ammonium salts, as outlined in Scheme 28. In the complex cation $[\{Ni(salen)\}_2Na(MeCN)_2]^+$ **(322)** two square planar [Ni(salen)] moieties are held together by one Na^+ cation which is surrounded by four oxygen atoms of the two Schiff bases and by two nitrogen atoms of two MeCN molecules (mean Na—O and Na—N distances, 241 and 249 pm respectively).[2348,2349] In the complexes $[\{Ni(salen)\}_3M]BPh_4{\cdot}2THF$ ($M = NH_4^+$, $C(NH_2)_3^+$) **(323)** the cation is encapsulated by six oxygen atoms of the three Ni(salen) molecules.[2348,2349,2351]



(322) (reprinted with permission from ref. 2349)

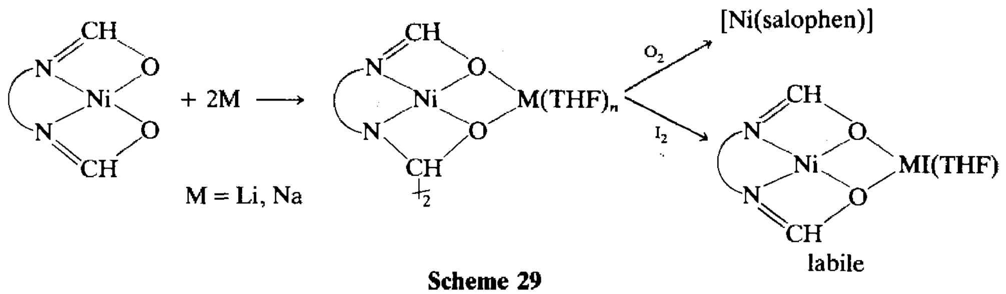


(323) (reprinted with permission from ref. 2349)



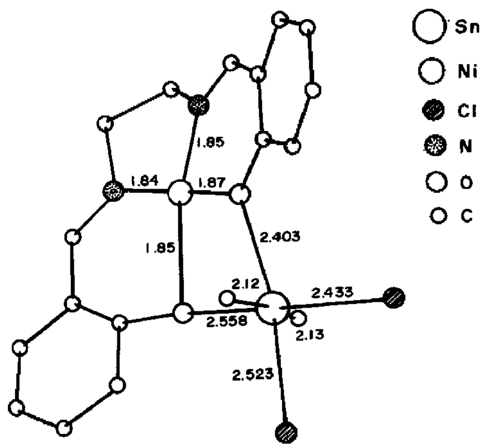
Scheme 28

The alkali metals Li and Na promote the dimerization of the complex *N,N'-o*-phenylenebis(salicylideneiminato)nickel(II), [Ni(salophen)], by means of the reductive coupling of two imino groups between two Ni(salophen) molecules (Scheme 29).[2352]



Scheme 29

Organotin(IV) chlorides react with Ni(salen) forming 1:1 complexes of the type $[Ni(salen)SnCl_{4-n}R_n]$ (R = Ph, Me; $n = 1, 2$) (**324**).[2353,2354] Similar complexes were also reported with $PbCl_2Ph_2$ and $TlCl_2Ph$,[2355] SbX_3 (X = Cl, Br) and $Mn(CO)_3X$.[2356] Di- and tri-nuclear complexes of nickel(II) were obtained by reacting $Ni(NO_3)_2$ hydrate with Schiff base complexes of nickel(II).[2357,2358] The donor–acceptor molecular complexes between 1,3,5-trinitrobenzene and bidentate Schiff base complexes were also investigated.[2359,2360]



(**324**) (reprinted with permission from ref. 2354)

(*iii*) *Complexes with Schiff bases derived from pyridine-2-carbaldehyde and related species and with hydrazones*

A number of representative nickel(II) complexes prepared with Schiff bases derived from pyridine-2-carbaldehyde, pyridine-2,6-dicarbaldehyde and related species are summarized in Table 98, together with some of their distinctive physicochemical properties and preparative routes. All of these complexes involve N and either O or S as donor atoms and exhibit various coordination numbers and geometries depending on the denticity of the ligands and on their steric and electronic requirements.

Noteworthy are the complexes obtained with the pentadentate ligands derived from the condensation of 2,6-diacetylpyridine with various substituted hydrazines (**XI**; Table 98). These complexes have been found to be seven-coordinate with pentagonal bipyramidal structure where the pentadentate ligand invariably has its five donor atoms in the equatorial plane. The two residual coordination sites in the axial positions are occupied by two water molecules (**325**).[2361–2364]

The condensation of *o*-aminobenzenethiol with pyridine-2,6-dicarbaldehyde does not form the corresponding Schiff base but a polyheterocyclic compound which behaves as a tridentate ligand towards nickel(II).[2365] In contrast the reaction of 2-(2-pyridyl)benzothiazoline with nickel(II) results in the opening of the heterocyclic ring and in the formation of a Schiff base ligand which coordinates to nickel(II) as a mononegative tridentate ligand.[2366,2367]

Table 98 Complexes with Schiff Bases Derived from Pyridine-2-carbaldehyde, Thiosemicarbazide, Dithiocarbazic Acid and with Hydrazones

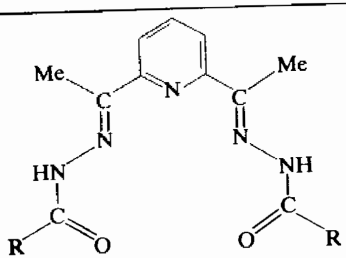
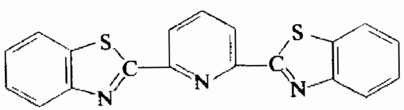
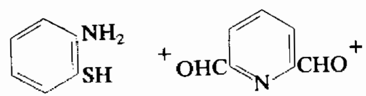
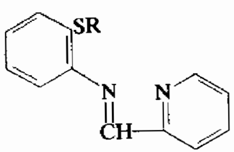
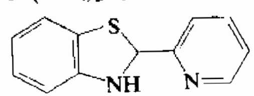
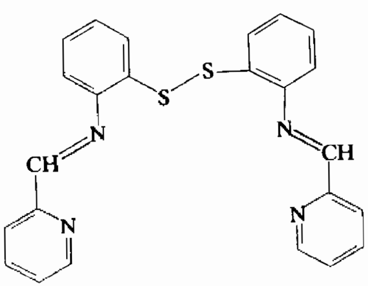
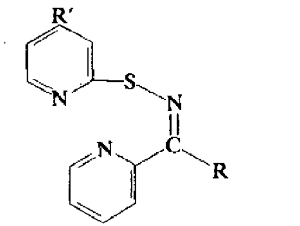
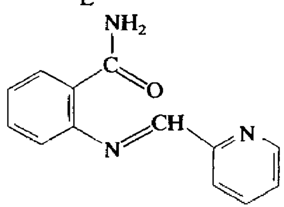
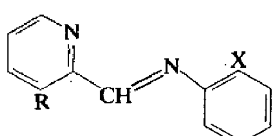
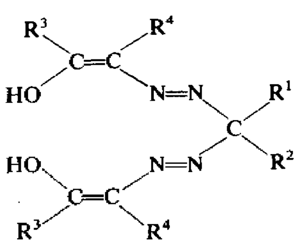
Schiff base	*Substituents*	*Preparation*	*Formula*	*Remarks* (μ_{eff} *in BM*)	*Ref.*
 (XI) L	R = Ph; NH_2 R = 2-py	$Ni(NO_3)_2 \cdot 6H_2O$ + ligand/H_2O, EtOH $NiCl_2 \cdot 6H_2O$ + ligand; EtOH/reflux	$[NiL(H_2O)_2](NO_3)_2$* (**325**) $[NiL(H_2O)_2]Cl_2 \cdot 3H_2O$*	Pentagonal bipyramidal Pentagonal bipyramidal; $\mu_{eff} = 3.2$	2361–2363 2364
 L		 $Ni(ClO_4)_2$ hydrate	$[NiL_2](ClO_4)_2 \cdot 6H_2O$	Oh	2365
	R = H (HL) R = Me (L)	 + $NiCl_2$ Ligand + NiX_2/EtOH	NiLCl NiLCl NiX_2L	SqPl $\mu_{eff} = 2.84$ Oh; X = halides; $\mu_{eff} = 3.0–3.1$	 2366 2367
 (XII) L		Ligand + NiX_2 hydrate/EtOH Ligand + NiY_2 hydrate + LiX/EtOH	[NiXL]Y $[NiClL]ClO_4$* (**326**)	Oh; X = Cl, Br; Y = Cl, Br, ClO_4, BF_4	2366 2368

Table 98 *(continued)*

Schiff base	*Substituents*	*Preparation*	*Formula*	*Remarks* (μ_{eff} *in BM*)	*Ref.*
 L	R, R′ = H, Me	Ligand + $Ni(ClO_4)_2$ hydrate/MeOH	$[NiL_2](ClO_4)_2$	Oh; μ_{eff} = 3.1–3.3; tridentate ligand	2369
 (XIII) L		Scheme 30 (see text)	$[NiLL'(H_2O)](NO_3)_2$*	Oh	2370
 L	R = H, Me; X = $AsMe_2$	Ligand + NiX_2	NiX_2L	Five-coordinate; X = halides, NCS; μ_{eff} = 3.1–3.3	2371
	R = H, Me; X = $AsEt_2$	Ligand + NiY_2 hydrate	$[NiL_2]Y_2$	Oh; Y = ClO, BF_4; μ_{eff} = 2.8–3.3	
 H_2L	R^1 = Me; R^2 = Me, Et, Pr^n, Bu^n, Ph; $R^3 = R^4$ = Ph	$Ni(OAc)_2 \cdot 4H_2O + R^1R^2CO$ + benzylmonohydrazone; EtOH/reflux	NiL	SqPl	2372
	$R^1 = R^2$ = Me; R^3 = Me, Bu^t; R^4 = Me, H	$Ni(OAc)_2 \cdot 4H_2O$ + acetone + 2,3-butanedione/EtOH	NiL	SqPl	2373

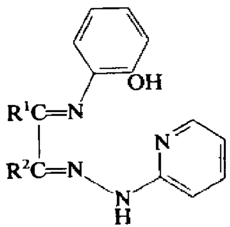
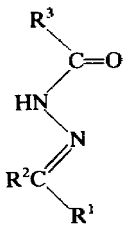
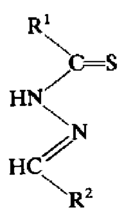
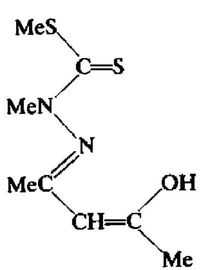
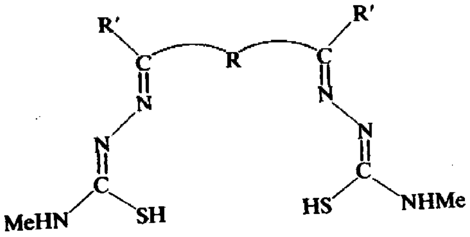
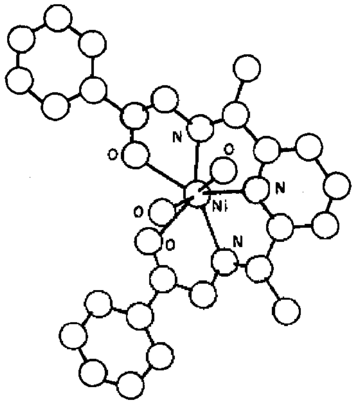
 H_2L	$R^1 = R^2 = H$, Me, Ph $R^1 = Me$; $R^2 = H$	Ligand + $Ni(OAc)_2 \cdot 4H_2O$/EtOH, H_2O	NiL (H_2O)	SqPl	2374
 HL	$R^1 = H$, Me; $R^2 = Me$, Ph, substituted phenyl; $R^3 = Ph$, substituted phenyl	Ligand + NiX_2/EtOH Ligand + $Ni(OAc)_2 \cdot 4H_2O + NH_3$; EtOH, H_2O/reflux	$Ni(HL)_2X_2$ NiL_2	Oh; X = halides, NCS; $\mu_{eff} = 3.1–3.2$ SqPl; bidentate ligand	2375
	$R^1 = 2$-py; $R^2 = H$; $R^3 = C_6H_4OH$-*o*	Ligand + $Ni(OAc)_2 \cdot 4H_2O$; EtOH/refluxing	NiL_2*	Oh	2376
	$R^1 = CO_2Me$; $R^2 = Me$; $R^3 = Ph$, Me, C_6H_4OH-*o*	As above; hydrolysis of the ligand and elimination of Me	$NiL'_2 \cdot 2H_2O$*	Oh	2377
	$R^1 = R^3 = 2$-py; $R^2 = H$, Me	Ligand + $NiCl_2$/EtOH; reflux	$Ni_2Cl_3L \cdot 3H_2O$	Oh; $\mu_{eff} = 3.0$; tetradentate ligand	2378
 HL	$R^1 = SMe$; $R^2 = py$	Ligand + NiX_2/EtOH	NiLX NiL_2	SqPl; X = halides Oh	2379
	$R^1 = NH_2$; $R^2 = py$, isoquinoline		NiL_2* (**328**)	Oh	2380, 2381
 HL		Ligand + NiX_2/EtOH	NiLX	SqPl; dinuclear; X = halides, NCS	2299

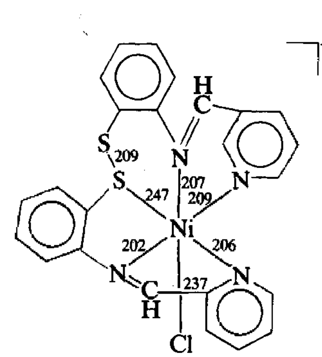
Table 98 (continued)

Schiff base	Substituents	Preparation	Formula	Remarks (μ_{eff} in BM)	Ref.
	R = CH_2CH_2; R′ = Me R = o-C_6H_4; R′ = H		NiL*	SqPl	2382

* Structures determined by X-ray analysis.



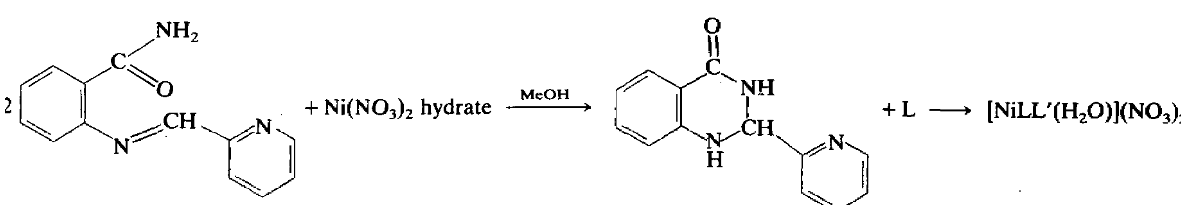
(**325**) (reprinted with permission from ref. 2361)



(**326**)

The X-ray structure of the six-coordinate complex $[NiClL]^+$ (**326**) has shown that the ligand (**XII**) containing the organic disulfide group coordinates intact to nickel(II) as pentadentate.[2368] Complexes containing a coordinated S-bonded disulfide group have also been obtained by oxidation with either H_2O_2 or air of the preformed complex with the tridentate ligand $pyCH_2NHCH_2CH_2SH$[2383]

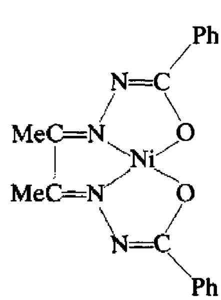
The ligand (**XIII**; Scheme 30) undergoes a cyclization reaction in the presence of $Ni(NO_3)_2$ hydrate and gives the new ligand (**XIV**). Both ligands coordinate to nickel in the resulting mixed-ligand complex.[2370]



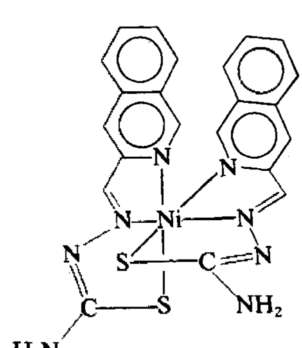
(**XIII**), L (**XIV**), L'

Scheme 30

The well-known square planar complex (diacetylbisbenzoylhydrazonato)nickel(II), Ni(dbh) (**327**) is capable of reacting with two molecules of monodentate base such as py, aliphatic amines, phosphines, *etc.*, to form six-coordinate bis adducts which are in equilibrium with the parent square planar complex.[2384] The base strengths towards Ni(dbh) have been measured spectrophotometrically. On the other hand the reaction of Ni(dbh) with phen in EtOH solution gives a 1:1 adduct which contains the monoanionic tridentate ligand $Hdbh^-$ (N,N,O donor set) and a coordinated ethoxy group besides the phen molecule.[2385] Square planar complexes analogous to (**327**) have been prepared with the tetradentate ligands formed by the condensation of aldehydes and ketones with monohydrazones[2372,2373,2382] and thiosemicarbazones. The crystal structures of two six-coordinate complexes $[NiL_2]$ (**328**) prepared with tridentate Schiff bases derived from thiosemicarbazone have been reported.[2380,2381]



(**327**)

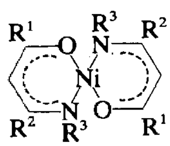


(**328**)

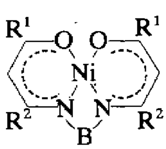
(*iv*) *Complexes with β-ketoamines and related ligands*

Nickel(II) complexes derived from β-ketoamines of general structures (**329**) and (**330**) bear some similarities with those formed by either bidentate or tetradentate salicylaldimines in that an extended conjugate chelate system with N,O donor atoms exists in both types of complexes. The stability of these complexes greatly depends upon the substituents in the chelate rings. It has been found that fluoroalkyl groups at R^1 and R^2 produce greatest stability as well as a two-carbon bridge between the β-ketoamines in complexes of type (**330**). Longer bridging chains reduce stability presumably by steric strain in the chelate ring.

Nickel(II) complexes with β-ketoamines are, in general, easily prepared. The most useful and general synthetic methods are the following: (i) reaction of the preformed ligands with nickel salts in basic solution using water, alcohol or their mixtures as medium; (ii) ligand exchange reactions; (iii) template reactions. Complexes of type (**329**) may be sensitive to moisture and are prepared in anhydrous conditions.



(**329**)



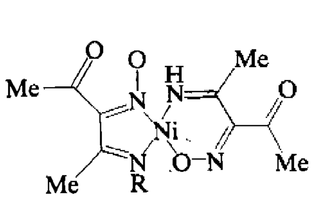
(**330**)

A summary of the preparative methods, formulas and physicochemical properties of selected complexes is given in Table 99.

The stereochemistry of complexes of type (**329**) parallels that of the bis(salicylaldiminato)nickel(II) complexes, being strongly dependent on the steric nature of the substituents R^3. The complexes are square planar when $R^3 = H$, *n*-alkyl and aryl, and tetrahedral both in the solid state and in solution when $R^3 = \alpha$-branched alkyl. The square planar complexes give rise to a diamagnetic⇌paramagnetic equilibrium in non-coordinating solvents,[2386,2410] and to paramagnetic bis adducts in coordinating solvents.[2411] The effect of sulfur substituents for oxygen atoms on complexes of type (**329**) is to favour the square planar species both in the solid state and in solution.

Tetradentate ligands with ethylene chains invariably give square planar complexes of the type (**330**)[2302,2393] and in some cases their structures were determined by X-ray analysis (bond distances: Ni—O, 183–184 pm; Ni—N, 185–186 pm).[2395,2397]

The reaction of the appropriate amine with the nickel complexes formed by isonitroacetylacetone in refluxing EtOH–$CHCl_3$ mixture affords the complexes (**331**).[2412]



(**331**)

The aerial oxidation of solutions of complexes (**330**) has been investigated. Chromatography separation led to the identification of products which underwent dehydrogenation of the ethylene bridge (Scheme 31).[2413] Such dehydrogenation reactions are inhibited by fluoroalkyl substituents and enhanced by alkyl substituents. Oxidation with hydrogen peroxide removes the ethylene bridge.

The reaction of 2,2′-bisbenzothiazoline with hydrated nickel acetate results in the Schiff base complex (**332**; Scheme 32). Complex (**332**) can be reduced to either monoanionic or dianionic species polarographically. The reduction to the monoanionic species can also be accomplished *via* chemical reduction with Bu_4NBH_4 or sodium analgam.[2414]

Table 99 Complexes with β-Ketoamines and Related Schiff Bases

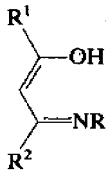
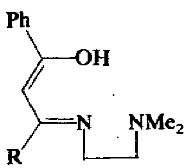
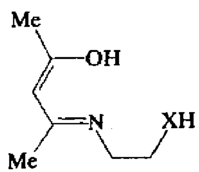
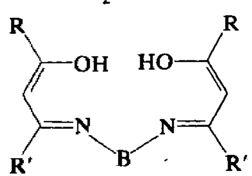
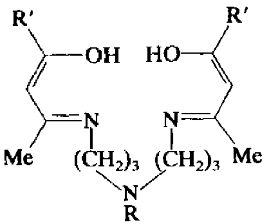
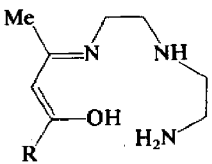
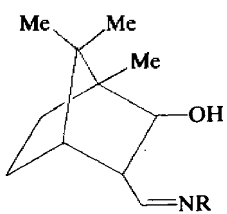
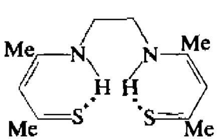
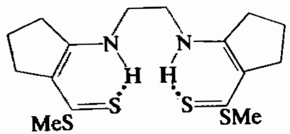
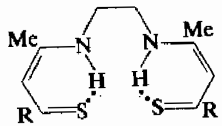
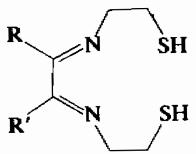
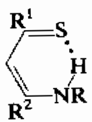
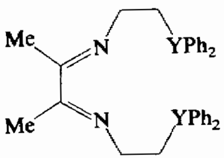
Schiff base[a]	Substituents	Preparation	Formula	Remarks (μ_{eff} in BM)	Ref.
 HL	$R = Pr^i, Bu^i; R^1 = H, Me; R^2 = Me, Ph$	Ligand + $NiBr_4^{2-}$; anhydrous conditions	NiL_2	Td; $\mu_{eff} = 3.2–3.4$	2386
	$R = n$-alkyl, aryl; $R^1 = Me; R^2 = Me, Ph$	As above	NiL_2	SqPl	2386–2388
 HL	R = Me, Ph	Ligand + NiX_2 + NaOEt; EtOH/dimethoxyethane	NiLBr	SqPl	2389, 2390
 H_2L	X = O		$[NiL(MeOH)]_4$*	Cubane-type structure	2391
	X = S	acac + $H_2NCH_2CH_2SH$ + $Ni(OAc)_2 \cdot 4H_2O$/MeOH	Ni_2L_2	SqPl	2392
 H_2L	$B = (CH_2)_2, CH_2CHMe, (CH_2)_3$, *cis*-1,2-cyclohexyl; R = Me, Ph; R′ = H, Me	Ligand + $Ni(OH)_2$/acetone	NiL	SqPl	2302, 2393, 2394
	$B = (CH_2)_2$; $R = Bu^t$; R′ = H, Me	Ligand + $Ni(OAc)_2 \cdot 4H_2O$/MeOH	NiL*	SqPl	2395
	$B = (CH_2)_2$; $R = CF_3$, Ph; R′ = Me		NiL*	SqPl	2396, 2397

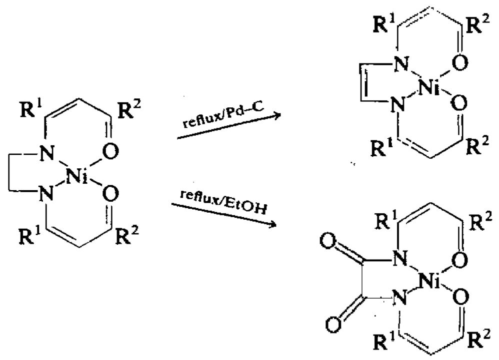
Table 99 *(continued)*

Schiff base[a]	*Substituents*	*Preparation*	*Formula*	*Remarks* (μ_{eff} *in BM*)	*Ref.*
 H_2L	R = H, Me, Ph; R′ = Me, CF_3, Ph, substituted phenyl	Ligand + $NiBr_4^{2-}$/Bu^tOH; Bu^tOK/N_2	NiL	Five-coordinate; μ_{eff} = 3.05–3.62	2398
 HL	R = Me, CF_3	$Ni(OH)_2$ + ligand/MeOH	NiLX	SqPl	2399
 HL	R = H, *n*-alkyl		NiL_2	SqPl	2400
	R = Pr^i, Ph, MeC_6H_4		NiL_2	Td; μ_{eff} = 3.0–3.3	2400
 H_2L		Ligand + $Ni(OAc)_2{\cdot}4H_2O$/MeOH	NiL	SqPl	2401

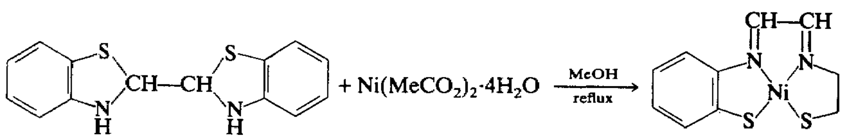
 H_2L		$NiCl_2$hydrate + $MeCO_2NH_4$ + ligand/MeOH, C_6H_6	NiL	SqPl	2402
 H_2L	$R = C_6H_4X$-*p* (X = Cl, Br, MeO, Me)	Ligand + $Ni(OAc)_2 \cdot 4H_2O$; MeOH, CH_2Cl_2/N_2	NiL	SqPl	2403
 H_2L	R = R′ = Me, Cy; R = Me; R′ = Et R = Me; R′ = Ph, Bu^n	$Ni(OAc)_2 \cdot 4H_2O$ + α-diketone + β-mercaptoamine/EtOH	NiL*	SqPl	2404–2406
 HL	$R = Bu^t, Pr^i$; R^1 = Ph; R^2 = H	Ligand + $NiBr_4^{2-}$/Bu^tOH; Bu^tOK	NiL_2	Td; $\mu_{eff} = 3.1$–3.3	2407
	$R = Pr^n$, $CHEt_2$; R^1 = Ph; R^2 = H, Me		NiL_2	SqPl	2407
	Y = P, As	Ligand + $Ni(ClO_4)_2$hydrate; BuOH, CH_2Cl_2/N_2	$[NiL](ClO_4)_2$	SqPl	2408
		NiX_2 + $Ni(ClO_4)_2$·hydrate; as above	$[NiXL]ClO_4$	Five-coordinate; polynuclear; diamagnetic	2409

* Structures determined by X-ray analysis.

[a] Only one limiting formula is given.



Scheme 31



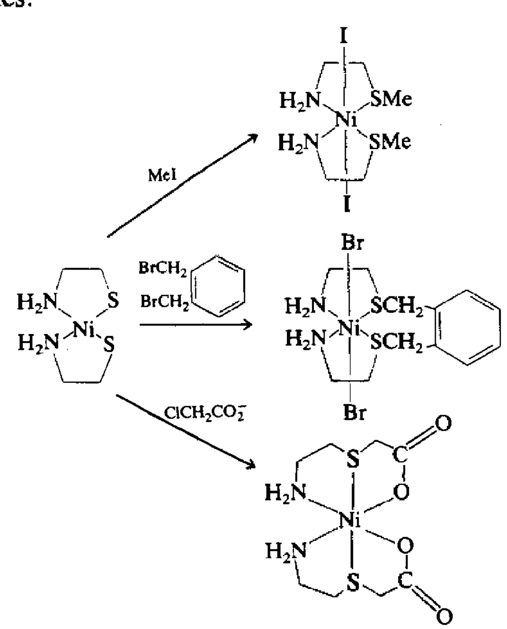
(332)

Scheme 32

50.5.8.2 Complexes with bidentate ligands having sulfur–nitrogen, oxygen–sulfur or oxygen–nitrogen donor atoms

(*i*) *Complexes with anionic and neutral sulfur–nitrogen chelates*[2415]

Nickel(II) complexes with various sulfur–nitrogen chelating ligands are reported in Table 100. 2-Aminoethanethiol (HL) is the simplest representative sulfur–nitrogen ligand acting as an anionic chelate. It forms two types of nickel(II) complex, namely the bis chelate [NiL_2] and the trinuclear $Ni_3L_4Cl_2$ (**333**).[2416,2417] Both complexes are square planar. Heterometallic complexes similar to (**333**), $[M(NiL_2)_2]^{n+}$, have been reported with different metals such as $M = Cu^{2+}$, Cu^+, Pd^{2+}, Pt^{2+} and Cd^{2+}.[2418] Most of the complexes with 2-aminoethanethiol have been prepared in aqueous solution, made basic with NH_3 or NaOH, by reacting the ligand hydrochloride with a nickel salt. The *S* alkylation of nickel complexes of 2-aminoethanethiol (Scheme 33) results in the formation of a thioether group which is still coordinated to nickel(II) in six-coordinate complexes.[2461]



Scheme 33

Table 100 Complexes with Miscellaneous Sulfur–Nitrogen Chelating Ligands

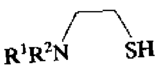
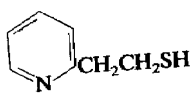
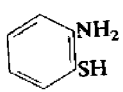
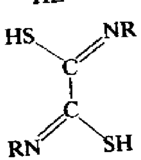
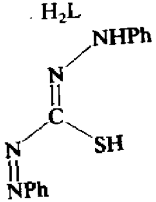
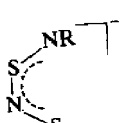
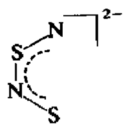
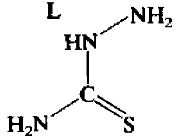
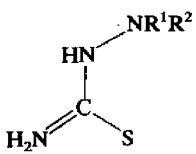
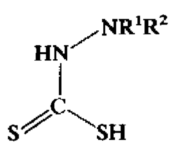
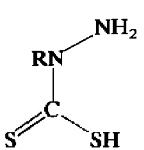
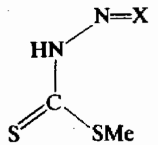
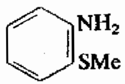
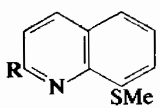
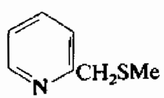
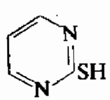
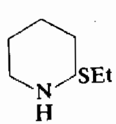
Ligand	*Substituents*	*Formula*	*Remarks*[a]	*Ref.*
 HL	$R^1 = R^2 = H$	NiL_2	SqPl	2416, 2417
	$R^1 = R^2 = H$	$Ni_3L_4Cl_2$* (**333**)	SqPl; Ni—S, 216 (av), 221; Ni—N, 190, 193	2416–2418
	$R^1 = H$; $R^2 = Pr^n$, Pr^i, hexyl, octyl, benzyl	NiL_2	SqPl	2419
	$R^1 = R^2 = Et$; $R^1 = R^2 = Bu^t$	NiL_2	SqPl; polynuclear	2419
	$R^1 = R^2 = Me$	NiL_2*	SqPl	2420
 HL		NiL_2; $Ni_3L_4X_2$	SqPl	2421
		$Ni_2L_2X_2$	SqPl; dinuclear	
 HL		NiL_2 (**334**)	SqPl	2422
 H_2L	R = H	NiL	SqPl; polynuclear	2423, 2424
	R = H, Me	Ni_4L_5; Ni_8L_9	$\mu_{eff} = 2.44, 2.09$	2425
 H_2L		NiL_2*	SqPl; Ni—S, 219; Ni—N, 187	2426
	R = H, Me, Et, CONHPh	NiL_2* (**335**)	SqPl; R = H, *cis*; R = Me, *trans*	2427–2432

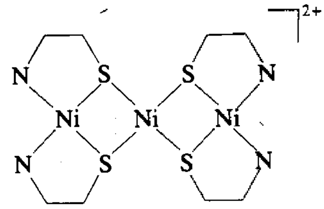
Table 100 *(continued)*

Ligand	*Substituents*	*Formula*	*Remarks*[a]	*Ref.*
 L		$[Ni_3L_4](Ph_4P)_2$ **(337)**	SqPl	2433
 HL		NiL_2* **(339)**	SqPl; grey and red forms	2434, 2435
		$[Ni(HL)_2]SO_4$*	*trans* SqPl, reddish-brown isomer, Ni—S, 217; Ni—N, 193	2436, 2437
			cis SqPl + *trans* SqPl, greenish-grey isomer	
		$[Ni(HL)_2](NO_3)_2$*	SqPl; two isomers, *cis* and *trans*	2438
		$Ni(HL)_2(NCS)_2$*	*trans* Oh; Ni—S, 240; Ni—N, 206	2439
		$[Ni(HL)_2(H_2O)_2](NO_3)_2$*	*trans* Oh	2440
		$[Ni(HL)_3]X_2$	Oh; X = halides	2441–2443
 HL	$R^1 = R^2 = Me$; R^1R^2 = cycloheptyl; $R^1 = Me$; $R^2 = Bu^i$	$[Ni(HL)_2X]X$	Supposed five-coordinate; X = Cl, Br	2444
 HL	$R^1 = R^2 = H, Me, Ph$; $R^1 = H, Me$; $R^2 = Ph$	NiL_2	SqPl	2434, 2445
 HL	$R = Me, Et, Pr^n, Bu$	NiL_2*	SqPl	2446

 HL	$X = CMe_2$, CHPh $NX = NPh_2$	NiL_2* NiL_2* $[NiX(HL)_2]X{\cdot}H_2O$	SqPl SqPl TBPy, X = Cl; Oh, $X = NO_3$	2447–2449 2450 2451
 L		NiX_2L_2	Oh; X = Cl, I; $\mu_{eff} = 3.1–3.3$	2452, 2453
 L	R = H R = Me	NiX_2L_2 NiX_2L	Oh; X = halides, NCS Td; X = Cl, Br; $\mu_{eff} = 3.1–3.2$	2454 2455
 L		NiX_2L_2	Oh; X = halides, NCS	2456
 L		NiX_2L_2	Oh; X = Cl, Br; $\mu_{eff} = 3.2$	2457
 L	R = Me, Et	NiX_2L_2	Oh; X = halides, NO_3; $\mu_{eff} = 3.0$	2458, 2459
 L		NiX_2L_2 $[NiL_3](ClO_4)_2$	Oh; X = halides, NCS; $\mu_{eff} = 3.2$ Oh; $\mu_{eff} = 3.2$	2460

* Structures determined by X-ray analysis.
[a] Bond distances are in pm; μ_{eff} are in BM.

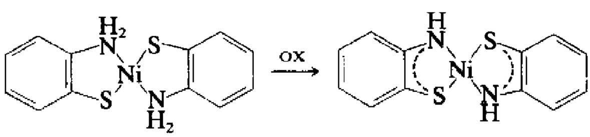
coc -H



(333)

Complexes with 2-(2-mercaptoethyl)pyridine are strictly similar to those obtained with 2-aminoethanethiol and were prepared in $MeOH/H_2O$ solution made alkaline with NH_3 by reacting the ligand with $NiSO_4$ hydrate.[2421]

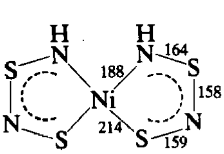
The buff-coloured bis chelate formed by 2-aminobenzenethiol (**334**) can be oxidized in alkaline solution to a blue-coloured complex of nickel(II) which contains the ligand in an oxidized form (Scheme 34).[2422,2462] Complex (**334**) reacts with MeI in acetone affording the six-coordinate complex NiL_2I_2 containing the *S*-methylated ligand.[2452]



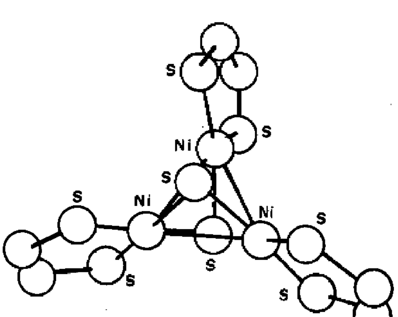
(334)

Scheme 34

The reaction of tetrasulfur tetranitride S_4N_4 with $NiCl_2$ in alcohol under anhydrous conditions produces a series of compounds which must be formulated as $Ni(S_2N_2H)_2$, $Ni(S_2N_2H)(S_3N)$ and $Ni(S_3N)_2$ (caution! S_4N_4 may be explosive). The latter two compounds have been obtained as by-products in the synthesis of the main product, the diamagnetic violet $Ni(S_2N_2H)_2$. The complexes have been separated and purified by means of chromatography. The structure of the main complex is *cis* square planar (**335**).[2430] The complexes $Ni(S_2N_2H)(S_3N)$ and $Ni(S_3N)_2$ presumably have the same structure as (**335**) where one or two NH groups are replaced by sulfur atoms. On the other hand the structure of the complex with the methyl-substituted ligand, $Ni(S_2N_2Me)_2$, is *trans* square planar.[2431] A trinuclear complex $[\{Ni(S_3N)\}_3S_2](Bu_4N)$ (**336**) has been obtained by reacting $NiCl_2$ hydrate with S_7NH in an MeOH solution made alkaline with KOH.[2463] The $[Ni(S_2N_2H)_2]$ complex reacts with alkaline hydroxide in EtOH affording the compounds $[Ni(S_2N_2H)(N_2S_2)]^-$ and $[Ni(N_2S_2)_2]^{2-}$. The latter acts as a bidentate ligand giving a trinuclear complex $[Ni_3(N_2S_2)_4](Ph_4P)_2$ (**337**).[2433] Other compounds have been prepared in which organic groups are substituted for one H atom in the complex $[Ni(S_2N_2H)_2]$ when it is reacted with phenyl isocyanate, aldehydes and amines.[2464] Bridged ligand complexes of general structure (**338**) have also been prepared.[2465] Other investigations concern the electronic structure of these compounds.[2466–2469]

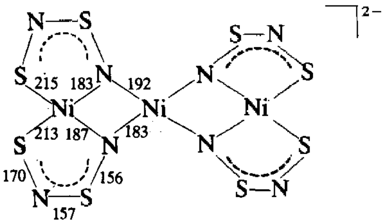


(335)

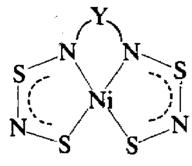


Average bond distances (pm): Ni—Ni, 290; Ni-μ^3-S, 220; Ni—S, 212; S—N, 145, 175

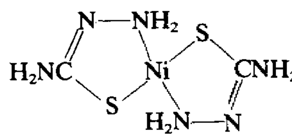
(**336**) (reprinted with permission from ref. 2463)



(337)



(338)



(339)

Neutral square planar complexes [NiL_2] (**339**) with deprotonated thiosemicarbazide have been obtained by the direct reaction of the reagents in aqueous ammonia solution.[2434] A summary of the spectroscopic studies carried out on the complexes with the various thiosemicarbazides is given in ref. 2470. Square planar complexes are also invariably given by deprotonated dithiocarbazic acids. The coordination mode (either S,S or N,S) adopted by these chelates depends on the substituents on the N atoms.[2434,2445,2446]

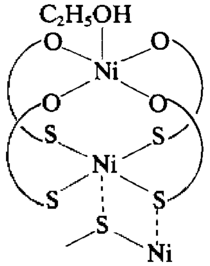
The nickel(II) complexes with thiosemicarbazides acting as neutral ligands, HL, are numerous and have been reviewed elsewhere.[2415] Selected examples of square planar and six-coordinate complexes are given in Table 100. Some examples of complexes prepared with tridentate Schiff bases derived from either thiosemicarbazide or dithiocarbazic acid are given in Tables 97 and 98, and examples of complexes with bidentate Schiff bases are reported in Table 100.

A summary of the representative neutral ligands constaining both thioether sulfur and amine nitrogen as donors is given in Table 100 together with the main properties of their nickel(II) complexes. Most of the complexes have the general formula NiX_2L_2 and are six-coordinate (X = coordinating anions) with the ligands acting as chelate. However, in the case of 2-methyl-8-thiomethylquinoline, the steric hindrance of the methyl groups in position 2 does not allow two molecules of the ligand to fit around the metal in either a *cis* or a *trans* square planar configuration, and a tetrahedral structure is preferred.[2455]

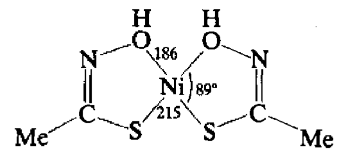
(*ii*) *Complexes with oxygen–sulfur chelating ligands*

The stability constants of mononuclear and polynuclear complexes of nickel(II) in either mercaptoacetic acid, $HSCH_2CO_2H$, or mercaptosuccinic acid, $HO_2CCH_2CH(SH)CO_2H$, have been investigated.[2471,2472] With the latter, six-coordinate polynuclear complexes with the formula $M(NiL)\cdot nH_2O$ (M = alkali metal)[2473] have been isolated in the solid state too, with the triply deprotonated ligand. Six-coordinate complexes of general formulas $NiL_2\cdot 2H_2O$ and [NiX_2L_2] have been reported with the deprotonated ligands $RSCH_2CO_2H$ (HL; R = Et, Pr^n, Bu^n, Bu^i, Bu^s),[2474] and the neutral ligands $RSCH_2CH_2OMe$ respectively.[2475]

The reaction of various monothiocarboxylic acids RC(S)OH (R = Ph, Et, Me) in alkaline solution with nickel(II) results in the isolation of complexes of general formula [{$Ni(RCOS)_2$}$_2\cdot$EtOH] (μ_{eff} = 2.3–2.4 BM).[2476] These complexes have a dinuclear structure exemplified by that of [{$Ni(PhC(S)O)_2$}$_2\cdot$EtOH] (**340**).[2477] In this complex both nickel atoms have five neighbours: one nickel is bound to four oxygen atoms of four different thiobenzoate anions, and to the oxygen atom of EtOH; the other nickel is bound to four sulfur atoms of thiobenzoates and to an additional sulfur atom belonging to the centrosymmetrically related molecule.



(340)



(341)

The dinuclear structure (**340**) is broken up by N donors which give mononuclear octahedral complexes $[Ni(RCOS)_2B_2]$ (B = py, substituted pyridines, ½bipy).[2478–2480] On the other hand the same dinuclear complexes are transformed into square planar complexes $[NiL_2B_2]$ by the reaction with phosphines.[2481]

Square planar complexes have been reported with deprotonated methylthiohydroxamic acid (**341**)[2482,2483] and other monoanionic chelating ligands.[2484–2486]

(*iii*) *Complexes with oxygen–nitrogen chelating ligands*

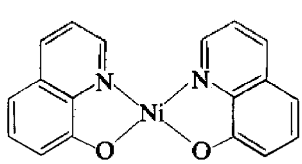
Besides the complexes with the various Schiff bases discussed in Sections 50.5.8.1.i–iv and with amino acids (Section 50.5.8.4.ii), nickel(II) complexes containing N,O chelates amount to hundreds. It is possible that molecules containing every conceivable bridging chain between the N and O donor atoms have been investigated as ligands towards nickel(II). Almost all of these complexes exhibit either square planar or octahedral coordination.

Amongst the simplest N,O chelating ligands, 1-amino-2-ethanol (ethanolamine) has been found to give six-coordinate tris chelates $[NiL_3]X_2$ (X = I,[2487] $\frac{1}{2}SO_4$;[2488] bond distances: Ni—O, 208; Ni—N, 215 pm) and square planar bis chelates $[NiL_2]SO_4$. The former have been easily obtained in H_2O/MeOH solution and the latter in MeOH solution under anhydrous conditions. Analogous complexes can be obtained with the ligand 1-amino-2-propanol. It has been found that the coordination of either the racemic or the optically active isomer of the latter ligand in *trans* octahedral complexes $Ni(NCS)_2L_2$ makes the difference in the complex stability very small[2489] (bond distances: Ni—O, 209–211; Ni—N, 207, 208 pm).

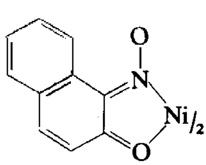
N,N-Dialkylethylenediamine *N*-oxide and 2,2′-bipyridine *N*-oxide form green octahedral $[NiL_3](ClO_4)_2$ and red square planar $[NiL_2](ClO_4)_2$ complexes.[2490,2491]

o-Phenolamine (HL) gives the paramagnetic (μ_{eff} = 3.2 BM) $NiL_2{\cdot}2H_2O$ complex[2492] which can be further deprotonated in liquid ammonia with KNH_2 to yield $K_2[Ni(o\text{-}C_6H_4NH)_2]$ (μ_{eff} = 3.1 BM) where the ligand acts as a binegative chelate.[2493]

Nickel(II) complexes of 8-hydroxyquinoline, HL, are well known from the viewpoint of analytical chemistry. The brown, diamagnetic complex NiL_2 has *cis* square planar coordination (**342**). The same coordination occurs in C_6H_6 and $CHCl_3$ solutions. In water, pyridine or dioxane, this complex is green and paramagnetic, as is the solid hydrate $NiL_2{\cdot}2H_2O$.



(**342**)



(**343**)

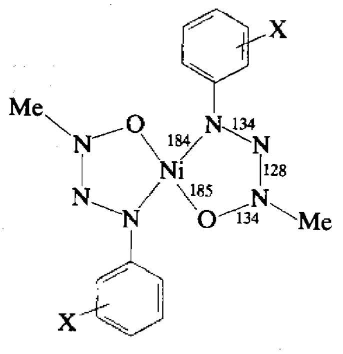
Nickel oximates were prepared by adding an EtOH solution of $NiSO_4$ to a solution of the ligand in 10% excess at boiling temperature and in the presence of enough HCl to obtain a clear solution.[2494]

Other simple chelate ligands which have been found to give six-coordinate complexes NiX_2L_2 are 2-acetylpyridine *N*-oxide oxime,[2495] 2-acetamidopyridine,[2496] pyridine-2-(acetic acid methyl ester)[2497] and *N*-substituted 2-aminopyridine *N*-oxides.[2498]

1-Nitroso-2-naphtholo (**343**) and 2-nitroso-1-naphtholo complexes $[NiL_2]$ exhibit some degree of association in the solid state, the extent of which depends upon the method of their preparation.[2499] Complex (**343**) reacts with the sodium salt of the deprotonated 1-nitroso-2-naphtholo ligand affording the tris chelate $Na[NiL_3]$, and with py affording $NiL_2{\cdot}2py$ adducts. Analogous complexes have been described with 2-nitroso-1-phenols.[2500]

Several square planar complexes have been characterized with chelating ligands derived from aromatic triazine 1-oxides of general formula ArNHN=N(R)O (HL).[2501,2502] The structure of some complexes has been determined by means of X-ray analysis (**344**).[2503]

Unlike other dioximes, as for example the well-known DMG (Section 50.5.3.7.ii), camphorquinone dioxime, H_2CQD, was found to coordinate with O and N atoms in the $Ni(HCQD)_2$ complex which has square planar coordination (**345**).[2504] The reaction of complex (**345**) with $AgNO_3$ in H_2O/MeOH solution gives a hexanuclear cluster of composition $[Ni(HCQD)_2Ag]_3$ (**346**).[2505] Each hexanuclear molecule consists of three $Ni(HCQD)_2^-$ anions



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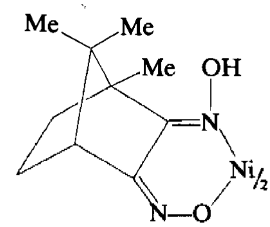

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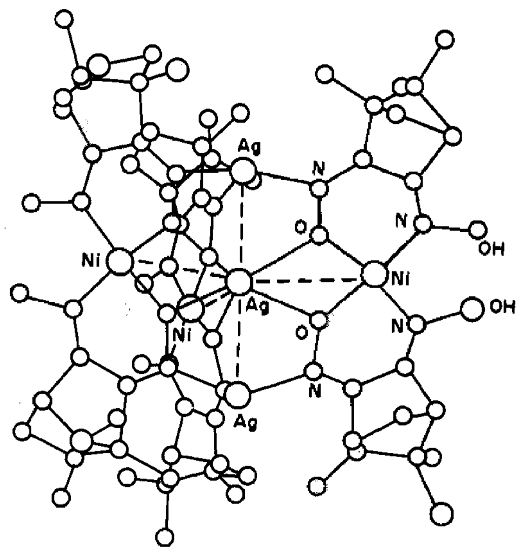
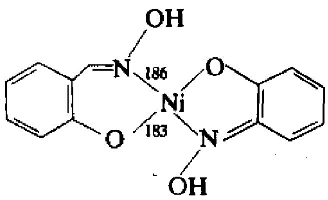


(346) (reproduced and adapted with permission from ref. 2505)

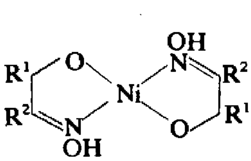
bound to three Ag atoms along a linear chain. The coordination around the nickel atom is *cis* square planar in contrast to the *trans* square planar coordination of the parent $Ni(HCQD)_2$ complex. The six metal atoms in the hexanuclear cluster are arranged in a trigonal bipyramid.

Two isomers of camphorquinone monooxime, known as isonitrosocamphor (HCQM) and isonitrosoepicamphor (HCQE), react with $Ni(NO_3)_2$ hydrate in the presence of py affording compounds of composition $[Ni(CQM)py_3(H_2O)]PF_6 \cdot H_2O$ and $[Ni(CQE)py_3(H_2O)]PF_6 \cdot \frac{1}{2}H_2O$ ($\mu_{eff} = 3.04$, 3.14 BM respectively). A dimeric structure with bridging oxime has been proposed.[2506]

Transition metal hydroxyoxime complexes have been reviewed very recently.[2507] Their use in both analytical chemistry and extraction metallurgy is well known. The square planar structure of the bis chelate complex NiL_2 (**347**) with the deprotonated 2-hydroxybenzaldoxime (HL) is typical of this series of nickel complexes.[2508] Their bis adducts, NiL_2B_2, with bases such as py, substituted pyridines and cyclomethyleneimines, are six-coordinate.[2509] The acyl oxime (H_2L) complexes are similar to the aforementioned complexes being either square planar bis chelates $Ni(HL)_2$ (**348**) or octahedral bis adducts, $Ni(HL)_2B_2$.[2507] When the acyl oxime acts as a dibasic ligand L^{2-}, the corresponding $(NiL)_n$ complexes are insoluble and involve extensive polymerization.



(347)



(348)

50.5.8.3 Complexes with 'hybrid' polydentate ligands

A summary of some nickel complexes which have been synthesized and characterized with saturated 'hybrid' polydentate ligands is given in Table 101. The complexes have generally been prepared by the direct reaction of various nickel salts with the appropriate ligand in alcoholic media. In the case of tridentate ligands with sterically unencumbered terminal donor groups the complexes are six-coordinate with the ligands, in general, facially coordinated to the nickel atom as found in the two complexes (**349**) and (**350**).[2510,2511] However, in the complex $NiBr_2L_2$ (**351**; L = 1,5-dihydroxy-3-thiapentane), the ligand acts as bilegate.[2512]

Table 101 Complexes with 'Hybrid' Polydentate Ligands

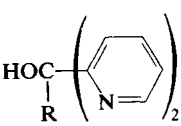
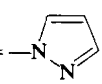
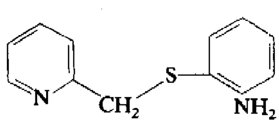
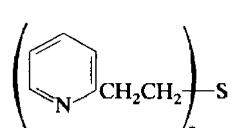
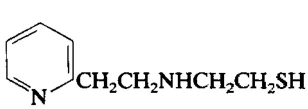
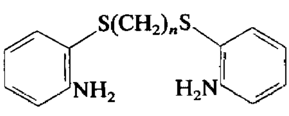
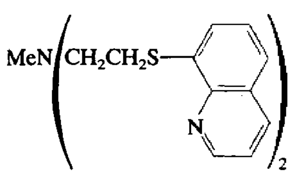
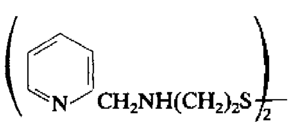
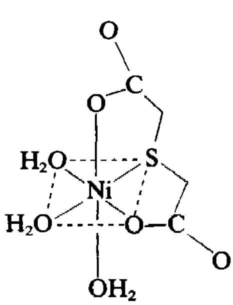
Ligand	*Substituents*	*Formula*	*Remarks* (μ_{eff} *in BM*)	*Ref.*
$S(CH_2CO_2H)_2H_2L$		$NiL(H_2O)_3$* (**349**)	Oh	2510
		$K_2[NiL_2]$* (**350**)	Oh	2511
$S(CH_2CH_2NH_2)_2$ L		NiL_2X_2	Oh; X = halides, PF_6, NO_3	2512
$S(CH_2CH_2OH)_2$ L		$NiBr_2L_2$* (**351**)	Oh; bilegate ligand	2513
$RN(CH_2CH_2OH)_2$	R = H: H_2L^1	$[Ni(H_2L^1)_2]X_2 \cdot xH_2O$	Oh; X = Cl, Br	2514, 2515
	R = Me: H_2L^2	$[Ni(H_2L^2)_2]X_2$	Oh; X = halides, NO_3; μ_{eff} = 3.2–3.3	
		$[Ni(HL^2)H_2O]X$	Oh, polynuclear; X = Cl, Br; μ_{eff} = 3.3–3.4	
		$[Ni(HL^2)(H_2L^2)]X$	Oh; X = NO_3, I; μ_{eff} = 3.1–3.2	
 (**XV**) L	R = , NHMe, NH_2	$[NiL_2](NO_3)_2$	Oh; μ_{eff} = 3.0–3.1	2516
 L		$NiL_2X_2 \cdot 2MeOH$	Oh; X = Br, ClO_4; μ_{eff} = 3.2–3.3	2438
$Y(CH_2CH_2NMe)_2$ L	Y = O, S	NiX_2L	Five-coordinate; X = Cl, Br, NCS; μ_{eff} = 3.1–3.4	2517
		NiX_2L	Five-coordinate; X = halides; μ_{eff} = 3.2–3.3	2518
$H_2N(CH_2)_nNH(CH_2)_2SH$	n = 2: HL^2	$NiClL^2 \cdot \frac{1}{2}MeOH$	SqPl	2519
		$[NiL^2]BPh_4$	SqPl	
	n = 3: HL^3	$[NiL^3]BPh_4 \cdot H_2O$	SqPl	
$MeN(CH_2CH_2SH)_2$ H_2L		$[NiL]_2$	SqPl; dinuclear	2520, 2521
 HL		$[NiL]_2(ClO_4)_2$* (**352**)	SqPl; dinuclear	2522
$ZCH_2CH_2N(CH_2CH_2NEt_2)_2$ (**XVI**) L	Z = OMe, SMe	$[NiXL]BPh_4$	TBPy; X = halides, NCS; μ_{eff} = 3.2–3.6	2523
	Z = OMe	$Ni(NCS)_2L$	Oh; μ_{eff} = 3.2	
	Z = SMe	$Ni(NCS)_2L$	Five coordinate; μ_{eff} = 3.4	
$(ZCH_2CH_2)_2NCH_2CH_2NEt_2$ (**XVII**) L	Z = OMe, SMe	$[NiXL]BPh_4$	TBPy; X = halides, NCS; μ_{eff} = 3.2–3.4	2523
		$Ni(NCS)_2L$	Oh; μ_{eff} = 3.2	

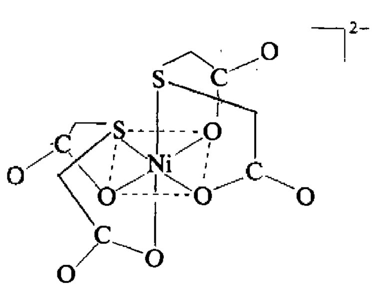
Table 101 (*continued*)

Ligand	*Substituents*	*Formula*	*Remarks* (μ_{eff} *in BM*)	*Ref.*
$N(CH_2CH_2Z)_3$ (**XVIII**) L	Z = OMe, SMe	$[NiXL]BPh_4$	Oh; X = halides, NCS; μ_{eff} = 3.1–3.3	2523, 2524
$HOCH_2CH_2N(CH_2CH_2NEt_2)_2$ (**XIX**) HL		$[NiL]_2(ClO_4)_2$* (**353**)	TBPy; dinuclear	2525
$N(CH_2CH_2OH)_3$ L		NiL_2X_2*	Oh; X = halides, NO_3; μ_{eff} = 3.0–3.3; trilegate ligand	2526, 2527
$N(CH_2CHMeOH)_3$		NiL_2SO_4	Oh; μ_{eff} = 3.13; trilegate ligand	2528
$2\text{-py}(CH_2)_nS(CH_2)_2S(CH_2)_n\text{py-}2$ L	n = 1, 2	NiX_2L	Oh; X = halides, NCS; μ_{eff} = 3.0–3.3	2529, 2530
	n = 2	$NiL(ClO_4)_2 \cdot xH_2O$	Different structures depending on the preparation	2531
 L	n = 2, 3, 4	NiX_2L	Oh; X = halides, NCS; μ_{eff} = 2.8–3.0	2532
$HN(CH_2CH_2SCH_2CH_2NR_2)_2$	R = Me; L	$[NiL(H_2O)](ClO_4)_2$	Oh; μ_{eff} = 3.56	2533
	R = H; HL	$[NiL(H_2O)]ClO_4 \cdot H_2O$	Oh; μ_{eff} = 2.91; deprotonated ligand	2534
 L		$[NiL(H_2O)](ClO_4)_2$	Oh; μ_{eff} = 3.04	2533
 L		$[NiXL]ClO_4$	Oh; pentalegate ligand X = Cl, Br	2383, 2534

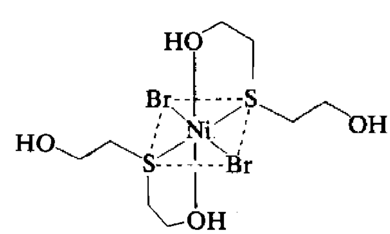
*Structures determined by X-ray analysis.



(**349**)



(**350**)

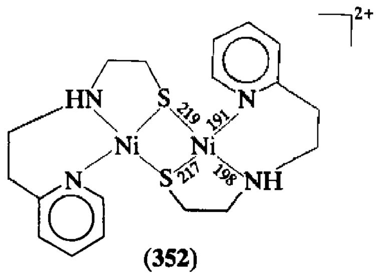


(**351**)

It has been found that di-2-pyridyl ketone (dpk) and reagents such as pz, $MeNH_2$, NH_3 and $PhNHNH_2$ react together in aqueous solution in the presence of hydrated $Ni(NO_3)_2$ affording tridentate ligands of the type (**XV**; Table 101) which coordinate to nickel(II) in the octahedral complexes $[NiL_2](NO_3)_2$.[2516]

When adequate steric hindrance on the donor atoms is provided in the tridentate ligands, high-spin five-coordinate NiX_2L complexes are obtained. Significant examples are the complex obtained with the two strictly correlatable ligands 1,5-bis(dimethylamino)-3-thiapentane and 1,5-bis(dimethylamino)-3-oxapentane.[2517] These compounds give rise in solution to equilibria between five- and six-coordinate species achieved *via* molecular association or solvolysis.

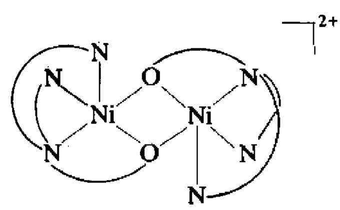
The tridentate ligands with terminal mercapto groups invariably give square planar complexes with a dinuclear structure achieved *via* mercapto bridges as found in the crystal structure of the complex (**352**).[2522] In this complex the Ni_2S_2 ring is severely folded to give an angle of 110° at the S—S diagonal, giving an Ni—Ni distance of 274 pm. Some such complexes react with MeI producing new complexes where the terminal sulfur atoms have reacted with the alkyl halide.



(**352**)

As outlined in Section 50.5.4.6 the tripod-shaped tetradentate ligands have the most favourable geometry for the formation of five-coordinated complexes with trigonal bipyramidal geometry. However, the presence of different donor groups in the donor set may give rise either to coordination distortion or to stereochemistries other than trigonal bipyramidal.

As a matter of fact the tetradentate tripodal ligands with donor sets N_2O_2, N_2S_2, N_3O and N_3S (**XVI**, **XVII**; Table 101) may give either five-coordinate $[NiXL]^+$ complexes or six-coordinate octahedral $NiL(NCS)_2$ complexes.[2523] Moreover, the ligands with donor sets NO_3 and NS_3 (**XVIII**) give polymeric six-coordinate $[NiXL]^+$ complexes.[2523,2524] The ligand (**XIX**) undergoes deprotonation with $Ni(ClO_4)_2$ affording the dinuclear five-coordinate complex (**353**).[2525] Most of the nickel complexes with ligands (**XVI**) and (**XVII**) retain their own five-coordinate structure in either nitroethane or 1,2-dichloroethane solutions.



(**353**)

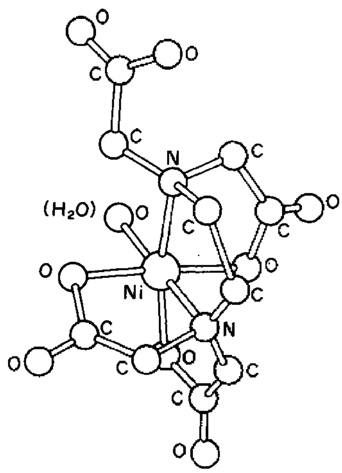
Linear quadridentate ligands with saturated connecting chains have sufficient flexibility to arrange themselves in either a planar or a non-planar arrangement. However, the non-planar arrangement around the nickel(II) atom is in general preferred in the case of bulky donor atoms such as sulfur because of the reduction of the steric strain. In general nickel complexes with hybrid linear quadridentate ligands are six-coordinate (Table 101).

50.5.8.4 Complexes with aminocarboxylic acids

(*i*) *Complexes with aminopolycarboxylic acids* (*complexones*)

Amongst the aminopolycarboxylic acids, also known as 'complexones', the potentially hexadentate ethylenediaminetetraacetic acid (usually called H_4edta and $H_{4-x}edta^{x-}$ according to the degree, if any, of deprotonation) is by far the most familiar. This ligand forms very stable 1:1 nickel complexes in aqueous solution ($\log K_1 = 18.6$ at 293 K and $\mu = 0.1$ in KNO_3).[2535] There are conflicting reports concerning the effective denticity of deprotonated H_4edta towards nickel(II) in aqueous solution. It is now ascertained that over the pH range 4–12 significant amounts of pentadentate ligand are present with an uncoordinated carboxylic group, corresponding to the formulation $[Ni(H_{2-x}edta)(H_2O)]^{x-}$.[2536,2537] The six-coordination of nickel(II) is completed by a coordinated water molecule. Actually such a structure has been found in the solid complex $[Ni(H_2edta)H_2O]$ (**354**)[2538] which can be prepared by the reaction of

H_4edta with nickel(II) hydroxide. A tetragonal distortion occurs in the complex, with two axial bonds longer than the normal ones (Ni—O, 216; Ni—N, 213 *vs.* the equatorial bond distances Ni—O, 203, 204; Ni—N, 208; distances in pm). Nickel(II) is six-coordinated by the fully deprotonated edta^{4-} in the complex $Ca[Ni(edta)]\cdot 4H_2O$.[2539] In the dinuclear complex $[Co^{III}(NH_3)_5\{(edta)Ni(H_2O)\}]ClO_4\cdot 2H_2O$, the edta ligand acts as quinquedentate towards nickel(II) and unidentate towards the $Co(NH_3)_5^{3+}$ moiety.[2540] The crystalline compound $Ni(H_2edta)\cdot 2H_2O$, which can be isolated from an acidic solution, is assumed to contain two uncoordinated CH_2CO_2H groups, while two water molecule complete the six-coordination of nickel(II).[2541]



(**354**) (adapted with permission from ref. 2538)

The kinetics of displacement of either trien or tetren from their nickel complexes by edta have been investigated.[2542,2543]

The complexes formed in solution by edta, propane-1,2-diaminetetraacetate, *trans*-1,2-cyclohexanetetraacetate and diethylenetriamine pentaacetate (H_5dtpa) have been investigated by means of ^{1}H NMR spectroscopy. It has been supposed that in the six-coordinate complexes the average ligand coordination is between five and six.[2544–2546] Mononuclear and dinuclear complexes are presumably formed in solutions of H_5dtpa. The solid compounds have formulas $Ni_2(Hdtpa)\cdot 7H_2O$ and $Ni(H_3dtpa)\cdot H_2O$.[2547] Mono and bis chelates $[Ni(nta)\cdot xH_2O^-]$ and $[Ni(nta)_2]^{4-}$ are formed in solutions of the deprotonated nitrilotriacetic acid (H_3nta = $N(CH_2CO_2H)_3$; log $K_1 = 11.5$ at 293 K and $\mu = 0.1$ in KNO_3).[2535] The structure of the bis chelate has been investigated in the solid $K_4[Ni(nta)_2]\cdot 8H_2O$.[2548] In this six-coordinate complex the ligand acts as tridentate with one free carboxylate arm for each ligand molecule. The structure of lithium bis(iminodiacetate)nickel(II) was also reported.[2549–2551]

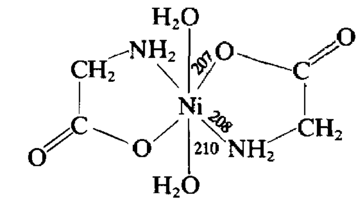
Nickel complexes with some sulfur analogues of complexones have also been investigated.[2552,2553]

(*ii*) *Complexes with simple amino acids and peptides*

The simplest α-amino acid is glycine, which is an excellent N,O chelating agent in the deprotonated form ($NH_2CH_2CO_2^-$, Gly) towards nickel(II). The complex $Na_2[Ni(Gly)_3]ClO_4\cdot D_2O$ contains the six-coordinate tris chelate tris(glycinato)nickelate(II).[2554] The neutral complex has the composition $[Ni(Gly)_2(H_2O)_2]$ and a *trans* octahedral structure (**355**).[2555] Other mixed-ligand complexes of the types $[Ni(Gly)_2(en)]$, $[Ni(Gly)(en)_2]^+$, $[Ni(Gly)_2(Im)_2]$ and $[Ni(Gly)_2(NH_3)_2]$ were also reported.[2556] The red-violet bis(thioglycinato) complex $Ni(H_2NCH_2COS)_2$ is diamagnetic and square planar.[2557]

Bis-aquo complexes were also reported with amino acids such as α- and β-alanine ($MeCH(NH_2)CO_2H$, $CH_2(NH_2)CH_2CO_2H$) and α-aminobutyric acid, $EtCH(NH_2)CO_2H$.[2558] The anhydrous complexes $[NiL_2]$ (L = glycinate, alaninate, α-aminobutyrate anions) are six-coordinate with a polymeric array of carboxylate groups both bidentate and bridging.[2558,2559]

The crystal structures of the following six-coordinated complexes were also determined: $[Ni(L\text{-}Ser)_2(H_2O)_2]$[2560] (Ser = $CH_2(OH)CH(NH_2)CO_2^-$), $[Ni(\beta\text{-}Ala)_2(H_2O)_2]$[2561] (Ala =

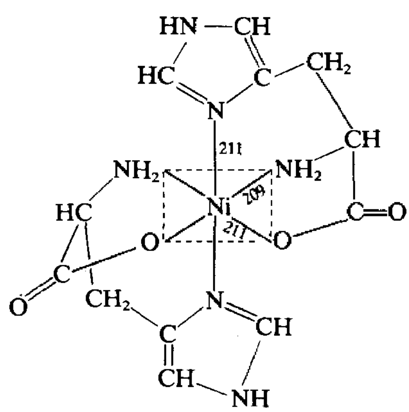


(355)

$CH_2(NH_2)CH_2CO_2^-$), $[Ni(Gly)_2(im)_2]$,[2562] $[Ni(L\text{-}Tyr)_2(H_2O)_2]\cdot H_2O$[2563] (Tyr = $HOC_6H_4CH_2$-$CH(NH_2)CO_2^-$) and $[Ni(Sar)_2(H_2O)_2]$[2564] (Sar = $MeNHCH_2CO_2^-$).

Transition metal complexes with potentially tridentate amino acids have recently been reviewed.[2559]

Amongst the numerous nickel(II) complexes with amino acids, those formed by histidine have been intensively studied because of the importance of the imidazole moiety in some enzymatic activities.[2565] In the solid state, the racemic $Ni(His)_2\cdot H_2O$ contains equimolar amounts of [Ni(D-His)$_2$] and [Ni(L-His)$_2$] (His = histidinate anion).[2566] The structure of [Ni(L-His)$_2$]·H_2O has also been determined.[2567] In both types of complex, the nickel(II) atom is six-coordinate with similar bond angles and distances (**356**). An analogous structure has been found in the complex Ni(D-pyAla)$_2$·$2H_2O$ (pyAlaH = β-(2-pyridyl)alanine, H_2NCH-$(CH_2C_5H_4N)CO_2H$).[2568,2569] Mixed-ligand complexes of amino acids (alanine, valine, leucine, phenylalanine, threonine) with *N*-(2-pyridylnaphthyl)-L-aspartic acid have been investigated. It has been found that the L isomers of the amino acids are coordinated preferentially for steric reasons.[2570] Other examples of stereoselectivity involving the coordination of deprotonated amino acids have been reported.[2571]



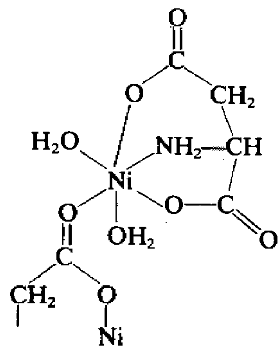
(356)

The coordination of methionine, $MeSCH_2CH_2CH(NH_2)CO_2H$, to nickel has been investigated in solution. It has been found that the complex [Ni(D-Met)(L-Met)] (Met = monoanionic methionine) is a little more stable than the optically active complex. The ligand is supposed to act as tridentate with at least weak Ni—S (thioether) bonding.[2572]

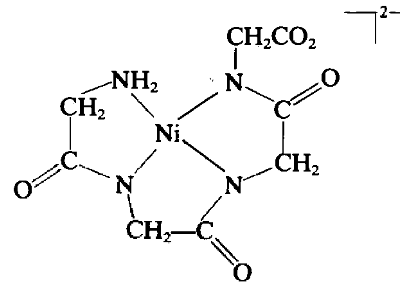
Using the dianionic ligand derived from aspartic acid, $HO_2CCH_2CH(NH_2)CO_2H$, the complex [Ni(L-aspartato)$(H_2O)_2$]H_2O has been synthesized and its structure determined (**357**).[2573] The mixed-ligand complex [Ni(L-Asp)(Im)$_3$] is mononuclear and six-coordinate.[2574]

The coordination of glycine peptides to nickel(II) has been investigated in aqueous solution by means of potentiometric and spectral measurements,[2575] and also in the solid compounds. In solution, as the pH increases, protons are lost progressively from the peptide groups and Ni—N (peptide) bonds are formed. The formation of Ni—N (peptide) linkages in general shifts the equilibrium between six- and four-coordinate species towards the latter. Actually, the structure of disodium tetraglycinatonickelate(II) octahydrate is square planar (**358**).[2576] This complex consumes O_2 in neutral solution and catalyzes the oxidation of the peptide affording a number of new products.[2577]

Various other Ni–peptide systems have been investigated in the solid state[2578] and in aqueous solution over a broad range of pH.[2579,2580]



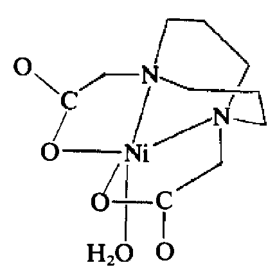
(357)



(358)

(iii) Miscellaneous complexes

Six-coordinate complexes were reported with pyridine-2-carboxylate, $[Ni(C_5H_4NCO_2)_2(H_2O)_2]\cdot 2H_2O$,[2581] with hydrogenopyridine-2,6-dicarboxylate, $[Ni\{C_5H_3N(CO_2H)CO_2\}_2]\cdot 3H_2O$[2582–2584] which acts as monoanionic tris chelate, and with the dianionic tris chelate pyridine-2,6-dicarboxylate $[Ni(en)_3][Ni\{C_5H_3N(CO_2)_2\}_2]\cdot 4H_2O$.[2585] Nickel complexes with the two closely related ligands 1,5-diazacyclooctane-*N,N'*-diacetic acid (dacoda) and 1,5-diazacyclooctane-*N*-monoacetic acid (dacoma) have been investigated. The square pyramidal coordination of the $[Ni(dacoda)H_2O]\cdot 2H_2O$ complex (**359**) is sterically forced by a methylene hydrogen which blocks the sixth coordination position.[2586,2587] The same five-coordination is also retained in solution. In solutions of $[Ni(dacoda)H_2O]$ containing variable amounts of $NaClO_4$, an equilibrium occurs between blue square pyramidal and yellow square planar species.[2588] Moreover, heating *in vacuo* converts the solid blue $[Ni(dacoda)H_2O]$ to yellow square planar [Ni(dacoda)]. In the case of the complex $[Ni(dacoma)(H_2O)_2]ClO_4$ the five-coordination is achieved with two coordinated water molecules.[2589]

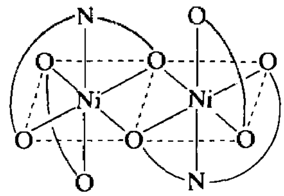


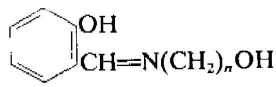
(359)

50.5.8.5 Di- and tri-nuclear complexes with dinucleating ligands

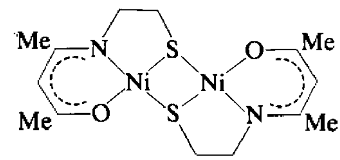
Many types of ligand have been designed or are known to favour the formation of di- and tri-nuclear nickel complexes. This field of coordination chemistry has recently been extensively reviewed.[2590,2591] For a specific discussion of the magnetic properties of dinuclear nickel(II) complexes, see Section 50.5.10.

Amongst the simplest ligands which have been found to give dinuclear complexes with nickel(II) are tridentate Schiff bases derived by the condensation of either salicylaldeyde or acetylacetone with amino alcohols (**360**),[2592] amino acids such as glycine, L-alanine, L-valine, L-leucine and L-methionine,[2593] 2-mercaptoethylamine (**361**)[2594] and *S*-methyldithiocarbazate.[2299] Most of the complexes with these ligands are six-coordinated but those with thiolo bridges are invariably square planar. Complexes of the type (**362**) where X = MeO, EtO, N_3, NH_2, OH and OCN are square planar and diamagnetic,[2595–2598] but those where X = Cl, $[Ni_2L(Cl)]\cdot n$DMSO ($n = 2, 4$), have magnetic moment values about 2.0 BM at room temperature. They contain presumably one diamagnetic square planar nickel(II) and one paramagnetic nickel(II).

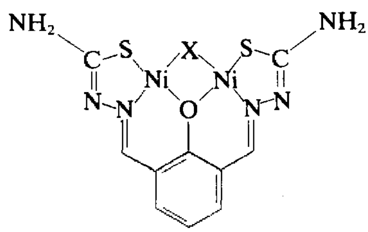


(360) O⌒N⌒O = 

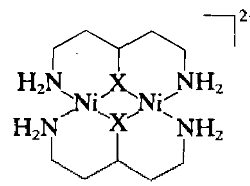
O⌒O is $MeOCH_2CH_2OH$



(361)



(362) X = MeO, EtO, N_3, NH_2, OH, OCN



(363) X = O, S

Square planar dinuclear complexes of type (363) formed by dinucleating ligands which have no unsaturated bonds have also been reported.[2599]

More examples of dinuclear homo- and hetero-metallic complexes which have been prepared with some dinucleating ligands are reported in Table 102 together with some physicochemical properties and preparative routes.

Table 102 Nickel(II) Complexes with some Dinucleating Ligands

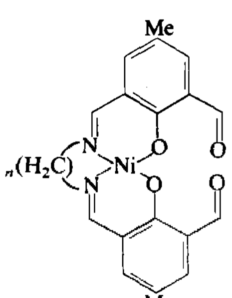
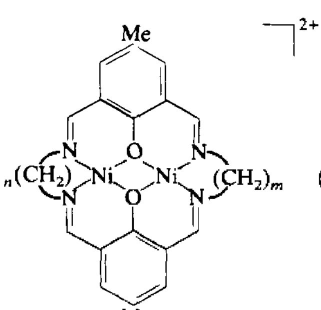
Complex	μ_{eff} (BM)	*Coordination geometry of nickel(II)*	*Remarks*	*Ref.*
 (XX)	Diamagnetic	SqPl	$n = 2, 3$; preformed ligand + $Ni(OAc)_2 \cdot 4H_2O$/EtOH, H_2O	2600
 (XXI)	Diamagnetic	SqPl Oh	$n = m = 2$; $n = 2$, $m = 3$; orange $n = m = 3$; green; Ni_2LCl_2	2600

Table 102 (*continued*)

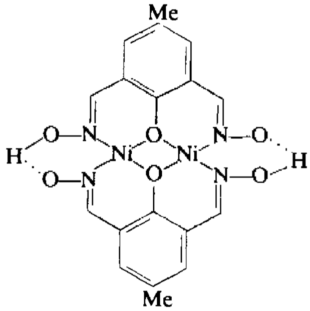
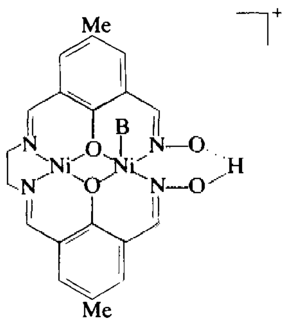
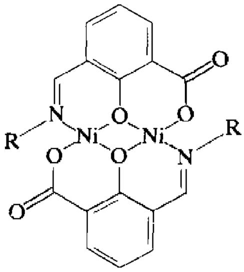
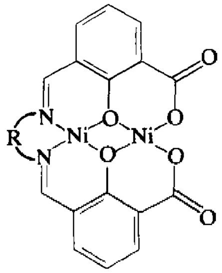
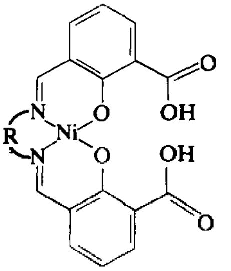
Complex	μ_{eff} (BM)	Coordination geometry of nickel(II)	Remarks	Ref.
	2.84[a]	Oh	$Ni_2L{\cdot}3H_2O$; antiferromagnetic interaction between nickel atoms	2600
	2.25[a]	SqPl + SqPy	$[Ni_2L]ClO_4{\cdot}DMF$; B = DMF; SqPl in DMF solution	2601
	3.06–3.17[a]	Oh	$Ni_2L_2{\cdot}nH_2O$; n = 2–4; R = Me, Et, Bu^n, CH_2CH_2OH; template synthesis: 3-formylsalicylic acid, amine, Na_2CO_3, $Ni(OAc)_2{\cdot}4H_2O$ in H_2O solution; presumably H_2O molecules in axial positions; antiferromagnetic behaviour	2602
 **(XXII)**	2.17–2.33[a]	SqPl + Oh	$Ni_2L{\cdot}nH_2O$; n = 3, 5; R = CH_2CH_2, CH_2CHMe, C_6H_4, C_6H_{10}; template synthesis as above.	2603
	3.36[a]	Oh	$Ni_2L{\cdot}5H_2O$; R = $(CH_2)_3$; antiferromagnetic behaviour	
 **(XXIII)**	Diamagnetic	SqPl	R = CH_2CH_2, CH_2CHMe; template synthesis as above	2603, 2604

Table 102 (*continued*)

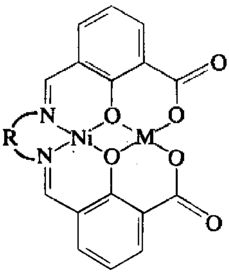
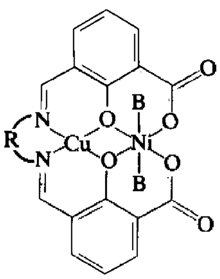
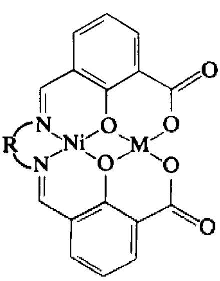
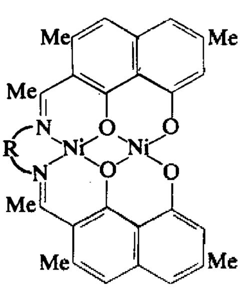
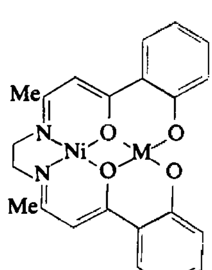
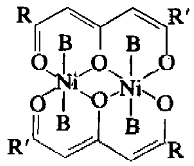
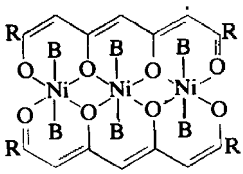
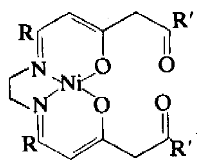
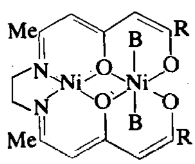
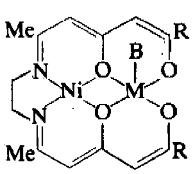
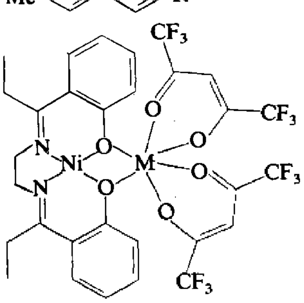
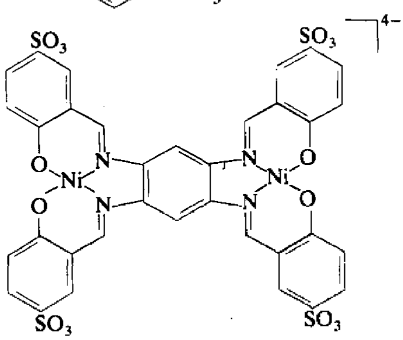
Complex	μ_{eff} (BM)	*Coordination geometry of nickel(II)*	*Remarks*	*Ref.*
 **(XXIV)**	Diamagnetic	SqPl	$NiM_xL{\cdot}nH_2O$; $x = 1, 2$; M = Li, Na, Mg, Sr, Ba; R = CH_2CHMe; preformed ligand + $Ni(OAc)_2{\cdot}4H_2O$ + MCl_x + NaOH/EtOH, H_2O	2605
 **(XXV)**	3.36–3.78[b]	Oh	$NiCuL{\cdot}xH_2O$; R = $(CH_2)_3$, $(CH_2)_4$, C_6H_4, C_6H_{10}; B = H_2O; antiferromagnetic behaviour; CuL + $Ni(OAc)_2{\cdot}4H_2O/H_2O$	2606
 **(XXVI)**	1.87–5.71[b]	SqPl	$NiML{\cdot}xH_2O$; R = CH_2CH_2; M^{2+} = Cu, UO_2, Co, Mn, Fe; NiL + MX_2/EtOH (MeOH)	2604, 2607
	2.53[a]		$Ni_2L{\cdot}H_2O$; R = $CH_2CH_2NHCH_2CH_2$; preformed ligand + $Ni(OAc)_2{\cdot}4H_2O$	2608
	0, 2.08[b] 2.99	SqPl SqPl + Oh	M^{2+} = UO_2, Cu M^{2+} = Ni NiL in pyridine + $Ni(OAc)_2{\cdot}4H_2O$ in MeOH + LiOH; six-coordination achieved, presumably *via* oligomerization in the solid state	2609

Table 102 *(continued)*

Complex	μ_{eff} (BM)	Coordination geometry of nickel(II)	Remarks	Ref.
 (XXVII)	2.75–3.30[a]	Oh	$[Ni_2L_2py_4]\cdot 4py$*; R = R′ = Ph R = Me, Ph, p-BrC_6H_4; R′ = Me, Ph, p-BrC_6H_4; B = H_2O, py; $NiCl_2$ + triketone + NaOH/acetone, H_2O	2610
	2.97[a]	Oh	$[Ni_2L_2py_4]$*; R = Me, R′ = CF_3	2611
	3.14[a]	Oh	B = H_2O; NiX_2 + ligand + NaOH ($MeCO_2Na$)/MeOH, H_2O	2612
 (XXVIII)	Diamagnetic	SqPl	R = R′ = Me; R = Me; R′ = Ph; preformed ligand + $Ni(OAc)_2\cdot 4H_2O$/EtOH	2613
 (XXIX)	3.05–3.16[b]	SqPl + Oh	Ni_2LB_2; B = H_2O, py; R = Me; prepared as above	2614
	3.16[b]	SqPl + Oh	$[Ni_2Lpy_2]py$*; R = Ph	2615
	0.5–2.0[b]	SqPl	NiML·xsolvent; R = Me, Ph; M^{2+} = Cu, VO, UO_2, Zn; NiL + $M(OAc)_2\cdot 4H_2O$/MeOH	2616, 2617
			NiZnL·py*; R = Me; Ni(VO)L*; R = Me	2617
		SqPl	$NiML(hfacac)_2$*; M^{2+} = Cu, Co, Mn (hfacac = hexafluoroacetylacetonate)	2618
		SqPl	$Na_4Ni_2L\cdot 4H_2O$; 1,2,4,5-benzenetetramine·4HCl + NaOMe in DMSO/MeOH + 5-sulfosalicylaldehyde in DMSO + $Ni(OAc)_2\cdot 4H_2O$	2619

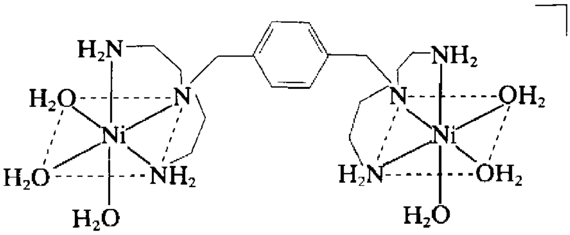
* Structure determined by X-ray analysis.
[a] Average magnetic moment per nickel(II) atom.
[b] Magnetic moment referred to the dimetallic complex.

The condensation of 2,6-diformyl-4-methylphenol with one molecule of diamine such as ethane-1,2-diamine or propane-1,3-diamine affords Schiff bases which have two adjacent coordination compartments[2591] where the donor atoms are different. The π system occurring in this type of ligand strongly favours a planar arrangement of each set of donor atoms, thus precluding six-coordination towards a single metal atom (**XX**; Table 102).[2600] When the complex (**XX**) reacts with one more molecule of the diamine, a cyclization of the complex occurs. The cyclic complex containing one nickel atom behaves by itself as a ligand and reacts with one additional nickel(II) to give dinuclear complexes of the types (**XXI**). In general, the nickel atom has square planar coordination when it is accommodated in the Schiff base compartment (N_2O_2 donor set; complexes **XXII–XXIV**, **XXVI**). On the other hand the nickel atom accommodated in the keto–enol-type compartment (O_4 donor set) may increase its coordination number up to six with two additional donors in the axial position (complexes **XXII**, **XXV**, **XXVII**, **XXIX**).[2610,2611,2613,2614]

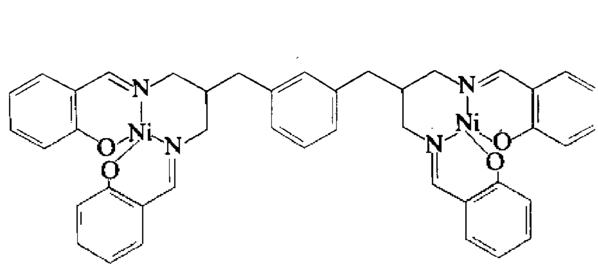
A different series of dinuclear nickel(II) complexes are those reported with more flexible ligands which hold one nickel atom well separated from the second metal centre. In general, these metal complexes are designed in such a way that interactions with substrates may occur.[2620,2621]

The ligand 1,4-bis{bis(2-aminoethyl)aminomethyl}benzene forms a polymeric 1:1 metal–ligand complex and a 2:1 complex (**364**) in aqueous solution.[2620]

The reaction of bis(salicylaldehydato)nickel(II)·$2H_2O$ with *m*-xylenebis-2-(1,3-propanediamine) in EtOH results in the formation of the dinuclear complex (**365**).[2621] This complex undergoes a quasi-reversible two-electron reduction at −1.47 V *vs.* SCE attributable to the formation of the corresponding dinuclear Ni^I complex. EPR measurements do not indicate any interaction between the two nickel(I) paramagnetic centres. The dinuclear nickel(I) complex forms adducts with CO and MeCN.



(**364**)



(**365**)

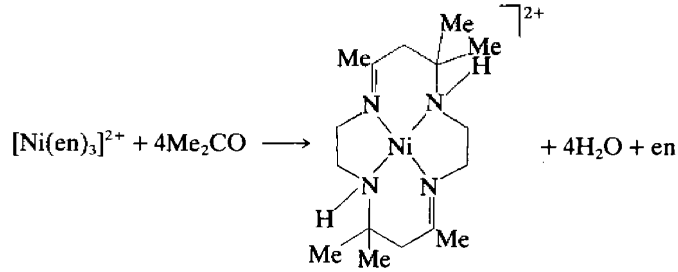
50.5.9 Nickel Complexes with Macrocyclic Ligands

The field of nickel complexes with macrocyclic ligands is enormous and continuous interest in this area in recent years has resulted in innumerable publications. A number of books and review articles are also available covering the general argument of the bonding capability of the various macrocyclic ligands towards transition and non-transition metals.[2622–2627] Synthetic procedures for metal complexes with some tetraaza macrocycles have been reported.[2628] Kinetics and mechanism of substitution reactions of six-coordinate macrocyclic complexes have also been reviewed.[2629]

The subject matter of this chapter will be subdivided into sections concerning template synthesis of the complexes; structural and thermodynamic properties of the complexes with synthetic cyclic polyamines; complexes with mixed-donor macrocycles; reactivity of the complexes; cryptates; and complexes with phthalocyanines and porphyrins.

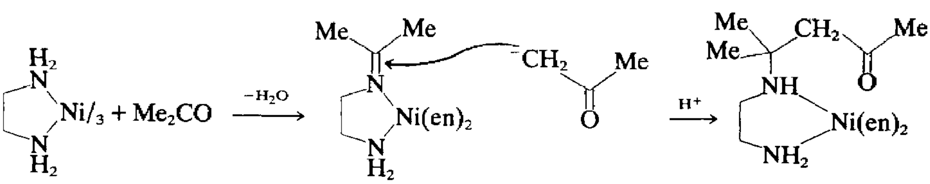
50.5.9.1 Template synthesis of macrocyclic complexes

Initially a great majority of tetradentate cyclic polyamines were prepared by condensation reactions assisted by a transition metal ion, typically nickel(II), which held the reacting molecules in favourable positions to facilitate their cyclic condensation (*template reactions*).[2625,2628,2630–2632] The archetypal template reaction was due to the pioneering work of N. F. Curtis, who found that $[Ni(en)_3](ClO_4)_2$ reacts with acetone at room temperature yielding a yellow crystalline compound (**366**; Scheme 35).[2633] In this scheme only one of the possible isomers, the *trans*, has been depicted for simplicity. In fact, three isomers can be isolated from Scheme 35. The *trans* isomer exists in two distinct forms in the solid state due to the asymmetric secondary nitrogen, namely the *meso* form (orange) and the racemic form (red). Only the racemic form of the *cis* isomer (**367**) has been isolated in the solid state. The same complexes were subsequently prepared in better yields by the condensation of $[Ni(en)_3]^{2+}$ with either mesityl oxide or diacetone alcohol in MeOH at refluxing temperature.[2634] A possible mechanism for the reaction of Scheme 35 is outlined in Scheme 36. The carbanion adds to a coordinated imine yielding an amino ketone which further condenses with one more molecule of en, and so on.



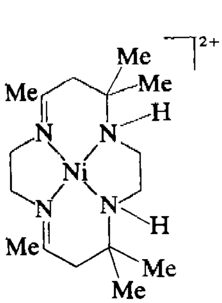
(**366**)

Scheme 35

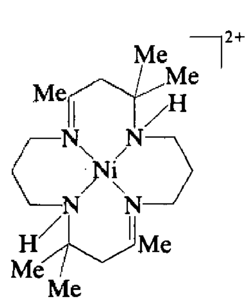


Scheme 36

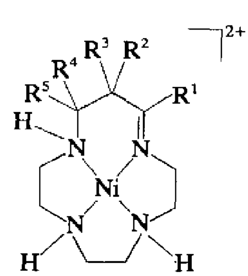
Reaction of Scheme 35 has been extended to other diamine complexes of nickel(II) and/or other carbonyl compounds producing macrocyclic complexes which differ from (**366**) or (**367**) in either ring size or substituents. For example, octamethylated analogues of either (**366**) or (**367**) have been obtained by the reaction of $[Ni(propane\text{-}1,2\text{-}diamine)_3]^{2+}$ with acetone. Complex (**368**) has been obtained by the cyclization reaction of $[Ni(tmd)_3]^{2+}$ with either acetone or diacetone alcohol.[2625,2635,2636] $Ni_2(trien)_3Cl_4{\cdot}2H_2O$ reacts with various aldehydes and with acetone to give macrocyclic complexes of type (**369**).[2637] Equimolar amounts of $[Ni(en)_3](ClO_4)_2{\cdot}0.5H_2O$ and $[Ni(tmd)_3](ClO_4)_2$ react with acetone which acts as the reaction medium affording complexes of type (**370**).[2638]



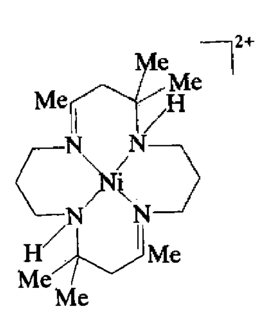
(**367**)



(**368**)



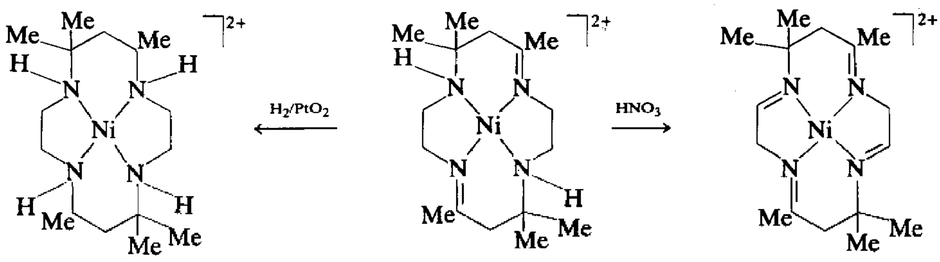
(**369**)



(**370**)

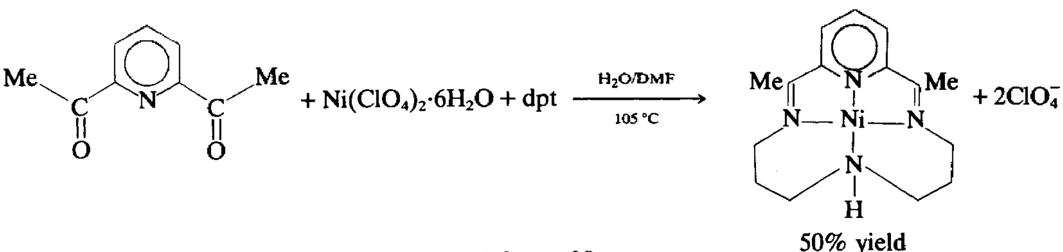
Cyclization reactions with aliphatic carbonyl compounds other than acetone are, in general, difficult and extremely slow. The reactant mixtures are often allowed to stand for weeks at room temperature and then refluxed in order to obtain appreciable amounts of the products.

Starting from complex (**366**) or (**367**) it is possible to produce a number of different complexes containing from zero to four imine linkages by means of reduction or oxidation reactions (Scheme 37).[2639] In these redox reactions the Ni donor atom set remains intact, thus indicating the remarkable stability and inertness of the macrocyclic complexes towards dissociation.

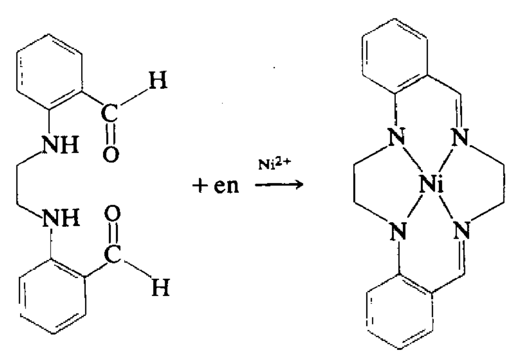


Scheme 37

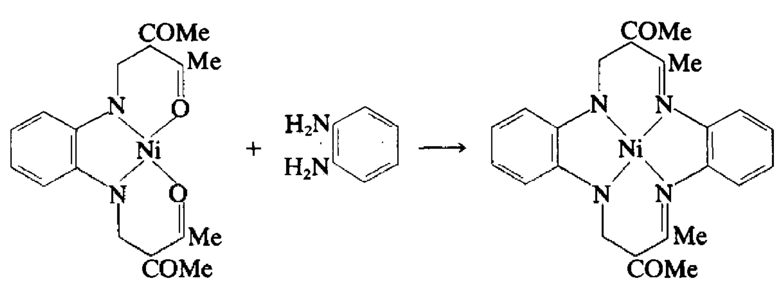
Another series of macrocyclic complexes has been prepared by Busch and co-workers by the condensation reaction of either pyridine-2,6-dicarboxaldehyde or 2,6-diacetylpyridine with various polyamines (Scheme 38).[2624,2628,2640–2645] Other examples of template reactions leading to different types of macrocyclic complexes are reported in Schemes 39–44.[2628,2646–2650] The self-condensation of 1-amino-2-carboxaldehyde in the presence of nickel(II) gives two types of macrocycle (Scheme 45).[2651]



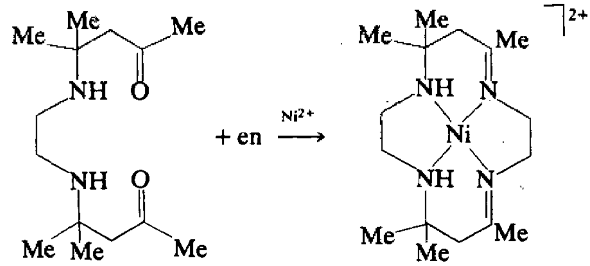
Scheme 38



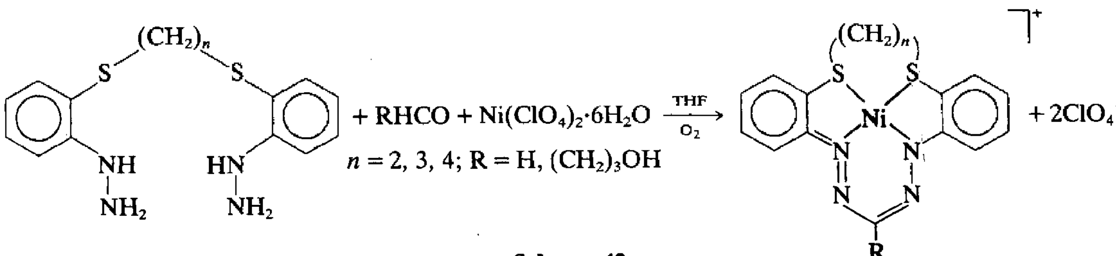
Scheme 39



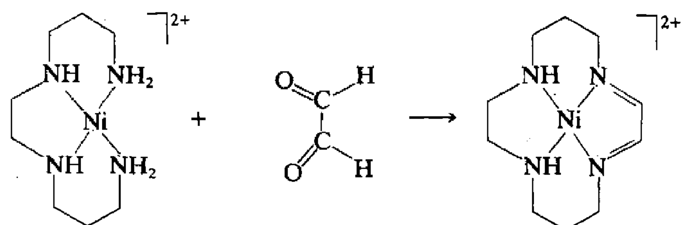
Scheme 40



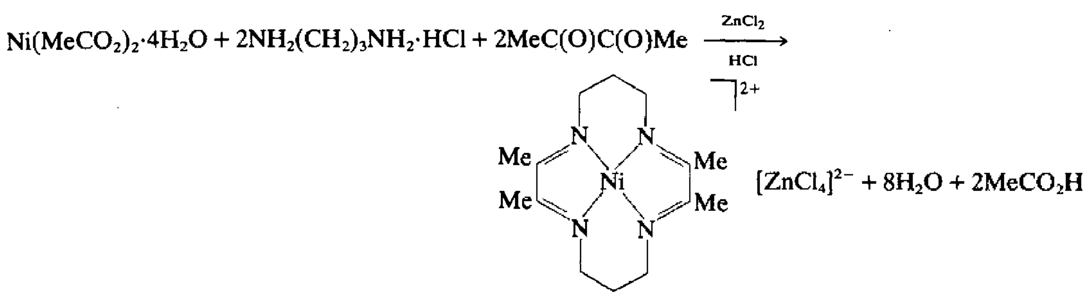
Scheme 41



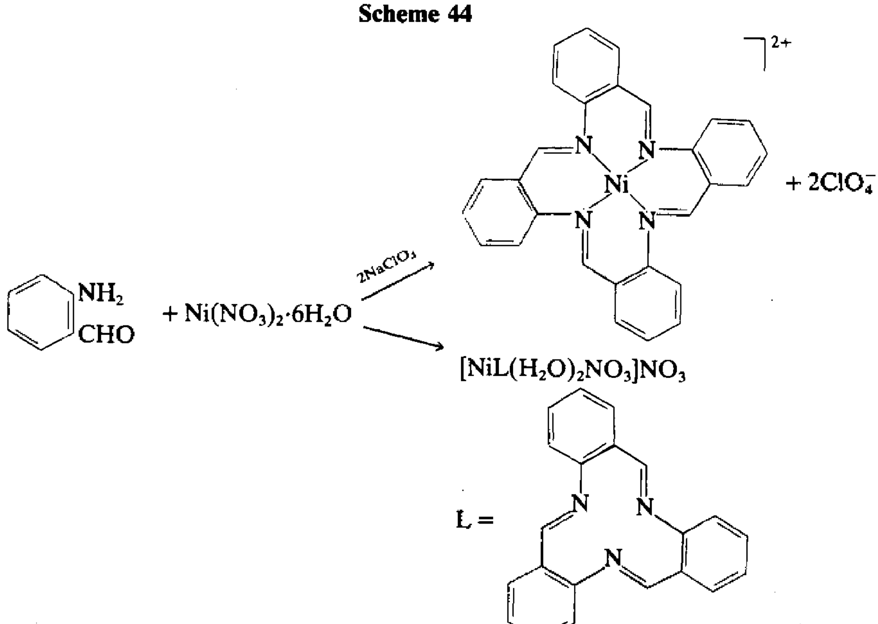
Scheme 42



Scheme 43

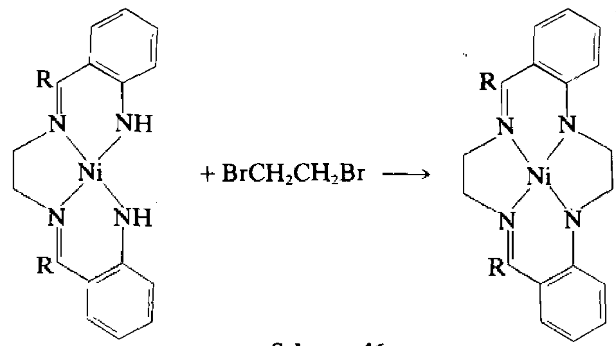


Scheme 44

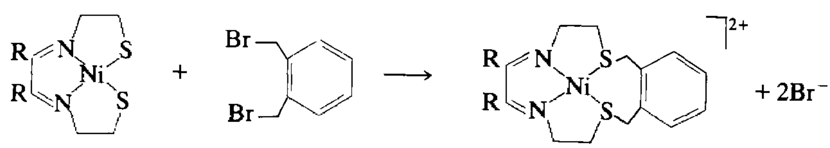


Scheme 45

Macrocyclic complexes were also obtained by the alkylation reaction of quadridentate chelates (Schemes 46 and 47).[2652–2654]

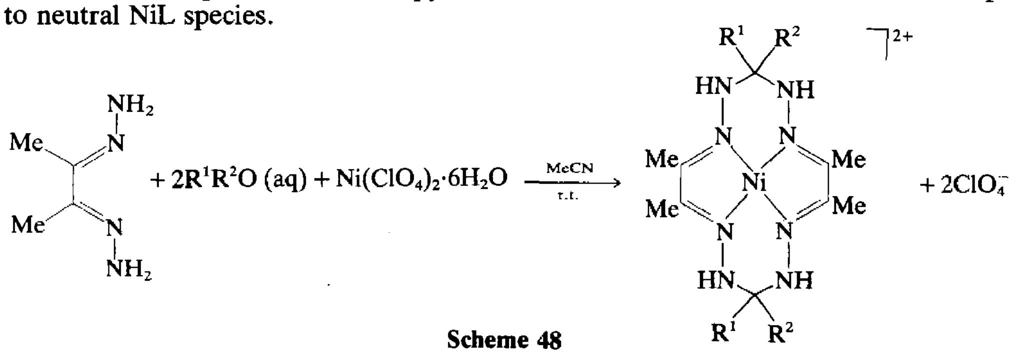


Scheme 46



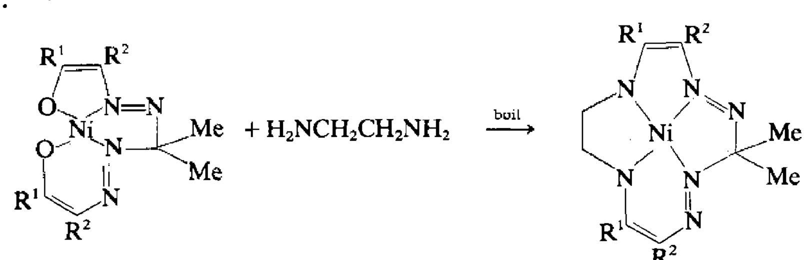
Scheme 47

The template condensation of 2,3-butanedione dihydrazone with aldehydes or ketones affords a variety of octaazabis(α-diimine) macrocyclic complexes of nickel(II), according to the Scheme 48.[2655] NH deprotonation with py or Et_3N of the aforementioned cationic complexes leads to neutral NiL species.



Scheme 48

Benzaldehyde monohydrazone, 2,3-butanedione monohydrazone and related hydrazones have been found to react with some ketones in the presence of nickel(II), affording compounds which, in turn, condense with either en or propane-1,2-diamine giving macrocyclic complexes (Scheme 49).[2656,2657]

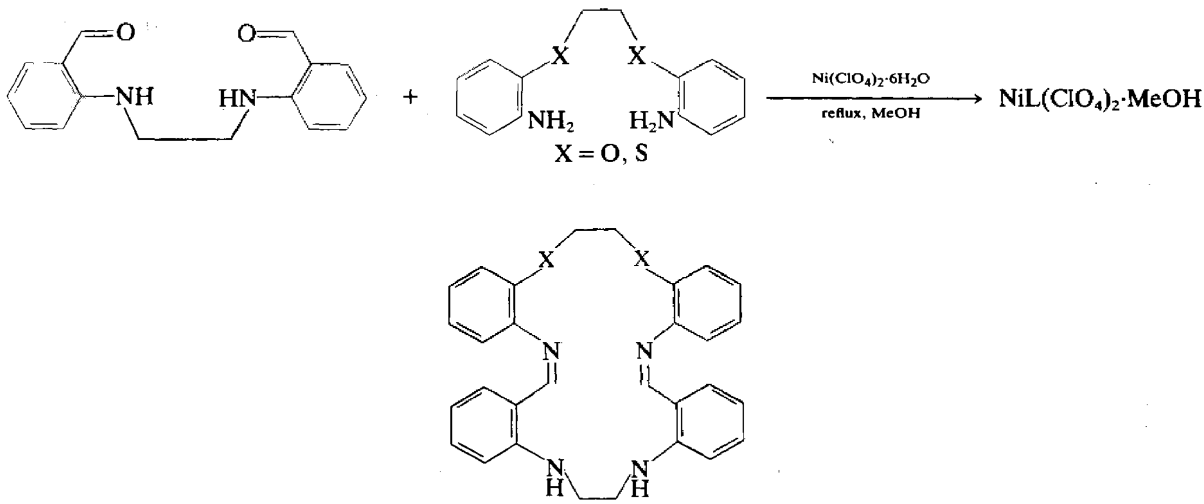


R^1, R^2 = Me, Ph; R^1 = Bu^t, R^2 = H

Scheme 49

The template synthesis has also been successfully employed for the preparation of macrocycles containing mixed donor atoms. Examples which refer to tetra- and hexa-dentate ligands are given in Schemes 42, 47 and 50.[2649,2653,2654,2658]

Apart from the template synthesis a number of nickel macrocycles have been prepared by direct combination of the appropriate nickel(II) salt with the preformed macrocyclic ligand in alcoholic medium, often MeOH (see also Tables 103, 106–108).

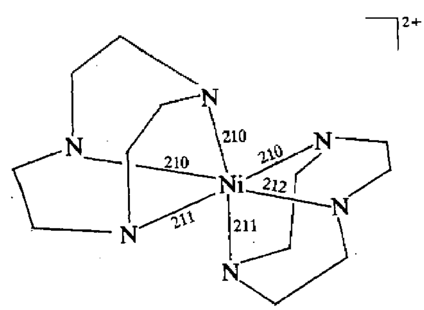


Scheme 50

50.5.9.2 *Structural and thermodynamic properties of complexes with saturated polyaza macrocycles*

A summary of nickel(II) complexes formed by representative saturated polyaza macrocycles is reported in Table 103, together with a concise description of the synthetic procedures and some of their physicochemical properties. Most studies are concerned with nickel(II) complexes with tetraaza macrocycles, but examples of complexes with triaza and pentaaza macrocycles are not rare.

Nickel(II) complexes with various saturated triaza macrocycles are six-coordinate in both the solid state and aqueous solution.[2659,2663] In the bis complexes the ligands are facially coordinated (**371**) with normal Ni—N bond distances (about 210–214 pm).[2661,2662]



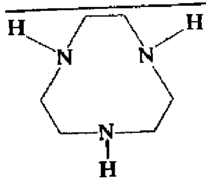
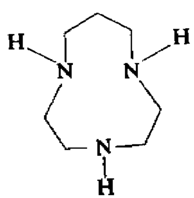
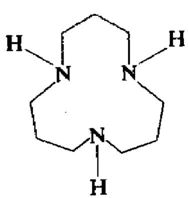
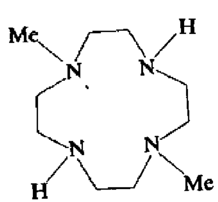
(**371**)

Formation constants in aqueous solution at 298 K indicate that the stability of the complexes decreases with increasing ring size. Kinetic studies indicate that the complex with the smallest macrocycle, namely [9]aneN_3, dissociates more rapidly in 1 M acid than that with the largest macrocycle, namely [12]aneN_3.[2660]

Saturated tetraaza macrocycles give rise to nickel(II) complexes with almost all of the main coordination geometries except tetrahedral. The preferred coordination in the solid state depends mainly on the ring size and substitution of the macrocyclic ligands, and on the coordinating capacity of the anions which neutralize the nickel(II) charge. In solution, equilibria often exist between different species, in most cases between diamagnetic square planar and high-spin octahedral species. The position of the equilibria is influenced by the donor capacity of both the solvent and any anions which are present in the solution, and also by the temperature. Typically, it has been found that the presence of 'inert' electrolytes such as $NaClO_4$ in aqueous solution strongly influences some equilibria favouring the square planar species.

The 12-membered cyclic tetramines, the smallest tetraaza macrocycles, have a cavity size too

Table 103 Complexes with Saturated Macrocycles (Eventually Incorporating Phenyl Rings)

Ligand (L)	*Complex*	μ_{eff} *(r.t.)* (BM)	*Preparation*	*Remarks*[a]	*Ref.*
 [9]aneN_3	$NiL_2Cl_2 \cdot 4H_2O$		Preformed ligand + NiX_2 hydrate in EtOH		2659
	$NiL_2(NO_3)_2 \cdot H_2O$			Oh; NiN_6 chromophore	2660
				Dissociation kinetics in 1.0 M acid	2661
	$NiLCl_2 \cdot 2.5H_2O$	2.80		Oh	
	$[NiL_2](NO_3)Cl \cdot H_2O$* **(371)**				
 [10]aneN_3	$[NiL_2](ClO_4)_2$*			Oh	2662
 [12]aneN_3	$[Ni(OH)L(H_2O)]ClO_4$	3.2	Preformed ligand + $Ni(ClO_4)_2$ hydrate in EtOH; reflux	Formation constants NiL^{2+} (log *K*): L = [9]aneN_3, 16.24; L = [10]aneN_3, 15.58; L = [12]aneN_3, 10.93	2663
				Dissociation kinetics of NiL^{2+} in 1.0 M acid	2660
 [illegible]	$NiLX_2 \cdot nH_2O$		Preformed ligand + NiX_2 hydrate in BuOH	X = Br, ClO_4	2664
	$[NiBrL(H_2O)]Br$* **(372)**			*cis*-Oh; Ni—N, 205–215; Ni—O, 214; Ni—Br, 261; folded macrocycle; $[NiL(H_2O)_2]^{2+}$ in H_2O	

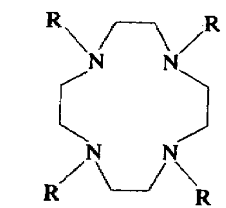
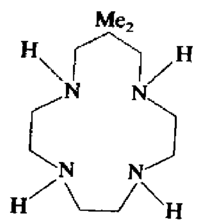
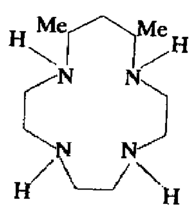
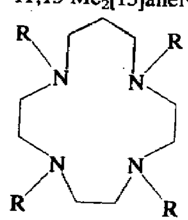
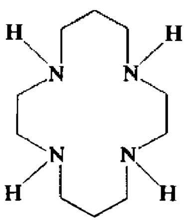
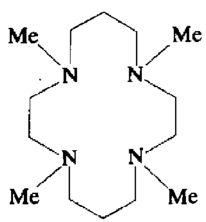
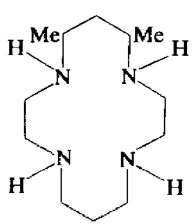
 [12]aneN_4R_4	$NiLX_2$	3.1–3.2		X = Cl, Br; R = H; Oh in the solid state and in solution; macrocycle not planar	2665
	$[Ni(NO_3)L]NO_3$				
	$NiLCl_2\cdot 0.5H_2O$	3.6	Preformed ligand + NiX_2 hydrate in EtOH	Oh (blue) ⇌ SqPl (yellow) in H_2O solution	2666
				Five-coordinate; folded macrocycle	2667
	$[NiClL]ClO_4\cdot H_2O$	3.7			
	$NiL(NO_3)_2\cdot 0.5H_2O$	3.2		Oh; R = CH_2Ph	
 12,12′-Me_2[13]aneN_4	$[NiL](ClO_4)_2$*	Diamagnetic		SqPl	2668
 11,13-Me_2[13]aneN_4	$[NiL]Y_2$	Diamagnetic	Reduction of the 11,13-diene complex with Raney Ni and H_2	SqPl; Y = I, PF_6	2669
	$[Ni_2L_2(C_2O_4)_2](PF_6)_2$		*cis* Oh; oxalate bridge; folded macrocycle		
 [13]aneN_4R_4	$NiL(ClO_4)_2$	Diamagnetic	Preformed ligand + $Ni(ClO_4)_2$ hydrate in EtOH	SqPl; R = Me; SqPl ⇌ five-coordinate equilibria in solution	2670, 2671
	$[Ni(N_3)L]ClO_4$	3.22	As above + NaN_3	R = H; SqPl ⇌ *cis* Oh equilibria in solution	2670, 2671
				Five-coordinate	2671

Table 103 (*continued*)

Ligand (L)	*Complex*	μ_{eff} (*r.t.*) (BM)	*Preparation*	*Remarks*[a]	*Ref.*
 [14]aneN_4(cyclam)	$NiLX_2$	3.06–3.09	Preformed ligand + NiX_2 hydrate in EtOH	X = Cl, Br, N_3, NCS; *trans* Oh;	2672
	$NiLX_2$	Diamagnetic		X = I, ClO_4; SqPl ⇌ Oh equilibria in H_2O	2673
	$[NiCl_2L]$* (**373**)			Elongated *trans* Oh	2674
	$[Ni(NO_3)_2L]$*			As above; *trans* ONO_2	2675
	$[NiLB_2](ClO_4)_2$			B = MeCN, DMSO, DMF; unstable	2676
				Thermodynamics of base (B) adduct formation	2677
	$[NiLB_2](ClO_4)_2$		NiL^{2+} + en; $NiL(en)^{2+}$ + HBr	*cis* Oh; B = $\frac{1}{2}$en, violet; *cis* Oh; B = H_2O, blue-violet	2678, 2679
				Isomerization of folded-to-planar coordination in H_2O solution	2679
 1,4,8,11-Me_4[14]aneN_4(Me_4cyclam)	$[NiL](ClO_4)_2$	Diamagnetic	Preformed ligand + NiX_2 hydrate in EtOH/H_2O	SqPl; red; diamagnetic ⇌ paramagnetic equilibria in H_2O	2680
	$[Ni(NCS)_2L]$	3.1		*cis* Oh; blue	
	$[NiXL]ClO_4$* (**379**)	3.2–3.3		SqPy; green; planar coordination of macrocycle; X = Cl, Br, NCS, N_3^*, Ni—N, 210, 211; Ni—N_3, 195	2680, 2681
	$[Ni_2(N_3)_3L_2]I$* (**380**)		$Ni(cyclam)^{2+}$ + MeI in DMSO + KOH and NaN_3	Oh; bridging and terminal N_3	2682
 5,7-Me_2[14]aneN_4	$[NiL]X_2$	Diamagnetic	Catalytic reduction of the 5,7-diene complex	SqPl; X = PF_6, I	2669
	$[NiX_2L]$	2.86–3.07		*trans* Oh; X = Cl, Br, NO_3; *cis* Oh; X = NCS; folded macrocycle	

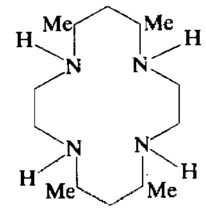
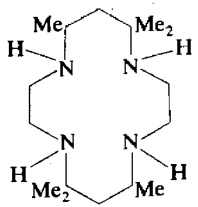
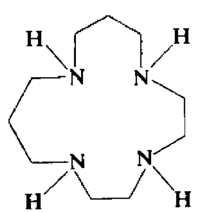
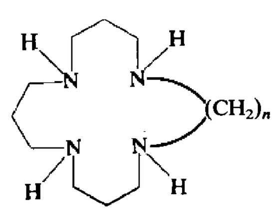
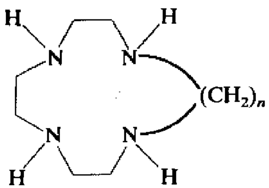
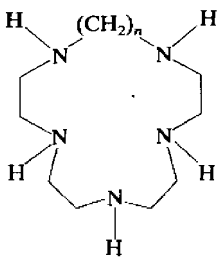
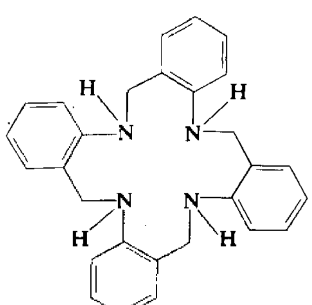
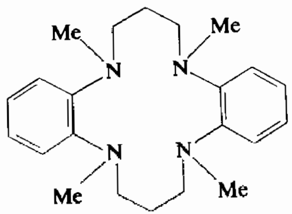
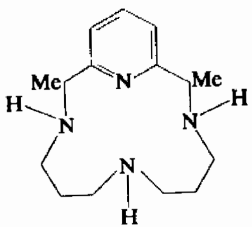
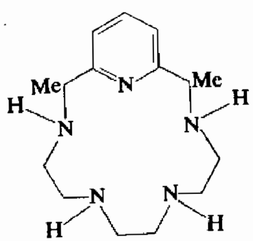
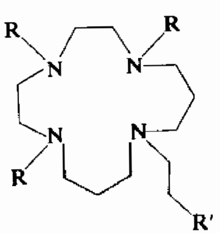
 5,7,12,14-Me_4[14]aneN_4	[NiL]$(ClO_4)_2$*		Reduction of the diene complex with $NaBH_4$	SqPl; Ni · · · · O ($OClO_3$), 281, orange; *trans* Oh; Ni—O ($OClO_3$), 222–224, violet	2683
	[$NiLB_2$]$(ClO_4)_2$			B = H_2O, Me_2CO	
 CTH (tet-a, *meso* form, tet-b racemic form)	Ni(tet-b)$(ClO_4)_2$	Diamagnetic	Catalytic reduction of the 1,7-diene complex	SqPl; three isomers designated as α (**374**), β (**375**) and γ (**376**); yellow to orange	2684–2686
	[Ni(tet-b)X]ClO_4 (**377**)	3.0–3.2	As above and metathetical reactions	*cis* Oh; X = Ac, NO_3, BH_4, $\frac{1}{2}C_2O_4$; folded coordination of macrocycle	2687, 2688
	Ni(tet-a)X_2	3.1	As above	*trans* Oh; X = NO_3, OAc, Cl, OH;	2688
	Ni(tet-a)C_2O_4·$3H_2O$	3.2	As above	polynuclear; bridging oxalate	
	[Ni(tet-a)acac]ClO_4*	3.1	$NiL(ClO_4)_2$ + acac + K_2CO_3 in aprotic solvents	*cis* Oh; folded macrocycle	2689
	$NiL(NCS)_2$	3.2		*trans* Oh; tet-a, tet-b = L	2685
	[$NiL(H_2O)_2$]Cl_2*		Obtained from $NiCl_2L$	*cis* Oh; optically active ligand	2690
	[Ni(tet-a)]Cl_2·$2H_2O$*	Diamagnetic	Ion exchange from $NiL(ClO_4)_2$	SqPl; yellow-orange	2691, 2692
	[$NiCl_2$(tet-a)]·$2CHCl_3$*		From $NiLCl_2$·$2H_2O$, upon heating	*trans* Oh; violet	2692
 1,4,7,11[14]aneN_4(isocylam)	$NiL(ClO_4)_2$	Diamagnetic	Preformed ligand + $Ni(ClO_4)_2$ hydrate in EtOH	SqPl; Orange; SqPl ⇌ Oh equilibria in H_2O	2693, 2694
	$NiLCl_2$	Diamagnetic	Metathetical reaction	SqPl; purple	
	$NiLX_2$	2.8	$Ni(OAc)_2$·$4H_2O$ + ligand + LiX	*trans* Oh; SqPl ⇌ Oh equilibria in H_2O; X = Cl, NCS	2695
	[NiL]$(ClO_4)_2$	Diamagnetic	Preformed ligand + NiX_2 hydrate in MeOH	SqPl; orange; n = 2, 3	2696
	[NiX_2L]	3.1–3.3		*trans* Oh; Blue-to-green; X = Cl, Br, N_3, NCS	

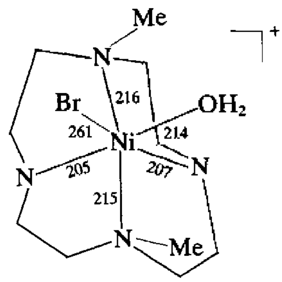
Table 103 *(continued)*

Ligand (L)	*Complex*	μ_{eff} *(r.t.)* (BM)	*Preparation*	*Remarks*[a]	*Ref.*
	$[NiL](ClO_4)_2$*	Diamagnetic	As above	SqPl, yellow; SqPl ⇌ Oh equilibria in H_2O; $n = 4$	2697, 2698
	$[NiX_2L]$*	3.1–3.3		*trans* Oh, violet-to-green; X = Cl, Br, NCS; $n = 5$; $n = 6$.	
	$[NiL](ClO_4)_2$	3.0–3.4	As above in EtOH	Six-coordinate in H_2O; folded macrocycle; $n = 2, 3$	2699
 H_8TAAB	$NiLX_2$	3.1–3.4	Reduction of the corresponding unsaturated complex with H_2/PtO_2 catalyst and metathetical reaction	*trans* Oh; coordinated X or H_2O or both; X = halides, NCS, NO_3, NO_2, ClO_4, BF_4, PF_6	2700

	$[NiL(NO_3)]NO_3$*	3.18	Preformed ligand + NiX_2hydrate in EtOH	*cis* Oh; bidentate NO_3 and folded macrocycle	2701
	$NiLX_2$		As above	X = Br, ClO_4	
 CRH	$[NiL](ClO_4)_2$*	Diamagnetic	Reduction of the corresponding $Ni(CR)(ClO_4)_2$ complex with H_2/PtO_2 catalyst	SqPl; red, *meso* form; yellow, racemic form	2702–2704
	$[Ni(ONO)(NO_2)L]\cdot 0.5H_2O$*			*trans* Oh; Ni—N, 197–209; Ni—N (NO_2), 222; Ni—O (ONO), 211	2705
	$NiX_2L\cdot nH_2O$	2.8–3.1	Metathetical reaction from $NiL(ClO_4)_2$	*trans* Oh; X = halides, NCS	2706
	$[NiL(en)](ClO_4)_2$*			*cis* Oh; folded macrocycle	2707
 pyaneN$_5$	$[NiXL]X\cdot nH_2O$	3.1–3.2	Preformed ligand + NiX_2 in MeOH and anhydrous conditions	Oh; X = halides, NCS; folded macrocycle	2708
	$[NiLB](PF_6)_2$		$L\cdot 4HNO_3 + Ni(OAc)_2\cdot 4H_2O + NH_4PF_6$ in H_2O	B = H_2O, MeCN, NH_3; as above	
	$[NiL](ClO_4)_2$*	3.65	Preformed ligand + $Ni(DMSO)_6(ClO_4)_2$ in MeOH	R = H; R′ = NMe_2; distorted TBPy; Ni—N, 204, 217; folded macrocycle; SqPl in acidic solution	2709
	$[Ni(NCS)L]ClO_4$	3.27	$NiL(ClO_4)_2$ + NaNCS in EtOH	R = H, R′ = NMe_2; Oh	2710
	$[NiL](ClO_4)_2$	Diamagnetic	Preformed ligand + $Ni(DMSO)_6(ClO_4)_2$ in EtOH	R = Me, R′ = NMe_2; SqPl	

* Structure determined by X-ray analysis.
[a] Bond distances are given in pm; colour is referred to solid compounds.
Formation constants are in H_2O at 298 K and at an ionic strength of 0.1 M KNO_3.

small to encompass high-spin or low-spin nickel(II) in a coplanar coordination of the four nitrogen atoms. In fact a folded coordination of the macrocycle around the face of either a trigonal bipyramidal or *cis* octahedral structure has been found in solid compounds (**372**).[2664,2667] However, the unsubstituted [12]aneN_4 ligand is assumed to encircle low-spin nickel(II) in a planar coordination in aqueous solution.[2666]

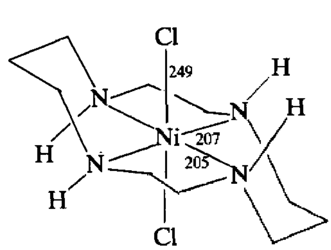


(372)

Most of the solid complexes with 13-membered macrocycles contain diamagnetic square planar nickel(II) as found in the complex [Ni(12,12′-Me_2[13]aneN_4)]$(ClO_4)_2$.[2668] As a matter of fact the calculated centre-nitrogen distances in the planar coordinated 13-membered macrocycles (192 pm) matches the Ni—N bond distances found in low-spin complexes with open-chain amines. In the case of the six-coordinate dinuclear complex [Ni_2(11,13-Me_2[13]aneN_4)$_2$(C_2O_4)]$(PF_6)_2$ the ligand exhibits a folded coordination to paramagnetic nickel(II).[2669] These structural properties seem to indicate that the 'cavity size' of the 13-membered macrocycles in planar coordination is adequate to encircle low-spin nickel(II) but too small in the case of high-spin nickel(II). In the latter case the folded coordination becomes preferred.

Macrocycles with 14–16-membered chelate rings all encircle both high-spin and low-spin nickel(II) in the solid compounds. With anions which have coordination tendency, e.g. halides, pseudohalides and in some cases NO_3^-, *trans* octahedral paramagnetic complexes are obtained which are often blue or violet. With anions such as ClO_4, PF_6 and BF_4 (and I, in some cases) which show little tendency to coordinate, square planar diamagnetic complexes are obtained which are generally yellow.

Typical examples of the rich coordination chemistry of saturated tetraaza macrocycles are the complexes given by 1,4,8,11-tetraazacyclotetradecane, also known as cyclam, with nickel(II) (Table 103).[2672–2677] Isomerism is expected to occur in the Ni–cyclam system due principally to the different configurations about the asymmetric coordinated secondary amines which, in turn, influence the possible conformations which can be adopted by the chelate rings. In the *trans* octahedral complexes [NiX_2(cyclam)] (**373**; X = Cl, NO_3[2674,2675]) and [NiI(cyclam)]I·H_2O[2711] the five- and six-membered chelate rings adopt *gauche* and chair conformations, respectively. The latter complex has a polynuclear structure with bridging iodide. The favourable coordination of cyclam in the complexes (**373**) is demonstrated by the very low ring strain of the chelate rings. A common feature of the three aforementioned *trans* octahedral complexes is the more or less pronounced lengthening of the axial bonds (Ni—Cl, 249; Ni—O (ONO_2), 217; Ni—I, 334; values in pm) which leads to a shortening of the in-plane Ni—N bonds (in the range 194–197 pm).

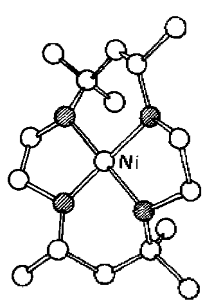


(373)

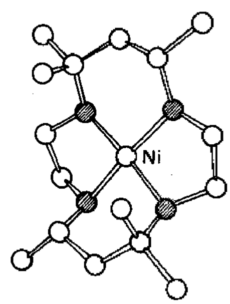
There are few exceptions to planar coordination of cyclam towards nickel(II). However, a facile conversion of Ni(cyclam)$^{2+}$ from square planar coordination to *cis* octahedral has been reported (equation 222). The latter complex slowly isomerizes in aqueous solution to a mixture of square planar $Ni(cyclam)^{2+}$ and *trans* octahedral $[Ni(cyclam)(H_2O)_2]^{2+}$.[2678,2679] It has been calculated that folding cyclam towards a *cis* octahedral structure would be favoured for M—N bond distances above 209 pm.[2675]

$$\underset{\text{SqPl}}{[\mathrm{Ni(cyclam)}]^{2+}} \xrightarrow{\text{en}} \underset{cis\text{-Oh}}{[\mathrm{Ni(cyclam)en}]^{2+}} \xrightarrow{2\mathrm{H}^+} \underset{cis\text{-Oh}}{[\mathrm{Ni(cyclam)(H_2O)_2}]^{2+}} \quad (222)$$

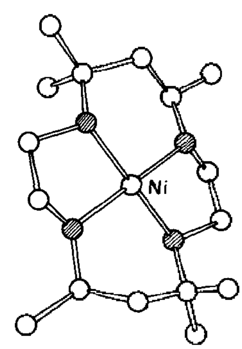
The introduction of a single substituent on a carbon atom of the chelate ring introduces further chiral centres, thereby resulting in further isomeric possibilities. For example, with the C-racemic 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (originally indicated as CTH or tet-b) three isomeric square planar complexes $[Ni(tet\text{-}b)]Y_2$ designated as α (**374**), β (**375**), and γ (**376**) have been investigated by means of X-ray diffraction methods.[2686] The α diastereoisomer is unstable and converts into the β form in neutral aqueous solution. The same ligand in the folded coordination forms a number of *cis* octahedral complexes with a chelate anion occupying the two additional *cis* positions (**377**)[2687] and, in the planar coordination, *trans* octahedral complexes.[2685] The C-*meso* form of the CTH ligand (originally indicated as tet-a) usually yields either square planar or *trans* octahedral complexes having a planar coordination. However, one complex, namely $[Ni(tet\text{-}a)acac]ClO_4$ (**378**), has been found to be *cis* octahedral with a folded coordination of the macrocycle.[2689] The configuration of the amine nitrogens is the same in the two similar complexes $[Ni(tet\text{-}b)(MeCO_2)]^+$ and $[Ni(tet\text{-}a)acac]^+$.



(**374**)

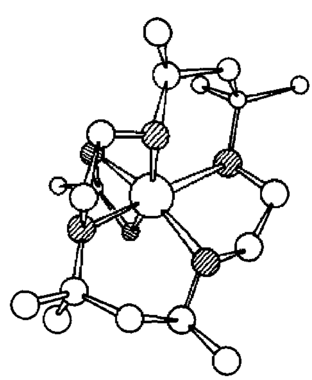


(**375**)

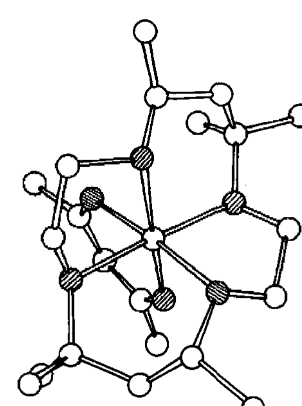


(**376**)

(reproduced with permission from refs. 2622 and 2686)



(**377**)

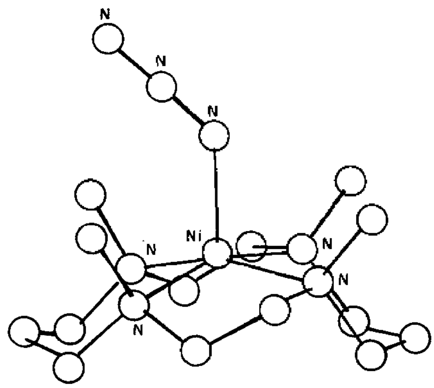


(**378**)

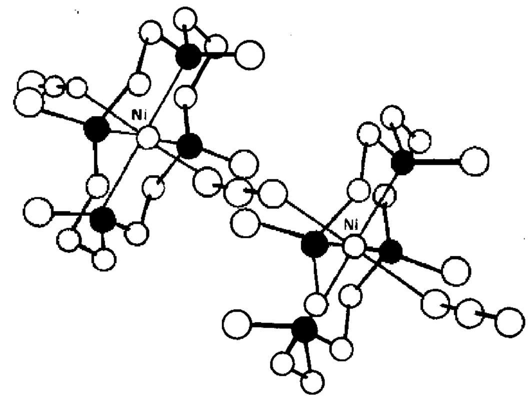
(reproduced with permission from refs. 2622, 2687 and 2689)

In the square pyramidal complex $[Ni(Me_4cyclam)N_3](ClO_4)$ (**379**) ($Me_4cyclam$ is 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) the coordinated azide anion is on the same side of the four methyl groups with the nickel atom 33 pm from the N_4 plane. The five- and six-membered chelate rings are in the usual *gauche* and chair conformations respectively.[2681] This complex is labile in comparison with the very inert dinuclear complex

$[Ni_2(Me_4cyclam)_2(N_3)_3]I$ (**380**) obtained by methylation of the $[Ni(cyclam)]^{2+}$ system.[2680] In the dinuclear six-coordinate complex which contains both terminal and bridging N_3 anions, the ligand has a more stable configuration than that in (**379**).



(**379**) (reproduced with permission from ref. 2681)



(**380**) (reproduced with permission from ref. 2680)

Tetraaza macrocycles incorporating phenyl groups in the chelate rings in general form nickel(II) complexes like those previously mentioned; most of them are either square planar or *trans* octahedral. In particular, two isomeric forms of the complex $[Ni(CRH)](ClO_4)_2$ (CRH = 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene) have been investigated by means of X-ray diffraction methods.[2702–2704] The red isomer is formed by the *C-meso* form and the yellow isomer by the *C-racemo* form of the ligand CRH. With coordinating monodentate anions *trans* octahedral complexes $[NiX_2CRH]$ are obtained,[2705,2706] whereas with additional chelating ligands *cis* octahedral complexes are formed with folded coordination of the macrocycle (Table 103).[2707]

In general tetraaza macrocycles strongly immobilize nickel(II) and the rates of both formation and decomposition of most of the complexes are exceptionally low. The nickel(II) complexes are, in general, extremely resistant to decomposition with boiling dilute acids, but they are less resistant to dilute mineral bases. Nearly all of the complexes, however, react with CN^- in anhydrous conditions affording the free ligand and $[Ni(CN)_4]^{2-}$. The complexes may undergo oxidation of the chelate ring with an HNO_3 solution, thereby forming up to tetraimine complexes of nickel(II) (see also Section 50.5.9.3).

Square planar nickel(II) complexes with the different tetraaza macrocycles dissolve in coordinating solvents such as H_2O, DMSO, MeCN and DMF giving rise to diamagnetic (yellow) $\rightleftharpoons$ paramagnetic (blue or green) equilibria. The relative amounts of the square planar and octahedral species depend upon many factors, mainly the ring size of the macrocycle, the nature of the solvents and temperature.[2670,2672,2673,2677,2679,2680,2712] In general, it is assumed that in coordinating solvents, 15- and 16-membered macrocycles favour the formation of high-spin nickel(II) which has greater ionic size, while 13- and 14-membered macrocycles favour the low-spin nickel(II) with its smaller ionic size.

Bis-solvent adducts $[Ni(cyclam)(solvent)_2](ClO_4)_2$ were also isolated in the solid state but in general they are unstable.[2676]

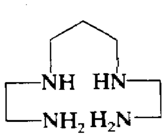
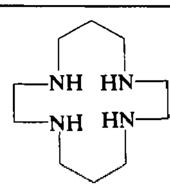
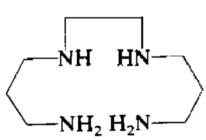
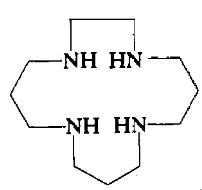
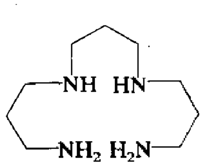
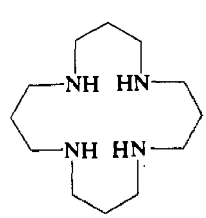
The formation of nickel(II) complexes with some saturated tetraaza macrocycles has been investigated in aqueous solution in spite of the experimental difficulties originating from the exceptionally low rates of formation and decomposition of the complexes which require a long time for the equilibria to be reached.[2670,2697,2713–2720] The role of the ring size of the various macrocyclic ligands in stabilizing different coordination geometries and/or spin states clearly results from the data reported in Table 104. The macrocycles with larger cavity size facilitate the formation of *trans* octahedral complexes of high-spin nickel(II) which has larger ionic size (205–210 pm), whereas the smallest macrocycle of this series, namely [12]aneN_4, is unable to encircle even low-spin nickel(II) (186–192 pm) and gives *cis* octahedral complexes with the ligand in a folded conformation. The two intermediate ligands [13]aneN_4 and [14]aneN_4 give square planar $\rightleftharpoons$ octahedral equilibria. Cyclam is the macrocycle which forms the most stable complexes of nickel(II). The stability of these complexes has also been compared with those of the corresponding complexes with open-chain tetramine ligands. The extra stability of the former relative to the latter, the so-called *macrocyclic effect,* differs substantially from one system to another (Table 105). The macrocyclic effect in the complex with cyclam is due to favourable enthalpy and entropy terms, whereas in the case of complexes with larger macrocyclic ligand hole, the macrocyclic effect is entropic in nature, the enthalpic term being unfavourable.

Table 104 Coordination Geometry and Thermodynamic Parameters for Nickel Complexes with Saturated Tetraaza Macrocycles in Aqueous Solution at 298 K

Ligand	*Coordination geometry*	$-\Delta H_f^{\circ a}$ (kJ mol^{-1}) (*Solution mixture*)	(*Oh complex*)	*log K*[b]
[12]aneN_4	*cis* Oh (more than 99%)		49.8[c]	
[13]aneN_4	SqPl (87%) ⇌ *cis* Oh (13%)[d]	56.5	83.7[c]	
[14]aneN_4	SqPl (71%) ⇌ *trans* Oh (29%)[d]	85.9	100.9[c]	21.9[e]
[15]aneN_4	*trans* Oh (more than 99%)		74.9[c]	18.4[f]
[16]aneN_4	*trans* Oh (more than 99%)		40.6[g]	13.2[f]

[a] Values relative to the reaction $Ni^{2+}_{aq} + ligand_{aq} \rightleftharpoons NiL^{2+}_{aq}$.
[b] Values for Oh complexes $NiL(H_2O)_2^{2+}$.
[c] Ref. 2710.
[d] Ref. 2670.
[e] Ref. 2711.
[f] Ref. 2712.
[g] Ref. 2713.

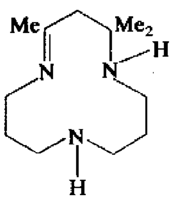
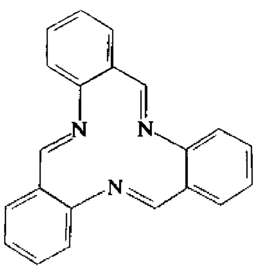
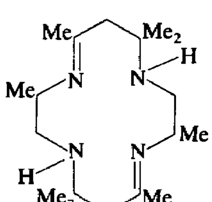
Table 105 Thermodynamic Parameters for the Reaction $[NiL_{open}]^{2+} + L_{cycl} \rightleftharpoons [NiL_{cycl}]^{2+} + L_{open}$ (values in kJ mol^{-1})[2714]

L_{open}	L_{cycl}	ΔG°	ΔH°	$T\Delta S^\circ$
		−33.7	−20.5	13.2
		−21.1	5.3	26.4
		−15.7	3.5	19.2

50.5.9.3 Properties of nickel(II) complexes with unsaturated macrocycles

The structures determined by X-ray analysis of the complexes $[Ni(Me_3[12]eneN_3)_2](NCS)_2$ ($Me_3[12]eneN_3$ = 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene) and $[Ni(TRI)(H_2O)NO_3]NO_3$ (TRI = tribenzo[*b*,*f*,*j*][1,5,9]triazacyclododecane) show that the two triaza macrocycles co-ordinate facially in both square pyramidal[2721] and octahedral complexes.[2724] Other complexes with triaza macrocycles have been prepared and are assumed to be either five- or six-coordinate.[2721–2725] Selected examples of nickel(II) complexes with unsaturated macrocycles are reported in Table 106.

Table 106 Complexes with Neutral Unsaturated Macrocycles

Ligand (L)	*Complex*	$\mu_{eff}(r.t.)$[a] (BM)	*Preparation*	*Remarks*[b]	*Ref.*
 $Me_3[12]eneN_3$	$NiL(NCS)_2 \cdot n$ solvent*		Template synthesis: $Ni(dpt)_2(NCS)_2$ + acetone	SqPy; deep blue; solvent = Me_2CO, H_2O, DMF, DMSO	2721
	$[NiXL]ClO_4$		$NiL(NCS)_2 + X$	5; X = Ac, acac	
	$[(NiL)_2(OH)_2](NCS)_2$		$NiL(NCS)_2$ + NaOH in MeOH	5; OH bridges	
	$[(NiL)_2X_2](ClO_4)_2$			5; X = Cl, $\frac{1}{2}C_2O_4$, OH, bridging	
	$[NiL(acac)NCS]$		$[(NiL)_2(OH)_2](NCS)_2$ + acac	Oh	
 TRI	$NiL(H_2O)_2X_2$	3.1–3.3	Self-condensation of *o*-aminobenzaldehyde with $Ni(NO_3)_2$ hydrate in EtOH	Oh; X = Br, I, NO_3, NCS, ClO_4	2722, 2723
	$[NiL(H_2O)_2NO_3]NO_3$*			Oh; Ni—N, 203; Ni—O (H_2O), 216; Ni—O (ONO_2), 208	2724
	NiL_2X_2	2.9–3.2		Oh; X = halides, NO_3, PF_6, ClO_4, NCS	2725
 $Me_8[14]4,11$-dieneN_4	$[NiL](ClO_4)_2$ (**366**)	D	Template synthesis: $Ni(en)_3(ClO_4)_2$ in acetone at r.t. for 3–4 days	SqPl; Aα = *racemo* form; Aβ = *meso* form; Ni—N, 190, 186	2726, 2727

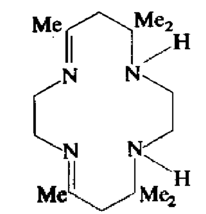
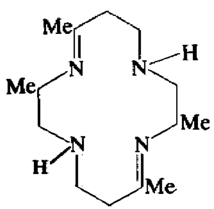
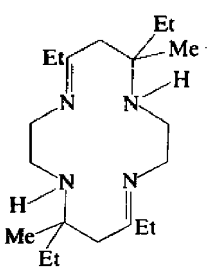
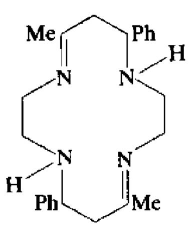
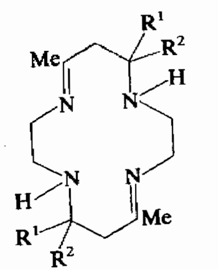
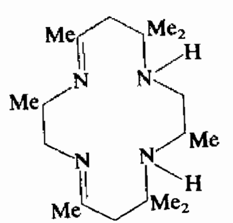
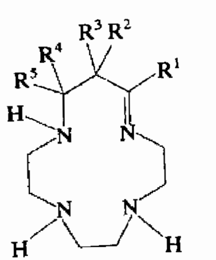
 Me$_6$[14]4,14-dieneN$_4$	[NiL](ClO$_4$)$_2$* (**367**)	D	As above	SqPl; B, *racemo* form; Ni—N, 189, 193	2726, 2728, 2729
	[NiL](NCS)$_2$	D	Metathetical reaction	SqPl; Aα, Aβ, B forms	2730
 Me$_4$[14]4,11-dieneN$_4$	[NiL](ClO$_4$)$_2$*	D	Preformed ligand + Ni(ClO$_4$)$_2$ hydrate	SqPl; *N-meso* and *C-meso*	2731
	[NiL′](ClO$_4$)$_2$*	D	As above	SqPl; L′ = 5,6,12,13-Me$_4$-1,4,8,11-tetraaza-4,11-cyclotetradecadiene isomer; *N-meso, C-meso*	2732, 2733
	[NiL](ClO$_4$)$_2$	D	Ni(en)$_3$(ClO$_4$)$_2$ + MeEtCO in pyridine	SqPl	2734
	[NiL′](ClO$_4$)$_2$	D	As above	SqPl; L′ = *cis* isomer ligand	
	[NiL]Y$_2$	D	Preformed ligand + NiY$_2$ hydrate in MeOH	SqPl; Y = I, ClO$_4$, BF$_4$, $\frac{1}{2}$ZnClO$_4$	2735
	NiLX$_2$	3.0–3.1	As above	*trans* Oh; X = Cl, NCS, NO$_3$, Ac	
	[NiL(en)](ClO$_4$)$_2$	2.9	NiL(ClO$_4$)$_2$ + en in MeOH	*cis* Oh	
	[Ni(acac)L]ClO$_4$	3.0	NiL(ClO$_4$)$_2$ + acac + K$_2$CO$_3$ in acetone	*cis* Oh	

Table 106 *(continued)*

Ligand (L)	*Complex*	μ_{eff}(r.t.)[a] (BM)	*Preparation*	*Remarks*[b]	*Ref.*
	[NiL]$(ClO_4)_2$	D	Preformed ligand + $Ni(ClO_4)_2$ hydrate	SqPl; $R^1 = R^2 = H$; $R^1 = H$; $R^2 = Me, Et, Pr^i$; *meso* and *racemo* isomers	2736
	[NiL]$(ClO_4)_2$*	D		SqPl; $R^1 = H$; $R^2 = Me$	2737
 Me$_8$[14]4,11-dieneN$_4$	[NiL]$(ClO_4)_2$*	D	$Ni(pn)_3(ClO_4)_2$ + acetone (r.t.)	SqPl; two non-interconvertible isomers; yellow = *racemo*; orange = *meso*	2738, 2739
	$NiLX_2$	D		SqPl; X = NCS, NO_3	
	[NiL]$ZnCl_4$	D	Template synthesis: $Ni_2(trien)_3Cl_4 \cdot 2H_2O + ZnCl_2$ in acetone	SqPl; $R'' = H, Me, Et, Pr^n$	2637, 2638

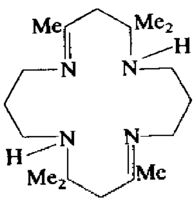
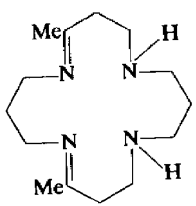
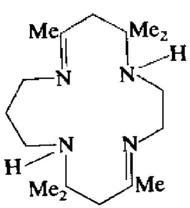
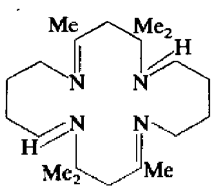
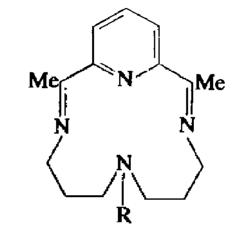
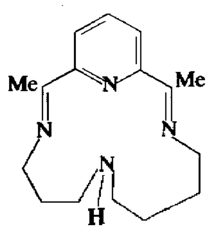
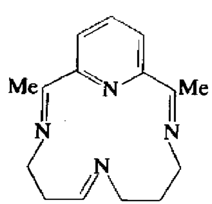
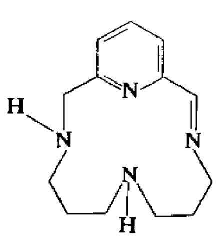
 $Me_6[16]5,13\text{-diene}N_4$	$[NiL](ClO_4)_2{\cdot}2H_2O$	D	Template synthesis: $Ni(tmd)_3(ClO_4)_2$ + diacetone alcohol in EtOH; reflux	SqPl; orange	2635, 2636
 $Me_2[16]1,12\text{-diene}N_4$	$[NiL]X_2$	D	Template synthesis: tmd·2HCl + methyl vinyl ketone in $MeOH/N_2$ + $Ni(OAc)_2{\cdot}4H_2O$ + NaX	SqPl; X = I, PF_6	2740
	$[NiX_2L]$	3.1		*trans* Oh; X = NCS, Cl	
	$[Ni(acac)L]PF_6$	3.1		*cis* Oh	
	$[NiCl(H_2O)_2L]Cl$*			*trans* Oh	2741
	$[Ni_2L_2(C_2O_4)_2](PF_6)_2$	3.1		Oh; dinuclear with oxalate bridges; folded macrocycle	2740
 $Me_6[15]5,12\text{-diene}N_4$	$[NiL](ClO_4)_2$	D	Template synthesis: $Ni(en)_3(ClO_4)_2$ + $Ni(tmd)_3(ClO_4)_2$ in acetone at room temperature	SqPl; yellow-orange	2638
	$NiL(NCS)_2$			Oh	
 $Me_6[18]6,15\text{-diene}N_4$	$NiLX_2$	D	Preformed ligand + NiX_2	SqPl; X = ClO_4, NCS; $NiL(NCS)_2$ is Oh in $CHCl_3$ solution	2742

Table 106 (*continued*)

Ligand (L)	*Complex*	$\mu_{eff}(r.t.)$[a] (BM)	*Preparation*	*Remarks*[b]	*Ref.*
 R = H: CR; R = Me: Me_3CR	$[NiL](ClO_4)_2$	D	Template synthesis: 2,6-diacetylpyridine + 3,3′-diaminodipropylamine + $Ni(ClO_4)_2$ hydrate	SqPl; SqPl ⇌ Oh equilibria in H_2O, MeOH, DMF, DMSO, MeCN	2743–2746
	$[NiBrL]Br^*$ (**381**)	D		SqPy; dark blue	2747
	$[NiX_2L]$			*trans* Oh; X = Cl, NCS	2743
	$NiLX_2$	D		SqPl; L = Me_3Cr; X = ClO_4, BF_4	2744
 CR 3,4	$[NiL](ClO_4)_2 \cdot 2H_2O$	D	Template synthesis as above using 1,5,10-triazadecane	SqPl	2645, 2748
	$[NiL](ClO_4)_2$	D	Oxidative dehydrogenation of $Ni(CR)(ClO_4)_2$ with HNO_3	SqPl	2745, 2746, 2749
	$[NiL](ClO_4)_2$	D	$Ni(CR)(ClO_4)_2 + NaBH_4$	SqPl	2745, 2746

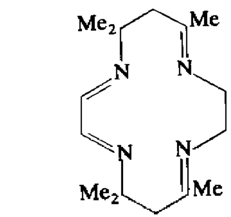
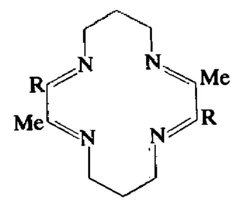
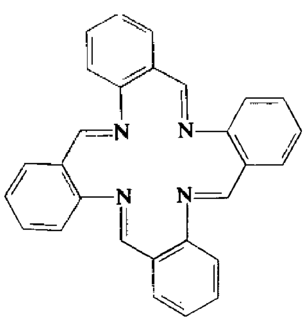
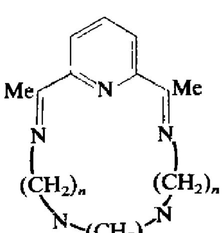
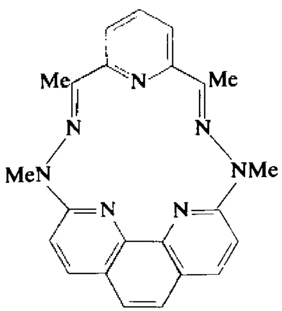
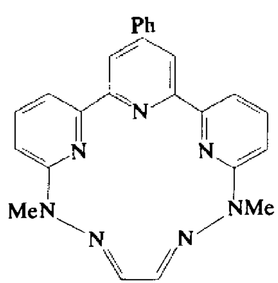
 cis-Me_6[14]1,3,7,11-tetraeneN_4	[NiL]Y_2	D	Oxidative dehydrogenation of the diene complex with conc. HNO_3	SqPl; Y = ClO_4, NO_3, PF_6; L = *cis* and *trans* isomers; reduction of NiLY_2 with H_3PO_2 affords triene and diene complexes	2750, 2751
	[NiL]$(ClO_4)_2$*			*α* form; Ni—N, 187–188	2729
 Me_2R_2[14]1,3,8,10-tetraeneN_4	[NiL]Y_2	D	Template synthesis: tmd + 1-phenyl-1,2-propanedione + $NiCl_2$ + $ZnCl_2$ in MeOH + HOAc	SqPl; Y = PF_6, $\frac{1}{2}ZnCl_4$; R = Ph	2752
	[NiL$(C_3H_4N_2)_2$]$(PF_6)_2$*			*trans* Oh; two imidazoles in axial positions	2753
 Bzo[16]octaeneN_4	[NiL]Y_2*	D	Self-condensation of *o*-aminobenzaldehyde in the presence of NiY_2	SqPl; Y = ClO_4, BF_4, BPh_4	2651, 2754
	[NiX_2L]	3.2		*trans* Oh; X = I, NO_3, NCS	
	NiLX_2·H_2O	1.47–1.68		Assumed spin equilibria	
	[NiIL(H_2O)]I*			*trans* Oh	2754
	[NiXL]ClO_4	3.12–3.26	Transmetallation reaction: AgLClO_4 + Ni$(ClO_4)_2$ hydrate in MeOH and metathetical reactions	Oh; X = ClO_4, NCS, N_3; $n = 3$, $m = 2$, stable complexes; $n = 2$, $m = 3$, unstable complexes	2755

Table 106 (*continued*)

Ligand (*L*)	*Complex*	$\mu_{eff}(r.t.)$[a] (BM)	*Preparation*	*Remarks*[b]	*Ref.*
 Me$_4$pyo[15]pentaeneN$_5$	[NiL(H_2O)$_2$](BF_4)$_2$*		Template synthesis: 2,6-diacetylpyridine + 2,9-di(1-methyl-hydrazino)-1,10-phenanthroline + Ni(BF_4)$_2$ hydrate in H_2O	Pentagonal bipyramidal; planar coordination of macrocycle and axial H_2O	2756
	[NiLB$_2$](BF_4)$_2$			B = monodentate bases such as py, quinoline, imidazole	
	[NiL(EtOH)$_2$](BF_4)$_2$*		Template synthesis: 6,6″-bis(methyl-hydrazino)-4″-phenyl-2,2′:6′,2″-terpyridine + glyoxal + Ni(OAc)$_2$·4H_2O and methathetical reaction	Pentagonal bipyramidal	2757

* Structures determined by X-ray analysis.
[a] D = diamagnetic.
[b] Coordination geometry or number is reported. Bond distances are in pm. Colour is that of the solid compounds.

In contrast to nickel(II) complexes with saturated tetraaza macrocycles, which exhibit a variety of coordination numbers and geometries, the ligands being in either a planar or a folded coordination, the majority of the complexes formed by unsaturated tetraaza macrocycles are square planar. Few six-coordinate complexes have been prepared with 14- and 16-membered macrocycles. It is expected that imino groups present in the chelate rings reduce the possibility of the folded coordination of the macrocycles and the conformational possibilities of the chelate rings.

The pioneering template reaction of $Ni(en)_3(ClO_4)_2$ in acetone (Scheme 35) gave three isomeric forms of the complex $[Ni(Me_6[14]dieneN_4)](ClO_4)_2$ which were originally distinguished as Aα,Aβ and B forms.[2722] With the aid of crystal structure analyses the complexes were unambiguously identified as the *trans* (form A, 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene; **366**) and *cis* (form B, 5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,14-diene; **367**) geometric isomers.[2723–2725] Two interconvertible forms of the *trans* isomer, indicated as α and β, due to the asymmetry of the two coordinated secondary amine groups, correspond to the *racemo* and *meso* conformers of the ligand, respectively. The NH groups are on the same side of the plane of the flattened macrocycle in the *racemo* form and on opposite sides in the *meso* form (Figure 28). On the other hand only the *racemo* form of the *cis* isomer has been identified. In the structures of the nickel(II) complexes with the $Me_6[14]4,11\text{-diene}N_4$ and $Me_6[14]4,14\text{-diene}N_4$ macrocycles, the conformation (A) of the six-membered chelate rings (Figure 29) is found in the *racemo* isomers and the conformation (B) in the *meso* isomer. The saturated chelate rings of the $Me_6[14]dieneN_4$ macrocycles adopt usually a *gauche* conformation. In the square planar complexes the Ni—N (imine) bond distances (186–189 pm) are generally shorter than the Ni—N (amine) bond distances (190–193 pm).

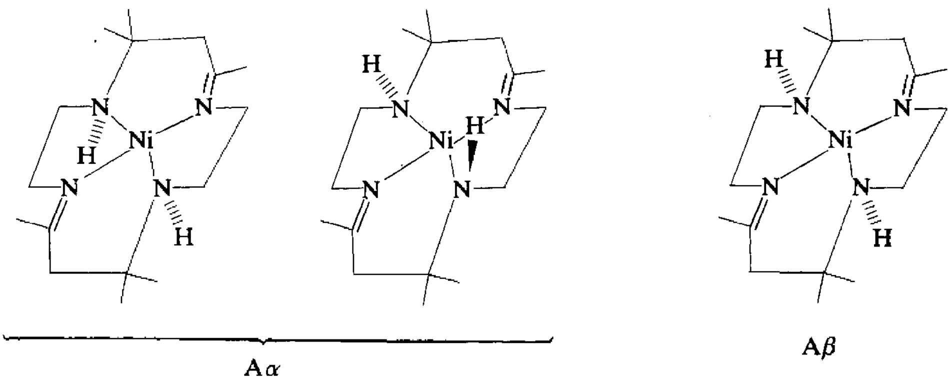


Figure 28 Schematic representation of the optical isomers of the complex $[Ni(Me_6[14]dieneN_4)](ClO_4)_2$ (*trans* isomer): Aα, racemic mixture; Aβ, *meso* form

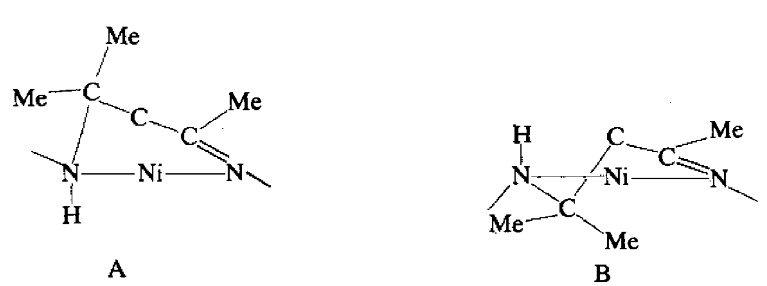
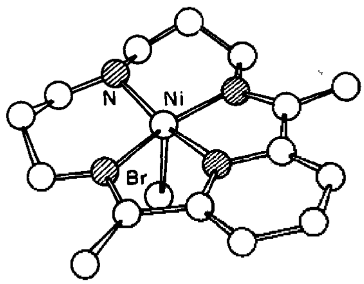


Figure 29 Conformation of the six-membered chelate rings in the *racemo* forms (A) and *meso* form (B) of $[Ni(Me_6[14]dieneN_4)](ClO_4)_2$ (*cis* and *trans* isomers)

The properties of nickel(II) complexes with unsaturated macrocycles which contain pyridyl groups are included in a very comprehensive review article.[2626] The complexes are usually square planar with the exceptions of the *trans* octahedral $NiX_2(CR)$[2743] (CR = 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene) and of the diamagnetic square pyramidal $[NiBr(CR)]Br\cdot H_2O$ (**381**).[2747] The diamagnetic complexes $Ni(CR)(ClO_4)_2$ give rise to square planar ⇌ octahedral equilibria in coordinating solvents,[2744,2746] whereas

$Ni(CR)X_2$ (X = halides) in NO_2Et solution gives rise to six- and five-coordinate complexes with coordinated halides.[2745]

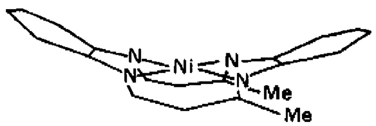


(**381**) (reproduced with permission from refs. 2622, 2747)

Reaction of $Ni(CR)(ClO_4)_2$ with HNO_3 solution produces a complex containing the macrocycle with an additional imino group.[2749]

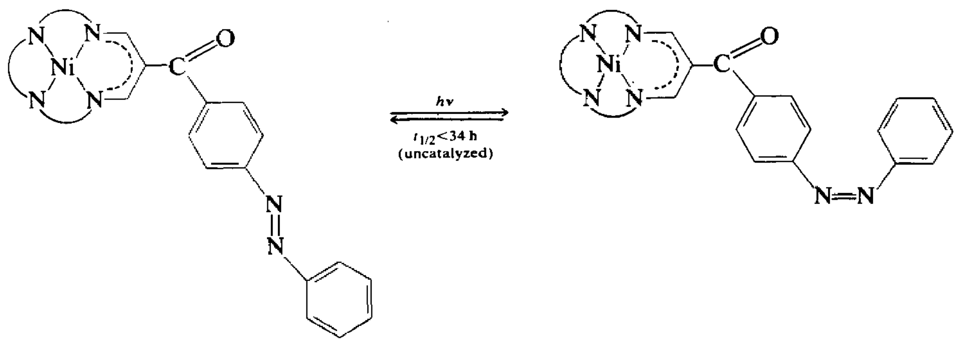
50.5.9.4 Nickel(II) complexes with deprotonated macrocycles

Amongst nickel complexes with anionic tetraaza macrocycles, the most thoroughly investigated are those with dianions derived by deprotonation of 1,8-dihydro[14]annulene, namely with the dibenzo[*b,i*][1,4,8,11]tetraazacyclotetradeca-2,4,6,9,11,13-hexaenato(2 −) macrocycle (**I**; Table 107). The electron delocalization within the six-membered 'diiminato' chelate rings makes these chelate rings planar, as the coordination of the entire macrocycle is square planar and gives complexes of general formula [NiL].[2774–2776] Complexes with dimethyl-substituted macrocycles exhibit a saddle-shaped configuration with the benzene rings and the diiminato rings tilted on opposites sides of the NiN_4 plane (**382**), whereas in the complex with the unsubstituted ligand the macrocycle adopts a planar conformation.



(**382**)

It has been found that the macrocyclic complex of type (**I**; Table 107) with azo compounds as substituents ($R^1 = C(O)C_6H_4N{=}NPh$) undergoes a photoisomerization reaction about the azo linkage (Scheme 51) giving the less stable *cis* isomer.[2784] The reisomerization to the *trans* form is accompanied by heat release, and can be catalytically accelerated by the presence of a cobalt macrocyclic complex. The aforementioned one is an example of the possible conversion of photo energy into heat energy. Nickel(II) complexes of deprotonated [14]annulenes have a stack packing structure and their partial oxidation with iodine yields a class of conductive materials[2777–2779] comparable to those formed by Ni(DMG) (see Section 50.5.3.7.ii). The packing of the stacking macrocycles and of the chains of iodine molecules in $[NiL]I_{2.58}$ is depicted in Figure 30. Room-temperature conductivity has a maximum value of 455 S cm^{-1} and the temperature dependence is metal-like.



Scheme 51

Table 107 Complexes with Deprotonated Macrocycles

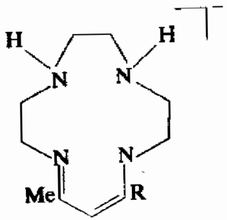
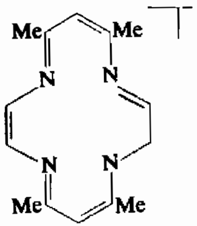
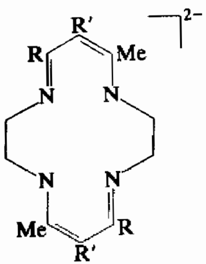
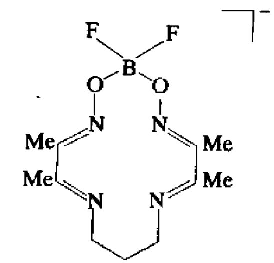
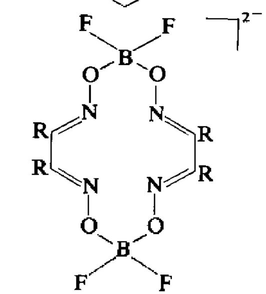
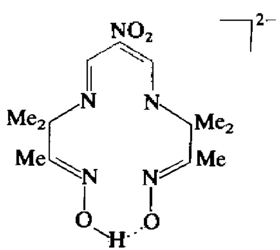
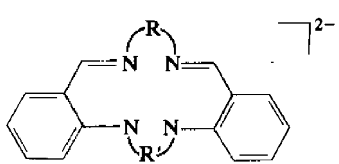
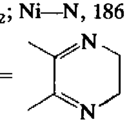
Ligand (L)[a]	*Complex*[b]	*Preparation*	*Remarks*[c]	*Ref.*
	$[NiL]ClO_4$*	Template synthesis: trien + β-diketone + $Ni(OAc)_2 \cdot 4H_2O$ + NaX in H_2O. Also starting from preformed ligand	R = Me; Ni—N, 183–188	2758
	[NiL]X		X = halides, NCS, NO_3, PF_6, BF_4; R = Me, CF_3	2759
	[NiL]Br*	As above	R = Me; Ni—N, 186–193	2760
	$[(NiL)_2](CF_3SO_3)_2$*		Confacial binuclear; Ni—Ni, 306	2761
	NiL	Preformed ligand + $Ni(OAc)_2 \cdot 4H_2O$	R = Me; R′ = H	2762
	NiL	Template synthesis	R = H; R′ = COMe	2763

Table 107 *(continued)*

Ligand (L)[a]	*Complex*[b]	*Preparation*	*Remarks*[c]	*Ref.*
	$[NiL]ClO_4$	$BF_3{\cdot}Et_2O$ + (3,3'-trimethylene-dinitrilo)bis(2-butanonedioximato)$Ni(ClO_4)_2$ in dioxane		2764
	$[NiXL]^*$	$NiLClO_4 + NaX$	SqPy; X = I*, NCS	2765, 2766
	$[NiLB]Y$	$NiLClO_4 + B$	SqPy; B = py, benzimidazole; Y = ClO_4, PF_6	2766
	$[Ni_2L_2X]ClO_4$	$NiLClO_4 + Bu_4NI/NaN_3$	SqPy; X = I, N_3; dinuclear structure	2766
	$[NiL]^*$	$BF_3{\cdot}Et_2O$ + bis(disubstituted glyoximato)nickel(II)	R = Me, Ph; the complexes are stacked in the crystal with alternating Ni—Ni distances of 321 and 465 pm	2767, 2768
	$[NiL]^*$	Oxidative dehydrogenation with O_2 of the parent $[NiL]^+$ complex	Ni—N, 186–188; O—H—O, 247	2769
	$[NiL]^*$	Template synthesis (Scheme 39)	R = R' = CH_2CH_2; Ni—N, 186 (av)	2770
			R = CH_2CH_2; R' = 	
	$[NiL]$	As above	R = CH_2CH_2, $(CH_2)_3$, $(CH_2)_4$, o-C_6H_4; R' = CH_2CH_2	2771, 2772

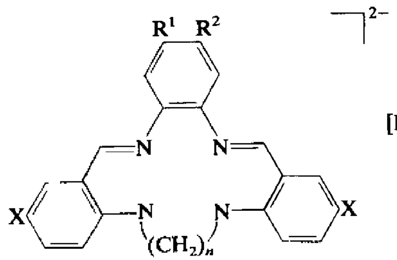
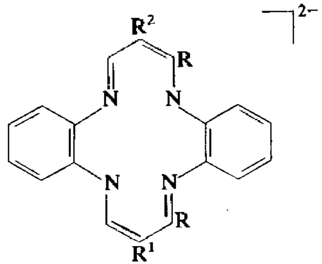
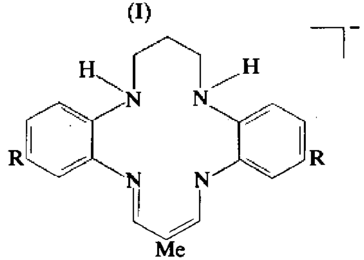
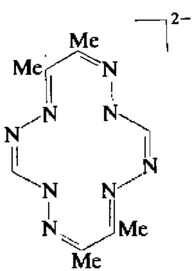
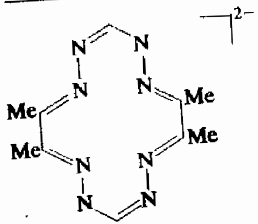
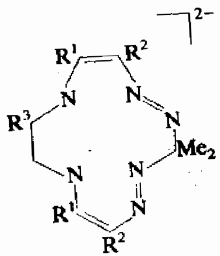
	[NiL]	Template synthesis: dialdehyde + diamine + $Ni(OAc)_2 \cdot 4H_2O$ in degassed DMF, under N_2; reflux	$n = 2, 3$; R^1, R^2 = H, Me, NO_2; $R^1R^2 = C_4H_4$; X = H, NO_2	2773
 (I)	[NiL]*	Template synthesis (Scheme 40)	$R = R^1 = R^2$ = H; Ni—N, 187	2774
	[NiL]* (382)		R = Me; $R^1 = R^2$ = H; Ni—N, 185	2775, 2776
	$[NiL]I_{2.58}$*	Oxidation of the parent NiL complex with I_2	R = H; $R^1 = R^2 = C_6H_4Me$-*p* (Figure 30)	2777
	$[NiL]I_n$	As above	$R = R^1 = R^2$ = H; n = 1.57, 2.0, 2.43	2778, 2779
	$[NiL]ClO_4$* [NiL]Y*	Preformed ligand + $Ni(ClO_4)_2$ hydrate in MeOH	R = H Y = $BF_4 \cdot H_2O$, $Cl \cdot H_2O$; R = Me	2780
 (II)	[NiL]*	Template synthesis: 2,3-butanedione + H_2CO + H_2NNH_2 in H_2O + $Ni(ClO_4)_2$ hydrate in MeCN under O_2, r.t.	Stacked structure with Ni–Ni distance of 486 pm	2781

Table 107 *(continued)*

Ligand (L)[a]	*Complex*[b]	*Preparation*	*Remarks*[c]	*Ref.*
 (III)	$[NiL]_2$* (386)	Oxidative dehydrogenation of the parent tetraimine complex in py with O_2 (Scheme 55)	Confacial dinuclear structure with Ni—Ni distance of 279 pm	2655
			Stacked structure with Ni—Ni distances of 380 pm	2781
	[NiL]*	Reduction of the parent complex with BH_4^- followed by oxidation with O_2 (Scheme 55)	mononuclear complex	2782
	NiL	Template synthesis (Scheme 49)	$R^1 = R^2 = Me$, Ph; $R^1 = Bu^t$, $R^2 = H$; $R^3 = H$, Me	2656, 2657, 2783

* Structures determined by X-ray analysis.
[a] Only one limiting formula is given for each macrocyclic ligand.
[b] All of the complexes are diamagnetic and square planar, unless otherwise stated.
[c] Distances are in pm.

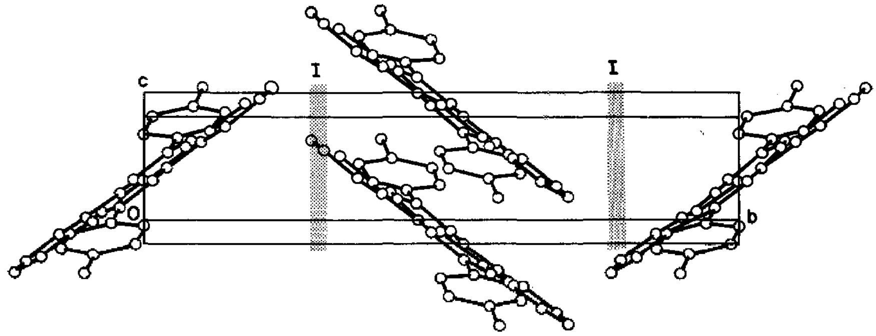
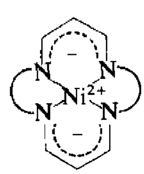
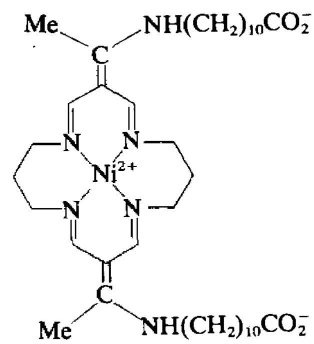


Figure 30 Stacking of the molecules of the complex $[NiL]I_{2.58}$ (L = deprotonated [14]annulene macrocycle, **I**, Table 107) (reproduced with permission from ref. 2777)

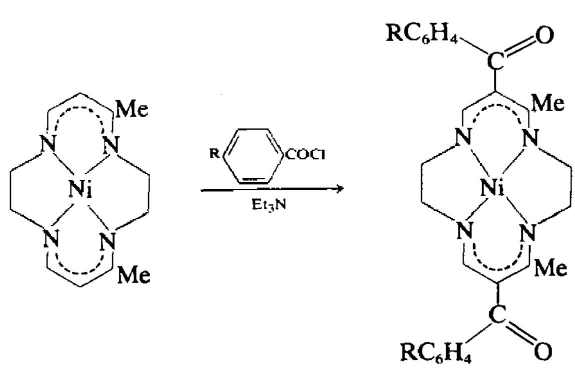
In complexes of anionic macrocycles, the charge-delocalized six-membered chelate rings containing the heteroatom nickel(II) (**383**) have been found to exhibit quasi-aromatic properties. The central carbon atom of each six-membered ring has pronounced nucleophilic character and this reactivity has been employed to introduce a variety of substituents in the chelate ring of the macrocycle.[2758–2760,2769,2780,2785–2790] An example of such reactions is outlined in Scheme 52.[2789] The introduction of peripheral functional groups provides facilities for the synthesis of macrocyclic ligands having superstructure components which may be useful models for biological molecules, as in the case of complex (**384**) with two hydrophilic moieties attached.[2790]



(383)

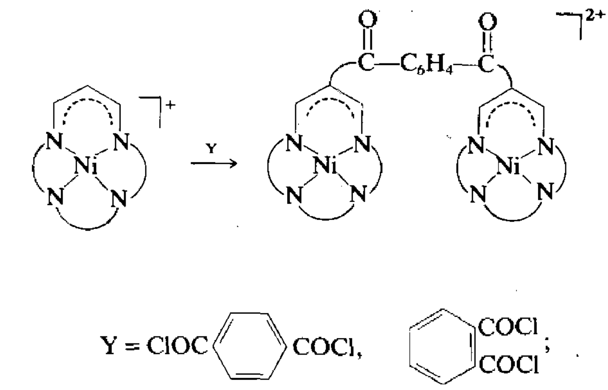


(384)

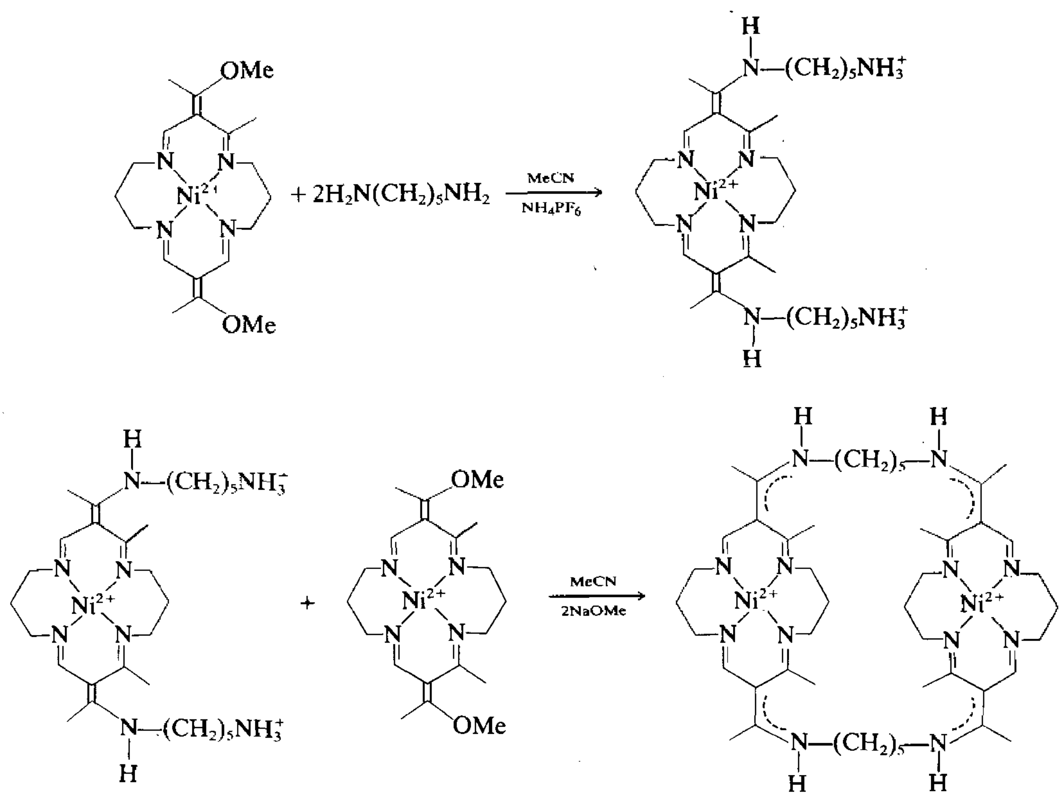


Scheme 52

Binuclear complexes have also been obtained by the electrophilic substitution reaction of $[Ni(Me_2[Z]dienatoN_4)]^+$ ($Z = 13, 14$) with *p*-substituted benzoyl chlorides (Scheme 53).[2791] A series of dimeric nickel(II) complexes of type (**385**) has been synthesized as outlined in Scheme 54.[2792] In the complex with *m*-xylene bridges the two nickel(II) atoms are 1360 pm apart, separated by the cavity of the pair of 16-membered macrocyclic ligands.



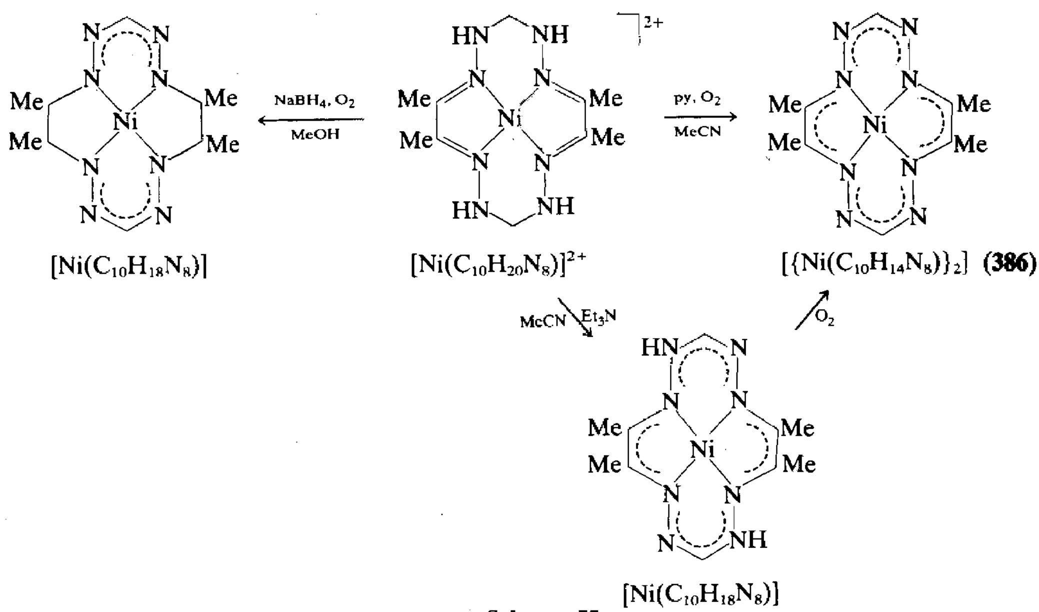
Scheme 53



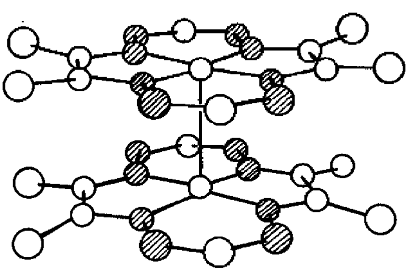
(385)

Scheme 54 (from ref. 2792)

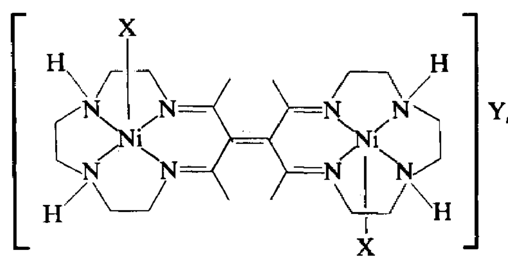
A number of nickel(II) complexes have been reported with different cyclic hydrazones (Table 107). The complexes have been prepared, in general, by template synthesis and are diamagnetic square planar with a planar coordination of the macrocyclic ligand. The cationic complex $[NiL](ClO_4)_2$ formed by the neutral ligand 6,7,13,14-tetramethyl-1,2,4,5,8,9,11,12-octaazacyclotetradeca-5,7,12,14-tetraene ($C_{10}H_{20}N_8$) can be easily deprotonated about the NH groups giving a neutral complex NiL (L = **III**; Table 107).[2655] The latter compound undergoes facile oxidative dehydrogenation in the chelate rings which results in the introduction of double bonds into the six-membered chelate rings (Scheme 55).[2781,2782] Different degrees of electronic delocalization have been supposed to exist in the chelate rings: in the case of the dinuclear complex (**386**) the bond lengths within the rings are equivalent, thereby indicating a nearly complete delocalization of the electronic charge. Isomerism in the complexes arises when different nitrogen atoms are coordinated to the nickel(II), as occurs in NiL (L = **II**; Table 107)[2781] and $[NiL]_2$ complexes (L = **III**; Table 107).



Scheme 55



(**386**) (reproduced with permission from refs. 2622, 2781).



(**387**)

The dinuclear complex (**387**; X = I, $Y_n = I_2$) was originally obtained in a low yield through the dimerization of $[NiMe_2[13]dienatoN_4]^+$.[2758,2759] The structure is square planar with the iodide completing the five-coordination.[2793] Analogous dinuclear complexes have been successively prepared (X = MeCN, $Y_n = (ClO_4)_4$) by oxidation of the same parent complex in MeCN solution.[2794]

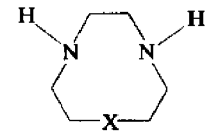
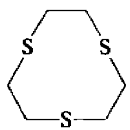
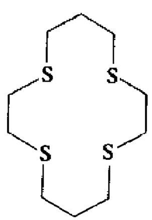
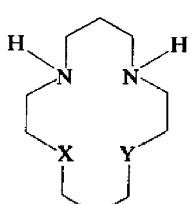
50.5.9.5 Complexes with mixed-donor macrocycles and with all-phosphorus and all-sulfur macrocycles

In Table 108 significant examples of nickel(II) complexes with mixed-donor macrocycles of various denticity are reported. Apart from the nitrogen atoms, the heteroatoms in the macrocyclic rings are usually either O or S, or in a few cases P. Few examples of nickel complexes with macrocycles containing all-sulfur or all-phosphorus donor atoms have been reported to date; they are also included in Table 108. In nickel(II) complexes formed by mixed-donor penta- and hexa-dentate ligands the oxygen atoms of the macrocycle are often only weakly coordinated or are not coordinated at all.

Compared with the nickel complexes formed by open-chain ligands containing the same donor set, nickel(II) complexes with mixed-donor macrocycles exhibit increased stability and kinetic inertness. However, compared with all-nitrogen donor macrocycles, the mixed-donor macrocyclic complexes of nickel(II) are less thermodynamically stable and kinetically inert, especially when some of the nitrogen atoms are replaced by oxygen atoms. Macrocyclic ligands containing all-oxygen atoms as donors do not appear to bind stably with nickel(II). Structures (**388**)–(**390**) refer to some of the complexes reported in Table 108.

Recently, several diamagnetic nickel(II) complexes were reported with 18-membered potentially hexadentate macrocycles containing four phosphane groups and two additional

Table 108 Complexes with Mixed-donor, All-phosphorus and All-sulfur Macrocycles

Ligand (L)	*Complex*	*Donor set*	μ_{eff} *(r.t.)*[a] (BM)	*Preparation*	*Remarks*[b]	*Ref.*
	$[NiL_2](NO_3)_2$* (**388**)	N_4S_2		Preformed ligand + $Ni(NO_3)_2$ hydrate in EtOH	Oh; X = S; Ni—N, 212; Ni—S, 242, log K_1 = 10.45; log K_2 = 9.6	2795
	$[NiL_2](NO_3)_2$				Oh; X = O; log K_1 = 8.59; log K_2 = 7.27	2796
	$[NiL_2](BF_4)_2$*	S_6		As above with $Ni(BF_4)_2$ hydrate	Oh; Ni—S, 238–240; complex stable in H_2O, MeCN solution	2797
	$[NiL](BF_4)_2$*	S_4	D	Preformed ligand + $Ni(BF_4)_2$ dehydrated in $MeNO_2$	SqPl; Ni—S, 218	2798, 2799
	$[NiX_2L]$	S_4X_2	3.04–3.18	$NiL(BF_4)_2$ + NaX in $MeNO_2$	Oh in the solid state and in solution	2799
	$[NiL(H_2O)_2]^{2+}$	N_3O_3			Oh; X = NH, Y = O; in aqueous solution; supposed folded macrocycle	2800
	$[NiL]^{2+}$				X = Y = S; Oh in H_2O solution; log K = 7.80–8.91 (0.5 M KNO_3)	2801

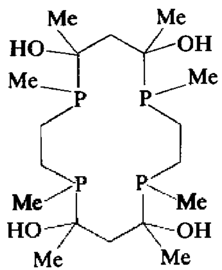
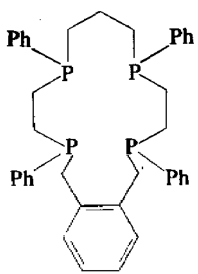
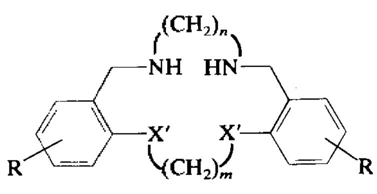
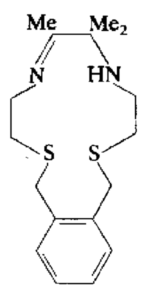
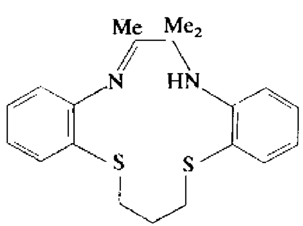
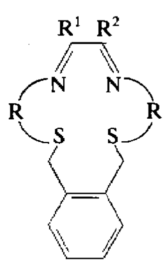
	$[NiL]Br_2$	P_4	D	Template synthesis: $Ni(MeHP(CH_2)_2PHMe)_2Br_2$ + Hacac in $EtOH/H_2O$	SqPl	2802
	$[NiL]X_2$	P_4	D	Cyclization reaction of the Ni^{II} complex with the open chain tetraphosphine (Scheme 47)	SqPl; X = Cl, NCS, BF_4	2803
	$[NiLCl_2]\cdot xH_2O$ (**389**)	$N_2S_2Cl_2$	3.21–3.25	Preformed ligand + $NiCl_2$ in MeOH	*trans* Oh; X′ = S; $m = 2$; $n = 3$; R = H; Ni—N, 208; Ni—S, 246 Ni—Cl, 244 *trans* Oh; $n = m = 3$	2804, 2805
	$[NiLX_2]$	$N_2O_2X_2$	3.11–3.31	As above with NiX_2	*trans* Oh; X′ = O; $n = 2, 3$; $m = 2, 3$; R = H, Cl, Br; X = Cl, Br, NCS; log $K = 3.5$–5.8	2806–2811
	$[NiLCl_2]^*$	$N_2O_2Cl_2$			*trans* Oh; X′ = O; $n = m = 3$; Ni—N, 204; Ni—O, 210–220; Ni—Cl, 240	2809
	$[NiLCl_2]^*$	$N_2O_2Cl_2$			*trans* Oh; X′ = O; $n = m = 2$; Ni—N, 200; Ni—O, 209; Ni—Cl, 244	2812

Table 108 (*continued*)

Ligand (*L*)	*Complex*	*Donor set*	μ_{eff} (*r.t.*)[a] (BM)	*Preparation*	*Remarks*[b]	*Ref.*
	[NiXL]X	N_2S_2X	2.80–3.01	Template synthesis: nickel complex with open-chain diamininodithio ligand and acetone	Five-coordinate	2813
	[NiL(NCS)$_2$]	N_4S_2	3.10		Oh	
	[NiL](ClO$_4$)$_2$	N_2S_2	D		SqPl	
	[NiLX$_2$]	$N_2S_2X_2$		Template synthesis as above	Oh; X = Br, I, NCS; weak axial coordination of X	2814
	[NiL]X$_2$	N_2S_2	D	Cyclization reaction (Scheme 47)	SqPl; X = ClO_4, I; R^1 = Me; R^2 = Et; R = CH_2CH_2	2815
	[NiLX$_2$]	$N_2S_2X_2$	2.99–3.23		Oh; X = Cl, N_3, NCS	
	[NiLX$_2$]	$N_2S_2X_2$	2.92–3.27		Oh; X = Br, I, NCS; $R^1 = R^2$ = Me; R^1R^2 = C_4H_8; R = o-C_6H_4	2816

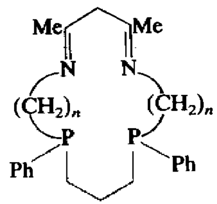
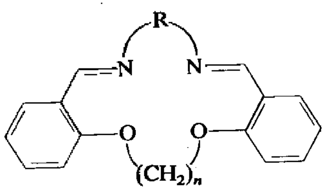
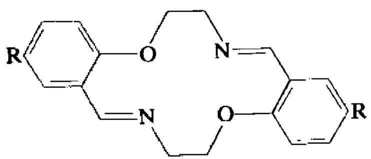
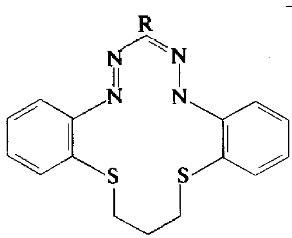
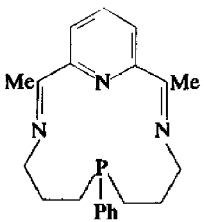
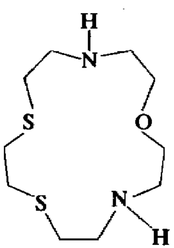
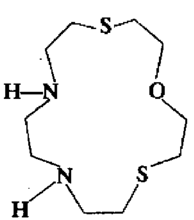
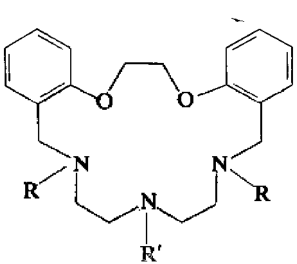
	[NiL]$(PF_6)_2\cdot 0.5H_2O$*	N_2P_2	D	Cyclization reaction of $Ni(OAc)_2\cdot 4H_2O$ with the open-chain phosphinoamine ligand in MeOH; reflux	SqPl; $n = 2, 3$; Ni—P, 219; Ni—N, 192	2817
	[NiLX_2]	$N_2O_2X_2$	3.08–3.29	Preformed ligand + NiX_2 in BuOH	Oh; $n = 2, 3$; R = CH_2CH_2, $(CH_2)_3$, $CH_2CH(CH_3)$; X = halides, NCS	2818
	[NiLBr_2]*	$N_2O_2Br_2$		Template synthesis: dialdehyde + diamine + NiX_2	*trans* Oh; $n = 3$; R = $(CH_2)_3$; Ni—N, 201; Ni—O, 214; Ni—Br, 254	2819
	[NiLI_2]*	$N_2O_2I_2$			*trans* Oh; R = H; Ni—N, 192; Ni—O, 207; Ni—I, 288	2820, 2821
					cis Oh; R = OMe; folded macrocycle; Ni—N, 205; Ni—O, 222; Ni—I, 273	2822
	[NiL]ClO_4*	N_2S_2	D	Template synthesis: Scheme 42	SqPl; R = H; Ni—N, 184; Ni—S, 216	2823, 2824
	[NiL]ClO_4*				SqPl; R = $(CH_2)_3OH$	

Table 108 *(continued)*

Ligand (L)	*Complex*	*Donor set*	μ_{eff} *(r.t.)*[a] (BM)	*Preparation*	*Remarks*[b]	*Ref.*
	$[NiL](PF_6)_2$	N_3P	D	Template synthesis: 2,6-diacetylpyridine + $PhP(CH_2CH_2CH_2NH_2)_2$ + NiX_2 hydrate + NH_4PF_6 in EtOH	SqPl	2825
	$[NiXL]PF_6$	N_3Px	D		TBPy; folded macrocycle	
	$[NiL(H_2O)](NO_3)_2$* **(390)**	$N_2S_2O_2$		Preformed ligand + $Ni(NO_3)_2$ hydrate in MeOH and BuOH	Oh; folded macrocycle; Ni—S, 242; Ni—O, 207; Ni—O (H_2O), 209; Ni—N, 206	2826
	$[Ni(NO_3)L]NO_3$*	$N_2O_2S_2$		As above	Oh; monodentate ONO_2; Ni—O, 224, Ni—N, 204, 208; Ni—S, 240, 243; Ni—O (ONO_2), 206	2827
	$NiLX_2$				Oh; R = H, Me; R′ = H, Me; X = Cl, Br, ClO_4; folded macrocycle; R = H, log K = 9.96; R = Me, log K < 7 in MeOH	2828

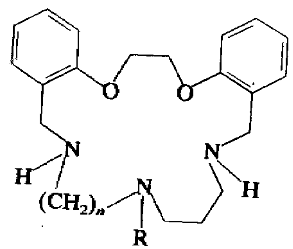
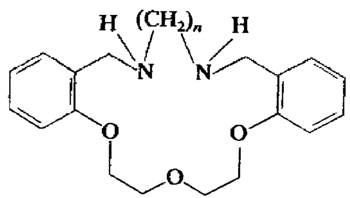
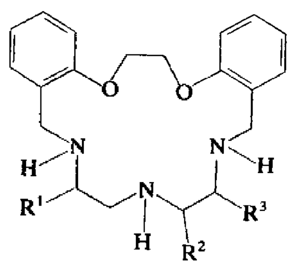
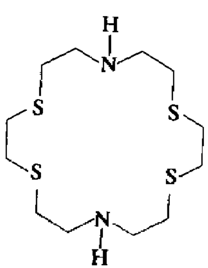
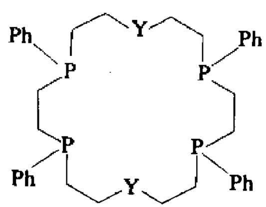
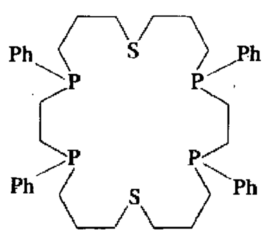
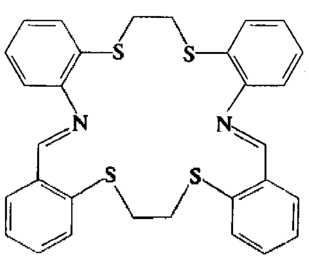
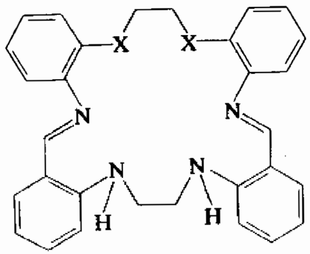
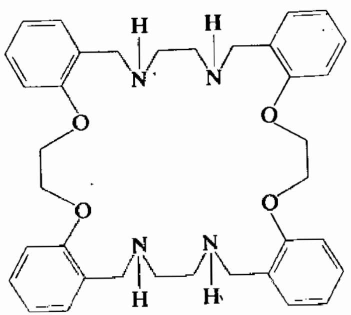
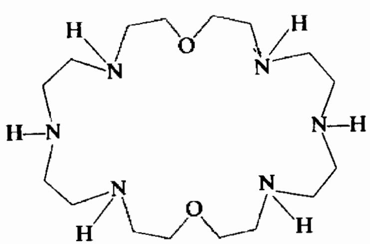
	$NiLCl_2$				Oh; R = H; $n = 2$; $\log K = 9.83$; R = H, $n = 3$; $\log K = 6.39$; R = Me, $n = 3$; $\log K = 6.4$	2828
					Oh; $n = 2$; $\log K = 6.50$; $n = 3$; $\log K = 4.77$	2828
	$[Ni(NCS)_2L]_2$*	N_6			Oh; bridging thiocyanates; $R^1 = R^2 = R^3 = H$; tridentate ligand	2829
	$[NiL(NCS)_2(H_2O)]$*	N_5O			Oh; $R^1 = R^2 = Me$; $R^3 = H$; tridentate ligand	
	$[Ni(NCS)_2L]$*	N_5			Five-coordinate; Ni—O, 267 and 319 pm	
	NiL(picrate)	S_4N_2	2.9	Preformed ligand + Ni(picrate)	Oh; folded macrocycle	2830

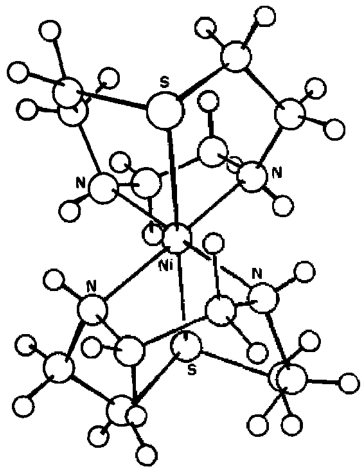
Table 108 *(continued)*

Ligand (L)	*Complex*	*Donor set*	μ_{eff} *(r.t.)*[a] (BM)	*Preparation*	*Remarks*[b]	*Ref.*
	$NiLBr_2 \cdot 2H_2O$* (**391**)	$P_4(S_2)$	D	Preformed ligand + $NiBr_2$ hydrate	Y = S; chiral ligand; β-diastereoisomer, elongated *trans* Oh; Ni—P, 220–222; axial Ni—S at about 294	2821
	$NiLBr_2 \cdot 5.5H_2O$* (**392**)	P_4S	D	As above	δ diastereoisomer; TBPy; Ni—P, 222–225; Ni—S, 235	2832
	$NiL(BPh_4)_2$	P_4	D	As above with $NaBPh_4$	γ diastereoisomer; SqPl	2833
	$NiL(BPh_4)_2$	P_4S		As above	α diastereoisomer; SqPy	2831
	$NiL(BPh_4)_2$	P_4	D	As above with additional $NaBPh_4$	Y = O; SqPl	2834
	$NiL(BPh)_4)_2$*	P_4	D	As above	Y = NPr^n; chiral ligand, SqPl; β diastereoisomer; Ni—P, 214, 223; Ni · · · N, 327	2835
					γ diastereoisomer; SqPl	
	$[NiL](BF_4)_2$	P_4	D	Preformed ligand + $Ni(BF_4)_2$ in $MeOH/CH_2Cl_2$	β diastereoisomer; SqPl	2836
	$[Ni_2Br_2L](BPh_4)_2$* (**393**)	P_2SBr	D	Preformed ligand + $NiBr_2$ in $MeOH/CH_2Cl_2$ + $NaBPh_4$ in acetone	SqPl; dinuclear	
	$[NiL]Y_2$	P_4S	D	As above	δ diastereoisomer; TBPy; Y = BF_4, BPh_4, I, CF_3CO_2	2837
	$[\{NiX_2\}_3L_2] \cdot nH_2O$		D		SqPl; X = Br, NCS; n = 6, 1	
	$NiLX_2$	S_4N_2	3.07–3.12	Template synthesis: 1,2-bis(2-aminophenylthioethane) + 1,4-bis(2-formylphenyl)-1,4-dithiobutane + $Ni(ClO_4)_2$ hydrate in acetone	Oh; X = I, ClO_4	2838

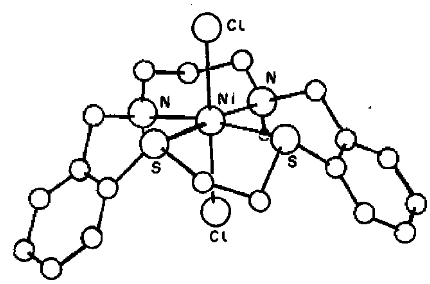
	$NiL(ClO_4)_2\cdot MeOH$	N_4X_2	3.17, 3.18	Template synthesis (Scheme 50)	Oh; X = O, S	2658
	$NiLX_2\cdot nH_2O$	N_4X_2	3.07–3.32	Preformed ligand + NiX_2 hydrate in MeOH/BuOH	Oh; X = Cl, Br, NCS, ClO_4; log K = 12.6 in MeOH	2839
	$NiL(NCS)_2\cdot DMF$*	N_6			Oh; oxygen atoms uncoordinated; folded macrocycle	
					1:1 complex in H_2O solution; ether oxygens uncoordinated; log K = 13.65	2840

* Structures determined by X-ray analysis.

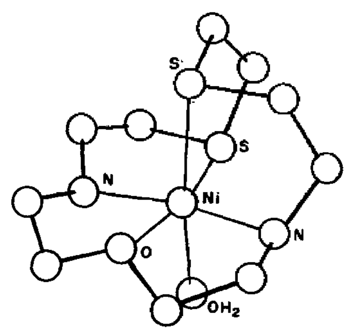
[a] Bond distances (average values, in general) are in pm; stability constants are in aqueous solutions at 25 °C and at an ionic strength of 0.1 M KNO_3, unless otherwise stated.



(388) (reproduced with permission from ref. 2795)

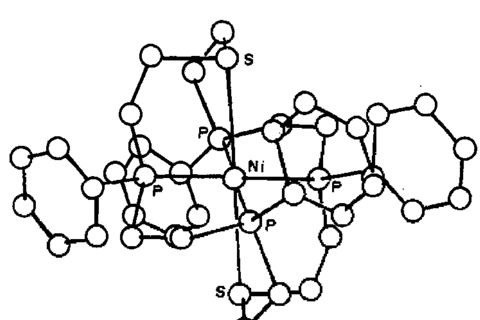


(389) (reproduced with permission from ref. 2805)

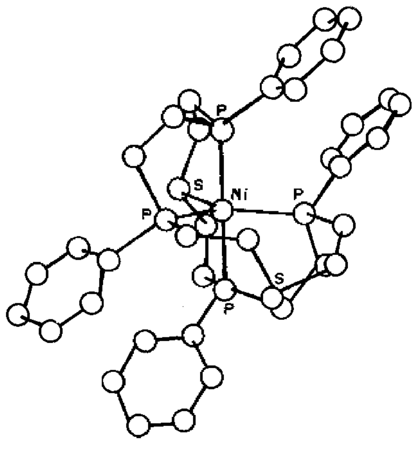


(390) (reproduced with permission from ref. 2826)

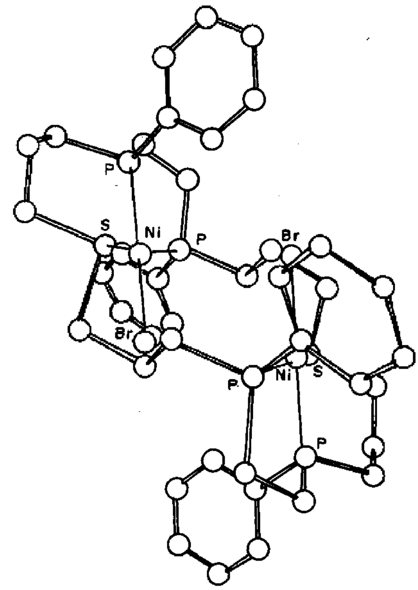
ether, thioether or amine groups.[2831–2837] Owing to the chiral nature of the phosphane groups, different diastereoisomers of each ligand were isolated, which generally exhibited different coordination behaviour towards nickel(II), according to the absolute configuration of the ligand and to the nature of the donor atoms (O, S, N). Examples of the rich coordination chemistry displayed by such types of ligand are given by the five possible diastereoisomers of the macrocycle 4,7,13,16-tetraphenyl-1,10-dithia-4,7,13,16-tetraphosphacyclooctadecane, indicated as α, β, γ, δ and ε, which yield diamagnetic mononuclear complexes of the same general formula [NiL]Y_2. The coordination geometries of these complexes are, respectively, square pyramidal, elongated *trans* octahedral (**391**), square planar, trigonal bipyramidal (**392**) and supposed *cis* octahedral (Table 108).[2831–2833] On the other hand the 22-membered macrocycle 5,8,16,19-tetraphenyl-1,12-dithia-5,8,16,19-tetraphosphacyclodocosane yields either dinuclear square planar complexes of the type $[Ni_2Br_2L](BPh_4)_2$ (**393**)[2836] or mononuclear five-coordinate complexes such as $[NiL](BF_4)_2$.[2837]



(391) (reproduced with permission from ref. 2831)



(392) (reproduced with permission from ref. 2832)



(393) (reproduced with permission from ref. 2836)

50.5.9.6 Reactivity of the complexes with synthetic macrocycles

(i) Redox properties involving coordinated macrocycles

Nickel(II) complexes with a variety of tetraaza macrocycles have been found to undergo facile one-electron redox reactions. Such reactions have been accomplished by means of both chemical and electrochemical procedures. The kinetic inertness and thermodynamic stability of the tetraaza macrocyclic complexes of nickel(II) make them particularly suitable systems for the study of redox processes. A very extensive summary of the potentials for the redox reactions of nickel(II) complexes with a variety of macrocycles is given in ref. 2622.

After the pioneering work of Olson and Vasilevskis,[2841] Busch and associates reported on the electrochemical properties of a large number of nickel complexes with different macrocycles.[2842] On the basis of EPR studies it is inferred that the one-electron oxidation of nickel(II) complexes with either neutral (*e.g.* cyclam) or dianionic ligands leads to the formation of authentic nickel(III) species (low-spin d^7 configuration). The influence of structural parameters such as the size of the chelate rings and the nature of ring substituents on the redox potential was investigated by other authors later.[2693,2749,2792,2843,2844] The easy oxidation of nickel(II) to nickel(III) in the case of 14-membered saturated macrocycles (in the range +0.7 to +0.9 V *vs.* Ag/Ag^+ reference electrode in MeCN; Table 109) has been correlated to the strong in-plane interaction of the four nitrogen atoms which increase the energy of the metal orbital from which the electron is extracted.[2693]

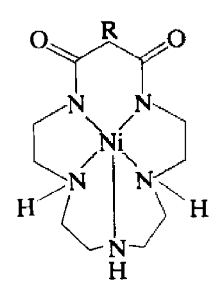
The electrochemical reduction of the complexes with saturated or non-conjugated macrocycles leads to the formation of nickel(I) complexes. An increase of the ring size of the macrocycle makes the reduction of nickel(II) to nickel(I) easier. In the case of macrocycles with α-diimine functions, the electrochemical reduction yields nickel(II)-stabilized ligand radicals.[2842] Both types of reduced complex react with CO affording paramagnetic 1:1 complexes, presumably of nickel(I).[2845] The use of protic solvents (*e.g.* MeOH) in place of MeCN in the reduction of $[Ni(CR)]^{2+}$ led to hydrogenation of the imine groups, eventually accompanied by the reduction of nickel(II).[2749] Neutral complexes with tetraazahexaenate macrocycles can be oxidatively dehydrogenated to mono- and di-positive cations. These redox reactions have been proved to be essentially ligand-based in nature on the basis of EPR evidence.[2846,2847] Chemical oxidation with Br_2, HNO_3 or Ph_3CBF_4 of complexes with saturated macrocycles results in the oxidative dehydrogenation of the starting complexes. In most cases the unsaturated linkages are introduced into nitrogen donor atoms (Scheme 37).[2639,2848–2851] Conversely, reductive hydrogenation of unsaturated linkages of coordinated macrocycles have been accomplished with a variety of specific reagents such as $NaBH_4$ in ethanol or H_2 over Pt catalyst. The ultimate products are complexes with saturated macrocyles.[2639,2642,2852,2853]

Table 109 Electrochemical Data for some Macrocyclic Complexes of Nickel[2842]

Ligand	*Oxidation potential*[a]	*Reduction potential*	
	$Ni(L)^{2+} \rightarrow Ni(L)^{3+}$	$Ni(L)^{2+} \rightarrow Ni(L)^{+}$	$Ni(L)^{+} \rightarrow Ni(L)$
[13]aneN_4	+0.7–+0.9	−1.70	
[14]aneN_4	+0.67	−1.70	
Me_2[14]aneN_4	+0.68	−1.73	
Me_4[14]aneN_4	+0.71	−1.66	
Me_6[14]aneN_4	+0.87	−1.57	
Me_6[14]4,11-dieneN_4	+0.98	−1.57	
Me_6[14]1,4,8,11-tetraeneN_4	+1.15	−1.35	−2.0
[15]aneN_4	+0.90	−1.5 (i)[b]	
Me_6[16]aneN_4	~+1.3	−1.40	
Me_6[16]4,12-dieneN_4	+1.3	−1.37	
Me_6[16]1,4,12-trieneN_4	+1.3	−1.30	
Me_2[14]1,3-dieneN_4	+0.86	−1.16	
CRH	+0.89	−1.53	
CR	+1.03	−0.96	−1.55
Me_6[14]1,3,7,11-tetraeneN_4	+1.05	−0.76	−1.62
Me_4[14]1,3,8,10-tetraeneN_4	+1.00	−0.82	−1.15
Me_2[14]4,7-dieneN_4	+0.72	~−1.5 (i)	
Me_2[15]8,11-dieneN_4	+0.94	~−1.5 (i)	
	$Ni(L)^{+} \rightarrow Ni(L)^{2+}$	$Ni(L)^{+} \rightarrow Ni(L)$	
Me_2[13]dienatoN_4^-	+0.27 (i)	−2.30	
Me_2[14]dienatoN_4^-	+0.23 (i)	−2.34	
	$Ni(L) \rightarrow Ni(L)^{+} \rightarrow Ni(L)^{2+}$		
$Me_2(MeCO)_2$[14]tetraenatoN_4^{2-}	+0.25	+0.97 (i)	
$Me_4(MeCO)_2$[14]tetraenatoN_4^{2-}	+0.26	+0.98 (i)	
$Me_2(MeCO)_2$[15]tetraenatoN_4^{2-}	+0.27	+0.92 (i)	
$Me_6(MeCO)_2$[15]tetraenatoN_4^{2-}	+0.28	+0.96	

[a] In MeCN solution and 0.1 M $Bu^n_4NBF_4$; V *vs.* Ag/Ag^+ (0.1 M) reference electrode.
[b] i = irreversible.

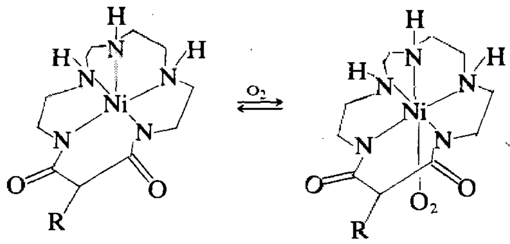
Some nickel(II) tetraaza macrocycles have been proved to act as efficient catalysts for the electrochemical reduction of CO_2 in H_2O/MeCN medium. This indirect electroreduction occurs at potentials in the range −1.3 to −1.6 V *vs.* SCE and mainly produces either CO or a CO/H_2 mixture, depending upon the type of complex.[2854] The five-coordinate complexes [NiL] **(394)** formed by some deprotonated dioxopentamine macrocycles have been found to display very low oxidation potentials Ni^{II}/Ni^{III} in aqueous solution (about 0.24–0.25 V *vs.* SCE at 25 °C and 0.5 M Na_2SO_4). Air oxidation of the same complexes in aqueous solution yields 1:1 NiL–O_2 adducts ($S = 1$) which are better formulated as superoxo complexes, $Ni^{III}L–O_2^-$ (Scheme 56). The activation of Ni-bound oxygen is such that it attacks benzene to give phenol.[2855]



(394) R = H, Me, Et, CH_2Ph, $CH_2C_{10}H_7$, $CH_2CH_2C_5H_4N$

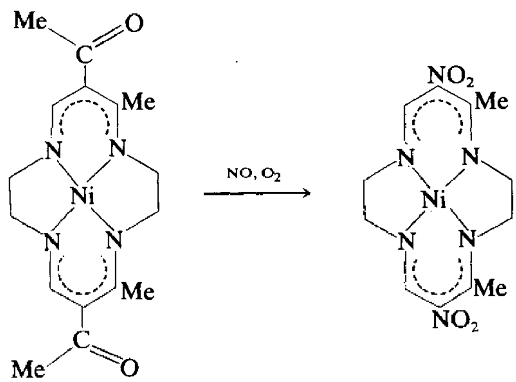
(ii) Substitution and addition reactions of macrocyclic ligands

Some electrophilic reagents have been found to react with unsaturated macrocyclic ligands, particularly those containing acetyl groups attached to charge-delocalized chelate rings.[2856,2857] The acetyl groups are displaced with a reaction mechanism which resembles the substitution



Scheme 56

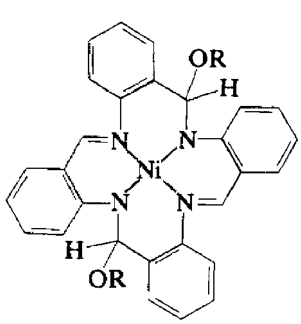
reaction into aromatic rings. A typical reaction which affords the dinitro derivative is reported in Scheme 57.[2857]



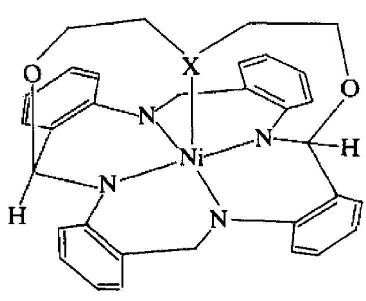
Scheme 57

N-Alkylation of some complexes has been accomplished by means of a variety of alkyl halides using KOH in DMSO.[2858,2859]

In the case of cationic complexes with unsaturated macrocycles two molecules of nucleophile, such as ammonia, amines and alkoxides, add to carbon atoms of two imine groups. For example, the reaction of $[Ni(Bzo[16]octaeneN_4)](ClO_4)_2$ (Table 106) with sodium methoxide or ethoxide yields the compounds (**395**),[2860] while with secondary amines and diamines complexes of type (**396**) are obtained.[2861] The reaction of (**396**) with acetone at room temperature yields complex (**397**) where the enolate anion of acetone, $MeC(O)CH_2^-$, replaces the diethylamide group (Scheme 58).[2862] The addition of molecules such as bis(2-hydroxyethyl)methylamine and bis(2-hydroxyethyl) sulfide, $HOCH_2CH_2YCH_2CH_2OH$ (Y = NMe, S) results in the formation of derivatives which possess one more coordination site just above the plane of the macrocyclic donors (**398**).[2863]

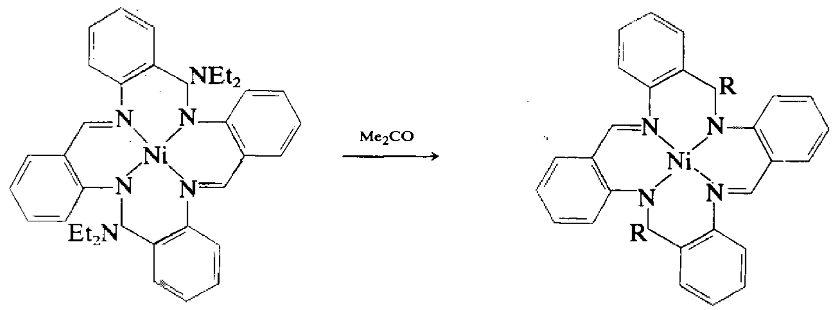


(**395**) R = Me, Et



(**398**) X = S, NMe

In general, the presence of reactive functional groups in the macrocyclic rings allows the synthesis of macrocycles with additional donor sites, bridging and pendant groups.[2864] These complexes have been designed as synthetic models for biological systems (Scheme 59). The various bridging groups in complexes of the type (**399**) form a protected cavity of variable size and form in the proximity of an empty coordination site of the nickel(II). In this hydrophobic cavity small molecules can be accommodated, in principle, becoming more reactive.[2865–2869]

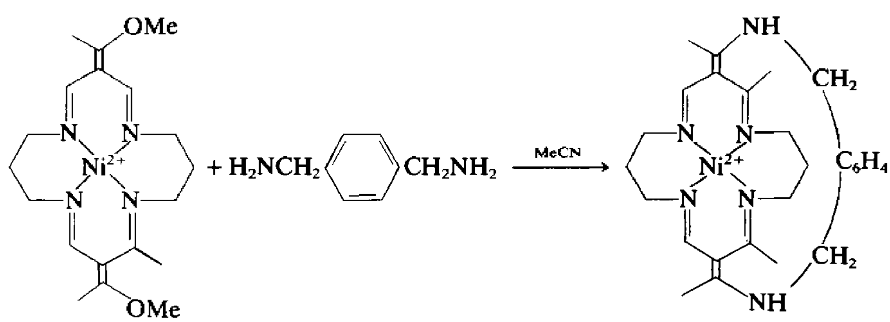


(396)

(397) R = CH_2COMe

Scheme 58

The structure of one such complex incorporating an MeCN molecule has been reported (Figure 31).[2868]



(399)

Scheme 59

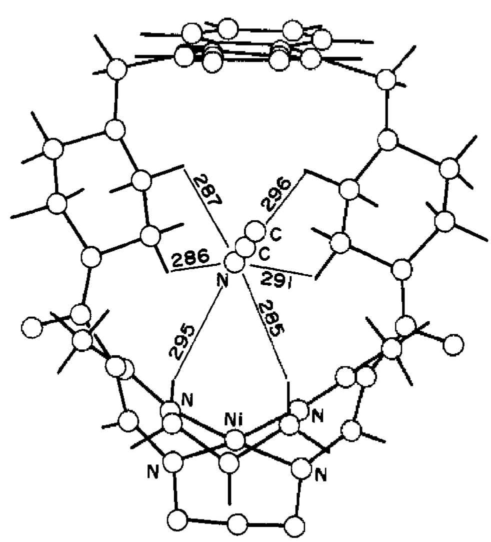
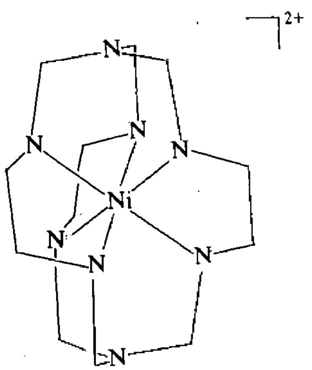


Figure 31 Interaction between an MeCN molecule and the host molecule Ni{9,10-anthracene(CH_2piperazine-Ethi)$_2$$Me_2$[16]tetraene}$(PF_6)_2$ (reproduced with permission from ref. 2868)

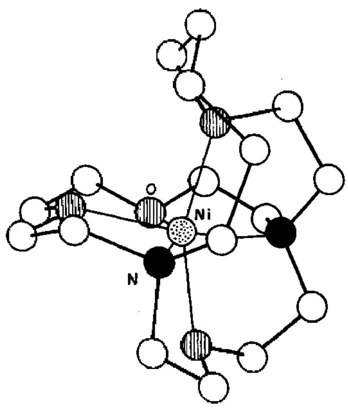
50.5.9.7 Nickel(II) complexes with macrobicyclic ligands (cryptands)

Nickel(II) complexes with cryptands are still rare. In general the encapsulation of nickel(II) in this type of macrocyclic ligand makes the complexes extraordinarily resistant to dissociation and substitution reactions.

By the template reaction of ammonia, ethane-1,2-diamine and formaldehyde, complex (**400**), trivial name nickel sepulchrate, was obtained in a very low yield (<1%).[2869] Bond distances and angles within the complex (Ni—N, 210 pm (ave)) are similar to those found in $[Ni(en)_3]^{2+}$. The X-ray structure of the distorted octahedral complex with a diazapentaoxa macrobicyclic ligand $[NiL](NO_3)_2$ (**401**) has also been reported (Ni—N, 211, 218 pm; Ni—O, 205–211 pm).[2870] A schematic representation of dinuclear cryptates of general formulas $[Ni_2L](ClO_4)_2$ (L = cryptand with two coordinating sites) is given in Figure 32. The complexes were prepared by direct synthesis with preformed ligands.[2871,2872]



(**400**)



(**401**) (reproduced with permission from ref. 2870)

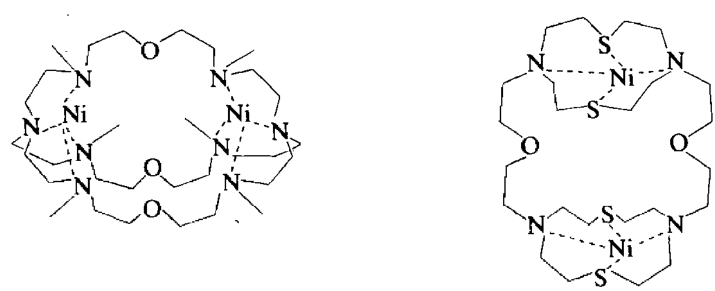
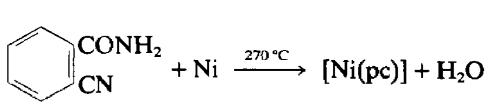


Figure 32 Schematic representation of dinuclear cryptates of general formula $[Ni_2L](ClO_4)_2$

50.5.9.8 Complexes with phthalocyanine,[2622,2873] porphyrins[2874–2877] and related macrocycles

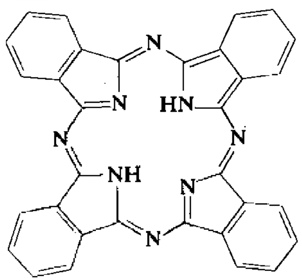
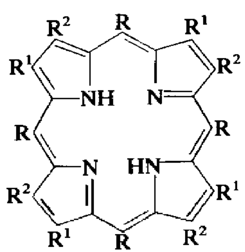
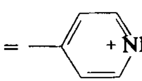
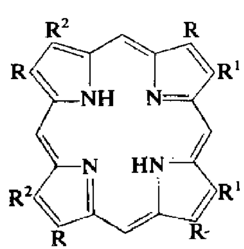
The first structural report on a phthalocyanine complex concerned [Ni(pc)] (Table 110; **I**).[2878] In the crystal lattice of this compound the square planar macrocycles are arrayed in slipped stacks such that the distance between the molecular planes along the perpendicular direction is 388 pm. [Ni(pc)] may be prepared by a variety of methods;[2873,2879,2880] a convenient one is heating a foil of elemental nickel in *o*-cyanobenzamide at 270 °C (Scheme 60).[2881] [Ni(pc)] is insoluble in the most common organic solvents, but soluble in concentrated sulfuric acid from which it is reprecipitated unchanged upon dilution. This complex is thermally very stable and may be sublimed *in vacuo*. The reduction of [Ni(pc)] can be accomplished by chemical or electrochemical methods and results in ligand-based reduced anions $[Ni(pc)]^{n-}$ ($n = 1, 2$). Analogously, the electrochemical oxidation results in the oxidized ligand.[2873]

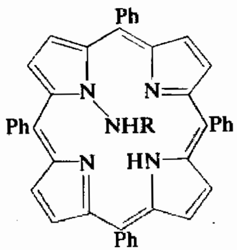
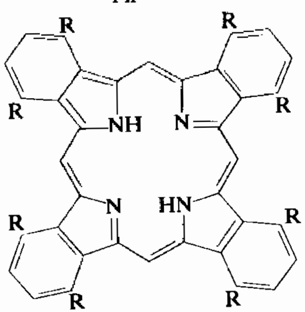
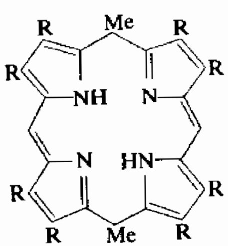
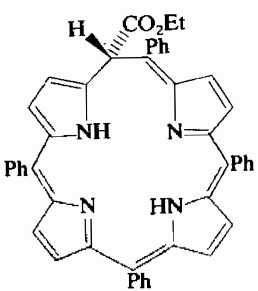


Scheme 60

The role of [Ni(pc)] as catalyst for the oxidation of various organic molecules has been investigated.[2622,2873] Hydrogenation reactions have also been accomplished in the presence of [Ni(pc)] as catalyst.[2873,2882]

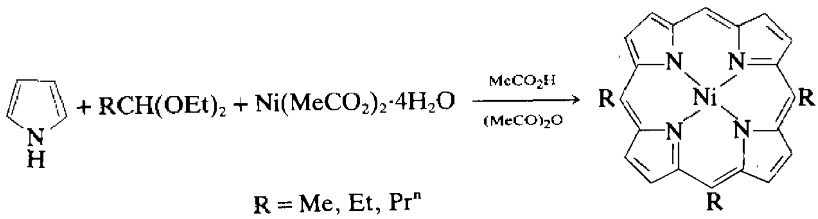
Table 110 Selected Nickel(II) Complexes with Porphyrins and Related Systems

Neutral ligand	*Substituents and formulas*	*Remarks*[a]	*Ref.*
	Phthalocyanine, H_2pc [Ni(Pc)] (**I**)	Slipped-stacked structure; Ni—N, 183 (av)	2878
	$R^1 = N^2 = H$; R =  +NMe (H_2tmpyp)		
	[Ni(tmpyp)($C_3H_4N_2$)$_2$](ClO_4)$_4$·Me_2CO (**II**)	*trans* Oh; $\mu_{eff} = 2.83$; Ni—N, 202, 205 (porph); Ni—N, 216 (imidazole); planar conformation of the macrocycle	2885
	$R^1 = R^2 = Et$; R = H (2,3,7,8,12,13,17,18-octaethylporphyrin, H_2oep) [Ni(oep)] (**402**)	Tetragonal form; Ni—N, 193; porphyrin not planar; angles between planes of adjacent pyrrole rings = 32.8° Triclinic form; Ni—N, 196; porphyrin planar	2886, 2887
	$R^1 = R^2 = H$; R = Me (5,10,15,20-tetramethylporphyrin, H_2tmp) [Ni(tmp)] (**403**)^2	Ni—N, 194, 196; planar conformation of macrocycle; slipped-stack arrangement of the molecules	2888, 2889
	[Ni(tmp)(TCNQ)][b]	Donor–acceptor π complex; alternating parallel molecules of Ni(tmp) and TCNQ stacking in columns. Intrastack spacing about 330 pm; conductivity $< 10^{-5}$ S cm^{-1}; Ni—N, 195	2890
	[Ni(tmp)]I	Partially oxidized complex; stacks of Ni(tmp) molecules (Ni—Ni spacing, 347 pm) and chains of I_3^-; conductivity about 110 S cm^{-1}	2891
	R = H; R^1 = Me; R^2 = Et (2,7,12,17-tetramethyl-3,8,13,18-tetraethylporphyrin, H_2ethp) [Ni(ethp)]	Ni—N, 196; porphyrin not planar	2892
	R = Me; $R^1 = CH_2CH_2CO_2Me$; R^2 = COMe (3,8-diacetyldeuteroporphyrin-IX dimethyl ester, H_2L) [NiL]	Ni—N, 196	2893

	R = $MeC_6H_4SO_2$ (*N*-tosylamino-5,10,15,20-tetraphenylporphyrin, H_2L) [NiL]	Nickel four-coordinated by three pyrrole nitrogens and by one extra nitrogen atom from the nitrene fragment; macrocycle not planar	2894
	R = H (tetrabenzoporphyrin, H_2tbp) [Ni(tbp)]I	Partially oxidized complex; stacks of Ni(tbp) molecules (Ni—Ni spacing, 332 pm) and chains of I_3^- ions; conductivity about 330 S cm^{-1}	2895
	R = Me (octamethyltetrabenzoporphyrin, H_2omtbp) [Ni(omtbp)]	As above (Ni—Ni spacing, 378 pm); conductivity about 125 S cm^{-1}	2896
	R = Et (5,10-dimethyl-5,10-dihydrooctaethylporphyrin, H_2L) [NiL]	Ni—N, 191 (av); macrocycle not planar	2897
	21-Ethoxycarbonyl-5,10,15,20-tetraphenyl-21*H*-21-homoporphyrin, H_2L [NiL]	Ni—N, 189–193; macrocycle not planar	2898

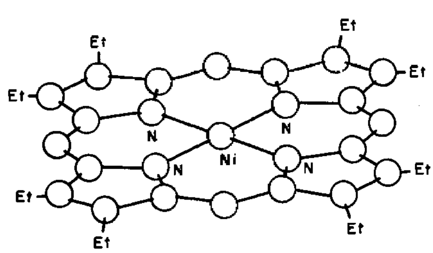
[a] All of the complexes are square planar unless otherwise stated; the structures have been determined by X-ray analysis. Bond distances are in pm and μ_{eff} in BM.
[b] TCNQ is tetracyanoquinodimethane.

Neutral nickel(II) complexes with a number of deprotonated porphyrins have been prepared in most cases by the direct reaction of a nickel salt, usually $Ni(ac)_2{\cdot}4H_2O$, with the preformed diacid macrocycle, using media such as DMF, $MeCO_2H$ or PhCl at refluxing temperature. Recently, the template synthesis of the complex with tetraalkylporphyrins has been reported (Scheme 61).[2883] On the other hand the condensation reaction of 1,3,4,7-tetraalkylisoindole and nickel acetate tetrahydrate gives the [Ni(omtbp)] complex (omtbp = octamethyltetrabenzoporphyrinate dianion).[2884]

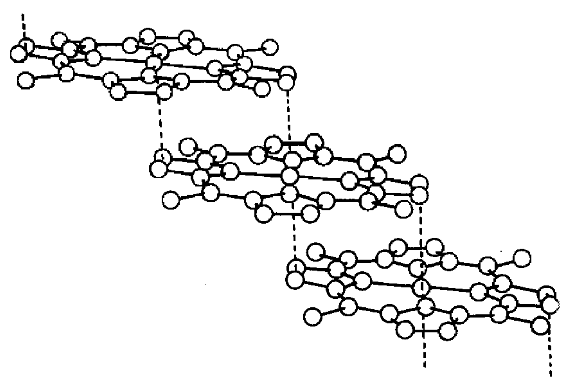


Scheme 61

The structures of some nickel(II) porphyrins have been investigated by means of X-ray diffraction (Table 110; **402, 403**). With one exception, the coordination of nickel(II) is square planar. However, the porphyrins have a rather flexible skeleton and give rise to different conformations of the macrocyclic moiety. It has generally been found that when the planar porphyrins distort to a ruffled conformation, a contraction of the macrocycle 'hole' results and, consequently, the Ni—Ni bond distances are reduced. From a solution of the water-soluble complex with 5,10,15,20-tetra(4-*N*-methylpyridyl)porphyrin (tmpyp; Table 110; **II**) containing a large excess of imidazole, the paramagnetic bis adduct $[Ni(tmpyp)(C_3H_4N_2)_2](ClO_4)_4{\cdot}2Me_2CO$ was obtained.[2885] This complex has a *trans* octahedral coordination with the porphyrin skeleton nearly planar.



(**402**) (reproduced with permission from ref. 2887)

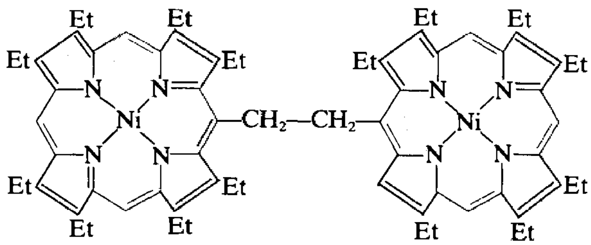


(**403**) (reproduced with permission from ref. 2889)

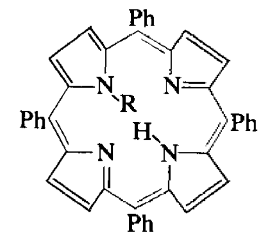
Solution studies on the adducts formed by various heterocyclic bases with some nickel porphyrins have been reported.[2899–2902] From these studies one can conclude that pyridine and substituted pyridines form predominantly 1:1 adducts while piperidine, imidazole and substituted imidazoles also form 1:2 complexes or a mixture of both 1:1 and 1:2 complexes. Electrochemical redox reactions of nickel porphyrins have been investigated.[2903,2904]

The bis-porphyrin complex (**404**) was prepared by simple heating of the parent complex nickel(II) *meso*-hydroxymethyloctaethylporphyrin, and its molecular structure has been ascertained.[2905,2906] The reaction of the *N*-substituted porphyrin (**405**) with nickel(II) acetylacetonate in the presence of NEt_3 as base, following some rearrangement, yields two isomers of the homoporphyrin (**III**; Table 110).[2898,2907] Further rearrangement reactions occur upon heating the neutral complex.[2908]

Partial oxidation of some nickel(II) complexes with phthalocyanine and porphyrins gives rise to conducting molecular solids of the type $Ni(pc)I_x$ ($x = 0$–3) and Ni(porphyrin)I (Table 110).[2884,2891,2895,2909] The oxidation of $Ni(pc)I_x$ is reversible and the iodine can be completely removed from the compound by heating it *in vacuo*. The aforementioned compounds may be



(404)



(405) R = CH_2CO_2Et

formulated as partially ring-oxidized species $[NiL]^{0.33+}[I_3^-]_{0.33}$ (L = phthalocyaninato, 5,10,15,20-tetramethylporphyrinato, tetrabenzoporphyrinato and octamethyltetrabenzoporphyrinato). Their crystal structures consist of macrocycle stacks and linear chains of disordered I_3^- anions parallel to the stacking axis. The iodine atoms lie in channels formed by neighbouring macrocycle stacks (Figure 33). Magnetic susceptibility values of the partially oxidized complexes, with one exception, are strongly reduced with respect to the $\frac{1}{3}$ spin/macrocycle value expected on the basis of the stoichiometry of the complexes. Conductivity along the stacking axis exhibits a metal-like temperature dependence and is in the range 150–750 S cm^{-1} at room temperature for the majority of the complexes.

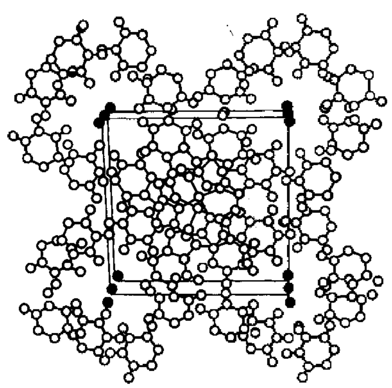
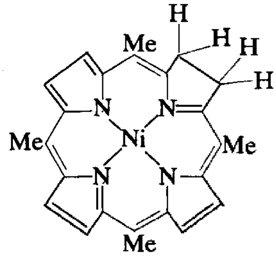


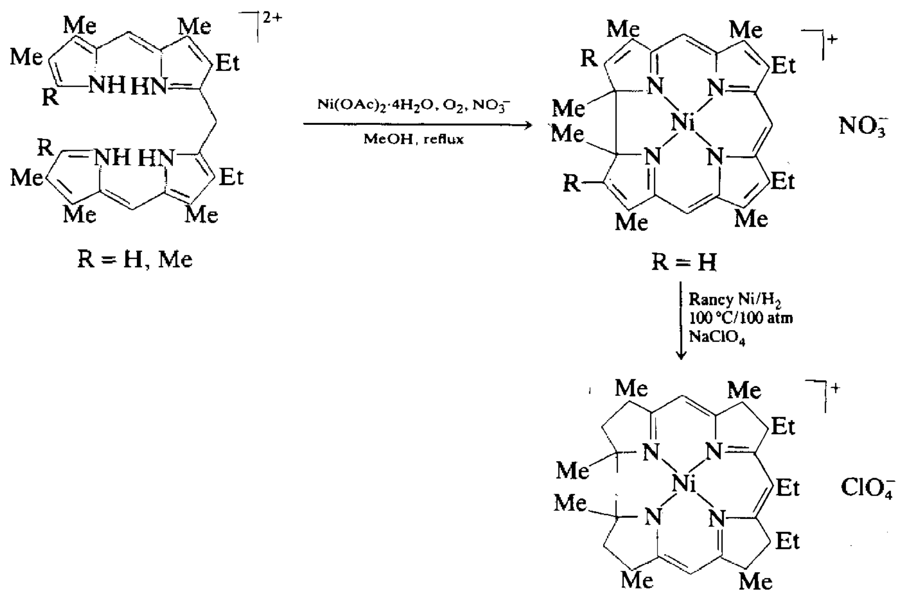
Figure 33 View of the crystal packing in [Ni(pc)]I (pc = phthalocyaninate(2−)) (reproduced with permission from ref. 2909)

Nickel(II) complexes have also been reported with reduced porphyrins, usually referred to as chlorins and corrins. Some nickel(II) complexes with chlorins (**406**)[2883] have been obtained as by-products in the template synthesis of tetraalkylporphyrins. The main difference between [Ni(tmc)] and [Ni(tmp)] (tmc = deprotonated tetramethylchlorin, tmp = deprotonated tetramethylporphyrin; Table 110) is the lack of symmetry in the former complex with respect to the latter. The synthesis and reactivity properties of a number of corrin–nickel(II) complexes have been reported, mostly by Johnson and co-workers.[2910–2915] Scheme 62 is a typical example of oxidative cyclization in the presence of a nickel salt.[2914]

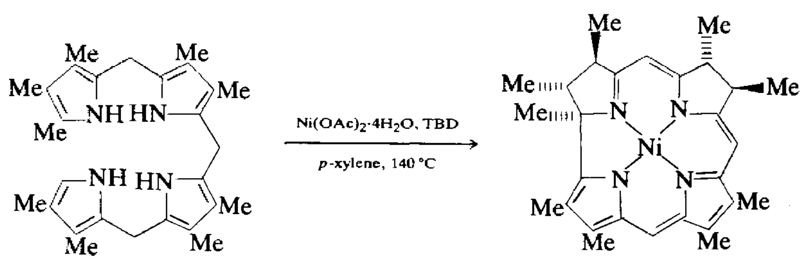


(**406**)

A mixture of diastereoisomers was obtained according to Scheme 63.[2916] The use of 1,5,7-triazabicyclo[4.4.0]deca-5-ene (TBD) as base is imperative, otherwise lower yields of the products or none at all are obtained. Complex (**407**) is square planar.



Scheme 62



(407)

Scheme 63

50.5.10 Magnetic Properties of Polynuclear Nickel(II) Complexes

Polynuclear high-spin nickel(II) complexes have been isolated with a large number of ligands and much attention has been devoted to the study of their magnetic properties, with particular emphasis on determining magnetic–structural correlations. The magnetic properties are determined by rather complicated interactions between the unpaired electrons in the magnetic orbitals of the metal atoms which are generally indicated as 'exchange' or 'superexchange' interactions and depend on the nature of the ligands around the metal atoms and on the relative orientation of the mononuclear moieties which form the polynuclear complex. The elucidation and understanding of the exchange interactions between transition metal ions are a severe test for all the theoretical models used to describe the electronic structure of metal complexes and present fundamental challenges to inorganic and theoretical chemists. Furthermore, the understanding of the magnetic–structural correlations is of considerable practical importance in the design and synthesis of new low-dimensional magnetic systems with specific magnetic properties as well as in all catalytic and electron transfer processes.

In this chapter we will present a series of polynuclear nickel(II) complexes, placing our attention mainly on those complexes for which the largest number of experimental observations are available. We will first review dimers and later oligonuclear complexes and extended systems in the order of increasing number of constituent metal ions.

50.5.10.1 Nickel(II) dimers

Dimers formed by exchange-coupled nickel(II) ions will be reviewed first, starting with dimers with monoatomic bridges. Mixed valence dimers and heterobimetallic dimers containing one nickel(II) ion will follow.

The exchange interactions between two nickel(II) ions are most commonly investigated by measuring the temperature dependence of the magnetic susceptibility. The main exchange interaction between two nickel(II) ions having orbitally non-degenerate ground states is generally described using the isotropic spin coupling Hamiltonian, $\mathcal{H} = -J\mathbf{s_1}\cdot\mathbf{s_2}$, where J is the isotropic exchange coupling constant to be measured and $\mathbf{s_1}$ and $\mathbf{s_2}$ are spin operators for the two ions forming the dimer. The eigenvalues of $\mathcal{H}$ can be labelled by means of S, the eigenvalues of $\mathbf{S}^2 = (\mathbf{s_1} + \mathbf{s_2})$, and M_S, the eigenvalues of $\mathbf{S}_z$, giving

$$E(S,M_S) = -J/2[S(S+1) - s_1(s_1+1) - s_2(s_2+1)] \qquad (223)$$

Equation (223) shows that the $E(S)$ levels are $(2S+1)$-fold degenerate. Since nickel(II) has two unpaired electrons, $s_1 = s_2 = 1$ and $S = 2, 1, 0$. The energies of the S levels are therefore $E(0) = 2J$, $E(1) = J$, $E(2) = -J$. A positive J value makes the $S = 2$ state (that having the highest multiplicity) the lowest in energy, and the exchange interaction is called ferromagnetic. A negative J value, on the other hand, makes the $S = 0$ state the ground state and the interaction is then called antiferromagnetic. J values can be obtained by measuring the temperature dependence of the magnetic susceptibility.

Ginsberg *et al.*[2917] made a detailed analysis of the average magnetic susceptibility of nickel(II) dimers and fitted the temperature dependence of the magnetic susceptibility of $[Ni_2(en)_4X_2]Y_2$ (X, Y = Cl, Br; X = NCS, Y = I). The model Hamiltonian they used is

$$\mathcal{H} = -J\mathbf{s_1}\cdot\mathbf{s_2} - D(s_{1z}^2 + s_{2z}^2) - g\mu_B\mathbf{S}_z - z'J'\mathbf{S}_z\langle S_z\rangle \qquad (224)$$

The terms on the right hand side of equation (224) represent the isotropic exchange interaction, the zero field splitting of the nickel(II) ions, the Zeeman interaction of the unpaired electrons with the magnetic field and the interdimer exchange interaction respectively. Detailed expressions of the magnetic susceptibility are reported in ref. 2917. In Figure 34 the computed dependence of the effective magnetic moment per Ni atom, $\mu_{eff} = \sqrt{(3k\chi T)}$ (BM), upon the reduced temperature $kT/|J|$ for a dimer complex is shown. Antiferromagnetic intradimer interactions are characterized by a regular decrease of μ_{eff} which is not much affected by either D or $z'J'$. For ferromagnetic dimers an increase of μ_{eff} with decreasing temperature is anticipated as a consequence of the increasing population of the $S = 2$ state until a plateau is reached corresponding to the complete depopulation of the excited $S = 1$ and $S = 0$ states (Figure 34a with $z'J' = 0$). The combined effect of antiferromagnetic interdimer exchange interactions and zero field splitting of nickel(II) ions causes a rapid low temperature decrease in μ_{eff}. It must be noted that measuring the D and $z'J'$ parameters from magnetic susceptibility data can be a difficult task since both interactions produce similar effects on the average magnetic susceptibility, which may result in large standard deviations and correlation coefficients between these two parameters.

In the literature different formulations of the Hamiltonian (equation 224) can be found, in particular $-J\mathbf{s_1}\cdot\mathbf{s_2}$ can be written as $J\mathbf{s_1}\cdot\mathbf{s_2}$ and $-2J\mathbf{s_1}\cdot\mathbf{s_2}$, and the interdimer exchange can be taken into account by multipling the susceptibility obtained from equation (224) by putting $z'J' = 0$, by $T/(T + \theta)$.

In Table 111 we have collected the most relevant structural features and magnetic parameters of selected nickel(II) dimers.

Much attention has been devoted to the characterization of the structural and magnetic properties of di-μ-halo complexes of nickel(II). These complexes can be obtained with a large variety of chelating ligands to form dimers with either six- or five-coordinate nickel(II) ions. A classical series of six-coordinate complexes having the general formula $[Ni_2(en)_4X_2]Y_2$ (X, Y = Cl, Br; X = Cl, Y = ClO_4, BPh_4) is formed using ethylenediamine as ligand. Joung *et al.*[2918] reported the single crystal magnetic susceptibilities of $[Ni_2(en)_4Cl_2]$ in the temperature range 1.5–25 K and confirmed the previous report of ferromagnetic intradimer interaction.[2917] Similar conclusions have also been reached by Journaux and Kahn[2919] who measured the average magnetic susceptibility of $[Ni_2(en)_4Cl_2]Y_2$ (Y = Cl, ClO_4, BPh_4) in the temperature range 3.6–300 K. The values obtained by the two groups are shown in Table 111. All the authors agree on the sign of the interaction, which is ferromagnetic, but they measure rather different absolute values. Since it has been shown[2972] that $[Ni_2(en)_4Cl_2]Cl_2$ undergoes a monoclinic–triclinic phase transition at about 19 K, it is probable that the maximum in the μ_{eff} *vs.* T curve, observed at 19 K, is somehow influenced by this phase transition. The parameters of Journaux

Table 111 Selected Examples of Dinuclear Nickel(II) Complexes[a]

Complex	Donor set	N[b]	Bridging atoms or groups	Bond distances Ni—X (pm)	Bond distances Ni—Ni (pm)	Bond angle Ni—X—Ni (°)	J	D	E/D	z'J'	θ	g	Ref.
$[Ni_2en_4Cl_2]Cl_2$	N_4Cl_2	2	Cl	247–256	375	96.55	7.0	9.7		−0.21		2.25	2918
$[Ni_2en_4Cl_2]Cl_2$	N_4Cl_2	2	Cl				13.3	3.6			2.1	2.21	2919
$[Ni_2en_4Cl_2](ClO_4)_2$	N_4Cl_2	2	Cl	246–251	368	95.4	17.8	4.3			2.1	2.17	2919, 2920
$[Ni_2EG_4Cl_2]Cl_2$	O_4Cl_2	2	Cl	238	346	93	1.3						2921, 2922
$[Ni_2(H_2O)_2Cl_8](PDA)_2$	OCl_5	2	Cl	243–246	361	95	16.2	4.9					2923
$[Ni_2Br_4(EtOH)_4]$	O_4Br_2	2	Br	252	362		7.1	6.8	0	−0.25			2924
$(dabc)Ni_2Cl_8$	Cl_5	2	Cl	237–245	367	99							2925
$[Ni(qnqn)Cl_2]_2$	N_2Cl_3	2	Cl	241–242	365	98	−8.8	−7		−0.03		2.25	2926, 2927
$[Ni(dmp)Cl_2]_2 \cdot CHCl_3$	N_2Cl_3	2	Cl	238–239	360	98	−10.2	−8.8		−0.03		2.20	2926, 2928
$[Ni(biq)Cl_2]_2$	N_2Cl_3	2	Cl	237–240	357	96.7	−10.7	−12.8	—	0.14		2.31	2929, 2930
$[Ni(dmp)Cl_2]_2$	N_2Cl_3	2	Cl	238–241	360	97.4	−14.5	−23.4	—	0.69		2.21	2929, 2930
$[Ni\{CH_2(dmpz)_2\}Cl_2]_2$	N_2Cl_3	2	Cl	232–246	359	97.4	5.2	2.2	—	−0.39		2.31	2931
$[Ni(dmp)Br_2]_2$	N_2Br_3	2	Br	247–265	383	96.7	−3.1	—	—	—		2.18	2929, 2930
$Ni_2(py)(acac)_4$	$O_6 + O_5N$	3	O	207	289	87.8	8.6	−11.4	—	0.29		2.20	2932, 2933
$Ni_2(pip)_2(acac)_4$	O_5N	2	O	216, 209	324	99.5	−12.2	−13.7	—	−0.41		2.24	2932, 2933
$Ni_2(acac)_4(Ph_3AsO)$	O_6	3	O	228, 200	290	82.6							2934
				206, 211		86.7							
				221, 203		90.3							
$[Ni_2(DBA)_2(py)_4] \cdot 4py$	O_4N_2	2	O	204	217	101.5	−26	—	—	—	—	2.0	2935
$[Ni_2(BAA)_2(H_2O)_4] \cdot H_2O$	O_6	2	O				−20	—	—	—	20.8	2.4	2935
$[Ni_2(DBA)_2(H_2O)_4]$	O_6	2	O				−16				20.8	2.5	2935
$[Ni_2(TFDAA)_2(py)_4]$	O_4N_2	2	O	205	316	101.1	−52				55.5	2.4	2936
$[Ni_2(trop)_4(H_2O)_2]$	O_6	2	O	201, 211	311	98.2							2937
$[Ni_2(bdhe)_2](ClO_4)_2$	N_3O_2	2	O	197	309	103	−35					2.4	2938, 2939
$[(triphos)_3Ni_2S](BPh_4)_2 \cdot 1.6DMF$	P_3S	1	S	203	406	180	Diamagnetic						2939
$[pipH][Ni_2(PhSal)_4ac]$	N_2O_4	2	O	203, 210	310	97.3	−9.4	|5|	—	|2|		2.30	2940
$[Ni_2(ps)_2(NO_3)_2(2\text{-}pic)_2]$	N_2O_4	2	O	200, 206		98.7	18	13		0.07		2.12	2941
$[Ni_2(ips)_2(NO_3)_2(EtOH)_2]$	N_2O_4	2	O	198, 205	301	96.4	32	15		0.2		2.15	2941
$[Ni_2(ips)_2(NO_3)_2(DMF)_2]$	N_2O_4	2	O	199, 206	300	99	−18.4	11		0.3		2.31	2941
$[Ni_2(slno)_2(NO_3)_2(EtOH)_2]$	N_2O_4	2	O	198, 204	299	95.9							2942
$[Ni_2(mcp)_2(NO_3)_2(EtOH)_2]$	N_2O_4	2	O	197, 206	303	82.1							2943
$[Ni_2en_4(NCS)_2]I_2$	N_5S	2	NCS^-	204 (N), 261 (S)	578		18	−6.9	—	−0.3		2.14	2917, 2944
$[Ni_2(NCS)_4(4\text{-}Mepy)_6]$	N_5S	2	NCS^-	205 (N), 258 (S)									2945
$[Ni_2(tren)_2(N_3)_2](BPh_4)_2$	N_6	2	N_3^-	207, 219	522		−70.2	6.8	—	0.72		2.32	2946
$[Ni_2(Me_6cyclam)_2(N_3)_3]I$	N_6	1	N_3^-	215, 211			−24.6	4.9	—	−1.7		2.23	2946, 2947
$[Ni_2(tren)_2(OCN)_2](BPh_4)_2$	N_5O	2	NCO^-	202 (N), 234 (O)	539		−8.8	−10.1	—	0.71		2.28	2948, 2949
$[Ni_2(tren)_2(SCN)_2](BPh_4)_2$	N_5S	2	NCS^-				4.8	−0.45	—	−0.16		2.25	2949

$[Ni_2(tren)_2(SeCN)_2](BPh_4)_2$	N_5Se	2	$NCSe^-$			3.2	−0.49	—	−0.07		2.25	2949
$[Ni_2(tren)_2(NCBH_3)_2](BPh_4)_2$	N_5H	2	BH_3CN^-	201 (N), 214 (H)	593							2950
$[Nien_2NO_2]_2(BPh_4)_2$	N_4O_2	2	NO_2^-	226 (O), 227 (O)		−25					2.23	2951
$[Ni_2en_4OX](NO_3)_2$	N_4O_2	1	$C_2O_4^{2-}$	210, 209		−66	—	—	—	52	2.19	2952, 2953
$[Ni_2py_6(NO_3)_2OX]\frac{1}{2}py$	N_3O_3	1	$C_2O_4^{2-}$	207, 207								2954
$[Ni_2(trien)_2OX](ClO_4)_2$	N_4O_2	1	$C_2O_4^{2-}$			−32	16	—	3.1		2.18	2955
$[Ni_2(Me_6cyclam)_2OX](ClO_4)_2$	N_4O_2	1	$C_2O_4^{2-}$			−32	20	—	0.3		2.19	2955
$[Ni_2(Me_6cyclam)_2SQ](ClO_4)_2$	N_4O_2	1	$C_4O_4^{2-}$			−0.8	15	—	0.6		2.20	2955
$[Ni_2(LZ)_2OX](ClO_4)_2 \cdot 2H_2O$	N_4O_2	1	$C_2O_4^{2-}$	209, 212								2956
$[Ni_2(tren)_2CA](BPh_4)_2$	N_4O_2	1	$C_6O_4Cl_2^{2-}$	204, 213	794	−3.6	3.8	—	—		2.30	2957
$[Ni_2(tren)_2DHBQ](BPh_4)_2$	N_4O_2	1	DHBQ			−2.2	|4.4|				2.17	2957
$[Ni_2(tren)_2RHZ](BPh_4)_2$	N_4O_2	1	RHZ			−8	|3.4|				2.10	2957
$[Ni_2(O_2CCMe_3)_4(quinal)_2]$	O_4N	4	$Me_3CCO_2^-$	204	—	−320					—	2958
$[Ni_2(Bz)_4(quinoline)_2]$	O_4N	4	$PhCO_2^-$			−250					2.20	2959
$[Ni_2(tmen)_2(prop)_4H_2O]$	O_4N_2	3	$EtCO_2^-$, H_2O	204, 203, 207 (H_2O)	356							2960
$[Ni_2(tmen)_2(O_2CCF_3)H_2O]$	O_4N_2	3	$CF_3CO_2^-$, H_2O	211, 207, 216 (H_2O)	368							2961
$[Ni_2(dhph)(py)Cl] \cdot 4H_2O$	N_4O_2	2	dhphpy, Cl	207, 237 (Cl)	360							2962
$[Ni_2(dhph)_2] \cdot 4H_2O$	N_4O_2	2	dhph	207, 208	379	−97.3					2.14	2953, 2963
$[Ni_2(BnAO\text{-}H)_2]Cl_2$	N_3O	2	N-OH	184, 186	363							2964
$[Ni_2\{tren(DO)\}_2](ClO_4)_2$	N_5O	2	N-OH		371	−158						2965
$[Ni_2(tren)_2DHNQ](BPh_4)_2$	N_4O_2	1	$DHNQ^-$			−0.2						2966
$[Ni_2LCl_2] \cdot 3H_2O$	N_2O_2Cl	2	L			−72					2.15	2967
$[Ni_2Lpy_4](BF_4)_2$	N_4O_2	2	L			−46						2968
$Ni_2Br_2(napy)_4]BPh_4$	N_4Br	4	napy	210 (N)	242	600						2969, 2970
$[Ni_2(tren)_2BIm](BPh_4)_2$	N_6	1	BIm			−2.5						2971

[a] The magnetic parameters are defined in the text. All values are in cm^{-1}. The reported bond distances and angles are with the bridging atoms.

[b] Number of bridging atoms.

Abbreviations: EG = ethyleneglycol; PDA = 1,3-propylenediaminium; dabc = *N*-ethyl-1,4-diazabicyclo[2.2.2]octonium; qnqn = *trans*-2-(2′-quinolyl)methylene-3-quinuclidone; dmp = 2,9-dimethyl-1,10-phenanthroline; biq = 2,2′-biquinolyl; dmpz = 3,5-dimethylpyrazolyl; pip = piperidine; DBA = 1,5-diphenyl-1,3,5-pentanetrionato; BAA = 1-phenyl-1,3,5-hexanetrionato; TFDAA = 1,1,1-trifluoro-2,4,6-heptanetrionato; trop = tropolonato; bdhe = *N,N*-bis(2-diethylaminoethyl)-2-hydroxyethylamine; PhSal = phenylsalicylaldime; ps = *N*-phenylsalicylaldimine; ips = *N*-isopropylsalicylaldimine; slno = 2-(*p*-nitrophenyliminomethyl)-phenolato; mcp = 4-chloro-2-[methylimino(phenyl)methyl]phenol; Me_4cyclam = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane; OX = oxalate; SQ = squarate; LZ = 3,5,5,10,10,12-hexamethyl-1,2,6,9,13,14-hexaazatetradeca-2,12-diene; CA = dianion of chloroanilic acid; DHBQ = dianion of 2,5-dihydroxy-1,4-benzoquinone; RHZ = rhodizonate; quinal = quinaldine; tmem = tetramethylethylenediamine; tren = 2,2′,2″-triaminoethylamine; dhph = 1,4-dihydrazinophthalazine; prop = propionate; BnAO-H = *N*-(6-amino-4-aza-3,3,6-trimethyl-2-heptylidenyl)-hydroxamato; trien DO = $(NH_2C_2H_4)_2N[C_2H_4NC(Me)\text{-}C(Me)NOH]$; DHNQ = dianion of 5,8-dihydroxy-1,4-naphthoquinone; L = macrocycle formed by condensation of 2,6-diformyl-4-methylphenol and 1,3-diaminepropane.

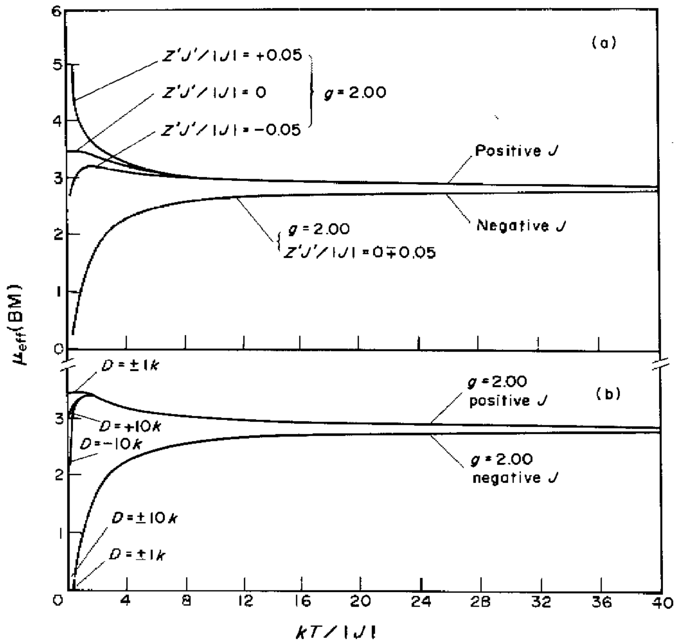
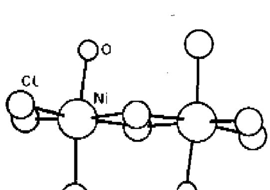


Figure 34 Theoretical dependence of μ_{eff} (BM) per Ni atom upon reduced temperature $kT/|J|$ for a dinuclear complex; (a) without zero field splitting; (b) including zero field splitting with $z'J' = 0$ (after ref. 2917)

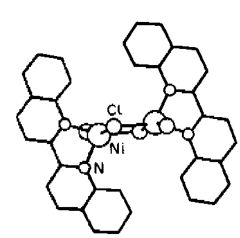
and Kahn[2919] were obtained by fitting the susceptibility in the range 27–300 K and probably give a better estimate of the exchange interactions.

Stebler *et al.*[2973] measured the transitions between the various spin states of $[Ni_2(enD)_4Br_2]Br_2$ (enD = deuteroethylenediamine) directly using inelastic neutron scattering techniques. They found $J = 7\ cm^{-1}$, $D = 6.8\ cm^{-1}$, $\lambda = 0$, $z'J' = -0.25\ cm^{-1}$ in good agreement with the other data reported in Table 111.

Landee and Willett[2923] obtained the complex $[Ni_2(H_2O)_2Cl_8](PDA)_2$ (**408**) (PDA = 1,3-propylenediaminium) by slow evaporation of equimolar solution of 1,3-propylenediamine dihydrochloride and anhydrous nickel(II) chloride in concentrated hydrochloric acid. The nickel atoms are octahedrally coordinated by five chlorine atoms and one oxygen from the water molecules. The Ni—Cl bonds average 241 pm and the Ni—OH_2 bond length is 212 pm. The *cis* Cl—Ni—Cl angles range from 83° to 94° while the *trans* O—Ni—Cl angle is 172.4°. The exchange interaction was found to be ferromagnetic ($J = 16.2\ cm^{-1}$).



(**408**)



(**409**)

Five-coordinate nickel(II) dimers with halogen bridges have been synthesized with N—N chelating ligands.[2926–2931] The synthesis has been generally performed by mixing equimolar amounts of ligand and nickel(II) halide in an appropriate solvent. The general structure of the complexes is exemplified by $[Ni(biq)Cl_2]_2$ (biq = biquinoline) (**409**). The structures are intermediate between a trigonal bipyramid and a square pyramid. In any reported complex an N atom lies in the apical position in a square pyramidal description. The largest distortion towards a trigonal bipyramid is seen in the complex $\{Ni[CH_2(dmpz)_2]Cl_2\}_2$ $[CH_2(dmpz)_2$ = bis(3,5-dimethylpyrazolyl)methane] where the N—Ni—Cl direction is the z axis of the trigonal bipyramid (the angle being 174°) and the equatorial N—Ni—Cl angles average 108°. The exchange interaction is antiferromagnetic for all the complexes except for $\{Ni[CH_2(dmpz)_2]Cl_2\}_2$ where a weak ferromagnetism was observed.

Various attempts have been made to rationalize the J values observed in nickel(II) dimers,[2917,2974] and special attention was given to dimers with monoatomic bridges. Barraclough and Brookes[2975] used a configuration interaction method, equivalent to the Anderson description[2976] of superexchange, to calculate J in a planar Ni_2Cl_2 geometry with Ni—Cl—Ni angles at 90°. In this framework the following pathways for electron transfer *via* the bridging anion must be responsible for the observed J:

$$d_{x^2-y^2}\,\|p_x \perp p_y\|\, d_{x^2-y^2} \tag{225}$$

$$d_{x^2-y^2}\,\|p_x \perp p_y\|\, d_{z^2} \tag{226}$$

$$d_{z^2}\,\|p_x \perp p_y\|\, d_{z^2} \tag{227}$$

$$d_{x^2-y^2}\,\|s\|\, d_{x^2-y^2} \tag{228}$$

$$d_{x^2-y^2}\,\|s\|\, d_{z^2} \tag{229}$$

$$d_{z^2}\,\|s\|\, d_{z^2} \tag{230}$$

where $d_{x^2-y^2}$ and d_{z^2} are the magnetic orbitals of the nickel(II) ions, and p_x, p_y and s are orbitals on the chlorine atoms. Three ferromagnetic pathways (225)–(227) (especially 225) predominate over the pathways for antiferromagnetic coupling (228, 229) determining a net ferromagnetic interaction.

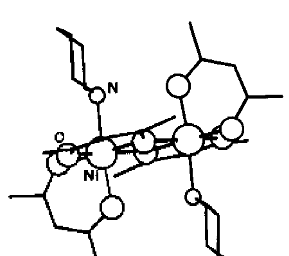
The theoretical expression which can be derived for J within the framework of the Hay, Thibeault and Hoffmann orbital model[2977] is

$$J = \tfrac{1}{4}\Sigma_i\Sigma_j K_{ij} - \tfrac{1}{4}\Sigma_i(\varepsilon_i - \varepsilon_{i-1})/(J_{i,i} - J_{i,j}) \tag{231}$$

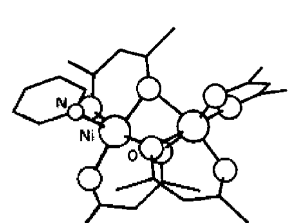
where the first summations run over the four combinations of electrons in the magnetic orbitals i on metal a and j on metal b and give ferromagnetic contributions to the exchange. The second sum is over all distinct pairs of MOs formed from equivalent pairs of magnetic orbitals on the two metal sites and gives the antiferromagnetic contributions. K_{ij} and $J_{i,j}$ indicate exchange and Coulomb integrals respectively. Equation (231) shows that the exchange interaction is always given by the sum of two opposite terms. The first favours the ferromagnetic coupling, the second the antiferromagnetic coupling. Since the last term depends on the energy difference $\varepsilon_i - \varepsilon_{i-1}$, which is largely determined by the overlap between the magnetic orbitals, it can be expected that a net ferromagnetic coupling occurs when the magnetic orbitals are orthogonal to each other.

Using extended Hückel calculations[2977] or the angular overlap formalism of Bencini and Gatteschi,[2978] it is possible to estimate the relative variations of $\varepsilon_i - \varepsilon_{i-1}$ within a series of similar complexes upon changes in the coordination geometry and to estimate the relative variation of the magnetic coupling constant. For nickel(II) dimers in five-coordinate environments the localized magnetic orbitals are essentially d_{z^2} and $d_{x^2-y^2}$ metal orbitals. On passing from a square pyramidal dimer to a trigonal bipyramidal one, it has been computed[2978] that the splitting of the $d_{x^2-y^2}$ orbitals decreases more rapidly than the increase of the splitting of the d_{z^2} orbitals, and this effect can explain the observed variation of the sign of J (see Table 111).

Base adducts of $[Ni_3(acac)_6]$ have been prepared[2932] and the crystal structures of the pyridine and piperidine derivatives have been determined.[2933] The complexes have the general structures (**410**) and (**411**). Type (**410**) complexes are antiferromagnetic while type (**411**) complexes are ferromagnetic. A series of antiferromagnetically coupled octahedral dimers[2935,2936] is also formed by the base adducts of 1,3,5-triketones. It must be noted that the Ni—O—Ni angles are about 100° in (**410**) and in these latter complexes, significantly larger than the angle (~95°) seen in the halo-bridged complexes. This causes a larger splitting of the MOs built up from the $d_{x^2-y^2}$ and d_{z^2} magnetic orbitals and can be one of the factors favouring the antiferromagnetic coupling.



(**410**)



(**411**)

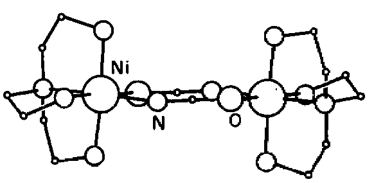
A number of nickel(II) dimers with bridging polyatomic molecules have been synthesized to date. Selected complexes are shown in Table 111 together with their most relevant structural and magnetic parameters.

(*i*) *Thiocyanides, azides and related bridges*

$[Ni_2(en)_4(NCS)_2]I_2$ is one of the first examples of ferromagnetic exchange *via* a polyatomic bridge. The two nickel(II) ions are octahedrally coordinated by four nitrogen atoms of two ethylenediamine molecules and one nitrogen and one sulfur of the bridging thiocyanate groups. The Ni—N—C and Ni—S—C angles are 176° and 100° respectively.[2944] The measured exchange coupling constant is $18\,cm^{-1}$. The main pathway responsible for the exchange interaction in this complex has been suggested to be $d_{xy}\,\|\sigma \perp \pi\|\,d_{z^2}$, where d_{xy} and d_{z^2} are the magnetic orbitals of the nickel atoms and σ and π are σ and π MOs of the thiocyanate groups.

Double thiocyanate bridges have also been found in the complex $[Ni_2(NCS)_4(4\text{-Mepy})_6]$.[2945]

Hendrickson and co-workers have synthesized a series of complexes with formulas $[Ni_2(tren)_2(NCX)_2](BPh_4)_2$ **(412)** where X = N, O, S and Se.[2946,2948,2949] In these complexes the nickel(II) ion is coordinated by four nitrogens of the tren ligand and by two X^- anions bridging in an end-to-end mode. The magnetic coupling between the nickel(II) ions in the azide complex is antiferromagnetic with $J = -70\,cm^{-1}$. The net antiferromagnetic interaction decreases on going to the NCO^- complex ($J = -8.8\,cm^{-1}$) and becomes net ferromagnetic for the NCS^- ($J = 4.8\,cm^{-1}$) and $NCSe^-$ ($J = 3.2\,cm^{-1}$) complexes. This behaviour has been related to the decrease of the Ni—X—C angle which goes from 135° in the azide complex to 100° in the NCS^- complex.[2949,2979] A smaller antiferromagnetic interaction has been measured in the monoazido complex $[Ni_2(Me_6\ cyclam)_2(N_3)_3]I$.[2946,2947]



(412)

(*ii*) *Carboxylate, oxalate, oxime and related bridges*

Carboxylate anions have a key role in the understanding of the magnetic exchange interactions propagated through multiatom bridges. The magnetic exchange and the electronic structure of the classic copper acetate hydrate dimer, $[Cu_2(O_2CMe)_4(H_2O)_2]$, are still a matter for investigation.[2979–2981]

Only a few nickel(II) complexes having the copper acetate type structure have been reported to date.[2958,2959] In the $[Ni_2(O_2CCMe_3)_4(quinoline)_2]$[2958] complex the nickel atoms are five-coordinate in a slightly distorted square pyramidal environment with the oxygens of the four carboxylate bridging groups occupying the equatorial positions and the nitrogen base in the axial position. A similar structure has also been assumed for $[Ni_2(bz)_4(quinoline)_2]$[2959] (bz = benzoate). The net exchange interaction measured in both complexes is antiferromagnetic, with $J = -320\,cm^{-1}$ and $-250\,cm^{-1}$ for the Me_3CCO_2 and the benzoate derivative respectively. These J values are the largest observed in nickel(II) dimers with polyatomic bridges and deserve some comments. The magnetic orbitals of nickel(II) in these complexes are predominantly d_{z^2} and $d_{x^2-y^2}$ metal orbitals and the exchange coupling constant can be decomposed according to equation (232):

$$J = J_{x^2-y^2,x^2-y^2} + J_{z^2,z^2} + 2J_{x^2-y^2,z^2} \tag{232}$$

where $J_{i,j}$ are the coupling constants relative to the coupling of the $|i\rangle$ and $|j\rangle$ magnetic orbitals.[2959] $J_{x^2-y^2}$ is expected to be negative (antiferromagnetic coupling) as already found in all the copper acetate type dimers ($\sim 300\,cm^{-1}$) and without any significant contribution from direct exchange.[2981] From the analysis of the EPR spectra of nickel(II)–copper(II) exchange-coupled pairs obtained by doping $[Cu_2(bz)_4(quinoline)_2]$ with Ni^{II}, $J_{x^2-y^2,z^2}$ was found to be positive (ferromagnetic coupling) and fairly large on account of the orthogonality of the two magnetic orbitals.[2959,2982] Assuming that the order of magnitude of the $J_{i,j}$ values does not significantly change on passing from copper(II) to nickel(II) complexes, the large negative J value can be justified only by assuming a sizeable antiferromagnetic contribution of J_{z^2,z^2} in equation (232). Since d_{z^2} is only moderately antibonding with respect to the benzoate bridging groups, J_{z^2,z^2} should be mainly determined by direct exchange between the two d_{z^2} orbitals which point towards each other in the molecule. This result is the first example of a significant contribution of direct exchange mechanisms to the magnetic coupling in transition metal complexes of copper acetate type.

Oxalate anion and dianions of oxamic acid and oxamide (as well as substituted forms) coordinate nickel(II) in a bis-bidentate fashion. The nickel atom can be six-,[2982–2986] five-[2983] and four-coordinated,[2984] and the observed coupling is always antiferromagnetic. On passing from oxalate to squarate[2955] the net exchange interaction drastically decreases. This was attributed to the larger electronic delocalization of the squarate dianions which causes a stabilization of the highest occupied molecular orbitals and consequently these orbitals interact less with the nickel d orbitals[2977] leading to smaller $\Delta\varepsilon$ values in equation (232).

(iii) *Heterocyclic amines and related bridges*

The aromatic diamine 1,8-naphthyridine (napy) forms the dinuclear complex $[Ni_2Br_2(napy)_4]BPh_4$.[2969] The four napy ligands bridge the two nickel atoms, which are in a slightly distorted square pyramidal environment with one bromine atom in the axial position. The formal oxidation state of nickel is 1.5 and the dimer can be described as a mixed valence compound containing Ni^I and Ni^{II}. The EPR spectra of $\{Ni_2Br_2(napy)_4]BPh_4$ can be interpreted as due to a spin quartet split by a large zero field splitting, the g values of the low lying Kramers doublet being $g_{\parallel} = 2.19$ and $g_{\perp} = 4.30$.[2970] This result agrees with the magnetic susceptibility data which were interpreted assuming that a ferromagnetic coupling is operative between the two nickel atoms, one having $S = 1$, the other having $S = \frac{1}{2}$. The separation between the ground quartet state and the first excited doublet state is $\frac{3}{2}J$ with $J > 600\,cm^{-1}$. Such a large coupling has been rationalized[2970] using an extension of the Hoffmann model[2977] and was attributed to a one-centre exchange integral which was found to contribute to the ferromagnetic term of the exchange integral.

(iv) *Heterodinuclear nickel(II) complexes*

Exchange interactions in heterodinuclear transition metal complexes have attracted the attention of many researchers in the last few years. Nickel(II)–copper(II) dimers are, in a sense, the simplest systems to be investigated and several complexes containing paramagnetic nickel(II) and copper(II) ions have been reported, as pure complexes[2985–2987] or as impurities in a parent lattice.[2959,2987–2991] Magnetic susceptibility or EPR spectroscopy has been used to

Table 112 Magnetic and EPR Parameters for M(II)–Nickel(II) Exchange-coupled Pairs

Complex	g_1	g_2	g_3	A_1	A_2	A_3	J	*Ref.*
$[Cu_2(Ni)(PNO)_2Cl_4(H_2O)_2]$	2.49	2.54	2.14			35		2987
$[Ni_2(Cu)(bdhe)_2](ClO_4)_2$	2.02	2.03	2.80					2992
$[Ni_2(Co)(bdhe)_2](ClO_4)_2$	3.47	0.66	0.77					2992
$[Ni_2(Co)(DBA)_2(py)_4]$	1.23	0.38	2.10					2989
$[Ni_2(Co)(dhph)_2(H_2O)_4]Cl_4\cdot 2H_2O$	0.93	2.09	0.60	—	36	84		2993
$[Ni_2(Cu)(DBA)_2(py)_4]$	2.21	2.25	2.15			45		2989
$[Ni_2(Cu)(dhph)_2(H_2O)_4]Cl_4\cdot 2H_2O$	2.21	2.25	2.07			47		2993
$[CuNiLCl_2]$	2.41	2.49	2.09			49	−206	2990, 2991
$[CuNi(fsa)_2en(H_2O)_2]\cdot H_2O$	2.28		2.20				−142	2985 2986
$[Cu\{(prp)_2en\}Ni(hfacac)_2]$							−96	2988
$[Cu_2(Ni)Bz_4(quinoline)_2]$	4.51	3.44	2.24			94		2959

Abbreviations: L, see Table 111; bdhe = *N,N*-bis(2-diethylaminoethyl)-2-hydroxyethylamine; DBA = 1,5-diphenyl-1,3,5-pentanetrionato; dhph = 1,4-dihydrazinophthalazine; $H_4(fsa)_2en$ = *N,N'*-bis(2-hydroxy-3-carboxybenzylidene)-1,2-diaminoethane; $(prp)_2en$ = *N,N'*-ethylenebis[2-hydroxypropiophenone iminato].

characterize the nature of the low-lying energy levels arising from the exchange interaction. For two complexes the two techniques have been used together.[2985,2986,2990,2991] The most relevant magnetic and EPR parameters for nickel(II)–copper(II) complexes are reported in Table 112.

The low-lying states arising from the coupling between nickel(II) ($S_1 = 1$) and copper(II) ($S_2 = \frac{1}{2}$) can be described, in a spin Hamiltonian formalism, using the total spin $S = S_1 + S_2$. Two states can arise with $S = \frac{3}{2}$ and $\frac{1}{2}$ respectively. In all the pure nickel(II)–copper(II) complexes reported to date[2985,2987–2991] the exchange interaction is antiferromagnetic making the $S = \frac{1}{2}$ state the lowest in energy with the $S = \frac{3}{2}$ state at $-\frac{3}{2}J$ above, while in nickel(II)-doped $[Cu_2(bz)_4(quinoline)_2]$ a ferromagnetic interaction was apparent from the analysis of the EPR spectra.[2959,2982]

The EPR spectra have always been interpreted[2994] using an effective $S' = \frac{1}{2}$ spin Hamiltonian including the Zeeman term, $\mu_B \boldsymbol{B}\cdot\boldsymbol{g}\cdot\boldsymbol{S}'$, and the hyperfine term, $\boldsymbol{I}_{Cu}\cdot\boldsymbol{A}\cdot\boldsymbol{S}'$, which describes the interaction of the unpaired electrons with the copper nucleus ($I_{Cu} = \frac{3}{2}$). The spectra are very sensitive to the ratio between the isotropic coupling constant J and the local zero field splitting of nickel(II), D_{Ni}.[2982] In the limit $J \gg D_{Ni}$ it can easily be shown that the following relations hold:

$$S = \tfrac{1}{2} \qquad M_s = \pm\tfrac{1}{2} \qquad g = \tfrac{4}{3}g_{Ni} - \tfrac{1}{3}g_{Cu} \qquad A = -\tfrac{1}{3}A_{Cu} \tag{233}$$

$$S = \tfrac{3}{2} \qquad M_s = \pm\tfrac{1}{2} \qquad g = \tfrac{2}{3}g_{Ni} + \tfrac{1}{3}g_{Cu} \qquad A = \tfrac{1}{3}A_{Cu} \tag{234}$$

$$M_s = \pm\tfrac{3}{2} \qquad g_{\parallel} = 2g_{\parallel Ni} + g_{\parallel Cu}; \qquad g_{\perp} = 0 \qquad A_{\parallel} = A_{\parallel Cu}; \qquad A_{\perp} = 0 \tag{235}$$

The deviation of g from the limit of equations (233)–(235) becomes sensitive from $J/D_{Ni} \leq 2$ while the A values are much more sensitive to J/D_{Ni}. In the general case equations (236) and (237) must be applied:

$$\boldsymbol{g} = \boldsymbol{M}_{Cu}\cdot\boldsymbol{g}_{Cu} + \boldsymbol{M}_{Ni}\cdot\boldsymbol{g}_{Ni} \tag{236}$$

$$\boldsymbol{A} = \boldsymbol{M}_{Cu}\cdot\boldsymbol{g}_{Cu} \tag{237}$$

where $\boldsymbol{M}_{Cu}$ and $\boldsymbol{M}_{Ni}$ are matrices defined in refs. 2994 and 2995.

Equations (236) and (237) have been used[2994] to interpret the spectra of some nickel(II)–copper(II) pairs for which hyperfine values were observed. The J/D_{Ni} ratios were found to be −1.2, 14 and 12 for $[Cu_2(Ni)(bz)_4(quinoline)_2]$, $[Cu_2(Ni)(pyO)_2Cl_4(H_2O)_2]$ and $[Cu_2(Ni)LCl_2]$ (L = dianion of 11,23-dimethyl-3,7,15,19-tetraazatetracyclo[9.3.1.1]hexacosa-2,7,9,11,13(26),14,19,21(25),22,24-decaene-25,26 diol) respectively.

Equations (233)–(235) can be used to guess the g values of the nickel(II), which is generally EPR silent, from the g values of the Cu–Ni pair once the g values of the copper(II) ion are known. g values of nickel(II) obtained in this way are shown in Table 113. Although the actual values can be affected by the zero field splitting of nickel(II), they reflect the symmetry of the complexes. In fact quasi-isotropic g values are computed for octahedral complexes, the anisotropy increasing on passing to square pyramidal and trigonal bipyramidal chromophores. In this last case the g values are very anisotropic. Since orbital degeneracy of the ground state can have measurable effects in trigonal bipyramidal chromophores a different treatment of the experimental data can be required.

Table 113 g Values of Nickel(II) Complexes Computed from the Spectra of Cu—Ni Pairs

Complex	*Donor set*	*Geometry*	g_1	g_2	g_3	*Ref.*
$[Ni_2(Cu)(DBA)_2py_4]$	O_4N_2	Oh	2.18	2.20	2.21	2989
$[Ni_2(Cu)(dhph)_2(H_2O)_4]Cl_4\cdot 2H_2O$	N_4O_2	Oh	2.16	2.17	2.21	2993
$[CuNi(fsa)_2en(H_2O)_2]\cdot H_2O$	O_6	Oh	2.20	2.24	2.24	2985
$[CuNiLCl_2]$	N_2O_2Cl	SqPl	2.12	2.32	2.38	2890
$[Cu_2(Ni)(PNO)_2Cl_2(H_2O)_2]$	O_2Cl_2O	SqPl	2.17	2.36	2.48	2987
$[Ni_2(Cu)(bdhe)_2](ClO_4)_2$	N_3O_2	TBPy	2.06	2.09	2.61	2992

50.5.10.2 Oligonuclear complexes and extended systems

Selected examples of oligonuclear and extended chain complexes of nickel(II) which have been magnetically characterized are shown in Table 114.

Table 114 Selected Examples of Oligonuclear and extended Chain Nickel(II) Complexes[a]

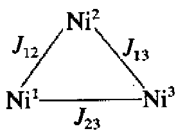
Complex	Type[b]	Donor set	N^c	Bridging atom or group	Bond distances Ni—X (pm)	Bond distances Ni—Ni (pm)	Bond angle Ni—X—Ni (°)	J_{ij}	D	E/D	g	Ref.
$[Ni_3(acac)_6]$	LT	O_6	3	O	199–291	286	75.2	25 −9	1.3	0	2.175	2996, 2997
$[Ni_3\{(triaz)_3(OH_2)_3\}_2](NO_3)_6$	LT	N_6	3	triaz				−18 8	—	—	2.048	2998, 2999
$[Ni_3\{(bztriaz)_3[N(C_3H_5)H_2]_3\}_2]\cdot 2PPh_3O$	LT	N_6	3	bztriaz		373		−10 0–8	—	—	2.13–2.16	3000, 3001
$[Ni_3(TFDAA)_2(OH)_2(H_2O)_6]$	LT	O_4O_2	2	O				20 −12	—	—	2.285	3002
$[Ni_4(OMe)_4(acac)_4(MeOH)_4]$	Cubane	O_6	3	O				14			2.17	3003
$[Ni_4(OMe)_4(o\text{-}OC_6H_4CHO)_4(EtOH)_4]$	Cubane	O_6	3	O	204		98	14			2.17	3004
$[Ni_4(OMe)_4(o\text{-}C_6H_4CHO)_4(MeOH)_4]$	Cubane	O_6	3	O				8 −18			2.21	3004
$[Ni_4(OMe)_4(OAc)_2(TMB)_4](BPh_4)_2$	Cubane	O_6	3	O	206	320	98	35 34			2.00	3005
$[Ni(en)_2NO_2]ClO_4$	LC	N_4NO	1	NO_2	216 (N) 218 (O)	515		−33	—	—	2.23, 2.15, 2.21	3006
$[Ni(en)_2NO_2]I_3$	LC	N_4NO	1	NO_2	220	523		−32	0.6		2.12	3006
$[Ni(bipy)(NCS)_2]$	Zigzag chain	$N_2N_2S_2$	2	NCS				8			2.21	3007
$[Ni(4\text{-}Phpy)_2Cl_2]$	LC	N_2Cl_4	2	Cl				11.8	3.6		2.06	3008
$[Ni(pz)_2Cl_2]$	LC	N_2Cl_4	2	Cl				9.7	18		2.32	3009
$[Ni(pz)_2Br_2]$	LC	N_2Br_4	2	Br				3.5	18		2.34	3009
$[Ni(py)_2Cl_2]$	LC	N_2Cl_4	2	Cl				6.9	17		2.32	3009
$[Ni(py)_2Br_2]$	LC	N_2Br_4	2	Br				4	16		2.32	3009
$[Ni(C_4O_4)(C_3N_2H_4)(H_2O)_2]$	Chain	$N_2O_2O_2$	1	C_4O_4	212			0	6		2.28	3010
$[Ni(acac)_2(2,5\text{-}Me_2pyr)]$	LC	N_2O_4	2	Pyrazine				−1	—		2.22	3011
$[Ni(hipp)_2(H_2O)_3]H_2O$	LC	O_4O_2	1	H_2O	212	394	137	−25.8	—		2.20	3012

[a] The magnetic parameters are defined in the text.
[b] LT = linear trimer; LC = linear chain.
[c] Number of bridging atoms.
Abbreviations: triaz = triazole; bztriaz = benzotriazole; TMB = 2,5-dimethyl-2,5-diisocyanohexane; pz = pyrazole; 2,5-Me_2pyr = 2,5-dimethylpyrazine; hipp = hippurato; TFDAA, 1,1,7-trifluoro-2,4,6-heptanetrionato.

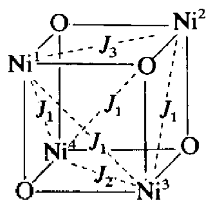
Several exchange interactions are possible in a trinuclear cluster of paramagnetic centres. The general configuration of a trinuclear cluster is shown in structure (413). The spin Hamiltonian for this configuration is

$$\mathscr{H} = -J_{12}(S_1 \cdot S_2) - J_{23}(S_2 \cdot S_3) - J_{13}(S_1 \cdot S_3) \tag{238}$$

In all of the trinuclear complexes reported in Table 114 the nickel atoms lies along the same axis forming a linear trimer. In this configuration $J_{12} = J_{23} = J$, $J_{13} = J'$ and the magnetic properties are essentially determined by J and J'/J. From the exchange interaction one $S = 3$ state, two $S = 2$ states, three $S = 1$ states and one $S = 0$ state originate. When J is positive the ground state is always paramagnetic the exact nature depending on the sign of J' and on the J'/J ratio. If $J' > 0$ or $J' \ll J$ the ground state is the $S = 3$ septet. When J is negative the ground state is diamagnetic for $0.5 < J'/J < 2$. A theoretical analysis of the temperature and field dependence of the magnetic susceptibility of linear nickel(II) trimers can be found in ref. 3013. The effect of the local zero field splitting of the nickel(II) ion has been considered in refs. 2997 and 2998.



(413)



(414)

A number of cubane-type complexes containing the $[Ni_4(OMe)_4]^{4+}$ species have been described.[2974,3003–3005] The possible exchange interactions occurring in a cubane-type complex are shown in (**414**). The exchange interactions occur between the nickel atoms which lie on one of the diagonals of the face of the cube. These nickel atoms are bridged by two oxygen atoms of the OMe groups. The general spin Hamiltonian which describes the magnetic coupling in these complexes is

$$\mathscr{H} = -\Sigma_{i>j} J_{ij} S_i \cdot S_j \tag{239}$$

where the summation runs over the four nickel atoms. Assuming that all the bond distances and angles are equal, the pairwise interactions are identical and only five spin states, among the 19 possible states arising from equation (239), have different energies. In this case the temperature dependence of the magnetic susceptibility becomes[3003]

$$\chi = (4N\mu_B^2 g^2/kT)\frac{5e^{20x} + 7e^{12x} + 5e^{6x} + e^{2x}}{3e^{20x} + 7e^{12x} + 10e^{6x} + 6e^{2x} + 1} \tag{240}$$

where $x = J/kT$ and N is Avogadro's number. Equation (240) was used to fit the temperature dependence of the magnetic susceptibility of $[Ni_4(OMe)_4(acac)_4(MeOH)_4]$,[3003] $[Ni_4(o\text{-}OC_6H_4CHO)_4(EtOH)_4]$[3004] and $[Ni_4(OMe)_4(o\text{-}OC_6H_4CHO)_4(MeOH)_4]$.[3004] In each case the net exchange interaction was found to be ferromagnetic. The sign of the interaction has been related to the approximately right angled Ni—O—Ni bridges.

In the case of $[Ni_4(OMe)_4(OAc)_2(TMB)_4](BPh_4)_2$[3005] equation (240) was found inadequate to fit the magnetic data and a more complicated expression for the temperature dependence of the magnetic susceptibility was derived[3005,3014] considering three different exchange interactions: $J_1 = J_{13} = J_{23} = J_{24} = J_{14}$, $J_2 = J_{34}$ and $J_3 = J_{12}$. The results of the fitting were $J_1 = 18.2\ \text{cm}^{-1}$, $J_2 \approx J_3 = 35\ \text{cm}^{-1}$. The difference in sign between the J values was attributed to the presence of the acetate groups which are bridging Ni¹—Ni² and Ni³—Ni⁴. This causes a distortion of the $[Ni_4(OMe)_4]^{4+}$ moiety and produces two types of Ni—O—Ni angle. The Ni¹—O—Ni² and Ni³—O—Ni⁴ angles are *ca.* 93°, the other angles being *ca.* 101°. It has been suggested that the 101° angles lead to a net antiferromagnetic interaction, J_1, while the 93° angles cause the net ferromagnetic interactions J^3 and J^4.

The physical properties of low dimensional magnetic materials have attracted the attention of many researchers.[3015] Several nickel(II) linear chain complexes have been synthesized and selected examples are reported in Table 114. The magnetic properties of linear chain complexes have been interpreted using the Hamiltonian

$$\mathscr{H} = -J\Sigma_{i<j}[aS_{iz}S_{jz} + b(S_{ix}S_{jx} + S_{iy}S_{jy})] \tag{241}$$

where J is the nearest neighbour exchange coupling constant. In the case $a = 1$, $b = 0$ the Ising model is found[3016] and for $a = 0$, $b = 1$ the XY model is reached.[3017] The isotropic or Heisenberg model[3018] is obtained when $a = b = 1$. An exact solution of equation (240) is possible in the case of the Ising model[3016] and the following expressions for the magnetic susceptibility parallel and perpendicular to the chain axis have been obtained:

$$\chi_{\parallel} = (N\mu_B^2 g^2/4kT)e^{2x} \tag{242}$$

$$\chi_{\perp} = (N\mu_B^2 g^2/16kT)(\tanh x + \mathrm{sech}^2 x) \tag{243}$$

where $x = J/kT$.

A closed expression for the temperature dependence of χ has also been obtained for a linear chain of $S = 1$ extrapolating the results of calculations performed on ring chains of increasing lengths[3019] as follows:

$$\chi = (N\mu_B^2 g^2/kT)\frac{2 + 0.019x + 0.777x^2}{3 + 4.346x + 3.232x^2 + 5.834x^3} \tag{244}$$

where $x = J/T$. Equation (244) is valid only for antiferromagnetic coupling and was used to fit the temperature dependence of the magnetic susceptibility of $[Ni(en)_2NO_2]I_3$[3006] in the temperature range 3.8–300 K.

The magnetic properties of compounds of general formula NiL_2X_2 (L = pyridine, pyrazole, 4-methylpyridine; X = Cl, Br) have been investitated in detail.[3008,3009] The metal ions are octahedrally coordinated by two L molecules and four X^- ions. The octahedra share an edge of X^- ions to form linear chains of metal ions. The temperature dependence of the magnetic susceptibility showed that the nickel(II) ions are ferromagnetically coupled and possess large single ion anisotropy. In order to fit the magnetic data a molecular field approach was used with the Hamiltonian[3020]

$$\mathscr{H} = -DS_z^2 + \mu_B g(B_xS_x + B_yS_y + B_zS_z) + A\boldsymbol{S}\langle \boldsymbol{S}\rangle \tag{245}$$

where the molecular field parameter A is related to the isotropic exchange by $-\sum J_{ij}\boldsymbol{S}_i \cdot \boldsymbol{S}_j \approx -ZJ\boldsymbol{S}\langle \boldsymbol{S}\rangle = A\boldsymbol{S}\langle \boldsymbol{S}\rangle$ where Z is the number of nearest neighbour spins ($Z = 2$ in a linear chain). For $kT \gg A$, D, the following equations hold:

$$\chi_{\parallel} = (2N\mu_B^2 g^2/3kT)[1 + (D - 4A)/6kT] \tag{246}$$

$$\chi_{\perp} = (2N\mu_B^2 g^2/3kT)[1 - (D - 2A)/3kT] \tag{247}$$

Equations (246) and (247) were used to fit the temperature dependence of the magnetic susceptibilities of NiL_2X_2 complexes from 20 to 300 K. The results of the fitting are shown in Table 114. At temperatures below 20 K long range antiferromagnetic interactions occurred which led to interesting behaviour of the compounds in applied magnetic fields. In particular the 4-methylpyridine complex showed a transition to a metamagnetic phase at about 9 K. From a magnetic point of view this complex can be described as an assembly of ferromagnetic linear chains with the single ion anisotropy larger than the intrachain interaction. In the ordered state the chains are coupled by an antiferromagnetic interchain interaction, J', with $J'/J \approx 10^{-2}$. This ordered state can undergo a metamagnetic phase transition when the applied field is large enough to overcome the interchain interaction causing the spins to 'flip' directly to the saturated paramagnetic state.

50.6 NICKEL(III) AND NICKEL(IV)

50.6.1 Introduction

Nickel(III) and nickel(IV) complexes are generally highly reactive leading to oxidation of a variety of organic substrates to form the more stable nickel(II) complexes.

The earliest examples of higher oxidation states of nickel were given in 1913[3021] and the first nickel(III) complex, $Ni(PEt_3)_2Br_3$, was isolated by Jensen in 1936.[3022] In 1907 Hall reported the occurrence of nickel(IV) in a heteropolymolybdate,[3023] and in 1951 Nyholm described the synthesis of a nickel(IV) complex with the chelating arsine *o*-phenylenebisdimethylarsine (diars).[3024] In the last 15 years the chemistry of nickel(III) and nickel(IV) complexes has largely developed due to the use of electrochemical methods of synthesis.

A review article describing nickel(I), nickel(III) and nickel(IV) complexes appeared in 1980[3025] and in 1981 another review article dealing specifically with nickel(III) was published.[3026] Other articles covering some general aspects of the chemistry of nickel(III) and nickel(IV) complexes are in refs. 3027–3030.

In the present article we will not try to give an exhaustive compilation of nickel(III) and nickel(IV) complexes due to the large amount of work which is currently being undertaken in the field. Particular attention will be placed on those complexes whose properties have been investigated with the largest number of experimental techniques to have a better description of the electronic and geometrical structure of the compounds.

We will first review the general synthetic routes and characteristics of nickel(III) and nickel(IV) complexes. A description of the features of the chemistry of the principal known systems arranged according to the nature of the ligands present will follow.

50.6.2 Electronic Structure and Methods of Study of Nickel(III) and Nickel(IV) Complexes

The stabilization of high oxidation states requires ligands with high electron density and/or one or more negative charges in order to allow for some charge delocalization from the ligand to the metal. This charge rearrangement due to bond formation should not however be so large as to give rise to ligand oxidation. The ability to form strong σ bonds is a necessary requisite for a ligand to stabilize the +3 and +4 states in nickel complexes.[3031,3032] As a matter of fact the large majority of well-characterized nickel(III) and nickel(IV) complexes contain F, O and N as donor atoms. In particular, most of the nickel(III) and nickel(IV) complexes have been obtained with the following ligands: open-chain and macrocyclic nitrogen donor systems, deprotonated amides (N donor atoms), and oximes (N donor atoms), oxides and fluorides.

Both nickel(III) and nickel(IV) complexes are usually found in octahedral environments. Less common geometries are the square planar and the trigonal bipyramidal ones.

Monomeric nickel(III) complexes are always paramagnetic with room temperature effective magnetic moments ranging between 1.7 and 2.1 BM, corresponding to one unpaired electron. EPR spectroscopy has been extensively used to characterize nickel(III) complexes in order to determine whether the unpaired electron is in an orbital with predominant metal or ligand character. In the latter case it is more appropriate to describe the complex as a nickel(II)-stabilized ligand radical complex and the $\boldsymbol{g}$ tensor will be almost isotropic and substantially equal to the free electron value ($g_e = 2.0023$). In a true nickel(III) complex the mixing of excited metal orbitals into the ground state, due to the spin–orbit coupling of nickel(III) (free ion spin–orbit coupling constant, $\xi = -715\,\mathrm{cm}^{-1}$), makes the $\boldsymbol{g}$ tensor different from g_e and anisotropic.[3033]

The electronic configuration of a nickel(III) complex is d^7. In a tetragonal ligand field[3034] the ground configuration will be $(d_{xz}d_{yz})^4(d_{xy})^2(d_{z^2})^1(d_{x^2-y^2})^0$ for a square planar or elongated octahedral complex and $(d_{xz}d_{yz})^4(d_{xy})^2(d_{x^2-y^2})^1(d_{z^2})^0$ for a compressed octahedron. In the first case the EPR spectra will show $g_\perp > g_\parallel \approx 2.00$ while in the latter situation the pattern $g_\parallel < g_\perp > 2.00$ will be observed.[3035,3036]

Nickel(IV) complexes have a d^6 electronic configuration and are always diamagnetic or weakly paramagnetic with a temperature-independent magnetic susceptibility. The characterization of these complexes is generally based on the stoichiometry and the electrochemical behaviour.

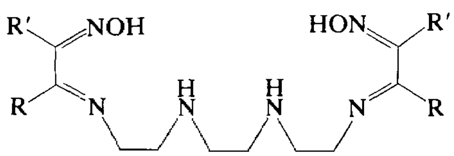
Dynamic voltammetry is currently employed in studying nickel(III) and nickel(IV) complexes, particularly for the characterization of short-lived species and of the kinetic and thermodynamic behaviour of the electron transfer reactions.[3026–3028]

50.6.3 Methods of Synthesis

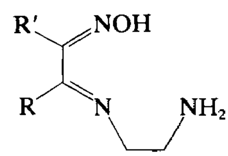
The synthesis of nickel(III) and nickel(IV) complexes is generally performed by oxidizing the parent nickel(II) complexes. The oxidation can be performed with a number of experimental techniques including chemical and electrochemical reactions in aqueous and non-aqueous media, pulse radiolytic techniques and photon irradiation of nickel(II) species (UV, γ or X-radiation) in solid matrices. In the following we will report some examples of the most commonly used synthetic procedures.

50.6.3.1 Chemical oxidation

Concentrated nitric acid has been used to obtain nickel(III) complexes like $[Ni^{III}L(NO_3)_2]ClO_4$ starting from $[Ni^{II}L](ClO_4)_2$ (L = cyclam, Me_6cyclam) in aqueous solutions.[3037] Oxidation of the parent nickel(II) with nitric acid complexes also afforded the nickel(IV) species $[Ni^{IV}L](ClO_4)_2$ where L is the amine–imine–oxime ligand (**415**) or (**416**).[3038–3041]



(**415**) R = R′ = Me
H_2L



(**416**) R = R′ = Me
HT

$S_2O_8^{2-}$ ion has been used in several instances to obtain nickel(III) macrocyclic complexes.[3042,3043]

Ce^{IV} and Co^{III} in dilute aqueous perchloric acid solutions were used to oxidize $[Ni^{II}cyclam]^{2+}$ to form stable nickel(III) complexes.[3044] The iron(III) ion was used in a mixture of water–ethanol to oxidize $[Ni^{II}(diphos)_2]ClO_4$ and $[Ni^{II}(diars)_2]ClO_4$ (diphos = *o*-phenylenebis(dimethylaminophosphine) to give the nickel(III) complexes $[Ni^{III}X_2(diphos)_2]ClO_4$ and $[Ni^{III}X_2(diars)_2]ClO_4$ (X = Cl, Br, I). The chloride derivatives were further oxidized with concentrated nitric acid to form the stable $[Ni^{IV}Cl_2(diphos)_2](ClO_4)_2$ and $[Ni^{IV}Cl_2(diars)_2](ClO_4)_2$ complexes.[3023,3044–3046]

$IrCl_6^{2-}$ has been used to prepare several nickel(III) complexes with peptides.[3047,3048]

The oxidation of nickel(II) complexes of cyclam and Me_6cyclam by NO^+ in acetonitrile solutions has been studied by Barefield and Busch.[3049]

Simek[3050] reported that a solution of nickel(II) dimethylglyoximate in 1–2 mol dm^{-3} KOH was easily oxidized by hypoiodite, hypobromite and peroxodisulfate to a solution containing a nickel(IV) complex. The complex $K_2[Ni^{IV}(DMG)_3]$ (DMG^{2-} = dimethylglyoximate) has been prepared[3051] in aqueous alkaline medium from nickel(II) and DMG^{2-} in the presence of two-electron oxidants such as Cl_2, OX^- (X = Cl, Br, I), $S_2O_8^{2-}$ or higher valent oxides of nickel.

50.6.3.2 Electrochemical methods

Electrochemical techniques are the most widely used methods to obtain nickel(III) complexes. Generally the oxidation of the nickel(II) complexes is performed in acetonitrile solutions under an inert atmosphere using a platinum electrode.[3052] A tetraalkylammonium salt, usually the perchlorate, is employed as supporting electrolyte (*ca.* 0.1 M). The complete procedure is often carried out in the dark at *ca.* 5 °C to prevent possible photoreduction reactions.[3053–3055]

These techniques were first employed[3052] in 1969 to prepare $[Ni^{III}L(MeCN)_2]^{3+}$ (L = cyclam, *rac*- (5,14)-*meso*-(5,12) – $Me_6[14]aneN_4$ and corresponding 4,11 and 4,13 dienes). An extensive study of the electrochemical behaviour of nickeltetraazamacrocyclic systems has been carried out by Busch and co-workers.[3056] Cocolios and Kadish investigated the redox behaviour of nickel(III) porphyrins.[3028]

Aqueous electrolysis has been used by Margerum and co-workers to oxidize oligopeptide complexes of nickel(II).[3047,3057–3059] They used a flow electrolysis system with a graphite powdered electrode packed in a porous glass column externally wrapped with a platinum wire electrode.

50.6.3.3 Pulse radiolytic techniques

Pulse radiolysis is a very powerful technique which can be employed to form solutions of nickel(III) and nickel(IV) complexes. The complexes cannot generally be isolated in the solid state, but their properties can be directly investigated by several physicochemical techniques.

Pulse radiolysis of water is used to generate both reducing (e^-_{aq}) and oxidizing (OH·) agents according to equation (248).[3060] Using appropriate solutes, however, it is possible to obtain completely oxidizing solutions.[3061] For example adding N_2O during radiolysis led to formation of oxidizing OH radicals (equation 249).

$$4H_2O \xrightarrow{100\,\text{eV}} 2.6e^-_{aq} + 2.6OH\cdot + 0.6H + 2.6H^+ + 0.4H_2 + 0.7H_2O \qquad (248)$$

$$e^-_{aq} + N_2O + H_2O \longrightarrow N_2 + OH^- + OH\cdot \qquad (249)$$

Extensive studies have been performed on the reactions of OH· with tetraaza macrocyclic complexes.[3054,3062–3065]

50.6.4 Cyano Complexes

No cyano complexes of nickel(III) and nickel(IV) have been isolated to date.

Pulse radiolytic oxidation of $Ni(CN)_4^{2-}$ by OH· radicals led to a nickel(III) species $Ni(CN)_4^-$ ($k = 9.1 \times 10^9\ M^{-1}\ s^{-1}$).[3066]

X-Ray irradiation of $K_2Ni(CN)_4$ doped into NaCl crystals afforded both nickel(I) and nickel(III) species, $Ni(CN)_4Cl_2^{5-}$ and $Ni(CN)_4Cl_2^{3-}$ which have been characterized by EPR spectroscopy.[3067,3068] The nickel(III) species has been associated with a two cation vacancy. The g values are $g_{\parallel} = 2.008$, $g_{\perp} = 2.153$ and are consistent with a *trans* octahedral structure. Similar results were obtained by electron (2 MeV) irradiation of $K_2Ni(CN)_4$ doped into KCl.[3069] In this case two isomers, *cis* and *trans*, were identified.

50.6.5 Complexes with Nitrogen-containing Ligands

Nitrogen-containing ligands are the most effective systems to stabilize nickel(III) and nickel(IV). The most studied complexes are those formed with macrocyclic ligands. The deprotonated O═CNH— group present in amides and peptides has also been found to be effective in stabilizing nickel(III) as well as the deprotonated oxime ═C═N—O group.

50.6.5.1 Complexes with amines and amino acids

Simple nickel(III) complexes with ammonia,[3070] ethylenediamine,[3061] glycine,[3061] edta[3071] and related species[3071,3072] have been generated in solution by pulse radiolytic techniques. The $Ni(NH_3)_n^{3+}$ species which are formed are considerably less stable than the corresponding $Ni(en)_n^{3+}$ species (half-life *ca.* 50 ms and *ca.* 1 s respectively). All the above species decay *via* a second order process into the corresponding nickel(II) complexes and oxidation products which have been reported to be H_2O_2 and/or N_2H_4 for NH_3 and NH_2CH_2CHO and NH_3 for en.

Nickel(III) complexes with aliphatic diamines have also been obtained by chemical oxidation (X_2 and HNO_3) and isolated as salts of general formula $[Ni(N—N)_2X_2]Y$ (N—N = ethylenediamine, 1,2-diaminopropane, 1,3-diaminopropane, 1,2-diaminocyclohexane, 2,3-diaminobutane, *o*-diaminobenzene; X = Cl, Br; Y = Cl, Br, NO_3, ClO_4).[3073–3078] With N—N = ethylenediamine and 1,2-diaminopropane, depending on the exact reaction conditions, both genuine nickel(III) complexes in a tetragonal coordination or mixed-valence $[Ni^{II}(N—N)_2Ni^{IV}(N—N)_2X_2]Y_4$ (X = Cl; Y = ClO_4) complexes were obtained.[3078]

Nickel(III) complexes of formula $[Ni(N—N)_3](ClO_4)_3$ with N—N = 2,2′-bipyridyl and 1,10-phenanthroline and substituted derivatives have been isolated as products of the electrolysis in acetonitrile of the corresponding nickel(II) salts. Electrode potentials for the Ni^{III}/Ni^{II} couples in MeCN (0.1 M $NaClO_4$) were in the range 1.51–1.82 V.[3079] The same diimine complexes have also been formed in strong acidic solutions.[3080,3081]

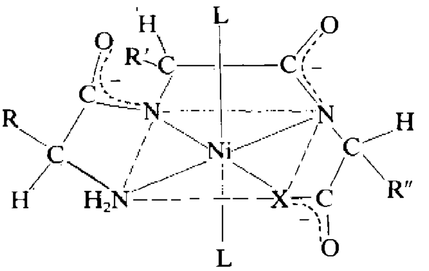
50.6.5.2 Complexes with amides, peptides and related ligands

Deprotonated amides can be very effective in stabilizing nickel(III). Complexes with biuret and substituted biurets have been reported.[3083,3084]

Ligands related to amides such as biguanides (Hbig) and amidinoisourea (ain) have also been reported to form pseudooctahedral complexes of formula $[Ni(Hbig)_2Cl_2]X$ (X = Cl, F), $[Ni(Hbig)_2Br_2]Br$, $[Ni(aiu)_2]Cl$, $[Ni(maiu)_2]_2SO_4\cdot2H_2O$ and $[Ni(eaiu)_2]_2SO_4\cdot2H_2O$ (maiu = methylamidinoisourea; eaiu = ethylamidinoisourea).[3085] Complexes of formula $[NiL_2(H_2O)_2]^{3+}$ (L = *N'*,*N'*-oxydiethylenebiguanide) and $[NiL_3]Cl_3$ (L = *N'*-chlorophenyl-N^5-isopropylbiguanide) have also been obtained.[3086]

Nickel(III) deprotonated peptide complexes can be easily obtained in solution by chemical or electrochemical oxidation of the corresponding nickel(II) complexes. They are moderately stable in aqueous solutions and have been widely characterized by EPR, electron spectroscopy and cyclic voltammetry.[3047,3058,3087,3088] Some selected examples of nickel(III) peptide complexes are reported in Table 115.

The polypeptide complexes have general formula (**417**) according to EPR results.[3087] In (**417**) $X = NH_2$ corresponds to a tripeptideamide.



(**417**)

$L = H_2O$	
R = R′ = R″ = H, X = O	$H_{-2}G_3$
R = R′ = R″ = Me, X = O	$H_{-2}A_3$
R = R′ = R″ = H, $X = NH_2$	$H_{-3}G_3a$
R = R′ = H, R″ = His, X = O	$H_{-2}G_2His$

Formation of the nickel(III) complexes is generally monitored by the changes in the UV-visible spectra which show up intense charge transfer bands[3047,3058] (27 000–31 000 and 38 000–40 000 cm^{-1}; see Table 115) in place of the less intense *d–d* bands observed in the parent nickel(II) complexes. The reduction potentials of the Ni^{III}/Ni^{II} peptide couples are in the range 0.79–0.96 V (*vs.* NHE)[3057] and are not very sensitive to the nature of the equatorial ligands.[3091] Nickel(III) peptide complexes are thus moderately strong oxidants in aqueous solutions. The electron transfer kinetics of the reduction reaction have been studied[3092,3093] as well as the electron transfer kinetics of the reactions between copper(III,II) and nickel(III,II) peptide complexes.[3094]

The complexes are moderately stable in the pH range 5–7; at higher pH decomposition occurs within several minutes.[3095] The behaviour of several complexes in acids has been investigated.[3096]

Tripeptide and tripeptideamide complexes undergo rapid substitution of axial water molecules to form 1:1 and 1:2 adducts with a number of molecules such as ammonia, imidazole, pyridine and terpyridine.[3087,3090,3097,3098] These substituted complexes are generally more stable to redox decomposition in neutral and basic solutions and have a lower reduction potential.

50.6.5.3 Complexes with oximes and related ligands

Oximes have long been known to stabilize higher oxidation states of nickel.[3021] Selected examples of nickel(III) and nickel(IV) complexes with oximes for which X-ray crystal data are available are shown in Table 116.

Alkaline solutions of nickel(II) salts and dimethylglyoxime (H_2DMG) can be readily oxidized to form strongly red coloured solutions[3110] which have been shown to contain nickel(III) and/or nickel(IV) species.[3025,3111–3113] Depending on the exact experimental conditions, nickel(III) or nickel(IV) salts have been obtained.[3050,3099,3112,3114–3118]

The $K_2[Ni(DMG)_3]$ salt has been prepared by oxidation of strongly alkaline solutions of nickel(II) and DMG^{2-} using two-electron oxidants such as Cl_2, OX^- (X = Cl, Br, I), $S_2O_8^{2-}$ or higher valent oxides of nickel.[3051] The solution behaviour of $Ni(DMG)_3^{2-}$ has been widely investigated.[3119]

Table 115 Selected Examples of Nickel(III) Deprotonated Peptide Complexes

Complex[a]	$\nu\ (\varepsilon_M)$[b]	$\nu\ (\varepsilon_M)$	E°[c]	g_x	g_y	g_z	$A_{\perp}$[d]	$A_{\parallel}$[d]	*Ref.*
$Ni(H_{-2}G_3)$	29 400 (4500)	40 000 (11 000)	0.85	2.242	2.295	2.015	—	—	3058, 3087
$Ni(H_{-2}A_3)$	28 980 (4270)	38 460 (10 600)	0.84	—	—	—	—	—	3058, 3087
$Ni(H_{-2}G_2His)$	—	—	0.95	2.256	2.279	2.015	—	—	3058, 3087
$Ni(H_{-3}G_4)^-$	30 580 (5240)	40 000 sh	0.79	2.297	2.278	2.010	—	—	3058, 3087
$Ni(H_{-3}G_5)^-$	30 770 (5820)	41 700 (11 300)	0.83	2.340	2.278	2.011	—	—	3058, 3087
$Ni(H_{-3}G_3a)$	30 770 (5360)	42 550 (10 700)	0.83	2.310	2.281	2.006	—	—	3058, 3087
$Ni(H_{-3}G_3a)NH_3$[e]			0.40	2.217		2.011	—	23.4	3087
$Ni(H_{-3}G_3a)(NH_3)_2$[e]			0.29	2.178		2.019	—	19.0	3087
$Ni(H_{-2}G_3)_2^{3-}$	21 460 (475)	32 470 (4194)	*0.66*	2.151		2.021	—	19.5	3089
	41 700 (14 019)		—						
$Ni(H_{-2}GAG)terpy$	29 500 (15 000)	36 700 (16 000)	0.56	2.168		2.018	16.7	19.8	3090
$Ni(H_{-1}G_2)_2^{2-}$	17 860 (500)	28 170 sh	*0.66*	2.070		2.220	—	—	3035
	39 200 (—)		—						
			0.83						
			—						

[a] The peptides are named according to the constituent amino acids (G = glycine, A = alanine, His = histidine; see text). H_{-n} indicates an *n*-deprotonated peptide.
[b] ν = position of the absorption maxima in cm^{-1}. ε_M = molar extinction coefficient.
[c] E° *vs.* NHE for the couple Ni^{III}/Ni^{II} measured by cyclic voltammetry: carbon paste electrode, scan rate $100\ mV\ s^{-1}$, pH = 9.6 in aqueous 0.1 M $NaClO_4$. Values in italics are estimated values.
[d] Nitrogen hyperfine coupling constant in gauss.
[e] E° measured with $[NH_3] = 1$ M.

Table 116 Selected Examples of Nickel(III) and Nickel(IV) Complexes with Oxime and Related Ligands

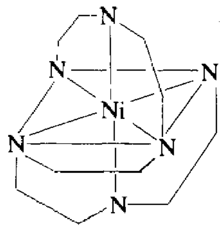
Complex	*Oxidation state*	*Bond distances (av)* (pm)	*Comments*	*Ref.*
$Ni(Hdpg)_2I$	+3	Ni—N, 187; Ni—Ni, 322; I—I, 322	Stacked $Ni(Hdpg)_2^+$ units staggered by 90° and disordered chains of I atoms extending in the *c* direction; semiconductor; $\sigma = 0.0023–0.011$	3098–3100
$Ni(Hbqd)_2I_{0.018}$	+3	Ni—N, 186, 194; Ni—Ni, 318		3101
$Ni(Hbqd)_2I_{0.52}$	+3	Ni—N, 191, 190; Ni—Ni, 315		3101–3103
$Ni(HL)(ClO_4)_2$	+3	—	Pseudoctahedral NiN_6 complex; $g_x = 2.13$, $g_y = 2.15$, $g_z = 2.05$	3104
$Ni(L')I_2$[b]	+3	Ni—C, 190; Ni—N, 204; Ni—I, 262	Square pyramidal complex with one I atom in the axial position; $g_x = 2.37$, $g_y = 2.22$, $g_z = 2.02$, $A_{\parallel}(I) = 140$ G	3105
$Ni(dapd)_2$	+4	Ni—N (pyridine), 184; Ni—N (oxime), 194	Pseudooctahedral NiN_6 complex (molecular symmetry S_4). The two tridentate ligands span meridionally	3106
$Ni(L)(ClO_4)_2$ **(418)**	+4	Ni—N (amine), 199; Ni—N (imine), 187; Ni—N (oxime), 195	Pseudooctahedral NiN_6 complex. The ligand is hexadentate with two amine, two imine and two oxime N atoms	3107
$Ni(T)_2(ClO_4)_2$ **(419)**	+4	Ni—N (amine), 201; Ni—N (imine), 187	Pseudooctahedral NiN_6 complex (molecular symmetry C_2). The two tridentate ligands span meridionally	3108
$Ni(HAO)_2$	+4	Ni—N (hydroxylamine), 180; Ni—N (oxime), 187	Square planar centrosymmetric NiN_4 complex	3109

[a] Electrical conductivity (σ) in Ω^{-1} cm^{-1}.
[b] $L' = o\text{-}C_6H_3(CH_2NMe_2)_2$.
Abbreviations: H_2dpg = diphenylglyoxime; H_2bqd = bisbenzoquinonedioximato; H_2L(**415**) = 3,14-dimethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime; H_2dapd = 2,6-diacetylpyridine dioxime; HT(**416**) = 2-(2-aminoethyl)-imino-3-butanone-oxime; H_2AO = α-Hydroxiamine oxime.

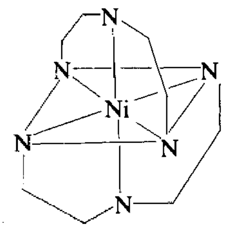
The halogenation (I_2 or Br_2) of $Ni(DPG)_2$ in the absence of coordinating bases yielded lustrous golden needles of composition $Ni(DPG)_2I$[3115] which possess electrical conductivities *ca.* 10^4 times greater than that of Ni(DPG).[3120] The X-ray crystal structure[3098–3100] showed that the crystals consist of stacking $Ni(HDPG)_2^+$ units intercalated by I_5^- species.[3100] Higher electrical conductivity was observed in $Ni(Hbqd)_2I_{0.52}$.[3101–3103]

A series of isomorphous complexes of composition $Ni(HDPG)_2X_p$ ($X = Br$, $p \leq 1.14$; $X = I$, $p \leq 1.02$) have been reported as well as interhalogen species $Ni(HDPG)_2(IBr)_{0.54}$ and $Ni(HDPG)_2I_{0.54}Br_{0.67}$.[3121]

The mixed amine–imine–oxime ligands HL (**415**) and HT (**416**) have been found to be effective in stabilizing nickel(IV). The complexes $Ni(L)(ClO_4)_2$ (**418**) and $Ni(T)_2(ClO_4)_2$ (**419**) can be obtained by oxidation of solutions of the parent nickel(II) complexes with various oxidizing agents (HNO_3, $S_2O_8^{2-}$, PbO_2, $Fe(bipy)_3^{3+}$) or electrochemically.[3038,3040,3122,3123]



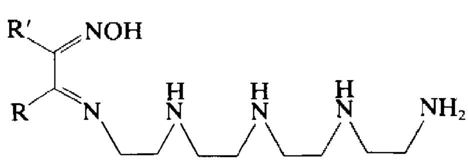
(**418**)



(**419**)

Reduction of $Ni^{IV}L^{2+}$ in aqueous media by two-electron reductants such as 1,2- or 1,4-dihydroxybenzene proceeds by consecutive two-electron transfer with formation of nickel(II) intermediates.[3124,3125] Nickel(III) complexes with (**415**) and (**416**) of formula $Ni^{III}(HL)(ClO_4)_2$ and $Ni^{III}(HT)(ClO_4)_2$ have been obtained by oxidation with $(NH_4)_2S_2O_8$ in borate buffer and alkaline solution respectively of nickel(II) complexes or by exposure of the nickel(IV) complexes to moist air.[3031] The g values of the nickel(III) species are $g_{\parallel} = 2.03–2.05$, $g_{\perp} = 2.15–2.16$.[3039,3104]

Using ligand HY (**420**) only the nickel(III) complex $Ni^{III}(Y)(ClO_4)_2$ was obtained ($g_{\parallel} = 2.03$, $g_{\perp} = 2.13$).[3041]



(**420**) R = R′ = Me
HY

A review article covering the synthesis, characterization and redox properties of imine–amine–oxime ligands has recently appeared.[3030]

50.6.5.4 Complexes with macrocyclic ligands

Macrocyclic ligands, mainly tetraaza macrocycles, have been widely used in stabilizing nickel(III). No nickel(IV) species has been isolated, although many nickel(III) complexes with dianionic macrocyclic ligands undergo one-electron oxidation. In this section we will use the nomenclature of Section 50.5.9 to indicate the macrocycles.

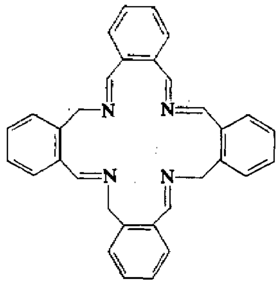
Complexes with macrocyclic ligands have been prepared using chemical oxidation, $(NH_4)_2S_2O_8$, HNO_3[3037,3126–3128] and $NOClO_4$,[3049,3129] electrochemical methods[3052,3130] or pulse radiolysis in aqueous solutions.[3054,3131,3132]

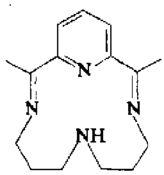
An extensive study of the redox properties of tetraaza macrocyclic complexes of nickel has been performed by Busch and co-workers.[3056,3133,3134] Electrochemical data for selected Ni^{III}/Ni^{II} couples are reported in Table 117. From an analysis of the EPR spectra it has been found that acetonitrile, as well as other molecules or ions like Cl and SO_4, can coordinate in axial position to give six-coordinate complexes.[3056,3141] The g values are indicative of a d_{z^2}

Table 117 Electrochemical Potentials[a] for Selected Ni^{III}/Ni^{II} Couples

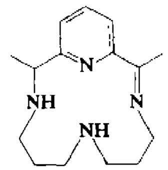
Ligand	E (V)	Ref.
Neutral ligands		
$[12]aneN_4$	+1.082	3035
$[13]aneN_4$	+0.7–+0.9	3056
Cyclam	+0.67	3056
$[15]aneN_4$	+0.90	3056
Me_2cyclam	+0.68	3056
Me_4cyclam	+0.71	3056
Me_6cyclam	+0.87	3056
$Me_6[16]aneN_4$	*ca.* +1.3	3056
$Me_6[14]4,11\text{-}dieneN_4$	+0.98	3056
$Me_6[14]1,4,8,11\text{-}tetraeneN_4$	+1.05	3056
$Me_6[16]4,12\text{-}dieneN_4$	+1.3	3056
$Me_6[16]1,4,12\text{-}trieneN_4$	+1.3	3056
$Me_2[14]1,3\text{-}dieneN_4$	+0.86	3056
TAAB	+1.24	3135
[CR + 4H]	+0.89	3056, 3136
[CR + 2H]	+0.93	3056, 3136
CR	+1.03	3056, 3136
[CR − 2H]	+1.05	3056, 3136
$Me_6[14]1,3,7,11\text{-}tetraeneN_4$	+1.05	3056
$Me_6[14]1,3,8,10\text{-}tetraeneN_4$	+1.00	3056
$Me_2[14]4,7\text{-}dieneN_4$	+0.72	3056
$Me_2[15]8,11\text{-}dieneN_4$	+0.95	3056
$pyaneN_5$	+0.78	3137
Isocyclam	+0.84	3138
$[NiLSO_4]^{3+}$ complexes[b]		
Cyclam	+0.49	3139
Me_6cyclam	+0.64	3139
$Me_6[14]4,11\text{-}dieneN_4$	+0.93	3139
Anionic ligands		
$Me_2[13]dieneN_4^-$	+0.27[c]	3056
$Me_2[14]dieneN_4^-$	+0.23[c]	3056
$Me_2(MeCO)_2[14]tetraeneN_4^{2-}$	+0.97[c]	3056
$Me_4(MeCO)_2[14]tetraeneN_4^{2-}$	+0.98[c]	3056
$Me_2(MeCO)_2[15]tetraeneN_4^{2-}$	+0.92[c]	3056
$Me_6(MeCO)_2[14]tetraeneN_4^{2-}$	+0.96[c]	3056
$Me_2[15]dieneN_5^{2-}$	−0.36[c]	3133, 3134
$Me_2(C_2H_4CO_2Et)_2[15]dieneN_4^{2-}$	−0.39[d]	3133, 3134, 3140
$Me_2(MeCO)[15]dieneN_4^{2-}$	−0.14[c,d]	3133, 3134, 3140
$Me_2(CONH\text{-}\alpha\text{-}C_{10}H_7)_2[15]dieneN_4^{2-}$	+0.003[d]	3133, 3134, 3140
$Me_2(COPh)_2[15]dieneN_4^{2-}$	+0.21[d]	3133, 3134, 3140
$Me_2(NO_2)_2[15]dieneN_4^{2-}$	+0.42[d]	3133, 3134, 3140
$Me_2(MeCO)_2[15]dieneN_4^{2-}$	+0.22	3133, 3134, 3140

[a] *vs.* $Ag/AgNO_3$ (0.1 M) in MeCN reference electrode.
[b] In aqueous solution. The reference electrode is Ag/AgCl.
[c] Irreversible polarograms.
[d] Solutions of DMF.
Abbreviations:

TAAB =




CR



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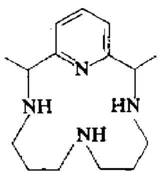

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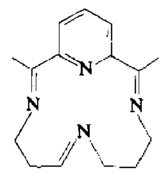
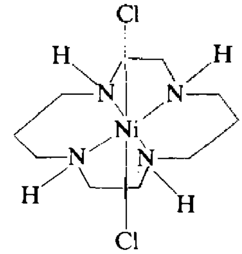


CR − 2H

ground state with $g_\perp$ (*ca.* 2.2) > $g_\parallel$ (*ca.* 2.01–2.03). A single crystal study on γ-irradiated nickel(II) complexes with *rac*-(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) and *rac*-(5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,14-diene) confirmed this interpretation.[3142]

In the case of $[Ni([12]aneN_4)]^{3+}$ a reverse *g* pattern was observed ($g_\parallel = 2.17$, $g_\perp = 2.06$), which was attributed to a larger *in-plane* ligand field strength which stabilizes the $d_{x^2-y^2}$ state as compared to other complexes with *n*-dentate amine macrocycles ($n = 5, 6$) which have the more common d_{z^2} ground state.[3035] The formation of nickel(III) complexes with tetraaza macrocycles is favoured by 14-membered macrocycles and is strongly dependent on the contraction or expansion of the ligand cavity. Penta- and hexa-aza macrocycles are more difficult to obtain than the tetraaza ones, but the ring-size-dependent redox selectivity was found to be drastically reduced in complexes with pentaaza macrocycles.[3035]

Despite the large number of nickel(III) complexes with macrocyclic ligands reported to date only three X-ray crystal structures have been determined. In the $[(Me_6cyclam)Ni(H_2PO_4)_2]ClO_4$[3143] and $[Ni(cyclam)Cl_2]ClO_4$ (**421**)[3144] complexes the nickel atom is in a tetragonal octahedral environment (average Ni—N bond length 200 pm). In the [Ni(TACNTA)] (TACNTA = 1,4,7-triazacyclononane-*N*,*N*′,*N*″-triacetate) the nickel atom is in a pseudooctahedral N_3O_3 environment (Ni—O = 191 pm (av.); Ni—N = 193 pm(av.)).[3145]



(421)

Some complexes of nickel(III) with porphyrins have been prepared electrochemically together with radical ligand species.[3028]

50.6.6 Compounds with Oxygen and Fluorine

Nickel(III) and nickel(IV) form a variety of compounds with oxygen, the most important being binary and ternary oxides and heterpolyanions. The first example of a nickel(IV) complex was a heteropolymolybdate, $Ba_3NiMo_9O_{32}$.[3023] Other polymolybdates and polyniobates are known, of compositions $(NH_4)_6NiMo_9O_{32}$,[3146,3147] $Na_{12}NiNb_{12}O_{38}\cdot xH_2O$ ($x = 48$–50)[3148] and $K_8Na_4NiNb_{12}O_{38}\cdot 12H_2O$.[3148] These salts can generally be prepared by persulfate oxidation of solutions containing $NiSO_4$ and the molybdate or niobate ions. Selected examples of nickel(III) and nickel(IV) compounds with oxygen are collected in Table 118.

NiF_6^{z-} ions have been isolated in a number of salts, for both nickel(III) and nickel(IV). Selected examples of these salts are shown in Table 118. NiF_6^{2-} is diamagnetic and the electronic spectra have been successfully interpreted in O_h symmetry (ground state $^1A_{1g}$).[3178–3180] Several spectroscopic and magnetic studies and molecular orbital calculations have been performed on NiF_6^{3-} ions.[3173,3175,3181,3182] The complex is low-spin with $^2A_{1g}$ as ground state in tetragonal symmetry, but unlike other nickel(III) complexes, the first excited quartet level $^4A_{2g}$ lies at *ca.* 700 cm^{-1} above and can be thermally populated at room temperature.

50.6.7 Complexes with Phosphines and Arsines

A number of nickel(III) complexes with phosphines and arsines have been isolated, but nickel(IV) complexes with the same ligands are still rare. *o*-phenylenebisdimethylarsine (diars) and *o*-phenylenebisdimethylphosphine (diphos) have been found very efficient in stabilizing nickel(IV). Selected examples of nickel(III) and nickel(IV) complexes with phosphines and arsines are shown in Table 119.

Table 118 Selected Compounds of Nickel(III) and Nickel(IV) with Oxygen and Fluorine

Compound	*Remarks*	*Ref.*
Binary oxides		
NiO_2, Ni_2O_3, Ni_3O_4	Oxidizing agents for various organics; never isolated as pure oxides	3149
$NiO(OH)$	Exists in three modifications (α, β and γ). The β form has the brucite structure. The γ form has a $CdCl_2$ structure with an elongated cell	3150–3153
Ternary oxides		
$LiNiO_2$	Rhombohedral with the α-$NaFeO_2$ structure	3154
$NaNiO_2$	Dimorphic. Transition temperature: 493 K. The low temperature phase is monoclinic	3154
$Li_xNi_{1-x}O$ $0<x<0.65$	Obtained by heating $LiNiO_2$ in oxygen atmosphere. For $x \geq 0.28$ the α-$NaFeO_2$ structure occurred. For $x<0.28$ a statistical distribution of cations in the NaCl structure was found	3155
$BaNiO_3$	Hexagonal close packing of BaO_3 sheets. Nickel atoms are aligned in chains through NiO_6 octahedra sharing faces. $SrNiO_3$ is isostructural	3156, 3157
$M_2Ni_2O_5$ (M = Sr, Ba)	Hexagonal layer structure	3156, 3158, 3159
$Ba_{1-x}Sr_xNiO_{3-y}$	Different layer structures according to the composition	3156, 3158, 3159
$Ba_3Ni_3O_8$	Layer structure	3160
$SrNiSbO_6$	Perovskite structure	3156, 3159
$LnNiO_3$ (Ln = La, Y)	$LaNiO_3$ is hexagonal. Metallic conductor between 573 and 77 K. $YNiO_3$ is orthorhombic	3158, 3161–3167
$Ni_{0.25}Pt_3O_4$	The formal oxidation state of Pt is 7/3 implying the presence of nickel(IV). Metallic conductor: $\sigma = 3000\ \Omega^{-1}\ cm^{-1}$ at 300 K	3168
$K_7NiV_{13}O_{38} \cdot 16H_2O$	The structure consists of $NiV_{13}O_{38}$ anions with one NiO_6 and 13 VO_6 octahedra sharing edges	3169, 3170
Compounds with fluorine		
K_3NiF_6	Obtained by fluorination of an $NiSO_4$–3 KCl mixture. Stable under vacuum at 720 K. Tetragonal	3171–3175
Na_3NiF_6	Monoclinic. Isomorphous with Na_3MF_6 (M = Al, Co, Fe)	3173, 3175
M_2NiF_6 (M = Na, K, Rb, Cs),	Obtained by fluorination of nickel(II) salts (300–3000 atm with temperatures up to 700 K). The M_2NiF_6 salts are isomorphous, space group *Fm3m*. Thermal decomposition: $3K_2NiF_6 \rightarrow 2K_3NiF_6 + NiF_2 + F_2$	3171–3173, 3176
$MNiF_6$ (M = Ba, Sr)		3177

Table 119 Selected Nickel(III) and Nickel(IV) Complexes with Phosphine and Arsines

Complex	*Oxidation state*	*Remarks*[a]	*Ref.*
$Ni(PR_3)_2X_3$ R = Me, Et, Pr^n, Bu^n; X = Cl, Br	+3	Obtained by oxidation with Br_2 or NOX (X = Cl, Br) of the parent nickel(II) complexes. μ_{eff} values at room temperature are in the range 1.8–2.2 BM. The stable complex is with PEt_3. No solid complex was obtained with R = phenyl or cyclohexyl	3022, 3183–3185
$Ni(PMe_2Ph)_2Br_3$	+3	Trigonal bipyramidal coordination. The compound crystallizes as $Ni(PMe_2Ph)_2Br_3 \cdot 0.5Ni(PMe_2Ph)_2Br_2 \cdot 0.6C_6H_6$. The crystal contains separated NiL_2X_3 units. Ni—Br = 236 pm; Ni—P = 227 pm; Ni—P—Ni = 178.8°. NiL_2X_2 complexes are square planar	3186, 3187
$Ni(P—P)Br_3$ P—P = $R_2P(CH_2)_2PR_2$(R = Et, Me), $Ph_2P(CH_2)_nPPh_2$(n = 2, 3)	+3	Obtained by bromination of the parent nickel(II) complexes. The complex with $Ph_2P(CH_2)_2PPh_2$ is square planar with the phosphine chelating in the basal plane (C_s symmetry). Ni—P = 224 pm; Ni—Br = 238 pm	3188–3190
$[Ni(diphos)_2X_2]ClO_4$ X = Cl, Br	+3	Prepared by oxidation of nickel(II) complexes with $FeCl_3 \cdot 6H_2O$. μ_{eff} = 1.90	3046
$[Ni(diphos)_2Cl_2](ClO_4)_2$	+4	Prepared by oxidation of $[Ni(diphos)_2Cl_2]ClO_4$ with concentrated nitric acid at 0 °C	3046
$[Ni(diars)_2Cl_2]Cl$	+3	Obtained by air oxidation of an alcoholic solution of $Ni(diars)_2Cl_2$ in the presence of HCl. The complex is in a pseudooctahedral environment with the diars molecules in the equatorial plane (C_{2h} symmetry). Ni—As = 234 pm; Ni—Cl = 242 pm	3024, 3191

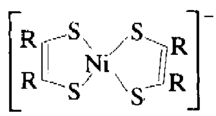
[a] Bond distances are average values over the non-equivalent atoms.

Complexes with monodentate phosphines always contain nickel(III). They have general formulas $Ni(PR_3)_2X_3$ (X = Cl, Br) and are quite unstable. The stability of the complexes increases through the series $PMe_3 \approx PEt_3 > PMe_2Ph \approx PBu_3 > PEt_2Ph > PMePh_2 > PPh_3$.[3185] Complexes with bidentate phosphines (P—P) and arsines (As—As) are considerably more stable. The properties of a number of complexes of general formula $Ni(P—P)X_3$ (X = Cl, Br) have recently been investigated.[3192] The EPR spectra of all the above compounds are generally ill resolved.

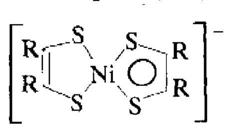
Diars and diphos have been found to stabilize both nickel(III) and nickel(IV). The reduction potentials measured in acetonitrile solutions of the Ni^{III}/Ni^{II} couples for $[NiLCl_2]^+$ are −0.11 and −0.26 (*vs.* SCE) for L = diphos and diars respectively. The reduction is reversible only in the presence of Cl^-. Reversible one-electron oxidation to nickel(IV) species $[NiL_2Cl_2]^{2+}$ occurs, the reduction potentials of the Ni^{IV}/Ni^{III} couples being +0.80 and +0.84 (*vs.* SCE) for L = diphos and diars respectively.[3046] The nature of the ground state in diphos[3193,3194] and diars[3195,3196] complexes has been widely investigated through EPR spectroscopy in frozen solutions and in single crystals of corresponding Co^{III} complexes doped with Ni^{III}. The single crystal spectrum of $[(Ni,Co)(diars)_2Cl_2]Cl$ is axial with $g_{\parallel} = 2.008$ and $g_{\perp} = 2.142$.[3195] For the analogous diphos complex the spectrum is rhombic with $g_x = 2.112$, $g_y = 2.116$ and $g_z = 2.009$.[3193] All the spectra showed well-resolved hyperfine structure due to the interaction of the unpaired electron with the P and As nuclei indicating that the molecular orbital which contains the unpaired electron is largely delocalized on to the ligands.[3033] From the analysis of the EPR spectra of $[Ni(diphos)_2Cl_2]ClO_4$ enriched with ^{61}Ni, Manoharan *et al.*[3194] concluded that the unpaired electron spends 58% of the time on the phosphorus nuclei. The observed *A* values were $A_x = 13 \times 10^{-4}$, $A_y = 12 \times 10^{-4}$ and $A_z = 25 \times 10^{-4}\,cm^{-1}$.

50.6.8 Complexes with Sulfur- and Selenium-containing Ligands

1,2-Dithiolenes have been found to stabilize nickel(III) and a number of structural investigations have been performed on nickel(III) dithiolene complexes. Structural data and physical properties of selected compounds are collected in Table 120. The EPR spectra of the $[NiS_4]^-$ unit have been extensively studied in order to decide whether the unpaired electron resides mainly on the metal or on the ligand[3202,3203,3210,3212–3217] giving rise to a true nickel(III) complex (**422**) or to a nickel(II)-stabilized ligand radical complex (**423**).



(**422**)



(**423**)

The analysis of the EPR spectra of $Ni^{III}S_4^-$ showed[3213,3217] that the ground state is $^2B_{2g}$ (d_{yz}^1) in D_{4h} symmetry with a large contribution (roughly 50%) from sulfur p_z orbitals. Many nickel(III) thiolate complexes have a polymeric structure and show electrical transport properties. Two structural motives have been found in these complexes: the segregated stack of donor (D^+) and acceptor (A^-) ions as in $[Et_4N][Ni(mnt)_2]$ or the integrated stack of planar complexes (A^-) and planar organic moieties (D^+). In the segregated stack complexes a pairwise interaction has been generally observed with measured singlet–triplet separation around $500\,cm^{-1}$. In the integrated stack complexes the DA unit can be repeated in a simple way as in $[POZ][Ni(tfd)_2]$ or in more complex arrangements such as $[TTF][Ni(tfd)_2]$ where the repeat unit along *b* is every three chains. The temperature dependence of the magnetic susceptibility in this latter complex has been interpreted in terms of linear antiferromagnetic trimers that are weakly ferromagnetically coupled along *c* to form a trimer ladder.[3204,3205]

The complex $[perylene]_2[Ni(mnt)_2]$ showed the largest electrical conductivity among the nickel dithiolate complexes ($\sigma = 50\,\Omega^{-1}\,cm^{-1}$ at room temperature on single crystals) but it has not yet been structurally characterized.[2218,3219]

The magnetic and charge transport properties of nickel(III) 1,2-dithiolene complexes have recently been reviewed.[3220,3221]

A nickel(IV) complex $(Ph_4As)_2[Ni(imns)_3]$ (imns = $Se_2C{=}C(CN)_2$) has been reported.[3222]

Dithiocarbamates (R_2dtc) stabilize both nickel(III) and nickel(IV) and a review article covering this chemistry has appeared.[3223]

Nickel(III) complexes with dithiocarbamates are still rare, the best examples being $Ni(Et_2dtc)_3$ and $Ni(Bu_2dtc)_2I$. $Ni(Et_2dtc)_3$ has been prepared by oxidation of $Ni(Et_2dtc)_2$ with

Table 120 Structural and Spectroscopic Data for Nickel(III) Dithiolene Complexes

Complex	*Remarks*[a]	*Ref.*
$[Et_4N][Ni(mnt)_2]$	Dimers. Segregated stacks. Ni—Ni′ = 414, 431; Ni—S = 215; Ni′—S = 352. μ_{eff} = 1.0 BM; J = 620 cm^{-1}. SC = 2.9 × 10^{-6} (sem); P = 10^{-8} (sem)	3197–3201
$[MePh_3P][Ni(mnt)_2]$	Dimers. Segregated stacks. Ni—Ni′ = 347, 362; Ni—S = 215; Ni′—S = 359. μ_{eff} = 0.79 BM; J = 490 cm^{-1}	3198, 3202
$[TMPD][Ni(mnt)_2]$	Segregated stacks along a. Ni—S = 215. Curie paramagnetism below 100 K; temperature-independent paramagnetism above 100 K. g_x = 2.14; g_y = 2.06; g_z = 1.991; the z direction is tilted by 40° from the normal to the $[Ni(mnt)_2]^-$ plane. $P < 10^{-9}$	3203
$[TTF][Ni(tfd)_2]$	DADA along a, c; repeat unit along b every three chains. Ferrimagnetic. $SC < 10^{-9}$	3204, 3205
$[PTZ][Ni(tfd)_2]$	DAADDA along b. D—A = 336; A—A = 383; D—D = 340, 390. Temperature-activated paramagnetism. $P \leq 10^{-8}$	3206, 3207
$[POZ][Ni(tfd)_2]$	DA along b. D—A = 366. Curie–Weiss paramagnetism. $P \leq 10^{-8}$	3206, 3207
$[TRP][Ni(tfd)_2]$	DA stacking with non-parallel planes. The angle between the planes is 17°, the distance between planes is 390. Curie–Weiss paramagnetism. g_x = 2.14; g_y = 2.04; g_z = 1.996	3208
$[NMe_3Ph][Ni(mnt)_2]$	Dimers. Segregated stacks along b. Ni—Ni′ = 382, 441; Ni—S = 214; Ni′—S = 380	3209
$[Ph_4As][Ni(cmt)_2]$	Two independent $[Ni(cmt)_2]^-$ units nearly orthogonal. Ni—S = 213. g_x = 2.063; g_y = 2.151; g_z = 1.986; x and y bisect the intraligand and interligand S—Ni—S angles respectively	3210
$[NEt_4][Ni(DDDT)_2]$	Monomeric $[Ni(DDDT)_2]^-$. Ni—S = 215; Ni—Ni′ = 815. Long range antiferromagnetic ordering below 15 K; J = 8.5 cm^{-1}. g_x = 2.119; g_y = 2.057; g_z = 2.022; A_x = 14.2 × 10^{-4} cm^{-1};[b] A_y, A_z < 2 × 10^{-4} cm^{-1} [b]	3211

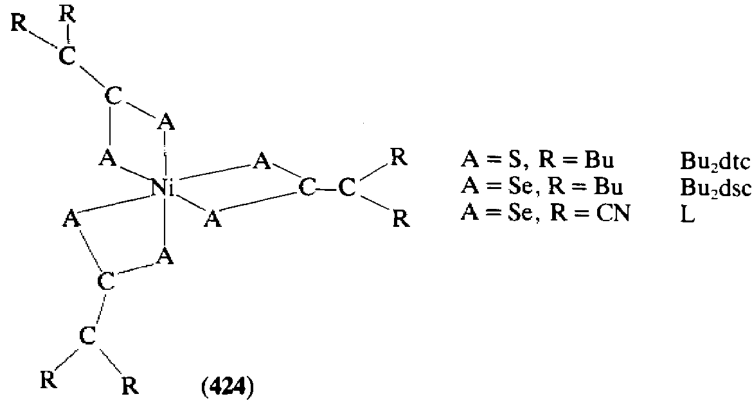
[a] Most relevant structural features and bond distances (pm), μ_{eff} is the effective magnetic moment at room temperature; J is the singlet triplet splitting in the dimeric Ni_2 unit. SC = single crystal conductivity and P = compressed pellets conductivity in Ω^{-1} cm^{-1} at room temperature; sem = semiconducting behaviour.
[b] Hyperfine coupling with ^{61}Ni.
Abbreviations: mnt = maleonitriledithiolato; TTF = tetrathiafulvalene; tfd = *cis*-1,2-bis(trifluoromethylethylene)-1,2-dithiolato; TMPD = *N*,*N*,*N′*,*N′*-tetramethyl-*p*-phenylenediamine; PTZ = phenothiazine; POZ = phenoxazine; TRP = tropylium; cmt = *cis*-1,2-dicarbomethoxyethylenedithiolato; DDDT = 5,6-dihydro-1,4-dithiin-2,3-dithiolato.

80-fold excess of Et_4tds (Et_4tds = thiuram disulfide) and characterized through EPR spectroscopy.[3224] The compound is highly unstable and disproportionates into nickel(II) and nickel(IV) complexes.[3225] $Ni(Bu_2dtc)_2I$ was obtained by iodine oxidation of $Ni(Bu_2dtc)_2$ at −30 °C.[3226]

Nickel(IV) complexes with dithiocarbamates are more stable than the nickel(III) ones. Complexes of formula $[Ni(R_2dtc)_3]X$ (R = Et, Bu; X = Br, I) are generally prepared by halogen oxidation of the parent nickel(II) complexes at room temperature.[3227–3229]

Nickel(IV) complexes having an $NiSe_6$ core have been reported with the ligands *N*,*N*-di-*n*-butyldiselenocarbamato[3230] (Bu_2dsc) and 2,2-diselenido-1,1-ethylenedicarbonitrile (L),[3231] namely $[Ni(Bu_2dsc)_3]Br$ and $[NiL_3][Ph_4As]$.

The X-ray crystal structures of $[Ni(Bu_2dtc)_3]Br$,[3227] $[Ni(Bu_2dsc)_3]Br$[3230] and $[NiL_3][Ph_4As]$[3231] showed that in each complex the nickel atom is in a pseudooctahedral NiA_6 environment (**424**; A = S, Se), slightly twisted towards a trigonal prismatic geometry.



(424)

50.7 REFERENCES

1. J. W. Mellor, 'A Comprehensive Treatise on Inorganic and Theoretical Chemistry', Longmans, London, 1961, vol. XV.
2. D. Nicholls, in 'Comprehensive Inorganic Chemistry', ed. J. C. Bailar, H. J. Emeleus, R. S. Nyholm and A. F. Trotman-Dickenson, Pergamon, Oxford, 1973, vol. 3, p. 1109.
3. R. L. Heath, 'Handbook of Chemistry and Physics', 49th edn., Chemical Rubber Company, Cleveland, OH, 1968.
4. L. J. Kirby, 'The Radiochemistry of Nickel', NAS–NRC Nuclear Science Series, no. 3051, Washington, DC, 1961.
5. F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry', 4th edn., Wiley-Interscience, New York, 1980, p. 785.
6. L. Sacconi, in 'Transition Metal Chemistry', ed. R. L. Carlin, Dekker, New York, 1968, vol. 4, p. 199.
7. P. L. Orioli, *Coord. Chem. Rev.*, 1971, **6**, 285.
8. R. Morassi, I. Bertini and L. Sacconi, *Coord. Chem. Rev.*, 1973, **11**, 343.
9. L. Sacconi, *Coord. Chem. Rev.*, 1972, **8**, 351.
10. E. Uhlig, *Coord. Chem. Rev.*, 1973, **10**, 227.
11. L. Malatesta and S. Cenini, 'Zerovalent Compounds of Metals', Academic, London, 1974.
12. K. Nag and A. Chakravorthy, *Coord. Chem. Rev.*, 1980, **33**, 87.
13. L. Mond, C. Langer and F. Quinke, *J. Chem. Soc.*, 1890, **57**, 749.
14. R. Ugo, *Coord. Chem. Rev.*, 1968, **3**, 319; R. S. Nyholm and M. L. Tobe, *Adv. Inorg. Chem. Radiochem.*, 1963, **5**, 1.
15. L. E. Orgel, 'An Introduction to Transition Metal Chemistry', Methuen, London, 1960.
16. A. G. Sharpe, 'The Chemistry of the Cyano Complexes of Transition Metals', Academic, 1976.
17. J. W. Eastes and W. M. Burgess, *J. Am. Chem. Soc.*, 1942, **64**, 1187.
18. R. Nast and H. Roos, *Z. Anorg. Allg. Chem.*, 1953, **272**, 242.
19. W. Hieber, R. Nast and E. Proeschel, *Z. Anorg. Allg. Chem.*, 1948, **256**, 145.
20. L. Veprek-Siska and S. Lunak, *Collect. Czech. Chem. Commun.*, 1972, **37**, 3846.
21. L. Malatesta and P. Pizzetti, *Gazz. Chim. Ital.*, 1942, **72**, 174.
22. H. Behrens and A. Muller, *Z. Anorg. Allg. Chem.*, 1965, **341**, 124.
23. L. Malatesta, *Prog. Inorg. Chem.*, 1959, **1**, 283.
24. Y. Yamamoto, *Coord. Chem. Rev.*, 1980, **32**, 193.
25. S. D. Ittel, *Inorg. Synth.*, 1977, **17**, 117.
26. S. Otsuka, A. Nakamura and Y. Tatsuno, *J. Am. Chem. Soc.*, 1969, **91**, 6994.
27. S. Otsuka, A. Nakamura, Y. Tatsuno and M. Miki, *J. Am. Chem. Soc.*, 1972, **94**, 3761.
28. M. Green, S. K. Shakshooki and F. G. A. Stone, *J. Chem. Soc. (A)*, 1971, 2828.
29. M. Matsumoto and K. Nakatsu, *Acta Crystallogr., Sect. B*, 1975, **31**, 2711.
30. S. D. Ittel, *Inorg. Chem.*, 1977, **16**, 2589.
31. C. A. McAuliffe, (ed.) 'Transition Metal Complexes of Phosphorus, Arsenic and Antimony Ligands', Macmillan, London, 1973.
32. G. Booth, *Adv. Inorg. Chem. Radiochem.*, 1964, **6**, 1.
33. W. Levason and C.A. McAuliffe, *Adv. Inorg. Chem. Radiochem.*, 1972, **14**, 173.
34. C. A. McAuliffe, *Adv. Inorg. Chem. Radiochem.*, 1975, **17**, 165.
35. W. A. Levason and C. A. McAuliffe, *Acc. Chem. Res.*, 1978, **11**, 363.
36. T. Kruck, *Angew. Chem., Int. Ed. Engl.*, 1967, **6**, 53.
37. P. G. Eller, D. C. Bradley, M. B. Hursthouse and D. W. Meek, *Coord. Chem. Rev.*, 1977, **24**, 1.
38. L. D. Quin, *J. Am. Chem. Soc.*, 1957, **79**, 3681.
39. L. Maier, *Angew. Chem.*, 1959, **71**, 574.
40. J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1960, 1378.
41. T. Kruck and K. Baur, *Chem. Ber.*, 1965, **98**, 3070.
42. G. Wilkinson, *J. Am. Chem. Soc.*, 1951, **73**, 5501.
43. J. F. Nixon, *J. Chem. Soc. (A)*, 1967, 1136.
44. J. F. Nixon and M. D. Sexton, *J. Chem. Soc. (A)*, 1969, 1089.
45. D. C. Staplin and R. W. Parry, *Inorg. Chem.*, 1979, **18**, 1473.
46. R. B. King and M. Chang, *Inorg. Chem.*, 1979, **18**, 364.
47. M. V. Andreocci, C. Cauletti, C. Furlani and R. B. King, *Inorg. Chem.*, 1979, **18**, 954.
48. J. W. Irvine, Jr. and G. Wilkinson, *Science*, 1951, **113**, 742.
49. M. Trabelsi, A. Loutellier and M. Bigorgne, *J. Organomet. Chem.*, 1972, **40**, C45.
50. R. A. Schunn, *Inorg. Chem.*, 1976, **15**, 208.
51. T. T. Tsou, J. C. Huffman and J. K. Kochi, *Inorg. Chem.*, 1979, **18**, 2311.
52. C. A. Tolman, D. H. Gerlach, J. P. Jesson and R. A. Schunn, *J. Organomet. Chem.*, 1974, **65**, C23.
53. C. S. Cundy, *J. Organomet. Chem.*, 1974, **69**, 305.
54. J. Browning, C. S. Cundy, M. Green and F. G. A. Stone, *J. Chem. Soc. (A)*, 1969, 20.
55. J. Browning, M. Green and F. G. A. Stone, *J. Chem. Soc. (A)*, 1971, 453.
56. P. E. Garrou and G. E. Hartwell, *Inorg. Chem.*, 1976, **15**, 730.
57. G. R. Van Hecke and W. de W. Horrocks, Jr., *Inorg. Chem.*, 1966, **5**, 1968.
58. M. Bigorgne and A. Zelwer, *Bull. Soc. Chim. Fr.*, 1960, 1986.
59. J. R. Leto and M. F. Leto, *J. Am. Chem. Soc.*, 1961, **83**, 2944.
60. R. F. Clark and C. D. Storr, *Chem. Abstr.*, 1962, **57**, 16 662c.
61. P. Cassoux, J. M. Savariault and J. F. Labarre, *Bull. Soc. Chim. Fr.*, 1969, 741.
62. C. W. Weston, A. W. Verstuyft, J. H. Nelson and H. B. Jonassen, *Inorg. Chem.*, 1977, **16**, 1313.
63. C. W. Weston, G. W. Bailey, J. H. Nelson and H. B. Jonassen, *J. Inorg. Nucl. Chem.*, 1972, **34**, 1752.
64. C. A. Tolman, W. C. Seidel and D. H. Gerlach, *J. Am. Chem. Soc.*, 1972, **94**, 2669.

65. R. J. De Pasquale, *J. Organomet. Chem.*, 1971, **32**, 381.
66. J. Chatt, F. A. Hart and H. R. Watson, *J. Chem. Soc.*, 1962, 2537.
67. B. Corain, M. Bressan and P. Rigo, *J. Organomet. Chem.*, 1971, **28**, 133.
68. M. Maier, F. Basolo and R. G. Pearson, *Inorg. Chem.*, 1969, **8**, 795.
69. R. S. Vinal and L. T. Reynolds, *Inorg. Chem.*, 1964, **3**, 1062.
70. C. A. Tolman, W. C. Seidel and L. W. Gosser, *J. Am. Chem. Soc.*, 1974, **96**, 53.
71. J. R. McLaughlin, *Inorg. Nucl. Chem. Lett.*, 1973, **9**, 565.
72. L. W. Gosser and C. A. Tolman, *Inorg. Chem.*, 1970, **9**, 2350.
73. C. A. Tolman, *Inorg. Chem.*, 1972, **11**, 3128.
74. T. Huttermann, Jr., B. Foxman, C. Sperati and J. Verkade, *Inorg. Chem.*, 1965, **4**, 950.
75. M. Aresta, C. F. Nobile and A. Sacco, *Inorg. Chim. Acta*, 1975, **12**, 167.
76. A. Morvillo and A. Turco, *J. Organomet. Chem.*, 1982, **224**, 387.
77. T. M. Balthazor and R. C. Grabiak, *J. Org. Chem.*, 1980, **45**, 5425.
78. P. L. Timms, *Chem. Commun.*, 1969, 1033.
79. T. Kruck, G. Mauler and G. Schmidgen, *Z. Anorg. Allg. Chem.*, 1975, **412**, 239.
80. T. Kruck, G. Mauler and G. Schmidgen, *Chem. Ber.*, 1974, **107**, 2421.
81. T. Kruck, M. Hofler and H. Jung, *Chem. Ber.*, 1974, **107**, 2133.
82. A. Almenningen, B. Andersen and E. E. Astrup, *Acta Chem. Scand.*, 1970, **24**, 1579.
83. J. C. Marriott, J. A. Salthouse, M. J. Ware and J. M. Freeman, *Chem. Commun.*, 1970, 595.
84. W. S. Sheldrick, *Acta Crystallogr., Sect. B*, 1975, **31**, 305.
85. C. Krüger and Y. H. Tsay, *Acta Crystallogr., Sect. B*, 1972, **28**, 1941.
86. S. Cenini, B. Ratcliff and R. Ugo, *Gazz. Chim. Ital.*, 1974, **104**, 1161.
87. K. Tanaka, Y. Kawata and T. Tanaka, *Chem. Lett.*, 1974, 831.
88. L. S. Meriwether and M. L. Fiene, *J. Am. Chem. Soc.*, 1959, **81**, 4200.
89. G. Bougnet and M. Bigorgne, *Bull. Soc. Chim. Fr.*, 1962, 433.
90. W. Reppe and W. J. Schweckendiek, *Liebigs Ann. Chem.*, 1948, **560**, 104; K. Jamamoto, *Bull. Chem. Soc. Jpn.*, 1954, **27**, 501.
91. L. S. Meriwether and J. R. Leto, *J. Am. Chem. Soc.*, 1961, **83**, 3192.
92. P. Rigo, M. Bressan and M. Basato, *Inorg. Chem.*, 1979, **18**, 860.
93. G. Booth and J. Chatt, *J. Chem. Soc.*, 1965, 3238.
94. H. D. Smith, Jr., M. A. Robinson and S. Papetti, *Inorg. Chem.*, 1967, **6**, 1014.
95. A. J. Carty, T. W. Nag and A. Efraty, *Can. J. Chem.*, 1969, **47**, 1429.
96. W. D. Horrocks, Jr. and G. R. Van Hecke, *Inorg. Chem.*, 1966, **5**, 1960.
97. R. S. Nyholm, *J. Chem. Soc.*, 1952, 2906.
98. J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1965, 812.
99. R. J. Clark and E. O. Brimm, *Inorg. Chem.*, 1965, **4**, 651.
100. L. Malatesta and A. Sacco, *Ann. Chim. (Rome)*, 1954, **44**, 134.
101. B. Corain, M. Bressan and G. Favero, *Inorg. Nucl. Chem. Lett.*, 1971, **7**, 197.
102. I. H. Sabherwal and A. B. Burg, *Inorg. Chem.*, 1973, **12**, 697.
103. C. A. Ghilardi, A. Sabatini and L. Sacconi, *Inorg. Chem.*, 1976, **15**, 2763.
104. B. Corain, M. Basato and G. Favero, *J. Chem. Soc., Dalton Trans.*, 1977, 2081.
105. B. Corain, L. De Nardo and G. Favero, *J. Organomet. Chem.*, 1977, **125**, 105.
106. C. Krüger and Y. H. Tsay, *Cryst. Struct. Commun.*, 1974, **3**, 455.
107. A. Del Pre, G. Zanotti, L. Pandolfo and P. Segala, *Crystal. Struct. Commun.*, 1981, **7**, 10.
108. M. Baacke, S. Morton, O. Stelzer and W. S. Sheldrick, *Chem. Ber.*, 1980, **113**, 1343.
109. J. Ladell, B. Post and I. Fankuchen, *Acta Crystallogr.*, 1952, **5**, 795.
110. S. Sakaki, K. Kitaura, K. Morokuma and K. Ohkubo, *Inorg. Chem.*, 1983, **22**, 104.
111. T. Ziegler and A. Rauk, *Inorg. Chem.*, 1979, **18**, 1558.
112. B. F. G. Johnson and J. A. McCleverty, *Prog. Inorg. Chem.*, 1966, **7**, 277.
113. N. G. Connelly, *Inorg. Chim. Acta Rev.*, 1972, **6**, 47.
114. K. G. Caulton, *Coord. Chem. Rev.*, 1975, **14**, 317.
115. J. H. Enemark and R. D. Feltman, *Coord. Chem. Rev.*, 1974, **13**, 339.
116. R. Eisenberg and C. D. Meyer, *Acc. Chem. Res.*, 1975, **8**, 26.
117. A. Z. Jahan, *Z. Anorg. Allg. Chem.*, 1959, **301**, 301.
118. G. Booth and J. Chatt, *J. Chem. Soc.*, 1962, 2099.
119. S. A. Bhaduri, I. Bratt, B. F. G. Johnson, A. Khair, J. A. Segal and R. Walters, *J. Chem. Soc., Dalton Trans.*, 1981, 234.
120. W. Hieber and I. Bauer, *Z. Anorg. Allg. Chem.*, 1963, **321**, 107.
121. D. Berglund and D. W. Meek, *Inorg. Chem.*, 1972, **11**, 1493.
122. R. D. Feltham, *Inorg. Chem.*, 1964, **3**, 116.
123. R. D. Feltham, *Inorg. Chem.*, 1964, **3**, 119.
124. W. P. Griffith, J. Lewis and G. Wilkinson, *J. Chem. Soc.*, 1961, 2259.
125. S. Badhuri, B. F. G. Johnson and T. W. Matheson, *J. Chem. Soc., Dalton Trans.*, 1977, 561.
126. P. Rigo, *Inorg. Chim. Acta*, 1980, **44**, L223.
127. M. Di Vaira, C. A. Ghilardi and L. Sacconi, *Inorg. Chem.*, 1976, **15**, 1555.
128. J. H. Meiners, C. J. Rix, J. C. Clardy and J. G. Verkade, *Inorg. Chem.*, 1975, **14**, 705.
129. W. Hieber and I. Z. Bauer, *Z. Naturforsch., Teil B*, 1961, **16**, 556.
130. K. S. Chong, S. J. Rettig, A. Storr and J. Trotter, *Can. J. Chem.*, 1979, **57**, 3090.
131. K. S. Chong, S. J. Rettig, A. Storr and J. Trotter, *Can. J. Chem.*, 1979, **57**, 3099.
132. H. Brunner, *Angew. Chem. Int., Ed. Engl.*, 1967, **6**, 566.
133. K. J. Haller and J. H. Enemark, *Inorg. Chem.*, 1978, **17**, 3552.
134. J. H. Enemark, *Inorg. Chem.*, 1971, **10**, 1952.
135. J. Kriege-Simondsen, G. Elbaze, M. Dartiguenave, R. D. Feltham and Y. Dartiguenave, *Inorg. Chem.*, 1982, **21**, 230.

136. J. Kriege-Simondsen and R. D. Feltham, *Inorg. Chim. Acta*, 1983, **71**, 185.
137. S. J. Rettig, A. Storr and J. Trotter, *Can. J. Chem.*, 1981, **59**, 2391.
138. K. S. Chong, S. J. Rettig, A. Storr and J. Trotter, *Can. J. Chem.*, 1979, **57**, 3107.
139. P. W. Jolly, K. Jonas, C. Krüger and Y. H. Tsay, *J. Organomet. Chem.*, 1971, **33**, 109.
140. G. Herrmann, Dissert. Thesis, Aachen, 1963.
141. K. Jonas, *J. Organomet. Chem.*, 1974, **78**, 273.
142. D. J. Brauer and C. Krüger, *Inorg. Chem.*, 1977, **16**, 884.
143. M. Englert, P. W. Jolly and G. Wilke, *Angew. Chem., Int. Ed. Engl.*, 1971, **10**, 77.
144. A. Greco, M. Green, S. K. Shakshooki and F. G. A. Stone, *Chem. Commun.*, 1970, 1374.
145. G. W. Parshall and F. N. Jones, *J. Chem. Soc.*, 1965, **87**, 5356.
146. J. Ashley-Smith, M. Green and F. G. A. Stone, *J. Chem. Soc. (A)*, 1969, 3019.
147. C. S. Cundy, M. Green and F. G. A. Stone, *J. Chem. Soc. (A)*, 1970, 1647.
148. P. K. Maples, M. Green and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1973, 388.
149. J. Browning and B. P. Penfold, *J. Chem. Soc., Chem. Commun.*, 1973, 198.
150. G. Wilke and G. Herrmann, *Angew. Chem., Int. Ed. Engl.*, 1962, **1**, 549.
151. E. O. Greaves, C. J. Lock and P. M. Maitlis, *Can. J. Chem.*, 1968, **46**, 3879.
152. W. C. Seidel and C. A. Tolman, *Inorg. Chem.*, 1970, **9**, 2354.
153. G. Wilke, E. W. Müller and M. Kroner, *Angew. Chem., Int. Ed. Engl.*, 1961, **73**, 33.
154. H. F. Klein and J. F. Nixon, *Chem. Commun.*, 1971, 42.
155. G. N. Schrauzer, *J. Am. Chem. Soc.*, 1960, **82**, 1008.
156. J. Ishizu, T. Yamamoto and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 2646.
157. P. W. Jolly, I. Tkatchenko and G. Wilke, *Angew. Chem., Int. Ed. Engl.*, 1971, **10**, 328
158. J. Browning, C. S. Cundy, M. Green and F. G. A. Stone, *J. Chem. Soc. (A)*, 1971, 448.
159. P. J. Cheng, C. D. Cook, C. H. Koo, S. C. Nyburg and M. T. Shiomi, *Acta Crystallogr.*, 1971, **27**, 1904.
160. W. Dreissig and H. Dietrich, *Acta Crystallogr., Sect. B*, 1968, **24**, 108.
161. W. Dreissig and H. Dietrich, *Acta Crystallogr., Sect. B*, 1981, **37**, 931.
162. L. J. Guggenberger, *Inorg. Chem.*, 1973, **12**, 499.
163. S. D. Ittel and J. A. Ibers, *J. Organomet. Chem.*, 1974, **74**, 121.
164. D. J. Brauer and C. Krüger, *J. Organomet. Chem.*, 1974, **77**, 423.
165. S. Komiya, J. Ishizu, A. Yamamoto, T. Yamamoto, A. Takenaka and Y. Sasada, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 1283.
166. G. D. Andreetti, G. Bocelli, P. Sgarabotto, G. P. Chiusoli, M. Costa, G. Terenghi and A. Biavati, *Transition. Met. Chem.*, 1980, **5**, 129.
167. M. J. S. Dewar, *Bull. Chem. Soc. Fr.*, 1951, **18**, 79.
168. J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 1953, 2939.
169. K. Tatsumi, T. Fueno, A. Nakamura and S. Otsuka, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 2170.
170. S. Sakaki, M. Kato and T. Kawamura, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 195.
171. K. S. Wheelock, J. H. Nelson, L. C. Cusachs and H. B. Jonassen, *J. Am. Chem. Soc.*, 1970, **92**, 5110.
172. J. H. Nelson, K. S. Wheelock, L. C. Cusachs and H. B. Jonassen, *Inorg. Chem.*, 1972, **11**, 422.
173. N. Rosch, R. P. Messmer and K. H. Johnson, *J. Am. Chem. Soc.*, 1974, **96**, 3855.
174. H. Basch, *J. Chem. Phys.*, 1972, **56**, 441.
175. H. F. Schaefer, III, *Mol. Phys.*, 1977, **34**, 2037.
176. K. Kitaura, S. Sakaki and K. Morokuma, *Inorg. Chem.*, 1981, **20**, 2292.
177. J. G. Norman, *J. Am. Chem. Soc.*, 1974, **96**, 3327.
178. J. K. Stalick and J. A. Ibers, *J. Am. Chem. Soc.*, 1970, **92**, 5333.
179. P. T. Cheng, C. D. Cook, S. C. Nyburg and K. Y. Wan, *Inorg. Chem.*, 1971, **10**, 2210.
180. C. A. Tolman, A. D. English and L. E. Manzer, *Inorg. Chem.*, 1975, **14**, 2353.
181. E. Uhlig and E. Dinjus, *Z. Anorg. Allg. Chem.*, 1975, **418**, 45.
182. D. Walter, *Z. Anorg. Allg. Chem.*, 1974, **465**, 8.
183. E. Uhlig, B. Hipler and P. Mueller, *Z. Anorg. Allg. Chem.*, 1978, **18**, 447.
184. C. A. Tolman, *J. Am. Chem. Soc.*, 1974, **96**, 2780.
185. D. Walther, *Z. Anorg. Allg. Chem.*, 1977, **431**, 17.
186. D. Walther, *J. Organomet. Chem.*, 1980, **190**, 393.
187. E. Dinjus, H. Langbein and D. Walther, *J. Organomet. Chem.*, 1978, **152**, 229.
188. D. J. Sepelak, C. P. Pierpont, E. K. Barefield, J. T. Budz and C. A. Poffenberger, *J. Am. Chem. Soc.*, 1976, **98**, 6178.
189. K. Krogmann and R. Mattes, *Angew. Chem. Int. Ed. Engl.*, 1966, **5**, 1046.
190. M. Matsumoto, K. Nakatsu, K. Tani, A. Nakamura and S. Otsuka, *J. Am. Chem. Soc.*, 1974, **96**, 6777.
191. H. Hoberg, V. Gotz, R. Goddard and C. Krüger, *J. Organomet. Chem.*, 1980, **190**, 315.
192. H. Hoberg, V. Gotz, C. Krüger and Y. H. Tsay, *J. Organomet. Chem.*, 1979, **169**, 209.
193. R. S. Berman and J. K. Kochi, *Inorg. Chem.*, 1980, **19**, 248.
194. S. Otsuka, Y. Aotani, Y. Tatsuno and T. Yoshida, *Inorg. Chem.*, 1976, **15**, 656.
195. A. H. Cowley, R. A. Jones, C. A. Stewart and A. L. Stuart, *J. Am. Chem. Soc.*, 1983, **105**, 3737.
196. R. Countryman and B. R. Penfold, *J. Cryst. Mol. Struct.*, 1972, **2**, 281.
197. J. Kaiser, J. Sieler, D. Walther, E. Dinjus and L. Golic, *Acta Crystallogr., Sect. B*, 1982, **38**, 1584.
198. I. W. Bassi, C. Benedicenti, M. Calcaterra, R. Intrito, G. Rucci and C. Santini, *J. Organomet. Chem.*, 1978, **144**, 225.
199. D. J. Yarrow, J. A. Ibers, Y. Tatsuno and S. Otsuka, *J. Am. Chem. Soc.*, 1973, **95**, 8590.
200. I. W. Bassi, C. Benedicenti, M. Calcaterra and G. Rucci, *J. Organomet. Chem.*, 1976, **117**, 285.
201. G. Favero, A. Morvillo and A. Turco, *J. Organomet. Chem.*, 1983, **241**, 251.
202. J. Clemens, R. E. Davis, M. Green, J. D. Oliver and F. G. A. Stone, *Chem. Commun.*, 1971, 1095.
203. T. A. van Der Knapp, L. W. Jenneskens, H. J. Meenwissen, F. Bickelhaupt, D. Walther, E. Dinjus, E. Uhlig and A. L. Spek, *J. Organomet. Chem.*, 1983, **254**, C33.
204. S. Otsuka, T. Yoshida and Y. Tatsuno, *Chem. Commun.*, 1971, 67.

205. S. Otsuka, T. Yoshida and Y. Tatsuno, *J. Am. Chem. Soc.*, 1971, **93,** 6462.
206. R. S. Dickson, J. A. Ibers, S. Otsuka and Y. Tatsuno, *J. Am. Chem. Soc.*, 1971, **93,** 4637.
207. R. S. Dickson and J. A. Ibers, *J. Am. Chem. Soc.*, 1972, **94,** 2988.
208. S. D. Ittel and J. A. Ibers, *J. Organomet. Chem.*, 1973, **57,** 389.
209. A. Nakamura, T. Yoshida, M. Cowie, S. Otsuka and J. Ibers, *J. Am. Chem. Soc.*, 1977, **99,** 2108.
210. S. D. Ittel and J. A. Ibers, *Inorg. Chem.*, 1975, **14,** 1183.
211. K. D. Schramm and J. A. Ibers, *Inorg. Chem.*, 1980, **19,** 2441.
212. B. Deppish and H. Schafer, *Acta Crystallogr., Sect. B*, 1982, **38,** 748.
213. S. Cenini and G. La Monica, *Inorg. Chim. Acta Rev.*, 1976, **18,** 179.
214. P. Overbosh, G. Van Koten and O. Orerbeek, *Inorg. Chem.*, 1982, **21,** 2373.
215. J. Ashley-Smith, H. Green and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1972, 1805.
216. P. Overbosh and G. Van Koten, *J. Organomet. Chem.*, 1982, **229,** 193.
217. P. Overbosh, G. Van Koten and K. Vrieze, *J. Organomet. Chem.*, 1981, **208,** C21.
218. D. A. Palmer and R. Van Eldik, *Chem. Rev.*, 1983, **83,** 651.
219. J. A. Ibers, *Chem. Soc. Rev.*, 1982, **11,** 57.
220. P. V. Yaneff, *Coord. Chem. Rev.*, 1977, **23,** 183.
221. I. S. Butler, *Acc. Chem. Res.*, 1977, **10,** 359.
222. M. Aresta, C. Nobile, V. G. Albano, E. Forni and M. Manassero, *J. Chem. Soc., Chem. Commun.*, 1975, 636.
223. M. Aresta and C. F. Nobile, *J. Chem. Soc., Dalton Trans.*, 1977, 709.
224. C. Bianchini, C. A. Ghilardi, A. Meli, S. Midollini and A. Orlandini, *J. Chem. Soc., Chem. Commun.*, 1983, 753.
225. S. Sakaki, K. Kitaura and K. Morokuma, *Inorg. Chem.*, 1982, **21,** 760.
226. M. G. Mason, P. N. Swepston and J. A. Ibers, *Inorg. Chem.*, 1983, **22,** 411.
227. M. C. Baird and G. Wilkinson, *J. Chem. Soc. (A)*, 1967, 865.
228. P. Dapporto, S. Midollini, A. Orlandini and L. Sacconi, *Inorg. Chem.*, 1976, **15,** 2768.
229. C. Bianchini, D. Masi, C. Mealli and A. Meli, *J. Organomet. Chem.*, 1983, **247,** C29.
230. C. Bianchini, C. A. Ghilardi, A. Meli and A. Orlandini, *J. Organomet. Chem.*, 1983, **246,** C13.
231. C. Bianchini and A. Meli, *J. Chem. Soc., Chem. Commun.*, 1983, 1309.
232. A. D. Allen, R. O. Harris, B. R. Loescher, J. R. Stevens and R. N. Whiteley, *Chem. Rev.*, 1973, **73,** 11.
233. D. Sellmann, *Angew. Chem., Int. Ed. Engl.*, 1974, **13,** 639.
234. J. Chatt, J. R. Kilworth and R. L. Richards, *Chem. Rev.*, 1978, **78,** 589.
235. P. W. Jolly and K. Jonas, *Angew. Chem., Int. Ed. Engl.*, 1968, **7,** 731.
236. M. G. Mason and J. A. Ibers, *J. Am. Chem. Soc.*, 1982, **104,** 5153.
237. C. Krüger and Y. H. Tsay, *Angew. Chem., Int. Ed. Engl.*, 1973, **12,** 998.
238. K. Jonas, *Angew. Chem., Int. Ed. Engl.*, 1973, **12,** 997.
239. K. Jonas, D. J. Brauer, C. Krüger, P. J. Roberts and Y. H. Tsay, *J. Am. Chem. Soc.*, 1976, **98,** 74.
240. J. K. Burdett and J. J. Turnes, *Chem. Commun.*, 1971, 885.
241. H. Huber, E. P. Kündig, M. Moskovits and G. A. Ozin, *J. Am. Chem. Soc.*, 1973, **95,** 332; W. Klotzbücher and G. A. Ozin, *J. Am. Chem. Soc.*, 1975, **97,** 2672
242. G. A. Ozin and W. E. Klotzbücher, *J. Am. Chem. Soc.*, 1975, **97,** 3965.
243. E. P. Kündig, M. Moskovits and G. A. Ozin, *Can. J. Chem.*, 1973, **51,** 2737.
244. A. J. Rest, *J. Organomet. Chem.*, 1972, **40,** C76.
245. J. J. Turner, M. B. Simpson, M. Poliakoff and W. B. Maier, II, *J. Am. Chem. Soc.*, 1983, **105,** 3898.
246. R. Mason, *Nature (London)*, 1968, **217,** 543.
247. K. Hori, Y. Asai and T. Yamabe, *Inorg. Chem.*, 1983, **22,** 3218.
248. K. I. Goldberg, D. M. Hoffmann and R. Hoffman, *Inorg. Chem.*, 1982, **21,** 3863.
249. J. A. Connor and E. A. V. Ebsworth, *Adv. Inorg. Chem. Radiochem.*, 1964, **6,** 280.
250. J. S. Valentine, *Chem. Rev.*, 1973, **73,** 235.
251. L. Vaska, *Acc. Chem. Res.*, 1976, **9,** 175.
252. R. W. Erskine and B. O. Field, *Struct. Bonding (Berlin)*, 1976, **28,** 3.
253. G. Wilke, H. Shott and P. Heimbach, *Angew. Chem., Int. Ed. Engl.*, 1967, **6,** 92.
254. S. Otsuka, A. Nakamura and Y. Tatsumo, *Chem. Commun.*, 1967, 836.
255. K. Hirota, M. Yamamoto, S. Otsuka, A. Nakamura and Y. Tatsumo, *Chem. Commun.*, 1968, 533.
256. S. Otsuka, A. Nakamura and M. Yamamoto, *J. Am. Chem. Soc.*, 1971, **93,** 6052.
257. K. Tatsumi, T. Fueno, A. Nakamura and S. Otsuka, *Bull. Chem. Soc. Jpn.*, 1976, **49,** 2164.
258. H. Huber, W. Klotzbücher, G. A. Ozin and A. Vander Voet, *Can. J. Chem.*, 1973, **51,** 2722.
259. R. R. Ryan, G. J. Kubas, D. C. Moody and P. G. Eller, *Struct. Bonding (Berlin)*, 1981, **46,** 47.
260. G. J. Kubas, *Inorg. Chem.*, 1979, **18,** 182.
261. C. Mealli, A. Orlandini, L. Sacconi and P. Stoppioni, *Inorg. Chem.*, 1978, **17,** 3020.
262. D. C. Moody and R. R. Ryan, *Inorg. Chem.*, 1979, **18,** 223.
263. L. Sacconi, C. A. Ghilardi, C. Mealli, and F. Zanobini, *Inorg. Chem.*, 1975, **14,** 1380.
264. L. Sacconi, A. Orlandi and S. Midollini, *Inorg. Chem.*, 1974, **13,** 2850.
265. P. Dapporto, S. Midollini and L. Sacconi, *Angew. Chem., Int. Ed. Engl.*, 1979, **18,** 469.
266. M. Di Vaira, M. Peruzzini and P. Stoppioni, *Inorg. Chem.*, 1983, **22,** 2196.
267. M. Di Vaira, M. Peruzzini and P. Stoppioni, *J. Organomet. Chem.*, 1983, **258,** 373.
268. K. Jonas and G. Wilke, *Angew. Chem., Int. Ed. Engl.*, 1969, **8,** 519.
269. R. A. Schunn, *Inorg. Chem.*, 1970, **9,** 394.
270. S. Otsuka, N. Naruto, T. Yoshida and A. Nakamura, *J. Chem. Soc., Chem. Commun.*, 1972, 396.
271. M. Hidai, T. Kashiwagi, T. Ikeuchi and Y. Uchida, *J. Organomet. Chem.*, 1971, **30,** 279.
272. T. Tsou and J. K. Kochi, *J. Am. Chem. Soc.*, 1979, **101,** 6319; C. S. Cundy, *J. Organomet. Chem.*, 1971, **30,** 135.
273. D. H. Gerlach, A. R. Kane, G. W. Parshall, J. P. Jesson and E. L. Muetterties, *J. Am. Chem. Soc.*, 1971, **93,** 3543.

274. E. Uhlig and W. Poppitz, *Z. Anorg. Allg. Chem.*, 1981, **477**, 167.
275. G. Favero, A. Frigo and A. Turco, *Gazz. Chim. Ital.*, 1974, **104**, 869.
276. G. Favero and A. Morvillo, *J. Organomet. Chem.*, 1984, **260**, 363.
277. A. Morvillo and A. Turco, *J. Organomet. Chem.*, 1981, **208**, 103.
278. H. Hoberg, D. Schaefer, G. Burkhart, C. Krüger and M. J. Romao, *J. Organomet. Chem.*, 1984, **266**, 203.
279. H. Hoberg, D. Schaefer and B. W. Oster, *J. Organomet. Chem.*, 1984, **266**, 313.
280. E. Dinjus, J. Kaiser, J. Sieler and D. Walther, *Z. Anorg. Allg. Chem.*, 1981, **483**, 63.
281. J. Kaiser, J. Sieler, U. Braun, L. Solic, E. Dinjus and D. Walther, *J. Organomet. Chem.*, 1982, **224**, 81.
282. H. Hoberg, B. W. Oster, C. Krüger and Y. H. Tsay, *J. Organomet. Chem.*, 1983, **252**, 365.
283. H. Hoberg and K. Summermann, *J. Organomet. Chem.*, 1984, **264**, 379.
284. C. Mealli, S. Midollini, S. Moneti and L. Sacconi, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 931.
285. C. Mealli, S. Midollini, S. Moneti, L. Sacconi, J. Silvestre and T. A. Albright, *J. Am. Chem. Soc.*, 1982, **104**, 95.
286. C. Mealli, S. Midollini, S. Moneti and L. Sacconi, *J. Organomet. Chem.*, 1981, **205**, 273.
287. R. M. Tuggle and D. L. Weaver, *Inorg. Chem.*, 1971, **10**, 2599.
288. R. M. Tuggle and D. L. Weaver, *Inorg. Chem.*, 1971, **10**, 1504.
289. E. W. Golign and S. F. A. Kettle, *Inorg. Chem.*, 1964, **3**, 604.
290. R. B. King and S. Ikai, *Inorg. Chem.*, 1979, **18**, 949.
291. C. Mealli, S. Midollini, S. Moneti and T. A. Albright, *Helv. Chim. Acta*, 1983, **66**, 558.
292. M. Di Vaira, S. Midollini, L. Sacconi and F. Zanobini, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 676; M. Di Vaira, S. Midollini and L. Sacconi, *J. Am. Chem. Soc.*, 1979, **101**, 1757.
293. L. Fabbrizzi and L. Sacconi, *Inorg. Chim. Acta*, 1979, **36**, L407.
294. C. Bianchini, M. Di Vaira, A. Meli and L. Sacconi, *Inorg. Chem.*, 1981, **20**, 1169.
295. C. Bianchini, M. Di Vaira, A. Meli and L. Sacconi, *J. Am. Chem. Soc.*, 1981, **103**, 1448.
296. M. Di Vaira and L. Sacconi, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 330.
297. M. Di Vaira, L. Sacconi and P. Stoppioni, *J. Organomet. Chem.*, 1983, **250**, 183; M. Di Vaira, M. Peruzzini and P. Stoppioni, *Acta Crystallogr., Sect. C*, 1983, **39**, 1210.
298. P. Stoppioni and M. Peruzzini, *J. Organomet. Chem.*, 1984, **262**, C5.
299. A. Bencini and D. Gatteschi, *Transition Met. Chem.*, 1982, **8**, 1.
300. A. Bencini, C. Benelli, D. Gatteschi and L. Sacconi, *Inorg. Chim. Acta*, 1979, **37**, 195.
301. R. Barbucci, A. Bencini and D. Gatteschi, *Inorg. Chem.*, 1977, **16**, 2117.
302. M. J. Nilges, E. K. Barefield, R. L. Belford and P. H. Davis, *J. Am. Chem. Soc.*, 1977, **99**, 755.
303. K. Nag and A. Chakravorty, *Coord. Chem. Rev.*, 1980, **33**, 87.
304. I. Bellucci and R. Corelli, *Atti Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Nat., Rend.*, 1913, **22** (2), 485; I. Bellucci and R. Corelli, *Z. Anorg. Allg. Chem.*, 1914, **86**, 88.
305. J. W. Eastes and W. M. Burgess, *J. Am. Chem. Soc.*, 1942, **64**, 1187; A. A. Vlcek, *Collect. Czech. Chem. Commun.*, 1957, **22**, 948; 1957, **22**, 1736.
306. O. Jarchow, H. Schuttz and R. Nast, *Angew. Chem., Int. Ed. Engl.*, 1970, **9**, 71.
307. W. P. Griffith and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1958, **7**, 295.
308. R. Nast and T. von Krakkay, *Z. Anorg. Allg. Chem.*, 1953, **272**, 233.
309. R. Nast and T. von Krakkay, *Z. Naturforsch., Teil B*, 1954, **9**, 798.
310. N. Tanaka, T. Ogata and S. Niizuma, *Inorg. Nucl. Chem. Lett.*, 1972, **8**, 965.
311. E. Uhlig, E. Dinijus, W. Poppitz and R. Winters, *Z. Chem.*, 1976, **16**, 161.
312. D. C. Olson and J. Vasilevskis, *Inorg. Chem.*, 1969, **8**, 1611.
313. F. V. Lovecchio, E. S. Gore and D. H. Busch, *J. Am. Chem. Soc.*, 1974, **96**, 3109.
314. A. M. Tait, M. Z. Hoffmann and E. Hayon, *Inorg. Chem.*, 1976, **15**, 934.
315. N. Jubran, G. Ginzburg, H. Cohen and D. Meyerstein, *J. Chem. Soc., Chem. Commun.*, 1982, 517.
316. C. W. G. Ansell, J. Lewis, P. R. Raithby, J. N. Ramsden and M. Schröder, *J. Chem. Soc., Chem. Commun.*, 1982, 546.
317. R. R. Gagné and D. M. Ingle, *Inorg. Chem.*, 1981, **20**, 420.
318. P. Heimbach, *Angew. Chem., Int. Ed. Engl.*, 1964, **3**, 648.
319. C. S. Cundy and H. Noth, *J. Organomet. Chem.*, 1971, **30**, 135.
320. L. Porri, M. C. Gallazzi and G. Vitulli, *Chem. Commun.*, 1967, 228.
321. D. G. Holah, A. N. Hughes, B. C. Hui and K. Wright, *Can. J. Chem.*, 1974, **52**, 2990.
322. C. Mealli, P. Dapporto, V. Sriyunyongwat and T. A. Albright, *Acta Crystallogr., Sect. C*, 1983, **39**, 995.
323. D. G. Holah, A. N. Hughes, B. C. Hui and C. T. Kan, *Can. J. Chem.*, 1978, **56**, 2552.
324. G. N. La Mar, E. O. Sherman and G. A. Fuches, *J. Coord. Chem.*, 1972, **1**, 289.
325. M. Aresta, C. F. Nobile and A. Sacco, *Inorg. Chim. Acta*, 1975, **12**, 167.
326. D. C. Bradley, M. B. Hursthouse, R. J. Smallwood and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 1972, 872.
327. C. F. Nobile, G. Vasapollo, P. Giannoccaro and A. Sacco, *Inorg. Chim. Acta*, 1981, **48**, 261.
328. B. Deppish and H. Shäfer, *Z. Anorg. Allg. Chem.*, 1982, **490**, 129.
329. A. Gleizes, M. Dartiguenave, Y. Dartiguenave and J. Galy, *J. Am. Chem. Soc.*, 1977, **99**, 5187.
330. B. Corain, M. Bressan, P. Rigo and A. Turco, *Chem. Commun.*, 1968, 509.
331. K. Jones and G. Wilke, *Angew. Chem., Int. Ed. Engl.*, 1970, **9**, 312.
332. B. L. Barnett, C. Krüger, Y. H. Tsay, R. H. Summerville and R. Hoffmann, *Chem. Ber.*, 1977, **110**, 3900.
333. L. Sacconi and S. Midollini, *J. Chem. Soc., Dalton Trans.*, 1972, 1213.
334. P. Dapporto, F. Fallani and L. Sacconi, *Inorg. Chem.*, 1974, **13**, 2847; P. Dapporto, G. Fallani, S. Midollini and L. Sacconi, *J. Chem. Soc., Chem. Commun.*, 1972, 1161.
335. C. Bianchini, D. Masi, C. Mealli and A. Meli, *Cryst. Struct. Commun.*, 1982, **11**, 1475.
336. C. Bianchini, C. Mealli, A. Meli and G. Scapacci, *Organometallics*, 1983, **2**, 141.
337. S. Midollini and F. Cecconi, *J. Chem. Soc., Dalton Trans.*, 1973, 681.
338. S. Midolini, S. Moneti, A. Orlandini and L. Sacconi, *Cryst. Struct. Commun.*, 1980, **9**, 1141; F. Cecconi, S. Midollini and A. Orlandini, *J. Chem. Soc., Dalton Trans.*, 1983, 2263.

339. L. Sacconi, C. A. Ghilardi, C. Mealli and F. Zanobini, *Inorg. Chem.*, 1975, **14**, 1380.
340. P. Dapporto and L. Sacconi, *Inorg. Chim. Acta*, 1980, **39**, 61.
341. P. Stoppioni, A. Biliotti and R. Morassi, *J. Organomet. Chem.*, 1982, **236**, 119.
342. L. Sacconi, P. Dapporto and P. Stoppioni, *Inorg. Chem.*, 1976, **15**, 325.
343. L. Sacconi, P. Dapporto and P. Stoppioni, *Inorg. Chem.*, 1977, **16**, 224.
344. G. Bontempelli, B. Corain and L. De Nardo, *J. Chem. Soc., Dalton Trans.*, 1977, 1887.
345. G. Bontempelli, F. Magno, L. Schiavon and B. Corain, *Inorg. Chem.*, 1981, **20**, 2579.
346. T. E. Mines and W. E. Geiger, Jr., *Inorg. Chem.*, 1973, **12**, 1189.
347. W. E. Geiger, Jr., T. E. Mines and F. C. Senftleber, *Inorg. Chem.*, 1975, **14**, 2141.
348. W. E. Geiger, Jr., C. S. Allen, T. E. Mines and F. C. Senftleber, *Inorg. Chem.*, 1977, **16**, 2003.
349. A. M. Bond, G. A. Heath and R. L. Martin, *Inorg. Chem.*, 1971, **10**, 2026.
350. W. L. Bowden, J. D. L. Holloway and W. E. Geiger, Jr., *Inorg. Chem.*, 1978, **17**, 256.
351. A. R. Hendrickson, R. L. Martin and N. M. Rohde, *Inorg. Chem.*, 1975, **14**, 2980.
352. G. A. Bowmaker, P. D. Boyd, G. K. Campbell, J. M. Hope and R. L. Martin, *Inorg. Chem.*, 1982, **21**, 1152, and refs. therein.
353. T. H. Randle, T. J. Cardwell and R. J. Magee, *Aust. J. Chem.*, 1976, **29**, 1191.
354. D. G. Hollah, A. N. Hughes and B. C. Hui, *Can. J. Chem.*, 1977, **55**, 4048.
355. C. Amano, T. Watanabe and S. Fujiwara, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 2586.
356. L. Sacconi, *Transition Met. Chem.*, 1968, **4**, 199.
357. R. Morassi, I. Bertini and L. Sacconi, *Coord. Chem. Rev.*, 1973, **11**, 343.
358. P. L. Orioli, *Coord. Chem. Rev.*, 1971, **6**, 285.
359. E. Uhlig, *Coord. Chem. Rev.*, 1973, **10**, 227.
360. M. Ciampolini, *Struct. Bonding (Berlin)*, 1969, **6**, 52.
361. J. S. Griffith, 'The Theory of Transition Metal Ions', Cambridge University Press, London, 1971.
362. C. K. Jorgensen, R. Pappalardo and H. H. Schmidtke, *J. Chem. Phys.*, 1963, **39**, 1422.
363. A. Bencini, C. Benelli and D. Gatteschi, *Coord. Chem. Rev.*, 1984, **60**, 131.
364. M. Gerloch and R. C. Slade, 'Ligand Field Parameters', Cambridge University Press, London, 1973.
365. I. Bertini, D. Gatteschi and A. Scozzafava, *Isr. J. Chem.*, 1976/77, **15**, 189.
366. J. Glerup, O. Monsted and C. E. Schaffer, *Inorg. Chem.*, 1976, **15**, 1399.
367. D. W. Smith, *Inorg. Chem.*, 1978, **17**, 3153.
368. C. E. Schaffer, in 'Wave Mechanics', ed. W. C. Price, S. S. Chissick and T. Ravensdale, Butterworths, London, 1973, p. 174.
369. C. E. Schaffer, *Struct. Bonding (Berlin)*, 1968, **5**, 68.
370. C. E. Schaffer, *Struct. Bonding (Berlin)*, 1973, **14**, 69.
371. M. Gerloch, J. H. Harding and R. G. Woolley, *Struct. Bonding (Berlin)*, 1981, **46**, 1.
372. E. Larsen, G. N. La Mar, B. E. Wagner, J. E. Parks and R. H. Holm, *Inorg. Chem.*, 1972, **11**, 2652.
373. A. B. P. Lever, G. London and P. J. McCarthy, *Can. J. Chem.*, 1977, **55**, 3172.
374. A. Bencini, and D. Gatteschi, *J. Phys. Chem.*, 1976, **80**, 2126.
375. B. N. Figgis, *Prog. Inorg. Chem.*, 1964, **6**, 37.
376. R. L. Carlin and A. J. Van Duyneveldt, 'Magnetic Properties of Transition Metal Compounds', Springer-Verlag, New York, 1977.
377. S. Mitra, *Prog. Inorg. Chem.*, 1977, **22**, 309.
378. S. Mitra, *Transition Met. Chem.*, 1972, **7**, 183.
379. C. J. O'Connor, *Prog. Inorg. Chem.*, 1982, **29**, 203.
380. L. Banci, A. Bencini, C. Benelli, D. Gatteschi and C. Zanchini, *Struct. Bonding (Berlin)*, 1982, **52**, 37.
381. R. S. Rubins, J. D. Clark and S. K. Jani, *J. Chem. Phys.*, 1977, **67**, 893.
382. R. S. Rubins and S. K. Jani, *J. Chem. Phys.*, 1977, **66**, 3297.
383. J. F. Suassuna, C. Rettori, H. Vargas, G. E. Barberis, C. E. Hennies and N. F. Oliveira, Jr., *J. Phys. Chem. Solids*, 1977, **38**, 1075.
384. W. M. Pontuschka, A. Piccini, C. J. A. Quadros and S. Isotani, *Phys. Lett. A*, 1973, **44**, 57.
385. R. S. Rubins, *J. Chem. Phys.*, 1974, **60**, 4189.
386. G. L. McPherson, R. C. Koch and G. D. Stucky, *J. Chem. Phys.*, 1974, **60**, 1424.
387. G. L. McPherson and K. O. Devaney, *Inorg. Chem.*, 1977, **16**, 1565.
388. Y. R. Chang, G. L. McPherson and J. L. Atwood, *Inorg. Chem.*, 1975, **14**, 3079.
389. H. Witteveen and J. A. R. Van Veen, *J. Phys. Chem. Solids*, 1974, **35**, 337.
390. P. B. Sczaniecki and J. Lesiak, *J. Magn. Reson.*, 1982, **46**, 185.
391. J. Reedijk and B. Nieuwenhuijse, *Recl. Trav. Chim. Pays-Bas*, 1972, **91**, 533.
392. J. A. Ochi, W. Sano, S. Isotani and C. E. Hennies, *J. Chem. Phys.*, 1975, **62**, 2115.
393. C. Trapp and C. I. Shyr, *J. Chem. Phys.*, 1971, **54**, 196.
394. S. Kirmse, S. Wartewig and R. Bottcher, *Chem. Phys. Lett.*, 1973, **22**, 427.
395. A. Bencini and D. Gatteschi, *Transition Met. Chem.*, 1982, **8**, 1.
396. F. W. King, *Chem. Rev.*, 1976, **76**, 157.
397. W. D. Horrocks, Jr., R. C. Taylor and G. N. La Mar, *J. Am. Chem. Soc.*, 1964, **86**, 3031.
398. R. W. Kluiber and W. D. Horrocks, Jr., *J. Am. Chem. Soc.*, 1965, **87**, 5350.
399. R. W. Kluiber and W. D. Horrocks, Jr., *J. Am. Chem. Soc.*, 1966, **88**, 1399.
400. J. A. Happe and R. L. Ward, *J. Chem. Phys.*, 1963, **39**, 1211.
401. G. N. La Mar, *Inorg. Chem.*, 1969, **8**, 581.
402. J. E. Parks and R. H. Holm, *Inorg. Chem.*, 1968, **7**, 1408.
403. M. Wicholas and R. S. Drago, *J. Am. Chem. Soc.*, 1969, **91**, 5963.
404. A. Chakravorty, J. P. Fennessey and R. H. Holm, *Inorg. Chem.*, 1965, **4**, 26.
405. J. D. Thwaites and L. Sacconi, *Inorg. Chem.*, 1966, **5**, 1029.
406. G. N. La Mar, *Mol. Phys.*, 1967, **12**, 427.
407. D. Doddrell and J. D. Roberts, *J. Am. Chem. Soc.*, 1970, **92**, 683.

408. R. E. Cramer and R. S. Drago, *J. Am. Chem. Soc.*, 1970, **92**, 66.
409. G. R. Underwood and H. S. Friedman, *J. Am. Chem. Soc.*, 1974, **96**, 4989.
410. T. Yonezawa, I. Morishima and Y. Ohmori, *J. Am. Chem. Soc.*, 1970, **92**, 1267.
411. I. Morishima and K. Toshikawa, *J. Am. Chem. Soc.*, 1975, **97**, 2950.
412. I. Morishima, K. Okada, T. Yonezawa and K. Goto, *J. Am. Chem. Soc.*, 1971, **93**, 3922.
413. I. Morishima, T. Yonezawa and K. Goto, *J. Am. Chem. Soc.*, 1979, **92**, 6551.
414. K. Tori, Y. Yoshimura and R. Muneyuki, *J. Am. Chem. Soc.*, 1971, **93**, 6324.
415. L. M. Stock and M. R. Wasielewski, *J. Am. Chem. Soc.*, 1972, **94**, 8276.
416. L. M. Stock and M. R. Wasielewski, *J. Am. Chem. Soc.*, 1973, **95**, 2743.
417. L. M. Stock and M. R. Wasielewski, *J. Am. Chem. Soc.*, 1974, **96**, 583.
418. R. W. Kluiber and W. D. Horrocks, Jr., *Inorg. Chem.*, 1967, **6**, 430.
419. T. Yonezawa, I. Morishima, Y. Akana and K. Fukuta, *Bull. Chem. Soc. Jpn.*, 1970, **43**, 379.
420. I. Morishima, K. Okada and T. Yonezawa, *J. Am. Chem. Soc.*, 1972, **94**, 1425.
421. R. H. Holm, G. W. Everett and W. D. Horrocks, Jr., *J. Am. Chem. Soc.*, 1966, **88**, 1071.
422. G. R. Underwood and K. E. Bayonmy, *J. Am. Chem. Soc.*, 1982, **104**, 3007.
423. D. Forster, *Inorg. Chim. Acta*, 1971, **5**, 465.
424. R. W. Kluiber and W. D. Horrocks, Jr., *Inorg. Chem.*, 1967, **6**, 166.
425. H. P. Fritz, B. M. Golla, H. J. Keller and K. E. Schwazhaus, *Z. Naturforsch., Teil B*, 1967, **22**, 216.
426. W. D. Horrocks, Jr. and D. L. Johnston, *Inorg. Chem.*, 1971, **10**, 1835.
427. D. Forster, *Inorg. Chem.*, 1973, **12**, 4.
428. W. D. Horrocks, Jr., *Inorg. Chem.*, 1973, **12**, 1211.
429. T. G. Campbell and F. L. Urbach, *Inorg. Chem.*, 1973, **12**, 1840.
430. P. F. Richardson and R. W. Kreilick, *Inorg. Chem.*, 1981, **20**, 1978.
431. M. Wicholas, R. Mustacich, B. Johnson, T. Smedley and J. May, *J. Am. Chem. Soc.*, 1975, **97**, 2113.
432. M. Wicholas, *Inorg. Chem.*, 1971, **10**, 1086.
433. G. N. La Mar and G. R. van Hecke, *Inorg. Chem.*, 1970, **9**, 1546.
434. R. J. Pell, H. W. Dodgen and J. P. Hunt, *Inorg. Chem.*, 1983, **22**, 529.
435. J. H. Coates, D. A. Hadi, S. F. Lincoln, H. W. Dodgen and J. P. Hunt, *Inorg. Chem.*, 1981, **20**, 707.
436. R. J. Kurland and B. R. McGarvey, *J. Magn. Reson.*, 1970, **2**, 286.
437. B. R. McGarvey, *J. Am. Chem. Soc.*, 1972, **94**, 1103.
438. W. D. Phillips and R. E. Benson, *J. Chem. Phys.*, 1960, **33**, 607.
439. D. R. Eaton, W. D. Phillips and D. J. Caldwell, *J. Am. Chem. Soc.*, 1963, **85**, 397.
440. D. R. Eaton, A. D. Josey and W. A. Sheppard, *J. Am. Chem. Soc.*, 1963, **85**, 2689.
441. D. R. Eaton, A. D. Josey, R. E. Benson, W. D. Phillips and T. L. Cairns, *J. Am. Chem. Soc.*, 1962, **84**, 4100.
442. D. R. Eaton, A. D. Josey, W. D. Phillips and R. E. Benson, *Mol. Phys.*, 1962, **5**, 407.
443. D. R. Eaton, R. E. Benson, G. G. Bottomley and A. D. Josey, *J. Am. Chem. Soc.*, 1972, **94**, 5996.
444. R. H. Holm, A. Chakravorty and G. O. Dudek, *J. Am. Chem. Soc.*, 1963, **85**, 821.
445. R. H. Holm, A. Chakravorty and G. O. Dudek, *J. Am. Chem. Soc.*, 1964, **86**, 379.
446. A. Chakravorty and R. H. Holm, *Inorg. Chem.*, 1964, **3**, 1010.
447. I. Bertini, D. L. Johnston and W. D. Horrocks, Jr., *Inorg. Chem.*, 1970, **9**, 693.
448. G. W. Everett and R. H. Holm, *Inorg. Chem.*, 1968, **7**, 776.
449. R. H. Holm, A. Chakravorty and L. J. Theriot, *Inorg. Chem.*, 1966, **5**, 625.
450. L. H. Pignolet and W. D. Horrocks, Jr., *J. Am. Chem. Soc.*, 1969, **91**, 3976.
451. G. N. La Mar and E. O. Sherman, *J. Am. Chem. Soc.*, 1970, **92**, 2691.
452. L. Que, Jr. and L. H. Pignolet, *Inorg. Chem.*, 1973, **12**, 157.
453. W. D. Horrocks, Jr. and E. S. Greenberger, *Inorg. Chem.*, 1971, **10**, 2190.
454. W. T. Scroggins, M. F. Rettig and R. M. Wing, *Inorg. Chem.*, 1976, **15**, 1381.
455. D. R. Eaton and W. D. Phillips, *Adv. Magn. Reson.*, 1965, **1**, 103.
456. I. Solomon, *Phys. Rev.*, 1955, **99**, 559.
457. J. Kowalewski, A. Laaksonen and L. Nordenskiold, *J. Magn. Reson.*, 1980, **53**, 346.
458. J. Kowalewski, A. Laaksonen, L. Nordenskiold and M. Blomberg, *J. Chem. Phys.*, 1981, **74**, 2927.
459. L. Nordenskiold, A. Laaksonen and J. Kowaleswki, *J. Am. Chem. Soc.*, 1982, **104**, 379.
460. C. K. Jorgensen, *Acta Chem. Scand.*, 1955, **9**, 1362.
461. R. B. Janes, *Phys. Rev.*, 1935, **48**, 78.
462. R. A. Palmer and C. R. Taylor, *Inorg. Chem.*, 1971, **10**, 2546.
463. M. D. Joesten and K. M. Nykerk, *Inorg. Chem.*, 1964, **3**, 548.
464. D. W. Herlocken, R. S. Drago and D. W. Meek, *Inorg. Chem.*, 1966, **5**, 2009.
465. D. J. Mackey and S. V. Evans, *J. Chem. Soc., Dalton Trans.*, 1976, 2004.
466. A. P. Filho, E. Sinn, R. D. Chirico and R. L. Carlin, *Inorg. Chem.*, 1981, **20**, 2688.
467. R. L. Carlin, C. J. O'Connor and S. N. Bathia, *J. Am. Chem. Soc.*, 1976, **98**, 3523.
468. D. J. Mackey, *J. Chem. Soc., Dalton Trans.*, 1977, 40.
469. J. Reedijk, *Inorg. Chim. Acta*, 1971, **5**, 687.
470. D. W. Meek, R. S. Drago and T. S. Piper, *Inorg. Chem.*, 1962, **1**, 285.
471. R. D. Hancock and G. J. McDougall, *J. Chem. Soc., Dalton Trans.*, 1977, 67.
472. J. Reedijk, *Recl. Trav. Chim. Pays-Bas*, 1970, **89**, 605.
473. J. S. Merrian and J. R. Perumareddi, *J. Phys. Chem.*, 1975, **79**, 140.
474. R. A. Palmer and T. S. Piper, *Inorg. Chem.*, 1966, **5**, 864.
475. C. W. Reimann, *J. Phys. Chem.*, 1970, **74**, 561.
476. R. Dingle and R. A. Palmer, *Theor. Chim. Acta*, 1966, **6**, 249.
477. S. Datta, *Philos. Mag.*, 1934, **17**, 585.
478. R. J. Fereday and B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1972, 197.
479. C. Furlani, G. Mattogno, A. Monaci and F. Tarli, *Inorg. Chim. Acta*, 1970, **4**, 187.
480. A. E. Wickenden and R. A. Krause, *Inorg. Chem.*, 1965, **4**, 404.

481. A. F. Schreiner and D. J. Hamm, *Inorg. Chem.*, 1973, **12,** 2037.
482. M. B. Palma-Vittorelli, M. V. Palma, G. W. J. Drewes and W. Koerts, *Physica (Amsterdam)*, 1960, **26,** 922.
483. G. L. McPherson, J. E. Wall, Jr. and A. M. Hermann, *Inorg. Chem.*, 1974, **13,** 2231.
484. N. Achiwa, *J. Phys. Soc. Jpn.*, 1969, **27,** 561.
485. R. W. Asmussen and H. Soling, *Z. Anorg. Allg. Chem.*, 1956, **283,** 1.
486. M. Steiner, W. Kruger and D. Babel, *Solid State Commun.*, 1972, **11,** 73.
487. D. A. Rowley and R. S. Drago, *Inorg. Chem.*, 1967, **6,** 1092.
488. P. J. McCarthy and J. Reedijk, *Inorg. Chim. Acta*, 1980, **40,** 239.
489. J. Reedijk, *Recl. Trav. Chim. Pays-Bas*, 1970, **89,** 993.
490. N. H. Agnew, R. J. Collin and L. F. Larkworthy, *J. Chem. Soc., Dalton Trans.*, 1974, 272.
491. A. V. Butcher, D. J. Phillips and J. P. Redfern, *J. Chem. Soc. (A)*, 1971, 2104.
492. A. B. P. Lever, S. M. Nelson and T. M. Shepherd, *Inorg. Chem.*, 1965, **4,** 810.
493. M. N. Hughes, J. R. Lusty and T. J. Barton, *J. Chem. Soc., Dalton Trans.*, 1979, 1478.
494. A. B. P. Lever, I. M. Walker and P. J. McCarthy, *Inorg. Chim. Acta*, 1980, **44,** L143.
495. A. B. P. Lever, I. M. Walker, P. J. McCarthy, K. B. Mertes, A. Jircitano and R. Sheldon, *Inorg. Chem.*, 1983, **22,** 2252.
496. B. N. Figgis, P. A. Reynolds, A. H. White, G. A. Williams and S. Wright, *J. Chem. Soc., Dalton Trans.*, 1981, 997.
497.. I. Bertini, D. Gatteschi and A. Scozzafava, *Inorg. Chem.*, 1976, **15,** 203.
498. W. K. Moseer and N. L. Hill, *Inorg. Chem.*, 1972, **11,** 710.
499. M. Gerloch, J. Lewis and W. R. Smail, *J. Chem. Soc. (A)*, 1963, 2686.
500. M. Gerloch, J. Lewis and W. R. Smail, *J. Chem. Soc. (A)*, 1971, 2434.
501. S. L. Holt, Jr. and R. L. Carlin, *J. Am. Chem. Soc.*, 1964, **86,** 3017.
502. H. G. Nelson, *Inorg. Chim. Acta*, 1979, **32,** L51.
503. C. T. Spencer and L. T. Taylor, *Inorg. Chem.*, 1971, **10,** 2407.
504. J. Catterick and P. Thornton, *J. Chem. Soc., Dalton Trans.*, 1975, 233.
505. P. L. Meredith and R. A. Palmer, *Inorg. Chem.*, 1971, **10,** 1049.
506. R. L. Chiang and R. S. Drago, *Inorg. Chem.*, 1971, **10,** 453.
507. P. Dapporto, M. Peruzzini and P. Stoppioni, *Inorg. Chim. Acta*, 1981, **47,** 213.
508. (a) M. J. Harding, S. F. Mason, D. J. Robbins and A. J. Thomson, *J. Chem. Soc. (A)*, 1971, 3047; (b) M. J. Harding, S. F. Mason, D. J. Robbins and A. J. Thomson, *J. Chem. Soc. (A)*, 1971, 3058.
509. E. Solomon and C. J. Ballhausen, *Mol. Phys.*, 1975, **29,** 279.
510. S. M. Hart, J. C. A. Boeyens and R. D. Hancock, *Inorg. Chem.*, 1983, **22,** 982.
511. B. E. Myers, L. G. Polgar and S. A. Friedberg, *Phys. Rev.*, 1972, **6,** 3488.
512. Y. Ajiro, S. A. Friedberg and N. S. Vander Ven, *Phys. Rev.*, 1975, **12,** 39.
513. J. N. McElearney, D. Bhosee, S. Merchant and R. L. Carlin, *Phys. Rev. B*, 1973, **7,** 3314.
514. B. K. Chandhuri, *J. Phys. C*, 1974, **7,** 3962.
515. S. N. Bathia, R. L. Carlin and A. P. Filho, *Physica, B + C (Amsterdam)*, 1977, **92B**, 330.
516. D. J. Mackey, S. V. Evans and R. L. Martin, *J. Chem. Soc., Dalton Trans.*, 1976, 1515.
517. M. Karnezos, D. L. Meier and S. A. Friedberg, *Phys. Rev. B*, 1978, **17,** 4375.
518. M. A. Hitchman, *Inorg. Chem.*, 1972, **11,** 2387.
519. D. J. Mackey and R. F. McMeeking, *J. Chem. Soc., Dalton Trans.*, 1977, 2186.
520. B. N. Figgis, P. A. Reynolds and S. Wright, *J. Am. Chem. Soc.*, 1983, **105,** 434.
521. B. N. Figgis, P. A. Reynolds and R. Mason, *J. Am. Chem. Soc.*, 1983, **105,** 440.
522. V. J. Koester and T. M. Dunn, *Inorg. Chem.*, 1975, **14,** 1811.
523. M. Gerloch and R. C. Slade, *J. Chem. Soc. (A)*, 1969, 1022.
524. G. P. Smith, C. H. Lin and T. R. Griffiths, *J. Am. Chem. Soc.*, 1964, **86,** 4796.
525. N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 1959, 3997.
526. L. Sacconi, M. Ciampolini and U. Campigli, *Inorg. Chem.*, 1965, **4,** 407.
527. R. Pappalardo, D. L. Wood and R. C. Linares, *J. Chem. Phys.*, 1961, **35,** 1460.
528. J. E. Ferguson and C. A. Ramsay, *J. Chem. Soc. (A)*, 1965, 5222.
529. Y. Murakami, Y. Matsuda and K. Sakata, *Inorg. Chem.*, 1971, **10,** 1728.
530. I. Bertini, D. Gatteschi and F. Mani, *Inorg. Chem.*, 1972, **11,** 2464.
531. M. Gerloch and L. R. Hanton, *Inorg. Chem.*, 1981, **20,** 1046.
532. B. B. Garrett, V. L. Goedken and J. V. Quagliano, *J. Am. Chem. Soc.*, 1970, **92,** 489.
533. M. Gerloch and M. R. Manning, *Inorg. Chem.*, 1981, **20,** 1051.
534. M. Gerloch and L. R. Hanton, *Inorg. Chem.*, 1980, **19,** 1692.
535. L. Sacconi and J. Gelsomini, *Inorg. Chem.*, 1968, **7,** 291.
536. R. J. Fereday, B. J. Hathaway and R. J. Dudley, *J. Chem. Soc. (A)*, 1970, 571.
537. J. E. Davies, M. Gerloch and D. J. Phillips, *J. Chem. Soc., Dalton Trans.*, 1979, 1836.
538. F. A. Cotton, D. D. Fant and D. M. L. Goodgame, *J. Am. Chem. Soc.*, 1961, **83,** 344.
539. S. F. Mason and R. D. Peacock, *J. Chem. Soc., Dalton Trans.*, 1973, 226.
540. S. Buffagni, L. M. Vallarino and J. V. Quagliano, *Inorg. Chem.*, 1964, **3,** 480.
541. I. Bertini, D. J. Johnston and W. D. Horrocks, Jr., *Inorg. Chem.*, 1970, **9,** 693.
542. M. Gerloch, L. R. Hanton and M. R. Manning, *Inorg. Chim. Acta*, 1981, **48,** 205.
543. D. A. Cruse and M. Gerloch, *J. Chem. Soc., Dalton Trans.*, 1977, 152.
544. F. A. Cotton and D. M. L. Goodgame, *J. Am. Chem. Soc.*, 1960, **82,** 5771.
545. D. M. L. Goodgame and F. A. Cotton, *J. Am. Chem. Soc.*, 1970, **92,** 5774.
546. G. W. Inman, Jr., W. E. Hatfield and E. R. Jones, Jr., *Inorg. Nucl. Chem. Lett.*, 1971, **7,** 721.
547. B. N. Figgis, J. Lewis, F. Mabbs and G. A. Webb, *J. Chem. Soc. (A)*, 1966, 1411.
548. M. Gerloch and R. C. Slade, *J. Chem. Soc. (A)*, 1969, 1012.
549. M. Gerloch and R. Mason, *Inorg. Chim. Acta*, 1981, **50,** 43.
550. R. Mason, and D. W. Meek, *Angew. Chem., Int. Ed. Engl.*, 1978, **17,** 183.

551. I. Bertini, M. Ciampolini, P. Dapporto and D. Gatteschi, *Inorg. Chem.*, 1972, **11,** 2254.
552. M. Ciampolini and N. Nardi, *Inorg. Chem.*, 1966, **5,** 41.
553. Z. Dori and H. B. Gray, *J. Am. Chem. Soc.*, 1966, **88,** 1394.
554. M. Ciampolini and G. P. Speroni, *Inorg. Chem.*, 1966, **5,** 45.
555. L. M. Vallarino, V. L. Goedken and J. V. Quagliano, *Inorg. Chem.*, 1972, **11,** 1466.
556. L. Sacconi, M. Ciampolini and G. P. Speroni, *J. Am. Chem. Soc.*, 1965, **87,** 3102.
557. V. L. Goedken, J. V. Quagliano and L. M. Vallarino, *Inorg. Chem.*, 1969, **8,** 2331.
558. A. M. Brodie, S. H. Hunter, G. A. Rodley and C. J. Wilkins, *Inorg. Chim. Acta,* 1968, **2,** 195.
559. S. H. Hunter, R. S. Nyholm and G. A. Rodley, *Inorg. Chim. Acta,* 1969, **3,** 631.
560. M. Gerloch, J. Kohl, J. Lewis and W. Urland, *J. Chem. Soc. (A)*, 1970, 3269.
561. L. Sacconi and R. Morassi, *J. Chem. Soc. (A)*, 1969, 2904.
562. A. T. Phillip, W. Mazurek and A. T. Casey, *Aust. J. Chem.*, 1971, **24,** 501.
563. V. L. Goedken, L. M. Vallarino and J. V. Quagliano, *J. Am. Chem. Soc.*, 1970, **92,** 303.
564. J. G. Gibson and E. D. McKenzie, *J. Chem. Soc. (A)*, 1971, 1029.
565. L. Sacconi, P. Mannelli and N. Nardi, *Inorg. Chem.*, 1965, **4,** 943.
566. D. A. Cruse and M. Gerloch, *J. Chem. Soc., Dalton Trans.*, 1977, 1613.
567. J. R. Angus, G. M. Woltermann and J. R. Wasson, *J. Inorg. Nucl. Chem.*, 1971, **33,** 3972.
568. C. Benelli, M. di Vaira, G. Noccioli and L. Sacconi, *Inorg. Chem.*, 1977, **16,** 182.
569. D. F. Averill, J. I. Legg and D. L. Smith, *Inorg. Chem.*, 1972, **11,** 2344.
570. A. A. G. Tomlinson and C. Furlani, *J. Chem. Soc., Dalton Trans.*, 1974, 1420.
571. I. Bertini and D. Gatteschi, *J. Coord. Chem.*, 1971, **1,** 285.
572. L. Banci, A. Bencini, A. Dei and D. Gatteschi, *Inorg. Chem.*, 1981, **20,** 393.
573. M. Ciampolini, *Inorg. Chem.*, 1966, **5,** 35.
574. J. S. Wood, *Inorg. Chem.*, 1968, **7,** 852.
575. M. di Vaira, *Inorg. Chim. Acta,* 1980, **32,** 81.
576. C. A. L. Becker, D. W. Meek and T. M. Dunn, *J. Phys. Chem.*, 1968, **72,** 3588.
577. C. A. L. Becker, D. W. Meek and T. M. Dunn, *J. Phys. Chem.*, 1968, **72,** 1568.
578. J. S. Wood and P. T. Greene, *Inorg. Chem.*, 1969, **8,** 491.
579. J. C. Hempel and M. E. Miller, *J. Chem. Phys.*, 1981, **75,** 2959.
580. L. Banci, C. Benelli and D. Gatteschi, *Inorg. Chem.*, 1984, **23,** 3262.
581. J. K. Burdett, *Inorg. Chem.*, 1975, **14,** 931.
582. L. Sacconi, *J. Chem. Soc. (A)*, 1970, 248.
583. H. B. Gray and C. J. Ballhausen, *J. Am. Chem. Soc.*, 1963, **85,** 260.
584. C. J. Ballhausen and A. D. Liehr, *J. Am. Chem. Soc.*, 1959, **71,** 538.
585. C. R. Hare and C. J. Ballhausen, *J. Chem. Phys.*, 1964, **46,** 788.
586. G. Maki, *J. Chem. Phys.*, 1958, **28,** 651.
587. (a) G. Maki, *J. Chem. Phys.*, 1958, **29,** 162; (b) G. Maki, *J. Chem. Phys.*, 1958, **29,** 1129.
588. B. B. Chastain, D. W. Meek, E. Billig, J. E. Mix and H. B. Gray, *Inorg. Chem.*, 1968, **7,** 2412.
589. J. W. Dawson, T. J. Lennan, W. Robinson, A. Merle, M. Dartiguenave, Y. Dartiguenave and H. B. Gray, *J. Am. Chem. Soc.*, 1974, **96,** 4428.
590. L. Baracco, M. T. Halfpenny and C. A. McAuliffe, *J. Chem. Soc., Dalton Trans.*, 1973, 1945.
591. J. W. Dawson, H. B. Gray, J. E. Hix, J. R. Preer and L. M. Venanzi, *J. Am. Chem. Soc.*, 1972, **94,** 2979.
592. G. Dyer, J. G. Hartley and L. M. Venanzi, *J. Chem. Soc. (A)*, 1965, 1293.
593. D. W. Meek and G. Dyer, *Inorg. Chem.*, 1965, **4,** 1398.
594. L. Sacconi and I. Bertini, *J. Am. Chem. Soc.*, 1967, **89,** 2235.
595. J. R. Preer and H. B. Gray, *J. Am. Chem. Soc.*, 1970, **92,** 7306.
596. M. O. Workman, G. Dyer and D. W. Meek, *Inorg. Chem.*, 1967, **6,** 1543.
597. C. A. McAuliffe, M. O. Workman and D. W. Meek, *J. Coord. Chem.*, 1972, **2,** 137.
598. J. C. Cloyd and D. W. Meek, *Inorg. Chim. Acta,* 1972, **6,** 607.
599. E. C. Alyea and D. W. Meek, *J. Am. Chem. Soc.*, 1969, **91,** 5761.
600. M. A. Atanassov and G. S. Nikolov, *Inorg. Chim. Acta,* 1983, **68,** 15.
601. M. A. Hitchman and J. B. Brenner, *Inorg. Chim. Acta,* 1978, **27,** L61.
602. B. G. Arrex and F. Kevinkrist, *J. Am. Chem. Soc.*, 1967, **89,** 6114.
603. C. D. Cowman, C. J. Ballhausen and H. B. Gray, *J. Am. Chem. Soc.*, 1973, **95,** 7873.
604. L. G. Vanquickenborne and A. Ceulemans, *Inorg. Chem.*, 1981, **20,** 796.
605. J. D. Lebedda and R. A. Palmer, *Inorg. Chem.*, 1972, **11,** 484.
606. A. A. G. Tomlinson and C. Furlani, *Inorg. Chim. Acta,* 1965, **3,** 487.
607. R. Dingle, *Inorg. Chem.*, 1971, **10,** 1141.
608. O. Siiman, D. D. Titus, C. D. Cowman, J. Fresco and H. B. Gray, *J. Am. Chem. Soc.*, 1974, **96,** 2353.
609. C. K. Jorgensen, *J. Inorg. Nucl. Chem.*, 1962, **24,** 1571.
610. Z. S. Herman, R. F. Kirchner, G. H. Loew, U. T. Mueller-Westerhoff, A. Nezzol and M. C. Zerner, *Inorg. Chem.*, 1982, **21,** 46.
611. A. R. Hendrickson and R. L. Martin, *Inorg. Chem.*, 1973, **12,** 2582.
612. O. Siimann and J. Fresco, *J. Am. Chem. Soc.*, 1970, **92,** 2652.
613. S. B. Piepho, P. N. Schatz and A. J. McCaffery, *J. Am. Chem. Soc.*, 1969, **91,** 5994.
614. J. Demuynck, A. Veillard and G. Vinot, *Chem. Phys. Lett.*, 1971, **10,** 522.
615. J. Demuynck and A. Veillard, *Theor. Chim. Acta,* 1973, **28,** 241.
616. Q. Looney and B. E. Douglas, *Inorg. Chem.*, 1970, **9,** 1955.
617. C. K. Jorgensen, *Inorg. Chim. Acta Rev.*, 1968, **2,** 65.
618. S. I. Shupack, E. Billig, R. J. H. Clark, R. Williams and H. B. Gray *J. Am. Chem. Soc.*, 1964, **86,** 4594 and refs. therein.
619. A. R. Lathorn, V. C. Hascall and H. B. Gray, *Inorg. Chem.*, 1965, **4,** 788.
620. R. W. Mason and H. B. Gray, *Inorg. Chem.*, 1968, **7,** 55.

621. A. G. Sharpe, 'The Chemistry of Cyano Complexes of the Transition Metals', Academic, London, 1976, p. 225.
622. W. P. Griffith, *Q. Rev., Chem. Soc.*, 1962, **16**, 188.
623. B. M. Chadwick and A. G. Sharpe, *Adv. Inorg. Chem. Radiochem.*, 1966, **8**, 84.
624. D. F. Shriver, *Struct. Bonding (Berlin)*, 1966, **1**, 32.
625. A. Lüdi and R. Hügi, *Helv. Chim. Acta*, 1967, **50**, 1283.
626. B. Corain, P. Rigo and G. Favero, *Inorg. Chem.*, 1971, **10**, 2329.
627. H. Freund and C. R. Schneider, *J. Am. Chem. Soc.*, 1959, **81**, 4780.
628. J. T. Christensen, R. M. Izatt, J. D. Hale, R. T. Pack and G. D. Watt, *Inorg. Chem.*, 1963, **2**, 337.
629. F. K. Larsen, R. G. Hazell and S. E. Rasmussen, *Acta Chem. Scand.*, 1969, **23**, 61.
630. R. L. Musselman, L. C. Stecher and S. F. Watkins, *Inorg. Chem.*, 1980, **19**, 3400.
631. K. N. Raymond and F. Basolo, *Inorg. Chem.*, 1966, **5**, 949.
632. F. A. Jurnak and K. N. Raymond, *Inorg. Chem.*, 1974, **13**, 2387.
633. K. N. Raymond, P. W. R. Corfield and J. A. Ibers, *Inorg. Chem.*, 1968, **7**, 1362.
634. J. H. Rayner and H. M. Powell, *J. Chem. Soc.*, 1958, 3412.
635. J. H. Rayner and H. M. Powell, *J. Chem. Soc.*, 1952, 319.
636. G. W. Watt, *Inorg. Synth.*, 1950, **3**, 194.
637. F. Ephraim and R. Linn, *Ber.*, 1913, **46**, 3742.
638. R. S. Drago, D. W. Meek, R. Longhi and M. D. Joesten, *Inorg. Chem.*, 1963, **2**, 1056.
639. E. Uhlig and K. Staiger, *Z. Anorg. Allg. Chem.*, 1965, **336**, 179.
640. S. Prasad and V. Krishnam, *J. Indian Chem. Soc.*, 1958, **35**, 52.
641. F. Ephraim, *Ber.*, 1913, **46**, 3103.
642. S. H. Yu, *Nature (London)*, 1942, **150**, 347.
643. B. Rapp and S. F. Paukovic, *Inorg. Chem.*, 1970, **9**, 2800.
644. E. Hertel, *Z. Anorg. Allg. Chem.*, 1929, **178**, 202.
645. K. Krogmann and R. Z. Mattes, *Kristallografiya*, 1963, **118**, 291.
646. M. A. Porai-Koshits, A. S. Antsyshkina, L. M. Dikareva and E. K. Yukhno, *Acta Crystallogr.*, 1957, **10**, 784.
647. T. B. Jackson and J. O. Edwards, *J. Am. Chem. Soc.*, 1961, **83**, 355.
648. R. W. Kiser and T. W. Lapp, *Inorg. Chem.*, 1962, **1**, 401.
649. C. A. Root and J. W. Allison, *Inorg. Chem.*, 1970, **9**, 2791.
650. M. N. Hughes and K. Shrimanker, *Inorg. Chim. Acta*, 1976, **18**, 69.
651. L. M. Englehardt, P. W. G. Newman, C. L. Raston and A. H. White, *Aust. J. Chem.*, 1974, **27**, 503.
652. R. Eggli and W. Ludwig, *Inorg. Chim. Acta*, 1973, **7**, 697.
653. J. V. Quagliano, A. K. Banerjee, V. L. Goedken and L. M. Vallarino, *J. Am. Chem. Soc.*, 1970, **92**, 482.
654. L. M. Vallarino, V. L. Goedken and J. V. Quagliano, *Inorg. Chem.*, 1972, **11**, 1466.
655. W. J. Rozell and J. S. Wood, *Inorg. Chem.*, 1977, **16**, 1827.
656. M. A. Buhamic and J. E. Guerchais, *Bull. Soc. Chim. Fr.*, 1971, 403.
657. M. A. Porai-Koshits, *Tr. Inst. Kristallogr. Akad. Nauk SSSR*, 1954, **10**, 269.
658. A. Werner, *Z. Anorg. Allg. Chem.*, 1899, **21**, 229.
659. D. D. Perrin, 'Stability Constants of Metal–Ion Complexes. Part B: Organic Ligands', Pergamon, Oxford, 1979.
660. T. Fujita and H. Ohtaki, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 455.
661. L. N. Swink and M. Atoji, *Acta Crystallogr.*, 1960, **13**, 639.
662. R. E. Cramer, W. van Doorne and J. T. Huneke, *Inorg. Chem.*, 1976, **15**, 529.
663. R. E. Cramer and J. T. Huneke, *Inorg. Chem.*, 1978, **17**, 365.
664. C. L. Raston, A. H. White and A. C. Willis, *Aust. J. Chem.*, 1978, **31**, 415.
665. J. D. Korp, I. Bernal, R. A. Palmer and J. C. Robinson, *Acta Crystallogr., Sect. B*, 1980, **36**, 560.
666. M. E. Farago, J. M. James and V. C. G. Trew, *J. Chem. Soc. (A)*, 1967, 820.
667. B. N. Brown and E. C. Lingafelter, *Acta Crystallogr.*, 1963, **16**, 753.
668. I. Bertini, D. Gatteschi and A. Scozzafava, *Inorg. Chem.*, 1976, **15**, 203.
669. A. A. G. Tomlinson, M. Bonamico, G. Dessy, V. Fares and L. Scaramuzzo, *J. Chem. Soc., Dalton Trans.*, 1972, 1671.
670. A. J. Finney, M. A. Hitchman, C. L. Raston, G. L. Rowbottom and A. H. White, *Aust. J. Chem.*, 1981, **34**, 2047.
671. A. J. Finney, M. A. Hitchman, C. L. Raston, G. L. Rowbottom and A. H. White, *Aust. J. Chem.*, 1981, **34**, 2159.
672. A. Meyer, A. Gleizes, J. J. Girerd, M. Verdaguer and O. Kahn, *Inorg. Chem.*, 1982, **21**, 1729.
673. A. Gelizes, A. Meyer, M. A. Hitchman and O. Kahn, *Inorg. Chem.*, 1982, **21**, 2257.
674. G. J. McDougall and R. D. Hancock, *J. Chem. Soc., Dalton Trans.* 1980, 654.
675. R. Stomberg, *Acta Chem. Scand.*, 1969, **23**, 3498.
676. A. S. Antsyshkina and M. A. Porai-Koshits, *Dokl. Akad. Nauk SSSR*, 1962, **143**, 105.
677. G. A. Bottomley, L. G. Glossop, C. L. Raston, A. H. White and A. C. Willis, *Aust. J. Chem.*, 1978, **31**, 285.
678. K. O. Joung, C. J. O'Connor, E. Sinn and R. L. Carlin, *Inorg. Chem.*, 1979, **18**, 804.
679. I. Bkouche-Waksman, Y. Journaux and O. Kahn, *Transition Met. Chem.*, 1981, **6**, 176.
680. A. E. Svelasvili, *Acta Crystallogr., Sect. A*, 1966, **21**, 153.
681. N. F. Curtis, I. Ross, N. McCormick and T. N. Waters, *J. Chem. Soc., Dalton Trans.*, 1973, 1537.
682. D. A. House and N. F. Curtis, *J. Am. Chem. Soc.*, 1964, **86**, 223.
683. L. Tschugaeff, *Ber.*, 1906, **39**, 3190.
684. D. A. House and N. F. Curtis, *J. Chem. Soc.*, 1963, 3149.
685. A. B. P. Lever, J. Lewis and R. S. Nyholm, *J. Chem. Soc.*, 1963, 2556.
686. N. F. Curtis and D. A. House, *J. Chem. Soc.*, 1965, 6194.
687. F. G. Beltran, A. V. Capilla and R. A. Aranda, *Cryst. Struct. Commun.*, 1978, **7**, 173.
688. S. C. Nyburg and J. S. Wood, *Inorg. Chem.*, 1964, **3**, 468.
689. W. C. E. Higginson, S. C. Nyburg and J. S. Wood, *Inorg. Chem.*, 1964, **3**, 463.
690. S. F. Pavkovic and D. W. Meek, *Inorg. Chem.*, 1965, **4**, 20.

691. D. M. L. Goodgame and L. M. Venanzi, *J. Chem. Soc.*, 1963, 616.
692. M. G. B. Drew, D. M. L. Goodgame, M. A. Hitchman and D. Rogers, *Proc. Chem. Soc.*, 1964, 363.
693. A. J. Finney, M. A. Hitchman, C. L. Raston, G. L. Rowbottom and A. H. White, *Aust. J. Chem.*, 1981, **34,** 2047.
694. A. B. P. Lever, I. M. Walker, P. J. McCarthy, K. B. Mertes, A. Jircitano and R. Sheldon, *Inorg. Chem.*, 1983, **22,** 2252.
695. I. Bertini and F. Mani, *Inorg. Chim. Acta,* 1969, **3,** 451.
696. L. Sacconi, I. Bertini and F. Mani, *Inorg. Chem.*, 1967, **6,** 262.
697. J. A. Cook, M. G. B. Drew and D. A. Rice, *J. Chem. Soc., Dalton Trans.* 1975, 1973.
698. D. B. Sowerby and I. Haiduc, *Inorg. Chim. Acta,* 1976, **17,** L15.
699. M. Ahlgren and U. Turpeinem, *Acta Crystallogr., Sect. B,* 1982, **38,** 276.
700. F. Basolo, Y. T. Chen and R. K. Murmann, *J. Am. Chem. Soc.*, 1954, **76,** 956.
701. I. Lifschitz, J. G. Bos and K. M. Dijkema, *Z. Anorg. Allg. Chem.*, 1939, **242,** 97.
702. I. Lifschitz and J. G. Bos, *Recl. Trav. Chim. Pays-Bas,* 1940, **59,** 407.
703. F. Hein and H. Muller, *Z. Anorg. Allg. Chem.*, 1956, **283,** 172.
704. W. A. Sadler and D. A. House, *J. Chem. Soc., Dalton Trans.*, 1973, 1937.
705. S. Arakawa, T. Nozawa and M. Matano, *Bull. Chem. Soc. Jpn.*, 1974, **47,** 2643.
706. D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, 1968, **7,** 1404.
707. D. L. Leussing, *Inorg. Chem.*, 1963, **2,** 77.
708. L. Fabbrizzi, M. Micheloni and P. Paoletti, *Inorg. Chem.*, 1974, **13,** 3019.
709. R. J. Pylkki, G. D. Willett and H. W. Dodgen, *Inorg. Chem.*, 1984, **23,** 594.
710. J. G. Breckenridge, *Can. J. Res.*, 1948, **26,** 11.
711. D. Bostrup and C. K. Jorgensen, *Acta Chem. Scand.*, 1957, **11,** 1223.
712. N. F. Curtis and Y. M. Curtis, *Inorg. Chem.*, 1965, **4,** 804.
713. N. F. Curtis and H. K. J. Powell, *J. Chem. Soc. (A)*, 1968, 3069.
714. M. Ciampolini, P. Paoletti and L. Sacconi, *J. Chem. Soc.*, 1961, 2994.
715. S. Biagini and M. Cannas, *J. Chem. Soc. (A)*, 1970, 2398.
716. G. Ponticelli and S. Preti, *J. Chem. Soc., Dalton Trans.*, 1972, 708.
717. M. T. Halfpenny, W. Levason, C. A. McAuliffe, W. E. Hill and F. P. McCullough, *Inorg. Chim. Acta,* 1979, **32,** 229.
718. I. Bertini, D. L. Johnston and W. D. Horrocks, Jr., *Inorg. Chim. Acta,* 1970, **4,** 79.
719. Z. Dori and H. B. Gray, *J. Am. Chem. Soc.*, 1966, **88,** 1394.
720. J. L. Burmeister, T. P. O'Sullivan and K. A. Johnson, *Inorg. Chem.*, 1971, **10,** 1803.
721. J. L. Burmeister, R. L. Hassel and K. A. Johnson, *Inorg. Chim. Acta,* 1974, **9,** 23.
722. J. L. Burmeister, T. P. O'Sullivan and K. A. Johnson, *Inorg. Chem.*, 1971, **10,** 1803.
723. M. Ciampolini and G. P. Speroni, *Inorg. Chem.*, 1966, **5,** 45.
724. P. D. Gradwick and D. Hall, *Acta Crystallogr., Sect. B,* 1970, **26,** 1384.
725. D. M. Duggan and D. N. Hendrickson, *Inorg. Chem.*, 1974, **13,** 2056.
726. C. G. Pierpont, D. N. Hendrickson, D. M. Duggan, F. Wagner and E. K. Barefield, *Inorg. Chem.*, 1975, **14,** 604.
727. B. G. Segal and S. J. Lippard, *Inorg. Chem.*, 1977, **16,** 1623.
728. C. G. Pierpont, L. C. Francesconi and D. N. Hendrickson, *Inorg. Chem.*, 1977, **16,** 2367.
729. K. R. Mann, D. M. Duggan and D. N. Hendrickson, *Inorg. Chem.*, 1975, **14,** 2577.
730. M. Ciampolini and N. Nardi, *Inorg. Chem.*, 1966, **5,** 41.
731. M. di Vaira and P. L. Orioli, *Acta Crystallogr., Sect. B,* 1968, **24,** 595.
732. I. Bertini, M. Ciampolini, P. Dapporto and D. Gatteschi, *Inorg. Chem.*, 1972, **11,** 2254.
733. P. L. Orioli and N. Nardi, *J. Chem. Soc., Chem. Commun.*, 1975, 229.
734. L. Sacconi and R. Morassi, *J. Chem. Soc. (A)*, 1969, 2904.
735. A. Dei and R. Morassi, *J. Chem. Soc. (A)*, 1971, 2024.
736. A. Dei, P. Paoletti and A. Vacca, *Inorg. Chem.*, 1968, **7,** 865.
737. A. Vacca and P. Paoletti, *J. Chem. Soc. (A)*, 1968, 2378.
738. A. McPherson, Jr., M. G. Rosmann, D. N. Margerum and M. R. James, *J. Coord. Chem.*, 1971, **1,** 39.
739. A. Clausen and A. C. Hazell, *Acta Chem. Scand.*, 1970, **24,** 2811.
740. C. K. Jorgensen, *Acta Chem. Scand.*, 1957, **11,** 399.
741. B. Bosnich, R. D. Gillard, E. D. McKenzie and G. A. Webb, *J. Chem. Soc. (A)*, 1966, 1331.
742. D. F. Cook and E. D. McKenzie, *Inorg. Chim. Acta,* 1978, **31,** 59.
743. R. Barbucci, P. Paoletti and G. Ponticelli, *J. Chem. Soc. (A)*, 1971, 1637.
744. N. F. Curtis and N. B. Milestone, *Aust. J. Chem.*, 1974, **27,** 1167.
745. J. G. Gibson and E. D. McKenzie, *J. Chem. Soc. (A)*, 1971, 1029.
746. J. G. Gibson and E. D. McKenzie, *J. Chem. Soc., Dalton Trans.*, 1974, 989.
747. J. Selbin, *J. Inorg. Nucl. Chem.*, 1961, **17,** 84.
748. A. Dei, *Inorg. Chim. Acta,* 1975, **12,** 79.
749. A. Vacca, D. Arenare and P. Paoletti, *Inorg. Chem.*, 1966, **5,** 1384.
750. C. K. Jorgensen, *Acta Chem. Scand.*, 1955, **9,** 1362.
751. H. B. Jonassen and B. E. Douglas, *J. Am. Chem. Soc.*, 1949, **71,** 4094.
752. A. Cristini, G. Ponticelli and A. Diaz, *J. Chem. Soc., Dalton Trans.*, 1972, 1361.
753. W. K. Musker and M. S. Hussain, *Inorg. Chem.*, 1966, **5,** 1416.
754. D. J. Royer, V. H. Schievelbeinm, A. R. Kalyanaman and J. A. Bertrand, *Inorg. Chim. Acta,* 1972, **6,** 307.
755. K. Musker and M. S. Hussain, *Inorg. Chem.*, 1969, **8,** 528.
756. M. S. Hussain, *J. Chem. Soc., Dalton Trans.*, 1982, 2545.
757. M. Nonayama, *Inorg. Chim. Acta,* 1976, **20,** 53.
758. R. A. D. Wentworth, *Inorg. Chem.*, 1968, **7,** 1030.
759. J. H. Ammeter, H. B. Burgi, E. Gamp, V. Meyer-Sandrin and W. P. Jensen, *Inorg. Chem.*, 1979, **18,** 733.

760. F. L. Urbach, J. E. Sarneski, L. J. Turner and D. H. Busch, *Inorg. Chem.*, 1968, **7**, 2169.
761. A. Sabatini and A. Vacca, *Coord. Chem. Rev.*, 1975, **16**, 161.
762. R. Saito and Y. Kidani, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 57.
763. R. Saito and Y. Kidani, *Chem. Lett.*, 1976, 123.
764. H. Okawa, M. Kakimuto, T. Izumitani and S. Kida, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 2671.
765. L. F. Audrieth and B. A. Ogg, 'The Chemistry of Hydrazine', Wiley, New York, 1951.
766. R. Y. Aliev, A. D. Kuliev and N. G. Klyuchnikov, *Russ. J. Inorg. Chem. (Engl Transl.)*, 1972, **17**, 1726.
767. R. Tsuchiya, M. Yonemura, A. Uehara and E. Kyuno, *Bull. Chem. Soc., Jpn.*, 1974, **47**, 660.
768. J. L. Dilworth, *Coord. Chem. Rev.*, 1976, **21**, 29.
769. D. Nicholls and R. Swindells, *J. Inorg. Nucl. Chem.*, 1968, **30**, 2211.
770. D. Nicholls, M. Rowley and R. S. Swindells, *J. Chem. Soc.*, 1966, 950.
771. B. Chiswell and F. Lyons, *Aust. J. Chem.*, 1969, **22**, 71.
772. T. S. Kuntsevich, I. S. Tarkhova and A. V. Ablov, *Dokl. Akad. Nauk SSSR*, 1978, **243**, 338.
773. R. C. Elder, D. Koran and H. B. Mark, *Inorg. Chem.*, 1974, **13**, 1644.
774. A. V. Butcher, D. J. Phillips and J. P. Redfern, *J. Chem. Soc. (A)*, 1968, 1064.
775. A. V. Butcher, D. J. Phillips and J. P. Redfern, *J. Chem. Soc. (A)*, 1971, 1640.
776. D. R. Marks, D. J. Phillips and J. P. Redfern, *J. Chem. Soc. (A)*, 1968, 2013.
777. B. J. A. Kakazai and G. A. Melson, *Inorg. Chim. Acta*, 1968, **2**, 186.
778. E. J. Duff, *J. Chem. Soc. (A)*, 1968, 434.
779. E. J. Duff, *J. Inorg. Nucl. Chem.*, 1968, **30**, 1257.
780. G. Bombieri, E. Forsellini, G. Bandoli, L. Sindellari. R. Graziani and C. Panattoni, *Inorg. Chim. Acta*, 1968, **2**, 27.
781. G. Bombieri, E. Forsellini, R. Graziani and E. Tondello, *J. Chem. Soc. (A)*, 1970, 3349.
782. M. R. Rosenthal and R. S. Drago, *Inorg. Chem.*, 1965, **4**, 840.
783. L. M. Vallarino, W. H. Will and J. V. Quagliano, *Inorg. Chem.*, 1965, **4**, 1598.
784. G. J. Long and P. J. Clarke, *Inorg. Chem.*, 1978, **17**, 1395.
785. A. S. Antsyshkina and M. A. Porai-Koshits, *Kristallografiya*, 1958, **3**, 676.
786. A. S. Antsyshkina and M. A. Porai-Koshits, *Kristallografiya*, 1958, **3**, 686.
787. D. H. Brown, R. H. Nuttal and D. W. A. Sharp, *J. Inorg. Nucl. Chem.*, 1963, **25**, 1067.
788. D. J. Hamm, J. Bordner and A. F. Schreiner, *Inorg. Chim. Acta*, 1973, **7**, 637.
789. S. M. Nelson and T. M. Shepherd, *J. Chem. Soc.*, 1965, 3284.
790. A. B. P. Lever, S. M. Nelson and T. M. Shepherd, *Inorg. Chem.*, 1965, **4**, 813.
791. I. S. Kerr and D. J. Williams, *Acta Crystallogr., Sect. B*, 1977, **33**, 3589.
792. J. Liprowski and G. D. Andretti, *Acta Crystallogr., Sect. B*, 1982, **38**, 607.
793. R. M. Morrison, R. C. Thompson and J. Trotter, *Can. J. Chem.*, 1980, **58**, 238.
794. N. Bose and H. Lynton, *Can. J. Chem.*, 1973, **51**, 1952.
795. S. Buffagni, L. M. Vallarino and J. V. Quagliano, *Inorg. Chem.*, 1964, **3**, 671.
796. W. Ludwig and G. Wittmann, *Helv. Chim. Acta*, 1964, **47**, 1265.
797. F. Madaule-Aubry, W. R. Busing and G. M. Brown, *Acta Crystallogr., Sect. B*, 1968, **24**, 754.
798. F. Madaule-Aubry and G. M. Brown, *Acta Crystallogr., Sect. B*, 1968, **24**, 745.
799. S. M. D. Glonek, C. Curran and J. V. Quagliano, *J. Am. Chem. Soc.*, 1962, **84**, 2014.
800. E. Konig and H. L. Shafer, *Z. Phys. Chem. (Leipzig)*, 1957, **26**, 1223.
801. S. Ooi and Q. Fernando, *Inorg. Chem.*, 1967, **6**, 1558.
802. M. M. Borel, A. Geffrouais and M. Ledesert, *Acta Crystallogr., Sect. B*, 1976, **32**, 2385.
803. E. Carmona, F. Gonzales, M. Poveda, J. L. Atwood and R. D. Rogers, *J. Chem. Soc., Dalton Trans.*, 1981, 777.
804. L. M. Venanzi, *J. Chem. Soc.*, 1958, 719.
805. C. E. Pfluger and R. L. Harlow, *Cryst. Struct. Commun.*, 1975, **4**, 633.
806. M. B. Hursthouse and D. B. New, *J. Chem. Soc., Dalton Trans.*, 1977, 1082.
807. S. Buffagni, L. M. Vallarino and J. V. Quagliano, *Inorg. Chem.*, 1964, **3**, 480.
808. W. L. Dargy and L. M. Vallarino, *Inorg. Chim. Acta*, 1976, **36**, 253.
809. D. M. L. Goodgame and M. Goodgame, *J. Chem. Soc.*, 1963, 207.
810. R. M. Morrison, R. C. Thompson and J. Trotter, *Can. J. Chem.*, 1983, **61**, 1651.
811. W. D. Horrocks, Jr., D. H. Templeton and A. Zalkin, *Inorg. Chem.*, 1968, **7**, 2303.
812. D. H. Brown, K. P. Forrest, R. H. Nuttal and D. W. A. Sharp, *J. Chem. Soc. (A)*, 1968, 2146.
813. J. Drew, M. B. Hursthouse and P. Thornton, *J. Chem. Soc., Dalton Trans.*, 1972, 1658.
814. A. F. Cameron, D. W. Taylor and R. H. Nuttal, *J. Chem. Soc., Dalton Trans.*, 1972, 422.
815. E. Durcanska, J. Garaj and M. Dunaj-Jurco, *Inorg. Chim. Acta*, 1978, **29**, 149.
816. J. Kopf, U. Behrens, M. Kastner, and G. Klar, *J. Inorg. Nucl. Chem.*, 1977, **39**, 889.
817. P. S. Shetty and Q. Fernando, *J. Am. Chem. Soc.*, 1970, **92**, 3964.
818. A. H. Norbury, E. A. Ryder and R. F. Williams, *J. Chem. Soc. (A)*, 1967, 1439.
819. R. V. Biagetti and H. M. Haendler, *Inorg. Chem.*, 1966, **5**, 383.
820. M. Jamnicky and E. Jona, *Z. Anorg. Allg. Chem.*, 1982, **487**, 225.
821. A. B. P. Lever, J. Lewis and R. S. Nyholm, *J. Chem. Soc.*, 1963, 5042; 1964, 4761.
822. M. Goldstein, F. B. Taylor and W. D. Unsworth, *J. Chem. Soc., Dalton Trans.*, 1972, 418.
823. F. D. Ayres, P. Pauling and G. B. Robertson, *Inorg. Chem.*, 1964, **3**, 1303.
824. D. E. Billing, A. E. Underhill and G. M. Smart, *J. Chem. Soc. (A)*, 1968, 8.
825. D. G. Hendricker and R. L. Bodner, *Inorg. Chem.*, 1970, **9**, 273.
826. R. L. Bodner and D. G. Hendricker, *Inorg. Chem.*, 1973, **12**, 33.
827. D. G. Hendricker and R. L. Foster, *Inorg. Chem.*, 1973, **12**, 349.
828. L. Sacconi, C. Mealli and D. Gatteschi, *Inorg. Chem.*, 1974, **13**, 1985.
829. R. W. Brookes and R. L. Martin, *Aust. J. Chem.*, 1974, **27**, 1569.
830. M. Brierley and W. J. Glary, *J. Chem. Soc. (A)*, 1967, 963.

831. D. A. Baldwin, A. B. P. Lever and R. V. Parish, *Inorg. Chem.*, 1969, **8**, 107.
832. P. J. Beadle, M. Goldstein, D. M. L. Goodgame and R. Grzeskowiak, *Inorg. Chem.*, 1969, **8**, 1490.
833. A. Bencini, D. Gatteschi and L. Sacconi, *Inorg. Chem.*, 1978, **17**, 2670.
834. M. Corbett and B. F. Hoskins, *Chem. Commun.*, 1968, 1602.
835. M. Corbett, D. F. Hoskins, N. J. McLeod and B. P. O'Day, *Aust. J. Chem.*, 1975, **28**, 2377.
836. L. F. Lindoy and S. E. Livingstone, *Coord. Chem. Rev.*, 1967, **2**, 173.
837. W. R. McWhinnie and J. D. Miller, *Adv. Inorg. Chem. Radiochem.*, 1969, **12**, 135.
838. E. D. McKenzie, *Coord. Chem. Rev.*, 1971, **6**, 187.
839. P. Pfeiffer and F. Tappermann, *Z. Anorg. Allg. Chem.*, 1933, **215**, 273.
840. G. B. Kauffman and L. T. Takahashi, *Inorg. Synth.*, 1966, **8**, 227.
841. G. Anderegg, *Helv. CHim. Acta*, 1963, **46**, 2397.
842. A. Wada, C. Katayama and J. Tanaka, *Acta Crystallogr., Sect. B*, 1976, **32**, 3194.
843. A. Wada, N. Sakabe and J. Tanaka, *Acta Crystallogr. Sect. B*, 1976, **32**, 1121.
844. K. R. Butler and M. R. Snow, *J. Chem. Soc. (A)*, 1971, 565.
845. B. A. Frenz and J. A. Ibers, *Inorg. Chem.*, 1972, **11**, 1109.
846. R. J. Butcher and E. Sinn, *Inorg. Chem.*, 1977, **16**, 2334.
847. R. J. Butcher, C. J. O'Connor and E. Sinn, *Inorg. Chem.*, 1979, **18**, 492.
848. S. K. Arora, D. E. Carter and Q. Fernando, *Acta Crystallogr., Sect. B*, 1977, **33**, 3230.
849. J. A. Broomhead and F. P. Dwyer, *Aust. J. Chem.*, 1962, **15**, 453.
850. C. M. Harris and E. D. McKenzie, *J. Inorg. Nucl. Chem.*, 1967, **29**, 1047.
851. H. Ojima and K. Nonoyama, *Z. Anorg. Allg. Chem.*, 1977, **429**, 282.
852. B. W. Dockum and W. H. Reiff, *Inorg. Chem.*, 1982, **21**, 2613.
853. J. A. Broomhead and F. P. Dwyer, *Aust. J. Chem.*, 1961, **14**, 250.
854. R. H. Lee, E. Griswold and J. Kleinberg, *Inorg. Chem.*, 1964, **3**, 1278.
855. T. R. Musgrave and C. E. Mattson, *Inorg. Chem.*, 1968, **7**, 1433.
856. V. A. Anagnostopoulos, *Inorg. Nucl. Chem. Lett.*, 1976, **12**, 225.
857. I. S. Ahuja, R. Singh and C. P. Rai, *J. Inorg. Nucl. Chem.*, 1978, **40**, 924.
858. F. Holmes, K. M. Jones and L. J. Torrible, *J. Chem. Soc.*, 1961, 4790.
859. R. J. Dosser and A. E. Underhill, *J. Chem. Soc., Dalton Trans.*, 1972, 611.
860. D. M. L. Goodgame and A. S. C. Machado, *Inorg. Chim. Acta*, 1972, **6**, 317.
861. A. D. Mighell, C. W. Reimann and F. A. Mauer, *Acta Crystallogr., Sect. B*, 1969, **25**, 60.
862. P. G. Rasmussen, R. L. Hough, J. E. Anderson, O. H. Bailey and J. C. Bayon, *J. Am. Chem. Soc.*, 1982, **104**, 6155.
863. G. Morgan and F. H. Borstall, *J. Chem. Soc.*, 1937, 1640.
864. J. S. Judge, W. M. Reiff, G. M. Intille, P. Ballway and W. A. Baker, Jr., *J. Inorg. Nucl. Chem.*, 1967, **29**, 1711.
865. J. S. Judge and W. A. Baker, Jr., *Inorg. Chim. Acta*, 1967, **1**, 239.
866. J. S. Judge and W. A. Baker, Jr., *Inorg. Chim. Acta*, 1967, **1**, 245.
867. W. J. Eilbeck, F. Holmes and A. E. Underhill, *J. Chem. Soc. (A)*, 1967, 757.
868. D. M. L. Goodgame, M. Goodgame, P. S. Hayward and G. W. Rayner-Canham, *Inorg. Chem.*, 1968, **7**, 2447.
869. J. Reedijk, *Recl. Trav. Chim. Pays-Bas*, 1971, **90**, 1135.
870. J. C. Van Dam, G. Hakvoort, J. C. Jansen and J. Reedijk, *J. Inorg. Nucl. Chem.*, 1975, **37**, 713.
871. A. D. van Ingen Schenan, *Acta Crystallogr., Sect. B*, 1975, **31**, 2736.
872. J. P. Konopelski, C. W. Reiman, C. R. Hubbard, A. D. Mighell and A. Santoro, *Acta Crystallogr., Sect. B*, 1976, **32**, 2911.
873. G. J. M. Ivarsson and W. Forsling, *Acta Crystallogr., Sect. B*, 1979, **35**, 1896.
874. C. E. Taylor and A. E. Underhill, *J. Chem. Soc., (A)*, 1969, 368.
875. D. M. L. Goodgame, M. Goodgame and G. W. Rayner-Canham, *Inorg. Chim. Acta*, 1969, **3**, 406.
876. K. C. Dash and P. Pujari, *J. Inorg. Nucl. Chem.*, 1977, **39**, 2167.
877. D. M. L. Goodgame, M. Goodgame and G. W. Rayner-Canham, *Inorg. Chim. Acta*, 1969, **3**, 399.
878. W. J. Eilbeck, F. Holmes, C. E. Taylor and A. E. Underhill, *J. Chem. Soc. (A)*, 1968, 128.
879. A. J. Finney, M. A. Hitchman, C. L. Raston, G. L. Rowbottom and A. H. White, *Aust. J. Chem.*, 1981, **34**, 2113.
880. D. M. L. Goodgame, M. Goodgame and G. W. Rayner-Canham, *J. Chem. Soc. (A)*, 1971, 1923.
881. J. Reedijk, *Recl. Trav. Chim. Pays-Bas*, 1974, **90**, 117.
882. J. Reedijk, *Recl. Trav. Chim. Pays-Bas*, 1973, **89**, 993.
883. D. M. L. Goodgame, M. Goodgame and M. J. Weeks, *J. Chem. Soc. (A)*, 1967, 1125.
884. M. G. B. Drew, D. H. Templeton and A. Zalkin, *Inorg. Chem.*, 1968, **7**, 2618.
885. D. M. L. Goodgame, M. Goodgame and M. J. Weeks, *J. Chem. Soc.*, 1964, 5194.
886. N. A. Daugherty and J. H. Swisher, *Inorg. Chem.*, 1968, **7**, 1657.
887. J. Reedijk and J. A. Smit, *Recl. Trav. Chim. Pays-Bas*, 1971, **90**, 1135.
888. R. W. M. Tenhoedt, W. L. Driessen and G. C. Verschoor, *Acta Crystallogr., Sect. C*, 1983, **39**, 71.
889. C. W. Reimann, A. Santoro and A. D. Mighell, *Acta Crystallogr., Sect. B*, 1970, **26**, 521.
890. C. W. Reimann, A. D. Mighell and F. A. Maner, *Acta Crystallogr.*, 1967, **23**, 135.
891. A. D. Mighell, C. W. Reimann and A. Santoro, *Acta Crystallogr., Sect. B*, 1969, **25**, 595.
892. D. Nicholls and B. A. Warburton, *J. Inorg. Nucl. Chem.*, 1970, **32**, 3871.
893. H. T. Wiheveen, W. L. C. Rutten and J. Reedijk, *J. Inorg. Nucl. Chem.*, 1975, **37**, 913.
894. J. Reedijk, *Recl. Trav. Chim. Pays-Bas*, 1970, **89**, 605.
895. P. J. McCarthy and J. Reedijk, *Inorg. Chim. Acta*, 1980, **40**, 239.
896. M. A. Guichelar, J. A. M. van Hest and J. Reedijk, *Delft Prog. Rep.*, 1976, **2**, 51.
897. M. J. Bagley, D. Nicholls and B. A. Warburton, *J. Chem. Soc. (A)*, 1970, 2694.
898. S. Trofimenko, *Chem. Rev.*, 1972, **72**, 497.
899. R. J. Sundberg and R. B. Martin, *Chem. Rev.*, 1974, **74**, 471.
900. A. Santoro, A. D. Mighell, M. Zocchi and C. W. Reiman, *Acta Crystallogr., Sect. B*, 1969, **25**, 842.

901. M. N. Hughes and K. J. Rutt, *Inorg. Chem.*, 1971, **10**, 414.
902. J. A. Weaver, P. Hambright, P. T. Talbert, E. Kang and A. N. Thorpe, *Inorg. Chem.*, 1970, **9**, 268.
903. E. J. Duff, M. N. Hughes and K. J. Rutt, *J. Chem. Soc.* (*A*), 1968, 2354.
904. M. Inque and M. Kubo, *Coord. Chem. Rev.*, 1976, **21**, 1.
905. J. G. Vos and W. L. Groeneveld, *Inorg. Chim. Acta,* 1977, **24**, 123; 1978, **26**, 71.
906. A. C. Fabretti, G. C. Franchini and G. Peyronel, *Transition Met. Chem.*, 1978, **3**, 363.
907. G. A. van Albada, R. A. G. De Graaf, J. G. Haasnoot and J. Reedijk, *Inorg. Chem.*, 1984, **23**, 1404.
908. C. W. Reimann and M. Zucchi, *Chem. Commun.*, 1968, 272.
909. J. E. Andrew and A. B. Blake, *J. Chem. Soc.* (*A*), 1969, 1408.
910. D. M. Bowers and A. I. Popou, *Inorg. Chem.*, 1968, **7**, 1594.
911. G. L. Gilbert and C. H. Brubaker, Jr., *Inorg. Chem.*, 1963, **2**, 1216.
912. L. Richards, S. N. Bow, J. L. Richards and K. Ralton, *Inorg. Chim. Acta,* 1977, **25**, L113.
913. R. D. Archer, *Inorg. Chem.*, 1965, **4**, 147.
914. N. M. Karayannis and C. M. Mikuski, *Inorg. Chim. Acta,* 1982, **65**, L233.
915. E. S. Raper, M. E. O'Neill and J. A. Daniels, *Inorg. Chim. Acta,* 1980, **41**, 201.
916. B. Piggot and A. C. Skapski, *Inorg. Chim. Acta,* 1983, **77**, L171.
917. M. L. Niven and L. R. Nassimbeni, *Cryst. Struct. Commun.*, 1980, **9**, 227.
918. J. J. Siirola and R. D. Ragsdale, *Inorg. Chem.*, 1965, **4**, 760.
919. E. Uhlig and M. Maaser, *Z. Anorg. Allg. Chem.*, 1963, **322**, 25.
920. E. Uhlig, R. Kramer and H. Wolf, *Z. Anorg. Allg. Chem.*, 1968, **361**, 157.
921. E. Uhlig, E. Unger and U. Dinjus, *Z. Anorg. Allg. Chem.*, 1971, **380**, 181.
922. E. Uhlig, J. Csaszar and M. Maaser, *Z. Anorg. Allg. Chem.*, 1964, **331**, 324.
923. E. Uhlig and E. Unger, *Z. Anorg. Allg. Chem.*, 1968, **363**, 151.
924. P. H. Nielsen and U. Dahl, *Acta Chem. Scand.*, 1966, **20**, 1113.
925. M. R. Litzow, L. F. Power and A. M. Tait, *J. Chem. Soc.* (*A*), 1970, 275.
926. L. F. Power, A. M. Tait, J. Pletcher and M. Sax, *J. Chem. Soc., Dalton Trans.*, 1975, 2494.
927. C. D. Burbridge and D. M. L. Goodgame, *J. Chem. Soc.* (*A*), 1968, 237.
928. T. J. Hurley and M. A. Robinson, *Inorg. Chem.*, 1968, **7**, 33.
929. W. R. McWhinnie, C. G. Kulasingam and J. C. Draper, *J. Chem. Soc.* (*A*), 1966, 1199; G. C. Kulasingam and W. R. McWhinnie, *J. Chem. Soc.* (*A*), 1967, 963.
930. J. K. Romary, J. D. Barger and J. E. Bunds, *Inorg. Chem.*, 1968, **7**, 1142.
931. S. M. Nelson and J. Rodgers, *J. Chem. Soc.* (*A*), 1968, 272.
932. M. M. Da Mota, J. Rodgers and S. M. Nelson, *J. Chem. Soc.* (*A*), 1969, 2036.
933. J. Rodgers and R. A. Jacobson, *J. Chem. Soc.* (*A*), 1970, 1826.
934. S. M. Nelson and J. Rodgers, *Inorg. Chem.*, 1967, **6**, 1390.
935. A. T. Casey, W. Peters and A. T. Phillip, *Aust. J. Chem.*, 1970, **23**, 2257.
936. R. G. Lacoste and A. E. Martell, *Inorg. Chem.*, 1964, **3**, 881.
937. S. Utsuno, *J. Inorg. Nucl. Chem.*, 1970, **32**, 1631.
938. N. F. Curtis, *J. Chem. Soc. Dalton Trans.*, 1975, 91.
939. R. K. Bogges and S. J. Boberg, *J. Inorg. Nucl. Chem.*, 1980, **42**, 21.
940. F. Mani and G. Scapacci, *Inorg. Chim. Acta,* 1980, **38**, 151.
941. F. Mani and C. Mealli, *Inorg. Chim. Acta,* 1982, **63**, 97.
942. J. G. Gibson and E. D. McKenzie, *J. Chem. Soc.* (*A*), 1971, 1666.
943. A. T. Phillip, A. T. Casey and C. R. Thompson, *Aust. J. Chem.*, 1970, **23**, 491.
944. W. Mazurek, A. T. Phillip, B. F. Hoskins and F. D. Whillans, *Chem. Commun.*, 1970, 184.
945. H. A. Goodwin, in 'Chelating Agents and Metal Chelates', ed. F. P. Dwyer and D. P. Mellor, New York, 1964, p. 143.
946. D. W. Gruenwedel, *Inorg. Chem.*, 1968, **7**, 495.
947. J. A. Timmons, A. E. Martell, W. R. Harris and I. Murase, *Inorg. Chem.*, 1982, **21**, 1525.
948. M. A. Robinson, J. D. Curry and D. H. Bush, *Inorg. Chem.*, 1963, **2**, 1178.
949. R. C. Stoufer and D. H. Busch, *J. Am. Chem. Soc.*, 1956, **78**, 6016.
950. R. C. Stoufer and D. H. Busch, *J. Am. Chem. Soc.*, 1960, **82**, 3491.
951. P. E. Figgins and D. H. Busch, *J. Am. Chem. Soc.*, 1960, **82**, 820.
952. H. M. Fisher and R. C. Stoufer, *Inorg. Chem.*, 1966, **5**, 1172.
953. M. A. Robinson and D. H. Busch, *Inorg. Chem.*, 1963, **2**, 1171.
954. I. Bertini, D. L. Jonston and W. D. Horrocks, Jr., *Inorg. Chem.*, 1970, **9**, 693.
955. J. D. Curry, M. A. Robinson and D. H. Busch, *Inorg. Chem.*, 1967, **6**, 1570.
956. L. Sacconi, R. Morassi and S. Midollini, *J. Chem. Soc.* (*A*), 1968, 1510.
957. E. C. Alyea, G. Ferguson and R. J. Restivo, *Inorg. Chem.*, 1975, **14**, 2491.
958. J. F. Geldard and F. Lions, *Inorg. Chem.*, 1963, **2**, 270.
959. B. Chiswell and D. S. Litster, *Inorg. Chim. Acta,* 1978, **29**, 17.
960. F. Lions, I. G. Dance and J. Lewis, *J. Chem. Soc.* (*A*), 1967, 565.
961. M. R. Litzow, L. F. Power and A. M. Tait, *J. Chem. Soc.* (*A*), 1970, 2908.
962. P. Bamfield, R. Price and R. G. J. Miller, *J. Chem. Soc.* (*A*), 1969, 1447.
963. B. Chiswell and F. Lions, *Aust. J. Chem.*, 1969, **22**, 71.
964. G. Zakrzewski and L. Sacconi, *Inorg. Chem.*, 1968, **7**, 1034.
965. L. Sacconi, I. Bertini and R. Morassi, *Inorg. Chem.*, 1967, **6**, 1548.
966. I. Bertini, D. L. Jonston and W. D. Horrocks, Jr., *Inorg. Chem.*, 1970, **9**, 698.
967. W. J. Stratton and D. H. Busch, *J. Am. Chem. Soc.*, 1958, **80**, 1286.
968. W. J. Stratton and D. H. Busch, *J. Am. Chem. Soc.*, 1958, **80**, 3191.
969. B. Chiswell and F. Lions, *Inorg. Chem.*, 1964, **3**, 490.
970. R. J. Olcott and R. H. Holm, *Inorg. Chim. Acta,* 1969, **3**, 431.

971. N. A. Bailey, T. A. James, J. A. McCleverty, E. D. McKenzie, R. D. Moore and J. M. Worthingon, *J. Chem. Soc., Chem. Commun.*, 1972, 681.
972. M. Bacci, F. Mani and S. Midollini, *Gazz. Chim. Ital.*, 1972, **102,** 1019.
973. J. Dekkers and H. A. Goodwin, *Aust. J. Chem.*, 1967, **20,** 69.
974. J. E. Parks, B. E. Wagner and R. H. Holm, *Inorg. Chem.*, 1971, **10,** 2472.
975. M. R. Churchill and A. H. Reis, Jr., *Chem. Commun.*, 1970, 679.
976. D. H. Busch, *Rec. Chem. Prog.*, 1964, **25,** 107.
977. W. O. Gillum, R. A. D. Wentworth and R. F. Childers, *Inorg. Chem.*, 1970, **9,** 1825.
978. E. B. Fleischer, A. E. Gebala, D. R. Swift and P. A. Tasker, *Inorg. Chem.*, 1972, **11,** 2775.
979. L. J. Wilson and N. J. Rose, *J. Am. Chem. Soc.*, 1968, **90,** 6041.
980. P. B. Donaldson, P. A. Tasker and N. N. Alcock, *J. Chem. Soc., Dalton Trans.*, 1977, 1161.
981. M. Bailey and E. C. Lingafelter, *Natl. Meet. Am. Chem. Soc., 156th, Abstr.*, 1968.
982. N. F. Curtis, *J. Chem. Soc.*, 1960, 4409.
983. M. M. Blight and N. F. Curtis, *J. Chem. Soc.*, 1962, 1204.
984. M. M. Blight and N. F. Curtis, *J. Chem. Soc.*, 1962, 3016.
985. D. A. House and N. F. Curtis, *J. Am. Chem. Soc.*, 1964, **86,** 1331.
986. T. E. MacDermott and D. H. Busch, *J. Am. Chem. Soc.*, 1967, **89,** 5780.
987. L. T. Taylor, N. J. Rose and D. H. Busch, *Inorg. Chem.*, 1968, **7,** 785.
988. W. Jehn, *Z. Chem.*, 1964, **4,** 307.
989. W. J. Rose, M. S. Elder and D. H. Busch, *Inorg. Chem.*, 1967, **6,** 1924.
990. D. E. Goldberg, *J. Chem. Soc. (A)*, 1968, 2671.
991. J. Lewis and K. P. Wainwright, *J. Chem. Soc., Dalton Trans.*, 1977, 734.
992. J. Lewis and K. P. Wainwright, *J. Chem. Soc., Dalton Trans.*, 1977, 739.
993. F. Feigl and M. Furth, *Monatsh. Chem.*, 1927, **48,** 445.
994. G. Swartz Hall and R. H. Soderberg, *Inorg. Chem.*, 1968, **7,** 2300.
995. A. L. Balch and R. H. Holm, *J. Am. Chem. Soc.*, 1966, **88,** 5201.
996. E. B. Fleischer, A. E. Gebala and P. A. Tasker, *Inorg. Chim. Acta*, 1972, **6,** 72.
997. R. H. Holm and M. J. O'Connor, *Prog. Inorg. Chem.*, 1971, **14,** 241.
998. D. R. Eaton and W. R. McClellan, *Inorg. Chem.*, 1967, **6,** 2134.
999. D. R. Eaton, A. D. Josey and R. E. Benson, *J. Am. Chem. Soc.*, 1967, **89,** 4040.
1000. D. R. Eaton, W. D. Phillips and D. J. Caldwell, *J. Am. Chem. Soc.*, 1963, **85,** 397 and refs. therein.
1001. P. Pfeiffer, T. Hesse, H. Pfitzner, W. Scholl and H. Thielert, *J. Prakt. Chem.*, 1937, **149,** 217.
1002. R. H. Holm and A. Chakravorty, *Inorg. Chem.*, 1966, **5,** 625.
1003. O. A. Osipov, A. D. Garnovskii and V. I. Minkin, *J. Struct. Chem. (Engl. Transl.)*, 1967, **8,** 817.
1004. D. Cummins, E. D. McKenzie, I. W. Nowell and J. M. Worthington, *Inorg. Chim. Acta*, 1975, **15,** L17.
1005. E. D. McKenzie, R. D. Moore and J. M. Worthington, *Inorg. Chim. Acta*, 1975, **14,** 37.
1006. N. A. Bailey and E. D. McKenzie, *Inorg. Chim. Acta*, 1980, **43,** 205.
1007. N. A. Bailey, E. D. McKenzie and J. M. Worthington, *J. Chem. Soc., Dalton Trans.*, 1974, 1363.
1008. M. Mulqi, F. S. Stephens and R. S. Vagg, *Inorg. Chim. Acta*, 1981, **52,** 73.
1009. F. S. Stephens and R. S. Vagg, *Inorg. Chim. Acta*, 1982, **57,** 9.
1010. S. C. Chang, D. Y. Park and N. C. Li, *Inorg. Chem.*, 1968, **7,** 2144.
1011. J. E. Parks and R. H. Holm, *Inorg. Chem.*, 1968, **7,** 1408.
1012. S. C. McGeachin, *Can. J. Chem.*, 1968, **46,** 1903.
1013. C. L. Honeybourne and A. G. Webb, *Chem. Phys. Lett.*, 1968, **2,** 426.
1014. C. L. Honeybourne and A. G. Webb, *Chem. Commun.*, 1968, 739.
1015. Y. Nishida, N. Oishi and S. Kida, *Inorg. Chim. Acta*, 1979, **32,** 7.
1016. P. C. Healy, M. R. Bendall, D. A. Doddrell, B. W. Skelton and A. H. White, *Aust. J. Chem.*, 1979, **32,** 727.
1017. H. M. N. H. Irving, J. B. Gill and W. R. Griss, *J. Chem. Soc.*, 1960, 2087.
1018. D. Dale, *J. Chem. Soc. (A)*, 1967, 278.
1019. A. Chakravorty, *Coord. Chem. Rev.*, 1974, **13,** 1.
1020. L. E. Godycki and R. E. Rundle, *Acta Crystallogr.*, 1953, **6,** 487.
1021. D. E. Williams, G. Wohlauer and R. E. Rundle, *J. Am. Chem. Soc.*, 1959, **81,** 755.
1022. K. Murmann and E. D. Schlemper, *Acta Crystallogr.*, 1967, **23,** 667.
1023. M. Calleri, G. Ferraris and D. Viterbo, *Acta Crystallogr.*, 1967, **22,** 468.
1024. E. Frasson and C. Panattoni, *Acta Crystallogr.*, 1960, **13,** 893.
1025. R. H. Bowers, C. V. Banks and R. A. Jacobson, *Acta Crystallogr., Sect. B*, 1972, **28,** 2318.
1026. I. Leichert and J. Weiss, *Acta Crystallogr., Sect. B*, 1975, **31,** 2877.
1027. H. Endres, T. Jannack and B. Prickner, *Acta Crystallogr., Sect. B*, 1980, **36,** 2230.
1028. S. Stephens and R. S. Vagg, *Acta Crystallogr., Sect. B*, 1977, **33,** 3159.
1029. C. K. Fair and E. O. Schlemper, *Acta Crystallogr., Sect. B*, 1978, **34,** 436.
1030. J. C. Ching and E. O. Schlemper, *Inorg. Chem.*, 1975, **14,** 2470.
1031. M. S. Hussain and E. O. Schlemper, *Inorg. Chem.*, 1979, **18,** 2275.
1032. E. G. Vassian and R. K. Murmann, *Inorg. Chem.*, 1967, **6,** 2043.
1033. E. O. Schlemper, W. C. Hamilton and S. J. La Placa, *J. Chem. Phys.*, 1971, **54,** 3990; E. O. Schlemper, *Inorg. Chem.*, 1968, **7,** 1130.
1034. P. S. Gomm, T. W. Thomas and A. E. Underhill, *J. Chem. Soc., (A)*, 1971, 2154.
1035. F. S. Stephens and R. S. Vagg, *Acta Crystallogr., Sect. B*, 1977, **33,** 3165.
1036. F. S. Stephens, R. S. Vagg and E. C. Watton, *Inorg. Chim. Acta*, 1981, **47,** 97.
1037. F. S. Stephens and R. S. Vagg, *Inorg. Chim. Acta*, 1981, **52,** 245; 1983, **69,** 103.
1038. F. S. Stephens and R. S. Vagg, *Inorg. Chim. Acta*, 1981, **51,** 163.
1039. J. A. Ibers, L. J. Pace, J. Martinsen and B. M. Hoffman, *Struct. Bonding (Berlin)*, 1982, **50,** 1.

1040. M. Cowie, A. Gleizes, G. W. Grynkewich, D. W. Kalina, M. S. McClure, R. P. Scaringe, R. C. Teitelbaum, S. L. Ruby, J. A. Ibers, C. R. Kannewurf and T. J. Marks, *J. Am. Chem. Soc.*, 1979, **101**, 2921.
1041. L. D. Brown, D. W. Kalina, M. S. McClure, S. Schultz, S. L. Ruby, J. A. Ibers, C. R. Kannewurf and T. J. Marks, *J. Am. Chem. Soc.*, 1979, **101**, 2937.
1042. H. Endres, H. J. Keller, W. Moroni and J. Weiss, *Acta Crystallogr., Sect. B*, 1975, **31**, 2357.
1043. H. Endres, H. J. Keller, M. Megnamisi-Belombe', W. Moroni, H. Pritzkow, J. Weiss and R. Comes, *Acta Crystallogr., Sect. A*, 1976, **32**, 954.
1044. L. E. Edelman, *J. Am. Chem. Soc.*, 1950, **72**, 5765.
1045. A. S. Foust and R. H. Soderberg, *J. Am. Chem. Soc.*, 1967, **89**, 5507.
1046. J. S. Miller and C. H. Griffiths, *J. Am. Chem. Soc.*, 1977, **99**, 749.
1047. D. W. Kalina, J. W. Lyding, M. T. Ratajack, C. R. Kannewurf and T. J. Marks, *J. Am. Chem. Soc.*, 1980, **102**, 7654.
1048. M. L. Bowers and C. L. Hill, *Inorg. Chim. Acta*, 1983, **72**, 149.
1049. H. Endres and A. Knieszner, *Acta Crystallogr., Sect. C*, 1984, **40**, 770.
1050. H. Endres and M. Schendzielorz, *Acta Crystallogr., Sect. C*, 1983, **39**, 1528.
1051. R. A. Krause and D. H. Busch, *J. Am. Chem. Soc.*, 1960, **82**, 4830.
1052. R. A. Krause and D. H. Busch, *Nature (London)*, 1958, **181**, 1529.
1053. R. A. Krause, C. Guy and M. L. Hooker, *Inorg. Chem.*, 1966, **5**, 1825.
1054. D. L. Cullen and E. C. Lingafelter, *Inorg. Chem.*, 1970, **9**, 1865.
1055. A. Nakamura, A. Konishi and S. Otsuka, *J. Chem. Soc., Dalton Trans.*, 1979, 488.
1056. M. S. Ma, R. J. Angelici, D. Powell and R. A. Jacobson, *J. Am. Chem. Soc.*, 1978, **100**, 7068.
1057. B. L. Holian and R. E. Marsch, *Acta Crystallogr., Sect. B*, 1970, **26**, 1040.
1058. L. Fabbrizzi, M. Micheloni and P. Paoletti, *Inorg. Chem.*, 1978, **17**, 495.
1059. L. Coghi, A. Mangia and M. Nardelli, *Ric. Sci.*, 1969, **39**, 438.
1060. A. Syamal and V. D. Ghanekar, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1606.
1061. S. Trofimenko, *Acc. Chem. Res.*, 1971, **4**, 17; S. Trofimenko, *Chem. Rev.*, 1972, **72**, 497; S. Trofimenko, *Adv. Chem. Ser.*, 1976, **150**, 289.
1062. S. Trofimenko, *Inorg. Synth.*, 1970, **12**, 99; S. Trofimenko, *J. Am. Chem. Soc.*, 1967, **89**, 3170.
1063. J. P. Jesson, S. Trofimenko and D. R. Eaton, *J. Am. Chem. Soc.*, 1967, **89**, 3148.
1064. H. M. Echols and D. Dennis, *Acta Crystallogr., Sect. B*, 1967, **23**, 1627.
1065. H. M. Echols and D. Dennis, *Acta Crystallogr., Sect. B*, 1974, **30**, 2173.
1066. F. A. Cotton and C. A. Murillo, *Inorg. Chim. Acta*, 1976, **17**, 121.
1067. E. Frauendorfer and G. Agrifoglio, *Inorg. Chem.*, 1982, **21**, 4122.
1068. F. Mani, *Inorg. Chim. Acta*, 1986, **117**, L1.
1069. K. R. Breakell, D. J. Patmore and A. Storr, *J. Chem. Soc., Dalton Trans.*, 1975, 749.
1070. D. F. Rendle, A. Storr and J. Trotter, *J. Chem. Soc., Dalton Trans.*, 1975, 176.
1071. S. J. Rettig, A. Storr and J. Trotter, *Can. J. Chem.*, 1979, **57**, 1823.
1072. S. Trofimenko, *J. Am. Chem. Soc.*, 1970, **92**, 5118.
1073. J. Verbiest, J. A. C. van Doijen and J. Reedijk, *J. Inorg. Nucl. Chem.*, 1980, **42**, 971.
1074. J. C. Jansen, H. van Koningsveld, J. A. C. van Ooijen and J. Reedijk, *Inorg. Chem.*, 1980, **19**, 170.
1075. S. Trofimenko, *J. Am. Chem. Soc.*, 1967, **89**, 6288.
1076. G. Bandoli, D. A. Clemente, G. Paolucci and L. Doretti, *Cryst. Struct. Commun.*, 1979, **8**, 965.
1077. J. R. Jezorek and W. H. McCurdy, Jr., *Inorg. Chem.*, 1975, **14**, 1939.
1078. A. H. Norbury, *Adv. Inorg. Chem. Radiochem.*, 1975, **17**, 231.
1079. P. P. Singh, *Coord. Chem. Rev.*, 1980, **32**, 33.
1080. D. Forster and D. M. L. Goodgame, *Inorg. Chem.*, 1965, **4**, 1712.
1081. R. A. Bailey, S. L. Kozak, T. W. Michelsen and W. N. Mills, *Coord. Chem. Rev.*, 1971, **6**, 407.
1082. D. Forster and D. M. L. Goodgame, *Inorg. Chem.*, 1965, **4**, 715, 823.
1083. Y. Y. Kharitonov, G. V. Tsintsadze and A. Y. Tsivadze, *Inorg. Nucl. Chem. Lett.*, 1970, **2**, 201.
1084. A. Rosenheim and R. Cohn, *Z. Anorg. Allg. Chem.*, 1901, **27**, 280.
1085. M. A. Porai-Koshits, *Acta Crystallogr., Suppl.*, 1963, **A42**, 472.
1086. A. Sabatini and I. Bertini, *Inorg. Chem.*, 1965, **4**, 959.
1087. J. L. Burmeister and L. E. Williams, *Inorg. Chem.*, 1966, **7**, 1113.
1088. D. Forster and D. M. L. Goodgame, *J. Chem. Soc.*, 1964, 2790.
1089. P. P. Singh and A. K. Gupta, *Inorg. Chem.*, 1978, **17**, 1.
1090. P. P. Singh, N. Singh and D. D. S. Yadav, *J. Inorg. Nucl. Chem.*, 1981, **43**, 77.
1091. P. P. Singh, S. Kumar and M. P. Reddy, *Inorg. Chem.*, 1981, **20**, 2711.
1092. P. P. Singh and K. Atreya, *Polyhedron*, 1982, **1**, 711.
1093. P. P. Singh and V. P. Singh, *Inorg. Chim. Acta*, 1983, **71**, 205.
1094. M. Duggan and D. N. Hendrickson, *J. Chem. Soc., Chem. Commun.*, 1973, 411.
1095. J. Nelson and S. M. Nelson, *J. Chem. Soc. (A)*, 1969, 1597.
1096. G. V. Tsintsadze, M. A. Porai-Koshits and A. S. Antsyshkina, *Zh. Strukt. Khim.*, 1967, **8**, 296.
1097. Z. Dori and R. F. Ziolo, *Chem. Rev.*, 1973, **73**, 247.
1098. H. Krishner, W. Dobramysl and H. P. Fritzer, *Z. Anorg. Allg. Chem.*, 1976, **423**, 255.
1099. F. Wagner, M. T. Mocella, M. J. D'Aniello, Jr., A. H. J. Wang and E. K. Barefield, *J. Am. Chem. Soc.*, 1974, **96**, 2625.
1100. K. Werner and W. Beck, *Chem. Ber.*, 1972, **105**, 3209.
1101. B. N. Storhoff and H. C. Lewis, Jr., *Coord. Chem. Rev.*, 1977, **23**, 1.
1102. R. A. Walton, *Q. Rev., Chem. Soc.*, 1965, **19**, 126.
1103. A. E. Wickenden and R. A. Krause, *Inorg. Chem.*, 1965, **4**, 404.
1104. B. J. Hathaway and D. G. Holah, *J. Chem. Soc.*, 1964, 2400.
1105. C. A. A. van Driel and W. L. Groeneveld, *Recl. Trav. Chim. Pays-Bas*, 1970, **90**, 389.
1106. A. P. Zuur, A. H. L. Reintjes and W. L. Groeneveld, *Recl. Trav. Chim. Pays-Bas*, 1970, **90**, 385.

1107. C. D. Jansen-Liathelm, W. L. Groeneveld and J. Reedijk, *Inorg. Chim. Acta*, 1973, **7**, 113.
1108. J. Reedijk and W. L. Groeneveld, *Recl. Trav. Chim. Pays-Bas*, 1968, **87**, 513.
1109. I. Sotofte, R. Gronbaer and S. E. Rasmussen, *Acta Crystallorg., Sect. B*, 1976, **32**, 1692.
1110. M. Wada and T. Shimohigashi, *Inorg. Chem.*, 1976, **15**, 954.
1111. R. Breslow, R. Fairweather and J. Keana, *J. Am. Chem. Soc.*, 1967, **89**, 2135.
1112. C. R. Clark and R. W. Hay, *J. Chem. Soc., Dalton Trans.*, 1974, 2148.
1113. K. Sakai, T. Itu and K. Watanabe, *Bull. Chem. Soc. Jpn.*, 1967, **40**, 1660.
1114. K. Watanabe, S. Komiya and S. Suzuki, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 2792.
1115. C. H. Yang, S. F. Lin, H. L. Chen and C. T. Chang, *Inorg. Chem.*, 1980, **19**, 3541.
1116. C. H. Yang and C. T. Chang, *J. Chem. Soc., Dalton Trans.*, 1982, 2539.
1117. M. Berthelot, *C. R. Hebd. Seances Acad. Sci.*, 1891, **112**, 1243.
1118. W. P. Griffith, J. Lewis and G. Wilkinson, *J. Chem. Soc.*, 1959, 1775.
1119. W. P. Griffith, J. Lewis and G. Wilkinson, *J. Chem. Soc.*, 1961, 775.
1120. C. C. Addison and B. F. G. Johnson, *Proc. Chem. Soc.*, 1962, 305.
1121. L. Malatesta and P. Pizzotti, *Gazz. Chim. Ital.*, 1942, **72**, 174.
1122. F. T. Bonner and M. J. Akhtar, *Inorg. Chem.*, 1981, **20**, 3155.
1123. D. C. Bradley and M. H. Chisholm, *Acc. Chem. Res.*, 1976, **9**, 273.
1124. H. Burger and U. Wannagat, *Monatsh. Chem.*, 1964, **95**, 1099.
1125. D. C. Bradley, M. B. Hursthouse, R. J. Smallwood and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 1972, 872.
1126. T. Yamamoto, T. Kohara and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 1720.
1127. A. Pidock, in 'Transition Metal Complexes of Phosphorus, Arsenic and Antimony Ligands', ed. C. A. McAuliffe, Wiley, New York, 1973.
1128. C. A. McAuliffe and W. Levason, 'Phosphine, Arsine and Stibine Complexes of Transition Metals', Elsevier, New York, 1978.
1129. G. Booth, *Adv. Inorg. Chem. Radiochem.*, 1964, **6**, 1.
1130. P. G. Eller, D. C. Bradley, M. B. Hursthouse and D. W. Meek *Coord. Chem. Rev.*, 1977, **24**, 1.
1131. W. A. Levason and C. A. McAuliffe, *Acc. Chem. Res.*, 1978, **11**, 363.
1132. M. A. A. Beg and H. C. Clark, *Can. J. Chem.*, 1961, **39**, 595.
1133. O. Dahl, *Acta Chem. Scand.*, 1969, **23**, 2342.
1134. A. Merle, M. Dartiguenave and Y. Dartiguenave, *J. Mol. Struct.*, 1972, **13**, 413.
1135. E. J. Lukosius and K. J. Coskran, *Inorg. Chem.*, 1975, **14**, 1922.
1136. A. Mari, A. Gleizes, M. Dartiguenave and Y. Dartiguenave, *Inorg. Chim. Acta*, 1981, **52**, 82.
1137. K. A. Jensen, *Z. Anorg. Allg. Chem.*, 1936, **229**, 265.
1138. G. Giacometti, V. Scatturin and A. Turco, *Gazz. Chim. Ital.*, 1958, **88**, 434.
1139. P. Rigo, C. Pecile and A. Turco, *Inorg. Chem.*, 1967, **6**, 1637; G. Bontempelli, B. Corain and L. De Nardo, *J. Chem. Soc., Dalton Trans.*, 1977, 1887.
1140. U. Blindheim, *Inorg. Chim. Acta*, 1970, **4**, 507.
1141. C. Udovich, J. Takemoto and K. Nakamoto, *J. Coord. Chem.*, 1971, **1**, 89.
1142. A. Turco, V. Scatturin and G. Giacometti, *Nature (London)*, 1959, **183**, 601.
1143. P. J. Stone and Z. Dori, *Inorg. Chim. Acta*, 1971, **5**, 434.
1144. L. Que and L. M. Pignolet, *Inorg. Chem.*, 1973, **12**, 156.
1145. B. B. Chastain, D. W. Meek, E. Billig, J. E. Hix, Jr. and H. B. Gray, *Inorg. Chem.*, 1968, **7**, 2412.
1146. A. Merle, M. Dartiguenave and Y. Dartiguenave, *C. R. Hebd. Seances Acad. Sci., Ser. C*, 1971, **272**, 2046.
1147. A. Merle, M. Dartiguenave and Y. Dartiguenave, *Bull. Soc. Chim. Fr.*, 1972, 87.
1148. P. F. Meier, A. E. Merbach, M. Dartiguenve and Y. Dartiguenave, *Inorg. Chim. Acta*, 1980, **39**, 19.
1149. A. Merle, M. Dartiguenave, Y. Dartiguenave, J. W. Dawson and H. B. Gray, *J. Coord. Chem.*, 1974, **3**, 199.
1150. J. W. Dawson, T. J. McLennan, W. Robinson, A. Merle, M. Dartiguenave, Y. Dartiguenave and H. B. Gray, *J. Am. Chem. Soc.*, 1974, **96**, 4428.
1151. M. Dartiguenave, Y. Dartiguenave, A. Gleizes, J. Galy, P. Meier, A. E. Merbach and C. Saint-Joly, *Inorg. Chem.*, 1978, **17**, 3503.
1152. P. Rigo and M. Bressan, *Inorg. Chem.*, 1972, **11**, 1314.
1153. C. D. Hem, M. Dartiguenave and Y. Dartiguenave, *Inorg. Nucl. Chem. Lett.*, 1974, **10**, 1039.
1154. M. F. Ludmann, M. Dartiguenave and Y. Dartiguenave, *Inorg. Chem.*, 1977, **16**, 440.
1155. F. A. Cotton, O. D. Fault and D. M. L. Goodgame, *J. Am. Chem. Soc.*, 1961, **83**, 344.
1156. G. N. LaMar, R. H. Fisher and W. D. Horrocks, Jr., *Inorg. Chem.*, 1967, **6**, 1798.
1157. M. Gerloch and L. R. Hanton, *Inorg. Chem.*, 1981, **20**, 1046.
1158. I. Bertini, D. Gatteschi and F. Mani, *Inorg. Chem.*, 1972, **11**, 2464.
1159. K. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1954, **27**, 501.
1160. L. M. Venanzi, *J. Chem. Soc.*, 1958, 719.
1161. C. R. C. Coussmaker, M. H. Hutchinson, J. R. Mellor, L. E. Sutton and L. M. Venanzi, *J. Chem. Soc.*, 1961, 2705.
1162. M. C. Browning, J. R. Mellor, D. J. Morgan, S. A. J. Pratt, L. E. Sutton and L. M. Venanzi, *J. Chem. Soc.*, 1962, 693.
1163. R. G. Hayter and F. S. Humic, *Inorg. Chem.*, 1965, **4**, 1701.
1164. J. T. Wang, C. Udovich, K. Nakamoto, A. Quattrochi and J. Ferraro, *Inorg. Chem.*, 1970, **9**, 2675.
1165. R. G. Hayter, *Inorg. Chem.*, 1963, **2**, 932.
1166. J. W. Dawson, L. M. Venanzi, J. R. Preer, J. E. Hix and H. B. Gray, *J. Am. Chem. Soc.*, 1971, **93**, 778.
1167. O. Stelzer, *Chem. Ber.*, 1974, **107**, 2329.
1168. O. Stelzer and E. Unger, *J. Chem. Soc., Dalton Trans.*, 1973, 1783.
1169. W. S. Sheldrick and O. Stelzer, *J. Chem. Soc., Dalton Trans.*, 1973, 926.
1170. D. W. Allen and S. J. R. Dommett, *Inorg. Chim. Acta*, 1978, **31**, L369.
1171. A. T. T. Hsieh, J. D. Ruddick and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1972, 1966.

1172. G. Elbaze, F. Dahan, M. Dartiguenave and Y. Dartiguenave, *Inorg. Chim. Acta,* 1984, **85,** L3.
1173. C. Saint Joly, A. Mari, A. Gleizes, M. Dartiguenave and Y. Dartiguenave, *Inorg. Chem.*, 1980, **19,** 2403.
1174. E. C. Alyea, A. Costin, G. Ferguson, G. T. Fey, R. G. Goel and R. J. Restivo, *J. Chem. Soc., Dalton Trans.*, 1975, 1294.
1175. L. R. Hanton and P. R. Raithby, *Acta Crystallogr., Sect. B,* 1980, **36,** 2417.
1176. R. P. Taylor, D. H. Templeton, A. Zalkin and W. D. Horrocks, Jr., *Inorg. Chem.*, 1968, **7,** 2629.
1177. J. K. Stalick and J. A. Ibers, *Inorg. Chem.*, 1970, **9,** 453.
1178. B. T. Kilbourn and H. M. Powell, *J. Chem. Soc. (A),* 1970, 1688.
1179. J. J. Macdougall, J. H. Nelson, M. W. Babich, C. C. Fuller and R. A. Jacobson, *Inorg. Chim. Acta,* 1978, **27,** 201.
1180. J. A. J. Jarvis, R. H. B. Mais and P. G. Owston, *J. Chem. Soc. (A),* 1968, 1473.
1181. J. A. Bertrand and D. L. Plymole, *Inorg. Chem.*, 1966, **5,** 879.
1182. J. K. Stalick and J. A. Ibers, *Inorg. Chem.*, 1969, **8,** 1090.
1183. H. Hope, M. M. Olmstead, P. P. Power and M. Viggiano, *Inorg. Chem.*, 1984, **23,** 926.
1184. M. G. B. Drew, D. F. Lewis and R. A. Walton, *Chem. Commun.*, 1969, 326.
1185. (a) B. M. Foxman and H. Mazurek, *Inorg. Chem.*, 1979, **18,** 113; (b) B. M. Foxman, P. L. Goldberg and H. Mazurek, *Inorg. Chem.*, 1981, **20,** 4368.
1186. D. G. Holah, A. N. Hughes and K. Wright, *Coord. Chem. Rev.*, 1975, **15,** 239.
1187. D. W. Allen, F. G. Mann, I. T. Millar, H. M. Powell and D. Watkin, *Chem. Commun.*, 1969, 1004.
1188. A. T. McPhail, R. C. Komson, J. F. Engel and L. D. Quin, *J. Chem. Soc., Dalton Trans.*, 1972, 874.
1189. E. C. Alyea, G. T. Fey and R. G. Goel, *J. Coord. Chem.*, 1976, **5,** 143.
1190. G. Garton, D. E. Henn, H. M. Powell and L. M. Venanzi, *J. Chem. Soc.*, 1963, 3625.
1191. P. F. Meier, A. E. Merbach, M. Dartiguenave and Y. Dartiguenave, *Inorg. Chem.*, 1979, **18,** 610.
1192. K. Cheng and B. M. Foxman, *J. Am. Chem. Soc.*, 1977, **99,** 8102.
1193. J. M. Huggins and R. G. Bergman, *J. Am. Chem. Soc.*, 1979, **101,** 4410.
1194. B. L. Barnett and C. Krüger, *J. Organomet. Chem.*, 1972, **42,** 169.
1195. F. A. Cotton, B. A. Frenz and D. L. Hunter, *J. Am. Chem. Soc.*, 1974, **96,** 4820.
1196. (a) M. R. Churchill, K. L. Kalra and M. V. Veidis, *Inorg. Chem.*, 1973, **12,** 1656; (b) M. Wada, K. Oguro and Y. Kawasaki, *J. Organomet. Chem.*, 1979, **178,** 261.
1197. M. R. Churchill and M. V. Veidis, *J. Chem. Soc., Dalton Trans.*, 1972, 670.
1198. M. R. Churchill and M. V. Veidis, *J. Chem. Soc. (A),* 1971, 3463.
1199. A. Gleizes, A. Kerkeni, M. Dartiguenave, Y. Dartiguenave and H. F. Klein, *Inorg. Chem.*, 1981, **20,** 2372.
1200. W. A. Spofford, P. D. Carfagna and E. L. Amma, *Inorg. Chem.*, 1967, **6,** 1553.
1201. E. Carmona, F. Gonzales, M. L. Poveda, J. L. Atwood and R. D. Rogers, *J. Chem. Soc., Dalton Trans.*, 1980, 2108.
1202. G. Huttner, O. Orama and V. Bejenke, *Chem. Ber.*, 1970, **109,** 2333.
1203. T. Saito, M. Nakajima, A. Kobayashi and Y. Sasaki, *J. Chem. Soc., Dalton Trans.*, 1978, 482.
1204. J. P. McCue, *Coord. Chem. Rev.*, 1973, **10,** 265.
1205. H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, 1972, **72,** 231.
1206. D. M. Roundhill, *Adv. Organomet. Chem.*, 1975, **13,** 273.
1207. A. N. Nesmelov, L. S. Isaeva and L. N. Lorens, *J. Organomet. Chem.*, 1977, **129,** 421.
1208. C. A. Tolman, *Inorg. Chem.*, 1972, **11,** 3128.
1209. M. Aresta, C. F. Nobile and A. Sacco, *Inorg. Chim. Acta,* 1975, **12,** 167.
1210. J. D. Druliner, A. D. English, P. J. Jesson, P. Meakin and C. A. Tolman, *J. Am. Chem. Soc.*, 1976, **98,** 2156.
1211. H. Imoto, H. Moriyama, T. Saito and Y. Sasaki, *J. Organomet. Chem.*, 1976, **120,** 453.
1212. T. Saito, H. Munakata and H. Imoto, *Inorg. Synth.*, 1977, **17,** 83.
1213. K. Jonas and G. Wilke, *Angew. Chem., Int. Ed. Engl.*, 1969, **8,** 519.
1214. A. Morvillo and A. Turco, *J. Organomet. Chem.*, 1981, **208,** 103.
1215. M. L. H. Green, T. Saito and P. J. Tanfield, *J. Chem. Soc. (A),* 1971, 152.
1216. H. C. Clark and A. Shower, *Can. J. Chem.*, 1975, **53,** 3462.
1217. T. Saito, *Chem. Lett.*, 1974, 1545.
1218. J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1960, 1718.
1219. P. W. Jolly, K. Jonas, C. Krüger and Y.-H. Tsay, *J. Organomet. Chem.*, 1971, **33,** 109.
1220. H. F. Klein and H. H. Korsch, *Chem. Ber.*, 1973, **106,** 1433.
1221. T. Yamamoto, Y. Nakamura and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1976, **49,** 191.
1222. K. Jacob, E. Pietzner, S. Vastag and K. H. Thiele, *Z. Anorg. Allg. Chem.*, 1977, **432,** 187.
1223. K. Maruyama, T. Ho and A. Yamamoto, *J. Organomet. Chem.*, 1978, **155,** 359; 1975, **90,** C28.
1224. M. D. Raush and F. E. Tibbets, *Inorg. Chem.*, 1970, **9,** 512.
1225. K. P. MacKinnon and B. O. West, *Aust. J. Chem.*, 1968, **21,** 2801.
1226. M. Wada, K. Kusabe and K. Oguro, *Inorg. Chem.*, 1977, **16,** 446.
1227. H. F. Klein, H. H. Karsch and W. Buchner, *Chem. Ber.*, 1974, **107,** 537.
1228. C. Arlen, M. Pfeffer, J. Fisher and A. Mitschler, *J. Chem. Soc., Chem. Commun.*, 1983, 928.
1229. M. Wada, K. Nishiwaki and Y. Kawasaki, *J. Chem. Soc., Dalton Trans.*, 1982, 1443.
1230. K. Oguro, M. Wada and N. Sonoda, *J. Organomet. Chem.*, 1979, **165,** C13.
1231. M. Wada and M. Kumazoe, *J. Organomet. Chem.*, 1983, **259,** 245.
1232. E. Uhlig and D. Walther, *Coord. Chem. Rev.*, 1980, **33,** 3.
1233. M. Hidai, T. Kashiwagi, T. Ikeuchi and Y. Uchida, *J. Organomet. Chem.*, 1971, **30,** 279.
1234. Y. Nakamura, K. Maruya and T. Mizoroki, *Bull. Chem. Soc. Jpn.*, 1980, **53,** 3089.
1235. T. T. Tsou and J. K. Kochi, *J. Am. Chem. Soc.*, 1979, **101,** 6319, 7547.
1236. D. R. Fahey and J. E. Mahan, *J. Am. Chem. Soc.*, 1977, **99,** 2501.
1237. G. W. Parshall, *J. Am. Chem. Soc.*, 1974, **96,** 2360.
1238. M. Foa and L. Cassar, *J. Chem. Soc. Dalton Trans.*, 1975, 2572.
1239. J. K. Stille and A. B. Cowell, *J. Organomet. Chem.*, 1977, **124,** 253.

1240. B. Hipler and E. Uhlig, *J. Organomet. Chem.*, 1980, **199**, C27.
1241. J. Ashley-Smith, M. Green and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1969, 3019.
1242. R. Nast and A. Beyer, *J. Organomet. Chem.*, 1981, **204**, 267.
1243. L. J. Krause and Y. A. Morisson, *J. Chem. Soc., Chem. Commun.*, 1981, 1282.
1244. H. D. Empsall, B. L. Shaw and B. L. Turtle, *J. Chem. Soc., Dalton Trans.*, 1976, 1500.
1245. M. Wada, *Inorg. Chem.*, 1975, **14**, 1415.
1246. M. Wada and T. Shimologashi, *Inorg. Chem.*, 1976, **15**, 954.
1247. H. F. Klein and H. H. Karsch, *Angew. Chem., Int. Ed. Engl.*, 1973, **12**, 402.
1248. H. F. Klein and H. H. Karsch, *Chem. Ber.*, 1976, **109**, 2524.
1249. M. Wada, N. Asada and K. Oguro, *Inorg. Chem.*, 1978, **17**, 2353.
1250. M. Wada and K. Oguro, *Inorg. Chem.*, 1976, **15**, 2346.
1251. S. J. Tremont and R. G. Bergman, *J. Organomet. Chem.*, 1977, **140**, C12.
1252. K. J. Coskran, J. M. Jenkins and J. G. Verkade, *J. Am. Chem. Soc.*, 1968, **90**, 5437.
1253. E. A. Rick and R. L. Pruett, *Chem. Commun.*, 1966, 697.
1254. B. B. Chastain, E. A. Rick, R. L. Pruett and H. B. Gray, *J. Am. Chem. Soc.*, 1968, **90**, 3994.
1255. C. A. Tolman, L. W. Yarbrough, II and J. G. Verkade, *Inorg. Chem.*, 1977, **16**, 479; K. J. Coskran, T. J. Huttemann and J. G. Verkade, *Adv. Chem.*, 1967, 590.
1256. T. J. Huttemann, Jr., B. M. Foxman, C. R. Sperati and J. G. Verkade, *Inorg. Chem.*, 1965, **4**, 950.
1257. P. Meakin and J. P. Jesson, *J. Am. Chem. Soc.*, 1974, **96**, 5751, 5760.
1258. G. D. Ginzburg, E. A. Zgadzai, N. S. Kolyubakima and P. A. Kirpichnikew, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1971, **16**, 1022; A. D. Troitskja, V. V. Sentemov and G. D. Ginzburg, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1973, **18**, 143.
1259. L. J. Vande Griend, J. C. Clardy and J. G. Verkade, *Inorg. Chem.*, 1975, **14**, 710.
1260. J. K. Stalick and J. A. Ibers, *Inorg. Chem.*, 1969, **8**, 1084.
1261. D. S. Milbrath, J. P. Springer, J. C. Clardy and J. G. Verkade, *Inorg. Chem.*, 1975, **14**, 2665.
1262. E. F. Riedel and R. A. Jacobson, *Inorg. Chim. Acta*, 1970, **4**, 407.
1263. W. C. Drinkard, D. R. Eaton, J. P. Jesson and R. V. Lindsey, Jr., *Inorg. Chem.*, 1970, **9**, 392.
1264. G. K. McEwen, C. J. Rix, M. F. Traynor and J. G. Verkade, *Inorg. Chem.*, 1974, **13**, 2800.
1265. W. Levason and C. A. McAuliffe, *Adv. Inorg. Chem. Radiochem.*, 1972, **14**, 173.
1266. E. C. Alyea, in 'Transition Metal Complexes of Phosphorus, Arsenic and Antimony Ligands', ed. C. A. McAuliffe, Macmillan, London 1973, p. 311.
1267. J. Chatt and F. G. Mann, *J. Chem. Soc.*, 1939, 1622.
1268. C. E. Wymore and J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, 1960, **14**, 42.
1269. K. Issleib and U. Giesder, *Z. Anorg. Allg. Chem.*, 1970, **379**, 9.
1270. K. Issleib, U. Giesder and H. Hartung, *Z. Anorg. Allg. Chem.*, 1972, **390**, 239.
1271. K. Issleib and G. Schwager, *Z. Anorg. Allg. Chem.*, 1961, **311**, 83.
1272. K. Issleib and G. Schwager, *Z. Anorg. Allg. Chem.*, 1961, **310**, 43.
1273. H. H. Karsch, *Chem. Ber.*, 1983, **116**, 1643.
1274. C. Ercolani, J. V. Quagliano and M. L. Vallarino, *Inorg. Chim. Acta*, 1973, **7**, 413.
1275. K. K. Chow and C. A. McAuliffe, *Inorg. Chim. Acta*, 1974, **10**, 197.
1276. G. Booth and J. Chatt, *J. Chem. Soc.*, 1965, 3238.
1277. G. R. van Hecke and W. D. Horrocks, Jr., *Inorg. Chem.*, 1966, **5**, 1968.
1278. W. W. Fogleman and H. B. Jonassen, *J. Inorg. Nucl. Chem.*, 1969, **31**, 1536.
1279. Von W. Seidel and M. Alexiev, *Z. Anorg. Allg. Chem.*, 1978, **438**, 68.
1280. J. A. Connor and P. I. Riley, *Inorg. Chim. Acta*, 1975, **15**, 197.
1281. E. C. Alyea and D. W. Meek, *Inorg. Chem.* 1972, **11**, 1029.
1282. J. M. Solar, M. A. Ozkan, H. Isci and W. R. Mason, *Inorg. Chem.*, 1984, **23**, 758.
1283. M. J. Hudson, R. S. Nyholm and M. H. B. Stiddard, *J. Chem. Soc.* (*A*), 1968, 40.
1284. C. A. McAuliffe and D. W. Meek, *Inorg. Chem.*, 1969, **8**, 904.
1285. P. Rigo, B. Corain and A. Turco, *Inorg. Chem.*, 1968, **7**, 1623.
1286. F. Cariati, R. Ugo and F. Bonati, *Inorg. Chem.*, 1966, **5**, 1128.
1287. J. Chatt, F. A. Hart and H. R. Watson, *J. Chem. Soc.*, 1962, 2537.
1288. M. Schmidt and G. G. Hoffmann, *Z. Anorg. Allg. Chem.*, 1980, **464**, 209.
1289. M. Schmidt and G. G. Hoffmann, *J. Organomet. Chem.*, 1977, **124**, C5.
1290. H. N. Ramaswamy, H. B. Jonassen and A. M. Aguiar, *Inorg. Chim. Acta*, 1967, **1**, 141.
1291. K. K. Chow, W. Levason and C. A. McAuliffe, *Inorg. Chim. Acta*, 1973, **7**, 589.
1292. A. J. Carty, D. K. Johnson and S. E. Jacobson, *J. Am. Chem. Soc.*, 1979, **101**, 5612.
1293. W. E. Hill, W. Levason and C. A. McAuliffe, *Inorg. Chem.*, 1974, **13**, 244.
1294. L. Campbell and J. J. McGarvey, *J. Chem. Soc., Chem. Commun.*, 1976, 749.
1295. J. J. McGarvey and J. Wilson, *J. Am. Chem. Soc.*, 1975, **97**, 2531.
1296. L. Sacconi and J. Gelsomini, *Inorg. Chem.*, 1968, **7**, 291.
1297. K. Issleib and G. Hohlfeld, *Z. Anorg. Allg. Chem.*, 1961, **312**, 170.
1298. W. E. Hill, J. G. Taylor, C. A. McAuliffe and W. Levason, *J. Chem. Soc., Dalton Trans.*, 1982, 841.
1299. L. Sacconi, I. Bertini and F. Mani, *Inorg. Chem.*, 1968, **7**, 1417.
1300. W. Levason and C. A. McAuliffe, *Inorg. Chim. Acta*, 1974, **11**, 33.
1301. W. Levason, C. A. McAuliffe and S. G. Murray, *Inorg. Chim. Acta*, 1977, **24**, 63.
1302. B. L. Booth, C. A. McAuliffe and G. L. Stanley, *J. Chem. Soc., Dalton Trans.*, 1982, 535.
1303. M. A. Bennet and J. D. Wild, *J. Chem. Soc.* (*A*), 1971, 536.
1304. K. K. Chow, W. Levason and C. A. McAuliffe, *Inorg. Chim. Acta*, 1976, **16**, 173.
1305. R. J. Dickinson, W. Levason, C. A. McAuliffe and R. V. Parish, *J. Chem. Soc., Chem. Commun.*, 1975, 272.
1306. K. K. Chow and C. A. McAuliffe, *Inorg. Chim. Acta*, 1975, **14**, 5.
1307. K. K. Chow, M. T. Halfpenny and C. A. McAuliffe, *J. Chem. Soc., Dalton Trans.*, 1973, 147.
1308. J. F. Sieckhaus and T. Layloff, *Inorg. Chem.*, 1967, **6**, 2185.

1309. P. Rigo and M. Bressan, *Inorg. Chem.*, 1975, **14,** 1491.
1310. E. Uhlig and M. Maasar, *Z. Anorg. Allg. Chem.*, 1966, **344,** 205.
1311. J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1960, 1378.
1312. P. G. Eller and D. W. Meek, *Inorg. Chem.*, 1972, **11,** 2518.
1313. L. F. Warren and M. A. Bennett, *Inorg. Chem.*, 1976, **15,** 3126.
1314. W. Levason and K. G. Smith, *Inorg. Chim. Acta,* 1980, **41,** 133.
1315. L. F. Warren and M. A. Bennett, *J. Am. Chem. Soc.*, 1974, **96,** 3340.
1316. T. D. DuBois and D. W. Meek, *Inorg. Chem.*, 1967, **6,** 1395.
1317. M. O. Workman, G. Dyer and D. W. Meek, *Inorg. Chem.*, 1967, **6,** 1543.
1318. R. S. Nyholm, *J. Chem. Soc.*, 1950, 2061.
1319. C. M. Harris, R. S. Nyholm and D. J. Phillips, *J. Chem. Soc.*, 1960, 4379.
1320. R. Ettore, G. Dolcetti and A. Peloso, *Gazz. Chim. Ital.*, 1967, **97,** 1681.
1321. J. R. Preer and H. B. Gray, *J. Am. Chem. Soc.*, 1970, **92,** 7306.
1322. N. K. Roberts and S. B. Wild, *Inorg. Chem.*, 1981, **20,** 1892.
1323. W. Levason and C. A. McAuliffe, *Inorg. Chim. Acta,* 1974, **11,** 33.
1324. B. R. Cook, C. A. McAuliffe and D. W. Meek, *Inorg. Chem.*, 1971, **10,** 2676.
1325. E. Schewchuk and S. B. Wild, *J. Organomet. Chem.*, 1977, **128,** 115.
1326. D. W. Allen, I. T. Millar, F. G. Mann, R. M. Canadine and J. Walker, *J. Chem. Soc.* (*A*), 1969, **1097.**
1327. D. W. Allen, D. F. Ashford, F. G. Mann and D. Hogarth, *J. Chem. Soc., Dalton Trans.*, 1977, 1597.
1328. M. Benettin, L. Sindellari, M. Vidali and R. Ros, *J. Inorg. Nucl. Chem.*, 1975, **37,** 2067.
1329. N. J. De Stefano, D. K. Johnson and L. M. Venanzi, *Angew. Chem., Int. Ed. Engl.*, 1974, **13,** 133.
1330. J. J. Bishop and A. Davison, *Inorg. Chem.*, 1971, **10,** 832.
1331. C. G. Pierpoint and R. Eisenberg, *Inorg. Chem.*, 1972, **11,** 828.
1332. N. E. Schore, L. S. Benner and B. E. LaBelle, *Inorg. Chem.*, 1981, **20,** 3200.
1333. B. Corain, M. Basato and G. Favero, *J. Chem. Soc., Dalton Trans.*, 1977, 2081.
1334. M. A. Bennet, P. W. Clark, G. B. Robertson and P. O. Whimp, *J. Organomet. Chem.*, 1973, **63,** C15.
1335. C. J. Moulton and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1976, 1020.
1336. P. T. Greene and L. Sacconi, *J. Chem. Soc.* (*A*), 1970, 866.
1337. P. Dapporto and L. Sacconi, *J. Chem. Soc.* (*A*), 1971, 1914.
1338. W. E. Hill, J. G. Taylor, C. A. McAuliffe, K. W. Muir and L. Manojlovic-Muir, *J. Chem. Soc., Dalton Trans.*, 1982, 833.
1339. N. C. Stephenson, *Acta Crystallogr.*, 1964, **17,** 592.
1340. R. Curran, J. A. Cunningham and R. Eisenberg, *Inorg. Chem.*, 1970, **9,** 2749.
1341. D. W. Allen, D. A. Kennedy and I. W. Nowell, *Inorg. Chim. Acta,* 1980, **40,** 171.
1342. H. J. Becher, W. Bensmann and D. Fenske, *Chem. Ber.*, 1977, **110,** 315.
1343. Von W. Haase, *Z. Anorg. Allg. Chem.*, 1974, **404,** 273.
1344. D. L. Allen, V. C. Gibson, M. L. H. Green, J. F. Skinner, J. Bashkin and P. D. Grebenik, *J. Chem. Soc., Chem. Commun.*, 1983, 895.
1345. V. Gramlich and C. H. Salomon, *J. Organomet. Chem.*, 1974, **73,** C61.
1346. I. Podlahova, B. Kratochvic and V. Langer, *Inorg. Chem.*, 1981, **20,** 2160.
1347. R. Morassi and A. Dei, *Inorg. Chim. Acta,* 1972, **6,** 314.
1348. B. Chiswell, in 'Transition Metal Complexes of Phosphorus, Arsenic and Antimony', ed. C. A. McAuliffe, Macmillan, London, 1973, p. 271.
1349. C. A. McAuliffe, *Adv. Inorg. Chem. Radiochem.*, 1975, **17,** 165.
1350. G. A. Barclay, R. S. Nyholm and R. V. Parish, *J. Chem. Soc.*, 1961, 4433.
1351. J. C. Lloyd and D. W. Meek, *Inorg. Chim. Acta,* 1972, **6,** 607.
1352. T. E. Nappier, Jr. and D. W. Meek, *Inorg. Chim. Acta,* 1973, **7,** 235.
1353. R. B. King, R. N. Kapoor, M. S. Saran and P. N. Kapoor, *Inorg. Chem.*, 1971, **10,** 1841.
1354. C. Mealli, M. Peruzzini and P. Stoppioni, *J. Organomet. Chem.*, 1980, **192,** 437.
1355. M. Baacke, S. Hietkamp, S. Morton and O. Stelzer, *Chem. Ber.*, 1981, **114,** 2568.
1356. G. A. Mair, H. M. Powell and D. E. Henn, *Proc. Chem. Soc.*, 1960, 415.
1357. C. A. McAuliffe, M. O. Workman and D. W. Meek, *J. Coord. Chem.*, 1972, **2,** 137.
1358. C. A. McAuliffe, K. Minten and D. G. Watson, *Inorg. Chim. Acta,* 1980, **39,** 249.
1359. W. Levason, C. A. McAuliffe and D. G. Watson, *J. Coord. Chem.* 1975, **4,** 173.
1360. R. G. Cunninghame, R. S. Nyholm and M. L. Tobe, *J. Chem. Soc., Dalton Trans.*, 1972, 229.
1361. W. E. Hill, J. Dalton and C. A. McAuliffe, *J. Chem. Soc., Dalton Trans.*, 1973, 143.
1362. B. Bosnich, R. Bramley, R. S. Nyholm and M. L. Tobe, *J. Am. Chem. Soc.*, 1966, **88,** 3926.
1363. B. Bosnich, R. S. Nyholm, P. S. Pauling and M. L. Tobe, *J. Am. Chem. Soc.*, 1968, **90,** 4741.
1364. C. Degischer and G. Schwarzenbach, *Helv. Chim. Acta,* 1966, **49,** 1927.
1365. L. Sacconi and R. Morassi, *J. Chem. Soc.* (*A*), 1968, 1927.
1366. P. L. Orioli and C. A. Ghilardi, *J. Chem. Soc.* (*A*), 1970, 1511.
1367. D. W. Meek and J. A. Ibers, *Inorg. Chem.*, 1969, **8,** 1915.
1368. W. S. J. Kelly, G. H. Ford and S. M. Nelson, *J. Chem. Soc.* (*A*), 1971, 388.
1369. W. V. Dahloff and S. M. Nelson, *J. Chem. Soc.* (*A*), 1971, 2184.
1370. P. Giannoccaro, G. Vasapollo, C. F. Nobile and A. Sacco, *Inorg. Chim. Acta,* 1982, **61,** 69.
1371. M. V. Andreocci, G. Mattogno, R. Zanoni, P. Giannoccaro and G. Vasapollo, *Inorg. Chim. Acta,* 1982, **63,** 225.
1372. M. D. Fryzuk and P. A. MacNeil, *J. Am. Chem. Soc.*, 1981, **103,** 3592.
1373. P. Giannoccaro, G. Vasapollo and A. Sacco, *J. Chem. Soc., Chem. Commun.*, 1980, 1136.
1374. R. B. King, *Acc. Chem. Res.*, 1972, **5,** 177.
1375. R. B. King, R. N. Saran, R. N. Kapoor and P. N. Kapoor, *Inorg. Chem.*, 1971, **10,** 1851.
1376. M. Bacci, S. Midollini, P. Stoppioni and L. Sacconi, *Inorg. Chem.*, 1973, **12,** 1801.
1377. M. Baacke, S. Hietkamp, S. Morton and O. Stelzer, *Chem. Ber.*, 1982, **115,** 1389.

1378. B. Bosnich, W. G. Jackson and S. T. D. Lo, *Inorg. Chem.*, 1975, **14**, 2998.
1379. T. D. DuBois and D. W. Meek, *Inorg. Chem.*, 1969, **8**, 146.
1380. W. Levason, C. McAuliffe and S. G. Murray, *J. Chem. Soc., Dalton Trans.*, 1976, 2321.
1381. K. Aurivillius and G. I. Bertinsson, *Acta Crystallogr., Sect. B*, 1980, **36**, 790.
1382. G. I. Bertinsson, *Acta Crystallogr., Sect. C*, 1983, **39**, 698.
1383. K. Aurivillius and G. I. Bertinsson, *Acta Crystallogr., Sect B*, 1981, **37**, 172.
1384. R. Schmelczer and D. Schwazenbach, *Cryst. Struct. Commun.*, 1981, **10**, 1317.
1385. L. Sacconi and A. Dei, *J. Coord. Chem.*, 1971, **1**, 229.
1386. A. Bianchi, C. A. Ghilardi, C. Mealli and L. Sacconi, *J. Chem. Soc., Chem. Commun.*, 1972, 652.
1387. L. Sacconi and D. Gatteschi, *J. Coord. Chem.*, 1972, **2**, 107.
1388. L. G. Scanlon, Y. Y. Tsao, K. Toman, S. C. Cummings and D. W. Meek, *Inorg. Chem.*, 1982, **21**, 2707.
1389. L. Sacconi, *Coord. Chem. Rev.*, 1972, **8**, 351.
1390. P. L. Orioli, *Coord. Chem. Rev.*, 1971, **6**, 285.
1391. C. A. McAuliffe, *Inorg. Chem.*, 1973, **12**, 2477.
1392. F. Mani and L. Sacconi, *Comm. Inorg. Chem.*, 1983, **2**, 157.
1393. L. Sacconi and F. Mani, *Transition Met. Chem.*, 1982, **7**, 179.
1394. R. Mason and D. W. Meek, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 183.
1395. D. Berglund, Ph.D. Dissertation, Ohio State University, 1969.
1396. R. Davis and J. E. Fergusson, *Inorg. Chim. Acta*, 1970, **4**, 23.
1397. C. Benelli, M. Di Vaira, G. Noccioli and L. Sacconi, *Inorg. Chem.*, 1977, **16**, 182.
1398. C. Bianchini, A. Meli, A. Orlandini and L. Sacconi, *J. Organomet. Chem.*, 1981, **209**, 219.
1399. F. Cecconi, S. Midollini, A. Orlandini and L. Sacconi, *Inorg. Chim. Acta*, 1980, **42**, 59.
1400. S. Midollini and F. Cecconi, *J. Chem. Soc., Dalton Trans.*, 1973, 681.
1401. L. M. Venanzi, *Angew. Chem. Int. Ed. Engl.*, 1964, **3**, 453.
1402. G. Dyer, J. G. Hartley and L. M. Venanzi, *J. Chem. Soc.*, 1965, 1293.
1403. B. R. Higginson, C. A. McAuliffe and L. M. Venanzi, *Inorg. Chim. Acta*, 1971, **5**, 37.
1404. O. St C. Headley, R. S. Nyholm, C. A. McAuliffe, L. Sindellari, M. L. Tobe and L. M. Venanzi, *Inorg. Chim. Acta*, 1970, **4**, 93.
1405. E. Grinley, J. M. Grinley, T. D. Li and D. Emerich, *Inorg. Chem.*, 1976, **15**, 1716.
1406. L. Baracco, M. T. Halfpenny and C. A. McAuliffe, *J. Chem. Soc., Dalton Trans.*, 1973, 1945.
1407. (a) W. Levason, C. A. McAuliffe and S. G. Murray, *J. Chem. Soc., Dalton Trans.*, 1977, 711. (b) W. Levason, C. A. McAuliffe and S. G. Murray, *J. Chem. Soc., Chem. Commun.*, 1975, 164.
1408. G. Dyer and D. W. Meek, *Inorg. Chem.*, 1965, **4**, 1398.
1409. L. P. Haugen and R. Eisenberg, *Inorg. Chem.*, 1969, **8**, 1072.
1410. G. Dyer and D. W. Meek, *Inorg. Chem.*, 1967, **6**, 149.
1411. M. Mathew, G. J. Palenik, G. Dyer and D. W. Meek, *J. Chem. Soc., Chem. Commun.*, 1972, 379.
1412. G. S. Benner, W. E. Hatfield and D. W. Meek, *Inorg. Chem.*, 1964, **3**, 1544.
1413. D. L. Stevenson and L. F. Dahl, *J. Am. Chem. Soc.*, 1967, **89**, 3424.
1414. G. S. Benner and D. W. Meek, *Inorg. Chem.*, 1967, **6**, 1399.
1415. C. A. McAuliffe and D. W. Meek, *Inorg. Chim. Acta*, 1971, **5**, 270.
1416. C. A. McAuliffe and D. G. Watson, *J. Organomet. Chem.*, 1974, **78**, C51.
1417. R. B. King, J. C. Cloyd, Jr. and R. H. Reimann, *Inorg. Chem.*, 1976, **15**, 449.
1418. L. Sacconi and I. Bertini, *J. Am. Chem. Soc.*, 1968, **90**, 5443.
1419. M. di Vaira and L. Sacconi, *J. Chem. Soc., Dalton Trans.*, 1975, 493.
1420. P. Dapporto and L. Sacconi, *J. Chem. Soc. (A)*, 1970, 1804.
1421. P. Stoppioni, R. Morassi and F. Zanobini, *Inorg. Chim. Acta*, 1981, **52**, 101.
1422. C. Bianchini, C. Mealli, S. Midollini and L. Sacconi, *Inorg. Chim. Acta*, 1978, **31**, L433.
1423. C. Bianchini, C. Mealli, A. Meli and L. Sacconi, *Inorg. Chim. Acta*, 1980, **43**, 223.
1424. P. Dapporto, M. Peruzzini and P. Stoppioni, *Inorg. Chim. Acta*, 1981, **47**, 213.
1425. L. Sacconi and R. Morassi, *J. Chem. Soc. (A)*, 1969, 2904.
1426. A. Bianchi, P. Dapporto, G. Fallani, C. A. Ghilardi and L. Sacconi, *J. Chem. Soc., Dalton Trans.*, 1973, 641.
1429. R. Morassi and L. Sacconi, *J. Chem. Soc. (A)*, 1971, 1487.
1428. I. Bertini, P. Dapporto, G. Fallani and L. Sacconi, *Inorg. Chem.*, 1971, **10**, 1703.
1429. M. Di Vaira and A. Bianchi Orlandini, *J. Chem. Soc., Dalton Trans.*, 1972, 1704.
1430. M. Di Vaira, *J. Chem. Soc. (A)*, 1971, 148.
1431. R. Morassi and L. Sacconi, *J. Chem. Soc. (A)*, 1971, 492.
1432. P. Dapporto, R. Morassi and L. Sacconi, *J. Chem. Soc. (A)*, 1970, 1298.
1433. M. Bacci, R. Morassi and L. Sacconi, *J. Chem. Soc. (A)*, 1971, 3686.
1434. A. Orlandini and L. Sacconi, *Inorg. Chem.*, 1976, **15**, 78.
1435. L. Sacconi, A. Orlandini and S. Midollini, *Inorg. Chem.*, 1974, **13**, 2850.
1436. C. A. Ghilardi, S. Midollini and L. Sacconi, *Inorg. Chem.*, 1975, **14**, 1790.
1437. C. Mealli, S. Midollini and L. Sacconi, *Inorg. Chem.*, 1978, **17**, 632.
1438. C. Mealli and S. Midollini, *Inorg. Chem.*, 1983, **22**, 2785.
1439. M. Di Vaira, S. Midollini and L. Sacconi, *Inorg. Chem.*, 1977, **16**, 1518.
1440. M. Di Vaira, S. Midollini and L. Sacconi, *Inorg. Chem.*, 1978, **17**, 816.
1441. C. A. Ghilardi, S. Midollini and L. Sacconi, *Inorg. Chem.*, 1977, **16**, 2377.
1442. C. A. Ghilardi, S. Midollini and S. Moneti, *J. Organomet. Chem.*, 1981, **217**, 391.
1443. L. Sacconi, P. Dapporto and P. Stoppioni, *Inorg. Chem.*, 1976, **15**, 325.
1444. L. Sacconi, P. Dapporto, P. Stoppioni, P. Innocenti and C. Benelli, *Inorg. Chem.*, 1977, **16**, 1669.
1445. P. Stoppioni, P. Dapporto and L. Sacconi, *Inorg. Chem.*, 1978, **17**, 718.
1446. S. Midollini, A. Orlandini and L. Sacconi, *J. Organomet. Chem.*, 1978, **162**, 109.
1447. J. P. Hunt and H. L. Friedman, *Prog. Inorg. Chem.*, 1983, **30**, 359.
1448. H. Taube, *Prog. Stereochem.*, 1962, **3**, 95.

1449. J. W. Neely and R. E. Connick, *J. Am. Chem. Soc.*, 1970, **92**, 3476.
1450. T. J. Swift and G. P. Weinberger, *J. Am. Chem. Soc.*, 1968, **90**, 2023.
1451. D. B. Bechtold, G. Liu, H. W. Dodgen and J. P. Hunt, *J. Phys. Chem.*, 1978, **82**, 333; B. B. Wayland and W. L. Rice, *Inorg. Chem.*, 1966, **5**, 54.
1452. A. K. Soper, G. W. Neilson, J. E. Enderby and R. A. Howe, *J. Phys. C*, 1977, **10**, 1793.
1453. A. G. Desai, H. W. Dodgen and J. P. Hunt, *J. Am. Chem. Soc.*, 1969, **91**, 5001; 1970, **92**, 798.
1454. M. W. Grant, H. W. Dodgen and J. P. Hunt, *J. Am. Chem. Soc.*, 1971, **93**, 6828.
1455. S. F. Lincoln, F. Aprile, H. W. Dodgen and J. P. Hunt, *Inorg. Chem.*, 1968, **7**, 929.
1456. T. J. Swift and R. E. Connick, *J. Chem. Phys.*, 1964, **41**, 2553.
1457. J. Mizuno, *J. Phys. Soc. Jpn.*, 1961, **16**, 1574.
1458. J. C. Barnes and C. S. Duncan, *J. Chem. Soc., Dalton Trans.*, 1972, 923.
1459. A. Zalkin, H. Ruben and D. H. Templeton, *Acta Crystallogr., Sect. B*, 1982, **38**, 610.
1460. H. Montgomery and B. H. Lingafelter, *Acta Crystallogr.*, 1964, **17**, 1478.
1461. C. A. Beevers and H. Lipson, *Z. Kristallogr.*, 1932, **83**, 123; H. L. Snyman and C. F. W. Pistorius, *Z. Kristallogr.*, 1964, **119**, 465.
1462. S. Baggio and L. N. Becka, *Acta Crystallogr., Sect. B*, 1969, **25**, 1150.
1463. F. Bigoli, A. Braibanti, A. Tiripicchio and M. Tiripicchio-Cammellini, *Acta Crystallogr., Sect. B*, 1971, **27**, 1427.
1464. W. H. Black, E. A. H. Griffith and B. E. Robertson, *Acta Crystallogr., Sect. B*, 1975, **31**, 615.
1465. H. Feoss, *Z. Anorg. Allg. Chem.*, 1970, **379**, 204.
1466. B. H. O'Connor and D. H. Dale, *Acta Crystallogr.*, 1966, **21**, 705.
1467. S. Ray, A. Zalkin and D. H. Templeton, *Acta Crystallogr., Sect. B*, 1973, **29**, 2741.
1468. K. A. Burkov, L. S. Lilic and L. G. Sillen, *Acta Chem. Scand.*, 1965, **19**, 14.
1469. H. Ohtaki and G. Biedermann, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 1822.
1470. K. A. Burkov, N. J. Zinevich and L. S. Lilich, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1971, **16**, 927.
1471. B. W. Clare and D. L. Kepert, *Aust. J. Chem.*, 1975, **28**, 1489.
1472. V. Baran, *Coord. Chem., Rev.*, 1971, **6**, 65.
1473. R. Scholder and E. Giesler, *Z. Anorg. Allg. Chem.*, 1962, **316**, 237.
1474. W. E. Hatfield, F. Anders and L. J. Rivela, *Inorg. Chem.*, 1965, **4**, 1088.
1475. W. P. Griffith, *Coord. Chem. Rev.*, 1970, **5**, 459.
1476. K. H. Schmidt and A. Muller, *Coord. Chem. Rev.*, 1974, **14**, 115.
1477. J. J. Lander, *J. Am. Chem. Soc.*, 1951, **73**, 2450.
1478. R. Boca, *Coord. Chem. Rev.*, 1983, **50**, 1.
1479. V. Imhof and R. S. Drago, *Inorg. Chem.*, 1965, **3**, 427.
1480. A. D. van Ingen Schenau, W. L. Groeneveld and J. Reedijk, *Recl. Trav. Chim. Pays-Bas*, 1972, **91**, 88.
1481. P. W. N. M. van Leeuwen, *Recl. Trav. Chim. Pays-Bas*, 1967, **86**, 247.
1482. L. G. L. Oward and J. R. Pipal, *Inorg. Synth.*, 1972, **13**, 154.
1483. B. P. Baranwal and R. C. Mehrotra, *Z. Anorg. Allg. Chem.*, 1978, **443**, 284.
1484. P. L'Haridon and I. Bkouche-Waksman, *J. Inorg. Nucl. Chem.*, 1978, **40**, 2025.
1485. R. C. Mehrotra, *Adv. Inorg. Chem. Radiochem.*, 1983, **26**, 269.
1486. D. C. Bradley, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 259.
1487. R. W. Adams, E. Bishop, R. L. Martin and G. Winter, *Aust. J. Chem.*, 1966, **19**, 207.
1488. R. C. Mehrotra, *Coord. Chem. Rev.*, 1981, **21**, 113.
1489. R. C. Mehrotra, P. C. Bharara and B. P. Baranwal, *Indian J. Chem., Sect. A*, 1977, **15**, 458.
1490. B. P. Baranwal, P. C. Bharara and R. C. Mehrotra, *Transition Met. Chem.*, 1977, **2**, 204.
1491. B. P. Baranwal and R. C. Mehrotra, *Transition. Met. Chem.*, 1978, **3**, 220.
1492. B. P. Baranwal, G. K. Parashar and R. C. Mehrotra, *Z. Naturforsch., Teil B*, 1979, **34**, 459.
1493. J. A. Bertrand and D. Caine, *J. Am. Chem. Soc.*, 1964, **86**, 2298.
1494. J. A. Bertrand, A. P. Ginsberg, R. I. Kaplan, C. E. Kirkwood, R. L. Martin and R. C. Sherwood, *Inorg. Chem.*, 1971, **10**, 240.
1495. A. G. Kruger and G. Winters, *Aust. J. Chem.*, 1970, **23**, 1.
1496. J. E. Andrew and A. B. Blake, *J. Chem. Soc. (A)*, 1969, 1456.
1497. A. Tettamanzi and B. Carli, *Gazz. Chim. Ital.*, 1933, **63**, 566.
1498. K. Nielsen, R. G. Hazel and S. E. Rasmussen, *Acta Chem. Scand.*, 1972, **26**, 889.
1499. J. L. Hall, J. A. Swisher, D. G. Brannon and T. M. Liden, *Inorg. Chem.*, 1962, **1**, 409.
1500. B. M. Foxman and H. Mazurek, *Inorg. Chem.*, 1979, **18**, 113.
1501. H. G. Biedermann, K. E. Schwarzhans and W. Wiedemann, *Z. Naturforsch., Teil B*, 1972, **27**, 1329.
1502. J. M. Stewart, E. C. Lingafelter and J. D. Breadzeale, *Acta Crystallogr., Sect. B*, 1961, **14**, 888.
1503. J. I. Bullock and S. L. Jones, *J. Chem. Soc. (A)*, 1970, 2742.
1504. J. I. Bullock, M. F. C. Ladd and D. C. Povey, *J. Chem. Soc., Dalton Trans.*, 1977, 2242.
1505. J. I. Bullock and R. V. Hobson, *Inorg. Chim. Acta*, 1976, **19**, 79.
1506. H. El Khadem and W. M. Orabi, *Z. Anorg. Allg. Chem.*, 1969, **365**, 315.
1507. F. J. Iaconianni, L. L. Pytlewski, C. M. Mikulski and N. M. Karayannis, *Inorg. Chim. Acta*, 1981, **53**, L21.
1508. W. L. Driessen and W. L. Groeneveld, *Recl. Trav. Chim. Pays-Bas*, 1969, **88**, 977.
1509. W. L. Driessen and W. L. Groeneveld, *Recl. Trav. Chim. Pays-Bas*, 1971, **111**, 258.
1510. M. W. G. de Bolster, W. L. Driessen, W. L. Groeneveld and C. J. van Kerkwijk, *Inorg. Chim. Acta*, 1973, **7**, 439.
1511. W. L. Driessen, W. L. Groeneveld and F. W. van der Wey, *Recl. Trav. Chim., Pays-Bas*, 1970, **89**, 353.
1512. W. L. Driessen and W. L. Groeneveld, *Recl. Trav. Chim. Pays-Bas*, 1960, **88**, 491.
1513. W. L. Driessen, L. M. van Geldrop and W. L. Groeneveld, *Recl. Trav. Chim. Pays-Bas*, 1970, **89**, 1271.
1514. W. L. Driessen and W. L. Groeneveld, *Recl. Trav. Chim. Pays-Bas*, 1971, **90**, 87.
1515. P. L. Verheijdt, P. H. van der Voort, W. L. Groeneveld and W. L. Driessen, *Recl. Trav. Chim. Pays-Bas*, 1972, **91**, 1201.
1516. W. L. Driessen and M. den Heijer, *Inorg. Chim. Acta*, 1979, **33**, 261.

1517. M. den Heijer and W. L. Driessen, *Inorg. Chim. Acta*, 1977, **26**, 227.
1518. K. Jackowski and Z. Keki, *J. Inorg. Nucl. Chem.*, 1977, **39**, 1073.
1519. V. Gutmann and H. Schmidt, *Monatsh. Chem.*, 1974, **105**, 653.
1520. J. H. Weber, *Inorg. Chem.*, 1969, **8**, 2813.
1521. F. Mani, *Inorg. Chim. Acta*, 1982, **65**, L197.
1522. Von W. Ludwig and H. P. Schroer, *Z. Anorg. Allg. Chem.*, 1968, **357**, 74.
1523. G. W. Fowles, D. A. Rice and R. A. Walton, *J. Inorg. Nucl. Chem.*, 1969, **31**, 3119.
1524. R. Junasz and L. F. Yntema, *J. Am. Chem. Soc.*, 1940, **62**, 3522.
1525. G. W. Fowles, D. A. Rice and R. A. Walton, *J. Chem. Soc. (A)*, 1968, 1842.
1526. J. C. Barnes and C. S. Duncan, *Inorg. Chim. Acta*, 1973, **7**, 404.
1527. J. C. Barnes and C. S. Duncan, *J. Chem. Soc.* (*A*), 1970, 1442.
1528. J. C. Barnes and C. S. Duncan, *J. Chem. Soc., Dalton Trans.*, 1972, 923.
1529. J. P. Fakler, Jr., *Prog. Inorg. Chem.*, 1966, **7**, 361.
1530. D. W. Thompson, *Struct. Bonding* (*Berlin*), 1971, **9**, 27.
1531. J. J. Fortman and R. E. Sievers, *Coord. Chem. Rev.*, 1971, **6**, 331.
1532. D. P. Graddon, *Coord. Chem. Rev.*, 1969, **4**, 1.
1533. D. Gibson, *Coord. Chem. Rev.*, 1969, **4**, 225.
1534. W. C. Fernelius and B. E. Bryant, *Inorg. Synth.*, 1978, **5**, 105.
1535. G. J. Bullen, R. Mason and P. Pauling, *Inorg. Chem.*, 1965, **4**, 456.
1536. H. Montgomery and E. C. Lingafelter, *Acta Crystallogr.*, 1964, **17**, 1481; R. E. Cramer, S. W. Cramer, K. F. Cramer, M. A. Chudyk and K. Seff, *Inorg. Chem.*, 1977, **16**, 219.
1537. R. C. Elder, *Inorg. Chem.*, 1968, **7**, 2316.
1538. C. E. Pfluger and R. L. Harlow, *Cryst. Struct. Commun.*, 1975, **4**, 633.
1539. W. D. Horrocks, Jr., D. H. Templeton and A. Zalkin, *Inorg. Chem.*, 1968, **7**, 1552.
1540. M. B. Hursthouse, M. A. Laffey, P. T. Moore, D. B. New, P. R. Raithby and P. Thornton, *J. Chem. Soc., Dalton Trans.*, 1982, 307.
1541. C. J. O'Connor, E. D. Stevens, C. E. Pfluser and K. A. Klanderman, *Inorg. Chim. Acta*, 1984, **81**, 91.
1542. J. H. Binks, L. S. D. Glasser, G. J. Dorward, R. A. Howie and G. P. McQuillan, *Inorg. Chim. Acta*, 1977, **22**, L17.
1543. S. Koda, S. Ooi, H. Kuroya, K. Isobe, Y. Nakamura and S. Kawaguichi, *Chem. Commun.*, 1971, 1321.
1544. Y. Nakamura, K. Isobe, H. Morita, S. Yamazaki and S. Kawaguichi, *Inorg. Chem.*, 1972, **11**, 1573.
1545. R. E. Cramer, S. W. Cramer, K. F. Cramer, M. A. Chudyk and K. Seff, *Inorg. Chem.*, 1977, **16**, 219.
1546. B. L. Barnett and C. Kruger, *J. Organomet. Chem.*, 1972, **42**, 169.
1547. F. A. Cotton, B. A. Frenz and D. L. Hunter, *J. Am. Chem. Soc.*, 1974, **96**, 4820.
1548. F. A. Cotton and J. J. Wise, *Inorg. Chem.*, 1966, **7**, 1200.
1549. M. N. Battacharjee, M. K. Chaudhuri, S. K. Ghosh, Z. Hiese and N. Roy, *J. Chem. Soc., Dalton Trans.*, 1983, 2561.
1550. J. A. Siegel and D. A. Rowley, *Inorg. Chim. Acta*, 1974, **9**, 19.
1551. J. P. Fackler, Jr. and F. A. Cotton, *J. Am. Chem. Soc.*, 1961, **83**, 3775; 1960, **82**, 5005.
1552. J. P. Fackler, Jr., *J. Am. Chem. Soc.*, 1962, **84**, 24.
1553. R. G. Pearson and J. W. Moore, *Inorg. Chem.*, 1966, **5**, 1523.
1554. R. J. Irving and M. A. V. Ribeiro da Silva, *J. Chem. Soc., Dalton Trans.*, 1978, 399.
1555. M. J. Hynes and B. D. O'Regan, *J. Chem. Soc., Dalton Trans.*, 1979, 162.
1556. W. D. Horrocks, Jr., R. C. Taylor and G. La Mar, *J. Am. Chem. Soc.*, 1964, **86**, 3031.
1557. R. W. Kluiber and W. D. Horrocks, Jr., *Inorg. Chem.*, 1966, **5**, 152.
1558. R. W. Kluiber and W. D. Horrocks, Jr., *J. Am. Chem. Soc.*, 1966, **88**, 1399.
1559. R. W. Kluiber and W. D. Horrocks, Jr., *Inorg. Chem.*, 1967, **6**, 166, 430.
1560. B. D. Santarsiero, A. Esmaili, V. Shomaker and E. C. Lingafelter, *Acta Crystallogr., Sect. A*, 1981, **37**, 234.
1561. W. D. Horrocks, Jr., R. H. Fischer, J. R. Hutchinson and G. La Mar, *J. Am. Chem. Soc.*, 1966, **88**, 2436.
1562. W. H. Watson and C. T. Lin, *Inorg. Chem.*, 1966, **5**, 1074.
1503. J. T. Hashagen and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, 1965, **87**, 2821.
1564. D. A. Fine, *Inorg. Chem.*, 1971, **10**, 1825.
1565. D. P. Graon and K. B. Heng, *Aust. J. Chem.*, 1972, **25**, 2247.
1566. R. W. Kluiber and S. Kopicinski, *J. Inorg. Nucl. Chem.*, 1968, **30**, 1891.
1567. M. K. Misra and D. V. Ramana Rao, *J. Inorg. Nucl. Chem.*, 1969, **31**, 3875.
1568. C. E. Pfluger, T. S. Burke and A. L. Bednowitz, *J. Cryst. Mol. Struct.*, 1973, **3**, 181.
1569. I. Yoshida, H. Kobayashi and K. Ueno, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 1411.
1570. A. N. Nesmeyanov, L. S. Isaeva, L. N. Morozova, P. V. Petrovskii, B. L. Lokshin and Z. S. Klemenkova, *Inorg. Chim. Acta*, 1980, **43**, 1.
1571. M. A. Laffey and P. Thornton, *J. Chem. Soc., Dalton Trans.*, 1982, 313.
1572. J. H. Binks, G. J. Dorward, R. A. Howie and G. P. McQuillan, *Inorg. Chim. Acta*, 1981, **49**, 251.
1573. S. Pinchas, B. L. Silver and I. Lanlight, *J. Chem. Phys*, 1967, **46**, 1506.
1574. P. W. N. M. van Leeuwen, *Recl. Trav. Chim. Pays-Bas*, 1968, **87**, 396.
1575. R. P. Eckberg, J. H. Nelson, J. W. Kenney, P. N. Howells and R. A. Henry, *Inorg. Chem.*, 1977, **16**, 3128.
1576. B. Corain, A. Del Pra, F. Filiro and G. Zanotti, *Inorg. Chem.*, 1979, **18**, 3523.
1577. A. Yamamoto, T. Yamamoto, T. Saruyama and Y. Nakamura, *J. Am. Chem. Soc.*, 1973, **95**, 4073.
1578. J. M. Huggins and R. G. Bergman, *J. Am. Chem. Soc.*, 1979, **101**, 4410.
1579. O. S. Mills and E. F. Paulus, *Chem. Commun.*, 1966, 738.
1580. C. S. Chamberlain and R. S. Drago, *Inorg. Chim. Acta*, 1979, **32**, 75.
1581. M. J. Collins and H. F. Henneike, *Inorg. Chem.*, 1973, **12**, 2983.
1582. V. A. Alekseevski and M. A. Reutova, *Zh. Neorg. Khim.*, 1979, **24**, 102.
1583. D. P. Graddon and T. T. Nyein, *Aust. J. Chem.*, 1974, **27**, 407.
1584. L. Nordenskiold and J. Kowaleswki, *J. Chem. Soc., Dalton Trans.*, 1980, 363.

1585. K. C. Joshi and V. N. Pathak, *Coord. Chem. Rev.*, 1977, **22,** 37.
1586. F. A. Cotton and B. H. C. Winquist, *Inorg. Chem.*, 1969, **8,** 1304.
1587. C. Reichert and J. B. Westmore, *Inorg. Chem.*, 1969, **8,** 1012.
1588. S. M. Schildcrout, *Inorg. Chem.*, 1980, **19,** 224.
1589. L. I. Katzin and E. Gulyas, *Inorg. Chem.*, 1971, **10,** 2411.
1590. J. Dillon and K. Nakonishi, *J. Am. Chem. Soc.*, 1975, **97,** 5409.
1591. H. D. Gafney and R. L. Lintvedt, *J. Am. Chem. Soc.*, 1970, **92,** 6996.
1592. R. D. Mouts and Q. Fernando, *Acta Crystallogr., Sect. B,* 1974, **30,** 542.
1593. I. Collamati, C. Ercolani and D. J. Machin, *J. Chem. Soc. (A)*, 1969, 1537.
1594. D. Attanasio, I. Collamati and C. Ercolani, *J. Chem. Soc., Dalton Trans.*, 1972, 772.
1595. R. L. Lindtvedt and A. M. Fatta, *Inorg. Chem.*, 1968, **7,** 2489.
1596. L. L. Borer and R. L. Lindtvedt, *Inorg. Chem.*, 1971, **10,** 2113.
1597. V. Schrig, *Inorg. Chem.*, 1972, **11,** 736.
1598. R. J. Irving, M. L. Post and D. C. Povey, *J. Chem. Soc., Dalton Trans.*, 1973, 697.
1599. E. L. Muetterties, H. Roesky and C. M. Wright, *J. Am. Chem. Soc.*, 1966, **88,** 4856.
1600. F. Rohrscheid, A. L. Balch and R. H. Holm, *Inorg. Chem.*, 1966, **5,** 1542.
1661. C. Floriani, R. Henzi and F. Calderazzo, *J. Chem. Soc., Dalton Trans.*, 1972, 2640.
1602. M. W. Lynch, R. M. Buchanan, C. G. Pierpoint and D. N. Hendrickson, *Inorg. Chem.*, 1981, **20,** 1038.
1603. P. J. Crowley and H. N. Haendler, *Inorg. Chem.*, 1962, **1,** 904.
1604. C. G. Pierpoint, L. C. Francesconi and D. N. Hendrickson, *Inorg. Chem.*, 1977, **16,** 2367.
1605. C. G. Pierpoint, L. C. Francesconi and D. N. Hendrickson, *Inorg. Chem.*, 1978, **17,** 3470.
1606. C. A. Tsipis, E. G. Bakalbassis, V. P. Papageorgiou and M. N. Bakola-Christianopoulou, *Can. J. Chem.*, 1982, **60,** 2477.
1607. R. S. Bottei and D. L. Greene, *J. Inorg. Nucl. Chem.*, 1968, **30,** 1469.
1608. H. Morita, S. Shimomura and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, 1978, **51,** 3213.
1609. C. C. Addison, N. Logan, S. C. Wallwork and C. D. Garner, *Q. Rev., Chem. Soc.*, 1971, **25,** 289.
1610. C. C. Addison and D. Sutton, *Prog. Inorg. Chem.*, 1967, **8,** 195.
1611. C. C. Addison and N. Logan, *Adv. Inorg. Chem., Radiochem.*, 1964, **6,** 72.
1612. D. K. Straub, R. S. Drago and J. T. Donoghue, *Inorg. Chem.*, 1962, **1,** 848.
1613. M. J. Begley, M. J. Haley, T. J. King, A. Morris, R. Pike and B. Smith, *Inorg. Nucl. Chem. Lett.*, 1976, **12,** 99.
1614. P. Gallezot, D. Weigel and M. Prettre, *Acta Crystallogr.*, 1967, **22,** 699.
1615. L. Berger and S. A. Friedberg, *Phys. Rev. A*, 1964, **136,** 158.
1616. A. F. Cameron, D. W. Taylor and R. H. Nuttall, *J. Chem. Soc., Dalton Trans.*, 1972, 422.
1617. R. Louis, Y. Agnus and R. Weiss, *Acta Crystallogr., Sect. B*, 1979, **35,** 2905.
1618. G. Bombieri, E. Forsellini, R. Graziani and E. Tondello, *J. Chem. Soc. (A)*, 1970, 3349.
1619. A. Laidoudi, N. Kheddar and M. C. Brianso, *Acta Crystallogr., Sect. B*, 1978, **34,** 778.
1620. E. C. Alyea, G. Ferguson and R. J. Restivo, *Inorg. Chem.*, 1975, **14,** 2491.
1621. L. F. Power, A. M. Tait, J. Pletcher and M. Sax, *J. Chem. Soc., Dalton Trans.*, 1975, 2494.
1622. M. Mathew, G. J. Palenik and G. R. Clark, *Inorg. Chem.*, 1973, **12,** 446.
1623. N. F. Curtis and Y. M. Curtis, *Inorg. Chem.*, 1965, **4,** 804.
1624. A. B. P. Lever, *Inorg. Chem.*, 1965, **4,** 1042.
1625. L. Sacconi, I. Bertini and F. Mani, *Inorg. Chem.*, 1967, **6,** 262.
1626. M. Ciampolini and N. Nardi, *Inorg. Chem.*, 1966, **5,** 41.
1627. K. A. Jensen, *Z. Anorg. Allg. Chem.*, 1936, **229,** 265.
1628. G. Dyer, J. G. Hartley and L. M. Venanzi, *J. Chem. Soc.*, 1965, 1293.
1629. E. Bannister and F. A. Cotton, *J. Chem. Soc.*, 1960, 2276.
1630. R. L. Carlin and M. J. Baker, *J. Chem. Soc.*, 1964, 5008.
1631. N. M. Karayannis, C. M. Mikulski, L. L. Pitlewski and M. M. Labes, *Inorg. Chem.*, 1974, **13,** 1146.
1632. M. Brierley and W. J. Geary, *J. Chem. Soc. (A)*, 1968, 2130.
1633. I. S. Ahuja, R. Singh and C. P. Rai, *J. Inorg. Nucl. Chem.*, 1978, **40,** 924.
1634. A. Guntz and M. Martin, *Bull. Soc. Chim. Fr.*, 1909, **5,** 1004.
1635. C. C. Addison and D. J. Chapman, *J. Chem. Soc.*, 1965, 819.
1636. B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 1960, 648.
1637. M. A. Hitchman and G. L. Rowbottom, *Coord. Chem. Rev.*, 1982, **42,** 55.
1638. S. Takagi, M. D. Joester and P. G. Lenhert, *Acta Crystallogr., Sect. B,* 1975, **31,** 1970.
1639. S. Takagi, M. D. Joester and P. G. Lenhert, *Acta Crystallogr., Sect. B,* 1975, **31,** 1968.
1640. S. Takagi, M. D. Joester and P. G. Lenhert, *Acta Crystallogr., Sect. B,* 1976, **32,** 2524.
1641. B. N. Figgis, P. A. Reynolds, A. H. White, G. A. Williams and S. Wright, *J. Chem. Soc., Dalton Trans.*, 1981, 997.
1642. A. J. Finney, M. A. Hitchman, C. L. Raston, G. L. Rowbottom and A. H. White, *Aust. J. Chem.*, 1981, **34,** 2047.
1643. A. J. Finney, M. A. Hitchman, C. L. Raston, G. L. Rowbottom and A. H. White, *Aust. J. Chem.*, 1981, **34,** 2085.
1644. A. J. Finney, B. W. Skelton and A. H. White, *Aust. J. Chem.*, 1981, **34,** 2095.
1645. A. J. Finney, M. A. Hitchman, C. L. Raston, G. L. Rowbottom and A. H. White, *Aust. J. Chem.*, 1981, **34,** 2113.
1646. A. J. Finney, M. A. Hitchman, C. L. Raston, G. L. Rowbottom and A. H. White, *Aust. J. Chem.*, 1981, **34,** 2069.
1647. M. G. B. Drew and D. Rogers, *Chem. Commun.*, 1965, 476.
1648. A. J. Finney, M. A. Hitchman, C. L. Raston, G. L. Rowbottom and A. H. White, *Aust. J. Chem.*, 1981, **34,** 2159.
1649. M. A. Hitchman, R. Thomas, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1983, 2273.
1650. R. Birdy, D. M. L. Goodgame, J. C. McConway and D. Rogers, *J. Chem. Soc., Dalton Trans.*, 1977, 1730.

1651. A. J. Finney, M. A. Hitchman, D. L. Kepert, C. L. Raston, G. L. Rowbottom and A. H. White, *Aust. J. Chem.*, 1981, **34**, 2177.
1652. A. Meyer, A. Gleizes, J. J. Girerd, M. Verdaguer and O. Kahn, *Inorg. Chem.*, 1982, **21**, 1729.
1653. D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, 1967, **6**, 813.
1654. D. M. L. Goodgame and L. M. Venanzi, *J. Chem. Soc.*, 1963, 616; 1963, 5909.
1655. D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, 1964, **3**, 1389.
1656. D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, 1966, **5**, 1303.
1657. K. C. Patel, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1631.
1658. J. R. Ferraro and L. Fabbrizzi, *Inorg. Chim. Acta*, 1978, **26**, L15.
1659. L. El-Sayed and R. O. Ragsdale, *Inorg. Chem.*, 1967, **6**, 1640.
1660. D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, 1965, **4**, 721.
1661. A. J. Finney, M. A. Hitchman, C. L. Raston, G. L. Rowbottom and A. H. White, *Aust. J. Chem.*, 1981, **34**, 2125.
1662. A. J. Finney, M. A. Hitchman, C. L. Raston, G. L. Rowbottom and A. H. White, *Aust. J. Chem.*, 1981, **34**, 2139.
1663. M. G. B. Drew, D. M. L. Goodgame, M. A. Hitchman and D. Rogers, *Chem. Commun.*, 1965, 477.
1664. A. Gleizes, A. Meyer, M. A. Hitchman and O. Kahn, *Inorg. Chem.*, 1982, **21**, 2257.
1665. I. Bertini, D. Gatteschi and A. Scozzafava, *Inorg. Chem.*, 1976, **15**, 203.
1666. C. R. Hare and C. J. Ballhausen, *J. Chem. Phys.*, 1964, **40**, 792.
1667. K. G. Caulton and R. F. Fenske, *Inorg. Chem.*, 1967, **6**, 562.
1668. M. A. Hitchman and G. L. Rowbottom, *Inorg. Chem.*, 1982, **21**, 823.
1669. D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chim. Acta*, 1969, **3**, 319.
1670. I. M. Walker, A. B. P. Lever and P. J. McCarthy, *Can. J. Chem.*, 1980, **58**, 823.
1671. K. Nakamoto, J. Fujita and H. Murata, *J. Am. Chem. Soc.*, 1958, **80**, 4817.
1672. I. Nakagawa, T. Shimanouchi and K. Yamasaki, *Inorg. Chem.*, 1968, **7**, 1332.
1673. A. Takeuchi, K. Sato, K. Sone, S. Yamada and K. Yamasaki, *Inorg. Chim. Acta*, 1967, **1**, 399.
1674. D. M. L. Goodgame, M. A. Hitchman, D. F. Marsham, P. Phavanantha and D. G. Rogers, *Chem. Commun.*, 1969, 1383.
1675. C. A. Lutz, A. Lomax and L. Toh, *J. Chem. Soc., Chem., Commun.*, 1977, 247.
1676. S. F. Pavkovic and D. W. Meek, *Inorg. Chem.*, 1964, **3**, 1091.
1677. M. R. Rosenthal and R. S. Drago, *Inorg. Chem.*, 1965, **4**, 840.
1678. D. H. Brown, R. H. Nuttal, J. McAvoy and D. W. A. Sharp, *J. Chem. Soc. (A)*, 1966, 892.
1679. S. Buffagni, L. M. Vallarino and J. V. Quagliano, *Inorg. Chem.*, 1964, **3**, 671.
1680. L. M. Vallarino, W. E. Hill and J. V. Quagliano, *Inorg. Chem.*, 1965, **4**, 1598.
1681. A. V. Butcher, D. J. Phillips and J. P. Redfern, *J. Chem. Soc.*, 1965, 1064.
1682. F. Mani, *Inorg. Nucl. Chem. Lett.*, 1971, **7**, 447.
1683. S. H. Hunter, R. S. Nyholm and G. A. Rodley, *Inorg. Chim. Acta*, 1969, **3**, 631.
1684. B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 1961, 3091.
1685. A. E. Wickenden and R. A. Krause, *Inorg. Chem.*, 1965, **4**, 404.
1686. R. W. Hay, B. Jeragh, G. Ferguson, B. Kaitner and B. L. Ruhl, *J. Chem. Soc., Dalton Trans.*, 1982, 1531.
1687. F. Mundale-Aubry and G. M. Brown, *Acta Crystallogr., Sect. B*, 1968, **24**, 745.
1688. H. C. Synman and C. W. F. T. Pistorius, *Z. Anorg. Allg. Chem.*, 1963, **324**, 157 and refs therein.
1689. C. Benelli, M. di Vaira, G. Noccioli and L. Sacconi, *Inorg. Chem.*, 1977, **16**, 182.
1690. P. J. C. Tedenac and E. Philippot, *Acta Crystallogr., Sect. B*, 1974, **30**, 2286; P. J. C. Tedenac, N. Dinhphung, C. Avinens and M. Maurin, *J. Inorg. Nucl. Chem.*, 1976, **38**, 85.
1691. N. M. Karayannis, C. M. Mikulski, L. L. Pytlewski and M. M. Labes, *Inorg. Chim. Acta*, 1974, **10**, 97.
1692. G. F. Gasperri, A. Mangia, A. Musatti and M. Nardelli, *Acta Crystallogr., Sect. B*, 1969, **25**, 203.
1693. E. J. Puff, *J. Chem. Soc. (A)*, 1968, 836.
1694. C. W. Dudley and C. Oldham, *Inorg. Chim. Acta*, 1968, **2**, 199.
1695. E. Lindner, I. P. Lorenz and G. Vitzthum, *Chem. Ber.*, 1973, **106**, 211.
1696. E. Konig, E. Lindner, I. P. Lorenz and G. Ritter, *Inorg. Chim. Acta*, 1972, **6**, 123.
1697. C. Preti, G. Tosi, D. de Filippo and G. Verani, *J. Inorg. Nucl. Chem.*, 1974, **36**, 2203.
1698. C. Preti and G. Tosi, *Inorg. Chem.*, 1977, **16**, 2805.
1699. R. C. Paul, V. P. Kapila, N. Polta and S. K. Sharma, *Indian J. Chem.*, 1974, **12**, 825.
1700. M. T. Janski and J. T. Yoke, *J. Inorg. Nucl. Chem.*, 1979, **41**, 1707.
1701. N. C. Johnson, J. T. Turk, W. E. Bull and H. G. Mayfield, Jr., *Inorg. Chim. Acta*, 1927, **25**, 235.
1702. A. R. Byington and W. E. Bull, *Inorg. Chim. Acta*, 1977, **21**, 239.
1703. P. E. C. Corbridge, in 'Topics in Phosphorus Chemistry', ed. E. J. Griffith and M. Grayson, Interscience, New York, 1966.
1704. M. G. Lyapilina, E. I. Krylov, V. Asherov and E. A. Nikomenko, *Zh. Neorg. Khim.*, 1975, **20**, 3379.
1705. A. Saavedra and D. Reinen, *Z. Anorg. Allg. Chem.*, 1977, **435**, 91.
1706. N. C. Johnson and W. E. Bull, *Inorg. Chim. Acta*, 1978, **27**, 191.
1707. D. M. Roundhill, R. P. Sperline and W. B. Beaulieu, *Coord. Chem. Rev.*, 1978, **26**, 263.
1708. V. Gutman and K. Penkart, *Monatsh. Chem.*, 1968, **99**, 1452.
1709. N. M. Karayannis, C. M. Mikulski, M. J. Strocko, L. L. Pytlewski and M. M. Labes, *Z. Anorg. Allg. Chem.*, 1971, **384**, 267.
1710. J. J. Pittis, M. A. Robinson and S. I. Trotz, *J. Inorg. Nucl. Chem.*, 1968, **30**, 1299.
1711. H. D. Gillmann, *Inorg. Chem.*, 1974, **13**, 1921.
1712. M. T. Youinau and J. E. Guerchais, *Inorg. Chim. Acta*, 1976, **19**, 257.
1713. H. Werner and T. N. Khac, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 324.
1714. R. P. Sperline and D. M. Roundhill, *Inorg. Chem.*, 1977, **16**, 2612.
1715. C. Oldham, *Prog. Inorg. Chem.*, 1968, **10**, 223.
1716. J. N. van Niekerk and F. R. L. Schoening, *Acta Crystallogr.*, 1953, **6**, 609.

1717. T. C. Downie, W. Harrison, E. S. Raper and M. A. Hepworth, *Acta Crystallogr., Sect. B,* 1971, **27**, 706.
1718. R. E. Cramer, W. van Doorne and R. Rubis, *Inorg. Chem.*, 1975, **14**, 2462.
1719. S. F. Pavkovic, F. C. Wilholm and J. N. Brown, *Acta Crystallogr., Sect. B,* 1978, **34**, 1337.
1720. J. Drew, M. B. Hursthouse and P. Thornton, *J. Chem. Soc., Dalton Trans.*, 1972, 1658.
1721. M. B. Hursthouse and D. B. New, *J. Chem. Soc., Dalton Trans.*, 1977, 1082.
1722. M. Klina, *Cryst. Struct. Commun.*, 1980, **9**, 439, 457, 567; 1981, **10**, 521.
1723. A. Pajumen and U. Turpeinen, *Suom. Kemistil. B,* 1973, **46**, 281.
1724. S. C. Nyburg and J. S. Wood, *Inorg. Chem.*, 1964, **3**, 469.
1725. P. O. Whimp, M. F. Bailey and N. F. Curtis, *J. Chem. Soc. (A)*, 1970, 1956.
1726. U. Turpeinen, M. Ahlgren and R. Hamalainen, *Finn. Chem. Lett.*, 1977, 246.
1727. U. Turpeinen, *Finn. Chem. Lett.*, 1976, 173.
1728. M. Ahlgren and U. Turpeinen, *Acta Crystallogr., Sect. B,* 1982, **38**, 276.
1729. M. Ahlgren and U. Turpeinen, *Acta Chem. Scand., Ser. A,* 1978, **32**, 18.
1730. U. Turpeinen, *Finn. Chem. Lett.*, 1977, **36**, 123.
1731. N. I. Kirillova, Yu. T. Struchkov, M. A. Porai-Koshits, A. A. Pasynskii, A. S. Antsyshkima, L. K. Minacheva, G. G. Sodikov, T. C. Idrisov and V. T. Kalinnikov, *Inorg. Chim. Acta,* 1980, **42**, 115.
1732. W. L. Gladfelter, M. W. Lynch, W. P. Schaefer, D. N. Hendrickson and H. B. Gray, *Inorg. Chem.*, 1981, **20**, 2390.
1733. C. K. Prout, C. Walker and F. J. C. Rossotti, *J. Chem. Soc. (A)*, 1971, 556.
1734. M. M. Borel, A. Geffrouais and M. Ledesert, *Acta Crystallogr., Sect. B,* 1976, **32**, 2385.
1735. M. M. Borel, A. Geffrouais and M. Ledesert, *Acta Crystallogr., Sect. B,* 1977, **33**, 571.
1736. M. M. Borel and M. L. Ledesert, *Acta Crystallogr., Sect. B,* 1977, **33**, 2993; M. M. Borel, A. Geffrouais and M. Ledesert, *Acta Crystallogr., Sect. B,* 1977, **33**, 568.
1737. M. Bonamico, G. Dessy and V. Fares, *Chem. Commun.*, 1969, 697.
1738. G. A. Melson, P. T. Green and R. F. Bryan, *Inorg. Chem.*, 1970, **9**, 1116.
1739. G. Adiwidjaja and H. Kuppers, *Acta Crystallogr., Sect. B,* 1976, **32**, 1571.
1740. N. F. Curtis, R. N. McCormick and T. N. Waters, *J. Chem. Soc., Dalton Trans.*, 1973, 1537.
1741. J. Kopf, U. Beherens, M. Kastner and G. Klar, *J. Inorg. Nucl. Chem.*, 1977, **39**, 889.
1742. D. O. Nielsen, M. L. Larsen, R. D. Willet and J. I. Legg, *J. Am. Chem. Soc.*, 1971, **93**, 5079.
1743. X. Solans and C. Miravitlles, *Acta Crystallogr., Sect. B,* 1981, **37**, 1407.
1744. E. N. Treushnikov, V. I. Kuskov, L. A. Aslanov and L. V. Soboleva, *Kristallografiya,* 1980, **25**, 287.
1745. D. W. Archer and C. B. Monk, *J. Chem. Soc.*, 1964, 3117.
1746. R. Fuentes, Jr., L. O. Morgen and N. A. Matwiyoff, *Inorg. Chem.*, 1975, **14**, 1837.
1747. A. Bonsen, F. Eggers and W. Knoche, *Inorg. Chem.*, 1976, **15**, 1212.
1748. P. W. N. M. van Leeuwen and W. L. Groeneveld, *Recl. Trav. Chim. Pays-Bas,* 1968, **87**, 86.
1749. K. Korgmann and R. Mattes, *Z. Kristallogr.*, 1963, **118**, 291.
1750. P. Bianco, M. Asso and J. Haladjian, *Bull. Soc. Chim. Fr.* 1971, 3943.
1751. S. F. Pavkovic, *J. Inorg. Nucl. Chem.*, 1971, **33**, 1475.
1752. F. C. Wilholm and S. F. Pavkovic, *J. Inorg. Nucl. Chem.*, 1975, **37**, 303.
1753. J. Catterick and P. Thornton, *J. Chem. Soc., Dalton Trans.*, 1975, 233.
1754. G. Marcotrigiano, G. C. Pellacani and C. Preti, *Z. Anorg. Allg. Chem.*, 1974, **408**, 313.
1755. A. B. P. Lever and D. Ogden, *J. Chem. Soc. (A)*, 1967, 2041.
1756. S. Amasa, D. H. Brown and D. W. A. Sharp, *J. Chem. Soc. (A)*, 1969, 2892.
1757. N. Kumar, P. L. Kachroo and R. Kant, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 1787.
1758. N. Kumar, P. L. Kachroo and R. Kant, *Indian J. Chem., Sect. A,* 1979, **18**, 265.
1759. P. G. Cookson and G. B. Deacon, *Aust. J. Chem.*, 1972, **25**, 2095.
1760. A. A. Pasynski, T. C. Idrisov, V. M. Novotortsev and V. T. Kalynnikov, *Koord. Khim.*, 1975, **1**, 1059.
1761. T. S. Kuntsevich, T. N. Tarkhova and A. V. Ablov, *Dokl. Akad. Nauk SSSR,* 1978, **243**, 108.
1762. T. S. Kuntsevich, T. N. Tarkhova and A. V. Ablov, *Dokl. Akad. Nauk SSSR,* 1978, **243**, 338.
1763. T. S. Kuntsevich, T. N. Tarkhova and A. V. Ablov, *Dokl. Adad. Nauk SSSR,* 1978, **243**, 649.
1764. A. B. P. Lever, I. M. Walker and P. J. McCarthy, *Inorg. Chim. Acta,* 1980, **44**, L143.
1765. D. M. L. Goodgame and L. M. Venanzi, *J. Chem. Soc.*, 1963, 5909.
1766. C. D. Rao, B. Paul, B. K. Mohapatra and S. Guru, *J. Inorg. Nucl. Chem.*, 1978, **40**, 134.
1767. A. Bencini, C. Benelli, D. Gatteschi and C. Zanchini, *J. Am. Chem. Soc.*, 1980, **102**, 5820.
1768. E. Cardarelli, G. D'Ascenzo, A. D. Macri and A. Pupella, *Thermochim. Acta,* 1979, **33**, 267.
1769. D. N. Dathyanarayana and V. V. Savant, *Z. Anorg. Allg. Chem.*, 1971, **385**, 329.
1770. F. W. Yerhoff and D. W. Larson, *Can. J. Chem.*, 1972, **50**, 826.
1771. D. F. Averill, J. I. Legg and D. L. Smith, *Inorg. Chem.*, 1972, **11**, 2344.
1772. M. H. West and J. I. Legg, *J. Am. Chem. Soc.*, 1976, **98**, 6945.
1773. J. I. Watters and R. Dewitt, *J. Am. Chem. Soc.*, 1960, **82**, 1333.
1774. G. H. Nancollas and N. Sutin, *Inorg. Chem.*, 1964, **3**, 360.
1775. S. R. Brinkley, *J. Am. Chem. Soc.*, 1939, **61**, 965.
1776. J. T. Morrison and W. A. Baker, Jr., *Inorg. Chim. Acta,* 1969, **3**, 463.
1777. D. Broadbent, D. Dollimore and J. Dollimore, *J. Chem. Soc. (A)*, 1966, 278.
1778. C. G. van Kralingen, J. A. C. van Ooijen and J. Reedijk, *Transition Met. Chem.*, 1978, **3**, 90.
1779. G. P. Singh, L. N. Srivastava and S. V. Chandra, *J. Inorg. Nucl. Chem.*, 1973, **35**, 2104.
1780. N. F. Curtis, *J. Chem. Soc. (A)*, 1968, 1584.
1781. N. F. Curtis, *J. Chem. Soc.*, 1963, 4109, 4115.
1782. R. West and H. Y. Niu, *J. Am. Chem. Soc.*, 1963, **85**, 2586.
1783. R. West and H. Y. Niu, *J. Am. Chem. Soc.*, 1963, **85**, 2589.
1784. A. Ludi and P. Schindler, *Angew. Chem., Int. Ed. Engl.*, 1968, **7**, 638.
1785. M. Habenschuss and B. C. Gerstein, *J. Chem. Phys.*, 1974, **61**, 852.
1786. R. A. Bailey, W. N. Willis and W. J. Tancredi, *J. Inorg. Nucl. Chem.*, 1971, **33**, 2387.

1787. P. H. Tedesco and H. F. Walton, *Inorg. Chem.*, 1969, **8,** 932.
1788. J. A. C. van Ooijen, J. Reedijk and A. L. Spek, *Inorg. Chem.*, 1979, **18,** 1184.
1789. E. Mentasti, E. Pelizzetti, F. Secco and M. Venturini, *Inorg. Chem.*, 1979, **18,** 2007.
1790. E. Mentasti, F. Secco and M. Venturini, *Inorg. Chem.*, 1980, **19,** 3528.
1791. D. G. Vartak and K. R. Menon, *J. Inorg. Nucl. Chem.*, 1971, **33,** 1003.
1792. Y. Z. Yousif and F. J. M. Al-Imarah, *J. Inorg. Nucl. Chem.*, 1980, **42,** 779.
1793. G. A. Melson and W. F. Pickering, *Aust. J. Chem.*, 1968, **21,** 1205.
1794. P. V. Khadikar, R. L. Ameria, M. G. Kekre and S. D. Chauhan, *J. Inorg. Nucl. Chem.*, 1973, **35,** 4301.
1795. K. N. Kovalenko, D. V. Kazachenko, V. P. Kurdatov and L. G. Kovaleva, *Russ. J. Inorg. Chem. (Engl. Transl)*, 1971, **16,** 1303.
1796. M. Tanaka, H. Okawa, I. Hanaoka and S. Kida, *Chem. Lett.*, 1974, 71.
1797. P. E. Rush, J. D. Oliver, G. D. Simpson and G. O. Carlisle, *J. Inorg. Nucl. Chem.*, 1975, **37,** 1393.
1798. J. Strouse, S. W. Layten and C. E. Strouse, *J. Am. Chem. Soc.*, 1977, **99,** 562.
1799. E. R. Still and P. Wikberg, *Inorg. Chim. Acta*, 1980, **46,** 153.
1800. N. M. Karayannis, C. M. Mikulski and L. L. Pytlewski, *Inorg. Chim. Acta*, 1971, **5,** 69.
1801. F. A. Cotton and E. Bannister, *J. Chem. Soc.*, 1960, 1873.
1802. M. W. G. de Bolster, I. E. Kortram and W. L. Groeneveld, *J. Inorg. Nucl. Chem.*, 1972, **34,** 575.
1803. J. Lewis, R. S. Nyholm and G. A. Rodley, *Nature (London)*, 1965, **207,** 72.
1804. A. M. Brodie, S. H. Hunter, G. A. Rodley and C. J. Wilkins, *Inorg. Chim. Acta*, 1968, **2,** 195.
1805. Y. S. Ng, G. A. Rodley and W. T. Robinson, *Inorg. Chem.*, 1976, **15,** 303.
1806. N. M. Karayannis, C. M. Mikulski, L. L. Pytlewski and M. M. Labes, *Inorg. Chem.*, 1970, **9,** 582.
1807. D. M. L. Goodgame and F. A. Cotton, *J. Am. Chem. Soc.*, 1960, **82,** 5774.
1808. F. A. Cotton and D. M. L. Goodgame, *J. Am. Chem. Soc.*, 1960, **82,** 5771.
1809. A. M. Brodie, J. E. Douglas and C. J. Wilkins, *J. Chem. Soc. (A)*, 1969, 1931.
1810. J. T. Donoghue and R. S. Drago, *Inorg. Chem.*, 1962, **1,** 866; 1963, **2,** 572.
1811. M. W. G. de Bolster and W. L. Groeneveld, *Recl. Trav. Chim. Pays-Bas*, 1972, **91,** 171, 185.
1812. B. B. Wayland and R. S. Drago, *J. Am. Chem. Soc.*, 1965, **87,** 2372.
1813. E. le Coz, J. E. Guerchois and D. M. L. Goodgame, *Bull. Soc. Chem. Fr.*, 1971, 409.
1814. N. M. Karayannis, C. M. Mikulski, M. J. Strocko, L. L. Pytlewski and M. M. Labes, *Inorg. Chim. Acta*, 1974, **8,** 91.
1815. N. M. Karayannis, E. E. Bradshow, L. L. Pytlewski and M. M. Labes, *J. Inorg. Nucl. Chem.*, 1970, **32,** 1079.
1816. N. M. Karayannis, C. M. Mikulski, M. J. Strocko, L. L. Pytlewski and M. M. Labes, *Inorg. Chim. Acta*, 1970, **4,** 557.
1817. N. M. Karayannis, C. Owens, L. L. Pytlewski and M. M. Labes, *J. Inorg. Nucl. Chem.*, 1969, **31,** 2059.
1818. N. M. Karayannis, L. L. Pytlewski and C. M. Mikulski, *Inorg. Chim. Acta*, 1977, **22,** L42.
1819. W. E. Daniels, *Inorg. Chem.*, 1964, **3,** 1800.
1820. E. le Coz, J. E. Guerchois and D. M. L. Goodgame, *Bull. Soc. Chem. Fr.*, 1969, 3855.
1821. A. S. Tryahin, V. V. Skopenko and D. A. Stakhov, *Zh. Neorg. Khim.*, 1973, **18,** 2658.
1822. J. C. Boubel, J. J. Delpuech and A. Peguy, *J. Chem. Soc., Dalton Trans.*, 1978, 1506.
1823. D. F. Peppard, *Adv. Inorg. Chem. Radiochem.*, 1966, **9,** 1.
1824. F. Mani and M. Bacci, *Inorg. Chim. Acta*, 1972, **6,** 487.
1825. F. Mani and A. Scozzafava, *Gazz. Chim. Ital.*, 1972, **102,** 1109.
1826. S. S. Sandhu and R. S. Sandhu, *Inorg. Chim. Acta*, 1972, **6,** 383.
1827. B. J. Brisdon, *J. Chem. Soc., Dalton Trans.*, 1972, 2247.
1828. B. J. Brisdon and D. Cocker, *Inorg. Nucl. Chem. Lett.*, 1974, **10,** 179.
1829. M. D. Joesten and K. M. Nykerk, *Inorg. Chem.*, 1964, **3,** 548.
1830. K. P. Lannert and M. D. Joesten, *Inorg. Chem.*, 1968, **7,** 2048.
1831. K. P. Lannert and M. D. Joesten, *Inorg. Chem.*, 1969, **8,** 1775.
1832. M. W. G. de Bolster and W. L. Groeneveld, *Recl. Trav. Chim. Pays-Bas*, 1971, **90,** 6871.
1833. M. W. G. de Bolster, F. J. Wiegerink and W. L. Groeneveld, *J. Inorg. Nucl. Chem.*, 1973, **35,** 89.
1834. M. W. G. de Bolster and W. L. Groeneveld, *Recl. Trav. Chim. Pays-Bas*, 1972, **91,** 185, 643.
1835. M. D. Joester and Y. T. Chen, *Inorg. Chem.*, 1972, **11,** 429.
1836. M. F. Prysak and M. D. Joester, *Inorg. Chim. Acta*, 1970, **4,** 383.
1837. J. A. Walmsley and S. Y. Tyree, *Inorg. Chem.*, 1963, **2,** 312.
1838. M. D. Joester and Y. T. Chen, *J. Inorg. Nucl. Chem.*, 1972, **34,** 237.
1839. C. M. Mikulski, W. Henry, L. L. Pytlewski and N. M. Karayannis, *J. Inorg. Nucl. Chem.*, 1978, **40,** 769.
1840. B. J. Brisdon and D. Cocker, *Inorg. Nucl. Chem. Lett.*, 1974, **10,** 179.
1841. C. M. Mikulski, W. Henry, L. L. Pytlewski and N. M. Karayannis, *Transition Met. Chem.*, 1977, **2,** 135.
1842. R. G. Garvey, J. H. Nelson and R. O. Ragsdale, *Coord. Chem. Rev.*, 1968, **3,** 375.
1843. N. M. Karayannis, L. L. Pytlewski and C. M. Mikulski, *Coord. Chem. Rev.*, 1973, **11,** 93.
1844. J. V. Quagliano, J. Fujita, G. Franz, D. J. Phillips, J. P. Walmsley and S. Y. Tyree, *J. Am. Chem. Soc.*, 1961, **83,** 3770.
1845. R. L. Carlin, *J. Am. Chem. Soc.*, 1961, **83,** 3773.
1846. D. W. Meek, R. S. Drago and T. S. Pyper, *Inorg. Chem.*, 1962, **1,** 285.
1847. R. L. Carlin, C. J. O'Connor and S. N. Bhatia, *J. Am. Chem. Soc.*, 1976, **98,** 3523.
1848. A. D. van Ingen Schenau, G. C. Verschoor and C. Romers, *Acta Crystallogr., Sect. B*, 1974, **30,** 1686.
1849. A. Paduan-Filho, E. Sinn, R. D. Chirico and R. L. Carlin, *Inorg. Chem.*, 1981, **20,** 2688.
1850. N. M. Karayannis, C. M. Paleos, L. L. Pytlewski and M. M. Labes, *Inorg. Chem.*, 1969, **8,** 2559.
1851. G. B. Aitken and G. P. McQuillan, *J. Chem. Soc., Dalton Trans.*, 1973, 2637.
1852. G. Schmauss and H. Specker, *Z. Anorg. Allg. Chem.*, 1969, **364,** 1.
1853. D. W. Herlocker, R. S. Drago and V. I. Meek, *Inorg. Chem.*, 1966, **5,** 2009.
1854. L. C. Nathan, J. H. Nelson, G. L. Rich and R. O. Ragsdale, *Inorg. Chem.*, 1969, **8,** 1499.
1855. J. H. Nelson and R. O. Ragsdale, *Inorg. Chim. Acta*, 1968, **2,** 439.

1856. N. M. Karayannis, L. L. Pytlewski and M. M. Labes, *Inorg. Chim. Acta,* 1969, **3,** 415.
1857. N. M. Karayannis, C. M. Mikulski, L. L. Pytlewski and M. M. Labes, *J. Inorg. Nucl. Chem.*, 1972, **34,** 3139.
1858. N. M. Karayannis, C. M. Mikulski, L. S. Gelfand, E. S. C. Schwartz and L. L. Pytlewski, *J. Inorg. Nucl. Chem.*, 1979, **39,** 1555.
1859. N. M. Karayannis, C. M. Mikulski, L. L. Pytlewski and M. M. Labes, *Inorg. Chim. Acta,* 1974, **10,** 97.
1860. J. H. Nelson and R. O. Ragsdale, *Inorg. Chim. Acta,* 1968, **2,** 230.
1861. J. H. Nelson, L. C. Nathan and R. O. Ragsdale, *Inorg. Chem.*, 1968, **7,** 1840.
1862. A. N. Speca, L. L. Pytlewski and N. M. Karayannis, *J. Inorg. Nucl. Chem.*, 1973, **35,** 4029.
1863. D. E. Chasan, L. L. Pytlewski, C. Owens and N. M. Karayannis, *Inorg. Chim. Acta,* 1976, **19,** L59.
1864. D. E. Chasan, L. L. Pytlewski, C. Owens and N. M. Karayannis, *J. Inorg. Nucl. Chem.*, 1979, **41,** 13.
1865. A. B. P. Lever, J. Lewis and R. S. Nyholm, *J. Chem. Soc.*, 1962, 5262.
1866. A. N. Speca, L. S. Gelfand, F. J. Iaconianni, L. L. Pytlewski, C. M. Mikulski and N. M. Karayannis, *J. Inorg. Nucl. Chem.*, 1979, **41,** 283.
1867. C. M. Mikulski, F. J. Iaconianni, L. L. Pytlewski, A. N. Speca and N. M. Karayannis, *Inorg. Chim. Acta,* 1980, **46,** L47.
1868. A. N. Speca, F. J. Iaconianni, L. S. Gelfand, L. L. Pytlewski, C. M. Mikulski and N. M. Karayannis, *J. Inorg. Nucl. Chem.*, 1979, **41,** 957.
1869. D. E. Chasan, L. L. Pytlewski, C. Owens and N. M. Karayannis, *J. Inorg. Nucl. Chem.*, 1978, **40,** 1019.
1870. A. N. Speca, L. S. Gelfand, F. J. Iaconianni, L. L. Pytlewski, C. M. Mikulski and N. M. Karayannis, *Inorg. Chim. Acta,* 1979, **33,** 195.
1871. D. X. West and M. A. Vanek, *J. Inorg. Nucl. Chem.*, 1978, **40,** 1027.
1872. L. H. Chartier, R. E. Kohrman and D. X. West, *J. Inorg. Nucl. Chem.*, 1979, **41,** 657, 663.
1873. H. Sigel and H. Brintzinger, *Helv. Chim. Acta,* 1963, **46,** 701.
1874. A. N. Speca, N. M. Karayannis, L. L. Pytlewski, L. J. Winters and D. Kandasamy, *Inorg. Chem.*, 1973, **12,** 1221.
1875. A. N. Speca, L. L. Pytlewski and N. M. Karayannis, *J. Inorg. Nucl. Chem.*, 1974, **36,** 1227.
1876. P. G. Simpson, A. Vinciguerra and J. V. Quagliano, *Inorg. Chem.*, 1963, **2,** 282.
1877. I. Bertini, D. Gatteschi and L. J. Wilson, *Inorg. Chim. Acta,* 1970, **4,** 629.
1878. R. S. Drago, J. J. Donoghue and D. W. Herlocker, *Inorg. Chem.*, 1965, **4,** 836.
1879. M. K. Mohan, J. C. Khera, S. G. Mittal and A. K. Srivastava, *Gazz. Chim. Ital.*, 1978, **108,** 523.
1880. N. M. Karayannis, C. M. Paleos, C. M. Mikulski, L. L. Pytlewski, H. Blum and M. M. Labes, *Inorg. Chim. Acta*, 1973, **7,** 74.
1881. W. L. Reynolds, *Prog. Inorg. Chem.*, 1970, **12,** 1.
1882. H. L. Schlafer and H. Popitz, *Angew. Chem.*, 1960, **72,** 618.
1883. R. Paetzold and G. Bochmann, *Z. Anorg. Allg. Chem.*, 1969, **368,** 202.
1884. C. V. Berney and J. H. Weber, *Inorg. Chim. Acta,* 1971, **5,** 375.
1885. W. F. Currier and J. H. Weber, *Inorg. Chem.*, 1967, **6,** 1539; C. V. Berney and J. H. Weber, *Inorg. Chem.*, 1968, **7,** 283.
1886. D. Richardson and A. P. Zipp, *Inorg. Chim. Acta,* 1979, **33,** 131 and refs. therein.
1887. P. W. N. M. van Leeuven and W. L. Groeneveld, *Recl. Trav. Chim. Pays-Bas,* 1976, **86,** 1217.
1888. A. H. M. Fleur and W. L. Groeneveld, *Recl. Trav. Chim. Pays-Bas,* 1972, **91,** 317.
1889. J. Reedijk, A. H. M. Fleur and W. L. Groeneveld, *Recl. Trav. Chim. Pays-Bas,* 1969, **88,** 1115.
1890. A. H. M. Driessen-Fleur and W. L. Groeneveld, *Inorg. Chim. Acta,* 1973, **7,** 139.
1891. S. K. Madan, C. M. Hull and L. J. Herman, *Inorg. Chem.*, 1968, **7,** 491.
1892. G. V. Tsintsadze, *Russ. J. Inorg. Chem. (Engl. Transl.),* 1971, **16,** 614.
1893. G. Griffiths and D. A. Thornton, *J. Mol. Struct.*, 1979, **52,** 39.
1894. R. Maylar, J. B. Gill and D. C. Goodell, *J. Chem. Soc., Dalton Trans.*, 1973, 534.
1895. R. S. Drago, D. W. Meek, M. D. Joester and L. la Roche, *Inorg. Chem.*, 1963, **2,** 124.
1896. W. K. Cunningham, R. S. Stephens and R. O. Ragsdale, *J. Inorg. Nucl. Chem.*, 1969, **31,** 3379.
1897. M. E. Stone and K. E. Johnson, *Can. J. Chem.*, 1973, **51,** 1260.
1898. M. B. Welch, R. S. Stephens and R. O. Ragsdale, *Inorg. Chim. Acta,* 1968, **2,** 367.
1899. R. W. Gray, M. B. Welch and R. O. Ragsdale, *Inorg. Chim. Acta,* 1969, **3,** 17.
1900. J. H. Bright, R. S. Drago, D. M. Hart and S. K. Madan, *Inorg. Chem.*, 1965, **4,** 18.
1901. G. V. Tsintsadze, M. A. Porai-Koshits and A. S. Antsyshkina, *Zh. Strukt. Khim.*, 1967, **8,** 296.
1902. C. D. Rao and B. K. Mohapatra, *J. Inorg. Nucl. Chem.*, 1977, **39,** 689.
1903. M. E. Stone, B. E. Robertson and E. Stanley, *J. Chem. Soc. (A),* 1971, 3632.
1904. M. Wicholas and R. S. Drago, *J. Am. Chem. Soc.*, 1969, **91,** 5963; B. B. Wayland, R. S. Drago and H. F. Henneike, *J. Am. Chem. Soc.*, 1966, **88,** 2455.
1905. K. M. Nykerk, D. P. Eyman and R. L. Smith, *Inorg. Chem.*, 1967, **6,** 2262.
1906. A. W. McLellan and G. A. Melson, *J. Chem. Soc. (A),* 1967, 137.
1907. B. B. Kedzia, P. X. Armendarez and K. Nakamoto, *J. Inorg. Nucl. Chem.*, 1968, **30,** 849.
1908. C. S. Kraihanzel and S. C. Grenda, *Inorg. Chem.*, 1965, **4,** 1037.
1909. W. E. Bull and R. G. Ziegler, *Inorg. Chem.*, 1966, **5,** 689.
1910. B. Chatterjee, *Coord. Chem. Rev.*, 1978, **26,** 281.
1911. S. Mizukami and K. Nagaka, *Coord. Chem. Rev.*, 1968, **3,** 267.
1912. D. A. Brown, D. McKeith and W. K. Glass, *Inorg. Chim. Acta,* 1979, **35,** 5.
1913. D. A. Brown, A. L. Roche, T. A. Pakkanen, T. T. Pakkanen and K. Smolanderi, *J. Chem. Soc., Chem. Commun.*, 1982, 676.
1914. T. Sato, K. Nagata, M. Shiro and H. Koyama, *Chem. Commun.*, 1966, 192.
1915. T. Sato, K. Nagata, Y. Tsukuda, M. Shiro and H. Koyama, *Chem. Commun.*, 1967, 215.
1916. W. Wendlandt, S. Iftikhar and C. H. Stembridge, *Anal. Chim. Acta,* 1964, **31,** 501.
1917. R. S. Bottei and R. G. Schneggenburger, *J. Inorg. Nucl. Chem.*, 1970, **32,** 1525.
1918. J. P. Freeman and J. J. Gannon, *J. Org. Chem.*, 1969, **34,** 194.

1919. R. S. Bottei, B. Kubuck and D. A. Lusardi, *J. Inorg. Nucl. Chem.*, 1980, **42**, 493.
1920. S. E. Livingstone, *Q. Rev., Chem. Soc.*, 1965, **19**, 386.
1921. S. E. Livingstone, *Coord. Chem. Rev.*, 1971, **7**, 59.
1922. M. Cox and J. Darken, *Coord. Chem. Rev.*, 1971, **7**, 29.
1923. G. N. Schrauzer, *Transition Met. Chem.*, 1968, **4**, 299.
1924. T. N. Lockyer and R. L. Martin, *Prog. Inorg. Chem.*, 1980, **27**, 5.
1925. J. A. McCleverty, *Prog. Inorg. Chem.*, 1968, **10**, 49.
1926. D. Coucouvanis, *Prog. Inorg. Chem.*, 1970, **11**, 233.
1927. R. Eisenberg, *Prog. Inorg. Chem.*, 1970, **11**, 295.
1928. S. G. Murray and F. R Hartley, *Chem. Rev.*, 1981, **81**, 365.
1929. C. J. Pedersen and K. Frensdorff, *Angew. Chem., Int. Ed. Engl.*, 1972, **11**, 16.
1930. H. Vahrenkamp, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 322.
1931. J. P. Fackler, Jr., *Prog. Inorg. Chem.*, 1980, **27**, 55.
1932. L. F. Lindoy, *Coord. Chem. Rev.*, 1969, **4**, 41.
1933. C. G. Kuehn and S. S. Isied, *Prog. Inorg. Chem.*, 1980, **27**, 153.
1934. C. K. Jorgensen, *Inorg. Chim. Acta Rev.*, 1968, **2**, 65.
1935. M. Sato, F. Sato, N. Takemoto and K. Iida, *J. Organomet. Chem.*, 1972, **34**, 205.
1936. M. Schmidt, G. G. Hofmann and R. Hollar, *Inorg. Chim. Acta*, 1979, **32**, L19; M. Schmidt and G. G. Hofmann, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 598.
1937. F. Cecconi, C. A. Ghilardi and S. Midollini, *Inorg. Chem.*, 1983, **22**, 3802.
1938. C. A. Ghilardi, S. Midollini, A. Orlandini, C. Battistoni and G. Mattogno, *J. Chem. Soc., Dalton Trans.*, 1984, 939.
1939. H. Vahrenkamp and L. F. Dahl, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 144; H. Vahrenkamp, V. A. Hutchman and L. F. Dahl, *J. Am. Chem. Soc.*, 1968, **90**, 3272.
1940. A. Muller, E. Krickmeyer, H. Bogge, W. Clegg and G. M. Sheldrick, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 1006.
1941. D. Swenson, N. C. Baenzinger and D. Coucouvanis, *J. Am. Chem. Soc.*, 1978, **100**, 1932.
1942. D. G. Holah and D. Coucouvanis, *J. Am. Chem. Soc.*, 1975, **97**, 6917.
1943. A. R. Dias and M. L. H. Green, *J. Chem. Soc. (A)*, 1971, 1951.
1944. P. Woodward, L. F. Dahl, E. W. Abel and B. C. Crosse, *J. Am. Chem. Soc.*, 1965, **87**, 5251.
1945. E. W. Abel and B. C. Crosse, *J. Chem. Soc. (A)*, 1966, 1377.
1946. W. Gaete, J. Ros, X. Solans, M. Font-Altaba and J. L. Brianso, *Inorg. Chem.*, 1984, **23**, 39.
1947. K. Prout, S. R. Critchley and G. V. Rees, *Acta Crystallogr., Sect. B*, 1974, **30**, 2305.
1948. T. Yamamoto and Y. Sekine, *Inorg. Chim. Acta*, 1984, **83**, 47.
1949. R. G. Hayter and F. S. Humiec, *J. Inorg. Nucl. Chem.*, 1964, **26**, 807.
1950. K. Osakada, T. Yamamoto, A. Yamamoto, A. Takenaka and Y. Sasada, *Acta Crystallogr., Sect. C*, 1984, **40**, 85.
1951. T. B. Rauchfuss, J. S. Shu and D. M. Roundhill, *Inorg. Chem.*, 1976, **15**, 2096.
1952. D. M. Roundhill, *Inorg. Chem.*, 1980, **19**, 557.
1953. D. L. Leussing and G. S. Alberts, *J. Am. Chem. Soc.*, 1960, **82**, 4458.
1954. D. L. Leussing, *J. Am. Chem. Soc.*, 1959, **81**, 4208.
1955. T. B. Rauchfuss and D. M. Roundhill, *J. Am. Chem. Soc.*, 1975, **97**, 3386.
1956. D. J. Baker, D. C. Goodall and D. S. Moss, *Chem. Commun.*, 1969, 325; G. A. Barklay, E. M. McPartlin and N. C. Stephenson, *Acta Crystallogr., Sect. B*, 1969, **25**, 1269.
1957. W. P. Bosman and H. G. M. van der Linden, *J. Chem. Soc., Chem. Commun.*, 1977, 714.
1958. R. Backhouse, M. E. Foss and R. S. Nyholm, *J. Chem. Soc. (A)*, 1967, 1714.
1959. C. D. Flint and M. Goodgame, *J. Chem. Soc. (A)*, 1968, 2178.
1960. N. N. Greenwood and G. Hunter, *J. Chem. Soc. (A)*, 1969, 929.
1961. W. K. Musker and N. L. Hill, *Inorg. Chem.*, 1972, **11**, 710.
1962. N. L. Hill and H. Hope, *Inorg. Chem.*, 1974, **13**, 2079.
1963. W. Levason, C. A. McAuliffe and S. G. Murray, *Inorg. Chim. Acta*, 1976, **17**, 247.
1964. W. Levason, C. A. McAuliffe and S. G. Murray, *J. Chem. Soc., Dalton Trans.*, 1976, 269.
1965. W. Levason, C. A. McAuliffe and S. G. Murray, *J. Chem. Soc., Dalton Trans.*, 1975, 1566.
1966. W. Rosen and D. Busch, *Inorg. Chem.*, 1970, **9**, 262.
1967. P. H. Davis, L. K. White and R. L. Belford, *Inorg. Chem.*, 1975, **14**, 1753.
1968. M. O. Workmann, G. Dyer and D. W. Meek, *Inorg. Chem.*, 1967, **6**, 1543.
1969. D. W. Meek and J. A. Ibers, *Inorg. Chem.*, 1969, **8**, 1915.
1970. G. Dyer and D. W. Meek, *Inorg. Chem.*, 1965, **4**, 1398.
1971. L. P. Hangen and R. Eisenberg, *Inorg. Chem.*, 1969, **8**, 1072.
1972. N. Nonoyama, *Inorg. Chim. Acta*, 1975, **13**, 5.
1973. G. Fava Gasparri, M. Nardelli and A. Villa, *Acta Crystallogr., Sect. B*, 1967, **23**, 384.
1974. M. Bonamico, G. Dessy, C. Mariani, A. Vaciago and L. Zambonelli, *Acta Crystallogr., Sect. B*, 1965, **19**, 619.
1975. M. Bonamico and G. Dessy, *J. Chem. Soc. (A)*, 1971, 264.
1976. J. H. Noordik and J. M. M. Smits, *Cryst. Struct. Commun.*, 1974, **3**, 253.
1977. H. W. Chen and J. P. Fackler, Jr., *Inorg. Chem.*, 1978, **17**, 22.
1978. P. C. Christidis and P. J. Rentzeperis, *Acta Crystallogr., Sect. B*, 1978, **34**, 2141.
1979. M. Bonamico, G. Dessy, V. Fares and L. Scaramuzza, *J. Chem. Soc., Dalton Trans.*, 1975, 2250.
1980. M. Bonamico, G. Dessy and V. Fares, *J. Chem. Soc., Dalton Trans.*, 1977, 2315.
1981. J. F. McConnell and V. Kastalski, *Acta Crystallogr., Sect. B*, 1967, **22**, 853; Q. Fernando and C. D. Green, *J. Inorg. Nucl. Chem.*, 1967, **29**, 647.
1982. S. Ooi and Q. Fernando, *Inorg. Chem.*, 1967, **6**, 1558.
1983. P. S. Shetty and Q. Fernando, *Acta Crystallogr., Sect. B*, 1969, **25**, 1294.
1984. L. Gastaldi and P. Porta, *Cryst. Struct. Commun.*, 1977, **6**, 175.

1985. S. P. Bone, D. B. Sowerby, R. Costantinescu and I. Haiduc, *J. Chem. Res.* (*S*), 1979, 69; (*M*), 1979, 933.
1986. F. Seel and G. Zindler, *Chem. Ber.*, 1980, **113**, 1837.
1987. S. K. Arora, D. M. Hayes and Q. Fernando, *Acta Crystallogr., Sect. B*, 1978, **34**, 3355.
1988. D. Coucouvanis, F. J. Hollander and M. L. Caffrey, *Inorg. Chem.*, 1976, **15**, 1853.
1989. J. McKechnie, S. L. Hiesel and I. C. Paul, *Chem. Commun.*, 1967, 152.
1990. M. Delepine, *Bull. Soc. Chim. Fr.*, 1908, **3**, 643.
1991. D. Coucouvanis and J. P. Fackler, *Inorg. Chem.*, 1967, **6**, 2047.
1992. G. S. Whitby and G. L. Matheson, *Trans. R. Soc. Can.*, 1924, **18**, 111.
1993. H. J. Carell and S. Sudgen, *J. Chem. Soc.*, 1935, 621.
1994. L. Malatesta and A. A. Mella, *Gazz. Chim. Ital.*, 1937, **67**, 738.
1995. W. Regenass, S. Fallab and H. Erlenmeyer, *Helv. Chim. Acta*, 1955, **38**, 1448.
1996. F. A. Cotton and J. A. McCleverty, *Inorg. Chem.*, 1964, **3**, 1398.
1997. B. Lorenz, R. Kirmse and E. Hoyer, *Z. Anorg. Allg. Chem.*, 1970, **378**, 144.
1998. D. de Filippo, P. Deplano, F. Devillanova and F. Trogu, *Inorg. Chim. Acta*, 1976, **17**, 199.
1999. P. W. G. Newman and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1972, 1460.
2000. C. L. Raston and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1972, 1460.
2001. C. Peyronel and A. Pignedoli, *Acta Crystallogr., Sect. B*, 1967, **23**, 398; A. Pignedoli and G. Peyronel, *Acta Crystallogr., Sect. B*, 1968, **24**, 433.
2002. P. W. G. Newman and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1972, 2239.
2003. C. L. Raston and A. H. White, *Aust. J. Chem.*, 1976, **29**, 523.
2004. M. Martin, P. W. G. Newman, B. W. Robinson and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1972, 2233.
2005. F. G. Herring, J. M. Park, S. J. Rettig and J. Trotter, *Can. J. Chem.*, 1979, **57**, 2379.
2006. J. Lokaj, F. Pavelick, V. Kettmann, J. Masarik, V. Vrabel and J. Garaj, *Acta Crystallogr., Sect. B*, 1981, **37**, 926.
2007. P. W. G. Newman, C. L. Raston and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1973, 1332.
2008. B. J. McCormick, B. P. Stormer and R. I. Kaplan, *Inorg. Chem.*, 1969, **8**, 2522.
2009. C. Battistoni, G. Mattogno, A. Monaci and F. Tarli, *J. Inorg. Nucl. Chem.*, 1971, **33**, 3815.
2010. K. J. Cavell, R. J. Magel and J. O. Hill, *J. Inorg. Nucl. Chem.*, 1979, **41**, 1281, 1379.
2011. A. A. G. Tomlinson and C. Furlani, *Inorg. Chim. Acta*, 1969, **3**, 487.
2012. M. A. Attanassou and G. St. Nikolou, *Inorg. Chim. Acta*, 1983, **68**, 15.
2013. R. Dingle, *Inorg. Chem.*, 1971, **10**, 1141.
2014. R. M. Golding, P. C. Healy, P. W. G. Newman, E. Sinn and A. H. White, *Inorg. Chem.*, 1972, **11**, 2435.
2015. J. P. Fackler, Jr., I. J. B. Lui and J. Andrews, *Inorg. Chem.*, 1977, **16**, 451.
2016. L. Tosi and A. Garnier, *J. Chem. Soc., Dalton Trans.*, 1978, 53.
2017. J. Chatt, L. A. Duncanson and L. M. Venanzi, *Nature (London)*, 1956, **177**, 1042; K. Nakamoto, J. Fujita, R. A. Condrate and Y. Morimoto, *J. Chem. Phys.*, 1963, **39**, 423.
2018. G. Granozzi, A. Vittadini, L. Sindellari and D. Ajo', *Inorg. Chem.*, 1984, **23**, 702.
2019. K. J. Carell, J. O. Hill and R. J. Magee, *J. Chem. Soc., Dalton Trans.*, 1980, 763.
2020. A. R. Hendrickson, R. L. Martin and N. M. Rohde, *Inorg. Chem.*, 1975, **14**, 2980.
2021. J. G. M. van der Linden and H. A. Dix, *Inorg. Chim. Acta*, 1979, **35**, 65.
2022. J. V. Dubsky, *J. Prakt. Chem.*, 1916, **93**, 142.
2023. F. Drawert, K. H. Reuther and F. Born, *Chem. Ber.*, 1960, **93**, 3056.
2024. C. W. Watt and B. J. McCormick, *J. Inorg. Nucl. Chem.*, 1965, **27**, 898.
2025. J. P. Fackler, Jr. and D. Coucouvanis, *J. Am. Chem. Soc.*, 1967, **89**, 1745.
2026. A. H. Ewald and E. Sinn, *Aust. J. Chem.*, 1968, **21**, 927.
2027. G. Corazza-Pelizzi and C. Pelizzi, *Inorg. Chim. Acta*, 1970, **4**, 618.
2028. M. Franzini, *Z. Kristallogr.*, 1963, **118**, 393.
2029. C. Cauletti and E. Cervone, *J. Inorg. Nucl. Chem.*, 1973, **35**, 593.
2030. W. Dietzsch, J. Sieler and T. Gyowiak, *Z. Anorg. Allg. Chem.*, 1977, **436**, 225.
2031. G. A. Stergioudis, P. C. Christidis and P. J. Rentzeperis, *Acta Crystallogr., Sect. B*, 1979, **35**, 616.
2032. M. Cusumano, *Inorg. Chem.*, 1979, **18**, 3612.
2033. D. R. Dakternieks and D. P. Graddon, *Aust. J. Chem.*, 1971, **24**, 2509.
2034. C. Furlani and M. L. Luciani, *Inorg. Chem.*, 1968, **7**, 1586.
2035. M. Bonamico, G. Dessy, V. Fares and L. Scaramuzza, *Cryst. Struct. Commun.*, 1973, **2**, 201.
2036. M. Bonamico, G. Dessy, V. Fares, A. Flamini and L. Scaramuzza, *J. Chem. Soc., Dalton Trans.*, 1976, 1743.
2037. B. Longato, F. Morandini and S. Bresadola, *Inorg. Chim. Acta*, 1978, **26**, 157.
2038. M. Bonamico, G. Dessy, V. Fares and L. Scaramuzza, *J. Chem. Soc., Dalton Trans.*, 1975, 2594.
2039. L. Malatesta and S. Pizzotti, *Chim. Ind. (Milan)*, 1945, **27**, 6.
2040. S. E. Livingstone and A. E. Mihkelson, *Inorg. Chem.*, 1970, **9**, 2545.
2041. C. P. Bhasin, G. Srivastava and R. C. Mehrotra, *Inorg. Chim. Acta*, 1983, **77**, L131.
2042. R. Micu-Semeniuc, L. Dumitrescu-Silaghi and I. Haiduc, *Inorg. Chim. Acta*, 1979, **33**, 281.
2043. J. R. Wasson, G. M. Woltermann and A. J. Stoklosa, *Top. Curr. Chem.*, 1973, **35**, 65.
2044. J. R. Angus, G. M. Woltermann, W. R. Vincent and J. R. Wasson, *J. Inorg. Nucl. Chem.*, 1971, **33**, 3041.
2045. V. Kastalski and J. F. McConnell, *Acta Crystallogr., Sect. B*, 1969, **25**, 909.
2046. W. Poll and H. Wunderlich, *Acta Crystallogr., Sect. B*, 1980, **36**, 1191.
2047. P. J. H. A. M. van der Leenput, T. W. Hummelink, J. H. Noodik and P. T. Beursekens, *Cryst. Struct. Commun.*, 1975, **4**, 167.
2048. W. Rudzinski, G. T. Behnke and Q. Fernando, *Inorg. Chem.*, 1977, **16**, 1206.
2049. J. R. Angus, G. M. Woltermann and J. R. Wasson, *J. Inorg. Nucl. Chem.*, 1971, **33**, 3937.
2050. H. E. Francis, G. L. Tincher, W. F. Wagner, J. R. Wasson and G. M. Woltermann, *Inorg. Chem.*, 1971, **16**, 2620.
2051. R. Costantinescu, F. Martinus and I. Haiduc, *Inorg. Chim. Acta*, 1976, **19**, 105.
2052. S. K. Arora, D. E. Carter, Q. Fernando and K. Seff, *Acta Crystallogr., Sect. B*, 1977, **33**, 3230.

2053. D. C. Craig, E. T. Pallister and N. C. Stephenson, *Acta Crystallogr., Sect. B*, 1971, **27,** 1163.
2054. D. B. Sowerby and I. Haiduc, *Inorg. Chim. Acta*, 1976, **17,** L15.
2055. P. S. Shetty, R. E. Ballard and Q. Fernando, *Chem. Commun.*, 1969, 717.
2056. M. J. Haynes and P. F. Brannick, *J. Chem. Soc., Chem. Commun.*, 1977, 942.
2057. A. A. G. Tomlinson and C. Furlani, *J. Chem. Soc., Dalton Trans.*, 1974, 1420.
2058. L. F. Black and D. P. Graddon, *Inorg. Chim. Acta*, 1978, **30,** L327.
2059. N. Yoon, M. J. Incorvia and J. I. Zink, *J. Chem. Soc., Chem. Commun.*, 1972, 499.
2060. L. Gastaldi, P. Porta and A. A. G. Tomlinson, *J. Chem. Soc., Dalton Trans.*, 1974, 1424.
2061. W. Kuchen, J. Metten and A. Jadat, *Chem. Ber.*, 1964, **97,** 2306.
2062. R. G. Cavell, W. Byers, E. D. Day and P. M. Watkins, *Inorg. Chem.*, 1972, **11,** 1598.
2063. K. Diemert and K. Kuchen, *Phosphorus Sulfur*, 1977, **3,** 131.
2064. K. Kuchen, M. Forster, H. Hertel and B. Hohn, *Chem. Ber.*, 1972, **105,** 3310.
2065. M. Forster, H. Hertel and W. Kuchen, *Angew. Chem., Int. Ed. Engl.*, 1970, **9,** 811.
2066. A. Muller, P. Christophliemk and V. V. K. Rao, *Chem. Ber.*, 1971, **104,** 1905.
2067. P. E. Jones, G. B. Ansell and L. Katz, *Acta Crystallogr., Sect. B*, 1969, **25,** 1939.
2068. H. Wunderlich, *Acta Crystallogr., Sect. B*, 1980, **36,** 717.
2069. H. Wunderlich and H. G. Wussow, *Acta Crystallogr., Sect. B*, 1979, **35,** 750.
2070. P. S. Shetty and Q. Fernando, *J. Am. Chem. Soc.*, 1970, **92,** 3964.
2071. P. Porta, A. Sgamellotti and N. Vinciguerra, *Inorg. Chem.*, 1971, **10,** 541.
2072. W. Rudzinski, M. Shiro and Q. Fernando, *Anal. Chem.*, 1975, **47,** 1194.
2073. D. A. Vu Thi, D. P. Graddon and V. A. K. Ng, *Aust. J. Chem.*, 1978, **31,** 2417.
2074. K. Diemert, P. Haas and W. Kuchen, *Z. Anorg. Allg. Chem.*, 1981, **480,** 65.
2075. B. G. Werden, E. Billig and H. B. Gray, *Inorg. Chem.*, 1966, **5,** 78.
2076. J. P. Fackler, Jr. and D. Coucouvanis, *J. Am. Chem. Soc.*, 1966, **88,** 3913.
2077. D. Coucouvanis and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, 1967, **89,** 1346.
2078. D. Coucouvanis, N. C. Baenziger and S. M. Johnson, *Inorg. Chem.*, 1974, **13,** 1191.
2079. R. D. Bereman and D. Nalewajek, *Inorg. Chem.*, 1976, **15,** 2981.
2080. W. von Dietzsch, J. Kaiser, R. Richter, L. Golic, J. Siftar and R. Heber, *Z. Anorg. Allg. Chem.*, 1981, **477,** 71.
2081. F. A. Cotton and C. B. Harris, *Inorg. Chem.*, 1968, **7,** 2141.
2082. J. M. Burke and J. P. Facker, *Inorg. Chem.*, 1972, **11,** 2744.
2083. A. Muller and E. Diemann, *Chem. Commun.*, 1971, 65.
2084. A. Muller, N. H. Heisen and G. Vandrish, *Inorg. Chem.*, 1974, **13,** 1001.
2085. I. Sotofte, *Acta Chem. Scand., Ser. A*, 1976, **30,** 157.
2086. K. P. Callahan and E. J. Cichon, *Inorg. Chem.*, 1981, **20,** 1941.
2087. E. Koniger-Ahlborn, A. Muller, A. D. Cormier, J. D. Brown and K. Nakamoto, *Inorg. Chem.*, 1975, **14,** 2009.
2088. C. W. Schlapfer and V. Nakamoto, *Inorg. Chem.*, 1975, **14,** 1338.
2089. W. Hieber and R. Bruck, *Z. Anorg. Allg. Chem.*, 1952, **269,** 13.
2090. J. P. Fackler, Jr., D. Coucouvanis, J. A. Fetchin and W. C. Seidel, *J. Am. Chem. Soc.*, 1968, **90,** 2784.
2091. A. Flamini, C. Furlani and O. Piovesana, *J. Inorg. Nucl. Chem.*, 1971, **33,** 1841.
2092. C. Furlani, A. Flamini, A. Sgamellotti, C. Bellitto and O. Piovesana, *J. Chem. Soc., Dalton Trans.*, 1973, 2404.
2093. M. Bonamico, G. Dessy, V. Fares and L. Scaramuzza, *J. Chem. Soc.*, (*A*), 1971, 3191.
2094. J. P. Fackler, Jr., J. A. Fetchin and D. C. Fries, *J. Am. Chem. Soc.*, 1972, **94,** 7323.
2095. J. D. Woollins, R. Grinter, M. K. Johnson and A. J. Thomson, *J. Chem. Soc., Dalton Trans.*, 1980, 1910.
2096. J. Bojes, T. Chivers, W. G. Laidlaw and M. Trsic, *J. Am. Chem. Soc.*, 1982, **104,** 4837.
2097. P. B. Blandon, R. Bruce and G. R. Knox, *Chem. Commun.*, 1965, 557.
2098. A. C. Villa, A. G. Manfredotti, M. Nardelli and C. Pelizzi, *Chem. Commun.*, 1970, 1322.
2099. J. M. Andrews, D. Coucouvanis and J. P. Fackler, Jr., *Inorg. Chem.*, 1972, **11,** 493.
2100. F. Sato, K. Ida and M. Sato, *J. Organomet. Chem.*, 1972, **39,** 197.
2101. C. Tsipis, G. E. Manoussakis, D. P. Kessissoglou, J. C. Huffman, L. N. Lewis, M. A. Adams and K. G. Caulton, *Inorg. Chem.*, 1980, **19,** 1458.
2102. F. Sato and M. Sato, *J. Organomet. Chem.*, 1972, **46,** C63.
2103. C. Bianchini, C. Mealli, A. Meli and G. Scapacci, *Organometallics*, 1983, **2,** 141.
2104. C. Bianchini and A. Meli, *J. Chem. Soc., Dalton Trans.*, 1983, 2419.
2105. C. Bianchini, C. Mealli, A. Meli and G. Scapacci, *J. Chem. Soc., Dalton Trans.*, 1982, 799.
2106. C. Bianchini, P. Innocenti and A. Meli, *J. Chem. Soc., Dalton Trans.*, 1983, 1777.
2107. C. Bianchini and A. Meli, *J. Organomet. Chem.*, 1982, **236,** C75.
2108. H. B. Gray, *Transition Met. Chem.*, 1965, **1,** 240.
2109. G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, 1965, **87,** 1483.
2110. A. Davison, N. Edelstein, R. H. Holm and A. H. Maki, *Inorg. Chem.*, 1963, **2,** 1227.
2111. A. Davison, D. V. Howe and E. T. Shawl, *Inorg. Chem.*, 1967, **6,** 458.
2112. E. Billig, R. Williams, I. Bernal, J. H. Waters and H. B. Gray, *Inorg. Chem.*, 1964, **3,** 663.
2113. G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, 1965, **87,** 3585.
2114. M. J. Baker-Hawkes, E. Billig and H. B. Gray, *J. Am. Chem. Soc.*, 1966, **88,** 4870.
2115. A. Davison, J. A. McCleverty, E. T. Shawl and E. J. Wharton, *J. Am. Chem. Soc.*, 1967, **89,** 830.
2116. A. Davison, N. Edelstein, R. H. Holm and A. H. Maki, *Inorg. Chem.*, 1964, **3,** 814.
2117. D. Sartain and M. R. Truter, *J. Chem. Soc. (A)*, 1967, 1264.
2118. R. D. Schmitt, R. M. Wing and A. H. Maki, *J. Am. Chem. Soc.*, 1969, **91,** 4394.
2119. R. M. Wing and R. L. Schlupp, *Inorg. Chem.*, 1970, **9,** 471.
2120. A. Singhabhandhu, P. D. Robinson, J. H. Fang and W. E. Geiger, Jr., *Inorg. Chem.*, 1975, **14,** 318.
2121. R. Eisenberg and J. A. Ibers, *Chem. Commun.*, 1965, 605.
2122. A. Kobayashi and Y. Sasaki, *Bull. Chem. Soc. Jpn.*, 1977, **50,** 2650.
2123. C. J. Fritchie, Jr., *Acta Crystallogr., Sect. B*, 1966, **20,** 107.
2124. I. G. Dance, P. J. Solstad and J. C. Calabrese, *Inorg. Chem.*, 1973, **12,** 2161.

2125. H. Endres, H. J. Keller, W. Moroni and D. Nothe, *Acta Crystallogr., Sect. B,* 1979, **35,** 353.
2126. M. J. Hove, B. M. Hoffman and J. A. Ibers, *J. Chem. Phys.,* 1972, **56,** 3490.
2127. Z. S. Herman, R. F. Kirchner, G. H. Loew, U. T. Mueller-Westerhoff, A. Nazzal and M. C. Zerner, *Inorg. Chem.,* 1982, **21,** 46.
2128. G. A. Bowmaker, P. D. W. Boyd and G. K. Campbell, *Inorg. Chem.,* 1983, **22,** 1208.
2129. G. A. Bowmaker, P. D. W. Boyd and G. K. Campbell, *J. Chem. Soc., Dalton Trans.,* 1983, 1019.
2130. W. E. Geiger, Jr., C. S. Allen, T. E. Mines and F. C. Senftleber, *Inorg. Chem.,* 1977, **16,** 2003.
2131. A. Vogler and H. Kunkely, *Inorg. Chem.,* 1982, **21,** 1172.
2132. L. V. Interrante, K. W. Browall, H. R. Hart, Jr., I. S. Jacobs, G. D. Watkins and S. H. Wee, *J. Am. Chem. Soc.,* 1975, **97,** 889.
2133. J. S. Kasper, L. V. Interrante and C. A. Secaur, *J. Am. Chem. Soc.,* 1975, **97,** 890.
2134. F. Wudl, C. H. Ho and A. Nagel, *J. Chem. Soc., Chem. Commun.,* 1973, 923.
2135. M. M. Ahmad and A. E. Underhill, *J. Chem. Soc., Dalton Trans.,* 1983, 165.
2136. D. R. Rosseinsky and R. E. Malpas, *J. Chem. Soc., Dalton Trans.,* 1979, 749.
2137. G. N. Schrauzer and H. N. Rabinowitz, *J. Am. Chem. Soc.,* 1968, **90,** 4297.
2138. P. Eckstein, R. Heber, J. Reinhold and E. Hoyer, *Z. Anorg. Allg. Chem.,* 1978, **440,** 253.
2139. A. Vlcek, Jr., *Inorg. Chim. Acta,* 1980, **43,** 35.
2140. R. M. Wing, G. C. Tustin and W. H. Okamura, *J. Am. Chem. Soc.,* 1970, **92,** 1935.
2141. A. Herman and R. M. Wing, *J. Am. Chem. Soc.,* 1973, **63,** 441.
2142. G. P. Khare, A. J. Schultz and R. Eisenberg, *J. Am. Chem. Soc.,* 1971, **93,** 3597.
2143. T. Herskovitz, C. E. Forbes and R. H. Holm, *Inorg. Chem.,* 1972, **11,** 1318.
2144. E. G. Cox, W. Wardlaw and K. C. Webster, *J. Chem. Soc.,* 1935, 1475.
2145. A. Gleizes, F. Clery, M. F. Bruniquel and P. Cassoux, *Inorg. Chim. Acta,* 1979, **37,** 19.
2146. D. Coucouvanis, N. C. Baezinger and S. M. Johnson, *J. Am. Chem. Soc.,* 1973, **95,** 3875.
2147. R. S. Czernuszewicz, K. Nakamoto and D. P. Strommen, *J. Am. Chem. Soc.,* 1982, **104,** 1515.
2148. A. R. Latham, V. C. Hascall and H. B. Gray, *Inorg. Chem.,* 1965, **4,** 788.
2149. G. A. Bowmaker, P. D. W. Boyd and G. K. Campbell, *Inorg. Chem.,* 1982, **21,** 3565.
2150. A. Gleizes and M. Verdaguer, *J. Am. Chem. Soc.,* 1981, **103,** 7373.
2151. D. Coucouvanis, D. G. Holah and F. J. Hollander, *Inorg. Chem.,* 1975, **14,** 2657.
2152. F. Gotzfried, W. Beck, A. Lerf and E. Sebald, *Angew. Chem., Int. Ed. Engl.,* 1979, **18,** 463.
2153. H. D. Smith, Jr., M. A. Robinson and S. Papetti, *Inorg. Chem.,* 1967, **6,** 1014.
2154. A. Pignedoli and G. Peyronel, *Acta Crystallogr., Sect. B,* 1977, **33,** 1439.
2155. A. Pignedoli, G. Peyronel and L. Antolini, *Acta Crystallogr., Sect. B,* 1974, **30,** 2181.
2156. R. L. Martin and I. M. Stewart, *Nature (London),* 1966, **210,** 622.
2157. G. A. Heath, R. L. Martin and I. M. Stewart, *Inorg. Nucl. Chem. Lett.,* 1969, **5,** 169.
2158. R. Beckett and B. F. Hoskins, *J. Chem. Soc., Dalton Trans.,* 1974, 622.
2159. A. Ouchi, N. Nakatani and Y. Takahashi, *Bull. Chem. Soc. Jpn.,* 1968, **41,** 2044.
2160. C. Blejean, *Inorg. Nucl. Chem., Lett.,* 1971, **7,** 1011.
2161. A. M. Bond, G. A. Heath and R. L. Martin, *Inorg. Chem.,* 1971, **10,** 2026.
2162. W. L. Bowden, J. D. L. Holloway and W. E. Geiger, Jr., *Inorg. Chem.,* 1978, **17,** 256.
2163. A. Furihashi, K. Watanuki and A. Ouchi, *Bull. Chem. Soc. Jpn.,* 1969, **42,** 260.
2164. G. A. Heath, R. L. Martin and I. M. Stewart, *Aust. J. Chem.,* 1969, **22,** 83.
2165. J. P. Fackler, Jr. and A. F. Masters, *Inorg. Chim. Acta,* 1980, **39,** 111.
2166. G. H. H. Chaston, S. E. Livingstone, T. N. Lockyer, V. A. Pickles and J. S. Shannon, *Aust. J. Chem.,* 1965, **18,** 673.
2167. R. K. Y. Ho and S. E. Livingstone, *Aust. J. Chem.,* 1968, **21,** 1781.
2168. O. Siiman, D. D. Titus, C. D. Cowman, J. Fresco and H. B. Gray, *J. Am. Chem. Soc.,* 1974, **96,** 2353.
2169. A. Ouchi, M. Hyodo and Y. Takahashi, *Bull. Chem. Soc. Jpn.,* 1967, **40,** 2819.
2170. C. G. Barraclough, R. L. Martin and I. M. Stewart, *Aust. J. Chem.,* 1969, **22,** 891.
2171. O. Siiman, *Inorg. Chem.,* 1980, **19,** 2889.
2172. O. Siiman and J. Fresco, *Inorg. Chem.,* 1969, **8,** 1846.
2173. R. K. Y. Ho and S. E. Livingstone, *Aust. J. Chem.,* 1968, **21,** 1781.
2174. S. H. H. Chaston, S. E. Livingstone and T. N. Lockyer, *Aust. J. Chem.,* 1966, **19,** 1401.
2175. R. L. Martin and A. F. Masters, *Inorg. Chem.,* 1975, **14,** 885.
2176. H. Luth, E. A. Hall, W. A. Spofford and E. L. Amma, *Chem. Commun.,* 1969, 520.
2177. A. Pignedoli, G. Peyronel and L. Antolini, *Acta Crystallogr., Sect. B,* 1973, **29,** 1490.
2178. T. Uechi, I. Ueda, N. Matsumoto and S. Kida, *Inorg. Chim. Acta,* 1979, **33,** 87.
2179. I. Ojima, T. Onishi, T. Iwamoto, N. Inamoto and K. Tamaru, *Bull. Chem. Soc. Jpn.,* 1971, **44,** 2156.
2180. A. Schmidpeter and H. Groeger, *Chem. Ber.,* 1967, **100,** 3216.
2181. T. Iwamoto, F. Ebina, H. Nakazawa and C. Nakatsuka, *Bull. Chem. Soc. Jpn.,* 1979, **52,** 185.
2182. J. Bodeker, *Z. Chem.,* 1971, **11,** 463.
2183. A. Ziegler, V. P. Botha and I. Haiduc, *Inorg. Chim. Acta,* 1975, **15,** 123.
2184. M. R. Churchill, J. Cooke, J. P. Fennessey and J. Wormald, *Inorg. Chem.,* 1971, **10,** 1031.
2185. M. S. Weiningen and E. L. Amma, *J. Coord. Chem.,* 1976, **5,** 91.
2186. S. L. Holt, R. J. Bouchard and R. L. Carlin, *J. Am. Chem. Soc.,* 1964, **86,** 519.
2187. E. C. Devore and S. L. Holt, *J. Inorg. Nucl. Chem.,* 1972, **34,** 2303.
2188. S. L. Holt, Jr. and R. L. Carlin, *J. Am. Chem. Soc.,* 1964, **86,** 3017.
2189. M. E. O'Neill, E. S. Raper, I. W. Nowell and J. A. Daniels, *Inorg. Chim. Acta,* 1981, **54,** L243.
2190. R. E. Oughtred, E. S. Raper and I. W. Nowell, *Inorg. Chim. Acta,* 1984, **84,** L5.
2191. M. E. O'Neill, E. S. Raper and J. A. Daniels, *Inorg. Chim. Acta,* 1980, **41,** 145; 1980, **41,** 201; 1981, **54,** L25.
2192. W. A. Spoffard, P. Boldrini and E. L. Amma, *Inorg. Chim. Acta,* 1971, **5,** 70.
2193. T. Tarantelli, P. Riccieri and C. Furlani, *J. Inorg. Nucl. Chem.,* 1969, **31,** 3585.

2194. A. Mangia and G. Pelizzi, *Cryst. Struct. Commun.*, 1973, **2,** 77.
2195. R. W. Olliff, *J. Chem. Soc.*, 1965, 2036.
2196. C. D. Flint and M. Goodgame, *J. Chem. Soc. (A)*, 1966, 744; 1967, 1718.
2197. M. S. Weininger, J. E. O'Connor and E. L. Amma, *Inorg. Chem.*, 1969, **8,** 424.
2198. C. Furlani, T. Tarantelli and P. Riccieri, *J. Inorg. Nucl. Chem.*, 1971, **33,** 1389.
2199. G. Yagudsky and R. Levitus, *Inorg. Chem.*, 1965, **4,** 1589.
2200. G. A. Bentley and J. N. Waters, *J. Inorg. Nucl. Chem.*, 1974, **36,** 2247.
2201. G. Fava Gasparri, A. Mangia, A. Musatti and M. Nardelli, *Acta Crystallogr., Sect. B*, 1969, **25,** 203.
2202. A. Lopez-Castro and M. R. Truter, *J. Chem. Soc.*, 1963, 1309.
2203. L. M. Amzel, S. Baggio and L. N. Becka, *J. Chem. Soc. (A)*, 1969, 2066.
2204. W. T. Robinson, S. L. Holt, Jr. and G. B. Carpenter, *Inorg. Chem.*, 1967, **6,** 605.
2205. H. Luth and M. R. Truter, *J. Chem. Soc. (A)*, 1968, 1879.
2206. R. L. Girling, J. E. O'Connor and E. L. Amma, *Acta Crystallogr., Sect. B*, 1972, **28,** 2640.
2207. M. Nardelli, G. Fava Gasparri, G. Giraldi Battistini and P. Domiano, *Acta Crystallogr.*, 1966, **20,** 349.
2208. C. Puglisi and R. Levitus, *J. Inorg. Nucl. Chem.*, 1967, **29,** 1069.
2209. M. Nardelli, G. Fava Gasparri, A. Musatti and A. Manfredotti, *Acta Crystallogr.*, 1966, **21,** 910.
2210. L. Capacchi, G. Fava Gasparri, M. Nardelli and G. Pelizzi, *Acta Crystallogr., Sect. B*, 1968, **24,** 1199.
2211. P. Rechberger and G. Gritzner, *Inorg. Chim. Acta*, 1978, **31,** 125.
2212. I. P. Evans and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1974, 946.
2213. T. Tarantelli, *J. Chem. Soc., Dalton Trans.*, 1974, 837.
2214. T. Tarantelli and B. Chiari, *J. Chem. Soc., Dalton Trans.*, 1975, 286.
2215. A. M. Brodie, J. E. Douglas and C. J. Wilkins, *J. Chem. Soc., Dalton Trans.*, 1969, 1931.
2216. W. E. Slinkard and D. W. Meek, *Inorg. Chem.*, 1969, **8,** 1811.
2217. F. Mani and A. Scozzafava, *Gazz. Chim. Ital.*, 1972, **102,** 1109.
2218. W. E. Slinkard and D. W. Meek, *J. Chem. Soc., Dalton Trans.*, 1973, 1024.
2219. F. Kober and P. Bachi, *Z. Anorg. Allg. Chem.*, 1981, **477,** 139.
2220. J. R. Miller, *Adv. Inorg. Chem. Radiochem.*, 1962, **4,** 133.
2221. M. Bizette, *C. R. Hebd. Seances Acad. Sci.*, 1956, **243,** 1295.
2222. N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 1959, 3997.
2223. F. A. Cotton, O. D. Faut and D. M. L. Goodgame, *J. Am. Chem. Soc.*, 1961, **83,** 344.
2224. D. M. L. Goodgame, M. Goodgame and F. A. Cotton, *J. Am. Chem. Soc.*, 1961, **83,** 4161.
2225. F. A. Cotton and R. Francis, *J. Am. Chem. Soc.*, 1960, **82,** 2986.
2226. A. Furuhashi, K. Watanuki and A. Ouchi, *Bull. Chem. Soc. Jpn.*, 1969, **42,** 260.
2227. G. Brun and G. Jourdan, *C. R. Hebd. Seances Acad. Sci., Ser. C*, 1974, **279,** 129.
2228. G. Brun, *C. R. Hebd. Seances Acad. Sci., Ser. C*, 1974, **279,** 105.
2229. W. Rudorff, J. Kandler and D. Babel, *Z. Anorg. Allg. Chem.*, 1962, **317,** 261.
2230. J. F. Weidenborne and A. L. Bednowitz, *Acta Crystallogr., Sect. B*, 1970, **26,** 1464.
2231. D. M. L. Goodgame, M. Goodgame and M. J. Weeks, *J. Chem. Soc.*, 1964, 5194.
2232. G. Stucky, S. D'Agostino and G. McPherson, *J. Am. Chem. Soc.*, 1966, **88,** 4828.
2233. D. M. L. Goodgame and M. Goodgame, *Inorg. Chem.*, 1965, **4,** 139.
2234. G. N. La Mar, R. H. Fisher and W. D. Horrocks, Jr., *Inorg. Chem.*, 1967, **6,** 1798.
2235. J. R. Weisner, R. C. Srivastava, C. H. L. Kennard, M. di Vaira and E. C. Lingafelter, *Acta Crystallogr.*, 1967, **23,** 565.
2236. P. Pauling, *Inorg. Chem.*, 1966, **5,** 1498.
2237. H. G. Schrering, *Z. Anorg. Allg. Chem.*, 1967, **353,** 1, 13.
2238. R. P. Taylor, D. H. Templeton, A. Zalkin and W. D. Horrocks, Jr., *Inorg. Chem.*, 1968, **7,** 2629.
2239. W. D. Horrocks, Jr., D. H. Templeton and A. Zalkin, *Inorg. Chem.*, 1968, **7,** 2303.
2240. A. Sabatini and L. Sacconi, *J. Am. Chem. Soc.*, 1964, **86,** 17.
2241. J. H. Clark and T. M. Dunn, *J. Chem. Soc.*, 1963, 1198.
2242. G. L. McPherson, J. E. Wall, Jr. and A. M. Hermann, *Inorg. Chem.*, 1974, **13,** 2230.
2243. C. A. Angell and D. M. Gruen, *J. Am. Chem. Soc.*, 1966, **88,** 5192.
2244. D. H. Brown, K. P. Forrest, R. H. Nuttal and D. W. A. Sharp, *J. Chem. Soc. (A)*, 1968, 2146.
2245. I. Bertini, D. Gatteschi and F. Mani, *Inorg. Chem.*, 1972, **11,** 2464.
2246. R. H. Holm, G. W. Everett and A. Chakravorty, *Prog. Inorg. Chem.*, 1966, **7,** 83.
2247. L. Sacconi, *Coord. Chem. Rev.*, 1966, **1,** 126, 192.
2248. S. Yamada, *Coord. Chem. Rev.*, 1966, **1,** 415.
2249. L. Sacconi, *Transition Met. Chem.*, 1968, **4,** 199.
2250. S. Yamada, E. Ohono, Y. Kuge, A. Takeuchi, K. Yamanouchi and K. Iwasaki, *Coord. Chem. Rev.*, 1968, **3,** 247.
2251. M. D. Hobday and T. D. Smith, *Coord. Chem. Rev.*, 1972, **9,** 311.
2252. R. H. Holm and M. J. O'Connor, *Prog. Inorg. Chem.*, 1971, **14,** 241.
2253. R. H. Holm and K. Swaminathan, *Inorg. Chem.*, 1962, **1,** 599.
2254. L. Sacconi and M. Ciampolini, *J. Am. Chem. Soc.*, 1963, **85,** 1750.
2255. L. Sacconi, P. Paoletti and M. Ciamploini, *J. Am. Chem. Soc.*, 1963, **85,** 411.
2256. L. Sacconi, P. Paoletti and G. Del Re, *J. Am. Chem. Soc.*, 1957, **79,** 4062.
2257. R. H. Holm and K. Swaminathan, *Inorg. Chem.*, 1963, **2,** 181.
2258. L. Sacconi, M. Ciampolini and U. Campligli, *Inorg. Chem.*, 1965, **4,** 407.
2259. E. Frasson, C. Panattoni and L. Sacconi, *J. Phys. Chem.*, 1959, **63,** 1908.
2260. M. R. Fox and E. C. Lingafelter, *Acta Crystallogr.*, 1967, **22,** 943.
2261. W. Steurer and W. Adlhart, *Acta Crystallogr., Sect. B*, 1983, **39,** 344.
2262. S. C. Bhatia, J. M. Bindlish, A. R. Saini and P. C. Jain, *J. Chem. Soc., Dalton Trans.*, 1981, 1773.
2263. S. C. Bhatia, V. K. Syal, R. P. Kashyap, P. C. Jain and C. J. Brown, *Acta Crystallogr., Sect. C*, 1983, **39,** 199.
2264. R. Grazziani and E. Forselli, *Inorg. Nucl. Chem. Lett.*, 1972, **8,** 775.

2265. M. R. Fox, P. L. Orioli, E. C. Lingafelter and L. Sacconi, *Acta Crystallogr.*, 1964, **17**, 1159.
2266. T. Ashida, S. Iwata, T. Yamane, M. Kakudo, A. Takeuchi and S. Yamada, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 3502.
2267. S. Yamada, K. Iwasaki and A. Takeuchi, *Inorg. Chim. Acta*, 1968, **2**, 395.
2268. S. Yamada, H. Tanaka and K. Yamanouchi, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 1464.
2269. R. J. Butcher, J. W. Overman and E. Sinn, *J. Am. Chem. Soc.*, 1980, **102**, 3276.
2270. E. D. McKenzie and F. S. Stephens, *Inorg. Chim. Acta*, 1978, **26**, 249.
2271. I. Bertini, L. Sacconi and G. P. Speroni, *Inorg. Chem.*, 1972, **11**, 1323.
2272. L. El-Sayed, M. F. Iskander, A. El-Tankhy and S. E. Zayan, *Inorg. Chim. Acta*, 1972, **6**, 663.
2273. L. S. Minkina, V. P. Kurbatov, O. A. Osipov, V. I. Minkin and L. E. Nivorozhkin, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1971, **16**, 571.
2274. H. R. Engeseth, D. R. McMillin and E. L. Ulrich, *Inorg. Chim. Acta*, 1982, **67**, 145.
2275. L. Sacconi, P. Nannelli and U. Campigli, *Inorg. Chem.*, 1965, **4**, 818.
2276. L. Sacconi, P. Nannelli, N. Nardi and U. Campigli, *Inorg. Chem.*, 1965, **4**, 943.
2277. P. L. Orioli, M. di Vaira and L. Sacconi, *J. Am. Chem. Soc.*, 1966, **88**, 4383.
2278. D. A. Cruse and M. Gerloch, *J. Chem. Soc., Dalton Trans.*, 1977, 1613.
2279. L. Sacconi, P. L. Orioli and M. di Vaira, *Chem. Commun.*, 1967, 849.
2280. L. Sacconi, N. Nardi and F. Zanobini, *Inorg. Chem.*, 1966, **5**, 1872.
2281. C. H. Harris, S. L. Lenzer and R. L. Martin, *Aust. J. Chem.*, 1961, **14**, 420.
2282. M. di Vaira and P. L. Orioli, *Inorg. Chem.*, 1967, **5**, 490.
2283. L. Sacconi and I. Bertini, *Inorg. Chem.*, 1968, **7**, 1178.
2284. P. L. Orioli and M. di Vaira, *J. Chem. Soc. (A)*, 1968, 2079.
2285. L. Sacconi and G. P. Speroni, *Inorg. Chem.*, 1968, **7**, 295.
2286. L. Sacconi, I. Bertini and R. Morassi, *Inorg. Chem.*, 1967, **6**, 1548.
2287. E. Uhlig and B. Machelett, *Z. Chem.*, 1969, **9**, 155.
2288. R. K. Mehta and V. G. Singhi, *Z. Naturforsch., Teil B*, 1972, **27**, 304.
2289. L. Sacconi, G. P. Speroni and R. Morassi, *Inorg. Chem.*, 1968, **7**, 1521.
2290. E. Uhlig and B. Machelett, *Z. Anorg. Allg. Chem.*, 1974, **409**, 320.
2291. B. Chiswell and K. W. Lee, *Aust. J. Chem.*, 1969, **22**, 2315.
2292. B. Chiswell and K. W. Lee, *Inorg. Chim. Acta*, 1973, **7**, 49.
2293. B. Chiswell and K. W. Lee, *Inorg. Chim. Acta*, 1972, **6**, 583.
2294. C. A. Root, B. A. Rising, M. C. van der Veer and C. F. Hellmuth, *Inorg. Chem.*, 1972, **11**, 1489.
2295. W. W. Fee, J. D. Pulsford and P. D. Vowles, *Aust. J. Chem.*, 1973, **26**, 675.
2296. Von E. Uhlemann and V. Pohl, *Z. Anorg. Allg. Chem.*, 1973, **397**, 162.
2297. S. E. Livingstone and J. D. Nolan, *Aust. J. Chem.*, 1969, **22**, 1817.
2298. A. V. Ablou and N. V. Gerbelev, *Russ. J. Inorg. Chem. (Engl. Transl)*, 1965, **10**, 624.
2299. M. A. Ali, S. E. Livingstone and D. J. Phillips, *Inorg. Chim. Acta*, 1973, **7**, 531, 553, 179.
2300. M. Akbar Ali and S. G. Teoh, *J. Inorg. Nucl. Chem.*, 1978, **40**, 2013.
2301. Y. K. Bhoon, *Polyhedron*, 1983, **2**, 365.
2302. R. H. Holm, *J. Am. Chem. Soc.*, 1960, **82**, 5632.
2303. A. Gaetani Manfredotti and C. Guastini, *Acta Crystallogr., Sect. C*, 1983, **39**, 863.
2304. W. C. Hoyt and G. W. Everett, Jr., *Inorg. Chem.*, 1969, **8**, 2013.
2305. G. M. Mockler, G. W. Chaffey, E. Sinn and H. Wong, *Inorg. Chem.*, 1972, **11**, 1308.
2306. F. Akhtar, *Acta Crystallogr., Sect. B*, 1981, **37**, 84.
2307. B. S. Tovrog and R. S. Drago, *J. Am. Chem. Soc.*, 1974, **96**, 2743.
2308. R. C. Coombes, J. P. Costes and D. E. Fenton, *Inorg. Chim. Acta*, 1983, **77**, L173.
2309. P. J. Burke and D. R. McMillin, *J. Chem. Soc., Dalton Trans.*, 1980, 1794.
2310. M. Nemiroff, P. Ganis, G. Avitabile and S. L. Holt, *Cryst. Struct. Commun.*, 1974, **3**, 619.
2311. E. Kwiatkowski and M. Kwiatkowski, *Inorg. Chim. Acta*, 1980, **42**, 197.
2312. J. P. Costes, G. Cros, M. H. Darbieu and J. P. Laurent, *Inorg. Chim. Acta*, 1982, **60**, 111.
2313. S. A. Patil and V. H. Kulkarni, *Inorg. Chim. Acta*, 1983, **73**, 125.
2314. J. C. Jeffery, T. B. Rauchfuss and P. A. Tucket, *Inorg. Chem.*, 1980, **19**, 306.
2315. L. T. Taylor and W. M. Coleman, *J. Am. Chem. Soc.*, 1970, **92**, 1449.
2316. W. M. Coleman and L. T. Taylor, *Inorg. Chem.*, 1971, **10**, 2195.
2317. K. Hori and K. Takahashi, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 3023.
2318. E. M. Boge, D. P. Freyberg, E. Kokot, G. M. Mockler and E. Sinn, *Inorg. Chem.*, 1977, **16**, 1655.
2319. E. M. Boge, G. M. Mockler and E. Sinn, *Inorg. Chem.*, 1977, **16**, 467.
2320. P. C. Healy, G. M. Mockler, D. P. Freyberg and E. Sinn, *J. Chem. Soc. Dalton Trans.*, 1975, 691.
2321. M. Seleborg, S. L. Holt and B. Post, *Inorg. Chem.*, 1971, **10**, 1501.
2322. M. di Vaira, P. L. Orioli and L. Sacconi, *Inorg. Chem.*, 1971, **10**, 553.
2323. L. Sacconi and I. Bertini, *J. Am. Chem. Soc.*, 1966, **88**, 5180.
2324. D. P. Freyberg, G. M. Mockler and E. Sinn, *Inorg. Chem.*, 1979, **18**, 808.
2325. J. W. Kolis, D. E. Hamilton and N. K. Kildahl, *Inorg. Chem.*, 1979, **18**, 1826.
2326. B. Das Sarma, K. R. Ray, R. E. Sievers and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, 1964, **86**, 14.
2327. H. J. Cumming, D. Hall and C. E. Wright, *Acta Crystallogr.*, 1977, **33**, 1636.
2328. F. P. J. Dwyer and F. Lions, *J. Am. Chem. Soc.*, 1950, **72**, 1545.
2329. I. Marase, K. Yamanouchi and S. Yamada, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 2138.
2330. D. A. Cruse and M. Gerloch, *J. Chem. Soc., Dalton Trans.*, 1977, 152.
2331. H. Ewald and E. Sinn, *Inorg. Chem.*, 1967, **6**, 40.
2332. C. Rosini, P. Salvadori and M. Zandomeneghi, *J. Chem. Soc., Dalton Trans.*, 1978, 822.
2333. I. Bertini and F. Mani, *Inorg. Chem.*, 1970, **9**, 248.
2334. K. R. Levan and C. A. Root, *Inorg. Chem.*, 1981, **20**, 3566.
2335. K. R. Levan, C. E. Strouse and C. A. Root, *Inorg. Chem.*, 1983, **22**, 853.

2336. G. A. Auld and A. Davison, *Inorg. Chem.*, 1968, **7**, 306.
2337. S. T. Chow, D. M. Johns, C. A. McAuliffe and D. J. Machin, *Inorg. Chim. Acta*, 1977, **22**, 1.
2338. Y. Nakao and A. Nakahara, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 3522.
2339. T. Sakurai, Y. Nakao and A. Nakahara, *J. Inorg. Nucl. Chem.*, 1980, **42**, 1673.
2340. M. Fujioka, Y. Nakao and A. Nakahara, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 477.
2341. K. Aoki and H. Yamazaki, *J. Chem. Soc., Chem. Commun.*, 1980, 363.
2342. A. Chakravorty and R. H. Holm, *Inorg. Chem.*, 1964, **3**, 1010.
2343. R. H. Holm, A. Chakravorty and G. O. Pudek, *J. Am. Chem. Soc.*, 1964, **86**, 379.
2344. G. N. La Mar, *J. Am. Chem. Soc.*, 1965, **87**, 3567.
2345. J. D. Thwaites, I. Bertini and L. Sacconi, *Inorg. Chem.*, 1966, **5**, 1036.
2346. G. N. La Mar and L. Sacconi, *J. Am. Chem. Soc.*, 1967, **89**, 2282.
2347. M. J. O'Connor, R. E. Ernst and R. H. Holm, *J. Am. Chem. Soc.*, 1968, **90**, 45, 61.
2348. C. Floriani, F. Calderazzo and L. Randaccio, *J. Chem. Soc., Chem. Commun.*, 1974, 384.
2349. N. Bresciani-Pahor, M. Calligaris, P. Delise, G. Nardini, L. Randaccio, E. Zotti, G. Fachinetti and C. Floriani, *J. Chem. Soc., Dalton Trans.*, 1976, 2310.
2350. L. G. Armstrong, H. P. Lip, L. F. Lindoy, M. McPartlin and P. A. Tasker, *J. Chem. Soc., Dalton Trans.*, 1977, 1771.
2351. A. Giacomelli, C. Floriani and G. Perego, *J. Chem. Soc., Chem. Commun.*, 1982, 650.
2352. S. Gambarotta, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Chem. Soc., Chem. Commun.*, 1982, 756.
2353. L. Pellerito, R. Cefalii, A. Gianguzza and R. Barbieri, *J. Organomet. Chem.*, 1974, **70**, 309.
2354. M. Calligaris, L. Randaccio, R. Barbieri and L. Pellerito, *J. Organomet. Chem.*, 1974, **76**, C56.
2355. L. Pellerito, R. Cefalu and A. Gianguzza, *J. Organomet. Chem.*, 1974, **70**, C27.
2356. M. D. Hobday and T. D. Smith, *J. Chem. Soc. (A)*, 1971, 3424.
2357. J. O. Miners, E. Sinn, R. B. Coles and C. M. Harris, *J. Chem. Soc., Dalton Trans.*, 1972, 1149.
2358. R. J. Butcher, J. Jasinski, G. M. Mockler and E. Sinn, *J. Chem. Soc., Dalton Trans.*, 1976, 1099.
2359. E. E. Castellano, O. I. R. Hodder, C. K. Prout and P. J. Sadler, *J. Chem. Soc. (A)*, 1971, 2620.
2360. N. Matsumoto, T. Hara, A. Hirano and A. Ohyoshi, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 2727.
2361. T. J. Giordano, G. J. Palenik, R. C. Palenik and D. A. Sullivan, *Inorg. Chem.*, 1979, **18**, 2445.
2362. D. Wester and G. J. Palenik, *J. Am. Chem. Soc.*, 1974, **96**, 7565.
2363. M. Gerloch and I. Morgenstern-Badarau, *Inorg. Chem.*, 1979, **18**, 3225.
2364. C. Pelizzi, G. Pelizzi, G. Predieri and S. Resola, *J. Chem. Soc., Dalton Trans.*, 1982, 1349.
2365. A. S. Salameh, H. A. Tayim and B. C. Uff, *Polyhedron*, 1982, **1**, 543.
2366. S. E. Livingstone and J. D. Nolan, *Aust. J. Chem.*, 1973, **26**, 961.
2367. P. S. K. Chia and S. E. Livingstone, *Aust. J. Chem.*, 1969, **22**, 1613.
2368. L. G. Warner, T. Ottersen and K. Seff, *Inorg. Chem.*, 1974, **13**, 2529.
2369. M. A. Robinson and T. J. Hurley, *Inorg. Chem.*, 1965, **4**, 1716.
2370. A. B. Corradi, C. G. Palmieri, M. Nardelli and C. Pelizzi, *J. Chem. Soc., Dalton Trans.*, 1974, 150.
2371. B. Chiswell and K. W. Lee, *Inorg. Chim. Acta*, 1973, **7**, 517.
2372. C. M. Kerwin and G. A. Melson, *Inorg. Chem.*, 1972, **11**, 726.
2373. G. A. Melson and D. B. Bonfey, *Inorg. Nucl. Chem. Lett.*, 1973, **9**, 875.
2374. B. Chiswell, *Inorg. Chim. Acta*, 1980, **41**, 165.
2375. M. F. Iskander and S. Saddeck, *Inorg. Chim. Acta*, 1977, **22**, 141.
2376. P. Domiano, A. Musatti and M. Nardelli, *J. Chem. Soc., Dalton Trans.*, 1975, 295.
2377. P. Domiano, P. L. Messori, C. Pelizzi and G. Predieri, *Inorg. Chim. Acta*, 1983, **70**, 21.
2378. M. Nonoyama, *Inorg. Chim. Acta*, 1974, **10**, 133.
2379. M. Akbar Ali, S. E. Livingstone and D. J. Phillips, *Inorg. Chim. Acta*, 1971, **5**, 493.
2380. G. R. Clark and G. J. Palenik, *Cryst. Struct. Commun.*, 1980, **9**, 449.
2381. M. Mathew and G. J. Palenik, *J. Am. Chem. Soc.*, 1968, **91**, 6310.
2382. N. A. Bailey, S. E. Hull, C. J. Jones and J. A. McCleverty, *J. Chem. Soc., Chem. Commun.*, 1978, 124.
2383. P. E. Riley and K. Seff, *Inorg. Chem.*, 1972, **11**, 2993.
2384. L. Sacconi, G. Lombardo and P. Paoletti, *J. Chem. Soc. (A)*, 1968, 848.
2385. D. Dåkternieks, A. Orlandini and L. Sacconi, *Inorg. Chim. Acta*, 1978, **29**, L205.
2386. G. W. Everett, Jr. and R. H. Holm, *J. Am. Chem. Soc.*, 1965, **87**, 2117.
2387. W. Ludwig, *Helv. Chim. Acta*, 1962, **45**, 277.
2388. T. M. Hsen, D. F. Martin and T. Moeller, *Inorg. Chem.*, 1963, **2**, 587.
2389. G. O. Dudek and E. P. Dudek, *Inorg. Chim. Acta*, 1974, **8**, 219.
2390. T. I. Benzer, L. Dann, C. R. Schwitzgebel, M. D. Tamburro and E. P. Dudek, *Inorg. Chem.*, 1971, **10**, 2204.
2391. J. A. Bertrand, C. Marabello and D. G. Vanderveer, *Inorg. Chim. Acta*, 1978, **26**, 113.
2392. G. Brubaker, J. C. Latta and D. C. Aquino, *Inorg. Chem.*, 1970, **9**, 2608.
2393. P. J. McCarthy, R. J. Hovey, K. Ueno and A. E. Martell, *J. Am. Chem. Soc.*, 1955, **77**, 5820.
2394. M. Honda and G. Schwarzenbach, *Helv. Chim. Acta*, 1957, **40**, 27.
2395. L. F. Lindoy, W. E. Moody and D. Taylor, *Inorg. Chem.*, 1977, **16**, 1962.
2396. V. Malatesta and A. Mugnoli, *Can. J. Chem.*, 1981, **59**, 2766.
2397. R. P. Scaringe and D. J. Hodgson, *Inorg. Chem.*, 1976, **15**, 1193.
2398. Y. Y. Chen, D. E. Chu, B. D. McKinney, L. J. Willis and S. Cummings, *Inorg. Chem.*, 1981, **20**, 1885.
2399. W. N. Wallis and S. C. Cummings, *Inorg. Chem.*, 1974, **13**, 991.
2400. C. R. Powers and G. W. Everett, Jr., *J. Am. Chem. Soc.*, 1969, **91**, 3468.
2401. P. R. Blum, R. M. C. Wei and S. E. Cummings, *Inorg. Chem.*, 1974, **13**, 450.
2402. S. K. Mondal, D. S. Joardan and K. Nag, *Inorg. Chem.*, 1978, **17**, 191.
2403. L. S. Chen and S. Cummings, *Inorg. Chem.*, 1978, **17**, 2358.
2404. M. C. Thompson and D. H. Busch, *J. Am. Chem. Soc.*, 1964, **86**, 213.
2405. A. Vogler and H. Kunkely, *Inorg. Chim. Acta*, 1981, **54**, L273.
2406. Q. Fernando and P. J. Wheatley, *Inorg. Chem.*, 1965, **4**, 1726.

2407. D. H. Gerlach and R. H. Holm, *J. Am. Chem. Soc.*, 1969, **91**, 3457.
2408. T. D. Dubois and F. T. Smith, *Inorg. Chem.*, 1973, **12**, 735.
2409. T. D. Dubois, *Inorg. Chem.*, 1972, **11**, 718.
2410. G. N. La Mar, *Inorg. Chem.*, 1969, **8**, 581.
2411. E. G. Jager, B. Kirchhof, E. Schmidt, B. Rende, A. Kipke and R. Muller, *Z. Anorg. Allg. Chem.*, 1982, **485**, 141.
2412. K. S. Bose, B. C. Sharma and C. C. Patel, *Inorg. Chem.*, 1973, **12**, 120.
2413. S. Dilli, A. M. Maitra and E. Patsalides, *Inorg. Chem.*, 1982, **21**, 2832.
2414. E. I. Stiefel, J. H. Waters, E. Billig and H. B. Gray, *J. Am. Chem. Soc.*, 1965, **87**, 3016.
2415. M. A. Ali and S. E. Livingstone, *Coord. Chem. Rev.*, 1974, **13**, 101.
2416. D. H. Busch and D. C. Jicha, *Inorg. Chem.*, 1962, **1**, 872, 878.
2417. C. H. Wei and L. F. Dahl, *Inorg. Chem.*, 1970, **9**, 1878.
2418. E. L. Blinn, C. T. Shirkey and C. R. Lishawa, *Inorg. Chim. Acta*, 1984, **84**, 161.
2419. C. A. Root and D. H. Busch, *Inorg. Chem.*, 1968, **7**, 789.
2420. R. L. Girling and E. L. Amma, *Inorg. Chem.*, 1967, **6**, 2009.
2421. J. W. Wrathall and D. H. Busch, *Inorg. Chem.*, 1963, **2**, 1182.
2422. W. Hieber and R. Bruck, *Z. Anorg. Allg. Chem.*, 1952, **269**, 13.
2423. C. R. Kanekar and A. T. Casey, *J. Inorg. Nucl. Chem.*, 1969, **31**, 3105.
2424. S. Son, N. Kinomura, F. Kanamaru and M. Koizumi, *J. Chem. Soc., Dalton Trans.*, 1980, 1029.
2425. L. Menabue, G. C. Pellacani and G. Peyronel, *Inorg. Nucl. Chem. Lett.*, 1974, **10**, 187.
2426. M. Laing, P. Sommerville and P. A. Alsop, *J. Chem. Soc. (A)*, 1971, 1247.
2427. M. Goehring, K. W. Daum and J. Weiss, *Z. Naturforsch., Teil B*, 1955, **10**, 298.
2428. T. S. Piper, *J. Am. Chem. Soc.*, 1958, **80**, 30.
2429. J. D. Woollins, R. Grinter, M. K. Johnson and A. J. Thomson, *J. Chem. Soc., Dalton Trans.*, 1980, 1910.
2430. J. Weiss and U. Thewalt, *Z. Anorg. Allg. Chem.*, 1968, **363**, 159.
2431. J. Weiss and M. Ziegler, *Z. Anorg. Allg. Chem.*, 1963, **322**, 184.
2432. J. Weiss and U. Thewalt, *Z. Anorg. Allg. Chem.*, 1966, **343**, 274.
2433. J. Weiss, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 225.
2434. K. A. Jensen, *Z. Anorg. Allg. Chem.*, 1934, **221**, 6, 11.
2435. L. Cavalca, M. Nardelli and G. Fava, *Acta Crystallogr.*, 1962, **15**, 1139.
2436. R. Gronbaek and S. E. Rasmussen, *Acta Chem. Scand.*, 1962, **16**, 2325.
2437. R. Gronbaek Hazell, *Acta Chem. Scand.*, 1968, **22**, 2171.
2438. R. Gronbaek Hazell, *Acta Chem. Scand.*, 1972, **26**, 1365.
2439. J. Garaj and M. Dunaj-Jurco, *Chem. Commun.*, 1968, 518.
2440. R. Gronbaek Hazell, *Acta Chem. Scand.*, 1968, **22**, 2809.
2441. R. E. Ballard, D. B. Powell and U. A. Jayasooriya, *Acta Crystallogr., Sect. B*, 1974, **30**, 1111.
2442. G. Dessy and V. Fares, *Acta Crystallogr., Sect. B*, 1980, **36**, 944.
2443. G. R. Burns, *Inorg. Chem.*, 1968, **7**, 277.
2444. B. Beecroft, M. J. M. Campbell and R. Grzeskowiak, *J. Inorg. Nucl. Chem.*, 1974, **36**, 55.
2445. C. Battistoni, G. Mattogono, A. Monaci and F. Farli, *J. Inorg. Nucl. Chem.*, 1971, **33**, 3815.
2446. L. Sastadi and P. Porta, *J. Inorg. Nucl. Chem.*, 1975, **4**, 693.
2447. M. Das and S. E. Livingstone, *Inorg. Chim. Acta*, 1976, **19**, 5.
2448. T. Glowiak and T. Ciszewska, *Inorg. Chim. Acta*, 1978, **27**, 27.
2449. T. Uechi and T. Oniki, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 971.
2450. G. Dessy and U. Fares, *Cryst. Struct. Commun.*, 1980, **9**, 1111.
2451. M. Mathew, G. J. Palenik and G. R. Clark, *Inorg. Chem.*, 1973, **12**, 446.
2452. L. F. Lindoy and S. E. Livingstone, *Inorg. Chem.*, 1968, **7**, 1149.
2453. N. Dunski and T. H. Crawford, *J. Inorg. Nucl. Chem.*, 1969, **31**, 2073.
2454. L. F. Lindoy, S. E. Livingstone and T. N. Lockyer, *Aust. J. Chem.*, 1966, **19**, 1391.
2455. P. S. K. Chia and S. E. Livingstone, *Aust. J. Chem.*, 1968, **21**, 339.
2456. P. S. K. Chia, S. E. Livingstone and T. N. Lockyer, *Aust. J. Chem.*, 1967, **20**, 239.
2457. J. Abbot, D. M. L. Goodgame and I. Jeeves, *J. Chem. Soc., Dalton Trans.*, 1978, 880.
2458. Von E. Uhlig, P. Schuler and D. Dielhmann, *Z. Anorg. Allg. Chem.*, 1965, **335**, 156.
2459. C. W. Schlapfer, Y. Saito and K. Nakamoto, *Inorg. Chim. Acta*, 1972, **6**, 284.
2460. E. Wenschuh, B. Wendelberger and H. Hartung, *J. Inorg. Nucl. Chem.*, 1969, **31**, 2759.
2461. N. J. Rose, C. A. Root and D. H. Busch, *Inorg. Chem.*, 1967, **6**, 1431.
2462. L. F. Larkworthy, J. M. Murphy and D. J. Phillips, *J. Am. Chem. Soc.*, 1966, **88**, 1570.
2463. J. Weiss, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 705.
2464. U. Thewalt and J. Weiss, *Z. Anorg. Allg. Chem.*, 1966, **348**, 238.
2465. J. Weiss and U. Thewalt, *Z. Anorg. Allg. Chem.*, 1967, **355**, 271.
2466. R. Grinter and J. D. Woollins, *Inorg. Chim. Acta*, 1980, **39**, 193.
2467. M. Bossa, C. Furlani, G. Mattogno and E. Paparazzo, *Inorg. Chim. Acta*, 1978, **27**, L117.
2468. R. Czernuszewicz, G. Y. Lin, D. T. Haworth and K. Nakamoto, *Inorg. Chim. Acta*, 1980, **44**, L167.
2469. S. Millefiori, A. Millefiori and G. Granozzi, *Inorg. Chim. Acta*, 1981, **48**, 233.
2470. M. J. M. Campbell, *Coord. Chem. Rev.*, 1975, **15**, 279.
2471. D. D. Perrin and I. G. Sayce, *J. Chem. Soc. (A)*, 1967, 82.
2472. L. J. Porter and D. D. Perrin, *Aust. J. Chem.*, 1969, **22**, 267.
2473. L. F. Larkworthy and D. Sattari, *J. Inorg. Nucl. Chem.*, 1980, **42**, 551.
2474. A. Ouchi, T. Takeuki and Y. Ohashi, *Bull. Chem. Soc., Jpn.*, 1971, **44**, 731.
2475. B. C. Bloodworth, B. Demetrion and R. Grzeskowiak, *Inorg. Chim. Acta*, 1981, **53**, L85.
2476. G. A. Melson, N. P. Crawford and B. J. Geddes, *Inorg. Chem.*, 1970, **9**, 1123.
2477. M. Bonamico, G. Dessy and V. Fares, *J. Chem. Soc. (A)*, 1969, 697.
2478. M. M. Borel, A. Geffrouais and M. Ledesert, *Acta Crystallogr., Sect. B*, 1976, **32**, 2385.

2479. M. M. Borel, A. Geffrouais and M. Ledesert, *Acta Crystallogr., Sect. B*, 1977, **33**, 568, 571.
2480. M. M. Borel and M. Ledesert, *Acta Crystallogr., Sect. B*, 1977, **33**, 2993.
2481. J. A. Goodfellow and T. A. Stephenson, *Inorg. Chim. Acta*, 1980, **41**, 19.
2482. T. Sato, K. Nagata, M. Shiro and H. Koyama, *Chem. Commun.*, 1966, 192.
2483. T. Sato, K. Nagata, Y. Tsukuda, M. Shiro and H. Koyama, *Chem. Commun.*, 1967, 215.
2484. L. Beyer, E. Hoyer and G. Kuhn, *Z. Anorg. Allg. Chem.*, 1967, **350**, 27.
2485. J. L. Davidson, P. N. Preston and M. U. Russo, *J. Chem. Soc., Dalton Trans.*, 1983, 783.
2486. S. L. Perry, R. S. Quinn and E. P. Dudek, *Inorg. Chem.*, 1968, **7**, 814.
2487. J. A. Bertrand, W. J. Howard and A. R. Kalyararaman, *Chem. Commun.*, 1971, 437.
2488. S. C. Rastorgi and G. N. Rao, *J. Inorg. Nucl. Chem.*, 1974, **36**, 1161.
2489. G. Nieuwpoort and G. C. Verschoor, *Inorg. Chem.*, 1981, **20**, 4079.
2490. S. Kida and T. Oniki, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 1078.
2491. A. N. Speca, N. M. Karayannis, L. L. Pytlewski, L. J. Winters and D. Kandasamy, *Inorg. Chem.*, 1973, **12**, 1221.
2492. N. Hieber and A. Schnackig, *Z. Anorg. Allg. Chem.*, 1936, **226**, 209.
2493. G. W. Watt and J. F. Knifton, *Inorg. Chem.*, 1968, 7, 1443.
2494. L. Morpurgo and R. J. P. Williams, *J. Chem. Soc.* (*A*), 1966, 73.
2495. A. E. Landers and D. J. Phillips, *Inorg. Chim. Acta*, 1982, **59**, 41.
2496. K. H. Shaw and G. J. Sutton, *Aust. J. Chem.*, 1969, **22**, 1841.
2497. E. Uhlig and D. Keil, *Z. Anorg. Allg. Chem.*, 1964, **332**, 69.
2498. D. X. West and T. J. O'Grady, *J. Inorg. Nucl. Chem.*, 1981, **43**, 2725.
2499. J. Charalambous, P. Maple, N. A. Nasset and F. B. Taylor, *Inorg. Chim. Acta*, 1978, **26**, 107.
2500. J. Charalambous, M. J. Frazer and F. B. Taylor, *J. Chem. Soc.* (*A*), 1971, 602.
2501. B. Behera and A. Chakravorty, *Inorg. Chim. Acta*, 1970, **4**, 372.
2502. P. S. Zacharias and A. Chakravorty, *Inorg. Chem.*, 1971, **10**, 1961.
2503. M. V. Rajasekharan, K. I. Varughese and P. T. Manoharan, *Inorg. Chem.*, 1979, **18**, 2221.
2504. M. S. Ma and R. J. Angelici, *Inorg. Chem.*, 1980, **19**, 363.
2505. M. S. Ma, R. J. Angelici, D. Powell and R. A. Jacobson, *Inorg. Chem.*, 1980, **19**, 3121.
2506. M. S. Ma and R. J. Angelici, *Inorg. Chem.*, 1980, **19**, 924.
2507. M. E. Keeney, K. Osseo-Asan and K. A. Woode, *Coord. Chem. Rev.*, 1984, **59**, 141.
2508. L. L. Merrit, C. Guare and A. E. Lessor, *Acta Crystallogr.*, 1956, **9**, 253.
2509. V. Romano, F. Maggio and T. Pizzino, *J. Inorg. Nucl. Chem.*, 1971, **33**, 2611.
2510. J. Delaunay, C. Kappenstein and R. Hugel, *J. Chem. Res.* (*S*), 1978, 48; (*M*), 0801.
2511. J. Delaunay, C. Kappenstein and R. Hugel, *Acta Crystallogr., Sect. B*, 1976, **32**, 2341.
2512. L. T. Taylor and E. K. Barefield, *J. Inorg. Nucl. Chem.*, 1969, **31**, 3831.
2513. M. R. Udupa and B. Krebs, *Inorg. Chim. Acta*, 1981, **52**, 215.
2514. M. N. Hughes, B. Waldron and K. J. Rutt, *Inorg. Chim. Acta*, 1972, **6**, 619.
2515. B. G. Sejekan, M. R. Udopa and G. Aravamudan, *Indian J. Chem.*, 1974, **12**, 533.
2516. M. C. Feller and R. Robson, *Aust. J. Chem.*, 1970, **23**, 1997.
2517. M. Ciampolini and N. Nardi, *Inorg. Chem.*, 1967, **6**, 1821, 445.
2518. S. M. Nelson and J. Rodgers, *Inorg. Chem.*, 1967, **6**, 1390.
2519. S. L. Rose, R. E. Hoskin, J. E. Cavanaugh, C. J. Smith and E. L. Blinn, *Inorg. Chim. Acta*, 1980, **40**, 7.
2520. J. Harley-Mason, *J. Chem. Soc.*, 1952, 146.
2521. D. H. Busch, D. C. Jicha, M. C. Thompson, J. W. Wrathall and E. Blinn, *J. Am. Chem. Soc.*, 1964, **86**, 3642.
2522. T. Blakevange, Jr., L. G. Warner and K. Seff, *Inorg. Chem.*, 1977, **16**, 2106.
2523. L. Sacconi and R. Morassi, *J. Chem. Soc.* (*A*), 1970, 575.
2524. M. Ciampolini, J. Gelsomini and N. Nardi, *Inorg. Chim. Acta*, 1968, **7**, 343.
2525. P. Dapporto and L. Sacconi, *J. Chem. Res.* (*M*), 1970, 618.
2526. M. N. Hughes and K. J. Rutt, *J. Chem. Soc.*, 1968, 2788.
2527. K. Nielsen, R. G. Hazell and S. E. Rasmussen, *Acta Chem. Scand.*, 1972, **26**, 889.
2528. S. C. Rustagi and G. N. Rao, *J. Inorg. Nucl. Chem.*, 1974, **36**, 1889.
2529. S. E. Livingstone and J. D. Nolan, *Aust. J. Chem.*, 1970, **23**, 1553.
2530. J. H. Worrell, J. J. Genova and T. D. Dubois, *J. Inorg. Nucl. Chem.*, 1978, **40**, 441.
2531. J. H. Worrell and J. J. Genova, *J. Am. Chem. Soc.*, 1970, **92**, 5282.
2532. W. Levason, C. A. McAuliffe, F. P. McCullough and A. M. Werfalli, *Inorg. Chim. Acta*, 1977, **25**, 247.
2533. D. St. C. Black and I. A. McLean, *Aust. J. Chem.*, 1971, **24**, 1391.
2534. L. G. Warner, M. M. Kadooka and K. Seff, *Inorg. Chem.*, 1975, **14**, 1773.
2535. C. F. Bell, 'Principles and Application of Metal Chelation'. Clarendon, Oxford, 1977.
2536. M. W. Grant, H. W. Dodgen and J. P. Hunt, *J. Am. Chem. Soc.*, 1971, **93**, 6826.
2537. D. S. Everhart and R. F. Evilia, *Inorg. Chem.*, 1975, **14**, 2755.
2538. G. S. Smith and J. G. Hoard, *J. Am. Chem. Soc.*, 1959, **81**, 556.
2539. J. M. Nestorova, M. A. Porai-Koshits and V. A. Logvinenko, *Zh. Strukt. Khim.*, 1980, **21**, 171.
2540. H. Ogino, K. Tsukahara and N. Tanaka, *Inorg. Chem.*, 1977, **16**, 1215.
2541. R. H. Nuttal and T. M. Stalken, *J. Inorg. Nucl. Chem.*, 1977, **39**, 373.
2542. D. B. Rorabacher and D. W. Margerum, *Inorg. Chem.*, 1964, **3**, 382.
2543. D. W. Margerum and J. D. Carr, *J. Am. Chem. Soc.*, 1966, **88**, 1645.
2544. L. E. Erickson, D. C. Young, F. F. L. Ho, S. R. Watkins, J. B. Terril and C. N. Reilley, *Inorg. Chem.*, 1971, **10**, 441.
2545. B. Jezowska-Trzebiatowska, L. Latos-Grazynski and H. Kozlowski, *Inorg. Chim. Acta*, 1977, **21**, 145.
2546. L. Latos-Grazynski and B. Jezowska-Trzebiatowska, *J. Inorg. Nucl. Chem.*, 1981, **43**, 1249.
2547. R. E. Sievers and J. C. Bailar, Jr., *Inorg. Chem.*, 1962, **1**, 174.
2548. V. V. Fomenko, T. N. Polyanova and M. A. Porai-Koshits, *Zh. Strukt. Khim.*, 1975, **16**, 651.

2549. F. G. Kramarenko, T. N. Polyanova, M. A. Porai-Koshits, V. P. Chalyi and N. D. Mitrofanova, *Zh. Strukt. Khim.*, 1974, **15**, 161.
2550. N. J. Manmano, D. H. Templeton and A. Zalkin, *Acta Crystallogr., Sect. B,* 1977, **33,** 1251.
2551. T. N. Polyanova, M. A. Porai-Koshits and N. D. Mitrofanova, *Zh. Strukt. Khim.*, 1978, **19,** 765.
2552. J. Podlaha and J. Podlahova, *Inorg. Chim. Acta,* 1971, **5,** 413.
2553. J. Podlahova, J. Lonb and C. Novak, *Acta Crystallogr., Sect. B,* 1972, **28,** 1623.
2554. C. F. Campana, D. F. Shepard and W. M. Litchman, *Inorg. Chem.*, 1981, **20,** 4039.
2555. E. E. Castellano, O. R. Nascimento and R. Calvo, *Acta Crystallogr., Sect. B,* 1982, **36,** 1303.
2556. C. K. Jorgensen, 'Inorganic Complexes', Academic, London, 1963.
2557. J. R. Ruble and K. Seff, *Acta Crystallogr., Sect. B,* 1972, **26,** 1272.
2558. C. A. McAuliffe and W. D. Perry, *J. Chem. Soc.* (*A*), 1969, 634.
2559. S. T. Cho and C. A. McAuliffe, *Prog. Inorg. Chem.*, 1975, **19,** 51.
2560. D. van der Helm and M. B. Hossain, *Acta Crystallogr., Sect. B,* 1969, **25,** 457.
2561. P. Jose, L. M. Pant and A. B. Biswas, *Acta Crystallogr.*, 1964, **17,** 24.
2562. H. C. Freeman and J. M. Guss, *Acta Crystallogr., Sect. B,* 1972, **28,** 2090.
2563. R. Hamalainen, M. Ahlgren, U. Turpeinen and T. Raikas, *Cryst. Struct. Commun.*, 1978, **7,** 379.
2564. S. Guha, *Acta Crystallogr., Sect. B,* 1973, **29,** 2167.
2565. L. D. Pettit and J. L. M. Swash, *J. Chem. Soc., Dalton Trans.*, 1976, 588.
2566. K. A. Fraser and M. M. Harding, *J. Chem. Soc.* (*A*), 1967, 415.
2567. T. Sakurai, H. Iwasaki, T. Katano and Y. Nakahashi, *Acta Crystallogr., Sect. B,* 1978, **34,** 660.
2568. S. R. Ebner, B. J. Helland, R. H. Jacobson and R. J. Angelici, *Inorg. Chem.*, 1980, **19,** 175.
2569. P. R. Rechani, R. Nakon and R. J. Angelici, *Bioinorg. Chem.*, 1976, **5,** 329.
2570. R. Nakon, P. R. Rechani and R. J. Angelici, *Inorg. Chem.*, 1973, **12,** 2431.
2571. S. A. Bedell, P. R. Rechani, R. J. Angelici and R. Nakon, *Inorg. Chem.*, 1977, **16,** 972.
2572. J. L. M. Swash and L. D. Pettit, *Inorg. Chim. Acta,* 1976, **19,** 19.
2573. L. Antolini, L. Menabue, G. C. Pellacani and G. Marcotrigiano, *J. Chem. Soc., Dalton Trans.*, 1982, 2541.
2574. L. P. Battaglia, A. Bonamartini Corradi, L. Antolini, L. Menabue and G. C. Pellacani, *J. Am. Chem. Soc.*, 1982, **104,** 2407.
2575. M. K. Kim and A. E. Martell, *J. Am. Chem. Soc.*, 1967, **89,** 5138.
2576. H. C. Freeman, J. M. Guss and R. L. Sinclair, *Acta Crystallogr., Sect. B,* 1978, **34,** 2459.
2577. E. B. Paniago, D. C. Weatherburn and D. W. Margerum, *Chem. Commun.*, 1971, 1427.
2578. H. C. Freeman and J. M. Guss, *Acta Crystallogr., Sect. B,* 1978, **34,** 2451.
2579. H. Kozlowski, *Inorg. Chim. Acta,* 1978, **31,** 135.
2580. G. Formicka-Kozlowska, H. Kozlowski and B. Jezowska-Trzebiatowska, *Inorg. Chim. Acta,* 1977, **25,** 1.
2581. H. Loiseleur, *Acta Crystallogr., Sect. B,* 1972, **28,** 816.
2582. H. Gaw, W. R. Robinson and R. A. Walton, *Inorg. Nucl. Chem. Lett.*, 1971, **7,** 695.
2583. A. Chiesi-Villa, C. Guastini, A. Musatti and M. Nardelli, *Gazz. Chim. Ital.*, 1972, **102,** 226.
2584. P. Quaglieri, H. Loiseleur and G. Thomas, *Acta Crystallogr., Sect. B,* 1972, **28,** 2583.
2585. J. G. H. du Preez, H. E. Rohwer, B. J. van Brecht and M. R. Caira, *J. Chem. Soc., Dalton Trans.*, 1984, 975.
2586. D. O. Nielson, M. L. Larsen, R. D. Willett and J. I. Legg, *J. Am. Chem. Soc.*, 1971, **93,** 5079.
2587. D. F. Averill, J. I. Legg and D. L. Smith, *Inorg. Chem.*, 1972, **11,** 2344.
2588. E. J. Billo, *Inorg. Chim. Acta,* 1979, **37,** L533.
2589. M. H. West and J. I. Legg, *J. Am. Chem. Soc.*, 1976, **98,** 6945.
2590. U. Casellato, P. A. Vigato and M. Vidali, *Coord. Chem. Rev.*, 1977, **23,** 31.
2591. U. Casellato, P. A. Vigato, P. E. Fenton and M. Vidali, *Chem. Soc. Rev.*, 1979, **8,** 199.
2592. J. O. Miners and E. Sinn, *Bull. Chem. Soc. Jpn.*, 1970, **43,** 1457.
2593. G. O. Carlisle and L. J. Theriot, *J. Inorg. Nucl. Chem.*, 1973, **35,** 2093.
2594. G. R. Brubaker, J. C. Calta and D. C. Aquino, *Inorg. Chem.*, 1970, **9,** 2608.
2595. B. F. Hoskins, R. Robson and M. Schaap, *Inorg. Nucl. Chem. Lett.*, 1972, **8,** 21.
2596. L. F. Lindoy and S. E. Livingstone, *Inorg. Chim. Acta,* 1967, **1,** 365.
2597. R. Robson and D. G. Vince, *Inorg. Chim. Acta,* 1977, **25,** 191.
2598. W. D. McFadyen, R. Robson and M. Schaap, *Inorg. Chem.*, 1972, **11,** 1777.
2599. I. Murase, S. Ueno and S. Kidà, *Bull. Chem. Soc. Jpn.*, 1983, **56,** 2748.
2600. H. Okawa and S. Kida, *Bull. Chem. Soc. Jpn.*, 1972, **45,** 1759.
2601. H. Okawa, T. Tokii, Y. Muto and S. Kida, *Bull. Chem. Soc. Jpn.*, 1973, **46,** 2464.
2602. M. Tanaka, H. Okawa, T. Tamura and S. Kida, *Bull. Chem. Soc. Jpn.*, 1974, **47,** 1669.
2603. M. Tanaka, M. Kitaoka, H. Okawa and S. Kida, *Bull. Chem. Soc. Jpn.*, 1976, **49,** 2469.
2604. M. Vidali, U. Casellato, P. A. Vigato, L. Doretti and F. Madalosso, *J. Inorg. Nucl. Chem.*, 1977, **39,** 1985.
2605. D. J. Phillips, N. S. Rawata and S. K. Tiwari, *J. Inorg. Nucl. Chem.*, 1977, **39,** 797.
2606. N. Torihara, H. Okawa and S. Kida, *Inorg. Chim. Acta,* 1976, **26,** 97.
2607. H. Okawa, Y. Nishida, M. Tanaka and S. Kida, *Bull. Chem. Soc. Jpn.*, 1977, **50,** 127.
2608. P. A. Vigato, U. Casellato, M. Vidali, R. Graziani, D. E. Fenton and C. M. Regan, *Inorg. Chim. Acta,* 1979, **32,** L27.
2609. D. E. Fenton, S. E. Gayda, U. Casellato, M. Vidali and P. A. Vigato, *Inorg. Chim. Acta,* 1978, **27,** 9.
2610. R. L. Lintvedt, L. L. Borer, D. P. Murtha, J. M. Kuszay and M. D. Glick, *Inorg. Chem.*, 1974, **13,** 18.
2611. J. W. Guthrie, R. L. Lintvedt and M. D. Glick, *Inorg. Chem.*, 1980, **19,** 2949.
2612. B. Andrelezyk and R. L. Lintvedt, *J. Am. Chem. Soc.*, 1972, **94,** 8633.
2613. D. E. Fenton and S. E. Gayda, *J. Chem. Soc., Dalton Trans.*, 1977, 2101.
2614. D. E. Fenton and S. E. Gayda, *J. Chem. Soc., Dalton Trans.*, 1977, 2109.
2615. M. D. Glick, R. L. Lintvedt, T. J. Anderson and J. L. Mack, *Inorg. Chem.*, 1976, **15,** 2258.
2616. R. L. Lintvedt, M. D. Glick, B. K. Tomlonovic and D. P. Gavel, *Inorg. Chem.*, 1976, **15,** 1646.
2617. M. D. Glick, R. L. Lintvedt, D. P. Gavel and B. Tomlonovic, *Inorg. Chem.*, 1976, **15,** 1654.
2618. C. J. O'Connor, D. P. Freyberg and E. Sinn, *Inorg. Chem.*, 1979, **18,** 1077.

2619. P. M. Merrell and M. Abrams, *Inorg. Chim. Acta,* 1979, **32,** 93.
2620. C. Y. Ng, R. J. Motekaitis and A. E. Martell, *Inorg. Chem.*, 1979, **18,** 2982.
2621. B. C. Whitmore and R. Eisenberg, *Inorg. Chem.*, 1983, **22,** 1.
2622. G. A. Nelson (ed.), 'Coordination Chemistry of Macrocyclic Compounds', Plenum, New York, 1979.
2623. J. J. Christensen, D. J. Eatough and R. M. Izatt, *Chem. Rev.*, 1974, **74,** 351.
2624. L. F. Lindoy, *Chem. Soc. Rev.*, 1975, **4,** 421.
2625. N. F. Curtis, *Coord. Chem. Rev.*, 1968, **3,** 3.
2626. G. R. Newkome, J. D. Sauer, J. M. Roper and D. C. Hager, *Chem. Rev.*, 1977, **77,** 513.
2627. D. H. Busch, *Acc. Chem. Res.*, 1978, **11,** 392.
2628. A. M. Tait and D. H. Busch, *Inorg. Synth.*, 1978, **18.**
2629. C. K. Poon, *Coord. Chem. Rev.*, 1973, **10,** 1.
2630. L. F. Lindoy, *Q. Rev., Chem. Soc.*, 1971, **25,** 379.
2631. D. St. C. Black and A. J. Hartshorn, *Coord. Chem. Rev.*, 1972, **9,** 219.
2632. L. F. Lindoy and D. H. Busch, *Prep. Inorg. React.*, 1971, **6,** 1.
2633. N. F. Curtis, *J. Chem. Soc.*, 1960, 4409.
2634. T. E. MacDermott and D. H. Busch, *J. Am. Chem. Soc.*, 1967, **89,** 5780.
2635. D. St. C. Black and H. Greenland, *Aust. J. Chem.*, 1972, **25,** 1314.
2636. D. A. House and N. F. Curtis, *J. Am. Chem. Soc.*, 1964, **86,** 223.
2637. D. A. House and N. F. Curtis, *J. Am. Chem. Soc.*, 1964, **86,** 1331.
2638. N. F. Curtis and D. A. House, *J. Chem. Soc. (A)*, 1967, 537.
2639. N. F. Curtis, *J. Chem. Soc. (A)*, 1971, 2834.
2640. M. de S. Healy and A. J. Rest, *Adv. Inorg. Chem. Radiochem.*, 1978, **21,** 1.
2641. J. L. Karn and D. H. Busch, *Nature (London)*, 1966, **211,** 160.
2642. J. L. Karn and D. H. Busch, *Inorg. Chem.*, 1969, **8,** 1149.
2643. M. C. Rakowski, M. Rycheck and D. H. Busch, *Inorg. Chem.*, 1975, **14,** 1194.
2644. D. H. Busch, *Helv. Chim. Acta, Fasciculus Extraodinarius Alfred Werner*, 1967, 174.
2045. R. H. Prince, D. A. Stotter and P. R. Woolley, *Inorg. Chim. Acta,* 1974, **9,** 51.
2646. M. Green, J. Smith and P. A. Tasker, *Inorg. Chim. Acta,* 1971, **5,** 17.
2647. E. G. Jaeger, *Z. Chem.*, 1964, **437,** 4.
2648. J. L. Love and H. K. J. Powell, *Chem. Commun.*, 1968, 39.
2649. S. K. Barefield, F. Wagner and K. P. Hodges, *Inorg. Chem.*, 1976, **15,** 1370.
2650. E. K. Barefield, F. Wagner, A. W. Herlinger and A. R. Dahl, *Inorg. Synth.*, 1976, **16,** 220.
2651. G. A. Melson and D. H. Busch, *J. Am. Chem. Soc.,* 1964, **86,** 4834, 4830.
2652. E. Uhlemann and M. Plath, *Z. Chem.*, 1969, **6,** 234.
2653. M. C. Thompson and D. H. Busch, *J. Am. Chem. Soc.*, 1964, **86,** 3651.
2654. R. W. Hay, A. L. Galyer and G. A. Lawrance, *J. Chem. Soc., Dalton Trans.*, 1976, 939.
2655. S. M. Peng, G. C. Gordon and V. L. Goedken, *Inorg. Chem.*, 1978, **17,** 119.
2656. C. M. Kerwin and G. A. Melson, *Inorg. Chem.*, 1973, **12,** 2410.
2657. D. B. Bonfoey and G. A. Melson, *Inorg. Chem.*, 1975, **14,** 309.
2658. P. A. Tasker and E. B. Fleischer, *J. Am. Chem. Soc.*, 1970, **92,** 7072.
2659. R. Yang and L. J. Zompa, *Inorg. Chem.*, 1976, **15,** 1499.
2660. L. J. Murphy, Jr. and L. J. Zompa, *Inorg. Chem.*, 1979, **18,** 3278.
2661. L. J. Zompa and T. N. Margulis, *Inorg. Chim. Acta,* 1978, **28,** L157.
2662. L. J. Zompa and T. N. Margulis, *Inorg. Chim. Acta,* 1980, **45,** L263.
2663. L. J. Zompa, *Inorg. Chem.*, 1978, **17,** 2531.
2664. M. Ciampolini, M. Micheloni, N. Nardi, P. Paoletti, D. Dapporto and F. Zanobini, *J. Chem. Soc., Dalton Trans.*, 1984, 1357.
2665. W. H. Plassman, R. G. Swisher and E. L. Blinn, *Inorg. Chem.*, 1980, **19,** 1101.
2666. L. Fabbrizzi, *Inorg. Chem.*, 1977, **16,** 2667.
2667. G. A. Kalligeros and E. L. Blinn, *Inorg. Chem.*, 1972, **11,** 1145.
2668. J. M. Waters and K. R. Whittle, *J. Inorg. Nucl. Chem.*, 1972, **34,** 155.
2669. M. S. Holtman and S. C. Cummings, *Inorg. Chem.*, 1976, **15,** 660.
2670. L. Fabbrizzi, *J. Chem. Soc., Dalton Trans.*, 1979, 1857.
2671. J. H. Coates, D. A. Hadi and S. F. Lincoln, *Aust. J. Chem.*, 1982, **35,** 903.
2672. B. Bosnich, M. L. Tobe and G. A. Webb, *Inorg. Chem.*, 1965, **4,** 1109.
2673. A. Anichini, L. Fabbrizzi, P. Paoletti and R. M. Clay, *Inorg. Chim. Acta,* 1977, **24,** L21.
2674. B. Bosnich, R. Mason, P. Pauling, G. B. Robertson and M. L. Tobe, *Chem. Commun.*, 1965, 97.
2675. V. J. Thom, C. C. Fox, J. C. A. Boeyens and R. D. Hancock, *J. Am. Chem. Soc.*, 1984, **106,** 5947.
2676. N. Herron and P. Moore, *Inorg. Chim. Acta,* 1979, **36,** 89.
2677. G. S. Vigfe, C. L. Watkins and H. F. Bowen, *Inorg. Chim. Acta,* 1979, **35,** 255.
2678. E. J. Billo, *Inorg. Chem.*, 1981, **20,** 4019.
2679. E. J. Billo, *Inorg. Chem.*, 1984, **23,** 236.
2680. E. K. Barefield and F. Wagner, *Inorg. Chem.*, 1973, **12,** 2435.
2681. M. J. D'Antello, Jr., M. T. Mocella, F. Wagner, E. K. Barefield and I. C. Paul, *J. Am. Chem. Soc.*, 1975, **97,** 192.
2682. F. Wagner, M. T. Mocella, M. J. D'Aniello, Jr., A. H. J. Wang and E. K. Barefield, *J. Am. Chem. Soc.*, 1974, **96,** 2625.
2683. R. W. Hay, B. Jeragh, G. Ferguson, B. Kaitner and B. L. Ruhl, *J. Chem. Soc., Dalton Trans.*, 1982, 1531.
2684. N. F. Curtis, *J. Chem. Soc.*, 1964, 2645.
2685. L. G. Warner and D. H. Busch, *J. Am. Chem. Soc.*, 1969, **91,** 4092.
2686. N. F. Curtis, D. A. Swann and T. N. Waters, *J. Chem. Soc., Dalton Trans.*, 1973, 1963.
2687. P. O. Whimp, M. F. Bailey and N. F. Curtis, *J. Chem. Soc. (A)*, 1970, 1956.
2688. N. F. Curtis and Y. M. Curtis, *Inorg. Nucl. Chem. Lett.*, 1965, **4,** 804.

2689. N. F. Curtis, D. A. Swann and T. N. Waters, *J. Chem. Soc., Dalton Trans.*, 1973, 1048.
2690. H. Ito, M. Sugimoto and T. Ito, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 1971.
2691. T. Ito, K. Toriumi and H. Ito, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 1096.
2692. T. Ito and K. Toriumi, *Acta Crystallogr., Sect. B*, 1981, **37**, 88.
2693. L. Sabatini and L. Fabbrizzi, *Inorg. Chem.*, 1979, **18**, 438.
2694. A. Dei, L. Fabbrizzi and P. Paoletti, *Inorg. Chem.*, 1981, **20**, 4036.
2695. R. G. Swisher, J. P. Dayhuff, D. J. Stuehr and E. L. Blinn, *Inorg. Chem.*, 1980, **19**, 1336.
2696. L. Y. Martin, C. R. Sperati and D. H. Busch, *J. Am. Chem. Soc.*, 1977, **99**, 2968.
2697. M. Sugimoto, M. Nonoyama, T. Ito and J. Fujita, *Inorg. Chem.*, 1983, **22**, 950.
2698. M. Sugimoto, J. Fujita, H. Ito, K. Toriumi and T. Ito, *Inorg. Chem.*, 1983, **22**, 955.
2699. L. Fabbrizzi, M. Micheloni, P. Paoletti, A. Poggi and A. B. P. Lever, *J. Chem. Soc., Dalton Trans.*, 1981, 1438.
2700. V. Katovic, L. T. Taylor, F. L. Urbach, W. H. White and D. H. Busch, *Inorg. Chem.*, 1972, **11**, 479.
2701. H. Elias, R. Grewe, D. D. Klaehn and M. Paulus, *Z. Naturforsch., Teil B*, 1984, **39**, 903.
2702. E. I. Ochiai and D. H. Busch, *Inorg. Chem.*, 1969, **8**, 1798.
2703. M. G. B. Drew and S. Hollis, *Acta Crystallogr., Sect. B*, 1980, **36**, 718.
2704. R. Dewar and E. Fleischer, *Nature (London)*, 1969, **222**, 372.
2705. M. G. B. Drew and S. Hollis, *Acta Crystallogr., Sect. B*, 1980, **36**, 1944.
2706. J. L. Karn and D. H. Busch, *Inorg. Chem.*, 1969, **8**, 1149.
2707. M. G. B. Drew and S. Hollis, *Acta Crystallogr., Sect. B*, 1980, **36**, 2629.
2708. M. C. Rakowski, M. Rycheck and D. H. Busch, *Inorg. Chem.*, 1975, **14**, 1194.
2709. N. W. Alcock, R. G. Kingston, P. Moore and C. Pierpoint, *J. Chem. Soc., Dalton Trans.*, 1984, 1937.
2710. N. W. Alcock, P. Moore and C. Pierpoint, *J. Chem. Soc., Dalton Trans.*, 1984, 2371.
2711. L. Prasad and A. McAuley, *Acta Crystallogr., Sect. C*, 1983, **39**, 1175.
2712. N. Herron and P. Moore, *Inorg. Chim. Acta*, 1979, **36**, 89.
2713. F. P. Hinz and D. W. Margerum, *Inorg. Chem.*, 1974, **13**, 2941.
2714. M. Micheloni, P. Paoletti and A. Sabatini, *J. Chem. Soc., Dalton Trans.*, 1983, 1189.
2715. E. Gallori, E. Martini, M. Micheloni and P. Paoletti, *J. Chem. Soc., Dalton Trans.*, 1980, 1722.
2716. L. Fabbrizzi, M. Micheloni and P. Paoletti, *Inorg. Chem.*, 1980, **19**, 535.
2717. L. Fabbrizzi, P. Paoletti and R. M. Clay, *Inorg. Chem.*, 1978, **17**, 1042.
2718. A. Bianchi, L. Bologni, P. Dapporto, M. Micheloni and P. Paoletti, *Inorg. Chem.*, 1984, **23**, 1201.
2719. M. Micheloni, P. Paoletti, A. Poggi and L. Fabbrizzi, *J. Chem. Soc., Dalton Trans.*, 1982, 61.
2720. L. Fabbrizzi, M. Micheloni and P. Paoletti, *J. Chem. Soc., Dalton Trans.*, 1980, 134.
2721. J. W. L. Martin, J. H. Johnston and N. F. Curtis, *J. Chem. Soc., Dalton Trans.*, 1978, 68.
2722. G. A. Melson and D. H. Busch, *J. Am. Chem. Soc.*, 1965, **87**, 1706.
2723. G. A. Melson and D. H. Busch, *J. Am. Chem. Soc.*, 1964, **86**, 4834.
2724. E. B. Fleischer and E. Klem, *Inorg. Chem.*, 1965, **4**, 637.
2725. L. T. Taylor and D. H. Busch, *Inorg. Chem.*, 1969, **8**, 1366.
2726. N. F. Curtis, Y. M. Curtis and H. K. J. Powell, *J. Chem. Soc. (A)*, 1966, 1015.
2727. M. F. Bailey and I. E. Maxwell, *J. Chem. Soc., Dalton Trans.*, 1972, 938.
2728. B. T. Kilbun, R. R. Ryan and J. D. Dunitz, *J. Chem. Soc. (A)*, 1969, 2407.
2729. I. E. Maxwell and M. F. Bailey, *J. Chem. Soc., Dalton Trans.*, 1972, 935.
2730. N. F. Curtis and Y. M. Curtis, *J. Chem. Soc. (A)*, 1966, 1653.
2731. J. Krajewski, Z. Urhanczyk and P. Gluzinski, *Rocz. Chem.*, 1974, **48**, 1821.
2732. G. Ferguson, F. J. Restivo and R. W. Hay, *Acta Crystallogr., Sect. B*, 1979, **35**, 159.
2733. P. Murray-Rust and J. Murray-Rust, *Acta Crystallogr., Sect.* 1979, **35**, 1704.
2734. N. F. Curtis, *J. Chem. Soc., Dalton Trans.*, 1974, 347.
2735. D. F. Cook, N. F. Curtis and R. W. Hay, *J. Chem. Soc., Dalton Trans.*, 1973, 1160.
2736. R. A. Kolinski and B. Korybut-Daszkiewicz, *Inorg. Chim. Acta*, 1975, **14**, 237.
2737. A. I. Gusiev, J. W. Krajewski and Z. Urbanczyk, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, 1974, **22**, 387.
2738. D. A. Swann, T. N. Waters and N. F. Curtis, *J. Chem. Soc., Dalton Trans.*, 1972, 1115.
2739. T. Ito and D. H. Busch, *Inorg. Chem.*, 1974, **13**, 1770.
2740. J. F. Myers and N. J. Rose, *Inorg. Chem.*, 1973, **12**, 1238.
2741. J. F. Myers and C. H. L. Kennard, *J. Chem. Soc., Chem. Commun.*, 1972, 77.
2742. J. W. L. Martin, J. H. Timmons, A. E. Martell and C. J. Willis, *Inorg. Chem.*, 1980, **19**, 2328.
2743. J. L. Karn and D. H. Busch, *Nature (London)*, 1966, **211**, 160.
2744. L. Rusnak and R. B. Jordan, *Inorg. Chem.*, 1971, **10**, 2199.
2745. K. Mochizuki, T. Ito and M. Fujimoto, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 543.
2746. K. Mochizuki, M. Fujimoto, T. Ito and H. Ito, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 2535.
2747. E. B. Fleischer and S. W. Hawkinson, *Inorg. Chem.*, 1968, **7**, 2312.
2748. L. Fabbrizzi and A. Poggi, *Inorg. Chim. Acta*, 1980, **39**, 207.
2749. E. K. Barefield, F. V. Lovecchio, N. E. Tokel, E. Ochiai and D. H. Busch, *Inorg. Chem.*, 1972, **11**, 283.
2750. N. F. Curtis, *J. Chem. Soc. (A)*, 1971, 2834.
2751. V. L. Goedken and D. H. Busch, *Inorg. Chem.*, 1971, **10**, 2679.
2752. D. S. Eggleston and S. C. Jackels, *Inorg. Chem.*, 1980, **19**, 1593.
2753. L. P. Torre and E. C. Lingafelter, *Proc. Am. Crystallogr. Assoc.*, 1971, 62.
2754. S. W. Hawkinson and E. B. Fleischer, *Inorg. Chem.*, 1969, **8**, 2402.
2755. C. Cairns, S. G. McFall, S. M. Nelson and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, 1979, 446.
2756. C. W. G. Ansell, J. Lewis, P. R. Raithby, J. N. Ramsden and M. Schroder, *J. Chem. Soc., Chem. Commun.*, 1982, 546.
2757. E. C. Constable, J. Lewis, M. C. Liptrot, P. R. Raithby and M. Schoder, *Polyhedron*, 1983, **2**, 301.
2758. M. F. Richardson and R. E. Sievers, *J. Am. Chem. Soc.*, 1972, **94**, 4134.
2759. S. C. Cummings and R. E. Sievers, *Inorg. Chem.*, 1970, **9**, 1131.
2760. P. W. R. Corfield, J. D. Mokren, C. J. Hipp and D. H. Busch, *J. Am. Chem. Soc.*, 1973, **95**, 4465.

2761. S. M. Peng, J. A. Ibers, M. Millar and R. H. Holm, *J. Am. Chem. Soc.*, 1976, **98**, 8037.
2762. T. J. Truex and R. H. Holm, *J. Am. Chem. Soc.*, 1971, **93**, 285.
2763. E. G. Jager, *Z. Chem.*, 1968, **8**, 470.
2764. R. R. Gagne and D. M. Ingle, *Inorg. Chem.*, 1981, **20**, 420.
2765. O. P. Anderson, *Acta Crystallogr., Sect. B*, 1981, **37**, 1194.
2766. A. W. Addison, B. Watts and M. Wicholas, *Inorg. Chem.*, 1984, **23**, 813.
2767. F. S. Stephens and R. S. Vagg, *Acta Crystallogr., Sect. B*, 1977, **33**, 3159.
2768. R. S. Vagg and E. C. Watton, *Acta Crystallogr., Sect. B*, 1978, **34**, 2715.
2769. M. S. Hussain, R. H. Murmann and E. O. Schlemper, *Inorg. Chem.*, 1980, **19**, 1445.
2770. E. N. Maslen, L. M. Engelhardt and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1974, 1799.
2771. M. Green, J. Smith and P. A. Tasker, *Inorg. Chim. Acta*, 1975, **5**, 17.
2772. K. Sakata, M. Hashimoto, N. Tagami and Y. Murakami, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 2262.
2773. D. St. C. Black, C. H. Bosvanderzalm and L. C. H. Wong, *Aust. J. Chem.*, 1979, **32**, 2303.
2774. M. C. Weiss, G. Gordon and V. L. Goedken, *Inorg. Chem.*, 1977, **16**, 305.
2775. F. Hanic, M. Handlovic and O. Lindgren, *Collect. Czech. Chem. Commun.*, 1972, **37**, 2119.
2776. E. G. Jager, *Z. Anorg. Allg. Chem.*, 1969, **364**, 177.
2777. M. Hunziker, H. Loeliger, G. Rihs and B. Hilti, *Helv. Chim. Acta*, 1981, **64**, 2544.
2778. Y. M. Wuu, S. M. Peng and H. Chang, *J. Inorg. Nucl. Chem.*, 1980, **42**, 839.
2779. M. Hunziker, B. Hilti and C. Rihs, *Helv. Chim. Acta*, 1981, **64**, 82.
2780. C. W. G. Ansell, M. F. H. Y. J. Chung, M. McPartlin and P. A. Tasker, *J. Chem. Soc., Dalton Trans.*, 1982, 2113.
2781. S. M. Peng and V. L. Goedken, *J. Am. Chem. Soc.*, 1976, **98**, 8500.
2782. G. C. Gordon, S. M. Peng and V. L. Goedken, *Inorg. Chem.*, 1978, **17**, 3578.
2783. G. A. Melson, *Inorg. Chem.*, 1974, **13**, 994.
2784. D. P. Fisher, V. Piermattie and J. C. Dabrowiak, *J. Am. Chem. Soc.*, 1977, **99**, 2812.
2785. W. Bachmann, S. Burki and T. Kapen, *J. Chem. Soc., Chem. Commun.*, 1981, 158.
2786. N. Motsumoto, K. Wakizaka and A. Ohyoshi, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 3165.
2787. L. O. Urban and E. G. Vassian, *Inorg. Chem.*, 1979, **18**, 867.
2788. C. J. Hipp and D. H. Busch, *Inorg. Chem.*, 1973, **12**, 894.
2789. J. A. Streeky, D. G. Pillsbury and D. H. Busch, *Inorg. Chem.*, 1980, **19**, 3148.
2790. W. P. Schammel, L. L. Zimmer and D. H. Busch, *Inorg. Chem.*, 1980, **19**, 3159.
2791. N. Matsumoto, A. Hirano and A. Ohyoshi, *Bull. Chem. Soc., Jpn.*, 1983, **56**, 891.
2792. D. H. Busch, G. G. Christoph, L. L. Zimmer, S. C. Jackels, J. J. Grzybowski, R. C. Callaham, M. Kojima, K. A. Holter, J. Mocak, N. Herron, M. Charanandw and P. Schammel, *J. Am. Chem. Soc.*, 1981, **103**, 5107.
2793. J. A. Cunningham and R. E. Sievers, *J. Am. Chem. Soc.*, 1973, **95**, 7183.
2794. K. Mochizuki, K. Toriumi and T. Ito, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 881.
2795. S. M. Hart, J. C. A. Boeyens, J. P. Michael and R. D. Hancock, *J. Chem. Soc., Dalton Trans.*, 1983, 1601.
2796. R. D. Hancock and V. J. Thom, *J. Am. Chem. Soc.*, 1982, **104**, 291.
2797. W. N. Setzer, C. A. Ogle, G. S. Wilson and K. S. Glass, *Inorg. Chem.*, 1983, **22**, 266.
2798. P. H. Davis, K. L. White and R. L. Bedford, *Inorg. Chem.*, 1975, **14**, 1753.
2799. W. Rosen and D. H. Busch, *J. Am. Chem. Soc.*, 1969, **91**, 1969.
2800. V. J. Thom and R. D. Hancock, *Inorg. Chim. Acta*, 1983, **77**, L231.
2801. M. Micheloni, P. Paoletti, L. Siegfried-Hertli and T. Kaden, *J. Chem. Soc., Dalton Trans.*, 1985, 1169.
2802. R. Bartsch, S. Hietkamp, S. Morton, H. Peters and O. Stelzer, *Inorg. Chem.*, 1983, **22**, 3624.
2803. T. A. Del Donno and W. Rosen, *Inorg. Chem.*, 1978, **17**, 3714.
2804. L. F. Lindoy and R. J. Smith, *Inorg. Chem.*, 1981, **20**, 1314.
2805. L. A. Drummond, K. Henrick, M. J. L. Kanagasundaram, L. F. Lindoy, M. McPartlin and P. A. Tasker, *Inorg. Chem.*, 1982, **21**, 3923.
2806. L.G. Armstrong, D. G. Grimsley, L. F. Lindoy, H. C. Lip, V. A. Norris and R. J. Smith, *Inorg. Chem.*, 1978, **17**, 2351.
2807. B. Wang and C. S. Chung, *J. Chem. Soc., Dalton Trans.*, 1982, 2565.
2808. G. Anderegg, A. Ekstrom, L. F. Lindoy and R. J. Smith, *J. Am. Chem. Soc.*, 1980, **102**, 2670.
2809. A. Ekstrom, L. F. Lindoy, H. C. Lip, R. J. Smith, H. J. Goodwin, M. McPartlin and P. A. Tasker, *J. Chem. Soc., Dalton Trans.*, 1979, 1.
2810. L. P. Battaglia, A. Bonamartini-Corradi and A. Mangia, *Inorg. Chim. Acta*, 1980, **39**, 211.
2811. K. R. Adam, L. F. Lindoy, R. J. Smith, G. Anderegg, K. Henrick, M. McPartlin and P. A. Tasker, *J. Chem. Soc., Chem. Commun.*, 1979, 812.
2812. K. Hendrick, L. F. Lindoy, M. McPartlin, P. A. Tasker and M. P. Wood, *J. Am. Chem. Soc.*, 1984, **106**, 1641.
2813. F. L. Urbach and D. H. Busch, *Inorg. Chem.*, 1973, **12**, 408.
2814. R. W. Hay, G. A. Lawrence and U. R. Shone, *J. Chem. Soc., Dalton Trans.*, 1976, 942.
2815. G. Brubaker and D. H. Busch, *Inorg. Chem.*, 1966, **5**, 2114.
2816. M. S. Elder, G. M. Prinz, P. Thornton and D. H. Busch, *Inorg. Chem.*, 1968, **7**, 2427.
2817. L. G. Scanlon, Y. Y. Tsoo, K. Toman, S. C. Cummings and D. W. Meek, *Inorg. Chem.*, 1982, **21**, 1215.
2818. L. G. Armstrong and L. F. Lindoy, *Inorg. Chem.*, 1975, **14**, 1322.
2819. H. J. Goodwin, K. Henick, L. F. Lindoy, M. McPartlin and P. A. Tasker, *Inorg. Chem.*, 1982, **21**, 3261.
2820. R. W. Kluiber and G. Sasso, *Inorg. Chim. Acta*, 1970, **4**, 226.
2821. D. L. Johnston and W. D. Horrocks, Jr., *Inorg. Chem.*, 1971, **10**, 687.
2822. R. A. Lalancette, D. J. Macchia and W. F. Furey, *Inorg. Chem.*, 1976, **15**, 548.
2823. P. B. Donaldson, P. A. Tasker and N. W. Alcock, *J. Chem. Soc., Dalton Trans.*, 1976, 2262.
2824. P. B. Donaldson, P. Haria and P. A. Tasker, *J. Chem. Soc., Dalton Trans.*, 1976, 2382.
2825. J. Riker-Nappier and D. W. Meek, *J. Chem. Soc., Chem. Commun.*, 1974, 442.
2826. R. Louis, B. Metz and R. Weiss, *Acta Crystallogr., Sect. B*, 1974, **30**, 774.
2827. R. Louis, Y. Agnus and R. Weiss, *Acta Crystallogr., Sect. B*, 1979, **35**, 2905.

2828. K. R. Adam, A. J. Leong, L. F. Lindoy, H. C. Lip, B. W. Skelton and A. H. White, *J. Am. Chem. Soc.*, 1983, **105**, 4645.
2829. P. A. Harding, K. Henrick, L. F. Lindoy, M. McPartlin and P. A. Tasker, *J. Chem. Soc., Chem. Commun.*, 1983, 1300.
2830. C. St. C. Black and I. A. McLean, *Chem. Commun.*, 1968, 1004.
2831. M. Ciampolini, N. Nardi, P. Dapporto and F. Zanobini, *J. Chem. Soc., Dalton Trans.*, 1984, 575.
2832. M. Ciampolini, N. Nardi, P. Dapporto and F. Zanobini, *J. Chem. Soc., Dalton Trans.*, 1984, 995.
2833. M. Ciampolini, N. Nardi, P. L. Orioli, S. Mangani and F. Zanobini, *J. Chem. Soc., Dalton Trans.*, 1985, 1425.
2834. M. Ciampolini, P. Dapporto, N. Nardi and F. Zanobini, *Inorg. Chem.*, 1983, **22**, 13.
2835. C. Mealli, M. Sabat, F. Zanobini, M. Ciampolini and N. Nardi, *J. Chem. Soc., Dalton Trans.*, 1985, 79.
2836. M. Ciampolini, N. Nardi, P. L. Orioli, S. Mangani and F. Zanobini, *J. Chem. Soc., Dalton Trans.*, 1984, 2265.
2837. M. Ciampolini, N. Nardi, P. L. Orioli, S. Mangani and F. Zanobini, *J. Chem. Soc., Dalton Trans.*, 1985, 1179.
2838. L. F. Lindoy and D. H. Busch, *J. Am. Chem. Soc.*, 1969, **91**, 4690.
2839. K. R. Adam, G. Anderegg, K. Henrick, A. J. Leong, L. F. Lindoy, H. C. Lip, M. McPartlin, R. J. Smith and P. A. Tasker, *Inorg. Chem.*, 1981, **20**, 4048.
2840. R. J. Motkeaitis, A. E. Martell, J. P. Lecompte and J. M. Lehn, *Inorg. Chem.*, 1983, **22**, 609.
2841. D. C. Olson and J. Vasilevskis, *Inorg. Chem.*, 1969, **8**, 1611.
2842. F. V. Lovecchio, E. S. Gore and D. H. Busch, *J. Am. Chem. Soc.*, 1974, **96**, 3109.
2843. D. G. Pillsbury and D. H. Busch, *J. Am. Chem. Soc.*, 1976, **98**, 78, 36.
2844. E. Zeigerson, I. Bar, J. Bernstein, L. J. Kirschenbaum and D. Meyerstein, *Inorg. Chem.*, 1982, **21**, 73.
2845. R. R. Gagne and D. M. Ingle, *J. Am. Chem. Soc.*, 1980, **102**, 1444.
2846. T. J. Truex and R. H. Holm, *J. Am. Chem. Soc.*, 1972, **94**, 4529.
2847. M. Millar and R. H. Holm, *J. Am. Chem. Soc.*, 1975, **97**, 6052.
2848. N. F. Curtis, *Chem. Commun.*, 1966, 882.
2849. C. J. Hipp, L. F. Lindoy and D. H. Busch, *Inorg. Chem.*, 1972, **11**, 1988.
2850. E. K. Barefield and D. H. Busch, *Inorg. Chem.*, 1971, **10**, 108.
2851. S. C. Tang and R. H. Holm, *J. Am. Chem. Soc.*, 1975, **97**, 3359.
2852. N. F. Curtis, *J. Chem. Soc.*, 1964, 2644.
2853. V. Katovic, L. T. Taylor, L. F. Urbach, W. H. White and D. H. Busch, *Inorg. Chem.*, 1972, **11**, 479.
2854. B. Fisher and R. Eisenberg, *J. Am. Chem. Soc.*, 1980, **102**, 7363.
2855. E. Kimura, R. Machida and M. Kodama, *J. Am. Chem. Soc.*, 1984, **106**, 5497.
2856. N. Matsumoto, K. Wakizaka and A. Ohyoshi, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 3165.
2857. C. J. Hipp and D. H. Busch, *Inorg. Chem.*, 1973, **12**, 894.
2858. F. Wagner and D. H. Barefield, *Inorg. Chem.*, 1976, **15**, 408.
2859. E. K. Barefield and F. Wagner, *Inorg. Chem.*, 1973, **12**, 2436.
2860. L. T. Taylor, F. L. Urbach and D. H. Busch, *J. Am. Chem. Soc.*, 1969, **91**, 1072.
2861. V. Katovic, L. T. Taylor and D. H. Busch, *Inorg. Chem.*, 1971, **10**, 458.
2862. B. Kamenar, B. Kaitner, V. Katovic and D. H. Busch, *Inorg. Chem.*, 1979, **18**, 815.
2863. V. Katovic, L. T. Taylor and D. H. Busch, *J. Am. Chem. Soc.*, 1969, **91**, 2122.
2864. N. P. Schammel, L. L. Zimmer and D. H. Busch, *Inorg. Chem.*, 1980, **19**, 3159.
2865. W. P. Shammel, K. S. B. Mertes, G. G. Christoph and D. H. Busch, *J. Am. Chem. Soc.*, 1979, **101**, 1622.
2866. B. Korybut-Daszkiewicz, M. Kojima, J. H. Cameron, N. Herron, M. Y. Chavan, A. J. Jircitano, B. K. Coltrain, G. L. Neer, N. W. Alcock and D. H. Busch, *Inorg. Chem.*, 1984, **23**, 903.
2867. N. Herron, M. Y. Chavan and D. H. Busch, *J. Chem. Soc., Dalton Trans.*, 1984, 1491.
2868. K. J. Takeuchi, D. H. Busch and N. Alcock, *J. Am. Chem. Soc.*, 1983, **105**, 4261.
2869. M. P. Suh, W. Shin, D. Kim and S. Kim, *Inorg. Chem.*, 1984, **23**, 618.
2870. S. B. Larson, J. N. Ramsden, S. H. Simonsen and J. J. Lagowski, *Acta Crystallogr., Sect. C*, 1983, **39**, 1646.
2871. J. M. Lehn, S. H. Pine, E. Watanabe and A. K. Willard, *J. Am. Chem. Soc.*, 1977, **99**, 6766.
2872. A. H. Alberts, J. M. Lehn and D. Parker, *J. Chem. Soc., Dalton Trans.*, 1985, 2311.
2873. A. B. P. Lever, *Adv. Inorg. Chem. Radiochem.*, 1965, **7**, 28.
2874. K. M. Smith (ed.), 'Porphyrins and Metalloporphyrins', Elsevier, Amsterdam, 1975.
2875. D. Dolphin (ed.), 'The Porphyrins', Academic, New York, 1978.
2876. J. E. Falk, 'Porphyrins and Metalloporphyrins', Elsevier, Amsterdam, 1964.
2877. A. W. Johnson, *Chem. Soc. Rev.*, 1975, **4**, 1.
2878. J. M. Robertson and I. Woodward, *J. Chem. Soc.*, 1937, 219.
2879. C. H. Yang and C. T. Chang, *J. Chem. Soc., Dalton Trans.*, 1982, 2539.
2880. N. A. Ebert and H. O. Gottlieb, *J. Am. Chem. Soc.*, 1952, **74**, 2806.
2881. P. A. Barrett, C. E. Dent and R. P. Linstead, *J. Chem. Soc.*, 1936, 1719.
2882. H. Kropf and D. J. Witt, *Z. Phys. Chem. (Leipzig)*, 1971, **76**, 331.
2883. A. Ulman, J. Gallucci, D. Fisher and J. Ibers, *J. Am. Chem. Soc.*, 1980, **102**, 6854.
2884. T. E. Phillips and B. M. Hoffman, *J. Am. Chem. Soc.*, 1977, **99**, 7734.
2885. J. F. Kirner, J. Garofalo, Jr. and W. R. Scheidt, *Inorg. Nucl. Chem. Lett.*, 1975, **11**, 107.
2886. E. F. Meyer, Jr., *Acta Crystallogr., Sect. B*, 1972, **28**, 2162.
2887. D. L. Cullen and E. F. Meyer, Jr., *J. Am. Chem. Soc.*, 1974, **96**, 2095.
2888. J. C. Gallucci, P. N. Swepston and J. A. Ibers, *Acta Crystallogr., Sect. B*, 1982, **38**, 2134.
2889. F. W. Kutzler, P. N. Swepston, Z. Berkovitch-Yellin, D. E. Ellis and J. A. Ibers, *J. Am. Chem. Soc.*, 1983, **105**, 2996.
2890. L. J. Pace, A. Ulman and J. Ibers, *Inorg. Chem.*, 1982, **21**, 199.
2891. L. J. Pace, J. Martinsen, A. Ulman, B. M. Hoffman and J. A. Ibers, *J. Am. Chem. Soc.*, 1983, **105**, 2612.
2892. E. B. Fleischer, *J. Am. Chem. Soc.*, 1963, **85**, 146.
2893. T. A. Hamor, W. S. Caughey and J. L. Haard, *J. Am. Chem. Soc.*, 1965, **87**, 2305.
2894. H. J. Callot, B. Chevrier and R. Weiss, *J. Am. Chem. Soc.*, 1979, **100**, 4733.
2895. J. Martinsen, L. J. Pace, T. E. Phillips, B. M. Hoffman and J. A. Ibers, *J. Am. Chem. Soc.*, 1982, **104**, 83.

2896 T. E. Phillips, R. P. Scaringe, B. M. Hoffman and J. A. Ibers, *J. Am. Chem. Soc.*, 1980, **102**, 3435.
2897. P. N. Dwyer, J. W. Buchler and W. R. Scheidt, *J. Am. Chem. Soc.*, 1974, **96**, 2789.
2898. B. Chevrier and W. Weiss, *J. Am. Chem. Soc.*, 1975, **97**, 1416.
2899. W. S. Caughey, R. M. Deal, B. D. McLees and J. O. Alben, *J. Am. Chem. Soc.*, 1962, **84**, 1735.
2900. A. MacCragh, C. B. Storm and W. S. Koski, *J. Am. Chem. Soc.*, 1965, **87**, 1470.
2901. S. J. Cole, G. C. Curthoys, E. A. Magnusson and J. N. Phillips, *Inorg. Chem.*, 1972, **11**, 1024.
2902. F. A. Walker, E. Hui and J. M. Walker, *J. Am. Chem. Soc.*, 1975, **97**, 2390.
2903. D. Dolphin, T. Niem, R. H. Felton and I. Fujita, *J. Am. Chem. Soc.*, 1975, **97**, 5288.
2904. K. M. Kadish and M. M. Morrison, *Inorg. Chem.*, 1976, **15**, 980.
2905. D. P. Arnold, A. W. Johnson and M. Winter, *J. Chem. Soc., Chem. Commun.*, 1976, 797.
2906. P. B. Hitchcock, *J. Chem. Soc., Dalton Trans.*, 1983, 2127.
2907. H. J. Callot and T. Tschamber, *J. Am. Chem. Soc.*, 1975, **97**, 6175.
2908. H. J. Callot, T. Tschamber and E. Schaeffer, *J. Am. Chem. Soc.*, 1975, **97**, 6178.
2909. C. J. Schramm, R. P. Scaringe, D. R. Stojakovic, B. M. Hoffman, J. A. Ibers and T. J. Marks, *J. Am. Chem. Soc.*, 1980, **102**, 6702.
2910. D. Dolphin, R. L. N. Harris, A. W. Johnson and I. T. Kay, *Proc. Chem. Soc.*, 1964, 359.
2911. A. Hamilton and A. W. Johnson, *Chem. Commun.*, 1971, 523.
2912. R. Grigg, A. W. Johnson, K. Richardson and K. W. Shelton, *Chem. Commun.*, 1967, 1192.
2913. D. Bormann, A. Fischli, R. Keese and A. Eschenmoser, *Angew. Chem., Int. Ed. Engl.*, 1967, **6**, 868.
2914. D. Dolphin, L. L. N. Harris, J. L. Huppartz, A. W. Johnson and I. T. Kay, *J. Chem. Soc. (C)*, 1966, 30.
2915. R. Grigg, A. W. Johnson and P. van den Brock, *Chem. Commun.*, 1967, 502.
2916. C. Angst, C. Kratky and A. Eschenmoser, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 263.
2917. A. P. Ginsberg, R. L. Martin, R. W. Brookes and R. C. Sherwood, *Inorg. Chem.*, 1972, **11**, 2884.
2918. K. O. Joung, C. J. O'Connor, E. Sinn and R. L. Carlin, *Inorg. Chem.*, 1979, **18**, 804.
2919. Y. Journaux and O. Kahn, *J. Chem. Soc., Dalton Trans.*, 1979, 1575.
2920. G. A. Bottomley, L. G. Glossop, C. L. Ralston, A. H. White and A. C. Willis, *Aust. J. Chem.*, 1978, **31**, 285.
2921. D. Knetsch and W. L. Groeneveld, *Inorg. Nucl. Chem. Lett.*, 1976, **12**, 27.
2922. B. M. Antti, *ACS Symp. Ser.*, 1975, **A29**, 76.
2923. C. P. Landee and R. D. Willett, *Inorg. Chem.*, 1981, **20**, 2521.
2924. P. L'Haridon and I. Bkouche-Waksman, *J. Inorg. Nucl. Chem.*, 1978, **40**, 2025.
2925. F. K. Ross and G. D. Stucky, *J. Am. Chem. Soc.*, 1970, **92**, 4538.
2926. E. J. Laskowski, T. R. Felthouse, D. N. Hendrickson and G. J. Long, *Inorg. Chem.*, 1976, **15**, 2908.
2927. G. J. Long and E. O. Schlemper, *Inorg. Chem.*, 1974, **13**, 279.
2928. H. S. Preston and C. H. L. Kennard, *J. Chem. Soc. (A)*, 1969, 2682.
2929. R. J. Butcher and E. Sinn, *Inorg. Chem.*, 1977, **16**, 2344.
2930. R. J. Butcher, C. J. O'Connor and E. Sinn, *Inorg. Chem.*, 1979, **18**, 492.
2931. J. C. Jansen, H. van Koningsveld, J. A. C. van Ooijen and J. Reedijk, *Inorg. Chem.*, 1980, **19**, 170.
2932. M. A. Laffey and P. Thornton, *J. Chem. Soc., Dalton Trans*, 1982, 313.
2933. M. B. Hursthouse, M. A. Laffey, P. T. Moore, D. B. New, P. P. Raithby and P. Thornton, *J. Chem. Soc. Dalton Trans.*, 1982, 307.
2934. J. H. Binks, G. J. Dorward, R. A. Howie and G. P. McQuillan, *Inorg. Chim. Acta*, 1981, **49**, 251.
2935. R. L. Lintvedt, L. L. Born, D. P. Murtha, J. M. Kuszaj and M. D. Glick, *Inorg. Chem.*, 1974, **13**, 18.
2936. J. W. Guthrie, R. L. Lintvedt and M. D. Glick, *Inorg. Chem.*, 1980, **19**, 2949.
2937. R. J. Irving, M. L. Post and D. C. Povey, *J. Chem. Soc., Dalton Trans.*, 1973, 697.
2938. P. Dapporto and L. Sacconi, *J. Chem. Soc. (A)*, 1970, 618; L. Banci and A. Dei, *Inorg. Chim. Acta*, 1980, **39**, 35.
2939. C. Mealli, S. Midollini and L. Sacconi, *Inorg. Chem.*, 1978, **17**, 632.
2940. R. J. Butcher, C. J. O'Connor and E. Sinn, *Inorg. Chem.*, 1982, **21**, 616.
2941. R. J. Butcher, C. J. O'Connor and E. Sinn, *Inorg. Chem.*, 1980, **20**, 3486.
2942. R. J. Butcher and E. Sinn, *Aust. J. Chem.*, 1979, **32**, 331.
2943. R. J. Butcher, J. Jasinski, G. M. Mackler and E. Sinn, *J. Chem. Soc. Dalton Trans.*, 1976, 1099.
2944. A. E. Svelasvili, *Acta Crystallogr., Sect A*, 1966, **21**, 153.
2945. J. Lipkowski and G. D. Andretti, *Met. Chem.*, 1978, **3**, 117.
2946. C. G. Pierpont, D. N. Hendrickson, D. M. Duggan, F. Wagner and E. K. Barefield, *Inorg. Chem.*, 1975, **14**, 604.
2947. F. Wagner, M. T. Mocella, M. J. D'Aniello, Jr., A. H.-J. Wang and E. K. Barefield, *J. Am. Chem. Soc.*, 1974, **96**, 2625.
2948. D. M. Duggan and D. N. Hendrickson, *Inorg. Chem.*, 1974, **13**, 2056.
2949. D. M. Duggan and D. N. Hendrickson, *Inorg. Chem.*, 1974, **13**, 2929.
2950. H. G. Segal and S. J. Lippard, *Inorg. Chem.*, 1977, **16**, 1623.
2951. A. Gleizes, A. Meyer, M. A. Hitchman and O. Kahn, *Inorg. Chem.*, 1982, **21**, 2257.
2952. N. F. Curtis, I. R. N. McCormick and T. N. Waters, *J. Chem. Soc., Dalton Trans.*, 1973, 1537.
2953. P. W. Ball and A. B. Blake, *J. Chem. Soc. (A)*, 1969, 1415.
2954. J. Kopf, U. Behrens, M. Kastner and G. Klar, *J. Inorg. Nucl. Chem.*, 1977, **39**, 889.
2955. D. M. Duggan, E. K. Barefield and D. N. Hendrickson, *Inorg. Chem.*, 1973, **12**, 985.
2956. A. R. Davis, F. W. B. Einstein and A. C. Willis, *Acta Crystallogr., Sect. B*, 1982, **38**, 443.
2957. C. G. Pierpont, L. C. Francesconi and D. N. Hendrickson, *Inorg. Chem.*, 1977, **16**, 2367.
2958. N. I. Kirillova, Yu. T. Struchkov, M. A. Porai-Koshits, A. A. Pasynskii, A. S. Antsyshkina, L. Kh. Minachfva, G. G. Sadikov, T. Ch. Idrisov and V. T. Kalinnikov, *Inorg. Chim. Acta*, 1980, **42**, 115.
2959. A. Bencini, C. Benelli, D. Gatteschi and C. Zanchini, *J. Am. Chem. Soc.*, 1980, **102**, 5820.
2960. M. Ahlgren, R. Hamalainen and U. Turpeinen, *Cryst. Struct. Commun.*, 1977, **6**, 829.
2961. M. Ahlgren and U. Turpeinen, *Acta Crystallogr., Sect. B*, 1982, **38**, 276.
2962. D. A. Sullivan and G. J. Palenik, *Inorg. Chem.*, 1977, **16**, 1127.

2963. J. E. Andrew and A. B. Blake, *J. Chem. Soc. (A)*, 1969, 1408.
2964. E. O. Schlemper and R. K. Murmann, *Inorg. Chem.*, 1974, **13**, 2424.
2965. I. Agnus, R. Louis, R. Jessen and R. Weiss, *Inorg. Nucl. Chem. Lett.*, 1976, **12**, 455.
2966. C. G. Pierpont, L. C. Francesconi and D. N. Hendrickson, *Inorg. Chem.*, 1978, **17**, 3470.
2967. S. L. Lambert and D. N. Hendrickson, *Inorg. Chem.*, 1979, **18**, 2683.
2968. C. L. Spiro, S. L. Lambert, T. J. Smith, E. N. Duesler, R. R. Gagne and D. N. Hendrickson, *Inorg. Chem.*, 1981, **20**, 1229.
2969. D. Gatteschi, C. Mealli and L. Sacconi, *J. Am. Chem. Soc.*, 1973, **95**, 2736.
2970. A. Bencini, D. Gatteschi and L. Sacconi, *Inorg. Chem.*, 1978, **17**, 2670.
2971. M. S. Haddad and D. N. Hendrickson, *Inorg. Chem.*, 1978, **17**, 2622.
2972. Y. Journaux, O. Kahn, B. Chevalier, J. Etourneau, R. Claude and A. Dworkin, *Chem. Phys. Lett.*, 1978, **55**, 140.
2973. A. Stebler, H. U. Gudel, A. Furrer and J. K. Kiems, *Inorg. Chem.*, 1982, **21**, 380.
2974. A. P. Ginsberg, *Inorg. Chim. Acta Rev.*, 1971, **5**, 45.
2975. C. G. Barraclough and R. W. Brookes, *J. Chem. Soc., Faraday Trans. 2*, 1974, **70**, 1364.
2976. P. W. Anderson, in 'Magnetism', ed. G. T. Rado and H. Suhl,, Academic, New York, 1983, vol. 1.
2977. P. J. Hay, J. C. Thibeault and R. Hoffmann, *J. Am. Chem. Soc.*, 1975, **97**, 4884.
2978. A. Bencini and D. Gatteschi, *Inorg. Chim. Acta*, 1978, **31**, 11.
2979. D. N. Hendrickson, in 'Magneto-structural Correlations in Exchange Coupled Systems', ed. R. D. Willett, D. Gatteschi and O. Kahn, Reidel, Dordrecht, 1985, p. 523.
2980. H. Gudel, in ref. 2979, p. 297.
2981. P. de Loth, P. Cassoux, J. P. Daudey and J. P. Malrieu, *J. Am. Chem. Soc.*, 1983, **103**, 4007.
2982. A. Bencini and D. Gatteschi, *Mol. Phys.*, 1985, **54**, 969.
2983. M. Nonoyama and K. Nonoyama, *J. Inorg. Nucl. Chem.*, 1981, **43**, 2567.
2984. M. Nonoyama, H. Ojima and K. Nonoyama, *Inorg. Chim. Acta*, 1982, **59**, 275.
2985. I. Morgenstern-Badarau, M. Rerat, O. Kahn, J. Jaud and J. Galy, *Inorg. Chem.*, 1982, **21**, 3050.
2986. S. Desjardins, I. Morgenstern-Badarau and O. Kahn, *Inorg. Chem.*, 1984, **23**, 3833.
2987. G. F. Kokoszka, H. C. Allen and G. Gordon, *J. Chem. Phys.*, 1965, **42**, 3020; E. Buluggiu, *J. Phys. Chem. Solids*, 1980, **41**, 1175.
2988. C. J. O'Connor, D. P. Freyberg and E. Sinn, *Inorg. Chem.*, 1979, **18**, 1077.
2989. L. Banci, A. Bencini, C. Benelli, A. Dei and D. Gatteschi, *Inorg. Chem.*, 1981, **20**, 1399.
2990. L. Banci, A. Bencini, D. Gatteschi and A. Dei, *Inorg. Chim. Acta*, 1979, **36**, L419.
2991. S. L. Lambert, C. L. Spiro, R. R. Gagne and D. N. Hendrickson, *Inorg. Chem.*, 1982, **21**, 68.
2992. L. Banci, A. Bencini, A. Dei and D. Gatteschi, *Inorg. Chem.*, 1981, **20**, 393.
2993. L. Banci, A. Bencini, C. Benelli and D. Gatteschi, *Inorg. Chem.*, 1982, **21**, 3868.
2994. A. Bencini and D. Gatteschi, in ref. 2979, p. 241.
2995. J. Hulliger, Ph.D. Thesis, University of Zurich, 1984.
2986. M. B. Hursthouse, M. A. Laffey, P. T. Moore, D. B. New, P. R. Raithby and P. Thornton, *J. Chem. Soc., Dalton Trans.*, 1982, 308.
2997. P. D. W. Boyd and R. L. Martin, *J. Chem. Soc. Dalton Trans.*, 1979, 92.
2998. C. W. Reimann and M. Zocchi, *Acta Crystallogr., Sect. B*, 1971, **27**, 682.
2999. D. J. Mackey and R. L. Martin, *J. Chem. Soc., Dalton Trans.*, 1978, 702.
3000. J. Meunier-Piret, P. Piret, J. Putzeys and M. van Meersche, *Acta Crystallogr., Sect. B*, 1976, **32**, 714.
3001. P. D. W. Boyd and R. L. Martin, *J. Chem. Soc., Dalton Trans.*, 1981, 1069.
3002. G. J. Long, D. Lindner, R. L. Lintvedt and J. W. Guthrie, *Inorg. Chem.*, 1982, **21**, 1431.
3003. J. A. Bertrand, A. P. Ginsberg, R. I. Kaplan, C. E. Kirkwood, R. L. Martin and R. C. Sherwood, *Inorg. Chem.*, 1971, **10**, 240.
3004. J. E. Andrew and A. B. Blake, *J. Chem. Soc. (A)*, 1969, 1456.
3005. W. L. Gladfelter, M. W. Lynch, W. P. Schaefer, D. N. Hendrickson and H. B. Gray, *Inorg. Chem.*, 1981, **20**, 2390.
3006. A. Meyer, A. Gleizes, J. J. Girerd, M. Verdaguer and O. Kahn, *Inorg. Chem.*, 1982, **21**, 1729.
3007. B. W. Dockum and W. M. Reiff, *Inorg. Chem.*, 1982, **21**, 2613.
3008. W. E. Estes, R. R. Weller and W. E. Hatfield, *Inorg. Chem.*, 1980, **19**, 26.
3009. H. T. Witteven, W. L. C. Rutten and J. Reedijk, *J. Inorg. Nucl. Chem.*, 1975, **37**, 913.
3010. J. A. C. van Oijen, J. Reedijk and L. Spek, *Inorg. Chem.*, 1979, **18**, 1184.
3011. A. B. Blake and W. E. Hatfield, *J. Chem. Soc., Dalton Trans.*, 1978, 868.
3012. M. M. Morelock, M. L. Good, L. M. Trefonas, D. Karraker, L. Maleki, H. R. Heichelberger, R. Majesteand and J. Dodge, *J. Am. Chem. Soc.*, 1979, **101**, 4858.
3013. A. P. Ginsberg, R. L. Martin and R. C. Sherwood, *Inorg. Chem.*, 1968, **7**, 932.
3014. L. Dubicki, G. A. Kakos and G. Winter, *Aust. J. Chem.*, 1968, **21**, 1461.
3015. L. J. de Jongh and A. R. Miedema, *Adv. Phys.*, 1974, **23**, **1**.
3016. M. E. Fisher, *J. Math. Phys.*, 1963, **4**, 124.
3017. S. Katsma, *Phys. Rev.*, 1962, **127**, 1508; 1963, **129**, 2835.
3018. J. C. Bonner and M. E. Fisher, *Phys. Rev. A*, 1964, **135**, 640.
3019. J. D. Dunitz, *Acta Crystallogr.*, 1957, **10**, 307.
3020. T. Watanabe, *J. Phys. Soc. Jpn.*, 1962, **17**, 1856.
3021. A. Hofman and W. Erhardt, *Ber.*, 1913, **46**, 1457.
3022. K. A. Jensen, *Z. Anorg. Allg. Chem.*, 1936, **229**, 275.
3023. R. D. Hall, *J. Am. Chem. Soc.*, 1907, **29**, 692.
3024. R. S. Nyholm, *J. Chem. Soc.*, 1951, 2602.
3025. K. Nag and A. Chakravorty, *Coord. Chem. Rev.*, 1980, **33**, 87.
3026. R. I. Haines and A. McAuley, *Coord. Chem. Rev.*, 1981, **39**, 77.
3027. A. McAuley and P. R. Norman, *Isr. J. Chem.*, 1985, **25**, 106.

3028. P. Cocolios and K. M. Kadish, *Isr. J. Chem.*, 1985, **25**, 138.
3029. L. Fabbrizzi, M. Licchelli, A. Perotti, A. Poggi and S. Soresi, *Isr. J. Chem.*, 1985, **25**, 112.
3030. A. Chakravorty, *Isr. J. Chem.*, 1985, **25**, 99.
3031. R. S. Nyholm and M. L. Tobe, *Adv. Inorg. Chem. Radiochem.*, 1963, **5**, 1.
3032. E. I. Baucom and R. S. Drago, *J. Am. Chem. Soc.*, 1971, **93**, 6469.
3033. A. Bencini and D. Gatteschi, *Transition Met. Chem.*, 1982, **8**, 1.
3034. A. H. Maki, N. Edelstein, A. Davison and R. H. Holm, *J. Am. Chem. Soc.*, 1964, **86**, 4580.
3035. A. Bencini, L. Fabbrizzi and A. Poggi, *Inorg. Chem.*, 1981, **20**, 2544.
3036. S. A. Jacobs and D. W. Margerum, *Inorg. Chem.*, 1984, **23**, 1195.
3037. C. F. Cook and N. F. Curtis, *Chem. Commun.*, 1967, 962.
3038. J. G. Mohanty, R. P. Singh and A. Chakravorty, *Inorg. Chem.*, 1975, **14**, 2178.
3039. J. G. Mohanty and A. Chakravorty, *Inorg. Chem.*, 1976, **15**, 2912.
3040. A. N. Singh, R. P. Singh, J. G. Mohanty and A. Chakravorty, *Inorg. Chem.*, 1977, **16**, 2597.
3041. A. N. Singh and A. Chakravorty, *Inorg. Chem.*, 1980, **19**, 969.
3042. E. S. Gore and D. H. Busch, *Inorg. Chem.*, 1973, **12**, 1.
3043. M. C. Rakowski, M. Rychek and D. H. Busch, *Inorg. Chem.*, 1975, **14**, 1194.
3044. J. C. Brodovitch and A. McAuley, *Inorg. Chem.*, 1981, **20**, 1667.
3045. R. S. Nyholm, *J. Chem. Soc.*, 1950, 20, 61.
3046. L. F. Warren and M. A. Bennett, *Inorg. Chem.*, 1976, **15**, 3126.
3047. F. P. Bossu and D. W. Margerum, *J. Am. Chem. Soc.*, 1976, **98**, 4003.
3048. Y. Sugima and Y. Mino, *Inorg. Chem.*, 1979, **18**, 1336.
3049. E. K. Barefield and D. H. Busch, *Chem. Commun.*, 1970, 523.
3050. M. Simek, *Collect. Czech. Chem. Commun.*, 1962, **27**, 220, 461.
3051. R. K. Panda, S. Acharya, G. Neogi and D. Ramaswamy, *J. Chem. Soc., Dalton Trans.*, 1983, 1225.
3052. D. C. Olsen and J. Vasilevskis, *Inorg. Chem.*, 1969, **8**, 1611.
3053. G. Ferraudi, *Inorg. Chem.*, 1979, **18**, 3230.
3054. G. Ferraudi and L. Patterson, *J. Chem. Soc., Chem. Commun.*, 1977, 755.
3055. G. Ferraudi and S. Muralidharan, *Inorg. Chem.*, 1981, **20**, 4262.
3056. F. V. Lovecchio, E. S. Gore and D. H. Busch, *J. Am. Chem. Soc.*, 1974, **96**, 3109.
3057. J. J. Czarnecki and D. W. Margerum, *Inorg. Chem.*, 1977, **16**, 1997.
3058. F. P. Bossu and D. W. Margerum, *Inorg. Chem.*, 1977, **16**, 1210.
3059. A. G. Lappin, C. K. Murray and D. W. Margerum, *Inorg. Chem.*, 1978, **17**, 1630.
3060. G. V. Buxton and R. M. Sellers, *Coord. Chem. Rev.*, 1977, **22**, 195.
3061. J. Lati and D. Meyerstein, *Inorg. Chem.*, 1972, **11**, 2397.
3062. H. Cohen, L. J. Kirschenbaum, E. Zeigerson, G. Ginsburg, M. Jaacobi, E. Fuchs and D. Meyerstein, *Inorg. Chem.*, 1979, **18**, 2763.
3063. K. D. Whitburn and G. S. Lawrence, *J. Chem. Soc., Dalton Trans.*, 1979, 139.
3064. P. Maruthanutha, L. K. Patterson and G. Ferraudi, *Inorg. Chem.*, 1978, **17**, 3157.
3065. M. Jaacobi, D. Meyerstein and J. Lilie, *Inorg. Chem.*, 1979, **18**, 429.
3066. Q. J. Mulazzini, M. D. Ward, G. Semerano, S. S. Emmi and P. Giordani, *Int. J. Radiat. Phys. Chem.*, 1974, **6**, 87.
3067. S. C. Jain, K. V. Reddy, C. L. Gupta and T. R. Reddy, *Chem. Phys. Lett.*, 1973, **21**, 150.
3068. S. C. Jain, K. V. Reddy and T. R. Reddy, *J. Chem. Phys.*, 1975, **62**, 4366.
3069. S. I. Zanette, A. O. Cardie and J. Danon, *J. Chem. Phys.*, 1976, **64**, 3381.
3070. J. Lati and D. Meyerstein, *Inorg. Chem.*, 1972, **11**, 2393.
3071. J. Lati, J. Koresh and D. Meyerstein, *Chem. Phys. Lett.*, 1975, **33**, 286.
3072. J. Lati and D. Meyerstein, *J. Chem. Soc., Dalton Trans.*, 1978, 1105.
3073. A. V. Babaeva, I. B. Baranovskii and G. G. Afanas'eva, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1965, **10**, 686.
3074. A. V. Babaeva, V. I. Belova, Ya. K. Sirkin and G. G. Afanas'eva, *Russ. J. Inorg. Chem.* (*Engl. Transl*), 1969, **13**, 660.
3075. I. B. Baranovskii and G. Ya. Mazo, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1975, **20**, 244.
3076. M. Yamashita, Y. Nonaka, S. Kida, Y. Hamane and R. Aoki, *Inorg. Chim. Acta*, 1981, **52**, 43.
3077. G. C. Papavassiliou and D. Layek, *Z. Naturforsch., Teil B*, 1982, **37**, 1406.
3078. D. A. Cooper, S. J. Higgins and W. Levason, *J. Chem. Soc., Dalton Trans.*, 1983, 2131.
3079. J. C. Brodovitch, R. I. Haines and A. McAuley, *Can. J. Chem.*, 1981, **59**, 1610.
3080. C. F. Wells and D. Fox, *J. Chem. Soc., Dalton Trans.*, 1977, 1498.
3081. C. F. Wells and D. Fox, *J. Chem. Soc., Dalton Trans.*, 1977, 1502.
3082. J. K. Brown, D. Fox, M. P. Heyward and C. F. Wells, *J. Chem. Soc., Dalton Trans.*, 1979, 735.
3083. J. J. Bour and J. J. Steggerda, *Chem. Commun.*, 1967, 2, 85.
3084, J. J. Bour, P. J. M. W. L. Birker and J. J. Steggerda, *Inorg. Chem.*, 1971, **10**, 1202.
3085. D. Sen and C. Saha, *J. Chem. Soc., Dalton Trans.*, 1976, 776.
3086. P. Spacu, C. Gheorgiu and A. Nicolaescu, *Inorg. Chim. Acta*, 1968, **2**, 413.
3087. A. G. Lappin, C. K. Murray and D. W. Margerum, *Inorg. Chem.*, 1978, **17**, 1630.
3088. M. P. Youngblood and D. W. Margerum, *Inorg. Chem.*, 1980, **19**, 3068.
3089. G. E. Kivan and D. W. Margerum, *Inorg. Chem.*, 1985, **24**, 3245.
3090. T. L. Pappenhagen, W. R. Kennedy, C. P. Bowers and D. W. Margerum, *Inorg. Chem.*, 1985, **24**, 4356.
3091. F. P. Bossu, K. L. Chellappa and D. W. Margerum, *J. Am. Chem. Soc.*, 1977, **99**, 2195.
3092. J. M. Raycheba and D. W. Margerum, *Inorg. Chem.*, 1981, **20**, 1441.
3093. C. K. Murray and D. W. Margerum, *Inorg. Chem.*, 1983, **22**, 463.
3094. G. D. Owens, D. A. Phillips, J. J. Czarnecki, J. M. T. Raycheba and D. W. Margerum, *Inorg. Chem.*, 1984, **23**, 1345.
3095. F. R. Bossu, E. B. Paniago, D. W. Margerum, S. T. Kirksey, Jr. and J. L. Kurtz, *Inorg. Chem.*, 1978, **17**, 1034.
3096. E. J. Subak, V. M. Loyola and D. W. Margerum, *Inorg. Chem.*, 1985, **24**, 4350.

3097. T. Sakuray, J. Hongo, A. Nakahara and Y. Nakao, *Inorg. Chim. Acta*, 1980, **46**, 205.
3098. A. Gleizes, T. J. Marks and J. A. Ibers, *J. Am. Chem. Soc.*, 1975, **97**, 3545.
3099. A. S. Foust and R. H. Soderberg, *J. Am. Chem. Soc.*, 1967, **89**, 5507.
3100. M. Cowie, A. Gleizes, G. W. Grynkewich, D. W. Kalina, M. S. McClure, R. P. Scaringe, R. C. Teitelbaum, S. L. Ruby, J. A. Ibers, C. R. Kannewurf and T. J. Marks, *J. Am. Chem. Soc.*, 1979, **101**, 2921.
3101. L. A. Brown, D. W. Kalina, M. S. McClure, S. Schultz, S. L. Ruby, J. A. Ibers, C. R. Kannewurf and T. J. Marks, *J. Am. Chem. Soc.*, 1979, **101**, 2937.
3102. H. Endres, H. J. Keller, W. Moroni and J. Weiss, *Acta Crystallogr., Sect. B*, 1975, **31**, 2357.
3103. H. Endres, H. J. Keller, M. Megnamisi-Belombe, W. Moroni, H. Pritzkow, J. Weiss and R. Comes, *Acta Crystallogr., Sect. A*, 1976, 32, 954.
3104. A. McAuley and K. F. Preston, *Inorg. Chem.*, 1983, **22**, 2111.
3105. D. M. Grove, G. van Koten, R. Zoet, N. W. Murral and A. J. Welch, *J. Am. Chem. Soc.*, 1983, **105**, 1379.
3106. G. Sproul and G. D. Stucky, *Inorg. Chem.*, 1973, **12**, 2898.
3107. J. Korvenranta, H. Saarinen and M. Nasakkala, *Inorg. Chem.*, 1982, **21**, 4296.
3108. H. Saarinen, J. Korvenranta and M. Nasakkala, *Acta Chem. Scand., Ser. A*, 1980, **34**, 443.
3109. E. O. Schlemper and R. K. Murray, *Inorg. Chem.*, 1983, **22**, 1077.
3110. F. Feigl, *Chem. Ber.*, 1924, **57**, 758.
3111. A. Chakravorty, *Coord. Chem. Rev.*, 1974, **13**, 1.
3112. J. Lati and D. Meyerstein, *Isr. J. Chem.*, 1972, **10**, 735.
3113. D. G. Batyr and L. Ya. Kistruga, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1975, **20**, 69.
3114. D. J. Davis and E. A. Boudreaux, *J. Electroanal. Chem.*, 1964, **8**, 434.
3115. L. E. Edelman, *J. Am. Chem. Soc.*, 1950, **72**, 5765, 5507.
3116. H. J. Keller and K. Seibold, *J. Am. Chem. Soc.*, 1971, **93**, 1309.
3117. I. N. Marov, E. K. Ivanova, A. T. Paniflov and N. P. Luneva, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1975, **20**, 67.
3118. L. F. Mehne and B. B. Wayland, *Inorg. Chem.*, 1975, **14**, 881.
3119. G. Neogi, S. Acharya, R. K. Panda and D. Ramaswamy, *J. Chem. Soc., Dalton Trans.*, 1983, 1233; 1983, 1239; 1984, 1477; 1984, 1471.
3120. A. E. Underhill, D. M. Watkins and R. Pethig, *Inorg. Nucl. Chem. Lett.*, 1973, **9**, 1269.
3121. J. S. Miller and C. H. Griffiths, *J. Am. Chem. Soc.*, 1977, **99**, 749.
3122. J. Mohanty, R. P. Singh, A. N. Singh and A. Chakravorty, *J. Indian Chem. Soc.*, 1977, **54**, 219.
3123. D. H. MacCartney and A. McAuley, *Can. J. Chem.*, 1983, **103**, 61.
3124. S. F. Munn, A. M. Lannon, M. C. M. Laranjeira and A. G. Lappin, *J. Chem. Soc., Dalton Trans.*, 1984, 1371.
3125. D. M. MacCartney and A. McAuley, *J. Chem. Soc., Dalton Trans.*, 1984, 103.
3126. E. S. Gore and D. H. Busch, *Inorg. Chem.*, 1973, **12**, 1.
3127. P. K. Chan and C. K. Poon, *J. Chem. Soc., Dalton Trans.*, 1976, 858.
3128. P. Marauthamuthu, L. K. Patterson and G. Ferraudi, *Inorg. Chem.*, 1978, **17**, 3157.
3129. E. K. Barefield and M. T. Mocella, *J. Am. Chem. Soc.*, 1975, **97**, 4238.
3130. D. P. Rillema, J. F. Endicott and E. Papaconstantinou, *Inorg. Chem.*, 1971, **10**, 1739.
3131. H. Cohen, L. J. Kirschenbaum, E. Zeigerson, M. Jaacobi, E. Fuchs, G. Ginsburg and D. Meyerstein, *Inorg. Chem.*, 1979, **18**, 2763.
3132. L. Fabbrizzi, H. Cohen and D. Meyerstein, *J. Chem. Soc., Dalton Trans.*, 1983, 2125.
3133. D. H. Busch, D. G. Pillsbury, F. V. Lovecchio, A. M. Tait, Y. Hung, S. Jackels, M. C. Ramovski, W. P. Schammel and L. Y. Martin, *ACS Symp. Ser.*, 1977, **30**, 32.
3134. D. G. Pillsbury and D. H. Busch, *J. Am. Chem. Soc.*, 1978, **98**, 7836.
3135. F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 1952, 3570.
3136. E. K. Barefield, F. V. Lovecchio, V. E. Tokel, E. Ochiai and D. H. Busch, *Inorg. Chem.*, 1972, **11**, 283.
3137. M. C. Rakowski, M. Rycheck and D. H. Busch, *Inorg. Chem.*, 1975, **14**, 1194.
3138. L. Sabatini and L. Fabbrizzi, *Inorg. Chem.*, 1979, **18**, 438.
3139. E. Zeigerson, G. Ginsburg, N. Schwartz, Z. Luz and D. Meyerstein, *J. Chem. Soc., Chem. Commun.*, 1979, 241.
3140. D. H. Busch, *Acc. Chem. Res.*, 1978, **11**, 392.
3141. L. J. Kirschenbaum and R. I. Haines, *Inorg. Chim. Acta*, 1983, **76**, L127.
3142. A. McAuley, J. R. Morton and K. F. Preston, *J. Am. Chem. Soc.*, 1982, **104**, 7561.
3143. E. Zeigerson, I. Bar, J. Berstein, L. J. Kirschenbaum and D. Meyerstein, *Inorg. Chem.*, 1982, **21**, 73.
3144. T. Ito, M. Sugimoto, K. Toriumi and H. Ito, *Chem. Lett.*, 1981, 1477.
3145. M. J. van der Merwe, J. C. A. Boyedens and R. D. Hancock, *Inorg. Chem.*, 1983, **22**, 3489.
3146. P. S. Ray, A. S. Bhaduri and B. Das Sarma, *J. Indian Chem. Soc.*, 1948, **25**, 51.
3147. L. C. Baker and T. J. R. Weakley, *J. Inorg. Nucl. Chem.*, 1966, **28**, 497.
3148. C. M. Flynn and G. D. Stucky, *Inorg. Chem.*, 1969, **8**, 332.
3149. M. V. George and K. S. Balachandran, *Chem. Rev.*, 1975, **75**, 491.
3150. R. S. McEwens, *J. Phys. Chem.*, 1971, **75**, 1782.
3151. O. Glemser and J. Einherand, *Z. Anorg. Allg. Chem.*, 1950, **261**, 26, 43.
3152. H. Bode, K. Dehmelt and J. Witte, *Z. Anorg. Allg. Chem.*, 1969, **366**, 1.
3153. H. Bartl, H. Bode, G. Sterr and J. Witte, *Electrochim. Acta*, 1971, **16**, 615.
3154. L. D. Dyer, B. S. Borie, Jr. and G. P. Smith, *J. Am. Chem. Soc.*, 1954, **76**, 1499.
3155. W. Bronger, H. Bade and W. Klemm, *Z. Anorg. Allg. Chem.*, 1964, **333**, 188.
3156. J. J. Lander and L. A. Wooten, *J. Am. Chem. Soc.*, 1951, **73**, 2452.
3157. Y. Takeda, F. Kanamaru, M. Shimada and M. Koizumi, *Acta Crystallogr., Sect. B*, 1976, **332**, 2464.
3158. M. Arjomand and D. J. Machin, *J. Chem. Soc., Dalton Trans.*, 1975, 1055.
3159. Y. Takeda, T. Hashino, H. Miyamoto, F. Kanamaru, S. Kurne and M. Koizumi, *J. Inorg. Nucl. Chem.*, 1972, **34**, 1599.
3160. R. J. Marcisak and L. Katz, *J. Solid State Chem.*, 1978, **24**, 295.
3161. G. Blasse, *J. Inorg. Nucl. Chem.*, 1965, **27**, 993.

3162. A. Wold, B. Post and E. Banks, *J. Am. Chem. Soc.*, 1957, **79**, 4911.
3163. A. Wold and R. J. Arnott, *J. Phys. Chem. Solids*, 1959, **9**, 176.
3164. G. Demazeau, A. Marbeuf, M. Ponchard, P. Hagenmuller and J. B. Goodenough, *C. R. Hebd. Seances Acad. Sci.*, 1971, **272**, 2163.
3165. G. Demazeau, A. Marbeuf, M. Ponchard and P. Hagenmuller, *J. Solid State Chem.*, 1971, **3**, 582.
3166. J. B. Goodenough and P. M. Raccah, *J. Appl. Phys.*, 1965, **36**, 1030.
3167. W. C. Koehler and E. D. Wollan, *J. Phys. Chem. Solids*, 1957, **2**, 100.
3168. D. Cahen, J. A. Ibers and R. D. Shanon, *Inorg. Chem.*, 1972, **11**, 3211.
3169. C. M. Flynn, Jr. and M. T. Pope, *J. Am. Chem. Soc.*, 1970, **92**, 85.
3170. A. Koleyashi and T. Saski, *Chem. Lett.*, 1975, 1123.
3171. T. L. Comt and M. F. A. Dove, *J. Chem. Soc., Dalton Trans.*, 1973, 1995.
3172. W. Klemm, W. Brandt and R. Hoppe, *Z. Anorg. Allg. Chem.*, 1961, **303**, 179.
3173. H. Henkel and R. Hoppe, *Z. Anorg. Allg. Chem.*, 1969, **364**, 253.
3174. C. Hebecker and R. Hoppe, *Naturwissenschaften*, 1966, **50**, 106.
3175. E. Aller and R. Hoppe, *Z. Anorg. Allg. Chem.*, 1974, **405**, 167.
3176. R. Hoppe, *Isr. J. Chem.*, 1978, **17**, 48.
3177. L. Stein, J. M. Neil and G. R. Alms, *Inorg. Chem.*, 1969, **8**, 2472.
3178. M. J. Reisfield, L. B. Asprey and R. B. Penneman, *J. Mol. Spectrosc.*, 1969, **29**, 109.
3179. A. D. Westland, R. Hoppe and S. S. I. Kaseno, *Z. Anorg. Allg. Chem.*, 1965, **338**, 319.
3180. G. C. Allen and K. D. Warren, *Inorg. Chem.*, 1969, **8**, 753.
3181. G. C. Allen and K. D. Warren, *Inorg. Chem.*, 1969, **8**, 1895.
3182. G. C. Allen, D. W. Clack and M. S. Farrimond, *J. Chem. Soc., (A)*, 1971, 2728.
3183. K. A. Jensen and B. Nygaard, *Acta Chem. Scand.*, 1949, **3**, 474.
3184. K. A. Jensen, B. Nygaard and C. T. Pedersen, *Acta Chem. Scand.*, 1963, **17**, 1126.
3185. S. J. Higgins, W. Levason and D. J. Wilkes, *Inorg. Chim. Acta*, 1984, **84**, 1.
3186. J. K. Stalick and J. A. Ibers, *Inorg. Chem.*, 1970, **9**, 453.
3187. D. W. Meek, E. C. Alyea, J. K. Stalick and J. A. Ibers, *J. Am. Chem. Soc.*, 1964, **91**, 4920.
3188. C. E. Wymore and J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, 1960, **14**, 42.
3189. G. Booth and J. Chatt, *J. Chem. Soc.*, 1965, 3238.
3190. G. R. van Heeke and W. D. Horrocks, Jr., *Inorg. Chem.*, 1966, **5**, 1968.
3191. P. K. Bernstein, G. A. Rodley, R. Marsh and H. B. Gray, *Inorg. Chem.*, 1972, **11**, 3040.
3192. L. S. Gray, S. J. Higgins, W. Levason and M. Webster, *J. Chem. Soc., Dalton Trans.*, 1984, 459.
3193. C. N. Sethulakshmi, S. Subramanian, M. A. Bennett and P. T. Manoharan, *Inorg. Chem.*, 1979, **18**, 2520.
3194. E. Balasivasubramanian, C. N. Sethulekshmi and P. T. Manoharan, *Inorg. Chem.*, 1982, **21**, 1684.
3195. P. T. Manoharan and M. T. Rogers, *J. Chem. Phys.*, 1970, **53**, 1682.
3196. P. K. Bernstein and H. B. Gray, *Inorg. Chem.*, 1972, **11**, 3035.
3197. A. Davison, N. Edelstein, R. H. Holm and A. M. Maki, *Inorg. Chem.*, 1963, **2**, 1227.
3198. J. F. Weiher, L. R. Melby and R. E. Benson, *J. Am. Chem. Soc.*, 1964, **86**, 4329.
3199. A. Kobayashi and S. Yukiyoshi, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 2650.
3200. N. A. Perez-Albuerne, L. C. Isett and R. K. Haller, *J. Chem. Soc., Chem. Commun.*, 1977, 417.
3201. A. Davison, N. Edelstein, R. H. Holm and A. H. Maki, *J. Am. Chem. Soc.*, 1963, **85**, 2029.
3202. C. J. Fritchie, Jr., *Acta Crystallogr.*, 1966, **20**, 107.
3203. B. L. Ramakrishna and P. T. Manoharan, *Inorg. Chem.*, 1983, **22**, 2113.
3204. I. S. Jacobs, H. R. Hart, L. V. Interrante, J. W. Bray, J. S. Kasper, G. D. Watkins, D. E. Prober, W. P. Wolf and J. C. Bonner, *Physica B + C (Amsterdam)*, 1977, **86–88**, 655.
3205. I. S. Jacobs, L. V. Interante and H. C. Hart, Jr., *AIP Conf. Proc.*, 1975, **24**, 355.
3206. W. E. Geiger, Jr. and A. H. Maki, *J. Phys. Chem.*, 1971, **75**, 2387.
3207. A. Singhabhandhu, P. D. Robinson, J. M. Fang and W. E. Geiger, Jr., *Inorg. Chem.*, 1975, **14**, 318.
3208. R. M. Wing and R. L. Schlupp, *Inorg. Chem.*, 1970, **9**, 471.
3209. C. Mahadevan, M. Seshasayee, B. V. R. Murthy, P. Kuppusamy and P. T. Manoharan, *Acta Crystallogr., Sect. C*, 1983, **39**, 1335.
3210. W. Levason and C. A. McAuliffe, *Coord. Chem. Rev.*, 1974, **12**, 171.
3211. C. T. Vance, R. D. Bereman, J. Bordner, W. E. Hatfield and H. Helms, *Inorg. Chem.*, 1985, **24**, 2905.
3212. R. H. Holm, A. K. Bolch, A. Davison, A. H. Maki and T. E. Berry, *J. Am. Chem. Soc.*, 1967, **89**, 2866.
3213. R. D. Schmitt and A. H. Maki, *J. Am. Chem. Soc.*, 1968, **90**, 2288.
3214. J. A. McCleverty, *Prog. Inorg. Chem.*, 1969, **10**, 49.
3215. G. N. Schrauzer, in 'Transition Metal Chemistry', ed. R. L. Carlin, Arnold, London, 1968, p. 299.
3216. A. Davison and E. T. Shard, *Inorg. Chem.*, 1970, **9**, 1821.
3217. A. H. Maki, N. Edelstein, A. Davison and R. H. Holm, *J. Am. Chem. Soc.*, 1964, **86**, 4580.
3218. L. Alcacer and A. H. Maki, *J. Phys. Chem.*, 1974, **78**, 215.
3219. L. Alcacer and A. H. Maki, *J. Phys. Chem.*, 1976, **80**, 1912.
3220. J. A. Ibers, L. J. Pace, J. Martinsen and B. M. Hoffman, *Struct. Bonding (Berlin)*, 1982, **50**, 3.
3221. B. M. Hoffman, J. Martinsen, L. J. Pace and J. A. Ibers, in 'Extended Linear Chain Compounds', ed. J. S. Miller, Plenum, New York, 1981, p. 459.
3222. W. Dietsch, K. Krimse, E. Hoyer, V. Belayeva and Z. N. Morov, *Inorg. Chem.*, 1978, **17**, 1665.
3223. J. Willemse, J. A. Cras, J. J. Steggerda and C. P. Keijzers, *Struct. Bonding (Berlin)*, 1976, **28**, 83.
3224. P. M. Solozjenkin and N. Kopitsja, *Dokl. Akad. Nauk Tadzh. SSR*, 1969, **12**, 30.
3225. D. Lachenal, *Inorg. Nucl. Chem. Lett.*, 1975, **11**, 101.
3226. J. Willemse and P. H. F. M. Rouwette, *Inorg. Nucl. Chem. Lett.*, 1972, **8**, 389.
3227. J. P. Fackler, Jr., A. Avderf and G. R. Fischer, *J. Am. Chem. Soc.*, 1973, **95**, 774.
3228. A. Avderf, J. P. Fackler, Jr. and R. G. Fisher, *J. Am. Chem. Soc.*, 1970, **92**, 6972.
3229. H. C. Brinkhoff, J. A. Cras, J. J. Steggerda and J. Willemse, *Recl. Trav. Chim. Pays-Bas*, 1969, **88**, 633.
3230. P. T. Beurskens and J. A. Cras, *J. Cryst. Mol. Struct.*, 1971, **1**, 63.
3231. J. Kaiser, W. Dietzsch, R. Richter, L. Golic and J. Siftar, *Acta Crystallogr., Sect. B*, 1980, **36**, 147.

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Palladium

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Because of factors beyond the editors' control, the submission of manuscripts for this chapter was delayed. In order to minimize any delay in publishing 'Comprehensive Coordination Chemistry' as a whole, the coverage of palladium appears at the end of this volume, commencing on page 1099.

52 Platinum

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52.1 INTRODUCTION

The chemistry of platinum has been studied for some 250 years. The metal has numerous uses in catalysis, jewelry and electrical applications, and the study of the complexes has been pivotal in the development of coordination chemistry. Among the landmarks in the coordination chemistry of platinum is the isolation of Zeise's salt $K[PtCl_3(C_2H_4)]\cdot H_2O$ in 1830.[1] The substitution chemistry of platinum(II) was also of early significance. The *trans* effect was discovered by carrying out substitution reactions on platinum(II) complexes.[2] These studies have been extensively used for the specific synthesis of *cis* and *trans* platinum(II) complexes. More recently platinum complexes having non-integral oxidation states have been studied because of their electrical conductivity, and the discovery of *cis*-$PtCl_2(NH_3)_2$ as a chemotherapeutic agent has led to the development of platinum chemistry with biological goals.

Complexes of platinum are commonly in oxidation states 0, II or IV. This is a rather unusual situation in transition metal chemistry. Although all the transition elements exhibit a range of oxidation states, platinum is one of the very few with three oxidation states differing by two electrons each. This has led to there being a wide range of oxidative addition chemistry in both oxidation state 0 and II. Since platinum is a third row transition element, the large values of the ligand field lead to low-spin, kinetically inert d^6 complexes of platinum(IV) with hexacoordinate structures, and low-spin kinetically inert d^8 complexes of platinum(II) having tetracoordinate planar geometry. Complexes of platinum(0) are fewer, and examples are known where the platinum is two, three or four coordinate. The ground state configuration can be considered to be d^{10} or d^9s^1. Stabilization of platinum(0) is accomplished with phosphine, arsine or isocyanide ligands, but $Pt(CO)_4$ is not thermally stable.

Mechanistic studies on platinum(II) complexes, primarily in the laboratories of Basolo and Pearson, have been fundamental in understanding substitution reactions at square planar platinum. This work has led to the identification of associative and dissociative pathways in these replacement reactions, and the effect of leaving and entering groups has been correlated in much the same way as has been done for substitution at saturated carbon. The concept of ligand nucleophilicity to platinum was developed by this group, and much of their work is collected in a book dealing with inorganic reaction mechanisms.[3]

Among the less common oxidation states those of I and III have the most significance. Complexes of platinum(III) have been of interest for many years because of their intermediacy in substitution reactions of platinum(II) and (IV). More recently binuclear platinum(I) and (III) complexes have been isolated, and the chemistry of these new complexes will be of increasing interest in platinum chemistry. Platinum forms strong homometallic bonds giving rise to multimetallic chain compounds and cluster complexes. The increasing use of X-ray crystallography, and ^{31}P and ^{195}Pt NMR will allow systematic studies to be made on these multimetallic platinum complexes.

Four comprehensive sources are available for platinum chemistry, three of which are written in the English language. The companion volume 'Comprehensive Organometallic Chemistry' has a chapter devoted to platinum,[4] and three books are of primary importance to readers with an interest in the coordination chemistry of platinum. The books by Belluco[5] and Muraveiskaya[6] are restricted to the organometallic and coordination chemistry of platinum, and Hartley's book is entitled, 'The Chemistry of Platinum and Palladium'.[7] It is assumed that readers will use these sources in conjunction with this chapter. For earlier literature this chapter will reference these sources or other review articles for extensive details. As a consequence this chapter will be comprehensive in coverage, but emphasis on detail will be primarily focused in the literature published in the last decade.

52.2 PLATINUM HYDRIDE COMPLEXES

52.2.1 Introduction

Hydride complexes of platinum have received considerable study since the preparation of $PtHCl(PEt_3)_2$.[8] Spectroscopic studies by ^1H NMR techniques have been widely used because of the structural information which can be obtained from coupling constant data to ^{195}Pt and other nuclei. Platinum is widely used as a heterogeneous catalyst, and vibrational studies on platinum hydride complexes have been useful for comparison of a hydrogen atom bonded to a single platinum with that bonded to a surface. Complexes of platinum have been used to catalyze hydrogenation, hydrosilylation and isomerization reactions with alkenes and alkynes, as well as H/D exchange reactions on alkanes. Hydride complexes are frequently proposed as intermediates in these reactions, and the pathways related to the known chemistry of hydride complexes.

A number of general reviews on transition metal hydride complexes have been written which include platinum hydrides,[9–13] and a specialist review on hydride complexes of the nickel triad gives a comprehensive treatment of platinum hydrides.[14] For hydrides bridging two metals the field has been reviewed for platinum complexes.[15] With hydride complexes the charge on the hydrogen ligand is always a subject of interest. A method using a modification of the Mulliken electronic population analysis has been used to show that there is at least partial negative charge on the hydride ligand in *trans*-$PtH_2(PH_3)_2$.[16] Using *ab initio* molecular orbital theory and effective potentials there is good agreement between experimental and calculated bond lengths, bond angles and vibrational frequencies.[17] These calculations also agree with XPES measurements where an effective charge of −0.6 for the H atom is obtained in $PtHCl(PR_3)_2$ and $PtH(SnCl_3)(PR_3)_2$.[18] Calculations have also been made using the CNDO method, and these data have correlated with the known high *trans* effect of the hydride ligand.[14,19]

52.2.2 Synthetic Methods

Platinum hydrides are among the most diverse for the range of synthetic methods used in their synthesis. Both protonation by strong acid and ligand substitution by hydride ligands have been used, in addition to methods involving the cleavage of strong O—H, N—H and C—H bonds. An earlier review outlines the scope of these reactions, and gives an extensive list of known platinum hydride complexes.[14]

52.2.2.1 Reaction with hydrazine

This method is not usually one of general use, but it was a method employed in the synthesis of the first hydride complex of platinum, $PtHCl(PEt_3)_2$.[8]

52.2.2.2 Reaction with metallohydrides such as borohydride and aluminum hydride

This method is a useful one for converting $PtCl_2L_2$ (L = tertiary phosphine) into $PtHClL_2$.[8] Alternatively high yields of *trans*-$PtHClL_2$ (L = tertiary phosphine) can be obtained on treating $PtCl_2$(cod) with 2 moles of phosphine L and one equivalent of $NaBH_4$.[20] If BH_3CN^- is used, the cyano group is also abstracted and complexes of the type $PtHCNL_2$ are formed (equation 1).[21]

$$PtCl_2(cod) + 2L + NaBH_4 \longrightarrow trans\text{-}PtHClL_2 + NaCl + cod + \tfrac{1}{2}B_2H_6 \qquad (1)$$

52.2.2.3 Protonation reactions

The earlier literature on patterns of reactivity in the formation of platinum hydrides by protonation reactions of platinum in zerovalent and divalent oxidation states has been briefly summarized in a short review.[22] The interaction of protonic acids with platinum(0) compounds involves initial protonation at platinum to yield a cationic hydride complex (**1**). For acids HX where X^- is a poor ligand for platinum(II), *e.g.* ClO_4^-, HSO_4^-, $MeCO_2^-$, NO_3^-, complex (**1**) is the final product. When X^- coordinates strongly to platinum(II), *e.g.* Cl^-, Br^-, I^-, CN^-, Ph_2PO^-, substitution occurs and the complex $PtHX(PPh_3)_2$ (**2**) is formed (equation 2).[23,24] The structure of $[PtH(PPh_3)_3](CF_3CO_2)_2H$ shows that the hydrogen atom occupies a stereochemical position[9] in the platinum(II) plane, but that the mutually *trans* phosphine ligands are bent toward the hydride with respective P—Pt—P angles of 99.7(2)° and 100.6(2)°.[25] The carboxylate ligand is not coordinated to platinum. The upfield hydride NMR resonance shows effects due to higher order transitions since the center line resonance shows an apparent difference in spin multiplicity from the lines resulting from coupling to ^{195}Pt.[24] Oxidative addition of carboxylic acids to the two-coordinate complex $Pt(PCy_3)_2$ (Cy = cyclohexyl) proceeds in a different manner to give $PtH(O_2CR)(PCy_3)_2$ (**3**) with the carboxylate group coordinated (equation 3).[26] Use of a thiocarboxylic acid with $Pt(PPh_3)_3$, however, results in the acid being a good conjugate base for platinum(II), and the neutral complex (**4**; equation 4) results. The *t*-butylphosphine complex $Pt(PBu^t_3)_2$ reacts in an analogous way to the cyclohexylphosphine complex with HX to give $PtHX(PBu^t_3)_2$ (X = Cl, Br, I, O_2CCF_3).[27] Subsequent metathetical replacement by NO_3^- or CN^- gives $PtHX(PBu^t_3)_2$ (X = ONO_2, CN).

$$Pt(PPh_3)_3 + HX \rightleftharpoons \underset{(\mathbf{1})}{PtH(PPh_3)_3^+X^-} \rightleftharpoons \underset{(\mathbf{2})}{PtHX(PPh_3)_2} + PPh_3 \qquad (2)$$

$$Pt(PCy_3)_2 + RCO_2H \longrightarrow \underset{(\mathbf{3})}{PtH(O_2CR)(PCy_3)_2} \qquad (3)$$

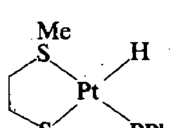
$$Pt(PPh_3)_3 + MeCOSH \longrightarrow \underset{(\mathbf{4})}{PtH(SCOMe)(PPh_3)_2} \qquad (4)$$

For thiolato ligands a series of complexes $PtH(SC_6H_4Y\text{-}p)(PPh_3)_2$ (Y = NO_2, Br, Cl, F, H, Me, MeO, NH_2) has been prepared. Good correlations have been obtained when ν(PtH) or *J*(PtH) is plotted against the Hammett substituent parameter σ_p.[28] These linear correlations are discussed in terms of electron density changes at platinum due to the mesomeric and inductive effects of the *para* substituent. These results complement earlier studies showing how values for ν(PtH), δ(PtH) or *J*(PtH) can be correlated with substituent effects on the *trans* ligand X (X = carboxylate), or with the *trans* influence of X.[14] Similar hydrides (**5**) have been obtained by the addition of areneselenols to $Pt(PPh_3)_3$ (equation 5).[29] In a detailed study, simple thiols RSH (R = Et) were found to undergo reversible oxidative addition to $Pt(PPh_3)_3$ (equation 6). When the thiol has a substituent with a potential complexing ligand for platinum(II) the resulting hydride (**6**) is stable (equation 7). This enhanced reactivity by intramolecular chelation has been referred to as 'chelate-assisted oxidative addition'.[30]

$$PtL_4 + p\text{-}YC_6H_4SeH \longrightarrow \underset{(\mathbf{5})}{PtH(SeC_6H_4Y\text{-}p)L_2} + L_2 \qquad (5)$$

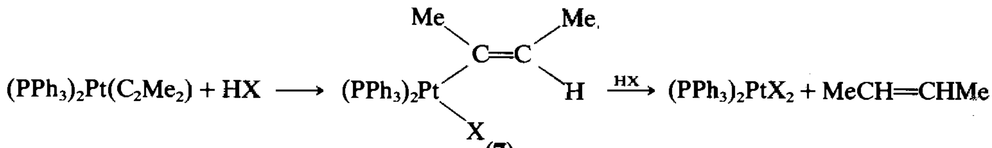
$$Pt(PPh_3)_3 + RSH \rightleftharpoons PtH(SR)(PPh_3)_2 + PPh_3 \qquad (6)$$

$$Pt(PPh_3)_2 + MeSCH_2CH_2SH \longrightarrow \qquad (7)$$



(**6**)

The reaction of $Pt(PPh_3)_4$, $Pt(C_2H_4)(PPh_3)_2$ and $Pt(C_2Me_2)(PPh_3)_2$ with strong acids can be compared.[31] The stability of hydrides $PtH(PPh_3)_3^+$ depends on the hydrogen ion concentrations, and for reactions of $Pt(C_2H_4)(PPh_3)_2$ and $Pt(C_2Me_2)(PPh_3)_2$ with proton acids HX the products are $PtX_2(PPh_3)_2$ and C_2H_6 or MeCH=CHMe.[32] In each case hydride intermediates are proposed, and in the case of $Pt(C_2Me_2)(PPh_3)_2$, a vinyl complex (**7**) has been isolated from the addition of 1 mole of HX (equation 8).[33,34]

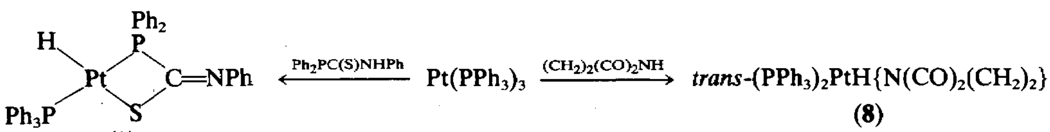


(7) (8)

The reactive compound $Pt(PCy_3)_2$ will react with a series of compounds RH which have an active hydrogen.[35] The compound reacts with hydrogen to give $PtH_2(PCy_3)_2$, and with RH to give $PtH(R)(PCy_3)_2$ (R = C_6F_5, 1,3,5-$C_6F_3H_2$, 1,3-$C_6F_2H_3$, C_6F_5O, PhO, C_6F_5NH and C_4H_4N). This reactivity resembles that found for $Pt(PEt_3)_3$.[36] Such compounds containing Pt—C bonds can, however, undergo protonolysis. The complex $PtH(CH_2CN)(PPh_3)_2$ reacts with HCl to give $PtHCl(PPh_3)_2$ (equation 9).[37]

$$PtH(CH_2CN)(PPh_3)_2 + HCl \longrightarrow PtHCl(PPh_3)_2 + MeCN \qquad (9)$$

The compound $Pt(PPh_3)_3$ will oxidatively add N—H bonds. Reaction of $Pt(PPh_3)_3$ with imides or the compound $Ph_2PC(S)NHPh$ yields isolable platinum(II) hydrides (**8**) and (**9**) with the complexed amido ligand (equation 10).[38,39] This reaction to form (**9**) is another example of chelate-assisted addition. The compound $Pt(PPh_3)_3$ will oxidatively add P—H bonds. When diphenylphosphine oxide reacts with PtL_3 (L = PPh_3, PPh_2Me), the P-bonded hydride $PtH\{(OPPh_2)_2H\}L$ is formed.[40]

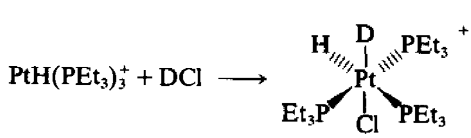


(9) (8) (10)

Although there are numerous examples of complexes $PtHXL_2$, there are fewer examples of six-coordinate hydride complexes $PtH_2X_2L_2$. Early examples are the addition of HCl to $PtHCl(PEt_3)_2$[41] and the addition of 1-ethynylcyclohexanol to $Pt(PPh_3)_3$.[42] In a number of cases involving HX addition to d^8 and d^{10} transition metal complexes, the product has stoichiometry MX_2 rather than MHX. A detailed study by Ebsworth *et al.* has addressed the question as to whether such reactions involve complexes MH_2X_2 as intermediates, and this study has focused on platinum complexes of type $PtH_2X_2L_2$ (L = tertiary phosphine). HX adds to *trans*-$PtHY(PEt_3)_2$ (X, Y = Cl, Br, I) to give *cis,trans*-$PtH_2XY(PEt_3)_2$. If $X \neq Y$, halogen exchange occurs to give a random mixture of dihydrides. Similarly HX adds to *trans*-$PtY_2(PEt_3)_2$ to give $PtHXY_2(PEt_3)_2$. Addition of X_2 to *trans*-$PtHX(PEt_3)_2$ (X = Cl, Br) does not give the expected $PtHX_3(PEt_3)_2$, but a mixture of $PtH_2X_2(PEt_3)_2$ and $PtX_4(PEt_3)_2$.[43] In a comparative study of the reactivities of H_2S and H_2Se, it is found that platinum(IV) complexes containing the SH ligand undergo H_2S elimination much more readily than the analogous SeH compounds.[44] The addition of H_2Se to $PtHI(PEt_3)_2$ gives the six-coordinate hydride complex $PtH_2I(SeH)(PEt_3)_2$, although it is in equilibrium with $PtH_2I_2(PEt_3)_2$ and $PtH_2(SeH)_2(PEt_3)_2$ (equation 11). These results explain how subsequent reductive elimination can readily yield complexes of type $PtX_2(PEt_3)_2$ after the addition of HX to $PtHX(PEt_3)_2$. As further support for the formation of six-coordinate platinum hydrides, the complexes $PtH_2X(CN)(PEt_3)_2$ (X = Cl, Br, I) have been identified in solution by NMR spectroscopy as the initial products from the reaction of *trans*-$PtH(CN)(PEt_3)_2$ and HX (equation 12). No distinction of *cis* or *trans* addition is possible, but in the addition of HCl to $PtH(PEt_3)_3^+$ to yield $PtH_2Cl(PEt_3)_3^+$, deuterium substitution indicates *trans* addition (equation 13).[45]

$$2PtI_2(PEt_3)_2 + 2H_2Se \longrightarrow PtH_2I(SeH)(PEt_3)_2 \rightleftharpoons PtH_2I_2(PEt_3)_2 \rightleftharpoons PtH_2(SeH)_2(PEt_3)_2 \qquad (11)$$

$$PtH(CN)(PEt_3)_2 + HX \xrightarrow{-90\,^\circ C} PtH_2X(CN)(PEt_3)_2 \xrightarrow{0\,^\circ C} PtX(CN)(PEt_3)_2 + H_2 \qquad (12)$$



(13)

Platinum hydrides bridged by a single phosphido bridge have been prepared by reacting the terminally bonded phosphido complex $PtH(PH_2)(PEt_3)_2$ with $PtHCl(PEt_3)_2$ (equation 14).[46] A terminal PF_2-bonded six-coordinate platinum hydride has been detected in the reaction of PF_2Cl with $PtHCl(PEt_3)_2$ (equation 15).[47] Low temperature NMR spectroscopy has also been used to detect hydride complexes $PtH_2Cl(PF_2S)(PEt_3)_2$ in the addition reaction of $PtHCl(PEt_3)_2$ with $PF_2H(S)$. Structures are elucidated and the elimination pathways to yield the final platinum(II) complexes discussed.[48]

$$PtH(PH_2)(PEt_3)_2 + PtHCl(PEt_3)_2 \longrightarrow [\{PtH(PEt_3)_2\}_2PH_2]Cl \qquad (14)$$

$$PtHCl(PEt_3)_2 + PF_2Cl \longrightarrow PtHCl_2(PF_2)(PEt_3)_2 \longrightarrow PtCl(PF_2)(PEt_3)_2 + HCl \qquad (15)$$

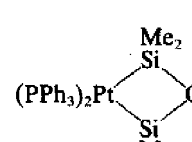
Using ^1H and $^{31}P\{^1H\}$ NMR spectroscopy it has been shown that there is a four-coordinate/five-coordinate exchange process occurring when PEt_3 is added to a solution of $PtH(PEt_3)_3^+$ (equation 16).[42] A line shape analysis has been carried out to evaluate k_1 and k_{-1}, as well as the rate processes corresponding to intramolecular rearrangement in both $PtH(PEt_3)_3^+$ and $PtH(PEt_3)_4^+$ species. The complex $PtH(PEt_3)_3^+$ has been isolated by the protonation reaction of $Pt(PEt_3)_4$ with ethanol.[50] This complex produces hydrogen and $Pt(PEt_3)_3$ on reduction in non-aqueous solvents, but the reduction cannot be effected by $Ru(bipy)_3^{2+*}$.[51] The cyclic voltammogram of $PtH(PEt_3)_3^+$ has been interpreted as an initial absorption with capture of two electrons to yield $PtH(PEt_3)_3^-$. Sustained hydrogen production occurs at -1.7 V *vs.* SCE after initiation.[52]

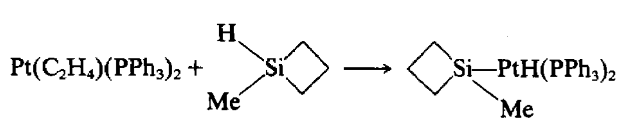
$$PtH(PEt_3)_3^+ + PEt_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} PtH(PEt_3)_4^+ \qquad (16)$$

52.2.2.4 Addition of Si—H bonds

The addition of Si—H bonds and the reactions of silyls with platinum complexes is of significance because of the early discovery of chloroplatinic acid as a hydrosilylation catalyst.[53] This section focuses on the formation of hydrides from silanes.

When the siloxane $(Me_2SiH)_2O$ reacts with $Pt(C_2H_4)(PPh_3)_2$ at 45 °C, the hydride *cis*-$PtH(Me_2SiOSiMe_2H)(PPh_3)_2$ is formed by Si—H addition. The complex is unstable to hydrogen loss at 75 °C (equation 17). Similar hydride complexes are formed from *o*-$C_6H_4(CH_2SiMe_2H)_2$ and $(CH_2)_4(SiMe_2H)_2$.[54] The hydrides $PtH(SiR_3)(PPh_3)_2$ ($R_3Si = Ph_3Si$, Ph_2MeSi, Ph_2HSi, $PhMe(CH_2{=}CH)Si$, Et_3Si, $(EtO)_3Si$ and $(Me_3SiO)_2SiMe$) have been prepared by addition to $Pt(C_2H_4)(PPh_3)_2$. With $SiHClMe_2$ the product is $Pt(SiMe_2Cl)_2(PPh_3)_2$.[55] The compound $SiHMePh_2$ reacts with $Pt(C_2Ph_2)(PPh_3)_2$ to give $PtH(SiMePh_2)(PPh_3)_2$, which is different from the reaction of $Pt(C_2Ph_2)(PPh_3)_2$ with strong acids where stilbene is obtained.[33] The major product of reaction between $Pt(CO_3)L_2$ ($L = PMe_2Ph$, PEt_2Ph, $PMePh_2$ and PPh_3) and silanes R_3SiH is the bis silyl complex $Pt(SiR_3)_2L_2$, but a low yield of $PtH\{Si(p\text{-}FC_6H_4)_3\}(PMe_2Ph)_2$ has been isolated from the appropriate reaction.[56] The reaction has also been used to effect Si—H addition in the silacyclobutane $HSi(Me)CH_2CH_2CH_2$ to yield the unstable platinum hydride product (**10**; equation 18).[57]

$Pt(C_2H_4)(PPh_3)_2 + (Me_2SiH)_2O \xrightarrow{45\,°C}$ *cis*-$PtH(Me_2SiOSiMe_2H)(PPh_3)_2 \xrightarrow{75\,°C}$  (17)

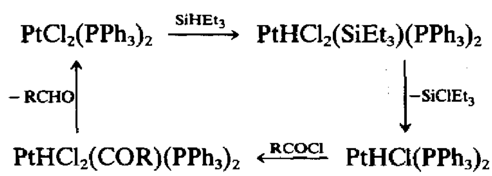
 (18)

(10)

Six-coordinate hydrides are also formed by Si—H addition. Treating a solution of *trans*-$PtI_2(PEt_3)_2$ with $HC{\equiv}CSiH_3$ gives $PtHI_2(SiH_2C{\equiv}CH)(PEt_3)_2$ by Si—H rather than C—H addition (equation 19).[58] These studies have been extended to a range of reactions between $Y(MH_3)_2$ ($Y = O$, S, Se; $M = Si$, Ge) and *trans*-$PtHX(PEt_3)_2$ ($X = Cl$, Br, I). The products have been characterized by ^1H and ^{31}P NMR spectroscopy, and the stabilities of the six-coordinate hydrides are discussed.[59] These authors have done a parallel study with $NH(SiH_3)_2$, $PH_2(SiH_3)$ and $PH(SiH_3)_2$, and the addition reactions discussed.[60] The reaction between $PtH_2(PCy_3)_2$ and MH_3X (M = Si, X = H, Cl, SiH_3; M = Ge, X = H) gives *trans*-$PtHY(PCy_3)_2$ (Y = MH_2X). Reaction intermediates, thought to be $PtH_3Y(PCy_3)_2$, have been detected by ^{31}P NMR spectroscopy (equation 20). The structure of $PtH(SiH_3)(PCy_3)_2$ has been confirmed by X-ray crystallography.[61] The acyl halides XC_6H_4COCl (X = H, *p*-Me, *p*-MeO, *o*-MeO, *p*-Cl, *p*-Br, *p*-NO_2) are converted to aldehydes *p*-XC_6H_4CHO in 50–84% yield on treatment with $SiHEt_3$ at 120 °C in the presence of catalytic amounts of *cis*-$PtCl_2(PPh_3)_2$. The pathway involving Si—H addition is shown in Scheme 1.[62]

$$\textit{trans}\text{-}PtI_2(PEt_3)_2 + HC{\equiv}CSiH_3 \longrightarrow PtHI_2(SiH_2C{\equiv}CH)(PEt_3)_2 \quad (19)$$

$$PtH_2(PCy_3)_2 + MH_3X \longrightarrow PtH_3(MH_2X)(PCy_3)_2 \longrightarrow PtH(MH_2X)(PCy_3)_2 \quad (20)$$



Scheme 1

52.2.2.5 Addition of Ge—H and Sn—H bonds

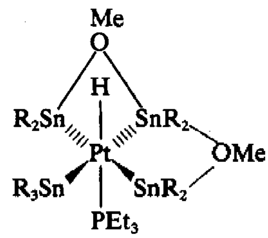
Simple germanes and silanes add to $PtH(PEt_3)_3^+$. An example is the formation of $PtH_2(GeH_2F)(PEt_3)_3^+$ from GeH_3F. The proposed stereochemistry has H, H and GeH_2F *trans* to PEt_3.[63] The addition of a Ge—H bond to $PtHCl(PEt_3)_2$ occurs with excess GeH_3Cl. The product contains a mixture of compounds $PtHX_3(PEt_3)_2$, where X = GeH_2Cl or $GeHCl_2$.[64] The addition of $(C_6F_5)_2GeHGe(C_6F_5)_2H$ to $Pt(PPh_3)_3$ to give $PtH\{Ge(C_6F_5)_2HGe(C_6F_5)_2\}(PPh_3)_2$ is an example of Ge—H addition to platinum(0).[65]

Organotin hydrides SnR_3H (R = Ph, $PhCH_2$, *o*-, *m*-, *p*-MeC_6H_4) react with $Pt(CO)_3(PMe_2Ph)_2$ to give *cis,trans,cis*-$PtH_2(SnR_3)_2(PMe_2Ph)_2$ in methanol solvent. In benzene solvent the H_2 is reversibly lost (equation 21).[66] Hydrides of platinum(II) have been formed from PtH_2L_2 (L = PCy_3, PPr^i_3, PPh_2Bu^t, $PMeBu^t_2$) and $SnHPh_3$, the addition of $SnHPh_3$ to PtL_2 (L = PPr^i_3, PPh_2Bu^t), and the reactions of PtH_2L_2 with $SnClR_3$ (R = Me, Bu^n) (equations 22 and 23).[67] The ^1H and ^{31}P NMR spectra of $PtH(SnCl_3)(PR_3)_2$ (R = Et, Ph) could only be obtained at low temperature, where large ^2J(SnH) values were found.[68] The series of complexes *trans*-$PtH(SnX_3)(PPh_3)_2$ (X = Cl, Br) have been used for *trans* influence studies on ν(PtH).[69] The complex $Pt(CO)_3(SEt_2)(PEt_3)$ reacts with $SnH(p\text{-}MeC_6H_4)_3$ in methanol to give a platinum(IV) complex with OMe groups bridging SnR_2 units. The structure (**11**) is verified by X-ray crystallography.[70]

$$Pt(CO)_3(PMe_2Ph)_2 + 2SnR_3H \longrightarrow PtH_2(SnR_3)_2(PMe_2Ph)_2 \quad (21)$$

$$PtH_2L_2 + SnHPh_3 \longrightarrow PtH(SnPh_3)L_2 + H_2 \quad (22)$$

$$PtL_2 + SnHPh_3 \longrightarrow PtH(SnPh_3)L_2 \quad (23)$$



(**11**)

52.2.2.6 Reactions involving hydrogen

Ab initio molecular orbital methods utilizing relativistic core potentials and correlated wave functions have been used to examine the addition of H_2 to $Pt(PH_3)_2$ and $Pt(PMe_3)_2$ to give *cis*-PtH_2L_2. For this symmetry-allowed process, an activation barrier of 71 kJ mol^{-1} and an exothermicity of 29 kJ mol^{-1} are calculated at the SCF level. The reaction is analyzed in terms of three phases: initial repulsion, partial transfer of charge from the platinum to the hydrogen, and final metal–hydrogen bond formation. The relative energies of *cis* and *trans* isomers are discussed.[71]

Although initial reports that H_2 would oxidatively add to $Pt(PPh_3)_2$ were erroneous,[14] hydrogen adds to $Pt(PEt_3)_3$ to give the thermally unstable $PtH_2(PEt_3)_3$ (equation 24).[72] Platinum hydrides can also be formed by hydrogenolysis reactions, an example being the preparation of $PtHCl(PEt_3)_2$ from $PtClPh(PEt_3)_2$ and hydrogen (equation 25).[73] Good yields of *cis*-$PtHCl\{P(p\text{-}XC_6H_4)_3\}_2$ (X = OMe, Me, H, F, Cl) can be obtained by treating the appropriate dichloroplatinum(II) complex with two equivalents of $SnCl_2$ and H_2 at ambient temperature.[74] Hydrogen will also add to the 14-electron compound $Pt(PCy_3)_2$ to give *trans*-$PtH_2(PCy_3)_2$ (equation 26), which shows ν(PtH) at 1710 cm^{-1}, and the ^1H NMR resonance at δ −3.10 ppm (J(PH) = 17 Hz, J(PtH) = 796 Hz).[75]

$$Pt(PEt_3)_3 + H_2 \longrightarrow PtH_2(PEt_3)_3 \quad (24)$$

$$PtClPh(PEt_3)_2 + H_2 \longrightarrow PtHCl(PEt_3)_2 + C_6H_6 \quad (25)$$

$$Pt(Cy_3)_2 + H_2 \longrightarrow trans\text{-}PtH_2(PCy_3)_2 \quad (26)$$

A platinum hydride is obtained by hydrogenation at both the platinum and the ligand in $Pt(BF_4)(NNAr)(PPh_3)_2$. The products which can be isolated are $[PtH(H_2NNHAr)(PPh_3)_2]BF_4$ and $[PtH(ArHNNC_3H_6)(PPh_3)_2]BF_4$.[19] The latter complex is formed by addition of acetone (equation 27),[76] and the structure confirms the presence of a complexed hydrazone. Hydrogen will undergo photoinduced elimination from $[Pt_2H_3(dppm)_2]PF_6$ and $[Pt_2H_2Cl(dppm)_2]PF_6$. The reaction is carried out in acetonitrile solvent (equation 28).[77] Similarly H_2 can be reversibly displaced from $Pt_2H_3(dppm)_2^+$ by addition of CO (equation 29).[78]

$$Pt(BF_4)(NNAr)(PPh_3)_2 \xrightarrow[EtOH]{H_2} [PtH(H_2NNHAr)(PPh_3)_2]BF_4 \xrightarrow[-H_2O]{acetone} [PtH(ArHNNC_3H_6)(PPh_3)_2]BF_4 \quad (27)$$

$$PtH_3(dppm)_2^+ + MeCN \xrightarrow{h\nu} [Pt_2H(MeCN)(dppm)_2]^+ + H_2 \quad (28)$$

$$Pt_2H_3(dppm)_2^+ + CO \rightleftharpoons Pt_2H(CO)(dppm)_2^+ + H_2 \quad (29)$$

52.2.2.7 Synthesis from water and alcohols

Water will oxidatively add to PtL_3 (L = PEt_3, PPr^i_3) to give $[PtHL_3]OH$, $[PtH(solvent)L_2]OH$, or $PtH(OH)L_2$, depending on the conditions. A quantitative study of this reversible water addition to PtL_3 in organic solvents has been carried out by pH and conductance measurements. For L = PPr^i_3, the equilibria shown in equations (30)–(32) occur. The equilibrium constants have been evaluated. Systems with PtL_3/H_2O catalyze H–D exchange of α-hydrogen atoms of ketones, aldehydes, sulfones, sulfoxides and nitroalkanes. The mechanism has been studied for H–D exchange of PhCOMe. The system also catalyzes alkene hydration.[79] Ligand hydrolysis will also yield hydride complexes, an example being the conversion of $PtCl(SiMe_3)(PEt_3)_2$ into $PtHCl(PEt_3)_2$ (equation 33).[80] The reaction of $[PtX(CO)L_2]BF_4$ (L = PEt_3, PPh_3; X = halide) with water gives $PtHXL_2$ (equation 34). The reaction involves nucleophilic attack at the carbonyl carbon atom, followed by decarboxylation to form the hydride complex.[81,82] Ethanol has been used as the hydride source by pressurizing $H_2PtCl_6 \cdot 6H_2O$ and triphenylphosphine with H_2 and CO in ethanol at 100 °C to give *trans*-$PtHCl(PPh_3)_2$.[83]

$$PtL_3 \rightleftharpoons PtL_2 + L \quad (30)$$

$$PtL_2 + H_2O \rightleftharpoons PtH(OH)L_2 \quad (31)$$

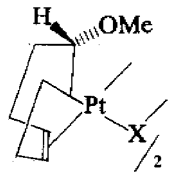
$$PtH(OH)L_2 + solvent \rightleftharpoons PtH(solvent)L_2^+ + OH^- \quad (32)$$

$$2PtCl(SiMe_3)(PEt_3)_2 + H_2O \longrightarrow 2PtHCl(PEt_3)_2 + (Me_3Si)_2O \quad (33)$$

$$[PtX(CO)L_2]BF_4 + H_2O \longrightarrow PtHXL_2 + CO_2 + HBF_4 \quad (34)$$

52.2.2.8 Elimination reactions

A new preparative route to platinum(II) hydrides, particularly for those containing bulky phosphine ligands, involves the reaction of phosphines with bis[(2-methoxy-5-cyclooctenyl)chloroplatinum] in methanol. The reaction (equation 35) involves the use of 4 moles of phosphine per mole of dimeric platinum complex.[84]



$$+ 4PR_3 \xrightarrow{MeOH} PtHCl(PR_3)_2 + C_9H_{14}O \quad (35)$$

$PR_3 = PPh_2Bu^t, PPr^i_3, PCy_3, PMeBu^t_2, PBu^nBu^t_2, PBu^t_3$

52.2.2.9 Ligand replacement

Complexes of platinum(II) having both hydride and alkyl ligands can be prepared. The compound *trans*-$PtHCl(PPh_3)_2$ reacts with MeMgBr to give *cis*-$PtH(Me)(PPh_3)_2$ (equation 36).[85] The compound is characterized at −80 °C, but it decomposes at −25 °C to give $Pt(PPh_3)_3$ and CH_4. The method has been extended to prepare a series of compounds $PtH(Me)L_2$ ($L = PCy_3$, PPr^i_3, PEt_3).[86] Alternatively these complexes can be prepared from $PtX(R)L_2$ (X = Cl, OH, NHCOMe) or *trans*-$PtR(MeOH)L_2^+$ by treatment with NaOMe/MeOH or $NaBH_4$.[87] The compounds are thermally fairly stable. No photochemistry is reported, but for complexes $PtH(CH_2CN)(PPh_3)_2$, photoinduced reductive elimination of MeCN occurs upon irradiation with 313 nm light (equation 37).[88] In relation to the stability of compounds PtH_2L_2, $PtH(Me)L_2$ and $Pt(Me)_2L_2$, a theoretical study has been made using the SCF–Xα–SW method.[89] A simple model is proposed to correlate the occupancy of antibonding M—H and M—C orbitals, and rates of reductive elimination with the relative electronegativities of M and H or C. By contrast to the methyl complex, the complexes *trans*-$PtH(CF_3)(PPh_3)_2$ and $PtH(CF_3)(dppe)$ are relatively thermally stable.[90] The structure of *trans*-$PtH(CF_3)(PPh_3)_2$ has been verified by X-ray crystallography.[91]

$$PtHCl(PPh_3)_2 + MeMgBr \longrightarrow cis\text{-}PtH(Me)(PPh_3)_2 \quad (36)$$

$$trans\text{-}PtH(R)(PPh_3)_2 \xrightarrow{h\nu} cis\text{-}PtH(R)(PPh_3)_2 \longrightarrow [Pt(PPh_3)_2] + RH \quad (37)$$

Cationic hydrides can be prepared by ligand replacement reactions. The complex $[PtH(py)(PPh_3)_2]ClO_4$ can be prepared by treating $PtH(ClO_4)(PPh_3)_2$ with pyridine (equation 38). The reaction is not a general one for amines.[92] The complex *trans*-$PtHI(PEt_3)_2$ will undergo substitution with phosphines L ($L = PH_3$, PH_2Me, $PHMe_2$, PMe_3, PEt_3) to give the ionic hydrides *trans*-$PtHL(PEt_3)_2^+$. Both four- and five-coordinate complexes are formed (equation 39), and the five-coordinate cations have a trigonal bipyramidal structure with the PEt_3 groups in equatorial positions.[93] Removal of the chloride ligand from *trans*-$PtHCl(PBu^t_3)_2$ by a non-coordinating anion X^- gives the three coordinate complexes $[PtH(PBu^t_3)_2]X$ ($X = PF_6$, BF_4, ClO_4, SO_3CF_3). The complex reacts with TCNE to give the four-coordinate complex having a π-bonded TCNE ligand (equation 40).[94] An extensive range of benzylphosphine platinum(II) hydrides has been synthesized.[95] The complexes have the general formula *trans*-$PtHX(PBz_3)_2$ or *trans*-$PtHL(Bz_3)_2^+$ (X = uninegative anion, Bz = benzyl, L = neutral donor). The complexes have been interconverted either by metathetical replacements with X^-, or by substitution of the X ligand by the neutral donor molecule. The list covers 123 compounds.

$$PtH(ClO_4)(PPh_3)_2 + py \longrightarrow [PtH(py)(PPh_3)_2]ClO_4 \quad (38)$$

$$PtHI(PEt_3)_2 + L \longrightarrow [PtHL(PEt_3)_2]I \xrightarrow{L} [PtHL_2(PEt_3)_2]I \quad (39)$$

$$PtHCl(PBu^t_3)_2 \xrightarrow[Cl^-]{X^-} [PtH(PBu^t_3)_2]X \xrightarrow{TCNE} [PtH(TCNE)(PBu^t_3)_2]X \quad (40)$$

The complex *trans*-$PtHClL_2$ (L = P(*o*-tolyl)$_3$, PPh_3, PPh_2Et, PBu^n_3, PEt_3, $AsEt_3$) reacts with pseudohalides X^- (X = NCO, NCS, CN, NCSe) to give $PtHXL_2$.[96,97] Linkage isomerism occurs only with the NCS ligand. The effects of temperature, solvent, concentration and nature of L on the linkage isomer ratio is discussed. The complexes undergo phosphine ligand exchange. In a detailed study of the solvent influence on the ambidentate bonding of the SCN ligand in these complexes, it is found that aromatic solvents stabilize the N-bonded isomer and that solvents capable of hydrogen bonding stabilize the S-bonded isomer.[98] NMR spectroscopy identifies N- and S-bonded isomers of the NCS ligand in *trans*-PtH(SCN)$(PEt_3)_2$.[99] This method has been reaffirmed using ^{14}N decoupling when the broad hydride resonance of the N-bonded isomer sharpened.[100]

Using metathetical replacement, *cis*- and *trans*-hydridocarborane complexes PtH(*o*-carborane)L_2 [L = PEt_3, PPh_3, PPh_2Me, $PPhMe_2$; carborane = 2-R-1,2- or 7-R-1,7-$B_{10}C_2H_{10}^-$ (R = H, Me, Ph)] have been prepared.[101] The *cis* complexes are the first examples of neutral *cis*-monohydrido platinum(II) complexes with a Pt—C σ bond.

Replacement reactions of the anionic ligand can be used to prepare cationic platinum(II) carbonyl and alkene complexes. The reaction of $PtHCl(PEt_3)_2$ with CO and $NaClO_4$ gives $[PtH(CO)(PEt_3)_2]ClO_4$ (equation 41).[102] Similarly ethylene reacts with $PtH(NO_3)(PEt_3)_2$ in the presence of $NaBPh_4$ to give $[PtH(C_2H_4)(PEt_3)_2]BPh_4$ (equation 42).[103]

$$PtHCl(PEt_3)_2 + CO + NaClO_4 \longrightarrow [PtH(CO)(PEt_3)_2]ClO_4 + NaCl \tag{41}$$

$$PtH(NO_3)(PEt_3)_2 + C_2H_4 + NaBPh_4 \longrightarrow [PtH(C_2H_4)(PEt_3)_2]BPh_4 + NaNO_3 \tag{42}$$

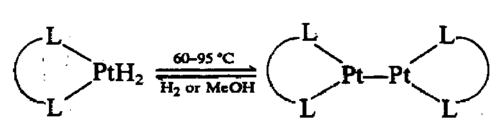
52.2.2.10 Formation of dihydrides

The dihydride complexes *trans*-PtH_2L_2 (L = PCy_3, PCy_2Pr^i, PCy_2Et) have been prepared by the reaction of $Pt(acac)_2$ with AlR_3 in the presence of L in ether solvent (equation 43).[104] The IR spectrum of $PtH_2(PCy_3)_2$ shows ν(PtH) at 1910 cm^{-1}. The compound reacts with CCl_4 to give $PtHCl(PCy_3)_2$ and $CHCl_3$. A similar series of complexes *trans*-PtH_2L_2 (L = PBu^tMe_2, PBu^tEt_2, $PBu^t(CH_2Ph)_2$, $PBu^t_2Pr^n$, $PBu^t_2CH_2Ph$, PCy_3) has been prepared by reacting $PtCl_2L_2$ or *trans*-$PtHClL_2$ with a large excess of $NaBH_4$ in ethanol (equation 44).[105] The stability of the complexes increases with the bulkier L groups. The first *cis*-dihydride was prepared by the reaction of the seven-membered chelate complex *cis*-$PtCl_2(Bu^t_2PCH_2C_6H_4CH_2PBu^t_2)$ with sodium borohydride in ethanol. The complex *cis*-$PtH_2(Bu^t_2PCH_2C_6H_4CH_2PBu^t_2)$ is obtained in high yield and shows ν(PtH) at 2023 cm^{-1}, with the hydride NMR resonance at δ −4.00 p.p.m. (^2J(PH) = 165 and 22 Hz; ^1J(PtH) = 1008 Hz).[106] An unusual synthesis of $PtH_2(PPr^i_3)_2$ is the reaction of $Pt(PPr^i_3)_2$ with methanol (equation 45).[107] This reaction differs from that for $Pt(PEt_3)_2$ where the reaction with methanol gives $PtH(OMe)(PEt_3)_2$.[36] Complexes of type *cis*-PtH_2L_2 ($L_2 = R_2P(CH_2)_nPR_2$, $n = 2, 3$) can be prepared by the sodium amalgam reaction with the dichloro complexes. At 60–95 °C, or *in vacuo*, the complexes lose hydrogen to give $(PtL)_2$. The reaction is reversible with added H_2 or methanol (equation 46).[108] The hydrogen is also displaced by alkynes to give zerovalent Pt(alkyne)L_2 complexes (equation 47). A range of R_2 substituents on the alkyne are used.

$$Pt(acac)_2 + 2L \xrightarrow{AlR_3} PtH_2L_2 \tag{43}$$

$$PtCl_2L_2 \text{ or } PtHClL_2 \xrightarrow{NaBH_4} trans\text{-}PtH_2L_2 \tag{44}$$

$$Pt(PPr^i_3)_2 \xrightarrow{MeOH} PtH_2(PPr^i_3)_2 \tag{45}$$



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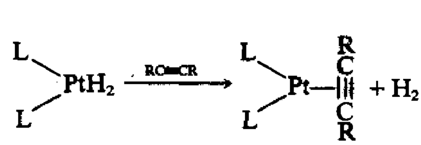


(47)

An alternative synthesis of *trans*-PtH_2L_2 (L = bulky tertiary phosphine) involves the reaction between the peroxycarbonato complexes $Pt(CO_4)L_2$ and $NaBH_4$. The method is preferable to a similar reaction of $NaBH_4$ with PtO_2L_2.[109] The structure of *trans*-$PtH_2(PBu^t_3)_2$ shows Pt—P distances of 2.277(1) Å.[110] The complexes PtH_2L_2 (L = bulky phosphine) form when the complex $[Pt(\mu\text{-}OMe)(C_8H_{12}OMe)]_2$ is reacted with bulky phosphines L.[111] The arsine analog *trans*-$PtH_2(AsBu^t_3)_2$ has been prepared from K_2PtCl_4 by treatment with $AsBu^t_3$ in ethanolic KOH (equation 48).[112] The complex reacts with HX to give $PtHX(AsBu^t_3)_2$ and with I_2 to give $PtHI(AsBu^t_3)_2$. No evidence is found for borohydride intermediates in the conversion of $PtHClL_2$ into PtH_2L_2 with $NaBH_4$, and when $LiBD_4$ is used, the complexes PtD_2L_2 with $\nu(PtD)$ at 1270 cm^{-1} are obtained (equation 49).[113]

$$K_2PtCl_4 + 2AsBu^t_3 + 2EtOH + 2KOH \longrightarrow PtH_2(AsBu^t_3)_2 + 2MeCHO + 4KCl + 2H_2O \quad (48)$$

$$PtHClL_2 \xrightarrow{LiBD_4} PtD_2L_2 \quad (49)$$

The hydrogen in these complexes PtH_2L_2 is displaced by CO, along with one phosphine (L) ligand. The product is $[Pt(CO)L]_3$.[114] The complex $PtH_2(PCy_3)_2$ does not react with C_2H_4, forms a 1:1 adduct at 213 K with TCNE which converts to $PtH\{C(CN){=}C(CN)_2\}(PCy_3)_2$ at ambient temperature, and undergoes an insertion reaction with C_2F_4.[115]

Stable but highly reactive complexes *cis*- and *trans*-PtH_2L_2 with small phosphines have been prepared by the reaction of H_2 with $Pt(C_2H_4)L_2$ (L = PMe_3, PEt_3) (equation 50).[116] The complexes isomerize in solution to produce an equilibrium mixture of *cis* and *trans* isomers. When $PtH_2(PEt_3)_2$ is placed under an atmosphere of D_2 in a toluene solution, both *trans*-$PtHD(PEt_3)_2$ and *trans*-$PtD_2(PEt_3)_2$ form, along with H_2 and HD (equation 51).

$$Pt(C_2H_4)L_2 + H_2 \rightleftharpoons PtH_2L_2 + C_2H_4 \quad (50)$$

$$2PtH_2(PEt_3)_2 + 2D_2 \longrightarrow PtHD(PEt_3)_2 + PtD_2(PEt_3)_2 + H_2 + HD \quad (51)$$

The dihydride complexes of platinum(IV), $PtH_2(CO)X_3^-$ (X = Cl, Br, I) have been prepared. For X = Cl, Br, the compounds are prepared from $Pt(CO)_2$ and HX in aqueous solution with added iron(III) ion (equation 52).[117] A reference to the preparation of $Pt(CO)_2$ from K_2PtCl_4 and CO in 1 M HCl is given, and the complex $PtH_2(CO)I_3^-$ prepared by metathetical replacement of Cl by I. The complexes are characterized by elemental analysis and IR spectroscopy ($\nu(PtH)$ are 2080–2100 cm^{-1}).

$$Pt(CO)_2 + 3HX + 2Fe^{3+} + H_2O \longrightarrow PtH_2(CO)X_3^- + CO_2 + 2Fe^{2+} + 3H^+ \quad (52)$$

52.2.3 Structure and Reactions

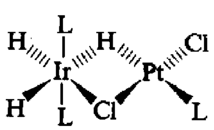
52.2.3.1 Geometry and stability of monomeric complexes

The presence of a hydride ligand on platinum is usually deduced by a combination of IR and ^1H NMR spectroscopic techniques. The bonding of the hydride has been correlated with the *trans* influence of the ligand *trans* to hydride (see Section 52.4), and one of the earliest attempts to rationalize the chemical shift and coupling constant parameters of hydrides was carried out on platinum hydrides.[118] Using single crystal X-ray structural techniques Ibers has shown that the hydride ligand occupies a stereochemical position in coordination at the metal,[9] although the hydride ligand is small and this is reflected in distortions in the coordination geometry.[25] Platinum(II) hydrides are stable and numerous,[14] and their stability and accessibility is comparable to those of iridium(III). Platinum(IV) hydrides are less common, frequently being unstable to reductive elimination to form platinum(II) complexes. We are unaware of any well-documented examples of platinum(0) or (III) hydrides, but the occurrence of hydrides of binuclear platinum(I) complexes is likely to increase.

The hydride ligand has a high *trans* influence (see Section 52.4) and a high *trans* effect,[119,120] properties which have been widely used in effecting metathetical replacement and substitution reactions. The complexes such as *trans*-$PtHCl(PPh_3)_2$, which are thermally stable, will decompose at 230 °C *in vacuo* to form $[PtCl(PPh_2)(PPh_3)]_2$ and benzene.[121] Complexes of type *trans*-$PtHXL_2$ are usually stereochemically rigid in solution, and isomerizations of platinum(II) complexes have been discussed mechanistically in terms of associative, or sometimes dissociative, pathways.[122] The compound *cis*-$PtH(SiR_3)(PPh_3)_2$ (R = Ph, *p*-ClC_6H_4, *p*-tolyl) undergoes spontaneous intramolecular interchange of the PPh_3 ligand positions in various solvents above 0 °C.[123]

52.2.3.2 Structure and reactions of bridging hydride complexes

The chemistry of bridging hydrides in transition metal complexes has received considerable attention over the past 10 years. A recent review on the subject[15] covers the whole range of transition metals, and bridging hydrides of platinum are interspersed through this article. Platinum complexes are known having both a single (μ-H) and a double (μ-H)$_2$ hydrogen bridge, and both homobimetallic and heterobimetallic complexes of platinum are known. An early heterobimetallic complex was assigned the structure (**12**), and was obtained by the reaction of IrH_5L_2 with $Pt_2Cl_4L_2$ (L = PPr_3).[124] The first diplatinum complexes $Pt_2(\mu\text{-H})_2(X_2)L_2$ (X = H, SiR_3, GeR_3; L = PCy_3) were prepared by the reaction of $Pt(C_2H_4)_2(PCy_3)_2$ with H_2 or R_3MH (M = Si, Ge; R = alkyl, aryl, alkoxy, Cl) (equation 53).[125] The structure of $Pt_2(\mu\text{-H})_2(SiEt_3)_2(PCy_3)_2$ has been confirmed by X-ray crystallography. The Pt–Pt distance is 2.692(3) Å, and the complex exhibits no high field ^{1}H NMR resonance. NMR studies on $Pt_2(\mu\text{-H})_2\{Si(OEt)_3\}_2(PMeBu^t_2)_2$ show that this class of complex shows dynamic behavior, and that the hydride signal for Pt—H is in the region of δ 3. This shift value, coupled with deuteration studies and bridge-cleavage reactions with C_2H_4, CO, $P(OPh)_3$, Bu^{t}NC, PMe_3 and $AsMe_2Ph$, provides evidence for asymmetric $Pt(\mu\text{-H})_2Pt$ bridges.[126,127]

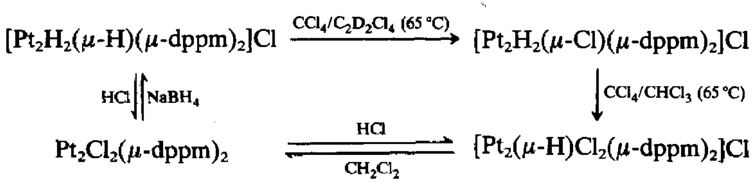


(**12**)

$$2Pt(C_2H_4)_2(PCy_3) + 2R_3MH \longrightarrow Pt_2(\mu\text{-H})_2(MR_3)_2(PCy_3)_2 + 4C_2H_4 \quad (53)$$

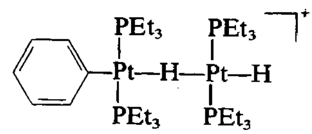
Reacting $PtCl_2(dppm)$ with $NaBH_4$ gives $Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2^+$ (equation 54).[128] The complex reacts with CCl_4 or HCl to give $Pt_2H_2(\mu\text{-Cl})(\mu\text{-dppm})_2^+$ and $Pt_2Cl_2(\mu\text{-H})(\mu\text{-dppm})_2^+$ (Scheme 2). The structures have been elucidated by a combination of ^{1}H and ^{31}P NMR spectroscopy. Vibrational bands due to bridging hydrides are not observed in these compounds. An analogous complex $[Pt_2H_2(\mu\text{-H})(L—L)_2]BF_4$ (L—L = dppe, dpae) has been isolated from the reaction between $[Pt(3,5\text{-dimethylpyrazole})_2(L—L)]BF_4$ and KBH_4 in alcohol solvent.[129] The bridging hydrogen is selectively replaced by reaction of $[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2]PF_6$ with methanethiol, when $[Pt_2H_2(\mu\text{-SMe})(\mu\text{-dppm})_2]PF_6$ is formed (equation 55).[130] In addition to $PtPh_2(PEt_3)_2$, the reaction of *trans*-$PtH(NO_3)(PEt_3)_2$ with $NaBPh_4$ gives a complex $[Pt_2H(\mu\text{-H})(Ph)(PEt_3)_4]BPh_4$ (equation 56). X-Ray crystallography shows a Pt–Pt distance of 3.09 Å. The C(phenyl)Pt(1)Pt(2) angle of 164.3° indicates that the singly bridged hydrogen in (**13**) is not collinear with the two metal centers. Addition of chloride ion to (**13**) results in reversible cleavage (equation 56).[131] Using this addition–elimination (reverse equation 56) method, this group has also prepared $[Pt_2H(\mu\text{-H})_2(PPh_3)_4]BF_4$ by reacting a 'hydride intermediate' formed from $Pt(cod)_2$, $2PPh_3$ and H_2, with *trans*-$[PtH(acetone)(PPh_3)_2]BF_4$.[132] This method is a useful one to systematically prepare heterobimetallic bridged hydride complexes. Treating a solution of *trans*-$PtR(MeOH)(PEt_3)_2^+$ (R = Ph, H) with $IrH_5(PEt_3)_2$ gives the complexes (**14a**) and (**14b**) with H_2 elimination. This complex is similar to (**12**), and the structure of the complex with R (phenyl) *cis* to terminal hydride shows a Pt–Ir separation of 2.687(2) Å. Chemical shift values for the bridging hydrides in this isomer are at δ −7.05 and −9.04.[133] The complex $(\eta^5\text{-Cp})_2W(\mu\text{-H})_2PtR(PEt_3)_2^+$ (R = H, Ph) is also briefly mentioned.[134] Mixed platinum–gold hydrides can be prepared by reacting *trans*-$PtH(C_6Cl_5)(PEt_3)_2$ with $[Au(THF)(PEt_3)]^+$ (equation 57). The complex shows a hydride resonance at δ −4.73 p.p.m. (^1J(PtH) = 537 Hz).[135] A bridging hydride $Pt_2(\mu\text{-H})Ph(\mu\text{-}PPh_2)(PPh_3)_3^+$ (**15**), resulting from P—phenyl cleavage in triphenylphosphine, has been obtained from the reaction of $Pt(cod)_2$, $[PtPh(acetone)(PPh_3)_2]BPh_4$, PPh_3 and H_2. The Pt–Pt distances are close to 2.9 Å, and the hydride NMR shows a resonance at δ −6.5 p.p.m. (^1J(PtH) = 600 Hz).[136] Using similar techniques the complexes $Pt_2(\mu\text{-H})Ar_2(PEt_3)_4^+$ (Ar = Ph, 4-MeC_6H_4, 2,4-$Me_2C_6H_3$) have been prepared. The structure of the Ph_2 complex shows a Pt–Pt distance of 3.238(1) Å. The weakness of the μ-H bridge is shown by the scrambling reaction of unsymmetrical compounds in the presence of a coordinating solvent such as acetone or methanol (equation 58).[137]

$$PtCl_2(dppm) \xrightarrow{NaBH_4} Pt_2H_2(\mu\text{-}H)(\mu\text{-}dppm)_2^+ \qquad (54)$$



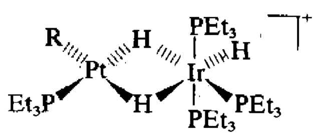
Scheme 2

$$Pt_2H_2(\mu\text{-}H)(\mu\text{-}dppm)_2^+ + MeSH \longrightarrow PtH_2(\mu\text{-}SMe)(\mu\text{-}dppm)_2^+ + H_2 \qquad (55)$$



(13)

$$[PtH(\mu\text{-}H)(Ph)(PEt_3)_4]^+ + Cl^- \rightleftharpoons trans\text{-}PtHCl(PEt_3)_2 + trans\text{-}PtH(Ph)(PEt_3)_2 \qquad (56)$$



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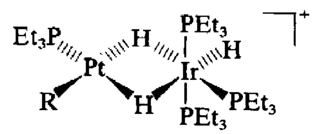

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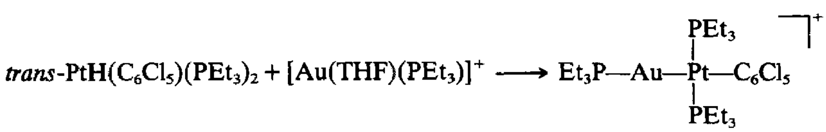

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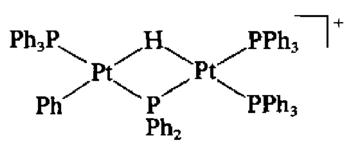

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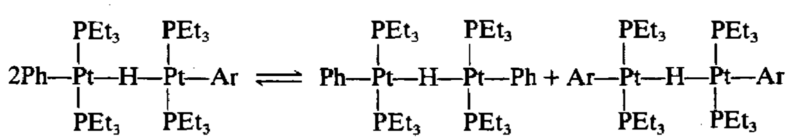
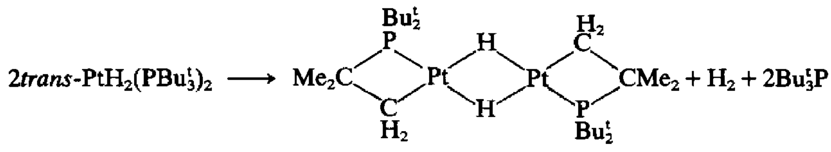


(58)

A doubly-hydrogen-bridged complex (**16**) has been formed from *trans*-$PtH_2(PBu^t_3)_2$, which undergoes facile intramolecular metalation with substitution of PBu^t_3 and elimination of H_2 (equation 59).[138] The static (X-ray crystal) structure of $[Pt_2H_3\{Bu^t_2P(CH_2)_3PBu^t_2\}_2]BPh_4$ shows a Pt–Pt separation of 2.768(2) Å and a dihedral angle between the two P—Pt—P coordination planes of 89°. The molecule is fluxional, and schemes are discussed for the interconversion of bridging and terminal hydrides by a Berry pseudorotation process.[139] The complex $[Pt_2H(\mu\text{-}H)_2(PEt_3)_4](O_2CH)$ is formed by irradiation of $Pt(C_2O_4)(PEt_3)_2$ in MeCN solvent under a hydrogen atmosphere. The compound can be prepared from $PtH_2(PEt_3)_2$ and $PtH(solvent)(PEt_3)_2^+$, and when $PtD_2(PEt_3)_2$ is used, deuterium is only incorporated into the bridging positions (equation 60).[140] The complex catalyzes the decomposition of formic acid at 25 °C, and factors affecting the equilibrium between monomers and $(\mu\text{-}H)_2$ bridged complexes are discussed. The complexes $[Pt_2H_3(L—L)_2]^+$ with a range of chelating L—L groups also show fluxionality down to −95 °C. The structure of the dppe compound at 115 K shows a Pt–Pt distance of 2.728(1) Å.[141] These authors note that the use of excess KBH_4 as a hydride source can lead to complexes of higher nuclearity such as $[Pt_3H_x(dppe)_3]^+$ and $[Pt_3H_x(dpae)_3]^+$.[142] The stoichiometry of a triplatinum hydride has been confirmed by X-ray crystallography.[143] The compound $[Pt_3(\mu\text{-}H)(\mu\text{-}PPh_2)_2(PPh_3)_3]BF_4$ (**17**) is prepared by UV irradiation of an ethanolic solution of $Pt(C_2O_4)(PPh_3)_2$ under a hydrogen atmosphere, followed by addition of $NaBF_4$ (equation 61).[144] The hydride could not be detected by direct ^1H NMR measurements but was established by ^{31}P and $^{31}P\{^1H\}$ experiments.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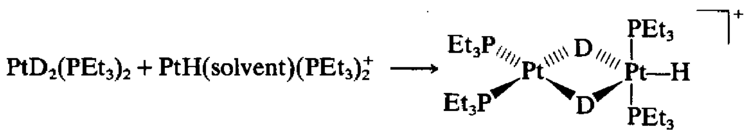
(**16**)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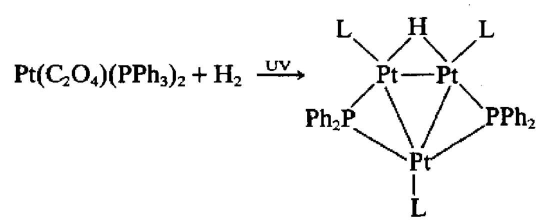
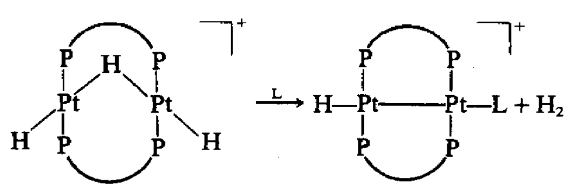

(61)

(**17**) L = PPh_3

The complex $Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2^+$ reacts with tertiary phosphines L to form $Pt_2HL(\mu\text{-dppm})_2^+$ (L = η^1-dppm, PMe_2Ph, $PMePh_2$, PPh_3) with reductive elimination of H_2 (equation 62).[145] The structure of the complex with L = η^1-dppm has been confirmed by X-ray crystallography.[146] Reductive elimination can also be photochemically induced. Photolysis of $Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2^+$ and $Pt_2H_2(\mu\text{-}Cl)(\mu\text{-dppm})_2^+$ results in hydrogen evolution, and the respective quantum yields are 0.62 and 0.06 (equations 63 and 64).[147] The complex $[Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2]^+$ is an active catalyst precursor for the water gas shift reaction at low CO pressure.[148]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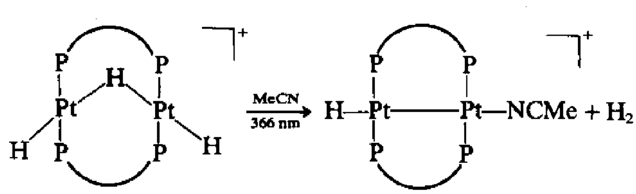
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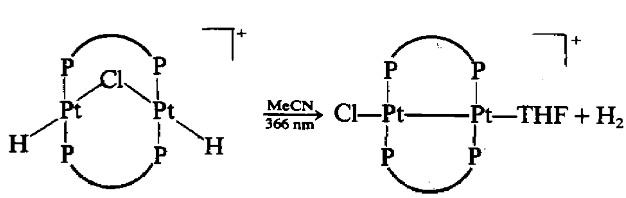
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52.2.3.3 Insertion reactions

Insertion of ethylene into the Pt—H bond of *trans*-$PtHCl(PEt_3)_2$ was reported by Chatt and Shaw,[73,149] who obtained a 25% yield of *trans*-$Pt(Et)Cl(PEt_3)_2$ after 18 hours when the reaction was carried out in cyclohexane at 95 °C/40 atm (equation 65). The reaction is reversible. If C_2F_4 is used, the stable complex *trans*-$Pt(CF_2CF_2H)Cl(PEt_3)_2$ is formed due to the stronger Pt—CF_2 bond (equation 66).[150]

$$trans\text{-}PtHCl(PEt_3)_2 + C_2H_4 \rightleftharpoons trans\text{-}Pt(Et)Cl(PEt_3)_2 \quad (65)$$

$$trans\text{-}PtHCl(PEt_3)_2 + C_2F_4 \longrightarrow trans\text{-}Pt(CF_2CF_2H)Cl(PEt_3)_2 \quad (66)$$

Both five-coordinate and four-coordinate pathways have been proposed for these reactions. The associative (five-coordinate) mechanism involves the formation of a trigonal bipyramidal or square pyramidal intermediate, which can revert back to tetracoordination by alkene insertion into the Pt—H bond.[151] The dissociative (four-coordinate) mechanism involves initial substitution of a ligand other than hydride by alkene, followed by insertion to form the alkyl product. The ligand which is substituted is usually the anionic ligand, and if this group is *trans* to hydride an isomerization will need to occur prior to insertion of the coordinated alkene into the Pt—H bond.

Support for the dissociative (four-coordinate) insertion pathway has primarily come from a series of papers by Clark and co-workers. The initial study shows that the insertion of ethylene or propene occurs readily (25 °C and 1 atm) with *trans*-$PtHBr(PMePh_2)_2$ when the reaction is carried out in a coordinating solvent such as acetone in the presence of added $AgPF_6$ and base (CO, 2,4,6-Me_3py) (equation 67).[152] Similarly *trans*-$PtH(NO_3)(PMePh_2)_2$ will insert C_2H_4 in acetone or dichloromethane solvent at 25 °C and 1 atm pressure (equation 68). Furthermore, the reaction of *trans*-$[PtH(acetone)(PMePh_2)_2]PF_6$ with ethylene at 25 °C gives *trans*-$[PtEt(C_2H_4)(PMePh_2)_2]PF_6$, but at −50 °C the proposed intermediate *trans*-$[PtH(C_2H_4)(PMePh_2)_2]PF_6$ (equation 69)[153] is obtained. Similarly in the alkene insertion into the Pt—H bond of *trans*-$PtH(NO_3)(PEt_3)_2$, the intermediate *trans*-$[PtH(C_2H_4)(PEt_3)_2]BPh_4$ has been isolated. Butadiene and allene insert to give π-allylic complexes, and 1,5-cod and norbornadiene give enyl systems.[154]

$$trans\text{-}PtHBr(PMePh_2)_2 + AgPF_6 \xrightarrow{S} [trans\text{-}PtH(S)(PMePh_2)_2]PF_6 + AgBr \xrightarrow[\text{ii, base (B)}]{\text{i, } C_2H_4} [trans\text{-}PtEt(B)(PMePh_2)_2]PF_6 \quad (67)$$

$$trans\text{-}PtH(NO_3)(PMePh_2)_2 + C_2H_4 \xrightarrow[25\,^{\circ}C]{(S)} trans\text{-}PtEt(NO_3)(PMePh_2)_2 \quad (68)$$

$$trans\text{-}[PtEt(C_2H_4)(PMePh_2)_2]PF_6 \xleftarrow{25\,^{\circ}C} trans\text{-}[PtH(L)(PMePh_2)_2]PF_6 + C_2H_4 \xrightarrow{-50\,^{\circ}C} trans\text{-}[PtH(C_2H_4)(PMePh_2)_2]PF_6 \quad (69)$$

L = acetone

The kinetics of the insertion reaction of methyl acrylate with *trans*-$PtH(NO_3)(PEt_3)_2$ have been interpreted in terms of the mechanism shown in Scheme 3.[155] Values of K_1, K_2 and k_3 have been found, and a kinetic isotope effect of 1.34 ± 0.06 observed for $k_3(H)/k_3(D)$. Further kinetic measurements have attempted to address the stereochemical questions about these insertion reactions. Schemes involving X^--assisted isomerization of *trans*-$PtH(C_2H_4)L_2^+$ to *cis*-$PtH(C_2H_4)L_2^+$ and the stabilization of five-coordinate intermediates have been proposed, but no unambiguous answers resulted.[156] For ethylene insertion into $PtH(acetone)(PEt_3)_2^+$ to give $PtEt(acetone)(PEt_3)_2^+$, the rate becomes zero order in C_2H_4 at high C_2H_4 concentrations. A mechanism is proposed involving rapid substitution of acetone by ethylene to give *trans*-$PtH(C_2H_4)(PEt_3)_2^+$, followed by a slow, rate-determining insertion step.[157] Although the question of solvation was not extensively discussed, the key ionic intermediates in these reactions have been assumed to be three coordinate rather than four coordinate.[158]

$$trans\text{-}PtH(NO_3)(PEt_3)_2 + \text{alkene} \overset{K_1}{\rightleftharpoons} trans\text{-}PtH(\text{alkene})(PEt_3)_2^+ + NO_3^-$$

$$trans\text{-}PtH(MeOH)(PEt_3)_2^+ + \text{alkene} \overset{K_2}{\rightleftharpoons} trans\text{-}PtH(\text{alkene})(PEt_3)_2^+ + MeOH$$

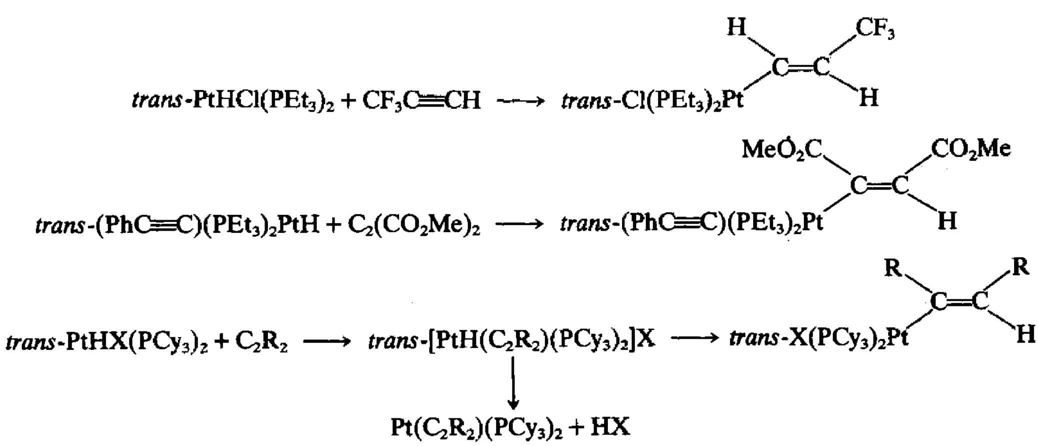
$$trans\text{-}PtH(\text{alkene})(PEt_3)_2^+ \xrightarrow{k_3} trans\text{-}PtR(PEt_3)_2^+$$

$$trans\text{-}PtR(PEt_3)_2^+ + NO_3^- \rightleftharpoons trans\text{-}PtR(NO_3)(PEt_3)_2$$

Scheme 3

Using a semiempirical (SCF–MO) method, the insertion of ethylene into the Pt—H bond of $PtHCl(PH_3)_2$ has been calculated. Assuming a five-coordinate intermediate, the favored path involves the H ligand approaching the ethylene as the Cl group moves to the *trans* position of the H ligand. The Pt—H bond energies for a series of compounds $PtHX(PH_3)_2$ are calculated, and an electron density of *ca.* 1.25 e^- is found on the hydride ligand.[159] Similar calculations by an all-valence-electron MO method for the insertion of CS_2, CO_2 and C_2H_4 into *trans*-$PtHCl(PH_3)_2$ concludes that following entry into coordination at Pt, transition state and product formation are largely dependent on steric effects.[160]

Platinum hydrides will also undergo insertion reactions with alkynes. 3,3,3-Trifluoropropyne reacts with *trans*-$PtHCl(PEt_3)_2$ to give *trans,trans*-$PtCl(CH{=}CHCF_3)(PEt_3)_2$ (equation 70).[161] Dicyanoacetylene only inserts into the Pt—H bond of *trans*-$PtHClL_2$ (L = PEt_3, PPh_3) when the reaction solvent is benzene.[162] For a series of complexes *trans*-$PtHL(PEt_3)_2^+$ (L = acetone, CO, PEt_3, $AsPh_3$, $P(OMe)_3$, $P(OPh)_3$) and *trans*-$PtHX(PEt_3)_2$ (X = Cl, NO_3, NO_2, CN), $PhC{\equiv}CMe$ is more reactive to insertion than C_2H_4, but the same relative reactivity order is found. These decrease in the order L = acetone $\gg$ CO > $AsPh_3$ > $P(OPh)_3$, $P(OMe)_3$, PEt_3 and X = NO_3 > Cl > NO_2, CN.[163] For a series of alkynes, the stereochemistry about platinum has been studied for the insertion products with *trans*-$PtHX(PEt_3)_2$. The stereochemistry depends on the electron-withdrawing capability of the alkyne substituents, the solvent or anion nucleophilicity, and the reaction temperature.[164] Dimethylacetylenedicarboxylate inserts into the Pt—H bond of *trans*-$PtH(C{\equiv}CPh)(PEt_3)_2$ to give *trans*-$Pt\{C(CO_2Me){=}CH(CO_2Me)\}(C{\equiv}CPh)(PEt_3)_2$ (equation 71).[165] The complexes *trans*-$PtH(acetone)(PEt_3)_2^+$ and *trans*-$PtH(CO)(PEt_3)_2^+$ follow an insertion pathway for alkynes analogous to that for alkenes. For the carbonyl complex, weakly activated alkynes insert *via* five-coordinate intermediates, but strongly activated alkynes insert by a pathway involving reversible CO loss.[166] For the complexes *trans*-$PtHX(PCy_3)_2$ the product is either the *cis*-alkenyl complex or the zerovalent complex formed by HX elimination from the intermediate *trans*-$[PtH(C_2R_2)(PCy_3)_2]X$ (equation 72).[167] The detailed mechanism is obviously more complex, since the use of spin traps shows that the reaction of $C_2(CO_2Me)_2$ with *trans*-$PtHCl(PEt_3)_2$ involves free radical participation.[168] Other reactions are possible in this chemistry. Although isopropenylacetylene and phenylacetylene insert into the Pt—H bond of *trans*-$PtHCl(PPh_3)_2$,[169] α-hydroxyalkynes $RC{\equiv}CH$ undergo substitution reactions to form *trans*-$PtCl(C{\equiv}CR)(PPh_3)_2$.[170]



(70)

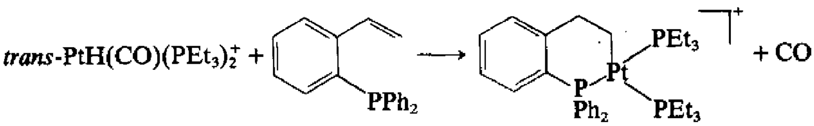
(71)

(72)

In a thermochemical study of the reaction (73), it is concluded that D(Pt—H) $\approx$ D(Pt—Cl) and that the reaction occurs primarily because of the formation of a strong H—Cl bond rather than because of the ease of rupture of the Pt—H bond.[171] Pressure effects on the insertion of alkynes into *trans*-$PtHCl(PEt_3)_2$ causes a large rate acceleration. The influence is large when ionic intermediates are involved, and in some cases a change of reaction mechanism is claimed.[172]

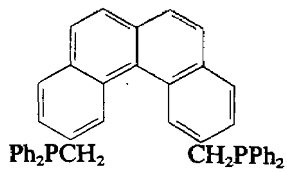
$$trans\text{-}PtHCl(PPh_3)_2(s) + C_2(CN)_4(g) \longrightarrow Pt\{C_2(CN)_4\}(PPh_3)_2(s) + HCl(g) \qquad (73)$$

These insertion reactions have been used to carry out reactions other than those with simple alkenes and alkynes. Stable products of alkene insertion are formed with (*o*-vinylphenyl)diphenylphosphine, when a five-membered ring complex is obtained. Reaction with *trans*-$PtH(CO)(PEt_3)_2^+$ gives complex (**18**; equation 74).[173] The question of the requirement of mutually *cis* hydride and alkene ligands prior to insertion has been addressed by using a *trans* spanning ligand. The complex PtHCl(L—L) has been prepared, where L—L is 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene (**19**), a *trans* spanning chelate ligand. The compound inserts ethylene even under relatively mild conditions.[174] The details of the synthesis of the platinum hydride complex are published later.[175]



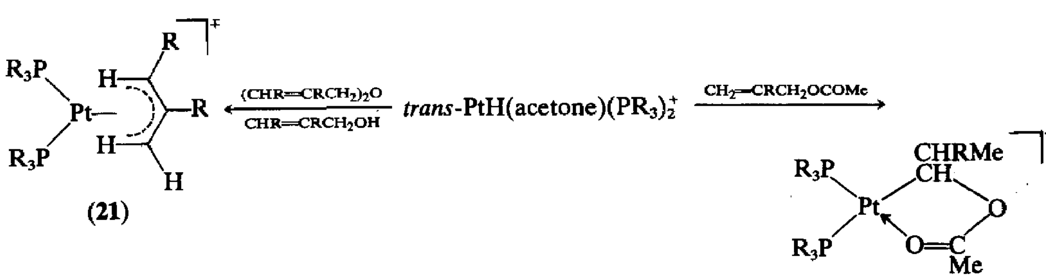
(74)

(**18**)

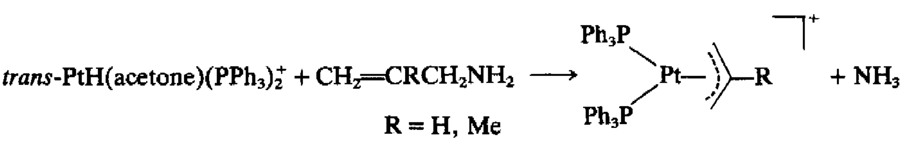


(**19**)

The complex *trans*-$PtH(acetone)(PR_3)_2^+$ undergoes insertion reactions with allylic acetates (CH_2=$CRCH_2OCOMe$), diallyl ethers [$(CHR$=$CRCH_2)_2O$] and allylic alcohols (CHR=$CRCH_2OH$) to give insertion products (**20**) and (**21**) (equation 75).[176] Complexes similar to (**21**) have been prepared starting from *trans*-$PtH(ClO_4)(PPh_3)_2$ and allyl alcohol.[177] Allylamine and 2-methylallylamine give π-allyl complexes by insertion into the Pt—H bond of *trans*-$PtH(acetone)(PPh_3)_2^+$ (equation 76).[178] Methylenecyclopropane derivatives also form allyl complexes of platinum on reaction with *trans*-$PtH(NO_3)L_2$ or *trans*-$PtH(solvent)L_2^+$ (equation 77).[179,180] The reaction involves a ring opening of the cyclopropane ring. When carboxylate substituents are present on the cyclopropane ring the carbonyl oxygen binds to platinum to form the cyclic compound (**22**).[180] A further product is the complex (**23**) which has been crystallographically confirmed.[181]



(**21**) (**20**) (75)



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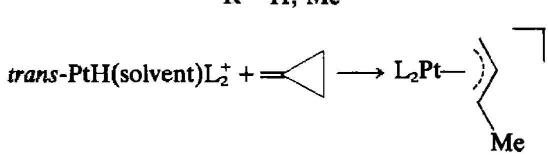

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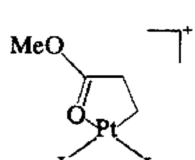
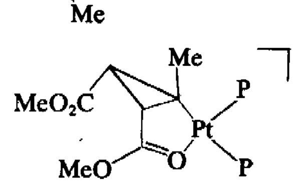


(**22**)



(**23**)

Isocyanides RNC undergo insertion into the Pt—H bond of *trans*-[PtH(CNR)L_2]Cl (R = *p*-tolyl; L = PEt_3, PMe_2Ph) in non-polar solvents to give formimidoyl complexes *trans*-PtCl(CHNR)L_2 (**24**; equation 78).[182] The *syn* and *anti* forms are present together in equilibrium. Carbon disulfide inserts into the Pt—H bond of *trans*-$PtHCl(PPh_3)_2$[183] and $PtH_2(PCy_3)_2$[184] to give *trans*-PtCl{SCH(S)}$(PPh_3)_2$ and *trans*-PtH{SCH(S)}$(PCy_3)_2$. The structure[184] shows the S_2CH group bonded to the metal through S as a monodentate thioformate anion. Carbon dioxide inserts into the Pt—H bond of *trans*-$PtH_2(PCy_3)_2$ to give *trans*-$PtH(O_2CH)(PCy_3)_2$. Monodentate O-coordination is confirmed by X-ray crystallography.[185] Tin(II) chloride will insert into the Pt—X bond of *trans*-$PtHX(PPh_3)_2$ (X = Cl, Br, I) to give *trans*-$PtH(SnX_3)(PPh_3)_2$.[186]

$$trans\text{-}[PtH(CNR)L_2]Cl + RNC \longrightarrow trans\text{-}Cl(PEt_3)_2PtC(H){=}NR \qquad (78)$$

(**24**)

52.2.3.4 Reactions with electrophiles

Complexes *trans*-$PtH(CN)(PEt_3)_2$ have a non-bonded N atom of a cyanide ligand which is susceptible to attack by electrophiles. Among the Lewis acid adducts which have been formed are ones of structure $HPt(PEt_3)_2CN{\rightarrow}X$ (X = BPh_3, $AlCl_3$, $CoCl_2$, $AlAr_3$, $ZnCl_2$, $B(OAr)_3$, AlR_3, $AlR_2(OR)$; equation 79).[187,188] The isomer *trans*-$HPt(PEt_3)_2NC{\rightarrow}BPh_3$ has also been prepared by treating *trans*-$PtHCl(PEt_3)_2$ with $NaBPh_3CN$ in THF solvent.[187] This isomer converts to the more stable form with the Pt—C bond with an activation energy of $63 \pm 8\ kJ\ mol^{-1}$.[189] A similar type of reactivity of a non-bonded N of a cyano group is the conversion of $PtH(CH_2)_3CN$(2=phos) into $[Pt(CH_2)_3CN(2{=}phos)]_2$ upon treatment with HBF_4.[190] A platinum(II) hydride also reacts as an acid (or electrophile) to a terminally bonded phosphido ligand to form a *μ*-phosphido biplatinum complex (**25**; equation 80).[191] The electrophile Ph_3C^+ attacks the hydride ligand to give Ph_3CH.[192]

$$trans\text{-}HPt(PEt_3)_2CN + X \longrightarrow trans\text{-}HPt(PEt_3)_2CN{\rightarrow}X \qquad (79)$$

$$\underset{L\,=\,PEt_3}{2\,trans\text{-}PtHCl(PEt_3)_2 + Me_3SiPH_2} \longrightarrow \left[\begin{array}{c} \;\;L \qquad\quad L \\ \;\;| \qquad\quad\; | \\ H{-}Pt{-}PH_2{-}Pt{-}H \\ \;\;| \qquad\quad\; | \\ \;\;L \qquad\quad L \end{array}\right]Cl + Me_3SiCl \qquad (80)$$

(**25**)

52.2.3.5 Reactions with bases

The reaction of *trans*-$PtHX(PPh_3)_2$ with KOH or KOR induces reductive elimination to form the species $Pt(PPh_3)_2$ (equation 81).[193] In a similar reaction the base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBu) can be used to convert *trans*-$PtHCl(PPh_3)_2$ to $Pt(C_2Ph_2)(PPh_3)_2$ (equation 82).[194] Treating $PtH(ClO_4)(PPh_3)_2$ with pyridine (py) gives the expected product $[PtH(py)(PPh_3)_2]ClO_4$. With NH_3 or Me_3N as bases, however, N—C and N—H cleavage occur giving amido complexes (equation 83).[92]

$$trans\text{-}PtHX(PPh_3)_2 + OH^- \longrightarrow Pt(PPh_3)_2 + H_2O + X^- \qquad (81)$$

$$trans\text{-}PtHCl(PPh_3)_2 \xrightarrow[C_2Ph_2]{DBU} Pt(C_2Ph_2)(PPh_3)_2 \qquad (82)$$

$$2PtH(ClO_4)(PPh_3)_2 + 2Me_3N \longrightarrow [Pt(NMe_2)(PPh_3)_2]_2(ClO_4)_2 + 2CH_4 \qquad (83)$$

52.2.4 Spectroscopy

Platinum hydrides have been primarily characterized by the Pt—H stretch in the IR spectrum and the high field shift of the hydride NMR resonance. The NMR technique is particularly useful because of the strong coupling of the hydride resonance to the ^{195}Pt ($I = 1/2$, 33% abundance) nucleus (^1J(PtH) = 500–1000 Hz). A review compiles the available IR and NMR data on platinum hydrides through 1974.[14] Two trends in the values for ν(PtH) and δ(PtH), ^1J(PtH) have been discussed. The values ν(PtH) and δ(PtH) in *trans*-$PtHXL_2$ are sensitive to the *trans* influence of X. The higher the *trans* influence of X the lower ν(PtH), and the smaller the high field shift of δ(PtH) (Table 1).[14] These spectral parameters are also sensitive to the pK_a of the *trans* ligand X. For a series of carboxylato complexes the value ν(PtH) increases with decreasing pK_a, and the trend in δ(PtH) is to upfield.[195]

Table 1 Spectral Parameters for *trans*-$PtHX(PEt_3)_2$

X	ν(*PtH*) (cm^{-1})	δ(*PtH*) (p.p.m.)	*J*(*PtH*) (Hz)
NO_3	2242	−23.8	15.5
Cl	2183	−16.9	14
Br	2178	−15.6	13.8
I	2156	−12.7	13
CN	2041	−7.8	15.5

The extinction coefficient of ν(PtH) for the series of complexes *trans*-$PtHX(PPh_3)_2$ has been measured. Comparison of the found E values with those for chemisorbed hydrogen on platinum shows that those in the complexes are higher by an order of magnitude.[196] The complexes *trans*-$PtHX(PEt_3)_2$ show intense MLCT bands in the UV spectral region due to MLCT transitions. Differences are small, but for a series of complexes it is found that the energy ordering of the MLCT bands generally parallels the σ donor strength of the ligands, with HX < EtX < MeX < X_2 (X = Cl, Br).[197]

52.2.4.1 ^{1}H NMR spectroscopy

Although the general features have been discussed in Section 52.2.4, a number of spectral features of the ^{1}H NMR of platinum hydrides require special note. In Section 52.2.2.3 it was noted that for the complex $[PtH(PPh_3)_3](CF_3CO_2)_2H$, second-order effects were required to interpret the ^{1}H NMR spectrum.[24] This problem has been further studied using a combination of ^{1}H and ^{31}P NMR spectroscopy. The spectrum must be interpreted on the basis of the AB_2X and AB_2MX (A = B = ^{31}P, M = ^{195}Pt, X = ^{1}H) spin system. When δ_{AB} is close to critical values it is not possible to neglect the effect on the X spectrum of remote magnetically active nuclei which are coupled to A or B. Thus in tertiary phosphine complexes it may not be possible to neglect the effects of remote hydrogens in the alkyl or aryl groups.[198] With the increasing use of ^{195}Pt NMR spectroscopy, temperature control is important. For platinum hydrides the temperature coefficient of the chemical shift is smaller than other complexes, but is still in the region of 0.15 p.p.m. K^{-1}.[199] The ^{195}Pt chemical shifts of *trans*-$PtHClL_2$ (L = PEt_3, PPh_3) are found to high field, a feature attributed to smaller ΔE values in Ramsey's equation.[200]

Table 2 Spectral Parameters for *trans*-$PtHY(PEt_3)_2$

Y	pK_a	δ(*PtH*) (p.p.m.)	*J*(*PtH*) (Hz)	ν(*PtH*) (cm^{-1})	*J*(*PH*) (Hz)
p-$MeC_6H_4CO_2$	4.373	−21.897	1176.2	2226	15.55
$PhCO_2$	4.212	−21.918	1179.1	—	15.65
p-$ClC_6H_4CO_2$	3.977	−22.036	1189.1	2231	15.6
m-$ClC_6H_4CO_2$	3.830	−22.095	1195.5	2232	15.5
p-$NO_2C_6H_4CO_2$	3.425	−22.200	1209.6	2235	15.8
$PhOCH_2CO_2$	3.171	−22.342	1202.9	2234	15.55
o-$BrC_6H_4CO_2$	2.824	−22.257	1205.2	2234	15.9
o-$NO_2C_6H_4CO_2$	2.173	−22.515	1226.2	2241	15.55
$CHCl_2CO_2$	1.25	−22.765	1255.8	2245	15.5
CF_3CO_2	0.23	−23.013	1285.5	2258	15.35

52.2.5 Catalytic Reactions

Although homogeneously catalyzed reactions of platinum complexes are mostly concerned with hydrogenation, hydroformylation, isomerization and hydrosilylation reactions, the complexes *trans*-$PtHX(PPh_3)_2$ (X = Cl, Br, I) have been used used as catalysts for the oxidative chlorination of *n*-pentane. H_2PtCl_6 and K_2PtCl_6 are used as oxidants.[201]

52.2.5.1 Homogeneous hydrogenation, hydroformylation and isomerization

These applications have been discussed in a review.[14] The most frequently used hydrogenation catalyst is one containing PtX_2L_2 or $PtHXL_2$, along with $SnCl_2$. The main application is for the partial hydrogenation of double bonds to monoenes.[202] This work followed the report that a mixture of H_2PtCl_6 and $SnCl_2$ in methanol solvent is an effective catalyst for alkene hydrogenation.[203] It has been suggested that an intermediate in the catalysis is $PtHCl_2(SnCl_3)^{2-}$,[204] which resembles the isolated complexes $PtH(SnCl_4)_4^{3-}$ and $PtH(SnCl_3)_2(PEt_3)_2^-$.[205] The complex *trans*-$PtH(NO_3)(PEt_3)_2$ is also an effective hydrogenation catalyst at 60 °C and 600 p.s.i. hydrogen. Both internal and terminal alkenes are hydrogenated, but not those with electron-withdrawing substituents.[206]

The cationic complexes $PtHL_3^+$ (L = PPh_3, PEt_3) are hydroformylation catalysts for alkenes to give a mixture of linear and branched aldehydes.[207] Using CO/H_2 at 100 °C and 3000 p.s.i., $PtH(SnCl_3)(CO)(PPh_3)_2$ is an active catalyst for the hydroformylation of pentene-1. The ratio of straight to branched chain aldehydes is about 20.[208] The complex $PtH(OPPh_2)(PPh_3)_2$ can be used for the hydroformylation of heptene-1. At 17.5% heptene conversion, 85% linear hydroformylated products form with an aldehyde : alcohol ratio of 0.8. Only 1.2% of heptane is formed.[209]

The systems used as hydrogenation catalysts usually catalyze alkene isomerization.[14] Both pathways involve insertion of alkene into a Pt—H bond, and the reverse of this process can lead to isomerization of the original alkene. In addition to complexes previously discussed,[14] octene-1 can be isomerized to internal alkenes using a mixture of *trans*-$PtHCl(PMe_2Ph)_2$ and $MeSO_3F$ in CH_2Cl_2 solvent.[210] Using deuterated compounds, the catalyzed migration of double bonds by platinum(II) hydrides has been found to involve the reversible anti-Markownikov addition of Pt—H across the terminal C═C bond before double-bond migration occurs.[211] The rate of isomerization of pentene-1 and pentene-2 at 80 °C by $PtH(SnCl_3)(PPh_3)_2$ has been compared with a series of iridium(I) and (III) complexes.[212] The mechanism involves the formation of pentyl platinum complexes.[213] Pentene-1 isomerization is catalyzed by $[PtH(PPh_3)_3]X$ (X = HSO_4, ClO_4), but only in ether solvents. High selectivity to *cis* isomer can be achieved.[214]

52.2.5.2 Hydrosilylation

Hydrosilylation of alkenes is catalyzed by H_2PtCl_6, Pt black and K_2PtCl_4.[215–217] The asymmetric hydrosilylation of α-methylstyrene with $SiHCl_2Me$ is catalyzed by (*R*)-benzylmethylphenylphosphine complexes of platinum(II).[218] The dimeric platinum(II) complex of (*R*)-(+)-benzylmethylphenylphosphine is an effective catalyst for the synthesis of asymmetric alcohols from $SiHCl_2Me$ and aromatic ketones (equation 84).[219] Zerovalent platinum complexes $Pt(PPh_3)_3$ and $Pt(C_2H_4)(PPh_3)_2$ have also been used as catalysts for the hydrosilylation of double bonds.[220,221] Kinetic data for the addition of $SiHCl_2Me$ to styrene with triphenylphosphine platinum(II) complexes as catalysts suggests an associative pathway. The *cis* and *trans* complexes show different dependence on their catalytic activity.[222]

$$\mathrm{RCOPh + SiHCl_2Me \xrightarrow{[PtCl_2\overset{*}{P}R_3]_2} R(\overset{*}{C}HO)PhSiMeCl_2 \xrightarrow[H^+]{MeLi} R(\overset{*}{C}HOH)Ph} \qquad (84)$$

The diplatinum complexes $[Pt(\mu\text{-}H)SiR_3(PCy_3)]_2$ catalyze the addition of silanes R_3SiH (R = Me, Et, $PhCH_2$, Ph, OEt, Cl) to pentene-1, hexene-1, styrene, allyl chloride and 2-methylpropene. The relative reactivity order in silane is given, and the catalyst : substrate ratio is 10^{-4}–10^{-6} : 1. The majority of the reactions are carried out at ambient temperature and are exothermic. Dienes are also hydrosilylated.[223] The complexes also catalyze the hydrosilylation of butyne-1, phenylacetylene, butyne-2 and diphenylacetylene in 70–90% yield. The stereochemistries of vinylsilanes formed are given.[224] For the addition of $SiHX_3$ to RC≡CH, RC≡CR, and RC≡CR′ the reaction is stereospecifically *cis*. For terminal alkynes, small amounts of internal adducts corresponding to Markownikov addition are also formed.[225] The relative reactivity to hydrosilylation follows the sequences: PhCH(OH)C≡CH ≪ Pr^{n}C≡CH < Bu^{n}C≡CH < *n*-pentC≡CH; PhCH(OH)C≡CH < $Me_2C(OH)$C≡CH < MeEtC(OH)C≡CH; EtC≡CEt < Pr^{n}C≡CMe < EtC≡CMe ≪ Pr^{n}C≡CH.[226]

52.3 PLATINUM COMPLEXES OF GROUP IIIA LIGANDS

52.3.1 Diphenylboron Complexes

The complex $PtCl(BPh_2)(PEt_3)_2$ has been prepared from the reaction of $PtHCl(PEt_3)_2$ with Ph_2BCl (equation 85).[227] A similar complex can also be obtained by the oxidative addition of Ph_2BX (X = Cl, Br) to $Pt(PPh_3)_3$ (equation 86).[228] The Pt^{II}—B bond is cleaved by Br_2.[227]

$$PtHCl(PEt_3)_2 + Ph_2BCl \longrightarrow PtCl(BPh_2)(PEt_3)_2 + HCl \quad (85)$$

$$Pt(PPh_3)_3 + Ph_2BX \longrightarrow PtX(BPh_2)(PPh_3)_2 + PPh_3 \quad (86)$$

52.3.2 Boron Hydride Complexes

Platinum(II) complexes of $B_3H_7^{2-}$ can be prepared from CsB_3H_8 (equation 87).[229] A π-allyl type structure is deduced from the NMR spectrum. A mixed platinum–osmium B_5H_7 complex has been obtained by treating the Na^+ salt of $Os(B_5H_8)CO(PPh_3)_2$ with $PtCl_2(PMe_2Ph)_2$. The complex has a seven-vertex *nido*-osmaplatinaborane cluster structure based on the dodecahedron with one five-connected vertex missing.[230] Metathesis of $K[B_5H_8]$ with complexes *cis*-$PtCl_2L_2$ (L = tertiary phosphine) gives complexes $PtX(B_5H_8)L_2$ in good yield. The B_5H_8 ligand is η^2-bonded to the metal *via* two of the basal boron atoms. ^1H, ^{11}B, ^{31}P and ^{195}Pt NMR data are discussed.[231] Hexaborane(10) reacts with $PtCl_3(C_2H_4)^-$ to give *trans*-$PtCl_2(B_6H_{10})$ (equation 88). The ligand is proposed to be bonded *via* a three-center, two-electron bond with Pt in the 4,5 bridging position.[232] Alcoholic degradation of the complex Pt{B_9H_{11}P(*p*-tolyl)$_3$}$(PEt_3)_2$ gives $Pt(B_8H_{12})(PEt_3)_2$.[233] A high yield of $Pt(B_8H_{12})(PMe_2Ph)_2$ has been obtained from the reaction of $B_9H_{14}^-$ with *cis*-$PtCl_2(PMe_2Ph)_2$ (equation 89).[234] The complex is formed in lower yield from other polyhedral borane derivatives. The structure has a nine-vertex *arachno*-platinanonaborane in which the B_8 unit shows trihapto bonding to the metal center. Treatment of the complex with KH and $PtCl_2(PMe_2Ph)_2$ gives the very stable compound $Pt_2(B_8H_{10})(PMe_2Ph)_4$ (equation 90). The complex $[(Pt_2B_8H_{14})(PMe_2Ph)_2]$ is an *iso-arachno*-diplatinadecaborane with four-vertex and eight-vertex subclusters Pt_2B_2 and Pt_2B_6 conjoined at a common Pt–Pt edge.[235] A similar procedure has been used to prepare the heterobimetallic compound $(Me_3P)_2Pt(PPh_3)(Ph_2PC_6H_4)HIrB_9H_{10}$. The overall yield is 40%.[236] These reactions are similar to those used to prepare earlier B_{10} complexes of Pt. Among the reported complexes are $Pt(B_{10}H_{12})(PPh_3)_2$ from $PtCl_2(PPh_3)_2$ and $Pt(PPh_3)_3$, and $(EtOB_{10}H_{11})Pt(PPh_3)_2$ formed from $PtCl_2(PPh_3)_2$ and $K_2[B_{10}H_{10}]$ in ethanol.[237] An improved synthesis of $Pt(B_{10}H_{12})(PMe_2Ph)_2$ involves deprotonation of $B_{10}H_{14}$ by tetramethylnaphthalene-1,8-diamine followed by treatment with $PtCl_2(PMe_2Ph)_2$. Similarly the cisoid and transoid complexes $(PtB_{10}H_{11})_2(PMe_2Ph)_2$ have been formed. Structural and fluxional NMR studies have been related to bonding features.[238] Extension of these reaction types to larger boron cages has been used to prepare [(Pt-η^4-*anti*-$B_{18}H_{20}$)$(PMe_2Ph)_2$], a μ-η^1-η^2 isomer with the $Pt(PMe_2Ph)_2$ group bridging the two edge-linked B_{10} clusters. The compound $[(Pt_2B_{18}H_{16})(PMe_2Ph)_4]$ has a confacial *conjuncto*-borane unit $B_{18}H_{16}$ η^4-bonded to one $Pt(PMe_2Ph)_2$ unit and ($\eta^4 + \eta^2$) bonded to the other. Use of *syn*-$B_{18}H_{22}$ provides a third isomer of $[(PtB_{18}H_{20})(PMe_2Ph)_2]$.[239] The compound [7-$(PMe_2Ph)${7-$PtB_{16}H_{18}$-9′-$(PMe_2Ph)$}] is a complex of a macropolyhedral 16-vertex borane ligand based on the structure of an unknown B_6–B_{10} *conjuncto*-borane. It is the first example of a contiguous 17-vertex cluster species.[240] The structure of the 17-vertex macropolyhedral trimetallaborane $Pt_3B_{14}H_{16}(PMe_2Ph)_4$ can be interpreted either in terms of a formal pentadecahapto complex of a 7,7′-(*arachno*-heptaboranyl) type ligand coordinated η^4, η^5 and η^6 to the three metal centers, or in terms of a *nido*-type 2,7,10-trimetallaundecaborane cluster conjoined to an *iso-arachno*-6,8-dimetallanonaborane cluster with three common adjacent PtBPt vertices.[241]

$$PtCl_2(PR_3)_2 + CsB_3H_8 \longrightarrow Pt(B_3H_7)(PR_3)_2 + CsCl + HCl \quad (87)$$

R = Et, Ph, *o*-tolyl

$$PtCl_3(C_2H_4)^- + B_6H_{10} \longrightarrow PtCl_2(B_6H_{10}) + C_2H_4 + Cl^- \quad (88)$$

$$PtCl_2(PMe_2Ph)_2 + B_9H_{14}^- \longrightarrow Pt(B_8H_{12})(PMe_2Ph)_2 + Cl^- + HCl \quad (89)$$

$$Pt(B_8H_{12})(PMe_2Ph)_2 + 2KH + PtCl_2(PMe_2Ph)_2 \longrightarrow Pt_2(B_8H_{10})(PMe_2Ph) + 2KCl \quad (90)$$

The interaction of platinum halides with boron hydrides has been used to couple boranes. In the presence of $PtBr_2$ at 25 °C the compound 1,2′-$(B_5H_8)_2$ can be formed from B_5H_9 (equation 91).[242]

$$2B_5H_9 \xrightarrow[25\,^\circ C]{PtBr_2} 1,2'\text{-}(B_5H_8)_2 + H_2 \quad (91)$$

52.3.3 Carborane Complexes

The first 1,2-dicarbollide platinum complex Pt(cod)(π-1,2-$B_9C_2H_{11}$) has been prepared from $K_2[B_9C_2H_{11}]$ and $PtCl_2$(cod) (equation 92).[243] Treatment with excess $K_2[B_9C_2H_{11}]$ did not yield the sandwich structure. In order to confirm Pt–C coordination in a Pt carborane, the crystal structure of the complex formed between $PtCl_2(PR_3)_2$ (R = Pr^n) and 1-Li-2-phenyl-1,2-dicarba-*closo*-dodecaborane(12) has been solved. The platinum(II) is coordinated by the carboranyl group through its C-1 atom, by one phosphine, and by phosphorus and carbon of a metalated propylphosphine ligand.[244]

$$PtCl_2(cod) + K_2[B_9C_2H_{11}] \longrightarrow Pt(cod)(B_9C_2H_{11}) + 2KCl \quad (92)$$

Reaction of *closo*-2,3-Me_2-2,3-$C_2B_9H_9$ with zerovalent platinum complexes $Pt(PEt_3)_3$, $Pt(PMe_3)_2$(*trans*-stilbene), $Pt(PMe_2Ph)_4$ gives the *closo*-metallacarbaboranes 1,1-L_2-2,4,Me_2-1,2,4-$PtC_2B_9H_9$ (L = PEt_3, PMe_3, PMe_2Ph). Treatment of 1-(η-Cp)-1,2,4-$CoC_2B_8H_{10}$ with $Pt(PEt_3)_2$(*trans*-stilbene) leads to a related insertion reaction to form 1-(η-Cp)-8,8-$(Et_3P)_2$-1,2,7,8-$CoC_2PtB_8H_{10}$ (equation 93).[245] A similar reaction between $Pt(PEt_3)_2$(stilbene) and 1,6-Me_2-1,6-$C_2B_7H_7$ gives $Pt(Me_2C_2B_7H_7)(PEt_3)_2$ in high yield. The polyhedral geometry approximates to that of a bicapped (B and C) square antiprism with the Pt in a CBBPt prism face, adjacent to the boron cap.[246] Further extension of the reaction has been used in the synthesis of *arachno*-5,9-C_2B_7 carbaboranes of platinum.[247] The structures of 1,1-bis(trimethylphosphine)-6,8-dicarba-1-platinaoctaborane and the 6,8-dimethyl derivative have *closo* polyhedral cages with geometries approximating to those of trapped trigonal prisms.[248] From the reaction of $Pt(PEt_3)_2$(*trans*-stilbene) and 1,6-R_2-1,6-$C_2B_6H_6$ (R = Me), a minor product is also formed which is *nido*-3,8-dimethyl-2,2-$(PEt_3)_2$-3,8-dicarba-2-platinanonaborane(6). Geometrically this nine-atom metallacage is based on a tricapped trigonal prism in which the metal lies in a prism face, adjacent to boron and carbon caps.[249] From $Pt(PEt_3)_3$ or $Pt(PR_3)_2$(stilbene) (R = Et, Me) and *closo*-1,7-R_2-1,7-$C_2B_6H_6$ (R = H, Me), *closo*-4,5-R_2-4,5-$C_2B_7H_7$ and *closo*-1,6-$C_2B_8H_{10}$ the carbametallaborane complexes *closo*-[4,5-R_2-6,6-(PEt_3)-4,5,6-$C_2PtB_6H_6$], *nido*-[4,5-R_2-7,7-(PEt_3)-4,5,7-$C_2PtB_6H_6$], *nido*-[2,8-R_2-10,10-(PEt_3)-2,8,10-$C_2PtB_7H_7$] and *nido*-[μ-(6,10)-[$Pt(PMe_3)_2$]-10,10-(PMe_3)-7,9,10-$C_2PtB_8H_{10}$] are formed. The latter compound with activated charcoal gives *nido*-[10,10-$(PMe_3)_2$-7,9,10-$C_2PtB_8H_{10}$]. The ^1H, ^{11}B and ^{31}P NMR spectra are reported for the complexes.[250] A series of complexes having both hydride and CB_5H_6, $C_2B_4H_4$ and $C_2B_4H_6$ ligands bonded to platinum have been obtained by insertion of platinum(0) into bridging B—H—B bonds of the appropriate carborane. The reactions involve the use of $Pt_2(\mu\text{-cod})(PEt_3)_4$.[251] The compound $Pt_2(\mu\text{-cod})(PEt_3)_4$ reacts with *nido*-5,6-$C_2B_8H_{12}$ to give 9-H-9,9-$(PEt_3)_2$-$\mu_{10,11}$-H-7,8,9-$C_2PtB_8H_{10}$, which on pyrolysis (100 °C) loses H_2 to form 9-H-9,10-$(PEt_3)_2$-7,8,9-$C_2PtB_8H_9$. Structural studies establish that direct insertion of a $Pt(PEt_3)_2$ fragment into the *nido*-carbaborane 5,6-$C_2B_8H_{12}$ involves incorporation of the metal into an expanded polyhedral framework. The first complex has Pt in a formal +4 state which reduces to +2 in the second pyrolysis product.[252] A pyrolysis procedure has also been used to convert [*nido*-$\mu_{4,5}$-{*trans*-$(PEt_3)_2$PtH}-$\mu_{5,6}$-H-2,3-Me_2-2,3-$C_2B_4H_4$] into the *closo*-carbametallaborane [1,1-$(PEt_3)_2$-2,3-Me_2-1,2,3-$PtC_2B_4H_4$]. The molecule has a highly distorted pentagonal bipyramidal cage with a

C_{2v} conformation of the $Pt(PEt_3)_2$ fragment.[253] The compound $Pt_2(\mu\text{-cod})(PEt_3)_4$ will also undergo double insertion of the platinum nucleophile into a *closo*-carbaborane. The complex 1,1-$(PEt_3)_2$-6,6-$(PEt_3)_2$-4,5-Me_2-1,4,5,6-$PtC_2PtB_5H_5$ has been structurally characterized.[254] A mixed Fe–Pt carbametallaborane $[FePt(Me_4C_4B_8H_8)(PEt_3)_2]$ with metal–metal connectivity has been prepared (equation 94).[255] The room-temperature reaction of $Pt_2(\mu\text{-cod})(PEt_3)_4$ with *nido*-5,6-$C_2B_8H_{12}$ gives 9-H-9,9-$(PEt_3)_2$-$\mu_{10,11}$-H-7,8,9-$C_2PtB_8H_{10}$, which shows a cage approximating a *nido* icosahedron with a CCPtBB open face. The complex undergoes thermolysis with H_2 loss.[256]

$$Pt(PEt_3)_2(stilbene) + CpCoC_2B_8H_{10} \longrightarrow (PEt_3)_2CpCoC_2PtB_8H_{10} + stilbene \quad (93)$$

$$[FeH_2(2,3\text{-}Me_2\text{-}2,3\text{-}C_2B_4H_2)_2] + \tfrac{1}{2}Pt_2(\mu\text{-cod})(PEt_3)_4 \longrightarrow FePt(Me_4C_4B_8H_8)(PEt_3)_2 \quad (94)$$

Extended Hückel molecular orbital calculations have been made for the icosahedral platinaboranes and carbaboranes $[B_{11}\{Pt(PH_3)_2\}H_{11}]^{2-}$, $[B_{10}C\{Pt(PH_3)_2\}H_{11}]^{2-}$, and $B_9C_2[Pt(PH_3)_2]H_{11}$. The failure of the polyhedral skeletal electron-counting rules is attributed to the unequal bonding capabilities of the platinum $5d_{xz}$ and $5d_{yz}$ orbitals in the $Pt(PH_3)_2$ fragment. The conformations of icosahedral carbaplatinaboranes are rationalized on the basis of the symmetry characteristics of the lowest unoccupied orbital of the carbaborane and the highest occupied orbital of the metal–phosphine moiety. Analogous d^8 metal compounds are predicted to be stable and to have conformations complementary to those found for d^{10} complexes.[257] The crystal structure of 3,3-$(PEt_3)_2$-1,2-dicarba-3-platinadodecaborane(11) shows a highly distorted icosahedron in which the platinum atom 'slips' toward B(8) and the metal-bonded face 'folds' across B(4)—B(7). Walsh diagrams derived from extended Hückel calculations suggest the 'slip' distortion will be dependent on the total number of valence electrons involved in M—L bonding and the conformation of the ML_2 fragment.[258] Extended Hückel MO calculations for the trigonal prismatic platinaboranes and carbaplatinaboranes $[B_8\{Pt(PH_3)_2\}H_8]^{2-}$ and $[B_6C_2\{Pt(PH_3)_2\}H_8]$ have been used to account for the observed conformations in terms of the nodal characteristics of the frontier orbitals of the constituent $Pt(PH_3)_2$ and carbaborane fragments.[259] Extension of this approach to comparison between small and large borane and carborane cages has concluded that differences in bond lengths associated with different classes of carbaplatinaboranes can be interpreted in terms of the different bonding capabilities of the two types of carborane ligand.[260]

Unsymmetrical *ortho*-carboranes $(R_2PC_2PR'R'')B_{10}H_{10}(L)$ (R = Ph, NMe; R′ = NMe_2; R″ = F and R = Ph; R′ = R″ = NMe_2 or F)[261] react with platinum salts to give complexes $PtCl_2L$. The structure of $PtCl(Ph_2PC_2B_{10}H_{10})(Ph_2PC_2B_{10}H_{11})$ shows a Pt—P—C—B metallacycle obtained by insertion of platinum into a B—H bond of L. Both *ortho*-carboranyl cages have approximately icosahedral geometries.[262] A similar reaction is found with the *ortho* carboranylphosphine *o*-$HCB_{10}H_{10}CCH_2PPh_2$ which gives a complex PtCl(PCB)(PR_3) when the ligand is reacted with $PtCl_2(PR_3)_2$.[263]

Carboranes have been prepared with a sulfur heteroatom. The reaction of PtL_4 (L = PMe_2Ph, PEt_3, PPh_3) with SB_9H_9 in dry refluxing alcohol gives 9,9-L_2-6,9-$SPtB_8H_{10}$. The platinum is square planar with three boron atoms acting as a bidentate moiety. The synthetic method (equation 95) is a degradative insertion reaction where the Pt moiety forms kinetically stable coordination complex after the thiaborane has been degraded to an SB_8 framework.[264] Mass spectrometry and ^{1}H NMR characterization show the framework electron count corresponds with the *nido* skeletal structure. The characterization of $Pt(PPh_3)_2(SB_8H_9)(OEt)$ from $Pt(C_2H_4)(PPh_3)_2$ as precursor is discussed, and the structure compared and related to earlier complexes.[265,266]

$$PtL_4 + SB_9H_9 \xrightarrow{EtOH} L_2Pt(SB_8H_{10}) + 2L \quad (95)$$

52.3.4 Boron Halide Complexes

Adducts of type $Pt(BX_3)_2(PPh_3)_2$ (X = F, Cl) have been prepared by reacting $Pt(C_2H_4)(PPh_3)_2$ or $Pt(PPh_3)_3$ with BX_3 (equation 96). The complexes have been isolated and characterized by ^{11}B NMR methods.[267]

$$Pt(PPh_3)_3 + 2BX_3 \longrightarrow Pt(BX_3)_2(PPh_3)_2 + PPh_3 \quad (96)$$

52.4 PLATINUM COMPLEXES OF GROUP IVA LIGANDS

52.4.1 Monomeric Platinum(II) Cyanide Complexes

Cyanide complexes of platinum occur most commonly in the divalent state, although there has been increasing interest in the complexes formed with platinum in a higher oxidation state. Among the complexes most recently studied have been the mixed valent complexes where platinum cyanides in the divalent state are partially oxidized. These complexes form one-dimensional stacks with Pt–Pt interactions. In the solid state these materials show interesting electrical conductivity properties, and these compounds are discussed by Underhill in Chapter 60. In this section the preparative procedures and spectroscopy of the complexes will be covered, but for solid state properties the reader is referred to Chapter 60.

The cyanide ion is isoelectronic with CO, and binds to platinum and other metal ions by σ donation of a pair of electrons in an *sp* hybrid orbital on the carbon atom, along with a complementary π back-donation from filled metal orbitals to empty π^* orbitals on CN^-. The anion is a poorer π acceptor than CO, but stable complexes are formed with platinum(II) and platinum(IV), and the ligand is high in the spectrochemical series.

The compound $Pt(CN)_2$ is a yellow water-insoluble compound formed by heating $(NH_4)_2Pt(CN)_4$ at 300 °C or by treating $K_2Pt(CN)_4$ with HCl (equation 97).[268] Synthesis of salts $Pt(CN)_4^{2-}$ is usually carried out by the addition of NaCN or KCN to an aqueous solution of $PtCl_4^{2-}$. The stability constant for complexation of CN^- to platinum(II) is very high, and it is not usually feasible to achieve partial substitution to form mixed halo cyanide complexes. Treatment of PtX_2L_2 (X = Cl, NO_2, NO_3; L = NH_3, en) with a stoichiometric amount of cyanide leads to the formation of $Pt(NH_3)_2(CN)_2$ (equation 98) and $Pt(en)(CN)_2$.[269,270] Monocyano complexes of type $Pt(CN)Cl(PPh_3)_2$ have also been prepared by refluxing $[PtCl(MeCN)(PPh_3)_2]Cl$ in benzene.[271] Mixed halo cyano platinum(II) complexes have also been prepared by the oxidative addition of XCN (X = Cl, Br, I) to $Pt(PPh_3)_3$ (equation 99).[272]

$$(NH_4)_2[Pt(CN)_4] \xrightarrow{300\,°C} Pt(CN)_2 \xleftarrow{HCl} K_2Pt(CN)_4 \quad (97)$$

$$PtX_2(NH_3)_2 + 2CN^- \longrightarrow Pt(CN)_2(NH_3)_2 + 2X^- \quad (98)$$

$$Pt(PPh_3)_3 + XCN \longrightarrow PtX(CN)(PPh_3)_2 + PPh_3 \quad (99)$$

The cyanide complex $Pt(CN)_4^{2-}$ has a stability constant of 10^{65-75} in aqueous solution, but the CN exchange rate is too fast to measure by radioisotope methods. Using ^{13}C NMR methods the exchange rate has been found to follow the rate law: rate = $k_2[Pt(CN)_4^{2-}][CN^-]$, and rate constants measured in the $26\,M^{-1}\,s^{-1}$ range. The experimental values for $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are $17 \pm 2\,kJ\,mol^{-1}$ and $-178 \pm 7\,J\,K^{-1}\,mol^{-1}$. It can be concluded that CN^- as a ligand for platinum(II) shows a high *trans* effect and forms thermodynamically stable yet kinetically labile complexes.[273]

Cyanide bonds to platinum(II) *via* the carbon atom. The nitrogen atom of the coordinated cyanide ligand reacts with electrophiles forming adducts. Along with examples in Section 52.3, the complex $Pt(CN)_4^{2-}$ reacts in a similar manner with $(\eta^5\text{-Cp})_2ZrI_2$ and $(\eta^5\text{-Cp})_2HfI_2$ in solution to yield polymeric amorphous solids of type $[(\eta^5\text{-Cp})_2ZrPt(CN)_4]_n$.[274]

52.4.1.1 *Spectroscopy and structure*

Raman studies have been made of the complexes $Pt(CN)_4^{2-}$, $Pt(^{13}CN)_4^{2-}$, and $Pt(C^{15}N)_4^{2-}$. Many of the vibrational frequencies have been determined. From force field calculations it is found that the Pt—C σ bond and Pt—CN 'back' π bond are both stronger than those found for the Ni and Pd analogs.[275]

The electronic structure of $Pt(CN)_4^{2-}$ has received considerable attention. The electronic spectrum shows a series of bands between 34 000 and 50 000 cm^{-1}, and at least six papers have discussed the assignments. A possible ordering of the platinum molecular orbitals shows a sequence $b_{1g}\ (d_{x^2-y^2}) \gg b_{2g}\ (d_{xy}) > e_g\ (d_{xz}, d_{yz}) > a_{1g}\ (d_{z^2})$. Alternatively the a_{1g} level has been proposed to be above the e_g and b_{2g} levels. The experimental data have recently been compared with the theoretical calculations, although the assignments of the MLCT absorptions still remain ambiguous.[276] The polarized absorption spectra of single crystals of $(\eta\text{-Bu}_4N)_2[Pt(CN)_4]$ at 5 K show that the excited states derived from $d \rightarrow a_{2u}$ transitions are strongly mixed by spin–orbit coupling. The σ and π polarizations have allowed a number of assignments to be unambiguously made.[277] The technique of chiral polymer and liquid crystalline polymer hosts has also been used for the characterization of intramolecular charge-transfer and exciton bands in $Cs_2Pt(CN)_4$ by circular dichroism spectropolarimetry.[278] In a study of the photophysics of aqueous $Pt(CN)_4^{2-}$, a detailed study of the non-Beer's-law behavior of the absorption features of the UV spectrum of aqueous $K_2Pt(CN)_4$ has led to a more definite set of excited state assignments. Concentration dependence, quenching and lifetime studies have shown that fluorescence and phosphorescence involve emission from oligomers.[279]

Hydrogen atoms generated by γ-radiolysis of aqueous sulfuric acid matrices at 77 K add to $Pt(CN)_4^{2-}$ to give $HPt(CN)_4^{2-}$ ions, the unpaired electron being in a σ^* orbital confined to hydrogen and platinum.[280]

Potassium tetracyanoplatinate trihydrate crystallizes in the orthorhombic form with planar $Pt(CN)_4^{2-}$ groups stacked parallel, forming linear Pt chains with a Pt–Pt separation of 3.478(1) Å. Alternate $Pt(CN)_4^{2-}$ groups are rotated giving an eclipsed configuration.[281] The structure of $Rb_2[Pt(CN)_4]\cdot1.5H_2O$ shows a bent Pt metal atom chain with a similar Pt–Pt separation of 3.421(2) Å. The largely staggered configuration of adjacent $Pt(CN)_4^{2-}$ groups may be due to $Rb^+\cdots N{\equiv}C$ attractive interactions and hydrogen bonding effects as well as to further reduction of repulsive cyanide π–π interactions.[282]

52.4.2 Partially Oxidized Cyanide Chain Complexes

The single crystal neutron diffraction structure of the partially oxidized $K_{1.75}[Pt(CN)_4]\cdot1.5H_2O$ shows a 'zigzag' metal atom chain with three crystallographically independent Pt atoms. The independent Pt separations are equal (2.961(1) and 2.965(1) Å). The short Pt–Pt separations and almost totally non-eclipsed configurations of adjacent $Pt(CN)_4^{1.75-}$ groups indicate considerable $Pt(5d_{z^2})$ metal overlap, strong metal–metal bond formation, and repulsive π–π cyanide interactions.[283] An X-ray structure of this material has also been carried out.[284]

Complexes of platinum having cyanide and non-stoichiometric quantities of halide ligand have been prepared. A review by Miller gives a broad coverage of this subject,[285] and a book series 'Extended Linear Chain Compounds' has a number of articles which are of direct interest and relevance to workers in this field.[286] This section will only briefly cover the topic, and will emphasize the more recent work.

A mixed halide complex $K_2Pt(CN)_4Br_{\sim0.16}Cl_{\sim0.16}\cdot xH_2O$ has been prepared by slow evaporation of a solution of $K_2Pt(CN)_4$, $K_2Pt(CN)_4Br_2$ and $K_2Pt(CN)_4Cl_2$. The complex cannot be prepared by electrolytic oxidation since $K_2Pt(CN)_4Cl_{0.3}$ will preferentially form, even in the presence of excess Br^-.[287] A difficulty in working with these materials is discussed with the reported preparation of $Mg[Pt(CN)_4]Cl_{0.28}$. Additional study suggests negligible chloride present in the compound, and that the blue color is due to structural changes within $Pt(CN)_4^{2-}$ itself, probably involving hydration differences.[288] The structure of the one-dimensional conductor $Rb_2[Pt(CN)_4]Cl_{0.3}\cdot3H_2O$ shows nearly planar $Pt(CN)_4$ moieties stacked to form a perfectly linear Pt–Pt chain. The crystal asymmetric unit contains two independent $Pt(CN)_4^{1.7-}$ groups with two unequal Pt–Pt chain distances of 2.877(8) and 2.924(8) Å.[289] A further combined neutron and X-ray structural study of $(NH_4)_2[Pt(CN)_4]Cl_{0.3}\cdot3H_2O$ shows again different Pt–Pt spacings. The neutron study shows the ammonium ion to be involved in hydrogen bonding.[290] The cesium salt $Cs_2[Pt(CN)_4]Cl_{0.3}$ again shows a perfectly linear Pt chain with Pt–Pt distances of 2.859(2) Å within the chain and 9.317 Å between chains. The compound is not hydrated and the separations between Cs^+ and Cl^- ions are significantly shorter than the sum of the ionic radii.[291] In order to investigate the ordering of Pt distances within a chain, the structure of $Rb_2[Pt(CN)_4]Cl_{0.3}\cdot3H_2O$ has been measured at 110 K and compared with that at 298 K. The lower temperature shows a decrease in both the average Pt–Pt spacing and the degree of dimerization. These results are discussed with respect to observed conductivity changes with temperature.[292]

The electrolytic method of synthesis has been used to prepare $K_2[Pt(CN)_4](FHF)_{0.30}\cdot xH_2O$. The medium used is a very acidic HF medium, and the added fluoride ion is present as FHF^- (equation 100).[293] The structure consists of columnar chains of square planar $Pt(CN)_4^{1.60-}$ groups separated by a Pt–Pt distance of 2.798(1) Å.[294] This distance is very close to that of 2.77 Å in Pt metal.

$$Pt(CN)_4^{2-} + FHF^- \xrightarrow{-e^-} Pt(CN)_4^{2-}(FHF)_{0.30} \tag{100}$$

Finally complexes have been obtained having two different cations and a partially oxidized $Pt(CN)_4^{2-}$ chain. These molecules show significant changes in electrical conductivity with small differences in cation composition.[295,296]

The distances found between platinum centers in these molecules have been correlated with the resonating valence bond theory of metals introduced by Pauling. The experimentally characterized partially oxidized one-dimensional platinum complexes fit a correlation of bond number *vs.* metal–metal distances, and evidence is presented that Pt—Pt bond formation in the one-dimensional chains is resonance stabilized to produce equivalent Pt—Pt distances.[297] The band structure of the $Pt(CN)_4^{2-}$ chain has also been studied by the extended Hückel method. From the band structure and the density of states it is possible to derive an expression for the total energy per unit cell as a function of partial oxidation of the polymer. The equilibrium Pt–Pt separation estimated from this calculation decreases to less than 3 Å for a loss of 0.3 electrons per platinum.[298]

52.4.3 Monomeric Platinum(IV) Cyanide Complexes

In addition to partially oxidized platinum cyano complexes, complexes of platinum(IV) have also been prepared. Potassium hexacyanoplatinate(IV) is obtained from K_2PtI_6 and KCN (equation 101).[299] With K_2PtCl_6 and KCN, reduction occurs. The complex $K_2Pt(CN)_6$ is water stable. Oxidation of $K_2Pt(CN)_4$ by halogen X_2 (X = Cl, Br, I) yields $K_2[Pt(CN)_4X_2]$.[300] Refluxing these compounds with ammonia gives $Pt(CN)_4(NH_3)_2$ (equation 102). The platinum(II) analog compounds $Pt(NH_3)_2(CN)_2$ are also known, having been prepared from either $PtCl_2(NH_3)_2$ or $Pt(CN)_2$ (equations 103a and 103b).[301] The electronic structures and MCD spectra of these compounds are compared with that of $Pt(CN)_4^{2-}$ and the spectral assignments given.

$$K_2PtI_6 + 6KCN \longrightarrow K_2Pt(CN)_6 + 6KI \tag{101}$$

$$K_2[Pt(CN)_4] + X_2 \longrightarrow K_2[Pt(CN)_4X_2] \xrightarrow{NH_3} Pt(CN)_4(NH_3)_2 + 2KX \tag{102}$$

$$\textit{trans}\text{-}PtCl_2(NH_3)_2 \xrightarrow[CN^-]{AgNO_3} \textit{trans}\text{-}Pt(CN)_2(NH_3)_2 \tag{103a}$$

$$Pt(CN)_2 + 2NH_3 \longrightarrow \textit{cis}\text{-}Pt(CN)_2(NH_3)_2 \tag{103b}$$

X-Ray diffraction shows that the $[Pt(CN)_6]^{2-}$ ion is regular octahedral with linear Pt—C—N bonds.[302] The IR and Raman spectra of $K_2[Pt(CN)_6]$ have C—N stretching vibrations at higher frequencies and C—N force constants which are larger than the corresponding divalent complexes.[303,304] This correlates with less π back-donation from the metal to the empty π^* orbitals of the cyanide ligand in the Pt^{IV} complexes.

52.4.4 Platinum Carbonyl Complexes

This section on platinum carbonyl complexes should be read in conjunction with the comparable chapter by Hartley in 'Comprehensive Organometallic Chemistry', Volume 6, Chapter 39. This section will emphasize very recent work and will omit compounds which are completely organometallic in nature.

52.4.4.1 Monomeric platinum carbonyls

The simple binary carbonyl $Pt(CO)_4$ is unstable and has only been prepared under matrix isolation conditions.[305] Clusters having a formula $[Pt_n(CO)_{2n}]^{2-}$ have been obtained by carbonylation of Na_2PtCl_4 in ethanol or by the reductive carbonylation of $Na_2PtCl_6{\cdot}6H_2O$ in methanol in the presence of NaOH or NaOAc.[306] The first product is $[Pt(CO)Cl_3]^-$. Large platinum carbonyl clusters have also been prepared from $PtCl_2(CO)_2$. The electronic and geometric structural properties of linear PtCO have been investigated using an *ab initio* calculation. This concludes that on complexation with a Pt atom the loss of C═O antibonding character in the carbon lone pair orbital dominates the decrease in π bonding due to the

Pt($5d_\pi$)–CO(π^*) interaction. Charge transfer between the Pt and CO fragments is dominated by the CO→Pt σ dative bond at larger Pt—CO distances and by Pt→CO π back-bonding at shorter bond lengths.[307]

When CO is passed through a suspension of K_2PtCl_4 in concentrated HCl the initial carbonyl species formed is $[Pt(CO)Cl_3]^-$. Continued reaction leads to the platinum(I) carbonyl complex $[Pt_2(CO)_2Cl_4]^{2-}$.[308] The structure shows two $PtCl_2(CO)^-$ groups linked by a short Pt—Pt bond of 2.584(2) Å.[309] The long Pt—Cl bond lengths indicate a large *trans* influence for the Pt^I—Pt^I bond.

Carbonyl halide complexes of platinum(II) are common. Treating $PtCl_3$ with CO under 40–120 atm at 110 °C yields $Pt(CO)_2Cl_2$ and phosgene.[310] The compound can also be obtained in higher yield by heating hydrated $PtCl_4$ in $SOCl_2$ at 110 °C under CO pressure.[311] A further synthesis involves the reaction of platinum atoms with oxalyl chloride (equation 104).[312] These monomeric complexes are thermally unstable to CO loss and formation of the chloro-bridged complex (equation 105). Treatment of $[Pt(CO)Cl_2]_2$ with HCl cleaves the chloride bridge to form anionic $Pt(CO)Cl_3^-$. This complex can also be formed by reaction of chloroplatinic acid in DMF for 20 min.

$$Pt + (COCl)_2 \longrightarrow Pt(CO)_2Cl_2 \tag{104}$$

$$2Pt(CO)_2Cl_2 \longrightarrow [Pt(CO)Cl_2]_2 + 2CO \tag{105}$$

Carbonyl halide complexes of platinum(IV) are less common. The reaction of $[Pt(CO)_2]_5$ with chloride ion in an aqueous solution of iron(III) ions gives $Pt(CO)H_2Cl_2$, which adds chloride to give $Pt(CO)H_2Cl_3^-$.[313,314] Addition of chlorine to a thionyl chloride solution of $Pt(CO)_2Cl_2$ at room temperature results in the rapid formation of $Pt(CO)Cl_5^-$ (equation 106), which shows a carbonyl stretch at 2191 cm^{-1}. The yellow-orange compound is stable toward Cl^- but reacts with water to form CO_2.[315]

$$Pt(CO)Cl_3^- + Cl_2 \longrightarrow Pt(CO)Cl_5^- \tag{106}$$

Carbonyl halides with ligands such as phosphines are known. When CO is passed through a solution of $PtCl_2L_2$ (L = PEt_3, $AsMePh_2$ or $AsCy_3$) containing $NaClO_4$, chloride is substituted by CO to give $[PtCl(CO)L_2](ClO_4)$ (equation 107).[315] Carbon monoxide will also substitute alkenes and alkynes from platinum(II) to give platinum(II) carbonyl complexes (equation 108).

Structural studies have been carried out on *trans*-$[PtCl(CO)(PEt_3)_2]BF_4$, *trans*-$[Pt(p\text{-}ClC_6H_4)(CO)(PEt_3)_2]PF_6$, *cis*-$PtCl_2(CO)(PPh_3)$, $NBu_4[PtCl_3(CO)]$ and $[PtMe\{HB(pz)_3\}CO]$, which show that the *trans* influence of the CO ligand is very small.[317–321]

$$PtCl_2L_2 + CO + NaClO_4 \longrightarrow [PtCl(CO)L_2]ClO_4 + NaCl \tag{107}$$

$$PtCl_2(C_2H_4)(RNH_2) + CO \longrightarrow PtCl_2(CO)(RNH_2) + C_2H_4 \tag{108}$$

A steady decrease in ν(CO) occurs in platinum(II) halogen carbonyl complexes as the atomic number of the halogen is increased, reflecting increasing importance of π back-donation from platinum(II) to CO as the electronegativity of the halogen decreases.[322,323] There is also a decrease in the Pt—C stretching frequency in ν(PtC) with increasing halogen size, but the trend is small. For a series of salts $PtCl_2R(CO)^-$ (R = Me, Et, Pr^n, Pr^i, Bu^n, Ph), comparisons have been made between ν(CO), ^1J(PtC) and $\delta(^{195}Pt)$. The most notable effect of β-methyl groups is to increase ^1J(PtC) of the carbonyl group, and since there are parallel decreases in ν(CO), this is ascribed to increased donation of electrons by the alkyl group to the metal.[324] The increase of ^1J(PtC) in the NMR on going from $PtX_2(CO)_2$ to $PtX_3(CO)^-$ is much less than the increase in the Pt—C stretching force constant.[325] This implies that the platinum 6*s* orbital is not especially involved in the Pt—C bond, which is therefore heavily dependent on the platinum $5d_{x^2-y^2}$ orbital. In the NMR spectra of PtX(CO)LL′ complexes, the ^{13}C chemical shift shows little dependence on the nature of the *cis* ligand, but a strong dependence on the nature of the *trans* ligand, the stronger σ donors moving the value closer toward the value in free CO.[323] Values for *J*(PtC) depend strongly on the *trans* ligand. Ligands with high *trans* influence give coupling constants in the range 960–990 Hz, while ligands of low *trans* influence give values in the 1658–1817 range.

In a kinetic study of the displacement of CO from $Pt(CO)Cl_3^-$ by bipyridyl there is rapid replacement of chloride to form Pt(CO)Cl(bipy), followed by slow replacement of CO by chloride to give $PtCl_2$(bipy) (equation 109).[326] A similar replacement reaction between

$PtCl_2X(CO)^-$ (X = Cl, Br, I) and *p*-substituted pyridines concludes that the equilibrium constant for equation (110) is quite sensitive to the *para* substituent Z, but relatively insensitive to the nature of X.[327] Cleavage of $[PtX_2L]_2$ (L = tertiary phosphine or arsine) gives *trans*-$PtX_2(CO)L$. These compounds readily lose CO and isomerize to the *cis* derivatives. The *trans* to *cis* isomerizations are catalyzed by free CO, phosphines, or halides, the latter being effective in the solid state. The *trans* to *cis* isomerizations are also accelerated by visible or UV light.[328] The analogous complexes $PtCl_2(CO)L$ (L = PEt_3, PBu^n_3, $PMePh_2$, PPh_3, $P(C_6H_4F\text{-}p)_3$ and PCy_3) can also be prepared by treating $PtCl_2(cod)$ with CO and tertiary phosphine (equation 111).[329]

$$Pt(CO)Cl_3^- + bipy \longrightarrow Pt(CO)Cl(bipy)^+ \xrightarrow{Cl^-} PtCl_2(bipy) \qquad (109)$$

$$Pt(CO)Cl_2X^- + Z\text{-}py \rightleftharpoons Pt(CO)ClX(Z\text{-}py) + Cl^- \qquad (110)$$

$$PtCl_2(cod) + CO + L \longrightarrow PtCl_2(CO)L + cod \qquad (111)$$

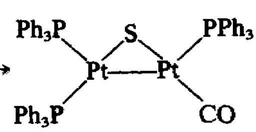
The coordinated carbonyl will undergo nucleophilic attack at carbon. It has been suggested that whether or not nucleophilic attack will occur can be predicted on the basis of the C—O stretching force constants.[330] This premise is based on the fact that the higher the force constant the greater is the fractional positive charge on the carbon atom. In agreement with this, *cis*-$PtCl_2(CO)_2$ reacts with diisopropylamine to yield the corresponding carbonyl complex (equation 112).[331] Carbonyl complexes also react with water to give CO_2 (equation 113).[332] These reactions proceed *via* hydrocarbonyl intermediates.

$$cis\text{-}PtCl_2(CO)_2 + HNPr^i_2 \longrightarrow \left[PtCl_2(CO)C(=O)NPr^i_2\right]^- + H^+ \qquad (112)$$

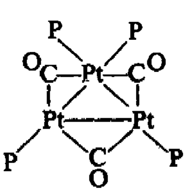
$$[PtCl_2(CO)]_2 + 2H_2O \longrightarrow 2Pt + 2CO_2 + 4HCl \qquad (113)$$

52.4.4.2 *Multimetallic platinum carbonyls*

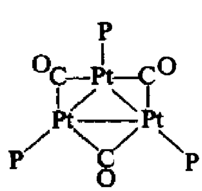
The binuclear platinum carbonyl $Pt_2S(CO)(PPh_3)_3$ is formed when $Pt(COS)(PPh_3)_2$ is heated in chloroform (equation 114). In the crystalline state the compound exists in two conformationally isomeric forms, the difference being due to changes in the phenyl ring orientations.[334] The recent structure determination of the compound $[Pt_2Br_2(\mu\text{-}CO)(PPh_3)_3]$ shows it to have an asymmetrically bridged CO ligand. This feature is believed to lead to some valence disproportionation, in contrast to its precursor $Pt_2Br_4(CO)_2^{2-}$.[335]

$2Pt(COS)(PPh_3)_2 \longrightarrow$  $+ COS + PPh_3$ (114)

Trinuclear clusters of platinum carbonyls are more common. These have been prepared by the reaction of $[Pt(CO)_2]_n$ with phosphine ligands,[336] the reduction of $PtHXL_2$ with hydrazine in the presence of CO,[337] and the reductive elimination of hydrogen from *trans*-$PtH_2(PCy_3)_2$ in the presence of CO.[338,339] The initially formed $Pt_3(CO)_4L_4$ has been isolated for L = PPh_3, PPh_2Me, PPh_2Et, PEt_3, PCy_3. The X-ray structure and solution ^{195}Pt NMR spectrum show two different types of platinum for these $Pt_3(CO)_4L_4$ compounds.[338,340] This is due to an unsymmetrical structure (**26**) where the apical platinum is bonded to two PCy_3 ligands. The structure of $Pt_3(CO)_3(PCy_3)_3$ is symmetrical with three bridging carbonyls in a similar arrangement (**27**).[341]



(**26**)



(**27**)

Mixed metal trimetallic carbonyls of platinum have also been synthesized and characterized crystallographically. Among those known are examples with carbonyls and phosphine ligands and a metal–metal bonded framework with $PtFe_2$,[342] Pt_2Fe,[343] Pt_2Ru,[344] and $PtOs_2$,[345] and phosphido-bridged complexes with $PtMn_2$.[346]

Tetranuclear clusters $Pt_4(CO)_5L_4$ and $Pt_4(CO)_5L_3$ have been prepared from the reaction of CO on the trinuclear species.[336,347] For tetrametallic compounds examples are found with Pt_2Mo_2, Pt_2Co_2 and Pt_2M_2 (M = Cr, Mo, W).[348,349] These latter complexes show an irreversible two-electron reduction leading to the rupture of the metallic core into identified fragments. These complexes are of the type $[PtM(\mu^3\text{-}CO)(\mu^2\text{-}CO)_2Cp(PPh_3)]_2$, and the first two oxidation waves indicate one-electron processes.[349] A tetrametallic carbonyl cluster $PtOs_3(\mu\text{-}H)_2(CO)_{10}(PR_3)$ has also been characterized.[350]

52.4.5 Isocyanide Complexes

As for carbonyl complexes, this section is relatively brief, omitting most references to complexes having no bonds to platinum other than from carbon. For a fuller and more detailed coverage the reader is directed to Chapter 39 of 'Comprehensive Organometallic Chemistry'. This section outlines the types of complexes which have been prepared, and indicates the range of reactions which have been carried out, without giving more details than are necessary to give the reader a broad outline and direction.

52.4.5.1 Synthesis

The zerovalent complex $Pt(CNCy)(PF_3)_3$ has been prepared by substitution of $Pt(PF_3)_4$ (equation 115).[351] Ethylene is also displaced from $Pt(C_2H_4)(PPh_3)_2$ by Bu^tNC at −20 °C to give the complex $Pt(CNBu^t)_2(PPh_3)_2$.[352] This complex undergoes oxidative addition of I_2 to give $[PtI(CNBu^t)_2(PPh_3)_2]I$.

$$Pt(PF_3)_4 + CyNC \longrightarrow Pt(CNCy)(PF_3)_3 + PF_3 \quad (115)$$

Platinum(I) isocyanide complexes are formed when Na_2PtCl_4 reacts with methyl isocyanide, and the product isolated by addition of $AgPF_6$ (equation 116). The structure has two square planar platinums linked by a Pt—Pt bond, with the two $Pt(CNMe)_3$ units perpendicular. The NMR spectrum shows that intramolecular rearrangements occur involving the tetrahedral deformation of one Pt center followed by rotation about the Pt—Pt bond.[353,354]

$$2PtCl_4^{2-} + 8MeNC + 2H_2O \longrightarrow [Pt_2(CNMe)_6]^{2+} + 8Cl^- + CO_2 + 2MeNH_2 + 2H^+ \quad (116)$$

Platinum(II) isocyanide complexes can be readily prepared by displacement of halide ligands by isocyanides. Reacting a solution of PtX_4^{2-} (X = Cl, Br, I, NO_2, CN) with two equivalents of isocyanide gives $PtX_2(CNR)_2$.[355–360] The compounds give the covalent form $PtX_2(CNR)_2$ and the Magnus green type salts $[Pt(CNR)_4][PtCl_4]$. Complexes PtX_2L_2 react with isocyanides with displacement of either an anionic (X) or a neutral (L) ligand.[361] An alternate route is the alkylation of a coordinated cyanide by methyl iodide or trimethyloxonium.[352,361,362] An example is shown in equation (117).

$$Pt(CN)_2(PPh_3)_2 + 2MeI \longrightarrow PtI_2(CNMe)_2 + 2PPh_3 \quad (117)$$

Platinum(IV) isocyanide complexes $PtCl_4(CNR)_2$ and $[PtCl_2(CNR)_2(PMe_2Ph)_2]^{2+}$ have been prepared by the addition of Cl_2 to the corresponding platinum(II) compounds (equation 118).[363] It is probable that the *trans* influence of the isocyanide ligand on platinum(IV) is greater than that of a tertiary phosphine.

$$PtCl_2(CNR)_2 + Cl_2 \longrightarrow PtCl_4(CNR)_2 \quad (118)$$

52.4.5.2 Physical properties of isocyanide complexes

The structures of $PtCl_2(CNEt)(PEt_2Ph)$,[364] *cis*-$PtCl_2(CNPh)(PEt_3)$, *cis*-$PtCl_2(CNPh)_2$[365] and $PtMe(CNBu^t)(HBpz_3)$[366] show that the isocyanide bonds through platinum. Bonding occurs *via*

σ donation of the lone pair of electrons in the *sp* hybrid orbital on carbon, along with a concomitant back-donation of electron density from filled Pt orbitals to empty π^* orbitals on the isocyanide. This π back-donation is less than that found in carbonyl complexes.

The C—N stretching frequencies are higher than in the free ligands.[367] This is caused by increased π donation from the doubly filled nitrogen 2*p* orbital to the empty 2*p* orbital on carbon. This effect is induced by coordination of the isocyanide carbon to platinum. From values of ν(PtCl) in a series of complexes *trans*-$[PtClL(PEt_3)_2]ClO_4$ (L = CNR), the *trans* influence of the CNR ligand is greater than CO but significantly less than that of tertiary phosphines.[368]

The electronic spectra of isocyanide complexes $[Pt(CNR)_4]X_2$ show intense charge transfer bands in the UV region caused by MLCT to a π^* orbital. The *d–d* bands have been assigned to ordering $d_{x^2-y^2} \gg d_{z^2} > d_{xz}, d_{yz} > d_{xy}$.[369] The spectral assignments have been used to construct a state diagram for comparison between $Pt(CNMe)_4^{2+}$ and $Pt(CN)_4^{2-}$. The complex $Pt(CNMe)_4^{2+}$ has not been partially oxidized, and this is likely because the 4+ charge difference will diminish the overlap of the a_{1g} wave functions between adjacent $Pt(CNMe)_4^{2+}$ ions relative to the overlap of wave functions for those of $Pt(CN)_4^{2-}$. As a consequence the probability of forming one-dimensional complexes decreases.

52.4.5.3 *Reactions of isocyanide complexes*

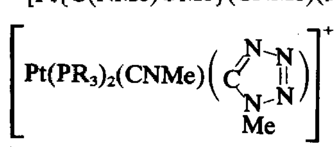
The most common reaction of platinum(II) isocyanides is their reaction with nucleophiles. This reaction is a useful one for the formation of platinum carbene complexes, and this will be discussed in the next section.

Platinum(II) isocyanide complexes are attacked by water, hydroxide,[370] alkoxide,[361] azide[361] and nitrite[361] to give complexes of type $PtC(R){=}NR_2$ (equations 119–123). The rate is faster with more nucleophilic substrates. The reaction is also promoted by electron-withdrawing substituents on the isocyanide ligand. The most prominent step involves direct attack of the nucleophile at the isocyanide carbon. The rate of the primary step is affected by the donor ability of the entering amine, by the electrophilic character of the isocyanide carbon, and by steric crowding around the reacting centers, with solvation being important. The reaction system is versatile with proper choice of substituent on the amine and isocyanide ligands, and with variation of ancillary ligands on the metal complex.[371]

$$[Pt(CNBu^t)_4]Cl_2 + 2H_2O \longrightarrow Pt(CN)_2(CNBu^t)_2 + 2BuOH + 2HCl \quad (119)$$

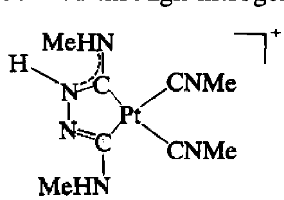
$$trans\text{-}[Pt(CNMe)_2(PPh_3)_2]^{2+} + OH^- \longrightarrow trans\text{-}[Pt\{C(O)NHMe\}(CNMe)(PPh_3)_2]^+ \quad (120)$$

$$trans\text{-}[Pt(CNMe)_2(PR_3)_2]^{2+} + OMe^- \longrightarrow [Pt\{C(NMe)OMe\}(CNMe)(PR_3)_2]^+ \quad (121)$$

$$[Pt(CNMe)_2(PR_3)_2]^{2+} + N_3^- \longrightarrow$$

(122)

$$[Pt(CNMe)_2(PR_3)_2]^{2+} + NO_2^- \longrightarrow [Pt\{C(O)NHMe\}(CNMe)(PR_3)_2]^+ \quad (123)$$

Reacting $PtCl_4^{2-}$ with RNC and then hydrazine gives compounds known as Chugaev's salts.[372,373] The structures of the two salts have been elucidated and are shown as (**28**) and (**29**).[374,375] Similar complexes are formed when isocyanides are inserted into a Pt—H bond. The reaction between *trans*-$PtHCl(PEt_3)_2$ and ArNC in acetone solvent in the presence of $AgClO_4$ gives a cationic isocyanide complex of platinum(II) which undergoes insertion to give an imino complex by equation (124). These complexes react with metal ions of the first transition series to form complexes bonded through nitrogen.[377]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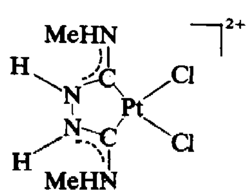
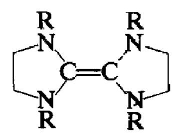

(29)

$$PtH(CNAr)(PEt_3)_2 \xrightarrow{CH_2Cl_2} PtCl\{C(NAr)H\}(PEt_3)_2 \quad (124)$$

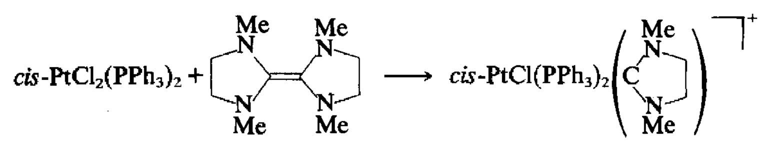
52.4.6 Carbene Complexes

The chemistry of carbene complexes is a field which has developed in the past 20 years. The current interest is primarily centered on the chemistry of the early transition elements, but much of the early work was carried out at low valent metal centers. The major complexes formed by platinum are those with the metal in a divalent oxidation state.

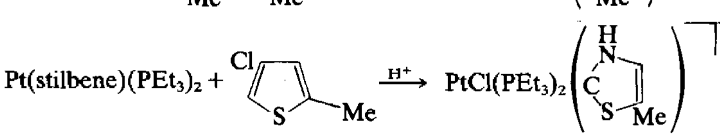
A logical route to the synthesis of platinum carbene complexes is by using a carbene precursor. This method has been successfully used with electron-rich alkenes. Reacting (**30**) with *cis*-$PtCl_2(PPh_3)_2$ and similar complexes leads to the formation of carbene complexes (equation 125).[378–380] Heterocyclic chloro compounds have also been used to prepare carbene complexes (equation 126).[381]



(**30**)

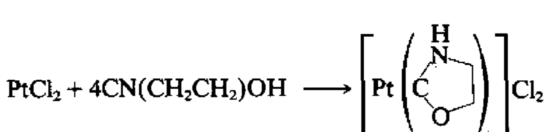


(125)



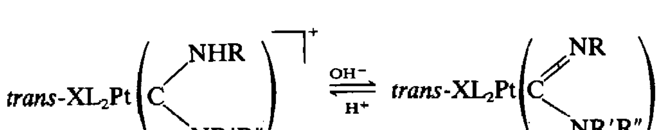
(126)

Carbene complexes can be readily prepared by nucleophilic attack at a coordinated isocyanide ligand. One of the earliest examples was found on reacting $CN(CH_2)_2OH$ with $PtCl_2$. Initial coordination of the isocyanide carbon occurs, then this complexed carbon undergoes intramolecular nucleophilic attack to give the carbene (equation 127).[382] A series of cationic carbene complexes *trans*-$[PtX\{C(NHR)NR'R''\}L_2]ClO_4$ (X = H, Cl, Br; R = Me, Ph, *p*-$O_2NC_6H_4$; R' = H, Me; R'' = Me, Et, Ph, *p*-MeC_6H_4; L = PEt_3, PBu^n_3, PPh_3, CNPh, $CNC_6H_4NO_2$-*p*) have been prepared by the reaction of base R'R''NH with the cationic isocyanide complexes *trans*-$[PtX(CNR)L_2]ClO_4$ (equation 128).[383] The complexes undergo a reversible reaction with base yielding the neutral amidino product formed by nucleophilic attack at a coordinated isocyanide ligand (equation 129). The binary isocyanide complex $[Pt(CNMe)_4]^{2+}$ reacts with methylamine to form the binary carbene complex (equation 130).[384] The complex $PtCl(CHNR)(PEt_3)_2$ reacts with HCl and dimethyl sulfate with protonation or alkylation at nitrogen to give carbene complexes (equation 131).[385] These complexes are characterized by a broad low field carbene C*H* signal in the ^1H NMR spectrum, and a strong absorption due to $\nu(C_{carbene}—N)$ in the 1500–1600 cm^{-1} region of the IR spectrum. The ^1H NMR spectrum shows evidence for restricted rotation about the C—N bond.

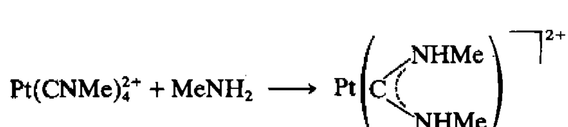


(127)

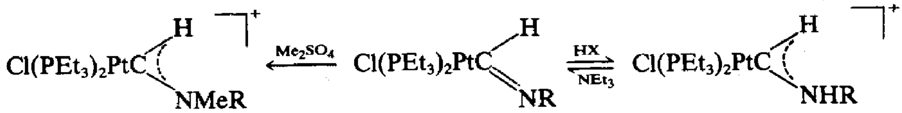
$$trans\text{-}PtX(CNR)L_2^+ + R'R''NH \longrightarrow trans\text{-}[XL_2Pt\{C(NHR)NR'R''\}]^+ \qquad (128)$$



(129)



(130)

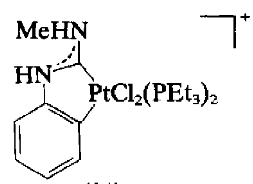


(131)

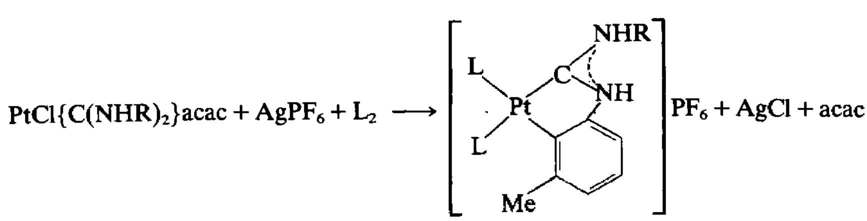
Ethanol will add across the C≡N triple bond in *cis*-$PtCl_2(CNPh)(PEt_3)$ to give the carbene complex *cis*-$[PtCl_2\{C(OEt)NHPh\}PEt_3]$ (equation 132).[386] The Pt—Cl distances are 2.361(5) and 2.367(7) Å, and the Pt—C(carbene) distance is 1.96(2) Å. This Pt—C distance is among the shorter Pt—C(carbenoid) distances which generally fall in the range 1.95(2)–2.13(2) Å. Complexes of this type can also be prepared by reaction of *trans*-$Pt(CNR)(CHNHR)(PEt_3)_2^{2+}$ with methoxide ion.[385] Carbon-13 NMR signals for carbene ligands occur at very low field. A compilation has been made of the ^1H, ^{13}C shift data, and the ^{195}Pt coupling constant values for a large series of platinum carbene complexes.[387] Carbene complexes of platinum(II) have also been prepared by the reaction of amines with complexes having a coordinated vinylogous aminoisonitrile.[388]

$$cis\text{-}PtCl_2(CNPh)(PEt_3) + EtOH \longrightarrow cis\text{-}[PtCl_2\{C(OEt)NHPh\}PEt_3] \qquad (132)$$

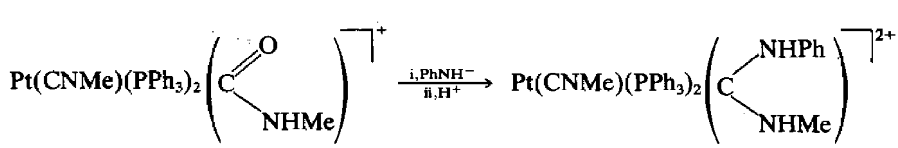
Carbene complexes of platinum(IV) have been prepared by similar reactions. The platinum(II) carbene complexes $PtCl_2\{C(NHR')(NHR'')\}PEt_3$ ($R' = R'' = Me$) undergo oxidative addition with chlorine to give the expected complexes $PtCl_4\{C(NHR')(NHR'')\}PEt_3$. When $R'' = Ph$ a different carbene complex (**31**) is formed involving metalation of the phenyl ring at the 2-position and chlorination at the 4-position.[389] The bonding of the carbene ligand resembles that in platinum(II) complexes. The carbene ligand is principally a σ donor. Possible mechanisms for the formation of this complex are discussed, but no definitive conclusions can be drawn.[390] An *ortho*-metalated carbene complex of platinum(II) has been isolated by reacting $PtCl\{C(NHR)_2\}acac$ ($R = p$-tolyl) with $AgPF_6$ followed by a ligand L_2 (L_2 = dppe; equation 133).[391] Amino carbenes can also be prepared by a replacement reaction. Treating $Pt(CNMe)(PPh_3)_2(CONHMe)$ with the anion from aniline, followed by protonation, yields the C(NHPh)(NHMe) carbene complex (equation 134).[370]



(31)

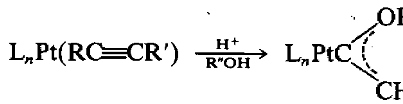


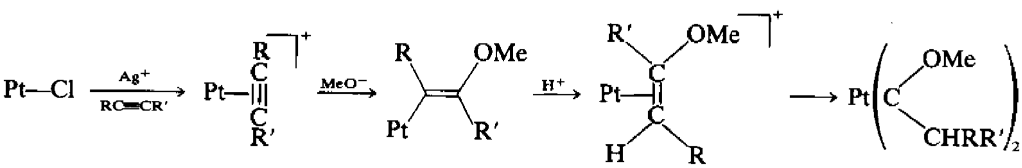
(133)



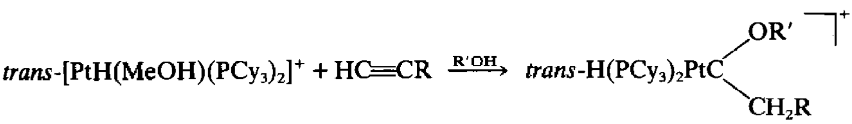
(134)

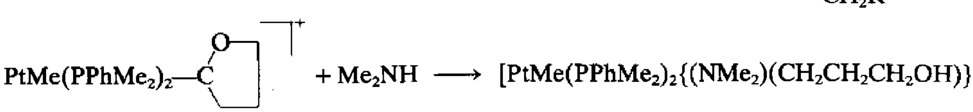
Carbene complexes can also be formed by nucleophilic attack on alkyne complexes (equation 135). This method has been pioneered by Clark and co-workers, and the pathway follows that shown in equation (136).[392–394] The reaction is sensitive to the nature of the alkyne, the supporting ligands, the solvent and the reaction conditions. This method has been used to prepare *trans*-$[PtMe\{C(Me)(OMe)\}(AsMe_3)_2]^+$, which reacts with *p*-substituted anilines to give the carbene complexes *trans*-$[PtMe\{C(Me)(NHC_6H_4X\text{-}p)\}(AsMe_3)_2]^+$ (equation 137).[395] Carbon-13 data for these complexes are plotted and discussed. The compound obtained using dimethylamine instead of *p*-substituted anilines has been structurally characterized.[396] The formation of these compounds appears to involve a highly amine-crowded transition state so that steric effects of the amino group are important.[397] The methanol-solvated complex *trans*-$[PtH(MeOH)(PCy_3)_2]^+$ reacts with terminal alkynes to give carbene complexes (equation 138).[398] Cyclic carbenes can undergo ring opening on reaction with dimethylamine *e.g.* equation (139); the product has been structurally characterized.[399]


(135)

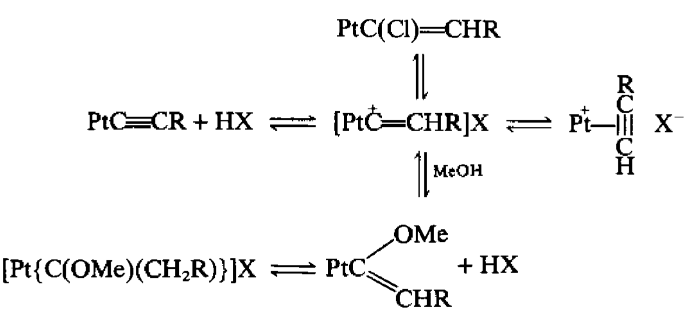

(136)

$$[PtMe\{C(Me)(OMe)\}(AsMe_3)_2]^+ + p\text{-}XC_6H_4NH_2 \longrightarrow [PtMe\{C(Me)(NHC_6H_4X\text{-}p)\}(AsMe_3)_2]^+ + MeOH \quad (137)$$


(138)


(139)

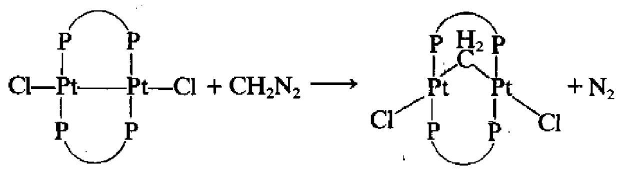
Carbene complexes are also obtained when platinum(II) acetylide complexes are treated with acids such as HPF_6 in alcohol, or when α-chlorovinyl complexes are reacted with alcohol. The reaction is outlined in Scheme 4. The reactions of platinum-stabilized vinyl carbonium ions formed from cationic π-alkynic complexes, protonation of platinum acetylides, and solvolysis of α-chlorovinylplatinum(II) compounds, are discussed along with H/D-labeled experiments.[400] The reaction of the platinum acetylide with protonic acids has been studied in more detail and the data interpreted on the basis of a platinum-stabilized vinyl cation.[401] The platinum(II) vinyl complexes undergo isomerization, a process dependent on the anion.[402] Neutral platinum(II) carbene complexes of this type have been prepared from the halo-bridged complexes $Pt_2X_2(\mu\text{-}X)_2L_2$ by reaction with terminal alkynes in alcohol solvent.[403,404] Both solid state and ^1H NMR techniques show a long Pt···H contact of 2.6(1) Å to a hydrogen atom of the ethoxy group in *cis*-$[PtX_2L\{C(OEt)CH_2R\}]$. The carbene complexes *cis*-$[PtCl_2(PR_3)\{C(OR')(CH_2R'')\}]$ react rapidly with CD_3OD to yield *cis*-$[PtCl_2(PR_3)\{C(OR')(CD_2R'')\}]$, then slowly to give *cis*-$[PtCl_2(PR_3)\{C(OCD_3)(CD_2R'')\}]$.



Scheme 4

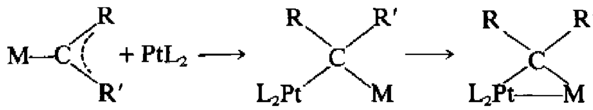
A number of other reactions have been used to prepare carbene complexes. When *trans*-$PtCl(C_6Cl_5)(PPhMe_2)_2$ reacts with $LiC{=}CH(CH_2)_nO$, followed by protonation with $HClO_4$, the cationic carbene complex *trans*-$[C_6Cl_5(PPhMe_2)_2Pt\{CCH_2(CH_2)_nO\}]^+$ is formed.[405] Carbene complexes $[PtCl\{C(SR)Y\}L_2]^+$ (R = Me, Et; Y = OMe, SEt, NMe_2; L = PPh_3, $PMePh_2$) have been prepared by alkylation of the sulfur of the parent thioester $PtCl\{C(S)XMe\}L_2$ (X = O, S) or the thiocarbamoyl complex $PtCl\{C(S)NMe_2\}L_2$ with Et_3O^+ or $MeOSO_2F$.[406] Cationic alkoxycarbene complexes of platinum(II) have been isolated using trimethylsilylalkynes. Cleavage of the C—Si bond occurs by nucleophilic attack of alcohol.[407]

Bridging ligands of the CRR′ type have been discussed as bridging carbenes. We will include them here for the sake of completeness of this section. Treating $Pt_2Cl_2(\mu\text{-dppm})_2$ with diazomethane gives the yellow complex $Pt_2Cl_2(\mu\text{-}CH_2)(\mu\text{-dppm})_2$ (equation 140).[123] The complex is stable and it has been characterized by ^1H and ^{31}P NMR spectroscopy. The reaction is first order in complex and diazomethane, and the rate constant of $41.2\,M^{-1}\,s^{-1}$ is found at 2 °C. The activation parameters are $\Delta H^{\neq} = 59.65 \pm 1.00\,kJ\,mol^{-1}$ and $\Delta S^{\neq} = 3.93 \pm 3.47\,J\,mol^{-1}\,K^{-1}$. The data are compared for a series of binuclear μ-dppm platinum complexes.[408]



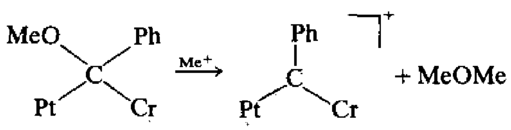
(140)

An impressive series of carbene- and carbyne-bridged complexes of platinum have been formed by reaction of metal carbene complexes with a platinum complex (equation 141). These complexes have been verified by X-ray crystallography, and the synthetic method appears to be one of some generality. Among the complexes of this type formed from carbenes are ones having metal frameworks with Pt—W,[409–413] Pt—Mn[414–418] and Pt—Cr[413,417] bonds.

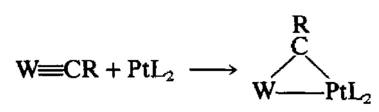


(141)

Bridging carbyne complexes of $PtCr(\mu\text{-CPh})$ structure have been prepared by alkylation of the carbene complex with Me_3O^+ (equation 142).[417] Alternatively bridging carbyne complexes with a PtW framework have been prepared by reacting a tungsten carbyne complex with $Pt(C_2H_4)(PR_3)_2$ (equation 143).[419] These carbyne complexes add a tertiary phosphine at carbon to form the bridged carbene complex.[418] A bridging thiocarbyne complex $[MnPt(\mu\text{-CSMe})(CO)_2(PMe_2Ph)_2Cp](BPh_4)$ has been prepared by methylation at sulfur of $MnPt(\mu\text{-CS})(CO)_2(PMe_2Ph)_2Cp$ with $[Me_3O]BF_4$.[420]



(142)



(143)

Extension to trimetallic complexes has led to the preparation of similar bridging carbene and carbyne complexes with Pt_3,[421] Pt_2W[422] and PtWFe[423] metal frameworks.

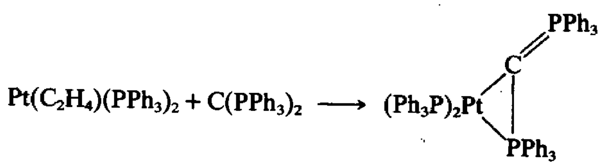
Conversion between carbyne and carbene complexes can also be carried out by methylene group transfer from $Cp_2Ti(\mu\text{-Cl})(\mu\text{-}CH_2)AlMe_2$ to the multiple metal–carbon bond of $Pt(\mu\text{-CR})W$ compounds.[424]

52.4.7 Ylide Complexes

A recent review discusses the chemistry of ylides and their reactions with transition metal complexes.[425] This article integrates platinum ylide chemistry with that of other metal ions, and has sections covering bonding.

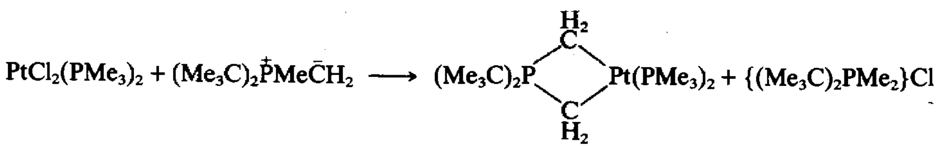
The alkylidenephosphoranes are among the most powerful bases known, and the displacement of a coordinated ligand is a useful method for the preparation of transition metal ylide complexes.

The zerovalent compound $Pt(C_2H_4)(PPh_3)_2$ reacts with $C(PPh_3)_2$ to give the platinum(0) ylide complex where partial triphenylphosphine transfer to platinum has occurred (equation 144).[426]



(144)

For platinum(II) complexes, the complex $PtCl_2(PMe_3)_2$ reacts with $(Me_3C)_2\overset{+}{P}Me—\overset{-}{C}H_2$ to give $[Pt\{(CH_2)_2P(CMe_3)_2\}(PMe_3)_2]Cl$ (equation 145).[427] The fully substituted platinum ylide is formed when $PtCl_2$(cod) is used (equation 146).[428] Sulfur ylide complexes of platinum(II) can also be prepared from $PtCl_2(SMe_2)_2$. The room temperature reaction with **(32)** gives a mixture of **(33)** and **(34**; equation 147).



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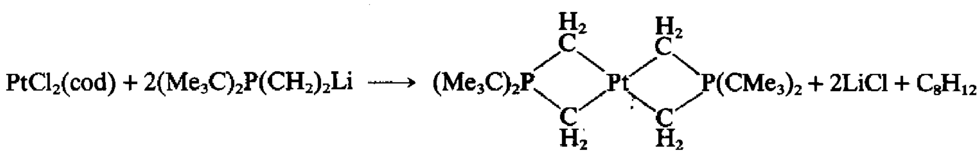
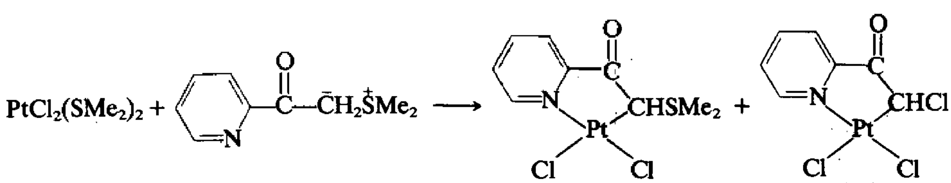


(146)



(32) **(33)** **(34)**

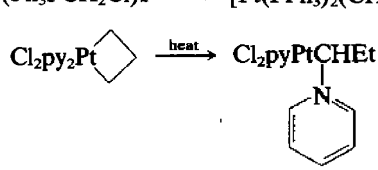
(147)

A direct synthesis of an ylide complex is the reaction between $Pt(PPh_3)_3$ and CH_2ClI, where the complex is formed by the series of reactions in equations (148–150).[429–431] When $PtCl_2(C_3H_6)py_2$ is heated in benzene the pyridinium propylide complex **(35)** is formed (equation 151).[432,433] The complex **(35)** on refluxing in $CHCl_3/CCl_4$ gives the tetrachloroplatinum(IV) complex.[432] Transylidation does not occur when the platinum(IV) complex $[PtMe_3]PF_6$ is treated with 3 equivalents of $Ph_3\overset{+}{P}—\overset{-}{C}H_2$. Ethane and methane are liberated and the cyclometalated complex **(36)** formed (equation 152).[434]

$$Pt(PPh_3)_3 \rightleftharpoons Pt(PPh_3)_2 + PPh_3 \tag{148}$$

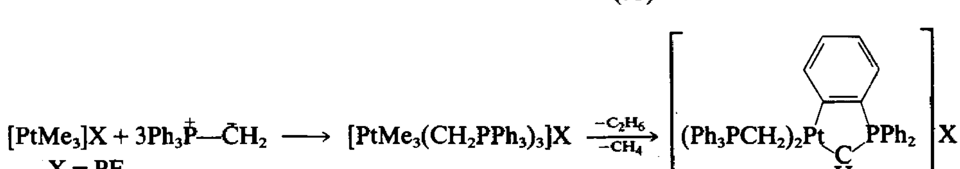
$$PPh_3 + CH_2ClI \longrightarrow (Ph_3PCH_2Cl)I \tag{149}$$

$$Pt(PPh_3)_2 + (Ph_3PCH_2Cl)I \longrightarrow [Pt(PPh_3)_2(CH_2PPh_3)Cl]I \tag{150}$$



(35)

(151)



(36)

(152)

In addition to sulfonium ylides of platinum(II),[435] platinum(II) halides of some phenacylides of nitrogen (p-$MeC_5H_4\overset{+}{N}\overset{-}{C}HC(O)Ph$), phosphorus and arsenic have been prepared.[436] The configurations have been elucidated by IR and ^1H NMR spectroscopy, and it has been found that $^2J(^{195}PtH_{methine})$ increases with increasing basicity of the ylide N > As > S > P.

Chloro platinum ylide complexes will undergo replacement of Cl for acetone in the presence of $NaBPh_4$.[437] The ylide complexes (**35**) undergo oxidative addition at platinum(II) by MeI, and substitution of pyridine by CO to give the carbonyl complex. The ylide ligand is not displaced.[438]

The platinum(II)–ylide bond involves donation of a pair of electrons in a formally sp^3 hybrid orbital on carbon to an empty orbital on platinum(II). The short bond lengths and XPES spectroscopy suggest some multiple bond character.

52.4.8 Platinum Alkyl and Aryl Complexes

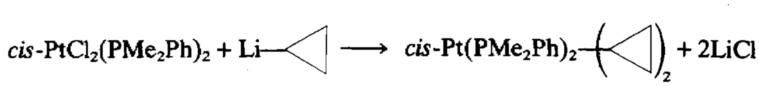
Platinum forms complexes containing metal–carbon σ bonds in its +2 and +4 oxidation states. Furthermore there are a few acetylide complexes of platinum(0) formed by treating $Pt(CN)_2$ with potassium acetylide in liquid ammonia,[439] and four reports of platinum(III) alkyl and aryl compounds.[440–443] A number of reviews on platinum–carbon σ-bonded complexes have been written, and these are summarized by Hartley in Chapter 39 of 'Comprehensive Organometallic Chemistry'. The preparation and reactions of these complexes are also given in some detail in the chapter by Hartley. This chapter will merely lead the reader to the different methods of synthesis, and include where possible a brief update of the chemistry as it has developed since 1980/1981. Selection of material will be guided by significance, variety and by the general guidelines of this series that complexes be omitted where the majority of bonds are of the Pt—C type.

52.4.8.1 Synthesis and structure

(i) Use of Grignard reagents or alkali metal salts

The complexes *cis-* or *trans*-$PtX_2(PR_3)_2$ react with MeLi or MeMgX to give $PtMe(X)(PR_3)_2$ and $PtMe_2(PR_3)_2$ (equation 153).[444] Alternatively Me_2Mg can be used.[445] The structures of $PtMeCl(PPh_3)_2$[445] and $PtMeCl(PMePh_2)_2$[447] show respective Pt—C distances of 2.08(1) and 2.081(6) Å for the Pt—methyl group *trans* to chloride. A cyclopropyl platinum(II) has been prepared by treating *cis*-$PtCl_2(PMe_2Ph)_2$ with cyclopropyllithium (equation 154).[448] The cyclopropyl rings are equilateral with average C—C distances of 1.506(13) Å. The Pt—C distances are 2.086(4) and 2.070(4) Å.[449] When *cis*-$PtCl_2(PCy_3)_2$ is reacted with cyclohexylmagnesium bromide the product is $PtHCl(PEt_3)_2$, probably by β-hydride transfer. The complex $Pt(CF_3)_2(PEt_3)_2$ has been prepared by treating $PtBr_2(PEt_3)_2$ with an excess of $Cd(CF_3)_2$·glyme. Short reaction times give $PtI(CF_3)(PBu^n_3)_2$ in 60–70% yield from $PtI_2(PBu^n_3)_2$ (equations 155 and 156).[450] Comparison of the Pt—C distances between *trans*-$PtClR(PMePh_2)_2$ (R = Me, CF_3, C_2F_5) shows that the values are 2.081(6) [2.09], and 2.013(12) and 1.990(12) Å for R = Me, CF_3 and C_2F_5 respectively.[447] The contracting of the Pt—C and Pt—Cl distances on going to the C_2F_5 compound is attributed to the electrostatic effect of a positive charge induced on the bonded carbon by the electronegative fluorines. Other structures have been solved for $Pt(CF_3)_2\{PMe_2(C_6F_5)\}_2$[451] and $PtF\{CH(CF_3)_2\}(PPh_3)_2$.[452] The signs and magnitudes of $^3J(PH)$ and $^3J(PF)$ have been measured by multiple resonance methods in Pt^{II}—CF_3, Pt^{IV}—Me and Pt^{IV}—CF_3 complexes. $^3J(PH)$ is more negative when P and Me are *trans* rather than *cis*, and the converse is true for the CF_3 complexes.[453]

$$PtX_2(PR_3)_2 \xrightarrow[\text{MeMgX}]{\text{MeLi}} PtMe(X)(PR_3)_2 \xrightarrow[\text{MeMgX}]{\text{MeLi}} PtMe_2(PR_3)_2 \quad (153)$$



(154)

$$PtBr_2(PEt_3)_2 + Cd(CF_3)_2 \longrightarrow Pt(CF_3)_2(PEt_3)_2 + CdBr_2 \quad (155)$$

$$PtI_2(PBu^n_3)_2 + Cd(CF_3)_2 \xrightarrow{5\text{ h}} PtI(CF_3)(PBu^n_3)_2 + CdI(CF_3) \quad (156)$$

Platinum(II) acetylide complexes are best prepared using Na or K acetylide in liquid ammonia solvent (equation 157).[454,455] Sodium dicyanomethanide can also be used to prepare platinum(II) complexes of this anion (equation 158).[456]

$$PtCl_2(AsEt_3)_2 + 2PhC{\equiv}CNa \longrightarrow Pt(C{\equiv}CPh)_2(AsEt_3)_2 + 2NaCl \quad (157)$$

$$Pt(PPh_3)_3 + R_2Hg \longrightarrow PtR_2(PPh_3)_2 + Hg + PPh_3 \quad (158)$$

(ii) Synthesis from organomercury, tin and silicon reagents

Organomercurials react with $Pt(PPh_3)_3$ to form dialkyl platinum(II) complexes (equation 158).[457,458] The method can be used for alkyl, aryl or vinyl complexes.

Organotin reagents are useful synthetic reagents for the synthesis of alkyl platinum complexes. The reactivity of $SnMe_3Ar$ compounds parallels the ease of electrophilic substitution at the Ar—H bond. Much of this work has been developed by Eaborn and Pidcock, and in equations (159)–(162) a number of examples are given where these reagents have been successfully used. When $SnMe_4$ is used, Pt^{II} methyl complexes can be obtained.[459–466]

$$PtCl_2(cod) + SnMe_3Ar \longrightarrow PtCl(Ar)(cod) \xrightarrow{SnMe_3Ar} PtAr_2(cod)_2 \quad (159)$$

$$2PtCl_2(C_2H_4)(PR_3) + 2SnMe_3Ar \longrightarrow [PtCl(Ar)(PR_3)]_2 + 2SnMe_3Cl \quad (160)$$

$$Pt(O_2CCF_3)_2(PPh_3)_2 + SnMe_3Ph \longrightarrow Pt(O_2CCF_3)(Me)(PPh_3)_2 + SnMe_2Ph(O_2CCF_3) \quad (161)$$

$$Pt(O_2CCF_3)_2(PMe_2Ph)_2 + SnMe_4 \longrightarrow Pt(O_2CCF_3)(Me)(PMe_2Ph)_2 + SnMe_3(O_2CCF_3) \quad (162)$$

(iii) Oxidative addition

Monoalkyl complexes have been prepared by oxidative addition to platinum(0) complexes, a reaction which has received much study. The reaction will be discussed later when the chemistry of platinum with phosphine ligands is discussed. The reaction has been used to prepare $PtI(Me)(PPh_3)_2$,[444] $PtBr(Ph)(PPh_3)_2$, $PtBr(CH{=}CHPh)(PPh_3)_2$, and $PtCl(CH{=}C{=}CR'R'')(PPh_3)_2$.[467] This latter reaction is an interesting one involving the addition of 3-chloropropyne to $Pt(PPh_3)_3$ (equation 163). The order of reactivity is RI > RBr > RCl. When secondary halides are used the dihalo complex may be formed (equation 164).[468]

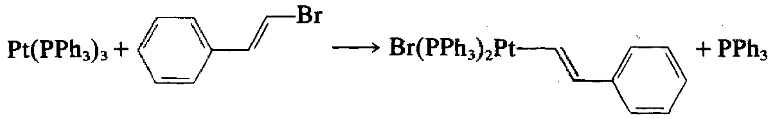
$$Pt(PPh_3)_3 + HC{\equiv}CCH_2Cl \longrightarrow PtCl(CH{=}C{=}CH_2)(PPh_3)_2 + PPh_3 \quad (163)$$

$$Pt(PEt_3)_4 + MeCHBrPh \longrightarrow PtBr_2(PEt_3)_2 \quad (164)$$

The reaction shows considerable dependence on the phosphine, both on electronic and steric grounds. Alkyl groups and arsines favor the reaction, as do substituents having the smaller cone angles. The correlations $AsMe_3 > PMe_3 > PPh_3$ and $PMe_3 > PMe_2Ph > PMePh_2 > PPh_3$ hold in general. Two primary mechanisms have been proposed.[469–473] The first involves S_N2 attack at platinum(0) followed by halide coordination or substitution at the cationic center. The second mechanism involves halogen abstraction by platinum from the alkyl halide to form a radical pair, possibly by electron transfer *via* a platinum(I) intermediate. Radical pair combination can give the product of oxidative addition. For unreactive alkyl halides with weak C—X bonds the product is frequently the dihalo complex. When the reaction between $PtMe_2(phen)$ and IPr^i is carried out in the presence of an alkene $CH_2{=}CHX$ as a radical trap, inserted alkene products are formed (equation 165).[474]

$$PtMe_2(phen) + IPr^i + CH_2{=}CHX \longrightarrow PtMe_2I(CHXCH_2Pr^i)(phen) \quad (165)$$

The structure of the oxidative addition product between $Pt(PPh_3)_3$ and *trans*-β-bromostyrene gives $PtBr(HC{=}CHPh)(PPh_3)_2$. The *trans* stereochemistry about the styryl double bond is retained (equation 166).[475,476] For aryl halides, fluorohalobenzenes react with $Pt(PEt_3)_4$ to give fluoroaryl platinum(II) complexes in high yield (equation 167).[477] There is no significant difference in the ease of oxidative addition between the *m*- and *p*-halofluorobenzenes, but the rate of reaction varies with the halide in the sequence I > Br > Cl > CN. The platinum complex is less reactive than the palladium or nickel analog. The C—C bond of an arenenitrile is cleaved (equation 168), a reaction not observed in the triphenylphosphine series of complexes. The ^{13}C chemical shifts and coupling constants of these aryl complexes correlate with both Taft and modified Swain–Lupton substituent constants.[478] These correlations, along with those for ^{19}F chemical shift data,[477] support the presence of significant π interactions between platinum and an aryl ligand. Nevertheless ^{13}C data for the cationic phenyl platinum(II) complexes *trans*-$[Pt(Ph)L(AsEt_3)_2]PF_6$ indicate that σ rather than π interactions are dominant in the phenyl–platinum bond.[479]



(166)

$$Pt(PEt_3)_4 + XC_6H_4F \longrightarrow PtX(C_6H_4F)(PEt_3)_2 + 2PEt_3 \quad (167)$$

$$Pt(PEt_3)_4 + NCC_6H_4F \longrightarrow Pt(CN)(C_6H_4F)(PEt_3)_2 + 2PEt_3 \quad (168)$$

The addition of nitromethane to $Pt(PPh_3)_4$ in a polar protic solution provides a route to the fulminate complex $Pt(CNO)_2(PPh_3)_2$ (equation 169).[480] The thermally stable complex rearranges to the isocyanato complex $Pt(NCO)_2(PPh_3)_2$ under the influence of carbonyl compounds as catalysts.[481] The fulminate compound gives $Pt(NCS)_2(PPh_3)_2$ with organic thiocarbonyl compounds, and is reduced to $Pt(CN)_2(PPh_3)_2$ by phosphines. Oxidative addition of CH_2Cl_2 to give $PtCl(CH_2Cl)(PPh_3)_2$ and *cis*-$PtCl_2(PPh_3)_2$ is photoinduced.[482] The rate of reaction is decreased by addition of duroquinone which is interpreted in terms of a free radical pathway. The oxidative addition reaction of C—Cl bonds can also be used to prepare alkoxalyl complexes of platinum(II). The reaction (equation 170) proceeds readily at room temperature to give the product in high yield.[483] A similar C—Cl addition reaction with $CF_2ClCOCF_2Cl$ gives *cis*-$PtCl(CF_2COCF_2Cl)(PPh_3)_2$, with a Pt—C bond length of 2.06(2) Å.[484] Chloromethyl methyl sulfide adds to $Pt(PPh_3)_3$ to give *trans*-$PtCl(CH_2SMe)(PPh_3)_2$ (equation 171).[485] This complex (**37**) reacts with methyl iodide by alkylation at sulfur to give $[PtCl(CH_2SMe_2)(PPh_3)_2]I$.[486] Protonation by trifluoroacetic acid occurs at sulfur.[487]

$$Pt(PPh_3)_3 + MeNO_2 \xrightarrow{80\,^{\circ}C} PtH(CNO)(PPh_3)_2 \longrightarrow Pt(CNO)_2(PPh_3)_2 + H_2 \quad (169)$$

$$Pt(PPh_3)_3 + ClCOCO_2R \longrightarrow PtCl(COCO_2R)(PPh_3)_2 + PPh_3 \quad (170)$$

$$Pt(PPh_3)_3 + ClCH_2SMe \longrightarrow \underset{(\mathbf{37})}{PtCl(CH_2SMe)(PPh_3)_2} + PPh_3 \quad (171)$$

(*iv*) *Replacement reactions*

Complexes *trans*-$PtX(R)(PR_3)_2$ undergo metathetical replacement of X by anionic Y^- or neutral ligands L and solvent. The high *trans* influence of the R group facilitates this reaction. The reaction has been used for the introduction of ligands such as Cl, Br, I, SCN, NO_2, NO_3, SPh, O_2CMe into complexes having RX bonded to platinum(II). For neutral ligands L, compounds frequently used are MeOH, Me_2CO, pyridine, PPh_3 and AsR_3. For the reaction of *trans*-$PtCl(R)L_2$ being converted to *trans*-$PtY(R)L_2$ by addition of Y^- (R = H, Et, *m*-$CF_3C_6H_4$, C_6F_5; L = PEt_3; Y = Br, I, N_3, NO_2, CN, SCN, thiourea) the first-order rate constant is correlated with the *trans* effect, and is H > Et > *m*-$CF_3C_6H_4$ > C_6F_5. When Y is a good π acceptor, contribution from the k_2 term becomes predominant, indicating that the driving force of the reaction is non-stabilization of the five-coordinate transition state.[488] Metathetical replacement of Cl by OH^- has been used to prepare Pt(OH)Me(dppe) in aqueous methanolic sodium hydroxide (equation 172).[489] A *trans* influence series is given for carbon donor (σ) ligands based on ^1J(PtP). For the anionic complexes $[PtCl_2R_2]^{2-}$ (R = C_6Cl_5), reaction with ligands L (L = PPh_3, PEt_3, py, $SbPh_3$) gives the monoanionic complexes $[PtClR_2L]^-$ by chloride ion substitution.[490] Replacement of dioxane in *trans*-$Pt(C_6F_5)_2(dioxane)_2$ has been used to prepare ketone adducts $Pt(C_6F_5)_2L$ (L = Me_2CO, EtMeCO, Et_2CO; equation 173).[491]

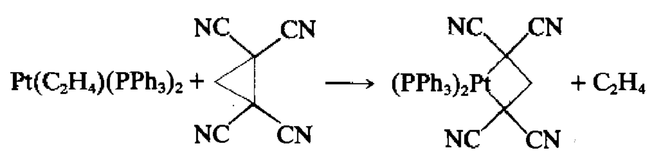
$$PtClMe(dppe) \xrightarrow{MeOH} [PtMe(MeOH)dppe]Cl \xrightarrow{OH^-} Pt(OH)Me(dppe) + Cl^- \quad (172)$$

$$trans\text{-}Pt(C_6F_5)_2(dioxane)_2 + L \longrightarrow Pt(C_6F_5)_2L + 2\ dioxane \quad (173)$$

Doubly bridged cationic diplatinum(II) complexes $[Pt(o\text{-}CH_2C_6H_4CN\text{-}\mu\mu')(2{=}phos)](BF_4)_2$ have been synthesized by halide replacement. The cyano group remains bonded to platinum both in the solid state and in solution.[492]

(v) *Ring-opening reactions*

One of the earliest such examples is the reaction between H_2PtCl_6 and cyclopropane. The structure of the pyridine adduct indicates that the complex is a platinum(IV) ylide.[493] The compounds *trans*-1-*n*-hexyl-*cis*-2,3-dideuterocyclopropane and *cis*-1-*n*-hexyl-*cis*-2,3-dideuterocyclopropane react with $Pt_2Cl_4(C_2H_4)_2$ by addition of Pt^{II} across the C(2)—C(3) bond. The reaction is stereospecific and involves retention of configuration at both reacting carbons. The reaction is interpreted in terms of a concerted cycloaddition mechanism.[494] Cyanocyclopropanes react with $Pt(C_2H_4)(PPh_3)_2$ by C—C cleavage at the bond possessing the largest number of cyano substituents (equation 174).[495] The reaction can be extended; two platinacyclobutane complexes have been prepared from tricyclooctene (**38**) and tetracyclononane (**39**).[496] A nortricycloplatinacyclopentane complex has been prepared using *endo*-tricyclo[3.2.1.0]oct-6-ene.[497] Bicyclo[1.1.0]butanes react with $Pt_2Cl_4(C_2H_4)_2$ to give a ring-opened complex which reacts with pyridine to give (**40**; equation 175).[498] The ring-opening reaction between $C_2(CN)_4O$ and PtL_4 ($L = PPh_3$, $P(p\text{-tolyl})_3$, $AsPh_3$) gives the complex (**41**; equation 176).[499] In some cases the reaction gives the opened isomer with a tricyanoethylenolato ligand O-bonded to platinum(II).[500] Four-membered carbocyclic rings with cyano substituents also undergo ring opening to give platinacyclopentane compounds (**42**; equation 177).[501] The structure of the compound is again verified by X-ray crystallography. Kinetic data for the ring opening of substituted cyclobutenediones by platinum(0) complexes show the activation energy and reaction pathway to be quite solvent dependent.[502]



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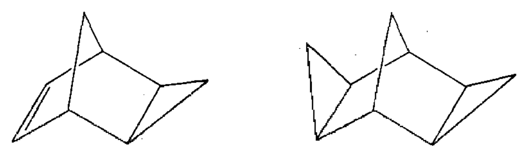
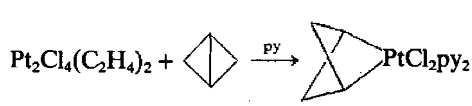


(**38**) (**39**)



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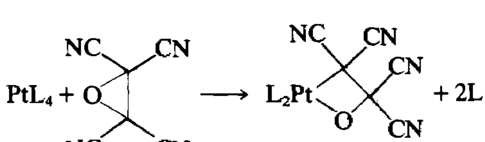
(**40**)



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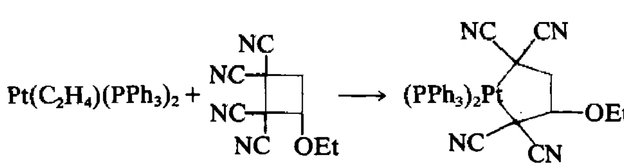
(**41**)



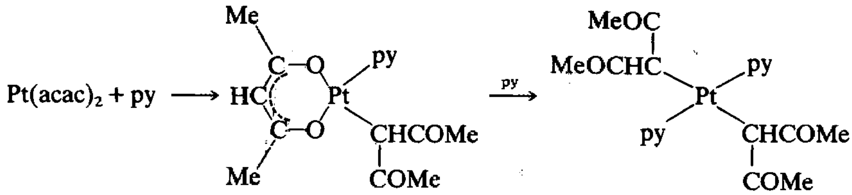
(177)

(**42**)

(vi) *Reactions with acetylacetonate*

Acetylacetone usually forms transition metal complexes by coordination through bidentate oxygens. Since platinum forms unusually strong bonds to carbon, acetylacetonato complexes of platinum(II) are frequently C-bonded. When $Pt(acac)_2$ is treated with 1 mole of pyridine, a bidentate oxygen-bonded acetylacetonate ligand is converted to a γ-carbon-bonded ligand.

When a further mole of pyridine is added the bis γ-carbon-bonded acetylacetonato complex (**43**) is formed (equation 178).[503]



(**43**)

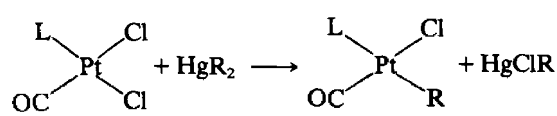
(178)

(*vii*) *Alkyl transfer between transition metals*

Platinum alkyl complexes can be prepared by alkyl transfer from a second alkyl transition metal complex.

The biomethylation reaction between platinum and methylcobalamin involves both platinum(II) and platinum(IV) oxidation states. An 'outer-sphere' complex is formed between the charged platinum(II) salts and the corrin macrocycle, which catalytically labilizes the Co—C σ bond to electrophilic attack. A two-electron 'redox switch' mechanism has been proposed between platinum(II) and platinum(IV). However, a mechanism consistent with the kinetic data is direct electrophilic attack by $PtCl_6^{2-}$ on the Co—C σ bond in MeB_{12}.[504] Studies on $[Pt(NH_3)_2(OH_2)_2]^{2+}$ indicate that the bases on cobalt interact in the coordination sphere of platinum(II).[505] Since both platinum(II) and platinum(IV) are together required to effect methyl transfer from methylcobalamin to platinum, ^{195}Pt and ^{13}C NMR spectroscopy have been used to show that the methyl group is transferred to the platinum of the platinum(II) reactant.[506] The kinetics of demethylation by mixtures of platinum(II) and platinum(IV) complexes show a lack of dependence on the axial ligand. The authors conclude therefore that it is unlikely that the reaction involves direct attack by the bound platinum on the Co—C bond, and instead favor electron transfer from an orbital on the corrin ring to the bound platinum group in the slow step, followed by rapid methyl transfer.[507]

For complexes *cis*-$PtCl_2(CO)L$ (L = tertiary phosphine), reaction with dialkyl mercury compounds leads to specific substitution *trans* to L (equation 179).[508] The critical factor is the bond-weakening *trans* influence of phosphines L,[509,510] which is the critical factor in making the *trans* ligands more likely to participate in an S_E2 (cyclic) exchange process through transition states of type (**44**).[508,511] σ-Bonded cyclopentadienyl ligands can also be transferred between platinums, and from platinum(II) to mercury(II). The cyclopentadienyl groups do not transfer as fast as chloride ions between the same species, but do so considerably faster than any accompanying CO scrambling processes.[512]



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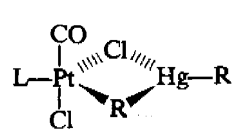
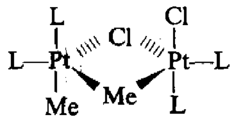


(**44**)

Methyl transfer between platinum(II) centers is a facile process. Homonuclear alkyl transfer occurs rapidly and stereospecifically when equimolar amounts of *cis*-$PtMe_2(PEt_3)_2$ and *cis*-$PtCl_2(PEt_3)_2$ in methanol or dichloromethane are mixed at 25 °C. The product *cis*-$PtClMe(PEt_3)_2$ is formed quantitatively (equation 180) in methanol solvent, and exclusively *trans* isomer is obtained in dichloromethane. The monomethylated complex *trans*-$PtBrMe(PMe_2Ph)_2$ is also formed by methyl transfer from *cis*-$PtMe_2(PMe_2Ph)_2$ to *cis*-$AuBrMe_2(PMe_2Ph)$. This reaction (equation 181) is one of a series of reactions involving methyl transfer between Au^I, Au^{III}, Pd^{II} and Pt^{II} centers.[514] The methyl exchange reaction can be considered to involve a bimolecular electrophilic substitution reaction at the methyl group, generally known as an S_E2 reaction. Stereochemical retention of configuration at platinum is explained on the basis of cyclic transition states or intermediates such as (**45**) and (**46**). Further work on the symmetrization reaction between PtR_2L_2 and $PtMe_2L_2$ shows that the reaction is catalyzed by $Pt_2Cl_4L_2$, but that the catalyst is destroyed in a competing reaction with PtR_2L_2 to give $Pt_2(\mu\text{-}Cl)_2Me_2L_2$.[515] Exchange occurs between dimethyl platinum(II) and dimethyl platinum(IV) complexes. *cis*-$PtMe_2(PMe_2Ph)_2$ reacts with $PtX_2Me_2(PMe_2Ph)_2$ ($X = I$, NO_2, NO_3) to give $PtXMe(PMe_2Ph)_2$ and $PtXMe_3(PMe_2Ph)_2$ (equation 182).[516] By labeling studies with CD_3 it has been shown that when $X = NO_3$, the reaction occurs by methyl for nitrate exchange rather than by a redox mechanism. *trans*-$PtHIL_2$ ($L = PMe_3$, PMe_2Ph) reacts with AuMeL or *cis*-$PtMe_2L_2$ to give *trans*-$PtIMeL_2$, apparently by methyl for hydride exchange. The complex $PtMe_2(SMe_2)_2$ exists in solution in equilibrium with $Pt_2Me_4(\mu\text{-}SMe_2)_2$ and SMe_2. Methyl for halogen exchange occurs on reaction of *cis*-$PtMe_2(SMe_2)_2$ with *cis*- or *trans*-$PtCl_2(SMe_2)_2$ to give *trans*-$PtClMe(SMe_2)_2$ as the only product (equation 183).[517] Kinetic studies show that the reaction rate is first order in each reagent, and that the reaction is strongly retarded in the presence of free SMe_2. The reactive intermediate is proposed to be $PtMe_2(SMe_2)$.

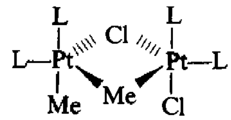
$$cis\text{-}PtMe_2(PEt_3)_2 + cis\text{-}PtCl_2(PEt_3)_2 \xrightarrow{MeOH} 2\,cis\text{-}PtClMe(PEt_3)_2 \quad (180)$$

$$trans\text{-}PtMe_2(PMe_2Ph)_2 + cis\text{-}AuBrMe_2(PMe_2Ph) \longrightarrow trans\text{-}PtBrMe(PMe_2Ph)_2 + AuMe_3(PMe_2Ph) \quad (181)$$



(45)

L = PMe$_2$Ph



(46)

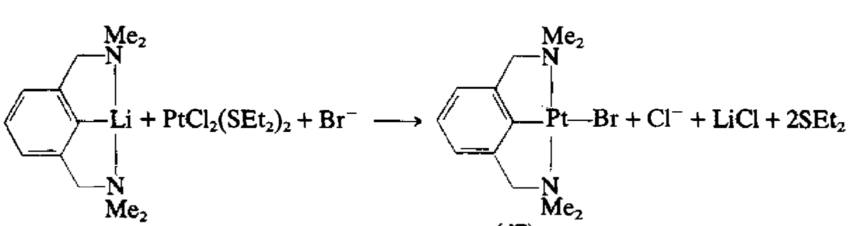
$$cis\text{-}PtMe_2(PMe_2Ph)_2 + PtX_2Me_2(PMe_2Ph)_2 \longrightarrow PtXMe(PMe_2Ph)_2 + PtXMe_3(PMe_2Ph)_2 \quad (182)$$

$$cis\text{-}PtMe_2(SMe_2)_2 + PtCl_2(SMe_2)_2 \longrightarrow 2\,trans\text{-}PtClMe(SMe_2)_2 \quad (183)$$

(*viii*) *Chelated aryl complexes*

This section is peripheral to the subject of *ortho*-metalation which will be discussed in the section covering the reactions of Group V ligands. A group of recent complexes included here has been prepared by reaction of a lithiated aryl anion with chloroplatinum(II) compounds. The aryl groups contain chelating groups and the complexes contain this multidentate aryl ligand.

The lithium salt $Li[C_6H_3(CH_2NMe_2)_2\text{-}o,o']$ reacts with $PtCl_2(SEt_2)_2$ in the presence of bromide ion to form $PtBr\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}$ (**47**; equation 184).[518,519] The bromide ligand can be replaced by water, and also two of the platinum centers can be coupled by a single halo bridge. The cationic complex (**48**) reacts with methyl iodide by alkylation of the phenyl ring (**49**; equation 185). The bidentate complex with a Pt—C σ-bonded methylene group (**50**) formed in equation (186) reacts with $Hg(O_2CMe)_2$ to give the six-coordinate platinum(IV) compound formed by oxidative addition of the Hg—O bond across the Pt^{II} center.[520] Similar formamidino and triazenido compounds having a Pt—Ag bond have been synthesized,[521] along with formamidino complexes having a Pt^{II} to Hg^{II} donor bond.[522]



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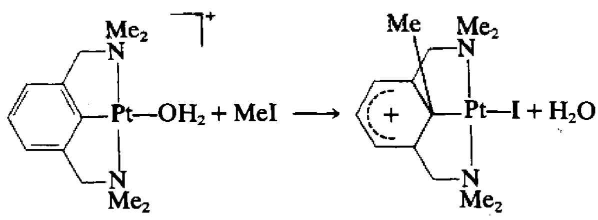
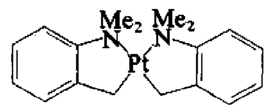
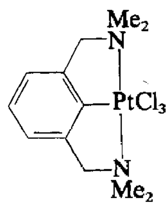


(48) (49) (185)

$PtCl_2(SEt_2)_2 + 2o\text{-}Me_2NC_6H_4CH_2Li \longrightarrow$  $+ 2LiCl + 2SEt_2$ (186)

(50)



(51)

For the tridentate ligand the tetravalent platinum(IV) complex $PtCl_3\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}$ (56) has been prepared.[523] If the cationic platinum(II) complex $[PtI\{MeC_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]BF_4$ (49) is considered to be a metal-substituted arenonium ion it should be susceptible to nucleophilic attack. This concept has been used to effect a fully reversible, aryl to cyclohexadiene conversion in a metal coordination sphere.[524]

52.4.8.2 Stability of Pt—C bonds

With respect to thermal stability, platinum–carbon σ-bonded complexes are among the most robust of the transition metal–carbon-bonded compounds. In terms of the stability order for organic ligands the sequence is o-phenyl > PhC≡C > p-phenyl ~ phenyl > Me > alkyl > HC≡C.[142] The bond energies for Pt—Ph and Pt—CPh=CHPh σ bonds have energies of 264 ± 15 and $215 \pm 23\ \mathrm{kJ\ mol^{-1}}$ respectively.[525,526] In terms of stability to reaction, a number of factors need to be considered. For transition metal complexes of higher alkyls, β-hydrogen transfer can lead to decomposition by alkene elimination. Secondly, the σ-bonded carbon may be susceptible to direct electrophilic attack resulting in its cleavage, or a similar type cleavage may occur by a sequential oxidative addition–reductive elimination sequence.

52.4.8.3 Chemical reactions: cleavage and isomerization

In order to integrate this section with that in ‘Comprehensive Organometallic Chemistry’, the reactions will again be collected into one of three categories: (i) cleavage reactions at the Pt—C bond; (ii) insertion reactions in which a reagent is ‘inserted’ into the Pt—C bond; and (iii) replacement reactions in which either the alkyl ligand or one of the other ligands bound to platinum(II) is replaced.

(i) Cleavage reactions: thermal cleavage

The major reaction that occurs on heating a metal alkyl is elimination, particularly of hydrogen.[527] In general it is the β hydrogen which is most susceptible toward transfer to the metal, followed by loss as hydrogen. The avoidance of β-hydrogen elimination as a decomposition pathway accounts for the much higher stability of both neopentyl and trimethylsilylmethyl complexes of platinum(II) such as *cis*-$Pt(CH_2SiMe_3)_2(PPh_3)_2$ as compared with the n-alkyl analogues.[528,529]

The thermal decomposition of *trans*-$PtXMeL_2$ (L = PEt_3; X = Cl, Br, I, CN) in decalin at high temperature gives CH_4, Pt and PtX_2L_2. The rate is independent of X, but a relative scale of Pt—Me bond dissociation energies obtained by measuring the appearance potentials of $PtXL_2^+$ shows a dependence on X.[530] The thermal decomposition of $Pt(Bu^n)_2(PPh_3)_2$ in dichloromethane solvent gives *n*-butane and butene-1 in a 1:1 ratio independent of the decomposition rate (equation 187). No octanes are observed, indicating that significant amounts of butyl radicals are not formed.[531] The rate of decomposition increases on the addition of triphenylphosphine. The reaction is intramolecular since heating a mixture of $Pt(CH_2CD_2CH_2Me)_2(PPh_3)_2$ and $Pt(n\text{-}C_8H_{17})_2(PPh_3)_2$ gives exclusively *n*-octane, C_8H_{18}, with no detectable deuterium. The proposed mechanism needs to account for three features: (i) a vacant coordination site on platinum needs to be generated; (ii) in the absence of added triphenylphosphine the rate-limiting step is the initial loss of phosphine but in the presence of added phosphine the slow step is the reductive elimination of butane; and (iii) the alkene in the intermediate is coordinated sufficiently strongly that it does not exchange with free alkene in solution, otherwise deuterium scrambling would be observed in the crossover experiment.

$$Pt(Bu^n)_2(PPh_3)_2 \xrightarrow{\text{heat}} Pt + n\text{-}C_4H_{10} + MeCH_2CH{=}CH_2 \qquad (187)$$

When an unsymmetrical dialkyl platinum(II) complex is thermolyzed, the distribution of alkane and alkene shows that the relative ease of β-hydrogen elimination from the two alkyl groups depends on the number of β hydrogens present in the two alkyl groups (equations 188 and 189).[532] The isopropyl ethyl complex isomerizes at room temperature to $PtEtPr^n(PPh_3)_2$. For a series of symmetrical and unsymmetrical dialkyl platinum(II) complexes of type *cis*-$PtRR'L_2$ (L = tertiary phosphine), thermolysis gives only the disproportionation products of the two alkyl groups by β elimination. In the presence of excess PPh_3, thermolysis proceeds mainly *via* a non-dissociative path in addition to the dissociative one. In the presence of excess PPh_3, thermolysis occurs mainly by a non-dissociative path in which the liberation of alkene after facile reversible β-elimination is probably rate determining. When *cis*-$PtRR'L_2$ is thermolyzed in the absence of excess PPh_3, the relative rate of β elimination involving the R group to that involving the R′ group is proportional to the ratio of the number of β hydrogens in R and R′.[533] The mechanism of the thermal decomposition of $PtEt_2(PEt_3)_2$ to $Pt(C_2H_4)(PEt_3)_2$ and C_2H_6 is also dependent on the concentration of triethylphosphine. The deuterium kinetic isotope effect for reductive elimination of ethane from $Pt(C_2H_5)_2L_2$ and $Pt(C_2D_5)_2L_2$ (L = PEt_3) shows a value of 3.3 for a situation where added [L] is 0.3 M. This value indicates C—H(D) bond making or breaking in the transition state, and is compatible with rate-limiting reductive elimination of alkane from the Pt—ethyl group.[534] Labeling experiments on the thermal decomposition of *trans*-$PtIMe(PR_3)_2$ (R = Me, CD_3, Et, Ph, C_6H_{11}; Me = CD_3) in deuterated and non-deuterated hydrocarbons at 120 °C gives MeH and/or MeD. The main route involves homolytic splitting of the Pt—methyl bond to give methyl radicals, which then form methane by H atom abstraction from the R groups of the phosphines or from the solvent. A minor pathway involves a molecular mechanism *via* coordinate methyl groups.[535]

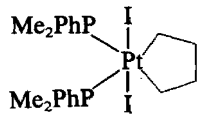
$$PtMeEt(PPh_3)_2 \longrightarrow CH_4 + C_2H_4 \qquad (188)$$

$$PtEtPr(PPh_3)_2 \longrightarrow \underset{1}{C_2H_4} + \underset{0.61}{C_2H_6} + \underset{0.64}{C_3H_6} + \underset{0.95}{C_3H_8} \qquad (189)$$

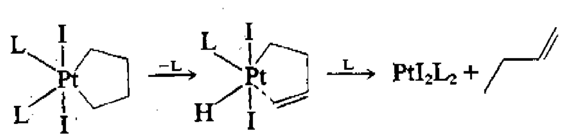
The condensed-phase thermolysis of the aryl complexes PtR_2L_2 and PtR_2(L—L) (R = Ph, *p*-MeC_6H_4; L = PPh_3, $P(C_6H_4Me\text{-}p)_3$; L—L = dppe, dppm) shows that the primary decomposition step is the concerted reductive elimination to form R_2 (equation 190). This elimination is intramolecular, and no scrambling of ligands occurs prior to pyrolysis.[536] This pyrolysis is again accelerated by added phosphine, and this suppresses secondary decomposition modes of the product platinum phosphine complexes.[537] The kinetics of the reaction shows that the reaction occurs by a primary concerted unimolecular reductive elimination of biaryl, and conforms to a first-order kinetic rate law. The elimination of 4,4′-bitolyl from *cis*-$Pt(p\text{-}MeC_6H_4)_2(PPh_3)_2$ has a negative entropy of activation. A transition state is suggested where C—C bond formation occurs while the Pt—C bonds are undergoing cleavage.[538] The compounds *cis*-$Pt(m\text{-}XC_6H_4)_2(PPh_3)_2$ (X = H, Me, OMe, NMe_2) and *cis*-$Pt(m\text{-}XC_6H_4)(m\text{-}YC_6H_4)(PPh_3)_2$ (X = H, Me, OMe; Y = Me, OMe, NMe_2) have been synthesized by the Grignard route. At temperatures in the 135–150 °C range the complexes stereospecifically eliminate biphenyls.[539] Complexes *trans*-$PtAr_2(PPh_3)_2$ have also been synthesized, the stereochemistry of the diphenyl complex being confirmed by X-ray crystallography. Again stereospecific reductive elimination of the biphenyl system occurs in a concerted reaction.[540]

$$PtR_2L_2 \longrightarrow PtL_2 + R{-}R \qquad (190)$$

Platinacycle complexes of both platinum(IV) and platinum(II) can be synthesized, and in general their thermal stabilities are higher than their open chain counterparts. A considerable amount of work has been carried out on the thermolysis of these complexes with a view to understanding factors affecting the stability of platinum–carbon bonds, and to understanding the pathways involved in their homolysis. The platinum(IV) complex $PtI_2\{(CH_2)_4\}(PMe_2Ph)_2$ (**52**) has been prepared by I_2 addition to the divalent platinacyclopentane, and the structure confirmed by X-ray crystallography.[541] Under thermolysis conditions complex (**52**) gives a mixture of *cis*- and *trans*-$PtI_2(PMe_2Ph)_2$ and butene-1. The proposed mechanism involves initial loss of PMe_2Ph followed by β-hydrogen elimination. Reductive elimination of butene from the intermediate alkyl hydride complex completes the reaction (equation 191).[542] As with the platinum(II) analogues, no reductive elimination to give cyclobutane or ethylene is found.[543]

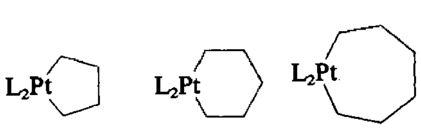


(**52**)



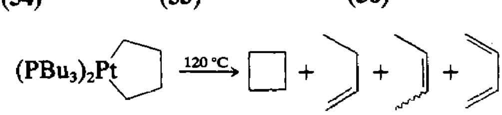
(191)

In a comparative study of platinacycles it has been found that (**53**) and (**54**) decompose more slowly than (**56**) and (**57**) by a factor of 10^4, but that (**55**), (**56**) and (**57**) decompose at comparable rates.[544] Decomposition of (**53**) and (**54**) is accelerated by added L ($L = PPh_3$), but the decomposition of (**57**) is inhibited. It is proposed that the high thermal stability of (**53**) and (**54**) reflects steric inhibition of the reaction resulting in *cis* elimination of platinum and β hydrogen. The relatively rigid five and six-membered platinacyclic rings do not permit the PtCCH dihedral angle to assume the value of 0°, which is optimal for the β-hydrogen transfer. Inhibition of this β-hydrogen transfer reaction can steer the elimination toward a different pathway. At 60 °C in CH_2Cl_2 solvent $PtEt_2(PBu_3)_2$ gives C_2H_4 and C_2H_6; at 120 °C $Pt\{(CH_2)_4\}(PBu_3)_2$ gives primarily cyclobutane (equation 192).[544] Further work on this system shows the organic product distribution to be sensitive to solvent. Thermal decomposition in hydrocarbon solvents at the same temperature leads only to open chain alkenes and alkanes.[545] Platinacyclobutanes decompose under thermal conditions to produce predominantly cyclopropanes. For $L = PEt_3$ in equation (193) mercury must be added to amalgamate the platinum formed and prevent it acting as a heterogeneous catalyst to decompose the products of the reaction. For $L = PPr^i_3$, PCy_3 the reaction gives PtL_2 as the platinum-containing product. The rate decrease on addition of L agrees with a mechanism involving reductive elimination from a three-coordinate platinacyclobutane intermediate. Arrhenius activation energies are in the region of 180 kJ mol^{-1} for the reaction.[546]

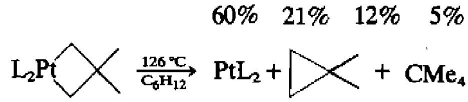


$L_2Pt(CH_2Me)_2$ $\qquad$ $L_2Pt(CH_2CH_2CH_2Me)_2$

(**53**) (**54**) (**55**) (**56**) (**57**)



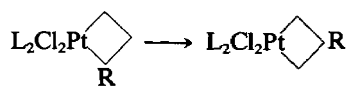
60% 21% 12% 5% (192)



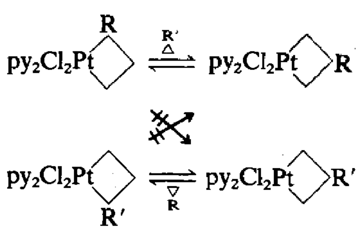
98% 2% (193)

$L = PPr^i_3$

Skeletal isomerization of platinacyclobutanes occurs (equation 194). The dominant effects favoring (**59**) are steric. The approach to equilibrium follows first-order kinetics, and a linear correlation is found between the reciprocal of the observed rate constant and [L] (L = pyridine). A mechanism is proposed involving reversible dissociation of L followed by skeletal isomerization of the resulting five-coordinate platinum(IV) complex.[547] No crossover products are found when the rearrangement is carried out in the presence of a different cyclopropane (Scheme 5).[548] The formation of platinacyclobutanes from cyclopropanes, skeletal isomerization of platinacyclobutanes, and reductive elimination of cyclopropane derivatives from platinacyclobutanes all occur with retention of stereochemistry about the ring. Concerted mechanisms, rather than mechanisms involving Zwitterionic intermediates or carbene–alkene complex intermediates, are proposed for these transformations.[549] Thermal decomposition of these platinacycles results in products being formed selectively from the least stable isomer of the platinacyclobutane.[550] Using deuterium-labeled compounds it has been found that two types of β-hydrogen transfer occur, although β-hydrogen transfer from the ring of the platinacyclobutane is favored over β-hydrogen abstraction from a methyl substituent. The α-hydrogen abstraction process does not occur.[551]

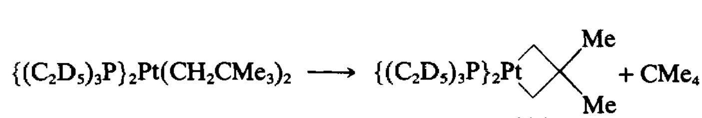


(**58**) (**59**) (194)

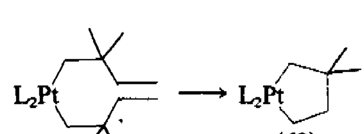


Scheme 5

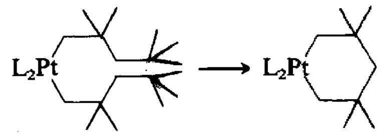
Heating a solution of $Pt(CH_2CMe_3)_2\{P(C_2D_5)_3\}_2$ (**60**) in cyclohexane gives bis(triethylphosphine-d_{30})-3,3-dimethylplatinacyclobutane (**61**; equation 195).[552] The other major product is neopentane. Selective deuteration experiments confirm that no significant fraction of the hydrogens in the ring or its thermolysis products comes from the trimethylphosphine or cyclohexane. The structures of (**60**) and (**61**) have been confirmed by single crystal X-ray studies.[553] The reaction pathway involves dissociation of one PEt_3 molecule, intramolecular oxidative addition of the C—H bond of a neopentyl methyl group to platinum, and reductive elimination of neopentane. The overall Arrhenius activation parameter E_a is approximately $210\ kJ\ mol^{-1}$.[554] Under thermal conditions $Pt(CH_2CMe_2CH_2Me)_2L_2$ and $Pt(CH_2CMe_2CH_2CMe_3)_2L_2$ decompose more rapidly than the neopentyl compound by a factor of 10^4 to give products (**62**) and (**63**) (equations 196 and 197). One equivalent of alkane is concurrently formed. It is concluded from free energy studies that the strain energy of the platinacyclobutanes is small. Free energies of activation for formation of four-, five- and six-membered platinacycloalkanes are small.[555] The complex $PtEt_2(PEt_3)_2$ under thermolysis first loses a PEt_3 group. This coordinately unsaturated intermediate $PtEt_2(PEt_3)$ loses hydrogen with equal probability from the ethyl groups. Thus, either side-to-side motion of the PEt_3 ligand within a T-shaped complex is fast relative to reductive elimination of ethane, or some other process or geometry causes the ethyl groups to be equivalent.[556]



(**60**) (**61**) (195)



(**62**) (196)

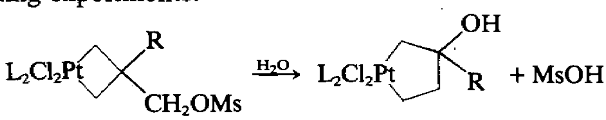


(197)

(63)

In a discussion on the conformational angles within a platinacyclobutane ring caution is expressed about the use of solid state X-ray crystallographic data. Using the Karplus relationship on coupling constant relationships to torsion angles, a good correlation is obtained in most cases between solution and solid state data. In two cases a wide discrepancy is noted and the conclusion is tentatively reached that the solid state data do not give an accurate description of the conformational properties in solution.[557]

Solvolysis of the complex (**64**) in aqueous acetone follows pseudo first-order kinetics with the formation of the ring-expanded compound (**65**; equation 198).[558] A carbonium ion pathway is supported by ^{13}C labeling experiments.

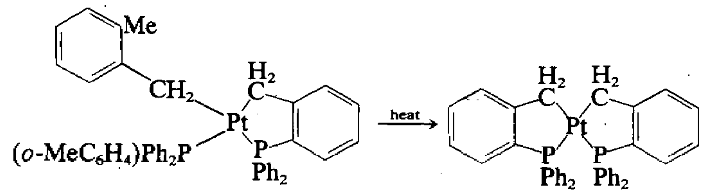


(198)

(64) **(65)**

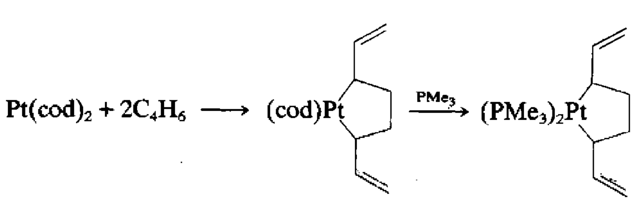
L = py; R = H; Ms = mesityl

A further reaction of interest is the δ-hydrogen abstraction, which has been used in the formation of benzoplatinacyclopentene complexes from coordinated *o*-methylbenzyl ligands (equation 199).[559]



(199)

A detailed recent study has been made to try and elucidate whether metallacyclobutanes rearrange to alkenes by β elimination or by α elimination to give an intermediate ylide complex, which can rearrange to an alkene complex. Using deuterium-labeled platinum(IV) platinacyclobutanes it is concluded that the pathway involves a [1,3] H shift (α elimination) rather than a [1,2] H shift (β elimination).[560] Platinacyclopentanes have also been formed by an alkene coupling between $Pt(cod)_2$ and butadiene. Addition of PMe_3 gives complex (**66**; equation 200).[561]



(200)

(66)

Compounds such as $PtCl(CO_2H)(PEt_3)_2$ will undergo a similar β-hydrogen transfer to give $PtHCl(PEt_3)_2$ and CO_2 (equation 201).[562]

$$PtCl(CO_2H)(PEt_3)_2 \longrightarrow PtHCl(PEt_3)_2 + CO_2 \qquad (201)$$

(ii) *Cleavage reactions: photochemical cleavage*

Platinum–carbon bond cleavage can be photoinduced. The photoinduced reductive elimination of cyanoalkanes from *trans*-$PtH(R)(PPh_3)_2$ ($R = CH_2CN$, $(CH_2)_2CN$, $(CH_2)_3CN$) involves initial isomerization to the *cis* isomer prior to reductive elimination.[563] Photolysis of platinacyclopentanes gives alkanes and alkenes.[564]

(*iii*) *Cleavage reactions: redox cleavage*

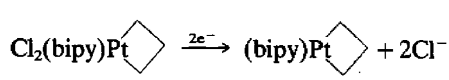
In a study of the electron transfer processes in organoplatinum chemistry, $PtR'_2(PR_3)_2$ complexes are oxidized by $IrCl_6^{2-}$ to give two principal types of products depending on the structure of the alkyl group and the coordinated phosphine. $PtMe_2(PMe_2Ph)_2$ undergoes oxidation to platinum(IV), *cis*-$PtEt_2L_2$ ($L = PMe_2Ph$, PPh_3) undergoes Pt—Et cleavage, and $PtMe_2(PPh_3)_2$ undergoes both oxidation and Pt—Me cleavage (equations 202–205).[565] Two equivalents of iridium(IV) are required in each reaction. The energetics and kinetics, as well as the observation of alkyl radicals by spin trapping and oxygen scavenging, support a mechanism involving the rate-limiting electron transfer from PtR_2 to $IrCl_6^{2-}$. The selectivity in product formation is associated directly with the paramagnetic formally platinum(III) intermediate $PtR_2L_2^+$. The platinacyclobutane complex (**67**) undergoes electrochemical reduction to (**68**) without Pt—C cleavage (equation 206).[566]

$$PtMe_2(PMe_2Ph)_2 \xrightarrow{IrCl_6^{2-}} PtMe_2Cl_2(PMe_2Ph)_2 \quad (202)$$

$$cis\text{-}PtEt_2(PMe_2Ph)_2 \xrightarrow[MeCN]{IrCl_6^{2-}} PtEt(MeCN)(PMe_2Ph)_2^+ + EtCl \quad (203)$$

$$PtMe_2(PPh_3)_2 \xrightarrow{IrCl_6^{2-}} PtMe_2Cl_2(PPh_3)_2 \quad (204)$$

$$PtMe_2(PPh_3)_2 \xrightarrow{IrCl_6^{2-}} PtMeCl(PPh_3)_2 + MeCl \quad (205)$$



(**67**) (**68**) (206)

(*iv*) *Cleavage reactions: binuclear elimination*

A formally β-elimination reaction occurs when $[Pt_2Et_3(\mu\text{-dppm})_2]^+$ is thermolyzed to give $[Pt_2Et_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$. This reaction across a biplatinum complex follows first-order kinetics, and is not retarded by added dppm. The β-elimination step is not rate determining.[567] Photolysis of $[Pt_2Me_3(\mu\text{-dppm})_2]^+$ in pyridine gives $PtMe_2(dppm)$ and $[PtMe(py)dppm]^+$, but in MeCN, acetone or CH_2Cl_2 solvent, reductive elimination of ethane occurs.[568]

(*v*) *Reductive elimination*

Theoretical analysis of the mechanism of reductive elimination leads to the following conclusions: (i) in the four-coordinate complex, the better the σ-donating capacity of the leaving groups, the more facile the elimination; (ii) stronger donor ligands *trans* to the leaving groups will increase the barrier to elimination; (iii) the reductive elimination barrier in four-coordinate complexes is controlled by the energy of an antisymmetric b_2 orbital, which in turn depends on the energy of the metal levels: the activation energy for such direct reductive elimination is substantially lower for Ni than for Pt or Pd; (iv) T-shaped *trans*-MR_2L arising from dissociation of L in MR_2L_2 will encounter a substantial barrier to polytopal rearrangement to *cis*-MR_2L_2, which has an open channel for reductive elimination of R_2; and (v) if the leaving groups are poor donors, *cis–trans* isomerization in the three-coordinate manifold should be easier than elimination. Conclusions (iv) and (v) were drawn for Pd compounds, and hence their extrapolation to platinum chemistry must be exercised with caution.[569]

(*vi*) *Electrophilic cleavage*

Platinum(II) alkyls are sensitive to cleavage by electrophiles. Hydrogen chloride in ethanol or benzene solvent causes cleavage (equation 207).[570] The alkyl aryl complexes *cis*-$PtMePh(PMePh_2)_2$ and *cis*-$PtMe(p\text{-}MeC_6H_4)(PMe_2Ph)_2$ react with the electrophiles HCl, $HgCl_2$ and $PtI_2(PMe_2Ph)_2$ by selective cleavage of the Pt—Me bond. This differs from

$PtMe(p\text{-}MeC_6H_4)(cod)$ where the Pt—aryl bond is cleaved. From the selectivities and rates, it is proposed that the S_E2 mechanism leads to selective Pt—aryl cleavage, and that a different mechanism, probably involving an oxidative addition–reductive elimination sequence, leads to selective Pt—Me bond cleavage.[571] Protolytic cleavage of one Pt—C σ bond in $Pt(YC_6H_4)_2(PEt_3)_2$ (Y = *p*-NMe₂, *p*-OMe, H, *m*-OMe, *p*-F, *p*-Cl, *m*-F, *o*-Me, *o*-Et, *m*-CF₃) to give *cis*-$PtCl(YC_6H_4)(PEt_3)_2$ and YC_6H_5 in methanol follows a sequence where electron-releasing substituents in the platinum–carbon-bonded aromatic rings increase the rates of electrophilic attack, and a fairly good LFER is found. The kinetic isotope effect for DCl is approximately 6.[572]

$$cis\text{-}PtMe_2(PEt_3)_2 + HCl \longrightarrow cis\text{-}PtMeCl(PEt_3)_2 \xrightarrow{HCl} cis\text{-}PtCl_2(PEt_3)_2 + 2CH_4 \qquad (207)$$

Phenylselenol, diphenylphosphine and diphenylarsine cleave Pt—Me bonds, but *N*-bromosuccinimide and 2-nitrobenzenesulfenyl chloride oxidize the methyl platinum(II) compounds to methyl platinum(IV) complexes (equations 208 and 209).[573] *m*-Chloroperbenzoic acid cleaves the Pt—benzyl bond in $PtCl(CHDPh)(PPh_3)_2$ with retention of configuration at carbon.[574]

$$cis\text{-}PtMe_2L_2 + PhSH \longrightarrow cis\text{-}PtMe(SPh)L_2 + MeH \qquad (208)$$

$$cis\text{-}PtMe_2L_2 + Ph_2MH \longrightarrow cis\text{-}PtMe(MPh_2)L_2 + MeH \qquad (209)$$

$$M = P,\ As$$

(*vii*) *Isomerization reactions*

The *cis*/*trans* isomerization of platinum(II) complexes is a subject which will be discussed in some detail when the halide (Group VII) complexes are covered. Nevertheless the importance of reductive elimination reactions of platinum(II) alkyl and aryl complexes makes it imperative that this reaction be discussed here for alkyl and aryl platinum(II) compounds.

For the complexes *cis*-$PtBr(R)(PEt_3)_2$ (R = Ph, *p*-MeC_6H_4, *o*-MeC_6H_4, *o*-EtC_6H_4, 2,4,6-$Me_3C_6H_2$) the isomerization rate is first order in platinum complex and is slowed by added Br^-. *Ortho* substitution in the phenyl ring only slightly affects the rates of isomerization. The reaction involves a dissociative asynchronous mechanism in which the rate-determining step is breaking of a Pt—X bond to yield the three-coordinate '*cis*-like' intermediate.[575] A phosphine dissociation assisted by a solvated platinum(II) complex has been proposed,[576] but refuted on kinetic grounds.[577] Large values for $\Delta H^{\neq}$ and large negative $\Delta S^{\neq}$ values are obtained for this isomerization. The rates correlate with the Hammett parameters of the Y substituents or with the set of Swain and Lupton dual-substituent parameters, which again indicates that σ rather than π interactions are dominant in the Pt—Ar bond.[578] In hydroxylic solvents and acetonitrile the role of the solvent is to promote the breaking of the Pt—Cl bond, leading to ligand substitution or uncatalyzed isomerization.[579]

A useful method to probe whether the reaction mechanism involves an associative or dissociative pathway is to measure $\Delta V^{\neq}$ (the volume of activation) for the reaction. High pressure kinetics in methanol give $\Delta V^{\neq} = -12\ cm^3\ mol^{-1}$ for an associative first step, and $+7.7\ cm^3\ mol^{-1}$ for the isomerization reaction. It is proposed that the faster reaction is a solvolytic replacement of Cl^- followed by a dissociative isomerization step with $[PtR(MeOH)(PEt_3)_2]^+$ (R = alkyl, aryl; equation 210).[580] Since isomerization and substitution reactions are mechanistically intertwined, it is useful to note here that for the rates of substitution of both *cis*- and *trans*-$PtBr(2,4,6\text{-}Me_3C_6H_2)(PEt_3)_2$ by I^- and thiourea, the volumes of activation are negative, in support of associative processes.[581] Further support for associative solvation as the first step in the isomerization of aryl platinum(II) complexes has been presented,[582] and the arguments in favor summarized.[583]

$$cis\text{-}PtClR(PEt_3)_2 \xrightarrow{MeOH} cis\text{-}PtR(MeOH)(PEt_3)_2^+ \xrightarrow{Cl^-} trans\text{-}PtClR(PEt_3)_2 \qquad (210)$$

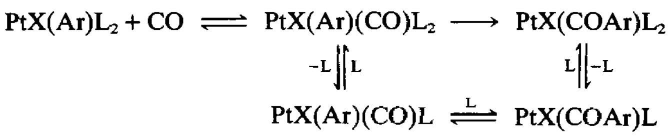
The photochemical isomerization of $PtClPh(PEt_3)_2$ in acetonitrile solvent occurs at 254, 280 and 313 nm. For *cis* → *trans* isomerization the quantum yield is close to 0.1 at all wavelengths, but for *trans* → *cis* isomerization the quantum yield varies from 0.5 to $<10^{-3}$ on changing λ from 254 to 313 nm.[584]

52.4.8.4 Insertion reactions

(i) Carbon monoxide

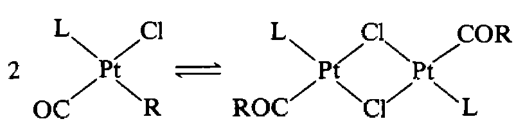
The insertion of CO into metal–carbon σ bonds has been reviewed.[585–590] Carbonylation of alkyl platinum(II) complexes usually requires elevated temperatures, although at higher temperatures the reaction is reversible (equation 211).[591] With $PtMe_2(dppe)$ insertion occurs into only one of the Pt—Me bonds. For complexes $PtX(Ar)L_2$, carbonylation follows pseudo first-order kinetics. Rates are decreased by addition of L to a maximum value where the carbonylation rate is independent of L. The pathway involves formation of a five-coordinate intermediate $PtX(Ar)(CO)L_2$, followed by dissociation to form PtX(Ar)(CO)L. The migratory step to yield PtX(COAr)L is unaffected by added L. This pathway is outlined in Scheme 6.[592]

$$trans\text{-}PtCl(Me)(PEt_3)_2 + CO \underset{140\,°C}{\overset{90\,°C,\ 80\ atm}{\rightleftharpoons}} trans\text{-}PtCl(COMe)(PEt_3)_2 \quad (211)$$



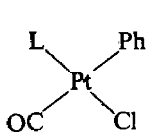
Scheme 6

For the three geometric isomers of $PtCl(Ph)CO(PMePh_2)$, (**69**), (**70**) and (**71**), only (**69**) undergoes carbonyl insertion (equation 212). Replacement of the phenyl group by other R groups affects the equilibrium position in equation (212), the tendency towards the acyl decreasing in the order R = Et > Ph > Me > CH_2Ph (≈ 0).[593] From the reaction of $HgPh_2$ with *cis*-$PtCl_2(CO)L$, benzoyl complexes $Pt_2(\mu\text{-}Cl)_2(COPh)_2L_2$ (L = PEt_3, PMe_2Ph, $PMePh_2$, PPh_3, PCy_3) or phenyl complexes PtCl(Ph)(CO)L (L = $P(o\text{-}MeC_6H_4)_3$, $AsMePh_2$, $AsPh_3$) can be obtained. Low temperature NMR studies show that the initial product is the phenyl carbonyl complex, and that acyl complexes are formed by a subsequent insertion reaction.[594] By using ^{31}P NMR techniques a number of intermediates resembling those discussed earlier are identified.[592,595] The use of elemental sulfur to remove PR_3 from the system is critically important in identifying some of these intermediates. In the equilibrium reaction (212) electron donating substituents in the *meta* and *para* positions of the aryl substituent promote formation of the insertion product, and a correlation with Hammett σ values is found. Enthalpies of the reaction became less negative with electron-withdrawing groups, which is ascribed to a strengthing of the Pt—Ar bond.[596] The five-coordinate intermediate $PtCl_2(CO)L_2$ is also a likely one for isomerization reactions, and carbon monoxide will catalyze *trans* to *cis* isomerizations of $PtCl_2L_2$.[597]

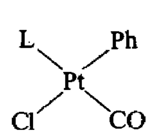


(212)

(**69**)



(**70**)

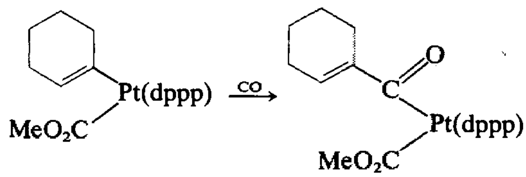


(**71**)

The decarbonylation of *trans*-$PtCl(COR)(PPh_3)_2$ (R = alkyl, aryl) complexes is promoted by tin(II) chloride.[598] Complexes *trans*-$Pt(SnCl_3)PhL_2$ (L = PPh_3, $PMePh_2$) react with CO to form *trans*-$[PtPh(CO)L_2]SnCl_3$, then slowly to give *trans*-$Pt(SnCl_3)(COPh)L_2$. The role of $SnCl_3^-$ appears to be to provide a good leaving group.[599] Consequently a mixture of *cis*-$PtCl_2(CO)(PPh_3)_2$ and $SnCl_2{\cdot}2H_2O$ in aqueous acetone is an active catalyst for alkene hydroformylation.[600] Solvent effects are important in the chemistry of *cis*-$PtCl_2(CO)(PPh_3)_2$ since in acetone and acetonitrile ligand rearrangement reactions occur, but in chloroform only the simple insertion of $SnCl_2$ into one Pt—Cl bond is observed.[601]

An interesting ligand effect is found by changing the ditertiary phosphine. The complex

$Pt(CO_2Me)C_6H_9(dppp)$ readily inserts CO to give an acyl complex (equation 213), but the dppe analog does not react.[602]



(213)

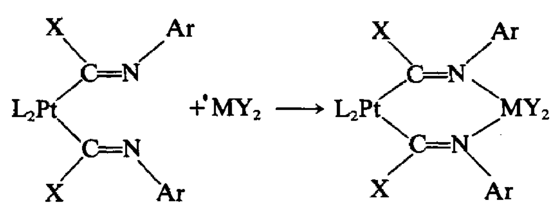
An MO study of CO insertion into the Me—Pt^{II} bond has considered a number of pathways, and the factors involved have been weighed. *Trans* influence arguments and the facility of the supporting ligands to migrate between different structures are considered. The relative stabilities of isomers and the potential barrier for isomerizations are investigated; the Y-shaped complex is unstable and isomerizes to a T-shape with no barrier. The relative stability of T-shaped complexes is explained by the *trans* influence effect.[603]

(*ii*) *Sulfur dioxide*

The complex *trans*-$PtClR(PEt_3)_2$ will insert SO_2 into the Pt—C σ bond.[604]

(*iii*) *Isocyanides*

Isocyanides will insert into platinum–carbon σ bonds. The compounds *trans*-$PtXR(PPh_3)_2$ (X = Br, I; R = Me, Ph) react with *p*-chlorophenyl isocyanide at ambient temperature to give [*trans*-$PtR(CNR')(PPh_3)_2$]X, which on refluxing undergoes insertion to form $PtX\{C({=}NR')R\}(PPh_3)_2$.[605,606] The rate increases as the nucleophilic character of the carbon atom of the alkyl or aryl group increases. The rate increases with increasing electrophilicity of the isocyanide ligand. Mechanisms have been proposed where the ionic compound is an intermediate[607] or by-product.[608] Complexes of this imino type have been used to prepare heterobimetallic complexes by using the imino nitrogen atom as a ligand to a second metal ion (equation 214).[609]



(214)

(*iv*) *Alkenes and alkynes*

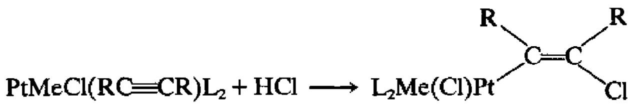
Insertion of alkenes and alkynes into a platinum–alkyl bond leads to the formation of platinum alkyl and vinyl complexes. Typical reactions are shown in equations (215) and (216). The reactivity shows little dependence on X, but for L the dependence is in the order L = $AsMe_2Ph > PMe_2Ph > PPh_3$. Electron-withdrawing substituents on the alkene or alkyne favor the reaction, possibly because such substituents stabilize both the formed alkyl and vinyl complexes, and the five-coordinate π-alkene and π-alkyne intermediates (equation 217).[610] Such five-coordinate intermediates need not yield product directly. A free radical route has been proposed for the insertion of alkynes where the five-coordinate intermediate (**72**) reacts with a radical $PtMeL_2\cdot$, formed by halogen loss from $PtMeClL_2$, to give a platinum(I) alkyne complex (**73**) which undergoes the insertion reaction (equation 218). Side reactions can occur. A radical pathway may result in the formation of HCl which can attack (**72**) to give the β-chlorovinyl platinum compound (**74**; equation 219).[612]

$$PtX(Me)L_2 \xrightarrow{C_2R_4} PtX(CR_2CR_2Me)L_2 \qquad (215)$$

$$PtX(Me)L_2 \xrightarrow{C_2R_2} PtX(CR{=}CRMe)L_2 \qquad (216)$$

$$trans\text{-}PtMeCl(PMe_2Ph)_2 + C_2(CN)_4 \longrightarrow PtMeCl\{C_2(CN)_4\}(PMe_2Ph)_2 \qquad (217)$$

$$\underset{(72)}{PtMeL_2\cdot + PtMeCl(RC{\equiv}CR)L_2} \longrightarrow \underset{(73)}{PtMeClL_2 + PtMe(RC{\equiv}CR)L_2\cdot} \qquad (218)$$

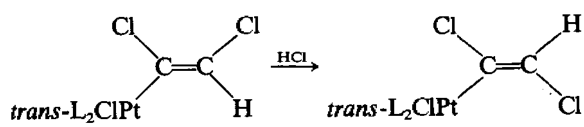


(72) (74)

$R = CO_2Me$ (219)

52.4.8.5 Reactions of vinyl and acetylide complexes

The reaction between protic acids and platinum(II) vinyl complexes is dependent on the particular σ-vinyl group.[613] For CH=CHCl, which has a hydrogen on the α carbon, Pt—C cleavage occurs, but for CCl=CHCl and CCl=CHMe, the reaction with HCl gives an equilibrium mixture of vinylic isomers (equation 220). α-Chlorovinyl platinum(II) complexes react with alcohols to give carbenes (see Section 52.4.6).[614] In considering reactivities of platinum(II) vinyl complexes, it may be worth noting that a survey of the available structural data concludes that there is little, if any, back donation from Pt to C in platinum–vinyl bonds.[615]



(220)

Chlorovinyl complexes undergo HCl elimination with amine bases to form the acetylide complexes.[668] The rate of this reaction (equation 221) is solvent dependent, decreasing in the order $PhNO_2 > CDCl_3 \approx CD_2Cl_2 \gg C_6D_6 \approx CCl_4$, and dependent on the group bonded *trans* to the vinyl. The order is $C{\equiv}CH \approx CCl = CH_2 > Cl \gg C(OMe)Me$.

$$trans\text{-}Pt(CCl{=}CH_2)_2L_2 + 2Me_3N \longrightarrow trans\text{-}Pt(C{\equiv}CH)_2L_2 + 2(Me_3NH)Cl \qquad (221)$$

The formation of carbene complexes by protonation of platinum(II) acetylides has been discussed. Both acetylide groups in *trans*-$Pt(C{\equiv}CR)_2(PMe_2Ph)_2$ (R = H, Me) can be cleaved by HCl (equation 222).[616]

$$trans\text{-}Pt(C{\equiv}CR)_2(PMe_2Ph)_2 + 2HCl \longrightarrow PtCl_2(PMe_2Ph)_2 + 2RC{\equiv}CH \qquad (222)$$

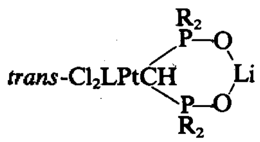
The triple bond can be reduced with hydrazine to form the vinyl complex with a *cis* stereochemistry about the carbon–carbon double bond (equation 223).[617] The five types of reaction between platinum acetylide complexes and aprotic compounds A—B have been summarized. These are (a) oxidative addition (A—B is I_2, IBr, ICN, MeI *etc.*); (b) insertion (A—B is $C_2(CN)_4$); (c) addition across the triple bond to form vinyl complexes (A—B is CF_3COCl, *o*-tetrachloroquinone, Br, NOCl); (d) insertion into the C—H bond (A—B is $(CF_3)_2CO$); and (e) formation of five-coordinate adducts.[618]

$$trans\text{-}Pt(C{\equiv}CR)_2(PMe_2Ph)_2 \xrightarrow{N_2H_4} trans\text{-}Pt(CH{=}CHR\text{-}cis)_2(PMe_2Ph)_2 \qquad (223)$$

52.4.8.6 Reactions of bis(diphenylphosphinyl)methanide complexes

Oxidation of dppm followed by addition of 1 mole of Bu^nLi gives the compound $Li[CH(Ph_2PO)_2]$, which reacts with $Pt_2Cl_4L_2$ (L = PBu^n_3, PPh_3, PEt_3) to give the Pt—C-bonded complex (**75**; equation 224). The structure of (**74**) has been confirmed by X-ray crystallography.[619]

$$\tfrac{1}{2}Pt_2Cl_4L_2 + Li\{CH(Ph_2PO)_2\} \longrightarrow \quad (224)$$



(**75**)

52.4.9 Platinum Alkene Complexes

Platinum alkene complexes have been known since 1830 when Zeise's salt was discovered. Alkene complexes of platinum(II) are kinetically more stable than their palladium counterparts, but this feature makes them less attractive for applications in homogeneous catalysis. A number of reviews have been written on alkene complexes.[620–623]

52.4.9.1 *Bonding*

Alkene complexes can be prepared with platinum in a divalent or a zerovalent oxidation state. The electron density at the platinum center exerts significant changes in bonding between the alkene and platinum. These effects exhibit themselves in both structural features and chemical reactivities.

An alkene complexed to platinum(II) is only slightly modified on coordination, but complexation to platinum(0) causes major changes. Platinum(0) alkene complexes show both weakening and lengthening of the carbon–carbon bond, as well as distortion of the plane of the double bond away from the platinum. In platinum(II) alkene complexes the double bond lies approximately perpendicular to the square plane of platinum(II), but in platinum(0) complexes there is only a small dihedral angle between the platinum and alkenic planes. For platinum(II) the energy barrier to free rotation of the alkene about the platinum(II)–alkene bond is only about 40–65 $kJ\ mol^{-1}$, whereas no rotation is observed with platinum(0) alkene complexes. Alkenes bonded to platinum(II) exert a large *trans* effect but only have a small *trans* influence.

The bonding in metal–alkene complexes[621,624] is described by a Chatt–Dewar–Duncanson model.[625,626] This model considers a σ (alkene to platinum) bond to be formed by donation of electron density from the filled $p\pi$ orbital on the alkene to the empty $5d_{z^2}5d_{x^2-y^2}6s6p_z$ hybrid orbital on platinum, and a π (platinum to alkene) bond being formed by back-donation of electron density from the $5d_{yz}6p_y$ hybrid orbital on platinum to the empty $p\pi^*$ antibonding orbital on the alkene. Calculations of the total energy of $PtCl_2(NH_3)(C_2H_4)$ as a function of torsion angle between the platinum and alkene planes shows a deep energy minimum at 90°,[627] although steric interactions cannot be ignored.[628] The near planarity of platinum(0) alkene complexes is considered to be due to the π back-donation causing the platinum center to become closer to the geometry required for a platinum(II) ion. Alternatively partial electron transfer to the alkene will cause the formally d^{10} platinum(0) center to have less than 10 electrons, which will lead to a Jahn–Teller distortion in which the tetrahedron is flattened.[629]

52.4.9.2 *Platinum(II) alkene complexes*

(*i*) *Synthesis*

Zeise's salt was originally prepared by refluxing a solution of K_2PtCl_6 in ethanol to give $K[PtCl_3(C_2H_4)]$ and acetaldehyde. Substitution reactions of platinum(II) complexes can be generally used for the direct synthesis of alkene platinum(II) complexes. The reaction of ethylene with $PtCl_4^{2-}$ is slow but can be accelerated by the addition of $SnCl_2$.[630,631] The reactions follow a usual two-term rate law *via* a first-order and a second-order pathway. The rate constant for reaction with $PtCl_3(H_2O)^-$ is greater than with $PtCl_4^{2-}$,[632–634] and the product $PtCl_3(C_2H_4)^-$ catalyzes the aquation of $PtCl_4^{2-}$.[635] The overall reaction is summarized in equation (225). Halide replacement to give cationic alkene complexes can be induced by the addition of a silver salt of a non-coordinating anion such as tetrafluoroborate (equation 226).[636]

Alkene complexes can also be prepared by bridge-cleavage reactions (equation 227).[637] The rate-determining step is probably the cleavage of one bridging halide. A ^{31}P NMR study shows that allene reacts with $Pt_2Cl_4(PMe_2Ph)_2$ at low temperatures to give *trans*-$PtCl_2(C_3H_4)(PMe_2Ph)$. At 20 °C, allene reacts with $Pt_2Cl_4(PR_3)_2$ ($PR_3 = PPr^n_3$, PMe_2Et, PMe_2Ph) to give *cis*-$PtCl_2(C_3H_4)(PR_3)$ (equation 228). The structure shows the allene complexed *via* one of the double bonds.[638]

$$PtCl_3(H_2O)^- \underset{k_{-1}}{\overset{H_2O,k_1}{\rightleftharpoons}} PtCl_4^{2-} \xrightarrow[C_2H_4]{k_2} PtCl_3(C_2H_4)^- \quad (k_3 \uparrow C_2H_4 \text{ from } PtCl_3(H_2O)^-) \qquad (225)$$

$$PtBr_2(1,5\text{-cod}) + acacH + 2AgBF_4 \longrightarrow [Pt(1,5\text{-cod})(acac)]BF_4 + 2AgBr + HBF_4 \qquad (226)$$

$$[PtCl_2(PR_3)]_2 + 2CH_2{=}CHCH_2OH \longrightarrow 2\,cis\text{-}PtCl_2(CH_2{=}CHCH_2OH)(PR_3) \qquad (227)$$

$$Pt_2Cl_4(PR_3)_2 + 2\text{ allene} \longrightarrow 2\,cis\text{-}PtCl_2(\text{allene})(PR_3)_2 \qquad (228)$$

Alkene substitution reactions can also be used to prepare new complexes. The rate of substitution of ethylene in *trans*-$PtCl_2(C_2H_4)py$ is markedly reduced by the presence of *ortho* substituents on the pyridine.[639] The substitution of styrene in *trans*-$PtCl_2(PhCH{=}CH_2)(p\text{-}ZC_6H_4NH_2)$ by pentene-1 in $CHCl_3$/EtOH follows a typical platinum(II) two-term rate law, the ethanol promoting the solvent-assisted pathway. The rate of substitution increases with increasing base strength on the aniline (equation 229).[640] Ethylene replacement in $PtCl(C_2H_4)(acac)$ is a route to the synthesis of the vinyl alcohol complex $PtCl(CH_2{=}CHOH)(acac)$ (**76**). The method involves displacement of ethylene by $CH_2{=}CHOSiMe_3$ followed by hydrolytic cleavage of the O—Si bond to give (**76**; equation 230).[641]

$$trans\text{-}PtCl_2(PhCH{=}CH_2)(p\text{-}ZC_6H_4NH_2) + C_5H_{10} \longrightarrow trans\text{-}PtCl_2(C_5H_{10})(p\text{-}ZC_6H_4NH_2) + PhCH{=}CH_2 \qquad (229)$$

$$PtCl(C_2H_4)(acac) + CH_2{=}CHOSiMe_3 \longrightarrow PtCl(CH_2{=}CHOSiMe_3)(acac) + C_2H_4 \xrightarrow{H_2O} PtCl(CH_2{=}CHOH)(acac) + Me_3SiOH \qquad (230)$$

(**76**)

Other supporting ligands will undergo substitution in platinum(II) alkene complexes to give new alkene complexes. The *trans* effect of alkenes on substitution rates is very high, and an explanation is usually given interrelating the alkene back-bonding ability with the stabilization of the pentacoordinate intermediate. Pentacoordinate platinum(II) alkene complexes are quite uncommon. One example is found when Zeise's salt is treated with bis(acetaldehyde methylphenylhydrazone).[642] Bidentate aliphatic diamines react with Zeise's salt to give complexes $PtCl_2(C_2H_4)L$ (L = *N,N,N',N'*-tetramethylethylenediamine (Me_4en), *N,N,N',N'*-tetramethylpropane-1,3-diamine (Me_4pn) or *N,N,N',N'*-tetramethylbutane-1,4-diamine (Me_4bn). In $CHCl_3$ solution the Me_4en complex has a five-coordinate structure for temperatures up to 10 °C, where ethylene dissociates. At 34 °C, the Me_4pn complex has a geometry intermediate between four- and five-coordinate, the five-coordinate compound becoming increasingly important as the solution temperature is lowered. The Me_4bn complex at 34 °C is four-coordinate, but is undergoing head-to-tail rearrangement.[643]

The characterization and calorimetric results for a series of displacement reactions (equations 231–233) show little difference between C_6H_6 and CH_2Cl_2 solvent.[644] The relative displacement energies are $P(OPh)_3 \gg$ ethylene > cyclooctene > *cis*-butene > styrene > cyclopentene > nitrostyrene > cyclohexene. These data are used to give a thermodynamic description of the *trans* effect.

$$[PtCl_2(\text{alkene})]_2 + 2py \longrightarrow 2PtCl_2(\text{alkene})py \qquad (231)$$

$$PtCl_2(\text{alkene})py + P(OPh)_3 \longrightarrow PtCl_2py\{P(OPh)_3\} + \text{alkene} \qquad (232)$$

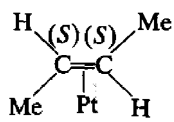
$$PtCl_2py\{P(OPh)_3\} + P(OPh)_3 \longrightarrow PtCl_2\{P(OPh)_3\}_2 + py \qquad (233)$$

Dienes such as norbornadiene, 1,5-cyclooctadiene and Dewar hexamethylbenzene will form mononuclear chelate complexes such as $PtX_2(\text{diene})$ (X = halogen).[645] Alkene isomerization may occur. Thus whereas complexes of 1,4- and 1,5-cyclooctadiene have been obtained which involve no isomerization,[646,647] under different experimental conditions phosphine complexes of platinum(II) cause isomerization to the 1,3-isomer.[648] Cationic chloride bridged complexes have been prepared from $PtCl_2$(diene) by reaction with $(Et_3O)BF_4$ (equation 234).[649]

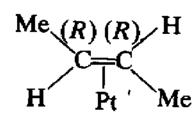
$$2PtCl_2(\text{diene}) + 2(Et_3O)BF_4 \longrightarrow [Pt_2Cl_2(\text{diene})_2](BF_4)_2 + 2Et_2O + 2EtCl \quad (234)$$

Chloroplatinate(II) salts can be used to prepare diene complexes of platinum(II), *e.g.* $PtCl_2(C_{12}H_{18})$ from Dewar hexamethylbenzene,[650,651] and $PtCl_2(\text{diene})_2$ from 4-vinylcyclohexene, 1,4-cyclohexadiene, *cis,cis*-1,4-cyclononadiene, bicyclo[3.3.1]nona-2,6-diene and methylenecyclopentene.[652–656]

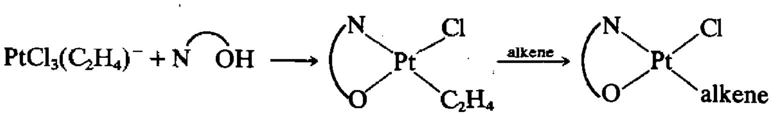
Alkenes which have no symmetry planes perpendicular to the plane of the double bond such as *trans*-butene-2 or propene can coordinate to platinum in two enantiomorphous ways (**77**) and (**78**). If an optically active ligand is also bound to platinum(II), then two diastereoisomers are found which can be separated by fractional crystallization[657,658] or by HPLC.[659] Both *cis* and *trans* isomers of complexes PtCl(N—O)(alkene) have been prepared, where N—O is an anion derived from an amino acid (equations 235a and 235b).[660–664] Epimerization cannot occur by simple rotation of the alkene about its bond axis, but only by a mechanism involving cleavage of the platinum(II)–alkene bond.



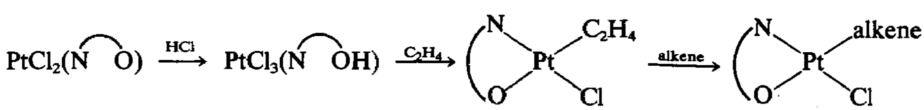
(**77**)



(**78**)



(235a)



(235b)

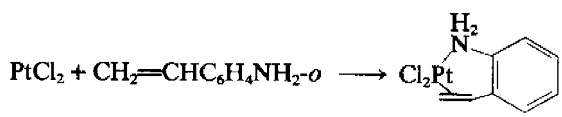
A series of complexes *cis*-$PtCl_2${(*S*)-TMSO}(alkene) (TMSO is *p*-tolyl methyl sulfoxide) have been prepared and characterized. The discriminatory effect of the chiral sulfoxide ligand is not large. Most alkenes are induced to prefer the (*R*) configuration, but butene-1 and 3,3-dimethylpropene-1 adopt the (*S*) configuration. Increasing the length or bulk of the aliphatic side chain of the alkene has only a small effect on the discrimination. No significant difference is found between disubstituted and monosubstituted alkenes. These authors stress the importance of the diastereotopic interaction as being that which leads to asymmetric discrimination. Relatively large discriminations are observed for the alkenic rotation barriers of the (*R*) and (*S*) alkene diastereomers; the (*S*) alkene rotates much more quickly than the (*R*) alkene diastereomer.[665] The rotation barriers are measured, and can be compared with the DMSO analogs.[666] The absolute configuration of $PtCl_2${(*S*)-methyl *p*-tolyl sulfoxide}{(*R*)-styrene} has been determined by X-ray crystallography. The Bijvoet method shows the absolute configuration at the asymmetric carbon atom which is formed upon alkene coordination is (*R*).[667] For the complex $PtCl_2${(*S*)-methyl *p*-tolyl sulfoxide}[$Me_2CHCH{=}CH_2$], a similar method shows the absolute configuration at the asymmetric carbon atom of the alkene to be (*S*).

The first crystalline optically active complex [PtCl(*o*-benzenediamine){(*S*)-2-methyl-2-butene}]BPh_4 shows that the ligands *cis* to the alkene affect the CD spectrum more than the *trans* ligand.[669] Substitution of *cis*-1,2-dichloroethylene for the coordinated (*S*)-2-methyl-2-butene proceeds in accordance with the second-order rate law, there being no contribution from the solvent path. For the complexes *trans*-$PtCl_2${R(Me)CHCH=CH_2}py (R = Et, Pr^i, Bu^t) the two diastereomers formed in the complexation of the chiral α alkene to Pt^{II} are present in different concentrations in solution, the diastereomer of opposite absolute configuration at the two chiral centers being the prevailing one.[670] Five-coordinate complexes $PtCl_2$(diamine)(alkene) (alkene = acrolein, acrylonitrile, fumarodinitrile, maleic anhydride and maleimide) have been isolated where the diamine is chiral of (*R*,*R*)-*N*,*N′* configuration. Structures have been solved for the ethylene and propylene analogues, and the two prochiral nitrogen atoms have equal absolute configurations identical with those of the asymmetric carbon atoms of the ligand.[671] Enantiomeric discrimination in platinum(II) alkene complexes has also been accomplished by using chiral lanthanide shift reagents.[672] Pentacoordinate platinum(II) alkene complexes with a chiral imine ligand have been prepared and the diastereomers identified through the use of high field ^{1}H and ^{13}C NMR spectroscopy.[673]

Cyclic monoenes and alkenes with chelating heteroatoms readily form complexes with platinum(II). The structure of $Pt_2Cl_2(\mu\text{-}Cl)_2$(cyclopentene)$_2$ shows only a slight elongation of the C═C double bond on coordination.[674]

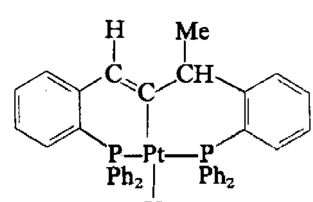
Among the heteroatom chelated alkene complexes, 2-allylpyridine coordinates to platinum through both nitrogen and alkene to give *cis*-$PtCl_2(2\text{-}CH_2{=}CHCH_2py)$ (equation 236).[675] *N*-Allylpyrazole reacts with K_2PtCl_4 in the presence of HCl to form the bidentate complex with N and the alkene coordinated.[676] The chelate complex $PtCl_2(CH_2{=}CHC_6H_4NH_2\text{-}o)$ is formed from *o*-vinylaniline (equation 237).[677] Similar platinum(II) complexes have been prepared using *o*-vinyl-*N*,*N*-dimethylaniline, *o*-isopropenylaniline and *o*-isopropenyl-*N*,*N*-dimethylaniline.[678–680] Deprotonation of $PtCl_2(CH_2{=}C(Me)C_6H_4NHMe\text{-}o)$ gives $[PtCl(CH_2{=}C(Me)C_6H_4NMe\text{-}o)]_2$ with bridging amido ligands and the alkenes in *trans* positions across the Pt_2 centers.[681]

$$PtCl_4^{2-} + 2\text{-}CH_2{=}CHCH_2py \longrightarrow PtCl_2(2\text{-}CH_2{=}CHCH_2py) + 2Cl^- \qquad (236)$$



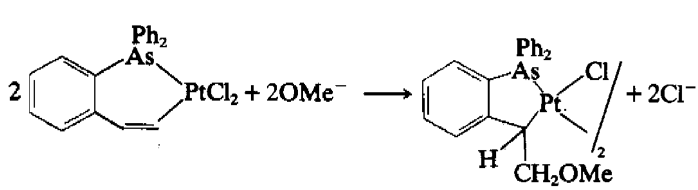
(237)

The pentenyl-phosphine and -arsine ligands $CH_2{=}CH(CH_2)_3EPh_2$ (E = P, As) form monomeric chelate complexes.[682] The compounds *o*-styryldiphenylphosphine, *o*-styryldimethylarsine and but-3-enyldi(cyclohexyl)phosphine form chelates PtX_2(L—L).[683–685] These complexes react with I^- and SCN^- to give a variety of complexes in which the double bond may or may not remain coordinated. In an approach directed toward the synthesis of alkene platinum(IV) complexes, iodine reacts with $PtMe_2(CH_2{=}CHC_6H_4PPh_2\text{-}o)$ to give $PtMeI(CH_2{=}CHC_6H_4PPh_2\text{-}o)$ by Pt—Me cleavage. The reaction with MeI is proposed to involve initial oxidative addition at platinum(II) followed by methyl transfer from platinum(IV) to the most substituted alkenic carbon.[686] The structures of $Pt(Me)_2(CH_2{=}CHC_6H_4PPh_2\text{-}o)$ and $Pt(CF_3)_2(CH_2{=}CHC_6H_4PPh_2\text{-}o)$ have been compared.[687] The alkenic di(tertiary phosphine) *o*-$Ph_2PC_6H_4$-*t*-CH═CHCH(Me)$C_6H_4PPh_2$-*o* reacts with chloroplatinum(II) complexes to give complexes of type (**79**), which have been formed by vinylic hydrogen abstraction.[688] Similar chelate complexes can be prepared from alkenic sulfides.[689]



(**79**)

The chelate complex $PtCl_2(CH_2{=}CHC_6H_4AsPh_2\text{-}o)$ reacts with methoxide ion at the coordinated double bond to give an alkyl complex (**80**; equation 238).[690] The structures of both compounds have been verified by X-ray crystallography. Analogous cationic complexes have been isolated, and their reactions with nucleophiles and electrophiles discussed.[691]



(**80**)

(238)

(*ii*) *Structure and reactions*

(*a*) *Diffraction studies and theoretical calculations.* Hartley's chapter on platinum chemistry in 'Comprehensive Organometallic Chemistry' gives an extensive list of the crystal structure data for platinum alkene complexes, and it would be superfluous to discuss the subject again here. A neutron diffraction study of Zeise's salt $K[PtCl_3(C_2H_4)]\cdot H_2O$ shows the Pt—Cl bond *trans* to ethylene as being significantly longer than the *cis* Pt—Cl bonds. The C—C distance of 1.375(4) Å is 0.038 Å longer than the value found in free ethylene, an indication of some $d\pi-p\pi^*$ back-bonding from Pt^{II} to ethylene. This is supported by the observed bending of the four hydrogen atoms away from the platinum atom. The carbon atoms are at an average distance of 0.164 Å from the plane of the four hydrogen atoms, and the angle between the normals to the methylene planes (the α angle) is 32.5°. Both the magnitude of α and the C—C bond lengthening are considerably smaller in Zeise's salt than in metal complexes of C_2F_4 and $C_2(CN)_4$, suggesting that the amount of $M\rightarrow L$ back-bonding is greater in these complexes than those of ethylene.[692]

Using the self-consistent-field $X\alpha$-scattered wave method, it has been concluded that the σ-bonding components are considerably more important than π back-bonding for the complexation of ethylene in Zeise's salt. These calculations are in agreement with the peak positions found in the optical spectra.[693] It appears likely, therefore, that even small contributions from π back-bonding overlap can cause marked geometric changes in the complexed alkene. The neutron diffraction structure has been compared with calculated structures of $PtCl_3(C_2H_4)^-$ by *ab initio* calculations using relativistic effective core potentials, and to incorporate the relativistic effects on the valence electrons. The calculated barrier to rotation (63 kJ mol^{-1}) agrees with the observed barriers (40–60 kJ mol^{-1}) in platinum alkene complexes. The barriers to rotation and binding energies both decrease in the order Pt > Pd.[694]

(*iii*) *NMR studies*

The NMR spectrum of polycrystalline $[PtCl_2(C_2H_4)]_2$ indicates the presence of a rocking motion perpendicular to the platinum(II)–alkene bond, and a wagging about the carbon–carbon double-bond axis.[695] A similar type of motion is observed in the NMR spectrum of single crystals of Zeise's salt.[696]

A ^{1}H NMR study of *trans*-$PtCl_2(C_2H_4)py$ in a nematic solution in CD_2Cl_2 shows the ratio of d_{gem}/d_{cis} to correspond with the structure obtained by neutron diffraction.[697] The plane of the pyridine ring is inclined at an angle to the $PtCl_2$ plane with rapid reorientation between the symmetry-related forms.[698]

In solution an alkene bonded to platinum(II) undergoes twisting about the axis of the alkenic double bond and rotation of the alkene about the platinum–alkene bond. From the coalescence temperature, the energy barrier to rotation is found to be between 41.8 and 62.8 kJ mol^{-1}, and this is almost independent of the alkene, the halogen, and other substituents on the supporting ligands. The five-coordinate pyrazoylborate complexes, however, show no evidence of alkene rotation. In a precise study of substituent effects on the energetics of alkene rotation, it appears that for a group of 4-substituted pyridine ligands there is an overall trend that $\Delta G^{\neq}$ decreases with decrease in pK_a of the pyridine.[699] This correlates with calculations showing little dependence of the rotational barrier on the strength of the Pt^{II}–alkene π bond.[700] A series of five-coordinate platinum alkene complexes PtX_2L_2(alkene) has been prepared where L_2 is a σ,σ, N,N′-bonded α-diimine or N,N′-disubstituted 1,2-diaminoethane. The five-coordinate structure is found both in the solid and solution state. The alkene is undergoing rotation with a barrier of 55 kJ mol^{-1} for styrene and 67 kJ mol^{-1} for methacrylate.[701]

Four-coordinate platinum(II) alkene complexes will undergo isomerization under photochemical[702] or thermal[703] conditions. The photochemical pathway is proposed to occur *via* a bridged dimeric intermediate.

Upon coordination of the carbon–carbon double bond to platinum(II), the alkenic proton is shifted upfield. In a series of complexes *trans*-$PtCl_2(C_2H_4)$(*p*-pyridine *N*-oxide), this shift is increasingly upfield as the *para* substituent becomes less electron releasing, because of increasing π back-donation of charge.[704] Protons in alkyl groups adjacent to alkenic double bonds shift downfield on coordination, the degree of shift depending on the distance between the alkyl groups and the platinum atom.[705] Carbon-13 data (δ and J) have been measured for the platinum(II) complexes *trans*-$PtCl_2$(alkene)Mepy, $PtCl_3(alkene)^-$ and [PtCl-

(alkene)$(NH_3)_2]BF_4$ where the alkene is p-$YC_6H_4CH{=}CH_2$, $RCH{=}CH_2$, $RCH{=}CHR$ or $CH_2{=}CH(CH_2)_nX$. The observed trends in $\delta(^{13}C)$ and J(PtC) have been qualitatively rationalized using a valence-bond description. The data support the view that for these platinum(II) complexes the donation from alkene π to a platinum σ orbital is the predominant component of the alkene–platinum bond.[706,707] A correlation has also been found between the Pt–alkene distance and the values of ^1J(PtC) for a series of *para*-substituted styryl (pyridyl) platinum complexes with substituents having different σ_p^+ values.[708]

(iv) Vibrational studies

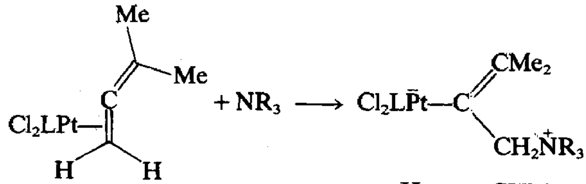
In Zeise's salt the accepted position of the ν_3 (C=C stretching) mode is at 1243 cm^{-1}.[709] This report corrected many earlier published claims, the problem being that the C=C double-bond stretching mode and the in-plane CH_2 deformation mode both have a_1 symmetry and similar frequencies. In view of this assignment problem, the best way of assessing the perturbation of alkenes on coordination is to sum the percentage lowering of the C=C stretching and CH_2 deformation modes.[710] For substituted platinum(II) alkene complexes, fine tuning of the electron density on the supporting ligand causes little influence on either the C=C or the PtC_2 stretching vibrations.

(v) Reactions of alkenes complexed to platinum(II)

Alkenes bonded to platinum(II) can be displaced by strongly coordinating ligands such as cyanide ion or tertiary phosphines. The displacement of ethylene from Zeise's salt by phosphines is a useful method of preparation of complexes *trans*-$PtCl_2(PR_3)_2$.[711] Amines will also displace alkenes from coordination to platinum(II), but this reaction can compete with nucleophilic attack at the coordinated alkenic carbon. The stability of platinum(II) alkene complexes follows the sequence $C_2H_4 > PhCH{=}CH_2 > Ph_2C{=}CH_2 \approx Ph(Me)C{=}CH_2$.[712]

The most important reaction of platinum(II) alkene complexes is nucleophilic attack at a coordinated carbon atom. The most studied nucleophile in this context is the amine nitrogen. Amines attack coordinated monoalkenes, and if tertiary phosphine or amine ligands are present these stabilize the Zwitterionic platinum–carbon σ-bonded complexes that are formed (equation 239).[713–715] The attack occurs *trans* to platinum.[715] Substituents adjacent to the alkenic double bond affect the direction of attack, forcing reactions anti-Markownikov.[716] Nucleophilic attack by amines on platinum(II) alkene complexes is reversible, the position of equilibrium depending largely on the steric bulk of the amine. Equilibrium constants for the reaction of $PtCl(Y)(Z)C_2H_4$ with amines have been measured. Lack of bulk in the amine is more important than its basicity. Data have been collected for Y = Cl, Z = amine and Y = Z = acac. Enthalpies and entropies are negative. The data are compared with those for pyridine as the nitrogen base where five-coordinate complexes are formed by attack at platinum(II).[717] When substituted alkenes are used, the direction of attack at the C=C double bond by amine nucleophiles is determined by electronic effects rather than steric effects, unless the latter are very large.[718] A similar reaction of *cis*-[$PtCl_2$(1,1-dimethylallene)L] (L = PPh_3, $AsPh_3$, p-$MeC_6H_4NH_2$, DMSO) with amines R_3N gives Zwitterionic alkenyl complexes (equation 240a).[719] The σ-bonded alkenyl group is perpendicular to the platinum coordination plane, and a short intramolecular contact between the N and a Cl suggests hydrogen bonding. These complexes will rearrange to the π-bonded alkene complex if the amine is a primary aromatic amine (equation 240b).[720] Although $PtCl_4^{2-}$ reacts with 4-pentenylammonium ion to form an alkene complex, this compound slowly converts back to $PtCl_4^{2-}$. The reaction involves intramolecular attack by amine at the coordinated double bond, and the intermediate (**81**) slowly converts back to $PtCl_4^{2-}$ by acid cleavage of the Pt—C bond.[721] A similar cyclization has been promoted by reaction with base on the Zwitterions formed by nucleophilic amine attack on a platinum(II) allene complex. Compounds (**82**) and (**83**) have been verified by X-ray crystallography.[722] For butadiene complexes of platinum(II), dimethylamine reacts rapidly at the terminal positions of both double bonds to form a diplatinum complex with two *trans*-fused five-membered rings.[723] Two other four-membered ring complexes similar to (**82**) have been verified by crystallography, the complexes being formed from Me_2NH and the respective ethylene and allene platinum(II) complexes.[724]

$$PtCl_2(C_2H_4)L + R_2NH \longrightarrow LCl_2\bar{P}tCH_2CH_2\overset{+}{N}HR_2 \qquad (239)$$



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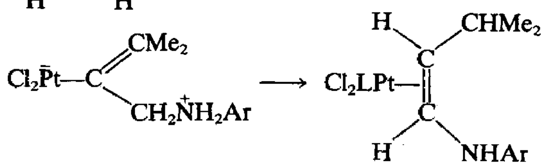

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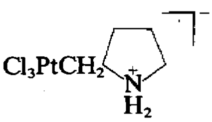

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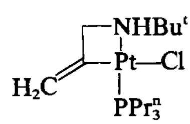

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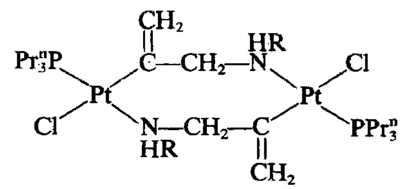
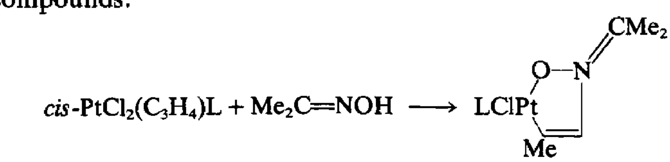


(83)

The more basic and less hindered pyridines undergo nucleophilic attack at an ethylene coordinated to platinum(II). Pyridine substitution reactions at platinum also occur, and in the presence of excess ethylene, alkene replacement is observed.[725]

Secondary and primary amines and ammonia undergo the amination reaction at ethylene in the cationic complexes $[PtCl(C_2H_4)L—L]^+$. The enhanced electrophilicity of the alkenic carbons, along with the absence of a formal negative charge on platinum in the product, stabilize the Pt—C σ bond. The product undergoes a further reaction with the initial cationic ethylene complex to form a binuclear platinum(II) complex with a single $C_2H_4N(Et_2)C_2H_4$ bridge.[726] These compounds undergo acidolysis to form polyalkylated ammonium ions.[727] For the polar alkene $H_2C{=}C(NMe_2)_2$, the product is a mixture of the η^1 and η^2 forms.[728] The compound $Me_2C{=}NOH$ reacts with *cis*-$PtCl_2$(allene)L to give $[PtCl\{ON({=}CMe_2)CH{=}CMe\}L]$ by nucleophilic attack by nitrogen followed by a [1,3] hydrogen shift and ring closure (equation 241).[729] Nucleophilic attack of cyanate ion at a coordinated alkene is a route to the synthesis of carbamoyl complexes (equation 242).[730] The reaction of 2-methyl-2-nitrosopropane with ethylene platinum(II) complexes similarly yields σ-alkylnitrone compounds.[731]



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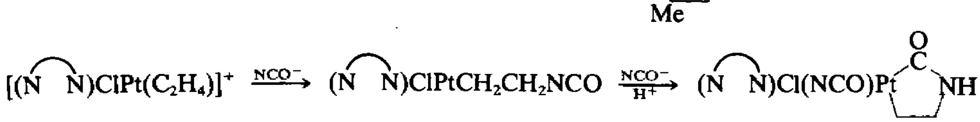
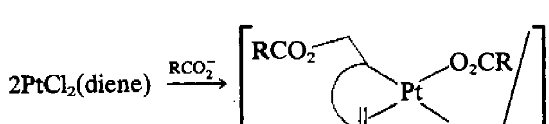


(242)

Nucleophilic attack by alkoxide usually results in reduction to platinum. Carboxylate ions react with $PtCl_2$(diene) by attack at both the platinum(II) and alkene centers (equation 243).[732] β-Diketonate anions react with platinum(II) dialkene complexes by similar nucleophilic attack at the double bond.[733,734] The complex $PtCl_2$(diene) (diene = norbornadiene or dicyclopentadiene) reacts with OPr^{i-}, NH_2Ph, SPh^- and SCN^-. The dicyclopentadiene complex undergoes attack at the diene in each case and the S nucleophiles also give substitution at platinum. Only the latter reaction occurs with the norbornadiene complexes and S nucleophiles, but attack at diene is found with OPr^{i-} and NH_2Ph. The reactions of these products with neutral uni- and bi-dentate ligands usually lead to bridge-splitting reactions, but in some cases the norbornenyl derivatives undergo rearrangement to nortricyclene systems.[735]



(243)

(vi) Catalyzed H–D exchange at saturated carbon

The platinum-catalyzed H–D exchange at saturated carbon is observed with alkenes. In the presence of a homogeneous platinum(II) complex as catalyst, alkenes $RCMe_2CH{=}CH_2$ (R = Et, Pr, Bu) undergo H–D exchange with a D_2O–$MeCO_2D$ solvent containing perchloric acid. Deuterium incorporation into the alkyl occurs exclusively at C-5, and exchange of alkenic protons is also observed. Dimeric chloro-bridged alkene platinum(II) complexes are recovered.[736] For complexes $Pt_2Cl_4L_2$ (L = PPr_3, PBu_3, PBu^tPr_2, PBu^t_2Pr, $PPrPh_2$, PPr_2Ph, PBu^tPh_2) deuterium incorporation into the alkyl groups of the tertiary phosphines occurs in the same solvent medium.[737] Site incorporation has also been analyzed by ^{13}C NMR spectroscopy.[738]

52.4.9.3 Platinum(0) alkene complexes

(i) Synthesis

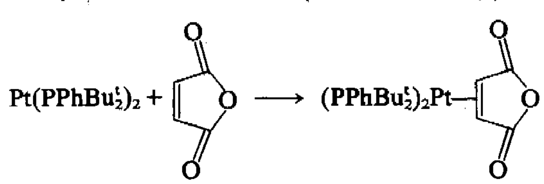
Alkene complexes of *trans*-stilbene, *trans*-4,4′-dinitrostilbene and acenaphthylene can be prepared by the reduction of *cis*-$PtCl_2(PPh_3)_2$ with hydrazine followed by alkene addition;[739,740] ethylene, hexene-1, cyclohexene, allyl alcohol, styrene and tetraphenylethylene do not react. Alternatively, treatment of $Pt(CO_3)L_2$ in ethanol with ethylene,[741] fluoroalkenes and tetracyanoethylene[742] gives Pt(alkene)L_2 (equation 244). An alternative preparation of alkene complexes and $Pt(C_2H_4)(PPh_3)_2$ involves using $NaBH_4$ and C_2H_4 with $Pt(CO_3)(PPh_3)_2$ in ethanol at 25 °C (equation 245).[743,744] Borohydride reduction can also be used to form $Pt(C_2H_4)(PPh_3)_2$ from $PtCl_2(PPh_3)_2$ in ethanol solvent under ethylene pressure, or without pressure in dichloromethane/ethanol.[745] A convenient high yield synthesis of $Pt(C_2H_4)(PEt_3)_2$ is achieved by the thermal decomposition of $PtEt_2(PEt_3)_2$. The method can be used to prepare other alkene complexes of platinum(0) with trialkylphosphine ligands, the yields and reaction temperatures being detailed.

$$Pt(CO_3)L_2 + \text{alkene} + EtOH \longrightarrow Pt(\text{alkene})L_2 + CO_2 + MeCHO + H_2O \qquad (244)$$

$$Pt(CO_3)(PPh_3)_2 + C_2H_4 + NaBH_4 \longrightarrow Pt(C_2H_4)(PPh_3)_2 \qquad (245)$$

Refluxing $Pt(PPh_3)_4$ in benzene solvent with alkenes gives complexes Pt(alkene)$(PPh_3)_2$ (alkene = chloroalkenes,[747,748] fluoroalkenes,[749] tetracyanoethylene[750] and fumaronitrile[751]) (equation 246). A similar displacement method can be used to prepare the series of complexes $Pt(C_2F_4)L_2$ (L = PPh_3, $PMePh_2$, PMe_2Ph, PBu_3; L_2 = dppe) by treating $Pt(C_2F_4)(AsPh_3)_2$ with the more strongly coordinating ligands L.[752,753] For bulky phosphine ligands where the stable platinum(0) complex is two coordinate, for example $Pt(PPhBu^t_2)_2$, addition of dimethyl fumarate or maleic anhydride gives the alkene complex (equation 247).[754] Displacement of ethylene from $Pt(C_2H_4)(PPh_3)_2$ is a useful method for the preparation of complexes Pt(alkene)$(PPh_3)_2$ under mild conditions.[755–757] The method has been used for the synthesis of a new structural class of cumulene complexes by coordination of η^2-butatriene,[758] and new methylene cyclopropane platinum(0) complexes (equation 248).[759]

$$Pt(PPh_3)_4 + CF_3CF{=}CFCF_3 \longrightarrow Pt(CF_3CF{=}CFCF_3)(PPh_3)_2 + 2PPh_3 \qquad (246)$$



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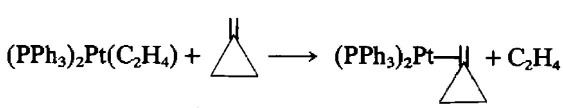
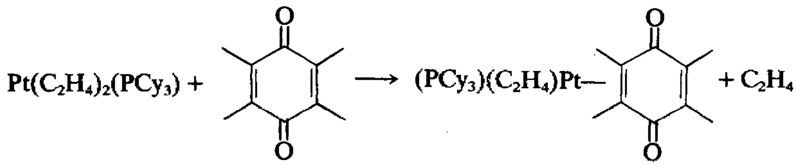


(248)

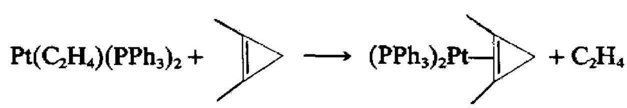
A series of complexes $Pt(\eta^2\text{-quinone})(C_2H_4)(PCy_3)$ has been prepared by displacement of one coordinated ethylene from $Pt(C_2H_4)_2(PCy_3)$ (equation 249).[760] On the NMR time scale the ethylene is undergoing rapid rotation but the η^2-bonded quinone is rigid. A similar reaction with tetrafluoroethylene yields $Pt(C_2F_4)(C_2H_4)(PCy_3)$.[761] The precursor ethylene compounds can be formed by treating $Pt(cod)_2$ with ethylene in the presence of one equivalent of tertiary phosphine or arsine (equation 250). The chemistry of these types of alkene platinum(0) complexes has been summarized by Stone.[762] Stable platinum(0) complexes of dibenzylideneacetone (dba) can be prepared, and the addition of phosphines L yields $Pt(dba)L_2$. In the presence of a second alkene the dibenzylideneacetone can be substituted to give $Pt(alkene)L_2$.[763]



(249)

$$Pt(cod)_2 + 2C_2H_4 + PR_3 \longrightarrow Pt(C_2H_4)_2(PR_3) + 2cod \qquad (250)$$

Cyclopropene can be stabilized by coordination to platinum(0). The complexes Pt(3-methylcyclopropene)$(PPh_3)_2$ and Pt(1,2-dimethylcyclopropene)$(PPh_3)_2$ can be prepared by displacement of ethylene from $Pt(C_2H_4)(PPh_3)_2$ (equation 251). The complexed ring has a C=C distance of 1.50 Å, and insertion of platinum into the ring has not occurred.[764] In a similar manner the compound bicyclo[2.2.0]hex-1,4-diene has been stabilized as a complex with $Pt(PPh_3)_2$.[765] These strained ring alkenes can be displaced by carbon disulfide, but upon dissolution in ethanol, addition across the double bond occurs.[766] The procedure has been used to prepare complexes of Bredt alkenes. The structure of (**84**) shows that the bridgehead double bond is bound on the *exo* side to the $Pt(PPh_3)_2$.[767] The Bredt alkene platinum(II) complexes are similarly stable.[768] The compound $Pt(cod)_2$ reacts with 2,3,4,5-tetraphenylfulvene and PR_3 to give a π-bonded fulvene complex $Pt(\eta^2\text{-}C_5H_4CPh_2)(PR_3)_2$ (equation 252). The structure of the PPh_3 complex shows the fulvene coordinated to the exocyclic double bond of the fulvene.[769] The C_5 fulvene ring is planar, and makes an angle of 108° with the coordination plane around the platinum. Replacement of stilbene in Pt(stilbene)$(PPh_3)_2$ by 1,2-disubstituted cyclobutenediones gives complexes which are not ring opened, but are platinum(0) cyclobutenedione compounds coordinated *via* the C=C double bond.[770] This displacement reaction can also be used to complex squaric acid to platinum(0) (equation 253). The synthesis cannot be accomplished from $Pt(PPh_3)_3$ since protonation at platinum occurs.[771] With 1,2-dicyanocyclobutene, the displacement of ethylene from $Pt(C_2H_4)(PPh_3)_2$ again gives the cyclic alkene complex and not the ring opened metallacycle.[772] Treating $Pt(C_2H_4)(PPh_3)_2$ or $Pt(PPh_3)_3$ with 1 equivalent of octafluorocyclooctatetraene rapidly gives the η^2 alkene complex, but in solution this rapidly transforms into the 1,2,3,6-η complex.[773]



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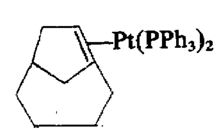
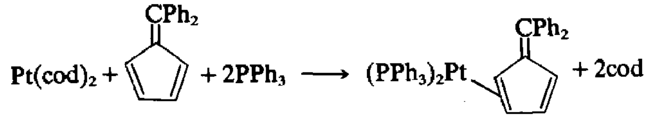


(**84**)



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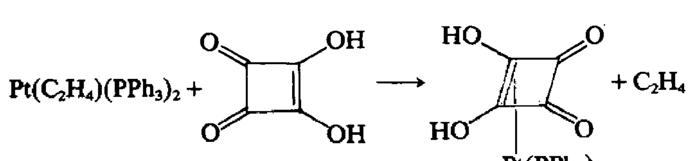
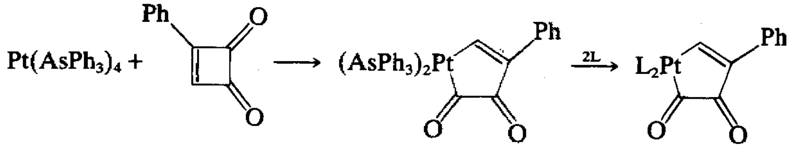


(253)

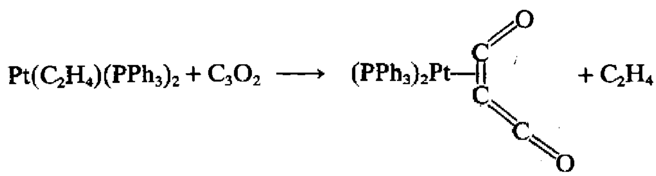
Ring opening can nevertheless occur. The synthesis and NMR spectroscopy have been described for a series of ring-opened platinacyclopent-4-ene-2,3-dione complexes

Pt{CH=C(Ph)(CO)(CO)}L_2 (L = $AsPh_3$, PPh_3, PEt_2Ph, PEt_3, $PMePh_2$, $P(OPh)_3$, py; L_2 = dppe, bipy, phen) (equation 254).[774]



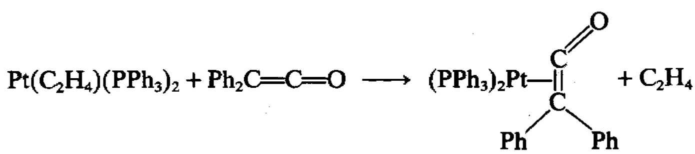
(254)

Platinum(0) complexes of allenes can be prepared by the hydrazine method or by displacement of triphenylphosphine from $Pt(PPh_3)_3$.[740,775] The displacement of ethylene from $Pt(C_2H_4)(PPh_3)_2$ has been used to prepare platinum(0) complexes of cyclic allenes.[776] On coordination to platinum(0), allene becomes non-linear with the uncoordinated carbon atom bent away from platinum by about 40°. Coordination lengthens the coordinated double bond.[777] Carbon suboxide (C_3O_2) reacts with $Pt(C_2H_4)(PPh_3)_2$ to give $Pt(C_3O_2)(PPh_3)_2$ (equation 255). The IR spectrum of (**85**) shows a strong ketene band (2080 cm^{-1}). Double-bond cleavage is suggested but not proven.[778] Ketenes also substitute ethylene in $Pt(C_2H_4)(PPh_3)_2$ to form η^2-bonded ketene complexes (equation 256).[779]



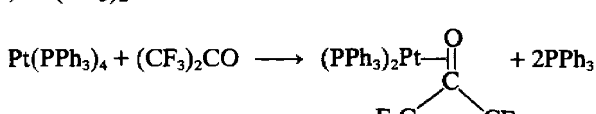
(255)

(**85**)



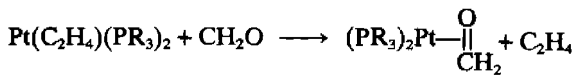
(256)

The carbonyl (C=O) and thiocarbonyl (C=S) functionalities will form η^2 (side-on)-bonded complexes to platinum(0). Hexafluoroacetone $(CF_3)_2CO$ reacts with $Pt(PPh_3)_3$ to form η^2 complexes (equation 257).[780] A similar type of product can be formed from $Pt(PPh_3)_4$ and indan-1,2,3-trione.[781] Hexafluoroacetone will also form η^2 complexes by replacement of $P(OMe)_3$ or $P(OPh)_3$ from PtL_4. Secondary reactions can occur. In some cases further addition of the carbonyl compound can lead to metallacycle formation, and in other cases isomerization to platinum(II) complexes can occur, an example being shown in equation (258).[782] An η^2-bonded complex of the parent formaldehyde has been prepared. Complexes $Pt(C_2H_4)(PR_3)_2$ (PR_3 = PEt_3, PPr^i_3, PPh_3, PEt_2Ph) react with formaldehyde to give the first examples of platinum formaldehyde complexes (equation 259).[783] Although CO_2 does not form a π complex with platinum(0), carbon disulfide and carbon diselenide will replace triphenylphosphine in $Pt(PPh_3)_3$ to give $Pt(CS_2)(PPh_3)_2$ and $Pt(CSe_2)(PPh_3)_2$ (equation 260).[784,785] An X-ray structure of the CS_2 complex shows that the SCS angle is 136.2° in the coordinated ligand, which is close to the 135° found in the lowest excited state of CS_2 ($^3A_2$) but much different from the ground state angle of 180°.[786,787] The ^{13}C NMR shows that the CS_2 ligand is not fluxional.[788] Other compounds which will substitute triphenylphosphine in $Pt(PPh_3)_3$ to form η^2-bonded complexes are COS,[784] $(CF_3)_2CS$,[784] $(CF_3)_2C{=}C{=}S$.[789]



(257)

$$(PPh_3)_2\{\eta^2\text{-}O{=}C(CF_2Cl)(CF_3)\} \longrightarrow (PPh_3)_2Pt(Cl)(CF_2COCF_3) \quad (258)$$

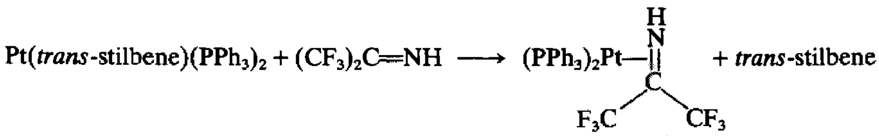


(259)

$$Pt(PPh_3)_3 + CX_2 \longrightarrow Pt(CX_2)(PPh_3)_2 + PPh_3 \quad (260)$$

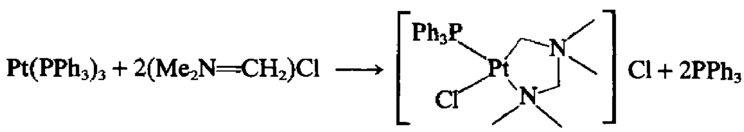
$$X = S, Se$$

Hexafluoroisopropylideneamine reacts with Pt(*trans*-stilbene)$(PPh_3)_2$ to give the η^2-bonded complex (**86**; equation 261).[790] As with hexafluoroacetone, addition of a second molecule of $(CF_3)_2C{=}NH$ gives platinacycles. The formation of (**86**) contrasts with the reaction of $Pt(PPh_3)_2$ with iminium salts $[Me_2N{=}CH_2]Cl$ where the first product is the platinacycle (**87**; equation 262).[791]



(261)

(**86**)



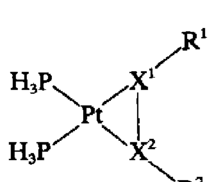
(262)

(**87**)

(*ii*) *Physical properties*

Hartley's review on platinum in 'Comprehensive Organometallic Chemistry' tabulates the crystal structure data on alkene complexes of platinum(0). Upon coordination to platinum(0) the substituents on the alkene are bent back out of the plane of the alkenic double bond away from the platinum by between 20° and 40°. There is a very significant increase in the C=C bond length of all the alkenes on coordination. The shortest Pt—C bond lengths are found with alkenes having electron-withdrawing substituents, in agreement with the concept that π back-donation into the antibonding orbitals of the alkenes is more important with platinum(0) complexes than with platinum(II) complexes. An inverse correlation is found between the Pt—C distance and that of the *trans* Pt—L bond. In Pt(*p*-$O_2NC_6H_4CH{=}CHC_6H_4NO_2$-*p*)$(PPh_3)_2$ the *p*-nitrophenyl substituents on the double bond are close to perpendicular with the PtC_2 plane, a geometry which maximizes π back-donation from metal to alkene.[792]

A CNDO-type approximate SCF–MO calculation method has been used to address the question of bonding and ligand distortion in Pt^0—L complexes where L = C_2H_2, C_2H_4, CO_2, CS_2. Graphs are presented correlating the total energy and bond strength in these complexes as the angle θ in (**88**) is varied. It is concluded that, besides the σ-donor and π-acceptor coordination bonds, the *s* orbital of the L ligand atom contributes substantially to the Pt—L interaction. The L ligand distortion is induced by the stabilization of the Pt—X^1, Pt—X^2, X^1—R^1 and X^2—R^2 bonds. Thus the driving forces of the L ligand distortion stem from the intraligand and the Pt–L interactions. In addition, the bond involved in the L ligand coordination is weakened by the extent to which the L ligand distortion is reduced.[793]



(**88**)

The complex $Pt(C_2H_4)(PPh_3)_2$ is stable in toluene solution, but the addition of ethylene causes associative exchange with E_a of 50 kJ mol^{-1} and $\Delta S^{\neq}$ of -59 J K^{-1} mol^{-1}.[794] The ethylene ligands in $Pt(C_2H_4)_2L$ undergo rotation with activation energies in the 41.0–54.4 kJ mol^{-1} range, but for complexes having alkenes with electron-withdrawing groups free rotation does not occur.[795] The small low-field shift of the ^{13}C NMR resonances of ethylene in $Pt(C_2H_4)(PPh_3)_2$ when compared with platinum(II) ethylene complexes is consistent with greater π back-donation in the zerovalent complex.[796] On coordination to Pt^0, there is also a decrease in ^1J(CH) of alkenes and alkynes. This result is consistent with the concept of reduced C=C bond order on coordination.[797] Similarly the geminal *J*(FF) in $Pt(CF_3CF{=}CF_2)(PPh_3)_2$ is comparable with that in a saturated fluorocarbon.[798] For a series of cyano- and methoxycarbonyl-substituted alkene complexes of $(PPh_3)_2Pt$, it has been found that, in contras to the corresponding alkyne complexes, there is little effect on $^1J(PtP)$ caused by changing th substituent. For the cyano complexes however, the monotonic deshielding in $\delta(^{195}Pt)$ corresponds with the same effect found in platinum alkyne complexes.[799]

Thermochemical data correspond with a decrease in the platinum(0)–alkene bond strength i the sequence $C_2H_4 > PhCH{=}CH_2 >$ *cis*-PhCH=CHPh > *trans*-PhCH=CHPh. Displacemen reactions show an expanded stability order for platinum(0) complexes to be TCNE > PhC≡CH > alkenes.[801] The relative weakness of alkene complexes relative to alkyne com plexes of platinum(0) is the reverse of that found with platinum(II).[802]

(*iii*) *Chemical reactions*

Coordination of an alkene to platinum(0) differs from complexation to platinum(II) Zerovalent platinum is an electron-rich metal center, whereas platinum(II) is electron poor. A a consequence alkenes coordinated to platinum(0) became more electron rich than in their fre state, and therefore susceptible to electrophilic attack. For alkenes complexed to platinum(II) their primary mode of reactivity is by attack from an external nucleophile.

Alkene complexes of platinum(0) react with strong acids to undergo protonation at th alkene and yield the alkyl complex (equation 263).[803] Since platinum alkyl complexes having n electron-withdrawing groups on carbon are frequently unstable to electrophiles, the products o HX on platinum(0) alkene complexes are often dihaloplatinum(II) complexes (equatio 264).

Haloalkene complexes of platinum(0) will undergo thermal isomerization to the viny complex.[804,805] The reaction occurs in coordinating solvents and is often promoted by th presence of additional ligands (equation 265).[806] When the alkene is C_2Cl_4 the rearrangemen probably involves an S_N1 displacement of chlorine by platinum(0) *via* a tight ion pair,[804,80 whereas when the alkene is $CHCl{=}CCl_2$ or $CFBr{=}CF_2$, the rearrangement i intramolecular.[808]

$$Pt(C_2F_4)(PPh_3)_2 + CF_3CO_2H \longrightarrow Pt(CF_2CF_2H)(OCOCF_3)(PPh_3)_2 \quad (263)$$

$$Pt(RCH{=}CHR)L_2 + 2HX \longrightarrow PtX_2L_2 + RCH_2CH_2R \quad (264)$$

$$Pt(CF_2{=}CFBr)(PPh_3)_2 + CO \longrightarrow [Pt(CF{=}CF_2)CO(PPh_3)_2]Br \quad (265)$$

52.4.10 Platinum Alkyne Complexes

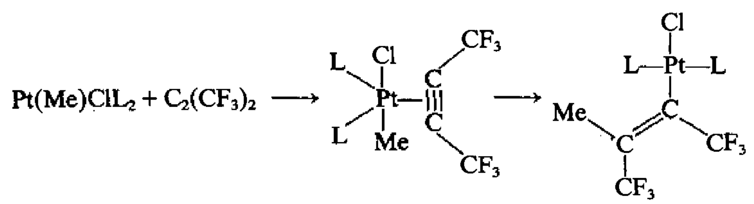
52.4.10.1 Synthesis

As with alkenes, alkynes coordinate to platinum in both the zerovalent and divalen oxidation states. Since the chemistry of platinum alkyne complexes is less extensive than that c alkene complexes, this section is not subdivided into complexes of the two types. The divalen compounds of platinum will be covered first, followed by the complexes of platinum in a form zerovalent oxidation state.

Many of the synthetic routes parallel those used to prepare alkene complexes c platinum(II). Replacement of chloride ion in $PtCl_4^{2-}$ by a water soluble alkyne is a frequentl used method (equation 266),[809–812] or the reaction can be assisted by the use of a silver salt t facilitate halide displacement (equation 267).[813] With hexafluorobutyne-2 the five-coordinat adduct can be isolated before it converts into the vinyl complex (**89**; equation 268).[814] Alkyn displace alkenes from platinum(II) complexes.

$$PtCl_4^{2-} + RC{\equiv}CR \longrightarrow PtCl_3(RC{\equiv}CR)^- + Cl^- \quad (266)$$

$$\textit{trans}\text{-}Pt(Me)Cl(PMe_2Ph)_2 + RC{\equiv}CR + AgPF_6 \longrightarrow \textit{trans}\text{-}[Pt(Me)(RC{\equiv}CR)(PMe_2Ph)_2]PF_6 + AgCl \quad (267)$$



(**89**) (268)

Hexafluorobutyne-2 will add to platinum(II) complexes. The insoluble complex PtMe{HB(pz)$_3$} reacts with dissolution and the five-coordinate alkyne complexes can be isolated (equation 269).[815] The coordination about platinum(II) is essentially trigonal bipyramidal. The C≡C triple bond is lengthened on coordination to 1.292(12) Å and the alkyne bend-back angle is 34.4(4)°.[816] These complexes have a π-bonded alkyne ligand, and show different structural and reaction chemistry than platinum(II) acetylide complexes.[817–821]

$$\mathrm{PtMe\{HB(pz)_3\} + CF_3C{\equiv}CCF_3 \longrightarrow PtMe\{HB(pz)_3\}(CF_3C{\equiv}CCF_3)} \tag{269}$$

Alkyne complexes of zerovalent platinum can be prepared by reduction of *cis*-$PtCl_2(PPh_3)_2$ in ethanol with hydrazine hydrate in the presence of the alkyne (equation 270).[822,823] When $Pt(PPh_3)_3$ is reacted with an alkyne in benzene at room temperature, complexes $Pt(alkyne)(PPh_3)_2$ are formed (equation 271).[824] With the monosubstituted alkyne $CF_3C{\equiv}CH$ the product can be the zerovalent compound $Pt(CF_3C{\equiv}CH)(PPh_3)_2$ or the platinum(II) acetylide complex $Pt(C{\equiv}CCF_3)_2(PPh_3)_2$ (equation 272).[825,826] As mentioned earlier, alkynes will readily replace alkenes in $Pt(alkene)(PPh_3)_2$. With dialkynes both monomeric and bridged complexes can be obtained.[827] With $C_6F_5C{\equiv}CH$, reaction with $Pt(C_2H_4)(PPh_3)_2$ gives the η^2-alkyne complex whereas $Pt(PPh_3)_3$ gives a platinum(II) hydride product *via* C—H oxidative addition.[828] Oxidative additions to give platinum(II) acetylide complexes are also observed with $PhC{\equiv}CSnEt_3$, $PhC{\equiv}CSnPh_3$, $Me_3SiC{\equiv}CI$, $Me_3SiC{\equiv}CBr$, $Et_3SiC{\equiv}CI$, $MeC{\equiv}CI$ and $Pt(C_2H_4)(PPh_3)_2$, but intermediate alkyne complexes are detectable for $PhC{\equiv}CSnEt_3$, $Me_3SiC{\equiv}CCl$ and $Me_3C{\equiv}CBr$. A triyne forms platinum(0) complexes by coordination with the central or terminal C≡C bond. Correlations of ^1J(PtP) and ^2J(PP) are made.[829]

$$\textit{cis}\text{-}\mathrm{PtCl_2 + RC{\equiv}CR \xrightarrow[\text{EtOH}]{N_2H_4} Pt(RC{\equiv}CR)(PPh_3)_2} \tag{270}$$

$$\mathrm{Pt(PPh_3)_3 + RC{\equiv}CR \longrightarrow Pt(RC{\equiv}CR)(PPh_3)_2} \tag{271}$$

$$\mathrm{Pt(PPh_3)_3 + CF_3C{\equiv}CH \longrightarrow (PPh_3)_2Pt(CF_3C{\equiv}CH) \xrightarrow{CF_3C{\equiv}CH} Pt(C{\equiv}CCF_3)_2(PPh_3)_2} \tag{272}$$

One alkyne will displace another from $Pt(alkyne)(PR_3)_2$ complexes, the order of alkyne displacement being C_2H_2 < alkylalkynes < arylalkynes < nitroalkynes. The reaction involves both a dissociative and an associative pathway.[824] The reaction may not lead to a single replacement product in all cases. Thus α-hydroxyalkynes lead to the formation of dialkynyl platinum(II) complexes.[830]

These reactions can be used to prepare a novel series of complexes where cyclic alkynes can be stabilized by coordination to platinum(0).[831,832] The compounds are feasible because coordination of a triple bond to platinum causes a distortion of the alkyne from linearity by displacement of the alkynic substituents back away from the platinum. Also these methods can be used to prepare platinum(0) alkyne complexes with substituents other than triphenylphosphine.[833–836]

52.4.10.2 Physical and chemical properties

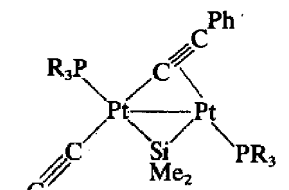
The structures of platinum(0) complexes of alkynes are fully summarized in Chapter 39 of 'Comprehensive Organometallic Chemistry' and need not be covered here.

The alkynic triple-bond stretching frequency is lowered by some 450 cm^{-1} on coordination to platinum(0). The value correlates with π back-bonding from platinum(0) to the alkyne,[837] but it is essentially independent of the substituent on the alkyne. From NMR coupling constant data it is apparent that alkyne rotation about platinum(0) is slow.[838] On complexation of acetylene to platinum(0) in $Pt(C_2H_2)\{P(C_6D_5)_3\}_2$ the value of J(CH) decreases from 250 to 210 Hz, consistent with a decrease in the *s* character of the hybrid orbitals about carbon.[839] Using ESCA, the platinum $4f_{7/2}$ binding energy in $Pt(PhC{\equiv}CPh)(PPh_3)_2$ of 72.3 eV is similar to that in $Pt(C_2H_4)(PPh_3)_2$.[840]

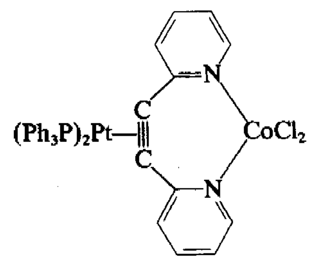
The platinum-195 NMR of a series of complexes $Pt(RC{\equiv}CR')(PPh_3)_2$ (R, R' = Ph, Ph; Ph, Me; Ph, OCOMe; Ph, H; Et, Et; Me, OCOMe; Me, Me; H, H; OCOEt, OCOEt; OCOMe, OCOMe; CF_3, CF_3; Ph, CN; $OCOCH_2CF_3$, $OCOCH_2CF_3$; Me, CN; H, CN; CN, CN) show that the platinum chemical shift dependence on the nature of the alkyne ligand is dominated by the electronic excitation energy, which is related to the π^* level of the alkyne. Values for J(PtP) are sensitive to the electron-withdrawing ability of the substituents on the alkyne.[841]

A theoretical approach addresses the question of alkynes bonded to PtL_2 fragments in both parallel and perpendicular geometries. With each mode of alkyne coordination there is required a different coordination geometry at platinum. The authors use the isolobal analogy to calculate the electronic structures of complexes, and propose several unknown complexes to be stable.[842]

Alkynes will also coordinate to more than one transition metal center. In the complex $Pt_2(\mu\text{-}SiMe_2)(\mu\text{-}C{\equiv}CPh)(C{\equiv}CPh)(PCy_3)_2$ (**90**) the bridging acetylide has a C≡C distance of 1.26(1) Å, which is significantly longer than the 1.20(2) Å distance in the terminal acetylide.[843] Binuclear platinum alkyne complexes can be prepared from $Pt(CO)_2(PPh_3)_2$, and the bonding appears to be analogous to that of a dimetalated alkene (equation 273).[844] The carbon–carbon bond is long at 1.34(2) Å. Structures have also been solved for alkynes bridging three platinums[845] or clusters with two platinums and one osmium atom.[846] Mixed metal complexes of alkynes can be prepared with no interaction between the metals. An example of such a complex is shown (**91**) where the *cis* bending of the alkynic substituents on coordination of the triple bond to platinum(0) creates a stereochemically useful environment for coordination to a second metal ion.[847]



(90)

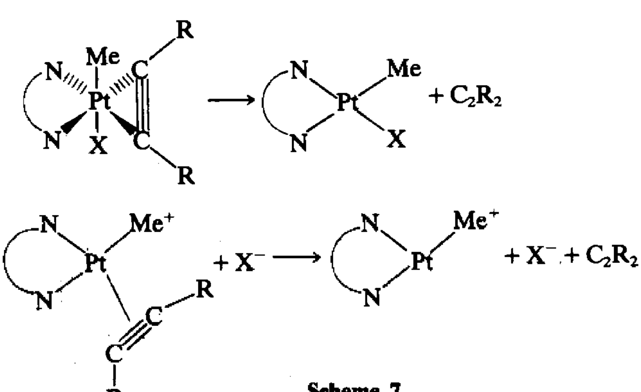


(91)

$$Pt(CO)_2(PPh_3)_2 + C_2R_2 \longrightarrow Pt_2(CO)_2(C_2R_2)(PPh_3)_2 \quad (273)$$

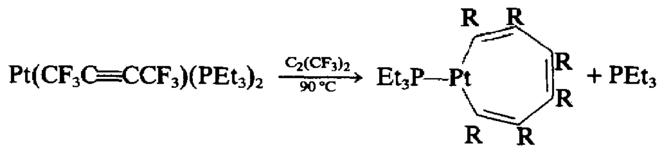
Alkynes coordinated to platinum(0) are susceptible to electrophilic attack. The reaction which has been most fully studied is the protonation of complexes $Pt(alkyne)(PPh_3)_2$ to give vinyl platinum(II) complexes then alkenes. The reaction has been discussed in Section 52. The vinyl complexes formed undergo isomerization in the final step, since the *cis* vinyl complex yields some *trans*-alkene. Carbene intermediates have been proposed in the pathway for this isomerization.[848] Platinum(II) alkyne complexes can be converted into carbene complexes, and this reaction has been discussed in Section 52.4.6. This pattern of differential reactivity is apparent in the IR spectra of the two sets of complexes. For alkyne complexes of platinum(0) the C≡C stretching frequency is lowered by some 450 cm^{-1} upon coordination, but with the platinum(II) analogs the difference is only in the region of 200 cm^{-1}.

The dissociation of the alkynes C_2R_2 ($R = CO_2Me$, CF_3) from $PtXMe(bipy)(C_2R_2)$ (X = Cl, Br) shows that two pathways need to be considered (Scheme 7). When X = Cl and $R = CO_2Me$, the reaction rate is strongly accelerated in more polar solvents and is retarded by added chloride, and a mechanism involving preliminary ionization of chloride is proposed. When X = Cl, I and $R = CF_3$, the rate is independent of solvent polarity and is not retarded by added halide. The route *via* a non-polar intermediate is proposed in this case.[849] Alkynes can also be displaced from $Pt(alkyne)(PPh_3)_2$ by the addition of excess triphenylphosphine.[824]

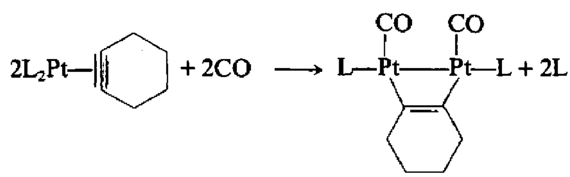


Scheme 7

Complexes Pt(alkyne)L_2 can react with further alkyne molecules to form metalacycles (equation 274).[850] With added carbon monoxide one can observe displacement, conversion to a 1,2-diplatinavinyl complex (equation 275) or, in the case of the hydroxyalkyne complexes of platinum(0), formation of a platinalactone complex (equation 276).[851] Complexes of platinum(0) with monosubstituted alkynes rearrange thermally to the acetylide hydride platinum(II) complexes (equation 277). The reaction is promoted by excess alkyne.[823,826,852] A similar situation exists with halogenated alkynes PhC≡CX where the zerovalent complexes $Pt(PhC{\equiv}CX)(PPh_3)_2$ will isomerize to the divalent compound $PtX(C{\equiv}CPh)(PPh_3)_2$.[853] Similarly with pseudohalogens $Pt\{C_2(CN)_2\}(PPh_3)_2$ very slowly isomerizes in sunlight to *cis*-$Pt(CN)(C{\equiv}CCN)(PPh_3)_2$.[854]


R = CF_3

(274)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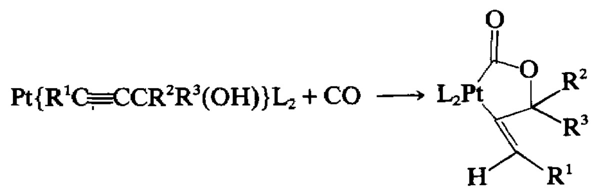
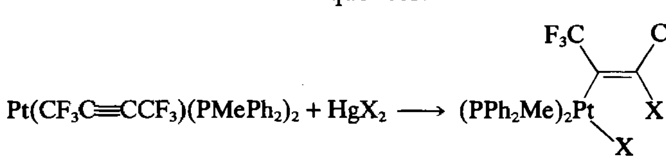

(276)

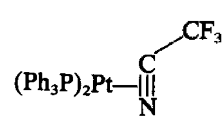
$$Pt(RC{\equiv}CH)(PPh_3)_2 \longrightarrow PtH(C{\equiv}CR)(PPh_3)_2 \quad (277)$$

Mercury(II) halides electrophilically attack $Pt(CF_3C{\equiv}CCF_3)(PMePh_2)_2$ at the alkynic carbon (equation 278).[855] Site migrations between PtCl(C≡CR)(CO)L and $Hg(C{\equiv}CR')_2$ involve oxidative addition and reductive elimination sequences.[856]


X = Cl, Br

(278)

By analogy with alkyne complexes, it is noteworthy that $Pt(stilbene)(PPh_3)_2$ reacts with trifluoroacetonitrile to give the η^2-bonded complex (**92**).[857]


(**92**)

52.4.11 Platinum Allyl and Delocalized Ligand Complexes

Although η^3-allyl complexes of platinum(II) are not rare, their occurrence is not as frequent as for η^2-alkene complexes. This situation is reversed for palladium(II) where η^3-allyl complexes are very common, and much of modern organopalladium chemistry is becoming dominated by the reactivity of η^3-allyl complexes.

52.4.11.1 Synthesis

Potassium tetrachloroplatinate(II) reacts with allyl chloride in the presence of tin(II) chloride to give $[PtCl(\pi\text{-}C_3H_5)]_4$ (equation 279).[858] The complex $Pt(\pi\text{-}C_3H_5)(PPh_3)_2$ can be conveniently prepared by treating $Pt(PPh_3)_3$ with C_3H_5HgCl in benzene solvent at room temperature (equation 280).[859]

$$K_2PtCl_4 + CH_2{=}CHCH_2Cl \xrightarrow{SnCl_2} [PtCl(\pi\text{-}C_3H_4)]_4 \tag{279}$$

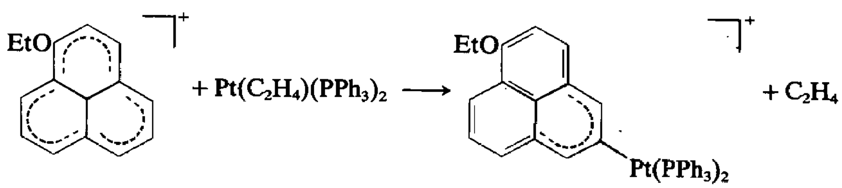
$$Pt(PPh_3)_3 + C_3H_5HgCl \longrightarrow [Pt(\pi\text{-}C_3H_5)(PPh_3)_2]Cl + Hg + PPh_3 \tag{280}$$

Under certain conditions, platinum alkene complexes can be converted to π-allyl complexes by hydrogen loss (equation 281).[860] Allyl alcohol insertion into a platinum(II) carbonyl bond gives an allyloxycarbonylplatinum(II) intermediate which can be decarboxylated to form the η^3-allyl complex (equation 282).[861,862]

$$[PtCl_2(CH_2{=}CMeR)]_2 \longrightarrow [PtCl(\pi\text{-R-allyl})]_2 + 2HCl \tag{281}$$

$$[PtCl(CO)(PR_3)_2]^+ + CH_2{=}CHCH_2OH \longrightarrow trans\text{-}PtCl(CH_2{=}CHCH_2CO_2)(PR_3)_2 \longrightarrow [Pt(\pi\text{-allyl})(PR_3)_2]Cl + CO_2 \tag{282}$$

Phenalenium cations replace ethylene from $Pt(C_2H_4)(PPh_3)_2$ to give cationic η^3-allyl complexes (equation 283).[863] Oxidative addition of Ph_3CCl to give platinum(0) followed by treatment with Tl(acac) gives the η^3-allyl complex of triphenylmethanide anion (equation 284).[864,865]



(283)

$$Pt_2(dba)_3 + Ph_3CCl \longrightarrow [PtCl(\eta^3\text{-}CPh_3)] \xrightarrow{Tlacac} Pt(acac)(\eta^3\text{-}CPh_3) \tag{284}$$

When the cyclopropyl platinum(II) complex cis-$Pt(CHCH_2CH_2)_2(PMe_2Ph)_2$ is treated with HCl then $AgNO_3$, the π-allyl complex is formed (equation 285).[866] η^2-Allyl complexes can also be formed by insertion of alkenes into platinum–hydride bonds, and this reaction is discussed in Section 52.2.3.3.

$$cis\text{-}Pt(CHCH_2CH_2)_2(PMe_2Ph)_2 \xrightarrow[\text{ii, }AgNO_3]{\text{i, HCl}} [Pt(\pi\text{-}C_3H_5)(PMe_2Ph)_2]^+ \tag{285}$$

Stable η^1-allyl complexes of platinum(II) have been prepared from $Pt(Ar)(\pi\text{-allyl})(PPh_3)$ and L (equation 286).[867] The ease of formation decreases in the order $MeCH{=}CHCH_2 \approx CH_2{=}CHCH_2 \gg CH_2CMeCH_2$; $PMe_2Ph > PPh_3$; and $Pt > Pd \gg Ni$. The cis η^1-allyl complexes $Pt(Ar)(C_3H_5)(dppe)$ can also be prepared. The η^1-allyl complex $trans$-$PtBr(\eta^1\text{-}C_3H_5)(PEt_3)_2$ can be prepared by oxidative addition of allyl bromide to $Pt(PEt_3)_4$ (equation 287).[868] Both η^3- and η^1-allyl complexes of platinum(II) can be obtained with a supporting 2,4-pentanedionato ligand.[869] The η^1–η^3-allyl rearrangement can be followed by NMR spectroscopy. Correlation with X-ray crystallographic data should be done with some caution, however, since the η^1–η^3 conversion may occur because of crystal packing forces.[870]

$$Pt(Ar)(\pi\text{-}C_3H_5)(PPh_3) + 2L \longrightarrow PtAr(C_3H_5)L_2 + PPh_3 \tag{286}$$

$$Pt(PEt_3)_4 + CH_2{=}CHCH_2Br \longrightarrow PtBr(\eta^1\text{-}CH_2CH{=}CH_2)(PEt_3)_2 + 2PEt_3 \tag{287}$$

Complexes of platinum with tetrahapto (η^4) cyclobutadiene ligands can be prepared; examples are shown in equations (288) and (289).[871,872]

$$2PtCl_2(CO)_2 + 4C_2R_2 \longrightarrow [PtCl(\mu\text{-}Cl)(\eta^4\text{-}C_4R_4)]_2 + 4CO \tag{288}$$

$$R = Et, Ph$$

$$PtCl_2(MeCN)_2 + 2C_2R_2 + SnCl_2 + (Ph_3P)_2N^+ \longrightarrow N(PPh_3)_2[Pt(SnCl_3)(\eta^4\text{-}C_4R_4)] \tag{289}$$

Cyclopentadienyl complexes of platinum are known for both the divalent and tetravalent oxidation states. Examples of both η^5 and η^1 complexes are shown in equations (290) and (291)[873,874]

$$[PtX_2(PR_3)]_2 + 2TlCp \longrightarrow 2PtX(\eta^5\text{-}Cp)(PR_3) + 2TlX \quad (290)$$

$$PtCl_2(SMe_2)_2 + 2NaCp \longrightarrow Pt(\eta^1\text{-}Cp)_2(SMe_2)_2 + 2NaCl \quad (291)$$

52.4.11.2 Structure and reactions

The structures of η^3-allyl complexes of platinum have been fully summarized by Hartley in Chapter 39 of 'Comprehensive Organometallic Chemistry'. This article also details the NMR methods used to investigate fluxionality of the η^3-allyl ligand.

Neutral ligands such as tertiary phosphines convert η^3-allyl complexes of platinum(II) into the η^1-allyl compound, and only in the presence of a large excess of added phosphine is the allyl ligand displaced.

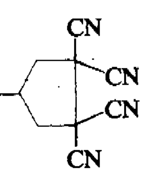
β-Diketo anions react with $[Pt(\eta^3\text{-allyl})(PPh_3)_2]^+$ with alkylation occurring at the coordinated allyl (equation 292).[875] A similar nucleophilic attack by methoxide ion at the η^3-allyl in $[Pt(\pi\text{-}C_3H_5)(PCy_3)_2]^+$ gives $PtH_2(PCy_3)_2$ and $CH_2{=}CHCH_2OMe$ (equation 293). The platinum–allyl bond is cleaved by HCl (equation 294).[876]

$$[Pt(\pi\text{-}C_3H_5)(PPh_3)_2]^+ + RCO\bar{C}HCOMe \longrightarrow CH_2{=}CHCH_2CH(COR)COMe \quad (292)$$

$$[Pt(\pi\text{-}C_3H_5)(PCy_3)_2]^+ + OMe^- \longrightarrow trans\text{-}PtH_2(PCy_3)_2 + CH_2{=}CHCH_2OMe \quad (293)$$

$$[Pt(\pi\text{-}C_3H_5)(PPh_3)_2]Cl + HCl \longrightarrow cis\text{-}PtCl_2(PPh_3)_2 + CH_2{=}CMe_2 \quad (294)$$

Carbon monoxide, sulfur dioxide and alkenes will insert into platinum(II)–η^3-allyl bonds. With $[Pt(\pi\text{-}C_3H_5)(PPh_3)_2]Cl$, CO reacts to give a 1:1 mixture of *cis*- and *trans*-2-butenoyl isomers of *cis*-$PtCl(COCH{=}CHMe)(PPh_3)_2$.[876] Sulfur dioxide similarly gives *cis*- and *trans*-$PtCl(SO_2CH{=}CHMe)(PPh_3)_2$.[876] The electrophilic alkene tetracyanoethylene undergoes a [3 + 2] cycloaddition reaction with the η^1-allyl complex $PtCl(CH_2CH{=}CH_2)L_2$ ($L = PPh_3$, $PMePh_2$, PCy_3; $L_2 = 2 = phos$) (equation 295). The structures of the PCy_3 and 2=phos complexes have been confirmed by X-ray crystallography.[877]

$L_2ClPtCH_2CH{=}CH_2 + C_2(CN)_4 \longrightarrow L_2ClPt$—  (295)

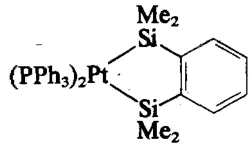
52.4.12 Platinum Complexes with Pt—Si Bonds

Complexes with Pt—Si bonds have been obtained by the oxidative addition of Si—H bonds to zerovalent platinum compounds. The products are usually silyl platinum hydrides, although in a number of cases reaction with a second mole of the silane gives bis silyl platinum(II) complexes (equation 296). These reactions have been covered with platinum hydrides in Section 52.2. Refluxing a benzene solution of *cis*-$PtCl_2(PMe_2Ph)_2$ with a trialkylsilane in the presence of trimethylamine gives the silane complex *trans*-$Pt(SiR_3)_2(PMe_2Ph)_2$ (equation 297).[878] The complex $Pt(C_2H_4)(PPh_3)_2$ reacts with $SiHMeCl_2$ to give $Pt(SiMeCl_2)_2(PPh_3)_2$ (equation 298).[879] Using an analogous methodology the chelated bis silyl complexes can be synthesized (equation 299).[880] The chelated Si—Pt bonded disiloxane complexes $Pt(SiMe_2OSiMe_2)L_2$ can be prepared,[880] but reaction of *cis*-$PtCl_2(PR_3)_2$ with $NaOSiMe_3$ gives the doubly oxygen-bonded complexes $Pt(OSiMe_3)_2(PR_3)_2$ (equation 300).[881] Alkylchlorosilanes add to platinum(0) by Si—C rather than Si—Cl cleavage, and Eaborn *et al.* have used this method to prepare methyl platinum(II) silyl complexes.

$$Pt^0 + R_3SiH \longrightarrow PtH(SiR_3) \xrightarrow{R_3SiH} Pt(SiR_3)_2 \quad (296)$$

$$cis\text{-}PtCl_2(PMe_2Ph)_2 + 2R_3SiH + 2Et_3N \longrightarrow trans\text{-}Pt(SiR_3)_2(PMe_2Ph)_2 + 2Et_3NHCl \quad (297)$$

$$Pt(C_2H_4)(PPh_3)_2 + 2SiHMeCl_2 \longrightarrow Pt(SiMeCl_2)_2(PPh_3)_2 + H_2 \quad (298)$$

$$Pt(C_2H_4)(PPh_3)_2 + 1,2\text{-}(HMe_2Si)_2C_6H_4 \longrightarrow$$  $+ H_2$ (299)

$$cis\text{-}PtCl_2(PR_3)_2 + 2NaOSiMe_3 \longrightarrow Pt(OSiMe_3)_2(PR_3)_2 + 2NaCl \quad (300)$$

Treatment of $H_2Si_4Ph_8$ with $Pt(C_2H_4)(PPh_3)_2$ gives $Pt[(SiPh_2)_3SiPh_2](PPh_3)_2$, which is the first example of incorporation of a transition metal into a silicon ring.[882]

The complex (+)-*trans*-$PtCl(\overset{*}{Si}R_3)(PMe_2Ph)_2$ is formed with a high degree of retention of configuration at silicon from (+)-$R_3\overset{*}{Si}H$ ($R_3\overset{*}{Si} = Me(1\text{-}C_{10}H_7)PhSi$) and *cis*-$PtCl_2(PMe_2Ph)_2$ in the presence of triethylamine. The (+)-$R_3\overset{*}{Si}H$ is regenerated with 93% overall retention of configuration when the complex is treated with $LiAlH_4$. The complex (−)-*cis*-$PtH(\overset{*}{Si}R_3)(PPh_3)_2$ is formed from $Pt(C_2H_4)(PPh_3)_2$ and (+)-$R_3\overset{*}{Si}H$ with little loss of optical activity, and probably with retention of configuration at silicon. The (+)-R_3SiH is regenerated with 97% overall retention on treatment with $LiAlH_4$.[883]

Platinum(II)–silicon bonds are cleaved by acids such as HCl and PhSH. Treating $Pt(SiR_3)_2(dppe)$ with HCl gives $PtCl(SiR_3)(dppe)$ then $PtCl_2(dppe)$ (equation 301).[878,884] With the complex *cis*-$Pt(SiMePh_2)_2(PMe_2Ph)_2$, the first Pt—Si bond (*trans* to P) cleaves to give $SiHMePh_2$, but the second Pt—Si bond (*trans* to Cl) gives $SiClMePh_2$ (equation 302).[878] These Pt—Si complexes are stable to water but are cleaved by halogens.[878] Methyl iodide will cleave Pt—Si bonds by methylation at silicon (equation 303).[878] Molecular hydrogen cleaves Pt—Si bonds by a reversible reaction. As with the majority of these reactions the pathway is believed to proceed by oxidative addition to form an intermediate six-coordinate platinum(IV) complex which can undergo reductive elimination by Pt—Si cleavage.

$$Pt(SiR_3)_2dppe + HCl \longrightarrow PtCl(SiR_3)dppe \xrightarrow{HCl} PtCl_2dppe + 2SiHR_3 \quad (301)$$

$$Pt(SiMePh_2)_2(PMe_2Ph)_2 + HCl \longrightarrow trans\text{-}PtCl(SiMePh_2)(PMe_2Ph)_2 + SiHMePh_2 \xrightarrow{HCl}$$
$$trans\text{-}PtHCl(PMe_2Ph)_2 + SiClMePh_2 \quad (302)$$

$$Pt(SiR_3)_2(PR_3)_2 + 2MeI \longrightarrow PtI_2(PR_3)_2 + 2MeSiR_3 \quad (303)$$

52.4.13 Platinum Complexes with Pt—Ge, Pt—Sn and Pt—Pb Bonds

The synthetic methods and chemistries of these complexes resemble those found for complexes with Pt—Si bonds. Platinum(II) germyl complexes can be readily prepared from the lithium reagents, although the reaction is a two-stage process with the second chloride on platinum(II) being replaced considerably faster than the first, reflecting the high *trans* effect of the germyl ligand (equation 304).[885] The complexes *trans*-$PtCl(GeMe_3)(PEt_3)_2$, as well as the $SiMe_3$, $PbPh_3$ analogues, have been prepared by reaction of the dichloro platinum(II) complexes with the required $Hg(ER_3)_2$ compound.[884,886,887] The Sn and Pb complexes $PtCl(EPh_3)(PPh_3)_2$ (E = Sn, Pb) can be prepared from *trans*-$PtHCl(PPh_3)_2$ and Ph_3ENO_3. The lead complex readily disproportionates to $PtCl(Ph)(PPh_3)_2$.[888] Preparations of Pt—ER_3 compounds involving Sn—Cl,[889] Sn—Sn,[890] Sn—H[884,891] and Sn—C[892,893] cleavage are reported. Similar methods have been used to prepare complexes $Pt(PbR_3)_2L_2$ and $PtCl\{Sn(OAr)_3\}L_2$.[894,895]

$$PtCl_2(PR_3)_2 + 2Ph_3GeLi \longrightarrow Pt(GePh_3)_2(PR_3)_2 + 2LiCl \quad (304)$$

Although the majority of these complexes contain phosphines as supporting ligands, compounds of platinum(IV) with Pt—Ge and Pt—Sn bonds have been formed by oxidative addition of Ge—X and Sn—X bonds to complexes $PtMe_2(L—L)$ (L—L = bipy, phen). Trace amounts of water cause hydrolysis of the Pt—Ge bond.[896,897] As expected Pt—Ge, Pt—Sn and Pt—Pb bonds are cleaved by HCl and halogens. 1,2-Dibromoethane cleaves Pt—Ge bonds (equation 305).[885]

$$Pt(GeR_3)_2(PEt_3)_2 + 2C_2H_4Br_2 \longrightarrow PtBr_2(PEt_3)_2 + 2GeR_3Br + 2C_2H_4 \quad (305)$$

By using ^{31}P, ^{195}Pt and ^{199}Hg NMR, it has been found that $Pt(GePh_3)(HgGePh_3)(PPh_3)_2$ is fluxional. Activation parameters are measured, and it is proposed that the intramolecular rearrangement occurs *via* a diagonal twist.[898]

Although only few complexes with Pt—$SiCl_3$ bonds have been characterized, a wide range of platinum complexes have been prepared with $GeCl_3$ and $SnCl_3$ ligands. Complexes with $GeCl_3^-$ are usually coordinated to the higher oxidation states (Pt^{II} or Pt^{IV}), whereas $SnCl_3^-$ is usually complexed to Pt^{II} or Pt^0. Complexes containing these ligands can be synthesized using $GeHCl_3$ or $SnCl_4$ (equations 306–309).[899–901] The air-sensitive compound $Pt(SnCl_3)_5^{3-}$ has a trigonal bipyramidal structure.[902] The complexes of $SnCl_3$ are particularly significant. The $SnCl_3$ ligand has a large *trans* effect, and complexes having this ligand complexed to platinum(II) have been variously used in homogeneous catalysis.

$$H_2PtCl_4 + GeHCl_3 \longrightarrow PtH(GeCl_3)_5^{2-} \quad (306)$$

$$K_2PtCl_4 + 5GeHCl_3 + 2PPh_3 \longrightarrow (Ph_3PH)_2[PtCl_4(GeCl_3)_2] + 2KCl \quad (307)$$

$$K_2PtCl_6 + 3SnCl_2 + 2PPh_3 \longrightarrow Pt(SnCl_3)_2(PPh_3)_2 + SnCl_4 + 2KCl \quad (308)$$

$$H_2PtCl_6 + 6SnCl_2 + Cl^- \longrightarrow [Pt(SnCl_3)_5]^{3-} + SnCl_4 + 2H^+ \quad (309)$$

The structure of $(Ph_3PMe)_3[Pt(SnCl_3)_5]$ shows a regular trigonal bipyramid about platinum with an average axial Pt—Sn bond length of 2.5530(7) Å and an equatorial distance of 2.5722(10) Å. This small difference between the axial and equatorial Pt—Sn bonds may be due to significant metal equatorial π bonding. The $SnCl_3^-$ ligand is a strong π acceptor, and metal equatorial π bonding is predicted to be stronger than metal axial π bonding in trigonal bipyramidal complexes.[903] In acetone solvent, ^{195}Pt and ^{119}Sn NMR spectroscopy show that $Pt(SnCl_3)_5^{3-}$ undergoes intramolecular rearrangement, and no dissociation of $SnCl_3^-$ occurs. By comparison the structure of $Pt(GeCl_3)_5^{3-}$ is highly distorted.[904] A comparison has been made between Pt—Sn bond lengths in $SnCl_3$ complexes and values for ^1J(PtSn). An inverse correlation is found with Pt—Sn distances falling in the range 2.356–2.601 Å, and the respective ^1J(PtSn) values being found between 23 000 and 29 000 Hz.[905] Similarly the Mössbauer isomer shifts for these $SnCl_3$ complexes correlate with ν(SnCl).[906] The electronic spectra of these complexes in aqueous hydrochloric acid have been reported.[907] The IR data on these complexes results in the finding of a *trans* influence series $Cl < PbPh_3 < Me < Ph < H < SiMe_3 < GeMe_3$ and $Cl < SnCl_3 < SnPh_3 < SnMe_3 \sim H < PbPh_3$.

Catalytic hydrogenation using mixtures of platinum(II) complexes and $SnCl_2$ as homogeneous catalyst has been discussed in Section 52.2. A recent comparison has been made between $SnCl_2$ and Ph_3SnX (X = H, Cl, Br, NO_3) as cocatalysts. In addition to summarizing the earlier work by this group, the article proposes a mechanism for the observed activity of Ph_3SnCl as a cocatalyst for isomerization.[908] Comparison of *cis*-$PtCl_2L(PR_3)$ with *cis*-$PtCl_2L_2$ and *cis*-$PtCl_2(PR_3)_2$ (L = SR_2, *p*-$XC_6H_4NH_2$, CO; R = aryl) shows that *cis*-$PtCl_2L(PR_3)_2$ is the most effective catalyst precursor in the presence of $SnCl_2$ for hydrogenation and hydroformylation. The catalytic activities of $[Pt_2(\mu\text{-}Cl)_2Cl_2(PR_3)_2]/SnCl_2{\cdot}2H_2O$ systems are very similar to those for mononuclear systems, particularly where the same catalyst precursor can be easily generated from the dinuclear species.[909] Finally a homogeneous catalyst for the water gas shift reaction has been prepared from platinum chloride and tin chloride. Previously the promoting activity of tin chloride with platinum(II) complexes was restricted to the ability of Pt—Sn complexes to achieve pentacoordination, the function of $SnCl_3^-$ as a good leaving ligand from platinum(II), or the subsequent effects from the high *trans* influence of the $SnCl_3$ ligand. In the catalyzed water gas shift reaction the tin chloride functions as a redox couple between the Sn^{II} and Sn^{IV} oxidation states.[910]

Cluster compounds can be formed with platinum and tin. Thus reduction of $PtCl_2(SnCl_3)_2^{2-}$ with $SnCl_2$ gives $Pt_3Sn_8Cl_{20}^{4-}$, which gives $[(cod)Pt_3Sn_2Cl_6]$ on treatment with cod.[902,911] Treating $Pt(C_2H_4)(PPh_3)_2$ with $Sn(acac)_2$ at ambient temperature gives $Pt\{Sn(acac)_2\}_2(PPh_3)_2$, but refluxing the mixture in toluene gives $Pt_2\{Sn(acac)_2\}_3(PPh_3)_2$.[912] The compound $Pt(PPh_3)_3$ will react with $K_4[Sn_9]$ and $K_4[Pb_9]$ to form complexes $Pt(Sn_9)(PPh_3)_2^{4-}$ and $Pt(Pb_9)(PPh_3)_2^{4-}$ (equation 310).[913] In understanding the bonding and geometries of these mixed metal clusters recent structural and electron-counting articles have been published.[914–916] This field is a relatively new one, and many new types of complexes will be synthesized in the near future.

$$Pt(PPh_3)_3 + K_4(Sn_9) \longrightarrow K_4[Pt(Sn_9)(PPh_3)_2] + PPh_3 \qquad (310)$$

52.5 PLATINUM COMPLEXES OF GROUP VA LIGANDS

52.5.1 Complexes of Nitrogen (N_2)

The simplest ligand is N_2 itself. Using matrix isolation techniques the IR spectra of $Pt(N_2)_n$ ($n = 1, 2, 3$) show $\nu(N{\equiv}N)$ in the range 2170.0–2211.5 cm^{-1} and $\nu(Pt{-}N)$ in the range 360–394 cm^{-1}. By using isotopically labeled N_2, accurate force constants have been calculated.[917] Using a similar experimental procedure, the compounds $Pt(O_2)(N_2)_n$ ($n = 1, 2$) have been observed in a cooled matrix by IR spectroscopy.[918]

52.5.2 Aliphatic and Aromatic Amine Complexes

52.5.2.1 Amine complexes of platinum(II)

Separate complexes *cis*-$PtCl_2(NH_3)_2$ and *trans*-$PtCl_2(NH_3)_2$ have been prepared by simple application of the *trans* effect. The *cis* isomer is formed by reacting $PtCl_4^{2-}$ with a buffered ammonia solution (equation 311),[919] and the *trans* isomer is obtained by chloride ion reaction with $Pt(NH_3)_4^{2+}$ (equation 312).[920–922] Ammonia in the gas phase reacts with solid β-$PtCl_2$ to give products of composition $PtCl_2{\cdot}xNH_3$ ($x = 1$–4). The compound $PtCl_2(NH_3)$ retains the basic β-$PtCl_2$ structure, but $PtCl_2(NH_3)_2$ is amorphous.[923] Trace detection of *trans*-$PtCl_2(NH_3)_2$ in a sample of *cis*-$PtCl_2(NH_3)_2$ can be achieved using HPLC techniques.[924]

$$PtCl_4^{2-} + 2NH_3 \longrightarrow PtCl_3(NH_3)^- \longrightarrow cis\text{-}PtCl_2(NH_3)_2 + 2Cl^- \qquad (311)$$

$$Pt(NH_3)_4^{2+} + 2Cl^- \longrightarrow PtCl(NH_3)_3^+ \longrightarrow trans\text{-}PtCl_2(NH_3)_2 + 2NH_3 \qquad (312)$$

Coordination isomers of $PtCl_2(NH_3)_2$ are also possible. When $[Pt(NH_3)_4]X_2$ (X = halide) reacts with PtX_4^{2-}, the ionic complexes $[Pt(NH_3)_4][PtX_4]$ are formed.[925] Complexes with a single amine ligand are synthesized by halide bridge cleavage with amines (equation 313).[926,927] For X = I, the equilibrium lies to the left. Except for a *cis*/*trans* mixture being formed when L = amine, the cleavage reaction leads to *trans* products. The complex *cis*-$PtCl_2(NH_3)_2$ has received considerable attention since its discovery as a chemotherapeutic agent.[928,929] This subject will not be discussed in this chapter since the field is being reviewed by Lock in Chapter 62.2. Furthermore complexes with X other than halide have been prepared and studied. These will not be included individually here, but will be referenced in the sections where substitution mechanisms are discussed.

$$Pt_2(\mu\text{-}X)_2X_2L_2 + 2NH_3 \rightleftharpoons 2PtX_2(NH_3)L \qquad (313)$$

Amines complex to platinum(II) by donation of an electron pair from an sp^3 hybrid orbital on nitrogen to an empty orbital of correct symmetry on platinum. Since there are no low-energy empty orbitals on nitrogen suitable for π back-donation, the Pt—N bond can be considered to be a pure σ bond. Ligands capable of π bonding strengthen the Pt—N bond, and coordination of NH_3 to Pt^{II} increases the acidity of the ammonia.[930] Amine ligands are low in the *trans* effect and *trans* influence series, low in the nephelauxetic series and high in the spectrochemical series.[931] This feature is evidenced where the singlet→singlet absorption is at 29 800 cm^{-1} in *cis*-$PtCl_2(NH_3)_2$, at 26 600 cm^{-1} in *trans*-$PtCl_2(NH_3)_2$, but at 21 000 cm^{-1} in K_2PtCl_4.[932]

The assignment of the low energy transitions to d–d bands of *cis*-$PtCl_2(NH_3)_2$ and *trans*-$PtCl_2(NH_3)_2$ is based on extinction data.[933] Later the solution and polarized single-crystal absorption spectrum of $PtCl_2(en)$ was measured and compared.[934,935] The complexes *cis*- and *trans*-$PtCl_2(NH_3)_2$ show respective luminescence energies of ~16 950 cm^{-1} and ~16 400 cm^{-1}. In conjunction with the absorption and MCD spectra, state assignments have been made.[936] Polarized single-crystal quartz UV spectroscopy of $PtCl_2(en)$ shows that the out-of-plane band at 35 000 cm^{-1} is associated with a metal-localized $5d_{z^2} \rightarrow 6p_z$ transition, and that the in-plane transition at 45 000 cm^{-1} is an LMCT band.[937] An asymmetric center in a complexed amine ligand interacts with the platinum d orbitals and gives rise to circular dichroism in the d–d transitions.[938] Complexes which contain simple C-substituted diamines with the (R) absolute configuration show positive CD in the region associated with the $^1A_{1g} \rightarrow {}^1E_g$ transition, both in solution and the solid state. There is no general consistency in the sign of the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition, and only for solution does the sign of the net CD show a correlation with the absolute configuration of the ligands.[939] The circular dichroism spectrum of $[Pt(NH_3)_2\{(S)\text{-3,3-dimethyl-1,2-butanediamine}\}]^{2+}$ has been compared with the spectrum of platinum complexes of other monosubstituted diamines. Solvent effects on the spectra are interpreted in terms of the creation of asymmetric nitrogen donors *via* the stereoselective solvation of the NH_2 protons.[940]

The IR ν(PtN) bands are found in the 500 cm^{-1} region. The NH_3 antisymmetric deformations in the region of 1610 cm^{-1} are split by between 65 and 100 cm^{-1} in platinum(II) complexes.[941] The stability constants for the replacement of chloride ion by amines in $PtCl_3(C_2H_4)^-$ follows the sequence $NH_3 < MeNH_2 > Me_2NH \gg Me_3N$.[942] Replacement of halide ion in *cis*-$PtCl_2(NH_3)_2$ can be readily effected by treatment with silver ion. Using this technique with $AgNO_3$, the complex *cis*-$Pt(NO_3)_2(NH_3)_2$ can be prepared (equation 314).[943] Each nitrate ion is coordinated through a single oxygen. Halide substitution apparently occurs on reaction of *cis*-$PtCl_2(NH_3)_2$ with calf thymus DNA. Extended X-ray absorption fine structure spectroscopy provides evidence against the possibility of Pt—Pt bonding in these complexes, and the data are consistent with four Pt—N (or —O) bonds about platinum(II).[944] Organocobalamins will replace water in $[Pt(NH_3)_2(H_2O)_2]^{2+}$. The interactions generate the 'base-off' form of the organocobalamin, and the reactions are first order in organocobalamin and first order in platinum complex. The rate determining step involves ligand exchange between N-3 of the 5,6-dimethylbenzimidazole ligand and a coordinated water.[945] For the reaction of *cis*-$PtCl_2(NH_3)_2$ and various nucleophiles, a linear free energy relationship is found between the logarithm of the second-order rate constant and either the electrode potential or the nucleophilic reactivity constant of the incoming ligand.[946]

$$cis\text{-}PtCl_2(NH_3)_2 + 2AgNO_3 \longrightarrow cis\text{-}Pt(NO_3)_2(NH_3)_2 + 2AgCl \qquad (314)$$

While aromatic amines in the ground state are good bases, the electron density at the amine nitrogen is drastically reduced in the first excited singlet state. On absorption of light an amine is therefore readily displaced from platinum(II). The complex *cis*-$PtCl_2$(1-naphthylamine)$_2$ is displaced with a quantum yield of 0.1 ± 0.02 on irradiation at 280 or 313 nm in aqueous DMF (equation 315).[947]

$$cis\text{-}PtCl_2(\text{1-naphthylamine})_2 + S \xrightarrow{h\nu} cis\text{-}PtCl_2(S)(\text{1-naphthylamine}) + \text{1-naphthylamine} \qquad (315)$$

The complex $[Pt(NH_3)_2(H_2O)_2]^{2+}$ will undergo oligomerization in aqueous solution in the pH range 4–5. The only observed product is $Pt_2(\mu\text{-}OH)_2(NH_3)_2$, which is formed from $[Pt(OH)(NH_3)_2(H_2O)]^+$.[948] Amine complexes of platinum(II) can be oxidized to the trivalent ions. In an N_2O-saturated solution of $Pt(en)_2^{2+}$, the initially observed product after irradiation by high energy electrons (2–20 MeV) has an absorption peak at 270 nm. Under these pulse radiolysis conditions the hydroxyl radical is formed, which has reacted to form $Pt(OH)(en)_2^{2+}$.[949] Between pH 5 and 10.5, these radiolysis conditions also generate solvated electrons and hydrogen atoms. Both these species react with $Pt(NH_3)_4^{2+}$ at near diffusion-controlled rates. For the electron reaction, the initial product is $Pt(NH_3)_4^+$, which in acid media rapidly releases two ammonia ligands (equation 318). In the reaction of the hydrogen atom the results support platinum hydride formation (equation 319).[950] The hydride product is unstable. The hydrated electron can also be used to prepare trivalent complexes from $[Pt(OH)_2(NH_3)_4]^{2+}$, although the product lifetime is short (equation 320). Alternatively ammine platinum(III) complexes are formed by hydroxyl radical oxidation of $Pt(NH_3)_4^{2+}$ (equation 321).[951]

$$Pt(en)_2^{2+} + OH\cdot \longrightarrow Pt(OH)(en)_2^{2+} \longrightarrow Pt(enH)(en)^{2+} + H_2O \qquad (316)$$

$$Pt(OH)(en)_2^{2+} + H^+ \longrightarrow Pt(en)_2(H_2O)^{3+} \qquad (317)$$

$$Pt(NH_3)_4^{2+} + e^- \longrightarrow Pt(NH_3)_4^+ \qquad (318)$$

$$Pt(NH_3)_4^{2+} + H\cdot \longrightarrow PtH(NH_3)_4^{2+} \qquad (319)$$

$$Pt(OH)_2(NH_3)_4^{2+} + e^- \longrightarrow Pt(OH)_2(NH_3)_4^+ \qquad (320)$$

$$Pt(NH_3)_4^{2+} + OH\cdot \longrightarrow Pt(OH)(H_2O)(NH_3)_4^{2+} \qquad (321)$$

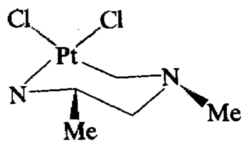
Although it will become readily apparent to the reader that many amines form *cis* chelate complexes with platinum(II) and platinum(IV), there are very few documented examples of bidentate amine ligands which span *trans* positions in platinum complexes. A successful method involves the synthesis of the six-coordinate platinum(IV) complex $[PtCl(NH_3)_2(H_2NCH_2CH_2N(R)CH_2CH_2NH_2)]^{3+}$, which has the NH_2 groups mutually *trans*. Reduction of this complex in HCl gives $Pt(NH_3)_2(H_2NCH_2CH_2N(R)CH_2CH_2NH_2)^{2+}$, where the required planar geometry about platinum(II) requires the central amine to dissociate.[952] These authors verify their complex by degradation and replacement reactions, and have since challenged the structure of [Pt(*sym*-Me dien)I]I.[953]

Cyclic amines will also form complexes to platinum(II). Using a method published by Dhara, the crystalline complex *cis*-$PtCl_2$(cyclopropylamine)$_2$ can be synthesized.[954] A preparation designed to produce the *cis* isomer, instead gives *trans*-$PtCl_2$(cyclobutylamine)$_2$. It is found that the *cis* procedure does give the correct isomer, but in the process of recrystallization the *cis* complex is converted to the *trans*.[955] In view of the selective chemotherapeutic action of the *cis* isomer of $PtCl_2(NH_3)_2$ it has become of significance to recognize isomers in planar platinum amine complexes. A spectrophotometric method has been developed which makes use of the different kinetic reactivities of the *cis* and *trans* isomers of $PtCl_2(NH_3)_2$ with allyl alcohol.[956] The isomeric structure can also affect potential barriers to internal rotation of the NH_3 groups since it has been found that the barriers are lower in *trans* complexes than in *cis*.[957] In another study, the slight distortions of $Pt(en)_2^{2+}$ and the anion from (*R*)-tartrate are incorporated into an ion-pairing model to suggest a cause for slow mutarotation in aqueous solutions of this salt.[958]

A wide range of multidentate amine ligands coordinate to platinum. The conformational analysis of chelate ring systems by NMR has been reviewed by Hawkins, and platinum complexes are included in this work.[959] Amine ligands with sulfur groups can also act as chelates, and this subject has also been reviewed.[960]

In addition to bidentate chelate complexes with ethylenediamine, tridentate chelate complexes can be prepared with diethylenetriamine (dien). The coordination plane about platinum(II) in [PtBr(dien)]Br is planar.[961] This compound substitutes halide ion by pyridine, but the rate is some 1000 to 10 000 times slower than is found for the tripyridine complex [PtX(tripy)]X. This faster exchange of the tripyridyl complex is explained on the basis of strain in this latter complex.[962] Substituents on the dien ligand can affect reactivity. For the dien compounds, their substitution reactions involve an associative mechanism, but by contrast the Et_4dien complexes of platinum(II) undergo replacement by a pathway having considerable dissociative character. The structure of [PtI(Et_4dien)]I shows the platinum atom slightly removed from the plane of its four ligands, and that plane shows some tetrahedral distortion. The iodide ion shows some hydrogen bonding to the ligand.[963]

For chelated amine complexes the question of ring conformation is a significant one since several conformations of the ring are formed on coordination. Variable temperature ^{1}H NMR studies show that for five- and six-membered rings, conformational equilibrium is rapidly achieved.[964,965] A number of (*S*)-*N*-methylpropylenediamine complexes of platinum(II) and platinum(IV) have been prepared. Equilibrium constant measurements for the axial–equatorial distributions of the NMe groups show there is very little free energy difference between the two internal diastereomers, but that small changes in the chelate ring or other groups complexed to platinum can cause major changes in the isomer distribution between (**93**) and (**94**).[966] The *d–d* CD spectra of the Pt^{II} complexes show additivity of the chelate ring and the asymmetrically coordinated N—Me group. The structure of $[Pt\{(S,S)\text{-2,4-pentanediamine}\}_2]^{2+}$ shows the six-membered chelate ring with a chair conformation. One methyl group is axial to the chelate ring and the other is equatorial. The effect of the (*S,S*)-ptn ligand on the CD spectra of $[Pt(NH_3)_2\{(S,S)\text{-ptn}\}]^{2+}$ and $[Pt\{(S,S)\text{-ptn}\}_2]^{2+}$ is not additive. The asymmetry factors responsible for the optical activity of these platinum(II) chelates are the chirality of the asymmetric carbon in the chelate ring and the chelate ring in the *skew* conformation. The non-additivity suggests that the CD spectrum of the bis chelate comprises the conformational contribution from the conformers with the *skew* ring.[967] The ^{13}C NMR spectra for 13 platinum(II) chelate complexes of type [Pt(bipy)(substituted 1,2-diaminoethane)]$^{2+}$ with different diamines have been measured to ascertain the conformational implications of ^3J(PtC) values. Values of ^2J(PtC) for *N*-methyl carbons vary from 10 to 25 Hz, decreasing for *N,N*-dimethyl substitution. The values for ^3J(PtC) are in the 20–50 Hz range, and from the known conformational properties of *gauche* five-membered diamine rings a Karplus-like dependence for ^3J(PtC) is suggested. It is noteworthy that ^{1}H NMR spectra of these complexes at various frequencies from 30 to 300 MHz show a pronounced broadening of platinum satellites at higher fields; at 300 MHz platinum satellites are broadened beyond recognition.[968] These correlations have allowed a combination of ^{13}C, ^{195}Pt and $J(PtC)$ techniques to be used to define the conformational behavior of platinum(II) complexes of methyl-substituted glycines. The chelates derived from $PtCl_2(gly)^-$ adopt an envelope conformation in solution with methyl substitution on the carbon and nitrogen atoms causing some puckering around the C—N bond of the chelate ring.[969] Extension of these methods can be made to the cyclic α-amino acids proline and pipecolic acid. Contrasts between the conformation and isomer preferences of these ligands in square planar platinum(II) and octahedral cobalt(III) complexes are related to the influence of apical ligands in the latter.[970] These techniques applied to the compounds $Pt(bipy)(aliphatic\ 1,3\text{-diamine})^{2+}$ show that the six-membered chelate ring is in a distorted-chair conformation, flattened in the region between the PtNN and NCCN planes.[971]



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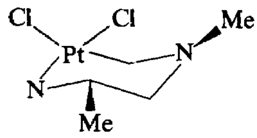


(94)

An X-ray crystal structure of Pt(malonato)(2,2-dimethyl-1,3-diaminopropane) addresses the conformational aspects of both rings. The diamino ring adopts a chair conformation strongly flattened at the PtN_2 end, and has an unusually large N—Pt—N angle of 97.2(2)°. The malonate ring has a boat conformation, and this structure is compared with previous chelating malonato complexes.[972] The molecular structure and absolute configuration of $(-)_{280}$-*cis*-dichloro{(1-methylamino)-2(*S*)-aminopropane}platinum(II) have been solved by X-ray crystallography. The absolute configuration of the chelate ring is δ, and the *N*-methyl substituent is in the axial position.[973]

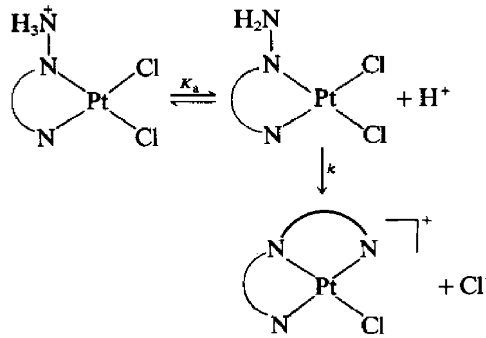
Although the main discussion on substitution reactions of platinum(II) complexes is in Section 52.9, some discussion is necessary here where reactions particularly relate to amine complexes. For mechanisms of reactions involving platinum(II) complexes, the reader has available several good sources of general reference. In particular the early work is well described in books by Basolo and Pearson,[3] Basolo and Johnson,[974] Langford and Gray,[975] and ACS Monographs 168 and 174 on Coordination Chemistry edited by Martell.[976] Furthermore useful examples of platinum substitution reactions are to be found in the book by Wilkins,[977] and in the review article by Pelozo.[978]

The reaction of propane-1,3-diamine (pn) with $PtCl_4^{2-}$ proceeds in two stages. The formation of $PtCl_2(pn)$ follows the usual two-term rate law for platinum complexes, with the first-order rate constant corresponding to the rate of hydrolysis of $PtCl_4^{2-}$. The rate of chelate ring closure is fast. In the second stage $[Pt(pn)_2]^{2+}$ is formed (equation 322).[979] The ring closure reaction is one of interest because of its direct relevance to the chelate effect. Nevertheless only a few papers have been published on ring closure in square planar complexes up through 1975.[980,981] Recently, however, a number of papers have been published on this subject. The complexes $[PtCl_2(bama{\cdot}HCl)]$ and $PtCl_2(taa{\cdot}2HCl)$ (bama = bis(2-aminoethyl)methylamine; taa = tris(2-aminoethyl)amine), with the tri- and quadri-dentate ligands acting as bidentate ligands, have been prepared. From stopped-flow measurements in basic media at 25 °C, the rate constants for the reactions (323) and (324) are $k_1 = 2.1 \pm 0.1$ and $4.3 \pm 0.2\ s^{-1}$. The overall reaction is shown in Scheme 8.[982] Similarly the chelate effect of *cis*-$[PtCl_2(DMSO)(enH)]^+$ converting to $[PtCl(DMSO)en]^+$ has been studied in both directions.[983] The reaction in equation (325) has also been kinetically studied in both directions. In particular, comparison is made between the values found for the (3-aminopropyl)ammonium and the (4-aminobutyl)ammonium complexes in order to understand ring size effects. The mechanism is the same as that found for the 1,2-diaminoethane complex.[983] The rate constants for the opening of the three rings are very similar. Under similar conditions of pH and temperature, the 1,2-diaminoethane complex undergoes ring closure much more rapidly than the 1,3-diaminopropane complex. This effect is almost entirely due to the difference in the basicities of the uncoordinated nitrogens and, once this has been taken into account, the rate constants for the closing of the ring differ by a factor of only 4. On the other hand, the 1,4-diaminobutane system is far less reactive and, even after accounting for any basicity difference, the rate constant for the formation of the seven-membered ring is some 10^2 times smaller than those for the closing of the five- and six-membered rings.[984] For the closing of eight-membered rings the rate constant is some 40 times smaller than that for the seven-membered ring.[985] These rates are compared against estimates for an analogous reaction with a monodentate amine.[984]

$$PtCl_4^{2-} + pn \longrightarrow PtCl_2(pn) \xrightarrow{pn} [Pt(pn)_2]Cl_2 \qquad (322)$$

$$PtCl_2(bama) \longrightarrow [PtCl(bama)]^+ + Cl^- \qquad (323)$$

$$PtCl_2(taa) \longrightarrow [PtCl(taa)]^+ + Cl^- \qquad (324)$$



Scheme 8

$$cis\text{-}[PtCl_2(DMSO)(N—NH)]^+ \rightleftharpoons [PtCl(DMSO)N—N]^+ + H^+ + Cl^- \qquad (325)$$

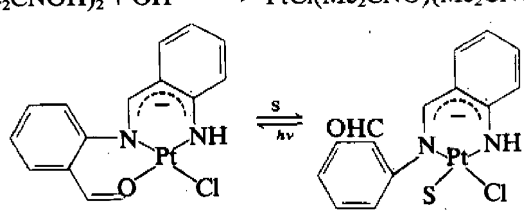
This work has been extended to the complexes *trans*-$[PtCl_2(NH_3)(N—NH)]^+$, because for the ring closure reaction in equation (326) it is possible to separate the rate constants for ring closing, k, from the acid dissociation constant of the protonated amine (K_a). Temperature data are given, and for the respective formation of ring sizes five, six and seven the values for $\Delta H^{\neq}$ are 50.6, 56.4 and 67.3 kJ mol^{-1}, and for $\Delta S^{\neq}$ −63, −63 and −71 J K^{-1} mol^{-1}.[986] The tetramethylated ligands have also been studied. The presence of two methyl substituents on the N atoms causes a 50–100 fold rate enhancement, which is a measure of the 'Thorpe–Ingold' or '*gem*-dimethyl' effect.[987]

$$trans\text{-}[PtCl_2(NH_3)(N—NH)]^+ \overset{K_a}{\rightleftharpoons} trans\text{-}PtCl_2(NH_3)(N—N) + H^+ \xrightarrow{k} [PtCl(NH_3)(N—N)]^+ + Cl^- \qquad (326)$$

In addition to chelate complexes, the cyclic amine 1,4,7-triazacyclononane will complex to platinum(II) and (IV). The hexacoordinate platinum(IV) complexes are bonded to two molecules of the tridentate ligand, but platinum(II) complexes with the ligand monodentate and bidentate.[988] Also the formation of platinum(II) ammine complexes from chloride complexes is a reversible process. The rate constants decrease as the basicity of the leaving amine increases.[989]

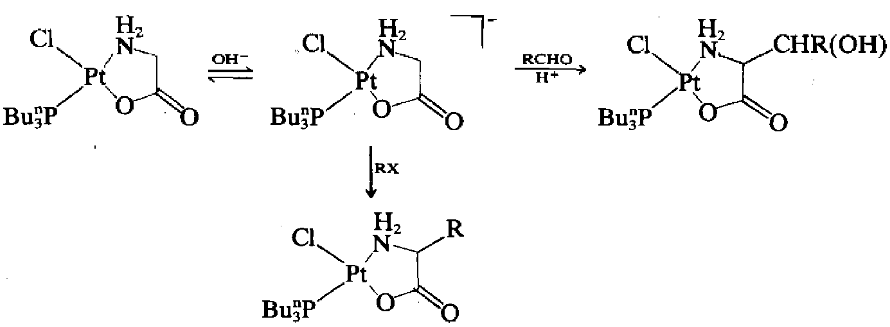
Stable bis(monoxime) complexes of platinum(II) formed with K_2PtCl_4 react directly with the monoxime. The oxime in these monomeric complexes is bonded to platinum(II) *via* the nitrogen atom. One oxime proton can be removed by base (equation 327).[990] Although platinum(II) complexes of Schiff bases are not common,[991] the ONNO type tetradentate ligands form complexes with platinum(II) which have highest stability when the ring size is five or six.[992] Using a similar NNO tridentate ligand, a platinum(II) complex has been prepared where a photochemically controlled 'swinging gate' ligand has been incorporated (equation 328).[993]

$$cis\text{-}PtCl_2(Me_2CNOH)_2 + OH^- \longrightarrow PtCl(Me_2CNO)(Me_2CNOH)^- + H_2O \qquad (327)$$



(328)

Glycine forms a series of complexes with platinum(II) of structure $[Pt(glycine)_4]^{2-}$, $[Pt(glycine)_3]^-$, *cis*- and *trans*-$Pt(glycine)_2$, and $[PtCl_2(glycine)]^-$.[994-1001] Where the glycinato ligand is unidentate coordination is *via* nitrogen. The IR spectra of $Pt(glycine)_2$ show asymmetric carboxylate stretching frequencies at higher wavenumbers, and symmetric carboxylate stretching frequencies at lower wavenumbers than most other divalent cations.[1000,1002,1003] IR spectroscopy can distinguish between unidentate and bidentate glycine ligands since unidentate glycine shows a band at 1700 cm^{-1} due to the C—O antisymmetric stretching mode which is absent in the bidentate complexes.[1004] Irradiation of *cis*-$Pt(glycine)_2$ in the *d–d* region of the spectrum in the absence of excess glycine isomerizes it to the *trans* isomer. Chlorination of the α-amino acid platinum(II) compounds *trans*-$PtCl_2(NH_2CHRCO_2H)_2$ and $PtCl_2(NH_2CH(CO_2H)CH_2CH_2SR)$ by PCl_5 gives the corresponding tetrachloroplatinum(IV) complexes with the carbonyl group converted to an acyl chloride. These functionalities will oxidatively add to $Pt(PPh_3)_3$.[1005] Glycinato complexes of platinum(II) react with aldehydes or alkylating agents to form chelate complexes with substituted amino acids (equation 329).[1006] The absorption and CD spectra in the *d–d* region of *cis*- and *trans*-$PtCl_2(ZH)_2$ (ZH = L-alanine, L-valine, L-norvaline, L-isoleucine and D-leucine) have been studied. The signs of the CD bands in the CD spectra are determined both by the absolute configuration of the ligand and by the geometric configuration of the complex.[1007] Interpretation of CD spectra is difficult and amino acid complexes of platinum(II) show a fairly consistent CD pattern which is opposite to that shown by platinum(II) dipeptide complexes.[1008] Other reactions of amino acid platinum(II) complexes involve studies of ring-opening and ring-closing reactions.[1009,1010]



(329)

Different types of anionic nitrogen ligands have been formed by *in situ* reactions. When $[PtR(NCR')L_2]BF_4$ is reacted with KOH, the methyl- or phenyl-*N*-carboxamido complexes of platinum(II) $PtR(NHCOR')L_2$ ($L = PEt_3$, R = Me, R′ = Me, $CH{=}CH_2$; $L = PEt_3$, R = Ph, R′ = Me; $L = PMe_2Ph$, R = Ph, R′ = Me, Ph; $L = PMePh_2$, R = Ph, R′ = Me; $L = PPh_3$, R = Ph, R′ = Me) are formed (equation 330).[1011]

$$PtR(NCR')L_2^+ + OH^- \longrightarrow PtR(NHCOR')L_2 \quad (330)$$

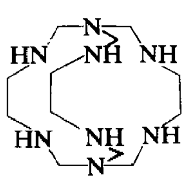
52.5.2.2 Partially oxidized and mixed-valence platinum amine complexes

Magnus's green salt $[Pt(NH_3)_4][PtCl_4]$ in $HClO_4$ reacts with various platinum(IV) chloro complexes to give a single phase partially oxidized conducting salt with directly interacting Pt atom chains (Pt—Pt 2.85 Å) adjacent to parallel chloride-bridged Pt^{II}—Pt^{IV} chains.[1012] This distance corresponds to a distance of 3.23 Å in Magnus's green salt itself.[1013,1014] Partial oxidation of $[Pt(NH_3)_4]Cl_2$ by hydrogen peroxide in 50% H_2SO_4 gives crystals of $[PtCl(NH_3)_4](HSO_4)_2$, an analog of Wolfram's red salt.[1015,1016] The bisulfate anions are hydrogen bonded to each other to form dimers. The extensive hydrogen bonding between the amine hydrogens and bisulfate oxygens stabilizes the crystal structure.

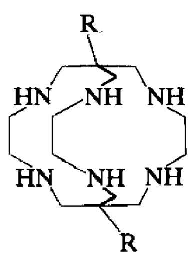
IR and Raman spectra have been measured for Magnus's green salt and the partially oxidized chains. The deuterated samples $[Pt(ND_3)_4][PtCl_4]$[1017,1018] have confirmed that a band in the far IR spectrum around 200 cm^{-1} is an NH_3 torsional motion and not an A_{2u} translational lattice mode involving the chain of platinum atoms. The resonance Raman spectra of the mixed-valence complexes $[PtX_2(en)][PtX_4(en)]$ and $[Pt(en)_2][PtX_2(en)_2][ClO_4]$ show an intense progression involving the symmetric X—Pt^{IV}—X stretching mode of platinum(IV).[1019] Similar spectra are observed with the analogous 1,3-diaminopropane compounds.[1020] Partial oxidation of platinum(II) complexes with a tetraaza macrocyclic ligand gives a complex with formal oxidation state of 2.7.[1021,1022]

52.5.2.3 Amine complexes of platinum(IV)

Amine complexes of platinum(IV) can be prepared by halogen oxidation of the platinum(II) complex or amine coordination to platinum(IV) halides.[988,1005] Reaction pathways in platinum(IV) amine complexes will be discussed in the section on reaction mechanisms. Macrobicyclic platinum(IV) complexes with ligands (**95**) and (**96**) have been prepared from $[Pt(en)_3]Cl_4$.[1023] The complexes are substitution inert diamagnetic octahedral ions which yield transient monomeric macrobicyclic platinum(III) ions on reduction. The lifetimes of the platinum(III) intermediates and the reduction pathways are discussed.[1024] Oxidation of platinum(II) complexes by iron(III) ion also provides a pathway to the synthesis of amine complexes of platinum(IV) (equation 331).[1025] The rate of oxidation of the platinum(II) complexes by Fe^{3+} is decreased by the presence of Fe^{2+}. The results are consistent with a redox mechanism involving two successive one-electron steps. The oxidation is kinetically and thermodynamically favored in the order $PrNH_2 < EtNH_2 < MeNH_2 < NH_3 <$ en, steric hindrance being responsible for the trends. Reduction of the series of platinum(IV) complexes $PtCl_6^{2-}$, *trans*-$PtCl_2(NH_3)_4^{2+}$, $PtCl_2(MeNH_2)_4^{2+}$, $PtCl(NH_3)_5^{3+}$, $PtBr(NH_3)_5^{3+}$ and *mer*-$PtCl_3(NH_3)_3^{+}$ by V^{2+} and $Ru(NH_3)_6^{2+}$ also involves successive one-equivalent changes. Analysis of the kinetic data shows consistency with outer-sphere reactions.[1026] For the synthesis of these and other platinum(IV) amine complexes the reader should consult Gmelin or Sidgwick's comprehensive two-volume book.[1027]



(**95**)



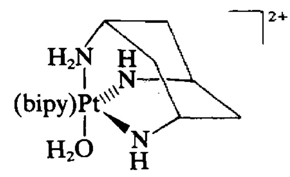
(**96**) $R = NO_2, NH_2$

$$PtL_4^{2+} + 2Fe^{3+} + 2Br^- \rightleftharpoons trans\text{-}PtBr_2L_4^{2+} + 2Fe^{2+} \quad (331)$$

$$L = NH_3,\ MeNH_2,\ EtNH_2,\ PrNH_2,\ \tfrac{1}{2}en$$

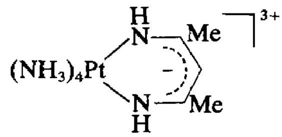
Since platinum(IV) complexes are also kinetically inert, optical diastereomers of $Pt(en)_2$(L-2,3-diaminopropionic acid)$^{4+}$ have been prepared.[1028] The first synthetic procedure involves the chlorine oxidation of $PtCl_2$(L-2,3-diaminopropionic acid) followed by reaction with ethylenediamine. Resolution is achieved through the (+)-tartrate salt. Alternatively the resolved complex can be prepared directly from the reaction of L-2,3-diaminopropionic acid on optically active *cis*-$[PtCl_2(en)_2]Cl_2$.

Since platinum(IV) is an electron-poor transition metal center, complexation of the amine nitrogen of ammonia or a primary or a secondary amine results in the hydrogen atoms of the ligand becoming acidic. The geometric isomers of $[PtCl_2(NH_3)(en)py]Cl_2$ may show stronger ($pK_1 = 8.15$) or weaker ($pK_1 = 10.35$) acidic properties than the analogous amine complex $[PtCl_2(NH_3)_2(en)]Cl_2$ ($pK_1 = 9.34$) depending on the configuration.[1029] In order to assess charge effects, the acidities of the complexes $[PtCl_2(NH_3)(en)(am)]Cl_2$, $[PtCl_2(en)(py)_2]Cl_2$ and $[PtCl(NH_3)_2(en)(am)]Cl_3$ (am = NH_3, py) have been compared. The change from the *trans* tetramine complexes to the pentamine compounds containing ammonia in the axial position is accompanied by a sharp increase in the acidic properties, which cannot be attributed entirely to charge effects. The results support Grinberg's theory that a positive contribution to the acid dissociation of amines is made by their *cis* interaction without metal atom participation.[1030] The ready deprotonation of two amines in Pt(bipy)(*cis,cis*-1,3,5-triaminocyclohexane)$^{2+}$ and oxidation of platinum to the tetravalent state gives the bis amido complex (**97**).[1031]



(**97**)

Ammine ligands complexed to platinum(IV) will undergo condensation reactions with acetylacetone. Thus $Pt(NH_3)_6^{2+}$ and acetylacetone react rapidly to give the diimine complex (equation 332).[1032]

$Pt(NH_3)_6^{2+} + MeCOCH_2COMe \longrightarrow$  $+ 2H_2O$ (332)

The reaction of PtX_6^{2-} and liquid ammonia gives mixtures of haloammine complexes $[PtX_n(NH_3)_{6-n}]X_{4-n}$ (X = Cl, Br, I; n = 3, 2, 1, 0). The salts $[Pt(NH_3)_6]X_4$ may be isolated as the main product only after several weeks of reaction. Interactions at room temperature of $PtCl_6^{2-}$ and $PtBr_6^{2-}$ salts with liquid ammonia yield the dinuclear μ-amido ammine complex $[(NH_3)_4Pt(\mu\text{-}NH_2)_2Pt(NH_3)_4]X_6$ quantitatively.[1033] The structure shows a Pt–Pt separation of 3.16(1) Å.[1034] Interaction of PtX_6^{2-} with liquid or gaseous ammonia followed by addition of excess KNH_2 yields the hexakis(amido) complex $K_2[Pt(NH_2)_6]$ (equation 333).[1033] Complexes of the anionic ligand NCl_2^- bonded to platinum(IV) have also been prepared. One method is by treatment of $[PtCl(NH_3)_5]Cl_3$ with chlorine (equation 334).[1035]

$$K_2PtX_6^{2-} + 6KNH_2 \longrightarrow K_2[Pt(NH_2)_6] + 6KCl \quad (333)$$

$$[PtCl(NH_3)_5]Cl_3 + 4Cl_2 \longrightarrow [PtCl(NCl_2)_2(NH_3)_3]Cl + 6HCl \quad (334)$$

Although platinum(IV) is a stable oxidation state of platinum, the complex $PtCl_6^{2-}$ will oxidize hydrazinium ion. Hydrogen ion does not affect the rate. The reaction proceeds *via* a platinum(III) intermediate and a protonated hydrazyl radical which decomposes to N_2 and NH_4^+.[1036]

52.5.2.4 Platinum(II) complexes with aromatic nitrogen ligands

Using similar preparative procedures as used for ammine complexes,[1037,1038] a series of pyridine platinum chloride complexes can be prepared.[1039] The *cis* and *trans* isomers of $PtCl_2(py)_2$ have been synthesized using the routes in equations (335–337), again making use of Chernyaev's *trans* effect method. In DMF solvent the sequence of compounds shown in equation (338) can be prepared where L is pyridine, picoline or lutidine.[1040] For the complexes $K[PtCl_3L]$ the yield decreases in the order 2,4-lutidine = picoline > 2,6-lutidine > 4-picoline = pyridine. The final product *trans*-$PtCl_2L_2$ is formed by a ligand catalyzed isomerization of *cis*-$PtCl_2L_2$. The compound $[Pt(py)_4]Cl_2$ can also be prepared in DMF solvent. Solvent differences are found between water and DMF. In water $[Pt(py)_4]Cl_2$ only converts to *trans*-$PtCl_2(py)_2$ by prolonged reflux in concentrated HCl solution; in DMF the conversion is spontaneous. Alternatively the halide compounds PtX_2 can be used as precursor synthons. In pyridine solvent PtI_2 gives a series of adducts $PtI_2 \cdot n$py (n = 2, 4, 6). The compound $PtI_2(py)_2$ has *trans* stereochemistry.[1041] Pyridine complexes of platinum(II) can be prepared by replacement of ligands other than halides. One DMSO ligand in *cis*-$PtCl_2(DMSO)_2$ is replaced by pyridine, picoline and lutidine (L) to give *cis*-$PtCl_2L(DMSO)$ (equation 339).[1042] Similarly dimethyl sulfide is replaced by pyridines (equation 340).[1043] The *trans* complexes are some 2.5 times more reactive than the *cis* isomers. The dependence of the second-order rate constant on the amine basicity is shown in Table 3, and follows the expression: $\log k_2 = 0.18pK_a(LH^+) + C$. Pyridine will also substitute an oxygen ligand of acetylacetonate, converting it into a monodentate C-bonded ligand.[1044]

$$2K_2PtCl_4 + 2py \longrightarrow cis\text{-}PtCl_2(py)_2 + 2KCl \quad (335)$$

$$cis\text{-}PtCl_2py_2 + 2py \longrightarrow [Pt(py)_4]Cl_2 \quad (336)$$

$$[Pt(py)_4]Cl_2 + 2HCl \xrightarrow{heat} trans\text{-}PtCl_2(py)_2 + 2py{\cdot}HCl \quad (337)$$

$$K_2PtCl_4 + L \longrightarrow K[PtCl_3L] \xrightarrow{L} cis\text{-}PtCl_2L_2 \longrightarrow trans\text{-}PtCl_2L_2 \quad (338)$$

$$cis\text{-}PtCl_2(DMSO)_2 + L \longrightarrow cis\text{-}PtCl_2L(DMSO) + DMSO \quad (339)$$

$$PtCl_2(Me_2S)_2 + L \longrightarrow PtCl_2L(Me_2S) + Me_2S \quad (340)$$

Table 3 Selected Rate Constants and Pyridines for Substitution of Me_2S in *trans*-$PtCl_2(Me_2S)_2$

L	pK_a *of* LH^+	10^3k_2 ($M^{-1}s^{-1}$)
4-Mepy	6.02	99 ± 3
Py	5.17	59 ± 1.3
4-CNpy	1.84	18.3 ± 0.2
3,4-Me_2py	6.44	106 ± 3
3,5-Me_2py	6.34	77 ± 4
3-Mepy	5.68	69.1 ± 0.6

Using conductivity measurements, the pressure dependence of the second-order rate constant for the substitution by pyridine in *trans*-$PtCl(NO_2)(py)_2$ shows $\Delta V^{\neq}$ values of -6.2 ± 0.4 at 10 °C, -8.8 ± 0.6 at 25 °C, -13.1 ± 0.8 at 25 °C and $-19.8 \pm 1.7\ cm^3\ mol^{-1}$ at 25 °C in $MeNO_2$, MeOH, EtOH and CH_2Cl_2 respectively. The volume change associated with the partial formation of the Pt—py bond is estimated to be $-4 \pm 1\ cm^3\ mol^{-1}$. Solvent effects are therefore important in deducing mechanism, and a large change in polarity or charge formation occurs during the activation step.[1045]

Luminescence, absorption and MCD spectra for *cis*- and *trans*-$PtCl_2(py)_2$ are used to identify transitions from $d \rightarrow d$, $d \rightarrow \pi^*$, and $n\pi \rightarrow \pi^*$ transitions. For the *cis* isomer two emission bands have been observed at 600 and 700 nm, which are assigned as $\pi^* \rightarrow d$ and $d \rightarrow d$ transitions. For the *trans* isomer, emission at 605 nm is from two excited π^* states separated by 240 cm^{-1}.[1045] For the *cis* isomer the LUMO is a metal *d* orbital.

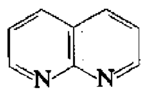
The platinum(II)–nitrogen distance in a *trans* pyridine complex is 2.085 Å.[1047] This distance is similar to the Pt—N distances of 2.011(6) and 2.013(6) Å found in the 2,6-lutidine complexes $PtCl_3$(2,6-lutidine)$^-$ and *trans*-$PtCl_2$(DMF)(2, 6-lutidine).[1048,1049]

A range of substituents other than methyl can be bonded to the pyridine (Table 3). The complex *cis*-$PtCl_2$(4-CNpy)$_2$ undergoes substitution with thiourea and the rate data measured in a variety of binary aqueous solvent mixtures. These data have been correlated with others to address problems of initial state and transition state solvation in inorganic reactions.[1050,1051] For the reaction with thiourea (equation 341), initial-state effects are considerably more important than transition-state effects. With a thienyl substituent bonded to pyridine in the 2,2′-position ligand, coordination in *trans*-$PtCl_2${2-(2′-thienyl)pyridine}$_2$ occurs only *via* nitrogen.[1052] Complexes bonded to platinum(II) with an N,N chelate are bis(pyridine-2-methylcarboxaldoximinato)platinum(II),[1053] and with an N,O chelate the compound is [$PtMe_3$(8-quinolinol)]$_2$.[1054]

$$cis\text{-}PtCl_2(4\text{-}CNpy)_2 + tu \longrightarrow cis\text{-}PtCl(tu)(4\text{-}CNpy)_2^+ + Cl^- \quad (341)$$

tu = thiourea

Two common aromatic nitrogen ligands which will form chelate complexes with platinum(II) are bipyridyl and 1,10-phenanthroline (**98**) and (**99**). A less common rigid ligand is dipyrrolylmethane.[1055] Bipyridyl reacts with $PtCl_4^{2-}$ but at a rate 33 times slower than is found for ethylenediamine because of the steric crowding in the initially formed monodentate intermediate.[1056] These unidentate intermediates are not produced in the formation of $PtCl_2$(phen) from 1,10-phenanthroline and $PtCl_4^{2-}$.[1057,1058] The reaction can be used to prepare $PtCl_2$(phen) and $PtBr_2$(phen); the complex PtI_2(phen) is very insoluble in aqueous solution (equation 342).[1059] Monodentate 1,10-phenanthroline complexes have, however, been isolated; the first observation of this feature in the solid state was with *cis*-$[PtCl(phen)(PEt_3)_2]BF_4$ (**100**). In solution the phenanthroline rapidly exchanges nitrogens bonded to platinum.[1060] This fluxionality is somewhat general, being observed with platinum(II) complexes of phen, bipy, 4-Me-1,8-naphthyridine, pyridazine and phthalazine. In the solid state the 1,8-naphthyridine complex is also monodentate. The fluxionality of platinum(II) between the two nitrogen sites is dependent on the suitability of the nitrogen lone pair orientation for bidentate coordination. For the pyridazine and phthalazine complexes the mechanism of fluxionality is dissociative rather than one involving pentacoordinate platinum.[1061,1062]



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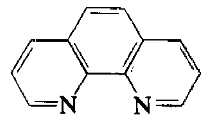

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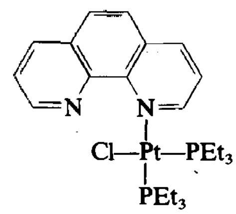
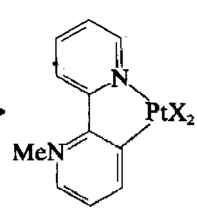


(100)

$$PtX_4^{2-} + phen \longrightarrow PtX_2(phen) + 2X^- \qquad (342)$$

Controversy surrounds the question of acidity found in aqueous solutions of $Pt(phen)_2^{2+}$ and $Pt(bipy)_2^{2+}$. The complexes react with hydroxide ion. One group argues that hydroxide attack occurs at the ring carbon adjacent to the coordinated nitrogen.[1063] but another research group argues that hydroxide reacts at the platinum center.[1064] The carbon-13 NMR spectrum is suggestive of the latter, and the Gillard 'pseudo base' mechanism seems to be in some doubt. Bipyridyl ligands will also undergo cyclometalation reactions. Cyclometalation of $PtX_3(Mebipy)$ ($X = Cl, Br$) occurs on heating the compound with an equimolar amount of $Mebipy^+$ (equation 343).[1065] The authors propose metalation *via* the aromatic group rather than *via* the methyl carbons. Redox chemistry can also be effected on these bipyridyl-type complexes. Reduction of $PtCl_4(N—N)$ by I^- and the oxidation of $PtCl_2(N—N)$ by $AuCl_4^-$ in the presence of chloride ions leads to the interchange between the compounds (equation 344).[1066] The reaction rates are insensitive to changes in N—N. The difference in substitution rates between platinum and palladium is very evident in bipyridyl complexes. In the complex $[Pd(bipy)en]Cl_2$, bipy is replaced by en in methanol at 25 °C within a few seconds, whereas in the platinum derivative bipy is totally inert toward substitution by en within a period of several weeks.[1067] Because of its chromophoric properties, *cis*-$[Pt(bipy)(H_2O)_2]^{2+}$ is useful as a bifunctional anchor for spin labels.[1068] Attachment of bipyridyl ligands to a polymer also leads to anchored catalysts with platinum bonded to the bipyridyl. The product is a hydrogenation catalyst which does not give discernible quantities of platinum metal.[1069]

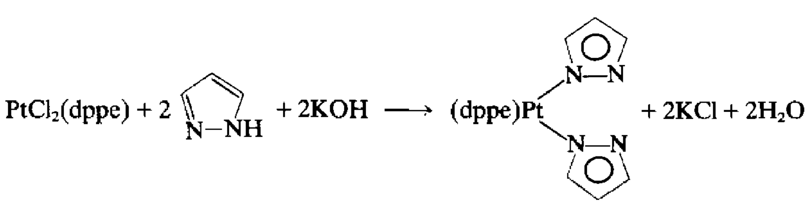
$PtX_3(Mebipy) + Mebipy^+ \longrightarrow$  $+ Mebipy^+ + HX$ (343)

$$PtCl_2(N—N) \underset{I^-/Cl^-}{\overset{AuCl_4^-/Cl^-}{\rightleftharpoons}} PtCl_4(N—N) \qquad (344)$$

The terpyridyl complex [PtCl(terpy)]Cl can be formed in 65% yield from K_2PtCl_4 (equation 345).[1070] Unusual substitution behavior is observed for the substitution reactions of $PtCl(terpy)^+$. The complex is some 10^3–10^4 times more reactive than its dien analog, and the relative reactivity order does not follow that expected from N_{Pt}° value (see Section 52.9). The reactions obey the usual two-term rate law, but the first-order constant k_1 is not common to all incoming groups. The data can be interpreted in terms of the ability of aromatic ligands to enter into π-bonding with the metal, and of the biphilic properties of the incoming groups involved.[1071]

$$K_2PtCl_4 + terpy + 2H_2O \longrightarrow [PtCl(terpy)]Cl{\cdot}2H_2O + 2KCl \qquad (345)$$

Platinum(II) also forms complexes with pyrazolates. The complexes with the pyrazolate ion can be prepared by treating $PtCl_2(dppe)$ with a basic solution of pyrazole; halide replacement occurs to give the bis(pyrazolate) complex $Pt(pz)_2(dppe)$ (equation 346).[1072] A similar reaction with $PtCl_2(diene)$ leads to incorporation of a single bridging pyrazolate.[1073] The platinum–nitrogen bond in these complexes is cleaved with HCl or I_2. With HBF_4 protonation of the uncoordinated nitrogen atom is observed (equation 347).[1074] Other electron-deficient centers which would react with this lone pair of electrons on the uncoordinated nitrogens are Zn^{II}, Ni^{II} and Co^{II} (equation 348).[1072,1075] Other complexes can be prepared where both pyrazolate and chloride or methoxide bridge two platinum(II) centers,[1076,1077] or where the L—L chelate ligand is a range of ditertiary phosphines or arsines.[1078] Monodentate phosphines PEt_3 and PMe_2Ph can be used in place of L—L, and the lone pair electrons on the nitrogens will form a chelate complex with $Cr(CO)_4$.[1079] Pyrazole ligands coordinated to platinum(II) are known for the trifluoro derivatives and indazole; coordination is again *via* a single nitrogen atom.[1080] These pyrazole complexes of platinum are static on the NMR time scale at room temperature, but the palladium complexes are fluxional.[1081]



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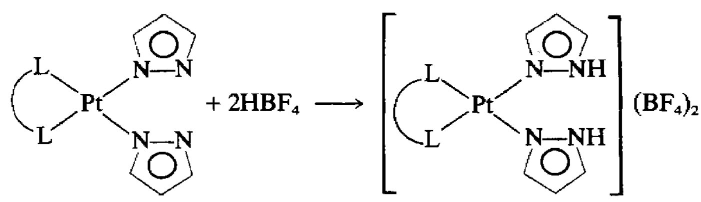

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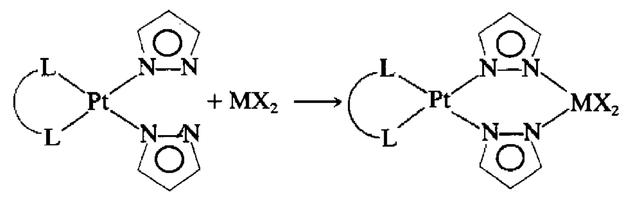
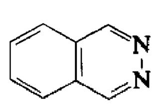


(348)

These pyrazole compounds show a strong resemblance to the nitrogen-bonded pyrazoylborate complexes. References to a number of these complexes are given in Sections 52.2 and 52.4; an example not previously mentioned is the complex $[PtMe(CNBu^t)\{HB(pz)_3\}]$. The Pt—N distances are in the range 2.0–2.1 Å. In this complex the ligand adopts bidentate coordination,[1082] but many complexes are known where tridentate coordination is observed.[1083] In addition to a boron atom fusing pyrazole ligands, platinum complexes have been prepared from ligands having pyrazole groups coupled by phosphazenes[1084] and a methane carbon.[1085]

Numerous other aromatic nitrogen compounds are known, and a significant number have been used to prepare complexes of platinum(II). Phthalazine (**101**) is one such compound, and the complex *cis*-$PtCl(phthalazine)(PEt_3)_2$ has been prepared in order to compare its fluxional properties with the phenanthroline and naphthyridine analogues. The monodentate complex is fluxional, but in this phthalazine case the orientation of the lone pairs is unsuitable for the five-coordinate intermediate required by an intramolecular process and the mechanism of exchange becomes dissociative.[1086]



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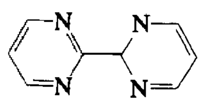
Pyrimidine (pm) complexes of platinum(II) can be isolated. The *cis* compound is obtained by treating K_2PtCl_4 with pyrimidine in water, while *trans*-$PtCl_2(pm)_2$ can be formed by isomerization of the *cis* isomer in DMSO (equation 349).[1087] The structures of *trans*-$PtX_2(pm)_2$

(X = Cl, Br) have been crystallographically confirmed.[1088] Three types of platinum(II) complexes have been prepared from 2,2′-bipyrimidyl (**102**). These are the covalent complexes $PtX_2(bipm)$ (X = Cl, CN, SCN; $X_2 = C_2O_4$), $[Pt(bipm)_2][PtCl_4]$ (X = Cl, CN) and $[Pt_2(NH_3)_4(bipm)][NO_3]_4$.[1089] Intense absorption bands in the visible region of the electronic spectrum are assigned to Pt–Pt interactions, and are related to strong hydrogen bonding involving the uncoordinated heterocyclic nitrogen atoms. This ligand (**102**) has also been used to prepare both homo- and hetero-bimetallic complexes of platinum(II); the second metal can be Hg or Mn.[1090] A further bidentate ligand having aromatic nitrogens is di-2-pyridyl ketone (**103**), from which the chelate complex $PtCl_2$(di-2-pyridyl ketone) can be prepared.[1091]

$$PtCl_4^{2-} + 2pm \xrightarrow{-2Cl^-} cis\text{-}PtCl_2(pm)_2 \xrightarrow{DMSO} trans\text{-}PtCl_2(pm)_2 \qquad (349)$$



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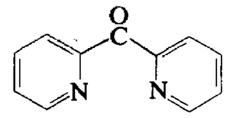

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Because of the discovery that platinum(II) complexes are useful chemotherapeutic agents, recent interest has centered on the coordination of platinum(II) to biologically interesting ligands. This work is covered in Chapter 62.2 by Lock. In this chapter only very brief mention will be made of the ligands which have been studied for their coordination to platinum, and, because of space limitation and duplication, no details of the complexes will be covered.

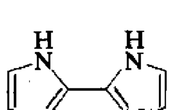
Imidazole complexes of platinum(II) are known. Using the Dhara method,[1092] the complexes *cis*-PtX_2(*N*-methylimidazole)$_2$ (X = Cl, Br) have been synthesized. Each imidazole is coordinated *via* a single nitrogen atom.[1093] The Magnus's green salt [Pt(*N*-methylimidazole)$_4$][$PtCl_4$] can also be prepared; dissolution in concentrated HCl and exposure to air result in oxidation (equation 350).[1094,1095] A range of procedures to prepare chloro-, bromo-, iodo- and aqua-substituted platinum(II) imidazoles has been published.[1096] These π-acceptor ligands can increase the redox potential at platinum. Comparative data are shown in Table 4, and for reference the potential for $[Pt(NH_3)_4]Cl_2$ is included.[1097] *N*-Acetylimidazole will acetylate alcohols in a reaction catalyzed by platinum(II).[1098]

$$[Pt(N\text{-}Meim)]_4[PtCl_4] \xrightarrow[HCl]{[O]} [Pt(N\text{-}Meim)_4][PtCl_6] \qquad (350)$$

Table 4 Redox Potentials for Platinum(II) Complexes with Aromatic Nitrogen Ligands

L in cis-PtCl$_2$L$_2$	$E°$ (mV)	*Ref.*
Imidazole	678	1097
Benzimidazole	747	1097
5,6-Dimethylbenzimidazole	742	1097
Pyridine	756	1097
$[Pt(NH_3)_4]Cl_2$	615	1097

Neutral complexes of platinum(II) can be prepared from the anions derived from biimidazolyl (**104**) and bibenzimidazolyl (**105**). The complexes have been prepared by treating $PtCl_2$(dppe) with the thallium salt of these ligands (equation 351).[1099,1100] A low yield of the platinum chelate complex of the anionic ligand derived from (**106**) has also been obtained. Other platinum(II) complexes with biologically important nitrogen ligands include compounds with platinum coordinated to guanine,[1101,1102] thiamine[1103] and xanthine.[1104,1105]



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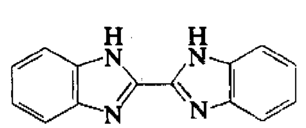

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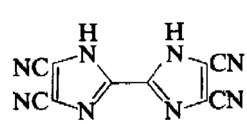


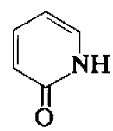
(106)

$$PtCl_2(dppe) + Tl_2(N\text{—}NH)_2 \longrightarrow Pt(N\text{—}N)(dppe) + 2TlCl + 2H^+ \qquad (351)$$

The macrocyclic phthalocyanine ligand will form a complex Pt(phthalocyanine).[1106] The crystal structure shows two polymorphs present because of molecular packing.[1107] The platinum is in a square planar coordination geometry with a mean Pt—N distance of 1.98 Å. The complex can be partially oxidized with iodine to give conducting mixed valence solids.[1108] Eighteen fundamental and overtone combination bands are observed in the resonance Raman spectrum of platinum phthalocyanine, and from this data the symmetry of the excited singlets are found to be D_{2h}, C_{2v} or D_2.[1109]

Platinum porphyrin complexes can be prepared by reaction with $PtCl_2(PhCN)_2$. Purification of the final complex is by medium pressure liquid chromatography on alumina. The strongly phosphorescent platinum(II) porphyrin complexes are efficient sensitizers for stilbene isomerization. The quantum yields for the *cis* to *trans* process are greater than unity because of a quantum chain process in which the metalloporphyrin serves both as an energy donor and an acceptor.[1110] Picosecond laser spectroscopy has been used to obtain time-resolved excited-state spectra of platinum octaethylporphyrin complexes, and to probe the excited-state energy levels.[1111] Tetrabenzoporphyrin complexes have been prepared for platinum in both the divalent and tetravalent oxidation states. The divalent complex shows strong phosphorescence at 745 nm.[1112]

Although 'platinblau' has been known for many years,[1113–1115] recent interest has grown because of its significance to chemotherapy. Dark blue crystals of $[Pt_2(\alpha\text{-pyridonato})_2(NH_3)_4]_2(NO_3)_5$ are obtained by reacting *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ with α-pyridone (**107**; equation 352).[1116] The molecular structure shows a chain of four platinum atoms with one unpaired electron per four platinum atoms. The separate Pt–Pt distances are 2.779 and 2.885 Å. The Pt 4*f* binding energy of this complex is similar to that of the platinum(II) complex *cis*-$PtCl_2(NH_3)_2$, in agreement with the formal valence of 2.25 for the platinums.[1117] Magnetic measurements on the complex show it to be a simple Curie paramagnet with a magnetic moment of 1.8 BM. Single-crystal EPR measurements show principal g values of 2.307, 2.455 and 1.975. The unpaired spin resides in an MO composed of d_{z^2} atomic orbitals directed along the platinum chain axis.[1118] The blue chromophores depend on the anions present and oxidative titrations using Ce^{IV} show that $1.75e^-/Pt$ are required for complete loss of the blue color, a result consistent with oxidation to Pt^{IV} from an oxidation state of 2.25.[1119]



(**107**)

$$4cis\text{-}Pt(NH_3)_2(H_2O)_2^{2+} + 2C_5H_5NO \longrightarrow [Pt_2(C_5H_4NO)_2(NH_3)_4]_2^{5+} \quad (352)$$

Binuclear platinum complexes with the α-pyridinato ligand can be formed with the metals in a divalent oxidation state. Two such complexes are the head-to-tail dimer $[Pt(C_5H_4NO)(NH_3)_2]_2^{2+}$ and the head-to-head tetramer $[Pt_2(C_5H_4NO)_2(NH_3)_4]_2^{4+}$. This tetrameric platinum(II)–(II) compound is prepared under experimental conditions where the pH is kept around neutrality to avoid the formation of the partially oxidized complex.[1120] Platinum-195 NMR spectroscopy can be used to show that the head-to-head to head-to-tail isomerization of these complexes involves dissociation of one ligand arm followed by an intramolecular linkage isomerization. Finally bond formation occurs between the divalent platinum with the vacant coordination site and the uncoordinated end of the ligand.[1121]

The success of this α-pyridonato work has spurred interest in investigating again the nature of 'platinblau', and the trimethylacetamide platinum blues.[1115,1122,1123] A combination of UV–visible spectral measurements, extended Hückel MO calculations, and Ce^{IV} redox titrations suggests that the trimethylacetamide platinum blues are a non-equilibrium mixture of oligomers of variable chain length in which there is again a strong Pt–Pt interaction, and in which platinum is in an average formal oxidation state greater than 2. A powder diffraction pattern on the material reveals the presence of platinum chains involving at least four or five platinum atoms and a Pt—Pt bond length of 2.76 Å. EXAFS can also be used to obtain structural information about these complexes. A purple platinum uridine complex has been subjected to this technique. The exact degree of oligomerization cannot be deduced but it verifies that Pt—Pt bonding is present in the complexes reminiscent of one-dimensional platinum complexes.[1124] A mixed valence tetraplatinum complex analogous to the α-pyridonato complexes can also be prepared from α-pyrrolidone (**108**). The structure of the product $[Pt_4(C_4H_6NO)_4(NH_3)_8]^{4+}$ is again head-to-head, but now the oxidation state of platinum is 2.5.[1125] The analogous 1-methylhydantoinato complex is tetrameric with a divalent oxidation state for platinum.[1126] The Pt—Pt distance found for these various dimeric and tetrameric platinum complexes with nitrogen ligands are grouped in Table 5, and compared with the pyridone blue distances. In the synthesis of these complexes care must be taken to ensure purity. HPLC on platinum pyrimidine blues has shown the presence of several colorless platinum impurity complexes.[1132]

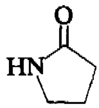


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Table 5 Pt—Pt Distances in Pt^{II}—Pt^{II} Complexes with N,O Ligands and with α-Pyridone Blue

Complex	*Pt—Pt* (Å)	*Ref.*	*Complex*	*Pt—Pt* (Å)	*Ref.*
1-Methylhydantoin	3.131	1126	1-Methylthymine(HH)	2.91	1128
α-Pyridone(HH) NH_3	2.877	1130	1-Methylthymine(HT)	2.97	1129
α-Pyridone(HT) NH_3	2.898	1130	1-Methyluracile	2.95	1127
α-Pyridone(HH) en	2.992	1131	α-Pyridone blue	2.77	1118

52.5.2.5 Platinum(III) and platinum(IV) complexes with aromatic nitrogen ligands

The mixed-valent α-pyridonato complex $[Pt_2(C_5H_4NO)_2(NH_3)_4]_2(NO_3)_5$ will undergo a concerted two-electron oxidation to give the head-to-tail isomer of the Pt^{III}–Pt^{III} complex *cis*-$[Pt_2(C_5H_4NO)_2(NO_3)(NH_3)_4(H_2O)](NO_3)_3$. The Pt—Pt distance in this complex has now decreased to 2.539(1) Å from the 2.77 Å of the mixed-valent α-pyridone blue complex. The head-to-tail platinum(II) dimer $[Pt_2(C_5H_4NO)_2(NH_3)_4](NO_3)_2$ also undergoes electrochemical oxidation to the Pt^{III}–Pt^{III} complex, a single wave being observed at $E_p = +0.63$ V.[1133] The platinum(III)–platinum(III) bond lengths are sensitive to the ligands substituted in the terminal axial ligand sites. Comparing the compound with O-bonded nitrate ligands against that with N-bonded nitrite ligands, the Pt^{III}—Pt^{III} distance in the nitro complex is greater by 0.028(1) Å, consistent with the greater *trans* influence of nitrite compared to nitrate ligands.[1134] If the nitric acid oxidation[1135] is carried out in the presence of NO_2^-, Cl^- or Br^-, head-to-tail bridged α-pyridonato Pt^{III}–Pt^{III} complexes are formed with the X groups ($X = NO_2$, Cl, Br) substituted in the axial positions (equation 353).[1136] The Pt—Pt bond lengths (2.582(1)–2.547(1) Å) vary as $X = Br \sim NO_2 > Cl > NO_3$, a trend which parallels the known *trans* influence series for these ligands. The axial Pt—X bonds are elongated by approximately 0.15 Å from 'normal' values, indicating a strong *trans* influence for the Pt—Pt bond. The α-pyridonato ligand does not always give multimetallic complexes with platinum. By judicious choice of synthetic conditions the monomeric platinum(II) complexes *cis*-$[PtCl(C_5H_4NOH)(NH_3)_2]NO_3$, *cis*-$[Pt(C_5H_4NOH)_2(NH_3)_2]Cl$ and the platinum(IV) complex *mer*-$PtCl_3(C_5H_4NO)(NH_3)_2$ have been isolated and characterized.[1137]

$$[Pt_2(C_5H_4NO)_2(NH_3)_4]^{2+} \xrightarrow[X^-]{HNO_3} [Pt_2(C_5H_4NO)_2(NH_3)_4X_2]^{2+} \qquad (353)$$

Studies on these complexes are leading to a better understanding of the physical and chemical properties of platinum chain compounds, and also to the biological function of platinum compounds. Examples of these concepts are found in the development of ideas about electron transfer in platinum chains. Magnetic susceptibility measurements on $[Pt_4(\mu$-α-pyrrolidonato$)_4(NH_3)_8](NO_3)_6$ which has formally two Pt^{II} and two Pt^{III} centers shows that the two unpaired electrons are strongly diamagnetically coupled and are delocalized over the four platinum atoms.[1138] Hush model calculations also support these data.[1139] Further investigation on 'platinblau' and acetamide complexes shows that the platinums are in a formally trivalent oxidation state,[1140,1141] and ^{15}N, ^{195}Pt NMR methods suggest that the initial coordination of amides to Pt^{II} is *via* the carbonyl oxygen.[1142]

The discussion of the origin of the acidity of platinum complexes of aromatic nitrogen ligands[1143] continues with the pyridine platinum(IV) complexes. Gillard argues that the acidity is caused by hydroxide ion addition at an aromatic carbon to give a species like a pseudo base,[1144,1145] but Nord argues the acidity is due to impurities, and that this fact has been known for a considerable time.[1146–1148]

52.5.2.6 Platinum complexes with other nitrogen-containing ligands

(*i*) *Nitriles*

Platinum(II) halides react with alkane- and arene-nitriles. Complexes *cis*-$PtCl_2(RCN)_2$ (R = Me, Ph) can be prepared by treating $PtCl_4^{2-}$ with RCN, or alternatively from $PtCl_2$.[1149–1151] The reaction of $PtCl_2$ in neat PhCN gives $PtCl_2(PhCN)_2$ as a mixture of *cis* and *trans* isomers, the ratio being temperature dependent (equation 354). The isomers can be separated by chromatography. By ^{13}C NMR spectroscopy the two isomer structures can be distinguished [nitrile carbon: δ 116.8 (^2J(PtC) = 289 Hz) *trans*; δ 115.3 (^2J(PtC) = 234 Hz) *cis*]. In benzonitrile solvent the *cis* form is favored at room temperature but the *trans* form at higher temperatures.[1152] The heats of formation of *cis*-$PtCl_2(RCN)_2$ are -122 ± 3 kJ mol^{-1} and -73 ± 1 kJ mol^{-1} for R = Me, Ph respectively.[1153] The small value for the benzonitrile complex is ascribed to steric reasons.

$$PtCl_2 + 2PhCN \longrightarrow PtCl_2(PhCN)_2(cis/trans) \qquad (354)$$

These nitrile complexes make very useful starting materials for the synthesis of new platinum complexes because the nitrile ligands can be readily substituted. Secondary reactions must be avoided, however. Coordinated nitriles can be attacked by hydroxide ion to give amides. Thus heating an aqueous solution of $PtCl_4^{2-}$ and acetonitrile in aqueous solution in the presence of oxygen gives 'platinblau'.[1154] Electron-withdrawing groups on the nitrile facilitate this reaction, and coordinated perfluorobenzonitrile will undergo attack by alcohols (equation 355).[1155]

$$trans\text{-}[Pt(Me)L_2(C_6F_5CN)]^+ + ROH \longrightarrow trans\text{-}[Pt(Me)L_2\{NH{=}C(OR)C_6F_5\}]^+ \qquad (355)$$

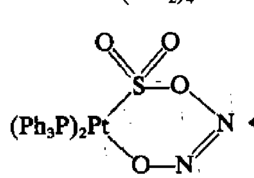
(*ii*) *N—O ligands*

The simplest of such ligands is nitric oxide, NO. A difficulty with forming complexes of platinum(II) with this ligand is that ready oxidation to NO_2 occurs, and the complexes formed may indeed be nitro complexes.[1156,1157] A useful method to prepare nitrosyl platinum complexes is from nitrosyl chloride (equation 356).[1157] Other methods involve the use of NO and HNO_3 (equations 357 and 358), although the former complex is worthy of further attention.[1157,1158] Slow passage of NO through a solution of $Pt(SO_2)(PPh_3)_3$ gives the nitro complex, but a fast stream leads to the formation of an insertion complex $Pt(N_2O_2)(SO_2)(PPh_3)_2$ (equation 359).[1159] An alternative method for the formation of nitrosyl complexes is the reduction of nitro compounds with carbon monoxide (equation 360).[1160] With zerovalent platinum complexes, dimerization of the ligand NO can occur (equation 361).[1160] Dialkyl platinum(II) complexes react with NO to give the nitro complex by an oxidative disproportionation reaction (equation 362).[1161,1162]

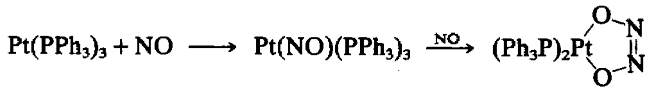
$$PtX_4^{2-} + NOCl \longrightarrow [PtX_4Cl(NO)]^{2-} \qquad (356)$$

$$[Pt(NH_3)_4]Cl_2 + NO \longrightarrow [PtCl(NO)(NH_3)_4] \qquad (357)$$

$$Pt(NO_2)_4^{2-} + HNO_3 \longrightarrow [Pt(NO_3)(NO_2)_4(NO)]^{2-} \qquad (358)$$


$\xleftarrow[\text{fast}]{NO}$ $Pt(SO_2)(PPh_3)_2$ $\xrightarrow[\text{slow}]{NO}$ $Pt(NO_2)_2(PPh_3)_2$ (359)

$$Pt(NO_2)_2(PEt_3)_2 + CO \longrightarrow Pt(NO_2)(NO)(PEt_3)_2 + CO_2 \qquad (360)$$



(361)

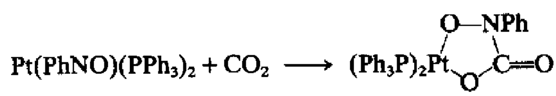
$$PtMe_2L_2 + 6NO \longrightarrow PtMe_2(NO_2)_2L_2 + 2N_2O \qquad (362)$$

$$L = PEt_3,\ PMe_2Ph$$

Nitrite complexes can be simply prepared by metathetical replacement with nitrite ion.[1163] The structure of *trans*-$Pt(NO_2)_2\{P\text{-}(p\text{-tol})_3\}_2$ has a Pt—N distance of 2.030(5) Å and N—O distances of 1.228(8) Å and 1.98(7) Å.[1164] Chemical shift (δ Pt) and coupling constant data have been tabulated for a large group of platinum(II) and (IV) nitro complexes. Both chemical shift and coupling constant changes upon ligand substitution are dominated by the nature of the *trans* ligand.[1165]

An unusual chloronitro(bipy)(*N,N'*-dinitroso-1,2-ethylenediaminato)platinum(IV) complex has been prepared by nitrosation of $[PtCl_2(en)(bipy)]Cl_2$.[1166] Similar arylnitroso complexes of platinum(0) can be formed from nitrosobenzene and an appropriate precursor platinum(0) complex (equation 363).[1167] This compound reacts with CO_2, CS_2, alkenes and alkynes to give metalacycles (equation 364).[1168]

$$Pt(C_2H_4)(PPh_3)_2 + PhNO \longrightarrow Pt(PhNO)(PPh_3)_2 + C_2H_4 \qquad (363)$$



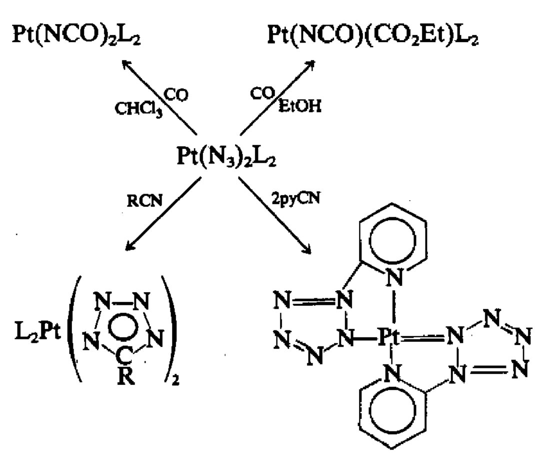
(364)

(iii) Azides

Sodium azide reacts with $(NH_4)_2PtCl_4$ to give the ion $Pt_2(N_3)_6^{2-}$, which gives $Pt(N_3)_4^{2-}$ if a large excess of azide is added (equation 365).[1169] Reaction with ligands L (L = PPh_3, bipy, phen) gives $Pt(N_3)_2L_2$. As a ligand, azide is comparable to iodide in the nephelauxetic series.[1169,1170] Azide ion will substitute chloride in *trans*-$[PtCl_2(NH_3)_4]Cl_2$ and *trans*-$[PtCl_2(en)_2]Cl_2$ to give the platinum(IV) azide complexes *trans*-$[PtCl(N_3)(NH_3)_4]Cl_2$ and *trans*-$[PtCl(N_3)(en)_2]Cl_2$.[1171] The fully substituted complex $Pt(N_3)_6^{2-}$ is also known.

$$PtCl_4^{2-} \xrightarrow{N_3^-} Pt_2(N_3)_6^{2-} \xrightarrow{N_3^-} Pt(N_3)_4^{2-} \qquad (365)$$

Coordinated azide ion will undergo a number of reactions which involve attack at the azide ligand. A number of examples are summarized in Scheme 9.[1172–1175] The azide ligand is photochemically dissociated from bis azide complexes. Irradiation of $Pt(CN)_4(N_3)_2^{2-}$ gives $Pt(CN)_4^{2-}$ and the azide radical (equation 366),[1176] whereas with $Pt(N_3)_2(PPh_3)_2$ the nitrogen-containing product is believed to be N_6 (equation 367).[1177]



Scheme 9

$$Pt(CN)_4(N_3)_2^{2-} \xrightarrow{h\nu} Pt(CN)_4^{2-} + 2N_3^{\cdot} \quad (366$$

$$Pt(N_3)_2(PPh_3)_2 \xrightarrow{h\nu} Pt(PPh_3)_2 + N_6 \quad (367$$

(iv) *Hydrazides, imines, diazo and triazendo ligands*

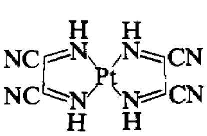
Hydrazine reacts with *cis*-$PtCl_2(PPh_3)_2$ to give $[Pt(\mu\text{-}N{=}NH)(PPh_3)_2]_2^{2+}$, $[Pt(\mu$ $NH_2)(PPh_3)_2]_2^{2+}$ and $[Pt_2(\mu\text{-}NH_2)(\mu\text{-}N{=}NH)(PPh_3)_4]^{2+}$.[1178,1179] The *p*-fluorophenylhydrazin complex *trans*-$[PtCl(H_2NNHC_6H_4F\text{-}p)(PEt_3)_2]^+$ has the hydrazine ligand lying in a plan approximately perpendicular to the platinum coordination plane.[1180] The synthesis of thi compound is achieved from the diazonium salt under conditions of catalyzed hydrogenatio (equation 368). Preparative procedures to the diimide and azo complexes are also given.[1180,118] Diazo ligands will also form π-bonded complexes to platinum(0).[1183]

$$PtCl(H_2NNHR)(PEt_3)_2 \xleftarrow{H_2} PtHCl(PEt_3)_2 + RN_2^+BF_4^- \longrightarrow$$
$$R = p\text{-}FC_6H_4$$
$$[PtCl(HN{=}NR)(PEt_3)_2]^+ \xrightarrow{OAc^-} PtCl(N{=}NR)(PEt_3)_2 \quad (368$$

Alkylideneamido ligands can be formed from the precursor compound $Me_3SnN{=}CR_2$ Reaction with platinum compounds gives both the η^2-type complexes $(Ph_3)_2Pt(\eta^2\text{-}HN{=}CR_2$ and the complexes containing the R_2CN^- ligand of type $Pt(N{=}CR_2)(PPh_3)_2$.[1184,1185]

1,3-Diaryltriazenes ArN=NNHAr react with $Pt(PPh_3)_3$ to form 1,3-diaryltriazenide com plexes, *cis*- and *trans*-$Pt(ArNNNAr)_2(PPh_3)_2$.[1186] The *cis* complex is the first definitive exampl of the monodentate bonding mode for the triazenido ligand.[1187,1188] For platinum(II) complexe of α-diimines, three types of metal complexation have been found: (i) σ,σ-N,N′ chelation; (ii σ-N monodentate coordination; and (iii) $\sigma\text{-N} \leftrightarrow \sigma\text{-N}'$ exchange. Reference is also given to th α-diimine bridging two platinums as a monodentate ligand to each Pt^{II}.[1189]

The diiminosuccinonitrilo platinum(II) complex (**109**) can be prepared from the divalen platinum halide and diaminomaleonitrile and base.[1190] These complexes resemble the diiminat chelates formed by condensation of diketones with platinum ammine complexes.[1032,1191] These complexes undergo rapid electron transfer reactions along the series of complexes with charg +1 to −2 (equation 369).[1192] Reversible electrochemistry is also found with the *o* phenylenediamine and *o*-quinonediimine complexes.[1193,1194] The complex $Pt\{(H_2N)_2C_6H_4\text{-}o\}$ undergoes photoxidation at $\lambda < 350$ nm to give $Pt\{(H_2N)_2C_6H_4\text{-}o\}_2^+$.



(109)

$$PtN_4^+ \rightleftharpoons PtN_4 \rightleftharpoons PtN_4^- \rightleftharpoons PtN_4^{2-} \quad (369$$

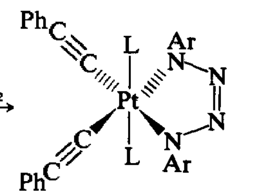
(v) *Oxime, glyoxime and diazabutadiene type ligands*

Glyoxime and dimethylglyoxime form platinum(II) complexes with the oxime complexe through nitrogen.[1195,1196] Several reviews of the coordination chemistry of α-dioximes hav been published.[1197–1200] Stable platinum(II) bis(monoxime) complexes can be prepared fron the direct reaction of $PtCl_4^{2-}$ and the monoxime. This technique has been used to prepare th N,N′-bonded camphorquinone dioxime complexes of platinum(II), the Pt—N bond strength i these complexes being greater than that with Pd^{II} or Ni^{II}.[1202] The diphenylglyoximato an pyridine-2-carboxaldoximinato compounds have been prepared in order to investigate thei solid state conductivity properties.[1203,1204]

Hydrazone complexes of platinum(II) can be prepared by treating Zeise's salt wit hydrazones (equation 370).[1205] Coordination is *via* the lone pair of electrons on nitrogen.[120 The reaction between (phenylazo)acetaldoxime (HL) and $PtCl_4^{2-}$ gives two isomers of PtL_2. Th *cis* isomer has been crystallographically confirmed.[1207] These arylazoacetaldoximat platinum(II) complexes on boiling in water in the presence of silver ion cause hydroxylation of one of the phenyl rings.[1208]

$$PtCl_3(C_2H_4)^- + Me_2C{=}NNR_2 \longrightarrow PtCl_2(C_2H_4)(Me_2C{=}NNR_2) + Cl^- \qquad (370)$$
$$R = H, Me, Ph$$

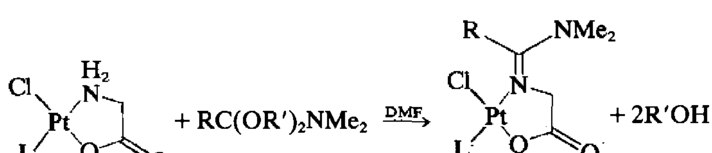
An unusual tetrazene complex of platinum(IV) is obtained from *trans*-$Pt(C{\equiv}CPh)_2(PEt_3)_2$ and 4-nitrophenylazide (equation 371).[1209] The structure has been verified by crystallography. The analogous platinum(II) complexes can be formed by reacting $Pt(cod)_2$ with aryl azides followed by triethylphosphine.[1210] The complexes with non-symmetrical RN_4R' ligands are also known.[1211]

trans-$Pt(C{\equiv}CPh)_2(PEt_3)_2 + 2O_2NC_6H_4N_3 \xrightarrow{-N_2}$  (371)

$L = PEt_3$; $Ar = O_2NC_6H_4$

(*vi*) *Schiff base type complexes*

Although complexes with these ligands are common in palladium(II) chemistry, their occurrence is more scarce in platinum(II) compounds. Nevertheless these complexes can be prepared, examples being platinum(II) complexes of the optically active quadridentate Schiff base of salicylaldehyde and (*R*)-1,2-diamines.[1212] An alternative synthesis involves formation of the Schiff base by reaction of a complexed amino ligand on platinum(II) with amide acetates (equation 372).[1213]

 (372)

(*vii*) *Complexes with* o-*metalated N ligands*

Again such complexes are more prevalent in palladium chemistry. Examples in platinum(II) chemistry are found with azobenzene,[1214–1216] *N,N*-dialkylbenzylamine,[1217] benzoquinoline,[1218] 8-methylquinoline,[1218] acetophenone oxime[1220] and *N*-alkyl-*N*-nitrosoanilines.[1221]

Finally, merely as a postscript, it is apparent that NMR techniques will become increasingly useful to study platinum complexes with nitrogen ligands.[1222,1223]

52.5.3 Phosphine Complexes

This constitutes a very significant class of ligands for platinum chemistry. The compounds grouped here are ones where the phosphorus ligand is the one of primary interest, but throughout this whole chapter the reader will find phosphine complexes where the coordinated phosphorus ligand has been used to stabilize Pt—H, Pt—B or Pt—C bonds. A number of reviews (Table 6) have been published on phosphine complexes, and the reader will find these articles contain numerous references to platinum complexes. The question of bonding in transition metal phosphine complexes is a frequently discussed topic. Such discussion is beyond the scope and limitations of this chapter, but two references will give the reader a guide to this literature.[1226,1232]

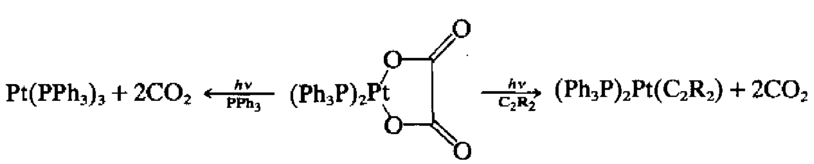
Table 6 Review Articles on Complexes with P, As and Sb Bonded Ligands

Title	*Ref.*
1. Phosphorus, Arsenic and Antimony Ligands	1224
2. Complexes of the Transition Metals with Phosphines, Arsines and Stibines	1225
3. Phosphine Complexes	1226
4. Homogeneous Catalysis with Metal Phosphine Complexes	1227
5. Chemistry of Bis(diphenylphosphino)methane	1228
6. ^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes	1229
7. Phosphite, Phosphonite, Phosphinite and Aminophosphine Complexes	1230
8. ^{31}P NMR Spectra of Coordination Compounds	1231

52.5.3.1 Zerovalent platinum complexes

(*i*) *Synthesis and structure*

The most common complex of platinum(0) is $Pt(PPh_3)_3$. The complex was first reported in 1958,[1233] and its early chemistry was reviewed in 1968.[1234] Both $Pt(PPh_3)_3$ and $Pt(PPh_3)_4$ have been reported in the solid state. Recrystallization gives $Pt(PPh_3)_3$, and indeed it is possible that the fourth triphenylphosphine is occluded in the lattice rather than coordinated to platinum.[1235,1236] There is evidence that $Pt(PPh_3)_4$ dissociates completely to $Pt(PPh_3)_3$ and PPh_3 in solvents such as benzene and toluene.[1224] Kinetic evidence suggests the chemically reactive intermediate in reactions of these compounds is $Pt(PPh_3)_2$,[1237,1238] but the original claims that $Pt(PPh_3)_2$ is an isolable monomeric complex remain unproven.[1239] A novel approach to prepare $Pt(PPh_3)_2$ involves the photochemical decomposition of the oxalato complex $Pt(C_2O_4)(PPh_3)_2$ (equation 373).[1240] In the presence of alkynes (C_2R_2) or triphenylphosphine, the complexes $Pt(C_2R_2)(PPh_3)_2$ and $Pt(PPh_3)_3$ can be prepared, but in the absence of added ligand a dimer is formed rather than $Pt(PPh_3)_2$. This method is a complementary one to the usual methods involving reduction of *cis*-$PtCl_2(PPh_3)_2$ with hydrazine or ethanolic potassium hydroxide (equation 374).


(373)

$$cis\text{-}PtCl_2(PPh_3)_2 + PPh_3 \xrightarrow[\text{or KOH/EtOH}]{N_2H_4\cdot H_2O} Pt(PPh_3)_3 \quad (374)$$

The low temperature ^{31}P NMR spectrum provides evidence for $Pt(PPh_3)_4$. The ^{31}P NMR spectrum for $Pt(PPh_3)_3$ at room temperature in toluene solvent is broad, but at −70 °C the spectrum sharpens and coincides with that for $Pt(PPh_3)_3$ (δ 49.3; $^1J(PtP) = 4438$ Hz).[124] Addition of 0.5 equivalents of PPh_3 to this solution causes broadening, but at −100 °C the NMR spectrum corresponds with that for $Pt(PPh_3)_3$ and $Pt(PPh_3)_4$ (equation 375). This equilibrium position correlates with that found for the analogous *p*-tolylphosphine complexes.[1242] The precise coordination number of these zerovalent platinum complexes is influenced by both steric and electronic factors.[1243,1244] The analogous triphenylarsine complex $Pt(AsPh_3)_4$ can be prepared as a colorless solid. The complex $Pt(PPh_3)_3$ will also luminesce and appears red under a UV light source.[1245]

$$Pt(PPh_3)_3 + PPh_3 \longrightarrow Pt(PPh_3)_4 \quad (375)$$

The complexes $Pt(PPh_2Me)_4$ and $Pt(PPhMe_2)_4$ have been prepared by the KOH method for the latter, and by using $NaBH_4$ to synthesize the former.[1246,1247] Low temperature NMR shows that below −30 °C, $Pt(PPh_2Me)_3$ is formed, but for both $Pt(PPhMe_2)_4$ and $Pt\{P(C_6F_5)Me_2\}_4$ there is no phosphine dissociation at this temperature. The sodium borohydride method can also be used to prepare $Pt(PPh_2CF_3)_3$ (equation 376).[1248] Variable temperature ^{19}F NMR shows that the rapid phosphine exchange occurring at room temperature is frozen out at *ca.* −50 °C and that at lower temperatures a further dynamic process, possibly associated with rotation of phosphine about the Pt—P bond, is reduced in rate. Zerovalent platinum complexes with other fluorinated phosphines include both $Pt(PF_3)_4$[1249] and mixed alkylfluorophosphine complexes PtL_4 ($L = PF_3$, PF_2CF_3, $PF(CF_3)_2$).[1250] These complexes are formed by reaction of the phosphine L with $PtCl_2$ at 60–80 °C (equation 377).

$$cis\text{-}PtCl_2\{P(C_6F_5)Me_2\}_2 + 2BH_4^- + 2P(C_6F_5)Me_2 \longrightarrow Pt\{P(C_6F_5)Me_2\}_4 + 2BH_3 + 2HCl \quad (376)$$

$$PtCl_2 + 5L \longrightarrow PtL_4 + LCl_2 \quad (377)$$

The triethylphosphine complex $Pt(PEt_3)_4$ can be prepared in high yield by the reaction of $PtCl_2$, PEt_3 and K in THF solvent (equation 378).[43] The complex is air sensitive and the synthesis must be carried out in a dry nitrogen atmosphere. The complex can also be prepared by the photolysis of $Pt(C_2O_4)(PEt_3)_2$ in the presence of triethylphosphine. If the photolysis is carried out in the presence of ligands such as CO, analogous reactions to the triphenylphosphine complex are observed. Using this reaction good yields of $Pt(CO)_2L_2$, Pt(alkene)L_2 and Pt(alkyne)L_2 ($L = PEt_3$, PPh_3) can be obtained.[1240,1251]

$$PtCl_2 + 4PEt_3 + 2K \longrightarrow Pt(PEt_3)_4 + 2KCl \quad (378)$$

When bulky substituents are present on the phosphine, the zerovalent platinum complexes are two coordinate PtL_2. Complexes $Pt(PCy_3)_2$, $Pt(PBu^t_3)_2$, $Pt(PPhBu^t_2)_2$, $Pt(PPr^i_3)_2$ and $Pt(PPr^i_3)_3$ can be prepared by sodium reaction of $PtClL_2$ complexes, or by substitution of the cyclooctadiene ligand in $Pt(cod)_2$ by the phosphine ligand L (equations 379 and 380). The structure of $Pt(PPhBu^t_2)_2$ shows a slightly bent geometry with an angle P—Pt—P of 177.0(1)°. The Pt—P distances are 2.252(1) Å, and the substituents on phosphorus form an eclipsed conformation with nearly parallel phenyl planes. The non-bonded Pt-*ortho*-hydrogen atom distance is estimated at 2.83 Å, and the shorter aliphatic hydrogen–Pt distance is 2.70 Å.[1252] Using the KOH/EtOH method, the tri-*t*-butylphosphine complex $Pt(PBu^t_3)_2$ can be prepared in 80% yield from K_2PtCl_4 (equation 381). The complex gives *trans*-$PtHCl(PBu^t_3)_2$ with $CHCl_3$, and undergoes carbonylation to form $[Pt(CO)(PBu^t_3)]_3$.[1253] An alternative method to the synthesis of PtL_2 ($L = PBu^t_3$, $PMeBu^t_2$, $PBu^nBu^t_2$) is to treat the methoxy-bridged binuclear platinum(II) complex $[Pt(\mu\text{-OMe})(C_8H_{12}OMe)]_2$ with two equivalents of L in an alcohol solvent.[1254] These PtL_2 complexes resemble $Pt(PPh_3)_3$ in their replacement chemistry giving $[Pt(CO)L]_3$ with CO, Pt(alkene)L_2 with dimethyl fumarate and maleic anhydride, and undergoing oxidative addition with HX and MeI.[100,1253] The tricyclohexylphosphine complex PtL_2 crystallizes at −15 °C in the presence of excess tricyclohexylphosphine to give PtL_3 ($L = PCy_3$; equation 382). The average Pt—P distance of 2.303(6) Å is longer than that of 2.231(6) Å for $Pt(PCy_3)_2$, but not unusually long for a Pt—P bond. The cyclohexyl groups have the chair conformation, and although the PCy_3 ligand has a cone angle of 157°, the interligand repulsions are minimized to a small value by intermeshing of the cyclohexyl groups.[1255] If desired, zerovalent complexes of platinum(0) having long chain tertiary phosphines (aliphatic or aromatic) can be synthesized.[1256]

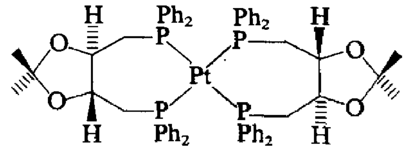
$$PtCl_2L_2 + 2Na \longrightarrow PtL_2 + 2NaCl \quad (379)$$

$$Pt(cod)_2 + 2L \longrightarrow PtL_2 + 2cod \quad (380)$$

$$\begin{array}{l} K_2PtCl_4 + 3PBu^t_3 + 2KOH \longrightarrow Pt(PBu^t_3)_2 + 4KCl + OPBu^t_3 + H_2O \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow CO,\ -PBu^t_3 \\ \qquad\qquad\qquad\qquad\qquad\qquad [Pt(CO)(PBu^t_3)]_3 \end{array} \quad (381)$$

$$Pt(PCy_3)_2 + PCy_3 \xrightarrow{-15\,°C} Pt(PCy_3)_3 \quad (382)$$

The asymmetric chelating ligand (*R*,*R*)-diop forms a four-coordinate platinum(0) complex (**110**) which exhibits conformational isomerism observable by ^{31}P NMR. Cooling the solution causes first broadening of the signals followed by resolution into an AA'XX' multiplet by an intramolecular process in the monomeric complex.[1257] As for the complex $Pt(PPh_3)_3$,[1241] ^{31}P NMR techniques show the existence of PtL_4 ($L = PMe_3$, $PPhMe_2$, PPh_2Me, PEt_3, PBu^n_3), PtL_3 ($L = PEt_3$, PBu^n_3, $P(p\text{-tolyl})_3$, $P(CH_2Ph)_3$, PPr^i_3, PCy_3) and PtL_2 ($L = PPr^i_3$, PCy_3, $PPhBu^t_2$) in solution. Where thermodynamic parameters have been obtained, it is found that there is no evidence for steric crowding affecting the enthalpy term, but the entropy terms are affected due to interaction of the ligands and resulting loss of motional freedom.[1258] In principle, platinum(0) complexes should possess no paramagnetic contribution to the platinum shift, which would therefore be in the region of -5900 p.p.m. to high frequency of 21.4 MHz. For $Pt(PPhMe_2)_4$ this shift is at δ -195 p.p.m., and for $Pt\{PF(OPh)_2\}_4$ the value is δ -1057 p.p.m., suggesting that there is some paramagnetic contribution, and that the electronic configuration of Pt^0 is not purely $5d^{10}$.[1259,1260]



(110)

Zerovalent platinum complexes can be prepared with the triphosphine ligand $MeC(CH_2PPh_2)_3$. These dissociatively stable complexes Pt(triphos)(PR_3) (R = Ph, *p*-tolyl, F, OPh; $PR_3 = PPh_2Me$, PF_2NMe, $P(OCH_2)_3CMe$) can be prepared by borohydride reduction and replacement reactions between PR_3 ligands to prepare the different analogues. With CO, Pt(triphos)CO is obtained.[1261]

Platinum(0) complexes with tertiary phosphines will catalyze the water gas shift reaction. With $Pt(PPh_3)_4$ no reaction occurs, but the complex $Pt(PPr^i_3)_3$ gives high turnover numbers in acetone solvent at temperatures above 100 °C.[1262] Other reactions can also occur in the presence of water with these complexes; thus under such conditions, systems with PtL_3/H_2O are efficient catalysts for H–D exchange in organic compounds such as ketones, aldehydes, sulfones, sulfoxides and nitroalkanes, and also for the hydration of organic unsaturated bonds. The initial step in these reactions involves the oxidative addition of water to PtL_3.[72]

The compound $PtH_2(Bu^t_2P(CH_2)_3PBu^t_2)$ loses hydrogen at 60–95 °C to give a dimeric complex $Pt_2(Bu^t_2P(CH_2)_3PBu^t_2)_2$ having a Pt—Pt bond. The Pt—Pt separation is 2.765(1) Å, and the angle between the two P—Pt—P planes is 82°. The compound has no bridging ligands, and represents a molecule with two formally d^{10} platinum centers having an interaction between two formally closed shells. Calculations on such molecules shows that an admixture of platinum *s* and *p* functions into MOs primarily composed of *d* functions converts, in part, bonding and antibonding interactions into more bonding and non-bonding ones, respectively.[101,1263] These calculations have been extended to the formation of clusters from the PtL_2 fragment, and can be compared with similar theoretical work on the incorporation of PtL_2 into mixed metal cluster compounds.[1264] An NMR approach to bonding in zerovalent platinum phosphine complexes can also be taken; values of ^1J(PtP) correlate with ^2J(PP), ^1J(PtP′) and the electronegativity of atoms or groups bonded to the phosphorus.[1265]

Two features are worthy of note here. Firstly the effect of solvent on reactivity of the complex $Pt(PPh_3)_3$. In Section 52.2 the reactions of $Pt(PPh_3)_3$ with protonic acids were shown to give hydrides. These reactions are carried out in organic solvents such as C_6H_6 or CH_2Cl_2. In liquid HCl, $Pt(PPh_3)_3$ gives $PtCl_2(PPh_3)_2$ (equation 383), and in anhydrous trifluoroacetic acid there is no reaction.[1266] Secondly the photophysics of complexes $PtXL_2$ ($X = C_2H_4$, $C_2(CN)_4$, fumaronitrile, tetracyanocyclopropane; $L = PPh_3$, $AsPh_3$) shows solvent effects on the ground state absorption bands, and a vibronic progression in the emission band. The observed emission is a ligand-centered π–π^* luminescence. The vibronic progression of $420 \pm 30\ cm^{-1}$ is present in the phosphorescence spectrum of triphenylphosphine itself, which implies that a P–Ph vibration is involved as a deactivation mode. The emission lifetimes are in the nanosecond range.[1267]

$$Pt(PPh_3)_3 + 4HCl \xrightarrow{\text{anhydrous HCl}} PtCl_2(PPh_3)_2 + H_2 + (Ph_3PH)(HCl_2) \quad (383)$$

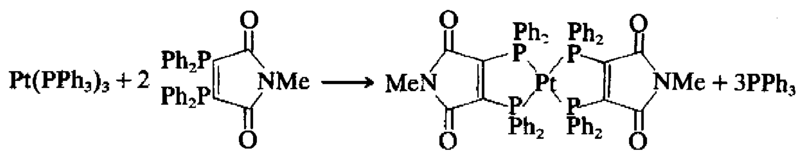
Tertiary phosphite complexes of platinum(0) can be prepared by the hydrazine reduction of $PtCl_2\{P(OR)_3\}_2$ (equation 384), or by replacement of triphenylphosphine in $Pt(PPh_3)_3$ (equation 385).[1233] Alternatively the complexes can be prepared from $Pt(\eta^3\text{-}C_3H_5)(\eta^5\text{-}Cp)$ and the phosphite.[1268] Heteronuclear INDOR measurements show that ^2J(PP) has a value of +81 Hz in $Pt\{P(OMe)_3\}_4$. A detailed synthesis of $Pt\{P(OEt)_3\}_4$ has been published from K_2PtCl_4 and triethyl phosphite with KOH (equation 386).[1269] The product is obtained as colorless crystals which can be handled in air.

$$PtCl_2\{P(OR)_3\}_2 + 2P(OR)_3 \xrightarrow{N_2H_4} Pt\{P(OR)_3\}_4 \quad (384)$$

$$Pt(PPh_3)_3 + nP(OR)_3 \longrightarrow Pt\{P(OR)_3\}_n + 3PPh_3 \quad (385)$$

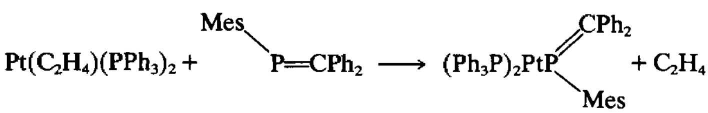
$$K_2PtCl_4 + 5P(OEt)_3 + 2KOH \longrightarrow Pt\{P(OEt)_3\}_4 + OP(OEt)_3 + 4KCl + H_2O \quad (386)$$

A number of less common phosphorus ligands have been used to prepare complexes of platinum(0). The complex $Pt(PPh_3)_3$ reacts with bis(diphenylphosphino)-*N*-methylmaleimide (equation 387).[1270] The complex $PtCl_2(dppe)$ reacts with $Li_2(PhP{=}PPh)$ at 25 °C in THF solution to give $Pt(PhP{=}PPh)dppe$. ^{31}P NMR data show very small *s* character in the Pt—P (diphosphene) bonds indicative of diphosphene complexed to Pt^0 rather than a diphosphido ligand coordinated to Pt^{II} (equation 388).[1271] Mesityl(diphenylmethylene)phosphine reacts with $Pt(C_2H_4)(PPh_3)_2$ to give dark red crystals of (**111**) in quantitative yield (equation 389).[1272] For the complex $Pt(PCBu^t)(PPh_3)_2$, an X-ray structure shows that the complex (**112**) adopts an η^2 configuration.[1273] The first example of an η^2-amino(imino)thiophosphorane complex has been observed in a coordination complex to platinum(0) (equation 390).[1274] Zerovalent complexes of platinum can be prepared with a P-bonded λ^3-phosphazene ligand. The complexes are prepared by ligand substitution reactions of $Pt(cod)_2$ (equation 391), and the structure of (**113**) verified by crystallography.[1275] The analogy of complex (**113**) to the zerovalent platinum complexes with triphenylphosphine ligands is fully shown in the reactions with alkenes and alkynes to form complexes $Pt(C_2R_4)L_2$ and $Pt(C_2R_2)L_2$ $[L = P({=}NBu^t)\{NBu^t(SiMe_3)\}]$.[1276] The hexakis(trifluoromethyl)benzene complex of platinum(0), $Pt\{C_6(CF_3)_6\}(PEt_3)_2$ can be prepared from $Pt(PEt_3)_3$ and the ligand.[1277]



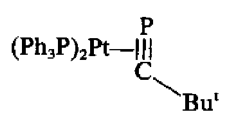
(387)

$$PtCl_2(dppe) + Li_2(PhP{=}PPh) \longrightarrow Pt(PhP{=}PPh)(dppe) + 2LiCl \qquad (388)$$

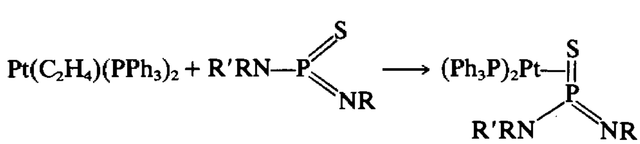


(389)

(**111**)



(**112**)



(390)

$R = Bu^t$, $R = SiMe_3$

$$Pt(cod)_2 + 3Bu^t(Me_3Si)NP{=}NBu^t \longrightarrow Pt[P{=}NBu^t\{NBu^t(SiMe_3)\}]_3 + 2cod \qquad (391)$$

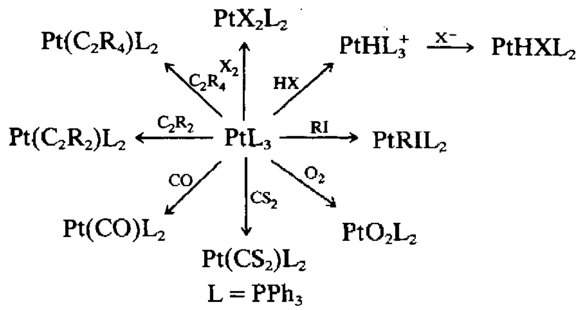
(**113**)

Platinum ($4f_{7/2}$) binding energies have been measured by X-ray photoelectron spectroscopy for 27 complexes. A binding energy of 71.6 eV for $Pt(PPh_3)_3$ is the smallest value in the list. The value of 73.2 for $PtO_2(PPh_3)_2$ is identical to that for the divalent complex *cis*-$PtCl_2(PPh_3)_2$.[1278]

(*ii*) *Reactions*

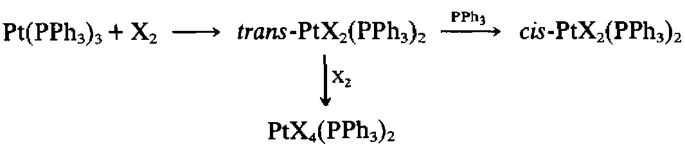
A number of reactions of platinum(0) complexes have been discussed in the earlier sections of this chapter. These reactions include protonation reactions of PtL_3 to give $PtHL_3^+$, oxidative addition of HX to give $PtHXL_2$, replacement with carboranes, alkenes and alkynes (L') to give complexes of type PtL_2L'. The most studied complex of platinum(0) is $Pt(PPh_3)_3$ and in Scheme 10 are outlined examples of the numerous reactions which this compound will undergo.

Hydrogen does not add to $Pt(PPh_3)_3$, but the triethylphosphine complex $Pt(PEt_3)_3$ does to give $PtH_2(PEt_3)_3$.[65]



Scheme 10

Bromine and iodine oxidatively add to $Pt(PPh_3)_3$ to give *cis*-$PtX_2(PPh_3)_2$ (X = Br, I),[1279] and a similar reaction with chlorine will likely yield *cis*-$PtCl_2(PPh_3)_2$. The *cis* isomer is the result of the kinetically formed *trans*-$PtX_2(PPh_3)_2$ undergoing triphenylphosphine-catalyzed isomerization to *cis*-$PtX_2(PPh_3)_2$.[1280] If the reaction of $Pt(PPh_3)_3$ is carried out for a short reaction time (3 min) with an excess of halogen, the complexes *trans*-$PtX_2(PPh_3)_2$ (X = Br, I) can be obtained in high yield. The excess halogen oxidizes free triphenylphosphine, and the short reaction time prevents the formation of significant quantities of $PtX_4(PPh_3)_2$ (Scheme 11).[1281]



Scheme 11

Metal halides will undergo oxidative addition to PtL_2 to form complexes having Pt—Pt, Pt—Ni, Pt—Cu, Pt—Au, Pt—Hg and Pt—Sn bonds.[1282–1284] Examples are shown in equations (392) and (393).

$$Pt(PPh_3)_3 + PtCl_2(PPh_3)_2 \longrightarrow Cl(PPh_3)_2Pt\text{—}Pt(PPh_3)_2Cl + PPh_3 \quad (392$$

$$Pt(PPh_3)_3 + XHg\text{—}Fe(py)_2(CO)_2\text{—}HgX \longrightarrow XHg\text{—}Fe(py)_2(CO)_2\text{—}Hg\text{—}Pt(PPh_3)_2X + PPh_3 \quad (393$$

Much of the mechanistic understanding of oxidative addition reactions comes from work or the reaction between alkyl halides and zerovalent platinum complexes. The work is fully summarized in texts covering organometallic chemistry;[1285,1286] no details will be given here but the work will be briefly outlined and the significant conclusions and references given. From earlier work by Halpern, Collman and others, it had become accepted that oxidative addition of alkyl halides to low-valent transition metal centers occurred by an S_N2 type mechanism involving nucleophilic attack by the metal ion at the saturated carbon of the electrophilic alkyl halide. A consequence of such a pathway is that the reaction involves inversion at carbon. Using *trans*-1-bromo-2-fluorocyclohexane, this inversion reaction was initially observed.[128] Subsequently this experiment was challenged by authors who were unable to reproduce the claimed reaction.[1288] At around the same time the oxidative addition reaction of alkyl halide to iridium(I) was being shown to occur with retention of configuration.[1289] The situation was clarified by further work with $Pt(PEt_3)_3$ which shows that a major (but not sole) pathway for the addition of alkyl halides to platinum(0) involves a radical chain process. The evidence presented is the radical scavenger duroquinone causing a 5×10^3 fold decrease in rate, the observation of benzyl platinum(II) complexes from the oxidative addition of neopentyl bromide in toluene solvent, the cyclization of 6-bromohexene-1, the racemization of ethyl-D (+)-α-chloropropionate, and the observation of CIDNP effects.[1290,1291] The rate with $Pt(PPh_3)$ and MeI does, however, still follow second-order kinetics, and $Pt(PPh_3)_2$ is the undetected intermediate.[1292]

52.5.3.2 Divalent monomeric platinum complexes

(*i*) *Synthesis*

The simplest phosphorus ligand is the element itself. The complex $[Pt(triphos)(\eta^3\text{-}P_3)]BF_4$ has been synthesized by adding an excess of white phosphorus in THF to a solution of $PtCl_2(PBu_3)_2$ and triphos in dichloromethane. Heating and subsequent addition of $[NBu_4]BF_4$ gives $[Pt(triphos)(\eta^3\text{-}P_3)]BF_4$ (equation 394).[1293]

$$PtCl_2(PBu_3)_2 + P_4 + \text{triphos} \xrightarrow{(NBu_4)BF_4} [Pt(\text{triphos})(\eta^3\text{-}P_3)]BF_4 \quad (394)$$

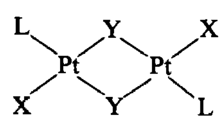
Tertiary phosphines form a wide range of complexes of the type $PtX_2(PR_3)_2$ (X = halide, pseudohalide; R = alkyl, aryl or mixed alkylaryl). Space limitations preclude this chapter becoming a compendium of known compounds, therefore for each individual complex the reader is directed to Chemical Abstracts, Gmelin or the book by McAuliffe which contains extensive tabulations of compounds.[1225] In this chapter we outline the general methods of synthesis, the properties, and the structures and spectral features which we expect to be found with this class of compounds.

Tertiary phosphines PR_3 react with PtX_4^{2-} to give complexes $PtX_2(PR_3)_2$ (equation 395).[1294,1295] When R is a lower alkyl group the initially formed ionic complex only slowly converts to the final product.[1296] If *cis* and *trans* isomers are formed, separation by fractional crystallization may be possible.[1295] Formation of complexes $PtX_2(PR_3)_2$ from $[Pt(PR_3)_4][PtX_4]$ is thermally accelerated.[1297] Preparative procedures have been developed to produce these platinum(II) phosphine complexes from $H_2PtCl_6{\cdot}H_2O$. The *cis* complexes $PtCl_2(PPh_3)_2$ or $PtCl_2(P\text{—}P)$ ($P\text{—}P = Ph_2P(CH_2)_nPPh_2$; $n = 1, 2, 4$) are prepared using excess phosphine and ethanol solvent (equation 396). To prepare the complex *trans*-$PtCl_2(PPh_3)_2$, aqueous formaldehyde is added (equation 397).[1298] A frequently used reaction to form phosphine complexes is bridge cleavage (equation 398). The strength of bridge bonds increases in the series Cl < Br < I and Cl < Et_2PO < RS < R_2P. The weaker bridges can be broken by phosphine ligands L′ to give monomeric phosphine complexes of platinum(II).[1299–1306] The addition of phosphine L to complexes $Pt_2(\mu\text{-}Cl)_2Cl_2L_2$ at low temperatures gives the ionic complexes $PtClL_3^+$ and $PtCl_3L^-$ as major products rather than the covalent complex $PtCl_2L_2$. If the covalent compound is the desired one, local accumulations of the added phosphine should be avoided during mixing.[1307] This bridge cleavage reaction can be reversed by fusion of the monomeric complex $PtCl_2L_2$ with $PtCl_2$.[1308]

$$2PtX_4^{2-} + 4PR_3 \longrightarrow [Pt(PR_3)_4][PtCl_4] \longrightarrow 2PtCl_2(PR_3)_2 \quad (395)$$

$$H_2PtCl_6{\cdot}H_2O \xrightarrow[EtOH]{PPh_3} cis\text{-}PtCl_2(PPh_3)_2 \quad (396)$$

$$H_2PtCl_6{\cdot}H_2O \xrightarrow[EtOH/CH_2O]{PPh_3} trans\text{-}PtCl_2(PPh_3)_2 \quad (397)$$



$$+ 2L' \longrightarrow 2PtXYLL' \quad (398)$$

(114)

This cleavage method can obviously be used to prepare complexes (**114**) with different phosphine ligands. Dropwise addition of L (L = PPh_3, $PMePh_2$, PPr^i_3, PCy_3, $AsPh_3$ or $SbPh_3$) to a dichloromethane solution of $[PrCl_2L']_2$ (L′ = PEt_3) gives *trans*-$PtCl_2LL'$ (*cis* for $SbPh_3$). Hydrazine reduction of these complexes gives extensive disproportionation, however treatment with $NaBH_4$ at 0 °C followed by HCl addition gives mixed-ligand hydrides (equation 399).[1309] The method can also be used to prepare complexes of platinum(II) with halogenated phosphine ligands, examples of such complexes being *cis*-PtX_2LL' (L′ = PPh_2Cl, PEt_2Cl, $AsPh_2Cl$, $AsMe_2Cl$).[1301] The PF_3 and PCl_3 complexes of platinum(II) have been formed from $PtCl_2$, presumably by bridge cleavage of this polymeric material (equation 400).[1310] The reaction of phosphine with $PtI_2(PPh_3)_2$ is reported to give $Pt_3I_2(PPh_3)_3(PH_3)_3$.[1311]

$$cis\text{-}PtCl_2(PEt_3)(AsPh_3) \xrightarrow[ii,\ HCl]{i,\ NaBH_4} PtHCl(PEt_3)(AsPh_3) \quad (399)$$

$$3PtCl_2 + 4PX_3 \longrightarrow PtCl_2(PX_3)_2 + [PtCl_2(PX_3)]_2 \quad (400)$$

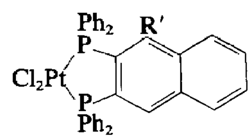
$$X = F, Cl$$

Recently there has been an interest for a variety of reasons in preparing phosphine complexes of the Group VIII metal ions where the phosphine ligands contain a variety of functionalities which are desired for subsequent chemistry. A number of examples will be discussed later where this second functional group also coordinates to platinum(II), but the other examples where the functional group remains free are covered here. This range of complexes shows the tolerance of the synthetic reactions to different functionalities on the ligand. For a good recent review on functionalized phosphine ligands the reader is directed to the chapter by Rauchfuss in ref. 1227. The alkyne-substituted phosphine $PBu^t_2(C{\equiv}CPh)$ reacts with $PtCl_2(CNBu^t)_2$ in toluene to give *trans*-$PtCl_2\{PBu^t_2(C{\equiv}CPh)\}_2$, which can be converted to the iodide complex by metathetical replacement with NaI (equation 401). Restricted rotation about the Pt—P bonds causes the complexes to exist as identifiable conformers.[1312] In the *cis* isomer of alkynic phosphine complexes the sterically less demanding $—C{\equiv}CR'$ group in $R_2PC{\equiv}CR'$ is forced into a configuration facilitating alkyne–alkyne interaction. The *cis* complex *cis*-$PtCl_2(Ph_2PC{\equiv}CPh)_2$ (**115**) has been prepared from $PtCl_2$(cod). Toluene reflux of complex (**115**) converts it into a platinum(II) complex of a naphthalene-substituted chelating phosphine ligand (**116**; equation 402).[1313] Alkynic groups on phosphorus coordinated to platinum(II) will also add HCl by *trans* addition across the triple bond (equation 403).[1314] Phosphine ligands with a cyclopropane functionality can be prepared. Using the platinum halide, the complex (**117**) with a coordinated PBu^t_2(cyclopropyl) ligand can be prepared and thermolyzed to the ring-opened complex (**118**; equation 404).[1315,1316]

$$PtCl_2(CNBu^t)_2 + 2PBu^t_2(C{\equiv}CPh) \longrightarrow trans\text{-}PtCl_2(PBu^t_2C{\equiv}CPh)_2 \xrightarrow{I^-} trans\text{-}PtI_2(PBu^t_2C{\equiv}CPh)_2 \quad (401)$$

$$PtCl_2(Ph_2PC{\equiv}CPh)_2 \xrightarrow{heat} \quad (402)$$

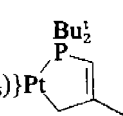
(**115**)



(**116**) R′ = Ph

$$cis\text{-}PtCl_2(Ph_2PC{\equiv}CCF_3)_2 + 2HCl \longrightarrow cis\text{-}PtCl_2\{Ph_2PCH{=}C(Cl)CF_3\text{-}trans\}_2 \quad (403)$$

$$trans\text{-}PtCl_2\{PBu^t_2CH_2(C_3H_5)\}_2 \longrightarrow Cl\{PBu^t_2CH_2(C_3H_5)\}Pt \quad (404)$$



(**117**) (**118**)

Cationic phosphine platinum(II) complexes can be readily synthesized. A usual method involves halide replacement from PtX_2L_2 by a series of neutral ligands L′ in the presence of $NaClO_4$, $AgBF_4$, $NaPF_6$ (equation 405).[1317] An alternative method uses the stereoretentive bridge cleavage of cationic platinum(II) dimers (equation 406).[1318] High yields of $[PtCl(PPh_3)_3]B_{12}Cl_{12}$ have been obtained from the reaction of K_2PtCl_4 with triphenylphosphine in the presence of $Cs_2B_{12}Cl_{12}$.[1319] Halide removal can also be carried out using direct reaction of *cis*-$PtCl_2L_2$ with the non-coordinating acid HBF_4 (equation 407).[1320]

$$PtX_2L_2 + L' \xrightarrow{Y^-} [PtXL_2L']Y + X^- \quad (405)$$

$$[Pt_2(\mu\text{-}X)_2L_4](ClO_4)_2 + 2L' \longrightarrow 2[PtXL_2L']ClO_4 \quad (406)$$

$$cis\text{-}PtCl_2L_2 + HBF_4 \xrightarrow{H_2O} [PtClL_2(OH_2)]BF_4 + HCl \quad (407)$$

Platinum(II) phosphite complexes can be prepared in many of the same ways. Two differences are noteworthy. Firstly phosphites differ from phosphines in that they are unstable to hydrolysis and careful precautions must be taken to exclude both water and oxygen when carrying out reactions using phosphites. Secondly, phosphite ligands coordinate to platinum(II) more strongly than do phosphine ligands, hence in replacement reactions the phosphite ligand may give complexes with a higher degree of phosphite substitution than the analogous reaction with tertiary phosphine ligands. A useful procedure for the synthesis of complexes $PtX_2\{P(OR)_3\}_2$ is the replacement of benzonitrile in $PtX_2(RCN)_2$ by phosphite $P(OR)_3$ (equation 408).[1321] An alternative route involves the *in situ* generation of the trialkyl phosphite ligand by solvolysis of the PCl_3 complex with the appropriate alcohol (equation 409).[1322] The first PtL_5^{2+} compound has been obtained using a phosphite ligand. Addition of trimethyl phosphite to a mixture of $PtCl_2$ and methanol becomes homogeneous when stirred. Addition of $NaBPh_4$ in methanol gives the complex $[Pt\{P(OMe)_3\}_5](BPh_4)_2$ as a white precipitate.[1323,1324] To prepare complexes with different phosphites it may be important to use either THF as reaction solvent, or if an alcohol solvent is desired, the alcohol having the same alkyl substituents as the phosphite must be used in order to avoid problems with transesterification of the phosphite ligand. The equilibrium between tetra- and penta-coordination (equation 410) is controlled by steric effects. Using similar synthetic procedures the alkyl diphenylphosphinite complexes of platinum $[Pt\{PPh_2(OR)\}_4](BPh_4)_2$ (R = Me, Et) can also be prepared.[1325] Unexpectedly the reaction between $Pt(1\text{-}\sigma,4,5\text{-}\eta\text{-}C_8H_{13})(cod)$ and $P(OR)_3$ (R = Me, Et, Ph) gives the hydride complex $[PtH\{P(OR)_3\}_4]^+$.[1326]

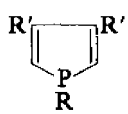
$$PtX_2(PhCN)_2 + 2P(OR)_3 \longrightarrow PtX_2\{P(OR)_3\}_2 + 2PhCN \tag{408}$$

$$Pt(PCl_3)_n + 3n\,ROH \longrightarrow Pt\{P(OR)_3\}_n + 3n\,HCl \tag{409}$$

$$PtL_4 + L \rightleftharpoons PtL_5 \tag{410}$$

The cationic ML_5 complexes, of which PtL_5^{2+} (L = tertiary phosphite) is an example, are stereochemically non-rigid at ambient temperatures. The rearrangements are intramolecular, and the barriers to this Berry pseudorotation process lie within the range 20–50 kJ mol^{-1}. This barrier increases with the steric bulk of the phosphite ligand up to the point where the bulk is too great for ML_5 complexes to be formed in the equilibrium in equation (410). For a given ligand the barriers are relatively insensitive to variation of the central metal, although the ordering follows the sequence Co > Ir ≈ Ni > Rh > Pt > Pd.[1327]

Both four- and five-coordinate platinum(II) complexes can be prepared with phosphole ligands L (**119**).[1328] The complexes *trans*-PtX_2L_2 (X = Cl, Br, I; R = Me, Bu^n, Bu^t, Ph, CH_2Ph; R′ = H, Me) are non-electrolytes in methanol solution. The formation of the five-coordinate adduct (equation 411) can be analyzed in terms of intra- and inter-molecular equilibria of the pentacoordinate species PtX_2L_3. The formation of PtX_2L_3 is enthalpy favored and entropy disfavored.



(119)

$$PtX_2L_2 + L \rightleftharpoons PtX_2L_3 \tag{411}$$

(ii) Structures and bond enthalpies

Platinum(II)–phosphorus distances in phosphine and phosphite complexes are usually between 2.2 and 2.4 Å. The distances are affected by the ligand *trans* to phosphorus in the square plane. For a complete listing of platinum–phosphorus distances in such structures the reader is directed to 'Molecular Structures and Dimensions' for structures from 1935–1976, and to the BIDICS series for structures published up through 1981. A list of representative structures and Pt—P bond distances is shown in Table 7. The Pt—Cl distance of 2.344(2) Å in *cis*-$PtCl_2(PEt_3)\{P(OPh)_3\}$ for the chloride *trans* to $P(OPh)_3$ is shorter than that (2.355(2) Å) for the chloride *trans* to PEt_3, implying a weaker *trans* influence of $P(OPh)_3$ than of PEt_3.[1336]

In order to assess steric and electronic effects on the bond enthalpies of reaction of phosphine and phosphite ligands to platinum(II), the enthalpies (ΔH) of reaction of these ligands L on reaction with $[PtMe(PPhMe_2)_2(THF)]PF_6$ have been measured (equation 412). These authors measured the enthalpies of 34 ligands, and correlated the measured enthalpy with the ligand cone angles.[1342,1343] Representative data are shown in Table 8.

$$[PtMe(PPhMe_2)_2(THF)]PF_6 + L \longrightarrow [PtMe(PPhMe_2)_2L]PF_6 + THF \tag{412}$$

Table 7 Pt—P Distances in Platinum(II) Phosphine and Phosphite Complexes

Compound	*Pt—P distance* (Å)	*Ref.*
cis-$PtCl_2(PMe_3)_2$	2.239(6), 2.256(8)	1329
trans-$PtCl_2(PEt_3)_2$	2.294(90)	1330
trans-$PtBr_2(PEt_3)_2$	2.315(4)	1330
trans-$PtHBr(PEt_3)_2$	2.26	1331
trans-$[PtCl(CO)(PEt_3)_2]BF_4$	2.345	1332
$[PtCl(PMe_3)_3]Cl$	2.242(3)(*trans*-P), 2.336(3)(*trans*-Cl)	1333
trans-$PtI_2(PMe_3)_2$	2.315(4)	1334
trans-$PtCl_2(PCy_3)_2$	2.337(2)	1335
cis-$PtCl_2(PEt_3)P(OPh)_3$	2.269(1)(PEt_3), 2.182(2)	1336
cis-$PtCl_2(PPhBu^t_2)_2$	2.358(6)	1337
trans-$PtHCl(PPh_2Et)_2$	2.268	1338
$Pt(CO_3)(PPh_3)_2$	2.24	1339
trans-$PtI_2\{P(tolyl\text{-}o)_3\}_2$	2.348(2)	1340
trans-$Pt_2Cl_2(\mu\text{-}Cl)_2(PPr_3)_2$	2.230(9)	1341

Table 8 Enthalpy and Cone Angle Correlations for the Reaction:
$[PtMe(PPhMe_2)_2(THF)]PF_6 + L \longrightarrow [PtMe(PPhMe_2)_2L]PF_6 + THF$

L	$-\Delta H$ (kJ mol^{-1})	*Cone angle* (°)
$P(OMe)_3$	111	107
PMe_3	110	118
PEt_3	102	130
$P(OPh)_3$	90	128
PPh_3	82	145
$P(CH_2CH_2CN)_3$	74	130
PCy_3	67	179
PBu^t_3	20	182

(iii) Nuclear magnetic resonance and vibrational spectra

The availability of Fourier transform NMR instruments with facilities for ^{31}P measurements has made this technique an important one in investigations involving phosphine and phosphite complexes. The technique is particularly useful for platinum complexes because of the strong coupling between the phosphorus ligand and the platinum nucleus (^{195}Pt, $I = 1/2$, 33% abundance). Even though the chemical shift range is large, the strong $^1J(PP)$ coupling in these complexes may make it necessary for the spectra to be analyzed using second-order methods. A large collection of data on ^{31}P chemical shifts and coupling constants is rapidly accumulating in the literature. It is, unfortunately, beyond the scope of this article to correlate all the known data. The chemical shifts of tertiary phosphines moved downfield on coordination,[1344] although upfield shifts are observed for phosphites.[1345] The ^{31}P chemical shifts of *cis* isomers are usually upfield of the *trans* isomers.[1346]

For platinum phosphine complexes values for $^2J(PP)$ and $^1J(PtP)$ may be obtainable. The magnitude of $^2J(PP)$ for mutually *cis* phosphines usually falls in the range 0–100 Hz, and for *trans* phosphines between 500 and 1000 Hz. This coupling constant depends directly on the value of the valence *s* orbitals at the phosphorus nuclei. The observed increase in coupling with the increasing electronegativity of the substituents correlates with the proposed increase in *s* character of the Pt—P bond.[1347] The coupling constant from the Pople and Santry expression depends inversely on the energy difference of the transition, hence on the effective nuclear charges of the metal and phosphorus nuclei. Platinum–phosphorus coupling constants are large (1000–7500 Hz), and are strongly dependent on the ligand *trans* to the phosphorus atom. Ligands with a strong σ-inductive character reduce the positive charge on the platinum atom and thereby weaken the overlap of the phosphorus and metal orbitals relative to *trans* ligands, which have weaker σ-inductive effects. For chelate complexes ring effects must also be taken into account. The effect on coupling constants is quite small, but the contribution of ring size to chemical shift data is quite significant.[1348,1349] Fine points such as ligand substituent effects can be observed. For the series of compounds *cis*-$[PtMe(L)(dppe)]PF_6$ (L is a *para*-substituted pyridine) the values for $\delta(^{31}P)$ and $^{1}J(PtP)$ decrease regularly as the ρ values of the substituents on pyridine decrease.[1350] Chemical shift and coupling constant data for 44 complexes of type *trans*-$PtXY(PEt_3)_2$ and $PtWXYZ(PEt_3)_2$ show that $^{1}J(PtP)$ is positive in sign, and that for hydrides (X = H), $^{1}J(PtH)$ is positive and $^{2}J(PH)$ negative.[1351] Values for $\delta(^{195}Pt)$ are reported for these complexes. Furthermore $\delta(^{195}Pt)$ has been measured for 78 platinum complexes having mainly Pt—C bonds. Detailed analyses of the shift magnitudes caused by changing ligands and substituents on ligands are given and correlated. Values for $^{1}J(PtP)$ decrease on going from Pt^{II} to Pt^{IV}, and increase with halogen substitution. The trends observed in $\delta(^{31}P)$ show increases in ^{31}P shielding associated with decreasing aromatic substitution on phosphorus and increasing halogen substitution on platinum. This detailed article gives the reader an excellent introduction to this NMR literature up to the mid-1970s.[1352]

For platinum(II) complexes with alkylphosphine ligands there is a small but marked dependence of the values $^{1}J(PC)$ on the nature of the group *trans* to phosphine.[1353] By analogy with the earlier method using ^{1}H NMR, $^{13}C\{^{1}H\}$ NMR techniques using 'virtual coupling' have been used for phosphite complexes of platinum(II), but it does not appear that the method can be generally used to determine stereochemistry.[1354]

Two features need to be noted. Firstly, platinum-195 chemical shifts are quite sensitive to temperature, and in order to obtain acceptably narrow lines the solution temperature should be kept constant over the data accumulation time. Secondly, solvent effects need to be considered. A study of *cis*- and *trans*-$PtCl_2(PBu^n_3)_2$ in 14 solvents shows a change in $\Delta\delta(P)$ of only 0.83 p.p.m., but a change in $\Delta^{1}J(PtP)$ of 84.2 Hz between *n*-hexane and acetonitrile.[1355] Further work on temperature, solvent, substituent, oxidation state and stereochemical effects on ^{31}P and ^{195}Pt NMR chemical shifts and complexes is needed, and further efforts to collect and correlate data will be very useful.[1356–1358]

Two other applications of NMR in platinum phosphine chemistry are noteworthy. Variable temperature ^{1}H and ^{19}F NMR spectroscopy can be used to show that in $PtX_2(C_6F_5)_2(PEt_3)_2$ the rotation of the phosphine ligands is prevented by steric interaction with the *cis*-pentafluorophenyl groups,[1359] and ^{31}P magic-angle spinning NMR can be used to investigate platinum(II) complexes attached to the phosphorus atoms of a polymer-immobilized phosphine ligand.[1360,1361]

Using empirical IR methods for complexes $PtXY(PPh_3)_2$ the stereochemistry can be assigned. A band at 550 cm^{-1} is very strong in the IR spectra of *cis* complexes, but weak in those of *trans* stereochemistry.[1362] This band is probably associated with a P—phenyl mode since bands due to $\nu(PtP)$ are usually weak and have not been assigned with certainty in many cases.

The electronic spectra of platinum(II) phosphine complexes are difficult to assign because the *d–d* bands are obscured by intense charge-transfer bands. Work with *trans*-$PtCl_2$(piperidine)(L) shows that the first allowed transition decreases in energy across the series: L = $P(OMe)_3 > PPr_3 >$ piperidine $> AsPr_3 > Et_2S > Et_2Se > Et_2Te$.[1363] There is no evidence of low-lying π combinations of phosphorus 3*d* orbitals in the absorption spectra.[1364]

(*iv*) *Reactions*

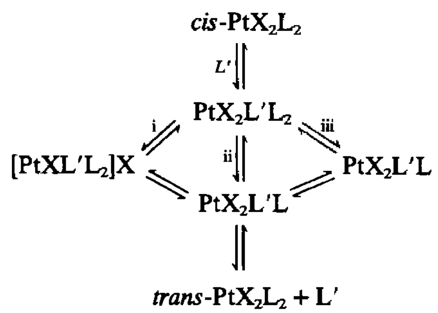
The chemistry of platinum(II) phosphine complexes usually centers around substitution reactions. The phosphine ligands bind strongly to platinum(II), and are not readily substituted. Much of the discussion involving these reactions is concerned with the *trans* influence and *trans* effect exerted by the phosphine ligands. In general the distinction between the two features is that the *trans* influence compares ground state effects, and the *trans* effect relates to differences in substitution rates. The *trans* influence has been reviewed in 1973.[509,510] Phosphine and phosphite ligands are high in both the *trans* influence and *trans* effect series. For the former these effects are apparent in $\nu(PtX)$, bond distances of *trans* ligands, $^{1}J(PtP)$, $\nu(PtH)$ and $^{1}J(PtH)$ in hydrides, as well as correlations of NQR and Mössbauer data.

Although the high *trans* effect of phosphine ligands is well known,[1365] a recent paper has made a comparison between phosphines and trimethyl phosphite. In a rate study it has been found that the relative *trans* effect depends on the reaction being studied, although in all cases the *trans* effect of $P(OMe)_3$ is greater than PMe_3, PEt_3, PBu^n_3 or PPh_3.[1366] All rates show that the *trans* effect of these P-bonded ligands is greater than that of $AsEt_3$, Me_2S or DMSO.

From these considerations it is clear that phosphorus ligands are strong σ donors, and that the order follows the sequence $PR_3 > PPh_3 > P(OR)_3 > PCl_3 > PF_3$.[1367]

A reaction which has been studied in some detail is the isomerization between *cis* and *trans* phosphine complexes of platinum(II). As mentioned earlier in this section on platinum(II) complexes with phosphorus ligands, synthetic routes to $PtX_2(PPh_3)_2$ usually give the *cis* isomer. An isolated yield of 42% for the *trans* isomer can be obtained by irradiation of *cis*-$PtX_2(PPh_3)_2$ at 336 nm (equation 413).[1368] Two different mechanisms were initially proposed for the *cis–trans* isomerization of square planar complexes PtX_2L_2 (L = monodentate phosphorus ligand). These were either the consecutive displacement of the anion X *via* the intermediate $[PtXL'L_2]^+$, where L′ is a catalyzing base, or the fluxional rotation in a pentacoordinate intermediate PtX_2L_2L' having a unique Pt—L′ bond. A third pathway has also been found which involves displacement of L from the pentacoordinate intermediate. Pathway i (in Scheme 12) should dominate in polar solvents, when X^- is poorly coordinating, and when L′ is a strong base. Pathway ii is fluxional rotation and should dominate in non-polar solvents when L and L′ have nearly the same basicity and are small. Pathway iii is consecutive displacement of ligand and should dominate in non-polar solvents when X^- is strongly coordinating.[1369] In the absence of added ligand L′ or a coordinating solvent or base, autocatalyzed isomerization can occur by phosphine dissociation from PtX_2L_2, followed by phosphine catalyzed isomerization of PtX_2L_2 (equation 414).[1370]

$$cis\text{-}PtX_2(PPh_3)_2 \xrightleftharpoons{366\,nm} trans\text{-}PtX_2(PPh_3)_2 \qquad (413)$$

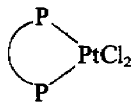


Scheme 12

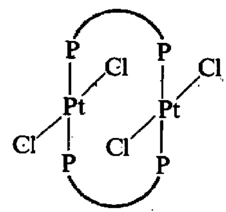
$$PtX_2L_2 \rightleftharpoons PtX_2L + L \rightleftharpoons PtX_2L_2 \qquad (414)$$

52.5.3.3 Chelating phosphorus ligands complexed to platinum(II)

The most common ligands are the ones $Ph_2P(CH_2)_nPPh_2$. These compounds will form chelate complexes PtX_2L_2 which necessarily have the *cis* geometry for X.[1225] The methods of synthesis parallel those used for the monodentate phosphine complexes. As will be discussed later, the complex with $n = 1$ (dppm) has a strong tendency to form a bridge across two platinum centers. Comparison between the ligands $Ph_2P(CH_2)_nPPh_2$ for coordination to platinum(II) shows monomeric complexes are formed when $n = 1$ and 2, dimeric complexes when $n = 3$ (N.B. monomer with Pd^{II}) and with $Ph_2PCH{=}CHPPh_2$, and trimers when $n = 4$ (**120–122**).[1371] If these chelating phosphines are used to replace cod in PtMeCl(cod), ligands $n = 2, 3$ give monomers PtMeCl(P—P), whereas dppm ($n = 1$) gives a trimeric complex $[PtMeCl(P—P)]_3$. Obviously all the features controlling molecular aggregation have not been identified. Using an analogous procedure the compounds $PtMe_2(P—P)$ ($n = 1–3$) can be prepared. For $PtMe_2$(dppm) and $PtMe_2$(dppe), methyl iodide addition gives $PtMe_3I$(dppm) and $PtMe_3I$(dppe), whereas $PtMe_2$(dppp) gives PtMeI(dppp).[1372] The complexes $PtCl_2(P—P)$ have also been obtained where methyl substituents are present on the phosphine $Me_2PCH_2CH_2PMe_2$; alternatively the neopentyl or *t*-butyl ligands $R_2PCH_2CH_2PR_2$ can be used.[1373–1375] Similarly the complexes $PtCl_2(P—P)$ can be formed with unsymmetrically substituted phosphine ligands $R_2PCH_2CH_2PAr_2$ (R = alkyl; Ar = aryl).[1373] An unsymmetrically substituted chelating phosphine complex (**123**) has been formed by an *in situ* reaction of $PtX_2(Ph_2C{\equiv}CR)_2$ with R′R″PH (R = CF_3, Ph; R′R″ = Ph, C_2H_4CN; R′ = Et, R″ = Ph) to give stereospecifically compound (**123**; equation 415).[1376] The less usual *cis* chelating ligands $Ph_2P(B_{10}H_{10}C_2)PRR'$ (R = R′ = Ph, NMe_2F; R = NMe_2, R′ = F) and $(Me_2N)_2P(B_{10}H_{10}C_2)$-PRR′ (R = R′ = C_6F_5; R = NMe_2, R′ = F) also form chelate complexes of the type $PtCl_2(P—P)_2$. NMR data are used to develop trends in *cis* and *trans* influences by comparison with other chelating phosphine ligands.[1377]

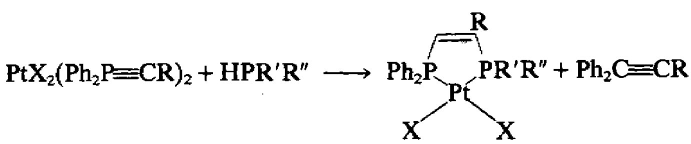


(120) $n = 1, 2$



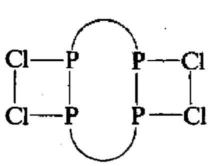
(121) $n = 3$, $Ph_2PCH{=}CHPPh_2$

$[PtCl_2\{Ph_2P(CH_2)_4PPh_2\}]_3$
(122)



(123) (415)

In a similar manner to the *trans* spanning aromatic ligand studied by Venanzi,[168] *trans* isomers, as well as *cis*, can be obtained using ditertiary phosphines which have long aliphatic chains between the two phosphorus atoms. The ligands which have been primarily used have either bulky aliphatic groups such as Bu^t bonded to phosphorus, or phenyl groups. Such ligands are $Bu^t_2P(CH_2)_nPBu^t_2$ ($n = 5$–10).[1378–1382] With $PtCl_2(PhCN)_2$, $Bu^t_2P(CH_2)_5PBu^t_2$ gives *trans*-$[PtCl_2(Bu^t_2P(CH_2)_5PBu^t_2)]_x$ and a cyclometalated product.[1380] Using ^{31}P NMR spectroscopy, it has been shown that the large-chelate mixed compounds containing PBu^t_2 groups in 'corner' positions are stable in solution relative to open-chain structures. This substituent promotion of rings is compared with the Thorpe–Ingold or *gem*-dimethyl effect.[1380] The ligands which form these strain-free large-ring binuclear complexes ('large' complexes) are ones with an even number of methylene groups between the two phosphorus atoms. The requirement of bulky terminal groups is not completely resolved, and more recently McAuliffe has suggested that bulky terminal substituents on the donor phosphorus atoms is not a prerequisite for *trans* chelation.[1383] The formation of *cis* and *trans* isomers of long-chain flexible bis(phosphine) ligands $Ph_2P(CH_2)_nPPh_2$ appears to be critically dependent on the choice of complex precursor; K_2PtCl_4 gives the *cis* isomer while $K[PtCl_3(C_2H_4)]$ gives the *trans* analogue. The *cis* dimers (**124**) are the most stable isomers for the majority of the *cis* complexes. The preferred ring sizes for the *cis* chelated monomers (**125**) are 14- and 19-membered chelate rings. The amount of *trans* monomer (**126**) increases with a chelate ring size of 15. Large flexible chelate rings (>19) are unstable in the *trans* configuration.[1383] A similar chemistry has been developed with the unsymmetrical chelate ligand $Ph_2P(CH_2)_6P(Et)Ph$.[1384] The design and synthesis of new chelating phosphine ligands which can form large rings or span *trans* positions will continue to develop. An example is the diphosphine complex (**128**) with an oxygen heteroatom in the ring. The complex undergoes ring metalation to (**129**) at 250 °C (equation 416).[1385]



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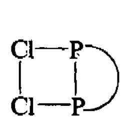

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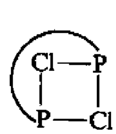

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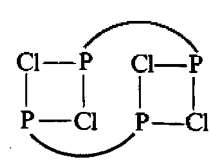

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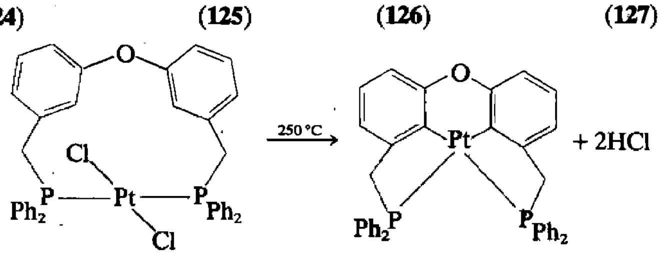
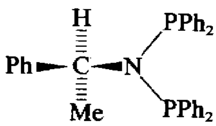
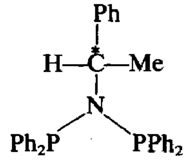


(128) (129) (416)

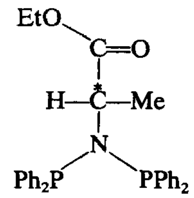
Platinum(II) complexes can be used to resolve triphosphamides.[1386] Also platinum(II) complexes with chiral bidentate phosphine ligands can be synthesized. The bidentate phosphine ligand (**130**) will form the chelate complex Pt{$C_2(CF_3)_2$}(P—P) (P—P is (−)-(*N,N*-bis(diphenylphosphino)-1-phenethylamine). The structural and spectral parameters show good correlation between the solid state and solution state.[1387] A series of platinum(II) complexes with ligands (**131**) and (**132**) has been prepared. The complexes are PtMeCl(L—L) and [PtMe(X)(L—L)]ClO_4 (X = acetone; *p*-Ypy where Y = Me, Et, CHO, CO_2Me, H, NMe_2; or X = PEt_3, PPr_3, $P(C_8H_{17})_3$, PPh_2Me, $PPhMe_2$, PPh_3, PPh_2Cy, $PPhCy_2$, PCy_3, $PPh_2(NEt_2)$, $AsPh_3$, $SbPh_3$).[1388] A partial resolution has been achieved for complexes PtMe($\overset{*}{P}$)(P—P) ($\overset{*}{P}$ is a chiral phosphine PPhR′R″; P—P is a chiral bidentate phosphine). The resolution can be monitored by ^{31}P NMR and ORD, and the configuration of the preferentially bound enantiomer obtained by X-ray crystallography.[1389]



(**130**)



(**131**)

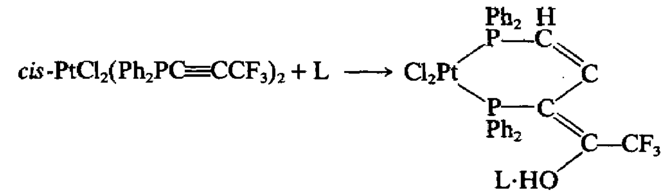


(**132**)

Although dppm is better known for complexes where the ligand bridges two transition metal centers, the homoleptic complex of the anion from dppm, $Pt(Ph_2PCHPPh_2)_2$ (**133**), can be synthesized from $PtCl_4^{2-}$ and dppm with KOH in ethanol. The complex gives $Pt(Ph_2PCHPPh_2)(dppm)^+$ on protonation, and $[Pt(dppm)_2]Cl_2$ on treatment with HCl (equation 417).[1390,1391] If the complex *cis*-$PtCl_2(Ph_2PC{\equiv}CCF_3)_2$ is treated with amine bases L, ligand coupling occurs to give a new bidentate ligand (equation 418).[1392]

$$PtCl_4^{2-} + 2dppm \xrightarrow{KOH} \underset{(\mathbf{133})}{Pt(Ph_2PCHPPh_2)_2} \xrightarrow{H^+} Pt(Ph_2PCHPPh_2)(dppm)^+ \quad (417)$$

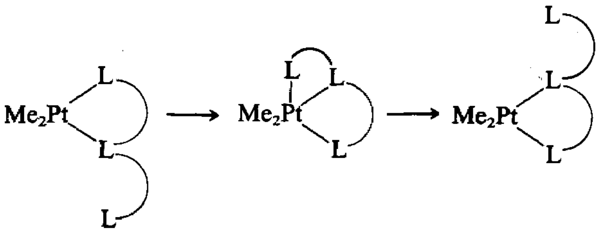
$$Pt(Ph_2PCHPPh_2)_2 \xrightarrow{HCl} [Pt(dppm)_2]Cl_2$$



(418)

52.5.3.4 Polydentate phosphorus ligands complexed to platinum(II)

Platinum(II) will form square planar complexes [PtCl(L—L—L)]X with the ligands $PhP(CH_2CH_2PMe_2)_2$, $PhP(CH_2CH_2PPh_2)_2$ and $Me_3CCH_2P\{CH_2CH_2P(CH_2CMe_3)_2\}_2$.[1373,1374] For recent reviews on both polydentate phosphine ligands and on polymer-bound phosphine catalysts the reader is referred to the chapters by Meek and by Holy in ref. 1227. The platinum(II) complexes with the tripod ligand $PhP(CH_2CH_2CH_2PPh_2)_2$(L—L—L) giving six-membered rings can be prepared for a wide range of X groups in [PtX(L—L—L)]$^+$ (X = Cl, NCS, NO_2, H, Me, CH_2CN, CO_2Me, $CH_2CH{=}CH_2$, Ph) and in [Pt(L—L—L)Y]$^{2+}$ (Y = PEt_3, $P(OMe)_3$).[1393] ^{31}P NMR spectroscopy of the methyl complexes $PtMe_2$(L—L—L) shows that one phosphine remains unbonded. For $PtMe_2$(L—L—L—L) two terminal phosphorus atoms are free. Exchange between the phosphorus atoms occurs by an associative pathway *via* a pentacoordinate intermediate (equation 419).[1394] A tetradentate phosphine ligand has been prepared which wraps around the platinum(II) center rather than chelating as a tripod-type ligand. Using the ligands $H_{2-n}R'_nP(CH_2)_3PR''(CH_2)_3PR''(CH_2)_3PR'_nH_{2-n}$, the five-coordinate complexes (**134**) can be prepared.[1395] Similar complexes with the tridentate analogue can be prepared (**135**).[1396]



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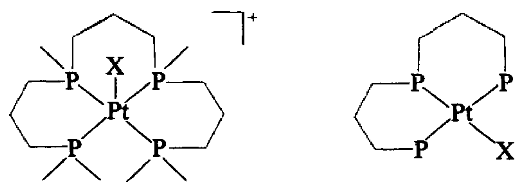


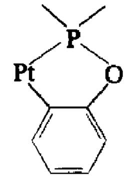
(**134**) (**135**)

Deprotonation of $HN(SiMe_2CH_2PPh_2)_2$ with Bu^nLi followed by reaction with $K[PtCl_3(C_2H_4)]$ gives $PtClN(SiMe_2CH_2PPh_2)_2$ (**136**; equation 420). With the amine protonated, reaction with $PtCl_2(cod)$ gives $PtCl_2\{HN(SiMe_2CH_2PPh_2)_2\}$.[1397] In the complex (**136**) the ligand is tridentate.

$$K[PtCl_3(C_2H_4)] + LiN(SiMe_2CH_2PPh_2)_2 \longrightarrow \underset{(\mathbf{136})}{PtClN(SiMe_2CH_2PPh_2)_2} + C_2H_4 + KCl + LiCl \quad (420)$$

52.5.3.5 Carbon-metalated phosphine and phosphite complexes

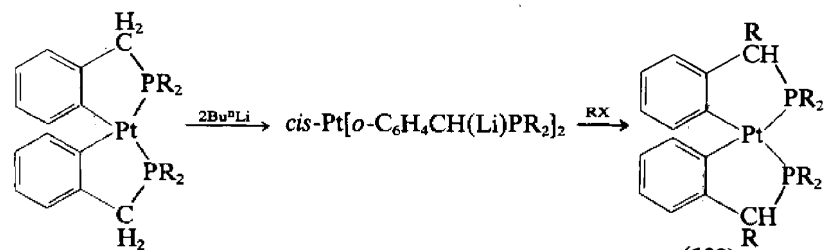
This reaction has been previously covered for amine ligands, but it needs to be reemphasized for phosphine and phosphite complexes because of its frequent occurrence with these P-bonded complexes. The reaction occurs with both aromatic and aliphatic phosphine and phosphite complexes, and is particularly observed for aryl phosphites $P(OAr)_3$, because metalation at the *ortho* position of the aryl ring leads to the formation of unstrained five-membered ring complexes (**137**). Refluxing *cis*-$PtCl_2\{P(OPh)_3\}_2$ in decalin gives $PtCl\{(PhO)_2POC_6H_4\}$-$\{P(OPh)_3\}$, probably by an initial C—H oxidative addition.[1398,1399] This metalation reaction is favored for platinum(II) over palladium(II), and the rate of ring closure follows the sequence Cl > Br > I, opposite to that found for phosphine complexes.[1400] In a detailed study with complexes of bulky phosphines, Shaw has carried out internal metalations of platinum(II) complexes *trans*-PtX_2L_2 (X = Cl, Br, I; L = PPh_2Bu^t, $P(p\text{-tolyl})_2Bu^t$, $PPhBu^t_2$, $P(p\text{-tolyl})Bu^t_2$, $PBu^tPr^n_2$, $PBu^t_2Pr^n$, $PPh(o\text{-tolyl})_2$, $P(o\text{-tolyl})Me_2$) to effect ring closure. Bulky substituents on tertiary phosphines promote internal Pt—C bond formation, and the reaction is favored with a greater number of bulky groups on phosphorus. *o*-Tolylphosphines can promote ring closure, but tertiary phosphines with smaller steric requirements do not metalate. The corresponding palladium(II) complexes with these bulky phosphines show no tendency to metalate.[1401] Analogous Pt—C metalated complexes of Pt^{II} are formed from PBu^t_3[1402–1404] and $PBu^t_2Bu^i$.[1405] In this latter case, metalation also occurs with palladium(II). In some cases the *ortho*-metalated carbon ligand can be coordinated to a platinum hydride without reductive elimination of alkane (equation 421a).[1406] Butyllithium can, however, attack the methylene group of a metalated benzylphosphine platinum(II) complex to give the dianion, which can be homologated by MeI or Me_3SiCl to give (**138**; equation 421b).[1407]



(**137**)

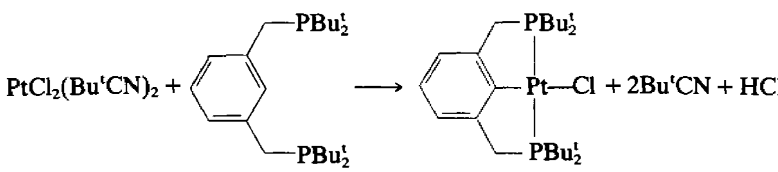
$$PtCl(P{-}C)(PR_3) + H^- \longrightarrow PtH(P{-}C)(PR_3) + Cl^- \qquad (421a)$$

$$P{-}C = Bu^t_2PCMe^t_2CH_2;\ PR_3 = PEt_3,\ PPh_3,\ PPr^i_3,\ PBu^t_2Me,\ PBu_3,\ P(tolyl)_3,\ P(OPh)_3$$

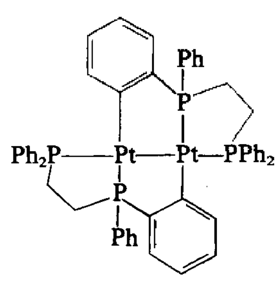


(138) (421b)

The *t*-butyldiphosphines with large chelate rings will also undergo metalation either by thermolysis reactions or as side-products in the synthesis of the chelate complexes.[1380,1382] The *trans* spanning ligand 1,3-{(di-*t*-butylphosphino)methyl}benzene will undergo very ready metalation to give (**139**) when treated with $PtCl_2(Bu^tCN)_2$ (equation 422).[1408] Thermolysis of PtMe(OH)dppe gives an unusual Pt^I—Pt^I complex (**140**) formed by metalation of one phenyl ring at each platinum.[1409] Other metalated complexes are ones with platinum(II) bonded to the vinylic carbon of 1,2-bis(diphenylphosphino)ethylene[1410] and the carbon of a phosphorus-substituted cyclopentadienylide.[1411]



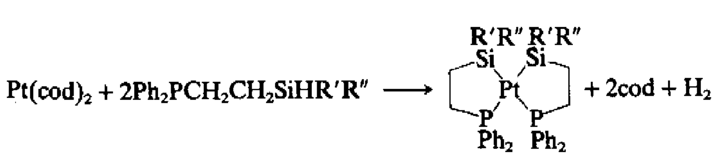
(139) (422)



(140)

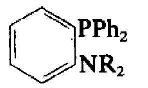
52.5.3.6 *Phosphine ligands chelated with other heteroatoms*

A platinum(II) complex has been prepared with a phosphine ligand chelated with a silyl. The complex (**141**) is formed by treating $Pt(cod)_2$ with $Ph_2PCH_2CH_2SiHR'R''$ (equation 423).[1412] When $R' \neq R''$, racemic and *meso* diasteromers are formed in varying ratios consistent with asymmetric induction during stepwise chelation. The complexes can be used for asymmetric hydrosilylation.[1413]

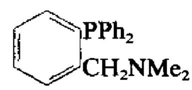


(141) (423)

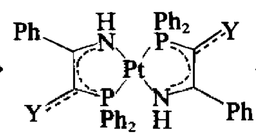
Phosphine complexes chelated with amine nitrogen ligands are more common. Early examples of such complexes include platinum(II) compounds with diphenylphosphino-substituted tertiary amines such as (**142**; R = Me) and (**143**). Both covalent $PtCl_2(o\text{-}Ph_2PC_6H_4NMe_2)$ and ionic $[Pt(o\text{-}Ph_2PC_6H_4NMe_2)_2](ClO_4)_2$ complexes can be prepared.[1414,1415] The primary amine derivative (**142**; R = H) presents more of a synthetic challenge, but the compound will also give the complex $[Pt(o\text{-}Ph_2PC_6H_4NH_2)_2]^{2+}$, which will deprotonate in base to give $[Pt(o\text{-}Ph_2PC_6H_4NH)(o\text{-}Ph_2PC_6H_4NH_2)]^+$ and $Pt(o\text{-}Ph_2PC_6H_4NH)_2$.[1416,1417] The *in situ* formation of a P—N chelate ligand occurs when $PtCl_2(NCPh)_2$ reacts with 2 equivalents of $Li[Ph_2PCHY]$ (Y = CN, CO_2Et) (equation 424).[1418] The platinum(II) complexes with 8-amino-, 8-diphenylphosphino- and 8-diphenylarsino-quinoline ligands can be prepared.[1419]



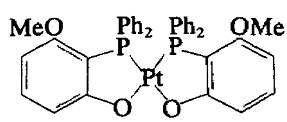
(142)



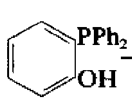
(143)

$PtCl_2(NCPh)_2 + 2Li[Ph_2PCHY] \longrightarrow$  $+ 2LiCl + 2PhCN$ (424)

Phosphine complexes have been prepared with an ether functionality in a suitable position for coordination. In contrast to the chelate complexes with (**142**) the analogous ether ligand coordinates to platinum(II) solely *via* phosphorus to give $PtCl_2(o\text{-}Ph_2PC_6H_4OMe)_2$.[1415] The compounds $PtBu^t_2R$ and PPh_2R (R = 2,3- or 2,6-dimethoxyphenyl) P-bond to platinum, and the complexes undergo O-demethylation. Stable complexes *cis*-$Pt\{OC_6H_3(OMe)(PPh_2)\}_2$ (**144**) and *trans*-$Pt\{OC_6H_3(OMe)(PBu^t_2)_2\}_2$ have been prepared where the ligand chelates through the phenoxy oxygen and the phosphino group. Bulky phosphines are demethylated more readily on coordination to platinum.[1420] Complexes of type (**144**) can be prepared from the monomethylated compound $o\text{-}Ph_2PC_6H_4OMe$[1421] and from $o\text{-}Ph_2PC_6H_4OH$.[1422] The reaction of $o\text{-}Ph_2PC_6H_4OH$ gives two intermediates (**145** and **146**; equation 425)[1422,1423] prior to the formation of the bis phenoxy complex (**144**).

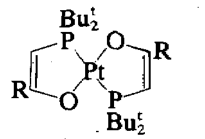


(144)

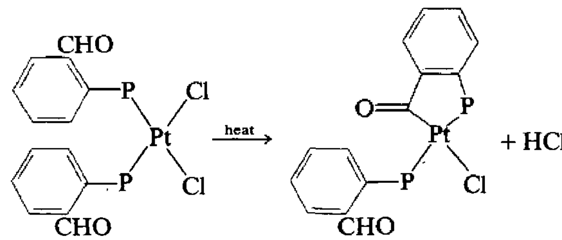
$PtCl_4^{2-} + 2$  $\longrightarrow Cl_2Pt(o\text{-}Ph_2PC_6H_4OH)_2 \longrightarrow ClPt(o\text{-}Ph_2PC_6H_4O)(o\text{-}Ph_2PC_6H_4OH)$ (425)

(145) **(146)**

Chelate complexes can be prepared with phosphine and ester oxygen functional groups bound to platinum(II). The ligands used are $Bu^t_2P(CH_2)_nCO_2Et$ ($n = 1, 2, 3$). Complexes of type $PtCl_2L_2$ with P bonded to platinum(II) have been formed, as well as binuclear complexes $Pt_2Cl_4L_2$ when $n = 2$ and 3. Refluxing in ethanol or toluene solvent leads to O-metalation ($n = 1$) to give $PtX(OCOCH_2PBu^t_2)(Bu^t_2PCH_2CO_2Et)$, or C-metalation ($n = 3$) to give $Pt_2Cl_2(Bu^t_2PCH_2CH_2CHCO_2Et)_2$.[1424] The complexes with ketophosphines *trans*-$PtCl_2\{Bu^t_2P(CH_2COR)\}_2$ remain unchanged on refluxing in alcohol, but treatment with sodium 2-methoxyethoxide causes ring closure to give $Pt\{Bu^t_2PCH{=}C(O)R\}_2$ (**147**).[1425] The compound *o*-diphenylphosphinobenzaldehyde complexes to platinum(II) *via* phosphorus in the compound *cis*-$PtCl_2(o\text{-}Ph_2PC_6H_4CHO)_2$. Vacuum thermolysis results in loss of HCl and chelation *via* carbon (equation 426).[1426] An acetylacetonate phosphine ligand has been prepared. The compound coordinates to platinum(II) *via* phosphorus but the acetylacetonate functionality will complex to subsequently added copper(II) ion.[1427]



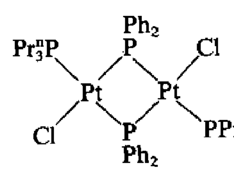
(**147**)



(426)

52.5.3.7 *Phosphido-bridged complexes*

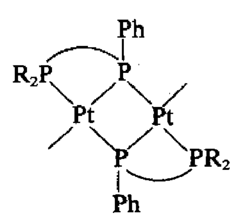
The compound $Pt_2Cl_2(\mu\text{-}Cl)_2(PPr^n_3)_2$ reacts with $PHPh_2$ to give *cis*-$PtCl_2(PPr^n_3)(PHPh_2)$, which reacts with base to form $Pt_2Cl_2(\mu\text{-}PPh_2)_2(PPr^n_3)_2$ (**148**). Alternatively the compound can be prepared from *cis*-$PtCl_2(PPr^n_3)_2$ and $LiPPh_2$.[1428] The dialkylphosphido and diarylphosphido ligands form strongly bridged complexes, although complexes of palladium(II) are more common than those of platinum(II). Treating $PtCl_2(PhCN)_2$ with $PHPh_2$ gives the diphenylphosphido-bridged diphenylphosphine complex $Pt_2Cl_2(\mu\text{-}PPh_2)_2(PHPh_2)_2$ with HCl loss (equation 427).[1429] The complex $[Pt_2(\mu\text{-}PPh_2)_2(dppe)_2]Cl_2$ has also been prepared, and the NMR spectrum solved using higher order methods of analysis. The structure of $[Pt_2(\mu\text{-}PPh_2)_2(dppe)_2]Cl_2$ shows a chelating diphosphine and a bridging diphenylphosphide group. The Pt—P—Pt angle is 103.9(0)°, and the platinums are non-bonding at a distance of 3.699(1) Å.[1430]



(**148**)

$$2PtCl_2(PhCN)_2 + 4PHPh_2 \xrightarrow[-4PhCN]{-2HCl} Pt_2Cl_2(\mu\text{-}PPh)_2(PHPh_2)_2 \quad (427)$$

Chelating phosphines can be used to generate phosphido bridges. Reacting either $Ph_2PCH_2CH_2CH_2P(H)Ph$, $Cy_2PCH_2CH_2CH_2P(H)Ph$ or (*pro-R,pro-S*)-$Cy_2PCH_2CH_2CH_2$-P(H)Ph with platinum(II) halides in the presence of base gives the bimetallic bridged complexes of type (**149**).[1431,1432]



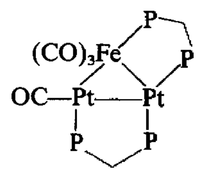
(**149**) ⌒ = $(CH_2)_3$

52.5.3.8 *Bridged binuclear complexes*

(*i*) *Complexes of dppm*

The chemistry of dppm has been recently reviewed by Puddephatt[1228,1433] and by Balch.[1227] The ligand will form either four-membered ring chelate complexes or bridged binuclear complexes.

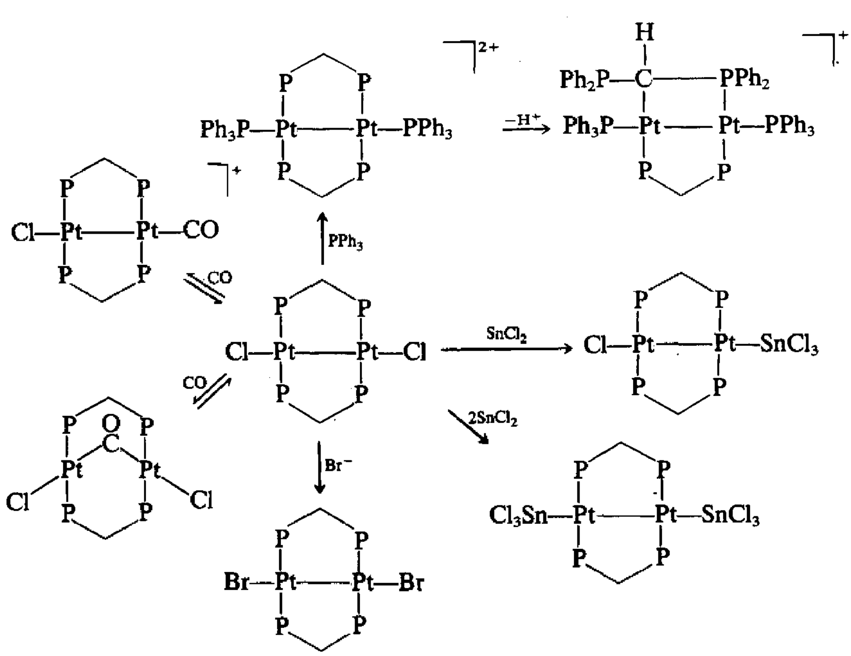
A bridged binuclear platinum(0) complex of dppm is $Pt_2(dppm)_3$. The compound appears to have been first prepared by Vaska,[1434] who found that the compound would catalyze the oxidation of CO to CO_2 with molecular oxygen, and the conversion of NO and CO into N_2O and CO_2. Subsequently the synthesis of the complex has been published, and the red compound can be obtained either by treating $Pt(PPh_3)_3$ with two equivalents of dppm, or by the reduction of $Pt_2Cl_2(\mu\text{-dppm})_2$ with ethanolic KOH in the presence of two equivalents of dppm. The complex is extremely reactive to CO, SO_2, S_8, O_2, MeI, EtI, CH_2Cl_2, CH_2I_2, C_2H_2, $AuCl(PPh_3)$, Ph_3SnCl, Bu_3SnCl_4 and $HgCl_2$.[1435] The structure of $Pt_2(dppm)$ shows a 'manxane'-type geometry with trigonal planar coordination about the platinums. The Pt—Pt separation is relatively long (3.023(1) Å), lying outside the usual range for Pt—Pt bonds in clusters (2.61–2.79 Å).[1436] The zerovalent platinum complexes $Pt_2Fe(dppm)_2(CO)_4$ and $PtPdFe(dppm)_2(CO)_4$ have been prepared by treating $Pt_2Cl_2(dppm)_2$ and $PtPdCl_2(dppm)_2$ with $Na_2Fe(CO)_4$. The diplatinum complex is shown by NMR spectroscopy to have structure **(150)**.[1437]



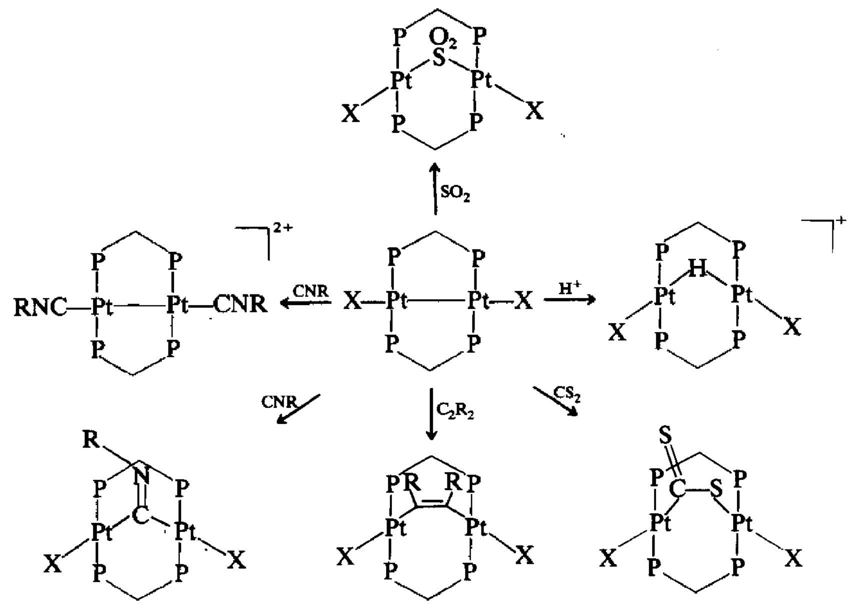
(150) P⌒P = dppm

A number of dppm complexes with hydride and methylene bridges have been referenced already in this chapter under the respective sections on hydrides and carbenes. These compounds will not be included again here. The binuclear platinum(I) chemistry of these complexes has also been developed. The complexes have a metal–metal bond between platinums, although this may be broken by formation of A-frame type molecules. This chemistry has been described in a series of papers, and the reaction types are outlined in Schemes 13 and 14.[1288,1438–1445] A similar chemistry will likely develop with the methylated ligand $Me_2PCH_2PMe_2$.[1450]

$$3PtMe_2(dppm) + HCl \longrightarrow PtClMe(dppm) + [Pt_2Me_2(\mu\text{-Cl})(\mu\text{-dppm})_2]Cl \quad (428)$$



Scheme 13



Scheme 14

$$2PtCl(COPh)(cod) + dppm \longrightarrow [Pt_2(COPh)_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]Cl + 2cod \quad (429)$$

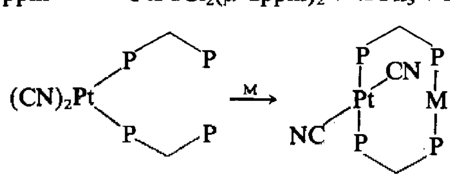
$$PtMe_2(dppm) + PtMeCl(dppm) \longrightarrow [Pt_2Me_3(\mu\text{-}dppm)_2]Cl \quad (430)$$

$$[Pt_2Me_3(\mu\text{-}dppm)_2]BF_4 + Ph_3C^+BF_4^- \longrightarrow [Pt_2Me_2(\mu\text{-}dppm)_2](BF_4)_2 \quad (431)$$

A-frame complexes which have a bridging hydride ligand, or which are capable of rearranging rapidly to a complex with a bridging hydride, undergo A-frame inversion on the NMR time scale. This A-frame inversion occurs through an intermediate with a linear Pt—H—Pt group.[1451]

Complexes having a bridging dppm ligand across two different metals have been recently prepared. Treating $Pd(PPh_3)_4$ with dppm and the complex $PtCl_2(NCBu^t)_2$ in stoichiometric ratios gives a very high yield of $PtPdCl_2(\mu\text{-}dppm)_2$ (equation 432).[1452] The monomeric complexes *trans*-$Pt(C{\equiv}CR)_2(\eta^1\text{-}dppm)_2$ can also be converted to $Pt_2(C{\equiv}CR)_4(\mu\text{-}dppm)_2$ by refluxing in toluene,[1453,1454] or used to prepare heterobimetallic complexes with Pt and Rh, Ir, W, Ag, Hg, Mo, Pd (equation 433).[1455–1460]

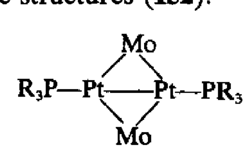
$$Pd(PPh_3)_4 + PtCl_2(NCBu^t)_2 + 2dppm \longrightarrow PtPdCl_2(\mu\text{-}dppm)_2 + 4PPh_3 + 2Bu^tCN \quad (432)$$

$Pt(dppm)_2^{2+} + 2CN^- \longrightarrow$  (433)

(151)

Analogous cyano complexes can be prepared. Treating the bis chelate complex $[Pt(dppm)_2]^{2+}$ with 2 equivalents of NaCN leads to stabilization of the η^1-dppm complex (**151**) which can be used to prepare heterobimetallic bridging complexes with added M ($M = Ag^+/I^-$, $HgCl_2$, $Rh_2Cl_2(CO)_4$) (equation 433).[1461] Similar complexes can be formed with dialkyl and diaryl substituents on platinum in place of cyanide.[1462]

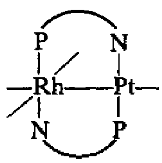
Tetrametallic complexes of type $Pt_2Mo_2Cp_2(CO)_6(PEt_3)_2$ can also be prepared. The complex has a triangulated parallelogram core structures (**152**).[1463]

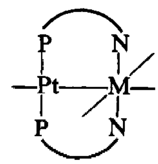


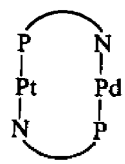
(152)

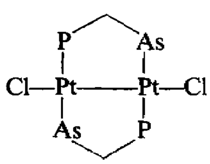
(ii) Complexes with P—N and P—As groups

Ligands with a single carbon atom between phosphorus and a heteroatom have been synthesized and used to prepare heterobimetallic complexes between platinum and a second metal ion. Examples of such complexes are shown in structures (**153**)–(**156**).[1464–1467]


(**153**)


(**154**) M = Mo, W


(also HH, PPt; HH, PPd)
(**155**) P͡N = *o*-Ph_2Ppy

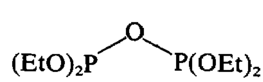

(also HH, PPt)
(**156**)

(iii) Trifunctional PPP ligands

Other modifications require brief mention. The tridentate ligand $Ph_2PCH_2P(Ph)CH_2PPh_2$ coordinates in a monodentate fashion to rhodium and chelates to platinum(II).[1468]

(iv) Ligands with PO and PS functionality

Functional groups other than methylene can be used to join the phosphorus atoms. Tetraethyl diphosphite (POP; **157**) can be used to bridge platinum(II) centers in compounds of type $Pt_2Cl_4(POP)_2$, $Pt_2Cl_4(POP)(PMe_2Ph)_2$ and $[Pt_2(POP)_2(PMe_2Ph)_4](BPh_4)_4$.[1469]

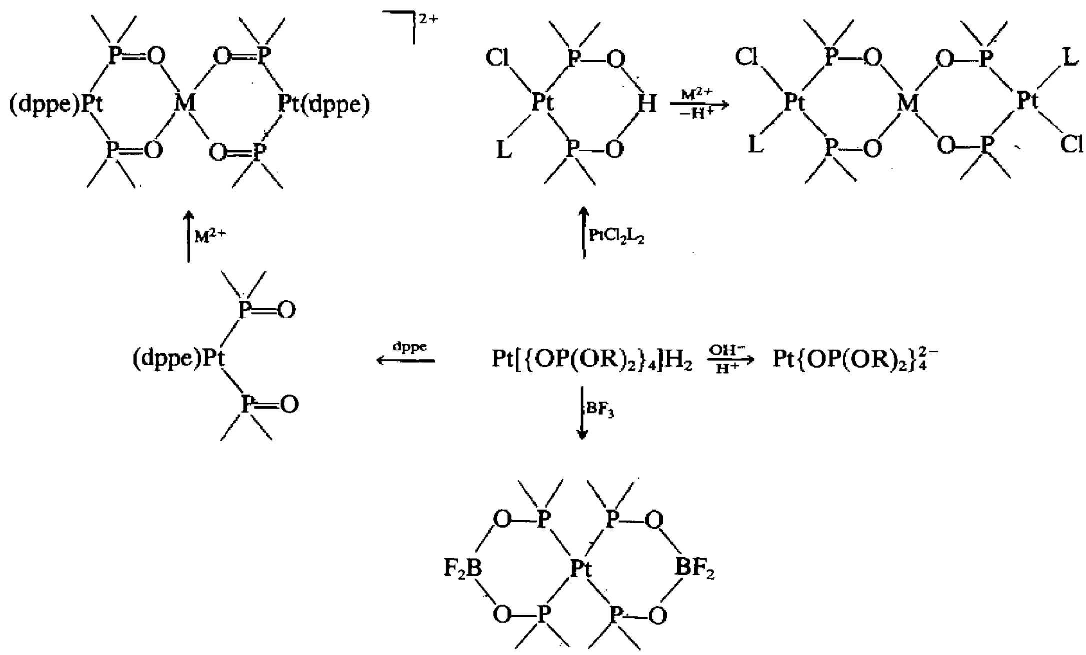

(**157**)

Ligands containing both phosphorus and oxygen functionality are phosphinous acids and secondary phosphites. The chemistry of these compounds with the platinum group of elements is becoming of increasing interest. The coordination chemistry of these compounds has been recently reviewed twice.[1470,1471] Three general methods are commonly used to prepare complexes of this type. These are the hydrolysis of transition metal chlorophosphine complexes, the demethylation of P-bonded methyl phosphite complexes with added nucleophile, and the direct reaction with diarylphosphinous acids or secondary phosphites. Examples of each of these reaction types is shown in equations (434)–(436). The first synthesis of $Pt\{(OPPh_2)_4H_2\}$ was by reaction (436)[1472] and also by the hydrolytic reaction between K_2PtCl_4 and Ph_2PCl.[1473] The phosphite analogues $Pt\{(OP(OR)_2)_4H_2\}$ have been known for a considerable time, having been first prepared by reacting K_2PtCl_4 with $P(OEt)_3$ in aqueous solution.[1474] Alternate routes to these complexes involve P—H addition to platinum(0).[33,1475] The hydroxylic proton in these platinum(II) complexes can be removed by base, or replaced with BF_2 or a second transition metal ion such as Co^{II}, Ni^{II}, Zn^{II}, UO_2, VO, Cu^{III} (Scheme 15).[33,1476,1477] The structures of two BF_2 complexes have confirmed that the PtPOBOP ring is puckered in a chair conformation.[1478,1479] Very recently the structure of $Pt\{(OP(OMe)_2)_4\}H_2$ shows the very short internuclear O···H···O separation of 2.381(1) Å required for the hydrogen bonded structure.[1480] The ^{31}P NMR spectra of these (dppe)$Pt\{OP(OR)_2\}_2$ complexes show an AA′BB′/AA′BB′X spin multiplicity which must be analyzed by second-order methods which include the platinum-195 couplings.

$$2cis\text{-}PtCl_2(PR_2Cl)(PEt_3) + 2H_2O \longrightarrow Pt_2(OH)_2(R_2PO)_2(PEt_3)_2 + 2HCl \quad (434)$$

$$Pt\{P(OMe)_3\}_4^{2+} + 4OH^- \longrightarrow Pt\{OP(OMe)_2\}_4^{2-} + 4MeOH \quad (435)$$

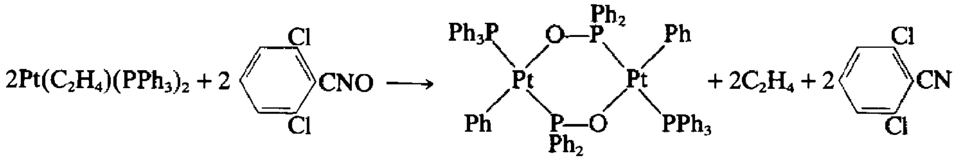
$$PtX_4^{2-} + Ph_2PH(O) \longrightarrow PtX\{(OPPh_2)_2H\}(PPh_2OH) \xrightarrow[Ph_2PH(O)]{AgNO_3} Pt\{(OPPh_2)_4H_2\} \quad (436)$$



Scheme 15

Michaelis–Arbuzov dealkylation of the compounds PF_2OR in the presence of $PtCl_2L_2$ ($L = t$-phosphine) gives *trans*-$PtCl(PF_2O)L_2$. Ionic complexes $Pt(PF_2O)_4^{2-}$ are formed with PF_2OR and $PtCl_2(NMe_3)_2$ (equation 437). The nucleophile present is chloride ion, and the electron-withdrawing fluoro substituents cause the hydrogen-bonded proton to be sufficiently acidic that it is the anion which is isolated.[1482,1483] A rather unusual method of preparing a bridged diphenylphosphinito complex is to react $Pt(C_2H_4)(PPh_3)_2$ with 2,6-dichlorophenylcyanate (equation 438).[1484] The diphenylphosphinite ligand is a moderate bridging group.

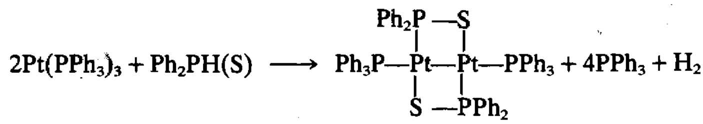
$$PtCl_2(NMe_3)_2 + PF_2OR \longrightarrow (NMe_3H)_2[Pt(PF_2O)_4] + 2RCl \quad (437)$$



(438)

Extension of these ligands to the triphosphorus compound $\{(EtO)_2PO\}_2PO^-$ allows bimetallic platinum(II) complexes to be synthesized where the phosphonato P coordinates to one platinum, and the phosphite P atoms chelate to the second platinum(II) center.[1485]

The diorganosulfide compounds $Ph_2PH(S)$ react with platinum(0) in a different way than do the compounds $Ph_2PH(O)$. Instead of forming hydrides the compound $Ph_2PH(S)$ reacts with $Pt(PPh_3)_3$ to give the bimetallic complex $Pt_2(\mu\text{-}SPPh_2)_2(PPh_3)_2$ (equation 439).[1486] Non-bridging compounds with both the $Pt(PS)_2$ and the PtPSHOP ligands bonded *via* platinum can, however, be prepared from $Pt(S_2CNR_2)(Ph_2PS)(solvent)$ with Ph_2PS^- and $Ph_2PH(O)$ respectively (equation 440).[1487]



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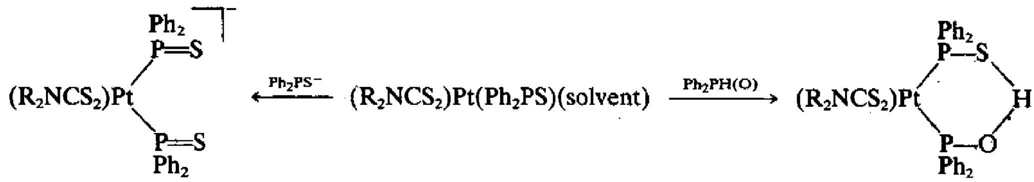
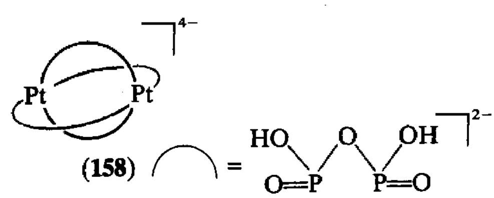


(440)

A diplatinum(II) complex (**158**) with a POP bridging ligand is formed when $PtCl_4^{2-}$ is heated with phosphorous acid at 100 °C (equation 441).[1488,1489] The Pt–Pt separation of 2.925(1) Å corresponds to little or no bonding between platinums. The complex shows a strong absorption peak at 368 nm and an intense phosphorescence at 514 nm. The absorption and emission spectroscopy of this complex has been interpreted in terms of transitions between MO levels at the platinums.[1490–1492] The complex reacts with small quantities of halogen to give solid state samples of the mixed-valent Pt^{II}–Pt^{III} compound (**159**) and with excess halogen or methyl iodide to give the binuclear tetra-bridged platinum(III) complexes $Pt_2(P_2O_5H_2)_4XY^{4-}$ (X = Y = Cl, Br, I; X = Me, Y = I).[1493,1494] The emission can be quenched by BSEP,[1491] sulfur dioxide[1495] and a series of aromatic amines.[1496] In the diplatinum(III) complexes, and in the excited state of the diplatinum(II) complex, the Pt–Pt distance shortens to approximately 2.7 Å, which corresponds to a bonding interaction between platinums.[1494,1497] This is confirmed by the calculated force constants between Pt^{III}–Pt^{III} in a normal coordinate analysis of the vibrational spectra of these complexes.[1498]

$$2K_2PtCl_4 + 8H_3PO_3 \longrightarrow K_4[Pt_2(P_2O_5H_2)_4] + 4H_2O + 8HCl \qquad (441)$$



(**158**)

$$\underset{(\mathbf{159})}{Pt_2(P_2O_5H_2)_4X_2^{4-}} \xleftarrow{X_2} \underset{(\mathbf{158})}{Pt_2(P_2O_5H_2)_4^{4-}} \xrightarrow{XY} \underset{(\mathbf{160})}{Pt_2(P_2O_5H_2)_4XY^{4-}}$$

The complex $Pt_2(P_2O_5H_2)_4^{4-}$ will undergo two-electron reduction with chromium(II) ion,[1495] and one-electron reduction with electrons from a van der Graaff generator to give a short-lived (~μs) complex $Pt_2(P_2O_5H_2)_4^{5-}$.[1499] Reaction with the one-electron oxidants Ir^{IV} and Ce^{IV} in the presence of chloride ion gives $Pt_2(P_2O_5H_2)_4Cl_2^{4-}$ (equation 442). Halide ion substitution in the complexes $Pt_2(P_2O_5H_2)_4X_2^{4-}$ is photochemically accelerated, and the reactions with halogens and interhalogens follow redox patterns.[1500]

$$Pt_2(P_2O_5H_2)_4^{4-} + 2Ce^{IV} + 2Cl^- \longrightarrow Pt_2(P_2O_5H_2)_4Cl_2^{4-} + 2Ce^{III} \qquad (442)$$

When the synthetic procedure to prepare $Pt_2(P_2O_5H_2)_4^{4-}$ (equation 441) is carried out at higher temperature, a higher oligomeric complex with platinum(II) centers coupled by an oligomeric condensed phosphorous acid ligand is formed. Little information is known about the complex except that the intense absorption chromophore is now at 580 nm and the emission in the red at 650 nm.[1501]

(*v*) *NMR spectroscopy*

In the absence of X-ray crystallographic data, ^{31}P and ^{195}Pt NMR spectroscopy is a useful method to investigate the nature of the products in the solution. In addition to earlier references to these topics, the Pople–Santry theory has been used to calculate the signs and relative magnitudes of the coupling constants for the type of phosphorus-bridged complexes covered in this section.[1502]

52.5.3.9 Complexes with phosphazenes

Cyclic and polymeric phosphazenes will form water-soluble platinum(II) complexes. The compounds contain square planar platinum bonded to the phosphazene *via* nitrogen.[1503–1506]

52.5.3.10 Cluster compounds

Platinum phosphine fragments can also be incorporated into cluster compounds with other transition metals and non-transition metals. A number of such compunds with bridging carbene ligands are described in Section 52.4, but stable compounds with direct metal–metal bonds can be formed without the necessity of bridging groups. The pentametallic cluster $Pt_5(CO)(\mu_2\text{-}CO)_5(PPh_3)_4$ reacts with $Co_2(CO)_8$ to give the new cluster compound $PtCo_2(CO)_7(\mu\text{-}CO)(PPh_3)$ (equation 443).[1507] This compound undergoes an irreversible one-electron reduction which results in the subsequent release of $Co(CO)_4^-$ from the cluster.[1508] Platinum–mercury-bonded complexes can be synthesized, and coordination to platinum cluster units can be used to stabilize dimercury. The complex $[\{Pt_3(\mu_2\text{-}CO)_3(PPhPr^i_2)_3\}_2Hg_2]$ is formed from the reaction between $Pt_3(\mu_2\text{-}CO)_3(PPhPr^i_2)_3$ and metallic mercury.[1509]

$$Pt_5(CO)(\mu_2\text{-}CO)_5(PPh_3)_4 + Co_2(CO)_8 \longrightarrow PtCo_2(CO)_7(\mu\text{-}CO)(PPh_3) \qquad (443)$$

52.5.3.11 Platinum(IV) phosphine complexes

Platinum(IV) phosphine complexes are much less common than their zerovalent or divalent counterparts. Since phosphines and phosphites are readily oxidized to phosphine oxides and phosphates respectively, the addition of these reduced ligands to platinum(IV) salts results in the formation of complexes of divalent platinum. If the platinum(IV) salts are desired, the usual synthetic method is halogenation of the precursor platinum(II) phosphine or phosphite complexes.[1510] As shown in equation (444), this method can be used to prepare $PtCl_4(PPr^n_3)_2$ from $PtCl_2(PPr^n_3)_2$.[1225] Similarly *trans*-$PtX_4(PEt_3)_2$ (X = Cl, Br, I), *cis*-$PtX_4(PEt_3)_2$ (X = Cl, Br), *cis*-$PtCl_4(PPhMe_2)_2$, and *cis*- and *trans*-$PtCl_4(PBu^n_3)_2$ can be prepared. The chloro and bromo complexes are yellow or orange.

$$PtCl_2(PPr^n_3)_2 + Cl_2 \longrightarrow PtCl_4(PPr^n_3)_2 \qquad (444)$$

52.5.3.12 Platinum complexes of tertiary arsines and stibines

Platinum compounds form stable complexes with As and Sb donor ligands. In many respects the complexes resemble those of phosphines, but one difference is that the As and Sb ligands stabilize platinum more effectively in its +4 oxidation state. For a general review on arsine and stibine complexes the reader is referred to McAuliffe's book,[1225] and for a survey of the complexes in higher oxidation states to a recent review article.[1511] A large number of complexes have been prepared of the types $PtX_2(AsR_3)_2$ and $PtX_2(SbR_3)_2$, where R is an alkyl or an aryl group. The compounds can be prepared by the standard methods of Jensen from K_2PtCl_4 (equation 445). As with the phosphine derivatives, chlorine oxidation gives $PtCl_4(ER_3)_2$, the first example being reported in 1950.[1512] Halide replacement with X^- gives the correspondingly substituted arsine or stibine complex.[1513] For the platinum(IV) complexes the reaction may be accompanied by reduction if iodide is the incoming halide ion (equation 446).[1514] Monomeric complexes $PtCl_2(AsR_3)_2$ can also be prepared with sterically hindered arsines such as $AsBu^t_3$.[1515] One difference appears to be that with SbR_3, the bulky stibine ligands preferentially form the *trans* isomer over the usual *cis*.[1516]

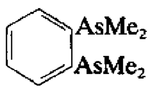
$$PtCl_4^{2-} + 2ER_3 \longrightarrow PtCl_2(ER_3)_2 + 2Cl^- \qquad E = As, Sb \tag{445}$$

$$PtCl_4(AsEt_3)_2 + 4I^- \longrightarrow PtI_2(AsEt_3)_2 + 4Cl^- + I_2 \tag{446}$$

The zerovalent complex $Pt(AsPh_3)_4$ can be prepared in an analogous manner to the triphenylphosphine complex.[1233] The color is white rather than yellow for $Pt(PPh_3)_3$. For triphenylstibine, reaction with $Pt(PPh_3)_3$ results in replacement of one PPh_3 ligand to give the insoluble compound $Pt(PPh_3)_2(SbPh_3)_2$ (equation 447).[1517]

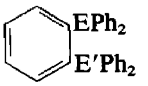
$$Pt(PPh_3)_3 + 2SbPh_3 \longrightarrow Pt(PPh_3)_2(SbPh_3)_2 + PPh_3 \tag{447}$$

In addition to these monodentate arsine and stibine ligands, chelate complexes of platinum with ditertiary arsine and stibine ligands have been isolated. The most common ligand of this group is diars (**161**).[1518,1519] More recently platinum complexes with this ligand of type PtXMe(diars) have been prepared.[1520] Diarsines can also be prepared having an aliphatic backbone yielding six-coordinate platinum(II) complexes of type $PtCl_2$(As—As), and NMR methods with the ring substituted deutero derivatives can be used to investigate ring conformations.[1521]



(161)

The analogous ligand o-$C_6H_4(AsMePh)_2$ can be prepared, and the four-coordinate square planar platinum complexes retain their structural integrity in solution. This allows NMR methods to be used to identify the diastereomers and enantiomers present.[1522] The phenylated derivatives (**162**) have also been prepared, and some 12 platinum(II) complexes prepared with the ligands.[1523] Other variations which have been used to prepare platinum compounds are diarsines with vinyl bridges,[1524] distibines,[1524,1525] tripod arsine ligands,[1526] *trans* chelating arsines[1527] and methoxyphenylstibines.[1528]



(162)

$E = E' = P, As$; $E = P, E' = As$;
$E = P, E' = Sb$; $E = As, E' = Sb$

Distibines fall lowest in the spectrochemical series $P_2 > As_2 > Sb_2$,[1529] a result which corresponds with the electronic spectra data for the monodentate series PEt_3, $AsEt_3$, $SbEt_3$.[1530] Mössbauer spectroscopy is a useful method for platinum stibine complexes. Coordination of the stibine causes a large increase in isomer shift and a decrease in quadrupole coupling constant in the ^{121}Sb spectrum, as expected for the formation of a donor bond.[1531]

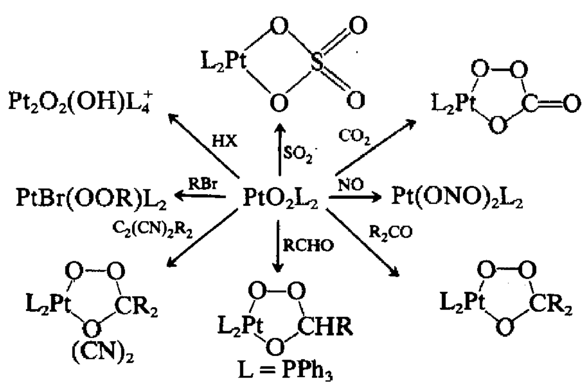
52.6 COMPLEXES WITH GROUP VI LIGANDS

52.6.1 Complexes with Platinum–Oxygen Bonds

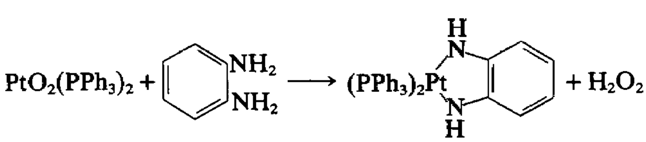
52.6.1.1 Complexes with molecular oxygen

The binding of oxygen to transition metal complexes is a field which has been reviewed several times in the past decade,[1532–1536] and a recent chapter by Roundhill in ref. 1227 covers this field with an emphasis on catalyzed oxidations. The most studied complex between oxygen and platinum is the complex $PtO_2(PPh_3)_2$. The compound can be prepared by passing oxygen through $Pt(PPh_3)_3$ (equation 448), and isolated as an off-white solid. Coordination of the oxygen molecule to the low-valent platinum center causes the oxygen to become electron rich, and indeed the complex can be conceptually viewed as a platinum(II) peroxide complex of polarity $Pt^{2+}O_2^{2-}(PPh_3)_2$.[1537,1538] The chemistry of the oxygen molecule complexed to platinum(0) becomes a study of its reactivity to electrophiles. Examples of these reactions are outlined in Scheme 16.[1227,1539,1540] A number of other reactions of $PtO_2(PPh_3)_2$ have been described which can be better described as substrate oxidation reactions. The complex $PtO_2(PPh_3)_2$ will catalyze the oxidation of triphenylphosphine by a pathway involving hydroperoxide,[1541] and the complex can be used to catalyze the oxidation of ketones to carboxylic acids by a free-radical autoxidation pathway.[1542] *o*-Phenylenediamines are also oxidized by $PtO_2(PPh_3)_2$. The reaction in ethanol gives the complexes (**163**; equation 449) as deeply colored compounds.[1543] Similar products to (**163**) are formed from catechol and from aroylhydroxylamine and aroylhydrazine.[1544] With the electron-poor alkyne $C_2(CF_3)_2$, the reaction differs from that with alkenes in Scheme 16. In the case of $C_2(CF_3)_2$ the product is that derived from O—O bond cleavage (**164**; equation 450). No intermediates have been suggested, and no explanation given for the difference in reactivity.[1545] When the ketone R_2CO in Scheme 16 is hexafluoroacetone, it is possible that ring expansion reactions can occur (equation 451).[1546] Attempts to verify this seven-membered ring by X-ray crystallography were unsuccessful, and the compound may be the six-membered ring complex (**165**).[1547]

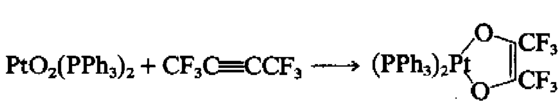
$$2Pt(PPh_3)_3 + 3O_2 \longrightarrow 2PtO_2(PPh_3)_2 + 2OPPh_3 \qquad (448)$$



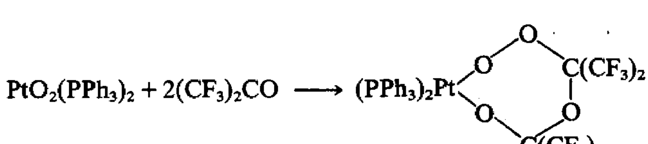
Scheme 16



(163) (449)



(164) (450)



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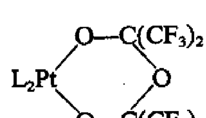


(165)

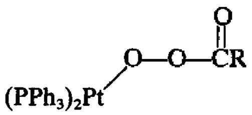
Photolysis of $PtO_2(PPh_3)_2$ in a nitrogen-saturated chloroform solution results in dissociation of singlet oxygen (equation 452).[1548]

$$PtO_2(PPh_3)_2 \longrightarrow Pt(PPh_3)_2 + {}^1O_2 \tag{452}$$

52.6.1.2 Complexes of hydroperoxides and peroxides

The reaction between $Pt(CF_3)(OH)L_2$ (L = monophosphine or L_2 = dppe) with ROOH (R = H, Bu^t) gives the hydroperoxide complexes $Pt(CF_3)(OOR)L_2$ (R = H, Bu^t; **166**; equation 453).[1549] The complexes (**166**; R = H) oxidize PPh_3, CO, NO and PhCHO to $OPPh_3$, CO_2, NO_2 and $PhCO_2H$ respectively, and for R = H, PPh_3 and CO to $OPPh_3$ and CO_2 respectively. The end-on bonding in $PtPh(OOBu^t)(PPh_3)_2$ is confirmed by single-crystal X-ray work, and the complexes are effective for the selective oxygenation of octene-1 to octanone-2.[1550] In addition to alkylperoxoplatinum(II) complexes formed by alkylation of $PtO_2(PPh_3)_2$ (Scheme 16),[1551] acyl halides will react with $PtO_2(PPh_3)_2$ to give the thermally unstable complexes (**167**).[1552] Attempts to prepare similar complexes from $Pt(PPh_3)_3$ and acetyl or benzoyl peroxide give *cis*-$Pt(OCOR)_2(PPh_3)_2$.[1553]

$$Pt(CF_3)(OH)L_2 + ROOH \longrightarrow \underset{\textbf{(166)}}{PtCF_3(OOR)L_2} + H_2O \tag{453}$$



(167)

52.6.1.3 Aqua, hydroxy, alcohol and ether complexes

Platinum(II) is classified as a 'soft' metal center which forms stable complexes with polarizable ligands. In this general classification, water will form the most stable compounds with the lighter transition metals, and compounds such as $Pt(H_2O)_n^{2+}$ and $Pt(H_2O)_m^{2+}$ ($n = 4$, $m = 6$) are not usually useful compounds. Nevertheless aqua complexes can be obtained from $PtCl_4^{2-}$ and $PtCl_3(NH_3)^-$ by chloride ion substitution by water (equation 454).[1554–1556] Coordination causes the hydrogens on water to become acidic, and addition of base can give hydroxy complexes (equation 455). Usually hydroxy complexes are bridged through this group, but the first stable crystalline hydroxy platinum(II) complex is the monomeric $Pt(OH)(GePh_3)(PEt_3)_2$.[1557] Monomeric hydroxy complexes of platinum(IV) can be obtained by the oxidation of platinum(II) complexes with hydrogen peroxide (equation 456).[1558,1559]

$$PtCl_3(NH_3)^- + H_2O \longrightarrow PtCl_2(NH_3)(H_2O) + Cl^- \tag{454}$$

$$PtCl_2(NH_3)(H_2O) \rightleftharpoons PtCl_2(NH_3)OH^- + H^+ \tag{455}$$

$$PtCl_2(NH_3)_2 + H_2O_2 \longrightarrow PtCl_2(OH)_2(NH_3)_2 \tag{456}$$

The recent interest in platinum complexes as antitumor agents has spurred considerable interest in the synthesis of hydroxy amine platinum(II) complexes. The cation $Pt_2(\mu\text{-}OH)_2(NH_3)_4^{2+}$ is a centrosymmetric complex with a long (>3 Å) separation between platinums.[1560,1561] The complex can be prepared directly from *cis*-$PtCl_2(NH_3)_2$ (equation 457), or by hydrolysis of the sulfato complex *trans*-$PtOH(SO_4)(NH_3)_4^+$.[1562] The ammonia ligands in these complexes can be replaced by amines or diamines.[1563] Using a combination of IR and Raman techniques the vibrational bands in these complexes can be assigned using a full normal coordinate analysis.[1564,1565]

$$2cis\text{-}PtCl_2(NH_3)_2 + 2Ag^+ \xrightarrow{OH^-} Pt_2(\mu\text{-}OH)_2(NH_3)_4^{2+} \tag{457}$$

Other possible compounds may be formed including mixed-valent[1566] and hydroxy-bridged trimeric complexes of type $[Pt_3(\mu\text{-}OH)_3(NH_3)_6](NO_3)_3$[1567] and $[Pt_3(\mu\text{-}OH)_3(NH_3)_6](SO_4)_3\cdot 6H_2O$.[1568]

Hydroxy-bridged complexes $[Pt_2(\mu\text{-}OH)_2(PEt_3)_4]^{2+}$ can also be prepared. The structure consists of two square planar platinum(II) centers bridged by hydroxide ligands with an angle of 36.4° between the mean plane normals.[1569] A useful method to prepare these complexes involves the use of phase-transfer catalysis with crown ethers to facilitate the reaction of KOH with platinum(II) chloro complexes.[1570]

Alcohol complexes of platinum(II) are usually not isolable, although their solution presence has been established.[1571]

Crown ether complexes of platinum can be prepared. The crown does not form a direct Pt—O bond but stabilizes amine complexes by a hydrogen-bonded attachment into the second coordination sphere.[1572–1574]

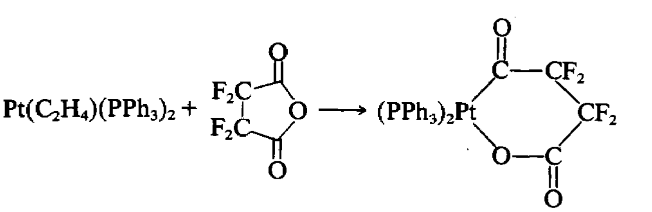
52.6.1.4 *Carboxylato complexes*

A compound initially characterized as diacetatoplatinum can be prepared by heating $Na_2Pt(OH)_6$ in nitric acid followed by refluxing in acetic acid. Addition of formic acid gives the complex as purple crystals which can be recrystallized from $CHCl_3/HCO_2H$.[1575] An X-ray structure of this compound shows it to be $Pt_4(OCOMe)_6(NO)_2$. The platinum atoms are joined together by double acetate bridges spanning the two shorter sides, while the other two sides are each bridged by one nitrosyl and one acetate group.[1576] A pure platinum acetate can be obtained using silver acetate. This compound $[Pt(OCOMe)_2]_4$ has a structure of D_{2d} symmetry in which each side of a Pt—Pt-bonded square of platinum atoms is spanned by two acetate groups.[1577]

If a solution of acetic acid and $Pt(PPh_3)_3$ in benzene solution is refluxed in air, the complex *cis*-$Pt(OCOMe)_2(PPh_3)_2$ is obtained as colorless crystals in 83% yield (equation 458).[1578] These carboxylate complexes are bound to platinum by a single monodentate oxygen atom, as is found with the glycine complexes $Pt(O_2CCH_2NH_3)_2(NH_3)_2^{2+}$.[1579] Trifluoroacetatic anhydride can be used to prepare the bis(trifluoroacetato) complexes of platinum (equation 459), although if $PtC_2H_4(PPh_3)_2$ is used with perfluorosuccinic anhydride, a chelated complex (**168**) is formed (equation 460).[1580] The compound $Pt(OCOCF_3)_2(PPh_3)_2$ can, however, be prepared from $Pt(C_2H_4)(PPh_3)_2$ if CF_3CO_2H is used.

$$Pt(PPh_3)_3 + 2MeCO_2H \xrightarrow{O_2} cis\text{-}Pt(OCOMe)_2(PPh_3)_2 + PPh_3 \qquad (458)$$

$$Pt(PPh_3)_3 + (CF_3CO)_2O \longrightarrow trans\text{-}Pt(OCOCF_3)_2(PPh_3)_2 + PPh_3 \qquad (459)$$



(460)

(**168**)

The Pt—O bond enthalpies for a series of amino acid complexes of platinum(II) fall in the range 322–397 kJ mol^{-1}.[1581]

Oxalic acid readily forms mono and bis oxalato complexes with platinum (equations 461 and 462).[1582–1584] Addition of thiocyanate ion to the chelate complex $Pt(NO_2)_2(C_2O_4)^{2-}$ gives the monodentate oxalato complexes *cis*-$Pt(NO_2)_2(SCN)(C_2O_4)^{3-}$ and *trans*-$Pt(NO_2)(SCN)_2$-$(C_2O_4)^{3-}$, on the pathway to $Pt(SCN)_4^{2-}$.[1585] Similarly the reaction of $[Pt(C_2O_4)_2]^{2-}$ with SCN^- gives the ring-opened monodentate oxalato complex $Pt(C_2O_4)_2(SCN)_2^{4-}$.[1586] A similar chemistry is observed between $Pt(C_2O_4)_2^{2-}$ and chloride ion.[1587]

$$K_2Pt(NO_2)_4 + H_2C_2O_4 \longrightarrow K_2[Pt(NO_2)_2(C_2O_4)] \xrightarrow{H_2C_2O_4} K_2[Pt(C_2O_4)_2] \qquad (461)$$

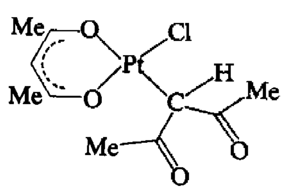
$$K_2PtCl_4 + 2K_2C_2O_4 \longrightarrow K_2[Pt(C_2O_4)_2] + 4KCl \qquad (462)$$

As with platinum cyanides, platinum oxalates can be partially oxidized to give one-dimensional conducting chain molecules.[1588,1589] The structure shows two Pt–Pt distances of 2.857(2) and 2.833(2) Å respectively, and bidentate oxalate ligands staggered (~45°) with respect to the ligands above and below.[1590] The structure has been rationalized on the basis of an intermolecular back-bonding model which involves overlap of a higher occupied MO on a molecular plane with a lower unoccupied molecular orbital on an adjacent molecular plane.[1591] Alternative cations for these partially oxidized molecules are Mg and Co in the complexes $M_{0.83}[Pt(C_2O_4)_2]$ (M = Mg, Co).[1592] With singly charged cations the isolated complexes are $M_{1.67}[Pt(C_2O_4)_2]$ (M = Rb, NR_4, where $R_4 = H_4$, Me_4, H_3Me, H_2Me_2).[1592,1594]

52.6.1.5 β-Diketonato complexes

When K_2PtCl_4 reacts with acetylacetone (acacH) in the presence of strong base, halide substitution by acetylacetonate occurs to give $K[PtCl_2(acac)]$, $K[PtCl(acac)_2]$, and with excess acetylacetone, $Pt(acac)_2$ (equation 463).[1595] The yellow crystalline $Pt(acac)_2$ is very soluble in chloroform. The O,O′ chelation of acetylacetonate in $Pt(acac)_2$ is confirmed by two independent crystal structure determinations. The geometry is planar about platinum(II) and the Pt—O distances are very close to 2.0 Å as expected.[1596,1597] Chelation *via* the O,O′-bidentate mode is the usual one for acetylacetonate complexes. Platinum is unusual among the transition elements in forming very stable complexes to carbon atoms, and the acetylacetonate group will form both O-bonded and C-bonded complexes with platinum(II). An example is $K[PtCl(acac)_2]$ which has one bidentate oxygen-bonded ligand and one acac moiety bound to platinum *via* the γ-carbon atom (**169**).[1598,1599] In the O-bonded complexes ν(CH) of the γ-hydrogen lies above 3000 cm^{-1}, but below 3000 cm^{-1} in the C-bonded compound. Also ν(C=O) in the C-bonded ligand is higher than in the bidentate oxygen-bonded ligand. ^1H NMR spectroscopy is diagnostic because $^2J(PtH)$ is ~120 Hz in (**169**), but $^4J(PtH)$ is ~10 Hz in the bidentate O-bonded ligand.[1600] Similar O- and C-bonding is found with the β-diketonato complexes of trifluoroacetylacetone and benzoylacetone.[1601,1602] The anion $[PtCl(acac)_2]^-$ can act as a terdentate (O,O′,O,O′) ligand to Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+}.[1603] The assignments due to ν(MO) (M = Ni, Cu, Zn, Fe) have been assigned by use of isotopic substitution with the metal M.[1604]

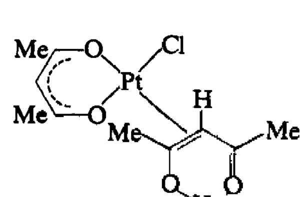
$$K_2PtCl_4 + 2acacH + 2KOH \longrightarrow Pt(acac)_2 + 4KCl + 2H_2O \qquad (463)$$



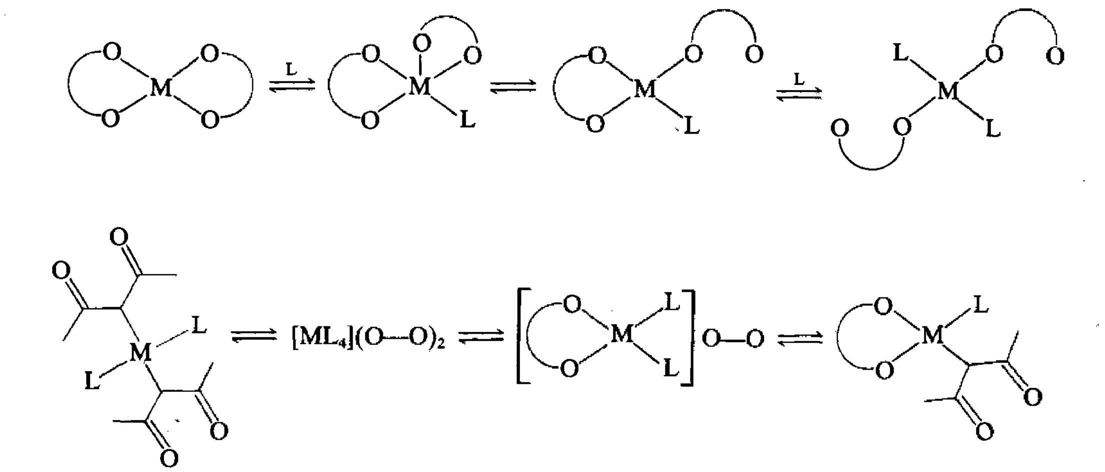
(**169**)

An acetylacetonate platinum(II) complex $[PtMe_3(acac)]_2$ is one of the few complexes for which ^{195}Pt chemical shift anisotropy has been measured in the solid state.[1605]

When $K[PtX(acac)_2]$ (X = Cl, Br) is treated with a strong proton acid the uncoordinated O,O′ site is protonated and complex (**170**) is formed.[1606,1607] If the alkyl groups on the O,O′-bonded acac ligand are non-equivalent, exchange can be observed. Although the mechanism has not been definitively proven, a dissociative mechanism is favored.[1608] This proposal correlates with the observations that the O,O′-bonded chelate complex $Pt(acac)_2$ will react with tertiary phosphines and nitrogen bases with substitution of one of the oxygen-bonded chelate arms.[1609,1610] A variety of products are formed as outlined in Scheme 17.



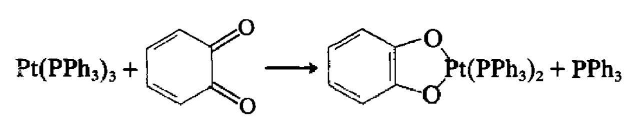
(**170**)



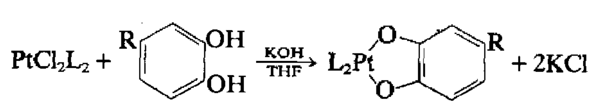
Scheme 17

52.6.1.6 Quinone and catecholate complexes

The first method to prepare these complexes is by addition to the zerovalent complex $Pt(PPh_3)_3$ (equation 464).[1611–1614] The second method which can be used is to react PtX_2L_2 with the corresponding alkali metal *o*-semiquinolates at room temperature.[1615] If desired the reaction can be carried out *in situ* with the free catechol in the presence of strong base (equation 465).[1616] These platinum catecholate complexes can be oxidized by Cu^{2+}, Fe^{3+} or CF_3CO_2Ag to give paramagnetic compounds where the unpaired electron is primarily located on the ligand.[1615,1617]



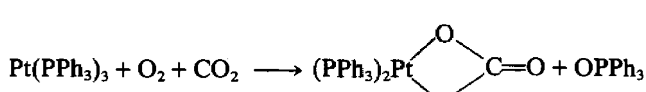
(464)



(465)

52.6.1.7 Carbonato complexes

In Scheme 16 the reaction between $PtO_2(PPh_3)_2$ and CO_2 was shown to give the peroxycarbonate complex $Pt(O_3CO)(PPh_3)_2$. If this reaction is carried out in the presence of free triphenylphosphine, or if the synthesis is achieved directly from $Pt(PPh_3)_3$ (equation 466), the carbonato complex (**171**) is formed.[1618] Alternatively carbonato complexes can be prepared from the dihalo complexes by treatment with silver carbonate (equation 467).[1619,1620] These complexes are air-stable but liberate CO_2 with added protonic acids.



(466)

(171)

$$PtX_2L_2 + 2AgNO_3 \longrightarrow Pt(NO_3)_2L_2 + 2AgX \qquad (467)$$

52.6.1.8 Nitrato complexes

The synthesis and chemistry of platinum nitrates has been recently reviewed.[1621] The only homoleptic nitrate complex is $K_2Pt(NO_3)_6$ formed from K_2PtBr_6 and N_2O_5. Oxidation of the nitrito complex $K_2Pt(NO_2)_4$ gives $K_2Pt(NO_2)_6$, and not the nitrate complex.

Platinum(II) nitrato complexes can be synthesized by metathesis, by addition of N_2O_4 to $PtO_2(PPh_3)_2$, by nitrosylation of $PtO_2(PPh_3)_2$ or by ligand transfer reactions (equations 467–471).

$$PtO_2(PPh_3)_2 + N_2O_4 \longrightarrow Pt(NO_3)_2(PPh_3)_2 \quad (468)$$

$$PtO_2(PPh_3)_2 + NOBF_4 \longrightarrow [(PPh_3)_2Pt(O_2)N{=}O]BF_4 \quad (469)$$

$$cis\text{-}PtMe_2L_2 + cis\text{-}Pt(NO_3)_2L_2 \longrightarrow 2cis\text{-}PtMe(NO_3)L_2 \quad (470)$$

$$Pt(OH)_2(bipy) + HNO_3 \longrightarrow Pt(OH)(NO_3)(bipy) \xrightarrow{HNO_3} Pt(NO_3)_2(bipy) \quad (471)$$

The *trans* influence of NO_3^- coordinated to platinum(II) places it very low in the series, and the high electronegativity of the NO_3^- group makes it a good leaving group from platinum(II). Infrared combination bands in the region of 1750 cm^{-1} can be used to distinguish between the coordination modes of nitrate. The magnitude of the splitting of these bands is usually larger for bidentate than for unidentate coordination.[1622]

52.6.1.9 Other nitrogen–oxygen ligands

An unusual O,O′-bonded hyponitrite ligand is formed by a coupling reaction of NO. The unstable complex is formed by reacting NO with $Pt(PPh_3)_3$ (equation 472). The Pt—O distances are equal (2.0 Å), and the N=N distance is short (1.21(5) Å).[1623]

$$Pt(PPh_3)_3 + 2NO \longrightarrow (PPh_3)_2Pt(ON{=}NO) + PPh_3 \quad (472)$$

As mentioned in Section 52.4, chelate-assisted aldehyde coordination can occur with platinum(II), but the Pt—O bond in the anthranilaldehyde complex will undergo ready substitution with rotation of the C=O functionality away from platinum.[1624]

In studies of reaction pathways, nitrosyl radicals are frequently used as spin traps to provide evidence for free radical pathways. A caution in interpretation of these results is that the probe or products will interact with the transition metal complex in the reaction and affect the reactivity of the probe with the organic substrate or free radicals produced. A number of reactions of the stable free radicals RNO and R_2NO with platinum(II) complexes have been carried out which show that such reactions must indeed be considered (equations 473–475).[1625–1627]

$$Pt(acac)_2 + CF_3NO \longrightarrow Pt(acac)\{acac\text{—}N(CF_3)O\} \quad (473)$$

$$Pt(C_2H_4)(PPh_3)_2 + 2(CF_3)_2NO \longrightarrow Pt\{ON(CF_3)_2\}_2(PPh_3)_2 + C_2H_4 \quad (474)$$

$$Pt(PPh_3)_3 + CF_3N(O)CF_2CF_2N(O)CF_3 \longrightarrow Pt\{ON(CF_3)CF_2CF_2N(CF_3)O\}(PPh_3)_2 \quad (475)$$

52.6.1.10 Ambidentate ligands

Platinum(II) halides react with cyanate salts to give cyanato complexes. Reacting the compounds $Pt(NCO)_4^{2-}$ with triphenylphosphine gives $Pt(NCO)_2(PPh_3)_2$.[1628] These platinum(II) complexes are N-bonded. Treatment with carbon monoxide and alcohol yields the complex (**172**; equation 476).[1629]

$$Pt(NCO)_2(PPh_3)_2 + 2ROH + CO \longrightarrow \underset{\mathbf{(172)}}{Pt(NCO)(CO_2R)(PPh_3)_2} + H_2NCO_2R \quad (476)$$

Nitrite complexes of platinum can be formed, and complexes are known where the NO_2^- ligand is N- or O-bonded. For platinum(II) the compounds are N-bonded, but for platinum(IV) complexes can be synthesized which are O- or N-bonded. Synthetic methods involve substitution reactions with nitrite ion or addition of NO to $PtO_2(PPh_3)_2$ (equations 477 and

478). The reaction of $[Pt(NH_3)_5(H_2O)]Cl_4$ with $NaNO_2$ in hydrochloric acid at 0 °C yields the O-bonded nitrito complex $[Pt(NH_3)_5(ONO)]Cl_3$, which isomerizes to the thermodynamically more stable N-bonded isomer (equation 479).[1630]

$$PtCl_4^{2-} + 4NO_2^- \longrightarrow Pt(NO_2)_4^{2-} + 4Cl^- \quad (477)$$

$$PtO_2(PPh_3)_2 + 2NO \longrightarrow Pt(NO_2)_2(PPh_3)_2 \quad (478)$$

$$[Pt(NH_3)_5(H_2O)]Cl_4 + NO_2^- \longrightarrow [Pt(NH_3)_5(ONO)]Cl_4 \longrightarrow [Pt(NH_3)_5(NO_2)]Cl_4 \quad (479)$$

Oxygen-bonded sulfito complexes of platinum(IV) can be prepared by the reaction of aqueous sulfite with $[Pt(NH_3)_5(H_2O)]^{4+}$ to give the O-bonded sulfito complex $[Pt(NH_3)_5(OSO_2)]^{2+}$. This compound rearranges to the S-bonded sulfite complex, or at elevated temperatures in acidic solution a single-step two-electron reduction occurs to yield a platinum(II) complex $Pt(SO_3)(NH_3)_3$ (equation 480).[1631] The O-bonded sulfite complexes show a series of IR bands in the range 460–960 cm^{-1}.[1632]

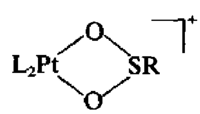
$$[Pt(NH_3)_5(H_2O)]^{4+} \xrightarrow{SO_3^{2-}} [Pt(NH_3)_5OSO_2]^{2+} \begin{cases} \longrightarrow [Pt(NH_3)_5SO_3]^{2+} \\ \xrightarrow[50-60\,^{\circ}C]{} Pt(SO_3)(NH_3)_3 \end{cases} \quad (480)$$

S-bonded alkyl and aryl sulfinato complexes can be prepared by the reaction of sulfonyl chlorides with $Pt(C_2H_4)(PPh_3)_2$,[1633] the phase-catalyzed reaction of $PtCl_2L_2$ with $NaSO_2R$,[1634] or the insertion of SO_2 into a platinum–alkyl bond[1635] as shown in equations (481)–(483). When $PtCl(SO_2R)L_2$ is treated with silver ion the O,O′-bonded chelate complex (**173**) is formed (equation 484).

$$Pt(C_2H_4)(PPh_3)_2 + RSO_2Cl \longrightarrow PtCl(SO_2R)(PPh_3)_2 + C_2H_4 \quad (481)$$

$$PtCl_2L_2 + NaSO_2R \longrightarrow PtCl(SO_2R)(PPh_3)_2 + NaCl \quad (482)$$

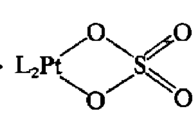
$$PtCl(Me)(PEt_3)_2 + SO_2 \longrightarrow PtCl(SO_2Me)(PEt_3)_2 \quad (483)$$

$PtCl(SO_2R)L_2 + Ag^+ \longrightarrow$  $+ AgCl$ (484)

(**173**)

52.6.1.11 Sulfato and substituted sulfato ligands

These compounds do not represent a wide ranging class of complexes for platinum. The synthesis of monomeric sulfato platinum complexes is represented in equations (485) and (486).[1636] The complexes are characterized by $\nu(S{=}O)$ bands in the 1100–1300 cm^{-1} region.

$L_2PtO_2 + SO_2 \longrightarrow$  (485)

$$Pt(NH_3)_4^{2+} + S_2O_8^{2-} \longrightarrow PtOHSO_4(NH_3)_4^+ + Pt(SO_4)_2(NH_3)_4 \quad (486)$$

A platinum(IV) complex of fluorosulfonic acid can be prepared from $Ag(SO_3F)_2$ and $Pt(SO_3F)_4$ at 25 °C in fluorosulfonic acid solvent (equation 487).[1637] The trifluoromethanesulfonate complex $Pt(OSO_2CF_3)(NH_3)_5^{3+}$ undergoes aquation to $Pt(H_2O)(NH_3)_5^{4+}$.[1638]

$$Ag(SO_3F)_2 + Pt(SO_3F)_4 \longrightarrow AgPt(SO_3F)_6 \quad (487)$$

52.6.1.12 *Perfluoropinacolate complexes*

Perfluoropinacol $(CF_3)_2C(OH)C(OH)(CF_3)_2$ (PFP) can be doubly deprotonated to give PFP^{2-}. The complex $Pt(PFP)_2^{2-}$ cannot be prepared, but the compound $Pt(PFP)(PPhMe_2)_2$ is isolable.[1639]

52.6.1.13 *Binuclear (μ-O,O′)-bridged Pt^{II}–Pt^{II} and Pt^{III}–Pt^{III} complexes*

A novel binuclear Pt^{II}–Pt^{II} complex $Ba_2[Pt_2(C_4O_4)_4]\cdot 6H_2O$ can be prepared from $Pt(H_2O)_4^{2+}$ and squaric acid. The tetrakis-bridged μ-O,O′ squarato complex has a Pt–Pt separation of 3.061 Å, indicative of negligible intermetallic bonding.[1640]

A series of binuclear Pt^{III}–Pt^{III} complexes has been prepared having μ-O,O′ sulfato or hydrogen phosphato bridges. When $K_2Pt(NO_2)_4$ is heated in sulfuric acid the yellow O,O′-bonded diplatinum(III) complex $K_2(H_3O)[Pt_2(OH)(H_2O)(\mu\text{-}SO_4)_4]$ is formed.[1641] The complex undergoes metathetical replacement with anions X^- or neutral ligands L to give complexes $Pt_2(\mu\text{-}SO_4)_4X_2^{4-}$ (X = Cl, Br, NO_2) and $Pt_2(\mu\text{-}SO_4)_4L_2^{2-}$ (L = NH_3, DMSO).[1642] The compounds are characterized by absorption bands in the 200–500 nm region. The Pt–Pt distances in the aqua and DMSO complexes are 2.466 Å and 2.471(1) Å.[1643,1644] The analogous Pt^{III}–Pt^{III} μ-O,O′-bridged hydrogen phosphate complexes $(NH_4)_2[Pt_2(\mu\text{-}HPO_4)_4(H_2O)_2]$ can be prepared along with the complexes where the axial water molecules are replaced by halide, NH_3, pyridine and methyl-substituted pyridines.[1645–1648] Where structural data have been collected, the Pt–Pt distances fall in the 2.45–2.50 Å range.

If the complex $K_2(H_3O)[Pt_2(OH)(H_2O)(\mu\text{-}SO_4)_4]$ is synthesized at higher reaction temperatures, violet-colored peroxo complexes such as $K_2[Pt_2(\mu\text{-}O_2^{2-})_2(\mu\text{-}SO_4)_2(H_2O)_2]$ are formed. The compounds have been verified by electronic spectroscopy and by ESCA, but no structural characterization has been published.[1649–1651]

The ^{31}P and ^{195}Pt NMR spectra of the binuclear μ-sulfato and μ-hydrogen phosphato complexes of platinum(III) show values of $^2J(PtP)$ in the range 40–100 Hz, and $^1J(PtPt)$ between 3500 and 5400 Hz. The $^1J(PtPt)$ values for the hydrogen phosphato complexes are significantly larger than those of complexes with bridging sulfato ligands.[1652]

Phosphate blues can also form. When *cis*-$PtCl_2(NH_3)_2$ and KH_2PO_4 in water at pH 4.5 and 40 °C are exposed to air, a deep blue color develops over several days. The reaction proceeds faster if $[Pt(NH_3)_2(H_2O)_2](NO_3)_2$ is used as precursor. The isolated blue solids are weakly paramagnetic (0.5 ± 0.2 BM per platinum atom) and give a complicated ESR spectrum with peaks centered at $g = 1.9$–2.4 and $g = 4.29$. The solids are insoluble in water and dissolve in alkali but with the loss of blue color.[1653]

52.6.2 Complexes with Platinum–Sulfur Bonds

Sulfur, thiolates and sulfide ligands form very stable complexes with platinum. Many complexes have platinum in the divalent state, but complexes with a Pt—S bond are formed with platinum in the zerovalent or tetravalent state. Several recent reviews have been written on various aspects of the platinum coordination chemistry of sulfur heteroatom ligands, and these are listed in Table 9.

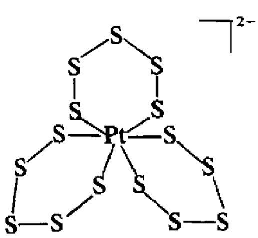
52.6.2.1 *Complexes with sulfur or sulfide ligands*

Platinum complexes can be formed where a single platinum(II) atom is present in a sulfur ring. Six-membered ring complexes such as (**174**) have been known for a considerable time.[1671] The all-chair conformation of the anion in the racemic solution is present in the solid state, although other conformations are possible where the C_3 axis has been lost, such as those with one PtS_5 ring inverted, or others with one or more rings in a non-chair conformation. Interconversions between these conformations can be observed using ^{195}Pt NMR.[1672] The inversion barriers have a $\Delta G^{\ne}$ in the region of 51 kJ mol^{-1}. The ammonium salt of (**174**) reacts with triphenylphosphine to give a five-membered thiometalacyclic complex (equation 488). The structure of this complex represents the first such proof of a complex having the PtS_4 ring structure.[1673,1674] These complexes resemble the well-known thionitrosyl-type complexes of

Table 9 Review Articles on the Coordination Chemistry of Sulfur Ligands

Title	Ref.
Coordination Chemistry of Thioethers, Selenoethers, and Telluroethers in Transition-Metal Complexes	1654
1,1-Dithiolato Complexes of the Transition Elements	1655
The X-Ray Photoelectron Spectra of Metal Complexes of Sulfur-Containing Ligands: Sulfur 2*p* Binding Energies	1656
Dithiolium Salts and Dithio-β-diketone Complexes of the Transition Metals	1657
Some Aspects of the Reactivity of Metal Ion–Sulfur Bonds	1658
The Chemistry of the Dithioacid and 1,1-Dithiolate Complexes, 1968–1977	1659
1,2-Dithiolene Complexes of Transition Metals	1660
Organometallic Intramolecular-Coordination Compounds. Recent Aspects in the Study of Sulfur Donor Ligands	1661
Oxidation and Other Products from the Reaction of Thiones and Phosphine Sulfides with Metal Salts and Halogens	1662
Monothio-β-diketones and their Metal Complexes	1663
Metal Complexes of Thio-β-diketones	1664
Structural Systematics of 1,1- and 1,2-Dithiolato Complexes	1665
The Chemistry of the Dithioacid and 1,1-Dithiolate Complexes	1666
Reactions involving Metal Complexes of Sulfur Ligands	1667
The Transition Metal Derivatives of Dithioketones and Ethylene(1,2)dithiolates	1668
Metal 1,2-Dithiolene and Related Complexes	1669
Metal Complexes of Ligands Containing Sulfur, Selenium, or Tellurium as Donor Atoms	1670

platinum. Recently the preparation of pure samples of $Pt(S_2N_2H)_2$, $Pt(S_2N_2H)(S_3N)$ and $Pt(S_3N)_2$ has been reported. The preferred route uses Na_2PtCl_6 and S_4N_4.[1675]



(174)

$$(NH_4)_2Pt(S_5)_3 + 12PPh_3 \longrightarrow PtS_4(PPh_3)_2 + (NH_4)_2S + 10Ph_3PS \quad (488)$$

Whereas $PtS_4(PPh_3)_2$ or $PtSe_4(PPh_3)_2$ is formed by heating $Pt(PPh_3)_4$ with 6 moles of sulfur or selenium, polymeric complexes $\{PtS(PPh_3)_2\}_n$ and $\{PtSe(PPh_3)_2\}_n$ containing sulfide or selenide bridges are formed if smaller amounts of S or Se are used.[1676] The μ-sulfide complex is inert to attack by CO, O_2 or C_2H_4, but gives an adduct with SO_2. Similar complexes can be readily formed by substitution reactions using sulfide salts. Examples are given in equations (489)–(493).[1677–1680] The triphenylphosphine and carbon monoxide ligands in $Pt_2(\mu\text{-}S)(CO)(PPh_3)_3$ can be replaced by dppe or isocyanides, but the Pt_2S core is robust. Methyl iodide alkylates at sulfur and CS_2 gives $Pt(S_2CS)(PPh_3)_2$ (equations 494 and 495). Isotopomer identification using ^{31}P NMR techniques has been effected by selective population transfer.[1681]

$$2cis\text{-}PtCl_2(PPhMe_2)_2 + 2Na_2S \longrightarrow Pt_2(\mu\text{-}S)_2(PPhMe_2)_4 + 4NaCl \quad (489)$$

$$3cis\text{-}PtCl_2(PPhMe_2)_2 + 2Na_2S + 2NaBF_4 \longrightarrow [Pt_3(\mu\text{-}S)_2(PPhMe_2)_6](BF_4)_2 + 6NaCl \quad (490)$$

$$2cis\text{-}PtCl_2(PPh_3)_2 + 2Na_2S \xrightarrow{EtOH} Pt_2(\mu\text{-}S)(CO)(PPh_3)_3 + 4NaCl + Ph_3PS \quad (491)$$

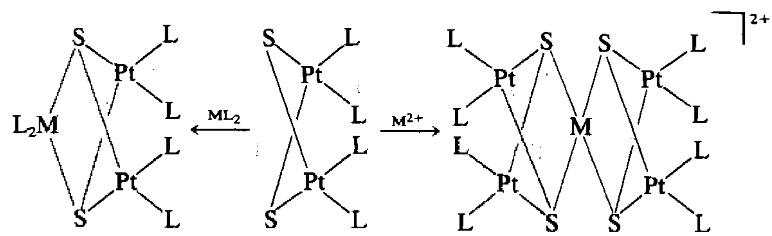
$$2Pt(COS)(PPh_3)_2 \xrightarrow[CHCl_3]{heat} Pt_2(\mu\text{-}S)(CO)(PPh_3)_3 + Ph_3PS \quad (492)$$

$$Pt(CS_2)(dppe) + Pt(C_2H_4)(PPh_3)_2 \longrightarrow Pt_2(\mu\text{-}S)(CS)(PPh_3)dppe + C_2H_4 + PPh_3 \quad (493)$$

$$Pt_2(\mu\text{-}S)(CO)(PPh_3)_3 + MeI \longrightarrow [Pt_2(\mu\text{-}SMe)(CO)(PPh_3)_3]I \quad (494)$$

$$Pt_2(\mu\text{-}S)(PPh_3)_4 + 2CS_2 \longrightarrow 2Pt(S_2CS)(PPh_3)_2 \quad (495)$$

Heteroatom multimetallic complexes having platinum as one of the transition metal ions can be prepared. These complexes can be assembled in a synthetically organized manner when it is appreciated that a bridging sulfide ligand of the type M(μ-S)M has available two electron pairs for reaction as a nucleophile (for example in equation 494), or as a ligand to transition metal ions leading to homometallic and heterometallic sulfido cluster complexes. Mingos has used this feature with $Pt_2(\mu\text{-}S)_2(PPh_3)_4$ as a synthon to prepare heterometallic sulfide cluster complexes of type (**175**) and (**176**) (equation 496).[1682,1683] Mixed Pt, Fe sulfido clusters can be prepared by the chloride ion replacement in *cis*-$PtCl_2(PPh_3)_2$ by $Fe_2(\mu\text{-}S)_2(CO)_6^{2-}$, or by the S—S addition reaction between $Pt(PPh_3)_3$ and $Fe_2(\mu\text{-}S)_2(CO)_6$ (equation 497).[1684] A similar procedure involving halide replacement on platinum(II) by a sulfide complexed to a second transition metal ion has been used to prepare the complexes $Pt(MS_4)_2^{2-}$ and $Pr(MOS_3)_2^{2-}$ (M = Mo, W). These complexes show bridging ν(MS) bands in the IR region between 450 and 500 cm^{-1}. The complexes $Pt(MS_4)_2^{2-}$ show a single reduction wave but it is probable that the observed reaction is the overlap of two different electrode processes.[1685,1686]



(496)

(**175**) (**176**)

M = Pd, Hg, Pd_2Cl_2, Ag_2, Pd(dppe), Hg(dppe), $PdCl(PPh_3)$

$$cis\text{-}PtCl_2(PPh_3)_2 + Fe_2(\mu\text{-}S)_2(CO)_6^{2-} \longrightarrow (PPh_3)_2Pt(\mu\text{-}S)_2Fe_2(CO)_6 \longleftarrow Pt(PPh_3)_3 + Fe_2(\mu\text{-}S)(CO)_6 \quad (497)$$

52.6.2.2 Complexes with hydrogen sulfide and hydrosulfides

Since H_2S is readily oxidized to elemental sulfur, any complexes of H_2S must be with metals in a low oxidation state. Although not fully proven, an H_2S adduct of platinum(0) was first published in 1967 when NMR methods were used to investigate the reaction of H_2S and H_2Se with $Pt(PPh_3)_3$ (equation 498).[1687] In addition to forming this simple adduct with $Pt(PPh_3)_2$, hydrogen sulfide also undergoes S—H addition to form $PtH(SH)(PPh_3)_2$.[1688] Monomeric hydrosulfide complexes can be prepared by reacting *cis*-$PtCl_2(PPh_3)_2$ with hydrogen sulfide and potassium carbonate as base (equation 499).[1689] The *cis* geometry has been verified by X-ray crystallography.[1690]

$$Pt(PPh_3)_3 + H_2S \rightleftharpoons Pt(SH_2)(PPh_3)_2 + PPh_3 \quad (498)$$

$$cis\text{-}PtCl_2(PPh_3)_2 + 2H_2S + K_2CO_3 \longrightarrow cis\text{-}Pt(SH)_2(PPh_3)_2 + 2KCl + CO_2 + H_2O \quad (499)$$

52.6.2.3 Complexes with thiolate ligands

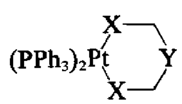
Thiolates form very strong bonds to platinum(II). Thiolato platinum(II) complexes have been known for a long time, but the characterization and chemistry of these complexes has been difficult because of the strong tendency of the thiolato ligand to form bridges to a second platinum center, resulting in the formation of insoluble bridged polymers. These reactions involve substitution polymerization processes which are shown schematically in equation (500). The position of equilibrium depends on M, R and X. Long chain polymers are favored by weakly bonded ligands X, small alkyl substituents R on sulfur, and for M the sequence Ni > Pd > Pt is followed for favored polymerization. Thus within the metal triad, platinum(II) is the most amenable for effecting the directed synthesis of monomeric or dimeric complexes, and these concepts have been fully discussed and compared.[30]

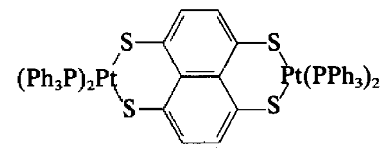
$$MX_2 + 2RS^- \longrightarrow MX_2(SR)_2^{2-} \rightleftharpoons [MX(SR)(\mu\text{-}SR)]_2^{2-} \rightleftharpoons [M(\mu\text{-}SR)_2]_n \quad (500)$$

The usual procedure to prepare thiolato complexes is to react halo platinum(II) complexes with the appropriate thiol and base, or with the preformed alkali metal or thallium thiolate salt. If the precursor complex is $PtCl_4^{2-}$, and excess thiolate is present, the product is polymeric (equation 501). Polymers of this type have been prepared with a wide range of thiolates.[1691–1694] Reversal of equation (500) can occur if a ligand X is added to the thiolate polymers which forms sufficiently strong bonds to platinum(II) to make bridge cleavage thermodynamically favored. Thiolato polymers can be cleaved by the addition of phosphine ligands. For the more strongly bridged complexes it may be necessary to add an alkylphosphine L or a chelating phosphine ligand L—L such as dppe (equation 502).[1695,1696] The chemistry of the chelating thiolate from ethanedithiol behaves in an analogous way. Extension to larger dithiolates allows for the synthesis of monomeric chelate complexes of platinum(II) with dithiolato ligands **(177)**–**(181)**.[1070,1697–1702]

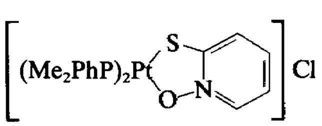
$$PtCl_4^{2-} + 2RS^- \longrightarrow [Pt(SR)_2]_n + 4Cl^- \quad (501)$$

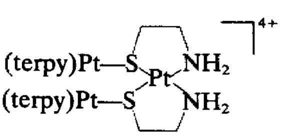
$$[Pt(SR)_2]_n + 2nL \longrightarrow nPt(SR)_2L_2 \quad (502)$$

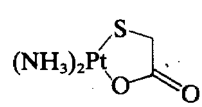




(177) X = S, Se; Y = S, CH_2 **(178)**





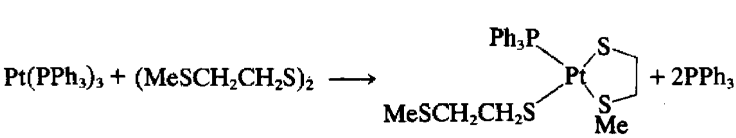


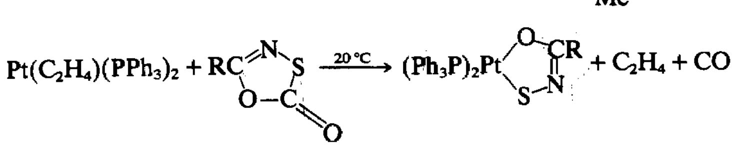
(179) **(180)** **(181)**

An alternative synthetic route to platinum(II) thiolates is by the oxidative addition of the S—S bond to platinum(0). When the sulfur atom has phenyl or electron-withdrawing substituents such as CF_3, this reaction is a useful one to synthesize the thiolato platinum(II) complexes (equation 503).[1703–1705] Simple alkyl disulfides such as Me_2S_2 and Et_2S_2 do not form stable dithiolato complexes of platinum(II) by S—S addition to $Pt(PPh_3)_3$, but if chelation can occur, 'chelate-assisted oxidative addition' can induce S—S cleavage (equation 504).[30] An unusual cyclic thiolato complex is obtained by the decarbonylative cleavage of a C—S bond (equation 505).[1707]

$$Pt(PPh_3)_3 + R_2S_2 \longrightarrow Pt(SR)_2(PPh_3)_2 + PPh_3 \quad (503)$$

$$R = CF_3,\ Ph,\ C_{10}Cl_6$$

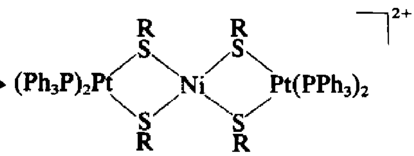
 (504)

 (505)

For complexes of type $Pt(SR)_2L_2$ with monodentate thiolate and ligands L the isolated product usually has *trans* stereochemistry. This is not necessarily the kinetic product, however, since exposure of the *cis* complexes to oxygen causes rearrangement to the *trans* isomer and other products.[1708]

Monomeric platinum(II) thiolates of type $Pt(SR)_2L_2$ can be converted into dimers or higher homologues by two methods. The first involves replacement of L to give a homobimetallic complex having bridging thiolate ligands (equation 506),[1709] and the second method (equation 507) is the analog of equation (496) in the sulfide series of complexes.[1710]

$$2Pt(SCH_2Ph)_2(PPh_2Me)_2 \xrightarrow[\text{in vacuo}]{210\,^\circ C} [Pt(SCH_2Ph)(\mu\text{-}SCH_2Ph)(PPh_2Me)]_2 + 2PPh_2Me \quad (506)$$

$2Pt(SR)_2(PPh_3)_2 + Ni^{2+} \longrightarrow$  (507)

Platinum(IV) thiolate complexes are uncommon, primarily because the thiolate ligand, and thiols in general, are unstable to oxidizing conditions. The reaction between thiophenol and $PtMe_2L_2$ may proceed *via* platinum(IV) thiolates as intermediates, but only the platinum(II) derivatives have been isolated (equation 508).[1711]

$$PtMe_2L_2 + PhSH \longrightarrow PtMe(SPh)L_2 + CH_4 \quad (508)$$

Bridging thiolato complexes with a $Pt_2(\mu\text{-}SR)_2$ core have a pseudotetrahedral geometry about sulfur, leading to an approximately 90° dihedral angle between the coordination planes of the two platinum centers.[1712] As a consequence, inversion through the bridging sulfurs can occur, a fluxional process whose rate is strongly dependent on the halide ligand X in $Pt_2X_2(\mu\text{-}SMe)_2(PPhMe_2)_2$ (X = Cl, Br, I). It is proposed that inversion at the sulfur *trans* to phosphorus is rapid on the NMR time scale, hence *syn* and *anti* isomers with respect to the two sulfur atoms cannot be detected.[1713]

Platinum(II) thiolates can be decomposed in strong acid because of protonation at sulfur (equation 509). This reaction is similar to electrophilic alkylation at the coordinated thiolate, although in this case the thioether complex may be isolable (equation 510). Thiolato ligands are unreactive to nucleophiles, and only under the most forcing conditions does ligand replacement occur.

$$Pt(SR)_2L_2 + 2HX \longrightarrow PtX_2L_2 + 2RSH \quad (509)$$

$$Pt(SR)_2L_2 + 2R'X \longrightarrow [Pt(SRR')_2L_2]X_2 \quad (510)$$

A platinum(II) complex with a monodentate isopropyl disulfide ligand has been reported.[1714] The complex (**182**) has been prepared by treating $Pt(C_2H_4)(PPh_3)_2$ with the N-substituted phthalimide compound $o\text{-}C_6H_4(CO)_2NSSPr^i$ (equation 511). The $PtSSCHMe_2$ group has an S—S distance of 2.037(4) Å and a torsion angle of 89.5°.

$$Pt(C_2H_4)(PPh_3)_2 + o\text{-}C_6H_4(CO)_2NSSPr^i \longrightarrow \underset{\textbf{(182)}}{cis\text{-}Pt(SSPr^i)\{N(CO)_2C_6H_4\text{-}o\}(PPh_3)_2} + C_2H_4 \quad (511)$$

52.6.2.4 Complexes with sulfide, selenide and telluride ligands

Platinum(II) forms both *cis* and *trans* complexes with compounds SR_2, SeR_2 and TeR_2. The complexes are usually formed by replacement reactions using the free ligand as reagent.[1715–1720] The complexes *trans*-$PtX_2(SR_2)_2$ (X = Cl, Br; R = Me, Et; $R_2 = (CH_2)_4$) are thermally stable, but the complex *trans*-$PtX_2\{S(CH_2)_5\}_2$ isomerizes in the solid state to the *cis* isomer.[1721] Ligand exchange studies on addition of free ZEt_2 to $MX_2(ZEt_2)_2$ (Z = S, Se, Te; M = Pd, Pt; X = Cl, Br, I) show that the rate of exchange decreases in the order $TeEt_2 \gg SeEt_2 > SEt_2$ and Pd > Pt.[1722] Carboxylato complexes of platinum(II) with diethyl sulfide ligands can be readily prepared using the silver carboxylate compound (equation 512). The complex *cis*-$Pt(OAc)_2(SEt_2)_2$ can be used to prepare a large variety of complexes, but the addition of tertiary phosphines leads to substitution and loss of the diethyl sulfide ligand.[1723]

$$PtCl_2(SEt_2)_2 + 2AgOAc \longrightarrow cis\text{-}Pt(OAc)_2(SR_2)_2 + 2AgCl \quad (512)$$

The replacement of Br^- in $[PtBr(dien)]^+$ by the sulfides SMe_2, S(Me)Et, SEt_2, $S(Me)C_2H_4Cl$-β, SPr^i_2, SBu^n_2, SBu^s_2, $S(CH_2)_4$ and thioxane show second-order rate constants which are insensitive to inductive effect changes in the organic groups attached to sulfur, but which decrease as the group bulkiness is increased (equation 513).[1724] This result correlates with the earlier observations that SEt_2 is less reactive toward *trans*-$PtCl_2py_2$ than is SMe_2.[1725] When ground state effects are considered, the *trans* influence of SR_2 is small, and comparable to NH_3 and Cl. Kinetic measurements on the replacement of the chloride *trans* to SR_2 in $PtCl_3(SR_2)^-$ by a variety of amines show that the *trans* effect of SR_2 is considerably greater than that of NH_3.[1726] The *cis* effect of SMe_2 is greater than that of an amine. This conclusion is drawn from kinetic data which show that for a variety of nucleophiles, the $Pt(SMe_2)(en)H_2O^{2+}$ complex is consistently more reactive than the analogous $Pt(dien)(H_2O)^{2+}$ compound. The relative reactivity varies by a factor of 2 or 3, and this is taken as the SMe_2:amine *cis* effect.[1727]

$$PtBr(dien)^+ + SR_2 \longrightarrow Pt(dien)(SR_2)^{2+} + Br^- \qquad (513)$$

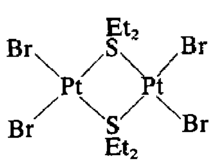
In addition, the complexes PtX_2L_2 (X = Cl, Br, I; L = SEt_2, $SeEt_2$, $TeEt_2$) are predominantly in the *trans* configuration. The complex $PtCl_2(TeEt_2)_2$ is isolated from solution as the *cis* isomer, but rapidly isomerizes back to *trans* in solution.[1728] The *trans* geometry is also found for the benzyl derivative $PtCl_2\{Te(CH_2Ph)_2\}_2$.[1729]

Binuclear-bridged platinum(II) complexes with ZR_2 ligands can be prepared. The complexes can be prepared by a number of different methods, and the range of earlier routes has been reviewed by Chatt and Venanzi.[1730] A number of the more general ones are listed in equations (514)–(516). Reaction (515) has been used in the earliest syntheses of complexes $Pt_2Cl_4(SEt_2)_2$ and $Pt_2Cl_4(SPr_2)_2$. The stabilities of these chloro-bridged complexes fall in the order $PR_3 \sim SR_2 > AsR_3 >$ amine $> TeR_2 > SbR_3 > SeR_2$. Bridging sulfide ligands are also known; the complex $Pt_2Br_4(SEt_2)_2$ (**183**) has terminal bromide ligands.[1731]

$$PtCl_2L_2 + PtCl_2 \longrightarrow Pt_2Cl_2(\mu\text{-}Cl)_2L_2 \qquad (514)$$

$$PtX_2L_2 + PtCl_4^{2-} \longrightarrow Pt_2Cl_2(\mu\text{-}Cl)_2L_2 + 2X^- \qquad (515)$$

$$2PtCl_2L(alkene) \longrightarrow Pt_2Cl_2(\mu\text{-}Cl)_2L_2 + 2alkene \qquad (516)$$

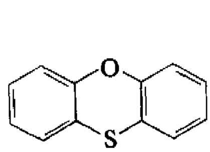


(**183**)

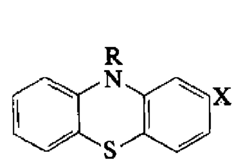
These platinum complexes with simple dialkyl sulfides show ν(PtS) in the region 310–350 cm^{-1}, and ν(PtSe) and ν(PtTe) in the region 170–230 cm^{-1}, the lowest energy band being due to the asymmetric stretch. In the electronic spectrum of a series of complexes *trans*-$PtCl_2L$(piperidine), the energies of the *d*–*d* transition decreases across the series L = $P(OMe)_3 > PPr_3 >$ piperidine $> AsPr_3 > SEt_2 > SeEt_2 > TeEt_2$, although the change is small.

Complexes have been prepared with more highly substituted, and also with chelating sulfide and selenide, ligands. Since intramolecular inversion through sulfur is sufficiently slow to be observed on the NMR time scale, the thrust of much of this work has been to understand this inversion process better.

Examples of multifunctional sulfides which bond to platinum(II) *via* the sulfide sulfur are phenoxathiin (**184**) and the phenothiazine drugs (**185**).[1732,1733]



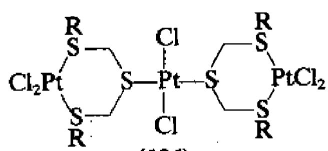
(**184**)



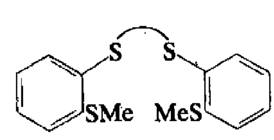
(**185**)

The sulfide group forms a large number of complexes where it is in chelation with a different heteroatom. Among the common heteroatoms are N, P and As. These complexes are too numerous to list here, but individual complexes can be found from Table 9 or from refs. 1224 and 1667. It is also possible to synthesize compounds which will form bi-, tri- and tetra-dentate complexes to platinum(II), where sulfur, selenium and tellurium are the only atoms which coordinate to the metal. A review of complexes formed from ligands of the type $RS(CH_2)_nSR$ has been recently published.[1734] This article outlines the synthesis, reactions and spectroscopy of these complexes, and allows the complexes of platinum to be placed in context with those of other transition metals.

Trifunctional sulfides $RSCH_2SCH_2SR$ can be prepared. With platinum(II) the chelate complexes can be synthesized, and the free sulfide group then utilized for coordination to a second platinum (**186**).[1735] The tetradentate ligands $MeS(CH_2)_nS(CH_2)_mS(CH_2)_nSMe$ and (**187**) can be prepared. Reaction with $PtCl_4^{2-}$ does not lead to complete replacement of all the chlorides by sulfide ligands. Use of $[Pt(MeCN)_4](ClO_4)_2$ does lead to complete substitution and the compounds PtL (L = S_4 tetradentate). The monomer structure is argued on the basis of the conductivity data.[1736] Sulfide ligands with strong electron-withdrawing ligands will also complex to platinum(II), the complex *cis*-$PtCl_2(CF_3SCH(Me)CH_2SCF_3)$ showing little difference in Pt—S bond distance due to the presence of the CF_3 substituents.[1737]

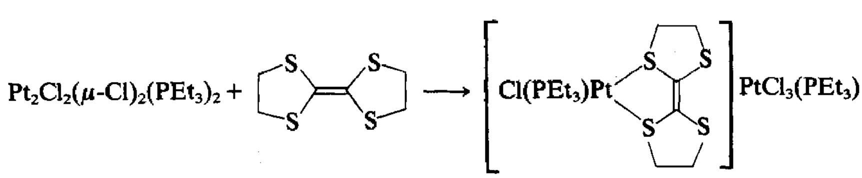


(**186**)



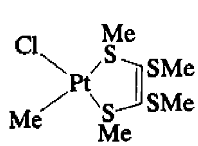
(**187**)

An unusual sulfide complex of platinum(II) is obtained with electron-rich alkenes (equation 517). These alkenes are often carbene precursors (Section 52.4), but the reaction with $Pt_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2$ gives a sulfide complex (**188**).[1738] With the compound $(MeS)_2C{=}C(SMe)_2$, the chelate complex (**189**) is formed with platinum(II), but with platinum(IV) the ligand will bridge two platinums (**190**).[1739]

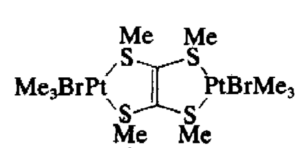


(517)

(**188**)

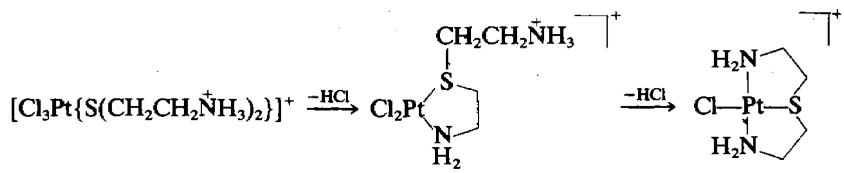


(**189**)



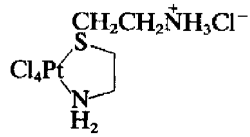
(**190**)

A number of platinum(II) complexes have been prepared where the sulfide group is in chelation with an amine.[1740–1742] With $S(CH_2CH_2NH_2)_2$, the monodentate S-bonded complex $[PtCl_3\{S(CH_2CH_2\overset{+}{N}H_3)_2\}]^+$ can be prepared. In basic media, ring closure occurs to form the tridentate complex (**192**; equation 518) with $\Delta H^{\neq}$ values in the region of 65 kJ mol^{-1} and $\Delta S^{\neq}$ of -38 J K^{-1} mol^{-1}. These enthalpies and entropies have been evaluated for each separate ring closure step.[1743] The intermediate (**191**) in this reaction has been oxidized by hydrogen peroxide in dilute HCl to give an early example of a platinum(IV) sulfide complex (**193**).[1744] Halogen (Cl_2 and Br_2) oxidation of sulfide complexes of platinum(II) appears to be a generally useful method to prepare complexes of type $PtX_4(S—S)$.[1745]



(518)

(191) (192)



(193)

(i) *Inversion at sulfur and selenium*

The inversion of configuration at the pyramidal sulfur atoms of sulfide complexes is amenable to study by NMR techniques.[1746–1750] The processes are intramolecular as evidenced by the retention of $^3J(PtH)$ coupling. The barriers to inversion for the complexes $PtX_2(ZEt_2)_2$ (X = Cl, Br, I; Z = S, Se, Te) follow the sequences Te > Se > S, and are sensitive to the *trans* influence of the opposite ligands. The inversion barriers are higher in the platinum complexes than in the analogous palladium complexes. The magnitudes of $\Delta G^{\neq}$ are in the range 51–84 kJ mol^{-1}.[1751,1752] Comparison between halides and sulfide ring size shows that the barrier energies in chloro complexes are 2–3 kJ mol^{-1} higher than in the corresponding bromides, which are in turn 4–5 kJ mol^{-1} higher than the iodo complexes. The dependence of pyramidal inversion energies on ring size in the series $PtX_2\{S(CH_2)_n\}_2$ follows a sequence where five- and six-membered rings are comparable with complexes of linear sulfides, but four-membered rings show an increased barrier, and three-membered rings do not invert at accessible temperatures.[1753] The difference in activation parameters has been ascribed to the effect of non-bonded interactions affecting the approach to the planar transition state, and for the palladium analogue this view is supported by $\Delta V^{\neq}$ measurements.[1754,1755] Heteroatom ring complexes such as 1,4-oxathiane and 1,4-oxaselenane coordinate through S or Se to platinum(II). The NMR coalescence in these cases is caused by site inversion about the ligand atom rather than by ring reversal of the cyclic ligand.[1756]

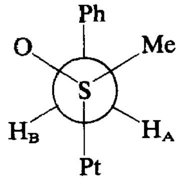
Platinum(IV) complexes with chelating bis(sulfide) or bis(selenide) ligands can be isolated. A specific synthetic route to the trimethyl platinum(IV) complexes involves cleavage of the tetranuclear complex $[(PtXMe_3)_4]$ with L—L [L—L = $MeECH_2EMe$, MeECH(Me)EMe, MeEEMe (E = S, Se)] to give the dinuclear complexes $[(PtXMe_3)_2(L—L)]$ (X = Cl, Br, I) (equation 519).[1757] The increase in barrier energy on going from S to Se in these complexes argues against the rate process being ring reversal since the barrier of the latter process is expected to decrease from S to Se.[1758] Further studies in this field have allowed separate barrier energies to be determined for ring reversal, pyramidal inversion of the S or Se atoms, S or Se atoms switching between Pt atoms, and a random cleavage of Pt—X bridge bonds allowing rotations which cause scrambling of the Pt—Me environments. The relative probabilities of simultaneous and non-simultaneous mechanisms for the inversion of pairs of chalcogen atoms are assessed.[1759–1762]

$$[(PtXMe_3)_4] + 2L—L \longrightarrow 2[(PtXMe_3)_2(L—L)] \quad (519)$$

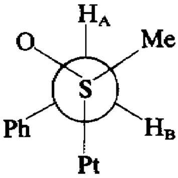
Comparative data have been collected for *cis*-PtX_2L_2 (X = Cl, Br, I; L = $MeS(CH_2)_2SMe$, $MeS(CH_2)_3SMe$, *o*-$(MeS)_2C_6H_3Me$, *cis*-MeSCH=CHSMe) and $[PtXMe(MeE(CH_2)_2E'Me)]$ (E = E′ = S or Se; E = S, E′ = Se; X = Cl, Br, I). Barrier energies decrease by 10–12 kJ mol^{-1} on going from aliphatic through aromatic to alkenic ligand backbones. Changing from Pt to Pd in MX_2L_2 causes a decrease in the S inversion barrier of 10–15 kJ mol^{-1}, and changing from platinum(II) to platinum(IV) causes a slight increase in the barrier. The halogen order for $\Delta G^{\neq}$ follows the sequence of Cl > Br > I, and the barrier decreases by 16 kJ mol^{-1} as the ring size increases from five to six.[1763] Stabilities of these complexes with chelating sulfide and selenide ligands can be correlated with $\delta(^{195}Pt)$ and $^{1}J(PtSe)$.[1764] For the compound $RS(CH_2)_5SR$ with five methylenes, barge complexes are formed.[1765] If chelating sulfides are used with CF_3 or C_6F_5 substituents terminally bound to sulfur, low temperature ^{19}F NMR methods can be used to identify *syn* and *anti* isomers, and to estimate inversion barriers.[1766] Cyclic ligands such as 1,3-dithiane and 1,3,5-trithiane also show configurational non-rigidity, and the exchange processes can be treated in the same manner.[1767]

52.6.2.5 Complexes with sulfoxide ligands

Dimethyl sulfoxide complexes $PtX_2(DMSO)_2$ (X = halide, NO_3, amine) have the ligand complexed to platinum(II) *via* sulfur both in the solid state and in solution. For O-bonded complexes of DMSO with first row transition metal ions, ν(S=O) is found between 910 and 960 cm^{-1}, which is at lower energy than ν(S—O) in free DMSO at 1055 cm^{-1}. For the S-bonded platinum(II) complex, ν(S—O) increases in energy on coordination to 1157, 1134 cm^{-1}. The complexes are *cis* in solution.[1768–1770] Analogous complexes $PtCl_2L_2$ (L = Et_2SO, $PhCH_2(Me)SO$, $(PhCH_2)_2SO$, $Me(Pr^i)SO$, $(Pr^i)_2SO$) can be prepared, and in each case coordination is *via* sulfur. Rotation about the Pt—S bond can interchange conformers, and values for J(PtH) can be used to deduce which conformer is the most favored. For $PtCl_2\{PhCH_2(Me)SO\}_2$, vicinal J(PtH) values can be assigned to the inequivalent methylene protons in both (±) and *meso* forms. From the magnitude of these couplings, conformers (**194**) and (**195**) are found to be favored.[1770]



(**194**)



(**195**)

Bridged complexes $Pt_2Z_2(\mu\text{-}X)_2(DMSO)_2$ can be prepared either by reacting $K[PtCl_3(DMSO)]$ with $AgNO_3$, or by treating $[PtCl_3(DMSO)]$ with KI to give $Pt_2I_2(\mu\text{-}I)_2(DMSO)_2$.[1771,1772] The Pt—S distances in the DMSO complex *cis*-$PtCl_2(DMSO)_2$ are 2.244 and 2.229 Å and the S—O distances 1.469 and 1.454 Å.[1773] The Pt—Cl distances are 2.306 and 2.312 Å, which are very normal distances, although the *trans* influence of DMSO has been claimed to be large.[1774]

Analysis of the forward and reverse steps for equation (520) shows that the strong *trans* effect of S-bonded DMSO is due to transition-state stabilization which results from the π-acceptor properties of the sulfur in this ligand.[1775] Comparative kinetics for chloride ion replacement in $[PtCl(DMSO)en]^+$ and $[PtCl(NH_3)(en)]^+$ by NH_3, N_3^-, NH_2OH, N_2H_4, Br^-, I^-, SCN^-, $SeCN^-$, SO_3^{2-} and $SC(NH_2)_2$ show that for the bimolecular step, the DMSO complex is at least one order of magnitude more labile than that of NH_3. The greater *cis* effect of DMSO arises from the greater nucleophilic discrimination factor of its complex.[1776] Using kinetic and equilibrium measurements, the *cis* and *trans* effects and influences for DMSO relative to other ligands are: (i) *trans* influence: $H_2O \approx Cl^- \approx Br^- < C_2H_4 \approx DMSO < NH_3$; (ii) *cis* influence: $DMSO \approx C_2H_4 < Br^- \approx Cl^- \approx H_2O < NH_3$; (iii) *trans* effect: $H_2O < NH_3 < Cl^- < Br^- < DMSO < C_2H_4$; (iv) *cis* effect: $C_2H_4 < Br^- \approx Cl^- < NH_3 \approx H_2O < DMSO$.[1777]

$$cis\text{-}[PtCl_2(DMSO)(amine)] + amine \rightleftharpoons cis\text{-}[PtCl(DMSO)(amine)_2]^+ + Cl^- \qquad (520)$$

As an entering group DMSO will substitute water in $Pt(H_2O)_4^{2+}$, in addition to chloride ion in $PtCl_4^{2-}$. The reaction with $Pt(H_2O)_4^{2+}$ can be followed by ^{195}Pt NMR techniques. The mechanism for water replacement by DMSO is mainly dissociative, but when more strongly coordinating ligands such as I^- are used instead of DMSO, the associative pathway becomes dominant.[1778] For chloro complexes of platinum(II) where the Cl^- is being substituted by DMSO, the associative pathway is sufficiently dominant that the five-coordinate transient is formed as an intermediate which can undergo a pseudorotation.[1779]

As a leaving group the sulfur-bonded DMSO ligand is some three orders of magnitude less labile than water, but the reactivity difference decreases with the nucleophilicity of the entering group.[1780]

As found for other ligands bonded to square planar platinum(II), photolysis can lead to isomerization in the complexes $PtCl_2(DMSO)_2$, $PtCl_2(Et_2SO)_2$ and $PtCl_2(Pr^n_2SO)_2$.[1781]

S-Oxides of methionine will also coordinate to platinum(II) *via* sulfur in an analogous manner to methionine itself. The carboxylate is uncoordinated and the methionine *S*-oxide ligand is complexed through nitrogen and sulfur. The coordination of the sulfoxide to platinum(II) introduces a second center of asymmetry into the compound.[1782] This concept is exemplified by the separation of the diastereoisomeric *meso* and *rac* forms of $PhS(O)CH_2CH_2S(O)Ph$, and coordination of the chelate ligands to $PtCl_2$.[1783]

52.6.2.6 Complexes of thiourea and related ligands

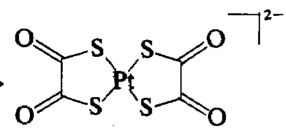
Thiourea, in common with other sulfur donors, forms stable complexes with platinum(II). Thiourea has a strong *trans* effect and will undergo substitution of both chloride and ammonia ligands in *cis*-$PtCl_2(NH_3)_2$ to give *cis*-$PtCl_2(NH_3)\{SC(NH_2)_2\}$, *cis*-$PtCl(NH_3)\{SC(NH_2)_2\}_2^+$, $PtCl\{SC(NH_2)_2\}_3^+$ and finally $Pt\{SC(NH_2)_2\}_4^{2+}$. With the chelating ligand bipyridyl, replacement of one chloride ion in $PtCl_2$(bipy) by thiourea leads to the singly substituted complex $PtCl\{SC(NH_2)_2\}(bipy)^+$ (equation 521).[1784] The cations PtL_4^{2+} (L = thiourea, thiocaprolactam, tetrahydro-2-pyrimidinethione, 2-imidazolidinethione, and 2-pyrimidinethione) will form mixed valence complexes $[PtL_4][PtCl_6]$.[1785] High-quality single crystals of the thiourea complex cannot be grown, but a microcrystalline powder shows mixed-valence bands at 532 and 470 nm.[1786] The ^{195}Pt chemical shifts of these compounds have been correlated with the σ-donor abilities of the ligands.[1787] Platinum complexes with ligands similar to thiourea have been prepared with isoperthiocyanic acid.[1788]

$$PtCl_2(bipy) + SC(NH_2)_2 \longrightarrow PtCl\{SC(NH_2)_2\}(bipy)^+ + Cl^- \qquad (521)$$

52.6.2.7 Complexes with thiocarboxylate ligands

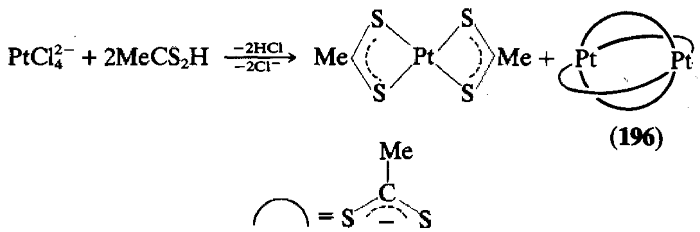
Thioacetic acid will oxidatively add to $Pt(PPh_3)_3$ to give a complex $PtH(SCOMe)(PPh_3)_2$, where the thioacetate group is S-bonded to platinum(II).[14] The compound Na_2PtCl_4 reacts with NaSCOPh to give the polymeric $[Pt(SCOPh)_2]_n$. These polymers can be cleaved by added ligand L (L = PPh_3, PPh_2Me, $PPhMe_2$, $AsPh_3$, $SbPh_3$, py) and L—L (L—L = bipy, dppm, dppe) to give the monodentate S-bonded complexes $Pt(SCOPh)_2L_2$ and $Pt(SCOPh)_2$(L—L) (equation 522).[1789] Unlike the carboxylate or dithiocarboxylate analogues, no evidence has been found for complexes of the type $[Pt(SCOPh)_2L]_n$ or $[M(SCOPh)L_2][SCOPh]$. Stable dithiooxalate complexes of platinum(II) can be prepared from $PtCl_2$ and $K_2(C_2O_2S_2)$ (equation 523).[1790,1791]

$$PtCl_4^{2-} + 2NaSCOPh \xrightarrow[-2Cl^-]{-2NaCl} [Pt(SCOPh)_2]_n \xrightarrow{2nL} nL_2Pt(SCOPh)_2 \qquad (522)$$

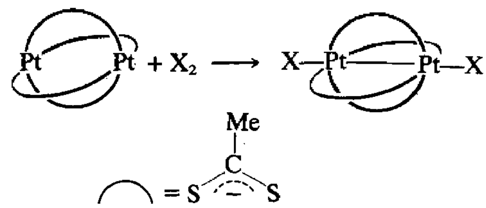
$PtCl_4^{2-} + 2K_2(C_2O_2S_2) \longrightarrow$  $+ 4KCl$ (523)

Chelate complexes are formed by platinum(II) with dithioacetates and dithiobenzoates.[1792,1793] The compound is prepared from K_2PtCl_4 in an analogous manner to the palladium complex.[1794] The compound appears to be in equilibrium with the dinuclear compound $Pt_2(S_2CMe)_4$ (**196**; equation 524). The complex (**196**) will add halogens X_2 (X = Cl, Br, I) to give the binuclear platinum(III)–(III) complexes $Pt_2(S_2CMe)_4X_2$ (equation 525).[1795] With a small amount of iodine, the mixed-valence platinum(II)–(III) complex $Pt_2(S_2CMe)_4X$

can be prepared.

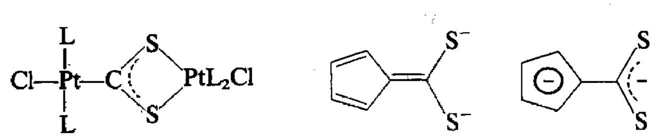


(196)



(525)

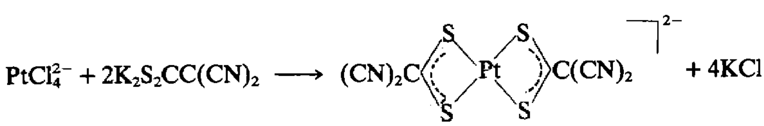
The complex (**197**) with a dithiocarboxylate ligand coordinated to platinum(II) bonded through both monodentate carbon and the chelating dithiocarboxylate ligand has been prepared from either the thiocarbonyl platinum(II) precursor or the carbon disulfide adduct of platinum(0).[1796,1797] A cyclopentadienyl-substituted dithiocarboxylate ligand (**198**) can be used to prepared S,S-bonded platinum(II) and (IV) complexes $Pt(C_5H_4CS_2)_2^{2-}$ and $Pt(C_5H_4CS_2)_3^{2-}$. The complexes show ν(PtS) at 340 cm^{-1}, and in each case electronic absorption bands of the Pt→L type are at 19 500 cm^{-1} and 29 500 cm^{-1}.[1798]



(**197**) L = PPh_3 (**198**)

52.6.2.8 Dithiocarbamate, diselenocarbamate, dithiophosphate and xanthate-type complexes

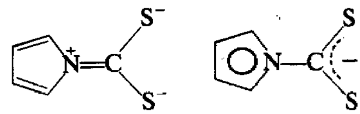
A monodentate S-bonded complex *cis*-$PtCl_2\{SC(OEt){=}NMe_2\}_2$ has been prepared with *N,N*-dimethyl-*O*-ethylthiocarbamate.[1799] The *N*-cyanodithiocarbamate complex of platinum(II) can be prepared by the reaction of $K_2S_2CC(CN)_2$ with K_2PtCl_4. The complex can be isolated as an orange solid (equation 526).[1800] An early preparation of the alkyl dithiocarbamate complexes of platinum(II) involves treatment of the precursor xanthate complexes with a secondary amine (equation 527), although these dithiocarbamate complexes have been known for a considerable time.[1802] A normal coordinate analysis of the bis dithiocarbamato complexes $Pt(S_2CNH_2)_2$ and $Pt(S_2CND_2)_2$ shows that the Pt—S stretching bands are at 375 and 288 cm^{-1}.[1803]



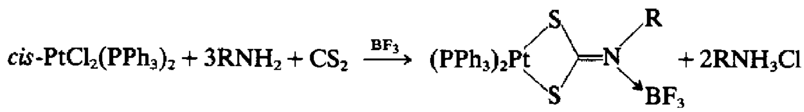
(526)

$$Pt(S_2COR)_2 + 2NHR'_2 \longrightarrow Pt(S_2CNR'_2)_2 + 2ROH \qquad (527)$$

The X-ray crystal structures of $Pt(S_2CNEt_2)_2$ and $PtCl(S_2CNEt_2)(PPh_3)$ show sulfur coordination of the dithiocarbamate ligand, with respective Pt—S distances of 2.349(7) Å and 2.294(7) Å for S atoms *trans* to P and Cl.[1804,1805] Analogous complexes can be prepared with an amino acid substituent on the dithiocarbamate.[1806] Other variations include the synthesis of bis complexes of platinum(II) with pyrrole ligand derivatives (**199**), which are similar to (**198**),[1807] and the synthesis of dithiocarbimidato complexes (**200**) from the reaction of *cis*-$PtCl_2(PPh_3)_2$ with primary amines in the presence of CS_2 and BF_3 (equation 528).[1808]



(**199**)



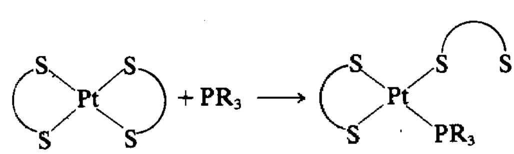
(528)

(**200**)

Unsymmetrically substituted dithiocarbamate complexes of platinum(II) can also be synthesized. Using NMR techniques, the barrier to rotation about the C═N bond is found to be in the region of 85 kJ mol^{-1}.[1809]

The availability of a convenient synthesis of CSe_2 has allowed the preparation of *N,N'*-dialkyldiselenocarbamate complexes of platinum(II).[1810,1811] From dialkyldiselenocarbamate salts the following platinum complexes have been prepared: $Pt(Se_2CNR_2)_2$ (R = Et, Bu^i), $PtCl(Se_2CNR_2)(PPh_3)$ (R = Et, Bu^i), $PtMe(Se_2CNEt_2)(PPh_3)$, *cis*-$PtX_2(Se_2CNBu^i_2)_2$ (X = Br, I), $PtI(Se_2CNEt_2)(PPh_3)$, $[Pt(Se_2CNBu^i_2)_3]Cl$. The structures of $Pt(Se_2CNBu^i_2)_2$[1810] and $PtMe(Se_2CNEt_2)(PPh_3)$[1812] have been confirmed by crystallography. Intramolecular rearrangements in these complexes can be followed by ^{77}Se NMR.[1813]

Bis chelating complexes of the S,S', S,Se and Se,Se' type can be prepared for platinum(II) where the heteroatom is phosphorus rather than nitrogen. An early review on metal complexes of thiophosphinic and selenophosphinic acids outlines the syntheses of the ligands as well as the complexes known up to that time.[1814] The later coordination chemistry of these ligands has led to the discovery of a variety of compound types.[1815–1818] Among these are the chelates $Pt(S_2PR_2)_2$ and $Pt\{S_2P(OR)_2\}_2$, the ionic complexes $[Pt(S_2PR_2)(PPh_3)_2](S_2PR_2)$, the monodentate dithiophosphate compounds $Pt(S_2PR_2)_2(PR_3)$ formed from the bis chelates and phosphine (equation 529), and the bis monodentate complexes (**201**). Rearrangements occur in these complexes *via* five-coordinate intermediates.[1818] In addition C—O cleavage in the dithiophosphate complexes $Pt\{S_2P(OR)_2\}_2$ can occur to give dithiocarbonates (**202**)[1801,1816,1819] which closely resemble the trithiocarbonato compounds (**203**).[1800]



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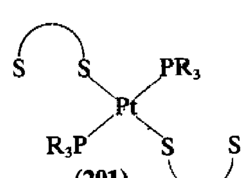

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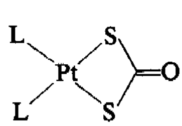
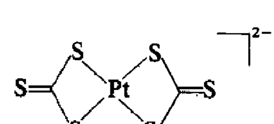


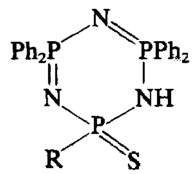
(**202**)



(**203**)

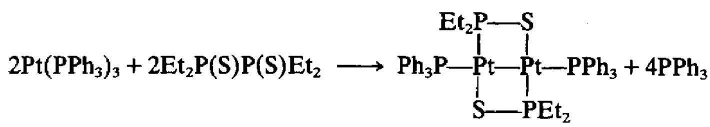
The MO schemes for the complexes $M\{S_2P(OEt)_2\}_2$ (M = Ni, Pd, Pt) have been discussed with respect to their UV photoelectron spectroscopy.[1820]

A rather unusual bis NS chelate complex of platinum(II) has been formed from the deprotonation of the compound (**204**).[1821]



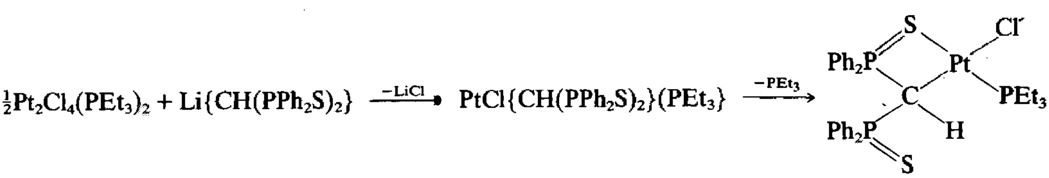
(204)

A dimeric thiophosphinato-bridged platinum complex (**204**) has been prepared by the addition of $Et_2P(S)P(S)Et_2$ to $Pt(PPh_3)_3$ (equation 530a). The compound has a Pt—Pt bond length of 2.628(1) Å, and is analogous to the compounds described earlier in ref. 1486.[1822] Treating $Pt_2Cl_4(PEt_3)_2$ in THF with $Li[CH(PPh_2S)_2]$ gives the complex $PtClCH(PPh_2S)_2(PEt_3)_2$, which isomerizes to $PtCl\{CH(PPh_2S)_2\}(PEt_3)$ (**206**; equation 530b).



(530a)

(205)

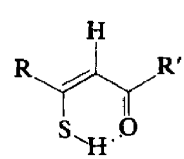


(530b)

(206)

52.6.2.9 Complexes with thio 1,3-β-diketonate ligands

Complexes of platinum(II) with β-monothiodiketonates, derived by deprotonation of the parent acid (**207**), can be prepared from $PtCl_4^{2-}$. The dark red complex $Pt\{C_3H(Ph)_2SO\}_2$ (R = R′ = Ph) shows IR bands at 1535 cm^{-1} [ν(C═C)], 1410 cm^{-1} [ν(C⩵O)] and 1270 cm^{-1} [ν(C⩵S)].[1824] Electronic spectra and dipole moment data for these complexes have been compared with the *O,O′*-diketonate complexes.[1825,1826] The structure of the phenyl derivative has been confirmed by X-ray crystallography.[1827] Detailed dipole moment measurements using static polarization have been made with fluorinated β-monothiodiketone complexes. Variations with substituent depend on the magnitude and vector directions of the Ph—X bond moments (aryl substituents), the inductive effect of the *meta* and *para* substituent on the phenyl ring, and the mesomeric effect of the substituent X.[1828] A useful separation method for bis(monothiotrifluoroacetylacetonates) of platinum(II) is gas chromatography.[1829]



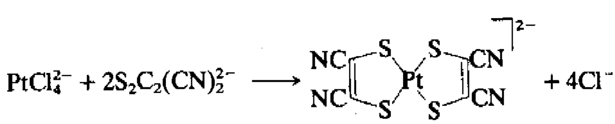
(207)

Complexes of dithioacetylacetone (SacSac) have been reviewed.[1830] As with acetylacetone complexes, the chemical shift of the ring methine proton has been carefully studied for metal and substituent effects in order to probe for any aromatic or anisotropic behavior in these six-membered ring complexes.[1830,1831] Much of the earlier work and theories on these complexes are summarized in an electrochemical study of the dithioketone complexes of Ni, Pd and Pt.[1832] The complexes undergo two successive reversible one-electron reductions in the range −0.8 to −1.8 V yielding the MS_4^- and MS_4^{2-} core.[1832,1833] The monoanion MS_4^- is usually unstable. The redox behavior of these 'odd-chain-number' compounds is similar to that of the 'even' 1,2-dithiolate complexes. Two differences, however, are that the odd dithiolate complexes have a lower electron affinity than the even dithiolate complexes with the same ligand substituent by about 1 V, and the MS_4 anions derived from the odd chelate are much less stable than those derived from the even ligand. Nevertheless the authors support the usefulness of Schrauzer's 'odd–even' theory.

Dithiomalonaldehyde forms an S,S′ chelate to platinum(II). The TCNQ charge transfer complex with bis(propene-3-thione-1-thiolato)platinum(II) shows a distorted square planar geometry about platinum with Pt—S distances of 2.282(1) and 2.278(1) Å.[1834]

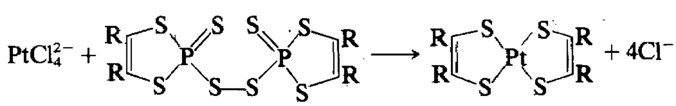
52.6.2.10 Complexes with 1,2-dithiolenes

1,2-Dithiolene complexes of transition metals can be prepared by a range of different routes. These are: (i) reaction of the divalent platinum halide with the sodium salt of the dithiolate anion in the presence of a bulky cation (equation 531);[1835,1836] (ii) addition of bis(trifluoromethyl)-1,2-dithietene to $Pt(PPh_3)_3$ to form $Pt\{S_2C_2(CF_3)_2\}(PPh_3)_2$ (equation 532);[1837] and (iii) reaction of K_2PtCl_4 with the appropriate thiophosphonic ester to give dimethyl- and diaryl-dithiolate derivatives (equation 533).[1838]



(531)

$$Pt(PPh_3)_3 + S_2C_2(CF_3)_2 \longrightarrow Pt\{S_2C_2(CF_3)\}_2(PPh_3)_2 + PPh_3 \quad (532)$$



(533)

These 1,2-dithiolene complexes have attracted considerable interest because of their facility to undergo sequential one-electron oxidations and reductions. A series of half-wave potentials are given in Table 10.[1660] It is apparent that the order of increasingly negative potentials for ML_2^-/ML_2^{2-} increases as the group R in the ligand $S_2C_2R_2^{2-}$ changes in the order R = CN > CF_3 > Ph > Me. Thus the dianions are stabilized by electron-withdrawing R groups such as CN^-, and destabilized by electron-releasing R groups such as methyl.[1839]

Table 10 Half-wave Potentials for Bis-1,2-dithiolene Complexes of Platinum in MeCN with a Calomel Scale

Ligand	ML_2^-/ML_2^{2-} (V)	ML_2/ML_2^- (V)
$S_2C_2(CN)_2$	+0.21	—
$S_2C_2(CF_3)_2$	−0.267	+0.819
$S_2C_2Ph_2$	−0.806	+0.06
$S_2C_2(p\text{-}MeOC_6H_4)_2$	−0.95	−0.03
$S_2C_2Me_2$	−1.10	−0.16

The IR spectrum of platinum(II) complexes of 1,2-dithiolenes shows bands due to ν(C═C), ν(C═S) and ν(PtS) in the respective ranges 1300–1500, 900–1200 cm^{-1} and 300–400 cm^{-1}. The electronic spectra show a number of very intense charge transfer bands in the visible region, which move to higher energy for the dianionic complexes. 1,2-Dithiolenes fall at the low end of the spectrochemical series in the sequence $S_2C_2(CN)_2^{2-} < Br^- < Cl^- < S_2C_2(CF_3)_2^{2-} < SCN^- < S_2P(OEt)_2^- < S_2CNR_2^- < H_2O \approx C_2O_4^{2-} < NH_3 < en < CN^-$.[1840,1841] The X-ray photoelectron spectroscopy of these platinum(II) dithiolene complexes shows that the charge on the metal remains essentially constant in the series of neutral, anionic and dianionic complexes, and that the change in electronic charge between the complexes resides principally on the ligand sulfur.[1842]

In addition to oxidation, maleonitriledithiolato complexes of platinum(II) will also undergo reduction with two closely spaced waves at −2.22 and −2.44 V. These processes are each one-electron reductions to $Pt\{S_2C_2(CN)_2\}_2^{3-}$ and $Pt\{S_2C_2(CN)_2\}_2^{4-}$ respectively.[1843] The highest published oxidation state for platinum in these dithiolene complexes is +5. This interpretation is based on the EPR spectra of the products obtained by bromine oxidation.[1844] Single crystal EPR spectra of the platinum(III) complex with bis(isotrithionedithiolato) shows these EPR signals at the g values 2.073, 2.168 and 1.858.[1845] The EPR spectra of the one-electron reduced species from $Pt(S_2C_2Ph_2)_2$ support the view, however, that these reductions are mainly ligand based.[1846] This result agrees with similar conclusions on dithiooxalato complexes of platinum.[1847]

Resonance Raman spectroscopy in conjunction with low temperature absorption spectroscopy can be used to assign the electronic levels in these complexes.[1848]

In chloroform solvent, the platinum dithiolene complexes $Pt(S_2C_2R_2)_2^{2-}$ are photooxidized between 300 and 350 nm, providing the complexes used are those for which the R groups result in redox potentials in the 0.1 to 0.5 V (*vs* SCE) range. The results are consistent with the reaction shown in equation (534).[1849] Further work on this system identifies the fact that several excited states are probably photoreactive in this process,[1850] and no definitive answer on the excited state reactivities is yet available. Very recently, however, highly structured solid-state emissions have been observed for $Pt\{S_2C_2(CN)_2\}\{P(OR)_3\}_2$, and this data may help resolve some of these questions.[1851]

$$Pt(S_2C_2R_2)_2^{2-} + CHCl_3 \longrightarrow Pt(S_2C_2R_2)_2^{-} + Cl^{-} + CHCl_2 \qquad (534)$$

The anionic dithiolene complexes will form salts with tetrathiafulvalene. Expectations were that the solids would be highly conducting, but the products are insulators or semiconductors.[1853]

Tetrathiolene complexes of platinum can be prepared from the sulfur-substituted derivatives of naphthalene, tetracene and chlorinated naphthalene.[1854]

52.6.2.11 Complexes with sulfur dioxide

As a Lewis acid, sulfur dioxide coordinates to platinum in its zerovalent oxidation state. Treating $Pt(PPh_3)_3$ with SO_2 gives the purple-colored complex $Pt(SO_2)(PPh_3)_3$, which readily loses triphenylphosphine to give $Pt(SO_2)(PPh_3)_2$ (equation 535).[1855,1856] Recently the chemistry of SO_2 with platinum complexes has received renewed attention, and the coordination chemistry of sulfur dioxide has been reviewed.[1857] When sulfur dioxide is passed through a toluene solution of $Pt(C_2H_4)(PPh_3)_2$, the brown-red complex $Pt(SO_2)_2(PPh_3)_2$ (**208**) is formed (equation 536). The geometry of (**208**) is a severely distorted tetrahedron with P—Pt—P and S—Pt—S angles of 158.58(6) and 106.33(8)°. Both S-bonded sulfur dioxide groups are pyramidal with the average angle between the Pt–S vectors and SO_2 planes being 119°, and an average Pt—S distance of 2.43 Å.[1858] A similar pyramidal sulfur dioxide coordinated to platinum is found in $Pt(SO_2)(PPh_3)_3$.[1859] The three-coordinate complexes $Pt(SO_2)(PCy_3)_2$ and $Pt(SO_2)(PBu^t_3)_2$ can be prepared. The complex $Pt(SO_2)(PCy_3)_2$ shows an η^1-pyramidal bonding for SO_2 with a Pt—S distance of 2.299(1) Å.[1860]

$$Pt(PPh_3)_3 + SO_2 \rightleftharpoons Pt(SO_2)(PPh_3)_3 \rightleftharpoons Pt(SO_2)(PPh_3)_2 + PPh_3 \qquad (535)$$

$$Pt(C_2H_4)(PPh_3)_2 + 2SO_2 \longrightarrow \underset{(\mathbf{208})}{Pt(SO_2)_2(PPh_3)_2} + C_2H_4 \qquad (536)$$

These monomeric sulfur dioxide adducts show $\nu(SO)$ in the region of 1030–1200 cm^{-1}, the band positions being diagnostic of the bonding mode.[1857,1860] The band $\delta(SO)$ is found in the region of 500 cm^{-1}. The complexes react with oxygen to give the corresponding sulfato compounds (equation 537). The reaction proceeds more slowly than does the corresponding reaction of the dioxygen complex of platinum with SO_2, and pathways requiring oxygen coordination prior to reaction are consistent with experimental data.[1860]

$$Pt(SO_2)L_n + O_2 \longrightarrow Pt(O_2SO_2)L_n \qquad (537)$$

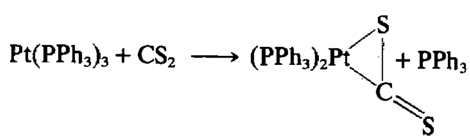
Slow removal of SO_2 from a toluene solution of $Pt(SO_2)_2(PPh_3)_2$ gives $Pt_3(SO_2)_3(PPh_3)_3$ (equation 538). The structure consists of a triangle of platinum atoms, each of which is bound to two bridging sulfur dioxide groups and a single triphenylphosphine.[1861] The analogous compounds $Pt_3(SO_2)_3L_3$ ($L = PCy_3$, PBu^t_3) can be similarly prepared.[1862] An alternative general synthetic route to SO_2 complexes of platinum clusters is the reaction of SO_2 with carbonyl clusters of platinum. Using as precursors $Pt_3(\mu\text{-}CO)_3(PPh_3)_4$, $Pt_4(\mu\text{-}CO)_5(PPhMe_2)_4$ and $Pt_5(\mu\text{-}CO)_5(CO)(PPh_3)_4$, the respective SO_2 complexes $Pt_3(\mu\text{-}SO_2)_3(PPh_3)_3$, $Pt_4(\mu\text{-}SO_2)_5(PPhMe_2)_4$ and $Pt_5(\mu\text{-}CO)_2(\mu\text{-}SO_2)_3(CO)(PPh_3)_4$ are formed.[1863]

$$3Pt(SO_2)_2(PPh_3)_2 \longrightarrow Pt_3(SO_2)_3(PPh_3)_3 + 3SO_2 + 3PPh_3 \qquad (538)$$

Sulfur dioxide will insert into Pt—carbon bonds (Section 52.4.8.4). Evidence has also been presented that sulfur dioxide will coordinate to the axial ends of the bimetallic Pt^{II}–Pt^{II} complex $Pt_2(P_2O_5H_2)_4^{4-}$; the reaction is an equilibrium process and no structural data are given.[1495]

52.6.2.12 Complexes with carbon disulfide and carbon diselenide

Carbon disulfide adds to $Pt(PPh_3)_3$ to give $Pt(CS_2)(PPh_3)_2$ (**209**; equation 539).[1864] The structure of (**209**) shows the CS_2 coordinated by a single π bond with distances of 1.72 Å and 1.54 Å for the coordinated and free C—S bonds respectively.[1865] The SCS bond angle is 136°.



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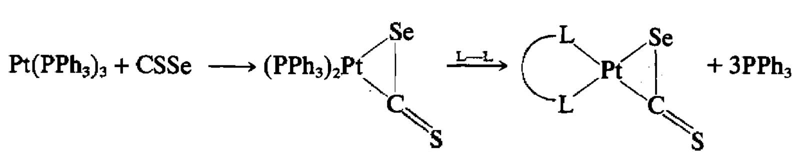
(**209**)

Carbon disulfide reacts with $Pt(PCy_3)_2$ to give the adduct $Pt(CS_2)(PCy_3)_2$. The compound can also be prepared from $Pt(SO_2)(PCy_3)_2$, the reaction being reversible (equation 540).[1860] With $Pt(PBu^t_3)_2$ a different reaction with CS_2 occurs to give $Pt_3(CS_2)_3(PBu^t_3)_3$. The PCy_3 analog $Pt_3(CS_2)_3(PCy_3)_3$ can be formed from $Pt(C_2H_4)_2(PCy_3)$.[1862]

$$Pt(SO_2)(PCy_3)_2 \underset{SO_2}{\overset{CS_2}{\rightleftharpoons}} Pt(CS_2)(PCy_3)_2 \qquad (540)$$

The carbon diselenide and carbon sulfide selenide complexes of platinum(0) can be synthesized from $Pt(PPh_3)_3$. Reaction of the compounds with chelating phosphines results in substitution of the triphenylphosphines (equation 541).[1866] With COS the C,S-bonded compound $Pt(COS)(PPh_3)_2$ is formed from $Pt(PPh_3)_3$. The reaction can also be used to prepare the dithiocarbonato complex $Pt(S_2CO)(PPh_3)_2$.[1867]



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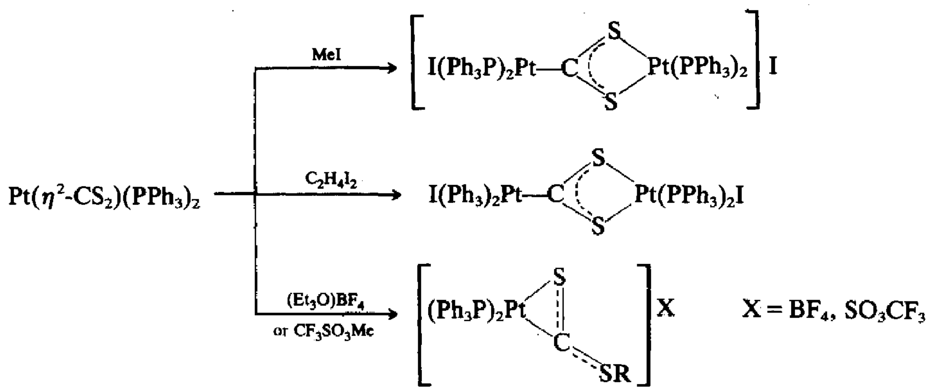
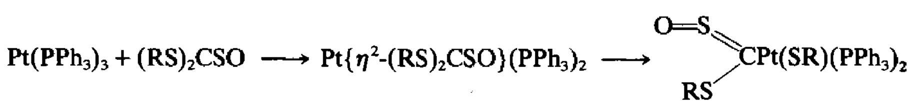
Coordination of a π-acceptor ligand makes it susceptible to electrophilic attack. The reactions of $Pt(\eta^2\text{-}CS_2)(PPh_3)_2$ with MeI, $C_2H_4I_2$, CF_3SO_3Me and $[Et_3O]BF_4$ are shown in

Scheme 18.[1868]



Scheme 18

Sulfine complexes of platinum(II) can be formed by oxidative addition to $Pt(PPh_3)_3$. The initial step involves the formation of an η^2-CS complex which undergoes intramolecular oxidative addition of a C—S bond (equation 542).[1869] Use of $Pt(cod)_2$ and PCy_3 gives the tricyclohexylphosphine analogue.[1870] The reaction gives two stereoisomers.[1871] The coordination stabilization of sulfines allows their synthesis in the coordination sphere of platinum, but the cyclic process is not very efficient.[1872]



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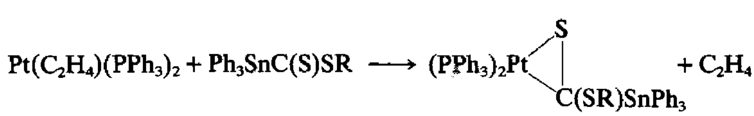
52.6.2.13 *Stannyldithioformate complexes*

The reaction between $Pt(C_2H_4)(PPh_3)_2$ and $Ph_3SnC(S)SR$ (R = Me, CH_2Ph, 2-propenyl) gives $Pt\{Ph_3SnC(S)SR\}(PPh_3)_2$ (equation 543), which has a structure analogous to the η^2-CS_2 complex of platinum(0).



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An *S*-methyl(triphenyl)dithioformate complex of platinum(0) has been prepared from $Pt(C_2H_4)(PPh_3)_2$ and $Ph_3SnC(S)SMe$.[1873]

52.6.2.14 *Thiocyanate complexes*

The coordination chemistry of the cyanate, thiocyanate and selenocyanate ligands has been recently reviewed.[1874] Platinum(II) forms the complex ion $Pt(SCN)_4^{2-}$, and the corresponding homoleptic platinum(IV) complex $Pt(SCN)_6^{2-}$ can be prepared. Numerous mixed ligand complexes of platinum(II) are known containing the thiocyanate ligand and other ligands, although there are fewer platinum(IV) examples.[1874]

Much discussion on the coordination chemistry of the thiocyanate ligand centers on its function as an ambidentate ligand. For coordination to platinum both N-bonded and S-bonded thiocyanate ligands are found and the small energy difference between the two bonding modes leads to small effects such as steric and electronic factors, as well as solvent changes, causing conversion between S- and N-bonded thiocyanate.

IR spectroscopy has been used to distinguish between the isomeric forms. For N-bonded isomers one finds $\nu(CN)$, $\delta(NCS)$ and $\nu(CS)$ at 2040–2100, 448–480 and 780–860 cm^{-1} respectively, and the corresponding positions for the S-bonded isomer are in the ranges 2080–2100, 410–470 and 690–720 cm^{-1}.[1875] Alternative methods include ^{14}N and ^{15}N NMR spectroscopy and nitrogen NQR methods.[1876,1877]

Complexes such as *cis*-$Pt(NCS)(SCN)(Ph_2PC{\equiv}CR)_2$ and $Pt(NCS)(SCN)(Ph_2PCH_2CCF_3\text{-}CHPPh_2)$ are known where both N- and S-bonded thiocyanate ligands are present in the same monomeric complex.[1878,1879] Many thiocyanate complexes of type PtX_2L_2 (X = NCS, SCN; L = tertiary phosphine) are known. Both $(SCN)_2$ and (NCS)(SCN) bonding modes are found with a range of bidentate phosphine and arsine ligands.[1880,1881] For the complexes PtX_3L^- (L = NMe_3, $PMe_{3-n}Et_n$ (n = 0–3), $AsMe_3$, $AsMe_2Et$, $SbMe_3$, SMe_2, $SeMe_2$, $TeMe_2$), N-bonding of the thiocyanate ion is favored when L contains a light donor atom, when the *trans* ligand has a high *trans* influence, or when a *cis* ligand is bulky.[1882] Similar effects are found for the complexes PtX_2L_2 with similar L ligands.[1883] The mixed pseudohalide complex *trans*-$Pt(NCS)(CN)(PPh_3)_2$ is also known.[1884]

The thiocyanate ligand will also bridge two metal ions. The α and β forms of $Pt_2Cl_2(NCS)_2(PPr_3)_2$ initially prepared by Chatt have been shown by crystallography to have the structures (**210**) and (**211**).[1885]

(**210**) (**211**)

Both $Pt(SeCN)_6^{2-}$ and $Pt(SeCN)_4^{2-}$ have been prepared, as have the mixed ligand complexes $Pt(SeCN)_2(bipy)$ and *trans*-$PtH(SeCN)L_2$ (P = PPh_3, PBu_3).[1874] Compared to the SCN^- ligand, $SeCN^-$ has a strong tendency to bond to platinum *via* the selenium atom.

52.7 COMPLEXES OF GROUP VII LIGANDS

52.7.1 Synthesis and Structure

Halide complexes of platinum(II) are commonly available compounds. The binary compounds $PtCl_2$, $PtBr_2$, PtI_2 are known, as are the platinum(IV) halides PtF_4, $PtCl_4$, $PtBr_4$ and PtI_4.[7] The structure of β-$PtCl_2$ shows it to be hexameric and composed of discrete Pt_6Cl_{12} units with Pt–Pt distances of 3.32 and 3.40 Å, and Pt—Cl distances of 2.34 and 2.39 Å.[1886] More commonly in coordination chemistry, the complex ions of these compounds are encountered. The anion $PtCl_4^{2-}$ can be formed by dissolving $PtCl_2$ in HCl, followed by the addition of an alkali metal chloride. The sodium and potassium salts dissolve in water to give red solutions. Replacement of chloride ion by Br^- or I^- gives $PtBr_4^{2-}$ and PtI_4^{2-}, although the conversion of the latter to $Pt_2I_6^{2-}$ casts doubt as to the solution existence of PtI_4^{2-}.[1887] Treating PtX_4^{2-} (X = Cl, Br) or PtI_2 with R_4NX or Ph_4AsCl (X = Cl) gives the complexes $Pt_2X_4(\mu\text{-}X)_2^{2-}$. These compounds have limited solubility in water, but the complexes are solution stable in this medium.[1888] The cyclopropenium salts are very soluble in dichloromethane.[1889] For platinum(IV), the fluoro complex K_2PtF_6 can be obtained by fluorination of $PtCl_4^{2-}$ or by treating Pt metal with a mixture of Br_2 and BrF_5 followed by KF. The complexes $PtCl_6^{2-}$ and $PtBr_6^{2-}$ can be obtained from the metal by oxidation with a mixture of the halogen and the hydrohalic acid. The parent acids H_2PtX_6 (X = Cl, Br) are water soluble and frequently used. These complex ions are much less soluble than their divalent counterparts, the potassium salts in this case being very insoluble. The iodo derivative can be formed from $PtCl_6^{2-}$ and KI, but aqueous solutions are not very stable. The detailed synthetic procedures for many of these halo complexes have been published, and the recovery of platinum from laboratory residues uses analogous procedures.[1890–1897]

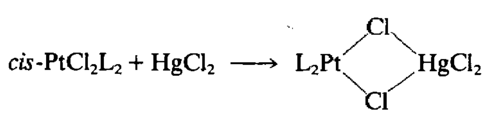
As a 'soft' metal on the Pearson scale, the heavier halide ions will readily substitute the lighter halogens bonded to platinum(II) and platinum(IV). As a consequence, fluoride complexes of platinum are relatively rare when compared to the large number of known complexes of platinum with complexed chloride, bromide or iodide ligands. Among the known fluoro complexes which are not simple binary complexes are $[PtF(PPh_3)_3]HF_2$, prepared from $Pt(PPh_3)_3$ and liquid HF,[1898] $[PtF(PEt_3)_2L]X$ (L = PEt_3, PPh_3, $P(OPh)_3$) formed from the corresponding chloro complexes by metathetical replacement with AgF,[1899,1900] and $PtF\{CH(CF_3)_2\}(PPh_3)_2$.[1901] Fluoro complexes of platinum can be readily detected by ^{19}F NMR spectroscopy, and $^1J(PtF)$ is in the region of 1000–2000 Hz. For chlorofluoro, fluorohydroxy and chlorofluorohydroxy platinum(IV) salts the ^{19}F chemical shifts correlate to $\delta = pC + qT$ where C and T are constants characteristic of Cl^- or OH^-, and p and q are the number of substituents *cis* and *trans* to the fluorine atom, respectively.[1902] More recently phase transfer has been used to substitute fluoride ion into platinum(IV) halo complexes to give mixed fluorohalo platinum(IV) complexes.[1903] The method can be extended for NO_2^-, CN^-, SCN^- and $C_2O_4^{2-}$.

Chloroplatinic acid, H_2PtCl_6, is a hydroscopic compound which is commercially available. The compound is probably $(H_3O)_2[PtCl_6]\cdot 2.04H_2O$. In the 110–125 °C range the water loss leaves $0.84\,H_2O$ in the compound, and at 220 °C the material is $PtCl_4$. Above 350 °C the product is $PtCl_2$ which then loses chlorine to give platinum metal at temperatures above 510 °C.[1904] Chloroplatinic acid is used for hydrosilylation; it will also effect H–D exchange reactions with aromatics (although $PtCl_4^{2-}$ is preferable),[1905] chlorination of alkanes,[1905] and undergo photochemical reaction with alkanes at room temperature.[1906] An unusual feature of the β-$PtCl_2$ lattice is that it can act as host to a range of small molecules such as Br_2, C_6H_6, CS_2, CCl_4, $CHCl_3$ or CH_2Cl_2. The adducts have a stoichiometry of one Pt_6Cl_{12} host to 1 or 0.75 inclusion molecules.[1907]

All the halide ions except fluoride are good bridging ligands. Their ability to act as bridging ligands relative to their ability to act as terminal ligands increases with increasing atomic number, so that I^- is equally effective as a terminal or a bridging ligand. In earlier sections halide bridging has been used to explain symmetrization reactions. Also the ready cleavage of halide bridges by neutral ligands L, or anionic ligands X^-, has been discussed as a method to prepare complexes of type $PtLX_3^-$ and PtX_2L_2.[1908,1909]

Halide bridges are commonly used to form bimetallic complexes between platinum(II) and a second transition metal or Group B metal. These complexes can be formed by symmetrization reactions between halide complexes of different metals (equation 544). All three complexes are in dynamic equilibrium and exchange occurs *via* a tetrameric intermediate involving four metal centers.[1910] The mixed metal complexes are not isolated, but they can be observed by ^{31}P NMR spectroscopy. Electrophilic metal ions like Hg^{II} will bridge to the chloride ligands of *cis*-$PtCl_2L_2$ to give the mixed metal complexes (**212**; equation 545).[1911] A third approach involves non-complementary redox reactions generating coordinatively unsaturated platinum cations which act as an electrophile to form halide bridges with the reduced oxidant (equation 546).[1912]

$$Pt_2Cl_4L_2 + Pd_2Cl_4L'_2 \rightleftharpoons 2PtPdCl_4LL' \qquad (544)$$
$$L = L' \text{ or } L \neq L'$$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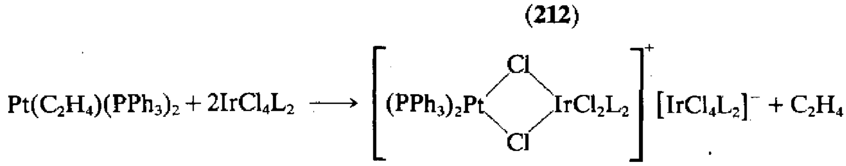
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52.7.2 Spectroscopy

52.7.2.1 Vibrational spectroscopy

The IR and Raman spectra of haloplatinum complexes have been studied in considerable detail. Values for $\nu(PtX)$ follow the sequence $X = Cl > Br > I$, and the precise band positions in complexes *cis*-PtX_2L_2 are sensitive to the *trans* influence of the *trans* ligand, groups with high *trans* influence causing a lowering of $\nu(PtCl)$.[1913] For the *trans* complexes PtX_2L_2 the positions of $\nu(PtX)$ are $340 \pm 3\,cm^{-1}$ ($X = Cl$) and $244 \pm 20\,cm^{-1}$ ($X = Br$), and these positions are quite insensitive to the nature of L.[1914] For the bridging complexes $Pt_2X_2(\mu\text{-}X)_2L_2$ the value for $\nu(PtX_{terminal})$ is independent of L as is $\nu(PtX_{bridging})$ which is *trans* to X. Values for these and $\nu(PtX_{bridging})$ which is *trans* to L are shown in Table 11. The Raman and IR bands, along with force constants, for both the platinum(II) and platinum(IV) halo complexes are shown in Table 12. It is noteworthy that the force constant f(PtX) for *both* platinum(II) and (IV) halides decreases in the sequence Pt—Cl > Pt—Br > Pt—I.

Table 11 Stretching Frequencies (cm^{-1}) in $Pt_2Cl_2(\mu\text{-}Cl)_2L_2$

L	$\nu(PtCl_t)^a$	$\nu(PtCl_b)^{b,c}$	$\nu(PtCl_b)^{b,d}$	*Ref.*
PMe_3	347	260	330	1915
PEt_3	351	265	327	1915
PPr^n_3	356	257	323	1915
$AsMe_3$	351	257	323	1915
$AsEt_3$	350	261	322	1915
C_2H_4	359	287	317	1915
CO	368	301	331	1915

[a] t = terminal. [b] b = bridging. [c] L *trans*. [d] X *trans*.

Table 12 Stretching Frequencies (cm^{-1}) and Force Constants (10^{-5} J $Å^{-1}$) for PtX_6^{2-}

Complex	$\nu(PtX)_{sym}$	$\nu(PtX)_{asym}$	$f(PtX)(A_{1g}$ *mode*)		*Ref.*
$PtCl_4^{2-}$	330	312	2.24	—	1916
$PtBr_4^{2-}$	208	194	1.97	—	1916
PtI_4^{2-}	155	142	1.79	—	1916
$PtCl_6^{2-}$	344	—	2.15	1917	1918
$PtBr_6^{2-}$	207	—	1.73	1917	1918
PtI_6^{2-}	150.3	—	1.06	1919	1918

Force constant calculations for the in-plane vibrations of $Pt_2X_4(\mu\text{-}X)_2^{2-}$ show that the terminal stretching force constants are larger than the bridging stretching force constants but that the difference diminishes for the heavier halides.[1920]

A number of less routine vibrational measurements have been made with haloplatinum complexes. On cooling below 100 K, new combination bands are found at 305 and 310 cm^{-1} for $PtCl_4^{2-}$. These assignments as combinations are tentative but are based on intensity characteristics.[1921] Detailed assignments of the vibrational modes in both $PtCl_4^{2-}$ and $PtBr_4^{2-}$ have been done with the aid of single crystal measurements.[1922,1923] The first systematic high pressure Raman study of inorganic complexes (P = 0–20 kbar) assigns $\Delta\nu/\Delta P$ for the different vibrational modes of $PtCl_6^{2-}$.[1924]

52.7.2.2 Electronic spectroscopy

Since platinum(II) is one of the few transition metal ions which strongly shows a preference for square planar geometry, the electronic spectra of these complexes have been studied in considerable detail. The early work on spectral assignment is well summarized in Hartley's book,[7] and more recent general references should be consulted by the reader who desires complete information.[1925–1928] A recent interpretation of the ligand field spectra of $PtCl_4^{2-}$ and $PtBr_4^{2-}$ addresses the question of the energy levels of the a_{1g} (d_{z^2}) orbital. The spectra are satisfactorily fitted if a parameter is added which accounts for *sd* orbital mixing.[1929] Detailed discussion of the spectral features is beyond the scope of this chapter, but this recent article along with earlier articles discussing charge-transfer bands, ligand–metal mixing, and UV transitions in PtX_4^{2-},[1930–1932] provide the reader with a comprehensive bibliography. Assignments have been supported by single crystal polarization measurements,[1933,1934] by analysis of the luminescence spectrum,[1935] and by Franck–Condon analysis of the vibronic structure in the single crystal polarized luminescence spectra of K_2PtCl_4 and K_2PtBr_4.[1936]

The electronic spectrum of the dimer $Pt_2(\mu\text{-}Cl)_2Cl_4^{2-}$ has been analyzed from single crystal measurements. The lowest excited states in the $Pt^{II}Cl_4$ chromophore increase energetically according to $^3E_g < {}^3A_{2g} < {}^3B_{1g} < {}^1A_{2g}$, and the intensity enhancement of the $^1A_g \rightarrow B_{2u}$ (^3A_u) transition and the 1650 cm^{-1} splitting observed for the $^1A_g \rightarrow B_{2u}$ ($^1B_{2u}$) bands show that moderate Pt–Pt interactions are present in $Pt_2Cl_6^{2-}$. The Pt–Pt separation is 3.481(2) Å.[1937] The corresponding dimeric bromo analog $Pt_2(\mu\text{-}Br)_2Br_4^{2-}$ has also been studied as a polarized single crystal. The *d–d* transition energies are comparable to those for $PtBr_4^{2-}$, but the Pt←L charge transfer transitions occur at lower energies in the dimer.[1938]

The electronic spectra of the platinum(IV) halo anions PtX_6^{2-}(X = F, Cl, Br, I) have also been assigned. The *d–d* bands are at 28 750 and 36 350 cm^{-1} for PtF_6^{2-}, at 22 100 and 28 300 cm^{-1} for $PtCl_6^{2-}$, and 19 100 and 23 000 cm^{-1} for $PtBr_6^{2-}$.[1939–1941] The charge transfer bands lie at lower energies than in the corresponding platinum(II) halo complexes. Doped salts of PtX_6^{2-} (X = F, Cl, Br, I) all show structured luminescence spectra at low temperatures.[1942] The spectrochemical series for platinum(IV) in the ions PtX_6^{2-} is $SeCN^- < Br^- < SCN^- < N_3^- < Cl^- < NH_3 \approx en < NO_2^- < CN^-$.[1941]

52.7.2.3 ESCA, NQR and Mössbauer spectroscopy

Both chlorine and platinum ESCA have been reported for halo complexes of platinum.[1943,1944] For complexes $PtCl_3L^-$ the *cis* and *trans* chlorides (to L) can be distinguished, and the binding energies follow the expected changes from *trans* influence effects. These Cl ($2p_{3/2}$) binding energies correlate with the NQR frequency of ^{35}Cl.[1944] NQR spectroscopy has also been used to estimate the percent ionic character in the Pt—X bonds of K_2PtCl_4 and K_2PtBr_4,[1945,1946] and of K_2PtCl_6, K_2PtBr_6 and K_2PtI_6.[1947–1949]

Iodine-129 Mössbauer spectroscopy can be used with iodo complexes. The shifts are sensitive to *cis* and *trans* ligands, and correlations can be made with ligand *trans* influences.[1950,1951]

52.7.3 Mixed-valence Chains

In many of these mixed-valence complexes of platinum, the halide ligand acts as a bridge between the two platinum centers. Complexes such as $PtBr_3(NH_3)_2$ can be prepared by evaporation of equimolar amounts of $PtBr_2(NH_3)_2$ and $PtBr_4(NH_3)_2$. The compounds have alternating stacks of platinum(II) and platinum(IV) centers with a single halide bridge joining them. The compounds have low electrical conductivities at ambient pressure but close to 10^{-1} ohm^{-1} cm^{-1} at 140 kbar.[1952–1954] Other similar Wolfram's red salt analogues can be prepared with ethylenediamine, propylenediamine, trimethylenediamine or pyridine, along with mixed palladium–platinum compounds.[1955–1958] All these complexes have infinite chains with single halide bridges.

The band structures of these complexes have been calculated by an extended Hückel method. The singly bridged $[PtL_4{\cdot}PtL_4X_2]^{4+}$ chain provides a partially filled band when all the metal-bridging halide bonds become identical in length.[1959] Similar calculations can be made on halide-bridged electrode reactions to calculate the activation energies for the electrochemical interconversion between platinum(IV) and platinum(II) complexes.[1960] The results suggest a platinum(III) intermediacy.

These complexes show intense broad intervalence bands ($Pt^{IV} \leftarrow Pt^{II}$) in the electronic spectra. Irradiation within the intervalence band leads to strong intensification of the Raman band attributed to the totally symmetric stretching mode $\nu_{sym}(X\text{—}Pt^{IV}\text{—}X)$ and its overtones. Data have been collected and analyzed for a wide range of these mixed valence compounds.[1961–1971] These complexes are discussed more fully by Underhill in Chapter 60.

52.8 COMPLEXES OF GROUP VIII LIGANDS

Although the product is not strictly a coordination compound of xenon, PtF_5 reacts with xenon in the presence of fluorine at 200 °C to give $[XeF_5]^+[PtF_6]^-$. Xenon is oxidized by PtF_6 to give both $Xe(PtF_6)$ and $Xe(PtF_6)_2$.[1972–1974] The former compound resembles $O_2(PtF_6)$. Similar ionic compounds are formed with krypton; treating KrF_2 with PtF_6 gives $[KrF]^+[PtF_6]^-$ (equation 547).[1975]

$$KrF_2 + PtF_6 \longrightarrow (KrF)^+[PtF_6]^- + \tfrac{1}{2}F_2 \qquad (547)$$

The optical spectra of Ni, Pd and Pt in noble gas matrices have been measured in order to search for complexes of these Group VIII ligands. Changes in the energy levels of the matrix isolated atoms occur because of a weak metal interaction. For platinum the frequency shifts follow the trend Xe > Ar > Kr, but whether this interaction is described as a Van der Waals interaction or a weak coordinate bond is open to speculation.[1976]

52.9 SUBSTITUTION REACTIONS AND REACTION MECHANISMS

In terms of the development of an understanding of the reactivity patterns of inorganic complexes, the two metals which have been pivotal are platinum and cobalt. This importance is to a large part a consequence of each metal having available one or more oxidation states which are kinetically inert. Platinum is a particularly useful element of this pair because it has two kinetically inert sets of complexes (divalent and tetravalent) in addition to the complexes of platinum(0), which is a kinetically labile center. The complexes of divalent and tetravalent platinum show significant differences. Divalent platinum forms four-coordinate planar complexes which have a coordinately unsaturated 16-electron d^8 platinum center, whereas tetravalent platinum is an 18-electron d^6 center which is coordinately saturated in its usual hexacoordination. In terms of mechanistic interpretation one must therefore consider both associative and dissociative substitution pathways, in addition to mechanisms involving electron transfer or inner-sphere atom transfer redox processes. A number of books and articles have been written about replacement reactions in platinum complexes, and a number of these are summarized in Table 13.

Table 13 Books and Reviews Covering Substitution Reactions of Platinum Complexes

Title	*Ref.*
Mechanisms of Inorganic Reactions	3
Organometallic and Coordination Chemistry of Platinum	5
The Chemistry of Platinum and Palladium	7
Coordination Chemistry	974
Ligand Substitution Processes	975
Inorganic Reaction Mechanisms	1977
The Intimate Mechanism of Replacement in d^8 Square-Planar Complexes	1978
Platinum(II)-Catalyzed Substitutions of Platinum(IV) Complexes	1979
Kinetics of Nickel, Palladium and Platinum Complexes	978
Isomerization Mechanisms of Square-Planar Complexes	1980
Anomalies in Ligand Exchange Reactions for Platinum(II) Complexes	1981
Inorganic Reaction Mechanisms	1982
The *cis* and *trans* Effects of Ligands	1983

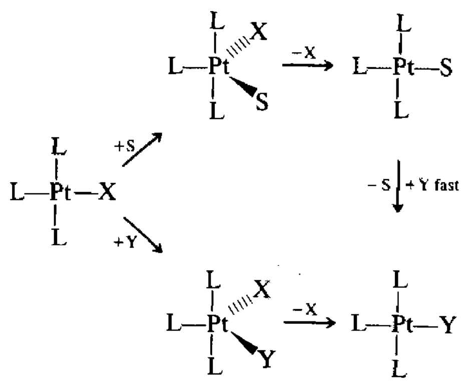
52.9.1 Planar Platinum(II) Complexes

Ligand substitution reactions of planar platinum(II) complexes occur with retention of configuration such that *cis* reactants give *cis* products, and *trans* reactants give *trans* products. Substitution reactions of X^- for Y^- in $PtXL_3$ (equation 548) follow a two-term rate law:

$$\text{Rate} = \{k_1 + k_2[Y]\}[PtXA_3]$$

This requires that a plot of k_{obs} against [Y] be linear with an intercept of k_1 for the reagent-independent path and a slope of k_2 for the reagent path. Such a two-term rate law requires a two-path reaction mechanism, and the experimental data fit the pathways shown in Scheme 19.

$$PtXL_3 + Y \longrightarrow PtYL_3 + X \quad (548)$$



Scheme 19

52.9.1.1 **Trans** ***effect***

An early factor to be considered when interpreting kinetic data for these complexes is the *trans* effect. Whereas *trans* influence considers ground state perturbations, the *trans* effect is a measure of the relative substitution rates, and must therefore be considered as a transition state perturbation. For platinum(II) the *trans* effect is: CO, CN^-, $C_2H_4 > PR_3$, $H^- > Me^-$, $SC(NH_2)_2 > Ph^-$, NO_2^-, I^-, $SCN^- > Br^-$, $Cl^- >$ py, NH_3, OH^-, H_2O. The *trans* effect variations are large, a factor of 10^6 or more in rate is found between a complex containing a good *trans* labilizing ligand and one with a ligand that is low in the *trans* effect series. Two theories which have been put forward to explain the *trans* effect series involve the effect of the *trans* ligand weakening the ligand-to-platinum(II) bond of the leaving group. The first theory invokes polarization to explain how the primary charge on platinum(II) induces a dipole in L, which in turn induces a dipole in the metal. The orientation of this second dipole is such as to repel negative charge in the group X. Thus the attraction of X for platinum(II) is reduced, and the Pt—X bond is lengthened and weakened. The second theory invokes π bonding to explain why ligands such as CO and C_2H_4 are high in the series. In this case a strongly π-bonding ligand L will weaken the *trans* ligand X, or more likely the effect of π bonding is to stabilize the five-coordinate trigonal bipyramidal intermediate, which thereby accelerates the substitution reaction.

Molecular orbital approaches to the problem were initially directed toward explaining the *trans* effect on the basis of the two *trans* ligands forming σ bonds with orbitals having the same symmetries, which can mix. As a consequence, a strongly bonding orbital to the *trans* ligand L will only be weakly bonding to L. Alternatively the σ-bond effect may be to stabilize the trigonal bipyramidal intermediate, which has more orbitals available for σ bonding in the trigonal plane than does the square planar complex.

Recently the angular overlap model of metal–ligand interactions has been used to derive a double-humped potential-energy surface for the substitution of a simple ligand in a d^8 square planar complex. This surface contains a transition state mainly associated with bond making, a trigonal bipyramidal intermediate, and a transition state mainly associated with bond breaking. The height of the entering barrier is found to dominate the rate in a large number of cases. The barrier height decreases and thus the reaction rate increases with (a) increasing σ strength of entering ligand; (b) π-acceptor orbitals on entering ligand; (c) good interaction with $(n+1)s$, p orbitals on metal by entering ligand; (d) entering ligand 'softness'; (e) decreasing σ strength of *trans* ligand (*trans* labilizing influence); (f) decreasing σ strength of leaving ligand; and (g) increasing σ strength of *cis* ligands (*cis* effect).[1984] These results can be compared with CNDO–MO calculations on *cis* and *trans* influences in platinum(II) iodide complexes.[1985]

Experimental data for the conversion of *trans*-$PtClL(PEt_3)_2$ into *trans*-$PtpyL(PEt_3)_2^+$ by pyridine (equation 549) are shown in Table 14.[1986] The *cis* effect in platinum(II) complexes is small.

$$trans\text{-}PtClL(PEt_3)_2 + py \rightleftharpoons trans\text{-}PtL(py)(PEt_3)_2^+ + Cl^- \quad (549)$$

Table 14 *Trans* Effect of L on Reaction Rates of Pyridine Substitution in *trans*-$PtClL(PEt_3)_2$ at 25 °C

L	k_1 (s^{-1})	k_2($M^{-1}s^{-1}$)
H^-	1.8×10^{-2a}	3.8^a
Me^-	1.7×10^{-4}	6.7×10^{-2}
Ph^-	3.3×10^{-5}	1.6×10^{-2}
p-$ClC_6H_4^-$	3.3×10^{-5}	1.6×10^{-2}
p-$MeOC_6H_4^-$	2.8×10^{-5}	1.3×10^{-2}
p-$PhC_6H_4^-$	1.7×10^{-5}	9.7×10^{-3}
Cl^-	1.0×10^{-6}	4.0×10^{-4}

[a] Rate at 0 °C.

52.9.1.2 *Effect of leaving group on substitution reactions*

The replacement of X by pyridine in the complex $PtX(dien)^+$ to give $Pt(dien)py^{2+}$ (equation 549) has been studied under controlled conditions with a range of leaving groups X. These data are shown in Table 15.[1987,1988] From these data the leaving group order is: $NO_3^- > H_2O > Cl^- > Br^- > I^- > N_3^- > SCN^- > NO_2^- > CN^-$. Reactions such as these must be carried out under thermal conditions for accurate comparison since photoaquation can occur, albeit with a rather low quantum yield.[1989] The volumes of activation of these reactions (equation 550) are all negative. An associative mechanism is proposed for the nucleophilic dependent path, but for the nucleophile independent pathway both associative and dissociative mechanisms need to be considered.[1990]

Table 15 Leaving Group Effect on Pyridine Substitution Rates in $PtX(dien)^+$

Ligand X	$10^6 k_{obs}$(s^{-1})
NO_3^-	Very fast
H_2O	1900
Cl^-	35
Br^-	23
I^-	10
N^-	0.83
SCN^-	0.30
NO_2^-	0.050
CN^-	0.017

$$PtX(dien)^+ + py \longrightarrow Ptpy(dien)^{2+} + X^- \quad (550)$$

52.9.1.3 *Effect of entering group on substitution reactions*

Evaluating entering group effects is the equivalent of assigning a nucleophilicity order to an incoming ligand. This nucleophilicity order depends on both the nucleophile and electrophile; there is no single scale for nucleophilic reactivities.[1991] The nucleophilicity order for reactivity to platinum(II) using *trans*-$PtCl_2(py)_2$ as standard is shown in Table 16. These nucleophilicity reactivity constants, n_{Pt}° are defined by:

$$\log (k_y/k_s)_0 = n_{Pt}^{\circ}$$

where k_y is the rate constant for the second-order pathway, and k_s the rate constant for the first-order pathway.

Table 16 Nucleophilicity Reactivity Constants (n°_{Pt}) to *trans*-$PtCl_2(py)_2$

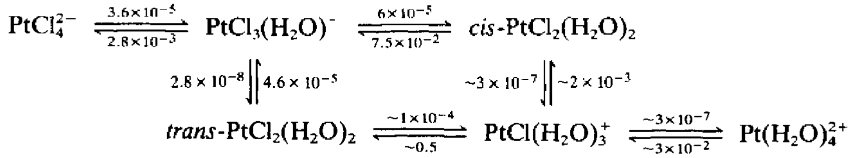
$MeCO_2^-$	<2.4	I^-	5.42
MeO^-	<2.4	Me_2Se	5.56
$PhNH_2$	3.02	SCN^-	6.65
Cl^-	3.04	SO_3^{2-}	5.79
NH_3	3.06	CyNC	6.20
Py	3.13	Ph_3Sb	6.65
NO_2^-	3.22	Ph_3As	6.75
$(PhCH_2)_2S$	3.29	CN^-	7.0
N_3^-	3.58	$(MeO)_3P$	7.08
NH_2OH	3.85	$SeCN^-$	7.10
N_2H_4	3.85	PhS^-	7.17
PhSH	4.15	$(NH_2)_2CS$	7.17
Br^-	4.18	$S_2O_3^{2-}$	7.34
Et_2S	4.38	Et_3As	7.54
Me_2S	4.73	Ph_3P	8.79
$(CH_2)_5S$	4.88	Bu_3P	8.82
$(CH_2)_4S$	5.00	Et_3P	8.85
$(PhCH_2)_2Se$	5.39		

Since charge effects are also important in affecting substitution rates, a recent suggestion has been made that the complex $[PtCl(NH_3)en]^+$ be used as a reference for n°_{Pt} with complexes of this charge type.[1992–1994] In particular, before comparison can be made it is emphasized that kinetic data must be collected under the same ionic strength conditions, and care must be exercised when fitting data for biphilic nucleophiles.

52.9.1.4 Solvent effects

Since these substitution reactions follow a two-term rate law, it is clear that solvent effects are very significant. Poorly coordinating solvents are benzene, carbon tetrachloride and sterically hindered alcohols; and strongly coordinating solvents are water, lower alcohols, DMF, DMSO, acetonitrile and nitromethane. The first-order rate constants are greater in DMSO than in water. Since the majority of precursor platinum complexes used in synthetic and mechanistic studies are halo complexes, the replacement of halide ligands by solvent and the reversibility of this reaction are important features of platinum halide chemistry.

In a series of papers the substitution of chloride ion in K_2PtCl_4 by water has been shown to occur in a stepwise manner.[1995–1997] At 25 °C an aqueous solution of $PtCl_4^{2-}$ gives both $PtCl_3(H_2O)_2^-$ and $PtCl_2(H_2O)_2$. The reaction is first order with respect to both chloride ion and the complex, and $PtCl_2(H_2O)_2$ can form both *cis* and *trans* isomers. The reverse chloride anations are also first order in each reagent. The pathway can be represented by Scheme 20, and the rate constants shown in this scheme are for conditions at 25 °C with added $HClO_4$. A similar chemistry is found for the platinum(II) bromo complexes. The aquation reaction of $PtCl_4^{2-}$ to $PtCl_3(H_2O)^-$ can be catalyzed by $PtCl_3(C_2H_4)^-$. The catalytic effect is nullified by added chloride, and the likely solution catalyst is *trans*-$PtCl_2(C_2H_4)(H_2O)$.[1998]



Scheme 20

In Scheme 20, the rate constants for the loss of the first and second chloride ions are comparable under these acidic conditions. Under conditions of higher pH, the replacement of the second chloride ion by water is slower than the first, but the first hydrolysis product is now $PtCl_3(OH)^{2-}$.[1999,2000] Aquation equilibria have also been studied for *cis*-$PtCl_2(NH_3)_2$, and the respective equilibrium constants for the formation of first *cis*-$PtCl(H_2O)(NH_3)^+$, and then *cis*-$Pt(H_2O)_2(NH_3)_2^{2+}$ are $3.63(22)\times10^{-3}$ M and $1.11(14)\times10^{-4}$ M.[2001] This article provides references to earlier work by this group who have shown that aquation is the first step in chloride exchange of chloro ammine platinum(II) complexes. With the bromo complex the situation is more complicated since now a second pathway becomes involved which has dimeric transition states.

The more recent availability of $Pt(H_2O)_4^{2+}$ allows for the reverse processes to be studied, namely the replacement of water by halide and pseudohalide ions. With a large excess of X^- the product is PtX_4^{2-}. The substitution reactions are sequential, and along the series $Pt(H_2O)_4^{2+}$, $PtX(H_2O)_3^+$ and $PtX_2(H_2O)_2$, the sequence for the anions to act as an entering ligand follows the order: $Cl^- < Br^- < SCN^- < I^-$.[2002] The mechanism of water replacement has been studied for the complex $Pt(dien)(H_2O)^{2+}$ because the rate must only involve substitution of a single water molecule. In a series of experiments Gray found that the first-order term in the substitution of H_2O by Y^- in $Pt(dien)(H_2O)^{2+}$ follows the sequence $OH^- \gg I^- > SCN^- > Br^- > Cl^- > NO_2^- >$ py (equation 551).[1988] The marked effect of OH^- is due to proton transfer rather than to its nucleophilic reactivity. Failure by others to observe the first-order rate term has led to criticism of this work, but recently a supportive article has been published offering the explanation that the original two-term rate law was observed by the reaction going to equilibrium rather than to completion in the presence of low chloride ion concentrations.[2003] The same entering group sequence is found for $PtCl_4^{2-}$, although this study added the ligand DMSO to the list, and found it to be only a poor entering group.[2004]

$$Pt(dien)(H_2O)^{2+} + Y^- \longrightarrow PtY(dien)^+ + H_2O \qquad (551)$$

Halide replacement occurs with other solvents. For the complexes $PtCl_2$(L—L), the equilibrium position in equation (552) is driven to the right by strongly coordinating solvents S. The observed sequence is $PR_3 \approx py > Me_2SO > DMF \gg MeCN \approx CO$.[2005]

$$PtCl_2(L\text{—}L) + S \longrightarrow PtCl(S)(L\text{—}L)^+ + Cl^- \qquad (552)$$

52.9.1.5 *Steric effects in substitution reactions*

Steric effects provide a useful method of probing mechanisms. If a bimolecular displacement is involved, the increased steric hindrance on the ligand causes a decrease in rate, whereas steric acceleration is generally observed for a dissociation process. The data in Table 17 show that increasing the steric bulk of the ligands L decreases the reaction rate, hence the data strongly support an associative mechanism.

Table 17 Steric Effects on Substitution Rates of $PtClL(PEt_3)_2$

L	*Temperature* (°C)	k_{obs} (s^{-1})
cis		
Phenyl	0	8.0×10^{-2}
o-Tolyl	0	2.1×10^{-4}
Mesityl	25	1.0×10^{-6}
trans		
Phenyl	25	1.2×10^{-4}
o-Tolyl	25	1.7×10^{-5}
Mesityl	25	3.4×10^{-6}

52.9.1.6 *Charge effects in substitution reactions*

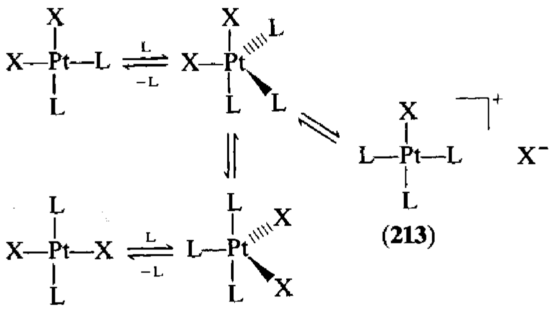
Charge effects are quite small in substitution reactions of platinum(II). This observation further supports a primarily associative pathway since the charge neutralization process of such a mechanism occurs with simultaneous bond-making and bond-breaking. The rates of such a reaction will be relatively insensitive to the charge on the complex. For the dissociative (k_1) portion of the mechanism the pathway involves separation of charges, then for an analogous series of complexes the rate will decrease for decreasing negative charge on the complex.

52.9.1.7 Isomerization reactions

This feature of platinum(II) chemistry has been very recently reviewed.[1980] In general for complexes of type PtX_2L_2 the *cis* isomers are enthalpy favored, but entropy changes in solution favor the *trans* form (equation 553). The free energy differences between the *cis* and *trans* forms are usually quite small, and changes in ligand, solvent or temperature can affect the equilibrium position.

$$cis\text{-}PtX_2L_2 \underset{\Delta H-\text{ve}}{\overset{\Delta S+\text{ve}}{\rightleftharpoons}} trans\text{-}PtX_2L_2 \qquad (553)$$

The best-documented pathways for isomerization involve pentacoordinate intermediates (see also Section 52.5.3.2). The pentacoordinate species formed by an associative pathway can then interconvert either *via* a four-coordinate ionic intermediate **(213)** or directly by a Berry pseudorotation process (Scheme 21).[2006,2007] These associatively induced isomerizations can be autocatalytic. The complex $PtCl_2(AsEt_3)_2$ isomerizes spontaneously in benzene solution, but if the complex $Pt_2Cl_2(\mu\text{-}Cl)_2(AsEt_3)_2$ is added to the solution as a scavenger for free $AsEt_3$, the isomerization is quenched. Photochemical isomerization of planar platinum(II) complexes occurs.[1980,2008] For platinum(II) it is likely that the tetrahedral geometry may be too high in energy to be a plausible intermediate, and that the pathway involves ligand dissociation.



(213)

Scheme 21

52.9.2 Six-coordinate Platinum(IV) Complexes

The substitution reactions of platinum(IV) complexes are considered separately because these compounds are coordinately saturated 18-electron molecules which do not undergo replacement reactions to any extent by associative substitution at the platinum(IV) center. Two reviews should be particularly consulted for current thinking on substitution mechanisms in platinum(IV) chemistry.[978,1979] Also as electron transfer mechanisms become increasingly significant, two recent articles by Chanon and Tobe[2009] and by Julliard and Chanon[2009] should be consulted for their in-depth coverage of electron-transfer catalysis, and for their integrative interpretation of organic and inorganic reaction mechanisms.

Platinum(IV) is kinetically inert, but substitution reactions are observed. Deceptively simple substitution reactions such as that in equation (554) do not proceed by a simple S_N1 or S_N2 process. In almost all cases the reaction mechanism involves redox steps. The platinum(II)-catalyzed substitution of platinum(IV) is the common kind of redox reaction which leads to 'formal nucleophilic substitution' of platinum(IV) complexes. In such cases substitution results from an atom-transfer redox reaction between the platinum(IV) complex and a five-coordinate adduct of the platinum(II) compound (Scheme 22). The platinum(II) complex can be added to the solution, or it may be present as an impurity, possibly being formed by a reductive elimination step. These reactions show characteristic third-order kinetics, first order each in the platinum(IV) complex, the entering ligand Y, and the platinum(II) complex. The pathway is catalytic in $Pt^{II}L_4$, but a consequence of such a mechanism is the transfer of platinum between the catalyst and the substrate.[2010] This premise has been verified using a ^{195}Pt tracer.[2011]

$$PtX_6 + Y \longrightarrow PtX_5Y + X \qquad (554)$$

$$Pt^{II}L_4 + Y \overset{fast}{\rightleftharpoons} Pt^{II}L_4Y$$

$$XPt^{IV}L_4Z + Pt^{II}L_4Y \rightleftharpoons XPtL_4ZPtL_4Y$$

$$XPtL_4ZPtL_4Y \rightleftharpoons XPt^{II}L_4 + ZPt^{IV}L_4Y$$

$$XPt^{II}L_4 \overset{fast}{\rightleftharpoons} Pt^{II}L_4 + X$$

Scheme 22

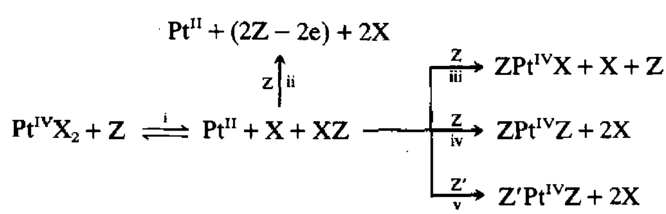
As expected the rates of these inner-sphere reactions are sensitive to the nature of the bridging ligand. In relation to Scheme 22, the relative order of reactivity for the bridging ligand Z follows the sequence: $I^- \gg Br^- > SCN^- > Cl^- \gg OH^-$. Also in agreement with inner-sphere bridged transition state processes, the values for $\Delta S^{\neq}$ are negative and those for $\Delta H^{\neq}$ small.[2012] The reactivity order for the entering groups Y follows the expected sequence for reactivity toward a planar platinum(II) center. The leaving group order for X is $py > Br^- > SCN^- > Cl^- > I^- > NH_3 \gg CN^-$, which generally correlates with the stability of the platinum(IV) substrate, the more stable complexes being the less reactive. For the equatorial ligands L, values of $\Delta G^{\neq}$ have been plotted against ΔG° for a series of different L groups. Linear plots of slope 0.5 have been interpreted as indicating a similarity between the bridged activated complex and products when the products are less stable than the reactants.[2013]

The base hydrolyses of $PtCl(NH_3)_5^{3+}$ and *cis*-$PtCl_2(NH_3)_4^{2+}$ are possibly examples of nucleophilic substitution reactions;[204] these remain the only cases which have not been proven otherwise. These reactions follow a rate law which is first order in the platinum(IV) complex, and a hydroxide ion dependence which is intermediate between zero and first order. The reaction is not catalyzed by $Pt(NH_3)_4^{2+}$.

In many other cases, detailed examination of platinum(IV) substitution reactions has shown that the mechanisms involve oxidation–reduction steps. These redox reactions can be collected into two classes according to whether a bielectronic or a monoelectronic redox species reacts with the platinum complex (*i.e.* complementary and non-complementary redox reactions, respectively).

52.9.2.1 Complementary redox reactions

All reactions belonging to this class involve an inner-sphere atom-transfer oxidation–reduction path. These reactions are generalized in Scheme 23. Path ii results in a net reduction to platinum(II) complexes, whereas pathways iii, iv and v represent net formal substitutions at platinum(IV). Each of these pathways can be regarded as an oxidative addition to the platinum(II) complex formed in step i. The combination of step i with iii, iv or v is therefore known as a reductive elimination oxidative addition (REOA) reaction.



Scheme 23

For the reaction sequence shown as steps i and ii, the reducing agent Z can be one of any of a large variety of cationic, anionic and uncharged species. When $PtCl_2(diars)_2^{2+}$ reacts with thiocyanate ion the product is $Pt(diars)_2^{2+}$ (equation 555).[2015] The rate shows first-order dependence on both $PtCl_2(diars)_2^{2+}$ and SCN^-, a rate law consistent with an inner-sphere atom-transfer redox mechanism. For the complex $PtBr_2(diars)_2^{2+}$ a similar pathway occurs, but now a parallel pathway is operative involving platinum(II) catalysis.[2016] For anionic reductants toward the same platinum(IV) complex the rate increases in the order $SCN^- < I^- < SeCN^- < S_2O_3^{2-}$, roughly paralleling their standard potentials. The reactivity of different complexes

PtX_4L_2 also depends on L and X. A linear free energy relationship

$$\log k_2 = r(X) + r_s$$

correlates the second-order rate constants of substrates *trans*-$PtCl_4L_2$ with different reducing anions (k_2 is the second-order rate constant; $r(X)$ is the value of $\log k_2$ for a standard substrate; and r_s is a ligand L dependent constant). The reactivity order for L is $AsEt_3 < PPr^n_3 < PEt_3 <$ py < pip < $SEt_2 \approx SMe_2$. As with the platinum(II)-catalyzed substitution reactions, the bridging halide plays a significant role in determining the reactivity. This is shown by the fact that *trans*-$PtCl_4(PEt_3)_2$ reacts much more slowly than *trans*-$PtBr_4(PEt_3)_2$, but $PtCl_2Br_2(PEt_3)_2$, where Br can bridge, reacts at a comparable rate to *trans*-$PtBr_4(PEt_3)_2$.

$$PtCl_2(diars)_2^{2+} + SCN^- \longrightarrow Pt(diars)_2^{2+} + Cl^- + ClSCN \qquad (555)$$

These REOA reactions are believed to occur in substitution reactions of platinum(IV) complexes which are not catalyzed by platinum(II) compounds. Two early examples are the hydrolysis of PtI_6^{2-} in the presence of free iodide ion (equation 556),[2017] and the $PtBr_6^{2-}$ interchange reaction with iodide ion (equation 557).[2018] Product formation in the latter case is pH dependent, and in a later study the complexes *trans*-$PtBr_4I(H_2O)^-$ and *trans*-$PtBr_4I(OH)^{2-}$ have been identified.[2019] An interesting effect ascribed to these pathways is the observation that $PtBr_5(H_2O)^-$ and *cis*-$PtBr_4(H_2O)_2$ undergo rapid substitution of water by Br^-, even in the absence of $PtBr_4^{2-}$; yet the complex *trans*-$PtBr_4(H_2O)_2$ in the absence of $PtBr_4^{2-}$ undergoes bromide ion substitution at a negligibly slow rate.[2020] The offered explanation is that a bromide ion Z (Scheme 23) is associated to a bromide ligand X in a *trans* position to the replaced water molecule, water being a poor bridging ligand ($X \neq H_2O$). For *cis*-$PtBr_4(H_2O)_2$ and $PtBr_5(H_2O)^-$ the aqua ligands are *trans* to the bromide ligands and can easily be replaced by Br^- *via* a bromide-assisted path. This possibility does not exist for *trans*-$PtBr_4(H_2O)_2$, which has the two water molecules opposite to each other. Halide anations of *trans*-$PtCl_4Br(H_2O)^-$ and *trans*-$PtBr_4Cl(H_2O)^-$ have also been shown to follow similar paths. The article also gives a useful summary of rate data for these various reactions collected from a number of sources.[2021] For LFER plots it is believed that the transition state $X \cdots Pt \cdots X \cdots Y$ bears a close resemblance to the products, and hence there is a considerable degree of bond making and breaking in the transition state.[2022]

$$PtI_6^{2-} + I^- \longrightarrow PtI_4^{2-} + I^- + I_2 \xrightarrow{H_2O} PtI_5(H_2O)^- + 2I^- \qquad (556)$$

$$PtBr_6^{2-} + I^- \longrightarrow PtBr_4^{2-} + IBr + Br^- \xrightarrow{I^-} PtBr_4I_2^{2-} + 2Br^- \qquad (557)$$

Other examples of complementary redox reactions are the reduction of $PtCl(NH_3)_5^{3+}$ by aquachromium(II),[2023] and the oxidation of $PtCl_4^{2-}$ by halogen (Scheme 24).[2024,2025] Other halogen oxidations of platinum(II) are the addition of Cl_2, Br_2, I_2, ICl, ICN, $(SCN)_2$ and NOCl to $PtX_2(phen)$. Although these reactions have not been fully characterized as complementary redox processes, the formation of $PtBr_3Cl(phen)$ from $PtBr_2(phen)$ and Br_2 in the presence of HCl (equation 558) suggests that this is probably the case.[2026,2027] Care must be taken in product determination with these reactions, however, since photoinduced scrambling can occur with these complexes.[2028]

$$PtCl_4^{2-} + Cl_2 \xrightarrow{fast} PtCl_4{\cdot}Cl_2^{2-}$$
$$PtCl_4Cl_2^{2-} + H_2O \longrightarrow PtCl_5OH^{2-} + H^+ + Cl^-$$
$$PtCl_4{\cdot}Cl_2^{2-} + PtCl_4^{2-} \longrightarrow Cl_4PtCl_2PtCl_4^{4-}$$
$$Cl_4PtCl_2PtCl_4^{4-} + H_2O \longrightarrow PtCl_5OH^{2-} + PtCl_4^{2-} + H^+ + Cl^-$$

Scheme 24

$$PtBr_2(phen) + Br_2 + HCl \longrightarrow PtBr_3Cl(phen) + HBr \qquad (558)$$

52.9.2.2 *Non-complementary redox reactions*

A general feature of these reactions, in which platinum reacts with monoelectronic reagents, is to undergo oxidation–reduction with formation of labile platinum(III) intermediates. These reactions can involve reduction of platinum(IV) complexes or oxidation of platinum(II) complexes, and the stoichiometry of these two sets of reactions is shown in equation (559).[978]

The reduction of platinum(IV) complexes can be carried out with outer-sphere as well as inner-sphere monoelectronic reductants. A possible first example of this outer-sphere pathway is in the reduction of platinum(IV) complexes by $Cr(bipy)_3^{2+}$.[2029] Other examples are the reduction of *trans*-$PtX_4(amine)_2$ (X = Cl, Br) by ferrocyanide,[2030] of *trans*-PtX_4L_2 (X = Cl, Br; L = neutral ligands) by ferrocene,[2031] of $PtCl_6^{2-}$ by V^{II},[2032] of $PtCl_2(pn)_2^{2+}$ by Eu^{2+},[2033] of $PtCl_6^{2-}$ by Sn^{II} and Cu^{I},[2034] and of $PtCl_4L_2$ (L = tertiary phosphine) by Ir^{I}.[2035] These reactions occur by a second-order rate law, first order in both the platinum(IV) complex and the reductant.

$$Pt^{II} + 2X^- + 2Z^n \rightleftharpoons Pt^{IV}X_2 + 2Z^{n-1} \qquad (559)$$

According to reaction (559) these reactions can occur by an oxidation reaction of platinum(II). With one-electron oxidants, the intermediate formation of platinum(III) complexes occurs. The best early example of this type of reaction is in the oxidation of $PtCl_4^{2-}$ and $Pt(en)_2^{2+}$ by $Ir^{IV}Cl_6^{2-}$ in the presence of free chloride ion. The presence of platinum(III) intermediates has been inferred from the rate law.[2036] For the oxidation of platinum(II) by gold(III) the kinetic data are consistent with a mechanism requiring a complementary two-electron transfer,[2037] with a rate independent of chloride ion. For the substituted pyridine derivatives $PtCl_2L_2$ (L = substituted pyridine) however, the third-order rate law is found with first-order dependencies on $PtCl_2L_2$, Au^{III} and Cl^-.[2038] Comparisons have been made with the amine complexes $PtCl_2L_2$ ($L = NH_2R$).[2039]

$$PtCl_6^{2-} \xrightarrow{h\nu} PtCl_5^{2-} + Cl \qquad (560)$$

Redox substitution reactions can be photoinitiated. Taube first proposed that the photocatalyzed substitution of $PtCl_6^{2-}$ occurs by an electron-transfer process (equation 560) to give a kinetically labile platinum(III) intermediate.[2040] Further work on this system has shown that the exchange occurs with quantum yields up to 1000,[2041–2043] and the intermediate has been assigned a lifetime in the μs range.[2044] Recently the binuclear platinum(III) complexes $Pt_2(P_2O_5H_2)_4X_2^{4-}$ (X = Cl, Br, I) have been found to show similar behavior and both photoreduction and complementary redox reactions are again proposed to explain the substitution behavior.[1500]

52.10 REFERENCES

1. W. C. Zeise, *Mag. Pharm.*, 1830, **35**, 105.
2. I. I. Chernyaev, *Izv. Inst. Izuch. Platiny Drugikh Blagorodn. Met., Akad. Nauk SSSR*, 1926, **4**, 243 (*Chem. Abstr.*, 1927, **21**, 2620).
3. F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions', 2nd edn., Wiley, New York, 1967.
4. F. R. Hartley, in 'Comprehensive Organometallic Chemistry', ed. G. Wilkinson, Pergamon, Oxford, 1982, vol. 6, chap. 39.
5. U. Belluco, 'Organometallic and Coordination Chemistry of Platinum', Academic, New York, 1974.
6. G. S. Muraveiskaya, 'The Chemistry of the Platinum and Heavy Metals', Moscow, 1975 (in Russian).
7. F. R. Hartley, 'The Chemistry of Platinum and Palladium', Wiley, New York, 1973.
8. J. Chatt, L. A. Duncanson and B. L. Shaw, *Proc. Chem. Soc.*, 1957, 343.
9. E. L. Muetterties, 'Transition Metal Hydrides', Dekker, New York, 1971.
10. M. L. H. Green and D. J. Jones, *Adv. Inorg. Chem. Radiochem.*, 1965, **7**, 115.
11. A. P. Ginsberg, *Transition Met. Chem.*, 1965, **1**, 111.
12. H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, 1972, **72**, 231.
13. J. P. McCue, *Coord. Chem. Rev.*, 1973, **10**, 265.
14. D. M. Roundhill, *Adv. Organomet. Chem.*, 1975, **13**, 273.
15. L. M. Venanzi, *Coord. Chem. Rev.*, 1982, **43**, 251.
16. J. O. Noell, *Inorg. Chem.*, 1982, **21**, 11.
17. J. O. Noell and J. P. Hay, *Inorg. Chem.*, 1982, **21**, 14.
18. C. Anderson and R. Larsson, *Chem. Scr.*, 1977, **11**, 140 (*Chem. Abstr.*, 1978, **89**, 120 405v).
19. O. V. Sizova, V. J. Baranovskii and M. J. Gel'fman, *Vestn. Leningr. Univ., Fiz. Khim*, 1975, 97 (*Chem. Abstr.*, 1976, **84**, 140 946x).
20. A. B. Goel and S. Goel, *Inorg. Chim. Acta*, 1982, **65**, L77.

21. D. G. Holah, A. N. Hughes, B. C. Hui and K. Wright, *Can. J. Chem.*, 1974, **52**, 2990.
22. D. M. Roundhill, *Adv. Chem. Ser.*, 1978, **167**, 160.
23. F. Cariati, R. Ugo and F. Bonati, *Inorg. Chem.*, 1966, **5**, 1128.
24. K. Thomas, J. T. Dumler, B. W. Renoe, C. J. Nyman and D. M. Roundhill, *Inorg. Chem.*, 1972, **11**, 1795.
25. R. E. Caputo, D. K. Mak, R. D. Willett, S. G. N. Roundhill and D. M. Roundhill, *Acta Crystallogr., Sect. B*, 1977, **33**, 215.
26. T. Yamamoto, K. Sano and A. Yamamoto, *Chem. Lett.*, 1982, 907.
27. R. G. Goel, W. O. Ogini and R. C. Srviastava, *Organometallics*, 1982, **1**, 819.
28. A. E. Keskinen and C. V. Senoff, *J. Organomet. Chem.*, 1972, **37**, 201.
29. K. Kawakami, Y. Ozaki and T. Tanaka, *J. Organomet. Chem.*, 1974, **69**, 151.
30. T. B. Rauchfuss and D. M. Roundhill, *J. Am. Chem. Soc.*, 1975, **97**, 3386.
31. P. Foley and G. M. Whitesides, *Inorg. Chem.*, 1980, **19**, 1402.
32. P. B. Tripathy and D. M. Roundhill, *J. Organomet. Chem.*, 1970, **24**, 247.
33. P. B. Tripathy and D. M. Roundhill, *J. Am. Chem. Soc.*, 1970, **92**, 3825.
34. B. E. Mann, B. L. Shaw and N. I. Tucker, *J. Chem. Soc. (A)*, 1971, 2667.
35. J. Fornies, M. Green, J. L. Spencer and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1977, 1006.
36. D. H. Gerlach, A. R. Kane, G. W. Parshall, J. P. Jesson and E. L. Muetterties, *J. Am. Chem. Soc.*, 1971, **93**, 3544.
37. P. Uguagliati, R. A. Michelin, U. Belluco and R. Ros, *J. Organomet. Chem.*, 1979, **169**, 115.
38. D. M. Roundhill, *Inorg. Chem.*, 1970, **9**, 254.
39. A. W. Gal, J. W. Gosselink and F. A.Vollenbroek, *J. Organomet. Chem.*, 1977, **142**, 357.
40. W. B. Beaulieu, T. B. Rauchfuss and D. M. Roundhill, *Inorg. Chem.*, 1975, **14**, 1732.
41. J. Chatt, L. A. Duncanson and B. L. Shaw, *Chem. Ind. (London)*, 1958, **36**, 859.
42. J. H. Nelson, H. B. Jonassen and D. M. Roundhill, *Inorg. Chem.*, 1969, **8**, 2591.
43. D. W. W. Anderson, E. A. V. Ebsworth and D. W. H. Rankin, *J. Chem. Soc., Dalton Trans.*, 1973, 854.
44. I. M. Blacklaws, E. A. V. Ebsworth, D. W. H. Rankin and H. E. Robertson, *J. Chem. Soc., Dalton Trans.*, 1978, 753.
45. I. M. Blacklaws, L. C. Brown, E. A. V. Ebsworth and F. J. S. Reed, *J. Chem. Soc., Dalton Trans.*, 1978, 877.
46. E. A. V. Ebsworth, B. J. L. Henner and F. J. S. Reed, *J. Chem. Soc., Dalton Trans.*, 1978, 272.
47. E. A. V. Ebsworth, D. W. H. Rankin and J. D. Whitelock, *J. Chem. Soc., Dalton Trans.*, 1981, 840.
48. J. A. S. Duncan, E. A. V. Ebsworth, R. O. Gould, C. L. Jones, D. W. H. Rankin and J. D. Whitelock, *J. Chem. Soc., Dalton Trans.*, 1981, 1028.
49. A. D. English, P. Meakin and J. P. Jesson, *J. Am. Chem. Soc.*, 1976, **98**, 422.
50. R. A. Schunn, *Inorg. Chem.*, 1976, **15**, 208.
51. R. F. Jones, J. R. Fisher and D. J. Cole-Hamilton, *J. Chem. Soc., Dalton Trans.*, 1981, 2550.
52. J. R. Fisher, R. G. Compton and D. J. Cole-Hamilton, *J. Chem. Soc., Chem. Commun.*, 1983, 555.
53. J. L. Speier, J. A. Webster and G. H. Barnes, *J. Am. Chem. Soc.*, 1957, **79**, 974.
54. C. Eaborn, T. N. Metham and A. Pidcock, *J. Organomet. Chem.*, 1973, **63**, 107.
55. C. Eaborn, B. Ratcliff and A. Pidcock, *J. Organomet. Chem.*, 1974, **65**, 181.
56. C. Eaborn, T. N. Metham and A. Pidcock, *J. Chem. Soc., Dalton Trans.*, 1975, 2212.
57. C. S. Cundy and M. F. Lappert, *J. Organomet. Chem.*, 1978, **144**, 217.
58. D. W. W. Anderson, E. A. V. Ebsworth, J. K. MacDougall and D. W. H. Rankin, *J. Inorg. Nucl. Chem.*, 1973, **35**, 2259.
59. E. A. V. Ebsworth, J. M. Edward and D. W. H. Rankin, *J. Chem. Soc., Dalton Trans.*, 1976, 1667.
60. E. A. V. Ebsworth, J. M. Edward and D. W. H. Rankin, *J. Chem. Soc., Dalton Trans.*, 1976, 1673.
61. E. A. V. Ebsworth, V. M. Marganian, F. J. S. Reed and R. O. Gould, *J. Chem. Soc., Dalton Trans.*, 1978, 1167.
62. S. P. Dent, C. Eaborn and A. Pidcock, *J. Chem. Soc., Dalton Trans.*, 1975, 2646.
63. E. A. V. Ebsworth, S. G. D. Henderson and D. W. H. Rankin, *Inorg. Chim. Acta*, 1981, **48**, 159.
64. J. E. Bentham and E. A. V. Ebsworth, *Inorg. Nucl. Chem. Lett.*, 1970, **6**, 671.
65. M. N. Bochkarev, L. P. Maiorova, S. E. Skobeleva and G. A. Razuvaev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 1854 (*Chem. Abstr.*, 1980, **92**, 6630b).
66. C. Eaborn, A. Pidcock and B. R. Steele, *J. Chem. Soc., Dalton Trans.*, 1975, 809.
67. H. C. Clark, A. B. Goel and C. Billard, *J. Organomet. Chem.*, 1979, **182**, 431.
68. K. A. O. Starzewski, H. Ruegger and P. S. Pregosin, *Inorg. Chim. Acta*, 1979, **36**, L445.
69. P. G. Antonov, Yu. N. Kukushnin, L. M. Mitronina, L. N. Vasil'ev and V. P. Sass, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1979, **24**, 557.
70. J. F. Almeida, K. R. Dixon, C. Eaborn, P. B. Hitchcock, A. Pidcock and J. Vinaixa, *J. Chem. Soc., Chem. Commun.*, 1982, 1315.
71. J. O. Noell and J. P. Hay, *J. Am. Chem. Soc.*, 1982, **104**, 4578.
72. D. H. Gerlach, A. R. Kane, G. W. Parshall, J. P. Jesson and E. L. Muetterties, *J. Am. Chem. Soc.*, 1971, **93**, 3544.
73. J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1962, 5075.
74. P. S. Pregosin and H. Ruegger, *Inorg. Chim. Acta*, 1981, **54**, L59.
75. M. Green, J. A. Howard, J. L. Spencer and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1975, 3.
76. S. Krogsrud, L. Toniolo, U. Croatto and J. A. Ibers, *J. Am. Chem. Soc.*, 1977, **96**, 5277.
77. H. C. Foley, R. H. Morris, T. S. Targos and G. L. Geoffroy, *J. Am. Chem. Soc.*, 1981, **103**, 7337.
78. J. R. Fisher, A. J. Mills, S. Sumner, M. P. Brown, M. A. Thomson, R. J. Puddephatt, A. A. Frew, L. Manojlovic-Muir and K. W. Muir, *Organometallics*, 1982, **1**, 1421.
79. T. Yoshida, T. Matsuda, T. Okano, T. Kitani and S. Otsuka, *J. Am. Chem. Soc.*, 1979, **101**, 2027.
80. F. Glockling and K. A. Hooton, *J. Chem. Soc. (A)*, 1967, 1066.
81. W. J. Cherwinski and H. C. Clark, *Inorg. Chem.*, 1971, **10**, 2263.
82. H. C. Clark and W. J. Jacobs, *Inorg. Chem.*, 1970, **9**, 1229.

83. G. Cavinato and L. Toniolo, *Inorg. Chim. Acta*, 1981, **52**, 39.
84. H. C. Clark, A. B. Goel and S. Goel, *J. Organomet. Chem.*, 1981, **216**, C25.
85. L. Abis, A. Sen and J. Halpern, *J. Am. Chem. Soc.*, 1978, **100**, 2915.
86. L. Abis, R. Santi and J. Halpern, *J. Organomet. Chem.*, 1981, **215**, 263.
87. D. P. Arnold and M. A. Bennett, *J. Organomet. Chem.*, 1980, **199**, C17.
88. S. Sostero, O. Traverso, R. Ros and R. A. Michelin, *J. Organomet. Chem.*, 1983, **246**, 325.
89. A. C. Balazs, K. H. Johnson and G. M. Whitesides, *Inorg. Chem.*, 1982, **21**, 2162.
90. R. A. Michelin, U. Belluco and R. Ros, *Inorg. Chim. Acta*, 1977, **24**, L33.
91. A. Del Pra, G. Zanotti, R. Bardi, U. Belluco and R. A. Michelin, *Cryst. Struct. Commun.*, 1979, **8**, 729 (*Chem. Abstr.*, 1979, **91**, 140 222c).
92. I. V. Gavrilova, M. I. Gel'man and V. V. Razumovskii, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1974, **19**, 1360.
93. E. A. V. Ebsworth, J. M. Edward, F. J. S. Reed and J. D. Whitelock, *J. Chem. Soc., Dalton Trans.*, 1978, 1161.
94. R. G. Goel and R. C. Srivastava, *Can. J. Chem.*, 1983, **61**, 1352.
95. T. Miyamoto, *J. Organomet. Chem.*, 1977, **134**, 335.
96. M. W. Adlard and G. Socrates, *J. Inorg. Nucl. Chem.*, 1972, **34**, 2339.
97. M. W. Adlard and G. Socrates, *J. Chem. Soc., Dalton Trans.*, 1972, 797.
98. M. W. Adlard and G. Socrates, *J. Inorg. Nucl. Chem.*, 1976, **38**, 531.
99. J. Powell and B. L. Shaw, *J. Chem. Soc.*, 1965, 3879.
100. B. E. Mann, B. L. Shaw and A. J. Stringer, *J. Organomet. Chem.*, 1974, **73**, 129.
101. B. Longato, F. Morandini and S. Bresadola, *J. Organomet. Chem.*, 1976, **121**, 113.
102. M. J. Church and M. J. Mays, *J. Chem. Soc.* (*A*), 1968, 3074.
103. A. J. Deeming, B. F. G. Johnson and J. Lewis, *J. Chem. Soc.* (*D*), 1970, 1703.
104. K. Kudo, M. Hidai and Y. Uchida, *J. Organomet. Chem.*, 1973, **56**, 413.
105. B. L. Shaw and M. F. Uttley, *J. Chem. Soc., Chem. Commun.*, 1974, 918.
106. C. J. Moulton and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1976, 365.
107. T. Yoshida and S. Otsuka, *J. Am. Chem. Soc.*, 1977, **99**, 2134.
108. T. Yoshida, Y. Yamagata, T. H. Tulip, J. A. Ibers and S. Otsuka, *J. Am. Chem. Soc.*, 1978, **100**, 2063.
109. H. C. Clark, A. B. Goel and C. S. Wong, *J. Organomet. Chem.*, 1978, **152**, C45.
110. G. Ferguson, P. Y. Siew and A. B. Goel, *J. Chem. Res.* (*S*), 1979, 362.
111. A. B. Goel, S. Goel and D. G. Vanderveer, *Inorg. Chim. Acta*, 1981, **54**, L169.
112. R. G. Goel, W. O. Ogini and R. S. Srivastava, *Inorg. Chem.*, 1982, **21**, 1627.
113. P. G. Leviston and M. G. H. Wallbridge, *J. Organomet. Chem.*, 1976, **110**, 271.
114. H. C. Clark, A. B. Goel and C. S. Wong, *Inorg. Chim. Acta*, 1979, **34**, 159.
115. G. K. Anderson, H. C. Clark and J. A. Davies, *Organometallics*, 1982, **1**, 550.
116. R. S. Paonessa and W. C. Trogler, *J. Am. Chem. Soc.*, 1982, **104**, 1138.
117. L. N. Rachkovskaya, N. K. Eremenko and K. I. Matveev, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1972, **17**, 1173.
118. A. D. Buckingham and P. J. Stephens, *J. Chem. Soc.*, 1964, 4583.
119. F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions', 2nd edn., Wiley, New York, 1967, p. 355.
120. I. V. Gavrilova, M. I. Gel'fman and V. V. Razumovskii, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1972, **17**, 727.
121. P. G. Antonov, L. N. Mitronina, V. V. Sokolov and E. S. Postnikova, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1980, **25**, 1422.
122. G. K. Anderson and R. J. Cross, *Chem. Soc. Rev.*, 1980, **9**, 185.
123. H. Azizian, K. R. Dixon, C. Eaborn, A. Pidcock, N. M. Shuaib and J. Vinaixa, *J. Chem. Soc., Chem. Commun.*, 1982, 1020.
124. J. P. C. M. van Dangen, C. Masters and J. P. Visser, *J. Organomet. Chem.*, 1975, **94**, C29.
125. M. Green, J. A. K. Howard, J. Proud, J. L. Spencer, F. G. A. Stone and C. A. Tsipsis, *J. Chem. Soc., Chem. Commun.*, 1976, 671.
126. M. Ciriano, M. Green, J. A. K. Howard, J. Proud, J. L. Spencer, F. G. A. Stone and C. A. Tsipsis, *J. Chem. Soc., Dalton Trans.*, 1978, 801.
127. M. Ciriano, M. Green, J. A. K. Howard, M. Murray, J. L. Spencer, F. G. A. Stone and C. A. Tsipsis, *Adv. Chem. Ser.*, 1978, **167**, 111.
128. M. P. Brown, R. J. Puddephatt, M. Rashidi and K. R. Seddon, *J. Chem. Soc., Dalton Trans.*, 1978, 516.
129. G. Minghetti, G. Banditelli and A. L. Bandini, *J. Organomet. Chem.*, 1977, **139**, C80.
130. M. P. Brown, J. R. Fisher, R. J. Puddephatt and K. R. Seddon, *Inorg. Chem.*, 1979, **18**, 2808.
131. G. Bracher, D. M. Grove, L. M. Venanzi, F. Bachechi, P. Mura and L. Zambonelli, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 778.
132. G. Bracher, D. M. Grove, P. S. Pregosin and L. M. Venanzi, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 155.
133. A. Immirzo, A. Musco, P. S. Pregosin and L. M. Venanzi, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 721.
134. P. S. Pregosin, A. Togni and L. M. Venanzi, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 668.
135. H. Lehner, D. Matt, P. S. Pregosin, L. M. Venanzi and A. Albinati, *J. Am. Chem. Soc.*, 1982, **104**, 6825.
136. J. Jans, R. Naegeli, L. M. Venanzi and A. Albinati, *J. Organomet. Chem.*, 1983, **247**, C37.
137. D. Carmona, R. Thouvenot, L. M. Venanzi, F. Bachechi and L. Zambonelli, *J. Organomet. Chem.*, 1983, **250**, 589.
138. H. C. Clark, A. B. Goel, R. G. Goel and W. O. Ogini, *J. Organomet. Chem.*, 1978, **157**, C16.
139. T. H. Tulip, T. Yamagata, T. Yoshida, R. D. Wilson, J. A. Ibers and S. Otsuka, *Inorg. Chem.*, 1979, **18**, 2239.
140. R. S. Paonessa and W. C. Trogler, *Inorg. Chem.*, 1983, **22**, 1038.
141. C. B. Knobler, H. D. Kaesz, G. Minghetti, A. L. Bandini, G. Banditelli and F. Bonati, *Inorg. Chem.*, 1983, **22**, 2324.
142. G. Minghetti, A. L. Bandini, G. Banditelli and F. Bonati, *J. Organomet. Chem.*, 1981, **214**, C50.
143. P. L. Bellon, A. Ceriotti, F. Demartin, G. Longoni and B. T. Heaton, *J. Chem. Soc., Dalton Trans.*, 1982, 1671.

144. D. M. Blake and L. M. Leung, *Inorg. Chem.*, 1972, **11**, 2879.
145. M. P. Brown, J. R. Fischer, R. H. Hill, R. J. Puddephatt and K. R. Seddon, *Inorg. Chem.*, 1981, **20**, 3516.
146. L. Manojlovic-Muir and K. W. Muir, *J. Organomet. Chem.*, 1981, **219**, 129.
147. H. C. Foley, R. H. Morris, T. S. Targos and G. L. Geoffroy, *J. Am. Chem. Soc.*, 1981, **103**, 7337.
148. A. A. Frew, R. H. Hill, L. Manojlovic-Muir, K. W. Muir and R. J. Puddephatt, *J. Chem. Soc., Chem. Commun.*, 1982, 198.
149. J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1959, 4020.
150. H. C. Clark, K. R. Dixon and J. W. Jacobs, *J. Am. Chem. Soc.*, 1968, **90**, 2259.
151. J. Chatt and R. S. Coffey, *J. Chem. Soc. (A)*, 1968, 190.
152. H. C. Clark and H. Kurosawa, *J. Chem. Soc. (D)*, 1971, 957.
153. H. C. Clark and H. Kurosawa, *Inorg. Chem.*, 1972, **11**, 1275.
154. A. J. Deeming, B. F. G. Johnson and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1973, 1848.
155. H. C. Clark and C. S. Wong, *J. Am. Chem. Soc.*, 1974, **96**, 7213.
156. H. C. Clark, C. Jablonski, J. Halpern, A. Mantovani and T. A. Weil, *Inorg. Chem.*, 1974, **13**, 1541.
157. H. C. Clark and C. R. Jablonski, *Inorg. Chem.*, 1974, **13**, 2213.
158. R. Romeo, D. Minniti and S. Lanza, *Inorg. Chim. Acta*, 1976, **18**, L15.
159. S. Sakaki, H. Kato, H. Kanai and K. Tarama, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 813.
160. D. R. Armstrong, R. Fortune and P. G. Perkins, *J. Catal.*, 1976, **41**, 51.
161. D. A. Harbourne, D. T. Rosevear and F. G. A. Stone, *Inorg. Nucl. Chem. Lett.*, 1966, **2**, 247.
162. G. L. McLure and W. H. Baddley, *J. Organomet. Chem.*, 1970, **25**, 261.
163. H. C. Clark, C. R. Jablonski and C. S. Wong, *Inorg. Chem.*, 1975, **14**, 1332.
164. H. C. Clark and C. S. Wong, *J. Organomet. Chem.*, 1975, **92**, C31.
165. Y. Tohda, K. Sonogashira and N. Hagihara, *J. Organomet. Chem.*, 1976, **110**, C53.
166. H. C. Clark, P. L. Fiess and C. S. Wong, *Can. J. Chem.*, 1977, **55**, 177.
167. T. G. Attig, H. C. Clark and C. S. Wong, *Can. J. Chem.*, 1977, **55**, 189.
168. H. C. Clark and C. S. Wong, *J. Am. Chem. Soc.*, 1977, **99**, 7073.
169. A. Furlani, M. V. Russo, A. Chiesi Villa, A. Gaetani Manfredotti and C. Guastini, *J. Chem. Soc., Dalton Trans.*, 1977, 2154.
170. A. Furlani, S. Licoccia, M. V. Russo and C. Guastini, *J. Chem. Soc., Dalton Trans.*, 1980, 1958.
171. C. T. Mortimer, M. P. Wilkinson and R. J. Puddephatt, *J. Organomet. Chem.*, 1979, **165**, 269.
172. T. Joh and N. Hagihara, *Chem. Lett.*, 1977, 1351 (*Chem. Abstr.*, 1978, **88**, 23 130y).
173. P. R. Brookes, *J. Organomet. Chem.*, 1973, **47**, 179.
174. G. Bracher, P. S. Pregosin and L. M. Venanzi, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 563.
175. P. N. Kapoor, P. S. Pregosin and L. M. Venanzi, *Helv. Chim. Acta*, 1982, **65**, 654.
176. H. C. Clark and H. Kurosawa, *Inorg. Chem.*, 1973, **12**, 357.
177. I. V. Gavrilova, M. I. Gel'fman, N. V. Ivannikova, V. M. Kiseleva and V. V. Razumovskii, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1973, **18**, 1390.
178. H. Kurosawa, *Inorg. Chem.*, 1976, **15**, 120.
179. R. L. Phillips and R. J. Puddephatt, *J. Chem. Soc., Dalton Trans.*, 1978, 1736.
180. T. G. Attig, *Inorg. Chem.*, 1978, **17**, 3097.
181. T. G. Attig, R. J. Ziegler and C. P. Brock, *Inorg. Chem.*, 1980, **19**, 2315.
182. D. F. Christian, H. C. Clark and R. F. Stepaniak, *J. Organomet. Chem.*, 1976, **112**, 209.
183. A. Palazzi, L. Busetto and M. Graziani, *J. Organomet. Chem.*, 1973, **30**, 273.
184. A. Albinati, A. Musco, G. Carturan and G. Strukul, *Inorg. Chim. Acta*, 1976, **18**, 219.
185. A. Immirzi and A. Musco, *Inorg. Chim. Acta*, 1977, **22**, L35.
186. A. B. Permin, V. I. Bogdashkina, Yu. E. Zubarev, V. S. Petrosyan and O. A. Reutov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 2840 (*Chem. Abstr.*, 1981, **94**, 184 706e).
187. L. E. Manzer and W. C. Seidel, *J. Am. Chem. Soc.*, 1975, **97**, 1956.
188. L. E. Manzer and G. W. Parshall, *Inorg. Chem.*, 1976, **15**, 3114.
189. L. E. Manzer and M. F. Anton, *Inorg. Chem.*, 1977, **16**, 1229.
190. R. Ros, R. A. Michelin, R. Bataillard and R. Roulet, *J. Organomet. Chem.*, 1978, **161**, 75.
191. E. A. V. Ebsworth, H. M. Ferrier, B. J. L. Henner, D. W. H. Rankin, F. J. S. Reed, H. E. Robertson and J. D. Whitelock, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 482.
192. Z. N. Parnes, G. D. Kolomnikova, M. I. Kalinkin, D. Kh. Shaapuni, S. M. Markosyan and D. N. Kursanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1976, 2506 (*Chem. Abstr.*, 1977, **86**, 89 300u).
193. R. Ugo, G. LaMonica, F. Cariati, S. Cenini and F. Conti, *Inorg. Chim. Acta*, 1970, **4**, 390.
194. K. R. Grundy, *Inorg. Chim. Acta*, 1981, **53**, L225.
195. P. W. Atkins, J. C. Green and M. L. H. Green, *J. Chem. Soc. (A)*, 1968, 2275.
196. D. J. Darensbourg and C. L. Hyde, *J. Chem. Phys.*, 1973, **59**, 3869.
197. D. A. Roberts, W. R. Mason and G. L. Geoffroy, *Inorg. Chem.*, 1981, **20**, 789.
198. T. W. Dingle and K. R. Dixon, *Inorg. Chem.*, 1974, **13**, 846.
199. S. M. Cohen and T. H. Brown, *J. Chem. Phys.*, 1974, **61**, 2985.
200. W. McFarlane, *J. Chem. Soc., Dalton Trans.*, 1974, 324.
201. Y. Wang and F. Dai, *Cuihua Xueboa*, 1982, **3**, 144 (*Chem. Abstr.*, 1982, **97**, 126 955m).
202. J. C. Bailar and H. Itatani, *J. Am. Chem. Soc.*, 1967, **89**, 1592.
203. R. D. Cramer, E. L. Jenner, R. V. Lindsey and U. G. Stolberg, *J. Am. Chem. Soc.*, 1963, **85**, 1691.
204. G. C. Bond and M. Hellier, *J. Catal.*, 1967, **7**, 217.
205. R. V. Lindsey, R. D. Cramer, C. J. Prewitt and U. G. Stolberg, *J. Am. Chem. Soc.*, 1965, **87**, 658.
206. H. C. Clark, C. Billard and C. S. Wong, *J. Organomet. Chem.*, 1979, **173**, 341.
207. J. J. Mrowca, *US Pat.* 3 876 672 (1975) (*Chem. Abstr.*, 1976, **84**, 30 432u).
208. C. Y. Hsu and M. Orchin, *J. Am. Chem. Soc.*, 1975, **97**, 3553.
209. P. W. N. M. Van Leeuwen and C. F. Roobeek, *Eur. Pat.* 82 576 (1983) (*Chem. Abstr.*, 1983, **99**, 121 813v).
210. C. Eaborn, N. Farrell and A. Pidcock, *J. Chem. Soc., Chem. Commun.*, 1973, 766.

211. H. C. Clark and H. Kurosawa, *Inorg. Chem.*, 1973, **12**, 1566.
212. D. Bingham, D. E. Webster and P. B. Wells, *J. Chem. Soc., Dalton Trans.*, 1974, 1514.
213. D. McMunn, R. B. Moyes and P. B. Wells, *J. Catal.*, 1978, **52**, 472.
214. H. Kanai and O. Hirako, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 953.
215. J. L. Speier, J. A. Webster and G. H. Barnes, *J. Am. Chem. Soc.*, 1957, **79**, 974.
216. J. C. Saam and J. L. Speier, *J. Am. Chem. Soc.*, 1958, **80**, 4104.
217. J. W. Ryan and J. L. Speier, *J. Am. Chem. Soc.*, 1964, **86**, 895.
218. K. Yamamoto, T. Hayashi and M. Kumada, *J. Am. Chem. Soc.*, 1971, **93**, 5301.
219. K. Yamamoto, T. Hayashi and M. Kumada, *J. Organomet. Chem.*, 1972, **46**, C65.
220. W. Fink, *Helv. Chim. Acta*, 1971, **54**, 1304.
221. K. Yamamoto, T. Hayashi and M. Kumada, *J. Organomet. Chem.*, 1971, **28**, C37.
222. V. O. Reikhsfel'd, M. I. Gel'fman, T. P. Khvatova, M. I. Astrakhanov and I. V. Gavrilova, *Zh. Obshch. Khim.*, 1977, **47**, 2093 (*Chem. Abstr.*, 1978, **88**, 5845f).
223. M. Green, J. L. Spencer, F. G. A. Stone and C. A. Tsipsis, *J. Chem. Soc., Dalton Trans.*, 1977, 1519.
224. M. Green, J. L. Spencer, F. G. A. Stone and C. A. Tsipsis, *J. Chem. Soc., Dalton Trans.*, 1977, 1525.
225. C. A. Tsipsis, *J. Organomet. Chem.*, 1980, **187**, 427.
226. C. A. Tsipsis, *J. Organomet. Chem.*, 1980, **188**, 53.
227. G. Schmid and H. Noth, *Z. Naturforsch., Teil B*, 1965, **20**, 1008.
228. G. Schmid, W. Petz, W. Arloth and H. Noth, *Angew. Chem., Int. Ed. Engl.*, 1967, **6**, 696.
229. A. R. Kane and E. L. Muetterties, *J. Am. Chem. Soc.*, 1970, **92**, 2571.
230. J. Bould, J. E. Crook, N. N. Greenwood and J. D. Kennedy, *J. Chem. Soc., Chem. Commun.*, 1983, 951.
231. N. N. Greenwood, J. D. Kennedy and J. Staves, *J. Chem. Soc., Dalton Trans.*, 1978, 1146.
232. A. Davison, D. D. Traficante and S. S. Wreford, *J. Am. Chem. Soc.*, 1974, **96**, 2802.
233. A. R. Kane, L. J. Guggenberger and E. L. Muetterties, *J. Am. Chem. Soc.*, 1970, **92**, 2571.
234. S. K. Boocock, N. N. Greenwood, M. J. Hails, J. D. Kennedy and W. S. McDonald, *J. Chem. Soc., Dalton Trans.*, 1981, 1415.
235. R. Ahmad, J. E. Crook, N. N. Greenwood, J. D. Kennedy and W. S. McDonald, *J. Chem. Soc., Chem. Commun.*, 1982, 1019.
236. J. Bould, J. E. Crook, N. N. Greenwood, J. D. Kennedy and W. S. McDonald, *J. Chem. Soc., Chem. Commun.*, 1983, 949.
237. T. E. Paxson and M. F. Hawthorne, *Inorg. Chem.*, 1975, **14**, 1604.
238. S. K. Boocock, N. N. Greenwood, J. D. Kennedy, W. S. McDonald and J. Staves, *J. Chem. Soc., Dalton Trans.*, 1981, 2573.
239. Y. M. Cheek, N. N. Greenwood, J. D. Kennedy and W. S. McDonald, *J. Chem. Soc., Chem. Commun.*, 1982, 80.
240. M. A. Beckett, J. E. Crook, N. N. Greenwood, J. D. Kennedy and W. S. McDonald, *J. Chem. Soc., Chem. Commun.*, 1982, 552.
241. M. A. Beckett, J. E. Crook, N. N. Greenwood and J. D. Kennedy, *J. Chem. Soc., Chem. Commun.*, 1983, 1228.
242. E. W. Corcoran, Jr. and L. G. Sneddon, *Inorg. Chem.*, 1983, **22**, 182.
243. L. F. Warren and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1970, **92**, 1157.
244. N. Bresciani, M. Calligaris, P. Delise, G. Nardin and L. Randaccio, *J. Am. Chem. Soc.*, 1974, **96**, 5642.
245. M. Green, J. L. Spencer and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1975, 179.
246. A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1975, 2270.
247. M. Green, J. A. K. Howard, J. L. Spencer and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1975, 2274.
248. A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1976, 225.
249. A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1977, 962.
250. M. Green, J. L. Spencer and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1979, 1679.
251. G. K. Barker, M. Green, F. G. A. Stone, A. J. Welch, T. P. Onak, and G. Siwapanyoyos, *J. Chem. Soc., Dalton Trans.*, 1979, 1687.
252. G. K. Barker, M. Green, F. G. A. Stone, A. J. Welch and W. C. Wolsey, *J. Chem. Soc., Chem. Commun.*, 1980, 627.
253. G. K. Barker, M. Green, F. G. A. Stone and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1980, 1186.
254. G. K. Barker, M. P. Garcia, M. Green, F. G. A. Stone and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 1982, 46.
255. G. K. Barker, M. P. Garcia, M. Green, F. G. A. Stone and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1982, 1679.
256. G. K. Barker, M. Green, F. G. A. Stone, W. C. Wolsey and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1984, 2063.
257. D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.*, 1977, 602.
258. D. M. P. Mingos, M. I. Forsyth and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1978, 1363.
259. D. M. P. Mingos and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1980, 1674.
260. M. J. Calhorda, D. M. P. Mingos and A. J. Welch, *J. Organomet. Chem.*, 1982, **228**, 309.
261. W. E. Hill and L. M. Silva-Trivino, *Inorg. Chem.*, 1979, **18**, 361.
262. L. Manojlovic-Muir, K. W. Muir and T. Solomon, *J. Chem. Soc., Dalton Trans.*, 1980, 317.
263. V. N. Kalinin, A. V. Usatov and L. I. Zakharkin, *J. Organomet. Chem.*, 1983, **254**, 127.
264. D. A. Thompson, T. K. Hilty and R. W. Rudolph, *J. Am. Chem. Soc.*, 1977, **99**, 6774.
265. T. K. Hilty, D. A. Thompson, W. M. Butler and R. W. Rudolph, *Inorg. Chem.*, 1979, **18**, 2642.
266. W. R. Hertler, F. Klanberg and E. L. Muetterties, *Inorg. Chem.*, 1967, **6**, 1696.
267. M. Fishwick, H. Noth, W. Petz and M. G. H. Wallbridge, *Inorg. Chem.*, 1976, **15**, 490.
268. A. A. Grinberg, *Izv. Inst. Izuch. Platiny Drugikh Blagorodn. Met., Akad. Nauk SSSR*, 1928, **6**, 155.
269. I. I. Chernyaev, N. N. Zheligovskaya and A. V. Babkov, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1961, **6**, 1328.
270. I. I. Chernyaev, A. V. Babkov and N. N. Zheligovskaya, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1963, **8**, 703.

271. P. M. Treichel and R. W. Hess, *J. Chem. Soc., Chem. Commun.*, 1970, 1626.
272. W. Beck and K. Schorpp, *Chem. Ber.*, 1975, **108**, 3317.
273. J. J. Pesek and W. R. Mason, *Inorg. Chem.*, 1983, **22**, 2958.
274. J. A. Abys, G. Ogar and W. M. Risen, *Inorg. Chem.*, 1981, **20**, 4446.
275. G. J. Kubas and L. H. Jones, *Inorg. Chem.*, 1974, **13**, 2816.
276. D. G. Marsh and J. S. Miller, *Inorg. Chem.*, 1976, **15**, 720.
277. C. D. Cowman and H. B. Gray, *Inorg. Chem.*, 1976, **15**, 2823.
278. F. D. Saeva, G. R. Olin, R. F. Ziolo and P. Day, *J. Am. Chem. Soc.*, 1979, **101**, 5419.
279. J. W. Schindler, R. C. Fukuda and A. W. Adamson, *J. Am. Chem. Soc.*, 1982, **104**, 3596.
280. M. C. R. Symons, M. M. Aly and J. L. Wyatt, *J. Chem. Soc., Chem. Commun.*, 1981, 176.
281. D. Washecheck, S. W. Peterson, A. H. Reis and J. M. Williams, *Inorg. Chem.*, 1976, **15**, 74.
282. T. R. Koch, P. L. Johnson and J. M. Williams, *Inorg. Chem.*, 1977, **16**, 640.
283. J. M. Williams, K. D. Keefer, D. M. Washecheck and N. P. Enright, *Inorg. Chem.*, 1976, **15**, 2446.
284. A. H. Reis, S. W. Peterson, D. M. Washecheck and J. S. Miller, *Inorg. Chem.*, 1976, **15**, 2455.
285. J. S. Miller and A. J. Epstein, *Prog. Inorg. Chem.*, 1976, **20**, 1.
286. J. S. Miller (ed.), 'Extended Linear Chain Compounds', Plenum, New York, vols. 1–3.
287. J. S. Miller and R. J. Weagley, *Inorg. Chem.*, 1977, **16**, 2965.
288. T. R. Koch, E. Gebert and J. M. Williams, *J. Am. Chem. Soc.*, 1976, **98**, 4017.
289. J. M. Williams, P. L. Johnson, A. J. Schultz and C. C. Coffey, *Inorg. Chem.*, 1978, **17**, 834.
290. P. L. Johnson, A. J. Schultz, A. E. Underhill, D. M. Watkins, D. J. Wood and J. M. Williams, *Inorg. Chem.*, 1978, **17**, 839.
291. R. K. Brown and J. M. Williams, *Inorg. Chem.*, 1978, **17**, 2607.
292. R. K. Brown and J. M. Williams, *Inorg. Chem.*, 1979, **18**, 1922.
293. J. M. Williams, D. P. Gerrity and A. J. Schultz, *J. Am. Chem. Soc.*, 1977, **99**, 1668.
294. A. J. Schultz, C. C. Coffey, G. C. Lee and J. M. Williams, *Inorg. Chem.*, 1977, **16**, 2129.
295. G. S. V. Coles, A. E. Underhill and K. Carneiro, *J. Chem. Soc., Dalton Trans.*, 1983, 1411.
296. G. S. V. Coles, A. E. Underhill, J. M. Williams and A. J. Schultz, *J. Chem. Soc., Dalton Trans.*, 1983, 2529.
297. A. H. Reis and S. W. Peterson, *Inorg. Chem.*, 1976, **15**, 3186.
298. M. H. Whangbo and R. Hoffmann, *J. Am. Chem. Soc.*, 1978, **100**, 6093.
299. I. I. Chernyaev and A. V. Babkov, *Dokl. Akad. Nauk SSSR*, 1963, **152**, 882 (*Chem. Abstr.*, 1964, **60**, 6510f).
300. I. I. Chernyaev, A. V. Babkov and N. N. Zheligovskaya, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1963, **8**, 1279.
301. H. Isci and W. R. Mason, *Inorg. Chem.*, 1975, **14**, 905.
302. A. Piccinin, *Bull. Soc. R. Sci. Liège*, 1967, 476 (*Chem. Abstr.*, 1968, **69**, 71 313).
303. H. Siebert and A. Siebert, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 600.
304. H. Siebert and A. Siebert, *Z. Naturforsch., Teil B*, 1967, **22**, 674.
305. E. P. Kundig, D. McIntosh, M. Moskovits and G. A. Ozin, *J. Am. Chem. Soc.*, 1973, **95**, 7234.
306. P. Chini, G. Longoni and V. G. Albano, *Adv. Organomet. Chem.*, 1976, **14**, 285.
307. H. Basch and D. Cohen, *J. Am. Chem. Soc.*, 1983, **105**, 3856.
308. P. L. Goggin and R. J. Goodfellow, *J. Chem. Soc., Dalton Trans.*, 1973, 2355.
309. A. Modinos and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1975, 1516.
310. J. M. Lutton and R. W. Parry, *J. Am. Chem. Soc.*, 1954, **76**, 4271.
311. D. B. Dell'Amico and F. Calderazzo, *Gazz. Chim. Ital.*, 1979, **109**, 99.
312. P. R. Brown, F. G. N. Cloke, M. L. H. Green and R. C. Tovey, *J. Chem. Soc., Chem. Commun.*, 1982, 519.
313. L. N. Rachkovskaya, N. K. Eremenko and K. I. Matveev, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1970, **5**, 78 (*Chem. Abstr.*, 1971, **74**, 60 302).
314. L. N. Rachkovskaya, N. K. Eremenko and K. I. Matveev, *Dokl. Akad. Nauk SSSR*, 1970, **190**, 1396 (*Chem. Abstr.*, 1970, **72**, 139 098).
315. D. B. Dell'Amico, F. Calderazzo, F. Marchetti and S. Merlino, *J. Chem. Soc., Dalton Trans.*, 1982, 2257.
316. M. J. Church and M. J. Mays, *J. Chem. Soc., Chem. Commun.*, 1968, 435.
317. H. C. Clark, P. W. R. Corfield, K. R. Dixon and J. A. Ibers, *J. Am. Chem. Soc.*, 1967, **89**, 3360.
318. J. S. Field and P. J. Wheatley, *J. Chem. Soc., Dalton Trans.*, 1974, 702.
319. L. Manojlovic-Muir, K. W. Muir and R. Walker, *J. Chem. Soc., Dalton Trans.*, 1976, 1279.
320. D. R. Russell, P. A. Tucker and S. Wilson, *J. Organomet. Chem.*, 1976, **104**, 397.
321. J. D. Oliver and P. E. Rush, *J. Organomet. Chem.*, 1976, **104**, 117.
322. K. Wade, *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 1.
323. J. Browning, P. L. Goggin, R. J. Goodfellow, M. G. Norton, A. J. M. Rattray, B. F. Taylor and J. Mink, *J. Chem. Soc., Dalton Trans.*, 1977, 2061.
324. J. Browning, P. L. Goggin, R. J. Goodfellow, N. W. Hurst, L. G. Mallinson and M. Murray, *J. Chem. Soc., Dalton Trans.*, 1978, 872.
325. W. J. Cherwinski, B. F. G. Johnson, J. Lewis and J. R. Norton, *J. Chem. Soc., Dalton Trans.*, 1975, 1156.
326. R. Pietropaolo, F. Faraone, D. Pietropaolo and P. Piraino, *J. Inorg. Nucl. Chem.*, 1974, **36**, 369.
327. F. Pesa, L. Spaulding and M. Orchin, *Inorg. Chem.*, 1974, **13**, 1289.
328. G. K. Anderson and R. J. Cross, *J. Chem. Soc., Dalton Trans.*, 1980, 1988.
329. G. K. Anderson, H. C. Clark and J. A. Davies, *Inorg. Chem.*, 1981, **20**, 1636.
330. R. J. Angelici, *Acc. Chem. Res.*, 1972, **5**, 335.
331. D. A. Dell'Amico, F. Calderazzo and G. Perlizzi, *Inorg. Chem.*, 1979, **18**, 1165.
332. T. Theophanides and P. C. Kong, *Inorg. Chim. Acta*, 1971, **5**, 485.
333. M. C. Baird and G. Wilkinson, *J. Chem. Soc. (A)*, 1967, 865.
334. A. C. Skapski and P. G. H. Troughton, *J. Chem. Soc. (A)*, 1969, 2772.
335. R. J. Goodfellow, I. R. Herbert and A. G. Orpen, *J. Chem. Soc., Chem. Commun.*, 1983, 1386.
336. J. Chatt and P. Chini, *J. Chem. Soc. (A)*, 1970, 1538.
337. G. Booth and J. Chatt, *J. Chem. Soc. (A)*, 1969, 2131.
338. A. Albinati, G. Carturan and A. Musco, *Inorg. Chim. Acta*, 1976, **16**, L3.

339. H. C. Clark, A. B. Goel and C. S. Wong, *Inorg. Chim. Acta,* 1979, **34,** 159.
340. A. Moor, P. S. Pregosin and L. M. Venanzi, *Inorg. Chim. Acta,* 1982, **61,** 135.
341. A. Albinati, *Inorg. Chim. Acta,* 1977, **22,** L31.
342. R. Mason and J. Zubieta, *J. Organomet. Chem.,* 1974, **66,** 289.
343. V. G. Albano and G. Ciani, *J. Organomet. Chem.,* 1974, **66,** 311.
344. A. Modinos and P. Woodward, *J. Chem. Soc., Dalton Trans.,* 1975, 1534.
345. L. J. Farrugia, J. A. K. Howard, P. Mitrprachachon, J. L. Spencer, F. G. A. Stone and P. Woodward, *J. Chem. Soc., Chem. Commun.,* 1978, 260.
346. P. Braunstein, D. Matt, O. Bars and D. Grandjean, *Angew. Chem., Int. Ed. Engl.,* 1979, **18,** 797.
347. R. Ugo, S. Cenini, M. F. Pilbrow, B. Deibl and G. Schneider, *Inorg. Chim. Acta,* 1976, **18,** 113.
348. R. Bender, P. Braunstein, Y. Dusausoy and J. Protas, *J. Organomet. Chem.,* 1979, **172,** C51.
349. R. Jund, P. Lemoine, M. Gross, R. Bender and P. Braunstein, *J. Chem. Soc., Chem. Commun.,* 1983, 86.
350. L. J. Farrugia, J. A. K. Howard, P. Mitrprachachon, F. G. A. Stone and P. Woodward, *J. Chem. Soc., Dalton Trans.,* 1981, 155.
351. R. D. Johnston, F. Basolo and R. G. Pearson, *Inorg. Chem.,* 1971, **10,** 247.
352. G. A. Larkin, R. Mason and M. G. H. Wallbridge, *J. Chem. Soc., Dalton Trans.,* 1975, 2305.
353. J. R. Boehm, D. J. Doonan and A. L. Balch, *J. Am. Chem. Soc.,* 1976, **98,** 4845.
354. J. R. Boehm and A. L. Balch, *Inorg. Chem.,* 1977, **16,** 778.
355. L. Chugaev and P. Teearu, *Chem. Ber.,* 1914, **159,** 188.
356. K. A. Hoffmann and G. Bugge, *Chem. Ber.,* 1907, **40,** 1772.
357. L. Ramberg, *Chem. Ber.,* 1907, **40,** 2578.
358. K. A. Jensen, *Z. Anorg. Allg. Chem.,* 1937, **231,** 365.
359. H. J. Keller, R. Lorentz, H. H. Rupp and J. Weiss, *Z. Naturforsch., Teil B,* 1972, **27,** 631.
360. H. J. Keller and R. Lorentz, *J. Organomet. Chem.,* 1975, **102,** 119.
361. P. M. Treichel, W. J. Knebel and R. W. Hess, *J. Am. Chem. Soc.,* 1971, **93,** 5424.
362. L. Malatesta and F. Bonati, 'Isocyanide Complexes of Metals', Wiley, London, 1969, p. 169.
363. B. Crociani, M. Nicolini and R. L. Richards, *Inorg. Chim. Acta,* 1975, **12,** 53.
364. B. Jovanovic and L. Manojlovic-Muir, *J. Chem. Soc., Dalton Trans.,* 1972, 1176.
365. W. M. Butler and J. H. Enemark, *Inorg. Chem.,* 1973, **12,** 540.
366. J. D. Oliver and N. C. Rice, *Inorg. Chem.,* 1976, **15,** 2741.
367. J. Browning, P. L. Goggin and R. J. Goodfellow, *J. Chem. Res. (S),* 1978, 328.
368. M. J. Church and M. J. Mays, *J. Chem. Soc. (A),* 1968, 3074.
369. J. S. Miller and D. G. Marsh, *Inorg. Chem.,* 1976, **15,** 2293.
370. P. M. Treichel and W. J. Knebel, *Inorg. Chem.,* 1972, **11,** 1285.
371. U. Belluco, R. A. Michelin, P. Uguagliato and B. Crociani, *J. Organomet. Chem.,* 1983, **250,** 565.
372. L. Chugaev and M. S. Grigorizewa, *Russ. J. Inorg. Chem. (Engl. Transl.),* 1915, **47,** 776.
373. L. Chugaev, M. S. Grigorizewa and A. Posniak, *Z. Anorg. Allg. Chem.* 1925, **148,** 37.
374. G. Rouschias and B. L. Shaw, *J. Chem. Soc. (A),* 1971, 2092.
375. W. M. Butler, J. H. Enemark, J. Parks and A. L. Balch, *Inorg. Chem.,* 1973, **12,** 451.
376. D. F. Christian and H. C. Clark, *J. Organomet. Chem.,* 1975, **85,** C9.
377. F. Bonati and H. C. Clark, *Can. J. Chem.,* 1979, **57,** 483.
378. B. Cetinkaya, P. Dixneuf and M. F. Lappert, *J. Chem. Soc., Chem. Commun.,* 1973, 206.
379. B. Cetinkaya, E. Cetinkaya and M. F. Lappert, *J. Chem. Soc., Chem. Commun.,* 1973, 906.
380. B. Cetinkaya, P. Dixneuf and M. Lappert, *J. Chem. Soc., Dalton Trans.,* 1974, 1827.
381. P. J. Fraser, W. R. Roper and F. G. A. Stone, *J. Organomet. Chem.,* 1973, **50,** C54.
382. K. Bartel and W. P. Fehlhammer, *Angew. Chem., Int. Ed. Engl.,* 1974, **13,** 599.
383. L. Busetto, A. Palazzi, B. Crociani, U. Belluco, E. M. Bradley, B. J. L. Kilby and R. L. Richards, *J. Chem. Soc., Dalton Trans.,* 1972, 1800.
384. J. S. Miller and A. L. Balch, *Inorg. Chem.,* 1972, **11,** 2069.
385. D. F. Christian, H. C. Clark and R. F. Stepaniak, *J. Organomet. Chem.,* 1976, **112,** 227.
386. E. M. Badley, K. W. Muir and G. A. Sim, *J. Chem. Soc., Dalton Trans.,* 1976, 1930.
387. M. H. Chisholm, H. C. Clark, J. E. H. Ward and K. Yasufuku, *Inorg. Chem.,* 1975, **14,** 893.
388. C. Heredeis and W. Beck, *Chem. Ber.,* 1983, **116,** 3205.
389. R. Walker and K. W. Muir, *J. Chem. Soc., Dalton Trans.,* 1975, 272.
390. J. Chatt, R. L. Richards and G. H. D. Royston, *J. Chem. Soc., Dalton Trans.,* 1976, 599.
391. D. F. Christian, D. A. Clarke, H. C. Clark, D. H. Farrar and N. C. Payne, *Can. J. Chem.,* 1978, **56,** 2516.
392. M. H. Chisholm and H. C. Clark, *Inorg. Chem.,* 1971, **10,** 1711.
393. M. H. Chisholm and H. C. Clark, *Inorg. Chem.,* 1971, **10,** 2557.
394. M. H. Chisholm and H. C. Clark, *J. Am. Chem. Soc.,* 1972, **94,** 1532.
395. H. C. Clark, J. E. H. Ward and K. Yasufuku, *Can. J. Chem.,* 1975, **53,** 186.
396. R. F. Stepaniak and N. C. Payne, *Inorg. Chem.,* 1974, **13,** 797.
397. M. H. Chisholm, H. C. Clark, W. S. Johns, J. E. H. Ward and K. Yasufuku, *Inorg. Chem.,* 1975, **14,** 900.
398. T. G. Attig and H. C. Clark, *Can. J. Chem.,* 1975, **53,** 3466.
399. R. Stepaniak and N. C. Payne, *Can. J. Chem.,* 1978, **56,** 1602.
400. R. A. Bell, M. H. Chisholm, D. A. Couch and L. A. Rankel, *Inorg. Chem.,* 1977, **16,** 677.
401. R. A. Bell and M. H. Chisholm, *Inorg. Chem.,* 1977, **16,** 687.
402. R. A. Bell and M. H. Chisholm, *Inorg. Chem.,* 1977, **16,** 698.
403. G. K. Anderson, R. J. Cross, L. Manojlovic-Muir, K. W. Muir and R. A. Wales, *J. Chem. Soc., Dalton Trans.,* 1979, 684.
404. G. K. Anderson and R. J. Cross, *J. Chem. Soc., Dalton Trans.,* 1979, 690.
405. M. Wada, Y. Koyama and K. Sameshinia, *J. Organomet. Chem.,* 1981, **209,** 115.
406. E. D. Dobrzynski and R. J. Angelici, *Inorg. Chem.,* 1975, **14,** 1513.
407. H. C. Clark, V. K. Jain and G. S. Rao, *J. Organomet. Chem.,* 1983, **259,** 275.

408. S. Muralidharan and J. H. Espenson, *Inorg. Chem.*, 1983, **22,** 2786.
409. T. V. Ashworth, J. A. K. Howard, M. Laguna and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1980, 1593.
410. J. C. Jeffrey, C. Sambale, M. F. Schmidt and F. G. A. Stone, *Organometallics,* 1982, **1,** 1597.
411. K. A. Mead, I. Moore, F. G. A. Stone and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1983, 2083.
412. M. Rasol Awang, J. C. Jeffrey and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1983, 2091.
413. J. A. K. Howard, K. A. Mead, J. R. Moss, R. Navarro, F. G. A. Stone and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1981, 743.
414. T. V. Ashworth, M. Berry, J. A. K. Howard, M. Laguna and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1980, 1615.
415. M. Berry, J. Martin-Gil, J. A. K. Howard and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1980, 1625.
416. M. Berry, J. A. K. Howard and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1980, 1601.
417. J. A. K. Howard, J. C. Jeffrey, M. Laguna, R. Navarro and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1981, 751.
418. J. C. Jeffrey, R. Navarro, H. Razay and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1981, 2471.
419. T. V. Ashworth, J. A. K. Howard and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1980, 1609.
420. J. C. Jeffrey, H. Razay and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1982, 1733.
421. J. C. Jeffrey, I. Moore, M. Murray and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1982, 1741.
422. M. J. Chetcuti, K. Marsden, I. Moore, F. G. A. Stone and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1982, 1749.
423. M. Chetcuti, J. A. K. Howard, R. M. Mills, F. G. A. Stone and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1982, 1757.
424. R. D. Barr, M. Green, J. A. K. Howard, T. B. Marder, I. Moore and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1983, 746.
425. W. C. Kaska, *Coord. Chem. Rev.*, 1983, **48,** 1.
426. W. C. Kaska, D. K. Mitchell and R. F. Reicheldefer, *J. Organomet. Chem.*, 1973, **47,** 391.
427. H. Schmidbaur, *Pure Appl. Chem.*, 1980, **52,** 1057.
428. H. Schmidbaur, *Acc. Chem. Res.*, 1975, **8,** 62.
429. N. J. Kermode, M. F. Lappert, B. W. Skelton and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1981, 698.
430. J. R. Moss and J. C. Spiers, *J. Organomet. Chem.*, 1979, **182,** C20.
431. O. J. Scherer and H. J. Jungmann, *J. Organomet. Chem.*, 1981, **208,** 153.
432. R. D. Gillard, M. Keeton, R. Mason, M. F. Pilbrow and D. R. Russell, *J. Organomet. Chem.*, 1971, **33,** 247.
433. M. Keeton, R. Mason and D. R. Russell, *J. Organomet. Chem.*, 1971, **33,** 259.
434. J. C. Baldwin and W. C. Kaska, *Inorg. Chem.*, 1979, **18,** 686.
435. H. Koezuka, G. E. Matsubayashi and T. Tanaka, *Inorg. Chem.*, 1974, **13,** 443.
436. H. Koezuka, G. E. Matsubayashi and T. Tanaka, *Inorg. Chem.*, 1976, **15,** 417.
437. M. Kato, H. Urabe, Y. Oosawa, T. Saito and Y. Sasaki, *J. Organomet. Chem.*, 1976, **121,** 81.
438. R. D. Gillard, M. F. Pilbrow, S. Leonard, M. C. Rendle and C. F. H. Tipper, *Polyhedron,* 1982, **1,** 689.
439. R. Nast and W. D. Henz, *Chem. Ber.*, 1962, **95,** 1478.
440. B. R. Steele and K. Vrieze, *Transition Met. Chem.*, 1976, **1,** 208.
441. J. Kuyper and K. Vrieze, *Transition Met. Chem.*, 1976, **1,** 208.
442. J. D. Schagen, A. R. Overbeek and H. Schenk, *Inorg. Chem.*, 1978, **17,** 1938.
443. C. M. Che, W. P. Schaefer, H. B. Gray, M. K. Dickson, P. B. Stein and D. M. Roundhill, *J. Am. Chem. Soc.*, 1982, **104,** 4253.
444. J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1959, 705.
445. F. Glockling, T. McBride and R. J. I. Pollock, *Inorg. Chim. Acta,* 1974, **8,** 77.
446. R. Bardi and A. M. Piazzesi, *Inorg. Chim. Acta,* 1980, **47,** 249.
447. M. A. Bennett, H. K. Chee and G. B. Robertson, *Inorg. Chem.*, 1979, **18,** 1061.
448. R. L. Phillips and R. J. Puddephatt, *J. Chem. Soc., Dalton Trans.*, 1978, 1732.
449. N. L. Jones and J. A. Ibers, *Organometallics,* 1982, **1,** 326.
450. L. J. Krause and J. A. Morrison, *J. Chem. Soc., Chem. Commun.*, 1981, 1282.
451. L. Manojlovic-Muir, K. W. Muir, T. Solomun, D. W. Meek and J. L. Peterson, *J. Organomet. Chem.*, 1978, **146,** C26.
452. D. B. Crump and N. C. Payne, *Inorg. Chem.*, 1973, **12,** 1663.
453. J. D. Kennedy, W. McFarlane and R. J. Puddephatt, *J. Chem. Soc., Dalton Trans.*, 1976, 745.
454. G. Calvin and G. E. Coates, *J. Chem. Soc.*, 1960, 2008.
455. R. Nast, J. Voss and R. Kramolowsky, *Chem. Ber.*, 1975, **108,** 1511.
456. W. H. Baddley and P. Choudhury, *J. Organomet. Chem.*, 1973, **60,** C74.
457. O. A. Reutov, V. I. Sokolov, G. Z. Suleimanov and V. V. Bahilov, *J. Organomet. Chem.*, 1978, **160,** 7.
458. V. I. Sokolov and O. A. Reutov, *Coord. Chem. Rev.*, 1978, **27,** 89.
459. C. Eaborn, K. Kundu and A. Pidcock, *J. Organomet. Chem.*, 1979, **170,** C18.
460. C. J. Cardin, D. J. Cardin and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 1977, 767.
461. C. Eaborn, K. J. Odell and A. Pidcock, *J. Chem. Soc., Dalton Trans.*, 1978, 357.
462. C. Eaborn, K. J. Odell and A. Pidcock, *J. Organomet. Chem.*, 1978, **146,** 17.
463. C. Eaborn, K. J. Odell and A. Pidcock, *J. Chem. Soc., Dalton Trans.*, 1979, 134.
464. C. Eaborn, K. J. Odell and A. Pidcock, *J. Chem. Soc., Dalton Trans.*, 1978, 1288.
465. C. Eaborn, K. J. Odell and A. Pidcock, *J. Chem. Soc., Dalton Trans.*, 1979, 758.
466. C. Eaborn, K. Kundu and A. Pidcock, *J. Chem. Soc., Dalton Trans.*, 1981, 933.
467. J. P. Collman, J. N. Cawse and J. W. Kang, *Inorg. Chem.*, 1969, **8,** 2574.
468. R. G. Pearson, W. Louw and J. Rajaram, *Inorg. Chim. Acta,* 1974, **9,** 251.
469. J. A. Osborn, in 'Organotransition Metal Chemistry', ed. Y. Ishii and M. Tsutsui, Plenum, New York, 1975, p. 65.
470. J. P. Collman, *Acc. Chem. Res.*, 1968, **1,** 136.
471. J. Halpern, *Acc. Chem. Res.*, 1970, **3,** 386.

472. F. G. A. Stone, *Pure Appl. Chem.*, 1972, **30**, 551.
473. T. L. Hall, M. F. Lappert and P. W. Lednor, *J. Chem. Soc., Dalton Trans.*, 1980, 1448.
474. P. K. Monaghan and R. J. Puddephatt, *Organometallics*, 1983, **2**, 1698.
475. C. D. Cook and G. S. Jauhal, *Can. J. Chem.*, 1967, **45**, 301.
476. J. Rajaram, R. G. Pearson and J. A. Ibers, *J. Am. Chem. Soc.*, 1974, **96**, 2103.
477. G. W. Parshall, *J. Am. Chem. Soc.*, 1974, **96**, 2360.
478. R. D. Coulson, *J. Am. Chem. Soc.*, 1976, **98**, 3111.
479. H. C. Clark and J. E. H. Ward, *J. Am. Chem. Soc.*, 1974, **96**, 1741.
480. K. Schorpp and W. Beck, *Chem. Ber.*, 1974, **107**, 1371.
481. W. Beck, K. Schorpp and C. Oetker, *Chem. Ber.*, 1974, **107**, 1380.
482. O. J. Scherer and H. Jungmann, *J. Organomet. Chem.*, 1981, **208**, 153.
483. E. D. Dobrzynski and R. J. Angelici, *Inorg. Chem.*, 1975, **14**, 59.
484. D. R. Russell and P. A. Tucker, *J. Chem. Soc., Dalton Trans.*, 1975, 2222.
485. G. Yoshida, H. Kurosawa and R. Okawara, *J. Organomet. Chem.*, 1977, **131**, 309.
486. H. D. McPherson and J. L. Wardell, *Inorg. Chim. Acta*, 1979, **35**, L353.
487. H. D. McPherson and J. L. Wardell, *J. Organomet. Chem.*, 1983, **254**, 261.
488. M. Cusumano, P. Marricchi, R. Romeo, V. Ricevuto and U. Belluco, *Inorg. Chim. Acta*, 1979, **34**, 169.
489. T. G. Appleton and M. A. Bennett, *Inorg. Chem.*, 1978, **17**, 738.
490. R. Uson, J. Fornies, F. Martinez, M. Tomas and I. Reoyo, *Organometallics*, 1983, **2**, 1386.
491. G. Lopez, G. Garcia, J. Galvez and N. Cutillas, *J. Organomet. Chem.*, 1983, **258**, 123.
492. D. Schwarzenbach, A. Pinkerton, G. Chapuis, J. Wenger, R. Ros and R. Roulet, *Inorg. Chim. Acta*, 1977, **25**, 255.
493. N. A. Bailey , R. D. Gillard, M. Keeton, R. Mason and D. R. Russell, *J. Chem. Soc., Chem. Commun.*, 1966, 396.
494. N. Dominelli and A. C. Oehlschlager, *Can. J. Chem.*, 1977, **55**, 364.
495. J. Rajaram and J. A. Ibers, *J. Am. Chem. Soc.*, 1978, **100**, 829.
496. M. D. Waddington and P. W. Jennings, *Organometallics*, 1982, **1**, 385.
497. M. D. Waddington, J. A. Campbell, P. W. Jennings and C. F. Campana, *Organometallics*, 1983, **2**, 1269.
498. A. Miyashita, M. Takahashi and H. Takaya, *J. Am. Chem. Soc.*, 1981, **103**, 6257.
499. R. Schlodder, J. A. Ibers, M. Lenarda and M. Graziani, *J. Am. Chem. Soc.*, 1974, **96**, 6893.
500. M. Lenarda, R. Ros, O. Traverso, W. D. Pitts, W. H. Baddley and M. Graziani, *Inorg. Chem.*, 1977, **16**, 3178.
501. R. Ros, M. Lenarda, N. Bresciani Pahor, M. Calligaris, P. Delise, L. Randaccio and M. Graziani, *J. Chem. Soc., Dalton Trans.*, 1976, 1937.
502. J. Burgess, R. I. Haines, E. R. Hamner, R. D. W. Kemmitt and M. A. R. Smith, *J. Chem. Soc., Dalton Trans.*, 1975, 2579.
503. T. Ito, T. Kiriyama, Y. Nakamura and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 3257.
504. Y. T. Fanchiang, W. P. Ridley and J. M. Wood, *J. Am. Chem. Soc.*, 1979, **101**, 1442.
505. H. P. C. Hogenkamp, N. A. Kohlmiller, R. Howsinger, T. E. Walker and N. A. Matwiyoff, *J. Chem. Soc., Dalton Trans.*, 1980, 1668.
506. Y. T. Fanchiang, J. J. Pignatello and J. M. Wood, *Organometallics*, 1983, **2**, 1748.
507. Y. T. Fanchiang, J. J. Pignatello and J. M. Wood, *Organometallics*, 1983, **2**, 1752.
508. R. J. Cross and A. J. McLennan, *J. Organomet. Chem.*, 1983, **255**, 113.
509. T. G. Appleton, H. C. Clark and L. E. Manzer, *Coord. Chem. Rev.*, 1973, **10**, 335.
510. F. R. Hartley, *Chem. Soc. Rev.*, 1973, **2**, 163.
511. J. Kupyer, *Inorg. Chem.*, 1978, **17**, 1458.
512. R. J. Cross and A. J. McLennan, *J. Chem. Soc., Dalton Trans.*, 1983, 359.
513. J. P. Visser, W. W. Jager and C. Masters, *Recl. Trav. Chim. Pays-Bas*, 1975, **94**, 70.
514. R. J. Puddephatt and P. J. Thompson, *J. Chem. Soc., Dalton Trans.*, 1975, 1810.
515. R. J. Puddephatt and P. J. Thompson, *J. Chem. Soc., Dalton Trans.*, 1977, 1219.
516. R. J. Puddephatt and P. J. Thompson, *J. Organomet. Chem.*, 1979, **166**, 251.
517. J. D. Scott and R. J. Puddephatt, *Organometallics*, 1983, **2**, 1643.
518. D. M. Grove, G. van Koten, H. J. C. Ubbels and A. L. Spek, *J. Am. Chem. Soc.*, 1982, **104**, 4285.
519. D. M. Grove, G. van Koten, J. N. Louwen, J. G. Noltes, A. L. Spek and H. J. C. Ubbels, *J. Am. Chem. Soc.*, 1982, **104**, 6609.
520. A. F. M. J. van der Ploeg, G. van Koten, K. Vrieze and A. L. Spek, *Inorg. Chem.*, 1982, **21**, 2014.
521. A. F. M. J. van der Ploeg, G. van Koten and K. Vrieze, *Inorg. Chem.*, 1982, **21**, 2026.
522. A. F. M. J. van der Ploeg, G. van Koten, K. Vrieze, A. L. Spek and A. J. M. Duisenberg, *Organometallics*, 1982, **1**, 1066.
523. J. Terheijden, G. Van Koten, J. L. deBooys, H. J. C. Ubbels and C. H. Stam, *Organometallics*, 1983, **2**, 1882
524. D. M. Grove, G. van Koten and H. J. C. Ubbels, *Organometallics*, 1982, **1**, 1366.
525. A. Evans, C. T. Mortimer and R. J. Puddephatt, *J. Organomet. Chem.*, 1975, **96**, C58.
526. S. J. Ashcroft and C. T. Mortimer, *J. Chem. Soc. (A)*, 1967, 930.
527. P. J. Davidson, M. F. Lappert and R. Pearce, *Chem. Rev.*, 1976, **76**, 219.
528. B. Wozniak, J. D. Ruddick and G. Wilkinson, *J. Chem. Soc. (A)*, 1971, 3116.
529. R. J. Cross, *Inorg. Chim. Acta Rev.*, 1969, **3**, 75.
530. A. Morvillo, G. Favero and A. Turco, *J. Organomet. Chem.*, 1983, **243**, 111.
531. G. M. Whitesides, J. F. Gaasch and E. R. Stedronsky, *J. Am. Chem. Soc.*, 1972, **94**, 5258.
532. S. Komiya, A. Yamamoto and T. Yamamoto, *Chem. Lett.*, 1978, **11**, 1273.
533. S. Komiya, Y. Morimoto, A. Yamamoto and T. Yamamoto, *Organometallics*, 1982, **1**, 1528.
534. T. J. McCarthy, R. G. Nuzzo and G. M. Whitesides, *J. Am. Chem. Soc.*, 1981, **903**, 3396.
535. A. Morvillo and A. Turco, *J. Organomet. Chem.*, 1983, **258**, 383.
536. P. S. Braterman, R. J. Cross and G. B. Young, *J. Chem. Soc., Dalton Trans.*, 1976, 1306.
537. P. S. Braterman, R. J. Cross and G. B. Young, *J. Chem. Soc., Dalton Trans.*, 1976, 1310.

538. P. S. Braterman, R. J. Cross and G. B. Young, *J. Chem. Soc., Dalton Trans.*, 1977, 1892.
539. H. A. Brune, J. Ertl, D. Grafl and G. Schmidtberg, *Chem. Ber.*, 1982, **115**, 1141.
540. J. Ertl, T. Debaerdemaeker and H. A. Brune, *Chem. Ber.*, 1982, **115**, 3860.
541. A. K. Cheetham, R. J. Puddephatt, A. Zalkin, D. H. Templeton and L. K. Templeton, *Inorg. Chem.*, 1976, **15**, 2997.
542. M. P. Brown, A. Hollings, K. J. Houston, R. J. Puddephatt and M. Rashidi, *J. Chem. Soc., Dalton Trans.*, 1976, 786.
543. J. X. McDermott, J. F. White and G. M. Whitesides, *J. Am. Chem. Soc.*, 1973, **95**, 4451.
544. J. X. McDermott, J. F. White and G. M. Whitesides, *J. Am. Chem. Soc.*, 1976, **98**, 6521.
545. G. B. Young and G. M. Whitesides, *J. Am. Chem. Soc.*, 1978, **100**, 5808.
546. R. DiCosimo and G. M. Whitesides, *J. Am. Chem. Soc.*, 1982, **104**, 3601.
547. R. J. Al-Essa, R. J. Puddephatt, M. A. Quyser and C. F. H. Tipper, *J. Am. Chem. Soc.*, 1979, **101**, 364.
548. C. P. Casey, D. M. Scheck and A. J. Shusterman, *J. Am. Chem. Soc.*, 1979, **101**, 4233.
549. R. J. Al-Essa, R. J. Puddephatt, P. J. Thompson and C. F. H. Tipper, *J. Am. Chem. Soc.*, 1980, **102**, 7546.
550. R. J. Al-Essa, R. J. Puddephatt, D. C. L. Perkins, M. C. Rendle and C. F. H. Tipper, *J. Chem. Soc., Dalton Trans.*, 1981, 1738.
551. T. H. Johnson and S. S. Cheng, *J. Am. Chem. Soc.*, 1979, **101**, 5277.
552. P. Foley and G. M. Whitesides, *J. Am. Chem. Soc.*, 1979, **101**, 2732.
553. J. A. Ibers, R. DiCosimo and G. M. Whitesides, *Organometallics*, 1982, **1**, 13.
554. P. Foley, R. DiCosimo and G. M. Whitesides, *J. Am. Chem. Soc.*, 1980, **102**, 6713.
555. R. DiCosimo, S. S. Moore, A. F. Sowinski and G. M. Whitesides, *J. Am. Chem. Soc.*, 1982, **104**, 124.
556. T. J. McCarthy, R. G. Nuzzo and G. M. Whitesides, *J. Am. Chem. Soc.*, 1981, **103**, 1676.
557. J. T. Burton, R. J. Puddephatt, N. L. Jones and J. A. Ibers, *Organometallics*, 1983, **2**, 1487.
558. J. T. Burton and R. J. Puddephatt, *J. Am. Chem. Soc.*, 1982, **104**, 4242.
559. S. D. Chappell and D. J. Cole-Hamilton, *J. Chem. Soc., Dalton Trans.*, 1983, 1051.
560. S. S. M. Ling and R. J. Puddephatt, *J. Chem. Soc., Chem. Commun.*, 1982, 412.
561. G. K. Barker, M. Green, J. A. K. Howard, J. L. Spencer and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1978, 1839.
562. M. Catellani and J. Halpern, *Inorg. Chem.*, 1980, **19**, 566.
563. S. Sostero, O. Traverso, R. Ros and R. A. Michelin, *J. Organomet. Chem.*, 1983, **246**, 325.
564. C. Bartocci, A. Maldotti, S. Sostero and O. Traverso, *J. Organomet. Chem.*, 1983, **253**, 253.
565. J. Y. Chen and J. K. Kochi, *J. Am. Chem. Soc.*, 1977, **99**, 1450.
566. R. J. Klingler, J. C. Huffman and J. K. Kochi, *J. Organomet. Chem.*, 1981, **206**, C7.
567. K. A. Azam, M. P. Brown, S. J. Cooper and R. J. Puddephatt, *Organometallics*, 1982, **1**, 1183.
568. R. H. Hill and R. J. Puddephatt, *Organometallics*, 1983, **2**, 1472.
569. K. Tatsumi, R. Hoffmann, A. Yamamoto and J. K. Stille, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 1857.
570. G. W. Parshall and J. J. Mrowca, *Adv. Organomet. Chem.*, 1968, **7**, 157.
571. J. K. Jawad, R. J. Puddephatt and M. A. Stalteri, *Inorg. Chem.*, 1982, **21**, 332.
572. R. Romeo, D. Minniti, S. Lanza, P. Uguagliati and U. Belluco, *Inorg. Chem.*, 1978, **17**, 2813.
573. R. J. Puddephatt and P. J. Thompson, *J. Organomet. Chem.*, 1976, **117**, 395.
574. I. J. Harvie and F. J. McQuillin, *J. Chem. Soc., Chem. Commun.*, 1977, 241.
575. R. Romeo, D. Minniti and M. Trozzi, *Inorg. Chem.*, 1976, **15**, 1134.
576. W. J. Louw, *Inorg. Chem.*, 1977, **16**, 2147.
577. R. Romeo, *Inorg. Chem.*, 1978, **17**, 2040.
578. R. Romeo, D. Minniti and S. Lanza, *Inorg. Chem.*, 1979, **18**, 2362.
579. R. Romeo, D. Minniti and S. Lanza, *Inorg. Chem.*, 1980, **19**, 3663.
580. H. Kelm, W. J. Louw and D. A. Palmer, *Inorg. Chem.*, 1980, **19**, 843.
581. R. van Eldik, D. A. Palmer and H. Kelm, *Inorg. Chem.*, 1979, **18**, 572.
582. W. J. Louw, R. van Eldik and H. Kelm, *Inorg. Chem.*, 1980, **19**, 2878.
583. R. van Eldik, D. A. Palmer, H. Kelm and W. J. Louw, *Inorg. Chem.*, 1980, **19**, 3551.
584. L. L. Costanzo, S. Giuffrida and R. Romeo, *Inorg. Chim. Acta*, 1980, **38**, 31.
585. M. Green, in 'MPT International Review of Science, Inorganic Chemistry', Butterworths, London, 1972, Series 1, vol. 6, chap. 5.
586. R. F. Heck, *Adv. Chem. Ser.*, 1964, **49**, 181.
587. M. F. Lappert and B. Prokai, *Adv. Organomet. Chem.*, 1967, **5**, 227.
588. A. Wojcicki, *Adv. Organomet. Chem.*, 1973, **11**, 88.
589. A. J. Deeming, in 'MTP International Review of Science, Inorganic Chemistry', Butterworths, London, 1972, Series 2, vol. 9, chap. 9.
590. (a) P. J. Davidson, R. R. Hignett and D. T. Thompson, in 'Catalysis', Chemical Society, London, 1977, vol. 1, p. 369. (b) F. Calderazzo, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 299.
591. G. Booth and J. Chatt, *J. Chem. Soc. (A)*, 1966, 634.
592. P. E. Garrou and R. F. Heck, *J. Am. Chem. Soc.*, 1976, **98**, 4115.
593. G. K. Anderson and R. J. Cross, *J. Chem. Soc., Dalton Trans.*, 1979, 1246.
594. G. K. Anderson and R. J. Cross, *J. Chem. Soc., Dalton Trans.*, 1980, 712.
595. G. K. Anderson and R. J. Cross, *J. Chem. Soc., Dalton Trans.*, 1980, 1434.
596. R. J. Cross and J. Gemmill, *J. Chem. Soc., Dalton Trans.*, 1981, 2317.
597. R. J. Cross and I. G. Phillips, *J. Chem. Soc., Dalton Trans.*, 1982, 2261.
598. M. Kubota, D. A. Phillips and J. E. Jacobsen, *J. Coord. Chem.*, 1980, **10**, 125.
599. G. K. Anderson, H. C. Clark and J. A. Davies, *Organometallics*, 1982, **1**, 64.
600. G. K. Anderson, H. C. Clark and J. A. Davies, *Inorg. Chem.*, 1983, **22**, 427.
601. G. K. Anderson, H. C. Clark and J. A. Davies, *Inorg. Chem.*, 1983, **22**, 434.
602. M. A. Bennett and A. Rokicki, *J. Organomet. Chem.*, 1983, **244**, C31.
603. S. Sakaki, K. Kitaura, K. Morokuma and K. Ohkubo, *J. Am. Chem. Soc.*, 1983, **105**, 2280.

604. F. Faraone, L. Silvestro, S. Sergi and R. Pietropaolo, *J. Organomet. Chem.*, 1972, **46**, 379.
605. P. M. Treichel and R. W. Hess, *J. Am. Chem. Soc.*, 1971, **93**, 5424.
606. S. Otsuka and K. Ataka, *J. Chem. Soc., Dalton Trans.*, 1976, 327.
607. P. M. Treichel, K. P. Wagner and R. W. Hess, *Inorg. Chem.*, 1973, **12**, 1471.
608. F. R. Hartley, in 'Comprehensive Organometallic Chemistry', ed. G. Wilkinson, Pergamon, Oxford, 1982, vol 6, chap. 39, p. 562.
609. G. Minghetti, F. Bonati and G. Banditelli, *Inorg. Chem.*, 1976, **15**, 2649.
610. C. T. Mortimer, M. P. Wilkinson and R. J. Puddephatt, *J. Organomet. Chem.*, 1979, **165**, 269.
611. T. G. Appleton, M. H. Chisholm and H. C. Clark, *J. Am. Chem. Soc.*, 1972, **94**, 8912.
612. T. G. Appleton, M. H. Chisholm, H. C. Clark and K. Yasufuku, *J. Am. Chem. Soc.*, 1974, **96**, 6600.
613. R. A. Bell and M. H. Chisholm, *Inorg. Chem.*, 1977, **16**, 698.
614. R. A. Bell, M. H. Chisholm and G. G. Christoph, *J. Am. Chem. Soc.*, 1976, **98**, 6046.
615. C. J. Cardin and K. W. Muir, *J. Chem. Soc., Dalton Trans.*, 1977, 1593.
616. M. A. Chisholm and D. A. Couch, *J. Chem. Soc., Chem. Commun.*, 1974, 42.
617. H. D. Empsall, B. L. Shaw and A. J. Stringer, *J. Organomet. Chem.*, 1975, **96**, 461.
618. M. H. Chisholm and L. A. Rankel, *Inorg. Chem.*, 1977, **16**, 2177.
619. J. Browning, G. W. Bushnell and K. R. Dixon, *Inorg. Chem.*, 1981, **20**, 3112.
620. J. H. Nelson and H. B. Jonassen, *Coord. Chem. Rev.*, 1971, **6**, 27.
621. F. R. Hartley, *Angew. Chem., Int. Ed. Engl.*, 1972, **11**, 596.
622. M. Herberhold, 'Metal π-Complexes', Elsevier, Amsterdam, 1972, vol. 2, part 2.
623. G. Deganello, 'Transition Metal Complexes of Cyclic Polyolefins', Academic, London, 1979.
624. S. D. Ittel and J. A. Ibers, *Adv. Organomet. Chem.*, 1976, **14**, 33.
625. M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, 1951, **18**, C79.
626. J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 1953, 2939.
627. J. H. Nelson, K. S. Wheelock, L. C. Cusachs and H. B. Jonassen, *Inorg. Chem.*, 1972, **11**, 422.
628. T. Ziegler and A. Rauk, *Inorg. Chem.*, 1979, **18**, 1558.
629. L. E. Orgel, 'An Introduction to Transition Metal Chemistry', Methuen, London, 1960, p. 65.
630. R. D. Cramer, E. L. Jenner, R. V. Lindsey and V. G. Stolberg, *J. Am. Chem. Soc.*, 1963, **85**, 1691.
631. J. Chatt and M. L. Searle, *Inorg. Synth.*, 1957, **5**, 210.
632. M. Green and C. J. Wilson, *J. Chem. Soc., Dalton Trans.*, 1977, 2302.
633. M. Green and C. J. Wilson, *J. Chem. Res. (S)*, 1978, 175.
634. L. I. Elding and A. B. Groning, *Inorg. Chim. Acta*, 1980, **38**, 59.
635. M. Green and M. G. Swanwick, *J. Chem. Soc., Dalton Trans.*, 1978, 158.
636. D. A. White, *Inorg. Synth.*, 1972, **13**, 55.
637. J. R. Briggs, C. Crocker, W. S. McDonald and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1980, 64.
638. J. R. Briggs, C. Crocker, W. S. McDonald and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1981, 121.
639. D. Mansuy, J. F. Bartoli and J. C. Chottard, *J. Organomet. Chem.*, 1974, **73**, C39.
640. S. S. Hupp and G. Dahlgren, *Inorg. Chem.*, 1976, **15**, 2349.
641. J. Hillis, J. Francis, M. Ori and M. Tsutsui, *J. Am. Chem. Soc.*, 1974, **96**, 4800.
642. L. Cattalini, F. Gasparrini, L. Maresca and G. Natile, *J. Chem. Soc., Chem. Commun.*, 1973, 369.
643. L. Maresca, G. Natile and L. Cattalini, *J. Chem. Soc., Dalton Trans.*, 1979, 1140.
644. W. Partenheimer, *J. Am. Chem. Soc.*, 1976, **98**, 2779.
645. C. R. Kistner, J. H. Hutchinson, J. R. Doyle and J. C. Storlie, *Inorg. Chem.*, 1963, **2**, 1255.
646. R. E. Rinehart and J. S. Lasky, *J. Am. Chem. Soc.*, 1964, **86**, 2516.
647. H. A. Tayim, A. Bouldoukian and M. Kharbousch, *Inorg. Nucl. Chem. Lett.*, 1972, **8**, 231.
648. H. A. Tayim and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, 1967, **89**, 3420.
649. C. Eaborn, N. Farrell and A. Pidcock, *J. Chem. Soc., Dalton Trans.*, 1976, 289.
650. R. Mason, G. B. Robertson, P. O. Whimp, B. L. Shaw and G. Shaw, *J. Chem. Soc., Chem. Commun.*, 1968 868.
651. B. L. Shaw and G. Shaw, *J. Chem. Soc., Chem. Commun.*, 1973, 264.
652. E. Kuljian and H. Frye, *Z. Naturforsch., Teil B*, 1965, **20**, 204.
653. N. Yagi, S. Kikkawa and I. Omae, *Nippon Kagaku Zasshi*, 1971, **92**, 634 (*Chem. Abstr.*, 1972, **76**, 127 146).
654. M. M. Bhagwat and D. Devaprabhakara, *J. Organomet. Chem.*, 1973, **52**, 425.
655. J. K. A. Clarke, E. McMahon, J. B. Thomson and B. Zeeh, *J. Organomet. Chem.*, 1971, **31**, 283.
656. C. B. Anderson and J. T. Michalowski, *J. Chem. Soc., Chem. Commun.*, 1972, 459.
657. A. C. Cope, C. R. Ganellin, H. W. Johnson, Jr., T. V. Van Auken and H. J. S. Winkler, *J. Am. Chem. Soc* 1963, **85**, 3276.
658. G. Paiaro, P. Corradini, R. Palumbo and A. Panunzi, *Makromol. Chem.*, 1964, **71**, 184.
659. M. Goldman, Z. Kustanovich, S. Weinstein, A. Tishbee, and E. Gil-Av, *J. Am. Chem. Soc.*, 1982, **104**, 1093.
660. A. Panunzi, R. Palumbo, C. Pedone and G. Paiaro, *J. Organomet. Chem.*, 1966, **5**, 586.
661. K. Konja, J. Fujita and K. Nakamoto, *Inorg. Chem.*, 1971, **10**, 1699.
662. S. Shinoda, Y. Yamaguchi and Y. Saito, *Inorg. Chem.*, 1979, **18**, 673.
663. Y. Terai and K. Saito, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 503.
664. Y. Terai, H. Kido, K. Kashiwabara and K. Saito, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 3245.
665. H. Boucher and B. Bosnich, *J. Am. Chem. Soc.*, 1977, **99**, 6253.
666. H. Boucher and B. Bosnich, *Inorg. Chem.*, 1977, **16**, 717.
667. R. G. Ball and N. C. Payne, *Inorg. Chem.*, 1976, **15**, 2494.
668. R. G. Ball and N. C. Payne, *Inorg. Chem.*, 1977, **16**, 1871.
669. S. Miya, K. Kashiwabara and K. Saito, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 2309.
670. R. Lazzaroni, P. Salvadori, C. Bartucci and C. A. Veracini, *J. Organomet. Chem.*, 1975, **99**, 475.
671. A. deRenzi, B. DiBlasio, A. Saporito, M. Scalone and A. Vitagliano, *Inorg. Chem.*, 1980, **19**, 960.
672. A. deRenzi, G. Morelli, A. Panunzi and S. Wurzburger, *Inorg. Chim. Acta*, 1983, **76**, L285.
673. H. van der Poel and G. van Koten, *Inorg. Chem.*, 1981, **20**, 2950.

674. J. Bordner and D. W. Wertz, *Inorg. Chem.*, 1974, **13**, 1639.
675. R. E. Yingst and B. E. Douglas, *Inorg. Chem.*, 1964, **3**, 1177.
676. T. Miyamoto, K. Fukushima, T. Saito and Y. Sasaki, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 138.
677. M. K. Cooper and D. W. Yaniuk, *J. Organomet. Chem.*, 1981, **221**, 231.
678. M. K. Cooper, N. J. Hair and D. W. Yaniuk, *J. Organomet. Chem.*, 1978, **150**, 157.
679. M. K. Cooper and D. W. Yaniuk, *J. Organomet. Chem.*, 1979, **164**, 211.
680. M. K. Cooper, D. W. Yaniuk and M. McPartlin, *J. Organomet. Chem.*, 1979, **166**, 241.
681. M. K. Cooper, P. V. Stevens and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, 1983, 553.
682. M. A. Bennett, H. W. Kouwenhaven, J. Lewis and R. S. Nyholm, *J. Chem. Soc.*, 1964, 4570.
683. K. Issleib and M. Haftendorn, *Z. Anorg. Allg. Chem.*, 1967, **351**, 9.
684. M. A. Bennett, J. Chatt, G. J. Erskin, J. Lewis, R. F. Long and R. S. Nyholm, *J. Chem. Soc. (A)*, 1967, 501.
685. M. A. Bennett, W. R. Kneen and R. S. Nyholm, *Inorg. Chem.*, 1968, **7**, 556.
686. T. G. Appleton and M. A. Bennett, *Inorg. Chem.*, 1974, **13**, 3023.
687. M. A. Bennett, H. K. Chee, J. C. Jeffrey and G. B. Robertson, *Inorg. Chem.*, 1979, **18**, 1071.
688. M. A. Bennett, R. N. Johnson, G. B. Robertson, I. B. Tomkins and P. O. Whimp, *J. Am. Chem. Soc.*, 1976, **98**, 3514.
689. D. C. Goodall, *J. Chem. Soc. (A)*, 1968, 887.
690. M. K. Cooper, P. J. Guerney and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, 1980, 349.
691. M. K. Cooper, P. J. Guerney, H. J. Goodwin and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, 1982, 757.
692. R. A. Love, T. F. Koetzle, G. J. B. Williams, L. C. Andrews and R. Bau, *Inorg. Chem.*, 1975, **14**, 2653.
693. N. Rosch, R. P. Messmer and K. H. Johnson, *J. Am. Chem. Soc.*, 1974, **96**, 3855.
694. P. J. Hay, *J. Am. Chem. Soc.*, 1981, **103**, 1390.
695. L. W. Reeves, *Can. J. Chem.*, 1960, **38**, 736.
696. S. Maricic, C. R. Redpath and J. A. S. Smith, *J. Chem. Soc.*, 1963, 4905.
697. D. R. McMillin and R. S. Drago, *Inorg. Chem.*, 1974, **13**, 546.
698. J. W. Emsley and J. Evans, *J. Chem. Soc., Dalton Trans.*, 1978, 1355.
699. S. Miya and K. Saito, *Inorg. Chem.*, 1981, **20**, 287.
700. T. A. Albright, R. Hoffmann, J. C. Thibeault and D. L. Thorn, *J. Am. Chem. Soc.*, 1979, **101**, 3801.
701. H. van der Poel, G. van Koten, M. Kokkes and C. H. Stam, *Inorg. Chem.*, 1981, **20**, 2941.
702. F. Pesa and M. Orchin, *Inorg. Chem.*, 1975, **14**, 994.
703. L. E. Erickson and D. C. Brower, *Inorg. Chem.*, 1982, **21**, 838.
704. P. D. Kaplan and M. Orchin, *Inorg. Chem.*, 1965, **4**, 1393.
705. R. Lazzaroni, P. Salvadori and P. Pino, *J. Organomet. Chem.*, 1972, **43**, 233.
706. D. G. Cooper and J. Powell, *Inorg. Chem.*, 1976, **15**, 1959.
707. D. G. Cooper and J. Powell, *Inorg. Chem.*, 1977, **16**, 142.
708. S. C. Nyburg, K. Simpson and W. Wong-Ng, *J. Chem. Soc., Dalton Trans.*, 1976, 1865.
709. J. Hiraishi, *Spectrochim. Acta, Part A*, 1969, **25**, 749.
710. D. B. Powell, J. G. V. Scott and N. Sheppard, *Spectrochim. Acta, Part A*, 1972, **28**, 327.
711. C. Y. Hus, B. T. Leshner and M. Orchin, *Inorg. Synth.*, 1979, **19**, 114.
712. J. S. Anderson, *J. Chem. Soc.*, 1936, 1042.
713. P. D. Kaplan, P. Schmidt and M. Orchin, *J. Am. Chem. Soc.*, 1968, **90**, 4175.
714. A. C. Cope and M. W. Fordice, *J. Am. Chem. Soc.*, 1967, **89**, 6187.
715. A. Panunzi, A. deRenzi and G. Paiaro, *J. Am. Chem. Soc.*, 1970, **92**, 3488.
716. A. Panunzi, A. deRenzi, R. Palumbo and G. Paiaro, *J. Am. Chem. Soc.*, 1969, **91**, 3879.
717. I. M. Al-Najjar and M. Green, *J. Chem. Soc., Dalton Trans.*, 1979, 1651.
718. M. Green, J. K. K. Sarhan and I. M. Al-Najjar, *J. Chem. Soc., Dalton Trans.*, 1981, 1565.
719. A. deRenzi, B. DiBlasio, A. Panunzi, C. Pedone and A. Vitagliano, *J. Chem. Soc., Dalton Trans.*, 1978, 1392.
720. A. deRenzi, P. Ganis, A. Panunzi, A. Vitagliano and G. Valle, *J. Am. Chem. Soc.*, 1980, **102**, 1722.
721. J. Ambuhl, P. S. Pregosin, L. M. Venanzi, G. Ughetto and L. Zambonelli, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 369.
722. J. R. Briggs, C. Crocker, W. S. McDonald and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1981, 575.
723. J. R. Briggs, C. Crocker, W. S. McDonald and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1982, 457.
724. A. deRenzi, B. DiBlasio, G. Morelli and A. Vitagliano, *Inorg. Chim. Acta*, 1982, **63**, 233.
725. G. Natile, L. Maresca and L. Cattalini, *J. Chem. Soc., Dalton Trans.*, 1977, 651.
726. G. Annibale, L. Maresca, G. Natile, A. Tiripicchio and M. Tiripicchio-Camellini, *J. Chem. Soc., Dalton Trans.*, 1982, 1587.
727. L. Maresca and G. Natile, *J. Chem. Soc., Dalton Trans.*, 1982, 1903.
728. P. P. Ponti, J. C. Baldwin and W. C. Kaska, *Inorg. Chem.*, 1979, **18**, 873.
729. A. T. Hutton, D. M. McEwan, B. L. Shaw and S. W. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1983, 2011.
730. L. Maresca and G. Natile, *J. Am. Chem. Soc.*, 1982, **104**, 7661.
731. D. Mansuy, M. Dreme, J. C. Chottard, J.-P. Girault and J. Guilhem, *J. Am. Chem. Soc.*, 1980, **102**, 844.
732. S. J. Betts, A. Harris, R. N. Haszeldine and R. V. Parish, *J. Chem. Soc. (A)*, 1971, 3699.
733. B. F. G. Johnson, J. Lewis and M. S. Subramanian, *J. Chem. Soc., Chem. Commun.*, 1966, 117.
734. J. K. Stille and D. B. Fox, *J. Am. Chem. Soc.*, 1970, **92**, 1274.
735. R. N. Haszeldine, R. V. Parish and D. W. Robbins, *J. Chem. Soc., Dalton Trans.*, 1976, 2355.
736. P. A. Kramer and C. Masters, *J. Chem. Soc., Dalton Trans.*, 1975, 849.
737. A. A. Kiffen, C. Masters and L. Raymond, *J. Chem. Soc., Dalton Trans.*, 1975, 853.
738. A. D. H. Clague and C. Masters, *J. Chem. Soc., Dalton Trans.*, 1975, 858.
739. J. Chatt, B. L. Shaw and A. A. Williams, *J. Chem. Soc.*, 1962, 3269.
740. S. Otsuka, A. Nakamura and K. Tani, *J. Organomet. Chem.*, 1968, **14**, P30.
741. D. M. Blake and R. Mersecchi, *J. Chem. Soc., Chem. Commun.*, 1971, 1045.
742. M. J. Hacker, G. W. Littlecott and R. D. W. Kemmitt, *J. Organomet. Chem.*, 1973, **47**, 189.
743. D. M. Blake, S. Shields and L. Wyman, *Inorg. Chem.*, 1974, **13**, 1595.

744. D. M. Blake and D. M. Roundhill, *Inorg. Synth.*, 1978, **18**, 120.
745. U. Nagel, *Chem. Ber.*, 1982, **115**, 1998.
746. R. J. Nuzzo, T. J. McCarthy and G. M. Whitesides, *Inorg. Chem.*, 1981, **20**, 1312.
747. W. J. Bland and R. D. W. Kemmitt, *J. Chem. Soc. (A)*, 1968, 1278.
748. K. Suzuki and H. Okuda, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 1938.
749. D. M. Roundhill and G. Wilkinson, *J. Chem. Soc. (A)*, 1968, 506.
750. W. H. Baddley and L. M. Venanzi, *Inorg. Chem.*, 1966, **5**, 33.
751. G. L. McClure and W. H. Baddley, *J. Organomet. Chem.*, 1971, **27**, 155.
752. R. D. W. Kemmitt and R. D. Moore, *J. Chem. Soc. (A)*, 1971, 2472.
753. P. K. Maples, M. Green and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1973, 388.
754. T. Yoshida and S. Otsuka, *J. Am. Chem. Soc.*, 1977, **99**, 2134.
755. J. P. Birk, J. Halpern and A. L. Pickard, *Inorg. Chem.*, 1968, **7**, 2672.
756. J. P. Visser, A. J. Schipperijn and J. Lukas, *J. Organomet. Chem.*, 1973, **47**, 433.
757. J. W. Fitch, K. C. Chan and J. A. Froelich, *J. Organomet. Chem.*, 1978, **160**, 477.
758. M. R. White and P. J. Stang, *Organometallics*, 1983, **2**, 1654.
759. M. Green, J. A. K. Howard, R. P. Hughes, S. C. Kellett and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1975, 2007.
760. M. J. Chetcuti, J. A. Herbert, J. A. K. Howard, M. Pfeffer, J. L. Spencer, F. G. A. Stone and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1981, 284.
761. J. A. K. Howard, P. Mitrprachachon and A. Roy, *J. Organomet. Chem.*, 1982, **235**, 375.
762. F. G. A. Stone, *Acc. Chem. Res.*, 1981, **14**, 318.
763. W. J. Cherwinski, B. F. G. Johnson and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1974, 1405.
764. J. J. deBoer and D. Bright, *J. Chem. Soc., Dalton Trans.*, 1975, 662.
765. M. E. Jason, J. A. McGinnety and K. B. Wiberg, *J. Am. Chem. Soc.*, 1974, **96**, 6531.
766. M. E. Jason and J. A. McGinnety, *Inorg. Chem.*, 1981, **20**, 4000.
767. E. Stamm, K. B. Becker, P. Engel, O. Ermer and R. Keese, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 685.
768. S. A. Godleski, R. S. Valpey and K. B. Gundlach, *Organometallics*, 1983, **2**, 1254.
769. A. Christofides, J. A. K. Howard, J. L. Spencer and F. G. A. Stone, *J. Organomet. Chem.*, 1982, **232**, 279.
770. D. R. Russell and P. A. Tucker, *J. Chem. Soc., Dalton Trans.*, 1976, 2181.
771. W. Beck, F. Goetzfried and M. W. Chen, *Chem. Ber.*, 1978, **111**, 3719.
772. R. B. Osborne, H. C. Lewis and J. A. Ibers, *J. Organomet. Chem.*, 1981, **208**, 125.
773. A. C. Barefoot, E. W. Corcoran, R. P. Hughes, D. M. Lemal, W. D. Saunders, B. B. Laird and R. E. Davis, *J. Am. Chem. Soc.*, 1981, **103**, 970.
774. E. R. Hamner, R. D. W. Kemmitt and M. A. R. Smith, *J. Chem. Soc., Dalton Trans.*, 1977, 261.
775. J. A. Osborn, *J. Chem. Soc., Chem. Commun.*, 1968, 1231.
776. J. P. Visser and J. E. Ramakers, *J. Chem. Soc., Chem. Commun.*, 1972, 178.
777. M. Kadonaga, N. Yasuoka and N. Kasai, *J. Chem. Soc., Chem. Commun.*, 1972, 178.
778. G. Paiaro and L. Pandolfo, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 288.
779. K. Schorpp and W. Beck, *Z. Naturforsch., Teil B*, 1973, **28**, 738.
780. I. S. Butler and A. E. Fenster, *J. Organomet. Chem.*, 1974, **66**, 161.
781. M. M. Hunt, R. D. W. Kemmitt, D. R. Russell and P. A. Tucker, *J. Chem. Soc., Dalton Trans.*, 1979, 287.
782. J. R. Burgess, J. G. Chambers, D. A. Clarke and R. D. W. Kemmitt, *J. Chem. Soc., Dalton Trans.*, 1977, 1906.
783. R. A. Head, *J. Chem. Soc., Dalton Trans.*, 1982, 1637.
784. M. C. Baird and G. Wilkinson, *J. Chem. Soc. (A)*, 1967, 865.
785. K. Kawakami, Y. Ozaki and T. Tanaka, *J. Organomet. Chem.*, 1974, **69**, 151.
786. R. Mason and A. I. M. Rae, *J. Chem. Soc. (A)*, 1970, 1767.
787. B. Kleman, *Can. J. Phys.*, 1963, **41**, 2034.
788. P. J. Vergamini and P. G. Eller, *Inorg. Chim. Acta*, 1979, **34**, L291.
789. M. Green, R. B. L. Osborn and F. G. A. Stone, *J. Chem. Soc. (A)*, 1970, 944.
790. J. Ashley-Smith, M. Green and F. G. A. Stone, *J. Chem. Soc. (A)*, 1970, 3161.
791. E. K. Barefield, A. M. Carrier, D. J. Sepelak and D. G. Van Derveer, *Organometallics*, 1982, **1**, 103.
792. J. M. Baraban and J. A. McGinnety, *Inorg. Chem.*, 1974, **13**, 2864.
793. S. Sakaki, N. Kudou and A. Ohyoshi, *Inorg. Chem.*, 1977, **16**, 202.
794. P. T. Cheng, C. D. Cook, S. C. Nyburg, and K. Y. Wan, *Inorg. Chem.*, 1971, **10**, 2210.
795. N. C. Harrison, M. Murray, J. L. Spencer and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1978, 1337.
796. M. H. Chisholm, H. C. Clark, L. E. Manzer and J. B. Stothers, *J. Am. Chem. Soc.*, 1972, **94**, 5087.
797. C. D. Cook and K. Y. Wan, *J. Am. Chem. Soc.*, 1970, **92**, 2595.
798. M. Green, R. B. L. Osborn, A. J. Rest and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1966, 502.
799. G. Pellizer, M. Graziani, M. Lenarda and B. T. Heaton, *Polyhedron*, 1983, **2**, 657.
800. W. G. Kirkham, M. W. Lister and R. B. Poyntz, *Thermochim. Acta*, 1975, **11**, 89.
801. S. J. Ashcroft, A. Maddock and G. Beech, *J. Chem. Soc., Dalton Trans.*, 1974, 462.
802. C. A. Tolman, W. C. Seidel and D. H. Gerlach, *J. Am. Chem. Soc.*, 1972, **94**, 2669.
803. R. D. W. Kemmitt, B. Y. Kimura, G. W. Littlecott and R. D. Moore, *J. Organomet. Chem.*, 1972, **44**, 403.
804. W. J. Bland, J. Burgess and R. D. W. Kemmitt, *J. Organomet. Chem.*, 1968, **15**, 217.
805. A. J. Mukhedar, M. Green and F. G. A. Stone, *J. Chem. Soc. (A)*, 1970, 947.
806. V. A. Mukhedar, B. J. Kavathekar and A. J. Mukhedar, *J. Inorg. Nucl. Chem.*, 1975, **37**, 483.
807. W. J. Bland, J. Burgess and R. D. W. Kemmitt, *J. Organomet. Chem.*, 1968, **14**, 201.
808. J. Burgess, M. M. Hunt and R. D. W. Kemmitt, *J. Organomet. Chem.*, 1977, **134**, 131.
809. S. V. Bukhovets and K. A. Molodova, *J. Inorg. Chem. (USSR)*, 1957, **2** (4), 104.
810. S. V. Bukhovets and N. K. Pukhov, *J. Inorg. Chem. (USSR)*, 1958, **3** (7) 326.
811. J. Chatt, R. G. Guy and L. A. Duncanson, *J. Chem. Soc.*, 1961, 827.
812. J. Chatt, R. G. Guy, L. A. Duncanson and D. T. Thompson, *J. Chem. Soc.*, 1963, 5170.
813. M. H. Chisholm and H. C. Clark, *Inorg. Chem.*, 1971, **10**, 2557.

814. B. W. Davies, R. J. Puddephatt and N. C. Payne, *Can. J. Chem.*, 1972, **50**, 2276.
815. H. C. Clark and L. E. Manzer, *Inorg. Chem.*, 1974, **13**, 1291.
816. B. W. Davis and N. C. Payne, *Inorg. Chem.*, 1974, **13**, 1843.
817. R. Nast, J. Voss and R. Kramolowsky, *Chem. Ber.*, 1975, **108**, 1511.
818. R. Nast and J. Moritz, *J. Organomet. Chem.*, 1976, **117**, 81.
819. C. J. Cardin, D. J. Cardin, M. F. Lappert and K. W. Muir, *J. Chem. Soc., Dalton Trans.*, 1978, 46.
820. A. Furlani, M. V. Russo, S. Licoccia and C. Guastini, *Inorg. Chim. Acta*, 1979, **33**, L125.
821. A. Sebald and B. Wrackmeyer, *J. Chem. Soc., Chem. Commun.*, 1983, 309.
822. P. B. Tripathy and D. M. Roundhill, *J. Organomet. Chem.*, 1970, **24**, 247.
823. J. H. Nelson and H. B. Jonassen, *Coord. Chem. Rev.*, 1971, **6**, 27.
824. J. Halpern and T. A. Weil, *J. Chem. Soc., Chem. Commun.*, 1973, 631.
825. D. A. Harbourne and F. G. A. Stone, *J. Chem. Soc. (A)*, 1968, 1765.
826. W. R. Cullen and F. L. Hou, *Can. J. Chem.*, 1971, **49**, 3404.
827. J. B. B. Heyns and F. G. A. Stone, *J. Organomet. Chem.*, 1978, **160**, 337.
828. O. M. Abu Salah and M. I. Bruce, *Aust. J. Chem.*, 1976, **29**, 73.
829. G. Butler, C. Eaborn and A. Pidcock, *J. Organomet. Chem.*, 1981, **210**, 403.
830. A. Furlani, P. Carusi and M. V. Russo, *J. Organomet. Chem.*, 1976, **116**, 113.
831. G. B. Robertson and P. O. Whimp, *J. Am. Chem. Soc.*, 1975, **97**, 1051.
832. M. A. Bennett and T. Yoshida, *J. Am. Chem. Soc.*, 1978, **100**, 1750.
833. B. W. Davis and N. C. Payne, *Inorg. Chem.*, 1974, **13**, 1848.
834. J. F. Richardson and N. C. Payne, *Can. J. Chem.*, 1977, **55**, 3203.
835. D. H. Farrar and N. C. Payne, *Inorg. Chem.*, 1981, **20**, 821.
836. D. H. Farrar and N. C. Payne, *J. Organomet. Chem.*, 1981, **220**, 239.
837. J. H. Nelson, H. B. Jonassen and D. M. Roundhill, *Inorg. Chem.*, 1969, **8**, 2591.
838. J. H. Nelson, J. J. R. Reed and H. B. Jonassen, *J. Organomet. Chem.*, 1971, **29**, 163.
839. C. D. Cook and K. Y. Wan, *J. Am. Chem. Soc.*, 1970, **92**, 2595.
840. C. D. Cook, K. Y. Wan, U. Gelius, K. Hamrin, G. Johansson, E. Olsson, H. Siegbahn, C. Nordling and K. Siegbahn, *J. Am. Chem. Soc.*, 1971, **93**, 1904.
841. Y. Koie, S. Shinoda and Y. Saito, *J. Chem. Soc., Dalton Trans.*, 1981, 1082.
842. D. M. Hoffman and R. Hoffmann, *J. Chem. Soc., Dalton Trans.*, 1982, 1471.
843. M. Ciriano, J. A. K. Howard, J. L. Spencer, F. G. A. Stone and H. Wadepohl, *J. Chem. Soc., Dalton Trans.*, 1979, 1749.
844. Y. Koie, S. Shinoda, Y. Saito, B. J. Fitzgerald and C. G. Pierpont, *Inorg. Chem.*, 1980, **19**, 770.
845. N. Boag, M. Green, J. A. K. Howard, J. L. Spencer, R. F. D. Stansfield, M. D. O. Thomas, F. G. A. Stone and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1980, 2182.
846. L. Farrugia, J. A. K. Howard, P. Mitrprachachon, F. G. A. Stone and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1981, 162.
847. G. R. Newkome and G. L. McClure, *J. Am. Chem. Soc.*, 1974, **96**, 617.
848. R. F. Heck, 'Organotransition Metal Chemistry', Academic, New York, 1974, p. 169.
849. N. Chaudbury and R. J. Puddephatt, *Inorg. Chem.*, 1981, **20**, 467.
850. J. Browning, M. Green, J. L. Spencer and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1974, 97.
851. H. D. Empsall, B. L. Shaw and A. J. Stringer, *J. Chem. Soc., Dalton Trans.*, 1976, 185.
852. D. M. Roundhill and H. B. Jonassen, *J. Chem. Soc., Chem. Commun.*, 1968, 1233.
853. J. Burgess, M. E. Howden, R. D. W. Kemmitt and N. S. Sridhara, *J. Chem. Soc., Dalton Trans.*, 1978, 1577.
854. W. H. Baddley, C. Panattoni, G. Bandoli, D. A. Clemente and U. Belluco, *J. Am. Chem. Soc.*, 1971, **93**, 5590.
855. R. D. W. Kemmitt, B. Y. Kimura and G. W. Littlecott, *J. Chem. Soc., Dalton Trans.*, 1973, 636.
856. R. J. Cross and J. Gemmill, *J. Chem. Soc., Chem. Commun.*, 1982, 1343.
857. W. J. Bland, R. D. W. Kemmitt and R. D. Moore, *J. Chem. Soc., Dalton Trans.*, 1973, 1292.
858. J. H. Lukas, *Inorg. Synth.*, 1974, **15**, 75.
859. A. N. Nesmeyanov and A. Z. Rubezhov, *J. Organomet. Chem.*, 1979, **164**, 259.
860. B. E. Mann, B. L. Shaw and G. Shaw, *J. Chem. Soc. (A)*, 1971, 3536.
861. H. Kurosawa, *Inorg. Chem.*, 1975, **14**, 2148.
862. J. D. Smith and J. D. Oliver, *Inorg. Chem.*, 1978, **17**, 2585.
863. A. Keasey, P. M. Bailey and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1978, 142.
864. B. E. Mann, A. Keasey, A. Sonoda and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1979, 338.
865. A. Sonoda, P. M. Bailey and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1979, 346.
866. R. L. Phillips and R. J. Puddephatt, *J. Organomet. Chem.*, 1977, **136**, C52.
867. S. Numata, R. Okawara and H. Kurosawa, *Inorg. Chem.*, 1977, **16**, 1737.
868. J. C. Huffman, M. P. Laurent and J. K. Kochi, *Inorg. Chem.*, 1977, **16**, 2639.
869. H. Kurosawa, *J. Chem. Soc., Dalton Trans.*, 1979, 939.
870. C. P. Brock and T. G. Attig, *J. Am. Chem. Soc.*, 1980, **102**, 1319.
871. A. Efraty, *Chem. Rev.*, 1977, **77**, 691.
872. J. Moreto and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1980, 1368.
873. R. J. Cross and R. Wardle, *J. Chem. Soc. (A)*, 1971, 2000.
874. H. P. Fritz and K. E. Schwarzhans, *J. Organomet. Chem.*, 1966, **5**, 181.
875. H. Kurosawa, *J. Chem. Soc., Dalton Trans.*, 1979, 939.
876. H. C. Voleger and K. Vrieze, *J. Organomet. Chem.*, 1968, **13**, 495.
877. M. Calligaris, G. Carturan, G. Nardin, A. Scrivanti and A. Wojcicki, *Organometallics*, 1983, **2**, 865.
878. J. Chatt, C. Eaborn, S. D. Ibekwe and P. N. Kapoor, *J. Chem. Soc. (A)*, 1970, 1343.
879. K. Yamamoto, T. Hayashi and M. Kumada, *J. Organomet. Chem.*, 1971, **28**, C37.
880. C. Eaborn, T. N. Metham and A. Pidcock, *J. Organomet. Chem.*, 1973, **54**, C3.
881. H. Schmidbaur and J. Adlkofer, *Chem. Ber.*, 1974, **107**, 3680.
882. M. F. Lemanski and E. P. Schram, *Inorg. Chem.*, 1976, **15**, 1489.

883. C. Eaborn, D. J. Tune and D. R. M. Walton, *J. Chem. Soc., Dalton Trans.*, 1973, 2255.
884. A. F. Clemmitt and F. Glockling, *J. Chem. Soc.* (*A*), 1971, 1164.
885. R. J. Cross and F. Glockling, *J. Chem. Soc.*, 1965, 5422.
886. F. Glockling and K. A. Hooton, *J. Chem. Soc.* (*A*), 1967, 1066.
887. G. Deganello, G. Carturan and P. Uguagliati, *J. Organomet. Chem.*, 1969, **17**, 179.
888. M. C. Baird, *J. Inorg. Nucl. Chem.*, 1967, **29**, 367.
889. A. J. Layton, R. S. Nyholm, G. A. Pneumaticakis and M. L. Tobe, *Chem. Ind.* (*London*), 1967, 465.
890. M. Akhtar and H. C. Clark, *J. Organomet. Chem.*, 1970, **22**, 233.
891. F. Glockling and R. J. I. Pollock, *J. Chem. Soc., Dalton Trans.*, 1975, 497.
892. C. Eaborn, A. Pidcock and B. R. Steele, *J. Chem. Soc., Dalton Trans.*, 1976, 767.
893. C. Eaborn, K. Kundu and A. Pidcock, *J. Chem. Soc., Dalton Trans.*, 1981, 1223.
894. S. Carr, R. Colton and D. Dakternieks, *J. Organomet. Chem.*, 1982, **240**, 143.
895. D. R. Coulson and L. P. Seiwell, *Inorg. Chem.*, 1976, **15**, 2563.
896. J. Kuyper, *Inorg. Chem.*, 1978, **17**, 77.
897. J. Kuyper, *Inorg. Chem.*, 1977, **16**, 2171.
898. Y. K. Grishin, V. A. Roznyatovsky, Y. A. Ustynyuk, S. N. Titova, G. A. Domrachev and G. A. Razuvaev, *Polyhedron*, 1983, **2**, 895.
899. J. K. Wittle and G. Urry, *Inorg. Chem.*, 1968, **7**, 560.
900. R. D. Cramer, E. L. Jenner, R. V. Lindsey and V. G. Stolberg, *J. Am. Chem. Soc.*, 1963, **85**, 1691.
901. R. D. Cramer, R. V. Lindsey, C. T. Prewitt and V. G. Stolberg, *J. Am. Chem. Soc.*, 1965, **87**, 658.
902. R. V. Lindsey, G. W. Parshall and V. G. Stolberg, *Inorg. Chem.*, 1966, **5**, 109.
903. J. H. Nelson and N. W. Alcock, *Inorg. Chem.*, 1982, **21**, 1196.
904. E. D. Estes and D. J. Hodgson, *Inorg. Chem.*, 1973, **12**, 2932.
905. A. Albinati, R. Naegeli, K. H. A. Ostoja Starzewski, P. S. Pregosin and H. Ruegger, *Inorg. Chim. Acta*, 1983, **76**, L231.
906. R. V. Parish and P. J. Rowbotham, *J. Chem. Soc., Dalton Trans.*, 1973, 37.
907. P. G. Antonov, Y. N. Kukushkin, V. G. Shtrele, Y. P. Kostikov and F. K. Egorov, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1982, **27**, 1770.
908. A. Vassilian and J. C. Bailar, Jr., *J. Catal.*, 1980, **62**, 389.
909. G. K. Anderson, C. Billard, H. C. Clark, J. A. Davies and C. S. Wong, *Inorg. Chem.*, 1983, **22**, 439.
910. C. H. Cheng and R. Eisenberg, *J. Am. Chem. Soc.*, 1978, **100**, 5968.
911. L. J. Guggenberger, *J. Chem. Soc., Chem. Commun.*, 1968, 512.
912. G. W. Bushnell, D. T. Eadie, A. Pidcock, A. R. Sam, R. D. Holmes-Smith and S. R. Stobart, *J. Am. Chem. Soc.*, 1982, **104**, 5837.
913. F. Teixidor, M. L. Luetkens and R. W. Rudolph, *J. Am. Chem. Soc.*, 1983, **105**, 149.
914. F. G. A. Stone, *Inorg. Chim. Acta*, 1981, **50**, 33.
915. Y. Yamamoto, H. Yamazaki and T. Sakurai, *J. Am. Chem. Soc.*, 1982, **104**, 2329.
916. D. M. P. Mingos and D. G. Evans, *J. Organomet. Chem.*, 1983, **251**, C13.
917. W. Klotzbucher and G. A. Ozin, *J. Am. Chem. Soc.*, 1975, **97**, 2672.
918. G. A. Ozin and W. E. Klotzbucher, *J. Am. Chem. Soc.*, 1975, **97**, 3965.
919. M. Peyrone, *Ann. Chem. Pharm.*, 1845, **51**, 15.
920. J. Reiset, *C.R. Hebd. Seances Acad. Sci.*, 1844, **18**, 1103.
921. R. N. Keller, *Inorg. Synth.*, 1946, **2**, 250.
922. G. B. Kauffman, *Inorg. Synth.*, 1963, **7**, 249.
923. A. E. Schweizer and G. T. Kerr, *Inorg. Chem.*, 1978, **17**, 2152.
924. J. D. Woollins, A. Woollins and B. Rosenberg, *Polyhedron*, 1983, **2**, 175.
925. E. G. Cox, F. W. Pinkard, G. H. Preston and W. Wardlaw, *J. Chem. Soc.*, 1932, 1895.
926. J. Chatt and F. G. Mann, *J. Chem. Soc.*, 1939, 1622.
927. J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 1957, 2445.
928. B. Rosenberg, L. VanCamp, J. E. Troska and V. M. Mansour, *Nature* (*London*), 1969, **222**, 385.
929. M. J. Cleare, *Coord. Chem. Rev.*, 1974, **12**, 349.
930. G. W. Watt and J. E. Cuddeback, *Inorg. Chem.*, 1971, **10**, 947.
931. C. K. Jørgensen, 'Absorption Spectra and Chemical Bonding in Complexes', Pergamon, Oxford, 1962.
932. A. V. Babaeva and R. I. Rudy, *J. Inorg. Chem.* (*USSR*), 1956, **1** (5), 42.
933. J. Chatt, G. A. Gamlen and L. E. Orgel, *J. Chem. Soc.*, 1958, 486.
934. D. S. Martin, L. D. Hunter, R. Kroening and R. F. Coley, *J. Am. Chem. Soc.*, 1971, **93**, 5433.
935. D. S. Martin, *Inorg. Chim. Acta Rev.*, 1971, **5**, 107.
936. H. H. Patterson, J. C. Tewksbury, M. Martin, M.-B. Krogh-Jesperson, J. A. LoMenzo, H. O. Hooper and A. K. Viswanath, *Inorg. Chem.*, 1981, **20**, 2297.
937. B. G. Anex and W. P. Peltier, *Inorg. Chem.*, 1983, **22**, 643.
938. B. Bosnich, *J. Chem. Soc.* (*A*), 1969, 1394.
939. E. A. Sullivan, *Can. J. Chem.*, 1979, **57**, 67.
940. C. J. Hawkins and J. Martin, *Inorg. Chem.*, 1982, **21**, 1074.
941. K. Nakamoto, P. J. McCarthy, J. Fujita, R. A. Condrate and G. T. Behnke, *Inorg. Chem.*, 1965, **4**, 36.
942. J. Chatt and G. A. Gamlen, *J. Chem. Soc.*, 1956, 2371.
943. B. Lippert, C. J. L. Lock, B. Rosenberg and M. Zvagulis, *Inorg. Chem.*, 1977, **16**, 1525.
944. B. K. Teo, P. Eisenberger, J. Reed, J. K. Barton and S. J. Lippard, *J. Am. Chem. Soc.*, 1978, **100**, 3225.
945. Y. T. Fanchiang, G. T. Bratt and H. P. C. Hogenkamp, *J. Chem. Soc., Dalton Trans.*, 1983, 1929.
946. C. M. Riley, L. A. Sternson, A. J. Repta and S. A. Slyter, *Polyhedron*, 1982, **1**, 201.
947. A. Vogler and A. Kern, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 625.
948. C. A. Bignozzi, C. Bartocci, C. Chiorboli and V. Carassiti, *Inorg. Chim. Acta*, 1983, **70**, 87.
949. W. L. Waltz, J. Lilie, R. T. Walters and R. J. Woods, *Inorg. Chem.*, 1980, **19**, 3284.
950. H. M. Khan, W. L. Waltz, R. J. Woods and J. Lilie, *Can. J. Chem.*, 1981, **59**, 3319.

951. H. M. Khan, W. L. Waltz and R. J. Woods, *Inorg. Chem.*, 1982, **21**, 1489.
952. I. Mochida, J. A. Mattern and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, 1975, **97**, 3021.
953. I. Mochida and J. C. Bailar, *Inorg. Chem.*, 1983, **22**, 1834.
954. H. E. Howard-Lock, C. J. L. Lock, G. Turner and M. Zvagulis, *Can. J. Chem.*, 1981, **59**, 2737.
955. C. J. L. Lock and M. Zvagulis, *Inorg. Chem.*, 1981, **20**, 1817.
956. C. P. Hicks and M. Spiro, *J. Chem. Soc., Chem. Commun.*, 1981, 131.
957. V. A. Palkin, T. A. Kuzina, N. N. Kuz'mina and R. N. Shchelokov, *Russ. J. Inorg. Chem.*, 1980, **25**, 573.
958. W. A. Freeman, *Inorg. Chem.*, 1976, **15**, 2235.
959. C. J. Hawkins and J. A. Palmer, *Coord. Chem. Rev.*, 1982, **44**, 1.
960. M. Akbar Ali and S. E. Livingstone, *Coord. Chem. Rev.*, 1974, **13**, 101.
961. R. Melanson, J. Hubert and F. D. Rochon, *Can. J. Chem.*, 1975, **53**, 1139.
962. F. Basolo, H. B. Gray and R. G. Pearson, *J. Am. Chem. Soc.*, 1960, **82**, 4200.
963. R. C. E. Durley, W. L. Waltz and B. E. Robertson, *Can. J. Chem.*, 1980, **58**, 664.
964. S. Yano, H. Ito, Y. Koike, J. Fujita and K. Saito, *J. Chem. Soc., Chem. Commun.*, 1969, 460.
965. T. G. Appleton and J. R. Hall, *Inorg. Chem.*, 1970, **9**, 1807.
966. B. Bosnich and E. A. Sullivan, *Inorg. Chem.*, 1975, **14**, 2768.
967. Y. Nakayama, S. Ooi and H. Kuroya, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 914.
968. L. E. Erickson, J. E. Sarneski and C. N. Reilley, *Inorg. Chem.*, 1975, **14**, 3007.
969. L. E. Erickson, J. E. Sarneski and C. N. Reilley, *Inorg. Chem.*, 1978, **17**, 1701.
970. L. E. Erickson, J. E. Sarneski and C. N. Reilley, *Inorg. Chem.*, 1978, **17**, 1711.
971. J. E. Sarneski, L. E. Erickson and C. N. Reilley, *Inorg. Chem.*, 1981, **20**, 2137.
972. C. G. vanKralingen, J. Reedijk and A. L. Spek, *Inorg. Chem.*, 1980, **19**, 1481.
973. R. G. Ball, N. J. Bowman and N. C. Payne, *Inorg. Chem.*, 1976, **15**, 1704.
974. F. Basolo and R. C. Johnson, 'Coordination Chemistry', Benjamin, New York, 1964.
975. C. H. Langford and H. B. Gray, 'Ligand Substitution Processes', Benjamin, New York, 1965.
976. A. E. Martell, *ACS Monogr. Ser.*, 1971, **168**; 1978, **174**.
977. R. G. Wilkins, 'The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes', Allyn and Bacon, Boston, 1974.
978. A. Peloso, *Coord. Chem. Rev.*, 1973, **10**, 123.
979. R. J. Mureinik, *J. Chem. Soc., Dalton Trans.*, 1976, 1036.
980. S. P. Tanner, F. Basolo and R. G. Pearson, *Inorg. Chem.*, 1967, **6**, 1089.
981. M. J. Carter and J. K. Beattie, *Inorg. Chem.*, 1970, **9**, 1233.
982. G. Natile, G. Albertin, E. Bordignon and A. A. Orio, *J. Chem. Soc., Dalton Trans.*, 1976, 626.
983. R. Romeo, S. Lanza and M. L. Tobe, *Inorg. Chem.*, 1977, **16**, 785.
984. R. Romeo, S. Lanza, D. Minniti and M. L. Tobe, *Inorg. Chem.*, 1978, **17**, 2436.
985. A. P. Schwab, M. L. Tobe and R. Romeo, *Inorg. Chim. Acta*, 1981, **58**, 161.
986. M. L. Tobe, A. P. Schwab and R. Romeo, *Inorg. Chem.*, 1982, **21**, 1185.
987. G. Annibale, L. Maresca, L. Cattalini and G. Natile, *J. Chem. Soc., Dalton Trans.*, 1982, 1.
988. K. Wieghardt, M. Koppen, W. Swiridoff and J. Weiss, *J. Chem. Soc., Dalton Trans.*, 1983, 1869.
989. R. Romeo and M. L. Tobe, *Inorg. Chem.*, 1974, **13**, 1991.
990. A. V. Babaeva and M. A. Mosyagina, *Dokl. Akad. Nauk SSSR*, 1953, **89**, 293 (*Chem. Abstr.*, 1953, **47**, 10 392).
991. R. H. Holm, G. W. Everett and A. Chakravorty, *Prog. Inorg. Chem.*, 1966, **7**, 83.
992. M. Riederer, E. Urban and W. Sawodny, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 860.
993. W. G. Rohly and K. B. Mertes, *J. Am. Chem. Soc.*, 1980, **102**, 7939.
994. A. A. Grinberg and L. H. Volshtein, *Dokl. Akad. Nauk SSSR*, 1935, **2**, 485 (*Chem. Abstr.*, 1935, **29**, 6860).
995. L. E. Erickson, J. W. McDonald, J. K. Howie and R. P. Clow, *J. Am. Chem. Soc.*, 1968, **90**, 6371.
996. F. W. Pinkard, E. Sharralt, W. Wardlaw and E. G. Cox, *J. Chem. Soc.*, 1934, 1012.
997. L. M. Volshtein and G. G. Motyagina, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1960, **5**, 840.
998. J. S. Coe and J. R. Lyons, *J. Chem. Soc. (A)*, 1971, 829.
999. V. Balzani, V. Carassiti, L. Moggi and F. Scandola, *Inorg. Chem.*, 1965, **4**, 1243.
1000. A. J. Saraceno, I. Nakagawa, S. Mizushima, C. Curran and J. V. Quagliano, *J. Am. Chem. Soc.*, 1958, **80**, 5018.
1001. L. M. Volshtein, M. F. Mogilevkina and G. G. Motyagina, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1961, **6**, 564.
1002. K. Nakamoto, Y. Morimoto and A. E. Martell, *J. Am. Chem. Soc.*, 1961, **83**, 4528.
1003. R. A. Condrate and K. Nakamoto, *J. Chem. Phys.*, 1965, **42**, 2590.
1004. J. A. Kieft and K. Nakamoto, *J. Inorg. Nucl. Chem.*, 1967, **29**, 2561.
1005. B. Purucker and W. Beck, *Chem. Ber.*, 1974, **107**, 3476.
1006. W. Beck and M. Girnth, *Chem. Ber.*, 1976, **109**, 965.
1007. O. P. Slyudkin, M. A. Kerzhentsev and L. M. Volshtein, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1981, **26**, 535.
1008. E. A. Sullivan, *Can. J. Chem.*, 1979, **57**, 62.
1009. W. Beck, H. Bissinger, M. Girnth-Weller, B. Purucker, G. Thiel, H. Zippel, H. Seidenberger, B. Wappes and H. Schonenberger, *Chem. Ber.*, 1982, **115**, 2256.
1010. V. I. Kazbanov, A. K. Starkov, T. K. Kazbanova and G. D. Mal'chikov, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1982, **27**, 840.
1011. D. P. Arnold and M. A. Bennett, *J. Organomet. Chem.*, 1980, **202**, 107.
1012. J. P. Catinat, T. Robert and G. Offergeld, *J. Chem. Soc., Chem. Commun.*, 1983, 1310.
1013. M. Atoji, J. W. Richardson and R. E. Rundlle, *J. Am. Chem. Soc.*, 1957, **79**, 3017.
1014. J. R. Miller, *Proc. Chem. Soc.*, 1960, 318.
1015. P. E. Fanwick and J. L. Huckaby, *Inorg. Chem.*, 1982, **21**, 3067.
1016. H. Wolfram, Dissertation, Konigsberg, 1900.
1017. J. R. Hall and D. A. Hirons, *Inorg. Chim. Acta*, 1979, **34**, L277.
1018. R. N. Keller, *Inorg. Synth.*, 1946, **2**, 250.
1019. J. R. Campbell, R. J. H. Clark and P. C. Turtle, *Inorg. Chem.*, 1978, **17**, 3622.

1020. R. J. H. Clark and M. Kurmoo, *Inorg. Chem.*, 1980, **19**, 3522.
1021. A. J. Jircitano, M. D. Timken, K. B. Mertes and J. R. Ferraro, *J. Am. Chem. Soc.*, 1979, **101**, 7661.
1022. A. J. Jircitano, M. C. Colton and K. B. Mertes, *Inorg. Chem.*, 1981, **20**, 890.
1023. D. C. Giedt and C. J. Nyman, *Inorg. Synth.*, 1966, **8**, 239.
1024. H. A. Boucher, G. A. Lawrance, P. A. Lay, A. M. Sargeson, A. M. Bond, D. F. Sangster and J. C. Sullivan, *J. Am. Chem. Soc.*, 1983, **105**, 4652.
1025. A. Peloso, *J. Chem. Soc., Dalton Trans.*, 1979, 1160.
1026. C. S. Glennon, T. D. Hand and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1980, 19.
1027. N. V. Sidgwick, 'Chemical Elements and their Compounds', Oxford University Press, 1950.
1028. C. F. Liu and M. K. Yoo, *Inorg. Chem.*, 1976, **15**, 2415.
1029. T. N. Fedotova and O. N. Adrianova, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1970, **15**, 1272.
1030. O. N. Adrianova and T. N. Fedotova, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1980, **25**, 105.
1031. J. E. Sarneski, A. T. McPhail, K. D. Onan, L. E. Erickson and C. N. Reilley, *J. Am. Chem. Soc.*, 1977, **99**, 7376.
1032. I. P. Evans, G. W. Everett and A. M. Sargeson, *J. Am. Chem. Soc.*, 1976, **98**, 8041.
1033. M. Kretschmer and L. Heck, *Z. Anorg. Allg. Chem.*, 1982, **490**, 205.
1034. M. Kretschmer and L. Heck, *Z. Anorg. Allg. Chem.*, 1982, **490**, 215.
1035. M. Zipprich, H. Pritzkow and J. Jander, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 225.
1036. K. K. Sen Gupta, P. K. Sen and S. S. Gupta, *Inorg. Chem.*, 1977, **16**, 1396.
1037. G. B. Kauffman, *Inorg. Synth.*, 1963, **7**, 236.
1038. G. B. Kauffman and D. O. Cowan, *Inorg. Synth.*, 1963, **7**, 239.
1039. G. B. Kauffman, *Inorg. Synth.*, 1963, **7**, 249.
1040. P. C. Kong and F. D. Rochon, *Can. J. Chem.*, 1978, **56**, 441.
1041. G. Thiele and D. Wagner, *Chem. Ber.*, 1978, **111**, 3162.
1042. P. C. Kong, D. Iyamuremye and F. D. Rochon, *Can. J. Chem.*, 1976, **54**, 3224.
1043. L. Canovese, L. Cattalini, G. Marangoni, G. Michelon and M. L. Tobe, *Inorg. Chem.*, 1981, **20**, 4166.
1044. S. Okeya, Y. Nakamura, S. Kawaguchi and T. Hinomoto, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 477.
1045. M. Kotowski, D. A. Palmer and H. Kelm, *Inorg. Chem.*, 1979, **18**, 2555.
1046. M. Martin, M.-B. Krogh-Jesperson, M. Hsu, J. Tewksbury, M. Laurent, K. Viswanath and H. Patterson, *Inorg. Chem.*, 1983, **22**, 647.
1047. E. Forsellini, G. Bombieri, B. Crociani and T. Boschi, *J. Chem. Soc., Chem. Commun.*, 1970, 1203.
1048. R. Melanson and F. D. Rochon, *Can. J. Chem.*, 1976, **54**, 1002.
1049. F. D. Rochon, P. C. Kong and R. Melanson, *Can. J. Chem.*, 1980, **58**, 97.
1050. M. J. Blandamer, J. Burgess and S. J. Hamshere, *J. Chem. Soc., Dalton Trans.*, 1979, 1539.
1051. M. J. Blandamer and J. Burgess, *Coord. Chem. Rev.*, 1980, **31**, 93.
1052. T. J. Giordano, W. M. Butler and P. G. Rasmussen, *Inorg. Chem.*, 1978, **17**, 1917.
1053. D. W. Phelps, W. F. Little and D. J. Hodgson, *Inorg. Chem.*, 1976, **15**, 2263.
1054. J. E. Lydon and M. R. Truter, *J. Chem. Soc.*, 1965, 6899.
1055. G. Calvin and G. E. Coates, *J. Chem. Soc.*, 1960, 2008.
1056. F. A. Palocsay and J. V. Rund, *Inorg. Chem.*, 1969, **8**, 524.
1057. J. V. Rund and F. A. Palocsay, *Inorg. Chem.*, 1969, **8**, 2242.
1058. J. V. Rund, *Inorg. Chem.*, 1970, **9**, 1211.
1059. J. V. Rund, *Inorg. Chem.*, 1974, **13**, 738.
1060. G. W. Bushnell, K. R. Dixon and M. A. Khan, *Can. J. Chem.*, 1974, **52**, 1367.
1061. K. R. Dixon, *Inorg. Chem.*, 1977, **16**, 2618.
1062. G. W. Bushnell, K. R. Dixon and M. A. Khan, *Can. J. Chem.*, 1978, **56**, 450.
1063. E. Bielli, R. D. Gillard and D. W. James, *J. Chem. Soc., Dalton Trans.*, 1976, 1837.
1064. O. Farver, O. Monsted and G. Nord, *J. Am. Chem. Soc.*, 1979, **101**, 6118.
1065. S. Dholakia, R. D. Gillard and F. L. Wimmer, *Inorg. Chim. Acta*, 1983, **69**, 179.
1066. A. Peloso, *J. Chem. Soc., Dalton Trans.*, 1976, 984.
1067. M. Cusumano, G. Guglielmo and V. Ricevuto, *J. Chem. Soc., Dalton Trans.*, 1981, 1722.
1068. Y. Y. H. Chao, A. Holtzer and S. H. Mastin, *J. Am. Chem. Soc.*, 1977, **99**, 8024.
1069. R. S. Drago, E. D. Nyberg and A. G. El A'mma, *Inorg. Chem.*, 1981, **20**, 2461.
1070. M. Howe-Grant and S. J. Lippard, *Inorg. Synth.*, 1980, **20**, 101.
1071. R. J. Mureinik and M. Bidani, *Inorg. Chim. Acta*, 1978, **29**, 37.
1072. G. Minghetti, G. Banditelli and F. Bonati, *Chem. Ind. (London)*, 1977, 123.
1073. G. Bonati and H. C. Clark, *Can. J. Chem.*, 1978, **56**, 2513.
1074. G. Minghetti, G. Banditelli and F. Bonati, *J. Chem. Soc., Dalton Trans.*, 1979, 1851.
1075. A. L. Bandini, G. Banditelli, G. Minghetti and F. Bonati, *Can. J. Chem.*, 1979, **57**, 3237.
1076. F. Bonati, H. C. Clark and C. S. Wong, *Can. J. Chem.*, 1980, **58**, 1435.
1077. W. C. Deese, D. A. Johnson and A. W. Cordes, *Inorg. Chem.*, 1981, **20**, 1519.
1078. G. Banditelli, A. L. Bandini, F. Bonati and G. Minghetti, *Inorg. Chim. Acta*, 1982, **60**, 93.
1079. S. R. Stobart, K. R. Dixon, D. T. Eadie, J. L. Atwood and M. D. Zaworotko, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 931.
1080. J. L. Atwood, K. R. Dixon, D. T. Eadie, S. R. Stobart and M. J. Zaworotko, *Inorg. Chem.*, 1983, **22**, 774.
1081. G. W. Bushnell, K. R. Dixon, D. T. Eadie and S. R. Stobart, *Inorg. Chem.*, 1981, **20**, 1545.
1082. J. D. Oliver and N. C. Rice, *Inorg. Chem.*, 1976, **15**, 2741.
1083. S. Trofimenko, *Acc. Chem. Res.*, 1971, **4**, 17.
1084. K. D. Gallicano and N. L. Paddock, *Can. J. Chem.*, 1982, **60**, 521.
1085. H. C. Clark, G. Ferguson, V. K. Jain and M. Parvez, *Organometallics*, 1983, **2**, 806.
1086. G. W. Bushnell and K. R. Dixon, *Can. J. Chem.*, 1978, **56**, 878.
1087. P. C. Kong and F. D. Rochon, *Can. J. Chem.*, 1979, **57**, 526.
1088. F. D. Rochon, P. C. Kong and R. Melanson, *Can. J. Chem.*, 1981, **59**, 195.

1089. P. M. Kiernan and A. Ludi, *J. Chem. Soc., Dalton Trans.*, 1978, 1127.
1090. S. Lanza, *Inorg. Chim. Acta*, 1983, **75**, 131.
1091. G. Annibale, L. Canovese, L. Cattalini, G. Natile, M. Biagini-Cingi, A. M. Manotti-Lanfredi and A. Tiripicchio, *J. Chem. Soc., Dalton Trans.*, 1981, 2280.
1092. S. C. Dhara, *Indian J. Chem.*, 1970, **8**, 193.
1093. B. J. Graves, D. J. Hodgson, C. G. Van Kralingen and J. Reedijk, *Inorg. Chem.*, 1978, **17**, 3007.
1094. C. G. Van Kralingen and J. Reedijk, *Inorg. Chim. Acta*, 1978, **30**, 171.
1095. M. B. Cingi, A. M. Manotti-Lanfredi, A. Tiripicchio, C. G. Van Kralingen and J. Reedijk, *Inorg. Chim. Acta*, 1980, **39**, 265.
1096. C. G. Van Kralingen, J. K. DeRidder and J. R. Reedijk, *Inorg. Chim. Acta*, 1979, **36**, 69.
1097. Y. N. Kukushkin, G. Kh. Khamnuev, V. N. Demidov and N. P. Kiseleva, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1981, **26**, 1533.
1098. J. C. Chottard, E. Mulliez and D. Mansuy, *J. Am. Chem. Soc.*, 1977, **99**, 3531.
1099. P. G. Rasmussen, R. L. Hough, J. E. Anderson, O. H. Bailey and J. C. Bayon, *J. Am. Chem. Soc.*, 1982, **104**, 6155.
1100. R. Uson, J. Gimeno, L. A. Oro, M. A. Aznar and J. A. Cabeza, *Polyhedron*, 1983, **2**, 163.
1101. J. D. Orbell, C. Solorzano, L. G. Marzilli and T. J. Kistenmacher, *Inorg. Chem.*, 1982, **21**, 3806.
1102. A. Terzis and D. Mentzafos, *Inorg. Chem.*, 1983, **22**, 1140.
1103. N. Hadjiliadis and J. Markopoulos, *J. Chem. Soc., Dalton Trans.*, 1981, 1635.
1104. J. D. Orbell, K. Wilkowski, L. G. Marzilli and T. J. Kistenmacher, *Inorg. Chem.*, 1982, **21**, 3478.
1105. A. T. M. Marcelis, H. J. Korte, B. Krebs and J. Reedijk, *Inorg. Chem.*, 1982, **21**, 4059.
1106. P. A. Barratt, C. E. Dent and R. P. Linstead, *J. Chem. Soc.*, 1936, 1719.
1107. C. J. Brown, *J. Chem. Soc. (A)*, 1968, 2494.
1108. J. L. Peterson, C. S. Schramm, D. R. Stojakovic, B. M. Hoffman and T. J. Marks, *J. Am. Chem. Soc.*, 1977, **99**, 286.
1109. T. H. Huang, K. E. Rieckhoff and E. M. Voigt, *Can. J. Chem.*, 1978, **56**, 976.
1110. J. A. Mercer-Smith and D. G. Whitten, *J. Am. Chem. Soc.*, 1978, **100**, 2620.
1111. G. Ponterini, N. Serpone, M. A. Bergkamp and T. L. Netzel, *J. Am. Chem. Soc.*, 1983, **105**, 4639.
1112. T. J. Aartsma, M. Gouterman, C. Jochum, A. L. Kwiram, B. V. Pepich and L. D. Williams, *J. Am. Chem. Soc.*, 1982, **104**, 6278.
1113. K. A. Hofmann and G. Bugge, *Ber.*, 1908, **41**, 312.
1114. R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 1964, 2835.
1115. D. B. Brown, R. D. Burbank and M. B. Robin, *J. Am. Chem. Soc.*, 1969, **91**, 2895.
1116. J. K. Barton, H. N. Rabinowitz, D. J. Szalda and S. J. Lippard, *J. Am. Chem. Soc.*, 1977, **99**, 2827.
1117. J. K. Barton, S. A. Best, S. J. Lippard and R. A. Walton, *J. Am. Chem. Soc.*, 1978, **100**, 3785.
1118. J. K. Barton, D. J. Szalda, H. N. Rabinowitz, J. V. Waszczak and S. J. Lippard, *J. Am. Chem. Soc.*, 1979, **101**, 1434.
1119. J. K. Barton, C. Caravana and S. J. Lippard, *J. Am. Chem. Soc.*, 1979, **101**, 7269.
1120. L. S. Hollis and S. J. Lippard, *J. Am. Chem. Soc.*, 1981, **103**, 1230.
1121. T. V. O'Halloran and S. J. Lippard, *J. Am. Chem. Soc.*, 1983, **105**, 3341.
1122. M. P. Laurent, J. C. Tewksbury, M.-B. Krogh-Jespersen and H. Patterson, *Inorg. Chem.*, 1980, **19**, 1656.
1123. M. P. Laurent, J. Briscoe and H. H. Patterson, *J. Am. Chem. Soc.*, 1980, **102**, 6575.
1124. B. K. Teo, K. Kijima and R. Bau, *J. Am. Chem. Soc.*, 1978, **100**, 621.
1125. K. Matsumoto and K. Fuwa, *J. Am. Chem. Soc.*, 1982, **104**, 897.
1126. J. P. Laurent, P. Lepage and F. Dahan, *J. Am. Chem. Soc.*, 1982, **104**, 7335.
1127. R. Faggiani, C. J. L. Lock, R. J. Pollock, B. Rosenberg and G. Turner, *Inorg. Chem.*, 1981, **20**, 804.
1128. B. Lippert, D. Neugebauer and U. Schubert, *Inorg. Chim. Acta*, 1980, **46**, L11.
1129. C. J. L. Lock, H. J. Peresie, B. Rosenberg and G. Turner, *J. Am. Chem. Soc.*, 1978, **100**, 3371.
1130. L. S. Hollis and S. J. Lippard, *J. Am. Chem. Soc.*, 1983, **105**, 3494.
1131. L. S. Hollis and S. J. Lippard, *Inorg. Chem.*, 1983, **22**, 2600.
1132. J. D. Woollins and B. Rosenberg, *Inorg. Chem.*, 1982, **21**, 1280.
1133. L. S. Hollis and S. J. Lippard, *J. Am. Chem. Soc.*, 1981, **103**, 6761.
1134. L. S. Hollis and S. J. Lippard, *Inorg. Chem.*, 1982, **21**, 2116.
1135. L. S. Hollis and S. J. Lippard, *Inorg. Chem.*, 1983, **22**, 2605.
1136. L. S. Hollis, M. M. Roberts and S. J. Lippard, *Inorg. Chem.*, 1983, **22**, 3637.
1137. L. S. Hollis and S. J. Lippard, *Inorg. Chem.*, 1983, **22**, 2708.
1138. K. Matsumoto, H. Takahashi and K. Fuwa, *Inorg. Chem.*, 1983, **22**, 4086.
1139. C. A. Chang, R. B. Marcotte and H. H. Patterson, *Inorg. Chem.*, 1981, **20**, 1632.
1140. B. Lippert, *J. Clin. Hematol. Oncol.*, 1977, **7**, 26.
1141. V. I. Nefedov, Ya. V. Salyn, I. B. Baranovskii and A. G. Maiorova, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1980, **25**, 116.
1142. S. J. S. Kerrison and P. J. Sadler, *J. Chem. Soc., Chem. Commun.*, 1981, 61.
1143. A. A. Grinberg, Kh. I. Gil'dengershel' and V. F. Budanova, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1966, **11**, 1351.
1144. R. D. Gillard and R. J. Wademan, *J. Chem. Soc., Chem. Commun.*, 1981, 448.
1145. R. D. Gillard and R. J. Wademan, *J. Chem. Soc., Dalton Trans.*, 1981, 2599.
1146. O. Monsted and G. Nord, *J. Chem. Soc., Dalton Trans.*, 1981, 2599.
1147. S. G. Hedin, *Acta Univ. Lund.*, Sect. 2, 1886, **22**, 1.
1148. 'Gmelins Handbuch der Anorganischen Chemie', Verlag Chemie, Weinheim, 1957, vol. 68, p. 510.
1149. K. A. Hofmann and G. Bugge, *Chem. Ber.*, 1970, **40**, 1772.
1150. K. A. Jensen, *Z. Anorg. Allg. Chem.* 1937, **231**, 365.
1151. R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 1964, 2835.
1152. T. Uchiyama, Y. Toshiyasu, Y. Nakamura, T. Miwa and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 181.
1153. G. Beech, G. Marr and S. J. Ashcroft, *J. Chem. Soc. (A)*, 1970, 2903.

1154. A. K. Johnson and J. D. Miller, *Inorg. Chim. Acta*, 1977, **22**, 219.
1155. H. C. Clark and L. E. Manzer, *Chem. Commun.*, 1971, 387.
1156. A. D. Gelman and Z. P. Maximova, *Dokl. Akad. Nauk SSSR*, 1939, **24**, 748 (*Chem. Abstr.*, 1940, **34**, 1930).
1157. W. P. Griffith, J. Lewis and G. Wilkinson, *J. Chem. Soc.*, 1961, 775.
1158. E. A. Hadow, *J. Chem. Soc.*, 1866, **19**, 345.
1159. S. Bhaduri, B. F. G. Johnson, A. Khair, I. Ghatak and D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.*, 1980, 1572.
1160. S. A. Bhaduri, I. Bratt, B. F. G. Johnson, A. Khair, J. A. Segal, R. Walters and C. Zuccaro, *J. Chem. Soc., Dalton Trans.*, 1981, 234.
1161. R. J. Puddephatt and P. J. Thompson, *J. Chem. Soc., Dalton Trans.*, 1976, 2091.
1162. A. R. Middleton, G. Wilkinson, M. B. Hursthouse and N. P. Walker, *J. Chem. Soc., Dalton Trans.*, 1982, 663.
1163. J. J. Levison and S. D. Robinson, *J. Chem. Soc. (A)*, 1971, 762.
1164. J. A. Kaduk and J. A. Ibers, *Inorg. Chem.*, 1977, **16**, 3278.
1165. S. J. S. Kerrison and P. J. Sadler, *J. Chem. Soc., Dalton Trans.*, 1982, 2363.
1166. W. A. Freeman, *J. Am. Chem. Soc.*, 1983, **105**, 2725.
1167. S. Otsuka, Y. Aotani, Y. Tatsuno and T. Yoshida, *Inorg. Chem.*, 1976, **15**, 656.
1168. P. L. Bellon, S. Cenini, F. Demartin, M. Pizzotti and F. Porta, *J. Chem. Soc., Chem. Commun.*, 1982, 265.
1169. W. Beck, W. P. Fehlhammer, P. Pollman, E. Schuierer and K. Fedl, *Chem. Ber.*, 1967, **100**, 2335.
1170. H. H. Schmidtke and D. Garthoff, *J. Am. Chem. Soc.*, 1967, **89**, 1317.
1171. H. A. Bryan, N. S. Pantaleo, W. L. Dickinson and R. C. Johnson, *Inorg. Chem.*, 1975, **14**, 1336.
1172. W. Beck, W. P. Fehlhammer, P. Pollmann and H. Schachl, *Chem. Ber.*, 1969, **102**, 1976.
1173. W. Beck, M. Bauder, G. LaMonica, S. Cenini and R. Ugo, *J. Chem. Soc. (A)*, 1971, 113.
1174. P. H. Kreutzer, J. C. Weis, H. Bock, J. Erbe and W. Beck, *Chem. Ber.*, 1983, **116**, 2691.
1175. J. Erbe and W. Beck, *Chem. Ber.*, 1983, **116**, 3867.
1176. A. Volger, A. Kern and J. Huttermann, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 524.
1177. A. Vogler, R. E. Wright and H. Kunkely, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 717.
1178. G. C. Dobinson, R. Mason, G. B. Robertson, R. Ugo, F. Conti, D. Morelli, S. Cenini and F. Bonati, *Chem. Commun.*, 1967, 739.
1179. M. Keubler, R. Ugo, S. Cenini and F. Conti, *J. Chem. Soc., Dalton Trans.*, 1975, 1081.
1180. S. D. Ittel and J. A. Ibers, *Inorg. Chem.*, 1975, **14**, 636.
1181. G. W. Parshall, *Inorg. Synth.*, 1970, **12**, 26.
1182. S. Krogsrud and J. A. Ibers, *Inorg. Chem.*, 1975, **14**, 2298.
1183. K. D. Schramm and J. A. Ibers, *Inorg. Chem.*, 1980, **19**, 2441.
1184. M. F. Lappert, J. McMeeking and D. E. Palmer, *J. Chem. Soc., Dalton Trans.*, 1973, 151.
1185. B. Cetinkaya, M. L. Lappert and J. McMeeking, *J. Chem. Soc., Dalton Trans.*, 1973, 1975.
1186. K. R. Laing, S. D. Robinson and M. F. Uttley, *J. Chem. Soc., Dalton Trans.*, 1974, 1205.
1187. L. D. Brown and J. A. Ibers, *J. Am. Chem. Soc.*, 1976, **98**, 1597.
1188. L. D. Brown and J. A. Ibers, *Inorg. Chem.*, 1976, **15**, 2794.
1189. H. van der Poel, G. van Koten and K. Vrieze, *Inorg. Chem.*, 1980, **19**, 1145.
1190. J. W. Lauher and J. A. Ibers, *Inorg. Chem.*, 1975, **14**, 640.
1191. S. A. Brawner, I. J. B. Lin, J. H. Kim and G. W. Everett, *Inorg. Chem.*, 1978, **17**, 1304.
1192. F. C. Senftleber and W. E. Geiger, *Inorg. Chem.*, 1978, **17**, 3615.
1193. A. L. Balch and R. H. Holm, *J. Am. Chem. Soc.*, 1966, **88**, 5201.
1194. A. Vogler and H. Kunkely, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 221.
1195. D. E. Williams, G. Wohlaver and R. E. Rundle, *J. Am. Chem. Soc.*, 1959, **81**, 755.
1196. G. Ferraris and D. Viterbo, *Acta Crystallogr., Sect. B*, 1969, **25**, 2066.
1197. R. H. Holm and M. J. O'Connor, *Prog. Inorg. Chem.*, 1971, **14**, 277.
1198. T. W. Thomas and A. E. Underhill, *Chem. Soc. Rev.*, 1972, **1**, 99.
1199. A. Chakravorty, *Coord. Chem. Rev.*, 1974, **13**, 1.
1200. G. N. Schrauzer, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 417.
1201. J. S. Miller and A. J. Epstein, *Prog. Inorg. Chem.*, 1976, **20**, 100.
1202. M. S. Ma and R. J. Angelici, *Inorg. Chem.*, 1980, **19**, 363.
1203. J. S. Miller and S. Z. Goldberg, *Inorg. Chem.*, 1975, **14**, 2294.
1204. K. W. Nordquest, D. W. Phelps, W. F. Little and D. J. Hodgson, *J. Am. Chem. Soc.*, 1976, **98**, 1104.
1205. L. Maresca, G. Natile, L. Cattalini and F. Gasparrini, *J. Chem. Soc., Dalton Trans.*, 1976, 1090.
1206. L. Maresca, G. Natile, M. Calligaris, P. Delise and L. Randaccio, *J. Chem. Soc., Dalton Trans.*, 1976, 2386.
1207. D. Bandyopadhyay, P. Bandyopadhyay, A. Chakravorty, F. A. Cotton and L. R. Falvello, *Inorg. Chem.*, 1983, **22**, 1315.
1208. P. Bandyopadhyay, D. Bandyopadhyay, A. Chakravorty, F. A. Cotton, L. R. Falvello and S. Han, *J. Am. Chem. Soc.*, 1983, **105**, 6327.
1209. J. Geisenberger, U. Nagel, A. Sebald and W. Beck, *Chem. Ber.*, 1983, **116**, 911.
1210. P. Overbosch, G. van Koten, D. M. Grove, A. L. Spek, and A. J. M. Duisenberg, *Inorg. Chem.*, 1982, **21**, 3253.
1211. P. Overbosch, G. van Koten and K. Vrieze, *J. Chem. Soc., Dalton Trans.*, 1982, 1541.
1212. E. Cesarotti, A. Pasini and R. Ugo, *J. Chem. Soc., Dalton Trans.*, 1981, 2147.
1213. E. Ambach, U. Nagel and W. Beck, *Chem. Ber.*, 1983, **116**, 659.
1214. A. C. Cope and R. W. Siekman, *J. Am. Chem. Soc.*, 1965, **87**, 3272.
1215. R. W. Siekman and D. L. Weaver, *J. Chem. Soc., Chem. Commun.*, 1968, 1021.
1216. R. C. Elder, R. D. Cruea and R. F. Morrison, *Inorg. Chem.*, 1976, **15**, 1623.
1217. A. C. Cope and E. C. Friedrich, *J. Am. Chem. Soc.*, 1968, **90**, 909.
1218. G. E. Hartwell, R. V. Lawrence and M. J. Smas, *Chem. Commun.*, 1970, 912.
1219. T. J. Giordano and P. G. Rasmussen, *Inorg. Chem.*, 1975, **14**, 1628.
1220. H. Onoue, K. Minami and K. Nakagawa, *Bull. Chem. Soc. Jpn.*, 1970, **43**, 3480.

1221. A. G. Constable, W. S. McDonald and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1980, 2282.
1222. A. F. M. J. van der Ploeg, G. van Koten and C. Brevard, *Inorg. Chem.*, 1982, **21**, 2878.
1223. I. M. Ismail, S. J. S. Kerrison and P. J. Sadler, *Polyhedron*, 1982, **1**, 57.
1224. C. A. McAuliffe (ed.), 'Transition Metal Complexes of Phosphorus, Arsenic and Antimony Ligands', Wiley, New York, 1973.
1225. G. Booth, *Adv. Inorg. Chem. Radiochem.*, 1964, **6**, 1.
1226. L. M. Venanzi, *Chem. Br.*, 1968, **4**, 162.
1227. L. H. Pignolet (ed.), 'Homogeneous Catalysis with Metal Phosphine Complexes', Plenum, New York, 1983.
1228. R. J. Puddephatt, *Chem. Soc. Rev.*, 1983, **12**, 99.
1229. P. S. Pregosin and R. W. Kunz, '^{31}P and ^{31}C NMR of Transition Metal Phosphine Complexes', Springer-Verlag, New York, 1978.
1230. J. G. Verkade, in 'Organic Phosphorus Compounds', ed. G. M. Kosolapoff and L. Maier, Wiley, New York, 1972, vol. 2, chap. 3B.
1231. J. F. Nixon and A. Pidcock, *Annu. Rev. NMR Spectrosc.*, 1969, **2**.
1232. S. X. Xiao, W. C. Trogler, D. E. Ellis and Z. Berkovitch-Yellin, *J. Am. Chem. Soc.*, 1983, **105**, 7033.
1233. L. Malatesta and C. Cariello, *J. Chem. Soc.*, 1958, 2323.
1234. R. Ugo, *Coord. Chem. Rev.*, 1968, **3**, 319.
1235. V. Albano, P. L. Bellon and V. Scatturin, *Chem. Commun.*, 1966, 507.
1236. J. P. Birk, J. Halpern and A. L. Pickard, *J. Am. Chem. Soc.*, 1968, **90**, 4491.
1237. J. Halpern and T. A. Weil, *J. Chem. Soc., Chem. Commun.*, 1973, 631.
1238. J. P. Birk, J. Halpern and A. L. Pickard, *J. Am. Chem. Soc.*, 1968, **7**, 2672.
1239. R. Ugo, G. LaMonica, F. Cariati, S. Cenini and F. Conti, *Inorg. Chim. Acta*, 1970, **4**, 390.
1240. D. M. Blake and C. J. Nyman, *J. Am. Chem. Soc.*, 1970, **92**, 5359.
1241. A. Sen and J. Halpern, *Inorg. Chem.*, 1980, **19**, 1073.
1242. C. A. Tolman, W. C. Seidel and D. H. Gerlach, *J. Am. Chem. Soc.*, 1972, **94**, 2669.
1243. C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313.
1244. L. Malatesta, R. Ugo and S. Cenini, *Adv. Chem. Ser.*, 1966, **62**, 318.
1245. R. F. Ziolo, S. Lipton and Z. Dori, *J. Chem. Soc., Chem. Commun.*, 1970, 1124.
1246. B. Clarke, M. Green, R. B. L. Osborn and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 167.
1247. H. C. Clark and K. Itoh, *Inorg. Chem.*, 1971, **10**, 1707.
1248. T. G. Attig, M. A. A. Beg and H. C. Clark, *Inorg. Chem.*, 1975, **14**, 2986.
1249. T. Kruck and K. Baur, *Angew. Chem., Int. Ed. Engl.*, 1965, **4**, 521.
1250. J. F. Nixon and M. D. Sexton, *J. Inorg. Nucl. Chem. Lett.*, 1968, **4**, 275.
1251. R. S. Paonessa and W. C. Trogler, *Organometallics*, 1982, **1**, 768.
1252. S. Otsuka, T. Yoshida, M. Matsumoto and K. Nakatsu, *J. Am. Chem. Soc.*, 1976, **98**, 5850.
1253. R. G. Goel, W. O. Ogini and R. C. Srivastava, *J. Organomet. Chem.*, 1981, **214**, 405.
1254. A. B. Goel and S. Goel, *Inorg. Chim. Acta*, 1983, **77**, L5.
1255. A. Immirzi, A. Musco and B. E. Mann, *Inorg. Chim. Acta*, 1977, **21**, L37.
1256. S. Franks and F. R. Hartley, *Inorg. Chim. Acta*, 1980, **47**, 235.
1257. J. M. Brown and P. A. Chaloner, *J. Am. Chem. Soc.*, 1978, **100**, 4307.
1258. B. E. Mann and A. Musco, *J. Chem. Soc., Dalton Trans.*, 1980, 776.
1259. P. L. Goggin, R. J. Goodfellow, S. R. Haddock, B. F. Taylor and I. R. H. Marshall, *J. Chem. Soc., Dalton Trans.*, 1976, 459.
1260. C. Crocker and R. J. Goodfellow, *J. Chem. Soc., Dalton Trans.*, 1977, 1687.
1261. J. Chatt, R. Mason and D. W. Meek, *J. Am. Chem. Soc.*, 1975, **97**, 3826.
1262. T. Yoshida, Y. Ueda and S. Otsuka, *J. Am. Chem. Soc.*, 1978, **100**, 3941.
1263. A. Dedieu and R. Hoffmann, *J. Am. Chem. Soc.*, 1978, **100**, 2074.
1264. D. G. Evans and D. M. P. Mingos, *J. Organomet. Chem.*, 1982, **240**, 321.
1265. A. R. Al-Ohaly and J. F. Nixon, *Inorg. Chim. Acta*, 1980, **47**, 105.
1266. K. B. Dillon, T. C. Waddington and D. Younger, *J. Chem. Soc., Dalton Trans.*, 1975, 790.
1267. S. Sostero, M. Lenarda, O. Traverso, W. J. Reed and T. J. Kemp, *Inorg. Chim. Acta*, 1981, **54**, L149.
1268. C. Crocker and R. J. Goodfellow, *J. Chem. Res.* (*S*), 1979, 378.
1269. M. Meier and F. Basolo, *Inorg. Synth.*, 1972, **13**, 112.
1270. W. Bensmann and D. Fenske, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 677.
1271. J. Chatt, P. B. Hitchcock, A. Pidcock, C. P. Warrens and K. R. Dixon, *J. Chem. Soc., Chem. Commun.*, 1982, 932.
1272. T. A. van der Knaap, F. Bickelhaupt, H. van der Poel, G. van Koten and C. H. Stam, *J. Am. Chem. Soc.*, 1982, **104**, 1756.
1273. J. C. T. R. Burckett-St. Laurent, P. B. Hitchcock, H. W. Kroto and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1981, 1141.
1274. O. J. Scherer and H. Jungmann, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 953.
1275. O. J. Scherer, R. Konrad, C. Kruger and Y.-H. Tsay, *Chem. Ber.*, 1982, **115**, 414.
1276. O. J. Scherer, R. Konrad, E. Guggolz and M. L. Ziegler, *Chem. Ber.*, 1983, **116**, 2676.
1277. J. Browning, M. Green, B. R. Penfold, J. L. Spencer and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1973, 31.
1278. W. M. Riggs, *Anal. Chem.*, 1972, **44**, 830.
1279. H. A. Tayim and N. S. Aky, *J. Inorg. Nucl. Chem.*, 1974, **36**, 1071.
1280. A. D. Allen and M. C. Baird, *Chem. Ind.* (*London*), 1965, 139.
1281. T. W. Lee and R. C. Stoufer, *J. Am. Chem. Soc.*, 1975, **97**, 195.
1282. A. J. Layton, R. S. Nyholm, G. A. Pneumaticakis and M. L. Tobe, *Chem. Ind.* (*London*), 1967, 465.
1283. V. I. Sokolov and G. Z. Suleimanov, *Inorg. Chim. Acta*, 1977, **25**, L149.
1284. M. C. Baird, *Prog. Inorg. Chem.*, 1968, **9**, 1.
1285. J. P. Collman and L. S. Hegedus, 'Principles and Applications of Organotransition Metal Chemistry', University Science Books, Mill Valley, CA, 1980.

1286. J. K. Kochi, 'Organometallic Mechanisms and Catalysis', Academic, New York, 1978.
1287. J. A. Labinger, R. J. Braus, D. Dolphin and J. A. Osborn, *Chem. Commun.*, 1970, 612.
1288. F. R. Jensen and B. Knickel, *J. Am. Chem. Soc.*, 1971, **93**, 6339.
1289. R. G. Pearson and R. W. Muir, *J. Am. Chem. Soc.*, 1970, **92**, 5519.
1290. A. V. Kramer, J. A. Labinger, J. S. Bradley and J. A. Osborn, *J. Am. Chem. Soc.*, 1974, **96**, 7145.
1291. A. V. Kramer and J. A. Osborn, *J. Am. Chem. Soc.*, 1974, **96**, 7832.
1292. R. G. Pearson and J. Rajaram, *Inorg. Chem.*, 1974, **13**, 246.
1293. P. Dapporto, L. Sacconi, P. Stoppioni and F. Zanolini, *Inorg. Chem.*, 1981, **20**, 3834.
1294. K. A. Jensen, *Z. Anorg. Allg. Chem.*, 1936, **229**, 237.
1295. J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 1951, 2532.
1296. G. B. Kauffman and L. A. Teter, *Inorg. Synth.*, 1963, **7**, 245.
1297. G. N. Sedova and L. N. Demchenko, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1981, **26**, 234.
1298. G. Cavinato and L. Toniolo, *Inorg. Chim. Acta*, 1981, **52**, 39.
1299. R. G. Pearson and M. M. Muir, *J. Am. Chem. Soc.*, 1966, **88**, 2163.
1300. F. Basolo, H. B. Gray and R. G. Pearson, *J. Am. Chem. Soc.*, 1960, **82**, 4200.
1301. J. Chatt and B. T. Heaton, *J. Chem. Soc. (A)*, 1968, 2745.
1302. J. Chatt and J. M. Davidson, *J. Chem. Soc.*, 1964, 2433.
1303. R. G. Hayter and S. F. Humiec, *Inorg. Chem.*, 1963, **2**, 306.
1304. G. W. Bushnell, K. R. Dixon, R. G. Hunter and J. J. McFarland, *Can. J. Chem.*, 1972, **50**, 3694.
1305. M. M. Muir and E. M. Cancio, *Inorg. Chim. Acta*, 1970, **4**, 565.
1306. M. M. Muir and E. M. Cancio, *Inorg. Chim. Acta*, 1970, 4, 568.
1307. R. J. Cross and I. G. Phillips, *J. Chem. Soc., Dalton Trans.*, 1981, 2132.
1308. J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 1955, 2787.
1309. H. C. Clark, A. B. Goel and C. S. Wong, *J. Organomet. Chem.*, 1980, **190**, C101.
1310. J. Chatt and A. A. Williams, *J. Chem. Soc.*, 1951, 3061.
1311. F. Klanberg and E. L. Muetterties, *J. Am. Chem. Soc.*, 1968, **90**, 3296.
1312. H. D. Empsall, E. M. Hyde, E. Mentzer and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1977, 2285.
1313. A. J. Carty, N. J. Taylor and D. K. Johnson, *J. Am. Chem. Soc.*, 1979, **101**, 5422.
1314. N. J. Taylor, S. E. Jacobson and A. J. Carty, *Inorg. Chem.*, 1975, **14**, 2648.
1315. W. J. Youngs and J. A. Ibers, *J. Am. Chem. Soc.*, 1983, **105**, 639.
1316. W. J. Youngs and J. A. Ibers, *Organometallics*, 1983, **2**, 979.
1317. M. J. Church and M. J. Mays, *J. Chem. Soc. (A)*, 1968, 3074.
1318. K. R. Dixon, K. C. Moss and M. A. R. Smith, *Can. J. Chem.*, 1974, **52**, 692.
1319. Yu. L. Gaft and N. T. Kuznetsov, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1981, **26**, 699.
1320. B. Olgemoller, L. Olgemoller and W. Beck, *Chem. Ber.*, 1981, **114**, 2971.
1321. M. J. Church and M. J. Mays, *J. Inorg. Nucl. Chem.*, 1971, **33**, 253.
1322. W. Strecker and M. Schurigin, *Chem. Ber.*, 1909, **42**, 1767.
1323. P. Meakin and J. P. Jesson, *J. Am. Chem. Soc.*, 1974, **96**, 5751.
1324. J. P. Jesson, M. A. Cushing and S. D. Ittel, *Inorg. Synth.*, 1980, **20**, 78.
1325. D. A. Couch and S. D. Robinson, *Inorg. Chem.*, 1974, **13**, 456.
1326. M. Green, D. M. Grove, J. L. Spencer and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1977, 2228.
1327. J. P. Jesson and P. Meakin, *J. Am. Chem. Soc.*, 1974, **96**, 5760.
1328. J. J. MacDougall, J. H. Nelson and F. Mathey, *Inorg. Chem.*, 1982, **21**, 2145.
1329. G. G. Messmer, E. L. Amma and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 725.
1330. G. G. Messmer and E. L. Amma, *Inorg. Chem.*, 1966, **5**, 1775.
1331. P. G. Owston, J. M. Partridge and J. M. Rowe, *Acta Cryst.*, 1960, **13**, 246.
1332. H. C. Clark, P. W. R. Corfield, K. R. Dixon and J. A. Ibers, *J. Am. Chem. Soc.*, 1967, **89**, 3360.
1333. R. Favez, R. Roulet, A. A. Pinkerton and D. Schwarzenbach, *Inorg. Chem.*, 1980, **19**, 1356.
1334. P. B. Hitchcock, B. Jacobson and A. Pidcock, *J. Chem. Soc., Dalton Trans.*, 1977, 2038.
1335. A. Del Pra and G. Zanotti, *Inorg. Chim. Acta*, 1980, **39**, 137.
1336. A. N. Caldwell, L. Manojlovic-Muir and K. W. Muir, *J. Chem. Soc., Dalton Trans.*, 1977, 2265.
1337. W. Porzio, A. Musco and A. Immirzi, *Inorg. Chem.*, 1980, **19**, 2537.
1338. R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 1965, **4**, 773.
1339. F. Cariati, R. Mason, G. B. Robertson and R. Ugo, *J. Chem. Soc., Chem. Commun.*, 1967, 408.
1340. E. C. Alyea, S. A. Dias, G. Ferguson and P. J. Roberts, *J. Chem. Soc., Dalton Trans.*, 1979, 948.
1341. M. Black, R. H. B. Mais and P. G. Owston, *Acta Crystallogr., Sect. B*, 1969, **25**, 1760.
1342. L. E. Manzer and C. A. Tolman, *J. Am. Chem. Soc.*, 1975, **97**, 1955.
1343. C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313.
1344. A. Pidcock, R. E. Richards and L. M. Venanzi, *J. Chem. Soc. (A)*, 1966, 1707.
1345. R. D. Bertrand, F. B. Ogilvie and J. G. Verkade, *J. Am. Chem. Soc.*, 1970, **92**, 1908.
1346. S. O. Grim, R. L. Keiter and W. McFarlane, *Inorg. Chem.*, 1967, **6**, 1133.
1347. F. B. Ogilvie, J. M. Jenkins and J. G. Verkade, *Inorg. Chem.*, 1969, **8**, 1904.
1348. P. E. Garrou, *Chem. Rev.*, 1981, **81**, 229.
1349. D. A. Slack and M. C. Baird, *Inorg. Chim. Acta*, 1977, **24**, 277.
1350. H. C. Clark and C. R. Milne, *Can. J. Chem.*, 1979, **57**, 958.
1351. D. W. W. Anderson, E. A. V. Ebsworth and D. W. H. Rankin, *J. Chem. Soc., Dalton Trans.*, 1973, 2370.
1352. J. D. Kennedy, W. McFarlane, R. J. Puddephatt and P. J. Thompson, *J. Chem. Soc., Dalton Trans.*, 1976, 874.
1353. G. Balimann and P. S. Pregosin, *J. Magn. Reson.*, 1976, **22**, 235.
1354. A. W. Verstuyft, J. H. Nelson and L. W. Cary, *Inorg. Chem.*, 1976, **15**, 732.
1355. K. R. Dixon, M. Fakley and A. Pidcock, *Can. J. Chem.*, 1976, **54**, 2733.
1356. C. Crocker, P. L. Goggin and R. J. Goodfellow, *J. Chem. Soc., Dalton Trans.*, 1976, 2494.
1357. C. Crocker and R. J. Goodfellow, *J. Chem. Res. (S)*, 1981, 38.
1358. C. Crocker and R. J. Goodfellow, *J. Chem. Res. (S)*, 1979, 378.

1359. C. Crocker, R. J. Goodfellow, J. Gimeno and R. Uson, *J. Chem. Soc., Dalton Trans.*, 1977, 1448.
1360. C. A. Fyfe, H. C. Clark, J. A. Davies, P. J. Hayes and R. E. Wasylishen, *J. Am. Chem. Soc.*, 1983, **105**, 6577.
1361. H. C. Clark, J. A. Davies, P. J. Hayes and R. E. Wasylishen, *Organometallics*, 1983, **2**, 177.
1362. S. H. Mastin, *Inorg. Chem.*, 1974, **13**, 1003.
1363. J. Chatt, G. A. Gamlen and L. E. Orgel, *J. Chem. Soc.*, 1959, 1047.
1364. J. Kozelka and W. Ludwig, *Helv. Chim. Acta*, 1983, **66**, 902.
1365. F. Basolo, J. Chatt, H. B. Gray, R. G. Pearson and B. L. Shaw, *J. Chem. Soc.*, 1961, 2207.
1366. R. Gosling and M. L. Tobe, *Inorg. Chem.*, 1983, **22**, 1235.
1367. P. B. Hitchcock, B. Jacobson and A. Pidcock, *J. Chem. Soc., Dalton Trans.*, 1977, 2043.
1368. S. H. Mastin and P. Haake, *Chem. Commun.*, 1970, 202.
1369. D. A. Redfield and J. H. Nelson, *J. Am. Chem. Soc.*, 1974, **96**, 6219.
1370. W. J. Louw and R. van Eldik, *Inorg. Chem.*, 1981, **20**, 1939.
1371. A. R. Sanger, *J. Chem. Soc., Dalton Trans.*, 1977, 1971.
1372. T. G. Appleton, M. A. Bennett and I. B. Tomkins, *J. Chem. Soc., Dalton Trans.*, 1976, 439.
1373. R. B. King and J. C. Cloyd, *Inorg. Chem.*, 1975, **14**, 1550.
1374. R. B. King, J. C. Cloyd and R. H. Reimann, *Inorg. Chem.*, 1976, **15**, 449.
1375. M. Harada, Y. Kai, N. Yasuoka and N. Kasai, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 390.
1376. A. J. Carty, D. K. Johnson and S. E. Jacobson, *J. Am. Chem. Soc.*, 1979, **101**, 5612.
1377. W. E. Hill, B. G. Rackley and L. M. Silva-Trivino, *Inorg. Chim. Acta*, 1983, **75**, 51.
1378. B. L. Shaw, *J. Am. Chem. Soc.*, 1975, **97**, 3856.
1379. A. Pyrde, B. L. Shaw and B. Weeks, *J. Chem. Soc., Dalton Trans.*, 1976, 322.
1380. N. A. Al-Salem, H. D. Empsall, R. Markham, B. L. Shaw and B. Weeks, *J. Chem. Soc., Dalton Trans.*, 1979, 1972.
1381. C. Crocker, R. J. Errington, R. Markham, C. J. Moulton, K. J. Odell and B. L. Shaw, *J. Am. Chem. Soc.*, 1980, **102**, 4373.
1382. J. R. Briggs, A. G. Constable, W. S. McDonald and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1982, 1225.
1383. W. E. Hill, C. M. A. Minahan, J. G. Taylor, and C. A. McAuliffe, *J. Am. Chem. Soc.*, 1982, **104**, 6001.
1384. J. C. Briggs, C. A. McAuliffe, W. E. Hill, D. M. A. Minahan, J. G. Taylor and G. Dyer, *Inorg. Chem.*, 1982, **21**, 4204.
1385. U. Baltensperger, J. R. Gunter, S. Kagi, G. Kahr and W. Marty, *Organometallics*, 1983, **2**, 571.
1386. A. E. Wroblewski, S. M. Socol, A. Okruszek and J. G. Verkade, *Inorg. Chem.*, 1980, **19**, 3713.
1387. D. H. Farrar and N. C. Payne, *J. Organomet. Chem.*, 1981, **220**, 251.
1388. N. C. Payne and D. W. Stephan, *J. Organomet. Chem.*, 1981, **221**, 203.
1389. N. C. Payne and D. W. Stephan, *J. Organomet. Chem.*, 1981, **221**, 223.
1390. M. P. Brown, A. Yavari, L. Manojlovic-Muir, K. W. Muir, R. P. Moulding and K. R. Seddon, *J. Organomet. Chem.*, 1982, **236**, C33.
1391. J. M. Bassett, J. R. Mandl and H. Schmidbaur, *Chem. Ber.*, 1980, **113**, 1145.
1392. A. J. Carty, S. E. Jacobson, N. J. Taylor and P. C. Chieh, *J. Chem. Soc., Dalton Trans.*, 1976, 1375.
1393. K. D. Tau and D. W. Meek, *Inorg. Chem.*, 1979, **18**, 3574.
1394. K. D. Tau, R. Uriarte, T. J. Mazanec and D. W. Meek, *J. Am. Chem. Soc.*, 1979, **101**, 6614,
1395. M. Baacke, O. Stelzer and V. Wray, *Chem. Ber.*, 1980, **113**, 1356.
1396. M. Baacke, S. Hietkamp, S. Morton and O. Stelzer, *Chem. Ber.*, 1981, **114**, 2568.
1397. M. D. Fryzuk, P. A. MacNeil, S. J. Rettig, A. S. Secco and J. Trotter, *Organometallics*, 1982, **1**, 918.
1398. E. W. Ainscough and S. D. Robinson, *Chem. Commun.*, 1971, 130.
1399. G. W. Parshall, *Acc. Chem. Res.*, 1970, **3**, 139.
1400. A. J. Cheney, B. E. Mann, B. L. Shaw and R. M. Slade, *Chem. Commun.*, 1970, 1176.
1401. A. J. Cheney, B. E. Mann, B. L. Shaw and R. M. Slade, *J. Chem. Soc. (A)*, 1971, 3833.
1402. R. G. Goel and R. G. Montemayor, *Inorg. Chem.*, 1977, **16**, 2183.
1403. H. C. Clark, A. B. Goel, R. G. Goel and S. Goel, *Inorg. Chem.*, 1980, **19**, 3220.
1404. R. G. Goel and W. O. Ogini, *Organometallics*, 1982, **1**, 654.
1405. A. R. H. Bottomley, C. Crocker and B. L. Shaw, *J. Organomet. Chem.*, 1983, **250**, 617.
1406. A. B. Goel and S. Goel, *Inorg. Chim. Acta*, 1983, **69**, 233.
1407. H. P. Abicht, P. Lehniger and K. Issleib, *J. Organomet. Chem.*, 1983, **250**, 609.
1408. C. J. Moulton and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1976, 1020.
1409. D. P. Arnold, M. A. Bennett, M. S. Bilton and G. B. Robertson, *J. Chem. Soc., Chem. Commun.*, 1982, 115.
1410. G. O. Robertson and P. O. Whimp, *Inorg. Chem.*, 1974, **13**, 2082.
1411. N. Holy, V. Deschler and H. Schmidbaur, *Chem. Ber.*, 1982, **115**, 1379.
1412. R. D. Holmes-Smith, S. R. Stobart, T. S. Cameron and K. Jochem, *J. Chem. Soc., Chem. Commun.*, 1981, 937.
1413. M. J. Auburn, R. D. Holmes-Smith and S. R. Stobart, *J. Am. Chem. Soc.*, 1984, **106**, 1314.
1414. H. P. Fritz, I. R. Gordon, K. E. Schwarzhans and L. M. Venanzi, *J. Chem. Soc. (A)*, 1965, 5210.
1415. T. B. Rauchfuss, F. T. Patino and D. M. Roundhill, *Inorg. Chem.*, 1975, **14**, 652.
1416. M. K. Cooper and J. M. Downes, *Inorg. Chem.*, 1978, **17**, 880.
1417. M. K. Cooper and J. M. Downes, *J. Chem. Soc., Chem. Commun.*, 1981, 381.
1418. P. Braunstein, D. Matt, Y. Dusausoy and J. Fischer, *Organometallics*, 1983, **2**, 1410.
1419. H. A. Hudali, J. V. Kingston and H. A. Tayim, *Inorg. Chem.*, 1979, **18**, 1391.
1420. H. D. Empsall, P. N. Heys and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1978, 257.
1421. C. E. Jones, B. L. Shaw and B. L. Turtle, *J. Chem. Soc., Dalton Trans.*, 1974, 992.
1422. H. D. Empsall, B. L. Shaw and B. L. Turtle, *J. Chem. Soc., Dalton Trans.*, 1976, 1500.
1423. T. B. Rauchfuss, *Inorg. Chem.*, 1977, **16**, 2966.
1424. H. D. Empsall, E. M. Hyde, D. Pawson and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1977, 1292.
1425. C. J. Moulton and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1980, 299.
1426. T. B. Rauchfuss, *J. Am. Chem. Soc.*, 1979, **101**, 1045.

1427. D. A. Wrobleski and T. B. Rauchfuss, *J. Am. Chem. Soc.*, 1982, **104**, 2314.
1428. J. Chatt and J. M. Davidson, *J. Chem. Soc.*, 1964, 2433.
1429. J. B. Brandon and K. R. Dixon, *Can. J. Chem.*, 1981, **59**, 1188.
1430. A. J. Carty, F. Hartstock and N. J. Taylor, *Inorg. Chem.*, 1982, **21**, 1349.
1431. D. W. Meek, R. Waid, K. D. Tau, R. M. Kirchner and C. N. Morimoto, *Inorg. Chim. Acta*, 1982, **64**, L221.
1432. R. Glaser, D. J. Kountz, J. C. Gallucci and D. W. Meek, *Inorg. Chim. Acta*, 1983, **77**, L207.
1433. M. P. Brown, J. R. Fisher, S. J. Franklin, R. J. Puddephatt and M. A. Thompson, *Adv. Chem. Ser.*, 1982, **196**, 231.
1434. C. S. Chin, M. S. Sennett, P. J. Wier and L. Vaska, *Inorg. Chim. Acta*, 1978, **31**, L443.
1435. M. C. Grossel, M. P. Brown, C. D. Nelson, A. Yavari, E. Kallas, R. P. Moulding and K. R. Seddon, *J. Organomet. Chem.*, 1982, **232**, C13.
1436. L. Manojlovic-Muir and K. W. Muir, *J. Chem. Soc., Chem. Commun.*, 1982, 1155.
1437. M. C. Grossel, R. P. Moulding and K. R. Seddon, *J. Organomet. Chem.*, 1983, **253**, C50.
1438. M. C. Grossel, R. P. Moulding and K. R. Seddon, *Inorg. Chim. Acta*, 1983, **64**, L275.
1439. M. P. Brown, A. Yavari, L. Manojlovic-Muir and K. W. Muir, *J. Organomet. Chem.*, 1983, **256**, C19.
1440. M. P. Brown, R. J. Puddephatt, M. Rashidi and K. R. Seddon, *J. Chem. Soc., Dalton Trans.*, 1978, 1540.
1441. T. S. Cameron, P. A. Gardner and K. R. Grundy, *J. Organomet. Chem.*, 1981, **212**, C19.
1442. K. R. Grundy and K. N. Robertson, *Organometallics*, 1983, **2**, 1736.
1443. A. L. Balch, L. S. Benner and M. M. Olmstead, *Inorg. Chem.*, 1979, **18**, 2996.
1444. M. P. Brown, S. J. Cooper, A. A. Frew, L. Manojlovic-Muir, K. W. Muir, R. J. Puddephatt and M. A. Thomson, *J. Chem. Soc., Dalton Trans.*, 1982, 299.
1445. M. P. Brown, R. J. Puddephatt, M. Rashidi and K. R. Seddon, *J. Chem. Soc., Dalton Trans.*, 1977, 951.
1446. S. J. Cooper, M. P. Brown and R. J. Puddephatt, *Inorg. Chem.*, 1981, **20**, 1374.
1447. G. K. Anderson, H. C. Clark and J. A. Davies, *J. Organomet. Chem.*, 1981, **210**, 135.
1448. M. P. Brown, S. J. Cooper, A. A. Frew, L. Manojlovic-Muir, K. W. Muir, R. J. Puddephatt, K. R. Seddon and M. A. Thompson, *Inorg. Chem.*, 1981, **20**, 1500.
1449. A. T. Hutton, B. Shabanzadeh and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1983, 1053.
1450. S. S. M. Ling, R. J. Puddephatt, L. Manojlovic-Muir and K. W. Muir, *Inorg. Chim. Acta*, 1983, **77**, L95.
1451. R. J. Puddephatt, K. A. Azam, R. H. Hill, M. P. Brown, C. D. Nelson, R. P. Moulding, K. R. Seddon and M. C. Grossel, *J. Am. Chem. Soc.*, 1983, **105**, 5642.
1452. P. G. Pringle and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1983, 889.
1453. P. G. Pringle and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1982, 581.
1454. R. J. Puddephatt and M. A. Thomson, *J. Organomet. Chem.*, 1982, **238**, 231.
1455. D. M. McEwan, P. G. Pringle and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1982, 859.
1456. W. S. McDonald, P. G. Pringle and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1982, 861.
1457. D. M. McEwan, P. G. Pringle and B. L. Shaw, *J. Organomet. Chem.*, 1983, 1240.
1458. C. R. Langrick, D. M. McEwan, P. G. Pringle and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1983, 2487.
1459. A. Blagg, A. T. Hutton, P. G. Pringle and B. L. Shaw, *Inorg. Chim. Acta*, 1983, **76**, L265.
1460. P. Braunstein, C. M. deBellefon and M. Ries, *J. Organomet. Chem.*, 1984, **262**, C14.
1461. P. G. Pringle and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1982, 956.
1462. P. G. Pringle and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1982, 1313.
1463. P. Braunstein, J. M. Jud, Y. Dusausoy and J. Fischer, *Organometallics*, 1983, **2**, 180.
1464. J. P. Farr, M. M. Ohmstead, N. M. Rutherford, F. E. Wood and A. L. Balch, *Organometallics*, 1983, **2**, 1758.
1465. J. P. Farr, F. E. Wood and A. L. Balch, *Inorg. Chem.*, 1983, **22**, 3387.
1466. J. P. Farr, M. M. Ohmstead, F. E. Wood and A. L. Balch, *J. Am. Chem. Soc.*, 1983, **105**, 792.
1467. R. R. Guimerans and A. L. Balch, *Inorg. Chim. Acta*, 1983, **77**, L177.
1468. R. R. Guimerans, M. M. Ohmstead and A. L. Balch, *Inorg. Chem.*, 1983, **22**, 2223.
1469. R. J. Haines, A. Pidcock and M. Safari, *J. Chem. Soc., Dalton Trans.*, 1977, 830.
1470. D. M. Roundhill, R. P. Sperline and W. B. Beaulieu, *Coord. Chem. Rev.*, 1978, **26**, 263.
1471. B. Walther, *Coord. Chem. Rev.*, 1984, **60**, 67.
1472. K. R. Dixon and A. D. Rattray, *Can. J. Chem.*, 1971, **49**, 3996.
1473. P. C. Kong and D. M. Roundhill, *Inorg. Chem.*, 1972, **11**, 749.
1474. A. A. Grinberg and A. D. Troitskaya, *Dokl. Akad. Nauk SSSR, Ser. Khim.*, 1944, 178 (*Chem. Abstr.*, 1945, **39**, 1604(4)).
1475. P. C. Kong and D. M. Roundhill, *J. Chem. Soc., Dalton Trans.*, 1974, 187.
1476. K. R. Dixon and A. D. Rattray, *Inorg. Chem.*, 1977, **16**, 209.
1477. R. P. Sperline and D. M. Roundhill, *Inorg. Chem.*, 1977, **16**, 2612.
1478. D. E. Berry, G. W. Bushnell and K. R. Dixon, *Inorg. Chem.*, 1982, **21**, 957.
1479. D. M. Roundhill and S. G. N. Roundhill, *Acta Crystallogr., Sect. B*, 1982, **38**, 2479.
1480. J. M. Solar, R. D. Rogers and W. R. Mason, *Inorg. Chem.*, 1984, **23**, 373.
1481. R. P. Sperline, W. B. Beaulieu and D. M. Roundhill, *Inorg. Chem.*, 1978, **17**, 2032.
1482. J. Grosse and R. Schmutzler, *J. Chem. Soc., Dalton Trans.*, 1976, 405.
1483. J. Grosse and R. Schmutzler, *J. Chem. Soc., Dalton Trans.*, 1976, 412.
1484. W. Beck, M. Keubler, E. Leidl, U. Nagel, M. Schaal, S. Cenini, P. del Buttero, E. Licandro, S. Maiorana and A. C. Villa, *J. Chem. Soc., Chem. Commun.*, 1981, 446.
1485. D. E. Berry, G. W. Busheil, K. R. Dixon and A. Pidcock, *Inorg. Chem.*, 1983, **22**, 1961.
1486. B. Messbauer, H. Meyer, B. Walther, M. J. Heeg, A. F. M. Magpudur Rahman and J. P. Oliver, *Inorg. Chem.*, 1983, **22**, 272.
1487. D. M. Anderson, E. A. V. Ebsworth, T. A. Stephenson and M. D. Walkinshaw, *J. Chem. Soc., Dalton Trans.*, 1982, 2343.
1488. R. P. Sperline, M. K. Dickson and D. M. Roundhill, *J. Chem. Soc., Chem. Commun.*, 1977, 62.
1489. M. A. F. D. R. Pinto, P. J. Sadler, S. Neidle, M. R. Sanderson, A. Subbiah and R. Kuroda, *J. Chem. Soc., Chem. Commun.*, 1980, 13.

1490. W. A. Fordyce, J. G. Brummer and G. A. Crosby, *J. Am. Chem. Soc.*, 1981, **103**, 7061.
1491. C. M. Che, L. G. Butler and H. B. Gray, *J. Am. Chem. Soc.*, 1981, **103**, 7796.
1492. S. F. Rice and H. B. Gray, *J. Am. Chem. Soc.*, 1983, **105**, 4571.
1493. C. M. Che, F. H. Herbstein, W. P. Schaefer, R. E. Marsh and H. B. Gray, *J. Am. Chem. Soc.*, 1983, **105**, 4604.
1494. C. M. Che, W. P. Schaefer, H. B. Gray, M. K. Dickson, P. B. Stein and D. M. Roundhill, *J. Am. Chem. Soc.*, 1982, **104**, 4253.
1495. K. A. Alexander, P. Stein, D. B. Hedden and D. M. Roundhill, *Polyhedron*, 1983, **2**, 1389.
1496. W. B. Heuer, M. D. Totten, G. S. Rodman, E. J. Hebert, H. J. Tracy and J. K. Nagle, *J. Am. Chem. Soc.*, 1984, **106**, 1163.
1497. C. M. Che, L. G. Butler, H. B. Gray, R. M. Crooks and W. H. Woodruff, *J. Am. Chem. Soc.*, 1983, **105**, 5492.
1498. P. Stein, M. K. Dickson and D. M. Roundhill, *J. Am. Chem. Soc.*, 1983, **105**, 3489.
1499. C. M. Che, S. J. Atherton, L. G. Butler and H. B. Gray, *J. Am. Chem. Soc.*, 1984, **106**, 5143.
1500. S. A. Bryan, M. K. Dickson and D. M. Roundhill, *J. Am. Chem. Soc.*, 1984, **106**, 1882.
1501. M. D. Dickson, W. A. Fordyce, D. M. Appel, K. Alexander, P. Stein and D. M. Roundhill, *Inorg. Chem.*, 1982, **21**, 3857.
1502. Y. Koie, S. Shinoda and Y. Saito, *Inorg. Chem.*, 1981, **20**, 4408.
1503. H. R. Allcock, R. W. Allen and J. P. O'Brien, *J. Am. Chem. Soc.*, 1977, **99**, 3984.
1504. R. W. Allen, J. P. O'Brien and H. R. Allcock, *J. Am. Chem. Soc.*, 1977, **99**, 3987.
1505. J. P. O'Brien, R. W. Allen and H. R. Allcock, *Inorg. Chem.*, 1979, **18**, 2230.
1506. N. L. Paddock, T. N. Ranganathan, S. J. Rettig, R. D. Sharma and J. Trotter, *Can. J. Chem.*, 1981, **59**, 2429.
1507. R. Bender, P. Braunstein, J. Fischer, L. Ricard and A. Mitschler, *Nouv. J. Chim.*, 1981, **5**, 81.
1508. P. Lemoine, A. Giraudeau, M. Gross, R. Bender and P. Braunstein, *J. Chem. Soc., Dalton Trans.*, 1981, 2059.
1509. A. Albinati, A. Moor, P. S. Pregosin and L. M. Venanzi, *J. Am. Chem. Soc.*, 1982, **104**, 7672.
1510. A. D. Troitskaya and Z. L. Shmakova, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1971, **16**, 872.
1511. D. J. Gulliver and W. Levason, *Coord. Chem. Rev.*, 1982, **46**, 1.
1512. R. S. Nyholm, *J. Chem. Soc.*, 1950, 843.
1513. J. Chatt, L. A. Duncanson, B. M. Gatehouse, J. Lewis, R. S. Nyholm, M. L. Tobe, P. F. Todd and L. M. Venanzi, *J. Chem. Soc.*, 1959, 4073.
1514. A. Peloso and G. Dolcetti, *J. Chem. Soc.*, 1967, 1944.
1515. R. G. Goel, W. O. Ogini and R. C. Srivastava, *Inorg. Chem.*, 1981, **20**, 3611.
1516. C. A. McAuliffe, I. E. Niven and R. V. Parish, *Inorg. Chim. Acta*, 1977, **22**, 239.
1517. P. E. Garrou and G. E. Hartwell, *Inorg. Chem.*, 1976, **15**, 730.
1518. C. M. Harris, R. S. Nyholm and D. J. Phillips, *J. Chem. Soc.*, 1960, 4379.
1519. G. Booth, *Adv. Inorg. Chem. Radiochem.*, 1964, **6**, 1.
1520. H. C. Clark and J. E. H. Ward, *Can. J. Chem.*, 1974, **52**, 570.
1521. W. R. Cullen, L. D. Hall, J. T. Price and G. Spendjian, *Can. J. Chem.*, 1975, **53**, 366.
1522. N. K. Roberts and S. B. Wild, *Inorg. Chem.*, 1981, **20**, 1900.
1523. W. Levason and C. A. McAuliffe, *Inorg. Chim. Acta*, 1976, **16**, 167.
1524. D. J. Gulliver, W. Levason and K. G. Smith, *J. Chem. Soc., Dalton Trans.*, 1981, 2153.
1525. R. J. Dickinson, W. Levason, C. A. McAuliffe and R. V. Parish, *J. Chem. Soc., Dalton Trans.*, 1978, 177.
1526. H. L. Collier and E. Grimley, *Inorg. Chem.*, 1980, **19**, 511.
1527. W. E. Hill, D. M. A. Minahan, C. A. McAuliffe and K. L. Minten, *Inorg. Chim. Acta*, 1983, **74**, 9.
1528. S. J. Higgins, W. Levason, F. P. McCullough and B. Sheikh, *Inorg. Chim. Acta*, 1983, **71**, 87.
1529. W. Levason and C. A. McAuliffe, *Inorg. Chem.*, 1974, **13**, 2765.
1530. P. L. Goggin, R. J. Knight, L. Sindellari and L. M. Venanzi, *Inorg. Chim. Acta*, 1971, **5**, 62.
1531. C. A. McAuliffe, I. E. Niven and R. V. Parish, *J. Chem. Soc., Dalton Trans.*, 1977, 1901.
1532. L. Vaska, *Acc. Chem. Res.*, 1976, **9**, 175.
1533. J. Valentine, *Chem. Rev.*, 1973, **73**, 235.
1534. V. J. Choy and C. J. O'Connor, *Coord. Chem. Rev.*, 1972, **9**, 145.
1535. B. R. James, *Adv. Chem. Ser.*, 1980, **191**, 253.
1536. R. VanAtta, J. Burstyn and J. S. Valentine, in 'Reactions of Coordinated Ligands', ed. P. S. Braterman, Plenum, New York, 1983.
1537. J. G. Norman, *Inorg. Chem.*, 1977, **16**, 1328.
1538. S. Sakaki, K. Hori and A. Ohyoshi, *Inorg. Chem.*, 1978, **17**, 3183.
1539. G. Read, A. M. R. Galas and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1983, 911.
1540. S. Bhaduri, L. Casella, R. Ugo, P. R. Raithby, C. Zuccaro and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1979, 1624.
1541. A. Sen and J. Halpern, *J. Am. Chem. Soc.*, 1977, **99**, 8337.
1542. G. D. Mercer, W. B. Beaulieu and D. M. Roundhill, *J. Am. Chem. Soc.*, 1977, **99**, 6551.
1543. M. Pizzotti, S. Cenini and G. LaMonica, *Inorg. Chim. Acta*, 1978, **33**, 161.
1544. P. L. Bellon, S. Cenini, F. Demartin, M. Manassero, M. Pizzotti and F. Porta, *J. Chem. Soc., Dalton Trans.*, 1980, 2060.
1545. H. C. Clark, A. B. Goel and C. S. Wong, *J. Am. Chem. Soc.*, 1978, **100**, 6241.
1546. P. J. Hayward and C. J. Nyman, *J. Am. Chem. Soc.*, 1971, **93**, 617.
1547. A. Modinos and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1975, 2134.
1548. A. Vogler and H. Kunkely, *J. Am. Chem. Soc.*, 1981, **103**, 6222.
1549. G. Strukul, R. Ros and R. A. Michelin, *Inorg. Chem.*, 1982, **21**, 495.
1550. G. Strukul, R. A. Michelin, J. D. Orbell and L. Randaccio, *Inorg. Chem.*, 1983, **22**, 3706.
1551. Y. Tatsuno and S. Otsuka, *J. Am. Chem. Soc.*, 1981, **103**, 5832.
1552. M. Y. Chen and J. K. Kochi, *J. Chem. Soc., Chem. Commun.*, 1977, 204.
1553. C. Bird, B. L. Booth, R. N. Haszeldine, G. R. N. Neuss, M. A. Smith and A. Flood, *J. Chem. Soc., Dalton Trans.*, 1982, 1109.

1554. L. Grantham, T. S. Elleman and D. S. Martin, *J. Am. Chem. Soc.*, 1955, **77**, 2965.
1555. T. S. Elleman, J. W. Reishus and D. S. Martin, *J. Am. Chem. Soc.*, 1958, **80**, 536.
1556. R. G. Denning, F. R. Hartley and L. M. Venanzi, *J. Chem. Soc. (A)*, 1967, 324.
1557. R. J. Cross and F. Glockling, *J. Chem. Soc.*, 1965, 5422.
1558. R. Kuroda, S. Neidle, I. M. Ismail and P. J. Sadler, *Inorg. Chem.*, 1983, **22**, 3620.
1559. R. Faggiani, H. E. Howard-Lock, C. J. L. Lock, B. Lippert and B. Rosenberg, *Can. J. Chem.*, 1982, **60**, 529.
1560. R. Faggiani, B. Lippert, C. J. L. Lock and B. Rosenberg, *J. Am. Chem. Soc.*, 1977, **99**, 777.
1561. B. Lippert, C. J. L. Lock, B. Rosenberg and M. Zvagulis, *Inorg. Chem.*, 1978, **17**, 2971.
1562. R. C. Johnson and C. G. Widmer, *Inorg. Chem.*, 1979, **18**, 2027.
1563. D. S. Gill and B. Rosenberg, *J. Am. Chem. Soc.*, 1982, **104**, 4598.
1564. M. Marfait, A. J. P. Alix, J. Delaunay-Zeches and T. Theophanides, *Can. J. Chem.*, 1982, **60**, 2216.
1565. A. J. P. Alix, M. Manfait, O. Krug and T. Theophanides, *Can. J. Chem.*, 1982, **60**, 2222.
1566. C. A. Bignozzi, C. Bartocci, A. Maldotti and V. Carassiti, *Inorg. Chim. Acta*, 1982, **62**, 187.
1567. R. Faggiani, B. Lippert, C. J. L. Lock and B. Rosenberg, *Inorg. Chem.*, 1977, **16**, 1192.
1568. R. Faggiani, B. Lippert, C. J. L. Lock and B. Rosenberg, *Inorg. Chem.*, 1978, **17**, 1941.
1569. G. W. Bushnell, *Can. J. Chem.*, 1978, **56**, 1773.
1570. M. E. Fakley and A. Pidcock, *J. Chem. Soc., Dalton Trans.*, 1977, 1444.
1571. U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson and A. Turco, *J. Am. Chem. Soc.*, 1965, **87**, 241.
1572. H. M. Colquhoun, J. F. Stoddart and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1981, 847.
1573. H. M. Colquhoun, J. F. Stoddart and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1981, 851.
1574. H. M. Colquhoun, J. F. Stoddart, D. J. Williams, J. B. Wolstenholme and R. Zarzycki, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 1051.
1575. T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer and G. Wilkinson, *J. Chem. Soc.*, 1965, 3632.
1576. P. de Meester and A. C. Skapski, *J. Chem. Soc., Dalton Trans.*, 1973, 1194.
1577. M. A. A. F. de C. T. Carrondo and A. C. Skapski, *J. Chem. Soc., Chem. Commun.*, 1976, 410.
1578. A. Dobson, S. D. Robinson and M. F. Uttley, *Inorg. Synth.*, 1977, **17**, 124.
1579. T. G. Appleton and J. R. Hall, *J. Chem. Soc., Chem. Commun.*, 1983, 911.
1580. D. M. Blake, S. Shields and L. Wyman, *Inorg. Chem.*, 1974, **13**, 1595.
1581. G. Al-Takhin, G. Pilcher, J. Bickerton and A. A. Zaki, *J. Chem. Soc., Dalton Trans.*, 1983, 2657.
1582. M. Vezes, *C. R. Hebd. Seances Acad. Sci.*, 1897, **125**, 525.
1583. M. Vezes, *Bull. Soc. Chim. Fr.*, 1899, **21**, 143.
1584. M. Vezes, *Bull. Soc. Chim. Fr.*, 1898, **19**, 875.
1585. A. Giacomelli, *Inorg. Chem.*, 1975, **14**, 1409.
1586. A. C. Villa, A. G. Manfredotti, A. Giacomelli, C. Guastini, and A. Indelli, *Inorg. Chem.*, 1975, **14**, 1654.
1587. J. Hoch and R. M. Milburn, *Inorg. Chem.*, 1979, **18**, 886.
1588. H. Soderbaum, *Ber.*, 1888, **21**, 567C.
1589. K. Krogmann and P. Dodel, *Chem. Ber.*, 1966, **99**, 3402.
1590. A. H. Reis, S. W. Peterson and S. C. Lin, *J. Am. Chem. Soc.*, 1976, **98**, 7839.
1591. J. S. Miller, *Inorg. Chem.*, 1976, **15**, 2357.
1592. A. J. Schultz, A. E. Underhill and J. M. Williams, *Inorg. Chem.*, 1978, **17**, 1313.
1593. A. Kobayashi, Y. Sasaki and H. Kobayashi, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 3682.
1594. A. E. Underhill and K. Carneiro, *J. Chem. Soc., Dalton Trans.*, 1983, 1770.
1595. A. A. Grinberg and I. N. Chapurskii, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1959, **4**, 137.
1596. S. Onuma, K. Horioka, H. Inoue and S. Shibata, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 2679.
1597. M. Katoh, K. Miki, Y. Kai, N. Tanaka and N. Kasai, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 611.
1598. B. N. Figgis, J. Lewis, R. Mason, R. S. Nyholm, P. J. Pauling and G. B. Robertson, *Nature (London)*, 1962, **195**, 1278.
1599. R. Mason, G. B. Robertson and P. J. Pauling, *J. Chem. Soc. (A)*, 1969, 485.
1600. J. Lewis, R. F. Long and C. Oldham, *J. Chem. Soc.*, 1965, 6740.
1601. D. Gibson, J. Lewis and C. Oldham, *J. Chem. Soc. (A)*, 1966, 1453.
1602. S. Okeya, Y. Nakamura, S. Kawaguchi and T. Hinomoto, *Inorg. Chem.*, 1981, **20**, 1576.
1603. J. Lewis and C. Oldham, *J. Chem. Soc. (A)*, 1966, 1456.
1604. Y. Nakamura and K. Nakamoto, *Inorg. Chem.*, 1975, **14**, 63.
1605. D. M. Doddrell, P. F. Barron, D. E. Clegg and C. Bowie, *J. Chem. Soc., Chem. Commun.*, 1982, 575.
1606. D. Gibson, J. Lewis and C. Oldham, *J. Chem. Soc. (A)*, 1967, 72.
1607. G. T. Behnke and K. Nakamoto, *Inorg. Chem.*, 1968, **7**, 2030.
1608. C. J. May and J. Powell, *Inorg. Chim. Acta*, 1978, **26**, L21.
1609. S. Okeya, Y. Nakamura and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 3396.
1610. S. Okeya, Y. Nakamura and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 1460.
1611. J. S. Valentine and D. Valentine, *J. Am. Chem. Soc.*, 1970, **92**, 5795.
1612. S. Cenini, R. Ugo and G. La Monica, *J. Chem. Soc. (A)*, 1971, 416.
1613. Y. S. Sohn and A. L. Balch, *J. Am. Chem. Soc.*, 1971, **93**, 1290.
1614. A. Y. Girgis, Y. S. Sohn and A. L. Balch, *Inorg. Chem.*, 1975, **14**, 2327.
1615. G. A. Abakumov, I. A. Teplova, V. K. Cherkasov and K. G. Shalnova, *Inorg. Chim. Acta*, 1979, **32**, L57.
1616. O. Gandolfi, G. Dolcetti, M. Ghedini and M. Cais, *Inorg. Chem.*, 1980, **19**, 1785.
1617. G. A. Razuvaev, G. A. Abakumov, I. A. Teplova, K. G. Shalnova and V. K. Cherkasov, *Inorg. Chim. Acta*, 1981, **53**, L267.
1618. P. J. Hayward, D. M. Blake, G. Wilkinson and C. J. Nyman, *J. Am. Chem. Soc.*, 1970, **92**, 5873.
1619. C. J. Nyman, C. E. Wymore and G. Wilkinson, *J. Chem. Soc. (A)*, 1968, 561.
1620. F. Cariati, R. Mason, G. B. Robertson and R. Ugo, *Chem. Commun.*, 1967, 408.
1621. P. B. Critchlow and S. D. Robinson, *Coord. Chem. Rev.*, 1978, **25**, 69.
1622. A. B. P. Lever, E. Mantovani and B. S. Ramaswamy, *Can. J. Chem.*, 1971, **49**, 1957.

1623. S. Bhaduri, B. F. G. Johnson, A. Pickard, P. R. Raithby, G. M. Sheldrick and C. I. Zuccaro, *J. Chem. Soc., Chem. Commun.*, 1977, 354.
1624. A. J. Jircitano, W. G. Rohly and K. B. Mertes, *J. Am. Chem. Soc.*, 1981, **103,** 4879.
1625. D. Plancherel and D. R. Eaton, *Can. J. Chem.*, 1981, **59,** 156.
1626. B. L. Booth, R. N. Haszeldine and R. G. G. Holmes, *J. Chem. Soc., Dalton Trans.*, 1982, 523.
1627. B. L. Booth, R. N. Haszeldine and R. G. G. Holmes, *J. Chem. Soc., Dalton Trans.*, 1982, 671.
1628. W. Beck and E. Schuierer, *Chem. Ber.*, 1965, **98,** 298.
1629. K. Werner, W. Beck and U. Böhner, *Chem. Ber.*, 1974, **107,** 2434.
1630. F. Basolo and G. S. Hammaker, *Inorg. Chem.*, 1962, **1,** 1.
1631. K. C. Koshy and G. M. Harris, *Inorg. Chem.*, 1983, **22,** 2947.
1632. K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds', Wiley-Interscience, New York, 1970, p. 177.
1633. S. P. Dent, C. Eaborn and A. Pidcock, *J. Organomet. Chem.*, 1975, **97,** 307.
1634. M. Kubota, R. R. Rothrock, M. R. Kernan and R. B. Haven, *Inorg. Chem.*, 1982, **21,** 2491.
1635. A. Wojcicki, *Adv. Organomet. Chem.*, 1974, **12,** 31.
1636. T. D. Harrigan and R. C. Johnson, *Inorg. Chem.*, 1977, **16,** 1741.
1637. P. C. Leung and F. Aubke, *Inorg. Chem.*, 1978, **17,** 1765.
1638. N. E. Dixon, G. A. Lawrance, P. A. Lay and A. M. Sargeson, *Inorg. Chem.*, 1983, **22,** 846.
1639. W. S. Cripps and C. J. Willis, *Can. J. Chem.*, 1975, **53,** 809.
1640. O. Simonsen and H. Toftlund, *Inorg. Chem.*, 1981, **20,** 4044.
1641. G. S. Muraveiskaya, V. S. Orlova and O. N. Evstaf'eva, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1974, **19,** 561.
1642. V. S. Orlova, G. S. Muraveiskaya and O. N. Evstaf'eva, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1975, **20,** 753.
1643. G. S. Muraveiskaya, G. A. Kukina, V. S. Orlova, O. N. Evstaf'eva and M. A. Porai-Koshits, *Dokl. Akad. Nauk SSSR*, 1976, **226,** 596.
1644. F. A. Cotton, L. R. Falvello and S. Han, *Inorg. Chem.*, 1982, **21,** 2889.
1645. G. S. Muraveiskaya, V. E. Abashkin, O. N. Evstaf'eva, I. F. Golovaneva and R. N. Shchelokov, *Sov. J. Coord. Chem. (Engl. Transl.)*, 1981, **6,** 218.
1646. F. A. Cotton, L. R. Falvello and S. Han, *Inorg. Chem.*, 1982, **21,** 1709.
1647. F. A. Cotton, S. Han, H. L. Conder and R. A. Walton, *Inorg. Chim. Acta*, 1983, **72,** 191.
1648. H. L. Conder, F. A. Cotton, L. R. Falvello, S. Han and R. A. Walton, *Inorg. Chem.*, 1983, **22,** 1887.
1649. V. S. Orlova, G. S. Muraveiskaya, I. F. Golovaneva and R. N. Shchelokov, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1980, **25,** 112.
1650. G. S. Muraveiskaya, V. S. Orlova, I. F. Golovaneva and R. N. Shchelokov, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1981, **26,** 994.
1651. G. S. Muraveiskaya, V. S. Orlova, I. F. Golovaneva and R. N. Shchelokov, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1981, **26,** 1770.
1652. T. G. Appleton, J. R. Hall, D. W. Neale and S. F. Ralph, *Inorg. Chim. Acta*, 1983, **77,** L149.
1653. T. G. Appleton, R. D. Berry and J. R. Hall, *Inorg. Chim. Acta*, 1982, **64,** L229.
1654. S. G. Murray and F. R. Hartley, *Chem. Rev.*, 1981, **81,** 365.
1655. R. P. Burns, F. P. McCullough and C. A. McAuliffe, *Adv. Inorg. Chem. Radiochem.*, 1980, **23,** 211.
1656. R. A. Walton, *Coord. Chem. Rev.*, 1980, **31,** 183.
1657. T. N. Lockyer and R. L. Martin, *Prog. Inorg. Chem.*, 1980, **27,** 223.
1658. C. G. Kuehn and S. S. Isied, *Prog. Inorg. Chem.*, 1980, **27,** 153.
1659. D. Coucouvanis, *Prog. Inorg. Chem.*, 1979, **26,** 301.
1660. R. P. Burns and C. A. McAuliffe, *Adv. Inorg. Chem. Radiochem.*, 1979, **22,** 303.
1661. I. Omae, *Coord. Chem. Rev.*, 1979, **28,** 97.
1662. E. W. Ainscough and A. M. Brodie, *Coord. Chem. Rev.*, 1978, **27,** 59.
1663. S. E. Livingstone, *Coord. Chem. Rev.*, 1971, **7,** 59.
1664. M. Cox and J. Darken, *Coord. Chem. Rev.*, 1971, **7,** 29.
1665. R. Eisenberg, *Prog. Inorg. Chem.*, 1970, **12,** 295.
1666. D. Coucouvanis, *Prog. Inorg. Chem.*, 1970, **11,** 233.
1667. L. F. Lindoy, *Coord. Chem. Rev.*, 1969, **4,** 41.
1668. G. N. Schrauzer, *Acc. Chem. Res.*, 1969, **2,** 72.
1669. J. A. McCleverty, *Prog. Inorg. Chem.*, 1968, **10,** 49.
1670. S. E. Livingstone, *Q. Rev., Chem. Soc.*, 1965, **19,** 386.
1671. K. A. Hofmann and F. Hochtlen, *Ber.*, 1903, **36,** 3090.
1672. F. G. Riddell, R. D. Gillard and F. L. Wimmer, *J. Chem. Soc., Chem. Commun.*, 1982, 332.
1673. D. Dudis and J. P. Fackler, *Inorg. Chem.*, 1982, **21,** 3577.
1674. C. E. Briant, M. J. Calhorda, T. S. Andy Hor, N. D. Howells and D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.*, 1983, 1325.
1675. J. D. Woollins, R. Grinter, M. K. Johnson and A. J. Thomson, *J. Chem. Soc., Dalton Trans.*, 1980, 1910.
1676. R. Ugo, G. LaMonica, S. Cenini, A. Segre and F. Conti, *J. Chem. Soc. (A)*, 1971, 522.
1677. J. Chatt and D. M. P. Mingos, *J. Chem. Soc. (A)*, 1970, 1243.
1678. M. C. Baird and G. Wilkinson, *J. Chem. Soc. (A)*, 1967, 865.
1679. A. C. Skapski and P. G. H. Troughton, *J. Chem. Soc. (A)*, 1969, 2772.
1680. W. M. Hawling, A. Walker and M. A. Woitzik, *J. Chem. Soc., Chem. Commun.*, 1983, 11.
1681. C. T. Hunt, G. B. Matson and A. L. Balch, *Inorg. Chem.*, 1981, **20,** 2270.
1682. C. E. Briant, T. S. Andy Hor, N. D. Howells and D. M. P. Mingos, *J. Chem. Soc., Chem. Commun.*, 1983, 1118.
1683. C. E. Briant, T. S. Andy Hor, N. D. Howells and D. M. P. Mingos, *J. Organomet. Chem.*, 1983, **256,** C15.
1684. A. M. Mazany, J. P. Fackler, M. K. Gallagher and D. Seyferth, *Inorg. Chem.*, 1983, **22,** 2593.
1685. K. P. Callahan and P. A. Piliero, *Inorg. Chem.*, 1980, **19,** 2619.
1686. K. P. Callahan and E. J. Cichon, *Inorg. Chem.*, 1981, **20,** 1941.

1687. D. Morelli, A. Segre, R. Ugo, G. LaMonica, S. Cenini, F. Conti and F. Bonati, *Chem. Commun.*, 1967, 524.
1688. R. Ugo, G. LaMonica, S. Cenini, A. Segre and F. Conti, *J. Chem. Soc. (A)*, 1971, 522.
1689. M. Schmidt and G. G. Hoffmann, *J. Organomet. Chem.*, 1977, **124,** C5.
1690. C. E. Briant, G. R. Hughes, P. C. Minshall and D. M. P. Mingos, *J. Organomet. Chem.*, 1980, **202,** C18.
1691. P. C. Ray, *Prog. Inorg. Chem.*, 1914, **30,** 304.
1692. P. C. Ray, *J. Chem. Soc.*, 1923, **123,** 133.
1693. R. G. Hayter and F. S. Humiec, *J. Inorg. Nucl. Chem.*, 1964, **26,** 807.
1694. F. G. Mann and D. Purdie, *J. Chem. Soc.*, 1935, 1549.
1695. T. B. Rauchfuss, J. S. Shu and D. M. Roundhill, *Inorg. Chem.*, 1976, **15,** 2096.
1696. S. A. Bryan and D. M. Roundhill, *Acta Crystallogr., Sect. C*, 1983, **39,** 184.
1697. M. Schmidt and G. G. Hoffmann, *Chem. Ber.*, 1979, **112,** 2190.
1698. B. K. Teo and P. A. Snyder-Robinson, *Inorg. Chem.*, 1978, **17,** 3489.
1699. B. K. Teo and P. A. Snyder-Robinson, *Inorg. Chem.*, 1981, **20,** 4235.
1700. J. L. Davidson, P. N. Preston and M. V. Russo, *J. Chem. Soc., Dalton Trans.*, 1983, 783.
1701. J. C. Dewan, S. J. Lippard and W. R. Bauer, *J. Am. Chem. Soc.*, 1980, **102,** 858.
1702. S. V. Kovalenko and G. D. Mal'chikov, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1982, **27,** 1767.
1703. K. R. Dixon, K. C. Moss and M. A. R. Smith, *J. Chem. Soc., Dalton Trans.*, 1973, 1528.
1704. K. R. Dixon, K. C. Moss and M. A. R. Smith, *J. Chem. Soc., Dalton Trans.*, 1975, 990.
1705. R. Zanella, R. Ros and M. Graziani, *Inorg. Chem.*, 1973, **12,** 2737.
1706. A. W. Gal, J. W. Gosselink and F. A. Vollenbroek, *Inorg. Chim. Acta*, 1979, **32,** 235.
1707. W. Beck, E. Leidl, M. Keubler and U. Nagel, *Chem. Ber.*, 1980, **113,** 1790.
1708. R. D. Lai and A. Shaver, *Inorg. Chem.*, 1981, **20,** 477.
1709. P. H. Bird, V. Siriwardane, R. D. Lai and A. Shaver, *Can. J. Chem.*, 1982, **60,** 2075.
1710. D. M. Roundhill, *Inorg. Chem.*, 1980, **19,** 557.
1711. A. Johnson and R. J. Puddephatt, *J. Chem. Soc., Dalton Trans.*, 1975, 115.
1712. J. P. Fackler, *Prog. Inorg. Chem.*, 1976, **21,** 55.
1713. M. P. Brown, R. J. Puddephatt and C. E. E. Upton, *J. Chem. Soc., Dalton Trans.*, 1976, 2490.
1714. A. Shaver, J. Hartgerink, R. D. Lai, P. Bird and N. Ansari, *Organometallics*, 1983, **2,** 938.
1715. L. A. Tschugaev and W. Subbotin, *Ber.*, 1910, **43,** 1200.
1716. K. A. Jensen, *Z. Anorg. Allg. Chem.*, 1935, **225,** 97.
1717. K. A. Jensen, *Z. Anorg. Allg. Chem.*, 1935, **225,** 115.
1718. J. E. Fritzmann, *Z. Anorg. Allg. Chem.*, 1911, **73,** 239.
1719. E. Fritzman and V. V. Krinitzkiv, *J. Appl. Chem. USSR (Engl. Transl.)*, 1939, **11,** 1610.
1720. G. B. Kauffman and D. O. Cowan, *Inorg. Synth.*, 1960, **6,** 211.
1721. E. A. Allen, N. P. Johnson, D. T. Rosevear and W. Wilkinson, *J. Chem. Soc., Chem. Commun.*, 1971, 171.
1722. R. J. Cross, T. H. Green, R. Keat and J. F. Paterson, *J. Chem. Soc., Dalton Trans.*, 1976, 1486.
1723. J. Kuyper, *Inorg. Chem.*, 1979, **18,** 1484.
1724. M. Bonivento, L. Canovese, L. Cattalini, G. Marangoni, G. Michelon and M. L. Tobe, *Inorg. Chem.*, 1983, **22,** 802.
1725. R. G. Pearson, H. Sobel and J. Sognstad, *J. Am. Chem. Soc.*, 1968, **90,** 319.
1726. R. Gosling and M. L. Tobe, *Inorg. Chim. Acta*, 1980, **42,** 223.
1727. M. Bonivento, L. Canovese, L. Cattalini, G. Marangoni, G. Michelon and M. L. Tobe, *Inorg. Chem.*, 1981, **20,** 3728.
1728. R. J. Cross, T. H. Green and R. Keat, *J. Chem. Soc., Dalton Trans.*, 1976, 382.
1729. E. Fritzmann, *Z. Anorg. Allg. Chem.*, 1924, **133,** 119, 133.
1730. J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 1955, 2787.
1731. D. L. Sales, J. Stokes and P. Woodward, *J. Chem. Soc. (A)*, 1968, 1852.
1732. W. L. Kwik and S. F. Tan, *J. Chem. Soc., Dalton Trans.*, 1976, 1072.
1733. W. J. Geary, N. J. Mason, I. W. Nowell and L. A. Nixon, *J. Chem. Soc., Dalton Trans.*, 1982, 1103.
1734. M. Schmidt and G. G. Hoffmann, *Phosphorus Sulfur*, 1978, **4,** 239.
1735. M. Schmidt and G. G. Hoffmann, *Phosphorus Sulfur*, 1978, **4,** 249.
1736. F. R. Hartley, S. G. Murray and C. A. McAuliffe, *Inorg. Chem.*, 1979, **18,** 1394.
1737. L. Manojlovic-Muir, K. W. Muir and T. Solomon, *Inorg. Chim. Acta*, 1977, **22,** 69.
1738. B. Cetinkaya, P. B. Hitchcock, M. F. Lappert, P. L. Pye and D. B. Shaw, *J. Chem. Soc., Dalton Trans.*, 1979, 434.
1739. E. W. Abel, K. Kite and B. L. Williams, *J. Chem. Soc., Dalton Trans.*, 1983, 1017.
1740. L. F. Lindroy, S. E. Livingstone and T. N. Lockyer, *Aust. J. Chem.*, 1967, **20,** 471.
1741. L. M. Volshstein and M. F. Mogilevkina, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1963, **8,** 304.
1742. C. A. McAuliffe, *J. Chem. Soc. (A)*, 1967, 641.
1743. G. Albertin, E. Bordignon, A. A. Orio, B. Pavoni and H. B. Gray, *Inorg. Chem.*, 1979, **18,** 1451.
1744. F. G. Mann, *J. Chem. Soc.*, 1930, 1745.
1745. D. J. Gulliver, W. Levason, K. G. Smith, M. J. Selwood and S. G. Murray, *J. Chem. Soc., Dalton Trans.*, 1980, 1872.
1746. P. Haake and P. C. Turley, *J. Am. Chem. Soc.*, 1967, **89,** 4611, 4617.
1747. E. W. Abel, R. P. Bush, F. J. Hopton and C. R. Jenkins, *Chem. Commun.*, 1966, 58.
1748. H. A. O. Hill and K. A. Simpson, *J. Chem. Soc. (A)*, 1970, 3266.
1749. R. J. Cross, I. G. Dalgleish, G. J. Smith and R. Wardle, *J. Chem. Soc., Dalton Trans.*, 1972, 992.
1750. A. R. Dias and M. L. H. Green, *J. Chem. Soc. (A)*, 1971, 1951.
1751. R. J. Cross, T. H. Green and R. Keat, *J. Chem. Soc., Dalton Trans.*, 1976, 1150.
1752. E. W. Abel, A. K. Shamsuddin Ahmed, G. W. Farrow, K. G. Orrell and V. Sik, *J. Chem. Soc., Dalton Trans.*, 1977, 47.
1753. E. W. Abel, M. Booth and K. G. Orrell, *J. Chem. Soc., Dalton Trans.*, 1979, 1994.
1754. E. W. Abel, M. Booth and K. G. Orrell, *J. Chem. Soc., Dalton Trans.*, 1980, 1582.

1755. R. L. Batstone-Cunningham, H. W. Dodgen, J. P. Hunt and D. M. Roundhill, *J. Chem. Soc., Dalton Trans.*, 1983, 1473.
1756. J. C. Barnes, G. Hunter and M. W. Lown, *J. Chem. Soc., Dalton Trans.*, 1976, 1227.
1757. E. W. Abel, A. R. Khan, K. Kite, K. G. Orrell and V. Sik, *J. Chem. Soc., Dalton Trans.*, 1980, 1169.
1758. E. W. Abel, A. R. Khan, K. Kite, K. G. Orrell and V. Sik, *J. Chem. Soc., Dalton Trans.*, 1980, 1175.
1759. E. W. Abel, A. R. Khan, K. Kite, K. G. Orrell and V. Sik, *J. Chem. Soc., Dalton Trans.*, 1980, 2208.
1760. E. W. Abel, A. R. Khan, K. Kite, K. G. Orrell and V. Sik, *J. Chem. Soc., Dalton Trans.*, 1980, 2220.
1761. E. W. Abel, A. R. Khan, K. Kite, K. G. Orrell, V. Sik and B. L. Williams, *J. Chem. Soc., Dalton Trans.*, 1981, 2439.
1762. E. W. Abel, S. K. Bhargava, K. Kite, K. G. Orrell, V. Sik and B. L. Williams, *J. Chem. Soc., Dalton Trans.*, 1982, 583.
1763. E. W. Abel, S. K. Bhargava, K. Kite, K. G. Orrell, V. Sik and B. L. Williams, *Polyhedron*, 1982, **1**, 289.
1764. E. W. Abel, K. G. Orrell and A. W. G. Platt, *J. Chem. Soc., Dalton Trans.*, 1983, 2345.
1765. J. Errington, W. S. McDonald and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1980, 2309.
1766. R. J. Cross, D. S. Rycroft, D. W. A. Sharp and H. Torrens, *J. Chem. Soc., Dalton Trans.*, 1980, 2434.
1767. E. W. Abel, M. Booth, G. King, K. G. Orrell, G. M. Pring and V. Sik, *J. Chem. Soc., Dalton Trans.*, 1981, 1846.
1768. F. A. Cotton, R. Francis and W. D. Horrocks, *J. Phys. Chem.*, 1960, **64**, 1534.
1769. J. Selbin, W. E. Bull and L. H. Holmes, *J. Inorg. Nucl. Chem.*, 1961, **16**, 219.
1770. W. Kitching, C. J. Moore and D. Doddrell, *Inorg. Chem.*, 1970, **9**, 541.
1771. P. C. Kong and F. D. Rochon, *Inorg. Chim. Acta*, 1979, **37**, L457.
1772. Yu. N. Kukushkin, Yu. E. Vyaz'menskii, L. I. Zorina and Yu. L. Pazukhina, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1968, **13**, 835.
1773. R. Melanson and F. D. Rochon, *Can. J. Chem.*, 1975, **53**, 2371.
1774. Yu. N. Kukushkin, Yu. E. Vyaz'menskii and L. I. Zorina, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1968, **13**, 1573.
1775. P. D. Braddock, R. Romeo and M. L. Tobe, *Inorg. Chem.*, 1974, **13**, 1170.
1776. M. Bonivento, L. Cattalini, G. Marangoni, G. Michelon, A. P. Schwab and M. L. Tobe, *Inorg. Chem.*, 1980, **19**, 1743.
1777. L. I. Elding and O. Groning, *Inorg. Chem.*, 1978, **17**, 1872.
1778. O. Groning, T. Drakenberg and L. I. Elding, *Inorg. Chem.*, 1982, **21**, 1820.
1779. L. E. Erickson, T. A. Ferrett and L. F. Buhse, *Inorg. Chem.*, 1983, **22**, 1461.
1780. R. Romeo and M. Cusumano, *Inorg. Chim. Acta*, 1981, **49**, 167.
1781. J. H. Price, J. P. Birk and B. B. Wayland, *Inorg. Chem.*, 1978, **17**, 2245.
1782. W. A. Freeman, L. J. Nicholls and C. F. Liu, *Inorg. Chem.*, 1978, **17**, 2989.
1783. L. Cattalini, G. Michelon, G. Marangoni and G. Pelizzi, *J. Chem. Soc., Dalton Trans.*, 1979, 96.
1784. M. J. Blandamer, J. Burgess and J. G. Chambers, *J. Chem. Soc., Dalton Trans.*, 1977, 60.
1785. J. M. Bret, P. Castan and J.-P. Laurent, *Inorg. Chim. Acta*, 1981, **51**, 103.
1786. P. Arrizabalaga, P. Castan, J.-P. Laurent and A. Salesse, *Chem. Phys. Lett.*, 1980, **76**, 548.
1787. J. M. Bret, P. Castan, G. Commenges and J.-P. Laurent, *Polyhedron*, 1983, **2**, 901.
1788. D. A. Edwards, R. Richards, R. E. Myers and R. A. Walton, *Inorg. Chim. Acta*, 1977, **23**, 215.
1789. (a) J. A. Goodfellow, T. A. Stephenson and M. C. Cornock, *J. Chem. Soc., Dalton Trans.*, 1978, 1195. (b) M. C. Cornock and T. A. Stephenson, *J. Chem. Soc., Dalton Trans.*, 1977, 683. (c) M. C. Cornock and T. A. Stephenson, *J. Chem. Soc., Dalton Trans.*, 1977, 501. (d) M. C. Cornock, R. O. Gould, C. L. Jones, J. D. Owen, D. F. Steele and T. A. Stephenson, *J. Chem. Soc., Dalton Trans.*, 1977, 496.
1790. C. S. Robinson and H. O. Jones, *J. Chem. Soc.*, 1912, **101**, 62.
1791. E. G. Cox, W. Wardlaw and K. C. Webster, *J. Chem. Soc.*, 1935, 1475.
1792. C. Bellito, A. Flamini, O. Piovesana and P. F. Zanazzi, *Inorg. Chem.*, 1980, **19**, 3632.
1793. M. Bonamico and G. Dessy, *J. Chem. Soc., Chem. Commun.*, 1968, 483.
1794. C. Bellito, A. Flamini, O. Piovesana and P. F. Zanazzi, *Inorg. Chem.*, 1979, **18**, 2258.
1795. C. Bellito, A. Flamini, L. Gastaldi and L. Scaramuzza, *Inorg. Chem.*, 1983, **22**, 444.
1796. J. M. Lisy, E. D. Dobrzynski, R. J. Angelici and J. Clardy, *J. Am. Chem. Soc.*, 1975, **97**, 656.
1797. W. P. Fehlhammer, A. Mayr and H. Stolzenberg, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 626.
1798. R. D. Bereman and D. Nalewajek, *Inorg. Chem.*, 1976, **15**, 2981.
1799. R. Bardi, A. M. Piazzesi and L. Sindellari, *Inorg. Chim. Acta*, 1980, **47**, 225.
1800. J. P. Fackler and D. Coucouvanis, *J. Am. Chem. Soc.*, 1966, **88**, 3913.
1801. J. P. Fackler and W. C. Seidel, *Inorg. Chem.*, 1969, **8**, 1631.
1802. J. Chatt, L. A. Duncanson and L. M. Venanzi, *Suom. Kemistil. B*, 1956, **29**, 75 (*Chem. Abstr.*, 1957, **51**, 5559d).
1803. K. Nakamoto, J. Fujita, R. A. Condrate and Y. Morimoto, *J. Chem. Phys.*,1963, **39**, 423.
1804. A. Z. Amanov, G. A. Kukina and M. A. Porai-Koshits, *Dokl. Akad. Nauk Az. SSR*, 1977, **33**, 24 (*Chem. Abstr.*, 1977, **87**, 209 741h).
1805. L. T. Chan, H. W. Chen, J. P. Fackler, A. F. Masters and W. H. Pan, *Inorg. Chem.*, 1982, **21**, 4291.
1806. W. Beck, M. Girnth, M. Castillo and H. Zippel, *Chem. Ber.*, 1978, **111**, 1246.
1807. R. D. Bereman and D. Nalewajek, *Inorg. Chem.*, 1977, **16**, 2687.
1808. R. Schierl and W. Beck, *Chem. Ber.*, 1982, **115**, 1665.
1809. J. P. Fackler, I. J. B. Lin and J. Andrews, *Inorg. Chem.*, 1977, **16**, 450.
1810. W. H. Pan, J. P. Fackler and H. W. Chen, *Inorg. Chem.*, 1981, **20**, 856.
1811. W. H. Pan and J. P. Fackler, *Inorg. Synth.*, 1982, **21**, 6.
1812. H. W. Chen, J. P. Fackler, A. F. Masters and W. H. Pan, *Inorg. Chim. Acta*, 1979, **35**, L333.
1813. J. P. Fackler and W. H. Pan, *J. Am. Chem. Soc.*, 1979, **101**, 1607.
1814. W. Kuchen and H. Hertel, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 89.
1815. J. M. C. Alison and T. A. Stephenson, *J. Chem. Soc., Chem. Commun.*, 1970, 1092.

1816. J. P. Fackler, J. A. Fetchin and W. C. Seidel, *J. Am. Chem. Soc.*, 1969, **91**, 1217.
1817. J. P. Fackler and L. D. Thompson, *Inorg. Chim. Acta*, 1981, **48**, 45.
1818. J. P. Fackler, L. D. Thompson, I. J. B. Lin, T. A. Stephenson, R. O. Gould, J. M. C. Alison and A. J. F. Fraser, *Inorg. Chem.*, 1982, **21**, 2397.
1819. I. J. B. Lin, H. W. Chen and J. P. Fackler, *Inorg. Chem.*, 1978, **17**, 394.
1820. J. P. Maier and D. A. Sweigart, *Inorg. Chem.*, 1976, **15**, 1989.
1821. A. Schmidpeter, K. Blanck and F. R. Ahmed, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 488.
1822. K. P. Wagner, R. W. Hess, P. M. Treichel and J. C. Calabrese, *Inorg. Chem.*, 1975, **14**, 1121.
1823. J. Browning, G. W. Bushnell, K. R. Dixon and A. Pidcock, *Inorg. Chem.*, 1983, **22**, 2226.
1824. S. H. H. Chaston and S. E. Livingstone, *Aust. J. Chem.*, 1967, **20**, 1065.
1825. S. H. H. Chaston and S. E. Livingstone, *Aust. J. Chem.*, 1967, **20**, 1079.
1826. L. P. Eddy, J. W. Hayes, S. E. Livingstone, H. L. Nigam and D. V. Radford, *Aust. J. Chem.*, 1971, **24**, 1071.
1827. E. A. Shugam, L. M. Shkol'nikova and S. E. Livingstone, *Zh. Strukt. Khim.*, 1967, **8**, 550 (*Chem. Abstr.*, 1968, **68**, 33 978g).
1828. M. Das and S. E. Livingstone, *J. Chem. Soc., Dalton Trans.*, 1975, 452.
1829. R. Belcher, W. I. Stephen, I. J. Thomson and P. C. Uden, *J. Chem. Soc., Chem. Commun.*, 1970, 1019.
1830. S. W. Schneller, *Int. J. Sulfur Chem.*, 1972, **78**, 295.
1831. A. R. Hendrickson and R. L. Martin, *Inorg. Chem.*, 1975, **14**, 979.
1832. W. L. Bowden, J. D. L. Holloway and W. E. Geiger, *Inorg. Chem.*, 1978, **17**, 256.
1833. G. A. Heath and J. H. Leslie, *J. Chem. Soc., Dalton Trans.*, 1983, 1587.
1834. J. J. Mayerle, *Inorg. Chem.*, 1977, **16**, 916.
1835. E. Billig, R. Williams, I. Bernal, J. H. Waters and H. B. Gray, *Inorg. Chem.*, 1964, **3**, 663.
1836. A. Davison and R. H. Holm, *Inorg. Synth.*, 1967, **10**, 8.
1837. A. Davison, N. Edelstein, R. H. Holm and A. H. Maki, *Inorg. Chem.*, 1964, **3**, 814.
1838. G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, 1965, **87**, 1483.
1839. D. C. Olson, V. P. Mayweg and G. N. Schrauzer, *J. Am. Chem. Soc.*, 1966, **88**, 4876.
1840. S. I. Shupack, E. Billig, R. J. H. Clark, R. Williams and H. B. Gray, *J. Am. Chem. Soc.*, 1964, **86**, 4594.
1841. H. B. Gray, *Transition Met. Chem.*, 1965, **1**, 240.
1842. S. O. Grim, L. J. Matienzo and W. E. Swartz, *Inorg. Chem.*, 1974, **13**, 447.
1843. W. E. Geiger, C. S. Allen, T. E. Mines and F. C. Senftleber, *Inorg. Chem.*, 1977, **16**, 2003.
1844. R. Kirmse, J. Stach and W. Dietzsch, *Inorg. Chim. Acta*, 1978, **29**, L181.
1845. R. Kirmse, J. Stach, W. Dietzsch, G. Steiniecke and E. Hoyer, *Inorg. Chem.*, 1980, **19**, 2679.
1846. G. A. Bowmaker, P. D. W. Boyd and G. K. Campbell, *Inorg. Chem.*, 1983, **22**, 1208.
1847. G. A. Bowmaker, P. D. W. Boyd and G. K. Campbell, *Inorg. Chem.*, 1982, **21**, 3565.
1848. R. J. H. Clark and P. C. Turtle, *J. Chem. Soc., Dalton Trans.*, 1977, 2142.
1849. A. Vogler and H. Kunkely, *Inorg. Chem.*, 1982, **21**, 1172.
1850. D. M. Dooley and B. M. Patterson, *Inorg. Chem.*, 1982, **21**, 4330.
1851. C. E. Johnson, R. Eisenberg, T. R. Evans and M. S. Burberry, *J. Am. Chem. Soc.*, 1983, **105**, 1795.
1852. L. V. Interrante, K. W. Browall, H. R. Hart, I. S. Jacobs, G. D. Watkins and S. H. Wee, *J. Am. Chem. Soc.*, 1975, **97**, 889.
1853. M. M. Ahmad and A. E. Underhill, *J. Chem. Soc., Dalton Trans.*, 1983, 165.
1854. B. K. Teo and P. A. Snyder-Robinson, *Inorg. Chem.*, 1979, **18**, 1490.
1855. J. J. Levison and S. D. Robinson, *J. Chem. Soc., Chem. Commun.*, 1967, 198.
1856. A. J. Layton, R. S. Nyholm, G. A. Pneumaticakis and M. L. Tobe, *Chem. Ind. (London)*, 1967, 465.
1857. R. R. Ryan, G. J. Kubas, D. C. Moody and P. G. Eller, *Struct. Bonding (Berlin)*, 1981, **46**, 47.
1858. D. C. Moody and R. R. Ryan, *Inorg. Chem.*, 1976, **15**, 1823.
1859. P. G. Eller, R. R. Ryan and D. C. Moody, *Inorg. Chem.*, 1976, **15**, 2442.
1860. J. M. Ritchey, D. C. Moody and R. R. Ryan, *Inorg. Chem.*, 1983, **22**, 2276.
1861. D. C. Moody and R. R. Ryan, *Inorg. Chem.*, 1977, **16**, 1052.
1862. J. M. Ritchey and D. C. Moody, *Inorg. Chim. Acta*, 1983, **74**, 271.
1863. C. E. Briant, D. G. Evans and D. M. P. Mingos, *J. Chem. Soc., Chem. Commun.*, 1982, 1144.
1864. M. C. Baird and G. Wilkinson, *J. Chem. Soc. (A)*, 1967, 865.
1865. R. Mason and A. I. M. Rae, *J. Chem. Soc. (A)*, 1970, 1767.
1866. H. Werner and M. Ebner, *J. Organomet. Chem.*, 1983, **258**, C52.
1867. T. R. Gaffney and J. A. Ibers, *Inorg. Chem.*, 1982, **21**, 2860.
1868. H. Stolzenberg and W. P. Fehlhammer, *J. Organomet. Chem.*, 1983, **246**, 105.
1869. J. W. Gosselink, G. van Koten, A. M. F. Brouwers and O. Overbeek, *J. Chem. Soc., Dalton Trans.*, 1981, 342.
1870. J. W. Gosselink, H. Bulthuis and G. van Koten, *J. Chem. Soc., Dalton Trans.*, 1981, 1342.
1871. J. W. Gosselink, G. van Koten, A. L. Spek and A. J. M. Duisenberg, *Inorg. Chem.*, 1981, **20**, 877.
1872. J. W. Gosselink, F. Paap and G. van Koten, *Inorg. Chim. Acta*, 1982, **59**, 155.
1873. S. W. Carr, R. Colton, D. Dakternieks, B. F. Hoskins and R. J. Steen, *Inorg. Chem.*, 1983, **22**, 3700.
1874. A. H. Norbury, *Adv. Inorg. Chem. Radiochem.*, 1975, **17**, 231.
1875. R. N. Keller, N. B. Johnson and L. L. Westmoreland, *J. Am. Chem. Soc.*, 1968, **90**, 2729.
1876. P. S. Pregosin, H. Streit and L. M. Venanzi, 1980, **38**, 237.
1877. C. P. Cheng, T. L. Brown, W. C. Fultz and J. L. Burmeister, *J. Chem. Soc., Chem. Commun.*, 1977, 599.
1878. Y. S. Wong, S. Jacobson, P. C. Chieh and A. J. Carty, *Inorg. Chem.*, 1974, **13**, 284.
1879. A. J. Carty, *Inorg. Chem.*, 1976, **15**, 1956.
1880. R. J. Dickinson, W. Levason, C. A. McAuliffe and R. V. Parish, *Inorg. Chem.*, 1976, **15**, 2934.
1881. G. P. McQuillan and I. A. Oxton, *J. Chem. Soc., Dalton Trans.*, 1978, 1460.
1882. S. J. Anderson and R. J. Goodfellow, *J. Chem. Soc., Dalton Trans.*, 1977, 1683.
1883. S. J. Anderson, P. L. Goggin and R. J. Goodfellow, *J. Chem. Soc., Dalton Trans.*, 1976, 1959.
1884. P. H. Kreutzer, K. T. Schorpp and W. Beck, *Z. Naturforsch., Teil B*, 1975, **30**, 544.
1885. U. A. Gregory, J. A. Jarvis, B. T. Kilbourn and P. J. Owston, *J. Chem. Soc. (A)*, 1970, 2770.

1886. K. Broderson, G. Thiele and H. G. Schnering, *Z. Anorg. Allg. Chem.*, 1965, **337**, 120.
1887. B. Corain and A. J. Poë, *J. Chem. Soc. (A)*, 1967, 1318.
1888. C. M. Harris, S. E. Livingstone and N. C. Stephenson, *J. Chem. Soc.*, 1958, 3697.
1889. D. C. Harris and H. B. Gray, *Inorg. Chem.*, 1974, **13**, 2250.
1890. R. N. Keller, *Inorg. Synth.*, 1946, **2**, 247.
1891. W. E. Cooley and D. H. Busch, *Inorg. Synth.*, 1957, **5**, 208.
1892. A. H. Cohen, *Inorg. Synth.*, 1960, **6**, 209.
1893. K. R. Dixon, D. W. A. Sharp and A. G. Sharpe, *Inorg. Synth.*, 1970, **12**, 232.
1894. L. E. Cox and D. G. Peters, *Inorg. Synth.*, 1972, **13**, 173.
1895. J. A. Abys, N. P. Enright, H. M. Gerdes, T. L. Hall and J. M. Williams, *Inorg. Synth.*, 1979, **19**, 2.
1896. G. T. Kerr and A. E. Schweizer, *Inorg. Synth.*, 1980, **20**, 48.
1897. G. B. Kauffman and L. A. Teter, *Inorg. Synth.*, 1963, **7**, 232.
1898. R. D. W. Kemmitt, R. D. Peacock and J. Stocks, *J. Chem. Soc. (A)*, 1971, 846.
1899. M. A. Cairns, K. R. Dixon and J. J. McFarland, *J. Chem. Soc., Dalton Trans.*, 1975, 1159.
1900. D. R. Russell, M. A. Mazid and P. A. Tucker, *J. Chem. Soc., Dalton Trans.*, 1980, 1737.
1901. J. Howard and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1973, 1840.
1902. D. F. Evans and G. K. Turner, *J. Chem. Soc., Dalton Trans.*, 1975, 1238.
1903. A. K. Shukla and W. Preetz, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 151.
1904. A. E. Schweizer and G. T. Kerr, *Inorg. Chem.*, 1978, **17**, 2326.
1905. D. E. Webster, *Adv. Organomet. Chem.*, 1977, **15**, 147.
1906. (a) J. R. Saunders, D. E. Webster and P. B. Wells, *J. Chem. Soc., Dalton Trans.*, 1975, 1191. (b) G. B. Shul'pin, G. V. Nizova and A. E. Shilov, *J. Chem. Soc., Chem. Commun.*, 1983, 671.
1907. M. F. Pilbrow, *J. Chem. Soc., Dalton Trans.*, 1975, 2432.
1908. G. W. Bushnell, A. Pidcock and M. A. R. Smith, *J. Chem. Soc., Dalton Trans.*, 1975, 572.
1909. G. K. Anderson, H. C. Clark and J. A. Davies, *Inorg. Chem.*, 1981, **20**, 944.
1910. A. A. Kiffen, C. Masters and J. P. Visser, *J. Chem. Soc., Dalton Trans.*, 1975, 1311.
1911. P. R. Brookes and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1973, 783.
1912. C. E. Briant, K. A. Rowland, C. T. Webber and D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.*, 1981, 1515.
1913. R. J. Goodfellow, P. L. Goggin and D. A. Duddell, *J. Chem. Soc. (A)*, 1968, 504.
1914. D. M. Adams, J. Chatt, J. Gerratt and A. D. Westland, *J. Chem. Soc.*, 1964, 734.
1915. R. J. Goodfellow, P. L. Goggin and L. M. Venanzi, *J. Chem. Soc. (A)*, 1967, 1897.
1916. P. L. Goggin and J. Mink, *J. Chem. Soc., Dalton Trans.*, 1974, 1479.
1917. L. A. Woodward and J. A. Creighton, *Spectrochim. Acta*, 1961, **17**, 594.
1918. P. Labonville, J. R. Ferraro, S. M. C. Wall and L. J. Basile, *Coord. Chem. Rev.*, 1972, **7**, 257.
1919. Y. M. Bosworth and R. J. H. Clark, *J. Chem. Soc., Dalton Trans.*, 1974, 1749.
1920. P. L. Goggin and J. Mink, *Inorg. Chim. Acta*, 1978, **26**, 119.
1921. D. M. Adams and R. W. Berg, *J. Chem. Soc., Dalton Trans.*, 1976, 52.
1922. D. M. Adams and D. C. Newton, *J. Chem. Soc. (A)*, 1969, 2998.
1923. D. M. Adams and D. J. Hills, *J. Chem. Soc., Dalton Trans.*, 1977, 947.
1924. D. M. Adams and S. J. Payne, *J. Chem. Soc., Dalton Trans.*, 1975, 215.
1925. C. K. Jørgensen, "Modern Aspects of Ligand Field Theory", Elsevier, New York, 1971.
1926. A. B. P. Lever, 'Inorganic Electronic Spectroscopy', Elsevier, New York, 1968.
1927. C. J. Ballhausen and H. B. Gray, *ACS Monogr. Ser.*, 1971, **168**, ACS Monograph 168, ed. A. E. Martell, Reinhold, New York, 1971.
1928. C. J. Ballhausen, 'Introduction to Ligand Field Theory', McGraw-Hill, New York, 1962.
1929. L. G. Van Quickenborne and A. Ceulemans, *Inorg. Chem.*, 1981, **20**, 796.
1930. J. L. H. Batiste and R. Rumfeldt, *Can. J. Chem.*, 1974, **52**, 174.
1931. R. P. Messmer, L. V. Interrante and K. H. Johnson, *J. Am. Chem. Soc.*, 1974, **96**, 3847.
1932. B. G. Anex and N. Takeuchi, *J. Am. Chem. Soc.*, 1974, **96**, 4411.
1933. R. F. Kroening, R. M. Rush, D. S. Martin and J. C. Clardy, *Inorg. Chem.*, 1974, **13**, 1366.
1934. T. J. Peters, R. F. Kroenig and D. S. Martin, *Inorg. Chem.*, 1978, **17**, 2302.
1935. H. H. Patterson, T. G. Harrison and R. J. Belair, *Inorg. Chem.*, 1976, **15**, 1461.
1936. H. Yersin, H. Otto, J. I. Zink and G. Gliemann, *J. Am. Chem. Soc.*, 1980, **102**, 951.
1937. C. D. Cowman, J. C. Thibeault, R. F. Ziolo and H. B. Gray, *J. Am. Chem. Soc.*, 1976, **98**, 3209.
1938. D. S. Martin, R. M. Rush and T. J. Peters, *Inorg. Chem.*, 1976, **15**, 669.
1939. C. K. Jørgensen, *Acta Chem. Scand.*, 1956, **10**, 518.
1940. G. N. Henning, P. A. Dobosh, A. J. McCaffery and P. N. Schatz, *J. Am. Chem. Soc.*, 1970, **92**, 5377.
1941. D. L. Swihart and W. R. Mason, *Inorg. Chem.*, 1970, **9**, 1749.
1942. H. H. Patterson, W. J. DeBerry, J. E. Byrne, M. T. Hsu and J. A. LoMenzo, *Inorg. Chem.*, 1977, **16**, 1698.
1943. W. Beck and F. Holsboer, *Z. Naturforsch., Teil B*, 1973, **28**, 511.
1944. D. T. Clark, D. Briggs and D. B. Adams, *J. Chem. Soc., Dalton Trans.*, 1973, 169.
1945. E. P. Marram, E. J. McNiff and J. L. Ragle, *J. Phys. Chem.*, 1963, **67**, 1719.
1946. K. Ito, D. Nakamura, Y. Kurito, K. Ito and M. Kubo, *J. Am. Chem. Soc.*, 1961, **83**, 4526.
1947. K. Ito, D. Nakamura and M. Kubo, *Bull. Chem. Soc. Jpn.*, 1962, **35**, 518.
1948. D. Nakamura and M. Kubo, *J. Phys. Chem.*, 1964, **68**, 2986.
1949. D. Nakamura, Y. Kurita, K. Ito and M. Kubo, *J. Am. Chem. Soc.*, 1960, **82**, 5783.
1950. R. J. Dickinson, R. V. Parish and B. W. Dale, *J. Chem. Soc., Dalton Trans.*, 1980, 895.
1951. G. M. Bancroft and K. D. Butler, *J. Am. Chem. Soc.*, 1974, **96**, 7208.
1952. L. V. Interrante, K. W. Browall and F. P. Bundy, *Inorg. Chem.*, 1974, **13**, 1158.
1953. L. V. Interrante and K. W. Browall, *Inorg. Chem.*, 1974, **13**, 1162.
1954. L. V. Interrante, *ACS Symp. Ser.*, 1975, **5**, "Transition Metal Complexes", ACS Symp. Ser., 1975, Vol. 5.
1955. O. Bekaroglu, H. Breer, H. Endres, H. J. Keller and H. N. Gung, *Inorg. Chim. Acta*, 1977, **21**, 183.
1956. N. Matsumoto, M. Yamashita and S. Kida, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 2334.

1957. N. Matsumoto, M. Yamashita and S. Kida, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 3514.
1958. T. N. Fedotova, I. F. Golovaneva and O. N. Adrianova, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1981, **26**, 1336.
1959. M. H. Whangbo and M. J. Foshee, *Inorg. Chem.*, 1981, **20**, 113.
1960. C. N. Lai and A. T. Hubbard, *Inorg. Chem.*, 1974, **13**, 1199.
1961. R. J. H. Clark and W. R. Trumble, *Inorg. Chem.*, 1976, **15**, 1030.
1962. R. J. H. Clark and P. C. Turtle, *Inorg. Chem.*, 1978, **17**, 2526.
1963. R. J. H. Clark, M. Kurmoo, H. J. Keller, B. Keppler and U. Traeger, *J. Chem. Soc., Dalton Trans.*, 1980, 2498.
1964. R. J. H. Clark and M. Kurmoo, *J. Chem. Soc., Dalton Trans.*, 1981, 524.
1965. R. J. H. Clark, M. Kurmoo, A. M. R. Galas and M. B. Hursthouse, *Inorg. Chem.*, 1981, **20**, 4206.
1966. S. Ahmad, R. J. H. Clark and M. Kurmoo, *J. Chem. Soc., Dalton Trans.*, 1982, 1371.
1967. R. J. H. Clark, M. Kurmoo, D. M. Mountney and H. Toftlund, *J. Chem. Soc., Dalton Trans.*, 1982, 1851.
1968. R. J. H. Clark, M. Kurmoo, A. M. R. Galas and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1982, 2505.
1969. R. J. H. Clark and M. Kurmoo, *J. Chem. Soc., Dalton Trans.*, 1982, 2515.
1970. R. J. H. Clark and M. Kurmoo, *J. Chem. Soc., Dalton Trans.*, 1983, 761.
1971. R. J. H. Clark, M. Kurmoo, A. M. R. Galas and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1983, 1583.
1972. N. Bartlett, *Proc. Chem. Soc.*, 1962, 218.
1973. N. Bartlett, F. Einstein, D. F. Stewart and J. Trotter, *Chem. Commun.*, 1966, 550.
1974. N. Bartlett, F. Einstein, D. F. Stewart and J. Trotter, *J. Chem. Soc.* (*A*), 1967, 1190.
1975. R. J. Gillespie and G. J. Schrobilgen, *Inorg. Chem.*, 1976, **15**, 22.
1976. W. Klotzbucher and G. A. Ozin, *Inorg. Chem.*, 1976, **15**, 292.
1977. J. O. Edwards, 'Inorganic Reaction Mechanisms', Benjamin, New York, 1964.
1978. L. Cattalini, *Prog. Inorg. Chem.*, 1970, **13**, 263.
1979. W. R. Mason, *Coord. Chem. Rev.*, 1972, **7**, 241.
1980. G. K. Anderson and R. J. Cross, *Chem. Soc. Rev.*, 1980, **9**, 185.
1981. D. S. Martin, *Inorg. Chim. Acta*, 1967, **1**, 87.
1982. M. L. Tobe, 'Inorganic Reaction Mechanisms', Nelson, London, 1972.
1983. F. R. Hartley, *Chem. Soc. Rev.*, 1973, **2**, 163.
1984. J. K. Burdett, *Inorg. Chem.*, 1977, **16**, 3013.
1985. D. R. Armstrong, R. Fortune, P. G. Perkins, R. J. Dickinson and R. V. Parish, *Inorg. Chim. Acta*, 1976, **17**, 73.
1986. F. Basolo, J. Chatt, H. B. Gray, R. G. Pearson and B. L. Shaw, *J. Chem. Soc.*, 1961, 2207.
1987. F. Basolo, H. B. Gray and R. G. Pearson, *J. Am. Chem. Soc.*, 1960, **82**, 4200.
1988. H. B. Gray and R. J. Olcott, *Inorg. Chem.*, 1962, **1**, 481.
1989. C. Bartocci, A. Ferri, V. Carassiti and F. Scandola, *Inorg. Chim. Acta*, 1977, **24**, 251.
1990. D. A. Palmer and H. Kelm, *Inorg. Chim. Acta*, 1976, **19**, 117.
1991. J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, 1962, **84**, 16.
1992. M. Bonivento, L. Cattalini, G. Marangoni, G. Michelon, A. Schwab and M. L. Tobe, *Inorg. Chem.*, 1980, **19**, 1743.
1993. G. Annibale, L. Canovese, L. Cattalini, G. Marangoni, G. Michelon and M. L. Tobe, *Inorg. Chem.*, 1981, **20**, 2428.
1994. G. Annibale, L. Canovese, L. Cattalini, G. Marangoni, G. Michelon and M. L. Tobe, *J. Chem. Soc., Dalton Trans.*, 1983, 775.
1995. C. I. Sanders and D. S. Martin, *J. Am. Chem. Soc.*, 1961, **83**, 807.
1996. L. I. Elding and I. Leden, *Acta Chem. Scand.*, 1966, **20**, 706.
1997. L. Elding, *Acta Chem. Scand.*, 1970, **24**, 1331, 1341, 1527, 2546, 2557.
1998. M. Green and M. G. Swanwick, *J. Chem. Soc., Dalton Trans.*, 1978, 158.
1999. A. K. Johnson and J. D. Miller, *Inorg. Chim. Acta*, 1976, **16**, 93.
2000. L. F. Grantham, T. S. Ellemann and D. S. Martin, *J. Am. Chem. Soc.*, 1955, **77**, 2965.
2001. K. W. Lee and D. S. Martin, *Inorg. Chim. Acta*, 1976, **17**, 105.
2002. L. I. Elding, *Inorg. Chim. Acta*, 1978, **28**, 255.
2003. J. K. Beattie, *Inorg. Chim. Acta*, 1983, **76**, L69.
2004. L. I. Elding and A. B. Groning, *Inorg. Chim. Acta*, 1978, **31**, 243.
2005. J. A. Davies, F. R. Hartley and S. G. Murray, *Inorg. Chem.*, 1980, **19**, 2299.
2006. L. Cattalini and M. Martelli, *J. Am. Chem. Soc.*, 1969, **91**, 312.
2007. W. J. Louw, *Inorg. Chem.*, 1977, **16**, 2147.
2008. J. R. Perumareddi and A. W. Adamson, *J. Phys. Chem.*, 1968, **72**, 414.
2009. (a) M. Chanon and M. L. Tobe, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 1. (b) M. Julliard and M. Chanon, *Chem. Rev.*, 1983, **83**, 425.
2010. G. M. Summa and B. A. Scott, *Inorg. Chem.*, 1980, **19**, 1079.
2011. L. T. Cox, S. B. Collins and D. S. Martin, *J. Inorg. Nucl. Chem.*, 1961, **17**, 383.
2012. H. Taube, *Adv. Inorg. Chem. Radiochem.*, 1959, **1**, 1.
2013. A. Peloso, *Gazz. Chim. Ital.*, 1969, **99**, 1025.
2014. R. C. Johnson, F. Basolo and R. G. Pearson, *J. Inorg. Nucl. Chem.*, 1962, **24**, 59.
2015. G. Dolcetti, A. Peloso and M. L. Tobe, *J. Chem. Soc.*, 1965, 5196.
2016. G. Dolcetti and A. Peloso, *Gazz. Chim. Ital.*, 1967, **97**, 1540.
2017. B. Corain and A. J. Poë, *J. Chem. Soc.* (*A*), 1967, 1633.
2018. E. J. Boounsall, D. J. Hewkin, D. Hopgood and A. J. Poë, *Inorg. Chim. Acta*, 1967, **1**, 281.
2019. D. W. Johnson and A. Poë, *Can. J. Chem.*, 1974, **52**, 3083.
2020. L. I. Elding and L. Gustafson, *Inorg. Chim. Acta*, 1977, **22**, 201.
2021. L. I. Elding and L. Gustafson, *Inorg. Chim. Acta*, 1977, **24**, 239.
2022. A. J. Poë and D. H. Vaughan, *J. Am. Chem. Soc.*, 1970, **92**, 7537.
2023. J. K. Beattie and F. Basolo, *Inorg. Chem.*, 1971, **10**, 486.

2024. M. M. Jones and K. A. Morgan, *J. Inorg. Nucl. Chem.*, 1972, **34**, 259.
2025. K. A. Morgan and M. M. Jones, *J. Inorg. Nucl. Chem.*, 1972, **34**, 275.
2026. K. D. Hodges and J. V. Rund, *Inorg. Chem.*, 1975, **14**, 525.
2027. K. D. Buse, H. J. Keller and H. Pritzkow, *Inorg. Chem.*, 1977, **16**, 1072.
2028. S. Al-Jibori, C. Crocker, W. S. McDonald and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1981, 2589.
2029. J. K. Beattie and F. Basolo, *Inorg. Chem.*, 1967, **6**, 2069.
2030. M. Basato and A. Peloso, *Gazz. Chim. Ital.*, 1972, **102**, 893.
2031. A. Peloso and M. Basato, *Coord. Chem. Rev.*, 1972, **8**, 111.
2032. A. Bakac, T. D. Hand and A. G. Sykes, *Inorg. Chem.*, 1975, **14**, 2540.
2033. J. K. Beattie and J. Starink, *Inorg. Chem.*, 1975, **14**, 996.
2034. K. G. Moodley and M. J. Nicol, *J. Chem. Soc., Dalton Trans.*, 1977, 239.
2035. S. Al-Jibori, C. Crocker and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1981, 319.
2036. J. Halpern and M. Pribanic, *J. Am. Chem. Soc.*, 1968, **90**, 5942.
2037. K. G. Moodley and M. J. Nicol, *J. Chem. Soc., Dalton Trans.*, 1977, 993.
2038. A. Peloso, *J. Chem. Soc., Dalton Trans.*, 1978, 699.
2039. A. Peloso, *J. Chem. Soc., Dalton Trans.*, 1983, 1285.
2040. R. L. Rich and H. Taube, *J. Am. Chem. Soc.*, 1954, **76**, 2608.
2041. A. W. Adamson and A. H. Sporer, *J. Am. Chem. Soc.*, 1958, **80**, 3865.
2042. R. Dreyer, K. Konig and H. Schmidt, *Z. Phys. Chem.* (*Leipzig*), 1964, **227**, 257.
2043. R. Dreyer, *Z. Phys. Chem.* (*Frankfurt am Main*), 1961, **29**, 347.
2044. R. C. Wright and G. S. Laurence, *J. Chem. Soc., Chem. Commun.*, 1972, 132.

53
Copper

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53.1 INTRODUCTION

Copper is one of the more abundant elements in the earth's crust (68 p.p.m.); it is about 20th in the order of abundance, occurring at a concentration of about 100 g per ton of the earth's crust.[1] It occurs in group Ib of the Mendeleev form of the periodic table (Table 1a),[2] or alternatively in the first-row transition metals (Ni, Cu, Zn) in the long form of the periodic table (Table 1b),[3] or in group 11*d* in the new long form of the periodic table (Table 1c) recently proposed by the American Chemical Society.[4]

Table 1 The Three Notations of the Periodic Table: (a) the Mendeleev Form, (b) the Long Form and (c) the New Long Form of the American Chemical Society

(a)	1A	2A	3A	4A	5A	6A	7A	8	8	8	1B	2B	3B	4B	5B	6B	7B	8B
(b)	I	II											III	IV	V	VI	VII	VIII
(c)	1	2	3*d*	4*d*	5*d*	6*d*	7*d*	8*d*	9*d*	10*d*	11*d*	12*d*	13	14	15	16	17	18
	H																	He
	Li	Be											B	C	N	O	F	Ne
	Na	Mg											Al	Si	P	S	Cl	Ar
	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
	Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
	Fr	Ra	Ac**															
			3*p**Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
			**Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

Copper has the electronic configuration (argon)$4s^23d^9$ and can occur naturally as the free element (see ref. 5 for the physical properties of the free metal), but it occurs more commonly combined in such minerals as malachite, $CuCO_3{\cdot}Cu(OH)_2$, and azurite, $[2\{Cu(CO_3)_2\}{\cdot}Cu(OH)_2]$.[6] The element is obtained from its ores by various reduction processes,[6] and is refined electrolytically.[5] Copper and its salts are highly toxic to lower organisms,[7] and it is also poisonous to man in large quantities, but at a much lower concentration it is an essential constituent of proteins and enzymes (see Section 53.4.8).[8] Like other transition metals copper is very important as a catalyst in the oxidation of organic molecules by atmospheric oxygen (see Section 53.3.4).[9]

Copper is a typical transition element in that it is a metal; it occurs in a range of oxidation states and the ions readily form complexes, yielding an extensive variety of coordination compounds. The oxidation states cover the range copper(0) in the metal, copper(I) in the cuprous compounds, copper(II) in cupric compounds, and copper(III) and (IV); the copper(0) and copper(IV) states are extremely limited. The copper(III) oxidation state is significantly more common, but has only been clearly characterized for 20–30 compounds or complexes,[10] although it is extensively invoked as an intermediate oxidation state in mechanistic studies,[11] especially those involving amino acid species. The copper(I) and copper(II) oxidation states are by far the most abundant oxidation states of copper; copper(II) is the more stable of the two under normal conditions and forms a wealth of simple compounds and coordination complexes (see Section 53.4.1).[12] The copper(I) state is less extensive and is readily oxidized to the copper(II) state (see Section 53.3).[5,12] The copper(II) oxidation state is not only the most stable of all the states, but is also the most prolific in the formation of complexes and in the formation of good crystals.[5,12,13] The latter circumstance has led to a wealth of crystal structure determinations to characterize the various regular and distorted stereochemistries of the copper(II) ion,[10,14] which are associated with the influence of the Jahn–Teller effect[15] (see Section 53.4.5).

The chemical literature on copper is now very extensive. Useful early source books on simple compounds of copper and its complexes must include the texts by J. R. Partington,[6] M. V. Sidgwick,[12] P. J. Durant and B. Durant,[16] and F. A. Cotton and G. Wilkinson.[17] The early structural chemistry of copper is described in Wychoff[18] and in the relevant sections of the five editions of A. F. Wells's 'Structural Inorganic Chemistry'.[10] More recent textbooks such as the fourth edition of 'Advanced Inorganic Chemistry' by F. A. Cotton and G. Wilkinson,[17] 'Introduction to Modern Inorganic Chemistry' by K. M. Mackay and R. A. Mackay,[19] the third edition of J. E. Huheey's 'Inorganic Chemistry'[20] and 'Chemistry of the Elements' by N. N. Greenwood and A. Earnshaw[21] contain the most up-to-date textbook accounts of the chemistry of copper(I), copper(II), copper(III) and copper(IV). More specific reviews of copper(II) complexes[22] and of copper(I) complexes[23] have been published and many specialized accounts of aspects of copper chemistry have been produced, especially since 1970, and will be referred to in the relevant sections. The increasing awareness of the importance of copper in biological systems has resulted in books devoted to copper, namely 'The Biochemistry of Copper' by J. Peisach, P. Aisen and W. E. Blumberg,[24] and 'Copper Proteins' by T. G. Spiro,[25] while a significant amount of copper chemistry appears in 'Biological Chemistry' by E. I. Ochiai,[26] 'Transition Metals in Biochemistry' by A. S. Brill,[27] 'The Inorganic Chemistry of Biological Systems' by M. N. Hughes[28] and 'An Introduction to Bio-Inorganic Chemistry' by R. W. Hays.[28] The series 'Metal Ions in Biological Systems', edited by H. Sigel,[29] contains a number of excellent reviews of the role of copper in biological systems, with Volumes 12 and 13 being devoted entirely to copper. However, the most up-to-date account of copper coordination chemistry appears in 'Copper Coordination Chemistry: Biochemical and Inorganic Perspectives' by K. D. Karlin and J. Zubieta.[30]

53.2 COPPER(0)

This is a very restricted oxidation state of copper but may be considered to occur in the polynuclear copper species Cu_2, Cu_3 and Cu_5,[31] which have been characterized by matrix isolation techniques. Copper(0) also occurs in species formed by the reaction of copper metal vapour and carbon monoxide gas. Matrix isolation techniques have characterized a monomeric $[Cu(CO)_3]$ trigonal planar species and a dimeric $[(CO)_3CuCu(CO)_3]$ species.[32]

53.3 COPPER(I)

The chemistry of copper(I) is very much less extensive than that of copper(II) and a number of accounts occur[5,6,10,12,17,20,21] which describe the chemistry of simple compounds of copper(I) with less emphasis on the formation of coordination compounds of copper(I).[10,13,17,22] During the past 20 years the realization that a copper(I) species may be involved as the precursor of the silent partner in the type III copper proteins[24,25,29] has resulted in a renaissance in the coordination chemistry of copper(I) compounds,[10,17,30] which is reflected in the amount of space given to the chemistry of copper(I) and (II) in 'Advanced Inorganic Chemistry' by F. A. Cotton and G. Wilkinson. In the first edition in 1952,[17a] more space was devoted to copper(II) than to copper(I), while in the fourth edition[17d] the space allocation is reversed. A useful account of the structural chemistry of copper(I) appears in the successive editions of 'Structural Inorganic Chemistry' by A. F. Wells[10] and the first clear description of the coordination chemistry of copper(I), by F. H. Jardine,[23] was published in 1975. A substantial account of three-coordinate copper(I) also appeared[33] in 1977 and two reviews of sulfur complexes which have included copper(I) complexes have appeared,[34,35] but due to the biological importance of copper(I) in coordination chemistry, the most up-to-date account[30] of a number of aspects of the chemistry of copper(I) appears in 'Copper Coordination Chemistry: Biochemical and Inorganic Perspectives' by K. D. Karlin and J. Zubieta. Various aspects of the coordination chemistry of copper(I), including preparative, structural, spectroscopic and redox properties, are discussed, and emphasize the possible role of copper(I) coordination chemistry, not only in biological systems (Section 53.3.5), but also in copper(I/II) systems as a catalyst in O_2 redox processes (Section 53.3.4), an area that may turn out to be of comparable importance to the biological origin in the renaissance in the coordination chemistry of copper(I).[30]

53.3.1 Preparation of Copper(I) Complexes

The copper(I)[23] and copper(II)[22] ions can readily form complexes in which the cations act a Lewis acids and the ligands as Lewis bases.[36] While copper(II) is generally considered borderline hard acid, copper(I) clearly behaves as a soft acid and the order of stability of th ligand to copper(I) is that of a soft base class b behaviour (Table 2).[36] In general the halide can form a wide range of complexes, with the Cl^-, Br^- and I^- ions predominant, but with ver few examples of the F^- ion acting as a ligand.[37] With O, S, N and P ligands, while O and N ligands dominate the chemistry of copper(II),[22] S and P ligands are more frequent in copper(I chemistry.[23] This reversal of ligand role is also influenced by the reducing properties of many S P and I^- ligands and the ready reduction of the copper(II) ion (equation 1) to a stabl copper(I) species with these ligands when this preparative reduction route is used (Figure 1) Where reduction is not required, as in preparations using copper(I), *e.g.* $Cu^{I}X$, or startin materials such as $[Cu(NCMe)_4](X)$ (Figures 2 and 3), copper(I) complexes involving nitroge ligands, such as pyridine, bipy, en and dien, are becoming more common (see later).[23,38] I aqueous solution the reaction (1) is a quantitative process that may be used for the estimation[4] of the copper(II) ion, and the electrode potentials of the reaction (equations 2 and 3) readil lead to the disproportionation shown in equation (4).[10] Consequently, the concentration of th Cu^+ ion in aqueous solution is extremely low (of the order of $K = 10^6$ for equation 4) compare with the indefinite stability of the Cu^{2+}(aq) cation. As a result there is virtually no aqueou solution chemistry of the copper(I) ion, compared with the extensive chemistry of th $[Cu(OH_2)_6]^{2+}$ ion. For this reason water is rarely found as a ligand to copper(I), but is common ligand in copper(II) chemistry (Section 53.4).[22] The electrode potentials of equation (2)–(4) are readily modified by complex formation with appropriate ligands (Table 3).[23] In thi way the concentration of copper(I) in aqueous solution can be significantly increased b complex formation, such as in the $[CuCl_2]^-$ and $[Cu(CN)_2]^-$ anions (Figure 1), by addition of a excess of the appropriate ligand. Alternatively, complex formation may be effected by the us of an appropriate nonaqueous solvent, for example acetonitrile,[39–41] in which the solvent i known to be a good ligand to the copper(I) ion and to form stable complexes, such as th $[Cu(NCMe)_4]^+$ cation,[40] which has been shown by X-ray crystallography to involve a regula tetrahedral CuN_4 chromophore stereochemistry.[43] As many ligands such as 2,2′-bipyrid (bipy) or triphenylphosphine are not very soluble in water, the use of acetonitrile or alcohol a a solvent increases the dissolution of the required ligand and the concentration of the require complex. Together they increase the possibility of obtaining crystalline products and hence th possibility of obtaining single crystals suitable for X-ray crystallographic analysis. An adde advantage of acetonitrile as a solvent is that a corresponding anhydrous copper(II) comple may also be soluble in this solvent and may be used as a starting material in the preparation followed by reduction by either: (a) a reducing ligand, PR_3, I^-, CN^-, *etc.* (Figure 1); (b refluxing a copper(II) complex with copper metal (Figures 1 and 3); or (c) electrolyti reduction in water, acetonitrile or dimethylformamide (DMF) (Figure 3). Thu $Cu(NO_3)_2 \cdot 3H_2O$ is readily soluble in acetonitrile and the solution can be dehydrated by boilin with dimethyloxypropane and the solution then reduced by refluxing with copper metal to yiel the anhydrous $[Cu(NCMe)_4]^+$ cation in a nonaqueous solution.[44]

Table 2 Classification of Hard and Soft Acids and Bases. (a) Metal Ion and (b) Ligands[36]

	Hard	*Borderline*	*Soft*
(a)	—	Copper(II)	Copper(I)
(b)	$F > Cl > Br > I$		$F^- < Cl^- < Br^- < I^-$
	$O \gg S > Se > Te$		$O \ll S \approx Se \approx Te$
	$N \gg P > As > Sb > Bi$		$N \ll P > As > Sb > Bi$

$$2Cu^{II} + 4I^- \longrightarrow Cu_2I_2 + I_2 \qquad (1)$$

(a) $CuCl_2 \cdot 3H_2O + KCl \xrightarrow{SO_2(aq)} K[CuCl_2]$

(b) $CuBr_2 + KBr \xrightarrow[aq]{boil} K[CuBr_2]$

(c) $K[CuI_2] \xleftarrow{excess\ KI} Cu^{2+}(aq) + KI \longrightarrow Cu_2I_2$

(d) $K[Cu(CN)_2] \xleftarrow{excess\ KCN} Cu^{2+} + KCN \longrightarrow Cu_2CN_2$

Figure 1 Preparation of copper(I)-halide-containing complexes[23]

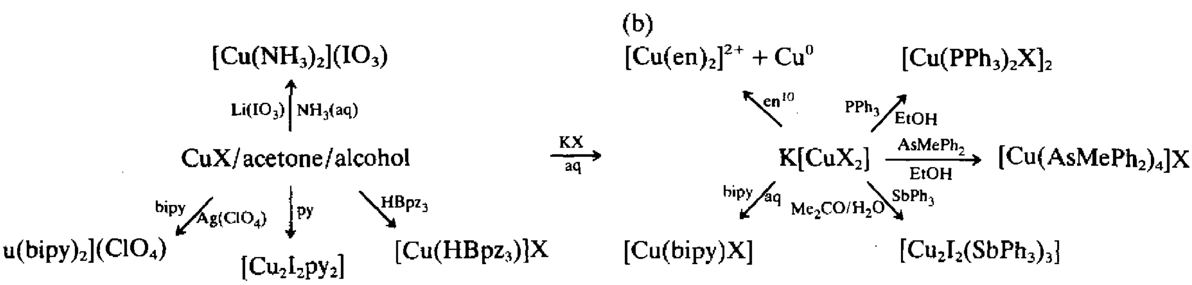


Figure 2 Preparations from (a) CuX and (b) $K[CuX_2]$[23,28]

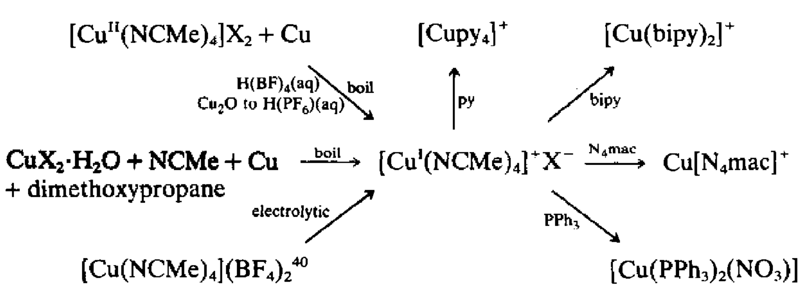


Figure 3 Preparation from $[Cu(NCMe)_4]X$ complexes[39–41,44]

$$Cu^+(aq) + e^- \longrightarrow Cu^0(aq) \qquad E^\circ = 0.52\ V \qquad (2)$$

$$Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq) \qquad E^\circ = 0.15\ V \qquad (3)$$

$$2Cu^+ \longrightarrow Cu^0 + Cu^{2+} \qquad E^\circ = 0.37\ V \qquad (4)$$

Table 3 (a) Reduction Potentials of Some $Cu^{II/I}$ Couples[26] and (b) Cu^{II}/Cu^{I2} Ratios[10]

(a) *I/II Couple*	*Potential* (mV)	(b) *Ligand*	Cu^{II}/Cu^{I2}
CN^-	+1120	en	10^5
I^-	+860	Me_3en	10^4
Cl^-	+460	Me_5en	3×10^{-2}
In laccasse	+420	NH_3	2×10^{-2}
In ceruloplasmin	+390		
py	+300		
phen	+170		
OH_2	+150		
bipy	+120		
NH_3	−10		
Glycinate	−160		
Oxalate	<−200		

Such preparative routes will be very dependent on the ligand lability of the $[Cu(NCMe)_4]^+$ cation to substitution by 'stronger' ligands, such as the traditional ligands like bipy and Ph_3P, but have assumed an even more sensitive preparative role where relatively 'weak' donor ligands [to copper(I)] are involved. Thus the formation of copper(I) carbonyl[38] and alkene[45] complexes (see Sections 53.3.2.9 and 53.3.2.10) has made fruitful use of the $[Cu(NCMe)_4]^+$ cation in nonaqueous solution as a preparative medium (Figure 3). For more details of the preparative routes using CuX and $MCuX_2$ complexes the reader is referred to refs. 23 and 38, and for the use of $[Cu(NCMe)_4]X$ complexes, to the original literature[39] and to the reviews in ref. 30.

In most of these preparations the products are sensitive to atmospheric oxygen and the preparations must be carried out under a nitrogen atmosphere and the product handled under a nitrogen atmosphere. In the X-ray structure determination of such oxygen sensitive materials, the general practice is to use a crystal mounted under nitrogen in a Lindemann glass capillary,[45] sometimes in the presence of a drop of the original mother liquor from which the crystals were grown.

53.3.2 Stereochemistry of Copper(I) Complexes

The electronic configuration of copper(I), (argon)$3d^{10}$, involves a filled $3d$ shell and hence spherical symmetry for the Cu^+ ion, in contrast to the nonspherical symmetry of the (argon)$3d^9$ configuration of the copper(II) ion (see Section 53.3).[46–48] As a consequence of the different charges, the copper(I) ion is larger than the copper(II) ion, but by how much is less clear. Pauling gives the crystal radius of the Cu^+ ion as 0.96 Å and that of Cu^{2+} as 0.73–0.77 Å.[49] More realistically, Huheey quotes different values for different coordination numbers (Table 4) and the most comparable coordination number of four-coordinate tetrahedral yields values of 0.74 and 0.71 Å, respectively.[20] These values are only slightly different from the values of 0.77 and 0.73 Å quoted by Greenwood and Earnshaw and suggest that the Cu^+ ion is only slightly larger than the Cu^{2+} ion.[21]

Table 4 Effective Ionic Radii[a] (Å) for the Cu^+, Cu^{2+} and Cu^{3+} Ions as a Function of Coordination Number

Coordination number	*Geometry*	Cu^+	Cu^{2+}	Cu^{3+}
Two-coordinate	Linear	0.60	—	—
Four-coordinate	Tetrahedral	0.74	0.71	—
Four-coordinate	Square coplanar	—	0.71	0.68
Four-coordinate	Square pyramidal/ trigonal bipyramidal	—	0.79	—
Six-coordinate	—	0.91[b]	0.87	—

[a] Values from R. D. Shannon, *Acta Crystallogr., Sect. A*, 1976, **32**, 751.
[b] As no examples of six-coordinate copper(I) species exist, this value must be an estimated value.

53.3.2.1 Mononuclear complexes

In the solid state the stereochemistry of copper(I) in its mononuclear complexes, as determined by X-ray crystallography (Figure 4.1), is dominated by four coordination. A significant number of three- and two-coordinate complexes are known, very few five-coordinate complexes exist and six coordination (or above) is unknown. This contrasts with the predominance of six coordination in the chemistry of copper(II) (see Section 53.4.2) and the absence of two or three coordination in the solid state, and with the formation of a significant number of seven- and eight-coordinate geometries.[47,48]

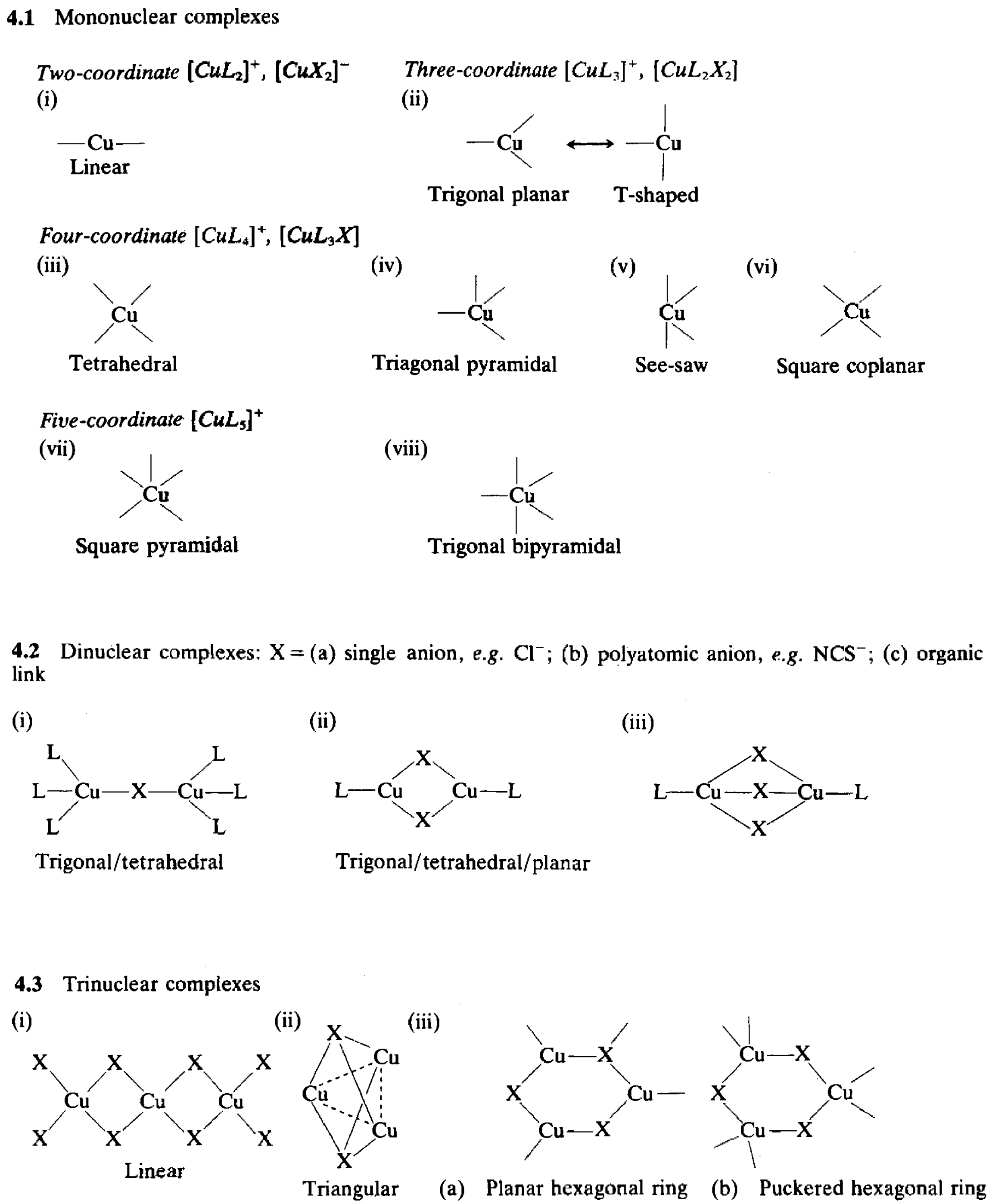
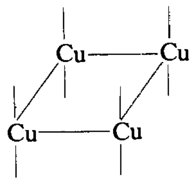


Figure 4 Stereochemistry of copper(I) complexes

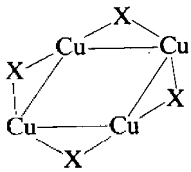
4.4 Tetranuclear complexes

(*A*) *Planar*

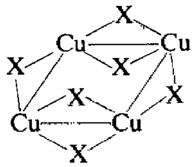
(i)



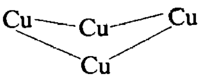
(ii)



(iii)



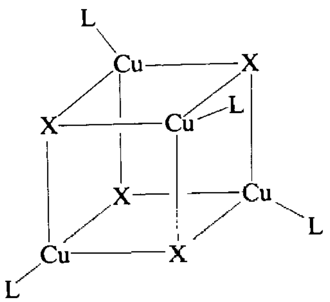
(iv)



Butterfly

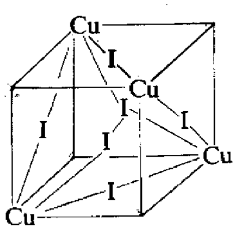
(*B*) *Tetrahedral*

(v)



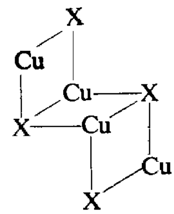
$[CuX]_4L_4$

(vi)



$[Cu_4I_6]$ — open cubane

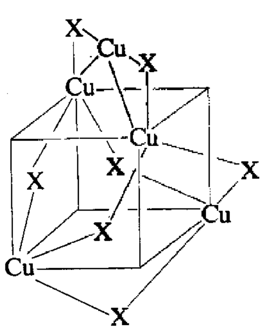
(vii)



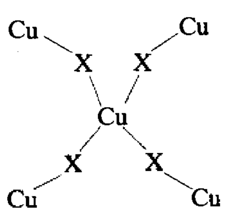
Cu_4X_4 — stepped cubane

4.5 Pentanuclear complexes

(i)

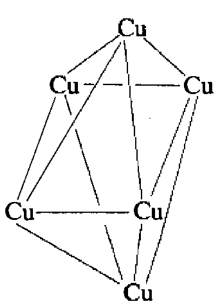


(ii)



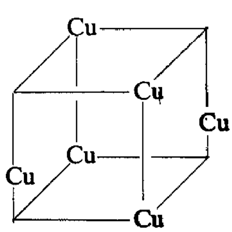
4.6 Hexanuclear complexes

(i)



Regular octahedral

(ii)

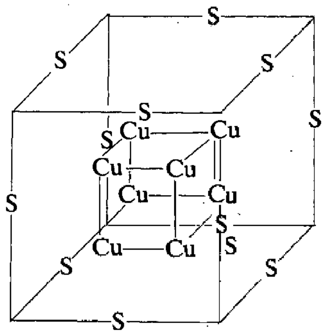


Distorted octahedral

Figure 4 (*continued*)

4.7 Octanuclear complexes

(i)

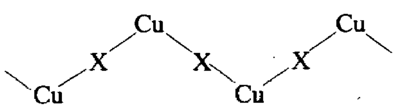


Cubic icosahedral

4.8 Chain and ribbon structures

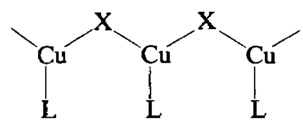
Single chain

(i)



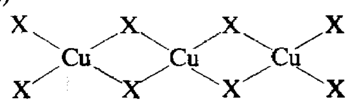
Two-coordinate

(ii)



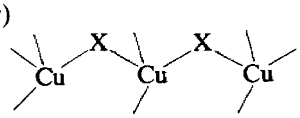
Three-coordinate — planar or stepped

(iii)



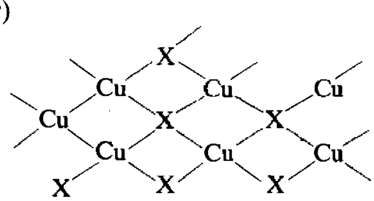
Tetrahedral

(iv)



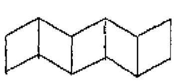
Double chain

(v)



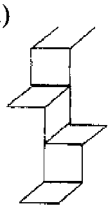
Four-coordinate

(vi)



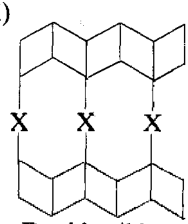
Stepped straight

(vii)



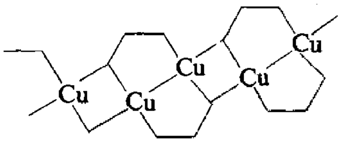
Twisted step

(viii)



Double ribbon

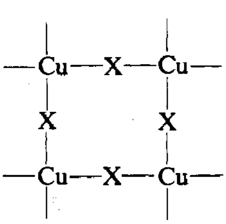
(ix)



Planar

4.9 Infinite two-dimensional sheets

(i)



(ii)

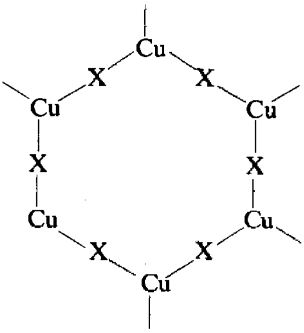


Figure 4 (*continued*)

4.10 Infinite three-dimensional lattices

(i)

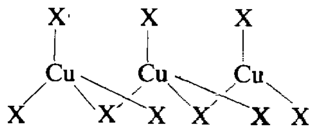


Figure 4 (*continued*)

The four-coordinate copper(I) complexes are generally tetrahedral (Figure 4.1, iii), especially when four equivalent ligands are involved as in $[Cu(NCMe)_4](ClO_4)$ (**1**)[43] and $[Cu(thioacetamide)_4]Cl$ (**2**).[50] No mononuclear $[CuX_4]^{3-}$ anions, where X = halide ion, are known, which is surprising in view of the frequent occurrence of the $[CuCl_4]^{2-}$ anion in copper(II) chemistry (see Section 53.4.2) and the frequent occurrence of the Cl^-, Br^- and I^- anions as bridging ligands in polynuclear copper(I) systems (Section 53.3.2.2).[22] Consistent with the soft acid behaviour of copper(I),[36] no mononuclear CuO_4 chromophores are observed, but a significant number of CuS_4 and CuP_4 chromophores are observed,[23] including the recently characterized CuP_4 chromophore of $[Cu(PPh_3)_4](ClO_4)$ (**3**).[51] The crystal structures of numerous monodentate phosphorus-containing ligands are known (CuP_{1-3}; Table 5); with PPh_3 some unusual ligands to copper(I) may be involved in coordination. Thus the fluoride ion coordinates in $[CuF(PPh_3)_3]$[37] and even the tetrafluoroborate anion in $[Cu(FBF_3)(PPh_3)_3]$ (**4**),[67] although it is not generally considered a strong ligand to any first-row transition metal (see Chapter 15.5). Even oxyanions may be involved in coordination as a bidentate ligand in $[Cu(O_2NO)(PPh_3)_2]$ (**5**)[80] and $[Cu(O_2CMe)(PPh_3)_2]$ (**6**).[82] With bidentate chelate ligands, $[Cu(chelate)_2]^+$ cations are well characterized, especially with potentially π-bonding donors as in $[Cu(2,9\text{-}Me_2phen)_2](NO_3)$ (**7**).[54] Only recently has a σ-bonding nitrogen chelate been characterized in $[Cu(N,N\text{-}Et_2en)_2][CuCl_2]$ (**8**).[53] With soft donor ligands, bis chelate chromophores are well represented: $Cu(P{-}P)_2$ in $[Cu(dppe)_2][CuCl_2]$,[59] $Cu(As{-}As)_2$ in $[Cu(diarsine)_2](PF_6)$ (**9**)[84] and $Cu(S{-}S)_2$ in $[Cu(3,6\text{-}thiaoctane)_2](BF_4)$ (**10**).[61] In these $[Cu(chelate)_2]^+$ cations a tetrahedral geometry is involved, although with considerable distortion, *e.g.* dihedral angles in the range 50–97° (Table 5). With macrocyclic ligands, such as 1,8-di(2-pyridyl)-3,6-dithiaoctane (L^1), a four-coordinate CuN_2S_2 chromophore may still be present, but with a rather distorted tetrahedral stereochemistry, *e.g.* $[Cu(L^1)](PF_6)$ (**11**).[73] With nonequivalent ligands CuX_2Y_2 chromophores predominate (Table 5), but CuX_3Y chromophores also exist; one of the more interesting is that of the CuS_3O chromophore of $[Cu(1,4\text{-}oxathiane)_3(OH_2)](BF_4)$ (**12**),[62] as it is one of the few copper(I) complexes containing coordinated water. In $[Cu(1,4\text{-}oxathiane)_3(OClO_3)]$ (**13**)[62] a similar CuS_3O chromophore involves the equally unusual coordinated perchlorato group (Chapter 15.5). No chromophores with four nonequivalent ligands appear in Table 5, but a number occur with three nonequivalent ligands, such as $[Cu(bipy)Cl(PPh_3)]$.[85] Although the regular undistorted tetrahedral stereochemistry predominates in these four-coordinate copper(I) complexes, other geometries occur to a limited extent, if ligand constraints are favourable. Thus, a unique square coplanar CuN_4 chromophore occurs in [Cu(cyclops)] (**14**),[86] where cyclops = difluoro-3,3′(trimethylenedinitrilo)bis(2-butanone oximato)borate, but even in (**14**) the macrocyclic ligand cyclops is distorted to produce a distinct tetrahedral twist to the CuN_4 chromophore of 23–27°. In other cases alternative descriptions of the stereochemistries are involved, as in the four-coordinate CuC_4 chromophore of $K_3[Cu(CN)_4]$.[90] The $[Cu(CN)_4]^{3-}$ anion occupies a three-fold crystallographic position with slightly different Cu—C distances of 2.014 and 1.992 Å (× 3), respectively. Thus, strictly, a trigonal pyramidal stereochemistry is involved, but, as the Cu—C distances are only just significantly different, a tetrahedral description is preferred. A better trigonal pyramidal structure (Figure 4.1, iv) occurs in $[Cu(pma)](BPh_4)$ (**15**),[88] where pma = 2-pyridylmethylbis(1-ethylthioethyl)amine, and a 'see-saw' structure (Figure 4.1, v) occurs in $[Cu(15\text{-}ane\text{-}S_5)]$ (**16**),[91] where $15\text{-}ane\text{-}S_5$ = 1,4,7,10,13-pentathiacyclopentadecane (see Table 5 for alternative examples). In both cases the nontetrahedral geometry arises from distortion imposed by the use of chelate macrocyclic ligands. In general the soft acid behaviour of copper(I) needs some qualification;[36] from Table 5 it can be seen that phosphorus is no longer more effective than nitrogen as a ligand, especially in macrocyclic systems; sulfur is a more common ligand than oxygen, but there are no selenium or tellurium atom ligands; Cl–

Table 5 Copper(I) Mononuclear Four-coordinate Chromophores

Complex	*Chromophore*	*Geometry*[b]	*Cu—L(1)* (Å)	*Cu—L(2)* (Å)	*Cu—L(3)* (Å)	*Cu—L(4)* (Å)	*Remarks*	*Ref.*
$[Cu(NCMe)_4](ClO_4)$ (**1**)	CuN_4	Td	1.99	—	—	—	—	43
$[Cu(N\text{-Meimidazole})_4](ClO_4)$	CuN_4	Td	2.054	—	—	—	Angles 108°, 112°	115
$[Cu(py)_4](ClO_4)$	CuN_4	Td	2.05	—	—	—	Angles 111°, 110°	52
$[Cu(N,N'\text{-}Et_2en)_2][CuCl_2]$ (**8**)	Cu(N—N)	Td	2.117	—	—	—	—	53(a)
$[Cu(phen)_2](ClO_4)$	$Cu(N—N)_2$	Td(C_2)	2.045	2.053	—	—	Dihedral angle, 49.9°	53(b)
$[Cu(phen)_2][CuBr_2]$	$Cu(N—N)_2$	Td(C_2)	2.006	2.071	—	—	Dihedral angle, 76.8°	53(b)
$[Cu(2,9\text{-}Me_2phen)_2](NO_3)$ (**7**)	$Cu(N—N)_2$	Td(C_2)	2.059	2.083	—	—	Dihedral angle, 67.6°	54
$[Cu(2,9\text{-}Me_2phen)_2]_2(TCNQ)_2$	$Cu(N—N)_2$	Td	2.038	2.082	2.041	2.093	Dihedral angle, 97.1°	55
$[Cu(6,6'\text{-}Me_2bipy)_2](BF_4)$	$Cu(N—N)_2$	Td	2.052	2.018	2.024	2.040	Dihedral angle 80.9°	56
$[Cu(2,2'\text{-bi-}4,5\text{-dihydrothiazine})_2](BPh_4)$	$Cu(N—N)_2$	Td(C_2)	2.010	2.024	—	—	Dihedral angle, 68.9°	57
[Cu(LH)(L)][a]	$Cu(N—N)_2$	Td(C_2)	1.985	1.997	1.988	1.996	Dihedral angle, 94.4°	58
$[Cu(dppe)_2][CuAr_2]$	$Cu(P—P)_2$	Td(C_2)	2.320	2.305	—	—	Dihedral angle, 90°	59
$[Cu(thioacetamide)_4]Cl$ (**2**)	CuS_4	Td	2.34	—	—	—	—	50
$[Cu(CH_4N_2S)_4][SiF_6]$	CuS_4	Distorted Td	2.357	2.335	2.362	2.340	Angles 94–118°	60
$[Cu(3,6\text{-dithiaoctane})_2](BF_4)$ (**10**)	$Cu(S—S)_2$		2.280	2.310	2.303	2.318	—	61
$[Cu(1,4\text{-oxathiane})_4](BF_4)$	CuS_4	Td(C_{3v})	2.281	2.342	2.310	2.291	—	62
$[Cu(2,5\text{-dithiahexane})_2](ClO_4)$	$Cu(S—S)_2$	Td	2.28	—	—	—	—	63
$[Cu(2,5\text{-dithiahexane-}1,6\text{-dicarboxylate})_2]$	CuS_4	Td(D_2)	2.30	2.34	—	—	—	64
$[Cu(Et_2\text{-}2,3,2\text{-}S_4)]$	$Cu(S—S)_2$	Td	2.28	2.30	2.31	2.33	—	65
$[Cu(14\text{-ane-}S_4)]$	CuS_4	Distorted Td	2.26	2.33	2.34	2.33	—	66
$[CuF(PPh_3)_3]$	$CuFP_3$	Td	F, 2.06	P, 2.325	P, 2.310	P, 2.316	—	37
$[Cu(FBF_3)(PPh_3)_3]$ (**4**)	$CuFP_3$	Td	F, 2.31	P, 2.298	—	—	No IR evidence of coordinated $(FBF_3)^-$	67

[a] L = (phenylazo)acetoxine-*N*,*N*′. [b] Td = tetrahedral.

Table 5 *(continued)*

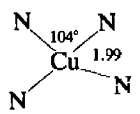
Complex	*Chromophore*	*Geometry*	*Cu—L(1)* (Å)	*Cu—L(2)* (Å)	*Cu—L(3)* (Å)	*Cu—L(4)* (Å)	*Remarks*	*Ref.*
$[Cu(H_2BH_2)(PPh_3)_2]$ **(18)**	CuH_2P_2	Td(C_2)	P, 2.276	H, 2.02	—	—	PCuP, 123.3	68
$[Cu(HBH_3)(PPh_2Me)_3]$ **(17)**	$CuHP_3$	Td	H, 1.697	P, 2.282	P, 2.283	P, 2.260	Neutron diffraction at 15 K	69
$[Cu(H_2B_3H_6)(PPh_3)_2]$	CuH_2P_2	Td	P, 2.274	P, 2.288	H, 1.84	H, 1.85	—	70
[CuBr-{2-(3,3-dimethyl-2-thiabutyl)}pyridine]	CuBr(N—S)S	Distorted Td	Br, 2.424	N, 2.109	S, 2.310	S, 2.357	—	71
$[Cu(2,9\text{-}Me_2phen)(H_2BH_2)]$	CuH_2(N—N)	Td(m)	H, 1.579	N, 2.023	N, 2.049	—	Mirror symmetry	72
[Cu{1,8-bis(2-pyridyl)-3,6-dithiaoctane}](PF_6) **(11)**	CuN_2S_2	Td(C_2)	N, 2.042	S, 2.345	—	—	—	73
$[Cu(1,4\text{-oxathiane})_3(OH_2)](BF_4)$ **(12)**	CuS_3O	Td	S, 2.272	S, 2.291	S, 2.230	OH_2, 2.234	Only $Cu^I—OH_2$ bond	62
$[Cu(1,4\text{-oxathiane})_3(OClO_3)]$ **(13)**	CuS_3O	Td	S, 2.262	S, 2.283	S, 2.269	O, 2.278	Monodentate $(OClO_3)^-$	62, 63
$[Cu\{HB(3,5\text{-}Me_2pz)_3\}(SC_6H_4NO_2)]\cdot 2C_3H_6O$	$CuSN_3$	Td	S, 2.19	N, 2.00	N, 2.06	N, 2.10	Trigonal distortion	74
$[Cu(PPh_3)_2(S_2CSO)]$	CuS_2P_2	Td	S, 2.452	S, 2.440	P, 2.255	P, 2.258	—	123
$[(Ph_3P)_4N][Cu(S_3N)_2]$	Cu(S—S)	Td	S, 2.291	S, 2.290	—	—	—	76
$[(Ph_3P)_2Cu(S_3N)]$	CuS_2P_2	Td	S, 2.304	P, 2.27	—	—	—	76
[Cu(Hmbt)(mbt-S-mbt)]$(ClO_4)\cdot 2CHCl_3$[c]	CuN_2S_2	Distorted Td	N, 2.040	N, 2.012	S, 2.486	Cl, 2.221	—	78
$[Cu(PPh_3)_2$(3-py carbonate)]	$CuNOP_2$	Distorted Td	N, 2.165	O, 2.135	P, 2.269	P, 2.258	—	79
$[Cu(PPh_3)_2$(2,3-pycarboxylate)]	$CuNOP_2$	Distorted Td	N, 2.109	O, 2.077	P, 2.237	P, 2.257	—	79
$[Cu(O_2NO)(PPh_3)_2]$ **(5)**	CuO_2P_2	C_2	O, 2.223	P, 2.256	—	—	—	80
$[Cu(O_2NO)\{P(C_6H_{11})_3\}_2]$	CuO_2P_2	Distorted Td	—	—	—	—	—	81
$[Cu(O_2CMe)(PPh_3)_2]$ **(6)**	CuO_2P_2	Distorted Td	O, 2.162	O, 2.257	P, 2.233	P, 2.240	—	82
$[Cu(PPh_3)_2$(thenoyltrifluoroacetonate)]	CuO_2P_2	Td	O, 2.104	O, 2.100	P, 2.242	P, 2.252	—	83
$[Cu(PPh_3)_2$(hexafluoroacetate)]	CuO_2P_2	Td	O, 2.123	O, 2.117	P, 2.239	P, 2.236	—	83
$[Cu(PPh_3)_2$(trifluoroacetate)]	CuO_2P_2	Td	O, 2.096	O, 2.077	P, 2.258	P, 2.256	—	83
[Cu(*o*-phenylenebis(dimethylarsine)]tetrakis(1-pyrazolylborato)-N^2,N^2	Cu(As—As)(N—N)	Td	N, 1.987	N, 2.016	As, 2.333	As, 2.370	—	84
[Cu(*o*-phenylenebis(dimethylarsine)}(PF_6) **(9)**	$Cu(As—As)_2$	Td	As, 2.360	—	—	—	—	84

[c] Hmbt = mercaptobenzothiazole.

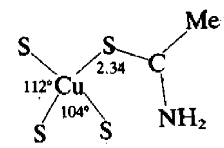
Table 5 *(continued)*

Complex	*Chromophore*	*Geometry*	*Cu—L(1) (Å)*	*Cu—L(2) (Å)*	*Cu—L(3) (Å)*	*Cu—L(4) (Å)*	*Remarks*	*Ref.*
[Cu(bipy)Cl(PPh_3)]	$CuClN_2P$	Td	N, 2.076	N, 2.087	Cl, 2.330	P, 2.180	—	85(a)
[CuCl{SP(PH)$_3$}$_3$]	$CuClSb_3$	Td	Cl, 2.235	Sb, 2.554	Sb, 2.564	Sb, 2.548	—	85(b)
[Cu(cyclops)] (**14**)	CuN_4	Square coplanar	N, 1.943	N, 1.937	N, 1.938	N, 1.939	Td twist 23–27°	86
[Cu(2,4-dithiobiuret)Cl]·DMF	$CuClS_2S'$	Trigonal pyramidal	S, 2.245	S, 2.258	Cl, 2.302	S, 2.880	—	77
[Cu(peas)]	CuN_2S_2	Trigonal pyramidal	N, 2.000	N, 2.192	S, 2.247	S, 2.343	—	87
[Cu(pma)](BPh_4) (**15**)	CuN_2S_2	Trigonal pyramidal	N, 2.035	N, 2.158	S, 2.230	S, 2.275	—	88
[Cu(PPh_2Me)$_3$(SPh)(SO_2)]	CuP_3S	Trigonal pyramidal	P, 2.404	P, 2.286	P, 2.280	S, 2.404	S—S 2.53 Å	75
[Cu(tepa)](PF_6)	CuN_4	Trigonal pyramidal	N, 2.192	N, 2.012	N, 2.021	N, 2.022	—	89
K_3[Cu(CN)$_4$]	$CuCC_3$	Trigonal pyramidal	C, 2.014	C, 1.992	C, 1.992	C, 1.992	—	90
[Cu(15-ane-S_5)] (**16**)	CuS_4	See-saw	S, 2.24	S, 2.24	S, 2.33	S, 2.33	—	91

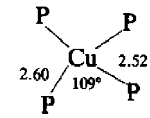
are are all effective bridging ligands (Section 53.3.2.2), and iodine occurs only as a bridging ligand. Even hydrogen has been characterized as a ligand to copper(I) in the coordination of the $(BH_4)^-$ anion as a monodentate ligand in $[Cu(HBH_3)(PPh_2Me)_3]$ **(17)**[69] and as the bidentate chelate ligand in $[Cu(H_2BH_2)(PPh_3)_2]$ **(18)**.[68]



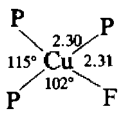
$[Cu(NCMe)_4](ClO_4)$ **(1)**[43]



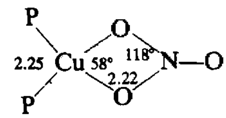
$[Cu(thioacetamide)_4]Cl$ **(2)**[50]



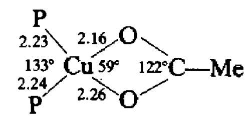
$[Cu(PPh_3)_4](ClO_4)$ **(3)**[51]



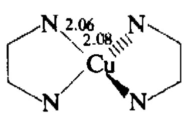
$[Cu(FBF_3)(PPh_3)_3]$ **(4)**[67]



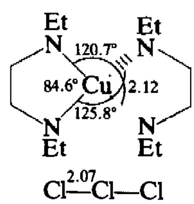
$[Cu(O_2NO)(PPh_3)_2]$ **(5)**[80]



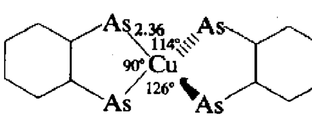
$[Cu(O_2CMe)(PPh_3)_2]$ **(6)**[82]



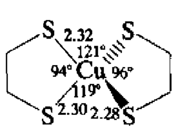
$[Cu(2,9\text{-}Me_2phen)_2](NO_3)$ **(7)**[54]



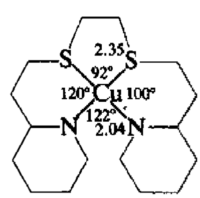
$[Cu(N,N'\text{-}Et_2en)_2][CuCl_2]$ **(8)**[53]



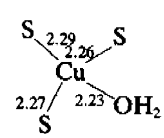
$[Cu(diarsine)_2](PF_6)$ **(9)**[84]



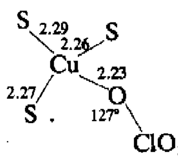
$[Cu(3,6\text{-dithiaoctane})_2](BF_4)$ **(10)**[61]



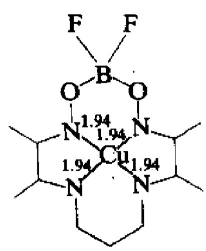
$[Cu(L^1)](PF_6)$ **(11)**[73]



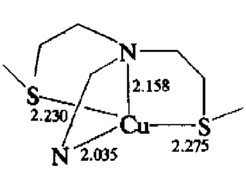
$[Cu(1,4\text{-oxathiane})_3(OH_2)](BF_4)$ **(12)**



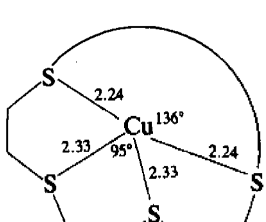
$[Cu(1,4\text{-oxathiane})_3(OClO_3)]$ **(13)**[62]



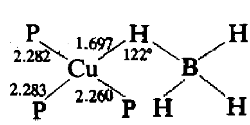
$[Cu(cyclops)]$ **(14)**[86]



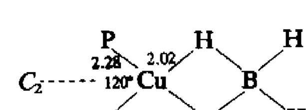
$[Cu(pma)](BPh_4)$ **(15)**[88]



$[Cu(15\text{-ane-}S_5)]$ **(16)**[91]

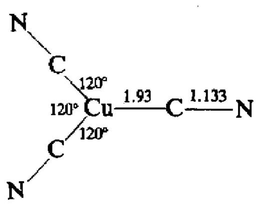


$[Cu(HBH_3)(PPh_2Me)_3]$ **(17)**[69]

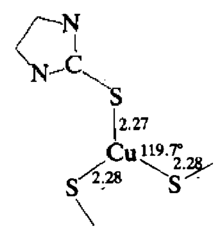


$[Cu(H_2BH_2)(PPh_3)_2]$ **(18)**[68]

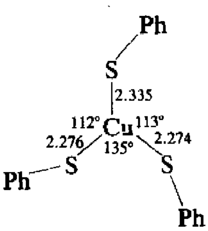
Coordination numbers of three are much less common than four for mononuclear complexes of copper(I) (Table 6). A number of trigonal copper(I) complexes occur for three equivalent ligands involving carbon, nitrogen and sulfur donor ligands. The CuC_3 chromophore of $Na_2[Cu(CN)_3]\cdot3H_2O$ (**19**)[97] has a crystallographic D_{3h} symmetry, and near D_{3h} symmetry occurs in $[Cu(ethylenethiourea)_3]_2(SO_4)$ (**20**),[92] but even with equivalent ligands distortion of the trigonal angles may occur as in $(PPh_4)_2[Cu(SPh)_3]$ (**21**)[93] with a back angle of 135° and the opposite Cu—S distance lengthened significantly from 2.274 to 2.335 Å. With nonequivalent ligands, angular distortion will also occur as in the 118° angle of $[Cu\{(Ph_2PS)_2CH_2\}Cl]$ (**22**).[101] With a simple bidentate chelate ligand such as in [CuBr(*N,N'*-diisopropylethylenediamine)] (**23**),[102] the angular distortion is reduced below 90° by the bite of the ligand and the two nonchelate angles are correspondingly increased to 137.5°. For macrocyclic type chelate ligands the angular distortion may be such that the CuN_2S chromophore of $[Cu(L^2)](BF_4)$ (**24**),[103a] where L^2 = 2,2′-{2-bis(*N*-propylbenzimidazolyl)diethyl sulfide, is best described as T-shaped (Figure 4.1, ii). An interesting mononuclear 'three-coordinate' structure occurs in $[Cu(OClO_3)(PCy_3)_2]$ (**25**),[104] where PCy_3 = tricyclohexylphosphine, and the percholate group is monodentate, giving formally a CuP_2O chromophore, but as the perchlorate is disordered over two positions related by a crystallographic two-fold axis through the Cu atom and as the PCuP and OCuO′ planes are at *ca.* 90°, the Cu chromophore is best described as a distorted four-coordinate CuP_2O_2 chromophore, with a P—Cu—P angle of 144° and an O—Cu—O′ angle of 36°.



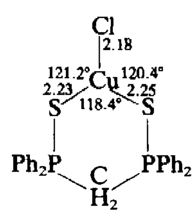
$Na_2[Cu(CN)_3]\cdot3H_2O$ (**19**)[97]



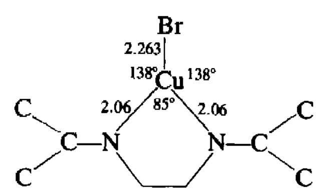
$[Cu(ethylenethiourea)_3]_2(SO_4)$ (**20**)[92]



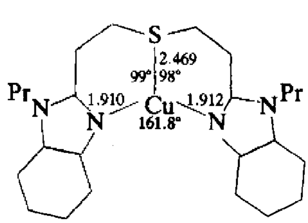
$(PPh_4)_2[Cu(SPh)_3]$ (**21**)[93]



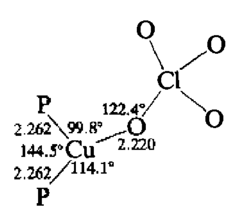
$[Cu\{(Ph_2PS)_2CH_2\}Cl]$ (**22**)[101]



[CuBr(*N,N'*-diisopropylethylenediamine)] (**23**)[102]



$[Cu(L^2)](BF_4)$ (**24**)[103]



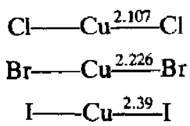
$[Cu(OClO_3)\{(cyclohexyl)_3P\}_2]$ (**25**)[104]

Classically, the linear two-coordinate copper(I) stereochemistry (Figure 4.1, i) is usually illustrated by the $[Cu(NH_3)_2]^+$ cation, but there is no X-ray crystallographic evidence for this linear species.[10] Nevertheless, the two-coordinate CuL_2 chromophore does occur in the halide anions $[CuX_2]^-$ (**26**; Table 7).[105a,b] Linear CuC_2,[59] CuN_2[108,109] and CuS_2[110] chromophores also occur (Table 7), but with bond angles slightly less than 180°, *e.g.* $[Cu(BBDHP)](PF_6)_{0.66}(BF_4)_{0.34}$ (**27**).[109] A characteristic feature of all these linear chromophores is that the CuL distances are significantly shorter than the corresponding distances in three- and four-coordinate copper(I) chromophores (see later). The five-coordinate geometry for mononuclear

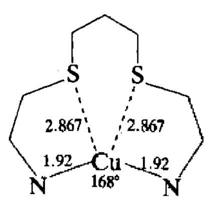
Table 6 Copper(I) Mononuclear Three-coordinate Complexes

Complex	*Chromophore*	*Symmetry*	*Cu—L(1)* (Å)	*Cu—L(2)* (Å)	*Cu—L(3)* (Å)	*Remarks*	*Ref.*
$[Cu(ethylenethiourea)_3]_2(SO_4)$ (**20**)	CuS_3	D_{3h}	2.27	2.28	2.28	—	92
$[Cu(tetramethylthiourea)_3](BF_4)$	CuS_3	Distorted D_{3h}	2.257	2.238	2.236	—	92
$(Ph_4P)_2[Cu(SPh)_3]$ (**21**)	CuS_3	Distorted D_{3h}	2.274	2.276	2.335	—	93
$[Cu(SPMe_3)_3](ClO_4)$	CuS_3	$\sim D_{3h}$	2.260	2.264	2.253	—	94
$[Cu(2\text{-picoline})_3](ClO_4)$	CuN_3	$\sim D_{3h}$	2.02	1.97	1.98	—	95
$[Cu(bpy\text{-}2)](PF_6)$	CuN_3	$\sim D_{3h}$	—	—	—	—	96
$Na_2[Cu(CN)_3]\cdot 3H_2O$	CuC_3	D_{3h}	C, 1.93	—	—	C—N, 1.133	97
$[CuI(2,6\text{-}Me_2py)_2]$	$CuIN_2$	$D_{3h}(C_2)$	I, 2.682	N, 1.984	N, 1.984	—	98
$[CuBr(PPh_3)_2]\cdot 0.5C_6H_6$	$CuBrP_2$	$\sim D_{3h}$	Br, 2.346	P, 2.282	P, 2.263	—	99
$[CuCl(2\text{-thiouracil})_2]\cdot DMF$	$CuClS_2$	$\sim D_{3h}$	Cl, 2.260	S, 2.225	S, 2.228	—	100
[CuCl{bis(diphenylphosphinothioyl)methane}] (**22**)	CuCl(S—S)		Cl, 2.18	S, 2.231	S, 2.251	118.4°	101
[CuBr(*N,N'*-diisopropylenediamine)] (**23**)	CuBr(N—N)	$\sim D_{3h}$	Br, 2.263	N, 2.062	—	NCuN, 85°; 137.5°	102
[Cu(2,2'-bis(2-*N*-propylbenziamidazolyl)	CuN_2S	T-shaped	S, 2.469	N, 1.912	N, 1.910	NCuN, 161.8°; 98°	103(a)
(diethyl sulfide)](BF_4) (**24**)						and 99°	103
[Cu(1-methylimidazoline-2(3*H*)-thione)$_3$](NO_3)	CuS_3	$\sim D_{3h}$	S, 2.235	S, 2.53	S, 2.58	—	103(b)
$[PMePh_3]_2[CuI_3]$	CuI_3	$\sim D_{3h}$	I, 2.537	I, 2.559	I, 2.566	116.5–122.9°	103(c)

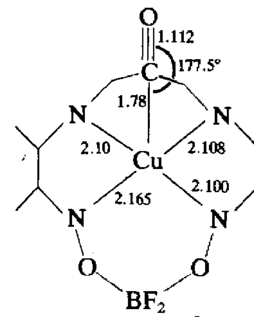
copper(I) complexes is the least common stereochemistry for copper(I), and generally occurs where macrocyclic ligands impose geometric constraints. It is best known (Figure 4.1, vi) in the square pyramidal geometry of [Cu(cyclops)(CO)] (**28**),[112] where cyclops = LBF_2 as in (**14**). In (**28**) the copper(I) atom is lifted well out of the plane of the N_4 ligand, $\rho = 0.96$ Å (see Section 53.3.2.10 for a discussion of copper(I) carbonyl complexes). The structure of $[Cu(L^3)](BPh_4)$ (**30**),[113] where L^3 = 2,15-dimethyl-7,10-dithia-3,14,20-triazabicyclo[14.3.1]icosa-1(20),2,14,16,18-pentaene (**29**), a potentially quinquidentate nitrogen sulfur macrocyclic ligand N_3S_2, is trigonal bipyramidal. This geometry arises from the geometric constraints of the ligand L^3 and involves significantly longer CuN_{ax} than CuN_{eq} distances. A number of potentially five-coordinate copper(I) structures also occur with alkene type ligands, but as the precise donor function (denticity) is sometimes not clearly defined, these complexes are dealt with in Section 53.3.2.10.



$[CuX_2]^-$ anions (**26**)[105a,b]

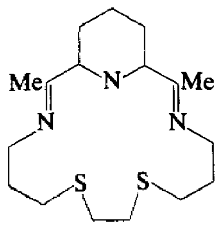


$[Cu(BBDHP)](PF_6)_{0.66}(BF_4)_{0.34}$ (**27**)[109]

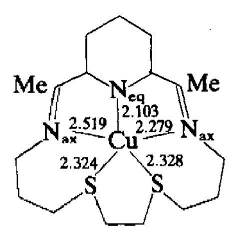


$\rho = 0.96$ Å

[Cu(cyclops)(CO)] (**28**)[112]



$L^3 = N_3S_2$-17-mac (**29**)[113]



$[Cu(L^3)](BPh_4)$ (**30**)[113]

The crystallographic data summarized in Tables 5–7 and molecular structures (**1**)–(**30**) provide a description of structures of mononuclear copper(I) complexes involving the basic geometries of Figure 4.1. In summary, the four-coordinate tetrahedral geometry (iii) predominates, while the two-coordinate linear (i) and three-coordinate trigonal planar (ii) make a significant contribution to the stereochemistry of copper(I). The four-coordinate trigonal pyramidal (iv), see-saw (v), and square planar (vi) geometries, the three-coordinate T-shaped (ii) and the five-coordinate square pyramidal (vii) geometries involve less than six examples each, and the five-coordinate trigonal bipyramidal geometry only involves one example (**30**). Table 8 summarizes the average Cu—L distances according to ligand type and coordination number, and includes the number of occurrences of a given Cu—L distance for mononuclear copper(I) complexes. Figure 5 shows plots of the average Cu—L distances against the coordination number for the different ligand atoms, and, in general, establishes that the Cu—L distances increase with increasing coordination number. As a number of the copper(I) structures are far from regular, *e.g.* see-saw (**16**), T-shaped (**24**) and (**25**), and bent (**27**), this suggests that notwithstanding the spherical symmetry of the d^{10} configuration of the copper(I) ion, the regular geometries of the copper(I) ion may be connected by the soft modes of vibration of the CuL_n chromophore to yield the possible structural relationships of Figure 6(a). This accounts for the structures involving clear bond-length and bond-angle distortions from the regular structures of Figure 6(a) (see Section 53.4.4.5 for a discussion of the structural pathways in copper(II) complexes).

Table 7 Copper(I) Mononuclear Two-coordinate Complexes

Complex	*Chromophore*	*Geometry*	*Cu—L(1)* (Å)	*Cu—L(2)* (Å)	*Angle* (°)	*Remarks*	*Ref.*
$(Bu_4N)[CuCl_2]$ (**26**)	$CuCl_2$	$C_{\infty v}$(i)	2.107	2.107	180	Linear(i)	105(a)
$[Cu(N,N'\text{-}Et_2en)_2][CuCl_2]$ (**8**)	$CuCl_2$	$C_{\infty v}$(i)	2.069	2.069	180	Linear(i)	53
$(Bu_4N)[CuBr_2]$ (**26**)	$CuBr_2$	$C_{\infty v}$(i)	2.226	2.226	180	Linear(i)	105(a)
$(Bu_4N)[CuBrCl]$	CuClBr	$C_{\infty v}$(v)	2.104	2.195	180	Statistical disorder	106
$[Cu^{II}(C_{44}H_{60}N_4)Cl][Cu^{I}Cl_2]$	$CuCl_2$	$C_{\infty v}$	2.066	2.088	179	Linear	107
$[Cu(dppe)_2][CuAr_2]$	CuC_2	$C_{\infty v}$(i)	1.915	—	180	Linear	59
$[Cu(diazoaminobenzene)_2]$	CuN_2	C_{2v}	1.92	—	—	Cu—Cu 2.45 Å	108
$[Cu(BBDHP)](PF_6)_{0.66}(BF_4)_{0.34}$ (**27**)	CuN_2	C_{2v}	1.92	—	168.5	—	109
$(NPr^n_4)[Cu(SC_{10}H_{13})_2]$	CuS_2	C_{2v}	2.137	—	178.6	Linear	110
$[Cu(im)_2](ClO_4)$	CuN_2	Linear	—	—	—	Powder data	111(a)
$[Li(12\text{-crown-}4)_2][CuMe_2]$	CuC_2	$C_{\infty v}$	1.935	—	—	Linear	111(b)
$[Li(12\text{-crown-}4)_2][CuPh_2]\cdot THF$	CuC_2	$C_{\infty v}$	1.925	—	178.5	Linear	111(b)
$[Li(12\text{-crown-}4)_2][CuBr\{CH(SiMe_3)_2\}]\cdot PhMe$	CuBrC	$C_{\infty v}$	Br, 2.267	C,1.920	—	Linear	111(b)
$[Li(THF)_4][Cu\{C(SiMe_3)_2\}]$	CuC_2	$C_{\infty v}$	2.027	—	—	Linear	111(c)
$[Cu_3(2,2'\text{-biquinolinyl})_2(CN)_3]$	CuN_2	$C_{\infty v}$	1.823	—	178.7	Linear	111(d)
$K[18\text{-crown-}6][CuI_2]$	CuI_2	$C_{\infty v}$	2.383	—	180	Linear	105(b)
$K[Cu(cyclohexane\text{-}18\text{-crown-}6)][CuI_2]$	CuI_2	$C_{\infty v}$	2.394	—	180	Linear	105(b)

Table 8 Average Cu—L Distances (Å) for Copper(I) 'Mononuclear' Complexes as a Function of Coordination Number

Coordination no.	F^-	Cl^-	Br^-	I^-	O	S	N	P	C
2	—	2.092	2.226	2.39	—	2.136	1.88	—	1.95
		4	2	4		2	6		8
3	—	2.220	2.305	2.55	—	2.259	1.967	2.273	1.93
		2	2	3		17	7	2	
4	2.047	2.336	2.424	(2.70)	—	2.312	2.04	2.257	2.00
	2	3	1	(10)		41	47	23	

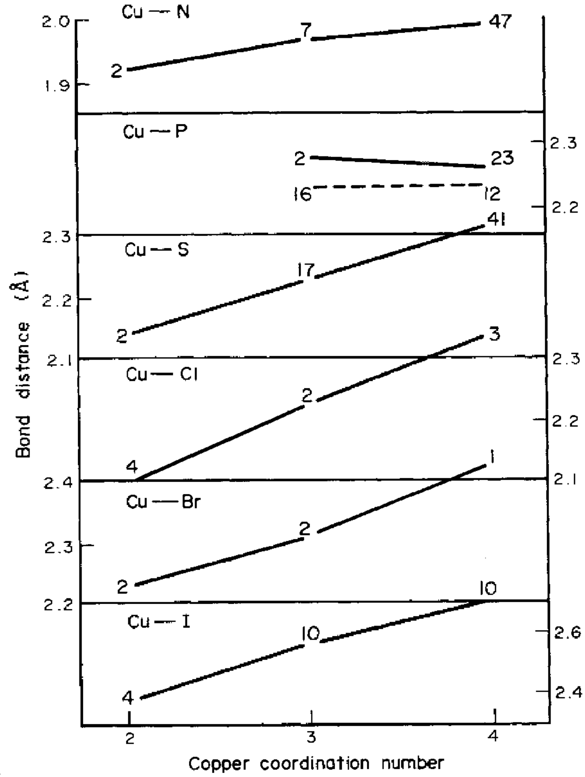


Figure 5 The average Cu—L distances for mainly mononuclear copper(I) complexes (data from Tables 5–7 and 9)

53.3.2.2 Binuclear complexes

Binuclear complexes form a significant class of copper(I) complexes involving bridging by one, two, but not three, ligand atoms, as in Figure 4.2 (i)–(iii).[33] In practice the bridging role is most common for halide ions (especially iodides) and mainly involves a symmetrical arrangement of two single-atom bridges, as in (**31**) to (**35**), with trigonal (**31**),[114] tetrahedral (**32**)[98] and mixed trigonal/tetrahedral copper stereochemistries (**33**).[119] Cu—Cu distances are in the limited range 2.9–3.2 Å for symmetrical two-atom bridging (Table 9). In general a planar Cu_2X_2 unit is involved, but a recent exception is the bent Cu_2I_2 unit of $(AsPh_4)_2[Cu_2I_2]$[122] in which the trigonal planar CuI_2 units are orientated at 147° to each other. In tetrahedral CuX_2Y_2 units, as in (**32**), the CuX_2 and CuY_2 planes are orientated at approximately 90° to each other. In most cases the terminal ligands are monodentate with a tetrahedral Cu atom geometry preferred to trigonal geometry (Table 9). In the former, chelate ligands may be involved as in [Cu(*N,N'*-diisopropylethylenediamine)I]$_2$ (**34**)[102] and [(*N,N,N',N'*-Me_4en)CuI]$_2$.[126] The dinuclear bridging iodide, Cu_2I_2, is sufficiently stable to occur with dimethyldiarsine (**35**) as a chelate ligand and a tetrahedral CuI_2As_2 chromophore.[127] The dinuclear bridging sulfur group Cu_2S_2 occurs in [Cu(2,4-dithiobiuret)Cl]$_2$·DMF (**36**),[128] while phenoxide and sulfide bridges occur in (**37**) and (**38**) respectively.[129,130] Dinuclear copper(I) complexes can also occur with polydentate

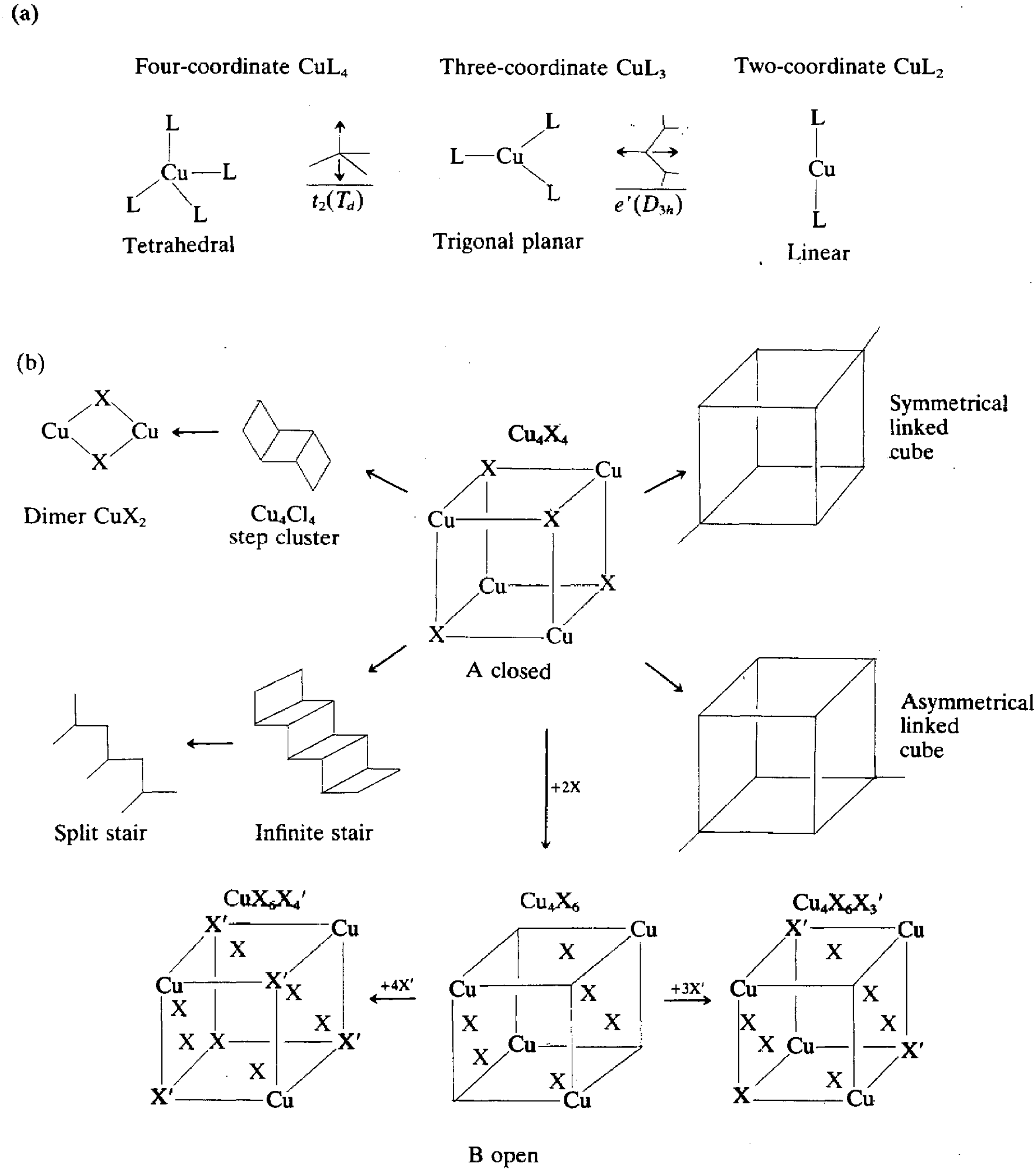
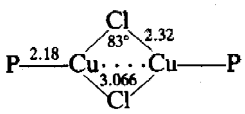


Figure 6 (a) Structural relationships in (a) copper(I) two-, three- and four-coordinate structures; and (b) structural relationships between the closed (A) and open (B) cubane structures

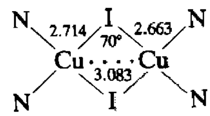
ligands, such as the hydrotris(1-pyrazolyl)borate in $[Cu(HBpz_3)]_2$ (**39**),[133] which forms a very compact Cu_2N_2 bridged complex with a very short Cu—Cu separation of 2.66 Å, which is comparable to that of 2.64 Å in $[Cu^{II}(O_2CMe)_2(OH_2)]_2$ (**316**; Section 53.4.2.3) and significantly shorter than the Cu—Cu distances of 2.9–3.23 Å in Table 9. In (**39**) the CuN_4 chromophores involve a very distorted tetrahedral stereochemistry, N—Cu—N angles of 94–145°, but with a normal Cu—N—Cu angle of 73° (see Table 9). Macrocyclic ligands may be used to hold together two copper centres close enough for bridging to occur as in $[Cu_2(L^4)(SCN)_2]$ (**40**),[134] where L^4 = (**41**). Dinuclear complexes occur with polynuclear bridging XY_n groups as in $[Cu(PPh_3)_2(NNN)]_2$ (**42**),[135] involving a tetrahedral CuP_2N_2 chromophore, with equivalent bridging $(NNN)^-$ anions.

Table 9 Copper(I) Dinuclear Complexes with Two Single X-atom Bridges (Figure 5)

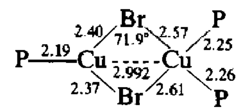
Complex	*Chromophore*	*CuCu coordination no.*	*Cu—Cu* (Å)	*Cu—X* (Å)	*Cu—L* (Å)	*Cu—X—Cu* (°)	*Remarks*	*Ref.*
$[Cu(tricyclohexylphosphine)Cl]_2$ (**31**)	$PCuCl_2CuP$	3–3	3.066	Cl, 2.322	P, 2.183	83.4	—	114
$[Cu\{2\text{-}(3,3\text{-dimethyl-2-thiabutyl})\text{-}pyridinium\}Br_2]_2$	$SBrCuBr_2CuBrS$	4–4	3.182	Br, 2.597	Br, 2.621	75.5	—	116
$(NEt_4)_2[Cu_2Br_4]$	$BrCuBr_2CuBr$	3–3	2.937	Br, 2.454	Br, 2.319	73.7	—	117
$[Cu(crotononitrile)Br]_2$	$NCuBr_2CuN$	3–3	—	Br, 2.464	Br, 2.538	—	—	118
$[Cu_2(triphenylphosphine)_3Br_2]$ (**33**)	$PCuBr_2CuP_2$	3–4	2.992	Br, 2.404	Br, 2.569	71.9	—	119
$[CuI(2,6\text{-}Me_2py)]_2$	$NCuI_2CuN$	3–3	2.586	Ir, 2.583	Ir, 2.544	60.1	N, 1.99, 2.00 Å	120
$[CuI(tmpip)]_2$	$NCuI_2CuN$	3–3	2.535	I, 2.505	I, 2.652	58.8	N, 2.12 Å	121
$(AsPh_4)_2[Cu_2I_4]$	$ICuI_2CuI$	3–3	2.663	I,2.578	I, 2.610	61.4	Cu—I, 2.49 Å, 147°	122
$[Cu_2I_2(triphenylphosphine)_3]$	$PCuI_2CuP_2$	3–4	3.109	I, 2.563	I, 2.820	70.4	Cu—P, 2.60 Å	124
$[Cu_2I_2(PPh_2Me)_4(SO_2)]$	$P_2CuI_2CuP_2$	4–4	—	I, 2.724	I, 2.714	83.4	I—SO_2, 3.407 Å	124
$[CuI(2\text{-methylpyridine})_2]_2$ (**32**)	$N_2CuI_2CuN_2$	4–4	3.083	I, 2.714	I, 2.663	70.0	Cu—N, 2.05 Å	98
$[CuI(quinoline)_2]_2$	$N_2CuI_2CuN_2$	4–4	3.364	I, 2.685	I, 2.687	77.6	—	125
$[Cu(died)I]_2$ (**34**)	$NNCuI_2CuNN$	4–4	2.73	I, 2.661	I, 2.579	—	Cu—N, 2.12–2.23 Å	102
$[Cu_2I_2(dimethylaminophenyldimethyl\text{-}arsine)_2]$ (**35**)	$AsNCuI_2CuAsN$	4–4	2.73	I, 2.53	I, 2.62	63.9	—	127
$[CuCl(2,4\text{-dithiobiuret})]_2 \cdot DMF$ (**36**)	$ClSCuS_2CuClS$	4–4	—	S, 2.245	S, 2.258	—	Cu—Cl, 2.302 Å	128
$[Cu(CNPh)_2(OPh)]_2$ (**37**)	$C_2CuO_2CuC_2$	4–4	3.223	O, 2.066	O, 2.082	101.9	—	129
$[Cu(SPh)(PPh_3)_2]_2$ (**38**)	$P_2CuS_2CuP_2$	4–4	3.662	S, 2.344	S, 2.415	98.6	—	130
$[CuCl\{bis(diphenylphosphino\text{-}thioyl)methane\}]_2$	$ClSCuS_2CuSCL$	4–4	2.900	S, 2.376	S, 2.459	73.7	—	101
$[Cu(1\text{-methylimidazoline-2-thione})_2Cl]_2$	$ClSCuS_2CuSCl$	4–4	2.914	S, 2.27	S, 2.30	73.2	—	131
$[Co(en)_2(SCH_2CH_2NH_2)Cu(NCMe)_2]_2(ClO_4)_6 \cdot 2H_2O$	$N_2CuS_2CuN_2$	4–4	3.140	S, 2.406	S, 2.342	83.0	—	132
$[Cu\{hydrotris(1\text{-pyrazolyl})borato\}]_2$ (**39**)	$N_2CuN_2CuN_2$	4–4	2.660	N, 2.254	N, 2.224	73.0	—	133



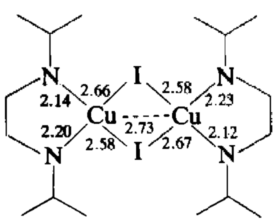
$[Cu\{P(cyclohexyl)_3\}Cl]_2$ (**31**)[114]



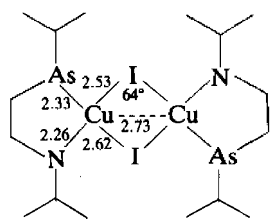
$[CuI(2\text{-methylpyridine})_2]_2$ (**32**)[98]



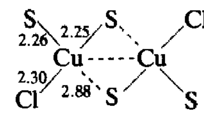
$[Cu_2(PPh_3)_3Br_2]$ (**33**)[119]



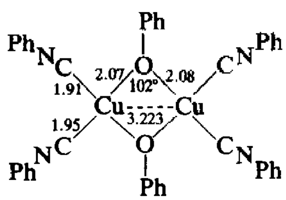
$[Cu(died)I]_2$ (**34**)[102]



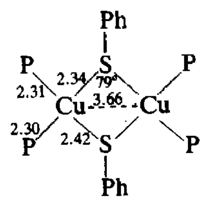
$[CuI(As—N)]_2$ (**35**)[127]



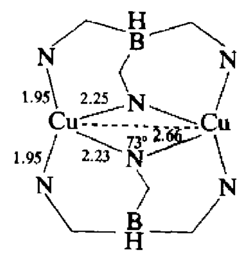
$[Cu(2,4\text{-dithiobiuret})Cl]_2{\cdot}DMF$ (**36**)[128]



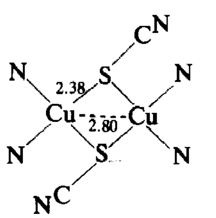
$[Cu(CNPh)_2(OPh)]_2$ (**37**)[129]



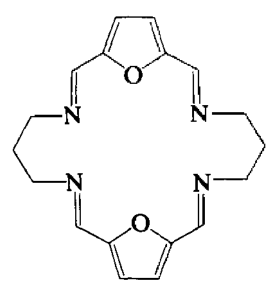
$[Cu(PPh_3)_2(SPh)]_2$ (**38**)[130]



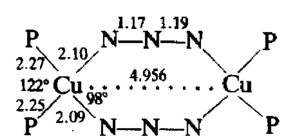
$[Cu(HBpz_3)]_2$ (**39**)[133]



$[Cu_2(L^4)(SCN)_2]$ (**40**)[134]

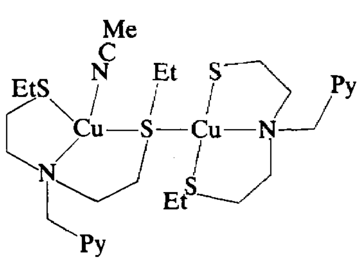


L^4 (**41**)[134]

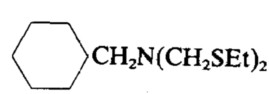


$[Cu(PPh_3)_2(NNN)]_2$ (**42**)[135]

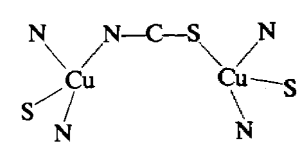
Dimeric copper(I) structures with single-X-atom bridging units (Figure 4.2, i) are much less common than two-X-atom bridging structures. A single-sulfur-atom bridge occurs in $[Cu(p\text{-}XYSEt)(NCMe)]_2(PF_6)_2$ (**43**),[136] where *p*-XYSEt = (**44**), while in $[Cu(L^5)(SCN)](ClO_4)$ (**45**),[137] where L^5 is the sulfur equivalent of L^4 (**41**), a single $(SCN)^-$ anion bridges two tetrahedral Cu chromophores. Equally, dinuclear complexes involving different bridging groups are not common, but do occur as in $[Cu_2(C_{23}H_{23}N_2O)(pyrazole)]$ (**46**),[138] which is of interest as not only does it involve a bridging pyrazole ligand (see Section 53.4.2.3), but the copper(I) environment involves a three-coordinate T-shaped CuN_2O chromophore, and a green product is obtained by reaction with O_2 in DMF solution (see Section 53.4.2.3). The largest group of dinuclear copper(I) complexes does not involve bridging ligands as such, but involves organic chains that constrain the two copper centres to lie close to each other; in these systems the atoms may be two, three and four coordinate with the copper atoms so far apart that the compounds may be considered to involve mononuclear copper atoms. Thus in the complex $[Cu(XYpz)]_2(BF_4)_2$ (**47**),[139] where XYpz = bis(3,5-dimethylpyrazolyl)-*m*-xylene, the bent two-coordinate CuN_2 chromophores, N(1)—Cu—N(2) = 159.7°, are well separated with a Cu—Cu separation of 6.35 Å, while in $[Cu_2(m\text{-}XYpy_2)](PF_6)_2$ (**48**),[140] the T-shaped CuN_3 chromophores are separated by 8.94 Å and in $[Cu_2(m\text{-}XYLSEt)(MeCN)_2](PF_6)_2$ (**49**)[141] the four-coordinate CuS_2NN' chromophores are 9.95 Å apart. Notwithstanding this large Cu—Cu separation in the solid state, in certain solutions all three complexes (**47**)–(**49**) are oxygen sensitive. This suggests that the oxygen sensitivity is not just a function of the low two and three coordination numbers of the copper(I) atom in these complexes. Significantly shorter Cu—Cu separations of 5.1 Å occur in the 3,5-dimethylpyrazole analogue of (**48**),[140] which is still oxygen sensitive, while the imidazole analogue is not.[142] Even shorter Cu—Cu separations result in a face to face approach of the three-coordinate copper chromophores, namely 3.77 Å as in the $CuPO_2$ chromophores of $[Cu(acacP)]_2$ (**50**),[143] where HacacP = *o*-[(diphenylphosphino)benzoyl]pinacolone, and 2.78 Å in the CuN_3 chromophores of $[Cu_2(TPEN)](BF_4)_2$ (**51**),[144] where TPEN = *N,N,N',N'*-tetrakis(2-pyridylmethyl)ethylenediamine. In (**50**) and (**51**), both three-coordinate Cu chromophores are intermediate in structure between trigonal and T-shaped with the largest angles being 150.4 and 146.8°, respectively, and the Cu atoms distorted out of the trigonal plane towards the second Cu atom by 0.009 and 0.07 Å, respectively. Although the latter corresponds to the shorter Cu—Cu separation of 2.78 Å, the stereochemistry is still best described as planar rather than pyramidal. The CuN_3 chromophore of (**51**) is also unusual in that the Cu—N distance of 2.30 Å is opposite the large N—Cu—N angle of 146.8° and is considerably longer than the average of 1.976 Å observed for the Cu—N distance in mononuclear three-coordinate copper(I) (Table 8). Even two-coordinate CuN_2 chromophores can involve short Cu—Cu distances of 3.04 Å, as in $[Cu_2(EDTB)](ClO_4)_2$ (**52**),[145] where EDTB = *N,N,N',N'*-tetrakis-(2-benzimidazolyl)methyl-1,2-ethanediamine, in which the N—Cu—N angles are nearly linear at 170.9°, and exceptionally short Cu—N distances of 1.88 Å, consistent with a two-coordinate CuN_2 chromophore, which suggest that the two further Cu—N contacts of 2.77 Å are clearly too long for any significant bonding. A slightly unusual dimerization for copper(I) of two bis chelate copper(I) systems in $[Cu(2,2'\text{-bithiazolidinyl})_2](ClO_4)_2$ (**53**)[146] involves tetrahedral CuN_3S chromophores, which bridge through a 2.428 Å Cu—S distance, with an additional long Cu—S distance of 3.039 Å, which is in the direction that makes the CuN_3SS' chromophore square-based pyramidal and is reminiscent of a copper(II) environment rather than the described copper(I). No examples are known of a dinuclear copper(I) complex involving three bridging ligands as in Figure 4.2, (iii).



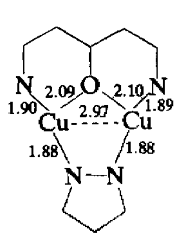
$[Cu(p\text{-}XYSEt)(NCMe)]_2(PF_6)_2$ (**43**)[136]



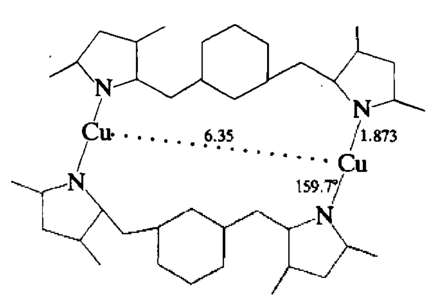
p-XYSEt (**44**)[136]



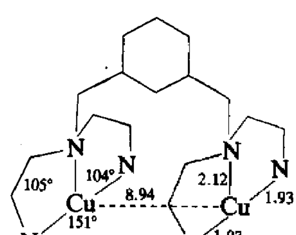
$[Cu(L^5)(SCN)](ClO_4)$ (**45**)[137]



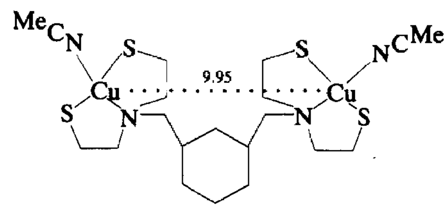
$[Cu_2(C_{23}H_{23}N_2O)(pyrazole)]$ (**46**)[138]



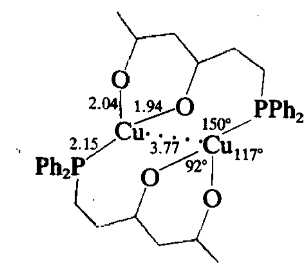
$[Cu(XYpz)]_2(BF_4)_2$ (**47**)[139]



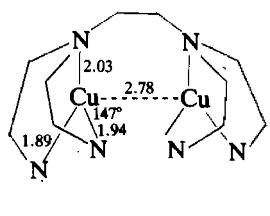
$[Cu_2(m\text{-}XYpy_2)](PF_6)_2$ (**48**)[140]



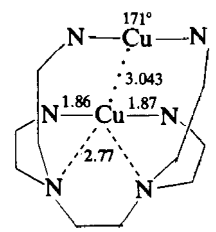
$[Cu_2(m\text{-}XYLSEt)(MeCN)_2](PF_6)_2$ **(49)**[141]



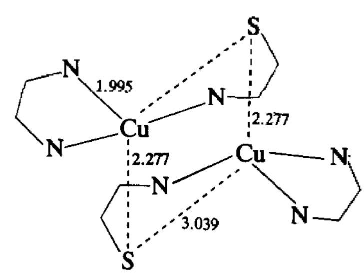
$[Cu(acacP)]_2$ **(50)**[143]



$[Cu_2(TPEN)](BF_4)_2$ **(51)**[144]



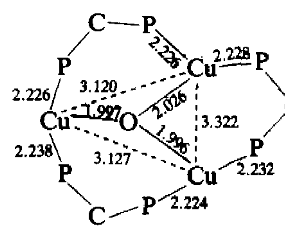
$[Cu_2(EDTB)](ClO_4)_2$ **(52)**[145]



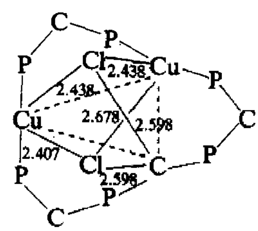
[Cu(2,2′-bithiazolidinyl)]$_2(ClO_4)$ **(53)**[146]

53.3.2.3 Trinuclear complexes

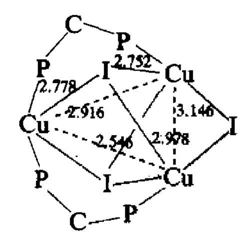
These are much less common than either mononuclear or dinuclear complexes of copper(I) and occur as a linear arrangement of bridged copper(I) atoms (Figure 4.3, i), as a triangular arrangement (Figure 4.3, ii), or as a six-membered ring with bridging X groups (Figure 4.3, iii). In general the bridging groups are monatomic anions such as Cl^-, OH^- and sulfur atoms. The triangular arrangement of Figure 4.3(ii) occurs with either a single capping ligand as in $[Cu_3(dppm)_3(OH)](BF_4)_2$ **(54)**,[147] where dppm = $Ph_2PCH_2PPh_2$, or with a bicapped trigonal bipyramidal arrangement, as in $[Cu_3(dppm)_3Cl_2](Cl)$ **(55)**,[148] or $[Cu_3(dppm)_2I_3]$ **(56)**.[149] In the $[Cu_3(dppm)_3(OH)]^{2+}$ cation of **(54)** the Cu core is situated in a 'picket-fence' type environment with the face opposite the OH group exposed and involving three sites of copper unsaturation, as each Cu is three coordinate, positioned in a hydrophobic cavity of the dppm ligand. In both **(55)** and **(56)** both faces of the Cu_3 triangle are capped by halide ions. The planar hexagonal bridged ring structure of Figure 4.3 (iii) (a) requires that the copper(I) atoms are three coordinate, as in $(Et_4N)_3[Cu_3S_{18}]$ **(57)**,[150] while the puckered hexagonal bridged ring structures of Figure 4.3 (iii) (b) could occur for both three- or four-coordinate copper(I) species, both of which can accommodate the boat or chair conformation of the Cu_3X_3 ring. Three-coordinate planar copper(I) occurs in $[Cu(Me_3PS)Cl]_3$ **(58)**[151] with a chair conformation of the Cu_3S_3 ring and a four-coordinate Cu_3S_3 puckered ring in $[Cu_4(tu)_{10}][SiF_6]_2{\cdot}H_2O$ **(59)**.[152] An unusual trinuclear structure occurs in $[Cu(Ph_2PHCPh_3)]_3$,[153] with mixed coordination numbers, two trigonal planar CuP_3 chromophores and two two-coordinate CuC_2 chromophores (C—Cu—C angle = 158°). The only trinuclear copper(I) structure involving more than one bridging type of atom occurs in $[Cu(CN)(phen)]_3$ **(60)**[154] in which the $Cu_3(CN)_3$ ring system is essentially planar with near linear Cu—CN—Cu links (174 and 173°); the CuN_2CN chromophore is distorted tetrahedral with the plane of the phen ligand at *ca.* 90° to the $Cu_3(CN)_3$ plane.



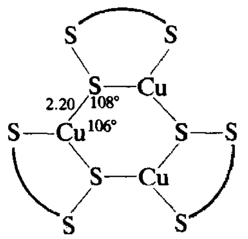
$[Cu_3(dppm)_3(OH)](BF_4)_2$ **(54)**[147]



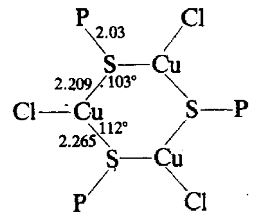
$[Cu_3(dppm)_3Cl_2]Cl$ **(55)**[148]



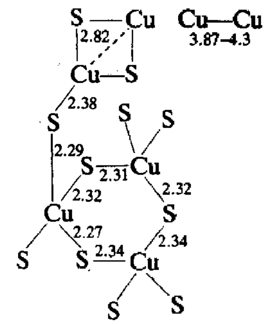
$[Cu_3(dppm)_2I_3]$ **(56)**[149]



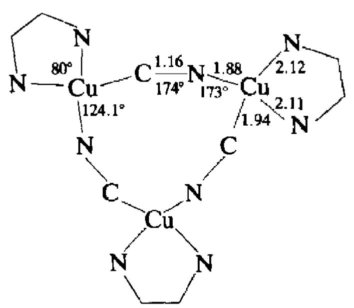
$(Et_4N)_3[Cu_3S_{18}]$ (**57**)[150]



$[Cu(Me_3PS)Cl]_3$ (**58**)[151]



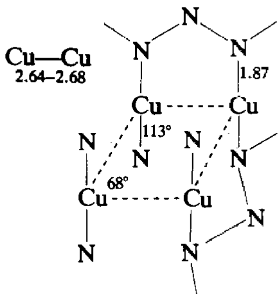
$[Cu_4(tu)_{10}](SiF_6)_2 \cdot H_2O$ (**59**)[152]



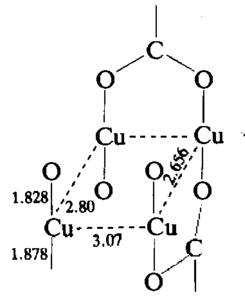
$[Cu(CN)(phen)]_3$ (**60**)[154]

53.3.2.4 Tetranuclear complexes

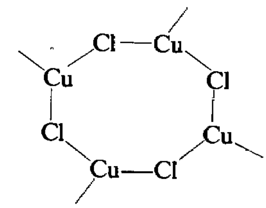
Tetranuclear complexes occur nearly as frequently as the dinuclear complexes, especially when iodide or sulfur ligands are present. No strictly linear tetranuclear Cu_4X_4 structures are known; square planar or rectangular Cu_4 units exist but these are much less common than the regular and distorted tetrahedral Cu_4 units. A near planar arrangement of four Cu atoms occurs (Figure 4.4) in $[Cu_4(MeN_3Me)_4]$ (**61**)[155] with Cu—Cu distances of 2.66 Å. In $[Cu_4(O_2CCF_3)_4] \cdot 2C_6H_6$ (**62**)[156] the Cu—Cu distances are significantly longer at 2.80 Å due to the presence of the more electronegative oxygen ligand and the coordination of the copper(I) atoms is increased by the formation of weak π bonds to the benzene molecule. In $[Cu_4(mhp)_4]$,[157] where mhp = 6-methyl-2-oxopyridine, a Cu_4N_8 chromophore is present, as in (**61**), but the Cu_4 is no longer planar. In [CuCl(2-butyne)] (**63**),[158] halide ions bridge the four planar copper atoms to give an eight-membered ring (Figure 4.4, ii) with the Cl atoms alternately out of the plane of the Cu atoms. In $[Cu_4(CH_2SiMe_3)_4]$[159] and $[Cu_4\{N(SiMe_3)_2\}_4]$ (**64**)[159] bulky nitrogen ligand groups[160] connect the four planar Cu atoms, with Cu—Cu distances of 2.42 and 2.69 Å, respectively. A similar planar Cu_4 chromophore with oxygen bridging occurs in $[Cu(OBu^t)]_4$[161] with a Cu—Cu distance of 2.71 Å. In [2-Cu-1-(dimethylaminomethyl)ferrocene]$_4$ (**65**),[162] the planar Cu_4 atoms are bridged in a most unusual way by single carbon atoms from a cyclopentadienyl ring, which then forms one ring of a ferrocene unit, $[Fe(Cp)_2]$. In $[Cu_4(tu)_9](NO_3)_4$ (**66**; tu = thiourea)[163] the four Cu atoms are bridged by two single S atom bridges and two pairs of S atom bridges (Figure 4.4, A, iii); see also $(NPr_4)_2[Cu_4Br_6]$[163b] with a short Cu—Cu distance of 2.71 Å and a sharp Cu—S—Cu angle of 69°. In (**66**) the Cu atoms are each coordinated by four thiourea ligands to give a tetrahedral CuS_4 chromophore, but two of these four sulfur ligand atoms bridge to a second Cu atom to yield a zigzag chain of Cu_4S_6 units. In $[Cu_4(dppm)_4(S_3C)_2]$ (**67**)[164] symmetrical bridging of a planar Cu_4 unit occurs by double-bridging trithiocarbonate sulfur atoms.



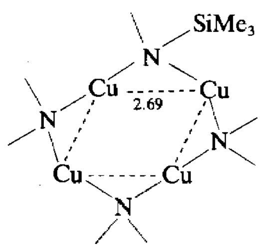
$[Cu_4(MeN_3Me)_4]$ (**61**)[155]



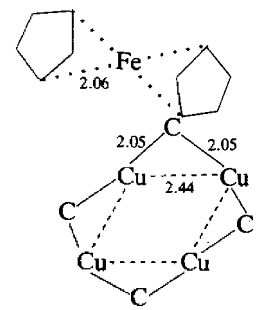
$[Cu_4(O_2CCF_3)_4]\cdot 2C_6H_6$ (**62**)[156]



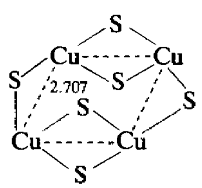
[CuCl(2-butyne)] (**63**)[158]



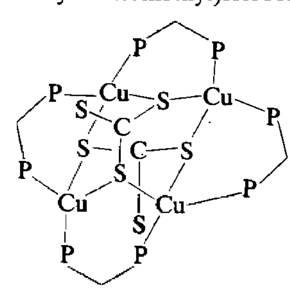
$[Cu_4\{N(SiMe_3)_2\}_4]$ (**64**)[159]



$[2\text{-Cu-1-(dimethylaminomethyl)ferrocene}]_4$ (**65**)[162]

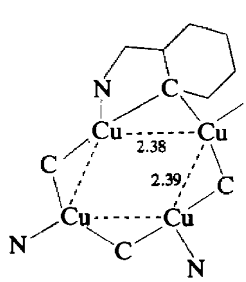


$[Cu_4(tu)_9](NO_3)_4$ (**66**)[163]

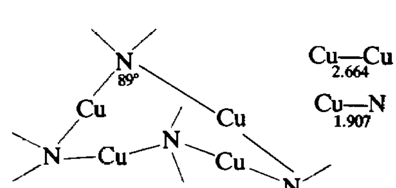


$[Cu_4(dppm)_4(S_2C)_2]$ (**67**)[164]

The butterfly configuration for a Cu_4 unit (Figure 4.4, iv) has been characterized in $[Cu(MDAP)]_4$ (**68**),[165] where MDAP = {5-methyl-2(dimethylamino)methyl}phenyl, in $[Cu\{(Pr^iO)_2PS_2\}]_4$[166] and, more recently, in $[Cu(NEt_2)]_4$ (**69**);[167] both the former structures involve an asymmetric bridging carbon atom from a phenyl ring, Cu—C = 1.97 and 2.16 Å, and the copper coordination number is increased to three by a Cu—N bond of 2.19 Å; the Cu—Cu distances are short at 2.38 and 2.74 Å, respectively. In (**69**) the separation is 2.66 Å and the CuN_2 units are nearly linear with an N—Cu—N angle of 175.4°.

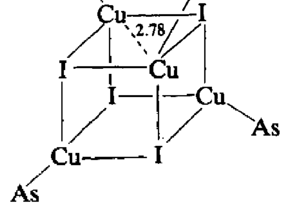


$[Cu(MDAP)]_4$ (**68**)[165]

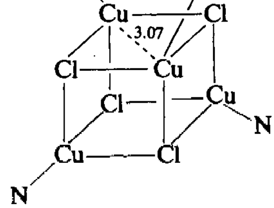


$[Cu(NEt_2)]_4$ (**69**)[167]

The tetrahedral Cu_4X_4 is the most common tetranuclear copper(I) species and primarily occurs (Figure 4.4, v) as the 'cubane' structure $Cu_4X_4L_4$, where X is Cl^-, Br^- or I^- and L is a monodentate (L) or bidentate (L_2) ligand. The basic cubane structure was first recognized in $[CuI(AsEt_3)]_4$ (**70**).[168] Two interpenetrating Cu_4 and I_4 tetrahedra are involved, approximately at the corners of a cube, but significant distortions of the regular 90° angles occur to give values of 97–113° (Table 10). With monodentate ligands L coordination to the copper(I) ions occurs approximately along the three-fold cube diagonal to generate a tetrahedral CuX_3L chromophore. In a series of $Cu_4X_4(PEt_3)_4$ complexes,[169] while the Cu—X distances increase with the size of the halide ion X, due to a significant change of the X—Cu—X angle from 97 to 109° in this series (Table 10a), the corresponding Cu—Cu distances show a significant decrease as the Cu—X distance increases. This suggests that the cubane Cu_4X_4 unit is best considered as a tetrahedron of X atoms with the Cu atoms in tetrahedral sites, with the copper atom moving nearer to the X_3 plane and the centre of the cube as the size of X increases. As the Cu—X distance increases, the Cu—L distance increases slightly for the same L (Table 10b).[170] A range of cubane structures is formed with $X = I^-$, but for $X = Cl^-$ large L groups, such as PPh_3, were thought to be required;[176] however the recent establishment of the corresponding $[CuX(NEt_3)]_4$ (**71**)[170] series, where $X = Cl^-$ and Br^-, questions this requirement (Table 10b). Ref. 170 includes a useful tabulation of the $Cu_4X_4L_4$ cubane structures. In a series of $Cu_4I_4L_4$ complexes (Table 10c) the Cu—I distances are not constant (2.54–2.77 Å) and the Cu—Cu separations vary from 2.60 to 3.18 Å, which again correlates with a decrease of the X—Cu—X angle from 115 to 101° in the same sequence (Table 10c). The cubane structure of $[CuBr\{P(Bu^t)_3\}]_4$ (**72**)[177] is unusual in having a crystallographic three-fold symmetry, while in $[Cu_4Cl_4(NEt_3)_3]$ (**73**),[121,176] the cubane structure is retained and has a crystallographic three-fold symmetry, but with the Cu_4I_4 units linked to give a linear chain of Cu—I bonds. In $[Cu_4I_4(SEt_2)_3]$ (**74**)[178] the Cu_4I_4 unit is present in a crystallographically general position, with CuI_3S chromophores, two of which involve a monodentate sulfur ligand and two involve a bridging sulfur ligand to give a linear zigzag chain structure. A relatively complex cubane type Cu_4S_4 unit occurs in $[Cu(S_2CNEt_2)]_4$ (**75**),[179] in which one of the S atoms constitutes the Cu_4S_4 unit and the second S of each S_2CNEt_2 group symmetrically bridges two copper atoms on the four side-face, Cu—Cu pairs. A comparable structure occurs in $[Cu\{S_2CN(Pr^i)_2]_4$.[180] While the cubane $Cu_4X_4L_4$ structure is of interest in its own right, it may also be considered the parent of a number of related copper(I) structures as shown in Figure 6(b), which also builds up to the open cubane structures in $(Ph_3MeP)_2[Cu_4I_6]$ (**76**).[181] The compact Cu_4I_4 cubane cage is lost and a more 'open cubane' tetrahedral structure (Figure 4.4, vi) results. The Cu—Cu separation is still 2.74–2.76 Å, well within the range of Cu—Cu distances of Table 10(b), but the interpenetrating tetrahedra of X_4 atoms of (**70**)–(**73**) are now missing and the six I^- atoms symmetrically bridge all six of the Cu—Cu edges of the tetrahedral Cu unit, with a Cu—I—Cu angle of 64–65°. An equivalent structure involving bridging sulfur ligands has been established for $[Cu_4\{SC(NH_2)_2\}_6](NO_3)_4{\cdot}4H_2O$,[182] and $(Ph_4P)_2[Cu_4(SPh)_6]$ (**77**).[93,183] Further examples of the $[Cu_4(SPh)_6]^{2-}$ anion have now been characterized[184] and the conformational isomerism that can arise has been discussed. In the open cubane Cu_4X_6 structure each Cu atom is trigonal pyramidal, with no terminal fourth ligand atoms. If some at least of these positions are occupied, this results in enhanced saturation, as in $[Cu_4\{SC(NH_2)_2\}_9](NO_3)_4{\cdot}4H_2O$ (**78**),[182] relative to the three-coordinate CuS_3 chromophores of $[Cu_4\{SC(NH_2)_2\}_6](NO_3)_4{\cdot}4H_2O$ (as in structure **77**).[182] A related $[Cu_4S_6]$ structure has been described for $[Cu_4(iptp)_3][CuCl_2]{\cdot}CCl_4$ (**79**),[185] where iptp = imidotetraphenyldithiodiphosphino-*S,S*, a chelate sulfur ligand, in which each iptp ligand chelates one Cu atom and bridges two others (*cf.* **75**). In (**79**) none of the four cubic X_4 tetrahedral positions is occupied to give an 'open cubane' structure and the presence of the chelate ligands imposes an approximate three-fold symmetry with each Cu atom involved in a trigonal pyramidal CuS_3 chromophore if Cu—Cu distances of 2.76–2.82 Å are excluded as bonding.



$[CuI(AsEt_3)]_4$ (**70**)[168]

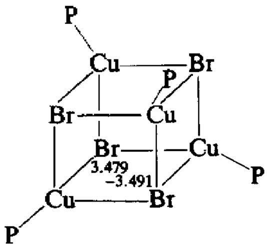


$[CuCl(NEt_3)]_4$ (**71**)[170]

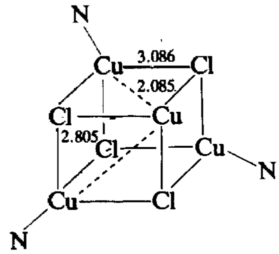
Table 10 Some Molecular Distances for $[Cu_4X_4L_4]$ Complexes[168–175]

X	*Cu—X* (Å)	*X—Cu—X* (°)	*Cu—Cu* (Å)	*Cu—L* (Å)	*Ref.*
(*a*) *L* = *PEt*$_3$					
Cl	2.43	97	3.21	2.18	169
Br	2.54	101	3.18	2.20	169
I	2.68	109	2.93	2.25	168
(*b*) *L* = *NEt*$_3$					
Cl	2.44	101	3.07	2.05	170
Br	2.54	104	3.04	2.06	170
(*c*) *X* = *I*					
2Mepy	2.70–2.77	111–115	2.67–2.72	1.99–2.07	171
py	2.70	113	2.60	2.02	172
denc[a]	2.70	113	2.68	2.04	173
$AsPh_3$	2.67–2.72	107–115	2.78–2.90	2.37–2.38	174
$AsEt_3$	2.67	112	2.78	2.36	168
PEt_3	2.54	101	3.18	2.19	168
PPh_3	2.65–2.73	103–115	2.87–3.16	2.25–2.26	175

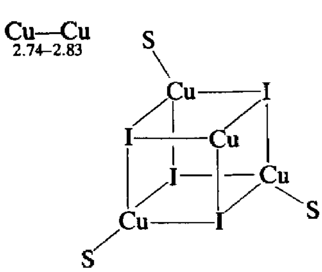
[a] denc = *N*,*N*-diethylnicotinamide.



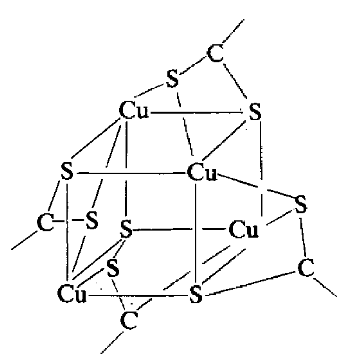
$[CuBr(PBu^t_3)]_4$ **(72)**[177]



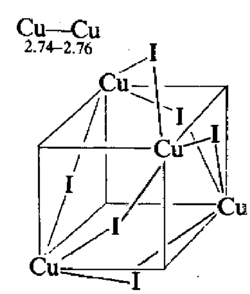
$[Cu_4Cl_4(NEt_3)_3]$ **(73)**[121,176]



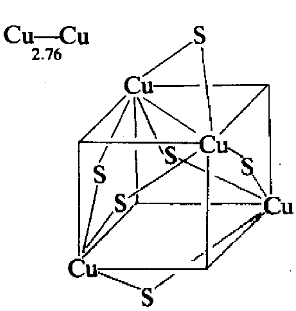
$[Cu_4I_4(SEt_2)_3]$ **(74)**[178]



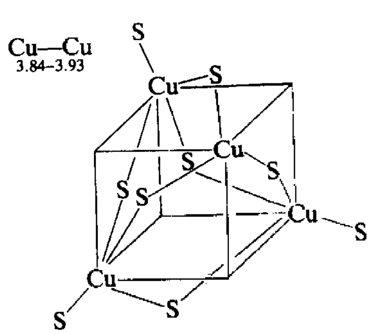
$[Cu(S_2CNEt_2)]_4$ **(75)**[179]



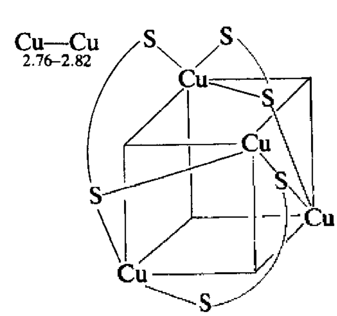
$(Ph_3MeP)_2[Cu_4I_6]$ **(76)**[181]



$(Ph_4P)_2[Cu_4(SPh)_6]$ **(77)**[93,183]

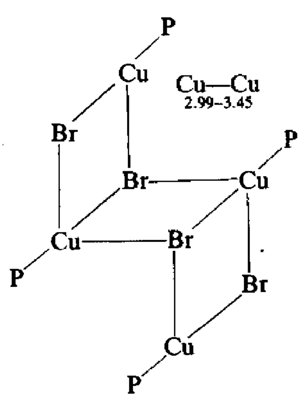


$[Cu_4\{SC(NH_2)_2\}_9](NO_3)_4 \cdot 4H_2O$ **(78)**[182]

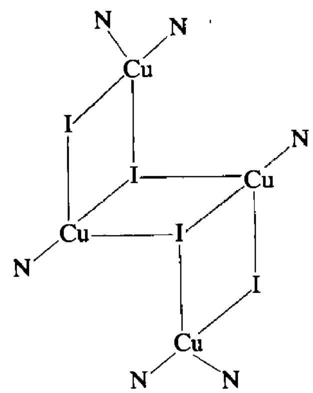


$[Cu_4(iptp)_3][CuCl_2] \cdot CCl_4$ **(79)**[18

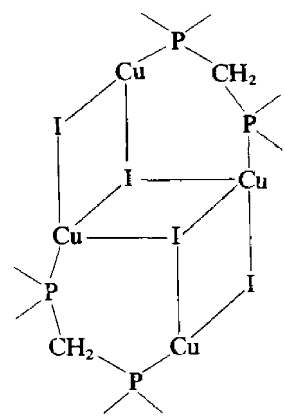
The basic Cu_4X_4 cubane structure may be further opened out into the stepped cubane structure of Figure 4.4 (vii), as in $[Cu_4Br_4(PPh_3)_4]\cdot 2CHCl_3$ (**80**)[186] and $[Cu_4I_4(dppm)_2]$ (**82a**),[187] both of which involve a mixed copper(I) stereochemistry with central tetrahedral $CuPX_3$ chromophore and terminal trigonal $CuPX_2$ chromophores. In the stepped structure of $[Cu_4I_4(2\text{-Mepy})_6]$ (**81**)[121] two additional nitrogen ligands increase the coordination number to make all four copper atoms four coordinate with two terminal CuI_2N_2 chromophores and two nonterminal CuI_3N chromophores. At all the steps, the Cu—I—Cu and I—Cu—I angles are opened out to 100–120° to yield a rather flattened 'staircase', which is then reminiscent of the ribbon-like structure of the unusual tetranuclear complex $[Me_2PCuC{\equiv}CPh]_4$ in (**82b**; Figure 8).[188] In (**82b**) the I atoms of the Cu_4I_4 unit are replaced by alkyne carbon atoms and the nonterminal copper atoms are involved in a long Cu—C distance of 2.22 Å to produce a distorted CuC_4 chromophore. The two terminal Cu atoms involve two P ligands to yield a tetrahedral CuC_2P_2 chromophore. In (**81**) and (**82**) the basic Cu_4 species of both structures could alternatively be described as a linear tetramer, but in view of the relationship to the Cu_4I_4 cubane cage, the stepped cubane description is preferred.



$[Cu_4Br_4(PPh_3)_4]\cdot 2CHCl_3$ (**80**)[186]



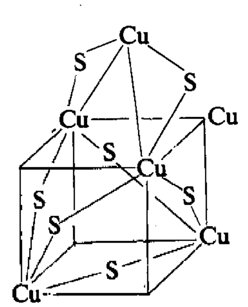
$[Cu_4I_4(2\text{-Mepy})_6]$ (**81**)[121]



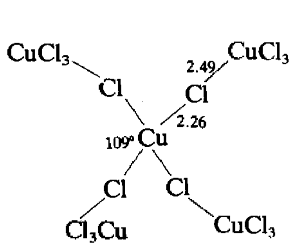
$[Cu_4I_4(dppm)_2]$ (**82a**)[187]

53.3.2.5 Pentanuclear complexes

Pentanuclear complexes are only of limited occurrence (Figure 4.5, i and ii). One of the best examples has only recently been recognized in $(Me_4N)_2[Cu_5(SPh)_7]$ (**83**),[189] and involves an open cubane structure with the top face bridged by a single S atom of the benzenethiolate ligands (Figure 4.5, i). The four Cu atoms of the original Cu tetrahedron involve near trigonal planar CuS_3 units, and the fifth Cu has a near linear CuS_2 unit with an S—Cu—S angle of 175.2°. The overall symmetry of the $[Cu_5S_7]$ chromophore is approximately C_{2v}, with Cu—S distances of 2.16–2.33 Å, and short Cu—Cu distances of 2.72–3.76 Å, in which the longest distance of 3.76 Å is associated with the two Cu atoms bridged by the fifth Cu atom. This suggests that the fifth Cu atom has significantly increased the Cu—Cu separation of the basic Cu_4S_4 unit of *ca.* 2.70 Å. A pentanuclear copper(I) complex involving bridging X atoms (Figure 4.5, ii) was first recognized in $[Co(NH_3)_6][Cu_5Cl_{17}]Cl$ (**84**),[190] which consists of an almost regular tetrahedral $CuCl_4$ chromophore, which is unknown in a monomeric copper(I) structure (see Figure 4.1, iii), bridged to four additional $CuCl_3$ chromophores.



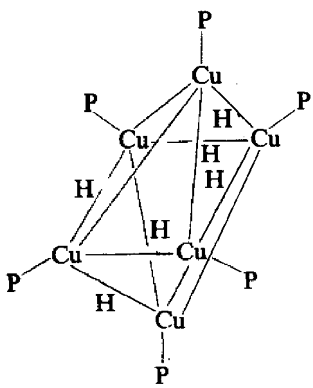
$(Me_4N)_2[Cu_5(SPh)_7]$ (**83**)[189]



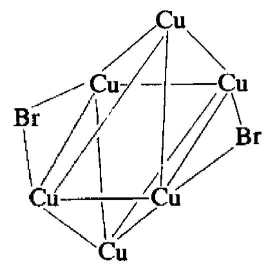
$[Co(NH_3)_6][Cu_5Cl_{17}]Cl$ (**84**)[190]

53.3.2.6 Hexanuclear complexes

Hexanuclear complexes are more common than pentanuclear complexes and are based upon a near regular octahedral Cu_6 unit (Figure 4.6, i) or a distorted Cu_6 unit (Figure 4.6, ii). The most regular octahedral structure is observed in $[H_6Cu_6(PPh_3)_6]$ (**85**)[191] and more recently $[H_6Cu_6\{P(totyl)_3\}_6]$;[192] in (**85**) the Cu_6 octahedron involves terminal PPh_3 ligands on each Cu atom; the Cu—P distance is 3.24 Å. Two mutually *trans* faces of the Cu octahedron are enlarged to Cu—Cu distances of 2.63–2.74 Å compared with 2.49–2.60 Å for the shorter Cu—Cu distances; the longer Cu—Cu distances are believed to involve bridging hydrogen ligands. A less regular octahedron due to nonequivalent ligands is present in $[Cu_6(2\text{-}Me_2NC_6H_4)_4Br_2]$ (**86**)[193] and in the comparable structure of $[Cu_6(2\text{-}Me_2NC_6H_4)_4(C{\equiv}CC_6H_4Me\text{-}4)_2]$.[194] A very distorted Cu_6 octahedron occurs in the structure of $(Ph_4P)_2[Cu_6(S_4)_3(S_5)]$;[195] the sense of the distortions (Figure 4.6, ii) suggest that two tetrahedra share a common edge and the faces of a Cu_6 unit are bridged by three S_4 chains and one S_5 chain of sulfur atoms.



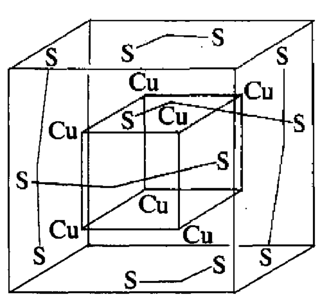
$[H_6Cu_6(PPh_3)_6]$ (**85**)[191]



$[Cu_6(2\text{-}Me_2NC_6H_4)_4Br_2]$ (**86**)[193]

53.3.2.7 Octanuclear complexes

Polynuclear complexes with more than six copper atoms are unusual, except for ones involving a Cu_8 unit (Figure 4.7). This involves a $[Cu_8(S_2R)_6]$ unit and occurs in $(PhMe_3As)_4[Cu_8\{S_2CC(CN)_2\}_6]$ (**87**),[196] but also occurs with the sulfur ligands $\{S_2C_2(CO)_2\}^{2-}$ and $\{S_2CC(CO_2Et)_2\}^{2-}$.[197] In all three complexes a basic cube of Cu_8 atoms is involved, which is capped by an octahedral array of S_2 ligand groups to yield a range of Cu—Cu distances of 2.77—2.91 Å.

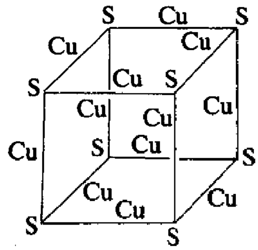


$[PhMe_3As]_4[Cu_8\{S_2C_2(CN)_2\}_6]$ (**87**)[196]

53.3.2.8 Dodecanuclear complexes

Recently the crystal structure of $(Ph_4P)_4[Cu_{12}S_8]$ (**88**) has been reported to involve a cube of eight S^{2-} anions with interpenetrating cubo-octahedral Cu_{12} units;[198] it represents an inverted

Cu_8S_{12} ratio as observed in (**87**). The arrangement of (**88**) is not strictly cubic as the Cu—Cu distances range from 2.774 to 2.980 Å, the Cu—S distances from 2.156 to 2.179 Å, and the S—Cu—S angles are 167–171°.

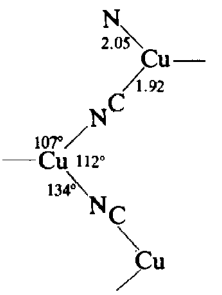


$(Ph_4P)_4[Cu_{12}S_8]$ (**88**)[198]

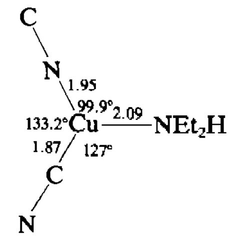
53.3.2.9 Infinite chains, sheets and three-dimensional lattices

While the structures so far described in Figure 4.1–4.7 involve distinct molecular and polynuclear copper(I) species, they are characterized by the relatively low coordination numbers of two, three and four. Such low coordination numbers are conducive[10] to bridging ligand functions and hence to infinite lattices involving chains (or ribbons), sheets and three-dimensional lattices.[199] Figure 4.8 summarizes the types of chain structures characteristic of copper(I).

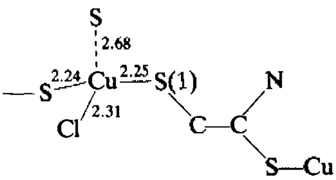
The most simple linear chain structure (Figure 4.8, i) involving two-coordinate copper(I) occurs in the helical chain structure of $K[Cu(CN)_2]$ (**89**)[200] and $Na[Cu(CN)_2{\cdot}2H_2O]$.[97] The linear chain structure involving three-coordinate copper(I) (Figure 4.8, ii) may occur as an essentially planar CuX_2L chromophore as in $[Cu(CN)(HNEt_2)]$ (**90**)[154] and $[Cu(CN)(NEt_3)]$,[201] with a tetrahedrally distorted CuX_2L_2 chromophore as in $[CuCl(Et_2S_2)]$,[202] or as a trigonal pyramidal $CuLX_3$ chromophore as in $[CuCl(C_2N_2S_2H_4)]$ (**91**).[203] In (**91**) the rubeanate ligand bridges the copper atoms along the chain and the Cl^- anions act as terminal ligands in the $CuClS_2S'$ chromophore. In (**91**) the chains are stacked in pairs and linked by a long Cu—S distance of 2.86 Å to form a distorted tetrahedral $CuClS_2S$ chromophore that is described as a (3 + 1)-type coordination with the Cu atom tilted 0.38 Å out of the $CuClS_2$ plane. In the three-coordinate tetrahedral chains of [CuI(2,4,6-trimethylpyridine)] (**92**)[204] and [CuI(acridine)][121] the tetrahedral distortion of the CuI_2N chromophore relates the chains of (**92**) to the double-stepped structure of Figure 4.8 (vi). For this reason these structures have been referred to as the split chain or stepped structures.[204] A chain of regular tetrahedral $CuCl_4$ chromophores occurs in $K_2[CuCl_3]$[205] and in (paraquat)$[CuCl_2]$.[206] In the former, single corners are shared to give a zigzag chain, while in the latter edge-sharing is involved to give a linear chain structure (Figure 4.8, v and iv, respectively). Mixed ligand atom bridging may also occur, as in the linear bridging chains of $[CuCl(C_8H_6N_4S_2)]{\cdot}H_2O$ (**93**)[207] or [CuBr(1,4-oxathiane-*S*)],[208] or in the nonbridging chelate-ligand chains of [Cu(dmphen)(NCS)] (**94**),[209] or in the bridging chelate chains of $[CuBr(Et_2PPEt_2)]$ (**95**)[210] and $[Cu(NC)(CH_2)_n(CN)](NO_3)$.[211] Linear chains with mixed trigonal and tetrahedral geometries may also occur as in $[Cu_2(CN)_2(4\text{-}Mepy)_3]$ (**96**)[154] and $\{S_2C_3(SMe)_3\}[Cu_2I_3]$ (**97**).[212] The double chain structures of copper(I) (Figure 4.8, v–viii) are even more common than the single chain structures of copper(I), and they generally involve tetrahedral CuX_4 chromophores or three-coordinate CuX_3 chromophores with a tetrahedral distortion. The former appears in the $[Cu_2Cl_3]^-$ anion of $Cs[Cu_2Cl_3]$[213a] (see also $(NEt_4)_3[Cu_7Cl_{10}]$),[213a] in the $[Cu_2Br_2]^-$ anion of $(Ph_2N_2)[Cu_2Br_3]$[214] and in the $[Cu_2I_3]^-$ anion of $Cs[Cu_2I_2]$,[213] in which each CuX_4 chromophore shares three edges and two vertices with adjacent groups in the chain. In $(Me_4N)[Cu_2I_3]$ (**98**)[215,216] a slight modification of the double tetrahedral chain occurs, involving the sharing of one edge and face, while in $[CuI(Et_2S_2)]$[217] an equally complicated double chain of shared CuI_3S tetrahedra is involved. In $[CuCl(C_2N_2S_2H_4)_{1.5}](OH_2)_{0.45}$ (**99**)[218] the CuS_3Cl tetrahedra are linked in two directions by the bidentate rubeanate ligand to form two interpenetrating zigzag helical chains. The stair or step polymer chain of Figure 4.8 (vi) and (vii) has been characterized in [CuX(py)], X = Cl (**100**)[120] or I, [CuX(NCR)],[219] X = Cl, Br and I, and R = Me and Ph. By changing from methyl cyanide to methyl isocyanide a linear polymer with a displaced stair structure is observed in [CuI(CNMe)] (**101**),[220] while in $[CuI(N_2Me_2)]$ (**102**)[221] a double stair polymer chain is formed by azomethane linkages. One of the most structurally intriguing complexes of copper(I) is $[Cu(O_2CMe)]$ (**103**),[222a] bearing in mind the dimeric structures of $[Cu(O_2CMe)_2(OH_2)]_2$ (see **316**, Section 53.4.2.3). Structure (**103**) retains the unique acetate ligand bridging role of the copper(II) complex, but this is now restricted to planar dimeric $[Cu_2(O_2CMe)_2]$ units, linked by further oxygen bridges into a staggered linear polymer which is planar overall. The Cu—Cu distance of 2.556(2) Å is significantly shorter than any of the Cu—Cu distances in the dimeric copper(II) carboxylates of *ca.* 2.64 Å, and, if considered a bond, the copper(I) environment is formally square coplanar, a geometry that is uncharacterized in the mononuclear stereochemistries of copper(I) (Figure 4.1), particularly for a CuO_4 chromophore (but see **14**). If for this reason alone the Cu—Cu distance is considered nonbonding, the CuO_3 chromophore is still most unusual as it has a T-shaped structure that involves two angles much less than 120°, namely 80.4 and 110.5°, with a third O—Cu—O angle nearly linear at 170.1°. More recently the electron diffraction structure of anhydrous copper(I) acetate has been reported[222b] to involve a dimeric planar structure related to the solid state structure (**103**), with relatively short Cu—O and Cu—Cu distances of 1.868 and 2.491 Å, respectively.



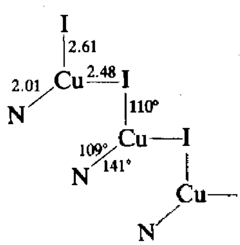
$K[Cu(CN)_2]$ (**89**)[200]



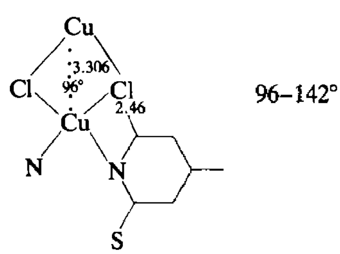
$[Cu(CN)H(NEt_2)]$ (**90**)[154]



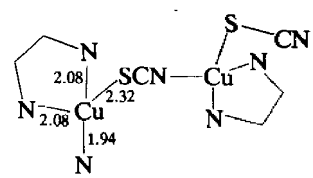
$[CuCl(C_2N_2S_2H_4)]$ (**91**)[203]



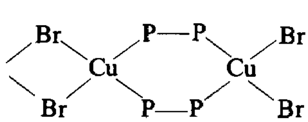
$[CuI(2,4,6\text{-}Me_3py)]$ (**92**)[204]



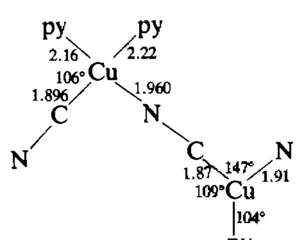
$[CuCl(C_8H_6N_4S_2)]\cdot H_2O$ (**93**)[207]



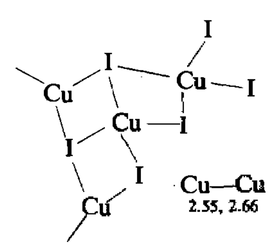
[Cu(dmphen)(NCS)] (**94**)[209]



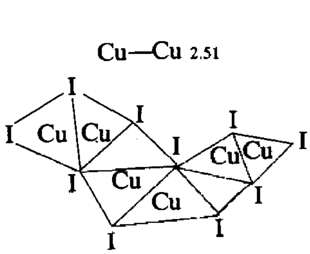
$[CuBr(Et_2PPEt_2)]$ (**95**)[210]



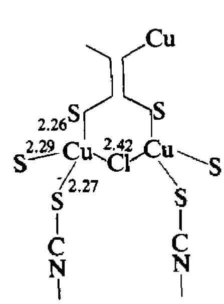
$[Cu_2(CN)_2(4\text{-}Mepy)_3]$ (**96**)[154]



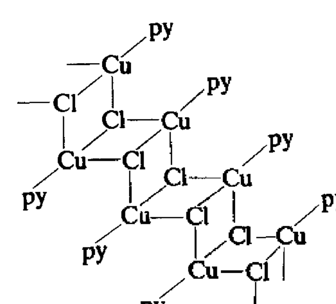
$[S_2C_3(SMe)_3][Cu_2I_3]$ (**97**)[212]



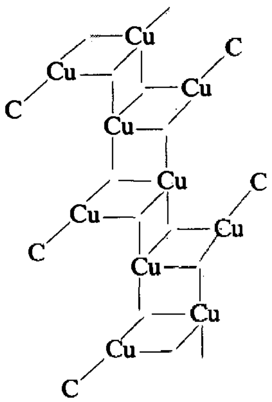
$(Me_4N)[Cu_2I_3]$ (**98**)[215,216]



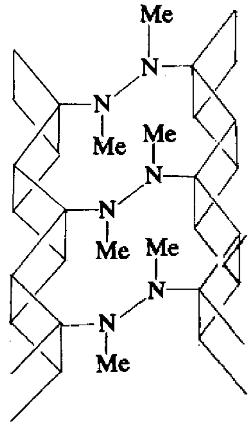
$[CuCl(C_2N_2S_2H_4)_{1.5}](OH_2)_{0.45}$ (**99**)[218]



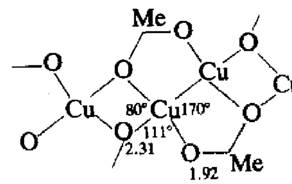
[CuCl(py)] (**100**)[120]



[CuI(CNMe)] (**101**)[120]

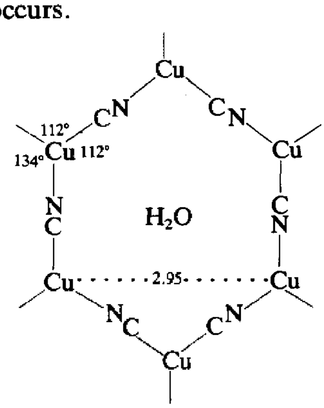


[CuI(N_2Me_2)] (**102**)[221]

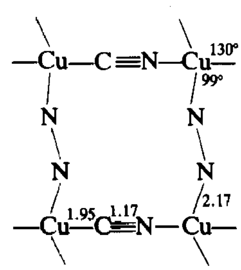


[Cu(O_2CMe)] (**103**)[222a]

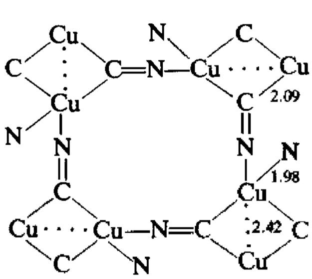
The formation of infinite two-dimensional sheet structures in copper(I) compounds (Figure 4.9) is much less extensive than the formation of tetranuclear or hexanuclear complexes might suggest. Rings of Cu_4 and Cu_6 atoms are still involved with intermediate bridging ligands; in the former the Cu atoms are three-coordinate trigonal planar, as in K[$Cu_2(CN)_3$]·H_2O (**104**)[223] with the water molecule at the centre of the rings. In the latter, puckered sheets of four-coordinate copper are involved, as in [Cu(CN)(N_2H_4)] (**105**).[224] A slightly different four-membered ring structure is formed in [Cu(CN)(NH_3)] (**106**)[225] in which the CN^- anions not only allow pairs of Cu atoms to bridge through the C atom, but also then form an additional Cu—N link. The NH_3 groups coordinate to each Cu atom either above or below the Cu–Cu planes to maintain a CuC_2N_2 chromophore if a relatively short Cu—Cu distance of 2.42 Å is considered nonbonding. [Cu(succinonitrile)$_2$](ClO_4)[226] also involves a Cu_4 ring system with tetrahedral CuN_4 chromophores. The sheet structure of the copper(I) halides[227] also involves 4:4 coordination, but even in Cu_2O this is complicated by two interpenetrating nets.[228] In β-[Cu(NCS)] (**107**)[229] there are sheets of tetrahedral CuS_3N chromophores linked by the bridging thiocyanate ligands, while in (C_5H_5N)[$Cu_2(SCN)_3$] (**108**)[230] a more complicated three-dimensional structure (Figure 4.10) is present, involving tetrahedrally twisted Cu_2S_2 units bridged by four $(SCN)^-$ anions in the plane and by four links out of the plane. In the Cu_2S_2 units a rather long Cu—Cu distance of 2.80 Å occurs.



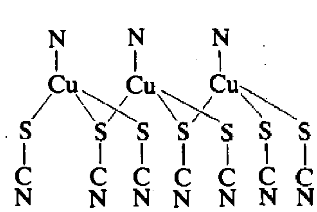
K[$Cu_2(CN)_3$]·H_2O (**104**)[223]



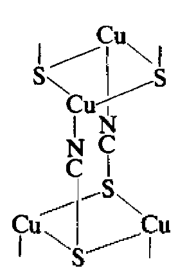
[Cu(CN)(N_2H_4)] (**105**)[224]



[Cu(CN)(NH_3)] (**106**)[225]



β-[Cu(NCS)] (**107**)[229]



(C_5H_5N)[$Cu_2(SCN)_3$] (**108**)[230]

53.3.2.10 Carbon monoxide complexes

A unique feature of copper(I) chemistry is the reversible fixation of carbon monoxide by solutions of copper(I) salts,[231] such as CuCl, in which the precise chemical species in solution has never been adequately defined.[232] Despite this lack of precise information, such solutions were extensively used for the estimation of CO gas.[233] The extent of the reaction and its reversibility are dependent on the nature of the solvent and the particular copper(I) salt used (*cf.* Figures 2 and 3). Presumably the solvent is involved in coordination to the copper(I) species and the stability of the $Cu(CO)_x(solvent)_y$ species will be determined by the coordinating ability of the solvent, not only to dissociation of the CO, but also towards disproportionation to copper(II) and copper metal. Since the first isolation of a solid copper(I) carbonyl, namely $[Cu^I(CF_3CO_2)(CO)]$,[234] as a polycrystalline sample, a significant literature has accumulated on the methods of preparation, characterization and crystal structure determination of the known copper(I) carbonyl complexes. These data were reviewed[231] in 1983 and the preparative routes and structural results are summarized in Figure 7. Against the general background of the structural chemistry of copper(I) summarized in Figure 4.1–4.10, the copper(I) carbonyl complexes at present characterized are restricted to mono- and bi-nuclear structures. In general the preparations are from the copper(I) halides (Figure 7) and the structures are stabilized by nitrogen donor ligands, and not by the phosphine type ligands so characteristic of the early copper(I) coordination chemistry. With one exception all the carbonyl complexes of known crystal structure involve coordination of the CO group *via* the carbon atom to a single metal and result in a characteristic[231] C—O stretching frequency in the range 2055–2117 cm^{-1} (Table 11). This contrasts with the C—O band at 1926 cm^{-1} in the only bridging carbonyl of known crystal structure, namely $[Cu_2(tmen)_2(\mu\text{-}PhCO_2)(\mu\text{-}CO)](BPh_4)$ (**116**; Figure 7).[240] In the dinuclear carbonyl complexes of Figure 7, the bridging ligands involve the halide ion[238] or carboxylate anion,[240] as might be anticipated, but also involve bridging ethylenediamine[237] (in $[Cu_2(en)_3(CO)_2](BPh_4)_2$, (**113**) and histamine[239] (in $[Cu_2(hm)_3(CO)_2](BPh_4)$, **115**), which are normally found as chelate ligands. Since the reviews summarized[231] in Figure 7 were published, further carbonyl complexes have been characterized: a dinuclear macrocyclic complex in $[Cu_2(tpen)(CO)_2](BF_4)$ (**117**),[144,247] where tpen = *N,N,N',N'*-tetrakis(1-pyridylmethyl)ethylenediamine, but of more significance, two tetranuclear carbonyl complexes. These are $[Cu(CO)(OBu^t)]_4$ (**118**)[246,247] and $[Cu(2\text{-methylquinolin-8-olato})(CO)]_4$ (**119**).[248] The latter is prepared from sodium 2-methylquinolin-8-olate in THF at 65 °C and 60 atm of CO pressure; the structure has S_4 symmetry of the cubane-like cage and the C—O stretch occurs at 2050 cm^{-1}. The unusual feature of (**118**) and (**119**) is that they both involve Cu—O bonds, which are much less common than Cu—N bonds, either in the complexes shown in Figure 7 or in the cubane-type structures of (**70**) to (**79**). Two further monomeric complexes involve a mixed tetrahedral $CuCN_2O$ chromophore in $[Cu(bipyam)(OClO_3)(CO)]$ (**120**), where bipyam = 2,2'-dipyridylamine,[249] and $[Cu(CO)(EtSO_3)]$ (**121**).[250] Structure (**120**) is also unusual in involving a coordinated perchlorate group (see Chapter 15.5) with a relatively long Cu—O distance of 2.4 Å and (**121**) involves a tridentate bridging ethanesulfonate anion to produce a double chain structure involving a local tetrahedral $CuCO_3$ chromophore.

Nonempirical LCAO–MO–SCF calculations[251] have been carried out on the hypothetical species $[Cu(NH_3)_2(CO)]^+$ and $[Cu(NH_3)_3(CO)]^+$ as models for the $[Cu(en)(CO)]^+$ (**112**) and $[Cu(dien)(CO)]^+$ (**111**) cations (Figure 7); each suggests that the Cu—C—O angle should be linear (as observed) and that the coordination energy of the CO is $-33.9\ kJ\ mol^{-1}$.

Table 11 The IR Spectra of Some Well-characterized Copper(I) Carbonyl Complexes of (a) Known and (b) Unknown Crystal Structure

Complex	*IR* (cm^{-1})	*Ref.*	*Complex*	*IR* (cm^{-1})	*Ref.*
(*a*) *Known crystal structures*			(*b*) *Unknown crystal structures*		
[Cu(cyclops)(CO)] (**28**)	2068	112	$[Cu(CF_3CO_2)(CO)]$	2155	241
$[Cu(HBpz_3)(CO)]$ (**110**)	2083	235	$[Cu(CO)(OH_2)_2](ClO_4)$	2131	242
$[Cu(dien)(CO)](BPh_4)$ (**111**)	2080	236	$[Cu^ICu^{II}L]$	2065	243
$[Cu(en)(CO)](BPh_4)$ (**112**)	2117	237	$[Cu^ICu^IL]$	2061	243
$[Cu_2(en)_3(CO)_2](BPh_4)_2$ (**113**)	2087	237	$[Cu(CO)](AsF_6)$	2180	244
$[\{Cu(tmen)(CO)\}_2Cl](BPh_4]$ (**114**)	2065	238	$[Cu_2(phen)_2Cl_2(CO)]$	2066	245
$[Cu_2(hm)_2(CO)](BPh_4)_2$ (**115**)	2055	239			
$[Cu_2(tmen)(\mu\text{-}PhCO)(\mu\text{-}CO)](BPh_4)$ (**116**)	1926	340			

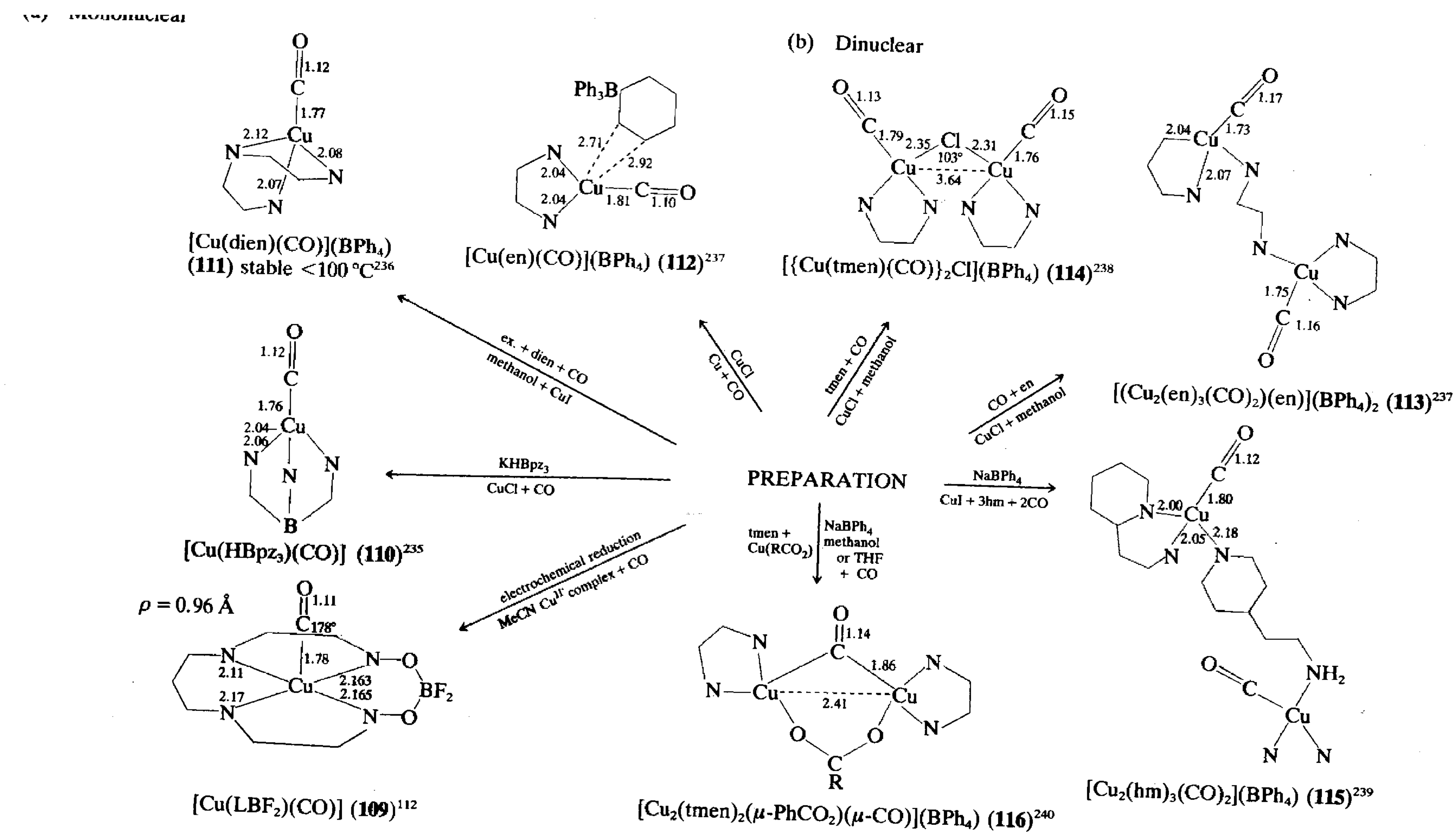
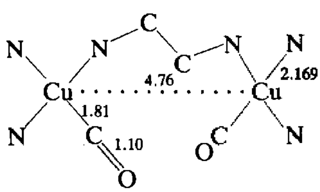
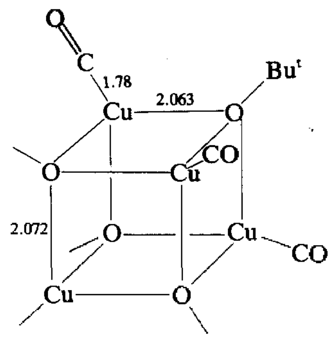


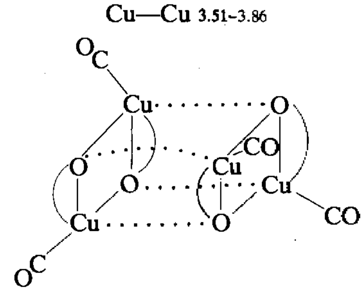
Figure 7 The preparations and crystal structures of copper(I) carbonyl (a) mononuclear and (b) dinuclear complexes



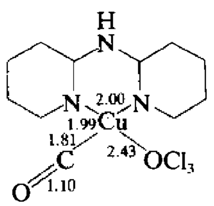
$[Cu_2(tpen)(CO)_2](BF_4)_2$ **(117)**[144]



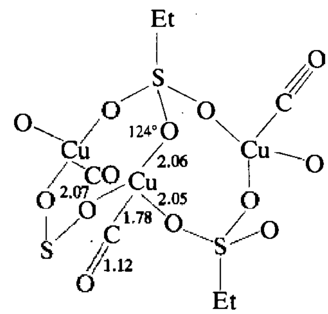
$[Cu(CO)(OBu^t)]_4$ **(118)**[247]



[Cu(2-Mequinolin-8-olato)(CO)]$_4$ **(119)**[248]



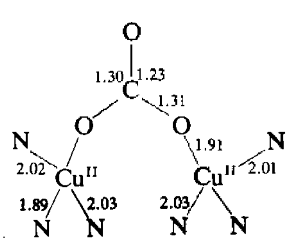
$[Cu(bipyam)(OClO_3)(CO)]$ **(120)**[249]



$[Cu(CO)(EtSO_3)]$ **(121)**[250]

A major reason for the interest in the carbonyl complexes of the copper(II) ion lies in the possible copper-promoted carbonylation of organic substrates[252] as in the Gatterman–Koch reaction (equation 5) and in the carbonylation of amines to *N*-alkylformamides.[252] Likewise the reduction of CO to methanol on copper-based catalysts is believed to occur through the formation of an intermediate Cu—CO unit. From an inorganic chemistry point of view, it is equally of interest that the stable carbonyl complex $[Cu(L^6)(CO)]$, where L^6 = 1,2-bis-{2-(4-methylpyridyl)imino}isoindoline,[253] can be oxidized by atmospheric oxygen to a copper(II) bridged carbonate complex $[\{Cu(L^6)\}_2(\mu\text{-}CO_3)]$ **(122)**,[254] suggesting that oxygen insertion has occurred to give an *in situ* carbonate anion (see Section 53.3.2). It may then be significant that copper(I) does form stable carbon monoxide complexes where O atom ligands are present **(118–121)** and equally that a suboxide, $[Cu_4O]$, has been recognized[255] on the surface of annealed copper metal that involves the oxygen at the centre of a rhombically distorted Cu_4 tetrahedron, a structure that may relate to the cubane structures of **(118)** and **(119)** (see Section 53.3.2.4).

$$PhMe + CO \xrightarrow[CuCl/AlCl_3]{HCl} p\text{-}MeC_6H_4CHO \qquad (5)$$



$[\{Cu(L^6)\}_2(\mu\text{-}CO_3)]$ **(122)**[254]

53.3.2.11 Alkene complexes

Solutions of copper(I) salts such as CuCl or $Cu(CF_3SO_3)$ readily absorb alkenes but it is frequently difficult to isolate crystalline solids with well defined stoichiometries, unless more traditional ligands are present, such as dien or pyridine.[256–259] Complexes may alternatively be prepared from the copper(II) salt in ethanol in the presence of an alkene by a suitable reducing agent (see Figures 1–3). If ethylene is added to an aqueous solution of copper metal and copper(II) perchlorate the disproportionation is reversed to the formation of a solid ethylene complex (equation 6; Danger: explosive), and while the structure of $[Cu(C_2H_4)(OH_2)_2](ClO_4)$[242] has not been determined, it is also unusual in containing water as a ligand to copper(I). The early literature[256] of the preparation and structure of ethylene and alkyne complexes is summarized in Figure 8, and was reviewed in 1968[256] and more completely in 1982.[257] Paralleling the normal coordination chemistry of copper(I), mononuclear,[260–262] dinuclear,[263] tetranuclear (cubane[264] and stepped[125,188] structures), hexanuclear[265] and linear chain[266] structures are formed. In general the C=C units are bonded symmetrically to the copper(I) ion and may be considered to occupy a single coordinate position stabilized by metal to ligand π back-bonding. Two- (**122**),[260] three- (**127**)[266] and four-coordinate (**123–125**) structures are involved with only the alkyne group involved in a near symmetrical bridging role through a single carbon atom as in (**82**)[188] and (**126**).[265]

$$Cu^0 + [Cu(OH_2)_6](ClO_4) + C_2H_4 \longrightarrow [Cu(C_2H_4)(OH_2)_2](ClO_4) \qquad (6)$$

More recently, crystal structures have been reported of copper(I) alkene complexes involving more traditional nitrogen chelate ligands; thus diethylenetriamine (dien) forms a complex with hex-1-ene, $[Cu(dien)(hex\text{-}1\text{-}ene)](BPh_4)$ (**128**),[268] while bipyam stabilizes three-coordinate complexes with both ethylene and acetylene, $[Cu(bipyam)(C_2H_4)](ClO_4)$ (**129**)[249] and $[Cu(bipyam)(C_2H_2)](BF_4)$ (**130**),[45] which offer a useful comparison of the relative bonding of C_2H_4 and C_2H_2 to the same $[Cu(bipyam)]^+$ cation. On the other hand while $HB(pz)_3$ forms a three-coordinate structure in $[Cu(HBpz_3)(C_2H_4)(CuCl)]$ (**131**),[270] along with a linear $[N—Cu—Cl]^-$ anion, in substituted $HBpz_3$ ligands (see ref. 271) a four-coordinate $CuN_3(C_2)$ chromophore is present, as in $[Cu\{HB(3,5\text{-}Me_2pz)_3\}(C_2H_4)]$ (**132**).[270] In the majority of these copper alkene complexes the Cu atoms are either three or four coordinate if the C_2 group is considered as a single unit with C atoms at comparable bonding distances of *ca.* 2.1 Å from the Cu atom.[259] In the former the $CuL_2(C_2)$ chromophore is trigonal planar with the C_2 unit lying in the plane of the CuL_2 unit and not perpendicular to this plane,[259] while in the latter the $CuL_3(C_2)$ unit is approximately tetrahedral. With a macrocyclic ligand L^7 (**133**)[272] a dinuclear complex $[Cu(L^7)]_2(BPh_4)_2$ (**134**)[272] is formed with a distorted tetrahedral $CuN_3(C_2)$ chromophore with the L^7 ligands bridging the separate Cu atoms, such that each involves a pyridine nitrogen and an imine nitrogen from one L^7 and imine nitrogen and an alkenic group from the second L^7, with a long Cu—Cu interaction of >4.0 Å. With substituted alkynes a more complex behaviour occurs, thus in the reaction of $[Cu(PhCO_2)]_4$, which has a tetranuclear structure similar to (**62**),[156] a dinuclear complex $[Cu_2(PhCO_2)_2(PhC{\equiv}CPh)_2]$ (**135**)[273] is formed with a Cu—Cu separation of 2.78 Å. With the macrocyclic ligand L^8 (**136**), a most unusual tetranuclear copper(I) structure is formed $[Cu_4(L^8)_2(PhC{\equiv}C)](ClO_4)_3{\cdot}DPDA$ (**137**),[274] where DPDA = diphenylacetylide anion. Four copper(I) atoms interact with a single C≡C unit: two appear to be σ-bonded to the alkyne carbon and two are π-bonded to the C≡C unit. The strong copper–alkyne π interaction is reflected in the relatively long C—C distance of 1.385 Å, compared to that of 1.3 Å normally observed for alkynes (Table 12), and the nonlinearity of the C—C—C(Ph) bond of (**137**).

Table 12 The C—C Distances (Å) of Alkene and Alkyne Complexes of Copper(I)

(*a*) *Alkene complexes*	*C=C*	*Ref.*
Ethylene, C_2H_4	1.34	—
$CuCl(C_8H_8)$ (**127**)	1.392	266
$[Cu(dien)(hex\text{-}1\text{-}ene)](BPh_4)$ (**128**)	—	268
$[Cu(bipyam)(C_2H_4)](ClO_4)$ (**129**)	1.359	249
$[Cu\{HB(3,5\text{-}Me_2pz_3\}(C_2H_4)]$ (**132**)	1.329	270
$[Cu(HBpz_3)(C_2H_4)(CuCl)]$ (**131**)	1.347	270
(*b*) *Alkyne complexes*	*C≡C*	*Ref.*
Acetylene, C_2H_2	1.20	—
$[Cu(bipyam)(C_2H_2)](BF_4)$ (**130**)	1.188	45
$[Cu_2(C_2Ph_2)_2(PhCO_2)_2]$ (**135**)	1.224	273
$[Cu_4(L^8)_2(C{\equiv}CPh)(ClO_4)_3{\cdot}DPDA]$ (**137**)	1.385	247

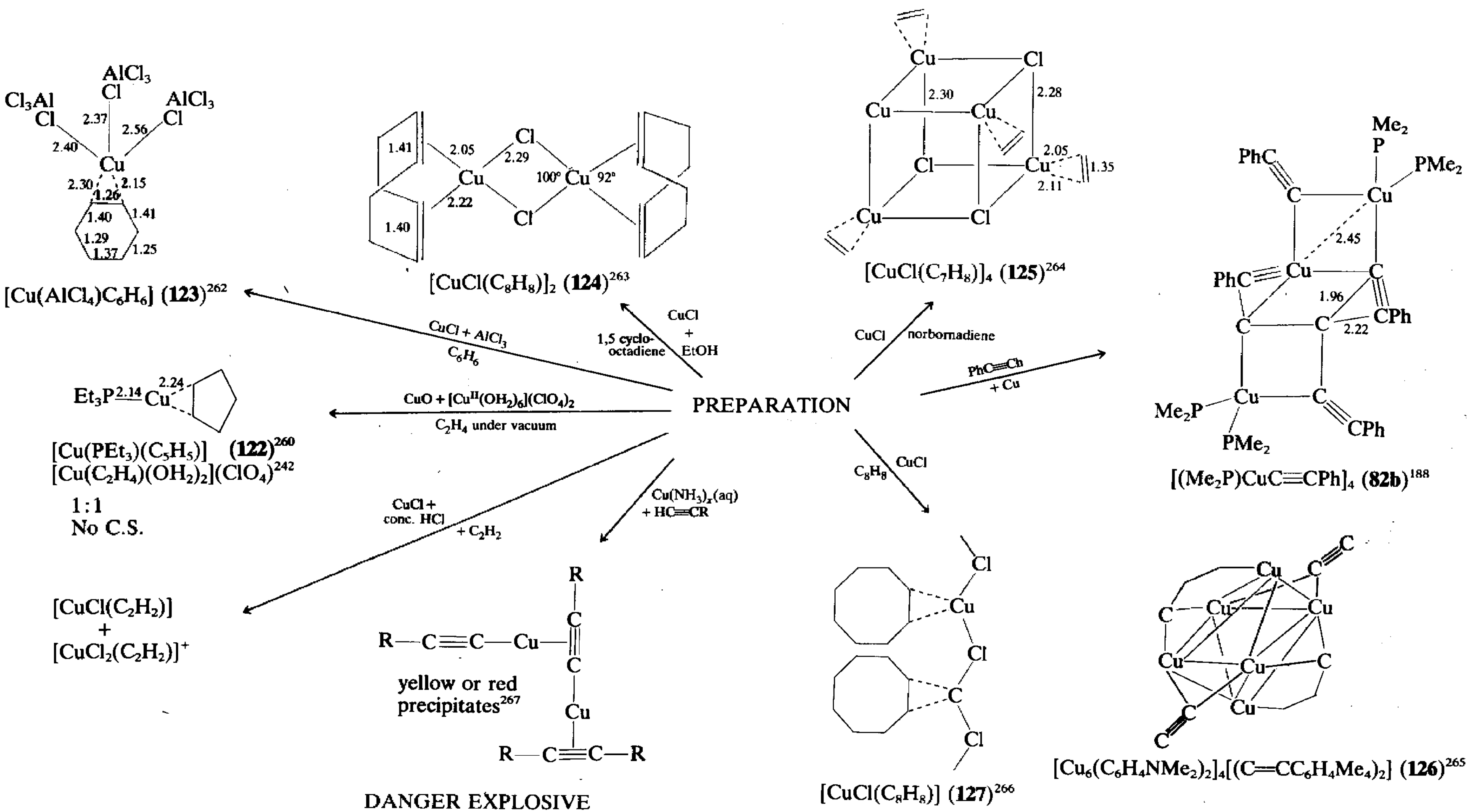
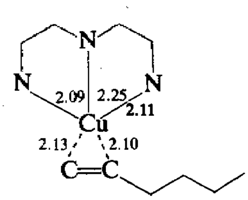
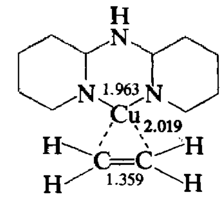


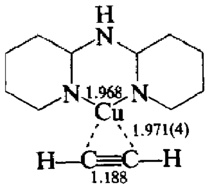
Figure 8 The preparations and crystal structures of copper(I) alkene and alkyne complexes



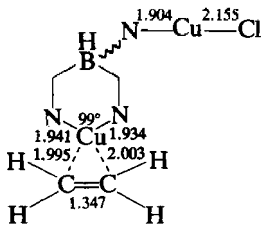
[Cu(dien)(hex-1-ene)](BPh_4) **(128)**[268]



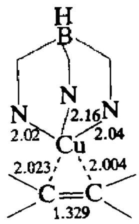
[Cu(bipyam)(C_2H_4)](ClO_4) **(129)**[249]



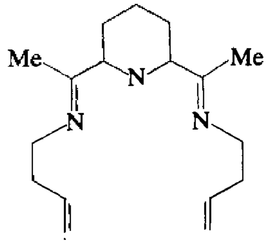
[Cu(bipyam)(C_2H_2)](BF_4) **(130)**[45]



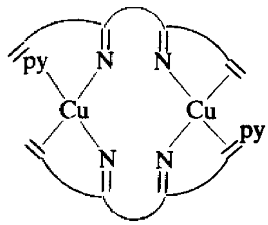
[Cu($HBpz_3$)(C_2H_4)(CuCl)] **(131)**[269,270]



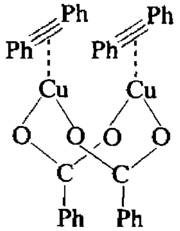
[Cu{HB(3,5-Me_2pz_3)}(C_2H_4)] **(132)**[270]



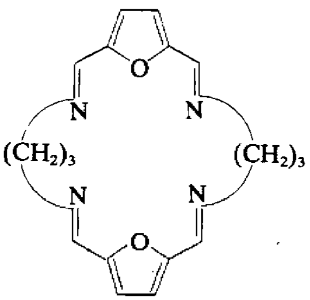
L^7 **(133)**[272]



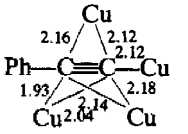
$[Cu(L^7)]_2(BPh_4)_2$ **(134)**[272]



[$Cu_2(PhCO_2)_2(PhC{\equiv}CPh)_2$] **(135)**[273]



L^8 **(136)**[274]



$[Cu_4(L^8)_2(C{\equiv}CPh)](ClO_4)_3$·DPDA **(137)**[274]

53.3.2.12 *Mixed metal complexes*

The copper(I) cation can form a number of complexes involving different copper(I) stereochemistries (Table 13), but in addition is able to form a number of mixed metal complexes involving one or more bridges to other metal atoms, which are potentially of interest as a number of enzymes and proteins (types III and IV) are known to contain more than one type of metal atom as a polynuclear structure (see Section 53.4.8).[24,25] In general the copper(I) atom and second metal atom may involve a completely independent structure (Figure 9) involving two single atom bridges with each metal displaying a typical stereochemistry as observed in its mononuclear complexes. In [VO(salen)Cl_2CuCl] (**138**)[275] the vanadium(IV) involves a square pyramidal VN_2Cl_2O chromophore and the copper(I) a trigonal planar $CuCl_3$ chromophore with a planar VCl_2Cu bridging group. More usually, more than two metal atoms may be linked by one or more bridging ligands where the local metal stereochemistry is still recognizably that of the component metal atoms, thus $(Ph_4P)_2[(MS_4)(CuCl_3)]$·MeCN may be prepared for M = Mo or W and have the same tetranuclear structures (**139**)[276] and (**140**)[277] with tetrahedral MS_4 units and trigonal planar CuS_2Cl units (Figure 9). By varying the Mo : Cu ratio to 1 : 4.3, the complex $(Ph_4P)_3[(MoOS_3)(CuCl)_3][CuCl_2]$ (**141**)[278] is formed with a tetrahedral $MoOS_3$ unit and the same peripheral trigonal planar CuS_2Cl units to yield a cation of C_{3v} symmetry and, in addition, a linear $[CuCl_2]^-$ anion. A trigonal planar CuS_3 chromophore occurs in both $(NPr^n_4)_2[(PhS)CuS_2MoS_2]$ (**142**)[279] and $(NPr^n_4)_2[(PhS)Cu(S_2MoS_2)Cu(SPh)]$ (**143**);[279] they are both double bridged through an MoS_4 chromophore. Consistent with the dinuclear bridging Cu_2Cl_2 unit (Table 9) this system occurs in the mixed metal complex [{piperidine *N*-oxide(−1)}$_2$Mo(μ_2-S)$_2${Cu(μ_2-Cl)}$_2$] (**144**; Figure 9),[280] while a monocubane structure occurs in $[(Ph_3PCu)_3ClS_3(WO)]$ (**145**),[281] and a dicubane structure occurs in $[\{(C_7H_7)_3P\}Cu_4(WOS_3)_2]$ (**146**).[282] In the Cu_6 group of $[\{(triphos)IrP_3\}_3Cu_5Br_4][CuBr_2]$ (**147**),[283] where triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane, five different copper(I) environments are present. In the tetrahedral Cu_4 unit the uppermost Cu has a tetrahedral $CuBrP_3$ chromophore to three separate P atoms. Each top surface Cu_4 triangle is symmetrically capped by three $[(triphos)IrP_3]$ units and the bottom Cu_3 triangle by a trigonal planar $CuBr_3$ chromophore. Each Cu atom of the Cu_3 bottom triangle has a $CuBrP_3$ chromophore from two different P_3Ir units and, finally, there is a separate $[CuBr_2]^-$ linear anion. An unusual mixed Cu : Re hydride complex has been prepared, $[\{ReH_5(PMePh_2)_3\}_2Cu](PF_6)$ (**148**; Figure 9),[284] with the Cu atom bridging to the two Re atoms by six H atom bridges, a most unusual environment for any metal atom. In the mixed metal hydride $[(\mu_5\text{-}C_5H_5)_2Re(H)Cu(\mu\text{-}I_2)Cu(H)Re(\mu_5\text{-}C_5H_5)_2]$ (**149**)[285] the position of the hydrogen atom was not located, but the structure contains an unusual bent CuI_2Cu chromophore (see ref. 122). A number of mixed metal carbonyl complexes are known such as $[Cu_2Rh_6(CO)_{15}(NCMe)_2]$[286] or, more recently, $[CuW(CO)_3(PPh_3)_2(\mu\text{-}C_5H_5)]$[287] and $[(PhMe)_2Cu_2Rh_6(CO)_{18}]$,[288] but as the oxidation state of the copper atom in these complexes is uncertain, and the carbonyl ligands are not coordinated to Cu, these complexes are not described in detail and the reader is referred to a recent review.[257]

Table 13 Copper(I) Complexes Containing Two Different Copper(I) Chromophores

Complex	*Chromophores*		*Ref.*
$[Cu_4(iptp)_3][CuCl_2]\cdot CCl_4$ (**79**)	CuS_3	$CuCl_2$	185
[Cu(*N*,*N*′-Et_2en)$_2$][$CuCl_2$] (**8**)	CuN_4	$CuCl_2$	53
$[Cu(dppe)_2][CuAr_2]$	$Cu(P—P)_2$	$CuCl_2$	59
$[Cu(C_{44}H_{60}N_4)][CuCl_2]$	CuN_4	$CuCl_2$	107
$(Me_4N)_2[Cu_5(SPh)_7]$ (**83**)	CuS_3	CuS_2	189
$[Cu(HBpz_3)(C_2H_4)(CuCl)]$ (**131**)	$CuN_3C{=}C$	CuNCl	270
$[Cu_4(tu)_{10}](SiF_6)_2\cdot H_2O$ (**59**)	CuS_4	CuS_3	152
$[Cu(Ph_2PHCPPh_2)]_3$	CuP_3	CuC_2	153

53.3.3 Spectroscopic Structural Data

While X-ray diffraction single-crystal data must always be the most accurate method for structure determination of copper(I) complexes in the solid state,[18] useful information can be obtained from other techniques. In general the stoichiometry *m* of a complex will provide

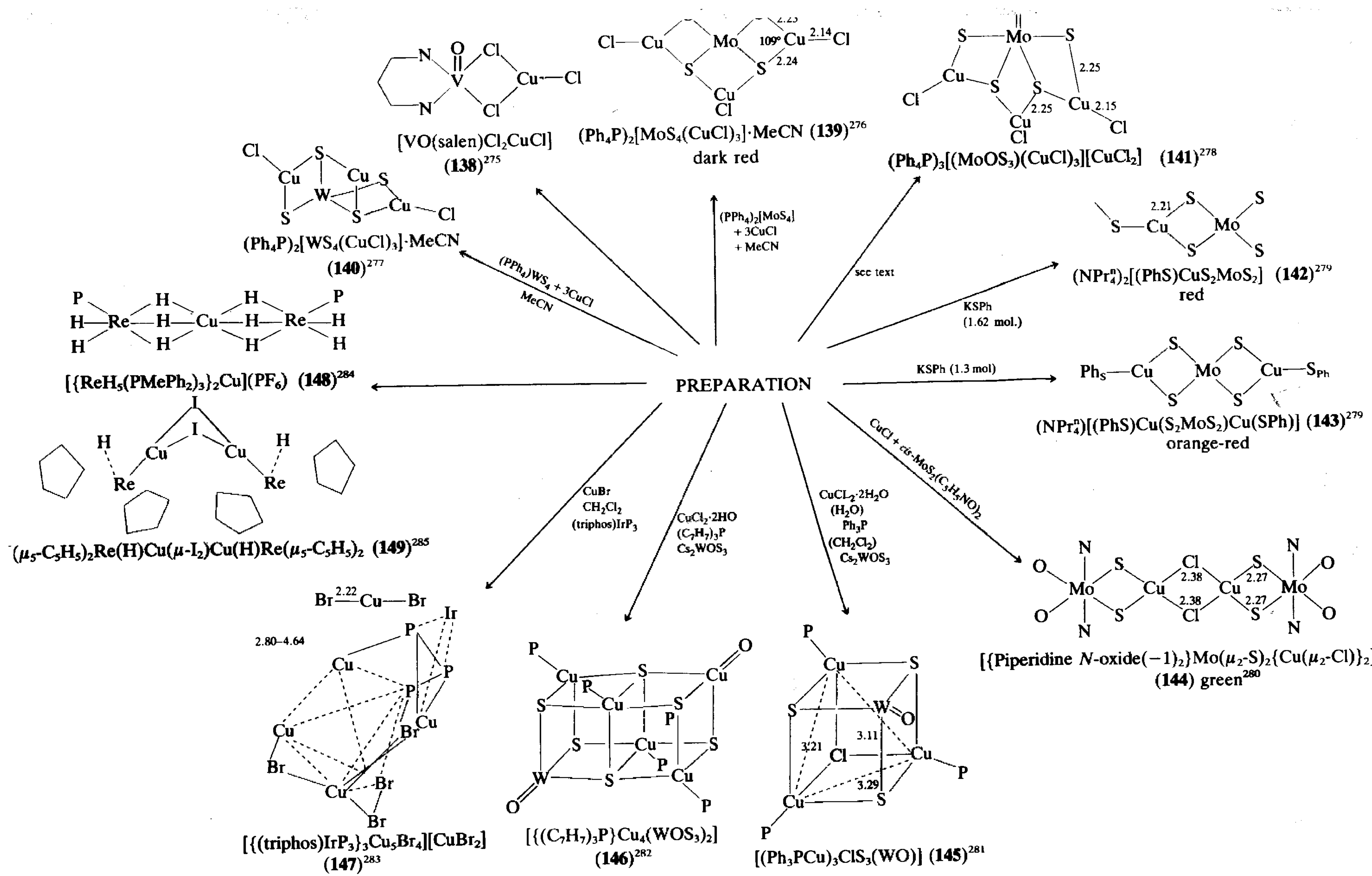
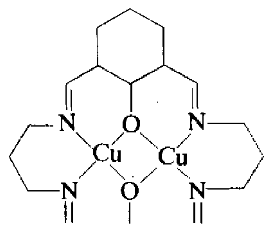


Figure 9 Mixed metal complexes of the copper(I) ion

information on the formal oxidation state of the Cu atom in binuclear species such as $[Cu_2(L^9)](ClO_4)_m$ (**150**).[289] In the series of Cu^ICu^I, Cu^ICu^{II} and $Cu^{II}Cu^{II}$ complexes,[243] X-ray photoelectron spectroscopy[289] may be used to distinguish Cu^I and Cu^{II} species, but as shifts of only 2 eV, on *ca.* 933 eV, are involved, care must be taken to compare the spectra with that of complexes with the Cu atoms in known oxidation states.



$[Cu_2(L^9)](X)_m$ (**150**)[289]

EXAFS spectroscopy[290] may be used to determine, in ideal situations, the length and number, *n*, of the Cu—L distances, but while the distances may be reliable to 0.01 Å, the *n* value may only be correct to one unit on three or four ligands.[290] A dicarbonyl copper(I) complex may be prepared by addition of the ligand L^9 (**150**) to CuI in dry methanol under a CO atmosphere; it crystallizes as $[\{Cu(CO)\}_2(L^9)](BPh_4)_2$.[291] EXAFS spectroscopy yielded evidence for Cu—N distances of 2.09 Å for this copper(I) complex with a reasonable Cu—Cu distance of 6.0 Å. In solutions of CuCN + NaCN the spectra[292] are best fitted as shown in Table 14(a); the short Cu—C distances of 1.95 Å indicate Cu–carbon coordination of the CN^- anions and the formation of tri- and tetra-cyano copper(I) species dependent upon the Cu/CN^- ratio. EXAFS spectroscopy[293] may be used to show that in the solid state the Cu atom environment can change upon electrolysis (Table 14b). In the CuI·sulfonium I^- electrolyte the Cu atom environment is changed from four I^- anions before electrolysis to three I^- anions after electrolysis (Table 14b).

Table 14 EXAFS Results for (a) CuCN + *n*NaCN Solution[292] and (b) CuI/sulfonium I^- Electrolytic cells[293]

(*a*) *CuCN + nNaCN*	$r_{Cu—C}$ (Å)	*n*	$r_{Cu—N}$ (Å)	*n*
$[Cu(CN)_4]^{3-}$	1.98	3.7	3.12	4.3
$[Cu(CN)_3]^{3-}$	1.94	3.3	3.06	3.6
(*b*) *CuI/sulfonium I^-*	$r_{Cu—I}$ (Å)	*n*		
CuI	2.54	4		
CuI/SI cell—before	2.54	4		
CuI/SI cell—after	2.58	3		

As the copper(I) ion has an (argon)$3d^{10}$ closed shell configuration it will be diamagnetic[5] and usually colourless, as there will be no *d–d* transitions associated with the Cu^I ion[17] and hence no stereochemical information provided on the CuL_n chromophore present or its geometry. In view of the diamagnetism, the NMR spectra of copper(I) complexes are not broadened by the presence of a paramagnetic centre, consequently both ^1H NMR[249] and ^{13}C NMR spectra[294] can be used to give information on the types of organic ligands present and their structures. Spectra measured in solution[295] indicate that the addition of bipy to $[Cu(NCMe)_4](ClO_4)$ shows only coordinated bipy, while the shifts in the ^1H NMR peaks with varying ligands L in these ternary complexes reflect the strong π acceptor properties of L, which delicately control the π back-bonding between the Cu^I and bipy ligands. More recently the ^{63}Cu NMR spectra[296] of the CuX halides have been reported (Figure 10); these show broad bands, with shifts in the region of 330–390 p.p.m., but 'magic angle spinning' considerably sharpens the peaks to produce shifts of 331, 354 and 388 p.p.m. for the copper(I) chloride, iodide and bromide, respectively. In the $[Cu(bipy)_2]^+$ cation an intense[295] MLCT band occurs at 22 727 cm^{-1}; replacement of one bipy ligand by two of the better π acceptor ligands results in a significant shift of the MLTC band to 27 777 cm^{-1}, as the bipy MLCT is reduced in preference to the LMCT.

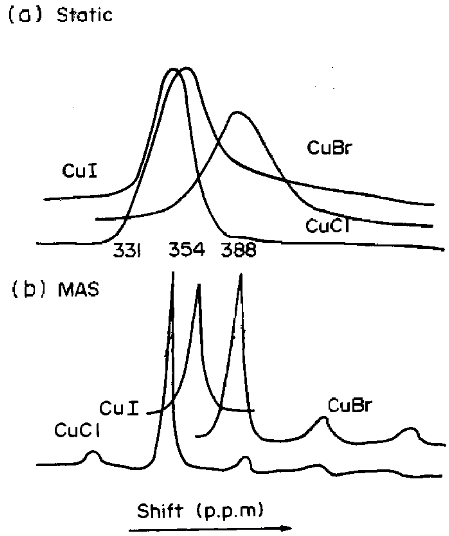


Figure 10 The effect of magic angle spinning on the broad band ^{63}Cu NMR spectrum of powdered copper(I) halide: (a) static; and (b) magic angle spinning

IR evidence of ligand–copper coordination occurs in copper(I) complexes, as described in standard textbooks on IR spectroscopy.[294,297] The IR spectra of coordinated polyanions are reviewed in Chapter 15.5 and Section 53.4.4.6 and will not be repeated here, except to mention that oxyanions are not good π acceptors or donors, but in the presence of a good π acceptor ligand form complexes such as $[Cu(PPh_3)_2(O_2NO)]$ (**5**)[80] or $[Cu(bipyam)(OClO_3)(CO)]$ (**120**).[120,249] In copper(I) halide chemistry the formation of $[CuX_2]^-$ species has been characterized by a single asymmetric stretching frequency at 406, 323 and 279 cm^{-1} for the $[CuCl_2]^-$, $[CuBr_2]^-$ and $[CuI_2]^-$ anions, respectively.[297–299] In a series of $CuBrP_n$ chromophores,[300] the ν_{CuBr} stretch has been shown to decrease from 380 to 179 cm^{-1} as the number of phosphine ligands increases from zero to four. At a more sophisticated level the normal coordinate analysis[301] of the adamantane-like cages of the $[Cu_4S_6]$ units (**77**) has been described. The resonance Raman spectra of copper(I) complexes are not extensively reported for mononuclear copper(I) complexes, but are more widely reported in biological copper systems (see refs. 25 and 30). The resonance Raman spectra of a series of α-diimine ligand perchlorate complexes have been reported[302] in the region of the MLCT band (16 667 to 21 882 cm^{-1}). The Raman spectra nicely show the IR forbidden ν_1 symmetric stretch of the ionic perchlorate group and the resonance-Raman-enhanced spectra allow a description of the electronic changes that are consistent with the published molecular orbital diagrams.[302]

Although the copper(I) cation has a closed d^{10} configuration and has no paramagnetism associated with this configuration, interest in calculating the electronic energy levels for this ion in its complexes is associated with the assignment of the MLTC bands of the copper(I) ligand environment.[303] As these transitions occur in the visible to near-UV region and are electronically allowed and hence very intense ($\varepsilon > 1000$), they are generally the primary origin of colour[304] in complexes of the copper(I) ion, which would otherwise be colourless. With diimine ligands such as bipy or 2,9-dimethyl-1,10-phenanthroline the intense colour is frequently used for the emission spectrophotometric analysis of traces of copper.[305] Equally, sulfur ligands are reducing towards copper(I) [and copper (II)], and generate low energy MLCT bands which are believed to be responsible for the intense colour[24,25,30] of the biologically important copper blue proteins (see Section 53.4.8). For this reason the molecular orbital calculations[306] on $[Cu(ethanediimine)_2]^+$ and $Cu^I(N_2S_2)$ chromophores have been carried out using extended Hückel and multiple scattering χ_α molecular orbital calculations in order to assign the electronic energy levels of these chromophores. In both series the origin of the colour in these systems is associated with an MLCT for both diimine and sulfur ligands. Ref. 303 gives a very readable account of the use of molecular orbital calculations in assigning the MLCT spectra of copper(I) and (II) sulfur ligand complexes, using a knowledge of the Cu atom stereochemistry as determined by X-ray crystallography, as this determines the nature of the highest energy d level [filled for copper(I) and half-filled for copper(II)]. It should be mentioned that the assignment of these charge-transfer bands as MLCT gives no information on the underlying stereochemistry or oxidation state of the Cu atom involved. In [Cu^I-(cyclops)CO] (**28**),[112] a molecular orbital calculation[307] suggests that the CO fifth ligand involves no formal σ bonding, but only extensive π back-bonding to the copper atom. The calculation also indicates that the $d_{x^2-y^2}$ level lies above a normally unoccupied ligand π^* level, which will result in internal electron transfer to the ligand (MLCT); it is suggested that (**28**) should be formulated as a copper(III) macrocyclic complex. In the copper(I) alkene complexes with symmetrical alkene coordination, (**123**) to (**137**), molecular orbital calculations[259,308] suggest that there is little direct σ bonding between the Cu atom and the π level of the alkene, but significant back-bonding. Nevertheless, probably the most significant contribution that molecular orbital calculations have made to copper(I) chemistry is in the discussion of the bonding of the polynuclear Cu_n species, especially in the tetrahedral Cu_4 cubane, octahedral Cu_6 and cubic Cu_8 structures as in (**70**) to (**88**). In general these calculations suggest[309–314] that there is only very weak or no Cu—Cu bonding present, as intuitively suggested by the seemingly wide range of Cu—Cu distances (Table 11), and for this reason it is generally considered that these Cu_n species are best described as copper aggregates and *not* copper clusters.[17]

Spectroscopic measurements and molecular orbital calculations have also been carried out[315] on Cu_n clusters, $n = 2$–6, and mass spectral measurements on the vapour of CuCl[316] suggest that the $[Cu_{14}Cl_{13}]^+$ cation has an enhanced stability; χ_α calculations[317] are consistent with an extended cluster model.

53.3.4 Redox Properties of Copper(I)/(II) Systems

These are associated with three processes:[5,17,30] (a) electrolytic oxidation or reduction (equation 7); (b) disproportionation (equation 8);[318] (c) the oxidation of copper(I) with molecular oxygen[319,320] ultimately yielding water (equation 9). It is this last process that is responsible for the air sensitivity of copper(I) compounds, but equally for the catalytic role of copper(I) in the oxidation of organic molecules,[321,322] and in biological systems.[24–30] Electrolytic reduction of copper(I) to copper metal is readily carried out as the second step in the electrolytic refining of copper metal and in the copper plating process, where the main interest is in the cost effectiveness of the process.[5] Although the disproportionation reaction (equation 8)[17,30] is favourable in aqueous solution,[10] the low solubility of the copper(I) species in water renders this reaction less important than the oxidation to copper(II). Complex formation in solution (Figures 1 and 2) notably increases the solubility, but also increases the stability of the copper(I) species to the disproportionation process. The use of $[Cu(NCMe)_4](X)$ complexes as a useful preparative[39–41] route to copper(I) complexes (Figure 3) is based on this enhanced stability and increased solubility in nonaqueous solvents, but even here the reactions are best carried out under nitrogen to avoid the oxidation of copper(I) to copper(II) (equation 7). Due to this the coordination chemistry of the copper(I)/(II) redox process is primarily concerned with the reduction of copper(II) to copper(I), a process that has been discussed in Table 3, Section 53.3.1.[26]

$$Cu^0 \xrightarrow{-e^-} Cu^+ \xrightarrow{-e^-} Cu^{2+} + 2e^- \quad (7)$$

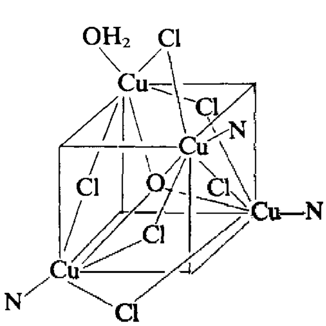
$$2Cu^+ \rightleftharpoons Cu^0 + Cu^{2+} \quad (8)$$

$$O_2 + 4e^- + 4H^+ \longrightarrow 2H_2O \quad (9)$$

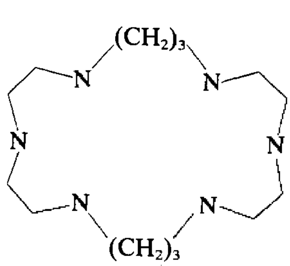
A striking feature of the chemistry of copper(I) is its ability to undergo reversible absorption of small molecules such as oxygen,[322] carbon monoxide (Figure 7) and alkenes (Figure 8). While to date there are no structural data on a dioxygen copper(I) complex, a number of copper(I) complexes do form solid oxygenated products (Table 15), the green colours of which suggest that they contain copper(II) rather than copper(I). Nevertheless, the interest in these complexes is not confined to their X-ray crystal structures, fascinating as these may be, but lies in their possible role as intermediates in the oxidation by molecular oxygen of the coordinated species, CO or alkenes. While oxidation of organic molecules in nonbiological and biological systems may be completely to CO_2 and water at temperatures well above room temperature, at ambient temperature less complete oxidation occurs and metal ions are required as a catalyst; copper(I) is a useful example,[320,321] as in the oxidation[319] of dimethyl sulfoxide to dimethyl sulfone using $[Cu(NCMe)_4][BF_4]$ (equation 10). This reaction is believed to take place *via* species such as Cu_2O^{2+} and the former has been isolated[321] as $[Cu_2^{II}O(DMSO)(dioxane)(BF_4)_2]$, but not characterized crystallographically (Table 15). Equally the $[Cu(chelate)_{1-2}]^+$ cation may be used in the catalytic oxidation[323] of primary and secondary alcohols to aldehydes and ketones, respectively. But with different complexes, rather more gentle 'oxygenation' processes may occur[324] as in the dehydrogenation reaction of O_2 of Figure 11(a) in which no oxidation of the copper(I) occurs, or in the oxygen insertion[325] of Figure 11(b) where oxidation to copper(II) does occur. Similarly copper(I), as CuCl in pyridine,[326–330] may catalyze the oxidative coupling of phenols to quinones (Figure 11c).[327,328] Aerial oxidation of a CuCl/pyridine slurry yields a brown solution containing equal mixtures of a brown $[(py)_mCuO]_2$ and a blue$[Cu(py)_2Cl_2]$ species, both involving copper(II) (equation 11). The separated brown $[(py)_mCuO]_2$ solution is unstable,[327,328] decomposing to CuO, but can still initiate reaction (11), and is ESR silent, notwithstanding the formal presence of *copper(II)*. Using oxygen donor solvents dimethyl sulfoxide (DMSO)[321] or *N*-methyl-2-pyrrolidinone (nmp)[331] in place of py in reaction (11) still yields a brown solution from which crystalline *copper(II)* complexes $[L_3Cu_4Cl_6O_2]$ are obtained. The crystal structure of $[(nmp)_3Cu_4Cl_6O_2]\cdot nmp$ (**151**)[331] reveals a novel μ_4-oxo-Cu_4 tetrahedral cage with a central oxygen atom, six bridging Cl atoms (see the structure of $(Ph_3MeP)_2[Cu_4I_6]$ (**76**)[181]) plus three terminal nmp ligands and a single OH_2 ligand. As solutions of (**151**) can still initiate reaction (11), it is reasonable to suppose that this μ_4-O unit exists in the primary initiation species, but then does not react with CO_2. For this reason, it has been suggested[327] that the latter may not contain a μ_4 oxygen, but can still be tetrameric as an $[L_4Cu_4^{II}Cl_4O_2]$ species has been identified in solution, where L = py or denc (*N,N*-diethylnicotinamide).[173,332] In the reaction product with O_2 two alternative structures may be formed as shown in Figure 12; structure (a) involves two surface bridging Cu—O—Cu units, which are exposed and react with CO_2 to form a $(CO_3)^{2-}$ species, while structure (b) has a μ_4 body-centred O atom, and one terminal Cu—O species, neither of which can react with CO_2 to form stable μ-$(CO_3)^{2-}$ complexes (see Section 53.3.2.2). In view of the identification of these copper(II) cubane-type cages, which have been shown to be so characteristic of copper(I) stereochemistry, it is then significant that the only crystallographic evidence for an O_2 species has been found[333] in a *copper(II)* complex involving a planar Cu_4 unit with two hexaammine macrocyclic ligands: L^{10} (**152**), $[Cu_4(O_2)_2(OH_2)_4(L^{10})_2](BF_4)_6$ (**153**).[333] In (**153**) each copper is part of a square pyramidal $CuN_3O(OH_2)_2$ unit with two bridging O—O links of 1.20 Å and a near linear Cu—O—O angle of 165° rather than the anticipated 120°; (**153**) then represents the first crystallographic evidence of a copper dioxygen species involving copper(II), and justifies the model compound approach[30] to the structural simulation of copper-catalyzed reactions, which are of importance in the oxidation of organic molecules[33,321,322] and in the biological copper system.[24,25,30] Table 15 lists a number of model copper(I) complexes that have been reported to form crystalline products in reactions with molecular oxygen, but for which no crystallographic structures were reported. In view of the importance of those oxygenated species these systems could justify further examination, preferably by single-crystal X-ray methods, but alternatively by X-ray powder profile analysis, if only to obtain approximate structural data.

$$Cu^+ + Me_2SO + O_2 \longrightarrow [Cu_2O]^{2+} + Me_2SO_2 \qquad (10)$$

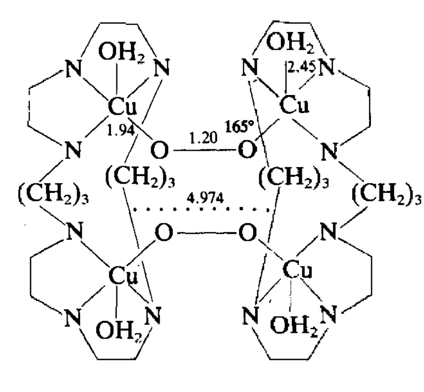
$$4CuCl + O_2 \xrightarrow{py} [(py)_mCu^{II}O]_2 + 2[Cu^{II}(py)_2Cl_2] \qquad (11)$$



$[(nmp)_3Cu_4Cl_6O_2]\cdot nmp$ (**151**)[331]



L^{10} (**152**)[333]

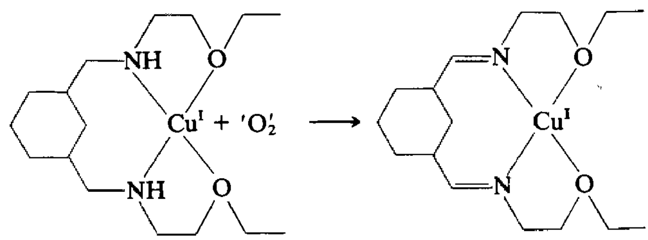


$[Cu_4(O_2)_2(OH_2)_4(L^{10})_2](BF_4)_6$ (**153**)[333]

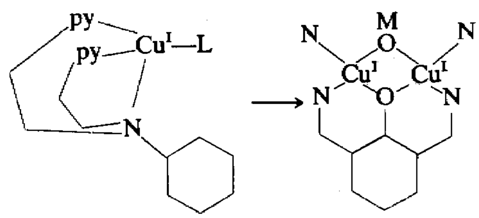
Table 15 Some Copper(I) Complexes that Yield Solid Reaction Products With Molecular Oxygen

Complex	*Solvent*	*Product*	*Colour*	*Properties*	*Ref.*
$[Cu_2(HBpz_3)_2]$	—	$[Cu_2(HBpz_3)_2O_2]$	Green	Paramagnetic	133
$[Cu_2(C_{23}H_{23}N_2O)(pyrazole)]$	DMF	$[Cu_2(C_{23}H_{23}N_2O)(pyrazole)(O)]$	Green or brown	—	138
$[Cu(phen)Cl]$	CH_2Br_2	$[\{Cu(phen)Cl\}_2O$	Green	—	334
$[Cu(C_{24}H_{40}N_2O_2S_4)](BF_4)_2$	—	—	Green	Diamagnetic	320
$[Cu\{HB(3,5\text{-}Me_2pz)_3\}(C_2H_4)]$	Acetone and CCl_2H_2	$[Cu(HB(3,5\text{-}Mepz)_3)(O_2)]$	Green	—	45
$[Cu(N,N\text{-}Et_4en)(C_2H_4)](ClO_4)$	Methanol	$[Cu_2(N,N\text{-}Et_4en)_2(OH_2)(O_2)](ClO_4)_2$	Blue	Diamagnetic	45
$[Cu(NCMe)_4](BF_4)$	DMSO	$[Cu_2O(DMSO)(dioxane)(BF_4)_2]$	Green	—	321

(a) Dehydrogenation[324]



(b) Oxygen insertion[140,141,135]



(c) Oxidative coupling[327,328]

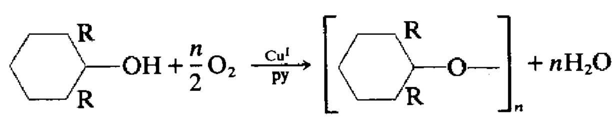


Figure 11 'Oxygenation' reactions involving copper(I)

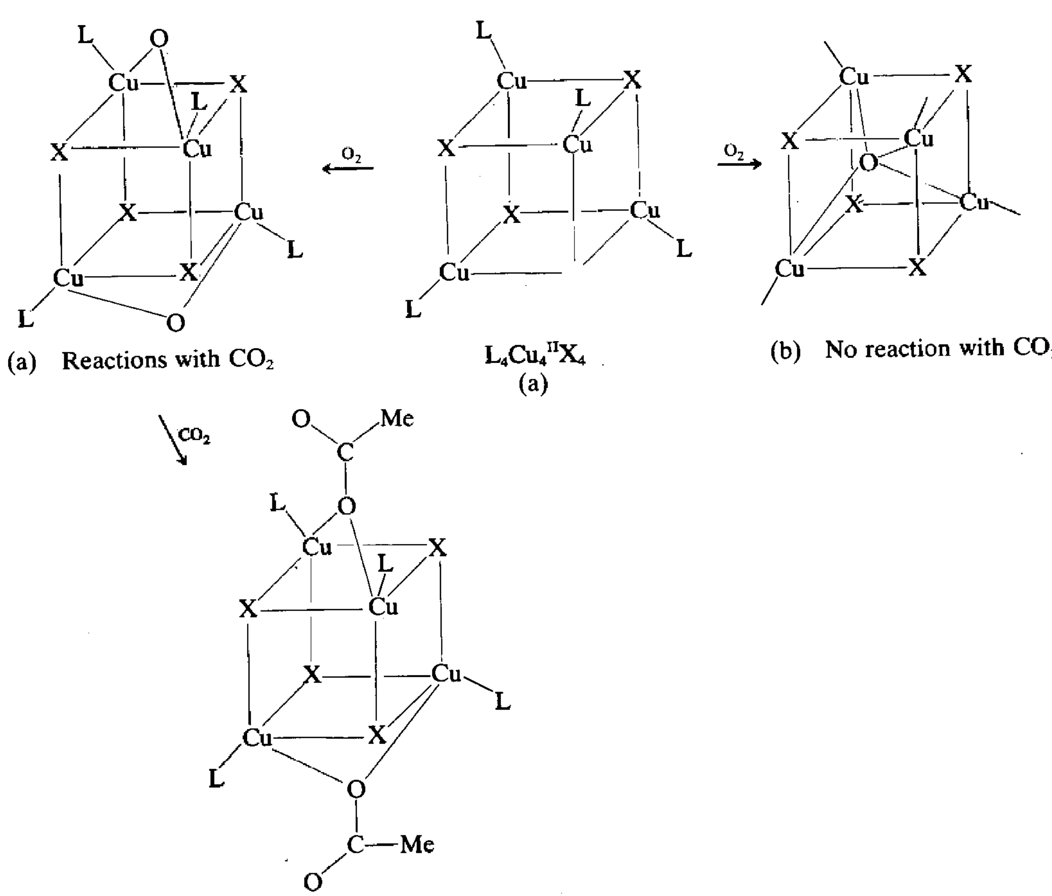
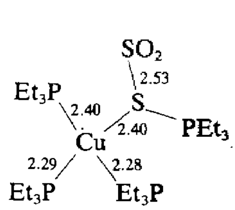


Figure 12 Proposed alternative reaction products of $L_4Cu_4X_4$ species with O_2[328]

An extensive literature[321,322] describes the catalytic role of the $[Cu^I(chelate)_2]^+$ cation with molecular oxygen as an oxidizing agent, where chelate = substituted 2,2′-bipyridyl or 1,10-phenanthroline, in the conversion of alcohols to aldehydes,[323] of the decarboxylation of ascorbic acid,[322] of Ph_3P to $Ph_3P{=}O$,[334] *etc.* In general these describe the oxidation products[335] and the kinetics[336] of these processes,[337–339] but little attention has been paid to the fate of the $[Cu(chelate)_2]^+$ species. Oxidation of $[Cu(bipy)_2](ClO_4)$ by O_2 in nonaqueous solutions such as nitromethane or acetonitrile[340] results in the formation of $[Cu(bipy)_2(ONO)](ClO_4)$,[341,342] with a structure shown to be comparable to that of the fluxional $[Cu(bipy)_2(ONO)](NO_3)$[342] (see Section 53.4.5). This oxygenation process is unusual as it suggests that $(NO_2)^-$ anions must be generated from nitromethane as a solvent, which is not too surprising, but equally from acetonitrile, which is surprising. It is also unexpected that the product of this reaction is the *cis*-distorted, octahedral CuN_4O_2 chromophore, one of the least common stereochemistries[47,48] of the copper(II) ion (see Section 53.4.2.1vii, Figure 19.1). Oxidation of $[Cu(phen)_2](ClO_4)$ in DMF with molecular oxygen forms the copper(II) complex $[Cu(phen)_2(O_3CH)]$-$(ClO_4)\cdot DMF$,[343] while $[Cu(2,9\text{-}Me_2phen)_2](ClO_4)$ in acetonitrile and excess trichloroacetic acid yields $[Cu(dmp)_2(O_2NO)](CCl_3CO_2)\cdot CCl_3CO_2H$,[335] both with *cis*-distorted CuN_4O_2 chromophores. Oxidation of the mixed ligand complexes $[Cu(bipy)_2(npm)](NO_3)$,[344] where npm = nitrophenylmethane, yields $[Cu(bipy)_2(ONO)](NO_3)$, containing the original[342] *cis*-distorted octahedral CuN_4O_2 chromophore. Taken together these reactions suggest that not only should the chemistry of copper(I)-catalyzed oxidation be further examined, but that the simple catalytic role of the copper(I) species should be further examined in the light of the above observations.

Reference has already been made to the use of dioxygen to oxidize copper(I) carbonyl complexes.[254] The reaction[345] of $[(Me)Cu^I\{P(C_6H_{11})_3\}]_4$ with CO_2 yields both an insertion product $[MeCO_2Cu\{P(C_6H_{11})_3\}]$[345] and an adduct $[(MeCO_2)Cu(CO_2)P(C_6H_{11})_3]$. The adduct is so stable that CO_2 is not given off until the complex is heated to 150 °C. Similar insertion adducts are formed with Ph_3P, *e.g.* $[RCO_2Cu(CO_2)(Ph_3P)_3]$,[346] and a bridging CO_2 group is suggested for $[Cu_2(CO_2)(Ph_3P)_4]$, but there is no crystallographic evidence to support this. With tertiary butoxide, $[(Bu^tO)Cu(Ph_3P)]_4$ in aqueous solution,[347] a copper(I) bicarbonate complex that is a water soluble reversible CO_2 carrier is formed. With aryl copper, carbon disulfide and dppm, a tetranuclear complex, $[Cu_4(dppm)_4(CS_2)_2]$ (**67**) is formed,[164] involving symmetrical bridging chelate S_2C and dppm ligands in an approximately planar Cu_4 unit. The reaction of SO_2 with $[Cu(SPh)(PPh_3)_3]$ also yields a simple addition complex in $[Cu(SO_2\cdot SPh)(PPh_3)_3]$ (**154**),[75] and in the dinuclear complex $[Cu_2I_2(PPh_2Me)_4(SO_2)]$.[124]



$[Cu(SO_2\cdot SPh)(PEt_3)_3]$ (**154**)[75]

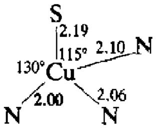
53.3.5 Biological Copper(I)

In biological copper systems the copper is involved in three basic processes:[24–30] (i) electrolytic redox processes, involving copper(III)/copper(I); (ii) (II)/(I) systems, oxygen atom processes, involving the absorption of O_2 molecules and their reduction ultimately to water;[321,322] and (iii) transport processes[348] through which copper is absorbed and rejected by the body. In general, copper(I) is the electron donor[349] for (i) and (ii) involving copper proteins, and copper(II) is primarily involved in (iii), but there is surprisingly little information available on the precise copper(I)–protein interaction.[350,351] There are two reasons for this: firstly, copper(I) is readily oxidized to copper(II),[10] but in aqueous solution also undergoes ready disproportionation to Cu^0 and Cu^{II} (equation 8) and as copper(II) is stable in aqueous solution, this oxidation state is readily formed. In nature the copper(I) site is generally considered to be in a hydrophobic area in the protein, while in model compounds, the copper(I) state can be stabilized by the formation of complexes using at least some soft ligands

(Table 1) such as the halides, acetonitrile, imine nitrogen chelates or sulfur (thiol to sulfide) ligands. In general the redox potential of the Cu^{II}/Cu^{I} couple is more positive the more stable the copper(I) species is relative to the copper(II) species, *i.e.* the softer the ligands involved (Tables 2 and 3). Consequently, the characteristically positive redox potentials of the copper biological systems (Table 3a) suggest that the reduced state of the copper is compatible with a stable copper(I) stereochemistry. This is generally assumed to involve a distorted tetrahedral geometry; however, in view of the stability of the trigonal planar CuL_3 chromophore this alternative coordination number and stereochemistry should not be ruled out. The more positive redox properties may also be associated with the 'similarity' of stereochemistry in both the copper(I) and (II) oxidation states, and in this respect a common tetrahedral stereochemistry might well be appropriate as this geometry is known to be stable for both oxidation states, while those of linear or trigonal coplanar species are unknown in the stereochemistry of copper(II) complexes involving normal ligands (Section 53.4.2.1). Equally, as the 'oxygenation' process[327,328] of copper(I) to copper(II) is generally agreed to involve an addition of molecular oxygen to a Cu, Cu_2 or Cu_4 species, such additions must involve an increase or change of coordination geometry in the addition species and the comparability of the initial and final stereochemistry of the mononuclear copper species may not be that important.

The nature of the structure of copper(I) in biological systems is not clear;[24,25,29,30] it is present in the type III copper, such as in the dinuclear species of the deoxyhemocyanin, but there are no X-ray crystal structure data available. EXAFS spectroscopy suggests[351] at least a two-coordinate copper nitrogen (CuN_2) environment, although a third ligand,[352] possibly oxygen, is not ruled out. Copper(I) also occurs in the multicopper type IV copper system, but always accompanied by at least one other type of copper, *i.e.* I–III. Because of the mixed copper types present, even EXAFS spectroscopy can not give precise information on the copper(I) ion environment. For this reason, particular interest awaits the further refinement of the 3.2 Å X-ray data on Panulirus Interruptus hemocyanin,[353a] which suggests two copper atoms 3.8 Å apart and each coordinated by three nitrogen ligands, probably histidine. But the most interesting set of data[353b] is that for Cu^{I} plastocyanin and deoxyplastocyanin ($Cu^{I}Pc$; Figure 16c, i and ii), which are pH dependent[353b,c] due to the protonation of a histidine nitrogen (87). At low pH the $CuNS_2$ chromophore is essentially trigonal coplanar but at high pH changes to distorted tetrahedral, with bond distances that are closely comparable to those of $Cu^{II}Pc$ (Figure 16c, iii; see Section 53.4.8). Even more interesting is the observation that the trigonal $HCu^{I}Pc$ is redox inactive, while the tetrahedral $Cu^{I}Pc$ is redox active, consistent with the principle that $Cu^{I/II}$ redox reactions are only possible for compatible Cu^{I} and Cu^{II} stereochemistries, namely tetrahedral (see Figure 60 and Section 53.4.4.5). It is then worth observing that while the crystals[53b] of $[Cu(phen)_2](ClO)_4$ and $[Cu(phen)_2][CuBr_2]$ (Table 5) both contain a CuN_4 chromophore, those of the near-regular (ClO_4) complex (dihedral angle 76.8°) are stable to aerial oxygenation, those of the more distorted $[CuBr_2]$ complex (dihedral angle 49.9°) are unstable to oxidation. In the latter the distortion present is closely comparable to that of the copper(II) $[Cu(phen)_2](PF_6)_2$,[526] with a dihedral angle 50.1°.

The part played by the synthesis of model compounds has assumed[30] significant importance. In the case of type I copper(II) (see Section 53.4.8), the distorted tetrahedral CuN_3S chromophore of $K[Cu\{HB(3,5\text{-}Me_2pz)_3\}(SC_6H_4NO_2)]\cdot 2Me_2CO$ (**155**)[74] deserves comment as the spectroscopic properties of the corresponding copper(II) chromophore $CuN_3(SR)$ are very similar to the type I copper blue proteins (see Section 53.4.8). For type III biological copper dimeric structures are more appropriate model compounds, *e.g.* the linear copper structures of $[Cu(XYpz)]_2(BF_4)_2$ (**47**)[139] and $[Cu_2(EDTB)](ClO_4)_2$ (**52**)[145] or the trigonal copper structures of $[Cu_2(C_{23}H_{23}N_2O)(pyrazole)]$ (**46**)[138] and $[Cu_2(m\text{-}XYpy_2)](PF_6)_2$ (**48**).[140] It is consequently gratifying that some at least of these model compounds (Table 15) do react with molecular oxygen to form solid products or even undergo oxygen insertion or oxidative coupling (Figures 12c and 12d, respectively).



$K[Cu\{HB(3,5\text{-}Me_2pz)_3\}(SC_6H_4NO_2)]\cdot 2Me_2CO$ (**155**)[74]

53.3.6 Survey of Copper(I) Ligands

The classification[36] of metals and ligands into hard and soft acids and bases respectively (Table 2b) usefully separates copper(I), which is a soft acid, from copper(II), which is a borderline hard acid, and predicts the sequence of soft base behaviour for the more common ligands as set out in Table 2(b). As this review of the coordination chemistry of copper(I) has emphasized the stereochemistry of copper(I) complexes of known structure, rather than their preparative chemistry (see ref. 23), Table 16 summarizes the complexes of known crystal structure (molecular structures (**1**) to (**155**), Tables 5, 6, 7 and 9 and Figures 7, 8 and 9) in which a given ligand donor atom occurs at least once, with no account taken of multiple appearances. In general, the predicted behaviour is not well obeyed and possible reasons for this are discussed in the following review of ligand behaviour as set out in Chapters 11–22.

Table 16 The Frequency of Occurrence of Donor Atoms in Copper(I) Complexes of Known Crystal Structure

N	≪	P	>	As	>	Sb	>	Bi
84		45		5		0		0
O	≪	S	=	Se	=	Te		
20		64		0		0		
F^-	<	Cl^-	<	Br^-	<	I^-		
3		347		17		27		
C		H						
50		7						

53.3.6.1 Mercury ligands

No examples of direct Cu—Hg bonds are known.

53.3.6.2 Carbon ligands

These must rate amongst the commonest ligands to copper(I), made up almost equally of the cyanide anion (coordinated *via* carbon and nitrogen), the carbon monoxide molecule (always through carbon), and alkene-type ligands; this does not include the 76 known examples of σ-bonded copper alkyls and aryls as listed in Table 1, p. 711 of ref. 23. Historically, the well-documented chemistry of the Cu^I cyanide system stems from the ready preparation of [CuCN] from copper(II) plus KCN (Figure 1d). It functions as a monodentate ligand to yield a trigonal planar anion in $Na_2[Cu(CN)_3]\cdot 3H_2O$ (**19**)[97] and as a tetrahedral anion in $K_3[Cu(CN)_4]$,[90] but more frequently occurs as a bridging ligand, as in $K[Cu(CN)_2]$ (**89**)[200] and in (**90**),[201] (**104**),[223] (**105**),[224] (**106**)[225] and more recently in the ring complex of $[Cu(phen)(CN)]_3$ (**60**).[154] In view of this extensive function as a ligand to copper(I), it is surprising that the $(CN)^-$ ligand does not form a linear $[Cu(CN)_2]^-$ anion. The coordination chemistry of carbon monoxide as a ligand has only developed since 1970; the early complexes are summarized in Figure 7 (**109** to **116**) and in molecular structures (**117**) to (**121**). The CO ligand is bonded through the carbon atom, never through the oxygen atom, with a near linear Cu—C—O angle. It is generally monodentate, but does occur as a bridging ligand in $[Cu_2(tmen)_2(\mu\text{-}PhCO_2)(\mu\text{-}CO)](BPh_4)$ (**116**).[240] Equally, the majority of copper(I) alkene coordination complexes have been developed since 1970 as summarized in Figure 8 (**122** to **127**) and more recently in molecular structures (**128**) to (**137**). The coordination of the C_2 unit usually involves symmetrical Cu—C distances to either a trigonal planar or tetrahedral copper(I) cation and π-type bonding to the metal.[308] Nevertheless, with alkyne ligands CuC σ-type bonding may also be involved, as in $[(Me_2P)_2Cu(C{\equiv}CPh)]_4$ (**82b**)[188] and $[Cu_4(L^8)_2(C{\equiv}CPh)](ClO_4)_3\cdot DPDA$ (**137**).[274]

No simple ligands involving silicon, tin or lead donor atoms to copper(I) are known.

53.3.6.3 Nitrogen ligands

Although it would be predicted that nitrogen, as a soft base, would be a less effective ligand than phosphorus (Table 2b), more complexes involving nitrogen as a ligand have been characterized crystallographically than with phosphorus as a ligand (Table 16). In contrast to the copper(II) ammonia system,[354] although copper(I) ammonia complexes are known,[23] they are too unstable to have been characterized by crystallography. Substituted ammonia ligands are known as in $[Cu_4Cl_4(NEt_3)_4]$ (**71**)[170] and $[CuCN(HNEt_2)]$ (**90**),[154] but potentially π-bonding ligands such as MeCN, as in $[Cu(NCMe)_4](ClO_4)$ (**1**),[43] pyridine, as in [CuClpy] (**100**),[120] or imidazole, as in $[Cu(imidazole)_4](ClO_4)$,[115] are preferred. In general the nitrogen ligands act as monodentate terminal ligands even when the copper atom is involved in a polynuclear structure, as in (**71**),[170] (**90**)[154] and (**100**)[120] above. Copper(I) complexes involving chelate nitrogen ligands outnumber those involving monodentate nitrogen ligands. Purely σ-bonding ligands occur only occasionally, as in [Cu(en)CO] (**112**)[237] and in $[Cu_2(en)_2(CO)_2(en)](PPh_4)_2$ (**113**);[237] in the latter complex en occurs in an unusual bridging role. Dien is also an unusual tridentate ligand to copper(I), but does occur in $[Cu(dien)(hex\text{-}1\text{-}ene)](BPh_4)$ with a bent conformation.[268] Diimine-type ligands, such as bipy, phen and bipyam, are well represented, as in [Cu(bipy)Cl(CO)],[245] [Cu(phen)(NCS)] (**94**)[209] and $[Cu(bipyam)(C_2H_4)](ClO_4)$ (**129**),[249] and seem well able to stabilize the trigonal planar copper(I) geometry. As a tridentate chelate ligand the trispyrazolylborate anion is useful for stabilizing the four-coordinate geometry of copper(I) as in $[Cu(HBpz_3)CO]$ (**110**)[235] and $[Cu\{HB(3,5\text{-}Me_2pz)_3\}(C_2H_4)]$ (**132**),[270] but may coordinate as a bidentate ligand as in $[Cu_2(HBpz_3)(C_2H_4)(CuCl)]$ (**131**).[270] Bis(nitrogen chelate) copper(II) complexes are well characterized, particularly with diimine-type ligands as in $[Cu(2,9\text{-}Me_2phen)_2](NO_3)$ (**7**),[54] with a near regular tetrahedral CuN_4 chromophore, but are much less common with σ-bonding nitrogen chelates, as in the recent structure of $[Cu(N,N'\text{-}Et_2en)_2][CuCl_2]$ (**8**),[53] where two independent copper(I) stereochemistries are present. Nitrogen chelates are also involved in generating the less common geometries of copper(I) such as the square coplanar CuN_4 chromophore of [Cu(cyclops)] (**14**),[86] although the structure involves a marked tetrahedral twist. A clear square-based pyramidal stereochemistry occurs in [Cu(cyclops)(CO)] (**28**)[112] with the Cu atom lifted 0.96 Å out of the plane of the four N atoms, while a bent CuN_2 chromophore occurs in $[Cu(BBDHP)](PF_6)_{0.66}(BF_4)_{0.34}$ (**27**),[109] presumably due to the constraints of the nitrogen chelates. Even more significant has been the role of nitrogen chelates in generating copper(I) dimers constrained by the bridging chelate ligands to produce Cu—Cu separations that may be of the order of magnitude of the separation in biological systems. These various structures are illustrated in the molecular structures of (**45**) to (**52**). Equally relevant to biological systems has been the bridging role of inorganic anions, such as the $(CNS)^-$ anion in $[Cu(L^5)(NCS)](ClO_4)$ (**45**)[137] and the $(N_3)^-$ anion, as in $[Cu(PPh_3)_2(NNN)]_2$ (**42**).[135] Finally, the role of MeCN as a ligand has already been mentioned in (**1**), but equally it appears as a nitrogen ligand in complexes due to its involvement as an extremely useful nonaqueous solvent (Figure 3) as in $[Cu_2(m\text{-}XYLSEt)(MeCN_2)](PF_6)_2$ (**49**).[141]

53.3.6.4 Phosphine ligands

Traditionally phosphorus has been considered one of the best soft base ligands for copper(I) and has generated a significant number of complexes of known crystal structure, primarily with monodenate ligands, especially PPh_3 and PEt_3 and in combination (see Tables 5, 6, 7 and 9 and 16). In general the monomeric phosphine ligands only coordinate as single ligand donors and do not involve any bridging role. In the polynuclear structures the bridging ligands are generally halide ions, oxygen atoms or sulfur atoms with the phosphines acting in a terminal ligand capacity, mainly to trigonal planar copper, as in $[Cu\{P(cyclohexyl)_3\}Cl]_2$ (**31**)[114] or tetrahedral copper $[Cu_4Br_4(PEt_3)_4]$.[169] In the $[Cu(PPh_3)_4](ClO_4)$ complex (**3**),[51] there is crystallographic evidence for a tetrahedral CuP_4 chromophore, and the hexameric Cu_6P_6 is known in $[H_6Cu_6(PPh_3)_6]$ (**85**)[191] and in the equivalent $[H_6Cu_6\{P(tolyl)_3\}_6]$ complex.[196] Chelate phosphine ligands are not very extensive; they are mainly restricted to dppm, and generate some interesting trimeric copper(I) complexes, such as $[Cu_3(dppm)_3Cl_2]Cl$ (**55**),[148] while the Et_2PPEt_2 ligand functions as a bridging ligand in $[CuBr(Et_2PPEt_2)]$ (**95**).[210] The bis(phosphine chelate) copper(I) systems are even less common, but do occur in $[Cu(dppe)_2][CuAr_2]$,[59] which involves the presence of a tetrahedral CuP_4 chromophore and a linear CuC_2 chromophore. Historically $AsEt_3$ was first characterized in the cubane-type cages of the tetranuclear complexes of copper(I) in $[Cu_4I_4(AsEt_3)_4]$ (**70**)[168] and in the corresponding $[Cu_4I_4(AsPh_3)_4]$ complex.[174] A tetrahedral bis(diarsine chelate) copper(I) complex is known in $[Cu(diarsine)_2](PF_6)$ (**9**).[84]

While a number of $SbPh_3$ complexes of copper(I) have been prepared,[23,355,356] only $[(Ph_3Sb)_3CuCl]\cdot CHCl_3$[85] has been characterized by crystallography.

53.3.6.5 *Oxygen ligands*

While oxygen-containing ligands have only a moderate representation as ligands to the copper(I) cation, they cover a wide range of ligand types. Due to the relative instability of the copper(I) ion in water, OH_2 as a ligand is not well represented, but does occur in $[Cu(1,4\text{-oxathiane})_3(OH_2)](BF_4)$ (**12**).[62] The oxide anion occurs in Cu_2O,[228] to give a linear CuO_2 chromophore, and as a triply bridging OH^- anion in $[Cu_3(dppm)_3(OH)](BF_4)_2$ (**54**).[147] Oxyanions are moderately well represented with $[Cu(PPh_3)_2(OXO)]$ complexes formed by $(OClO_3)$, as in (**25**),[104] $(O_2NO)^-$ as in (**5**),[89] and $(MeCO_2)^-$ as in (**6**).[82] The butoxide ligand forms a tetranuclear ring structure[161] involving linear CuO_2 chromophores, but equally forms a stable tetranuclear cubane-type structure in $[Cu_4(OBu^t)_4(CO)_4]$ (**118**).[247] The square planar Cu_4O_8 unit is formed by bridging $(CF_3CO_2)^-$ anions in $[Cu_4(O_2CCF_3)_4]\cdot 2C_6H_6$ (**62**),[156] while copper(I) acetate has a linear dimeric planar Cu_2O_4 structure (**103**).[222]

53.3.6.6 *Sulfur ligands*

Consistent with the soft base behaviour[36] of sulfur as a ligand (Table 16) sulfur considerably exceeds oxygen as a ligand to copper(I). It is a good monodentate ligand as in the trigonal planar CuS_3 chromophore of $[Cu(tetraethylenethiourea)_3](SO_4)$ (**20**)[92] and in the tetrahedral CuS_4 chromophore of $[Cu(thioacetamide)_4]Cl$ (**2**).[50] In the thiophenolate anion sulfur readily behaves as a monodentate ligand as in $(PPh_4)[Cu(SPh)_3]$ (**21**),[93] but is equally good as a bridging ligand, as in $[Cu(PPh_3)_2(SPh)]_2$ (**38**),[130] and in the extensive bridging role of $(Ph_4P)_2[Cu_4(SPh)_6]$ (**77**).[93,183] This role is only exceeded by that of the thiourea ligand in $[Cu_4tu_9](NO_3)_4\cdot 4H_2O$ (**78**),[182] where additional terminal sulfur ligands are present on three of the corner Cu atoms. These polynuclear aggregates are further extended to the Cu_5 species $(Me_4N)_2[Cu_5(SPh)_7]$ (**83**),[189] to the highly symmetrical Cu_8 species $(Me_3As)_2[Cu_8\{S_2C(CN)_2\}_6]$,[197] and to the Cu_{12} species $(Ph_4P)[Cu_{12}S_8]$ (**88**).[198] While the sulfide ion may also act as a three-dimensional bridging ligand in ZnS, the polysulfide anion also forms complex metal aggregates, as in the irregular Cu_6 species $(Ph_4P)[Cu_6(S_4)_3(S_5)]$.[195] Simple sulfides form terminal ligands in the cubane-type structures, such as $[Cu_4I_4(SEt_2)_3]$ (**74**),[178] in which only two of the sulfide ligands are terminal; the remaining two bridge to yield a cubane chain structure. Chelate thio ligands are also known as in $[Cu(3,6\text{-thiaoctane})_2](BF_4)$ (**10**),[61] and in the search for model compounds to simulate biological sulfur systems, complex chelate sulfides have been prepared, such as in $[Cu(p\text{-XYSEt})(NMe)]_2(PF_6)_2$ (**43**)[136] and $[Cu(15\text{-ane-}S_5)]$ (**16**).[91] Sulfur coordination also occurs by coordination of the thiocyanate anion as a ligand, as in the three-atom bridging present in $[Cu(dmphen)(SCN)]$ (**94**),[209] or in the single-sulfur-atom bridging of $[Cu(L^4)(SCN)_2]$ (**40**).[134] Addition of CS_2 to the $[Cu(dppm)]^+$ cation results in the formation of a tetranuclear Cu_4 species with formation of a thiocarbonate ligand as in $[Cu_4(dppm)_4(S_2C)]$ (**67**),[164] while addition of SO_2 to $[Cu(SPh)(PEt_3)_3]$ results in the coordination of SO_2 to the thiophenolate ligand, as in $[Cu(PPh_2Me)_3(SO_2\cdot SPh)]$ (**154**).[75] Notwithstanding that Se and Te ligands are predicted to have a stability comparable to that of sulfur ligands[36] with copper(I), and although both selenium and tellurium complexes have been prepared, there are no crystallographic data available concerning their structures.[23,357–359]

53.3.6.7 *Halide ligands*

As predicted by the soft acid behaviour[36] of copper(I), very few examples of the fluoride ion coordinated to copper(I) are known (Table 16). It occurs on the fluoride ion in $[Cu(PPh_3)_3F]$,[37] and on the coordinated tetrafluoroborate anion in $[Cu(PPh_3)_3(FBF_3)]$ (**4**);[67] in both cases a tetrahedral CuP_3F chromophore is present.

In contrast, although the chloride anion should also be considered to be a weaker ligand to copper(I) than either the bromide or especially the iodide anions, considerably more chloride-containing structures are known than for the bromide and iodide anions together (Table 16). As all three copper(I) halides (chloride, bromide and iodide) can be obtained commercially, the preponderance of the chloro complexes cannot be ascribed to the greater availability of CuCl. The chloride ion has only limited occurrence as a terminal ligand, as in [Cu(bipy)(PPh$_3$)Cl][85] with a tetrahedral CuN_2PCl chromophore. It has a much more extensive occurrence of the linear $[CuCl_2]^-$ anion, as in $(NBu^t_4)[CuCl_2]$ (**26**),[105] and frequently occurs as a counterion in more complex copper(I) species and cations, as in $[Cu(N,N'\text{-}Et_2en)_2][CuCl_2]$ (**8**).[53] See Section 53.3.7 for examples of the $[CuCl_2]^-$ anion in copper mixed oxidation state complexes and $[Mo(SPh)_3Cu_3Cl_3][CuCl_2]$ (**141**)[278] as an example of the $[CuCl_2]^-$ anion in a mixed metal complex. The predominant occurrence of the chloride ion is as a bridging ligand in dimers such as [Cu{P(cyclohexyl)$_3$}Cl]$_2$ (**37**),[129] and in trimers, such as [Cu(2-butene)Cl]$_4$ (**63**),[158] in which Cu—Cl—Cu bridging occurs. Chloride ion bridging to three separate Cu(1) atoms occurs in $[Cu_3(dppm)_3Cl_2]$ (**55**),[148] but even more extensively in the cubane cage structures of $[Cu_4Cl_4(NEt_3)_4]$ (**71**).[170] The only Cu_5 species occurs in $[Co(NH_3)_6][Cu_5Cl_{17}]$ (**84**)[190] with no evidence for the higher Cu_n aggregates. A linear chain structure of tetrahedral $CuCl_4$ chromophores, linked through two chloride bridges to give a zigzag chain, occurs in $K_2[CuCl_3]$,[205] while a double chain structure occurs in $Cs[Cu_2Cl_3]$[213] (Figure 4.8, iii and v, respectively). A regular bridged tetrahedral $CuCl_4$ chromophore occurs in the infinite zinc blende structure of CuCl.[227]

Cu—Br bonds are less extensive than the Cu—Cl or Cu—I bonds (Table 18). Single terminal Br ligands occur in the trigonal planar compound [CuBr(*N,N'*-diisopropyldiamine)$_2$] (**23**)[102] and a linear $[CuBr_2]^-$ anion in $(NBu_4)[CuBr_2]$ (**26**)[105] and [{(triphos)IrP$_3$}$_3$Cu$_5$Br$_4$][CuBr$_2$] (**147**).[283] Simple bridging dimers occur as in $(NEt_4)[Cu_2Br_4]$;[177] $[Cu_2(PPh_3)_3Br_2]$ (**33**)[119] is unusual as the bromide bridge connects a trigonal planar $CuPBr_2$ and tetrahedral CuP_2Br_2 chromophore. No Cu_3 aggregates are of known structure, but the $Cu_4Br_4L_4$ cubane structures are known, with L = PEt$_3$[169] and NEt$_3$,[170] and also the stepped structures of $[Cu_4Br_4(PPh_3)_4]\cdot 2CHCl_3$ (**80**).[186] Linear chains of a half-stepped structure [CuI(2,4,6-Me$_3$py)] (**92**)[204] occur in [CuBr(NCMe)],[219] and in the alternate Br^- and Et_2PPEt_2 bridges of [CuBr(Et$_2$PPEt$_2$)] (**95**).[210] The zigzag linear chain structure, involving tetrahedral $CuBr_4$ chromophores, occurs in $(Ph_2N_2)[Cu_2Br_3]$.[214] As predicted from Table 16, the Cu—I bonds are more extensive than the Cu—Br bonds. Single terminal Cu—I structures are very limited (see [CuI(2,6-Me$_2$py)][98]), but dimeric bridged structures are well represented, as in [CuI(died)$_2$] (**34**).[102] A Cu_3 cluster occurs in $[Cu_3(dppm)_2I_3]$ (**56**),[149] involving *one* Cu-bridging I^- and *two* three-Cu-bridging I^- ions. However, the predominant Cu—I structure is that of the $Cu_4I_4L_4$ cubane-type structure of $[Cu_4I_4(AsEt_3)_4]$ (**70**),[168] with each I^- ion bridging to three Cu atoms and each Cu clearly tetrahedral. The same basic cage exists in $[Cu_4I_4(SEt_2)_3]$ (**74**),[178] but with two of the terminal SEt_2 ligands involved in bridging, to give a linear cubane-type chain. Unlike the Cl^- and Br^- ions, but like the S atom, the I^- ion can form the more open cubane structures, as in $(Ph_3MeP)_2[Cu_4I_6]$ (**76**),[181] in which the Cu_4 tetrahedron involves six I^- ions bridging the six Cu_2 edges to give a more open structure. In addition the Cu_4I_4 stepped structure occurs in $[Cu_4I_4(PPh_3)_4]$[187] (see **80**) and in [Cu$_4$I$_4$(2-Mepy)$_6$] (**81**),[121] where the two additional 2-Mepy ligands increase the coordination of the two terminal Cu atoms from trigonal planar (CuI_2N) to tetrahedral (CuI_2N_2). The I^- ion forms a split chair structure in the infinite chains of [CuI(2,4,6-Me$_3$py)] (**92**),[204] involving three-coordinate CuI_2N chromophores and a linear zigzag infinite chain in $(Me_4N)[Cu_2I_3]$ (**98**).[215,216] In [CuI(CNMe)] (**101**)[120] an infinite chain of displaced chair structures is formed, while in [CuI(N$_2$Me$_2$)] (**102**)[221] a double chain of Cu_2I_2 ribbons is linked by bridging MeN—NMe ligands.

53.3.6.8 Hydrogen ligands

Hydrogen is involved as a ligand to copper(I) in a very restricted sense. In mononuclear copper(I) complexes it is restricted to the monodentate $(BH_4)^-$ anion in the four-coordinate CuP_3H chromophore of $[Cu(PPh_2Me)_3(HBH_3)]$ (**17**)[69] and to the bidentate $(BH_4)^-$ anion in the CuP_2H_2 chromophore of $[Cu(PPh_3)_2(H_2BH_2)]$ (**18**) (see Table 5).[68] It is believed to occur as a bridging H atom in the hexamer $[H_6Cu_6(PPh_3)_6]$ (**85**)[191] and more convincingly in the neutron diffraction structure of [H$_6$Cu$_6${P(tolyl)$_3$}$_6$],[192] in which the hydrogen bridges account for the slightly longer Cu—Cu distances in the two *trans* faces of the Cu_6 octahedron. A mixture of terminal and bridging H atoms is believed to be present in the mixed metal structure of [ReH$_5${P(Me)Ph$_2$}$_2$Cu](PF$_6$) (**148**).[284]

53.3.6.9 Mixed donor atom ligands

While there are no crystal structures of mononuclear Schiff base complexes of copper(I) (N—O ligands) available, these do occur as in the dimeric structure of $[Cu_2(C_{23}H_{23}N_2O)(pyrazole)]$ **(46)**[138] and in the tetranuclear structure of $[Cu(2\text{-}Mequinoline)(CO)]_4$ **(119)**.[248] Mixed N—S ligands are more frequent in view of the biological interest in CuS bonds. The tetrahedral distorted CuN_2S_2 chromophore occurs in $[CuL^1](PF_6)$ **(11)**,[73] a trigonal pyramidal CuN_2S_2 chromophore occurs in $[Cu(pma)](BPh_4)$[88] and a T-shaped CuN_2S chromophore occurs in $[Cu(L^2)](BF_4)$.[103] In $[Cu(L^3)]$ **(30)**[113] a unique five-coordinate trigonal bipyramidal geometry occurs. A number of N—S ligands have been prepared to produce not only Cu—S bonds, but also polynuclear copper(I) species as in $[Cu(p\text{-}XYSEt)(MeCN)_2](PF_6)$ **(43)**[136] and $[Cu_2(m\text{-}XYLSEt)(MeCN)_2](PF_6)_2$ **(49)**.[141] No mixed O—S ligands have been described that complex with copper(I), but a mixed O—P ligand is known for the complex $[Cu(acacP)]_2$ **(50)**,[143] and yields a T-shaped $CuPO_2$ chromophore. A mixed As—N chelate ligand occurs in the dimeric $[Cu_2I_2(As\text{—}N)_2]$ **(35)**,[127] where As—N = dimethylaminophenyldimethylarsine (Table 9).

A number of the above complexes may be alternatively considered as macrocyclic ligands or compartmental ligands, but as the emphasis has been primarily in terms of the local copper(I) stereochemistry and the polynuclear nature of the complexes, they have been included above. As there is no crystallographic data on biological copper(I) systems, this section will have to await the further refinement of the structure of Panutirus Interruptus hemocyanin.[353]

53.3.7 Copper(I)/(II) Mixed Oxidation State Complexes

While the bulk of copper complexes can be separated into copper(I) and copper(II) oxidation states, a number of complexes involve a mixture of the (I) and (II) oxidation states, and a smaller number involve an intermediate oxidation state. Robin and Day[360] have classified the behaviour of mixed valence complexes in general, and have divided the behaviour into three classes, I–III, as summarized[361] in Table 17, and applied to the element copper. Some reference to the properties of mixed valence compounds of copper are included in the original reference in an update[362] and in a more theoretical review.[363] A substantial review of the stereochemistry of mixed valence complexes of copper has been published.[364] For this reason the present section only summarizes the stereochemical situation and the related electronic properties. In general, the three types of mixed oxidation state complexes of copper are prepared from a mixture of copper(I) and copper(II) starting materials or from a copper(II) starting material and mild chemical reduction (Figure 13) or carefully controlled electrochemical reduction.[375–377] In chemical reduction $(CN)^-$, $(SO_3)^{2-}$ and S^{2-} anions frequently occur and consequently appear[378] as ligands in the mixed valence complexes shown in Figure 13. In class I complexes the copper(I) and (II) units are clearly different and the stereochemistries are, separately, consistent with the known stereochemistries of the copper(I) ion (Figure 4) and of the copper(II) ion (Figure 19.1, Section 53.4.2). Simple mononuclear copper(II) complex units may be involved, *e.g.* **(156)**[365] and **(157)**,[366] and those in Table 18, along with mononuclear copper(I) units, but the tendency of copper(I) to involve polynuclear anionic structures is reflected in the linear chain structure of the $[Cu(S_2O_3)_2]^{3-}$ anions of **(157)**,[366] the Cu_2- and Cu_6-membered ring structures of **(158)**[367] and in the Cu_3 linear chain structure of **(159)**.[368] With ligand bridges between the copper(I) and copper(II) ions, Cu–Cu interactions may or may not occur. In general, if the copper(I) and copper(II) geometries are different, *no* magnetic interaction occurs and the copper(II) ion gives rise to a normal spin-only magnetic moment of *ca.* 2.0 BM. Thus $[Cu_2(acacP)_2(3\text{-}MeOC_6H_4CO_2)]$ **(160)**[369] involves a bridged tetrahedral $Cu^IP_2O_2$ chromophore and a square pyramidal $Cu^{II}O_4O'$ chromophore and $[Cu^ICu^{II}(4\text{-}metz)_4Cl_3]$ **(161)**[370] involves a bridged tetrahedral CuN_2Cl_2 chromophore and a square pyramidal CuN_2Cl_2Cl' chromophore, where 4-metz = 4-methylthiazole, with a μ_{eff} of 1.96 and 1.89 BM, respectively. Even with the same tetrahedral stereochemistry of different CuL_4 chromophores, the copper(I) and (II) centres are still identifiable as a compressed tetrahedral $[Cu^{II}Cl_4]$ species and a tetrahedral $[Cu^{II}Cl_2S_2]_3$ species in $[Cu^I_3Cu^{II}(tetrahydrothiophene)_3Cl_5]$ **(162)**[371] and there is no evidence for $Cu^{I/II}$ interaction. Likewise the coplanar $Cu^{II}N_2N'_2$ chromophore of the dark red $[Cu_4(CN)_6\{Cu(NH_3)_2\}]_n$ **(163)**[372] complex and the two copper(I) units, a linear $[Cu(CN)_2]$ and a trigonal $[Cu(CN)_3]$, are all bridged by nearly linear bridging cyanide ligands and yet the spin-only magnetic moment of **(163)**,[372] 1.87 BM, suggests that the copper(I) and (II) centres are independent (see Section 53.4.4.3). The structure of $[Cu_2(NCS)_3(NH_3)_2]$ (**164**)[373] involves linear chains of dinuclear bridging $(NCS)^-$ anions involving tetrahedral CuS_2N_2 chromophores, the chains of which are further bridged by elongated rhombic octahedral $CuN_3N'S_2$ chromophores. In $[Cu_4(O_2CMe)_6(PPh_3)_2]$ (**165**),[374] the dimeric $[Cu^{II}_2(O_2CMe)_4]$ unit is clearly identifiable from the electronic properties of (**165**), notwithstanding that this dimeric unit is linked *via* an acetate oxygen atom to two separate $[Cu^{I}P_2O_2]$ chromophores having a distorted tetrahedral geometry. This contrasts with the near symmetrical bridging role of the acetate anion in the mononuclear $[Cu(O_2CMe)(PPh_3)_2]$ (**6**) complex.[82] Thus, while there is a wealth of interesting and sometimes novel structural stereochemistries involved in the mixed valence structures of (**156**) to (**165**) (Figure 13), the electronic properties show no evidence for significant copper(I)–copper(II) interaction and are typical of Robin and Day class I behaviour.[360–662]

In the extreme class III behaviour,[360–362] two types of structures were envisaged: clusters and infinite lattices (Table 17). The latter, class IIIB behaviour, has been known for a number of years in the nonstoichiometric sulfides of copper (see ref. 10, p. 1142), and particularly in the double layer structure of $K[Cu_4S_3]$,[382] which exhibits the electrical conductivity and the reflectivity typical of a metal. The former, class IIIA behaviour, was looked for in the polynuclear clusters of copper(I) $Cu_{4-8}X_n$ species, especially where X = sulfur, but no mixed valence copper(I)/(II) clusters with class IIIA behaviour have been identified to date. Mixed valence copper(I)/(II) complexes of class II behaviour (Table 17) have properties intermediate between those of class I and class III. The local copper(I)/(II) stereochemistry is well defined and the *same* for all Cu atoms present, and the single odd electron is associated with both Cu atoms, *i.e.* delocalized between them, but will have a normal spin-only magnetic moment. The complexes will be semiconductors and the *d–d* spectra of the odd electron will involve a near normal copper(II)-type spectrum (see Section 53.4.4.5), but in addition a unique band may be observed associated with an intervalence Cu^I/Cu^{II} charge transfer band (IVTC) (Table 19). While these requirements are fairly clear,[360,362] their realization for specific systems is not so clearly established.

The first mixed valence copper(I)/(II) class II system to be suggested occurs in acetate-buffered ethanol solution.[383] When $[Cu(MeCN)_4](ClO_4)$ is added to $[Cu(OH_2)_6](ClO_4)_2$, a deep violet colouration is formed with bands at 19 700 and 11 000 cm^{-1} (Figure 14a) and a seven-line ESR spectrum is observed at room temperature (see Section 53.4.4.4), neither of which can arise from the electronic properties of the components. Unfortunately, no crystallographic data are available to characterize the species responsible for these electronic properties, but both or either of the electronic bands could be associated with IVCT bands. Likewise in the deep black colour[384] of $(N_2H_5)_2[Cu_3Cl_6]$ the stoichiometry suggests a mixed valence complex, which on the basis of the IR spectrum of the $(N_2H_5)^+$ cation is formulated as $[Cu(N_2H_5)_2Cl_2][CuCl_2]_2$, consistent with the measured spin-only magnetic moment of 1.88 BM per formula weight and suggesting one copper(II) ion per molecule. Unfortunately, no crystallographic structure or electronic spectrum is available for this complex. The first crystallographic evidence for a class II mixed valence complex was obtained in $[Cu_2Cl_3(MeNN)_2]$ (**166**),[385] where MeNN = 4-methyl-1,8-naphthyridine. Both CuN_2Cl_2 chromophores involve a distorted tetrahedral stereochemistry; these are *nearly* equivalent crystallographically and bridged by a single chloride ion, resulting in a short Cu—Cu separation of 2.89 Å. The spin-only magnetic moment of 1.99 BM per Cu_2 unit indicates a copper(I)/(II) species, and the two bands at 8000 and 10 300 cm^{-1} in the electronic spectra (Figure 14b) are assigned as *d–d* transitions and that at 14 600 as an MLCT or possibly IVCT. The solution ESR spectrum shows a characteristic seven-line splitting of $g_{\parallel}$ with a small $A_{\parallel}$ coupling constant of 72 gauss, indicating that the dimerization with two equivalent tetrahedral copper chromophores is retained in solution (see Section 53.4.4.4).

The macrocyclic ligand L^9 (**150**) has been shown to form a binuclear copper(II) complex[289,386] when 1,3-diaminopropane is condensed with 2-hydroxy-5-methylisophthalaldehyde in the presence of $[Cu(OH_2)_6](ClO_4)_2$ to give $[Cu^{II}Cu^{II}(L^9)Cl_2]_2$. One-electron electrochemical reduction[387] yields a mixed valence complex $[Cu^{I}Cu^{II}(L^9)](ClO_4)$ (**167**)[388] as dark brown needles, and involves a rhombic coplanar $Cu^{II}N_2O_2$ unit and a distorted square pyramidal $Cu^{I}N_2O_2O'$ chromophore with a short internuclear Cu—Cu contact of 2.55 Å, and some disorder associated with the $Cu^{II}N_2O_2O'$ chromophore. Notwithstanding the disorder, distinct Cu^I and Cu^{II} units are recognized in the solid state, suggesting class I Robin and Day behaviour. Nevertheless when (**167**) is dissolved in acetonitrile, a seven-line ESR spectrum is observed,[387] indicating that the single electron experiences two equivalent copper interactions and the electronic spectrum (Figure 13c) shows a new band in the near IR at *ca.* 12 000 cm^{-1},

Table 17 The Robin and Day Classification of Mixed Valence Complexes of the Copper(I) and (II) Ions[360,362]

Class	*(I)*	*(II)*	*(III)*
Stereochemistry	Localized stererochemistry different for different oxidation states	Same stereochemistry for different oxidation states—distinguishable	Same stereochemistry for different oxidation states—indistinguishable. (A) Clusters; (B) infinite lattices
Electronic properties	Localized Cu^I and Cu^{II}	Delocalized electron	Delocalized
Magnetics	Cu^I—diamagnetic Cu^{II}—paramagnetic	—	Metallic ferromagnetic
Conductivity	Insulator	Semiconductor	Conductor
Electronic spectra	Cu^I—colourless Cu^{II}—normal *d–d*	Cu^I—colourless Cu^{II}—near normal *d–d*. Characteristic (I)–(II) charge transfer spectra	No spectra of constituent Cu^I and Cu^{II} ions. Characteristic charge transfer spectra. Metallic reflectivity
Examples	See Figure 13	$[Cu_2^{II}(N_2O_2N_2)]$ $[Cu_2(L'')(ClO_4)_3]$[389] $[Cu(2,5\text{-}DTH)_2](ClO_4)_{4/3}$ (Figure 15)[63]	CuS Cu_2S $K[Cu_4S_3]$[382]

Table 18 Some Mixed Oxidation State Class I Cu^I and Cu^{II} Complexes

Complex	*Copper(II)*	*Stereochemistry*[a]	*Copper(I)*	*Stereochemistry*[a]	*ESR (g)*	*Ref.*
$[Cu(NH_3)_4][CuCl_2]\cdot H_2O$	CuN_4Cl_2	ERO	$CuCl_2$	L	—	378
$[Cu(NH_3)_4][CuBr_2]$	CuN_4Br_2	ERO	$CuBr_2$	L	—	378
$[Cu(NH_3)_4][CuI_2]$	CuN_4I_2	ERO	CuI_2	L	—	378
$[Cu(bipy)_2Cl][CuCl_2]_2$	CuN_4Cl	TB	$CuCl_2$	L	2.091	379
			$CuCl_4$	Td	—	—
$[Cu(C_{44}H_{60}N_4)Cl][CuCl_2]$	CuN_4Cl	SBP	$CuCl_2$	L	2.066, 2.088	380b
$[Cu(Ph_3AsO)_4][CuCl_2]$ (**156**)	CuO_4	SP	$CuCl_2$	—	2.06	365
$[Cu_2(SO_3)Cu(SO_3)]\cdot 2H_2O$	CuO_6	ERO	$CuSO_3$	Td	—	380b
$[Cu(NH_3)_3(CN)_4]$ (**163**)	CuN_6	ERO	CuC_3	Tr	—	372, 381

[a] ERO = elongated rhombic octahedral; TB = trigonal bipyramidal; SBP = square-based pyramidal; L = linear; Td = tetrahedral; Tr = trigonal.

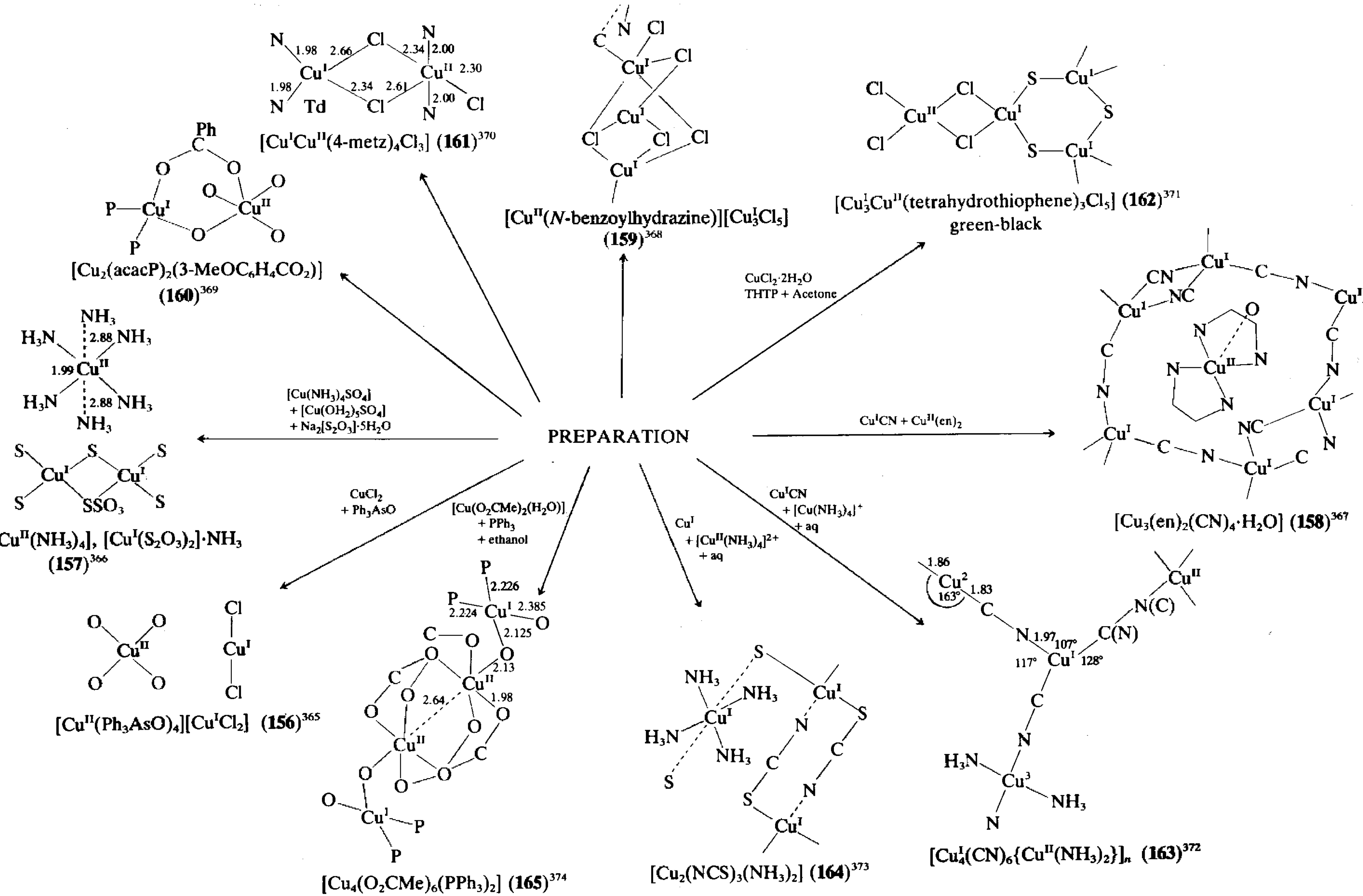


Figure 13 The preparation and crystal structures of some mixed oxidation state copper(I) and (II) complexes

Table 19 The Electronic Properties of Some Class II Mixed Valence Copper(I/II) Systems

Complex	μ_{eff} (*BM*)	*Electronic spectra* (cm^{-1})	*ESR*	*Hyperfine*
$[Cu^I(NCMe)]_4^+/[Cu^{II}(OH_2)_6]^{2+}/(OAc)^-$	—	19 685, 11 111	$g_{\parallel}$ 2.37	Seven line
$[Cu_2Cl_3(MeNN)_2]$ **(166)**	1.99	14 600;[a] 10 300, 8 000	2.14	Seven line
$[Cu^{II}Cu^I(L^9)](ClO_4)$ **(167)**	1.81	16 666; 12 000[a]	2.26	Seven line
$[Cu^ICu^{II}(L^{11})]ClO_4)_3$ **(169)**	1.87	—	$g_{\perp}$ 2.09	—
$[Cu(2,5\text{-dithiohexane})_2](ClO_4)_{4/3}$ (Figure 15)	1.90	22 222; 16 807	$g_{\parallel}$ 2.22, $g_{\perp}$ 2.05	—
			$A_{\parallel}$ 153 gauss	—

[a] Intervalence charge transfer (IVCT) spectrum.

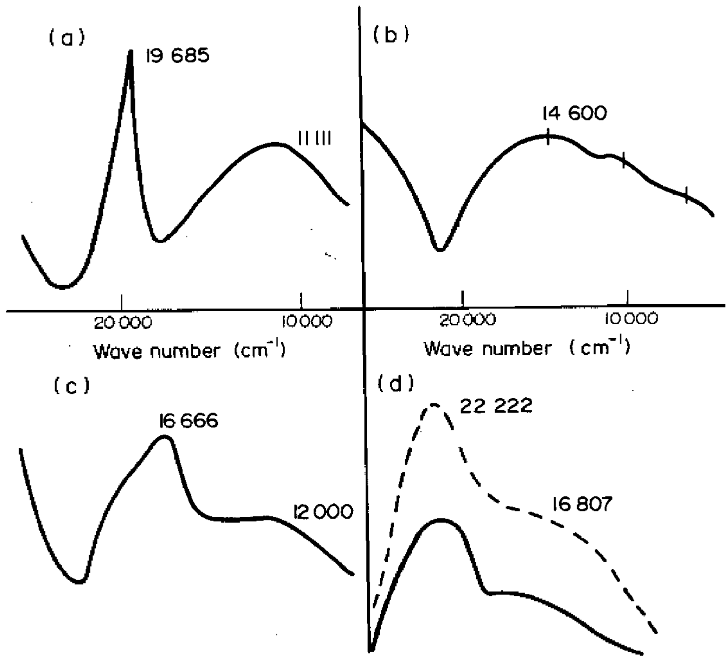
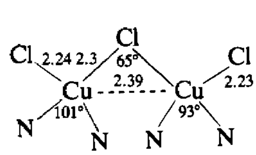
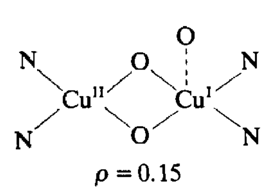


Figure 14 The IVCT[375–377] spectra of some class II copper(I/II) systems: (a) $[Cu(NCMe)_4Cu(OH_2)_6(OAc)_2]$;[383] (b) $[Cu_2Cl_3(MeNN)_2]$ **(166)**;[385] (c) $[Cu^{II}Cu^I(L^9)](ClO_4)$ **(167)**;[387] and (d) $[Cu_2^ICu^{II}(2,5\text{-DTH})_6](ClO_4)$[63]

which has been assigned as an intervalence charge-transfer band associated with the $Cu^{I/II}$ species. Together these properties suggest that **(167)** must be considered as a class II, Cu^I/Cu^{II} complex, at least in solution. However, the ESR spectrum of **(167)** in solution changes[387] to a normal four-line spectrum at 77 K suggesting that the odd electron is no longer under the influence of both copper centres and is now localized on a single copper(II) centre, consistent with normal class I Robin and Day behaviour.[360,362]

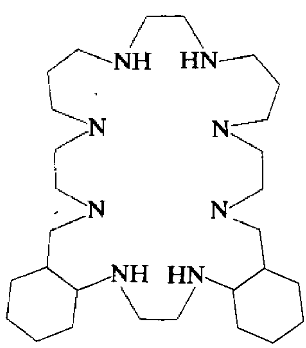


$[Cu_2Cl_3(MeNN)_2]$ **(166)**[385]

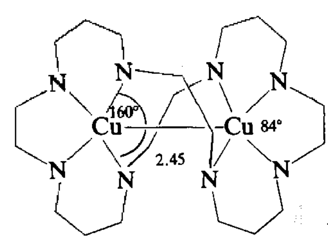


$[Cu^ICu^{II}(L^9)](ClO_4)$ **(167)**[388]

When a suspension of L^{11} **(168)**[389] in THF is treated with a methanolic solution of $[Cu(OH_2)_6](ClO_4)_2$, the solution yields green crystals of $[Cu^ICu^{II}(L^{11})](ClO_4)_3$ **(169)**,[389] whose structure involves a symmetrical Cu—Cu bond of length 2.445 Å. Each Cu atom involves a CuN_4 chromophore with a very distorted tetrahedral or trigonal pyramidal geometry (if the Cu—Cu direction is considered a bond with near two-fold symmetry). The structure confirms a $[Cu^ICu^{II}(L^9)]$ mixed valence cation, $\mu_{eff} = 1.87$ BM. The ESR spectrum shows a single g value of 2.07, but no evidence of any copper hyperfine structure and no electronic spectrum was reported. However, the two equivalent Cu environments suggest the best crystallographic evidence to date for class II type Robin and Day behaviour.[360–362] The ligand 2,5-dithiohexane[63] reacts with $[Cu(OH_2)_6](ClO_4)_2$ to yield three different products:[390] $[Cu(2,5\text{-}DTH)_2](ClO_4)_2$ (a), $[Cu(2,5\text{-}DTH)_2](ClO_4)$ (b), and $[Cu(2,5\text{-}DTH)_2](ClO_4)_{4/3}$ (c) (Figure 15). In (b) a tetrahedral Cu^IS_4 chromophore is present, while (a) has an elongated rhombic octahedral $Cu^{II}S_4O_2$ chromophore. In (c) the crystals are isomorphous with those of (b), but with a different occupation of the perchlorate positions to give a Cu^I/Cu^{II} ratio of 2:1 and indistinguishable CuS_4 environments, consistent with class II Robin and Day behaviour. The magnetic properties are consistent with a single unpaired electron per Cu_2 unit, and the ESR spectrum (Table 19) displays normal axial *g* and *A* values, which are hardly typical of a compressed CuS_4 tetrahedral geometry (see Section 53.4.4.4). Likewise the electronic spectrum of (c) (Figure 14d) shows little difference from that of the elongated rhombic octahedral geometry of (a). This suggests that the most intense band at $22\,222\ cm^{-1}$ is most probably associated with LMCT, which is insensitive to the change in stereochemistry of (a) and (b). The low energy shoulder at *ca.* $15\,000\ cm^{-1}$ probably masks any *d–d* transitions, as is usual with sulfur ligands, and there is no indication of any low energy IVCT bands.



L^{11} (**168**)[389]



$[Cu_2(L^{11})](ClO_4)_3$ (**169**)[398]

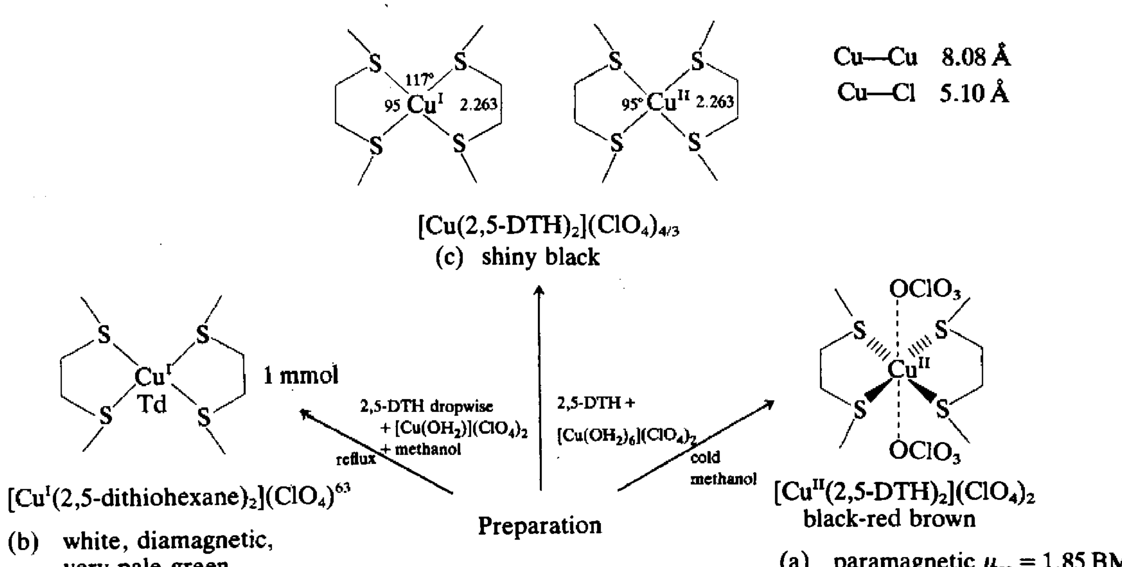


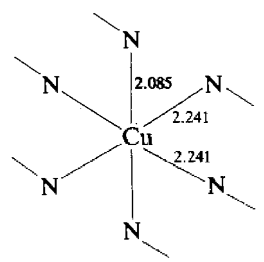
Figure 15 The preparations and structures of the copper(I), copper(I/II) and copper(II) 2,5-dithiohexane (2,5-DTH) complexes—copper thioethers[63,390]

53.3.8 Biological Copper(I)/(II) Systems

Mixed valence copper(I)/(II) complexes might reasonably be expected to have some relevance to the type I–IV systems of biological copper (see Section 53.4.8). Consequently, the recognition that D-penicillamine (D-H_2pen) is effective[391] in promoting the urinary excretion of excess copper from patients with Wilson's disease has led to a number of studies of the reaction of D-H_2pen and copper(II) ions. At physiological pH an intense purple complex is formed and isolated as the Tl_5 complex, the composition and structure of which were established[391] as $Tl_5[Cu^{II}_6Cu^{I}_8$(D-pen$)_{12}$Cl]·$n$$H_2O$ (Figure 16a) and is related to that of $(PhMe_3As)_2[Cu_8\{S_2C(CN)_2\}_6]$ (**87**).[196] It involves a high symmetry cube of Cu^I atoms with a central Cl^- anion with D-pen sulfur atoms bridging all the Cu^I atoms. Each face of the cube is capped by a copper(II) ion bridging a pair of sulfur atoms and itself coordinated by two nitrogen ligands to give a tetrahedrally distorted square coplanar *cis*-$Cu^{II}N_2S_2$ chromophore. If the Cu–Cu interactions are ignored the Cu^I atoms are involved in a trigonal CuS_3 chromophore. The stoichiometry and structure of the complex clearly establish a mixed valence copper(I)/(II) system, but with different geometries at the copper(I) and copper(II) atoms, which indicates class I Robin and Day behaviour. Consequently, the magnetic properties, μ_{eff}/Cu^{II} 1.75–2.20 BM, are consistent with a ferromagnetic coupling between the six copper(II) ions of an octahedral Cu_6 array. Likewise the very broad featureless ESR spectrum is associated with exchange coupling of the misaligned copper(II) ions, and the intense visible absorption band at 19 305 cm^{-1} is associated with an $S \rightarrow Cu^{II}$ LMCT. More recently, using alternative sulfur-containing ligands, very comparable structures have been characterized, such as $Tl_5[Cu^{II}_6Cu^{I}_8$(*o*-mercaptoisobutyric acid$)_{12}$Cl]·$n$$H_2O$,[392] and $[Cu^{II}_6Cu^{I}_8(SCMe_2CH_2NH_2)_{12}Cl](SO_4)_{3.5}\cdot 20H_2O$.[393]

Equally, attempts to use biologically relevant ligands such as imidazole and triazole have produced mixed valence copper(I)/(II) systems, such as in $[Cu^{I}_{10}Cu^{II}_2$(1-methyl-2-mercaptoimidazole$)_{12}(MeCN)_4](BPh_4)_2\cdot 4MeCN$[394,400] which involves eight tetrahedral Cu^IS_4 chromophores, two linear Cu^IN_2 chromophores and two square-based pyramidal CuN_2S_2 chromophores (see refs. 394 and 400). Likewise the use of the benzotriazole anion (BTA) has produced a $[Cu_5(BTA)_6(Bu^tNC)_4]$ (**170**)[395] complex, which involves a single $Cu^{II}N_6$ chromophore surrounded by four tetrahedral Cu^IN_3C chromophores with the former having [396] the uncommon compressed tetragonal octahedral stereochemistry (see Section 53.4.2.1 vi). Consistent with this pseudo copper(II) geometry (see Section 53.4.4.3) the ESR spectrum of the single copper(II) ion displays a reversed type spectrum[47] at room temperature $g_\perp > g_\parallel > 2.0$, which changes to a normal type spectrum at 77 K with $g_\parallel > g_\perp > 2.0$. It is surprising that such a biologically relevant set of ligands should produce such a nice example of fluxional copper(II) stereochemistry,[397] but does not disguise the clearly different Cu^I and Cu^{II} geometries and hence the class I Robin and Day behaviour.[360–362] Notwithstanding the lack of structural information[345] on the environment of the copper(I) centres in type III deoxyhemocyanin (Figure 16b), stepwise oxidation procedures of various types have produced a range[398] of Cu—Cu pairs involving single and double bridged systems involving various combinations of Cu^I and Cu^{II} centres (mixed oxidation states), ultimately to the *proposed* nonequivalent ligand-bridged species of oxyhemocyanin (Figure 16b). Included in the mixed valence systems, especially ones involving a potentially bridging azide anion, has been the report of some intervalence charge-transfer spectra (ref. 399, Figure 25), but without any structural data on the proposed class II Robin and Day behaviour (see Section 53.3.7).

This review of mixed valence copper(I)/(II) systems has clearly established the predominance of the class I Robin and Day behaviour (Table 17),[360–362] but equally has shown how few copper class II or III systems have been well defined. This particularly applies to the class II systems, which can still be considered well-defined coordination complexes, with the electronic properties of these systems in the solid state and in solution. This suggests a fruitful area of research in these copper(I)/(II) mixed valence systems, especially of class II behaviour.



$[Cu_5(BTA)_6(Bu^tNC)_4]$ (**170**)[395]

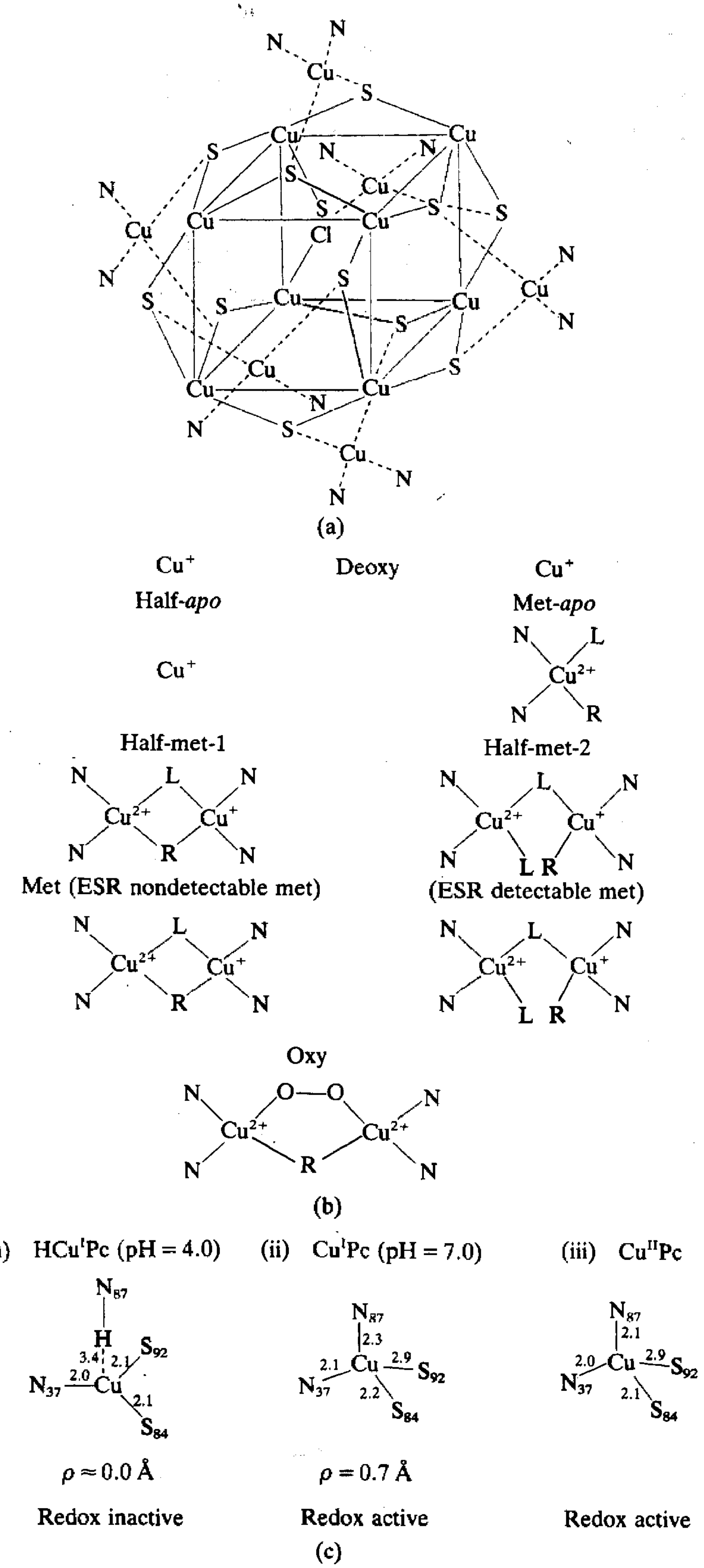


Figure 16 (a) The molecular geometry of $Tl_5[Cu^{II}_6Cu^{I}_8(\text{D-pen})_{12}Cl]\cdot nH_2O$;[391] (b) notation for the decay to oxyhemocyanin dinuclear copper species; and (c) the structural relationships between (i) HCu^{I}Pc; (ii) Cu^{I}Pc; (iii) Cu^{II}Pc and their redox activity

53.4 COPPER(II)

53.4.1 Introduction and Preparation

The copper(II) ion is the commonest oxidation state of copper, as copper(I) is readily oxidized[5,6] up to copper(II) and disproportionates into copper(II) and copper metal (equations (3) and (4); Section 53.3.1), while copper(III) can only be prepared[11] by strong oxidation of copper(II) (Section 53.6). The copper(II) ion is particularly stable in aqueous solution as the $[Cu(OH_2)_6]^{2+}$ cation from which complexes may frequently be prepared directly by the addition of the appropriate ligand, usually in water or in a nonaqueous solvent such as alcohol, acetonitrile or dimethylformamide, to increase the solubility. By using appropriate concentrations of a copper salt and the ligand, heating the mixed solution to boiling, filtering and slow cooling well-formed crystals suitable for a range of physical techniques, including X-ray crystallography can usually be produced.[354] In general most copper(II) crystals are air and moisture stable and are free of the handling problems associated with copper(I) complexes. In the case of moisture sensitive complexes such as anhydrous $[Cu(NO_3)_2]$[401] or $[Cu(ClO_4)_2]$[402] nonaqueous solutions may have to be used, such as liquid N_2O_4/ethyl acetate mixtures[401] in the preparation of $[Cu(NO_3)_2]$, and it is necessary to handle the products in a special filtration and dry box facility.[403] For systems involving only slightly less moisture sensitive systems, dehydration of a solvent, such as ethanol or acetonitrile, may be effected *in situ* by boiling with 10% by volume of dimethoxymethane, although care must be taken as a hydrate may be formed in the wet solvent, and the anhydrous complex in the dry solvent, as in the preparation of $[Cu(phen)_2(O_2CMe)](BF_4)\cdot 0$ or $2H_2O$.[404]

The copper(II) cation may be stabilized by complex formation against reduction to copper(I) by reducing anions[23] such as the iodide and cyanide anions (see Figure 1). Thus while these anions will reduce Cu^{II} to Cu^{I} in aqueous solution with the precipitation of Cu_2I_2 and CuCN, respectively, the addition of bipy to the solution prior to the addition of the I^- or $(CN)^-$ anions prevents reduction and allows the preparation[405,406] of a $[Cu(bipy)_2X]^+$ cation involving coordinated I^- and $(CN)^-$, respectively.

While the copper(I) cation is considered to be a soft acid,[36] the copper(II) ion is best considered as a borderline hard acid (Table 2). With the copper(II) cation the hard base function of the ligands is complicated by the tendency to reduce Cu^{II} to Cu^{I} by even mild reducing ligands, unless the copper(II) ion is stabilized by complex formation, as above. Thus although oxygen ligands are more abundant than sulfur ligands, the latter are well characterized,[30] notwithstanding their reducing properties. Nitrogen is probably the best donor to copper(II), virtually to the exclusion of phosphorus as a ligand (see Section 53.4.2.3). On the other hand, while fluoride is predicted to be the best halide ligand towards copper(II),[36] it is relatively uncommon and Cl^- is much more common;[5,10,22] the I^- anion is a relatively uncommon ligand. Thus on balance the copper(II) cation must be considered as a borderline hard acid, with O, N and Cl^- the most abundant ligands with S only slightly less common. The main difference compared to copper(I) (see Table 16) is the greater occurrence of σ donors and the virtual absence of π donors.

Like all the first-row transition metal(II) cations, copper(II) readily forms coordination complexes involving mainly the coordination numbers four, five and six, but unlike the majority of the first-row metal ions,[10] the copper(II) complexes are characterized by a seemingly infinite variety of distortions,[47,396] the sense of which can only be determined by X-ray crystallography. For this reason there are probably *five* times as many compounds and complexes of the copper(II) ion of known crystal structure than, for example, of nickel(II) or zinc(II).[407] Thus while the stereochemistry of the nickel(II) ion is characterized by the formation of near regular octahedral and tetrahedral geometries (Figure 17a),[10] the former stereochemistry is limited to less than 10 compounds for the copper(II) ion, and the latter stereochemistry is unknown. The majority of six-coordinate copper(II) complexes[47,48] involve an elongated tetragonal or rhombic octahedral structure (Figure 17b), with only a few involving a compressed tetragonal (or rhombic) octahedral structure. The tetrahedral geometry for the copper(II) ion always involves a significant compression along the S_4 symmetry axis (Figure 17b). Only the square coplanar geometry is regular for both the nickel(II) and copper(II) ions, but even here the latter sometimes involves a slight tetrahedral distortion. In five-coordinate geometries (Figure 17) the nickel(II) ion forms mainly regular structures,[408] while the copper(II) ion rarely involves a regular square pyramidal stereochemistry, but generally involves both an elongation (– – –) and a trigonal in-plane distortion[396] or, less frequently, a tetrahedral distortion. In the trigonal bipyramidal stereochemistry, the nickel(II) ion forms regular structures,[408] while the copper(II) may be regular, but is more frequently involved in a distortion towards square pyramidal (Figure 17b).

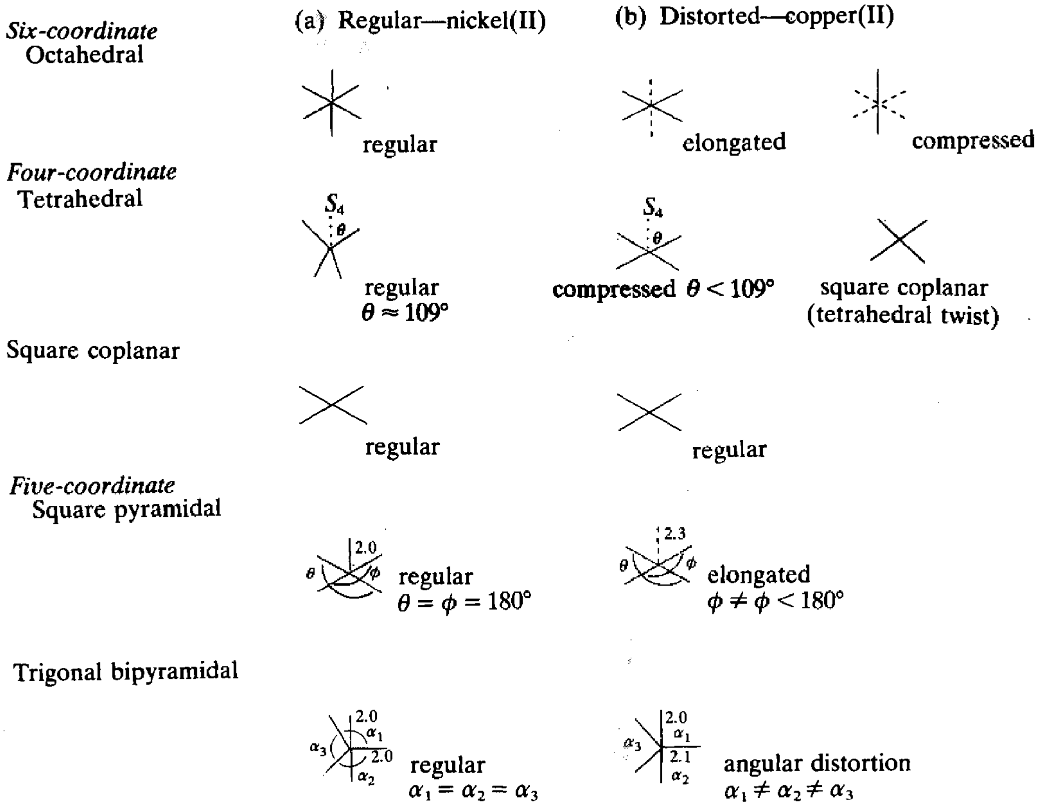
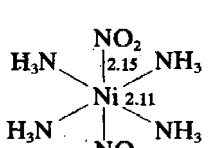
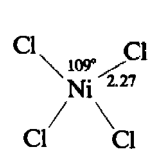


Figure 17 Comparison of the broad stereochemistries of (a) the nickel(II) ion; and (b) the copper(II) ion

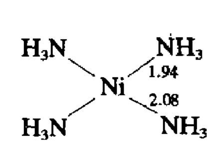
Some of the small bond-length and bond-angle distortions of the copper(II) complexes are also found in the corresponding nickel(II) complexes for the same ligands,[407,408,410,411] especially where chelate ligands are involved. Thus ethylenediamine (en), diethylenetriamine (dien) and tris(2-aminoethyl)amine (tren) can all produce bond-length distortions of 0.1 Å and bond-angle distortions of *ca.* 5°. Substituents such as ethyl or tertiary butyl groups can produce distortions due to their conformation and due to their bulk, which may also block coordination sites. These relative effects are illustrated for some pairs of nickel(II) and copper(II) complexes in the molecular structures **(171)** to **(176)** and show how much greater are the bond-length and bond-angle distortions of the copper(II) complexes.[407–411]



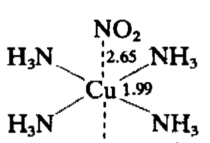
$[i(NH_3)_4(NO_2)_2]$ **(171)**[408,410,411]



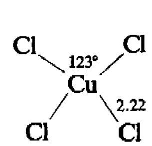
$(Ph_3MeAs)_2[NiCl_4]$ **(172)**[408,410,411]



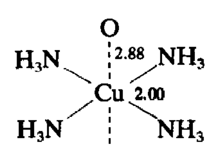
$Na_4[Ni(NH_3)_4][Ag(S_2O_3)_2]_2 \cdot NH_3$ **(173)**[409]



$[Cu(NH_3)_4(NO_2)_2]$ **(174)**[439]



$Cs_2[CuCl_4]$ **(175)**[483]



$Na_4[Cu(NH_3)_4][Cu(S_2O_3)_2] \cdot OH_2$ **(176)**[366,475]

A qualitative understanding of the more regular structures of the six-coordinate nickel(II) and zinc(II) ions may be associated with the spherical symmetry of the d^n configuration of these two ions in an octahedral ligand field, namely $t_{2g}^6e_g^2$ and $t_{2g}^6e_g^4$, respectively. In contrast the copper(II) ion, with a $t_{2g}^6e_g^3$ configuration, may be considered to be nonspherically symmetrical with a prolate ellipsoidal shape in the elongated octahedral stereochemistry (Figure 18) and an oblate ellipsoidal shape in the compressed octahedral stereochemistry.[412,47,48]

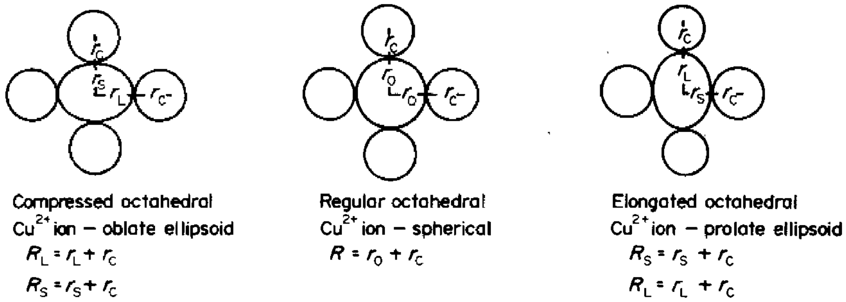


Figure 18 The copper atom and ligand atom covalent radii in octahedral and tetragonal octahedral stereochemistries (two dimensional)[412,47,48]

53.4.2 Copper(II) Stereochemistry

53.4.2.1 Mononuclear complexes

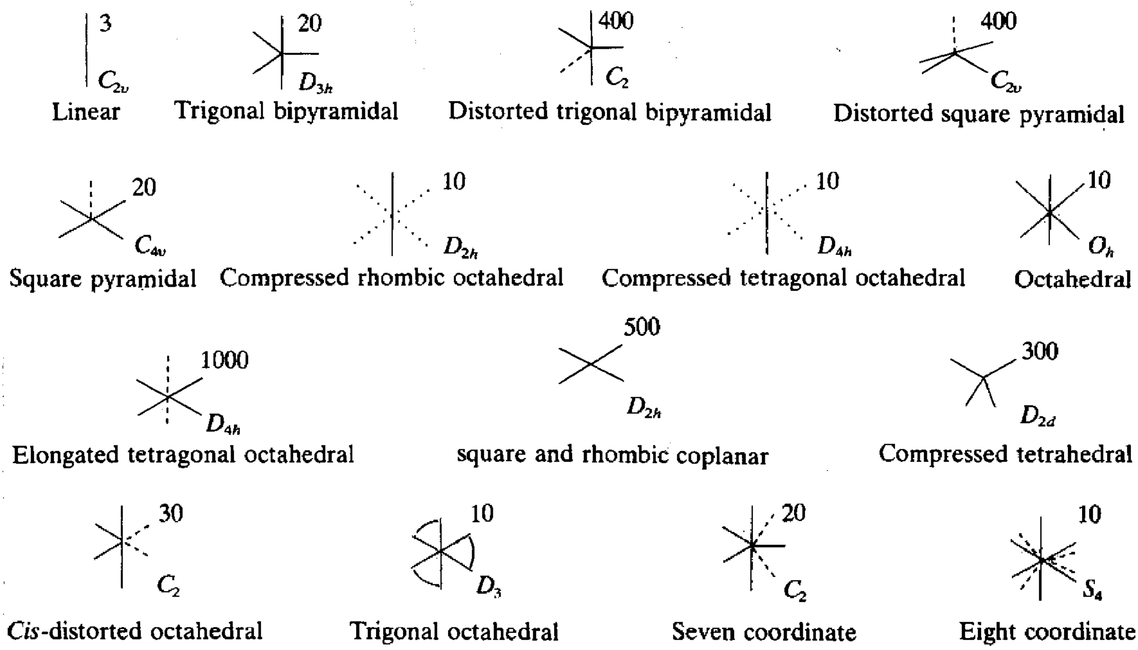
Figure 19.1 summarizes the range of stereochemistries occurring in the mononucleai compounds and complexes of the copper(II) ion and the post superscript to each structure gives a 'quantitative' indication[407] of the approximate number of known structure determinations foi each structure. Single-crystal X-ray crystallography[407] is the predominant method for determining the structure of copper(II) complexes in the solid state, with a much less frequent, but most important, contribution from neutron diffraction determinations.[413] Powder profile analysis[414,415] is beginning to make a contribution to structure determination, initially by neutron diffraction[414] and more recently *via* the high intensity of synchrotron radiatior sources.[416] Electron diffraction of molecules in the gaseous state and in solution has found only limited application, but has been used for the structure determination of $[CuCl_2]$,[41] $[Cu(O_2NO)_2]$[418] and $[Cu(acac)_2]$,[419] and of cations in solution.[420,421] EXAFS spectroscopy[42] also yields copper–ligand distances in the solid state,[423] but care has to be observed in the estimation of long Cu—L distances.[424]

The following section attempts to summarize the various stereochemistries of the copper(II) ion (Figure 19)[47,48] in terms of their regular and distorted geometries and to discuss the factors which contribute not only to the regular structures but also to the distorted geometries.[396] The structures of Figure 19 are characterized by three ranges of Cu—L distances: short, 1.9–2.1 Å (——); intermediate, 2.1–2.4 Å (···); and long 2.4–3.0 Å (---). For oxygen and nitrogen donor atom ligands all three ranges of Cu—L distances are observed, but for ligand atoms involving larger donor atom radii (Table 20),[49] as determined by their covalent or ionic radii only intermediate and long distances are observed, as summarized in Table 20, assuming an approximate copper(II) radius of 0.7 Å. Consequently, the longer Cu—L distances observed for Cl^-, Br^-, I^- and S arise simply from the larger size of the donor atom present and do no imply weaker binding.

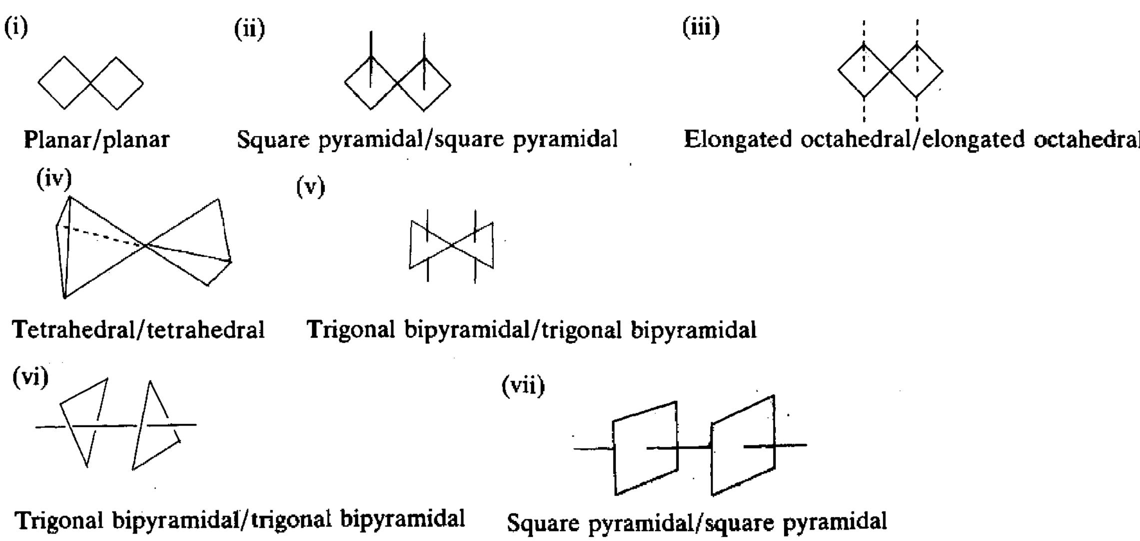
(*i*) *Octahedral and trigonal octahedral*

A regular octahedral CuL_6 chromophore for the copper(II) ion is very uncommon (Figure 19.1) but does occur for the $[Cu(NO_2)_6]^{4-}$ anion when stabilized by high symmetry lattices such as the face-centred-cubic lattice of $K_2Pb[Cu(NO_2)_6]$ (**177**),[426] at 298 K. All six Cu—N distances of 2.11 Å are equivalent from the copper site symmetry, with the actual symmetry o the anion lowered to T_h by the conformation of the nitro oxygen atoms. The six nitro ligand are also involved in bidentate nitro coordination to the Pb^{2+} cations at 2.77 Å, a distance consistent with intermediate Pb—O bonding, and which must be mainly responsible fo

19.1 Mononuclear: a summary of the stereochemistries of the copper(II) ion, their approximate point group symmetries and the relationship between the regular and distorted geometries: —, short (1.9–2.1 Å); · · ·, intermediate (2.1–2.4 Å); – – – –, long (2.4–3.0 Å)



19.2(a) Dinuclear Type I: CuXCu bridged



19.2(b) Dinuclear Type II: CuX_2Cu bridged

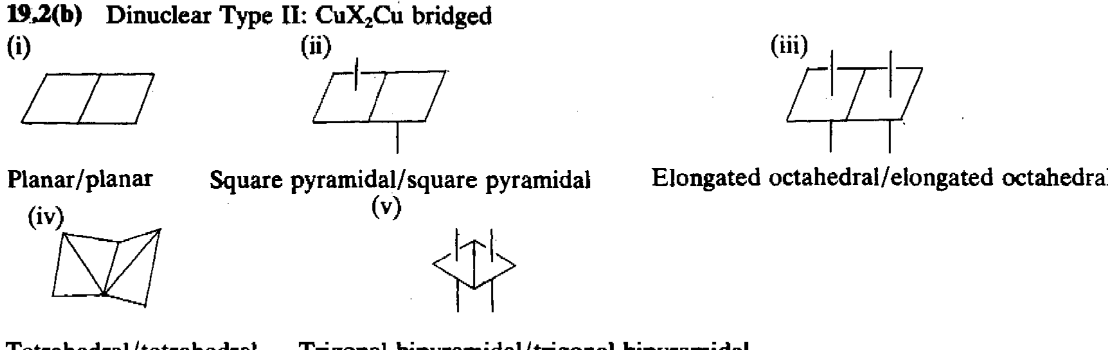
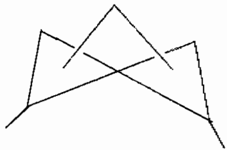


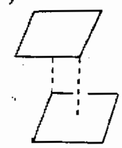
Figure 19 Stereochemistry of copper(II) complexes

(vi)



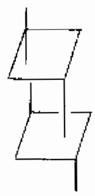
Trigonal bipyramidal/trigonal bipyramidal

(vii)



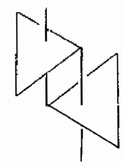
Square pyramidal/square pyramidal

(viii)



Elongated rhombohedral/elongated rhombohedral

(ix)



Trigonal bipyramidal/trigonal bipyramidal

19.2(c) Dinuclear Type III: CuX_3Cu bridged

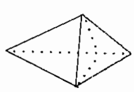
(i)

Square pyramidal/square pyramidal

(ii)

Elongated octahedral/elongated octahedral

(iii)

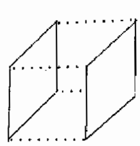


Tetrahedral/tetrahedral

(iv)

Trigonal bipyramidal/trigonal bipyramidal

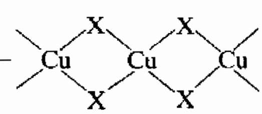
19.2(d) Type IV: CuX_4Cu bridged
(i)



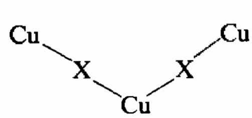
Square coplanar/square coplanar

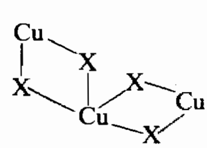
19.3 Trinuclear

(i) Linear Cu—X—Cu—X—Cu—



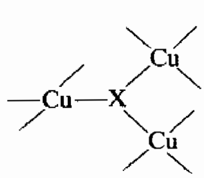
(ii) Bent





(iii) Triangular

(a) planar



(b) pyramidal

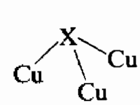
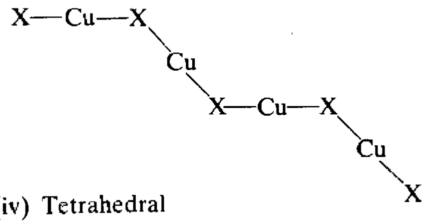


Figure 19 (*continued*)

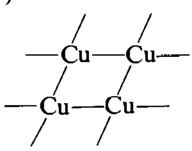
19.4 Tetranuclear

(i) Linear X—Cu—X—Cu—X—Cu—X—Cu—X

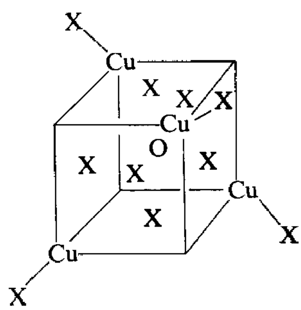
(ii) Zigzag or stepped



(iii) Planar

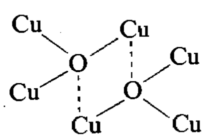


(iv) Tetrahedral



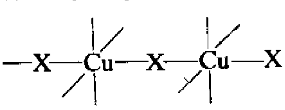
19.5 Hexanuclear

(i)

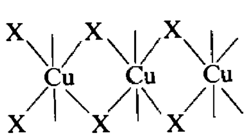


19.6 Dimensional chains and ribbons

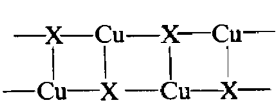
(i) Single ligand bridge



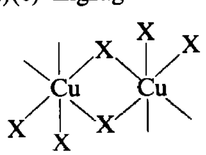
(ii)(a) Double ligand bridge straight chain



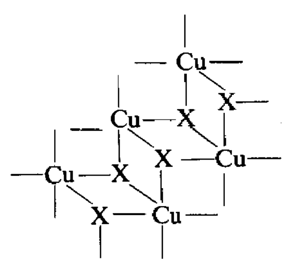
(ii)(b) Zigzag chain planar



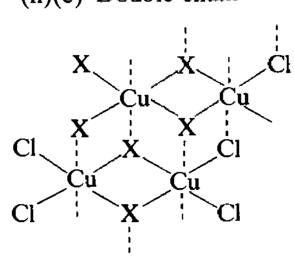
(ii)(c) Zigzag chain bent



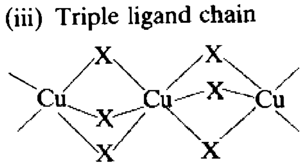
(ii)(d) Stepped chain



(ii)(e) Double chain



(iii) Triple ligand chain



(iii)

(ii)(f) Linear double chain

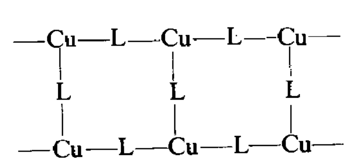
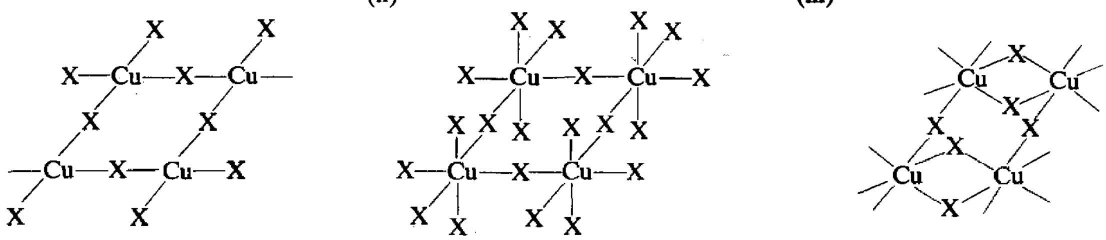


Figure 19 (*continued*)

19.7 Two-dimensional layers

(i) (ii) (iii)



Elongated rhombohedral, six coordinate, $a = b$

Square pyramidal, five coordinate, $a \neq b$

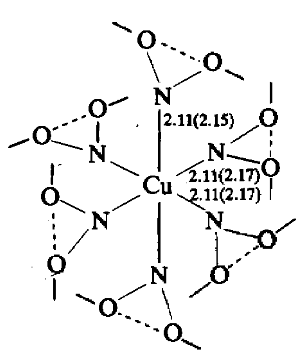
Trigonal bipyramidal, five coordinate, chain linl

Figure 19 (*continued*)

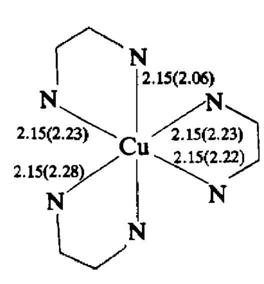
Table 20 The Difference Between the Observed R_S Bond Lengths and the Pauling Covalent Radii[49] (P.C.R.) giving the 'Apparent' In-plane Radii of the Copper(II) Ion R_{Cu}

Ligand	R_S (Å)	*P.C.R.* (Å)	R_{Cu} (Å)
F^-	1.91	0.64	1.27
O	1.99	0.66	1.33
N	2.03	0.70	1.33
Cl^-	2.29	0.99	1.30
Br^-	2.45	1.14	1.31

maintaining the $[Cu(NO_2)_6]^{4-}$ anion in this uncommon regular octahedral stereochemistry. A regular trigonal octahedral CuL_6 chromophore is more common than the regular octahedral chromophore. It is most common in the tris(chelate) copper(II) complexes such as $[Cu(en)_3](SO_4)$ (**178**)[427] or $[Cu(ompha)_3](ClO_4)_2$ (**179**),[428] where ompha = octamethylpyrophosphoramide, but also occurs with tridentate chelate ligands as in $[Cu(metri)_2]$ (**180**),[429] where metri = tri(4-methylbenzo)(b,f,j)[1,5,9]triazacyclododecane. It also occurs with monodentate ligands as in $[Cu(pyNO)_6](ClO_4)_2$[430] and in the high temperature form of $Cs[CuCl_3]$ (**181**),[431] where Cl^- anions bridge at two nearly equal distances. In the tris(chelate) copper(II) complexes (**178**)–(**180**) the chelate ligands impose a D_3 symmetry, whereas in $[Cu(pyNO)_6](ClO_4)_2$ this can only be imposed by the packing of the pyNO ligands and in (**181**) by the spiral chain of bridging Cl^- anions. In (**178**) and (**179**) the trigonal lattice is maintained by the three-fold symmetry of the anions present, which are also present in crystallographic positions of three-fold symmetry (the cooperative Jahn–Teller Effect,[432] see Section 53.4.5).

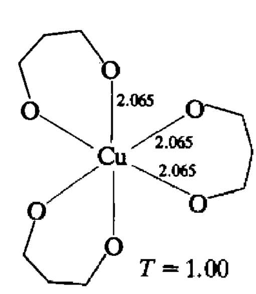


$K_2Pb[Cu(NO_2)_6]$ (**177**)[426]

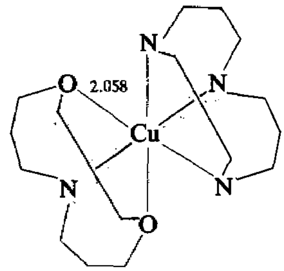


298 K (120 K) $T = 1.00(1.08)$

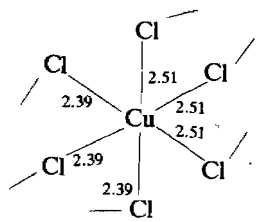
$[Cu(en)_3](SO_4)$ (**178**)[427,573]



$[Cu(ompha)_3](ClO_4)_2$ (**179**)[428]



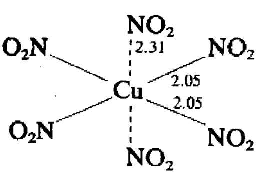
[Cu(metri)$_2$] **(180)**[429]



Cs[CuCl$_3$] **(181)**[431]

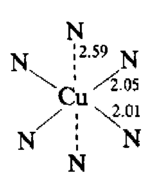
(*ii*) *Elongated tetragonal and rhombic octahedral*

Together these two stereochemistries account for the bulk of six-coordinate copper(II) structures (Figure 19.1). The former can only occur with monodentate ligands, as in $K_2Ba[Cu(NO_2)_6]$ **(182)**,[433] [Cu(imidazole)$_6$](NO_3)$_2$ **(183)**,[434] $Cs_2[Cu(OH_2)_6](SO_4)_2$ **(184)**,[435] $Ba_2[Cu(OH)_6]$ **(185)**,[436] $Ba_2[CuF_6]$ **(186)**[437] and $(NH_4)_2[CuCl_4]$ **(187)**.[438] It also occurs with four equivalent ligands, as in $[Cu(NH_3)_4(NO_2)_2]$ **(174)**,[439] [Cu(imidazole)$_4$(OH_2)$_2$]F_2 **(188)**,[440] [Cu(cyclam)(SPh)$_2$] **(189)**,[441] where cyclam or 14-ane-N_4 = 1,4,8,11-tetrazacyclotetradecane, and [Cu(14-ane-S_4)($OClO_3$)$_2$] **(190)**.[442] In general with nonequivalent ligands an elongated rhombic octahedral stereochemistry results, as in $Ba_2[Cu(OH_2)_2(O_2CH)_4](HCO_2)_2{\cdot}2H_2O$ **(191)**[443] or $[CuCl_2(OH_2)_2]$ **(192)**.[444] In **(192)** the in-plane rhombic distortion of 0.4 Å arises mainly from the differing covalent radii of the oxygen and chloride ligands (Table 20). With chelate[49] ligands both bond-length and bond-angle distortions arises as in the case of ethylenediamine, diethylenetriamine and ethylenediaminetetraacetic acid, *e.g.* in [Cu(en)$_2$(FBF_3)$_2$] **(193)**,[445] [Cu(dien)$_2$]$Br_2{\cdot}H_2O$ **(194)**[446] and [Cu(H_2edta)OH_2] **(195)**.[447] Not only may there be distortion of the bond angles, but more significantly, with out-of-plane chelation, a reduction of the observed out-of-plane distortion as in **(194)**, **(195)**, [Cu(phen)$_3$](ClO_4)$_2$ **(196)**,[448] [Cu(hfacac)$_2$(bipy)] **(197)**,[449] [Cu(phen)$_2$(NCS)$_2$] **(198)**[450] and [Cu(HBpz$_3$)$_2$] **(199)**.[451] With nonequivalent ligands bonding out of the plane, asymmetry in the axial bond lengths occurs as in **(195)** and [Cu(en)$_2$(OH_2)Cl] **(200)**,[452] where despite the longer Cu—Cl distance of 2.87 Å, the chloride ion is probably more strongly bonding than the OH_2 at 2.68 Å, due to the larger covalent radius of the chloride ion (Table 20). In the case of [Cu(bipy)$_2$(FBF_3)](BF_4) **(201)**[453,454] not only are there equivalent axial ligands bonding at unequal Cu—F distances ($\Delta F \approx 0.1$ Å), but the in-plane CuN_4 chromophore has a marked tetrahedral distortion, dihedral angle 44.6°, due to the steric interference of the two 2,9-hydrogen atoms preventing the two bipy rings from lying coplanar.[455]



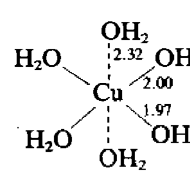
$T = 0.89$

$K_2Ba[Cu(NO_2)_6]$ **(182)**[433]



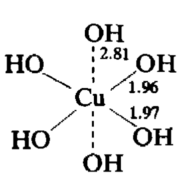
$T = 0.78$

[Cu(imidazole)$_6$](NO_3)$_2$ **(183)**[434]



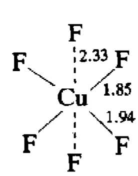
$T = 0.86$

$Cs_2[Cu(OH_2)_6](SO_4)_2$ **(184)**[435]



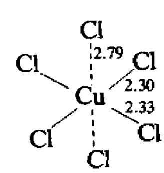
$T = 0.70$

$Ba_2[Cu(OH)_6]$ **(185)**[436]



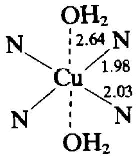
$T = 0.81$

$Ba_2[CuF_6]$ **(186)**[437,534]



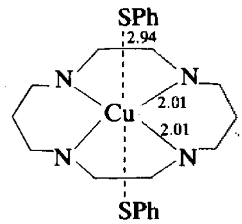
$T = 0.83$

$(NH_4)_2[CuCl_4]$ **(187)**[438]

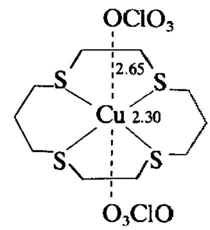


$T = 0.76$

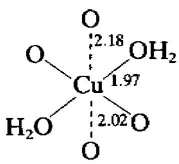
$[Cu(imidazole)_4(OH_2)_2]F_2$ **(188)**[440]



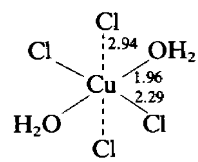
$[Cu(cyclam)(SPh)_2]$ **(189)**[441]



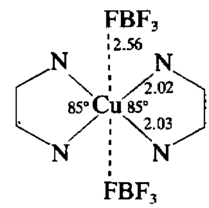
$[Cu(14\text{-ane-}S_4)(OClO_3)_2]$ **(190)**[442]



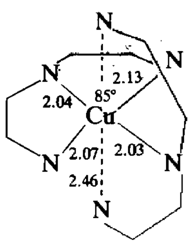
$Ba_2[Cu(OH_2)_2(O_2CH)_4][HCO_2]_2{\cdot}2H_2O$ **(191)**[433]



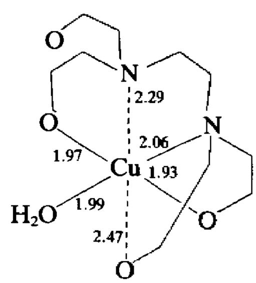
$[CuCl_2(OH_2)_2]$ **(192)**[444]



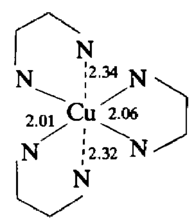
$[Cu(en)_2(FBF_3)_2]$ **(193)**[445]



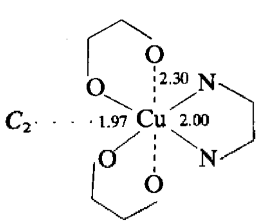
$[Cu(dien)_2]Br_2{\cdot}H_2O$[446] **(194)**



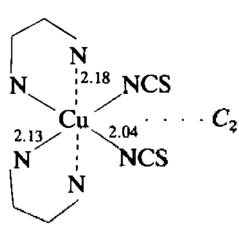
$[Cu(H_2edta)(OH_2)]$ **(195)**[447]



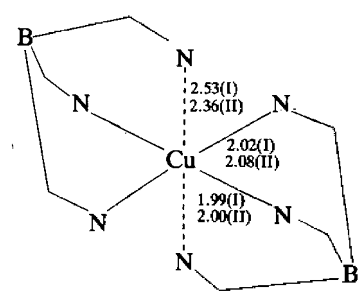
$[Cu(phen)_3](ClO_4)_2$ **(196)**[448]



$[Cu(hfacac)_2(bipy)]$ **(197)**[449]

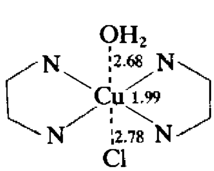


$[Cu(phen)_2(NCS)_2]$ **(198)**[450]

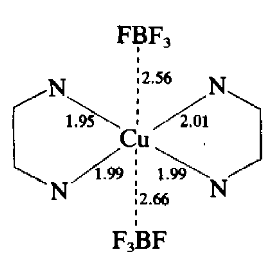


$T = 0.87(I);\ 0.79(II)$

$[Cu(HBpz_3)_2]$ I and II **(199)**[451]



$[Cu(en)_2(OH_2)Cl]Cl$ **(200)**[452]



$[Cu(bipy)_2(FBF_3)](BF_4)$ **(201)**[453,454]

In all of these elongated tetragonal and rhombic octahedral copper(II) complexes (**174**) and (**182**)–(**201**) there are clearly longer out-of-plane bond lengths, R_L, than in-plane lengths, R_S. For equivalent ligands the term tetragonality, T,[456] has been introduced, where T = (mean in-plane distance R_S)/(mean out-of-plane distance R_L), and is readily determined to be 0.80 ± 0.02 (Table 21). The tetragonality, T^*, of complexes involving nonequivalent ligands may also be estimated if the values of R_S and R_L are corrected to a standard Cu—L distance, such as that for nitrogen, using the respective values of the Pauling covalent radii and the expression R_L (corrected) = R_L (observed) $\times R_S^N/R_S^X$. When applied to a limited range of ligands such as water and ammonia (Table 21), the tetragonalities are reasonably constant at *ca.* 0.8, but with more crystallographic data now available,[407] a significant number of elongated rhombic octahedral complexes have been found to have appreciably higher T values of 0.85–0.95. One reason for this is the presence of out-of-plane chelate ligand bonding, which restricts the extent of axial elongation that is possible as in (**194**) to (**199**) and whose general stereochemistry is understandable in terms of the nonspherical symmetry of the copper(II) ion[412] (prolate ellipsoid, Figure 18). Nevertheless, a number of elongated rhombic octahedral complexes involving monodentate ligands also have high tetragonalities of *ca.* 0.9 as in $(NH_4)_2[Cu(OH_2)_6](SO_4)_2$ (**202**), $T = 0.91$.[457,458] When the tetragonality T is plotted against the separate R_S and R_L values (Figure 20a)[459] or R_L *vs.* R_S (Figure 20b),[460–462] the data suggest that the tetragonality of the copper(II) ion prolate ellipsoid is not fixed, but may vary over a finite range of values.[459] This variable tetragonal distortion has been termed the plasticity effect[461] in copper(II) stereochemistry and has been developed more recently in the concept of the mutual influence of ligands,[463] namely R_L *vs.* R_S (Figure 20b). The data of Figure 20 suggest that the stereochemistry of the copper(II) ion may vary continuously[461] from regular octahedral through elongated tetragonal octahedral to ultimately square coplanar, where the two axial ligands are no longer bonding. Consequently, each observed structure (**182**)–(**201**) simply represents a point in a continuous structural pathway connecting the two stereochemistries, regular octahedral to regular square coplanar, connected by the appropriate mode of vibration of the CuL_n chromophore (Figure 21).[464–467,396] In (**194**) the nonequivalent axial Cu—N distances of 2.34 and 2.44 Å suggest that an appropriate mode of vibration of the octahedral CuL_6 chromophore may take the stereochemistry from elongated tetragonal octahedral along a structural pathway towards the square base pyramidal stereochemistry of Figure 21.

Table 21 Copper–Ligand Bond Lengths (Å) R_S, R_L and R_S/R_L (= T)[456]

	R_S		R_L			
Ligand atom	*Range*	*Mean*	*Range*	*Mean*	$R_L - R_S$	$R_S/R_L = T$
F	1.89–1.93	1.91(10)	2.21–2.86	2.36(12)	0.45	0.809
O[a]	1.92–2.16	1.99(42)	2.22–2.89	2.50(16)	0.51	0.796
N[b]	1.99–2.14	2.03(40)	—	—	—	—
Cl	2.25–2.34	2.31(48)	2.73–3.19	2.93(32)	0.62	0.792
Br	2.40–2.56	2.45(12)	3.08–3.19	3.15(6)	0.70	0.777

[a] Water. [b] Ammonia.

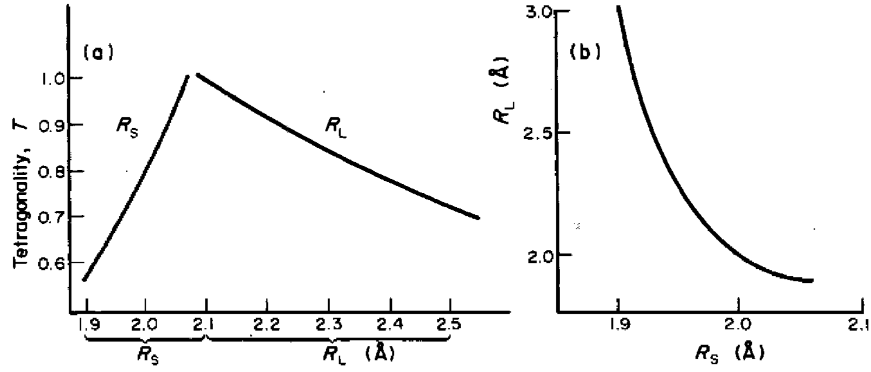


Figure 20 (a) Tetragonality *vs.* R_S and R_L;[459] and (b) R_L *vs.* R_S[463]

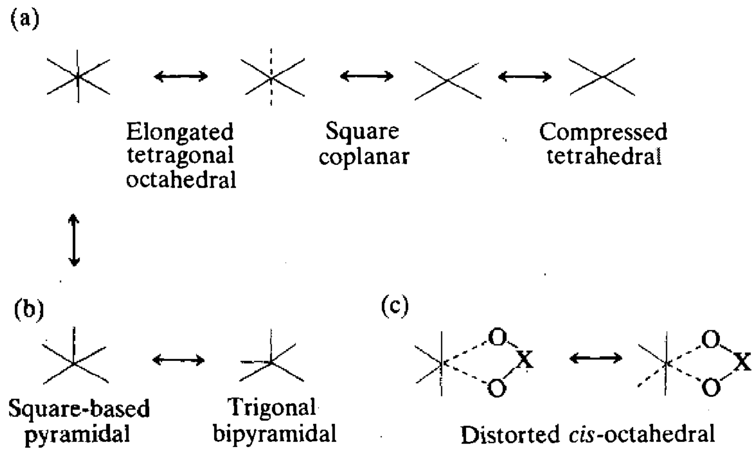
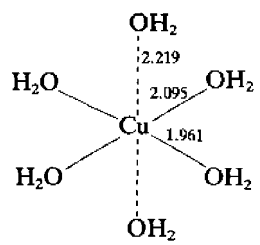


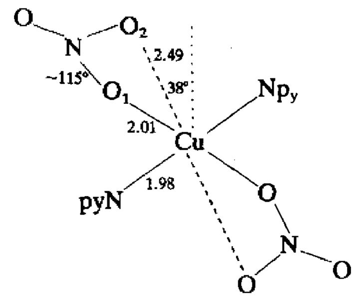
Figure 21 Structural pathways for some copper(II) stereochemistries



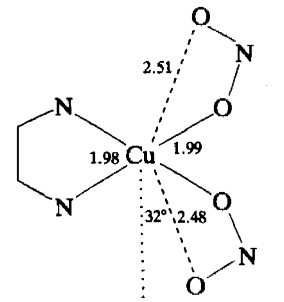
$(NH_4)_2[Cu(OH_2)_6](SO_4)_2$ **(202)**[457,458]

The term semi-coordination[468] has been introduced to describe the long-bonding role (R_L) o the axial ligands of these elongated tetragonal and rhombic octahedral stereochemistries of th copper(II) ion and while receiving some criticism[469] the term is generally accepted. Neverthe less, it should be remembered that the term semi-coordination does not imply a different sor of covalent bond, but rather recognizes the presence of some weak bonding to the copper(II ion, notwithstanding the relatively long copper ligand distances (R_L) involved, which ar generally 0.4–0.8 Å longer than the corresponding in-plane distances (R_S) of *ca.* 2.0 Å.

A further type of ligand bonding role is associated with the elongated rhombic octahedra stereochemistry of the copper(II) ion; this involves off-the-*z*-axis bonding.[470] This is associate with the bonding role to the copper(II) ion of trigonal oxyanions (see Chapter 15.5) such as th nitrite, nitrate and acetate anions, all of which form good primary ligands to the copper(II) io as in $[Cu(pyrazine)_2(O_2NO)_2]$ **(203)**[471] and $[Cu(bipy)(ONO)_2]$ **(204)**.[472] By virtue of th coordination of the first oxygen atom, O(1), to the copper(II) ion, with a Cu—O(1)—N angl of 110–120°, a second oxyanion oxygen atom, O(2), is constrained to be at a distance o 2.5–2.7 Å from the copper(II) ion (see Chapter 15.5, Figure 1) such that the O(1)—N—O(2 plane is at 90° to the plane of the CuL_4 chromophore and the Cu—O(2) direction makes a angle of 30–40° to the perpendicular (*z*) to the CuL_4 plane. This O(2) atom cannot be involve in direct bonding along the *z* axis, but is close enough to the *z* direction to involve at least som weak or semi-coordination of the O(2) atom to the copper(II) ion.[48] Consequently th stereochemistries of **(203)** and **(204)** should not be considered to involve four-coordinat rhombic coplanar CuO_2N_2 chromophores, but six-coordinate elongated rhombic octahedra $CuO_2N_2O'_2$ chromophores with a (4 + 2*)-type coordination. In this off-the-*z*-axis bonding rol of these trigonal planar oxyanions, the criterion has been introduced[473] for the nitrate ion tha if $\Delta O = \{Cu—O(2)\} - \{Cu—O(1)\} < 0.7$ Å, weak off-axis bonding of the O(2) atom i involved, while if $\Delta O > 0.7$ Å, no off-axis bonding is involved; this criterion is readily extende to other trigonal planar oxyanions (see Figure 1, Chapter 15.5) and also to tetrahedra oxyanions.



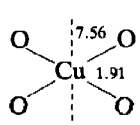
$[Cu(pyrazine)_2(O_2NO)_2]$ **(203)**[471]



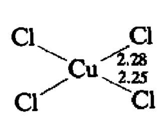
$[Cu(bipy)(ONO)_2]$ **(204)**[472]

(*iii*) *Square and rhombic coplanar*

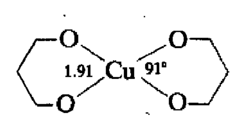
Together the square and rhombic coplanar stereochemistries of the copper(II) ion are comparable in frequency to that of the compressed tetrahedral stereochemistry (Figure 19.1) but less than that of the five-coordinate and elongated rhombic octahedral structures. The strictly square coplanar CuL_4 chromophore with monodentate ligands occurs in gillespite, $Ca[CuSi_4O_{10}]$ **(205)**,[474] $Na_4[Cu(NH_3)_4][Cu(S_2O_3)_2]_2{\cdot}OH_2$ **(176)**[475] and $(modphma)_2[CuCl_4]$ **(206)**.[476] All must involve some minor interactions along the z-axis, but the CuL_4 chromophore is considered to be square coplanar if these involve distances >3.0 Å. In this four-coordinate geometry the majority of complexes involve bidentate chelate ligands as in $[Cu(3\text{-}Meacac)_2]$ **(207)**,[477] $[Cu(N,N\text{-}Et_2en)_2](NO_3)_2$ **(208)**[478] and $[Cu(diethylthiocarbamate)_2]$ **(209)**.[479] In all of these coplanar structures the Cu—O, N distances are short (1.9–2.0 Å) and the Cu—Cl, S distances relatively short at 2.25–2.35 Å. With chelate ligands the internal L—Cu—L angles are >90° for six-membered rings **(207)**, but <90° for five- **(208)** and four-membered **(209)** rings. With the macrocyclic ligand as in [Cu(phthalocyanine)] **(210)**[480] the whole molecular is planar, but a feature of some of the mixed donor CuO_2N_2 chromophores is that the molecule involves a stepped structure **(211)**[481] with an δ angle of *ca.* 15° and a step distance of *ca.* 1.0 Å. With oxygen donor ligands, as in **(205)** and **(207)**, the coplanar CuO_4 chromophore may be stabilized by out-of-plane π bonding,[470] but as the geometry also occurs for σ-bonding ligands, such as NH_3 as in **(176)** and **(208)**, π bonding is clearly not a strict requirement for this geometry. For a number of ligands, bulky substituents may effectively block the fifth and sixth coordinate positions and prevent coordination numbers above four, as in the case of **(208)**. In the series of substituted [Cu(salicylaldehyde)] **(212)**[481,482] complexes the planar CuO_2N_2 chromophore is only retained for small groups and straight chain substituents, H, Me and n-propyl; for bulky substituents, such as isopropyl, the CuO_2N_2 chromophore has a compressed tetrahedral stereochemistry.



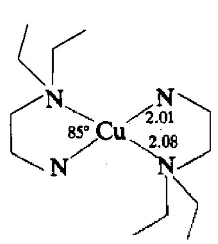
$Ca[CuSi_4O_{10}]$ **(205)**[474]



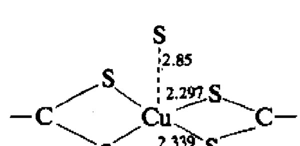
$(modphma)_2[CuCl_4]$ **(206)**[476]



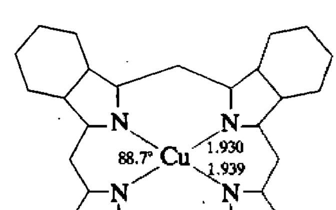
$[Cu(3\text{-}Meacac)_2]$ **(207)**[477]



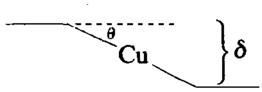
$[Cu(N,N\text{-}Et_2en)_2](NO_3)_2$ **(208)**[478]



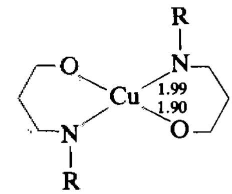
$[Cu(diethylthiocarbamate)_2]$ **(209)**[479]



[Cu(phthalocyanine)] **(210)**[480]



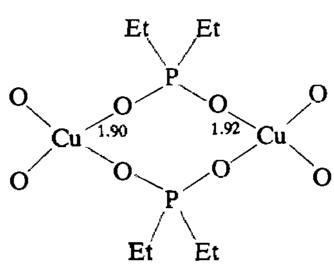
Stepped structure (211)[481]



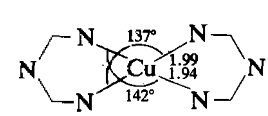
$[Cu(N\text{-Mesalim})_2)]$ (212)[481,482]

(*iv*) *Compressed tetrahedral*

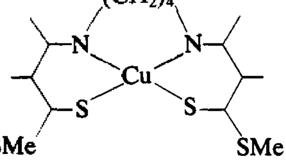
The regular four-coordinate tetrahedral stereochemistry is unknown for the copper(II) ion, but the compressed tetrahedral geometry is as well known as the square and rhombic coplanar stereochemistries (Figure 19.1). The classic example of the compressed tetrahedral geometry is in the $[CuCl_4]^{2-}$ anion of $Cs_2[CuCl_4]$ (**175**),[483] but is less common with monodentate oxygen donor ligands, however it can be found in the anhydrous $\{Cu[(n\text{-hexyl})_2PO_2]_2\}$ (**213**),[484] involving linear chains of bridging $\{OP(Et_2)O\}^-$ anions. The compressed tetrahedral stereochemistry is most common with chelate ligands,[485] especially with nitrogen donors such as in $[Cu(bipyam)_2](ClO_4)_2$ (**214**),[485] where a dihedral angle of 58.8° is involved. A compressed tetrahedral CuS_4 chromophore is unknown for copper(II); a CuN_2S_2 chromophore occurs in $[Cu(L^{12})]$ (**215**),[486] with $n = 2$, 3 or 4, and the dihedral angles = 20, 53 or 57° respectively. Other mixed ligand chromophores occur: the CuO_2Cl_2 in $[Cu(Ph_3PO)_2Cl_2]$ (**216**)[487] and $CuNCl_3$ in $[Cu\{(NPMe_2)_4H\}CuCl_3]$.[488] Within series of four-coordinate complexes there is again no fixed compressed tetrahedral stereochemistry for the copper(II) ion, but a range of distortion from square coplanar to compressed tetrahedral through a range of dihedral angles from 0–70°. In the $[CuCl_4]$ anions, the Cl—Cu—Cl angles range from 129–159° (see Table 2, ref. 489). For the CuN_4 and CuO_4 chromophores less structural data are available and the range of dihedral angles is more limited (Table 22). These purely angular variations again suggest a structural pathway connecting these two stereochemistries (Figure 21a), and linkage by a suitable mode of vibration of the CuL_4 chromophore.



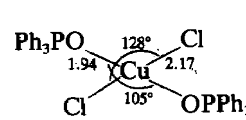
$[Cu\{(n\text{-hexyl})_2PO_2\}_2]$ (213)[484]



$[Cu(bipyam)_2](ClO_4)_2$ (214)[485]



$[Cu(L^{12})]$ (215)[486]



$[Cu(Ph_3PO)_2Cl_2]$ (216)[487]

(*v*) *Five-coordinate*

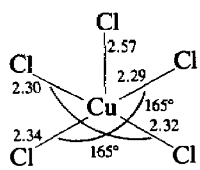
Five-coordination is as abundant in copper(II) complexes as the six-coordinate elongated rhombic octahedral stereochemistry (Figure 19.1). The regular square-based pyramidal geometry with five equivalent ligands is only of limited occurrence, but does arise in

Table 22 Compressed Tetrahedral CuN_4 and CuO_4 Chromophores (Bidentate Ligands)

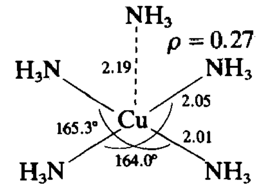
Complex	*Chromophore*	*Cu–X* (Å)	*Dihedral angle* (°)	*Ref.*
[Cu(dipyromethane)$_2$]	CuN_4	1.99	66	490
[Cu(bipyam)$_2$](ClO_4)$_2$ (**214**)	CuN_4	1.94, 1.99	55.6	485
[Cu($C_{17}H_{17}N_4$)$_2$][a]	CuN_4	1.95–1.98	67	491
[Cu(3,3′-Me_2bipyam)$_2$]	CuN_4	1.94–1.96	57.4	492
[Cu(*N*-*t*-butylpyrrole-2-carbaldimine)$_2$]	CuN_4	1.94–2.05	61.3	493
		1.92–2.04	60.1	493
[Cu(bipy)$_2$](PF_6)$_2$	CuN_4	1.99	44.6	494
[Cu(phen)$_2$](PF_6)$_2$	CuN_4	1.98, 2.00	50.1	497
[Cu{(*n*-butyl)$_2PO_2$}]$_2$	CuO_4	1.92–1.93	—	495
[Cu(Et_2PO_2)$_2$(PO_2)$_2$]	CuO_4	1.92	—	496
[Cu{(*n*-hexyl)$_2PO_2$}$_2$] (**213**)	CuO_4	1.90–1.93	—	484

[a] $C_{17}H_{17}N_4$ = 4-phenylamino-2-phenyliminopent-3-enato-*N*,*N*′. [b] 3,3′-Me_2bipyam = 3,3′-dimethyl-2,2′-dipyridylamine.

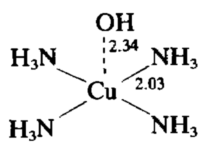
{*N*-(2-amet)pipzH_3}[$CuCl_5$]·2H_2O (**217**),[498] where *N*-(2amet)pipzH_3 = *N*-(2-ammoniomethyl)-piperaziniumH_3, and K[Cu(NH_3)$_5$](PF_6)$_3$ (**218**),[499] with nonequivalent ligands in [Cu(NH_3)$_4$-(OH_2)](SO_4) (**219**)[500] and with macrocyclic ligands, as in [Cu(cyclops)(CN)] (**220**).[501] In all of these square-based pyramidal structures the four in-plane distances are of normal length, *ca.* 2.0 Å for O, N ligands and *ca.* 2.3 Å for Cl, but the fifth ligand distance is 0.2–0.5 Å longer. The copper(II) ion is also lifted out of the plane of the four in-plane ligand atoms by a distance ρ (ρ = 0.1–0.5 Å) with an inverse correlation with the fifth ligand distance, *i.e.* the shorter the Cu—L_5 distance the larger is ρ (Figure 22a). The net result is that both the *trans* in-plane ligands are never linear (180°) but in the range 160–170° (**217**–**220**). The regular trigonal bipyramidal geometry with five equivalent ligands is also of limited occurrence, but does arise in [Cu(NH_3)$_6$][$CuCl_5$] (**221**)[502] and in [CuGaInO_4] (**222**)[503] and also, with nonequivalent ligands, in [Cu(NH_3)$_2$Ag(NCS)$_3$] (**223**)[504] and [Cu(tren)(NH_3)](ClO_4) (**224**).[499] All four of these complexes have at least a strict C_3 symmetry imposed by the crystallographic site symmetry and by the conformation of the ligands present as in (**223**) and (**224**). In all four complexes the two axial Cu—L distances are *ca.* 0.1 Å shorter than the three equatorial Cu—L distances. A nearly regular trigonal bipyramidal geometry also occurs in [Cu(bipy)$_2$Cl](PF_6) (**225**)[505] with clearly nonequivalent ligands and the Cu—L axial/equatorial difference still exists when due allowance is made for the presence of nonequivalent ligands. By far the largest group[506] of five-coordinate geometries of the copper(II) ion involves distortion away from the regular square-based pyramidal and trigonal bipyramidal geometries above. In general the distortion is restricted to a trigonal distortion of the square pyramidal stereochemistry and a square pyramidal distortion of the trigonal bipyramidal stereochemistry (Figure 21b), with the sense of the distortion related by the mechanistic pathway of the Berry twist[507] for these five-coordinate geometries. The bond-length changes are described by the tetragonality T^5, defined[470] as the ratio of the four in-plane Cu—L distances and the single long Cu—L distance. The in-plane angular distortions may also be described by the ratio τ, defined as in (**226**)[508] and representing a percentage trigonal distortion of a square pyramidal stereochemistry. Table 23 lists the structural data for a series of five-coordinate copper(II) complexes containing the CuN_5 chromophore and the resulting T^5 and τ values are plotted in Figure 22(b). In general the T^5 values are in the range 0.90–0.96, significantly higher than the range of T^6 values (Figure 20a) and show a significant increase with increasing τ value. Notwithstanding the significant scatter of the data of Figure 22(b), arising from the presence of nonequivalent nitrogen donor ligands and chelate ligand effects, the data tend to an extrapolated T^5 value of *ca.* 0.96 for a τ value of 100% consistent with an $R_{ax} - R_{eq}$ value of *ca.* 0.1 Å, as found for the regular trigonal bipyramidal copper(II) stereochemistry with $R_{ax} < R_{eq}$. Within the data of Table 23, the three complexes [Cu(dien)(bipyam)]X_2 (**227**),[514] with X = $(ClO_4)^-$, H_2O, Cl^-, 5H_2O and $(NO_3)^-$, represent a series of three cation distortion isomers[514] in which the *same* cation is present in three different lattice environments (a solid state solvent effect) and gives rise to a range of angular distortions of 11 and 24° in the θ and ϕ angles, respectively. These structures span the range of the trigonally distorted square pyramidal copper(II) stereochemistries (see Section 53.4.5) and again suggest individual points along the structural pathway[464] connecting the two regular five-coordinate geometries of the copper(II) ion.



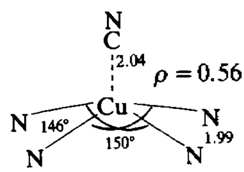
$\{N\text{-(2-amet)pipzH}_3\}[CuCl_5]\cdot 2H_2O$ **(217)**[498]



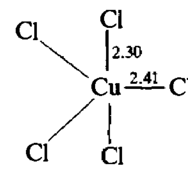
$K[Cu(NH_3)_5](PF_6)_3$ **(218)**[499]



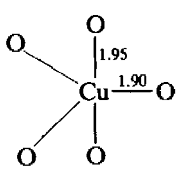
$[Cu(NH_3)_4(OH_2)](SO_4)$ **(219)**[500]



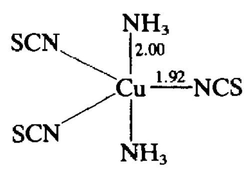
[Cu(cyclops)(CN)] **(220)**[501]



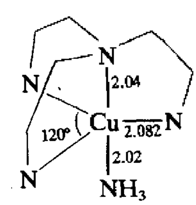
$[Co(NH_3)_6][CuCl_5]$ **(221)**[502]



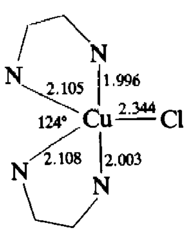
$[CuGaInO_4]$ **(222)**[503]



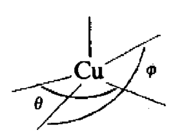
$[Cu(NH_3)_2Ag(NCS)_3]$ **(223)**[504]



$[Cu(tren)(NH_3)](ClO_4)_2$ **(224)**[499]

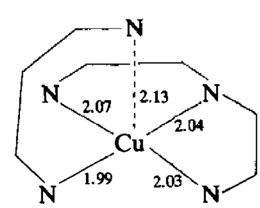


$[Cu(bipy)_2Cl](PF_6)$ **(225)**[505]



$$\tau = \frac{\theta - \phi}{60} \times 100$$

distorted five-coordinate **(226)**[508]



$[Cu(dien)(bipyam)]X_2$ **(227)**[514]

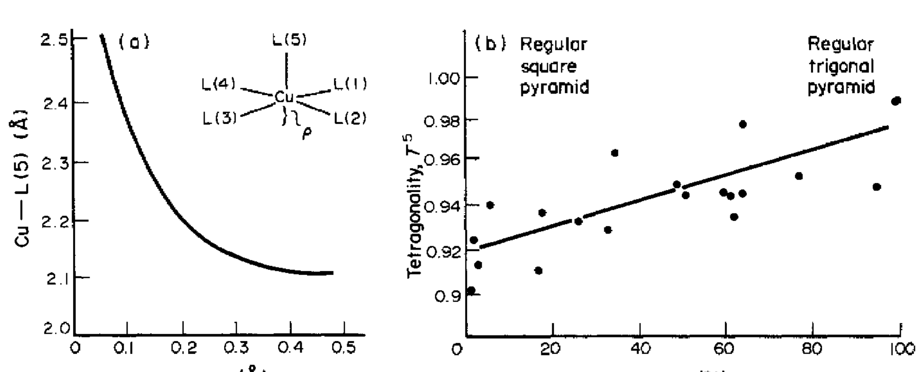


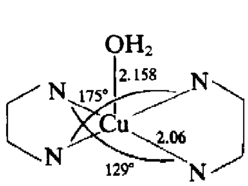
Figure 22 (a) Correlation of the Cu—L(5) distance with the distance ρ that the copper(II) is displaced from the plane of the four in-plane ligands L(1)–L(4) for the regular square-based pyramidal CuL_5 chromophore; and (b) tetragonality T^5 *vs.* angular difference τ [$\tau = \{(\theta - \phi)/60\} \times 100$]

Table 23 CuN_5 Chromophores—Some Structural Data Correlating the Square Pyramidal and Trigonal Bipyramidal Stereochemistries

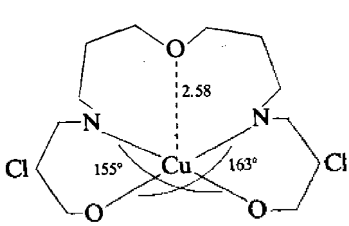
Complex	Mean $Cu{-}L_4$ (Å)	Mean $Cu{-}L_5$ (Å)	T^5	ρ (Å)[a]	θ (°)	ϕ (°)	τ (%)[b]	Ref.
$[Cu(cyclops)py](ClO_4)$	1.972	2.171	0.908	0.40	156.4	156.1	0.5	509
$[Cu(dien)]_2[Fe(CN)_6]\cdot 6H_2O$	2.015	2.210	0.912	—	164.7	163.8	1.5	511
$[Cu(dibenzocyclam)(N_3)](ClO_4)$	2.082	2.160	0.964	0.21	168.8	167.7	1.8	510
$K[Cu(NH_3)_5](PF_6)_3$ (**218**)	2.029	2.193	0.925	0.27	165.3	164.0	2.2	499
[Cu(DMG)(im)]	1.955	2.141	0.913	0.35	160	158	3.0	512
$[Cu(en)_2NH_3](BF_4)_2$	2.01	2.21	0.910	0.22	169	165	7.0	513
$[Cu(dien)(bipyam)](Cl_2)\cdot 2H_2O$ (**227**)	2.005	2.126	0.943	0.32	162.7	159.1	6	514
$[Cu(Me_5dien)(NCBH_3)_2]$	2.038	2.153	0.947	0.36	175.6	165.0	18	515
$[Cu(dien)(bipyam)](ClO_4)_2\cdot H_2O$ (**227**)	2.024	2.170	0.933	0.34	167.9	151.9	26	514
[Cu(3,6-diazaoctane-1,8-diamine)	2.045	2.120	0.965	0.43	165	144	35	516
$(NCS)](ClO_4)$	2.035	2.190	0.929	0.39	167	147	33	—
[Cu(1,7-bis(2-pyridyl)-2,6-diazaheptane)	2.011	2.119	0.949	—	174.5	145.1	49	517
(NCS)](NCS)	2.020	2.162	0.934	—	176.7	139.3	62	—
[Cu(tren)(NCS)](NCS)	2.025	2.144	0.945	—	180	129.5	51	518
$[Cu(dien)(bipyam)](NO_3)_2$ (**227**)	2.033	2.150	0.946	0.44	172.0	135.5	60	514
$[Cu(bipy)_2(NCS)](BF_4)_2$	2.002	2.120	0.944	—	174.7	137.9	61	519
$[Cu(bipy)_2(NCS)](NCS)$	2.008	2.126	0.945	—	173.5	134.8	64	520
	1.998	2.108	0.948	—	175.3	118.5	95	—
$[Cu(bipy)_2(NH_3)](BF_4)_2$	2.014	2.112	0.954	—	175.7	129.5	77*	521
$[Cu(tren)(NH_3)](ClO_4)_2$ (**224**)	2.057	2.082	0.988	—	180	120	100	499
$[Cu(NH_3)_2Ag(NCS)_3]$ (**223**)	1.96	1.92	1.02	—	180	120	100	504

[a] Figure 22(a); [b] (**226**)[508]

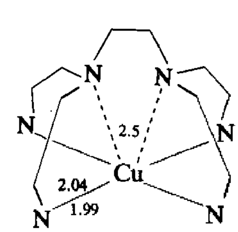
While the trigonally distorted square pyramidal stereochemistry dominates the five-coordinate copper(II) geometry,[515–521] there are a few clear five-coordinate CuL_5 geometries that involve a tetrahedral distortion of an otherwise trigonal bipyramidal stereochemistry, as in $[Cu(bipy)_2(OH_2)](S_2O_6)$ (**228**)[522] or in a square pyramidal stereochemistry, as in [Cu(cbpo)] (**229**),[523] where cbpo = *N,N'*-bis[(5-chloro-2-hydroxyphenyl)phenylmethylene]-4-oxaheptane-1,7-diamine. The sense of the distortion is towards the elongated rhombic octahedral geometry of the CuN_4O_2 chromophore of $[Cu(bipy)_2(F_2BF_2)](BF_4)$ (**201**),[453] with the dihedral angle between the bipy rings being 46.4°, as the bipy rings cannot lie coplanar for steric reasons.[453,454] This tetrahedral twist is also apparent in the bicapped square pyramidal geometry (Table 24a) of [Cu(ebtd)] (**230**),[524] where ebtd = *N,N,N',N'*-tetrakis(2-benzimidazoylmethyl)-1,2-ethanediamine, but the in-plane distortion reverts to trigonal in the less symmetric bicapped nitrate coordination of $[Cu(metaab)(O_2NO)](NO_3)\cdot H_2O$,[525] where metaab = tetrabenzo[*b,f,j,r*]-[1,5,9,13]tetraazacyclohexadecane, with θ and ϕ 166 and 175°, and the two Cu—O distances asymmetric at 2.66 and 2.50 Å. However the most convincing short-bonded bicapped nitrate group is in $[Cu(phen)_2(O_2NO)](NO_3)$ (**231**)[526] with near equivalent Cu—O distances of 2.43 and 2.46 Å, respectively. On the borderline between a five- and a six-coordinate geometry lies the structure of $[Cu(babz)(O_2NO)][HOMe](NO_3)$ (**232**),[527] where babz = *N,N*-bis(2-benzimidazolylmethyl)benzylamine. In general the square-based pyramidal geometry involves no ligand atoms in the sixth coordinate position within 3.0 Å of the copper(II) ion, but where trigonal planar oxyanions are involved in short Cu—O(1) distances (see Section 53.4.2.1ii), the conformation of the oxyanion results in the involvement of the O(2) atom in a short Cu—O(2) distance of 2.64 Å, clearly off-the-*z*-axis, but within bonding distance of the Cu^{II} ion and generating a $(4+1+1^*)$-type structure, intermediate between five- and six-coordination. A trigonal distortion is usually present in these $(4+1+1^*)$ structures, with $\theta = 170$–$180°$ and $\phi = 140$–$160°$ (Table 24b).



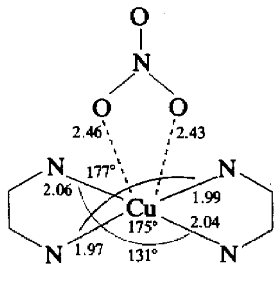
$[Cu(bipy)_2(OH_2)](S_2O_6)$ (**228**)[522]



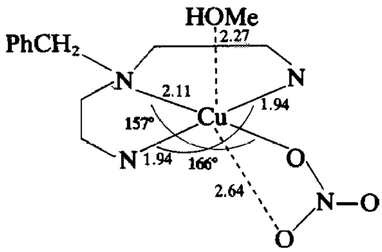
[Cu(cbpo)] (**229**)[523]



$[Cu(ebtd)](BF_4)(BF_3OEt)\cdot H_2O$ (**230**)[524]



$[Cu(phen)_2(O_2NO)](NO_3)$ (**231**)[526]



$[Cu(babz)(O_2NO)(HOMe)](NO_3)$ (**232**)[527]

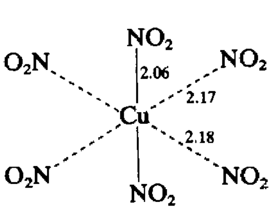
Table 24 Copper(II) Stereochemistries (a) Bicapped CuN_4O_2 (4 + 2*) and (b) $CuN_3OO'O''$ (4 + 1 + 1*)

	Chromophore	*Cu–N* (Å)	*Cu–O,N* (Å)	θ (°)	φ (°)	*Ref.*
(*a*) *Bicapped* (4 + 2*)						
$[Cu(ebtd)](BF_4)(BF_3OMe)\cdot H_2O$ (**230**)	CuN_4N_2	1.99–2.03	2.50, 2.50	142.6	165.3	524
$[Cu(metaab)(O_2NO)](NO_3)\cdot H_2O$	CuN_4O_2	1.95–2.01	2.50, 2.66	165.6	175.3	525
$[Cu(phen)_2(O_2NO)](NO_3)$ (**231**)	CuN_4O_2	1.97–2.06	2.43, 2.46	130.9	177.1	526
(*B*) *Square pyramidal* (4 + 1 + 1*)						
$[Cu(babz)(O_2NO)(HOMe)](NO_3)$ (**232**)	$CuN_3OO'O^*$	1.94–2.11	2.27, 2.64	157.2	163.4	527
$[Cu(Me_4bim)_2(O_2NO)](NO_3)$[a]	$CuN_3ON'O^*$	1.99–2.01	2.28, 2.57	163.8	178.3	528
$[Cu(amtd)(O_2NO)](NO_3)$	$CuN_3ON'O^*$	2.00	2.2, 2.8	140	180	529
$[Cu(terpy)(ONO)(OH_2)](NO_2)$	$CuN_2OO'O^*$	2.01, 1.97	1.97, 2.63	156.1	179.2	530

[a] Me_4bim = 4,4′,5,5′-tetramethyl-2,2′-biimidazolyl.

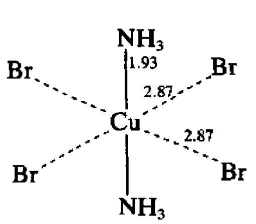
(*vi*) *Compressed tetragonal and rhombic octahedral*

The compressed tetragonal octahedral stereochemistry (Figure 19.1) with six equivalent ligands is restricted (Table 25) to the $[Cu(NO_2)_6]^{4-}$ anion in the rubidium (**223**)[531] and caesium complexes (**251**).[532] The original suggestion that this stereochemistry occurs in $K_2[CuF_4]$[533] and $Ba_2[CuF_6]$[437,534] is now considered incorrect, and an alternative choice of space group yields an elongated rhombic octahedral CuF_6 chromophore in each structure.[535,437] The compressed rhombic octahedral stereochemistry is more common (Table 23) than the tetragonal form, but both together only constitute a very restricted class of copper(II) structures. It was first recognized in β-$[Cu(NH_3)_2Br_2]$ (**234**),[536] but more recently in the CuN_6 chromophores of $[Cu(dien)_2](NO_3)_2$ (**235**),[537] $[Cu(terpy)_2](NO_3)_2$ (**436**),[538] $[Cu(terpy)_2](PF_6)_2$[539] and in the near octahedral structure of $[Cu(tach)_2](NO_3)_2$ (**236**).[540] It occurs in the CuO_6 chromophore of $[Cu(methoxyacetate)_2(OH_2)_2]$ (**237**)[541] and in the CuO_4N_2 chromophore of the unusual structure of $[Cu(ttbz)_2(O_2NO)_2]$ (**238**),[542] both of which involve nonequivalent ligands and (**238**) involves a novel bonding role for the nitrato group. In (**233**)[531] and (**177**)[426,427] the nitrito coordination of the $(NO_2)^-$ anions to the Pb^{2+} ion (see **38** Chapter 15.5) may account for the occurrence of this uncommon compressed six-coordinate structure, while in (**235**)[537] and (**236**)[540] it could be associated with the restricted bite of the chelate ligands present, but no such explanation is available to account for the formation of the compressed geometry in (**237**)[541] and (**238**).[542]

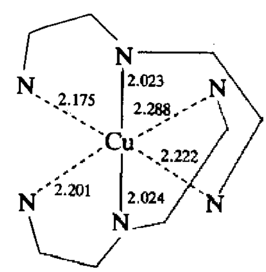


$T = 1.056$

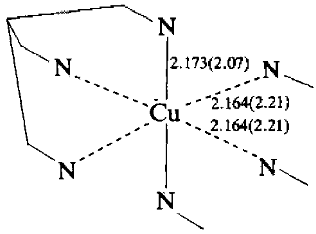
$Rb_2Pb[Cu(NO_2)_6]$ (**233**)[531]



β-$[Cu(NH_3)_2Br_2]$ (**234**)[536]

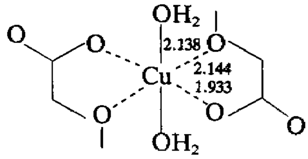


$[Cu(dien)_2](NO_3)_2$ (**235**)[537]

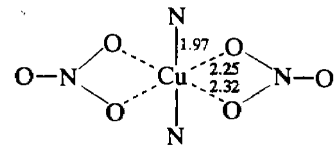


295 K (120 K) $T = 0.99(1.073)$

[Cu(tach)$_2$](NO$_3$)$_2$ (**236**)[540]



[Cu(methoxyacetate)$_2$(OH$_2$)$_2$] (**237**)[541]



[Cu(ttbz)$_2$(O$_2$NO)$_2$] (**238**)[542]

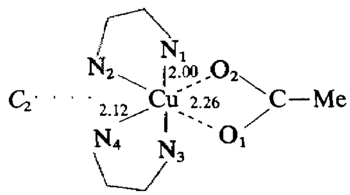
Table 25 Compressed Tetragonal and Rhombic Octahedral Copper(II) Complexes (298 K)

Complex	*Chromophore*	*Cu—L$_S$* (Å)	*Cu—L$_l$* (Å)	*Ref.*
Rb$_2$Pb[Cu(NO$_2$)$_6$] (**233**)	CuN$_2$N$'_4$	2.06	2.17, 2.18	531
Cs$_2$Pb[Cu(NO$_2$)$_6$] (**250**)–(**252**)	CuN$_2$N$_4$	2.07	2.27, 2.27	532
β-[Cu(NH$_3$)$_2$Br$_2$] (**234**)	CuN$_2$Br$_4$	1.93	2.54	536
[Cu(dien)$_2$](NO$_3$)$_2$ (**235**)	CuN$_2$N$'_4$	2.02	2.20, 2.22, 2.18, 2.29	537
[Cu(terpy)$_2$](NO$_3$)$_2$ (**436**)	CuN$_2$N$'_2$N$''_2$	1.99	2.09, 2.29	538, 1267
[Cu(terpy)$_2$](PF$_5$)$_2$	CuN$_1$N$'_2$N$''_2$	1.98	2.18	539
[Cu(tach)$_2$](NO$_3$)$_2$ (**236**)[a]	CuN$_2$N$'_2$N$''_2$	2.17	2.16, 2.16	540
[Cu$_5$(benzotriazole)$_6$(Bu^{t}NC)] (**170**)	CuN$_2$N$_4$	2.085	2.241, 2.241	395
[Cu(methoxyacetate)$_2$(OH$_2$)$_2$] (**237**)	CuO$_2$O$_2$O$_2$	1.94	2.14, 2.15	541
[Cu(ttbz)$_2$(O$_2$NO)$_2$] (**238**)[b]	CuN$_2$O$_4$	1.97	2.32, 2.25	542

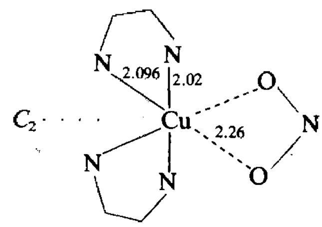
[a] tach = *cis,cis*-1,3,5-triaminocyclohexane. [b] ttbz = 2-(2-thienyl)-1-(2-thienylmethyl)benzimidazole.

(*vii*) *Cis-distorted octahedral*

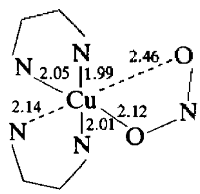
The *cis*-distorted octahedral stereochemistry is only a limited class of copper(II) structures (Figure 19.1 and Table 26) and occurs only slightly more frequently than the compressed octahedral class (Table 25). It is unknown for six equivalent ligands, but does occur with non-equivalent ligands in the CuN$_4$O$_2$ chromophore and is restricted to complexes involving two bidentate chelate nitrogen ligands and one chelate oxyanion ligand, [Cu(chelate)$_2$(OXO)]$^-$, with trigonal planar oxyanions such as (ONO)$^-$, (O$_2$NO)$^-$, (O$_2$CMe)$^-$ and (O$_2$CH)$^-$ which when acting as a bidentate chelate ligand involve a restricted bite to form a *four*-membered chelate ring. The symmetrical CuN$_4$O$_2$ chromophore (C_2 symmetry) occurs in [Cu(phen)$_2$(O$_2$CMe)](BF$_4$)·2H$_2$O (**239**),[543] [Cu(phen)$_2$(O$_2$CH)](ClO$_4$),[544] [Cu(bipyam)$_2$-(ONO)](NO$_2$) (**240**)[545] and in a more distorted structure in [Cu(bipy)$_2$(ONO)](BF$_4$) (**241**).[547] In all three symmetrical complexes the restricted bite of the out-of-plane chelate ligands impose the overall compressed six-coordinate structure and the bite of the oxyanion must influence the *cis* configuration, but does not explain the *cis* distortion, especially in view of the more usual elongated rhombic octahedral structure of [Cu(hfacac)$_2$(bipy)] (**197**),[449] where hfacac = hexafluoroacetylacetone, and [Cu(phen)$_2$(NCS)$_2$] (**198**),[450] neither of which involves an in-plane *cis* distortion. In the complexes of Table 26, there is considerable variation in the distortions present. With the distortions defined as in Table 26, the asymmetry in the Cu—O(1) and Cu—O(2) distances, $\Delta O_{2,1}$, varies from zero in (**239**) and (**240**) to 0.35 Å in (**241**). The asymmetry in the Cu—N distance is considerably smaller, $\Delta N_{4,2}$ is *ca.* 0.2 Å and $\Delta N_{3,1}$ is hardly significant at *ca.* 0.02 Å. Once again the series of *cis*-distorted octahedral CuN$_4$O$_2$ chromophores of Table 26 suggests a series of structures along the structural pathway[464] from a regular to an asymmetric *cis*-distorted octahedral stereochemistry (Figure 21c). Alternatively, the latter may be described as basically five-coordinate (4 + 1) or six-coordinate stereochemistry with a long off-the-z-axis O(2) ligand, to give a (4 + 1 + 1*) structure, as in (**232**).[527]



$[Cu(phen)_2(O_2CMe)](BF_4)\cdot 2H_2O$ **(239)**[543]



$[Cu(bipyam)_2(ONO)](NO_2)$ **(240)**[545]



$[Cu(bipy)_2(ONO)](BF_4)$ **(241)**[547]

Table 26 *Cis*-distorted Octahedral Copper(II) Complexes, CuN_4O_2 Chromophores (298 K)

Complex	*Symmetry*	$\Delta O_{2,1}$[a] (Å)	$\Delta N_{4,2}$[a] (Å)	$\Delta N_{1,3}$[a] (Å)	*Ref.*
$[Cu(phen)_2(O_2CMe)](BF_4)\cdot 2H_2O$ **(239)**	C_2 sym.	0.0	0.0	0.0	543
$[Cu(phen)_2(O_2CH)](ClO_4)$	C_2 sym.	0.0	0.0	0.0	544
$[Cu(bipyam)_2(ONO)](NO_2)$ **(240)**	C_2 sym.	0.0	0.0	0.0	545
$[Cu(bipy)_2(ONO)](NO_3)$	C_1	0.091	0.035	0.026	546
$[Cu(bipy)_2(ONO)](BF_4)$ **(241)**	C_1	0.346	0.088	0.015	547
$[Cu(bipy)_2(O_2CH)](BF_4)$	C_1	0.845	0.097	0.023	548
$[Cu(bipy)_2(O_2CMe)](ClO_4)\cdot H_2O$	C_1	0.617	0.112	0.023	549
$[Cu(bipy)_2(O_2NO)](NO_3)$	C_1	0.42	0.085	0.011	550
$[Cu_2(bipy)_2(pydca)_2]\cdot 4H_2O$[c,d]	C_1	0.85	0.053	0.001	551
$[Cu(dmphen)_2(O_2NO)](CCl_3CO_2)\cdot CCl_3CO_2H$[b,e]	C_1	0.33	0.07	0.03	552

[a] See (239) for the atom labelling. [b] The sense of distortion of CuN_4O_2 is different in this complex (see ref. 553). [c] This complex is dimeric. [d] pydca = pyridine-2,6-dicarboxylate. [e] dmphen = 2,9-dimethyl-1,10-phenanthroline.

(*viii*) *Linear*

This stereochemistry for the copper(II) ion (Figure 19.1) is unknown in the solid state, but does occur for the copper(II) halides in the vapour state, *e.g.* $CuCl_2$ **(242)**, as determined by electron diffraction in the gaseous state.[417]

Cl—Cu—Cl

Br—Cu—Br

$[CuCl_2]$, $[CuBr_2]$ **(242)**[417]

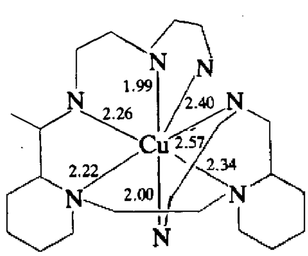
(*ix*) *Seven-, eight- and nine-coordinate*

These coordination numbers are unknown for copper(II) structures involving *n* Cu—L distances <2.1 Å, where *n* = 7, 8 or 9 (Figure 19.1). In general a mixture of three, four or five short Cu—L distances are involved and the remainder are long Cu—L distances up to 2.9Å. In all three coordination numbers the majority of the long Cu—L distances involve off-axis bonding through trigonal planar oxyanion ligands, such as $(ONO)^-$, $(ONO_2)^-$ and $(O_2CMe)^-$, *etc.* There are two exceptions: one is the seven-coordinate CuN_7 chromophore of $[Cu(L^{12})](ClO_4)_2$ **(243)**[554] with five intermediate Cu—N distances and two short linear Cu—N distances. The second is the $CuN_2N_3O_2$ chromophore of [Cu(dapse)]$(NO_3)_2 \cdot 3H_2O$[555] with two short Cu—N distances and five intermediate Cu—N and Cu—O distances (Table 27a). In general, seven coordination occurs more frequently than eight coordination, and nine coordination is very uncommon. Seven coordination is illustrated by **(243)**, [Cu(py)$_3$(O$_2$NO)$_2$] **(244)**[556] and [Cu(OH$_2$)$_2$(O$_2$NO)$_2$]·0.5H$_2$O **(245)**.[558] In all these seven-coordinate complexes (Table 27a), an approximate pentagonal bipyramid is involved (D_{5h} symmetry) but in all cases the symmetry is lowered to approximately C_2 symmetry. Eight coordination is dominated by the distorted dodecahedral geometry (Table 27b), as in Ca[Cu(O$_2$CMe)$_4$]·6H$_2$O **(246)** (S_4 symmetry)[563,564] with four short and four long Cu—O distances, $\Delta O = 0.89$ Å, which is rather on the limit for off-the-z-axis bonding. The only alternative geometry observed for eight coordination is that of (AsPh$_4$)$_2$[Cu(O$_2$NO)$_4$] **(247)**.[566] Nine coordination is restricted to that in Ca[Cu(2-cpa)$_4$(OH$_2$)$_4$] **(248)**,[567] with the in-plane CuO_4 chromomophore involving a slight tetrahedral distortion which reduces the overall C_{4v} symmetry to that of C_2.

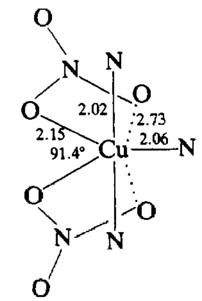
Table 27 Seven-, Eight- and Nine-coordinate Stereochemistries of the Copper(II) Ion

Complex	*Chromophore*	*Cu—L$_{ax}$* (Å)	*Cu—L$_{eq}$* (Å)	*Geometry*[d]	*Ref.*
) *Seven coordinate*					
Ju(L^{12})](ClO$_4$)$_2$ **(243)**	CuN_2N_5	1.99, 2.00	2.22, 2.26, 2.34, 2.40, 2.57	C_1 PB	554
Ju(dapsc)](NO$_3$)$_2$·3H$_2$O[a]	$CuO_2O_3O_2$	1.92, 1.92	2.26, 2.26, 2.27, 2.35, 2.35	C_2 PB	555
Ju(py)$_3$(O$_2$NO)$_2$] **(244)**	$CuN_2NO_2O'_2$	2.02, 2.02	2.06, 2.15, 2.15, 2.73, 2.73	C_2PB	556
Ju(*cis, trans*-pmk)(O$_2$NO)$_2$][b]	$CuN_2NO_2O'_2$	1.96, 1.96	2.03, 2.15, 2.15, 2.76, 2.76	C_2 PB	557
Ju(OH$_2$)$_2$(O$_2$NO)$_2$]·0.5H$_2$O **(245)**	$CuO_2O'_2O''_2O'''$	2.39, 2.65, 2.68	1.96, 1.96, 1.99, 1.99	C_1 PSP	558
Ju(OH$_2$)$_2$(O$_2$CPh)$_2$(OH$_2$)]	$CuO_2O'_2O''_2O'''$	2.27, 2.96, 2.97	1.96, 1.96, 2.03, 2.02	C_1 PSP	559
Ju(py)$_2$(cmpa)$_2$(OH$_2$)]	$CuN_2O_2O'_2O''$	2.27	2.06, 2.06, 1.95, 1.95	C_2 PSP	560
Ju(methylamine)$_2$(O$_2$CPh)$_2$(OH$_2$)]	$CuN_2O_2O'_2O'$	2.22	2.02, 2.02, 1.97, 1.97	C_2 PSP	561
Ju(β-pic)$_2$(O$_2$CPh)$_2$(OH$_2$)]	$CuN_2O_2O'_2O'$	2.30	1.99, 2.02, 1.92, 1.96	C_1 PSP	562
) *Eight coordinate*					
a[Cu(O$_2$CMe)$_4$]·6H$_2$O **(246)**	$CuO_4O'_4$	2.78 × 4	1.97 × 4	S_4 D	563, 564
Ju(6-aminohexanoic acid)$_4$](ClO$_4$)$_2$	$CuO_4O'_4$	2.77 × 4	1.97 × 4	S_4 D	565
AsPh$_4$)$_2$[Cu(O$_2$NO)$_4$] **(247)**	$CuO_4O'_4$	2.67 × 2, 2.79 × 2	1.92 × 2, 1.97 × 2	C_i—	566
) *Nine coordinates*					
a[Cu(2-cpa)$_4$(OH$_2$)]·3H$_2$O[c] **(248)**	$CuO_4O'_4O''$	2.27 × 1	2.2 × 4, 1.97 × 2, 1.99 × 2	C_1 SBd	567

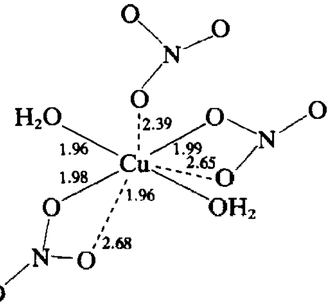
[a] dapsc = 2,6-diacetylpyridine. [b] *cis,trans*-pmk = bis(2-pyridylmethyl)ketazine. [c] 2-cpa = 2-chlorophenoxyacetaet. [d] PB = pentayonal pyramidal; PSP = pentagonal square pyramidal; D = dodecahedral; SBd = square based.



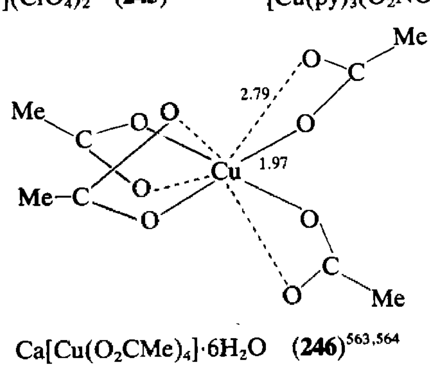
[Cu(L^{12})](ClO$_4$)$_2$ **(243)**[554]



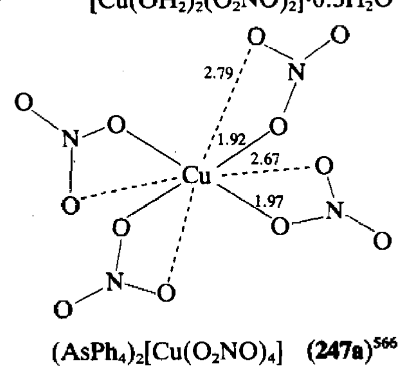
[Cu(py)$_3$(O$_2$NO)$_2$] **(244)**[556]



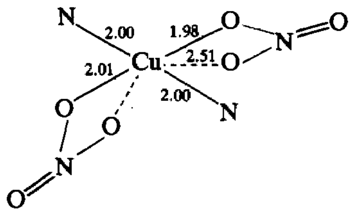
[Cu(OH$_2$)$_2$(O$_2$NO)$_2$]·0.5H$_2$O **(245)**[558]



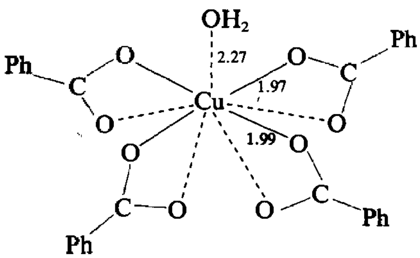
Ca[Cu(O$_2$CMe)$_4$]·6H$_2$O **(246)**[563,564]



(AsPh$_4$)$_2$[Cu(O$_2$NO)$_4$] **(247a)**[566]

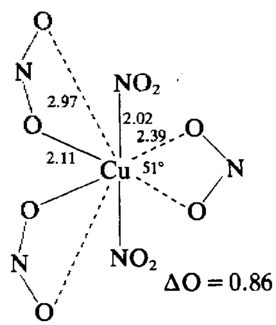


$[Cu(\alpha\text{-pic})_2(O_2NO)_2]$ (**247b**)[569]

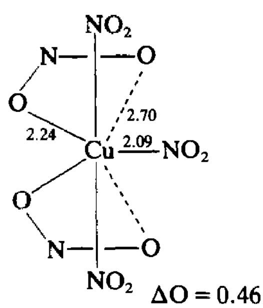


$Ca[Cu(2\text{-cpa})_4(OH_2)]\cdot 4H_2O$ (**248**)[567]

Off-axis coordination to copper(II) is highlighted in the two independent chromophores of $K_3[Cu(NO_2)_5]$ I and II (**249**);[568] neither is five coordinate as the formula might suggest. I involves a basic six-coordinate $CuN_2O_2O'_2$ chromophore with a *cis* distortion that is unique outside the $[Cu(chelate)_2(OXO)]Y$ complexes[543–553] of Section 53.4.2.1(vii), but with two additional asymmetric nitrito oxygen atoms at 2.97 Å ($\Delta O = 0.86$ Å) giving a formally eight-coordinate $CuN_2O_2O'_2O''_2$ chromophore with a distorted hexagonal bipyramidal geometry. II involves a pentagonal bipyramidal $CuN_2NO_2O'_2$ chromophore with three nitro ligands and two asymmetric bidentate nitrito ligands with off-axis coordination $\Delta O = 0.46$ Å.



$K_3[Cu(NO_2)_5]I$ (**249a**)[568]



$K_3[Cu(NO_2)_5]II$ (**249b**)[568]

With the exception of (**243**),[554] these coordination numbers of the copper(II) ion above six, as in (**224**)–(**240**), are generated by coordination of a range of trigonal coplanar OXO or OXO_2 oxyanions, which suggests that these trigonal oxyanions must play a unique bonding role. They are well known as symmetrical bidentate ligands (Figure 23a, i) to other transition metal ions (see Chapter 15.5), but more usually bond to copper(II) as an asymmetric ligand (Figure 23a, ii) with $\Delta O = [Cu—O(2)] - [Cu—O(1)] = 0.4–0.9$ Å. With low ΔO values of 0.4–0.7 Å there is little question that the off-axis oxygen atoms are involved in weak bonding to the copper(II) ion, but for ΔO values greater than 0.8 Å, this becomes increasingly questionable. For monodentate copper(II) oxyanion coordination the orientation of the short-bonded oxyanion (OXO) is most commonly *cis* rather than *trans* (Figure 23a, ii and iii), as in (**203**)[471] and (**204**).[472] The *cis* conformation even predominates in the bridging function of (**347**). In the clearly bidentate (OXO) anion coordination to copper(II) relatively long Cu—O distances of *ca.* 2.5 Å are involved as in the bicapped square pyramidal geometry of (**231**)[525] or of 2.25 Å in the *cis* distorted octahedral stereochemistry of (**239**)[543] and (**240**)[545] (Figure 23b, i and ii), both of which relate to the more common asymmetric bonding $(4+1+1^*)$ of (**241**) (Figure 23b, iii).[547]

With two symmetrically long-bonded bidentate OXO anions, as in (**238**) (Figure 23c, i),[542] symmetric distortion (Figure 23c, ii) may occur to give the most common $(4+2^*)$ type of coordination as in (**203**).[471] However the alternative asymmetric distortion (Figure 23c, iii) is known in $[Cu(\alpha\text{-pic})_2(O_2NO)_2]$ (**247b**),[569] where a distorted $(4+2^*)$ geometry may be considered the parent of the two alternative seven-coordinate geometries $(4+1+2^*)$, as in (**244**)[556] and (**245**),[558] by involvement of an additional donor ligand.

While no regular compressed hexagonal $(2+6^*)$ structures are known (Figure 23d, i), a distorted eight-coordinate hexagonal $(2+2+4^*)$ geometry is observed in (**249**)-I[568] (Figure 23d, ii) with the alternative independent stereochemistry of (**249**)-II[568] exhibiting the

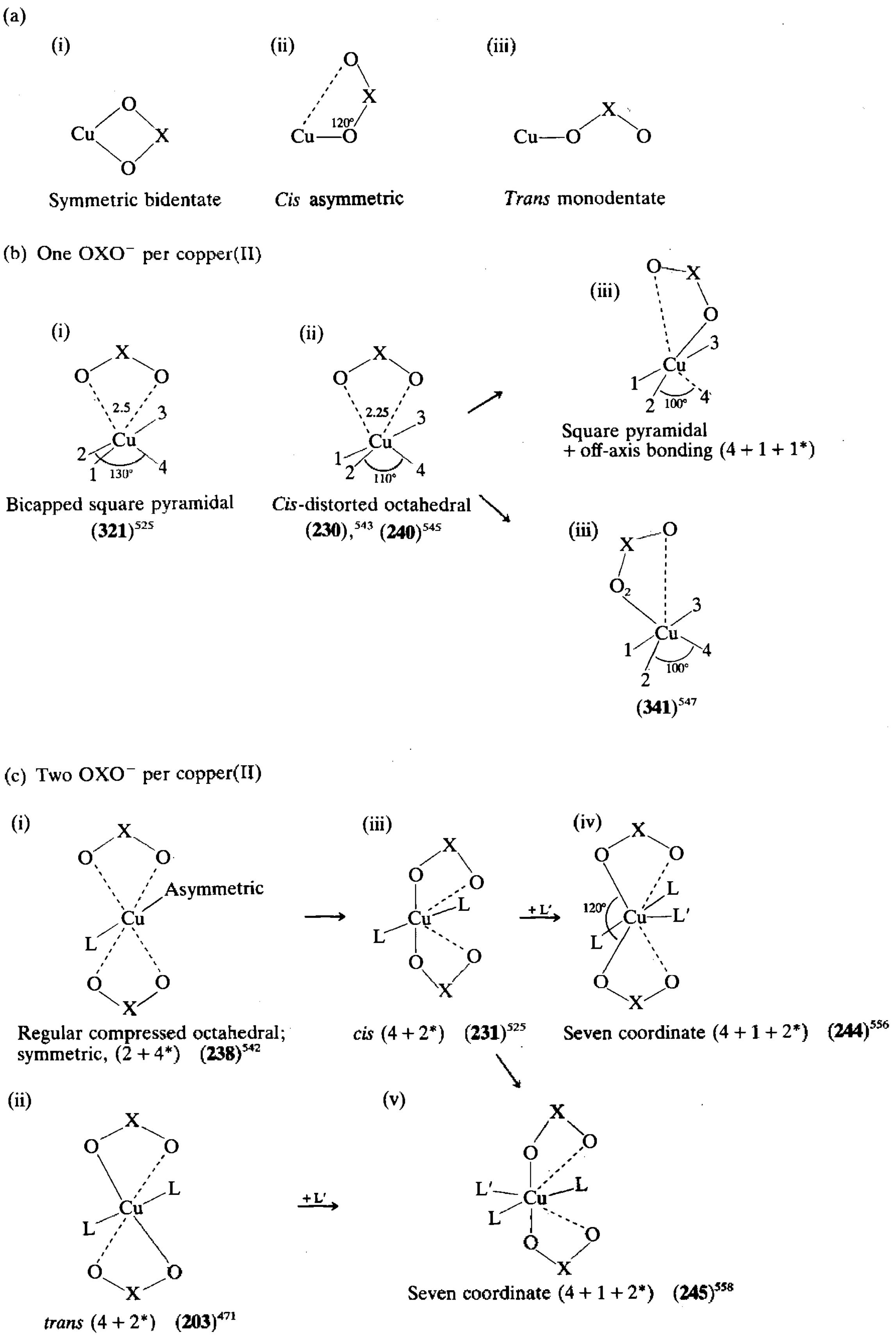
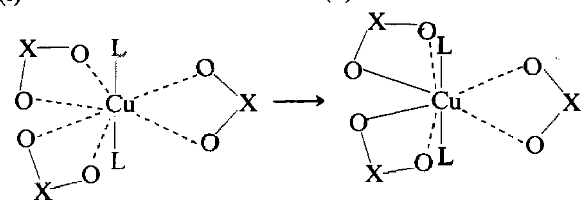


Figure 23 Trigonal oxyanion coordination to the copper(II) cation

(d) Three OXO^- per copper(II)

(i) (ii)

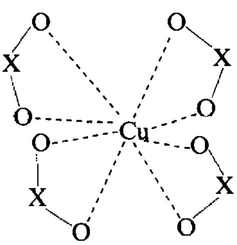


Regular compressed hexagonal (2 + 6*)

Eight-coordinate nonequivalent hexagonal (2 + 2 + 4*) (249)[568]

(e) Four OXO^- per copper(II)

(i)

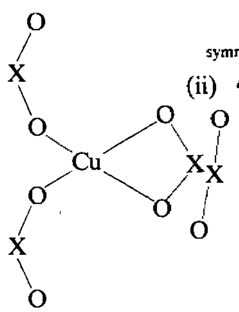


(4 + 4) hypothetical

symmetric

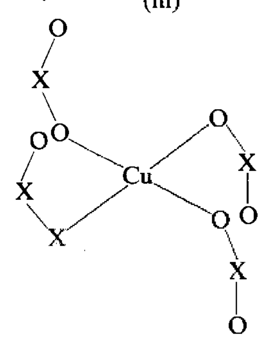
asymmetric

(ii)



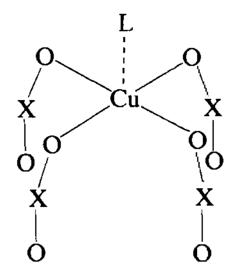
Two up, two down (S_4) eight-coordinate *trans* (4 + 4*) (**246**)[563,564]

(iii)



Two up, two down (C_{2h}) eight-coordinate *cis* (4 + 4*) (**247**)[566]

(iv)



Four down + L up, (C_{4v}) eight-coordinate (4 + 1 + 4*) (**248**)[567]

Figure 23 (*continued*)

seven-coordinate (4 + 1 + 2*) geometry of Figure 23(c) (iv). Equally, the regular eight-coordinate $Cu(OXO)_4$ chromophore is unknown at present, but may then be considered to be the parent (Figure 23e, i) of the three distorted geometries of Figure 23(e) (ii)–(iv). Two eight-coordinate geometries (4 + 4*) are formed as in the symmetric two up/two down structure (S_4 symmetry) of Figure 23(e) (ii), as in (**246**),[563,564] and in the asymmetric two up/two down structure (C_{2h} symmetry) of Figure 23(e) (iii), as in (**247**).[566] But addition of a ninth ligand to Figure 23(e) (i) can also generate the nine-coordinate (4 + 1 + 4*) stereochemistry (C_{4v} symmetry) of Figure 23(c) (iv), as in (**248**).[567]

In this way the symmetric and asymmetric bonding of the OXO anions as ligands to the copper(II) ion may be considered responsible for a significant range of the six- to nine-coordinate geometries of the copper(II) ion.

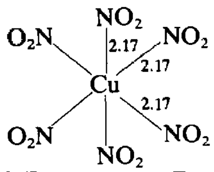
(*x*) *Temperature variable copper(II) structures*

The above description of the mononuclear structures of the copper(II) ion presupposes that the structures are all determined at room temperature. If they were determined at a temperature either below or above room temperature (subject to thermal stability in the latter case), and subject to no change of phase in both cases, this account has presumed that there would be *no* significant change of structure. For the vast majority of copper(II) complexes this is the case, and for copper(II) complexes involving coordination numbers four, five, seven, eight and nine, there is no evidence for any significant variation with temperature of the crystal structure. As this accounts for over 65% of the known crystal structures of copper(II), the majority of copper(II) structures may be considered to involve *static* non-temperature-variable crystal structures.[396] In the remaining 35% of *six*-coordinate geometries, again the majority of complexes involve an elongated tetragonal or rhombic octahedral geometry and for these complexes in the range of tetragonalities $T = 0.75$–0.85, a static non-temperature-variable stereochemistry is involved. This applies to 90% of the complexes in the elongated octahedral class and is illustrated for the structure of anhydrous α-[$Cu(O_2CH)_2$],[570] whose structure has been determined at 296, 80 and 4.2 K (Table 28) by powder profile analysis.[570] In these complexes neither the Cu—L distances nor the tetragonalities vary significantly with decreasing temperature, namely by >1%, but for a small number of six-coordinate copper(II) complexes having tetragonalities >0.85,[396,397] it has been found that the crystal structures are temperature variable and very dependent upon the temperature at which the structure determination is carried out. The classic example of this involves the structure of $Cs_2Pb[Cu(NO_2)_6]$ (**250–252**). At 420 K the CuN_6 chromophore involves a regular octahedral geometry in a cubic lattice,[571] at 293 K the geometry is compressed tetragonal octahedral in an orthorhombic lattice,[532] while at 160 K the structure is elongated rhombic octahedral,[572] although still with a relatively high tetragonality T of 0.91 in a monoclinic lattice. In the case of the trigonal octahedral CuN_6 chromophore of $[Cu(en)_3](SO_4)$ (**178**),[427] the change[573] is to a compressed rhombic octahedral stereochemistry at 120 K. The observation of a temperature variable crystal structure is not restricted to high symmetry lattices or to equivalent ligands. Figure 24(a) shows how the Cu—O distances of the compressed rhombic octahedral CuO_6 chromophore of [Cu(methoxyacetate)$_2$(OH_2)$_2$] (**237**)[541] vary down to 4 K[574,575] and Figure 24(b) shows how the Cu—O distances of the *cis*-distorted octahedral CuN_4O_6 chromophore of [Cu(bipy)$_2$(ONO)](NO_3) (**253**),[576,577] vary from 298[546] to 20 K.[576,577] In (**237**) the Cu—O(1) distance increases, the Cu—O(3) distance decreases and the Cu—O(4) distance is almost temperature invariant. In (**254**) (Figure 23b) the Cu—O(2) length increases by 0.22 Å, and the Cu—O(1) length decreases by 0.18 Å with decreasing temperature; a smaller increase, 0.06 Å, occurs with the Cu—N(4) distance and a small decrease, 0.04 Å, occurs with the Cu—N(2) distance. The Cu—N(1) and Cu—N(3) distances show no significant change with temperature. Even the simple $[Cu(OH_2)_6]^{2+}$ cation in $(NH_4)_2[Cu(OH_2)_6](SO_4)_2$ (**254**)[457,458] with an elongated rhombic octahedral stereochemistry and tetragonality of 0.914 at 298 K shows a significant drop in tetragonality to 0.874 and a more elongated rhombic octahedral stereochemistry at 123 K,[578] and to a tetragonality of 0.85 at 5 K (determined by powder profile analysis).[579] The extent of temperature variation required to produce a significant change of structure varies considerably; with $K_2[PbCu(NO_2)_6]$ (**177**) only a change from 298 to 276 K[580] was required to produce the change from an octahedral to a compressed octahedral CuN_6 chromophore, but in the case of [Cu(metri)$_2$] (**180**)[429] the trigonal octahedral CuN_6 chromophore showed no change from 298 to 120 K, and the compressed octahedral CuN_6 chromophore of [Cu(dien)$_2$](NO_3)$_2$ (**235**)[537] also showed no change over the same temperature range.[581] In the case of [Cu(pyNO)$_6$](BF_4)$_2$ (**255**)[582] the C_3 symmetry of the trigonal octahedral CuO_6 chromophore is retained even at 20 K.[582]

Table 28 The Crystal Structure Data for Two Static Copper(II) Structures at a Range of Temperatures for α-[$Cu(HCO_2)_2$] Neutron Diffraction Using Powder Profile Analysis[569,570]

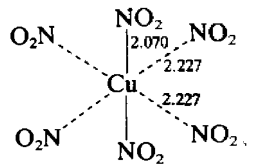
	296 K	*80 K*	*4.2 K*
Cu—O(1)[a]	1.950(5)	1.949(5)	1.947(5)
Cu—O(2)[a]	1.987(5)	1.968(5)	1.968(5)
Cu—O(3′)[a]	2.410(5)	2.389(5)	2.371(5)
T (full data)	0.756	0.758	0.762

[a] In Å.



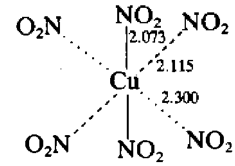
420 K $T = 1.0$

$Cs_2Pb[Cu(NO_2)_6]$ **(250)**[571]



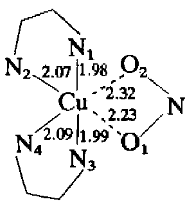
293 K $T = 1.076$

$Cs_2Pb[Cu(NO_2)_6]$ **(251)**[532]

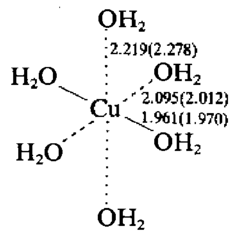


160 K $T = 0.91$

$Cs_2Pb[Cu(NO_2)_6]$ **(252)**[572]

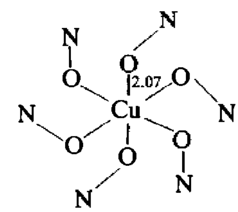


$[Cu(bipy)_2(ONO)](NO_3)$ **(253)**[546]



295 K (123 K) $T = 0.914\ (0.874)$

$(NH_4)_2[Cu(OH_2)_6](SO_4)_2$ **(254)**[578]



$[Cu(pyNO)_6](BF_4)_2$ **(255)**[582]

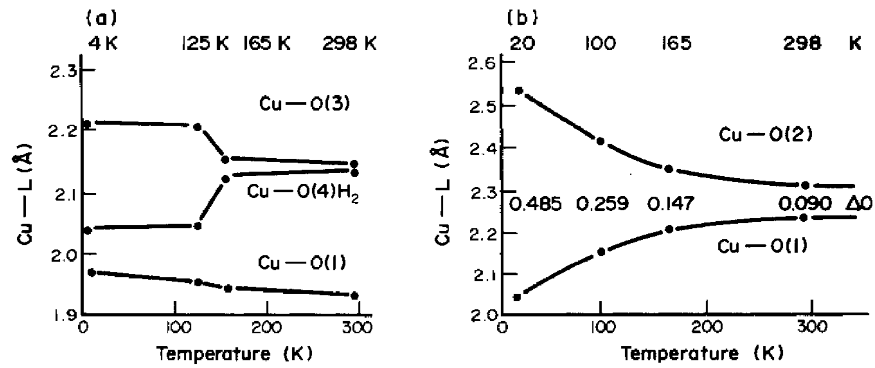


Figure 24 The effect of temperature on the copper–ligand distances of (a) $[Cu(methoxyacetate)_2(OH_2)_2]$ **(237)**; and (b) $[Cu(bipy_2)_2(ONO)](NO_3)$

The observation of temperature variable structures for six-coordinate copper(II) complexes involving tetragonalities greater than 0.85 enables the various stereochemistries of Figure 19 to be subdivided into their temperature variable and non-temperature-variable stereochemistries,[396] as summarized in Table 29. In this sense they may be divided into the static and nonstatic stereochemistries of the copper(II) ion, but it should always be remembered that 95% of the observed structures of the copper(II) ion involve *static* stereochemistries, which are non temperature variable.

Table 29 The Classification of the Various Stereochemistries of Copper(II) into their Static Non Temperature Variable and Nonstatic Temperature Variable Stereochemistries

(a) *Static — nontemperature variable*	(b) *Nonstatic — temperature variable*
(1) Elongated tetragonal octahedral ($T < 0.85$)	(1) Octahedral
(2) Elongated rhombic octahedral ($T < 0.85$)	(2) Trigonal octahedral
(3) Trigonal bipyramidal	(3) Elongated tetragonal octahedral ($T > 0.85$)
(4) Square pyramidal	(4) Elongated rhombic octahedral ($T > 0.85$)
(5) Square coplanar	(5) Compressed tetragonal octahedral
(6) Rhombic coplanar	(6) Compressed rhombic octahedral
(7) Seven-, eight- and nine-coordinate	(7) *Cis*-distorted octahedral
(8) Compressed tetrahedral	
(9) Linear	

53.4.2.2 Summary of the stereochemistries of mononuclear copper(II) complexes

For the mononuclear complexes of the copper(II) ion, as summarized in the molecular structures (**174**)–(**255**). Tables 21–27 and Figures 17–25, the following generalizations may be made:

(i) the coordination numbers 2, 4, 5, 6, 7, 8 and 9 occur, with the order of abundance being $6 = 5 > 4 \gg 7 > 8 \gg 9 \approx 2$, with no three-coordinate structures;
(ii) coordination numbers of 5 and 6 are characterized by distorted geometries, (4 + 1), (4 + 2) and (4 + 1 + 1) coordination;
(iii) off-axis coordination by oxyanions is responsible for the long bonds in some of the (4 + 2*), and (4 + 1 + 1*) six-coordinate structures and is the main geometric origin of the higher coordination numbers of 7, 8 and 9 as in (4 + 1 + 2*), (4 + 4*) and (4 + 1 + 4*) geometries;
(iv) in the four-, five- and six-coordinate structures regular geometries are uncommon, and distorted geometries predominate, characterized by a range of bond-length and bond-angle distortions along structural pathways connecting the more regular geometries (Figure 21);
(v) these pathways are dominated by rhombic, trigonal and tetrahedral modes of distortion (Figure 25a), and may be related to the appropriate nuclear modes of vibration of the elongated tetragonal octahedral CuL_6 chromophore, (Figure 25b);
(vi) in a small group of the six-coordinate complexes (5%) with $T > 0.85$, the structures are found to have temperature variable or fluxional stereochemistries, with Cu—L varying with temperature by 0.1–0.3 Å.

53.4.2.3 Dinuclear complexes

These form a major group of copper(II) complexes for three reasons: (i) they are readily prepared by the normal methods used in preparing monomeric complexes;[5,22,47] (ii) they provide useful simple models for the study of the magnetic interaction of two unpaired *d* electrons;[583–586] and (iii) they are useful models of the type III–IV biological copper systems.[30,27]

In the past ten years it is probably (ii) and (iii) above that have provided the major incentive in the synthesis of novel dimeric structures in copper(II) systems.[30] Reference 10 includes a review of polynuclear copper(II) complexes in general and ref. 30 includes reference to a large range of biologically relevant dinuclear copper(II) complexes. The structural chemistry of binuclear copper(II) complexes was reviewed in 1977.[586] In order to systematize the description of copper(II) polynuclear structures the following notation is introduced.

(i) X is defined as a monatomic bridging ligand such as Cl^-, Br^- and including the OH^- anion, and also including polyatomic ligands bridging through one terminal atom, such as $(NO_3)^-$, $(O_2Me)^-$ and $(N_3)^-$ anions.
(ii) Y is defined as a polyatomic bridging ligand which has a generally *rigid* stereochemistry in its own right, such as the $(NO_3)^-$, $(O_2Me)^-$, $(C_2O_4)^{2-}$ and imidazole anions.
(iii) Z is defined a polyatomic bridging ligand which has a nonrigid stereochemistry in its own right, such as a polydentate chelate ligand. In practice X-type ligands produce rigid bridges with short Cu—Cu distances of *ca.* 3.5 Å, while with Z-type ligands flexible bridges occur and the Cu—Cu distance can range from 3–10 Å, but equally important the Cu—Cu separation is not 'rigidly' determined. Depending upon the conformation of the flexible bridging ligand the Cu—Cu separation is not fixed, but varies over a range of values, ±2.0 Å, especially in solution.

In general, it is not possible to predict the stereochemistry about the separate copper(II) ions; in most cases they are the same and may or may not be related by a centre of symmetry. The actual stereochemistries produced are recognizably the same as those occurring in mononuclear copper(II) complexes (Figure 19.1). The most common is that of square-based pyramidal with rhombic coplanar, compressed tetrahedral, trigonal bipyramidal and elongated rhombic octahedral stereochemistries all occurring.

Figure 19.2 summarizes the range of stereochemistries for dinuclear copper(II) complexes, I–IV for one to four bridging ligands. As each ligand may be of an X-, Y- or Z-type and for II–IV may be the same or different, as each L may bond at a short (*ca.* 2.0 Å), intermediate

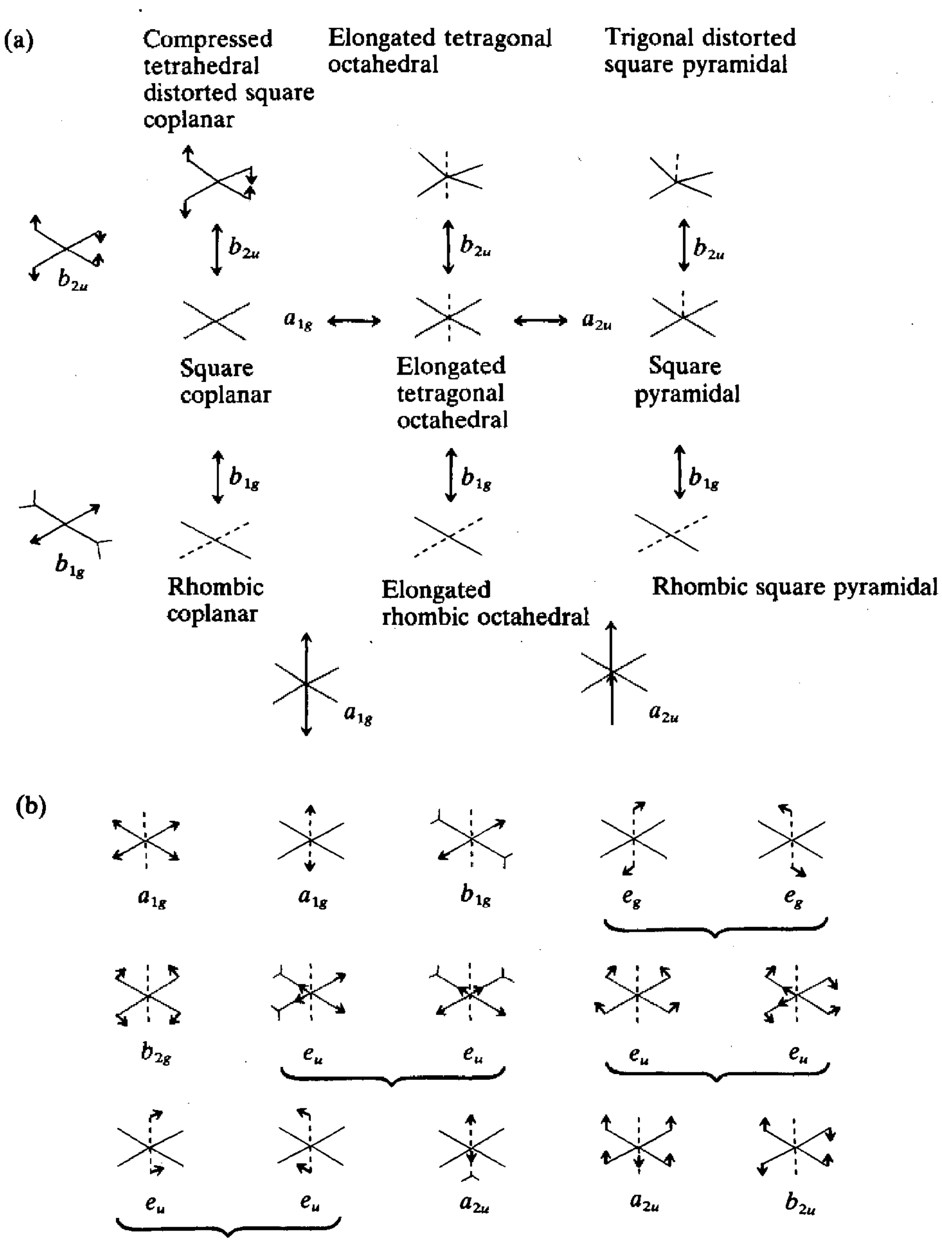
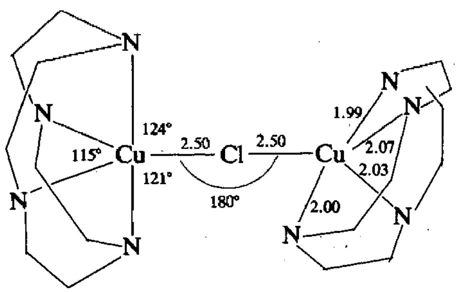
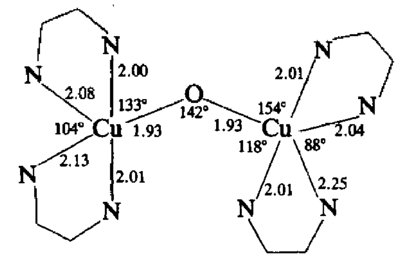


Figure 25 (a) Copper(II) stereochemical structural pathways; and (b) the normal modes of vibration of an elongated tetragonal octahedral complex of copper(II), *e.g.* $[Cu(NH_3)_4(SCN)_2]$

(2.3–2.6 Å) or long (2.7–3.0 Å) Cu—L distance, and as each Cu^{II} may have a choice (usually the same) of the five most common mononuclear copper(II) stereochemistries of Figure 19, there is a wealth of different structural types of dinuclear copper(II) structures (Table 30). Type I dinuclear copper(II) structures involving a single bridging ligand are the least common, a linear type I(v) structure occurs in $[Cu_2(tet\text{-}b)_2Cl](ClO_4)_3$ (**256**)[587] and a bent type I(v) structure occurs in $[Cu_2(bipy)_4(OH)](ClO_4)_3$ (**257**).[588] In (**256**) two equivalent CuN_4Cl chromophores are involved, with near trigonal bipyramidal geometries and the principal axis aligned at 90° as the two Cu atoms are related by a 180° Cu—Cl—Cu angle. In (**257**) the Cu—O—Cu angle of 142° is significantly distorted from linear and the CuN_4O chromophores are considerably distorted from trigonal bipyramidal with the principal axis misaligned by 90°. In both chromophores the sense of the distortion is along the structural pathway of the Berry twist towards square pyramidal and in the second chromophore the distortion is so extensive that the geometry is best described as trigonally distorted square pyramidal. This probably arises from the proximity of a perchlorate anion in the long sixth Cu—L position at a distance of 3.05 Å, too long for even semi-coordination. In both structures the origin of the 90° misalignment of the trigonal axes of the local Cu chromophores is not clear; in (**256**) there can be no steric requirements of the two separate nitrogen ligands, while in (**257**) the physical separation afforded by the bridging atom (Cu—Cu, 3.5 Å) restricts any steric interaction of the bulky bipy rings. Nevertheless, the misalignment does allow two of the bipy rings on the separate Cu atoms to be parallel to each other and perpendicular to the Cu—Cu direction, at a distance of 3.5 Å, suggestive of some $\pi-\pi$ interaction, possibly sufficient to cause the observed misalignment.[588]



$[Cu_2(tet\text{-}b)_2Cl](ClO_4)_3$ (**256**)[587]



$[Cu_2(bipy)_4(OH)](ClO_4)_3$ (**257**)[588]

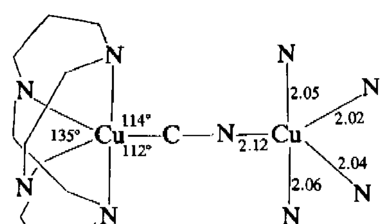
With single polyatomic bridging ligands (Table 30) linear bridging may still arise as in the $(CN)^-$ anion bridging in $[Cu_2(14\text{-}4,11\text{-diene-}N_4)_2(CN)](ClO_4)_3$ (**258**)[589] containing two centre-related square pyramidal or distorted trigonal bipyramidal $CuN_4C(N)$ chromophores of type I(v) or (vii). In (**258**) the centre of symmetry present ensures that the principal axes of the Cu environments are aligned parallel whether or not the geometry is best considered trigonal bipyramidal or square pyramidal. With a rigid planar imidazole bridge as in $Na[Cu_2(Gly\text{-}Gly\text{-}o)_2(im)]\cdot 6H_2O$ (**259**)[592] the bridging angle may deviate from linear, namely to 150° with the plane of the im ligand lying in the plane of the CuN_3O chromophore of the rhombic coplanar (type I, i), or square pyramidal (type II, ii) Cu environments (Table 30). In $[Cu_2(pip)_2(im)](NO_3)_3\cdot 2.5H_2O$[593] (Table 30) the plane of the im ligand is at $90 \pm 10°$ to the plane of the CuN_4 chromophore of the rhombic octahedral Cu environment, and a bridging angle of *ca.* 160° is still involved. With the more flexible bridging ligands, such as the $-(CH_2)_2-$ linkage in $[Cu_2(metgb)F_2](BF_4)_4\cdot 2H_2O$ (**260**),[594] where metgb = 1,1,10,10-tetrakis(1-methylbenzimidazole-2-methyl)-1,10-diaza-4,7-dioxadecane, two square pyramidal CuN_3FO chromophores (type I, vii) are linked *via* the fifth oxygen ligand position, but still approximately aligned with respect to each other. With even longer organic chains involving benzene rings, even longer Cu—Cu separations may be present, such as 11.7 Å in $[Cu_2(p\text{-}XYLpy_2)Cl_4]$ (**261**),[595] where square pyramidal CuN_3ClCl' chromophores (type II, ii) are still approximately aligned. In $[Cu_2(tren)_2(benzidine)](NO_3)_4$ (**262**)[596] the Cu—Cu separations of *ca.* 12.0 Å involve not only a zigzag Cu—benzidine—Cu chain with Cu—N—C angles of 133–118°, but also the benzene rings are twisted through angles of 14.3–22.5°. Consequently, the four square pyramidal distorted trigonal bipyramidal CuN_2N_3 chromophores (type I, vi) are misaligned by *ca.* 20°.

Type II dinuclear structures (Figure 19.2) are the most common dinuclear structures for the copper(II) ion and primarily involve a planar Cu_2L_2 unit (type II, i–x) and only occasionally a bent Cu_2L_2 unit. In the planar CuX_2Cu structures with monatomic bridging atoms, short copper ligand distances occur and result in a planar stereochemistry for the terminal ligands as well. Thus in $[Cu_2(OH)_2(tmen)_2]Br_2$ (**263**)[598] the Cu_2O_2 is planar type II(i), and the N atoms only involve a slight tetrahedral twist out of the plane of the Cu_2O_2 chromophore, which involves a Cu—O distance of 1.90 Å, and a Cu—O—Cu angle of 104°. A series of planar Cu_2O_2 complexes exists (see Table 31a) with Cu—O—Cu angles in the range 95–105° (see ref. 603 for a more extensive listing). Symmetrical bridging chloride ions occur in $[Cu_2Cl_2(HBpz_3)_2]$ (**264**)[603] and fluoride ions in $[Cu_2F_2(mppzH)_4(F_2BF_2)_2]$ (**265**);[604] in (**264**) the Cu stereochemistry is square pyramidal (type II, ii) and in (**265**) elongated rhombic octahedral (type II, iii). In both cases the short-bonded in-plane CuL_4 chromophore is coplanar with the bridging CuX_2Cu unit, and both dimeric units are centrosymmetric, consequently in (**264**) one long fifth ligand direction lies above the $Cu_2Cl_2N_4$ plane and one lies below this plane. Table 31(b) lists some further examples of asymmetric bridging $CuCl_2Cu$ units (type II, vii) and Table 31(c) lists some

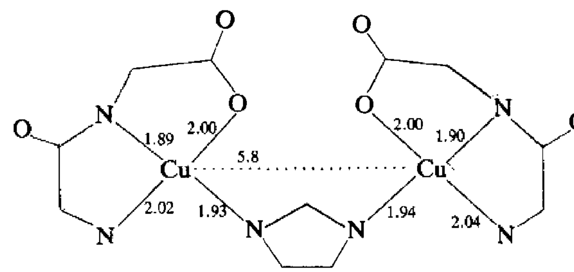
Table 30 Type I Bridged CuXCu Complexes

Type I	*Bridge*	*Bridge angle* (°)	*Chromophore*	*Type*	*Align A* (°)	μ(BM)	J(cm^{-1})	*Ref.*
$[Cu_2(tet\text{-}b)_2Cl](ClO_4)_3$ (**256**)	Cu—Cl—Cu	180	CuN_4Cl	I(v)	90	1.53	−144	587
$[Cu_2(bipy)_4(OH)](ClO_4)_3$ (**257**)	Cu—OH—Cu	142	CuN_4O	I(v)	90	1.56	−161	588
$[Cu_2(14\text{-}4,11\text{-}diene\text{-}N_4)_2(CN)](ClO_4)_3$ (**258**)	Cu—CN—Cu	180	$CuN_4C(N)$	I(v) or (vii)	0	1.53	−4.8	589
$[Cu_2L_2(CO_3)]$	Cu—OCO—Cu	—	$CuN_3O(O')$	I(i) or (ii)(4 + 1*)	90	—	—	590
$[Cu_2($*trans,trans*-pmk$)Cl_4]$	Cu—C—N—Cu	90	CuN_2Cl_2	I(i)	90	—	−52	557
$Na[Cu_2(Gly\text{-}Gly\text{-}o)_2(im)]\cdot 6H_2O$ (**259**)	Cu—im—Cu	150	CuN_2ONO'	I(i) and (ii)	0	—	−19	592
$[Cu_2(pip)_2im](NO_3)_3\cdot 2.5H_2O$	Cu—im—Cu	160	CuN_3NO_2	I(i)	0	—	—	593
$[Cu_2(metgb)F_2](BF_4)_2\cdot 2H_2O$ (**260**)	Cu—$O(CH_2)_2O$—Cu	—	CuN_3FO'	I(vii)	0	—	—	594
$[Cu_2(p\text{XYLpy2})Cl_4]$ (**261**)	Cu—NC_6H_4N—Cu	—	CuN_3ClCl'	I(ii)	0, 11.7	—	—	595
$[Cu_2(tren)_2(benzidine)](NO_3)_4$ (**262**)	Cu—$NC_6H_4C_6H_4N$—Cu	—	CuN_3N_2	I(vi)	Various	—	—	596
$[Cu_2(tren)_2(CN)_2](BPh_4)_2$	Hydrogen bonded	—	$CuNN_3C$	I(v) and (vi)	—	—	−1.8	589
$[Cu_2(px\text{-}saldpt)]$	$C_6H_4\{p\text{-}CH_2N[(CH_2)_3NH_2]_2\}_2$	—	CuN_2O_2	I(i)	—	—	—	597
$[Cu_2(teta)(OH_2)]\cdot 5H_2O$	Cu—$(CH_2)_3$—Cu	—	CuN_2O_2O'	—	0	—	—	591

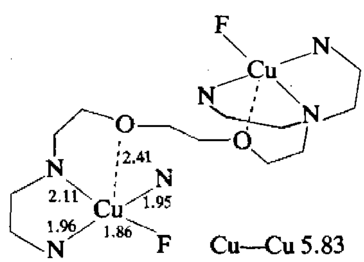
asymmetric bridging $CuBr_2Cu$ units, (type II, vii). Single atom bridging groups occur as in the alkoxide ligand in di(benzyloxo)bis(2,2,6,6-tetramethylheptane-3,5-dionato)copper(II) (**266**)[612] or with the 1,1-azide ligand of $[Cu_2(Bu^tpy)_4(N_3)_2](ClO_4)_2$ (**267**).[613] Planar Cu_2X_2 units may also occur with nonplanar Cu stereochemistries, thus in $(Ph_4As)_2[Cu_2Cl_6]$ (**268**)[614] both $CuCl_4$ chromophores have a compressed tetrahedral stereochemistry (type II, iv) with a dihedral angle of 66°, while $[Cu_2Br_4(pyNO)_4]$ (**269**)[615] has a very unusual short bridged Cu_2O_2 unit with trigonal pyramidal CuO_2Br_2O chromophores (type II, ix). Much less common are the bent (or roof-top) structures (type II, ii) as in $[Cu_2(cyclohexamine)_4(OH)_2](ClO_4)_2$ (**270**),[616] which has a Cu_2O_2 roof-top angle of 147.5° with a Cu—Cu distance of 2.93 Å. Even smaller bridge angles of 132.9° and 129° occur in the two independent roof-top structures in $[Cu_2(MeNH_2)_4(OH)_2](SO_4)\cdot H_2O$ (**271**),[617] with an even smaller Cu—Cu distance of 2.78 Å. While in (**270**) the CuN_2O_2 chromophores are square coplanar, in (**271**) one CuN_2O_2 chromophore has a fifth ligand (OH_2) at 2.37 Å and the other has an intermolecular contact of 2.40 Å to the adjacent bridge. Both are consequently square pyramidal (type II, ii) and, as in the mononuclear structures, the Cu atom is lifted out of the plane of the CuN_2O_2 chromophore by 0.07 and 0.41 Å, respectively.



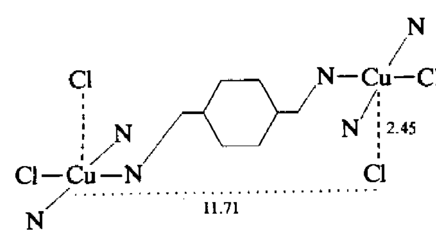
$[Cu_2(14\text{-}4,11\text{-diene-}N_4)_2(CN)](CLO_4)_3$ (**258**)[589]



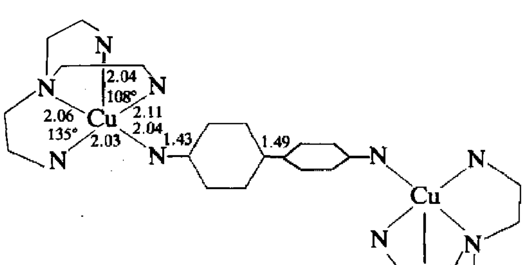
$Na[Cu_2(Gly\text{-}Gly\text{-}O)_2(im)]\cdot 6H_2O$ (**259**)[592]



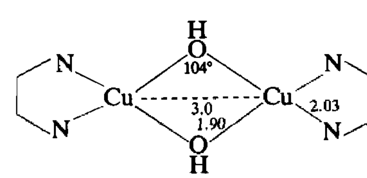
$[Cu_2(metgb)F_2](BF_4)_2\cdot 2H_2O$ (**260**)[594]



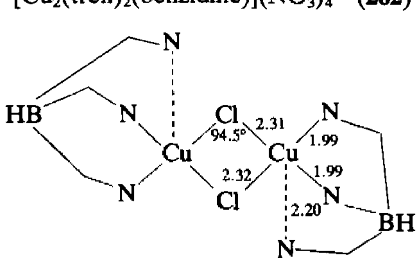
$[(Cu_2(p\text{-}XYLpy2)Cl_4]$ (**261**)[595]



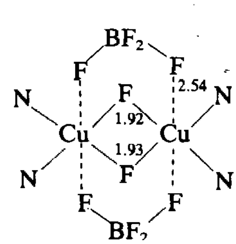
$[Cu_2(tren)_2(benzidine)](NO_3)_4$ (**262**)[596]



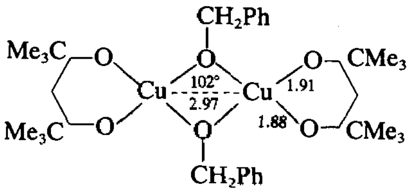
$[Cu_2(OH)_2(tmen)_2]Br_2$ (**263**)[598]



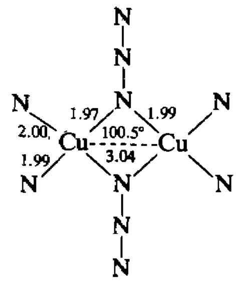
$[Cu_2Cl_2(HBpz_3)_2]$ (**264**)[603]



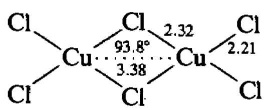
$[Cu_2F_2(mppzH)_4(F_2BF_2)_2]$ (**265**)[604]



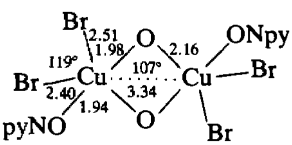
$[Cu_2(tmhd)_2(OCH_2Ph)_2]$ **(266)**[612]



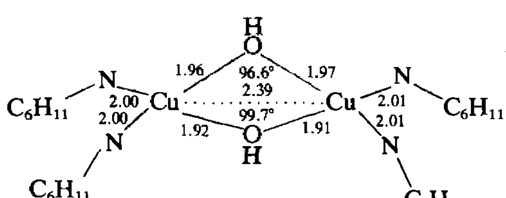
$[Cu_2(Bu^tpy)_4(N_3)_2](ClO_4)_2$ **(267)**[613]



$(Ph_4As)_2[Cu_2Cl_6]$ **(268)**[614]

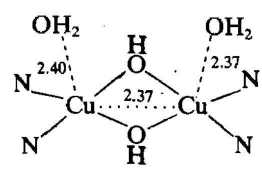


$[Cu_2Br_4(pyNO)_4]$ **(269)**[615]



roof angle = 147.5°

$[Cu_2(cyclohexamine)_4(OH)_2](ClO_4)_2$ **(270)**[616]



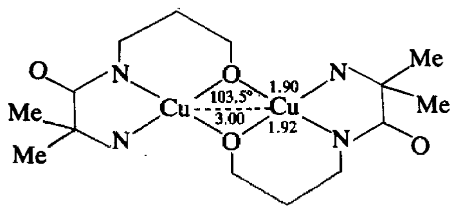
roof angle = 132.9°

$[Cu_2(Me(NH_2)_4(OH)_2](SO_4)\cdot H_2O$ **(271)**[617]

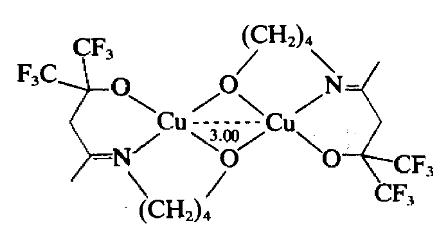
Table 31 Type II Bridged CuX_2Cu Complexes

	Type	*Chromophore*	*Cu—Cu* (Å)	*Cu—L*$_x$ (Å)	*Cu—X—Cu* (°)	μ(BM)	*Ref.*
(*a*) *X = hydroxide*							
$[Cu_2(OH)_2(tmen)_2]Br_2$ **(263)**	II(i)	CuN_2O_2	3.00	—	104	1.4	598
$[Cu_2(OH)_2(tmen)_2](NO_3)_2$	II(i)	CuN_2O_2	2.98	—	103	1.38	599
$[Cu_2(dmaep)_2(OH)_2](ClO_4)_2$	II(ii)	CuO_6	2.94	—	100	1.49	600
$[Cu_2(eaep)_2(OH)_2](ClO_4)_2$	II(ii)	CuN_2O_2O'	2.92	—	99, 100	1.63	601
$[Cu_2(bipy)_2(OH)_2](SO_4)\cdot H_2O$	—	CuN_2O_2	2.89	—	97	1.94	602
(*b*) *X = chloride*							
$[Cu_2Cl_4(HBpz_3)_2]$ **(264)**	II(ii)	CuN_2Cl_2N	—	—	95	—	603
$[Cu_2Cl_4(DMG)_2]$	II(ii)	CuN_2Cl_2Cl'	3.45	2.70	88	—	605
$[Cu_2Cl_2(dmen)_2]$	II(vii)	CuN_2Cl_2Cl'	3.46	2.73	86	—	606
$[Cu_2Cl_4(tmpd)_2]$	II(vii)	CuN_2Cl_2Cl'	3.76	2.98	97	—	607
$[Cu_2Cl_4(tmen)_2]$	II(vii)	CuN_2Cl_2Cl'	4.08	3.15	97	—	608
$[Cu_2Cl_4(C_4H_8SO)_4]$	II(vii)	CuO_2Cl_2Cl'	3.74	3.74	88.5	—	637
$[Cu_2Cl_4(pinacol)_2]$	II(vii)	CuO_2Cl_2Cl'	3.64	2.66, 3.08	85, 109	—	638
$[Cu_2(C_6H_{10}N_2O_2)_2Cl_4]$	II(vii)	CuN_2Cl_2Cl'	3.57	2.82	87.4	—	639
$[Cu_2(terpy)_2Cl_2](PF_6)$	II(vii)	CuN_3ClCl'	—	2.71	—	—	640
$[Cu_2(Et_3en)_2Cl_4]$	II(vii)	CuN_2Cl_2Cl'	3.70	2.73	94.8	—	641
$[Cu_2(dien)_2Cl_2](ClO_4)_2$	II(vii)	CuN_3ClCl'	3.64	2.77	92.2	—	642
$[Cu_2(benzotriazole)_4Cl_4]$	II(vii)	CuN_2Cl_2Cl'	3.45	2.69	89.3	—	643
$[Cu_2Cl_4(tmp)_2]$	II(vii)	CuO_2Cl_2Cl	3.47	2.69	—	—	644
(*c*) *X = bromide*							
$[Cu_2(DMG)_2Br_4]$	II(vi)	CuN_2Br_2Br'	3.60	2.88	86	—	609
$[Cu_2(tmen)_2Br_4]$	II(vii)	CuN_2Br_2Br'	4.20	3.2	96	—	610
$[Cu_2(2\text{-}pic)_4Br_4]$	II(vii)	CuN_2Br_2Br'	4.93	3.87	100	—	611
$[Cu_2(4\text{-}methyloxazole)_2Br_4]$	II(vii)	CuN_2Br_2Br'	3.63	2.71	92	—	634

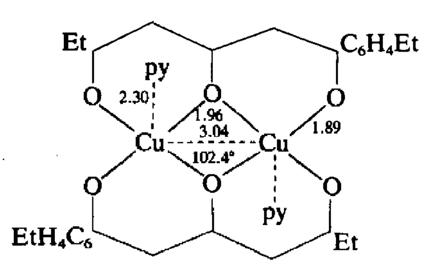
With tridentate chelate ligands an extensive series of binuclear copper(II) complexes is known, such as [Cu_2(aiba-nno)$_2$] (**272**),[618] in which the centrosymmetric Cu_2O_2 unit involves two rhombic coplanar CuO_2N_2 chromophores (type II, j) with a Cu—Cu separation of 3.0 Å and a Cu—O—Cu angle of 103.5°. A similar type II(ii) centrosymmetric $Cu_2O_4N_2$ chromophore occurs in [$Cu_2C_{20}H_{26}F_{12}N_2O_4$] (**273**)[619] with a Cu—Cu separation of 3.0 Å, a planar Cu_2O_2 unit and with a slight tetrahedral distortion of the CuO_3N chromophores, dihedral angle 6.8°. With triketone ligands base adducts may be formed to give a dual square pyramidal stereochemistry (type II, ii) as in [Cu_2(dana)$_2$(py)$_2$] (**274**)[620] with an out-of-plane Cu—N distance of 2.30 Å, and a ρ value of 0.24 Å. The structural chemistry of polynuclear transition metal polyketonates has been reviewed[621] with an emphasis on dinuclear copper(II) complexes with planar type (II) (i), (ii) and (iii) structures (Figure 19.2). With the more rigid ligand L^8 a centrosymmetric square pyramidal $Cu_2O_2N_4Cl_2$ unit is formed as in [$Cu_2(L^8)_2Cl_2$]·$6H_2O$ (**275**).[622]



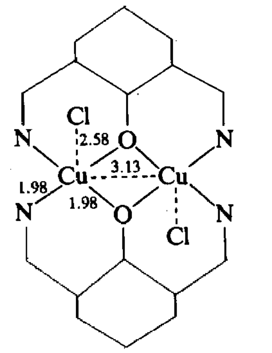
[Cu_2(aiba-nno)$_2$] (**272**)[618]



[$Cu_2C_{20}H_{26}F_{12}N_2O_4$] (**273**)[619]

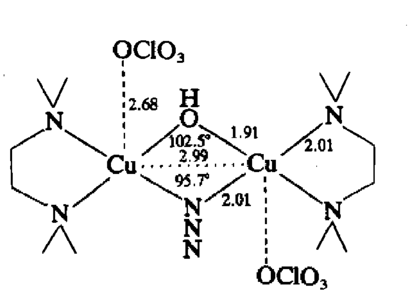


[Cu_2(dana)$_2$(py)$_2$] (**274**)[620]

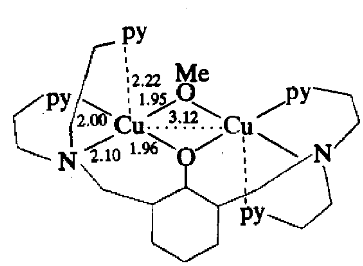


[Cu_2(L)Cl_2]·$6H_2O$ (**275**)[622]

Binuclear copper(II) complexes involving nonequivalent bridging ligands bonding at short Cu—ligand distances occur, as in [Cu_2(tmen)$_2$(N_3)(OH)](ClO_4)$_2$ (**276**),[623] notwithstanding the disorder associated with the bridging OH^- and N_3^- groups. The Cu_2ONN_4 unit is strictly planar and the perchlorate anions are involved in semi-coordination to the copper(II) ion (type II, ii), which is still coplanar with four in-plane ligands. Nonequivalent ligands are also present with polydentate ligands, as in [Cu_2{$OC_6H_3[CH_2N(CH_2CH_2py)_2]_2$-2,6-(OMe)}] (**277**),[140,141,624] which is of interest as the product of oxygenation of the copper(I) complex (see Section 53.3.7). A comparable $N_3Cu_2CuN_3$ chromophore also occurs in [$Cu_2(N_6O)(OH)](BF_4)_2$,[625] where N_6O = 2,6-[{bis[2-(1-pyrazolyl)ethyl]amino}methyl]-*p*-cresol.

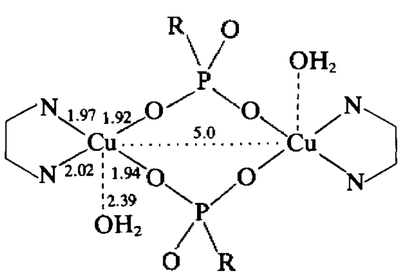


[Cu_2(tmen)$_2$(N_3)(OH)(ClO_4)$_2$ (**276**)[623]

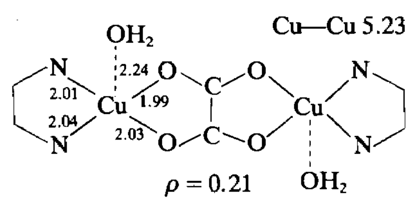


[Cu_2{$OC_6H_3[CH_2N(CH_2CH_2py)_2]$-2,6-(OMe)}] (**277**)[624]

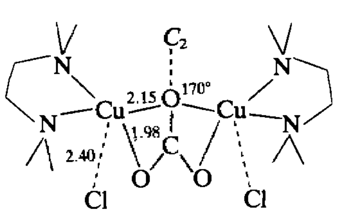
With polyatomic anions short copper–ligand bridging may occur, but must result in longer Cu—Cu distances. In $[Cu(5'\text{-AMP})(bipy)(OH_2)]_2(NO_3)_2{\cdot}6H_2O$ (**278**),[626] where 5′-AMP is a nucleotide base with a terminal phosphate group, the phosphate group bonds as a symmetrical bridging ligand with a Cu—Cu separation of *ca.* 5.0 Å. In $[Cu_2(Me_4en)_2(C_2O_4)(OH_2)_2](PF_6)_2{\cdot}2H_2O$ (**279**)[627] a planar oxalate anion forms four short Cu—O distances to two square pyramidal CuN_2O_2O chromophores (with $\rho = 0.21$ Å) with a Cu—Cu separation of 5.23 Å; an overall linear and an approximately planar $N_2CuO_4CuN_2$ chromophore is involved. A comparable linear planar structure is involved with the nonsymmetrical bridging carbonate ligand of $[Cu_2(Me_4pn)_2Cl_2(O_2CO)]$ (**280**).[628] Two square pyramidal CuN_2O_2Cl chromophores are involved ($\rho = 0.42$ Å) with the two-coordinate carbonate anion (see Chapter 15.5) involved in two slightly asymmetric bidentate Cu—O distances of 1.98 and 2.15 Å to the two separate Cu atoms. Due to the trigonal shape of the carbonate anion, the Cu—C—Cu angle is *ca.* 120°, but with a near linear Cu—O(1)—Cu angle of 170° (type II, ii). In $[Cu_2(\text{sal-}m\text{-pda})_2]{\cdot}CHCl_3$ (**281**),[629] where sal-*m*-pda = bis(salicylidene)-*m*-*N*,*N*′-phenylenediamine, an increased Cu—Cu separation of 7.4 Å is involved with a stepped structure to two rhombic coplanar CuN_2O_2 chromophores, both with a slight tetrahedral twist (type II, ii) and a dihedral angle of 6.9°. In $[Cu_2$(3,3′-dimethoxy-4,4′-bis(3-methyltriazine 3-oxide)biphenyl)] (**282**)[630] two tetrahedrally distorted CuO_2N_2 chromophores of type II (i) (dihedral angle 9°) are separated by two biphenyl links to give a Cu—Cu separation of 12.0 Å, and as the phenyl rings involve a twist of 26°, the planes of the CuO_2N_2 chromophores are inclined at 70° to each other, with a significant distortion from the planarity normally found for short Cu—L systems.



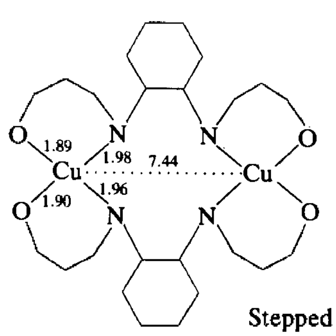
$[Cu(5'\text{-AMP})(bipy)(OH_2)]_2(NO_3)_2{\cdot}6H_2O$ (**278**)[626]



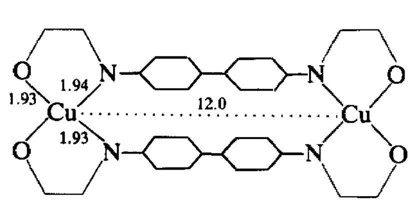
$[Cu_2(Me_4en)_2(C_2O_4)(OH_2)_2](PF_6)_2{\cdot}2H_2O$ (**279**)[627]



$[Cu_2(Me_4pn)_2Cl_2(O_2CO)]$ (**280**)[628]

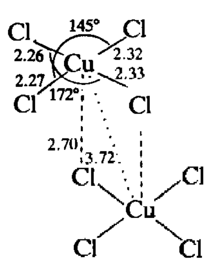


$[Cu_2(\text{sal-}m\text{-pda})_2]$ (**281**)[629]

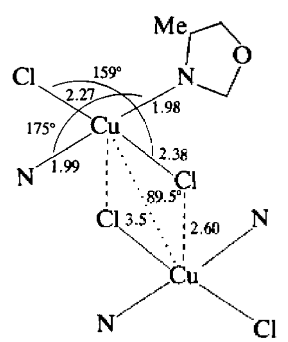


$[Cu_2N_{12}O_8C_{32}H_{36}]$ (**282**)[630]

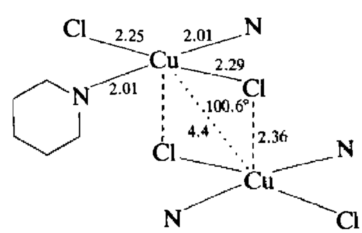
The largest group of dinuclear copper(II) complexes, with two bridging ligands, involves unequal Cu—X distances within the bridging Cu_2X_2 unit, in which, rather than the edge sharing of the CuL_4 chromophore of Figure 19.2, type II (i–iv), the planar/planar overlap of Figure 19.2, type II (vii)–(x) is involved, to give a long Cu—fifth ligand distance of ~2.3–3.0 Å, to yield two square pyramidal CuX_4X' chromophores with some distortion of the Cu atom out of the plane to ρ distances of 0.1–0.4 Å. The most simple example is in the dinuclear structure of $[Co(en)_3]_2[Cu_2Cl_8]Cl_2{\cdot}2H_2O$ (**283**)[631] in which two coplanar $CuCl_4$ chromophores relate by forming long Cu—Cl contacts of 2.70 Å to give two centre-related square pyramidal $CuCl_4Cl'$ chromophores. While the original publication suggested that this involved two trigonal bipyramidal $CuCl_5$ chromophores sharing a common edge, there is no obvious reason why a trigonal bipyramidal chromophore should involve such a long Cu—Cl distance of 2.70 Å and a distorted square pyramidal description is preferred. The latter is clearly not regular and has the marked trigonal distortion ($\theta = 145°$) of the majority of the monomeric square pyramidal copper(II) chromophores. In (**283**) the dimerization of the two $CuCl_4$ chromophores results in a slight tetrahedral twist, as the two basal angles of 172° and 145° are in the opposite sense. This type of long bond dimerization occurs most frequently with $[Cu(monodentate)_2Cl_2]_2$ complexes, such as in $[Cu(4\text{-}Meox)_2Cl_2]_2$ (**284**),[632] where 4-Meox = 4-methyloxazole with a short Cu—Cl distance of 2.60 Å, and a Cu—Cu distance of 3.50 Å, and in $[Cu(2\text{-}pic)_2Cl_2]_2$ (**285**).[633] More examples of this type of dimerization are shown in Table 31(b) and for some corresponding bromide complexes in Table 31(c), and illustrated in the molecular structures of $[Cu(4\text{-}Meox)_2Br_2]_2$ (**286**) (Table 31c).[634] In all the structures of Table 31, the bridging short copper–halogen distance is approximately 0.1 Å longer than the terminal copper–halogen distance and the bridging angle ranges from 84 to 100°. Bridging asymmetric Cu_2F_2 units are less common than either of the corresponding chloride or bromide units, but have been characterized recently as in $[Cu_2(dmpz)_2(mpz)_4F_2](BF_4)_2$ (**287**),[635] where dmpz = 3,5-dimethylpyrazole and mpx = 5-methylpyrazole and also in $[Cu_2F_2(tmpz)_6](BF_4)_2$ and $[Cu_2F_2(dmpz)_4(mpz)_2](BF_4)_2$.[636] In contrast to its frequent occurrence in copper(I) chemistry the structural unit Cu_2I_2 is unknown in copper(II) chemistry (Section 53.3.2.2).



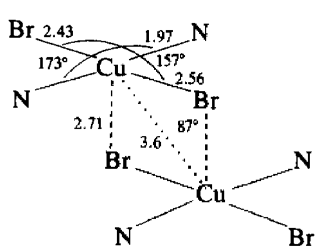
$[Co(en)_3]_2[Cu_2Cl_8]Cl_2{\cdot}2H_2O$ (**283**)[631]



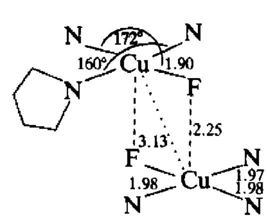
$[Cu(4\text{-}Meox)_2Cl_2]_2$ (**284**)[632]



$[Cu(2\text{-}pic)_2Cl_2]_2$ (**285**)[633]

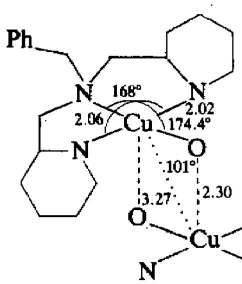


$[Cu(4\text{-}Meox)_2Br_2]_2$ (**286**)[634]

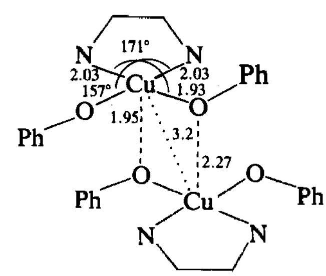


$[Cu_2(dmpz)_2(mpz)_4F_2](BF_4)_2$ (**287**)[635]

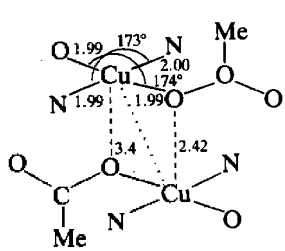
Asymmetric Cu_2O_2 units are reasonably common, as in $[Cu(bpy2)(OH)]_2(PF_6)_2{\cdot}2H_2O$ (**288**).[645] Relatively short bridging Cu—O distances are involved in (**288**) (*cf.* **284**) and the smaller trigonal basal angle of 168° is involved with the Cu—N bonds at right angles to the plane of the Cu_2O_2 unit, as also occurs in (**287**). In structures (**283**) to (**286**) this smaller trigonal angle lies in the Cu_2X_2 plane. Asymmetric bridging Cu_2O_2 units also occur with the phenoxide ligand, as in $[Cu_2(en)_2(OPh)_4]{\cdot}2PhOH$ (**289**),[646] with the acetate ligand, as in $[Cu_2(1\text{-}Meim)_4(O_2CMe)_4]{\cdot}6H_2O$ (**290**),[647] where 1-Meim = 1-methylimidazole. While (**289**) has a marked trigonal distortion of the CuN_2O_2O' chromophore, that of (**290**) is almost regular, notwithstanding the relatively short fifth ligand distance of 2.42 Å. A possible reason for this is that the bridging acetate is involved in off-z-axis bonding to the copper(II) ion to yield a (4+1+1*) six-coordinate $CuN_2O_2O'_2$ chromophore and not a (4+1) five-coordinate chromophore.[470] Probably the best known dimer of the present type involving a Cu_2O_2 chromophore is that involved in $[Cu_2(pyNO)_2(O_2NO)_2]$ (**291**),[648] in view of its magnetic properties (see Section 53.4.4.3). It involves a CuO_4O' square pyramidal chromophore, with a relatively short fifth ligand distance of 2.44 Å, but in contrast to the previous dimer structures (**283**) to (**290**) it involves a clear tetrahedral twist to the in-plane CuO_4 chromophore compared to the trigonal distortion normally observed. As with (**290**) a possible reason is that the two nonbridging nitrate groups may be involved in off-z-axis bonding at 2.75 and 2.80 Å, and suggests that the stereochemistry is really seven coordinate with (4+1+2*) stereochemistry (see Section 53.3.2.1).



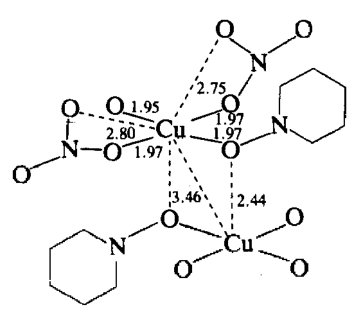
$[Cu(bpy2)(OH)]_2(PF_6)_2\cdot 2H_2O$ (**288**)[645]



$[Cu_2(en)_2(OPh)_4]\cdot 2PhOH$ (**289**)[646]

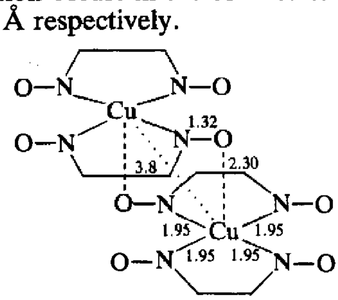


$[Cu_2(1\text{-}Meim)_4(MeCO_2)_4]\cdot 6H_2O$ (**290**)[647]

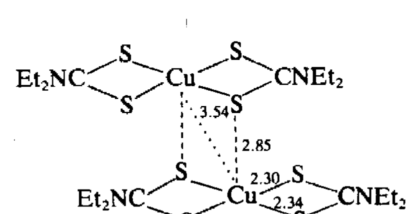


$[Cu_2(pyNO)_2(O_2NO)_2]$ (**291**)[648]

In the essentially rhombic coplanar complexes $[Cu(DMG)_2]_2$ (**292**)[649] and $[Cu(ditc)_2]_2$ (**293**),[650] where DMG = dimethylglyoxime and ditc = diethylthiocarbomate (type II, vii), dimerization occurs in the solid state by planar overlap to produce a Cu—Cu separation of 3.8 and 3.54 Å respectively.

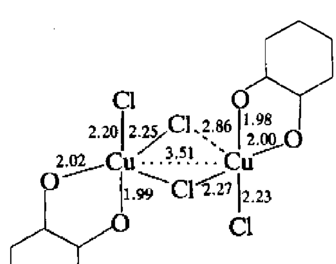


$[Cu(DMG)_2]_2$ (**292**)[649]



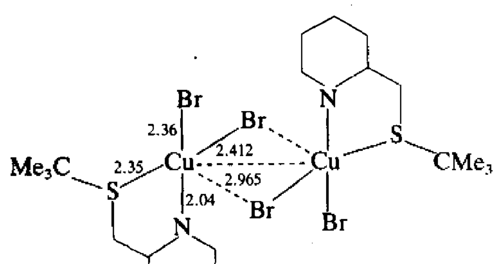
$[Cu(ditc)_2]_2$ (**293**)[650]

With monatomic bridging atoms (type I (i)–(iv) and type II (i) structures, Figure 19.2) type II structures predominate in the dimeric copper(II) structures, but one or two examples of the bent or roof-top structure (type II (i)–(v), Figure 19.2) exist. In $[Cu(\textit{trans}\text{-chd})_2Cl_2]_2\cdot THF$ (**294**),[651] where *trans*-chd = 1,2-cyclohexanediol, the Cu_2Cl_2 is nonplanar with a roof angle of 147°, while in the structure of $[Cu_2(dmthbp)_2Br_4]$ (**295**),[652] where dmthbp = 2-(3,3-dimethyl-2-thiabutyl)pyridine, the bridge angle is 140° and the $CuBr_2NS$ chromophore has a tetrahedral twist with a dihedral angle of 28.9°. But the most unusual dimeric copper(II) structure, with mixed copper(II) stereochemistries, involves a rhombic coplanar CuN_2ClO chromophore plus a tetrahedral $CuCl_4$ chromophore, and occurs in $[Cu_2(medpco)Cl_4]$ (**296**),[653] where medpco = *N,N'*-bis(2-*N,N*-dimethylaminoethyl)pyridine-2,6-dicarboxamide 1-oxide. One Cu—Cl—Cu bridge involves short Cu—Cl distances, while the second involves one short plus one long Cu—Cl distance of 2.64 Å to produce a normal square pyramidal CuN_2OClCl' chromophore with a reasonable Cu—Cu distance of 3.45 Å. The asymmetric type bridging of Figure 19.2, type II (vi), also occurs with polyatomic Y-type anions (Table 32), such as the $(N_3)^-$ anion, which involves restricted asymmetry in $[Cu_2(Me_5dien)_2(N_3)_2](BPh_4)_2$ (**297**)[654] with only a 2.25 Å Cu—N distance out of the plane and trigonal in-plane angular distortion ($\tau = 28\%$). The bridging $(N_3)^-$ anions are not linear (176.7°) and coordinate to the copper(II) ions with angles of 124° and 140° to give an increased Cu—Cu distance of 5.20 Å. A slightly greater asymmetry in the $(N_3)^-$ anion bridging role occurs in the comparable structure of $[Cu(Me_4en)(N_3)_2]$ (**298**)[655] with an out-of-plane Cu—N distance of 2.46 Å and in which a second $(N_3)^-$ anion forms a terminal in-plane nitrogen ligand. With a series of $[Cu_2(tren)_2(anion)_2](Ph_4B)_2$ complexes,[656] where anion = Cl^-, $(NCO)^-$ or $(NCS)^-$ and illustrated for the NCO^- anion in (**299**), each anion is involved in a normal Cu—X ligand distance to a trigonal bipyramidal CuN_4X chromophore, but linked to a second chromophore by hydrogen bonding between the coordinated anion and an amine hydrogen atom of the tren ligand of the second chromophore (**299**). In the case of the $(NCS)^-$ complex the terminal S atoms form two hydrogen bonds (Table 32). In all three complexes the dimerization aligns the principal axes of the two trigonal pyramidal CuN_4X chromophores. With polyatomic bridging ligands asymmetric bridging can occur, as with the oxalate anion in $[Cu_2(Et_5dien)_2(C_2O_2)](PF_6)_2{\cdot}2H_2O$ (**300**),[627] to give a planar centrosymmetric structure, which contrasts with the short Cu—O symmetric bridging of this anion in $[Cu_2(Me_4en)_2(C_2O_4)(OH_2)_2](PF_6)_2{\cdot}2H_2O$ (**279**).[627] A square pyramidal CuN_3OO' chromophore is involved with a τ value of 42% ($\rho = 0.21$ Å) and a Cu—Cu separation of 5.46 Å. A similar structure involving an asymmetric bridging biimidazolate anion occurs in $[Cu_2(Me_5dien)(biim)](Ph_4B)_2$,[657] also with a type II (vii) structure.



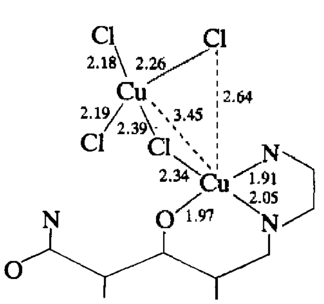
roof angle = 147°

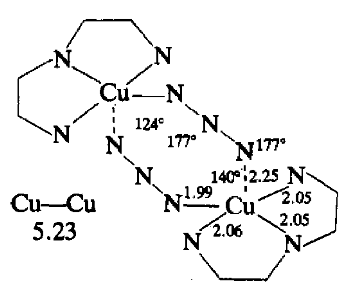
$[Cu(trans\text{-}chd)_2Cl_2]_2$ (**294**)[651]

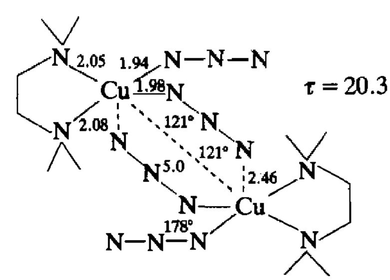


roof angle = 140°

$[Cu_2(dmthbp)_2Br_4]$ (**295**)[652]

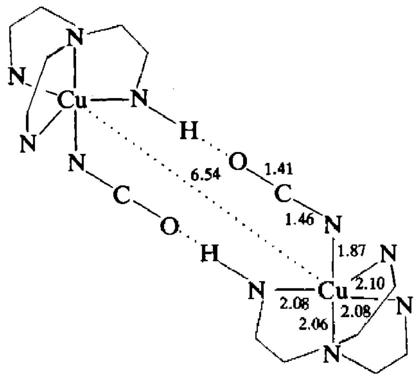




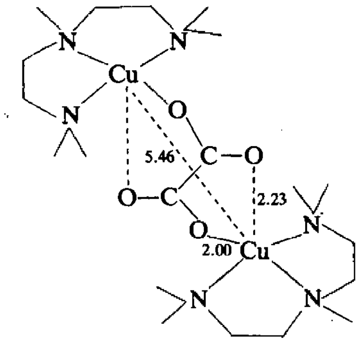


$[Cu_2(medpco)Cl_4]$ (**296**)[653] $[Cu_2(Me_5dien)_2(N_3)_2](BPh_4)_2$ (**297**)[654] $[Cu(Me_4en)(N_3)_2]_2$ (**298**)[655]

In order to introduce more flexibility into the structure of dinuclear copper(II) complexes, bridging ligands of type Y, such as p-$XYLpy_2$ (**261**),[595] have been combined with simple anion bridging ligands, such as Cl^-, OH^-, $(CN)^-$, $(OPh)^-$ and $(N_3)^-$, to produce very asymmetric

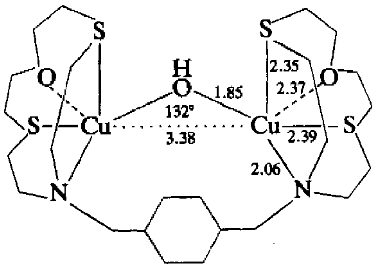


$[Cu_2(tren)_2(NCO)_2](BPh_4)_2$ **(299)**[656]

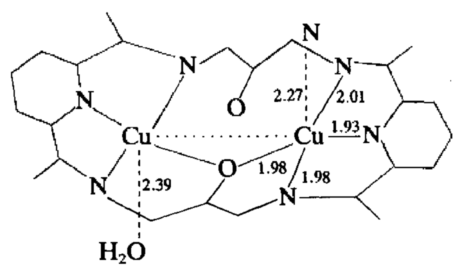


$[Cu_2(Et_5dien)_2(C_2O_4)](PF_6)_2\cdot 2H_2O$ **(300)**[627]

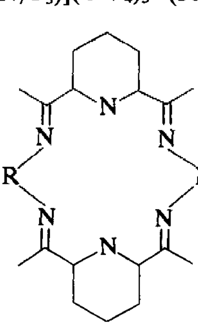
dimeric structures involving significantly different bridging groups. Thus the *p*-$CH_2(C_6H_4)CH_2$— link of $[Cu(p\text{-}XYLpy2)(OH)](BF_4)_3$ **(301)**[658] holds the two Cu atoms sufficiently close together to form a short bonded Cu—(OH)—Cu bridge (1.85 Å), which has been described as the 'earmuff' structure.[659] The Cu—(OH)—Cu bridge is bent with a Cu—O—Cu angle of 132° and the environment is square pyramidal with a Cu—O out-of-plane distance of 2.37 Å. The in-plane $CuONS_2$ chromophore has a definite tetrahedral twist with angles of 167° and 160°, directed in opposite directions, due to the comformational constraints of the macrocyclic ligand. Even more common are single bridging units with two organic linkages as listed in Table 33(a), and illustrated for an endogenous alkoxy bridge in $[Cu_2(C_{26}H_{34}N_7O_{15})Cl_3]$ **(302)**.[660] A bent Cu—(OR)—Cu link is present with a Cu—O—Cu angle of 136°, generating a Cu—Cu separation of 3.64 Å, between two square pyramidal CuN_3OX chromophores, where $X = N_3^-$ and OH_2 for the two distinct copper(II) environments. In $[Cu_2(L^F)(N_3)_2(1,3\text{-}N_3)](ClO_4)$ **(303)**,[661] where L^F is defined in **(304)**, a 1,3-azide bridge occurs, bridging two long Cu—N distances and involving nonlinear Cu—N—N angles which together produce misaligned CuN_4 planes (*ca.* 45°) with a Cu—Cu separation of 6.02 Å (see also Table 33a).[662–665]



$[Cu_2(p\text{-}XYLpy2)(OH)](BF_4)_3$ **(301)**[658,659]

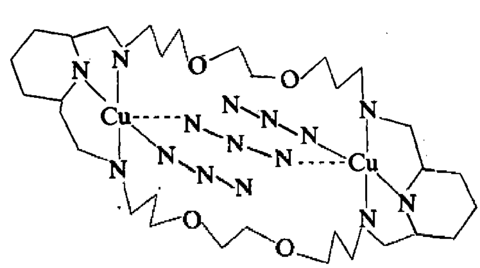


$[Cu_2(C_{26}H_{34}N_7O_3)](ClO_4)_3$ **(302)**[660]



L^A–L^F **(304)**[661]

L^A, R = —$(CH_2)_4$—
L^B, R = —$(CH_2)_5$—
L^C, R = —$(CH_2)_2S(CH_2)_2$—
L^D, R = —$(CH_2)_2NH(CH_2)_2$—
L^E, R = —$(CH_2)_3NH(CH_2)_3$—
L^F, R = – $(CH_2)_2O(CH_2)_2O(CH_2)_2$—



$[Cu_2(L^F)(N_3)_2(1,3\text{-}N_3)](ClO_4)$ **(303)**[661]

Table 32 Some $[Cu_2(chelate)_2(anion)_2]X_2$ Dimers

Complex	*Chromophore*	*Cu—Cu* (Å)	*Cu—anion* (Å)	*Cu—anion* (Å)	*Stereochemistry*[a]	*Ref.*
$[Cu_2(Me_5dien)_2(N_3)_2](BPh_4)_2$ (**297**)	CuN_4N	5.2	1.99	2.25	SBP	654
$[Cu_2(Me_4en)(N_3)_2]$ (**298**)	CuN_4N	5.0	1.98	2.46	SBP	655
$[Cu_2(tren)_2Cl_2](BPh_4)_2$	CuN_4Cl	5.79	2.25	2.47	TB	656
$[Cu_2(tren)_2(NCO)_2](BPh_4)_2$ (**299**)	CuN_4N	6.54	2.95	2.95	TB	656
$[Cu_2(tren)_2(NCS)_2](BPh_4)_2$	CuN_4N	6.14	3.46	3.46	TB	656
			3.73	3.73		

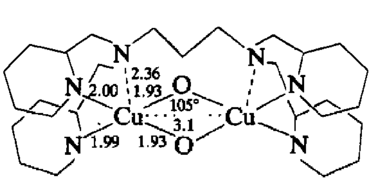
[a] SBP = square-based pyramidal; TB = trigonal bipyramidal.

Table 33 Dinuclear Copper(II) Complexes with Bridging Organic Groups

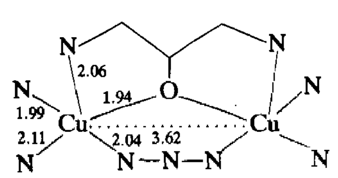
Complex	*Chromophore*	*Cu—Cu* (Å)	*X*	*Cu—X* (Å)	*Cu—X—Cu* (°)	*Stereochemistry*[b]	*Alignment*	*Ref.*
(*a*) *CuX_1L_2 structures*								
$[Cu_2(p\text{-}XYLpy2)(OH)](BF_4)_3$ (**301**)	—	3.1	HO^-	—	141.7	—	Aligned	658, 659
$[Cu(C_{26}H_{34}N_7O_{15})Cl_3]$ (**302**)	$CuN_3O(NNN)$	3.64	RO^-	1.977	135.5	SBP	*ca.* 35°	660
	$CuN_3O(OH_2)$	—	—	—	—	SBP	—	661
$[Cu_2(L^F)(N_3)_2(1,3\text{-}N_3)](ClO_4)$[a] (**303**)	$CuN_4(NNN)$	6.02	NNN^-	—	—	—	—	—
$[Cu_2(imH)_2(L^G)(im)](ClO_4)_3$[a]	CuN_5	—	im	1.976	135	TB	25°	662, 663
$[Cu_2(L^C)(im)](ClO_4)_3 \cdot H_2O$[a]	CuN_4O_2	5.87	im	—	—	ERO	Misaligned	664
$[Cu_2(L^F)(im)](ClO_4)_3$[a]	CuN_4	5.99	im	1.92, 1.98	—	RC	130°	665
$[Cu_2(L^F)(OH)](ClO_4)_3 \cdot H_2O$	CuN_4O	3.57	OH	1.87, 1.91	—	SBP	Misaligned	665
(*b*) *$Cu_2X_2L_2$ structures*								
$[Cu_2(OH)_2(H_2L^C)](ClO_4)_2 \cdot MeNO_2$	CuN_2O_2	2.99	OH^-	—	—	RC	—	668
$[Cu_2(L^B)(N_3)_2(1,3\text{-}N_3)_2]$ (**307**)	CuN_4S_2	5.15	NNN^-	2.0	—	ERO	Aligned	669
$[Cu_2(C_{16}H_{38}N_6O_2)(N_3)_2(1,3\text{-}N_3)_2]$	CuN_4N_2	—	NNN^-	1.963, 3.0	—	ERO	Aligned	670
$[Cu_2(LC^1)(pdc)1,3\text{-}N_3)]$ (**308**)	CuN_4S_2	—	NNN^-	—	—	ERO	Aligned	671
$[Cu_2(L^B)(OH)(OH_2)](ClO_4)_3$[a]	CuN_3OO'	3.2	OH^-	1.92	110	SBP	*ca.* 90°	672
	—	—	OH_2	2.52	77	—	—	—
$[Cu_2(L^G)(OH)(O_2ClO_2)](ClO_4) \cdot CHCl_3$	CuN_3OO'	3.6	OH^-	1.92	144	SBP	*ca.* 35°	673
	—	—	$(OClO_3)^-$	2.6	—	—	—	—
$[Cu_2(LC^5)(pdc)(OClO_3)]$ (**310**)	CuN_2S_2OO'	4.1	N—N,O	2.00, 2.85	—	SBP	*ca.* 40°	674
$[Cu_2(LC^3)(N_3)_3]$ (**311**)	CuN_5	—	{—$(CH_2)_3$—}	—	—	SBP	Aligned	675
$[Cu_2(LC^3)(NCS)_4]$	CuN_4N'	—	{—$(CH_2)_3$—}	—	—	SBP	—	676
$[Cu(LC^5)Cl_2]Cl_2$	$CuNS_2ClCl'$	7.3	{—$(CH_2)_5$—}	—	—	SBP	—	677
$[Cu(ppda)(OSO_2)] \cdot 13H_2O$	CuN_2O_2O'	3.9	$(OSO_3)^{2-}$	2.3	—	SBP	—	678
$[Cu_2(nmebtd)(ONO_2)_3](NO_3) \cdot 4H_2O$	$CuN_3OO'O''$	5.2	$(O_2NO)^-$	—	—	SBP	—	679

[a] L^B = —$(CH_2)_5$—; L^C = —$(CH_2)_2S(CH_2)_2$—; L^F = —$(CH_2)_3O(CH_2)_2O(CH_2)_2$—; L^G = 1,4,7,13,16,19-hexaaza-10,22-dioxacyclotetracosane. [b] SBP = square-based pyramidal; TB = trigonal bipyramidal; ERO = elongated rhombic octahedral; RC = rhombic coplanar.

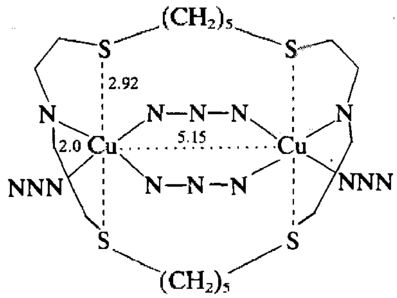
The presence of an organic bridging group also occurs with two small bridging ligands as in $Cu_2X_2L_2$; symmetrical short MeO^- bridging ligands occur in $[Cu_2(N_3py2)(OMe)_2](ClO_4)_2$ (**305**),[666] in which the Cu_2O_2 unit is planar with a Cu—Cu separation of 3.1 Å. Both CuN_2O_2N chromophores are square pyramidal with a trigonal distortion ($\tau = 27\%$), and the fifth ligand distance of 2.36 Å restricted by the bite of the chelate ligand. Equally nonequivalent short-bonded bridging ligands may be present plus an additional bridging organic chain, as in $[Cu_2(ehpdtb)(N_3)](ClO_4)_3$ (**306**).[667] With two bridging organic links two short bridging ligands predominate for CuX_2L systems (Table 30b). In $[Cu_2(H_2L^A)(OH_2)_2](ClO_4)_2 \cdot 2MeNO_2$, L^A = (**304**) (Table 30b),[668] two short Cu—OH—Cu bridges are formed along with a rhombic coplanar $N_2CuO_2CuN_2$ chromophore, linked further by two flexible N—$(CH_2)_4$—N linkages. Likewise the two short-bonded 1,3-N_3 links of $[Cu_2(L^B)(N_3)_2(1,3\text{-}N_3)_2]$ (**307**), L^B = (**304**),[669] yield a unique planar $Cu(N_3)_2Cu$ unit linked by two S—$(CH_3)_5$—S chains, to hold together two elongated rhombic octahedral $CuN_2N_2'S_2$ chromophores at the relatively long Cu—Cu distance of 5.2 Å. In $[Cu_2(C_{16}H_{38}N_6O_2)(N_3)_2(1,3\text{-}N_3)_2]$[670] two N—N linkages hold together a very asymmetric $Cu(N_3)_2Cu$ bridging unit, as observed previously in (**297**) and (**298**). Two S—$(CH_2)_5$—S linkages also hold together the very asymmetric short-bonded $Cu(N_2)(N_3)Cu$ bridge of $[Cu_2(LC^1)(pdc)(1,3\text{-}N_3)]$ (**308**),[671] where pdc = pyrazole dicarboxylate anion, again with two aligned elongated rhombic octahedral $CuNN'N''OS_2$ chromophores at the intermediate Cu—Cu distance of 4.45 Å. In $[Cu_2(L^B)(OH)(OH_2)](ClO_4)_3$,[672] two organic links hold two nonequivalent oxygen bridges, a hydroxy bridge involving two short Cu—O distances of 1.92 Å, and a bridging water molecule at an appreciably longer Cu—O distance of 2.52 Å, to yield a Cu—Cu separation of 3.2 Å. In this asymmetric Cu_2O_2 unit the Cu—O—Cu angles are considerably different: 110° at the OH bridge and 77° at the OH_2 bridge. In $[Cu_2(L^G)(OH)(O_2ClO_2)](ClO_4) \cdot CHCl_3$ (**309**)[673] and $[Cu_2(LC^5)(pdc)(OClO_3)](ClO_4)_2 \cdot H_2O$ (**310**),[674] two organic links hold two very asymmetric copper bonds in place, in the former a short bonded Cu—OH—Cu bridge, Cu—O at 1.92 Å, with a Cu—O—Cu bond angle of 144°, and in the latter the two nitrogens of an imidazole ring with equivalent Cu—N distances. In both (**309**) and (**310**) the second long-bonded bridging unit is a perchlorate anion, in the former bridging symmetrically at 2.61 Å as a bidentate perchlorato group at a semi-coordinate distance, in the latter occurring as an unsymmetrically bridging monodentate perchlorate at distances of 2.85 and 3.07 Å, two rather long distances, even for semi-coordination. In a number of dimeric copper(II) complexes (Table 33b) involving two organic chain links, the links are sufficiently long and flexible for no short ligand bridging to occur, and the copper chromophores can be considered as separate mononuclear copper(II) centres linked by the two organic chains.[675–678] This occurs in the structure of $[Cu_2(LC^3)(N_3)_2(N_3)](ClO_4)$ (**311**),[675] where the two square pyramidal CuN_5 chromophores are independent and only constrained by the organic links to produce a Cu—Cu separation of 4.1 Å with no short bridging ligands present. In $[Cu(ppda)(OSO_4)]_2 \cdot 13H_2O$ (**312**),[678] where ppds = *N,N'*-dipicolinoyl-1,3-propanediamine, two square pyramidal CuN_2O_2O' chromophores are aligned base to base (*cf.* type I, vii), with two organic links, but no direct axial bridging ligand and a Cu—Cu separation of 3.9 Å. In (**312**) a monodentate $(SO_4)^{2-}$ oxyanion completes the long fifth ligand Cu—O bond of 2.3 Å. In $[Cu_3\{N(Me)edtb\}(O_2NO)_3](NO_3) \cdot H_2O$ (**313**),[145] where N(Me)edtb = *N,N,N',N'*-tetrakis[(1-methyl-2-benzimidazolyl)methyl]-1,2-ethanediamine, a single en linkage connects two coplanar CuN_2O_2 chromophores, and a bridging nitrato group forms a second linkage *via* long Cu—O distances of 2.41 Å to give a square pyramidal CuN_3OO_2' chromophore with an additional off-the-*z*-axis nitrate oxygen at 2.63 Å to form a (4 + 1 + 1*) structure of two misaligned chromophores. The ultimate loosely bonded dimeric structure is that of the hydrogen-bonded structure of (**299**).



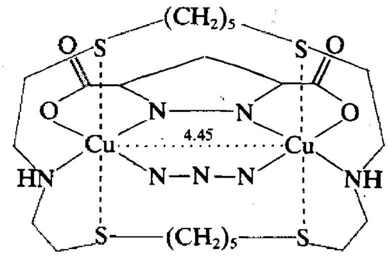
$[Cu_2(N_3py2)(OMe)_2](ClO_4)_2$ (**305**)[666]



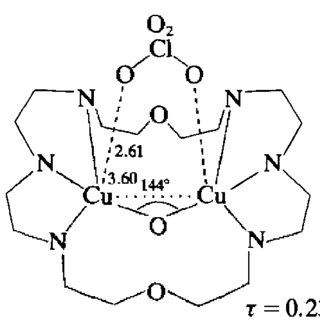
$[Cu_2(ehpdtb)(N_3)](ClO_4)_3$ (**306**)[667]



$[Cu_2(L^B)(N_3)_2(1,3\text{-}N_3)_2]$ **(307)**[669]

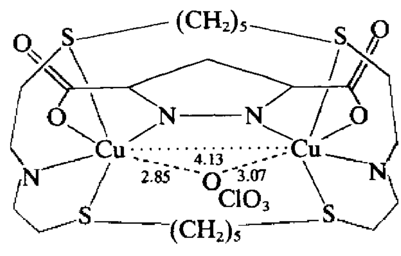


$[Cu_2(LC^1)(pdc)(1,3\text{-}N_3)]$ **(308)**[671]



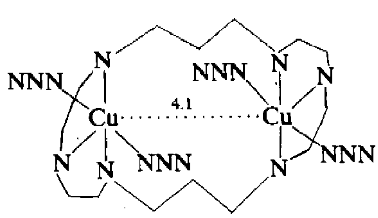
$\tau = 0.23\%$

$[Cu_2(L^G)(OH)(O_2ClO_2)](ClO_4)_2\cdot CHCl_3$ **(309)**[673]

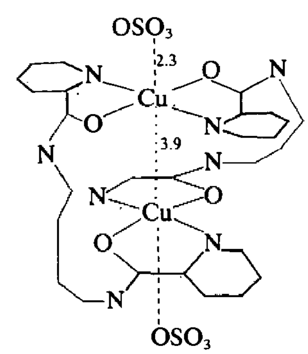


$(ClO_4)_2\cdot H_2O$

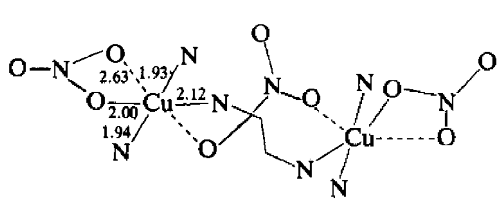
$[Cu_2(LC^5)(pdc)(OClO_3)](ClO_4)_2\cdot H_2O$ **(310)**[674]



$[Cu_2(LC^3)(N_3)_2\mu\text{-}(N_3)](ClO_4)$ **(311)**[675]

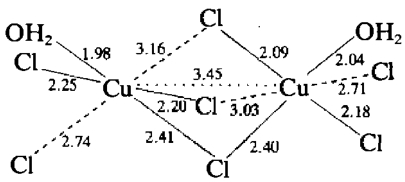


$[Cu(ppda)(OSO_3)]_2\cdot 13H_2O$ **(312)**[678]

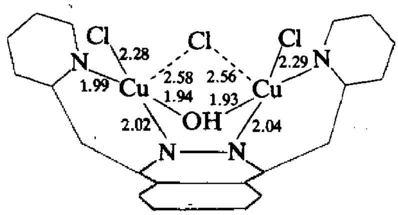


$[Cu_2\{N(Me)edtb\}(O_2NO)_3](NO_3)\cdot H_2O$ **(313)**[145]

Dinuclear copper(II) complexes involving three short-bonding rigid ligands (Figure 19.2, type III) are unknown as this would require a trigonal pyramidal CuL'_3 chromophore which is only known in the pseudo structures of copper(II) such as $K_2Pb[Cu(NO_2)_6]$ **(177)** and $Cs(CuCl_3)$ **(181)**. Two short and one long copper bridging distances are only found rarely, but they do occur in $Cs_3[Cu_2Cl_7(OH_2)_2]$ **(314)**[679] and in $[Cu_2(C_{18}H_{14}N_6)Cl_3(OH)]\cdot 5H_2O$ **(315)**.[680,681] In the former, two elongated rhombic octahedral $CuCl_3OCl_2$ chromophores share a face with one short/short and two short/long bridging Cl^- anions, to produce a Cu—Cu separation of 3.45 Å. In **(315)** two square pyramidal CuN_2OClCl' chromophores share a common face, but with two short/short OH^- and N_2 bridges and one long/long Cl^- bridge. In both **(314)** and **(315)** there is significant misalignment of the two Cu centres.

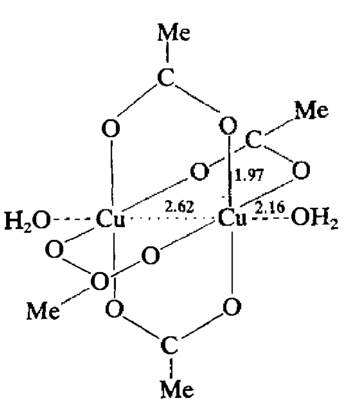


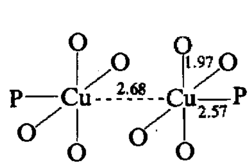
$Cs_3[Cu_2Cl_7(OH_2)_2]$ **(314)**[679]

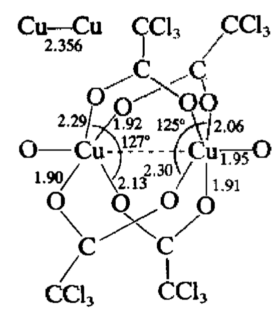


$[Cu_2(C_{18}H_{14}N_6)Cl_3(OH)]\cdot 1.5H_2O$ **(315)**[680,681]

For dinuclear copper(II) complexes with four equivalent bridges (Figure 19.2, type IV) the $[Cu_2(O_2Me)_4]$ structure predominates. It was first recognized in $[Cu_2(O_2CMe)_4(OH_2)_2]$ **(316)**,[682–684] but due to the interest in the magnetic properties[685] and bonding in this type of complex, it has been extensively studied and reviewed.[685–687] In **(316)** the two Cu atoms are bridged by four symmetrically bridging acetate groups to give a dimeric structure with a short Cu—Cu distance of 2.62 Å. The copper(II) involves four short Cu—O distances of 1.97 Å and a further fifth ligand distance for Cu—OH_2 of 2.16 Å. If the Cu—Cu direction is ignored as a bonding direction in **(316)**, the complex has two square pyramidal CuO_4O' chromophores sitting back to back (see **312**). Numerous acetate structures have been determined with different fifth ligands (Table 34[688–694]), and also with substituted carboxylate groups,[695–697] but because of the restricted bite of the carboxylate oxygen atoms the geometry varies very little and the Cu—Cu separation only changes by *ca.* 0.3 Å. While the rigid geometry of the $[Cu_2(O_2CMe)_4]^{2-}$ unit is the norm, this stabilizes the copper(II) ion to reduction even by Ph_3P and the formation of a stable Cu^{II}—P bond (2.56 Å) in $[Cu_2(O_2CR)_4(PPh_3)_2]$ **(317)**,[698] where RCO_2H_2 = 2,9-bis(methoxymethyl)-2,9-dimethyl-4,7-dioxadecanedioic acid. More recently a trigonally distorted square pyramidal CuO_4O chromophore has been characterized in $[Cu_2(O_2CCCl_3)_4(tempo)_2]$ **(318)**,[699] where tempo = the stable nitroxyl radical 2,2,6,6-tetramethylpiperidinyl-1-oxy. Each CuO_4O chromophore is still five coordinate, but one of the Cu—O(acetate) distances forms the elongated fifth ligand direction, rather than the terminal ligand as in **(316)** and **(317)** and the τ values of the two Cu centres of **(318)** are 73 and 95% respectively; the latter is very close to a trigonal bipyramidal CuO_5 chromophore. In **(318)** the acetate bridges involve one short and one long Cu—O distance and link the two principal O—Cu—O axes at *ca.* 90° misalignment.





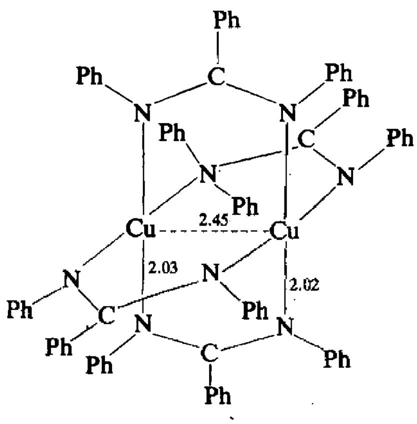


$[Cu_2(O_2CMe)_4(OH_2)_2]$ **(316)**[682–684] $[Cu_2(O_2CR)_4(PPh_3)_2]$ **(317)**[698] $[Cu_2(O_2CCCL_3)_4(tempo)_2]$ **(318)**[6

The acetate type structure can also occur with nitrogen ligands, but is only of limite occurrence. It occurs in $[Cu_2(NPhCPhNPh)_4]$ **(319)**,[700] where bridging NPhCPhNPh ligan(result in an even shorter Cu—Cu distance of 2.45 Å.

Table 34 Some Crystallographic Data for Dinuclear Acetate-type Structures

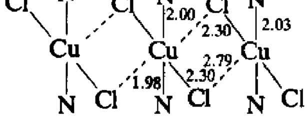
Complex	*Cu—Cu* (Å)	*Cu—O$_{eq}$* (Å)	*Cu—OH$_2$* (Å)	*Ref.*
$[Cu_2(O_2CMe)_4(pz)_2]$	2.58	1.96	2.17	688
$[Cu_2(O_2CMe)_4(MeCO_2H)]$	2.58	1.97	2.20	689
$[Cu_2(O_2CMe)_4(OH_2)_2]$ (**316**)	2.62	1.97	2.16	682–684
$[Cu_2(O_2CMe)_4(urea)_2]\cdot H_2O$	2.64	2.00	2.09	690
$[Cu_2(O_2CMe)_4(NCS)_2]$	2.64	2.03	2.08	691
$[Cu_2(O_2CMe)_4(2\text{-pic})_2]$	2.67	1.98	2.24	692
$[Cu_2(O_2CMe)_4(dien)]$	2.56	1.95	2.23	693
$[Cu_2(O_2CPh)_4(dien)_{2.5}]$	2.57	1.96	2.18	694
$[Cu_2(O_2CCH_2Cl)_4(3\text{-pic})_2]$	2.69	1.97	2.27	695
$[Cu_2(O_2CCCl_3)_4(2\text{-Clpy})_2]$	2.77	1.96	2.15	696
$[Cu_2(O_2CCF_3)_4(quin)_2]$	2.89	1.97	2.11	697



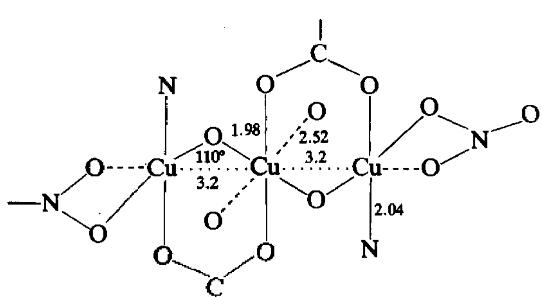
$[Cu_2(NPhCPhNPh)_4]$ (**319**)[700]

5.3.4.2.4 *Trinuclear complexes*

These are far less extensive than are dinuclear copper(II) systems and limited to only two or three types, which are shown in Figure 19.3(i)–(iii). A bridging chloride trimer occurs in the trinuclear $[Cu(denc)_2Cl_2]_3$ (**320**),[701] whence denc = *N*,*N*-diethylnicotinamide; a planar Cu_3Cl_6 ribbon occurs with two *trans* nitrogen atoms from denc coordinating out of the plane. Due to the stoichiometry the central Cu atom has a $CuCl_4N_2$ chromophore and the terminal Cu atoms have a $CuCl_3N_2$ chromophore. In both environments the *trans* Cu—Cl directions are elongated and aligned parallel in all three chromophores. At the central copper atom the tetragonality is 0.77 and the terminal CuN_2Cl_3 chromophores are almost regular square pyramidal with a τ value of 7.5%. In $[Cu_3(C_{10}H_{22}NO)_2(C_7H_5O_2)_4(C_2H_6O)_2]$ (**321**)[702] the copper atoms form a linear array with a Cu—Cu separation of 3.2 Å. The central atom has an octahedral stereochemistry and the two terminal atoms involve a rhombic coplanar (4 + 1*) stereochemistry with the carboxylate oxygen involved in off-axis bonding. Due to the short Cu—O bridging distances and the 110° Cu—O—Cu angle, the two outer Cu centres have their principal axes approximately aligned, but they are both misaligned by *ca.* 70° with the principal axis of the central copper atom.

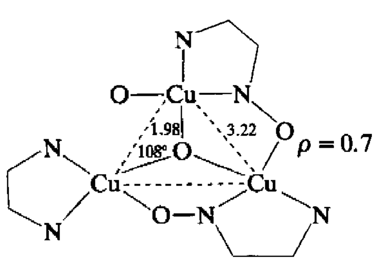


$[Cu(denc)_2Cl_2]_3$ (**320**)[701]

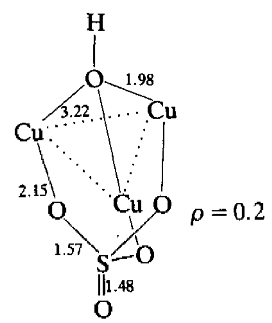


$[Cu_3(C_{10}H_{22}NO)_2(C_7H_5O_2)_4(C_2H_6O)_2]$ (**321**)[702]

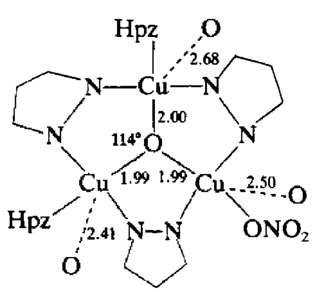
No type III (ii) bent trinuclear copper(II) systems are known, but a number of type III (iii) systems with a symmetrical tridentate bridging ligand to three copper(II) ions are known. In the trinuclear complex, $[Cu_3(OH)(pao)_3](SO_4)\cdot10.5H_2O$ (**322**),[703] where pao = 2-pyridinecarbaldehyde oxime, the three equivalent copper atoms are bridged by a single three-coordinate hydroxide group at 1.98 Å and each copper atom involves an approximately planar CuN_2O_2 group with an apical Cu—O distance of 2.15 Å to a symmetrically tridentate sulfate anion, which symmetrically caps the underside of the $Cu_3(OH)$ group (**323**). The $CuN_2O_2O_2$ chromophores are square pyramidal with $\rho = 0.2$ Å. A very similar symmetrical structure occurs in $[Cu_3(prao)_3(OH)_{0.5}(ClO_4)_{0.5}](ClO_4)\cdot4H_2O$, where prao = 2-2-methyl-2-propylamino-3-butanone oxime, and more recently in $[Cu_3(OH)(phbo)_3]$, where phbo = 3-(phenylimino)butanone 2-oxime.[704,705] In $[Cu_3(OH)(pz)_3(Hpz)_2(ONO_2)_2]\cdot H_2O$ (**324**)[706] a less symmetrical $[Cu_3(OH)]$ unit occurs, still with a pyramidal geometry and $\rho = 0.48$ Å. Each pair of Cu atoms is bridged in the trigonal plane by an N—N pyrazole group, but two kinds of Cu environment occur: two Cu atoms involve a terminal Hpz ligand while the third involves a nitrato group that is also involved in off-axis coordination, Cu—O = 2.87 Å. All three Cu atoms have a distorted square pyramidal environment completed by a nitrate oxygen to give a (4 + 1) or (4 + 1 + 1*) stereochemistry. The nitrate is tridentate (see **49**, Chapter 15.5) and semi-coordinates to two Cu atoms of one Cu_3O unit and one Cu atom of a second Cu_3O unit, thus generating a linear lattice structure. Less symmetric single-atom bridging of a Cu_3 unit occurs *via* a 1,1,1-azide ligand in $[Cu_3(2\text{-bzpy})_2(N_3)(N_3)_5]$ (**325**),[707] where bzpy = 2-benzoylpyridine. All three Cu—Cu separations are bridged by a short-bonded 1,1-azide ligand. Two of the copper environments are then elongated rhombic octahedral with out-of-plane chelation of the benzoylpyridine ligand and the third Cu environment is distorted square pyramidal, with 1,1-azide ligands bridging to other Cu_3N units to give a one-dimensional chain structure.



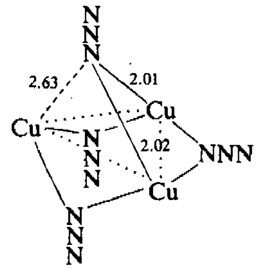
$[Cu_3(OH)(pao)_3](SO_4)\cdot10.5H_2O$ (**322**)[703]



(**323**) $[Cu_3(OH)(O_2SO)]$ group of (**322**)[703]



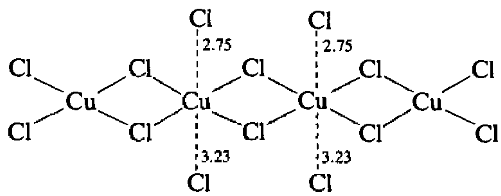
$[Cu_3(OH)(pz)_3(Hpz)_2(ONO_2)_2]\cdot H_2O$ (**324**)[706]



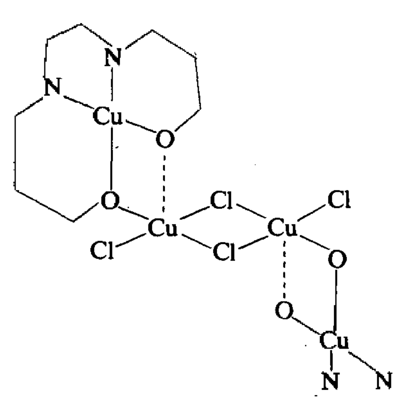
$[Cu_3(2\text{-bzpy})_2(N_3)(N_3)_5]$ (**325**)[707]

53.4.2.5 Tetranuclear complexes

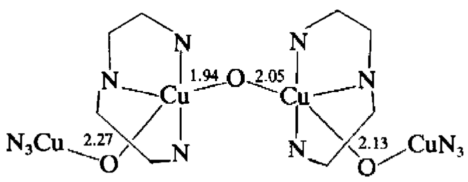
These complexes are again much less common than dinuclear complexes, but slightly mor extensive than trinuclear complexes. Four main structural types arise (Figure 19.4), namel linear (IV, i), zigzag or stepped (IV, ii), planar (IV, iii) and tetrahedral (IV, iv). The line systems IV (i) are the least common, but do occur in the linear chain of $(Me_3NH)_2[Cu_4Cl_1$ (**326**)[708] involving four coplanar $CuCl_4$ chromophores; the centre two of the chain bridge t adjacent chloride ions at 2.75 and 3.23 Å, to yield a rhombic octahedral $CuCl_6$ (4 + 1 + 1 structure. In $[Cu(salen)CuCl_2]_2$ (**327**),[709] where salen = *N,N'*-ethylenebis(salicylaldimine), a zigzag or stepped Cu_4 unit is present, with a planar Cu_2Cl_2 central unit and two terminal CuO_2Cu bridges. The two central $CuCl_3O_2O'$ chromophores are square pyramidal and the two terminal CuN_2O_2 chromophores[710] are rhombic coplanar; due to the two-atom bridging, the elongation axes of the central and terminal copper(II) centres are misaligned by *ca.* 90°. In $[(CuL)_3(CuLO)(\text{-}\mu\text{-}OH)_3]$ (**328**),[254] where HL = 1,3-bis{2-(4-methylpyridyl)imino}isoindoline, a bent Cu—O—Cu bridged tetramer occurs with a trigonal bipyramidal central CuN_3O_2 chromophore and tetrahedrally distorted terminal CuN_3O chromophores. An essentially planar Cu_4 unit of type IV (iii) occurs in $[Cu_2(bpim)(im)]_2(NO_3)_4{\cdot}3H_2O$ (**329**),[593] where bpim = 4,5-bis{(2-pyridyl)ethylimine}methylimidazolate. All four Cu atoms are bridged by imidazole ligands and further coordinated by two nitrogens of the bpim ligand to form four essentially planar CuN_4 chromophores with the im rings of the bpim ligands coplanar with the CuN_4 chromophore and the planes of the remaining two im ligands perpendicular to this plane. Two Cu—Cu separations of 5.91 and 8.63 Å are involved. An essentially planar cyclic Cu_4 eight-membered ring occurs in $[Cu_4(mpz)_4(acmpz)_2(ONO_2)_2]$ (**330**),[711] where mpzH = 3(5)-methylpyrazole and acmpzH = 1-(1-ethanoyl)-5-methylpyrazole, with four bridging pyrazole N—N groups; in addition the two Cu_2 pairs are bridged by an ethoxy group. Two copper environments are present: a tetrahedrally distorted CuN_3O chromophore, and an essentially planar CuN_2OO' chromophore, where O' is a nitrate oxygen ligand with a second off-axis oxygen at 2.57 Å to give a (4 + 1*) square pyramidal stereochemistry. In this rather irregular Cu_4 structure there are four distinct Cu—Cu distances of 3.32, 3.42, 4.39 and 5.11 Å. The most regular type of tetrahedral Cu_4 unit is involved in the $[Cu_4OX_6L_4]$ structure (**331**),[712] where $X = Cl^-$ and Br^- and L may be Cl^- or OH_2 or an organic ligand such as triphenyl phosphine oxide, *N*-methyl-2-pyrrolidinone (nmp), or 2-methylpyridine as listed in Table 35(a). In all of these structures,[711–715] the Cu_4 tetrahedron is nearly regular with a central tetrahedral O atom. The six edges of the Cu_4 tetrahedron are bridged by the halide anions, X^-, and the L ligands form terminal groups on the Cu atoms. Each Cu has a trigonal bipyramidal CuX_3OL chromophore and the four principal axes are misaligned by the tetrahedral orientation about the central O atom. All the Cu—Cu separations are *ca.* 3.0 Å. A less regular tetrameric Cu_4 structure occurs with the dialkylaminoethanolate anion, in which $[Cu_2\{O(CH_2)_2NR_2\}_2]$[716–722] dimers are further associated in pairs by longer Cu—O distances to form a distorted Cu_4O_4 chromophore (**332**). No central μ_4-O atom is present, but two interpenetrating tetrahedral Cu_4 and O_4 units are present with the nitrogen atom of the $O(CH_2)_2NR_2$ anion also involved as a terminal ligand to the copper(II) ion to give a distorted square pyramidal stereochemistry (Table 35b). In $[Cu_4(C_5H_{13}N_2O)_4](SO_4){\cdot}8H_2O$,[720] $[Cu_4(C_5H_{13}N_2O)_4](NO_3)_2{\cdot}2H_2O$[721] and $[Cu_4(dmae)_4(O_2CCF_3)_4]$[722,723] the same basic tetrameric unit (**332**) is present, except that the copper(II) environment is elongated rhombic octahedral rather than square pyramidal. This arises from semi-coordination of an oxygen from the oxyanion in the nitrate complex to give a bridged chain structure, in the sulfate complex to give a bridged sheet structure and by internal off-axis bonding in the carboxylate to give a molecular tetrameric structure. While the $[Cu_4OX_6L_4]$ chromophore is unique in copper(II) stereochemistry, the $[Cu_4O_4L_4]$ structure is comparable to the closed cubane structure of copper(I) chemistry (Figure 4.4(v), Section 53.3.2.4) and without the central O atom the former resembles the open cubane structure of Figure 4.4(vi).



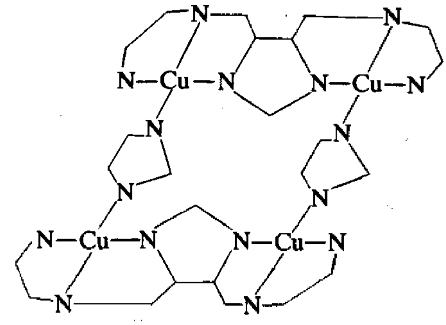
$(Me_3NH)_2[Cu_4Cl_{10}]$ (**326**)[708]



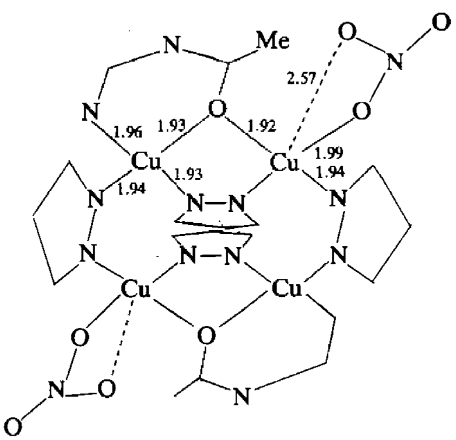
$[Cu(salen)CuCl_2]_2$ (**327**)[709]



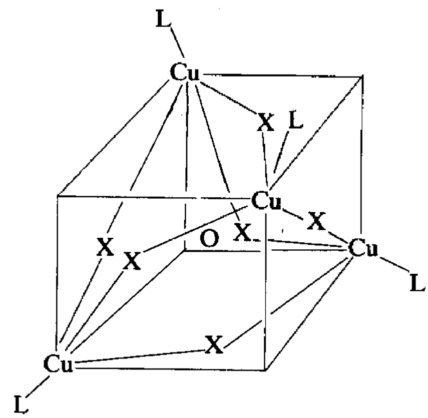
$[(CuL)_3(CuLO)(\text{-}\mu\text{-}OH)_3]$ **(328)**[254]



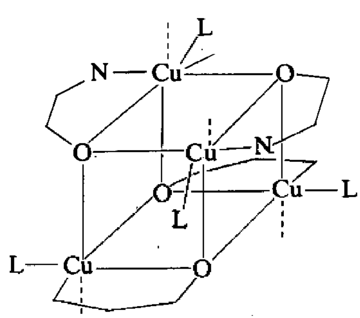
$[Cu_2(bpim)(im)]_2(NO_3)_4 \cdot 3H_2O$ **(329)**[593]



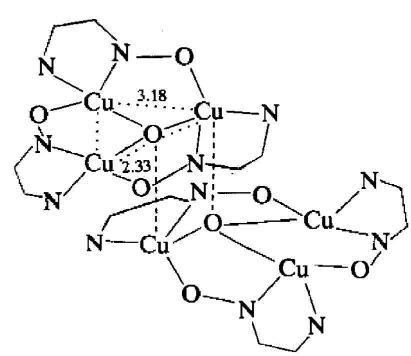
$[Cu_4(mpz)_4(acmpz)(ONO_2)_2]$ **(330)**[711]



$[Cu_4OX_6L_4]$ **(331)**[712]



$[Cu_4\{O(CH_2)_4NR\}_4L_4]$ **(332)**[716]



$[Cu_3O(dpeo)_3]_2$ **(333)**[723]

53.4.2.6 Hexanuclear complexes

Unlike copper(I) Cu_5 and Cu_6 units are very limited in copper(II) structures. The former is unknown but the latter occurs (Figure 19.5) in $[Cu_3O(dpeo)_3]_2$ (**333**),[705] where dpeo = 1,2-diphenyl-2-(methylimino)ethanone 1-oxime and results from the dimerization of the trinuclear $[Cu_3O(dpeo)_3]$ units (see **321**) with a relatively short Cu—O separation of 2.33 Å and a short Cu—Cu separation of 3.18 Å.

Table 35 Crystallographic Data for Some Tetranuclear Cubane Copper(II) Complexes

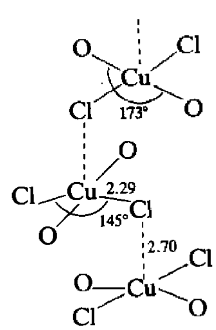
Complex	*Chromophore*	*Cu stereo-chemistry*[e]	*Cu—Cu* (Å)	*Cu—O* (Å)	*Cu—X*[f] (Å)	*Cu—L* (Å)	*Remarks*	*Ref.*
(*a*) $[Cu_4OX_6L_4]$								
$[teedH_2]_2[Cu_4OCl_6Cl_4]$[a] (**331**)	$CuCl_3OCl'$	TB	—	1.92	2.40	Cl, 2.24	—	712
$[Cu_4OCl_6(nmp)_3(OH)_2]nmp$[b] (**151**)	$CuCl_3ON$	TB	3.10	1.90	—	O, 1.91–1.94	—	331
	$CuCl_3OO'$	—	—	—	—	—	—	
$(Me_4N)_4[CuOCl]_4$	$CuCl_3OCl'$	TB	—	1.93	2.21	—	—	713
$[Cu_4OCl_6(OPPh_3)_4]$	$CuCl_3OO'$	—	—	1.90	2.38	—	—	713
$[Cu_4OCl_6(py)_4]$	$CuCl_3ON$	TB	—	1.90	2.41	—	—	714
$[Cu_4OCl_6(2\text{-Mepy})_4]\cdot xH_2O$	$CuCl_3ON$	TB	3.04, 3.21	1.86–1.93	2.31–2.45	1.96–2.1	—	715
(*b*) $[CuLCO(CH_2)_nNR_2]_4$								
$[CuBr(OCH_2CH_2NEt_2)]_4\cdot 4CCl_4$ (**332**)	$CuNBrO_3$	DSBP	3.18, 3.52	1.92–1.98	2.52	Br, 2.39	—	716
$[Cu(NCO)(OCH_2CH_2NMe_2)]_4$	$CuNNO_3$	DSBP	2.9–3.5	1.95–1.97	2.50	N, 1.88	—	717
$[Cu(NCO)(OCH_2CH_2N(Bu)_2]_4$	$CuNNO_3$	DSBP	3.03–3.24	1.93–2.0	2.25	N, —	—	717
[Di-μ-ethoxobis{4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dionato}$Cu_2]_2$	CuO_4O'	DSBP	2.97–3.28	1.95	2.41	O, 1.95	—	718
$[Cu(L)]_4\cdot 9MeOH$[c]	CuO_4O'	DSBP	3.01–3.49	1.92	2.33–2.69	O, 2.06	—	719
$[Cu_4(C_5H_{13}N_2O)_4](SO_4)\cdot 8H_2O$	$CuNO_3O'O''$	DERO	3.2–3.5	1.95–1.97	2.57–2.58	2.02	(SO_4)-bridged-sheet	720
$[Cu_4(C_5H_{13}N_2O)_4](NO_3)_2\cdot 2H_2O$	$CuNO_3O'O''$	DERO	3.2–3.4	1.94–1.98	2.50–2.63	1.99	(NO_3)-bridged-chain	721
$[Cu_4(dmae)_4(O_2CCF_3)_4]$[d]	$CuNO_3O'O''$	DERO	3.2–3.8	1.91–1.97	2.7–2.9	2.06	Molecular	722

[a] teed = *N,N,N',N'*-tetraethylethylenediamine. [b] nmp = *N*-methyl-2-pyrrolidinone. [c] H_2L = 3-hydroxy-4-[4-(3,4-dichlorophenyl)-4-hydroxy-2-azabut-1-en-1-yl]-5-hydroxymethyl-2-methylpyridine. [d] dmae = 2-dimethylaminoethanolate anion. [e] TB = trigonal bipyramidal; DSBP = distorted square-based pyramidal; DERO = distorted elongated rhombic octahedral. [f] (a) $X = Cl_{ax}$, (b) $X = O'$.

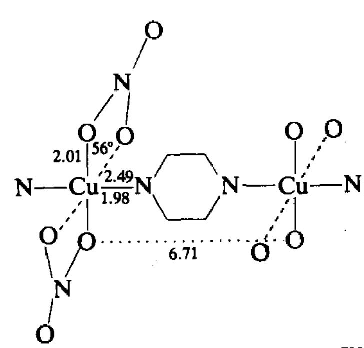
53.4.2.7 *One-dimensional chains*

While the three-dimensional structures of copper(I) are dominated by the trigonal three-coordinate and tetrahedral four-coordinate geometries, the three-dimensional structures of copper(II) (Figure 19.6) are dominated by the square pyramidal five-coordinate and octahedral six-coordinate geometries. In both cases regular structures are not involved, but elongated tetragonal and rhombic, square pyramidal and octahedral stereochemistries occur. In general a short-bonded mononuclear rhombic or tetragonal CuL_4 chromophore is present, which is then bridged through a single long bond (square pyramidal) or two *trans* long bonds (octahedral) to build up an infinite lattice in one, two or three dimensions.[10] Occasionally dinuclear chromophores are involved as the bridged unit.

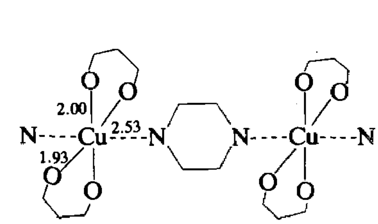
There are no linear chain structures for the copper(II) ion involving a single short-bonded monatomic bridging anion (Figure 19.6, i), but a twisted linear chain occurs, as in $[CuCl_2(DMSO)_2]$ (**334**)[724] and similar structures in Table 36. In general a trigonally distorted $CuCl_2L_2Cl'$ chromophore is involved, $\tau = 17–45\%$, with a long Cu—Cl bridging distance, a nonlinear Cu—Cl—Cu angle of 114–145° and a Cu—Cu separation of 4.3–4.8 Å. Linear Cu—Cu chains do occur with polyatomic bridging ligands such as pyrazine, as in $[Cu(pyrazine)(O_2NO)_2]$ (**335**)[728] involving short Cu—N distances of 1.98 Å, but this is uncommon. More common is a bridging role involving long or semi-coordinate Cu—L distances of 2.3–2.8 Å, as in $[Cu(hfacac)_2(pyrazine)]$ (**336**),[729] and $[Cu(hfacac)_2$(1,4-diazabicyclo[2.2.2]octane)][730] and especially oxyanions (Table 37).[731–735] In (**335**) a short Cu—N distance occurs, with the coordinated nitrate anion involved to give an off-axis long Cu—O distance and an overall $CuN_2O_2O'_2$ chromophore with a (4 + 2*) structure. In (**336**) the *trans* pyrazine ligand is involved in a long Cu—N distance (2.53 Å) and a CuO_4N_2 chromophore is present with a normal (4 + 2) structure. In $[Cu(1,3\text{-propanediamine})_2(OSO_3)]$[736] a very asymmetric bridging single sulfate oxygen atom occurs, 2.75 and 3.34 Å, but the latter is too long to be considered even semi-coordinate; the structure is described as a weak chain-like arrangement. Unsymmetrical bridging occurs in the mixed long/short bridging role of the planar crotonate anion of $[Cu(OH_2)_3(C_5O_5)]$ (**337**)[737] or of the planar oxalate anion of $[Cu(NH_3)_2(C_2O_4)]\cdot 2H_2O$ (**338**).[738] In (**337**) the bridging crotonate anion results in misalignment of the principal axis of the local elongated rhombic octahedral stereochemistry, while in (**338**) the alignment of the axes of the very rhombic $CuN_2O_2O'_2$ chromophore is retained.



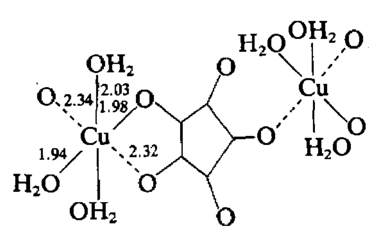
$[Cu(DMSO)_2Cl_2]$ (**334**)[724]



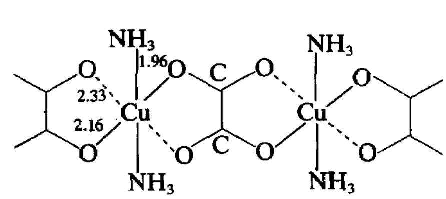
$[Cu(pyrazine)(O_2NO)_2]$ (**335**)[728]



$[Cu(hfacac)_2(pyrazine)]$ (**336**)[729]



$[(Cu(OH_2)_3(C_5O_5)]$ (**337**)[737]



$[Cu(NH_3)_2(C_2O_4)]\cdot 2H_2O$ (**338**)[738]

Double ligand bridges (Figure 19.6, ii) involve a four-coordinate CuL_4 chromophore chain of $[CuCl_2]$,[739] but the Cu environment is increased to elongated tetragonal octahedral by further overlap to give a $CuCl_4Cl'_2$ chromophore to give a two-dimensional sheet structure. A linear

Table 36 Crystallographic Data on $[CuCl_2L_2]$ Complexes Involving a Single Bridge Linear Chain

Complex	*Chromophore*	*Stereo-chemistry*[c]	τ (%)[c]	$Cu—Cl_{eq}$ (Å)	$Cu—Cl_6$ (Å)	$Cu—Cl_6—Cl$ (°)	*Cu—Cu* (Å)	*Ref.*
$[CuCl_2(DMSO)_2]$ (**234**)	$CuCl_2O_2Cl'$	SBP	44.8	2.29	2.70	145	4.76	724
$[Cu(imH)_2Cl_2]$	$CuCl_2N_2Cl$	SBP	29.0	2.37	2.75	117	4.37	725
$[Cu(caf)(OH_2)Cl_2]$[a]	Cu	SBP	29.7	2.32	2.79	128	4.60	726
$[Cu(maep)Cl_2]$[b]	$CuCl_2N_2Cl_2$	SBP	17.2	2.30	2.79	114	4.26	727

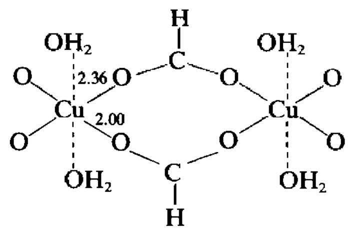
[a] caf = caffeine. [b] maep = 2-(2-methylaminoethyl)pyridine. SBP = square-based pyramidal. [c] See (**226**).[508]

Table 37 Crystallographic Data on Bridging Oxyanions (Linear, Figure 19.2, i)

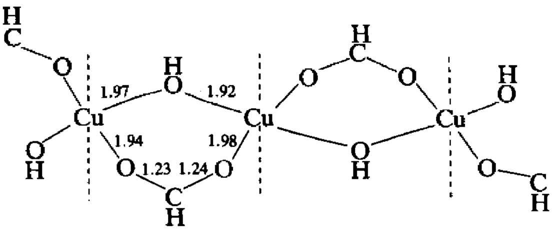
	CuL_n	*Stereochemistry*[a]	*Bridging anion*	*Cu---O* (Å)	*Units bridged*	*Ref.*
$(NO_3)^-$						
$[Cu_4(C_5H_{13}N_2O)_4](NO_3)_2\cdot 2H_2O$	$CuNO_3$	ERO	$(O_2NO)^-$	2.50–2.63	CuO_4	721
$(SO_4)^{2-}$						
$[Cu_4(C_5H_{13}N_2O)_4](SO_4)\cdot 8H_2O$	$CuNO_3$	ERO	$(O_2SO_2)^{2-}$	2.57, 2.58	CuO_4	720
$[Cu(OH_2)_2(O_2SO_2)]\cdot H_2O$	CuO_4O_2	ERO	$(O_2SO_2)^{2-}$	—	CuO_4	731
$[Cu(en)(OH_2)_2(O_2SO_2)]$	$CuN_2O_2O'_2$	ERO	$(O_2SO_2)^{2-}$	2.49, 2.49	CuN_4	732
$[Cu(bipy)(OH_2)_2(O_2SO_2)]$	$CuN_2O_2O'_2$	ERO	$(O_2SO_2)^{2-}$	2.44, 2.44	CuN_4	733
$(ClO_4)^-$						
$[Cu(bipy)_2(O_2ClO_2)](ClO_4)$	CuN_4O_2	ERO	$(O_2ClO_2)^-$	2.51, 2.75	CuN_4	734
$[Cu(bipyam)(O_2CMe)(O_2ClO_2)]$	$CuN_2O_2O'_2$	ERO	$(O_2ClO_2)^-$	2.54, 2.54	CuN_2O_2	735
$(BF_4)^-$						
$[Cu(bipy)_2(F_2BF_2)](BF_4)$	CuN_4F_2	ERO	$(F_2BF_2)^-$	2.56, 2.66	CuN_4	453, 454
$[Cu(en)_2(F_2BF_2)](BF_4)$	CuN_4F_2	ERO	$(F_2BF_2)^-$	2.56, 2.56	CuN_4	445

[a] ERO = elongated rhombic octahedral.

chain structure of pairs of (1,1-N_3)$^-$ bridges occurs in the structure of [Cu(N_3)$_2$],[740] but again with an increase of the four coplanar CuN_4 chromophores to six-coordination by longer Cu—N distances of 2.5–2.7 Å to the terminal azide nitrogen atom, the 1,1-bridging (N_3)$^-$ anions involve a tetrahedral stereochemistry at the bridging nitrogen atom. A genuine double-bridged linear chain involving a short Cu—L distance occurs in the structures of [Cu{(*n*-butyl)$_2$$PO_2$}$_2$][495] and [Cu{(*n*-hexyl)$_2$$PO_2$}$_2$] (**213**),[484] both involving symmetrically bridging (R_2PO_2)$^-$ anions, and both involving a compressed tetrahedral CuO_4 chromophore, which is as uncommon as a mononuclear CuO_4 chromophore (Table 22). A comparable chain of bridging oxyanions occurs in [Cu(O_2CH)$_2$(OH_2)$_2$]·2H_2O (**339**),[741] but with the more usual $CuO_4O'_2$ chromophore completed by two long bonded OH_2 groups which terminate cross-linking to give a clear-cut linear chain structure, but even here the terminal OH_2 groups are linked by hydrogen bonding. A less symmetrical linear chain form is present in [Cu(O_2CH)(OH)] (**340**)[742] in which short Cu—O bonded OH^- and $OCHO^-$ bridges form a linear [CuO_4] chain, but again further long Cu—O bonds of 2.58 and 2.62 Å complete an elongated octahedral CuO_6 chromophore. The structure of α-[Cu(NH_3)$_2$$Br_2$] (**243**)[536] is of interest as it has a compressed tetragonal octahedral CuN_2Br_4 chromophore involving a short axial Cu—N distance of 1.93 Å and four 'long' Cu—Br distances of 2.87 Å involving double ligand bridging (Figure 19.6, ii). While the presence of four bridging bonds is unique, it is an artifact of the temperature as a change of phase occurs at 298 K to give a normal elongated rhombic octahedral $CuN_2Br_2Br'_2$ chromophore (see **414**[1097]).[536]



[Cu(O_2CH)$_2$(OH_2)$_2$]·2H_2O (**339**)[741]



[Cu(O_2CH)(OH)] (**340**)[742]

Large planar molecules such as [Cu(phthalocyanine)] (**341**)[480] stack with their Cu atoms aligned to form an infinite chain, with a Cu—Cu separation of 3.4 Å, while in [Cu(*N*-methylsalicylaldiminato)$_2$] (**342**),[743] the planar CuN_2O_2 chromophores stack with the Cu—Cu separations aligned, but with alternate molecules rotated through 90° to facilitate packing and to give a reduced Cu—Cu distance of 3.3 Å. With planar CuO_2O_2 chromophores a more common packing involves a sideways displacement of the planar CuO_2O_2 units to give a Cu—O contact at *ca.* 3.0 Å, as in Na_2[Cu(C_2O_4)$_2$]·2H_2O (**343**),[744] where the CuO_4 chromophore has two out-of-plane contracts at 2.83 Å, to produce a Cu—Cu separation at 3.58 Å. Due to the rigid planar CuO_4 chromophore this type of linear chain results in aligned chromophores; further examples with different types of ligand atoms are given in Table 38. The sideways displacement may occur over greater distances than just one Cu—O distance, as in (propylenediammonium)[Cu(C_2O_4)$_2$] (**344**),[755] where the overlap occurs through a terminal oxygen and significantly increases the Cu—Cu separation from <4.0 Å (Table 38) to 4.9 Å in (**344**). Equally this type of planar overlap may occur through an independent bridging anion or molecule as in the semi-coordinate bridging (SO_4)$^{2-}$ anion of [Cu_2[S_2C_2{N(CH_2)$_2$OH}$_2$]-(O_2SO_2)]·2H_2O (**345**)[756] or as with the dioxane molecule of [Cu(*p*-nitrobenzoyltrifluoroacetonate)$_2$(dioxane)] (**346**).[757] Less symmetrical bridging roles of the coordinated HCO_2^- anion occur in [Cu(dien)(O_2CH)](HCO_2) (**347**),[758] in the comparable bridging role of the nitrate ion in [Cu(dien)(O_2NO)](NO_3)[759] and in [Cu(OH_2)$_2$(O_2NO)$_2$]·0.5H_2O (**245**).[558] In (**347**) the rhombic pyramidal CuN_3OO' is bridged by an off-axis formate oxygen atom to give a (4 + 1 + 1*) type of structure linked through a single bridging O atom at two long Cu—O distances of 2.17 and 2.61 Å with the CuN_2O planes stacked approximately parallel and a Cu—Cu distance of 4.7 Å. Planar overlap may also occur to give a zigzag Cu atom chain as in [Cu(en)Cl_2] (**348**),[760] and [Cu(2-aminomethylpyridine)Br_2].[761] In general bridging polydentate ligands, especially oxyanions, tend to bridge by out-of-plane chelation to produce a zigzag Cu atom chain (Figure 19.6, ii, c), while both the elongation axes and the plane of the four short in-plane bonds of the CuL_4 chromophore of the octahedron remain essentially parallel. This occurs in [Cu(bipy)(C_2O_4)]·2H_2O (**349**)[762] and contrasts with the linear copper atom chain of

$[Cu(NH_3)_2(C_2O_4)]\cdot 2H_2O$ (**338**),[738] a difference that arises from the *cis* Cu—N bonds in (**349**) compared with the *trans* arrangement in (**338**). A *cis* arrangement of the quadridentate bridging ligand of [Cu(pyrdic)(HCl)] (**350**),[763] where H_2pyrdic = 2,3-pyrazinedicarboxylic acid, results in a linear Cu chain, but with the elongation axes of the square pyramidal CuN_2ClOO' chromophore, alternating through 90° along the chains. In $[Cu(NH_3)_2(O_2CO)]$ (**351**)[764] the restricted bite of the carbonate oxyanion imposes a *cis* Cu—N arrangement and a further out-of-the-CuN_2O_2-plane Cu—O link forms a square pyramidal CuN_2O_2O' chromophore to produce a zigzag chain of Cu atoms (**351**) with hydrogen bonds linking the chains into an infinite sheet. This results in the basal planes of adjacent CuN_2O_2 chromophores being misaligned at a Cu—Cu distance of 3.5 Å. When dinuclear planar Cu_2X_2 chromophores are involved in out-of-plane long bonding, a ribbon structure of parallel Cu chains is produced with a stepped structure (Figure 19.6, ii, d). This occurs in $Li[CuCl_3(OH_2)_2]$ (**352**)[765] to give a stepped ribbon chain structure, while more complete overlap as in $(NH_4)_2[Cu_2Cl_6]$ (**353**)[766] and $[CuCl_2(MeCN)_2]$[767] gives the less pronounced stepped ribbon structure of Figure 19.6 (ii) (e). In all of these structures the bridging Cl^- anions are involved in a trigonal pyramidal coordination to three separate Cu atoms at nonequivalent distances of 2.30, 2.31 and 2.59 Å, a structural situation that is comparable to that of the unsymmetrical bridging 1,1,1-azide anion in $[Cu_3(2\text{-bzpy})_2(N_3)(N_3)_5]$ (**325**).[707] The linking of dimers may also take place *via* a single organic linkage as in $[Cu(L)(O_2CMe)]\cdot 2MeOH$ (**354**),[768] where LH_2 = *N,N'*-bis[2-{(α-hydroxybenzhydrylidene)amino}ethyl-1,2-ethanediamine]. In (**354**) the CuN_2O_2 chromophores are involved in dimerization with an adjacent chromophore with an out-of-plane Cu—O distance of 2.50 Å and acetate ligands are involved in off-axis bonding. Consequently the Cu environment is best described as (4 + 1 + 1*) six-coordinate and there are two Cu—Cu distances, 3.38 Å across the Cu_2O_2 dimer and 7.35 Å *via* the ethylenediamine link. In $[Cu_2(O_2CMe)_2(CA)]$ (**355**)[673] where CA = 1,4,7,13,16,19-hexaaza-10,22-dioxacyclotetracosane, the planar diacetates (*syn, anti*) bridged Cu_2 dimer is linked by four —$(CH_2)_3$— links to two adjacent $[Cu(O_2CMe)_2Cu]$ units to form a linear double ribbon-type chain (Figure 19.6, ii, f). In $[Cu(succinate)(OH_2)]_2$ (**356**),[769] the dinuclear $[Cu(O_2CCH_2)_4Cu]$ units are similarly linked into linear double-ribbon-type chain by the parallel —$(CH_2)_2$— linkages of the succinate anion, while in $[\{Cu(O_2CMe)_2\}(hmta)]$ (**357**),[770] where hmta = hexamethylenetetramine, the $[Cu(O_2CMe)_4Cu]$ units are combined in a zigzag chain by the tetrahedral arrangement of the nitrogen donors of the bridging hmta ligands. In $[Cu_3(im)_2(imH)_8](ClO_4)_4$ (**358**)[771] parallel chains of CuN_4O_2 chromophores are linked by bridging im ligands and bidentate semi-coordinate $(ClO_4)^-$ anions to give linear chains of Cu_3 atoms, which are coplanar with the chain lengths (**358**). This contrasts with the Cu_3 units of $[Cu_3(2\text{-bzpy})_2(N_3)(N_3)_5]$ (**325**),[707] which are triangular, and the Cu_3 planes, which are parallel to the chain length, are alternatively rotated through 90° along the chain.

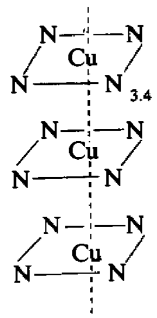
A few copper(II) complexes involve alternating CuL_n chromophore stereochemistries: chains of $[Cu_3Cl_6(C_6H_7NO)_2(OH_2)_2]$ (**359**)[772] contain alternating elongated rhombic octahedral $CuO_2Cl_2Cl'_2$ and square pyramidal CuO_2Cl_2Cl' chromophores are present and in addition there are bridging $CuCl_2Cu$ and CuO_2Cu units. In the chains of $[Cu(3\text{-pic})(1,1\text{-}N_3)(1,3\text{-}N_3)]$ (**360**),[773] while all the CuN_5 chromophores are equivalent with a square pyramidal geometry (with a tetrahedral twist), alternating pairs of bridging azide links occur, *i.e.* a symmetrical 1,1-N_3 bridging link and an unsymmetrical 1,3-N_3 bridging link. In $[CuCl_2(\textit{trans}\text{-}1,2\text{-cyclohexanediol})(THF)_2]$[774] alternating *cis*- and *trans*-$CuCl_4O_2$ chromophores are linked into a twisted chain by $CuCl_2Cu$ links. The structure of $[Cu(aep)Cl_2]$,[775] where aep = 2-(2-aminoethyl)pyridine, has been described as a twisted chain structure, but involves very long Cu—Cl distances of 3.5 Å, too long for significant bonding (Table 21). Likewise the alternate $CuCl_2Cu$ and CuS_2Cu units of $[CuCl_2(3,6\text{-dithiaoctane})]$[776] contain some rather long Cu—Cl (3.2 Å) and Cu—S (3.4 Å) distances for a twisted chain description to be appropriate.

One of the more interesting linear chain structures of copper(II) is in $Cs[CuCl_3]$ (**181**)[431] in which $CuCl_6$ chromophores with six equivalent CuCl distance of 2.39 and 2.51 Å share opposite faces to form a helical chain structure. This structure only occurs in the high temperature phase[431] and reverts to an asymmetric $CuCl_6$ chromophore (elongated rhombic octahedral) at room temperature (see Section 53.4.5).[777] The high temperature phase is associated with a crystallographic special position, which explains the presence of the unusual regular trigonal octahedral $CuCl_6$ stereochemistry. A regular $CuBr_6$ chromophore also occurs in the comparable structure of $Cs[CuBr_3]$.[778] A linear chain of elongated rhombic octahedral $CuCl_6$ chromophores sharing opposite Cl_3 faces occurs in $(ipa)[CuCl_3]$ (**361**),[779] where ipa = the isopropylammonium cation. This complex also undergoes a phase change at 51 °C, associated

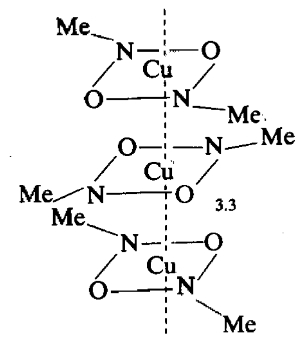
Table 38 Crystallographic Data on Planar CuX_4Y_2 Chromophores Involved in Overlap Bridging

Complex	*Chromophore Stereochemistry*[a]	*Cu—X* (Å)	*Cu—Y* (Å)	*Cu—Cu* (Å)	*Alignment* (°)	*Ref.*
$Na_2[Cu(C_2O_4)_2]\cdot 2H_2O$ (**343**)	$CuO_4O'_2$	O, 1.93	O, 2.83	2.58	0	744
Cu_2Br_2(3,5-dimethylpyridine)$_2$	$CuBr_2N_2Br'_2$	N, 2.02; Br, 2.45	Br, 3.214	4.05	0	745
Cu_2Cl_2(4-methylpyridine)$_2$	$CuCl_2N_2Cl'_2$	N, 2.07; Cl, 2.35	3.19	3.93	0	746
Cu_2Cl_2(pyridine)$_2$	$CuCl_2N_2Cl'_2$	N, 2.00; Cl, 2.30	3.03	—	0	747
Cu_2Br_2(pyridine)$_2$	$CuBr_2N_2Br'_2$	N, 2.00; Br, 2.41	2.93	—	0	748
[Cu(maleate)$_2(OH_2)_4$]	$CuO_4O'_4$	O, 1.93; O, 1.96	2.68	3.60, 9.7	0	749
$[Cu(C_2H_5N_4O_2)_2]\cdot C_2H_6N_4O_2$	$CuN_4N'_2$	N, 1.93; O, 1.93	2.89	—	0	750
[Cu(semicarbazide)Cl_2]	$CuNOCl_2Cl'_2$	N, O, 1.93; Cl, 2.27	2.90	—	0	751
[CuBr(3-*N*,*N*-dimethylamino-1-propanolate)]	$CuNOCl_2Br'$	N, O, 2.01; Cl, 2.40	3.13	3.06	0	752
$CuF_2\cdot 2H_2O$	$CuO_2F_2F'_2$	O, 1.94; F, 1.90	2.47	—	0	753
$CuCl_2\cdot 2H_2O$	$CuO_2Cl_2Cl'_2$	O, 1.96; Cl, 2.29	2.94	—	0	754

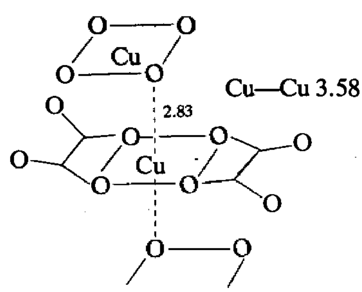
[a] ERO = elongated rhombic octahedral.



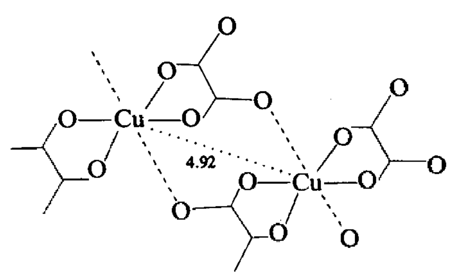
[Cu(phthalocyanine)] (**341**)[480]



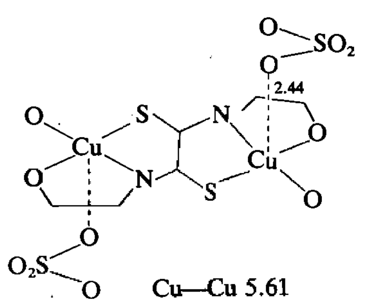
[Cu(*N*-methylsalicylaldiminato)$_2$] (**342**)[743]



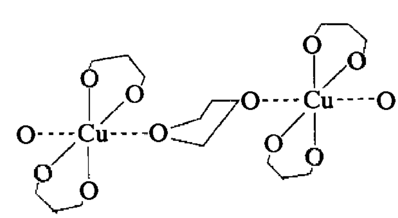
$Na_2[Cu(C_2O_4)_2]\cdot 2H_2O$ (**343**)[744]



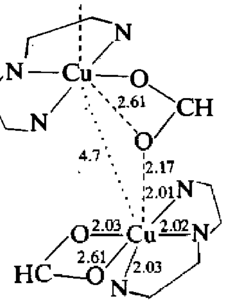
[propylenediammonium][$Cu(C_2O_4)_2$] (**344**)[755]



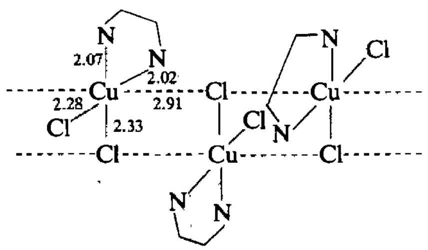
$[Cu_2\{S_2C_2[N(CH_2)_2OH]_2\}(O_2SO_2)]\cdot 2H_2O$ (**345**)[756]



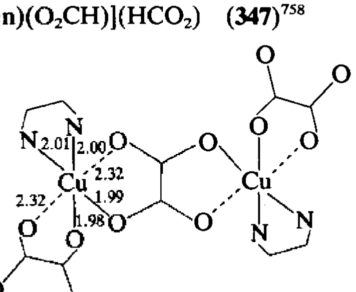
[Cu(*p*-NO_2btfa)$_2$(dioxane)] (**346**)[757]



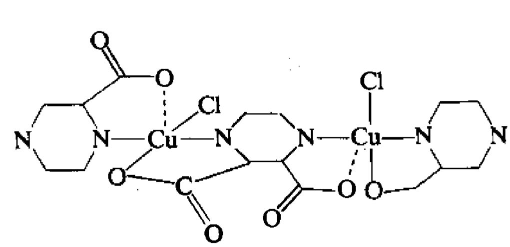
[Cu(dien)(O_2CH)](HCO_2) (**347**)[758]



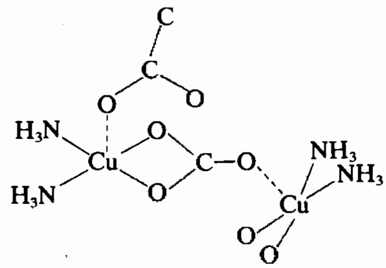
[Cu(en)Cl_2] (**348**)[760]



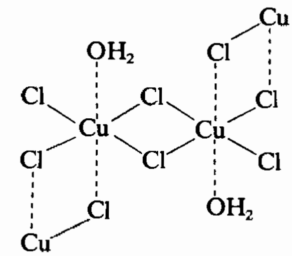
[Cu(bipy)(C_2O_4)]·$2H_2O$ (**349**)[762]



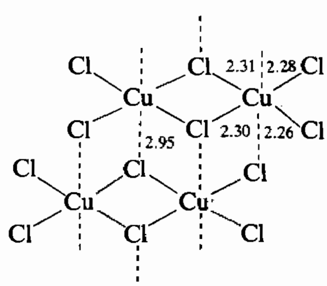
[Cu(pyridic)(HCl)] (**350**)[763]



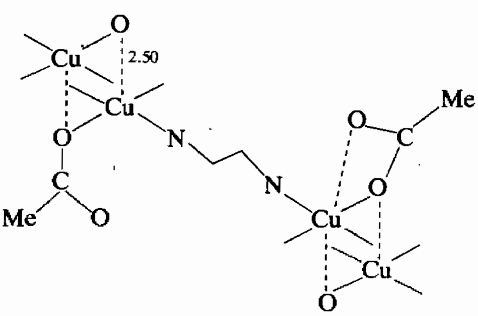
$[Cu(NH_3)_2(O_2CO)]$ (**351**)[764]



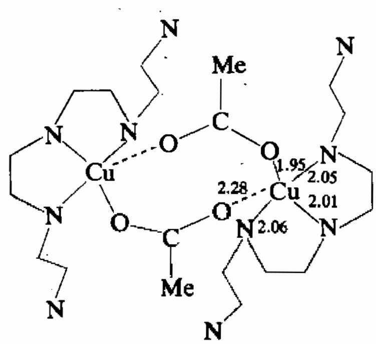
$Li[CuCl_3(OH_2)_2]$ (**352**)[765]



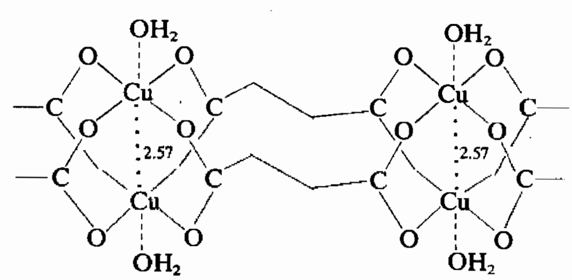
$(NH_4)_2[Cu_2Cl_6]$ (**353**)[766]



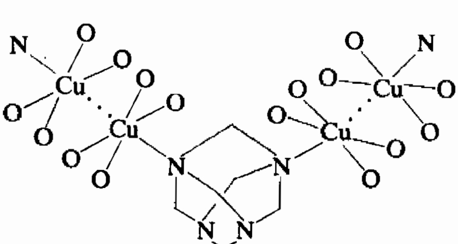
$[Cu(L)(O_2CMe)]\cdot 2MeOH$ (**354**)[768]



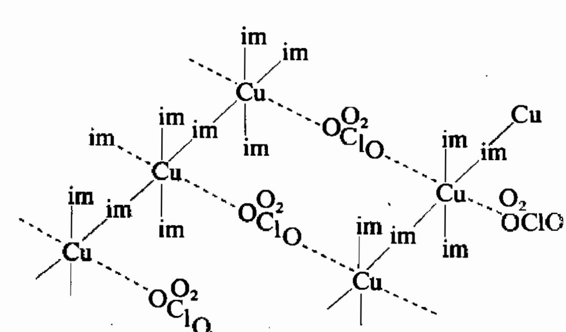
$[Cu_2(O_2CMe)_2(CA)]$ (**355**)[673]



$[Cu(succinate)(OH_2)]_2$ (**356**)[769]

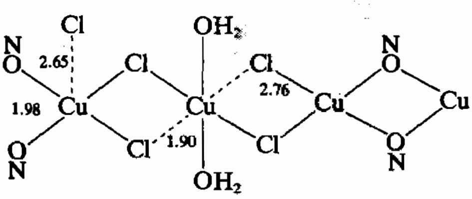


$[\{Cu(O_2CMe)_2\}_2(hmta)]$ (**357**)[770]

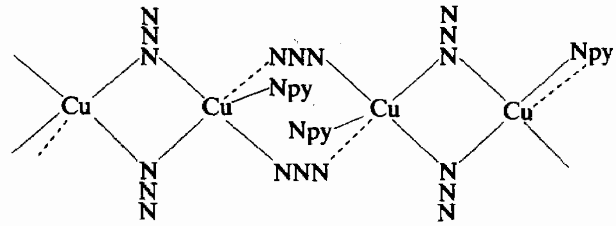


$[Cu_3(im)_2(imH)_8](ClO_4)_4$ (**358**)[771]

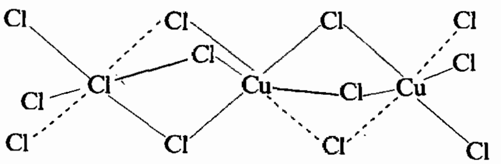
not with the structure of the $[CuCl_3]_n$ chain but with disorder of the ipa cation. Three nonequivalent bridging monatomic ligands also occur in the elongated rhombic octahedral $CuCl_4O_2$ chromophore of $[CuCl_2(TMSO)]$ (**362**)[780] and $[CuCl_2(DMSO)]$,[780] where TMSO = tetramethylene sulfoxide and DMSO = dimethyl sulfoxide. With polyatomic bridging ligands three bridges can still occur as in $[CuCl_2(1,2,4\text{-triazole})]$ (**363**)[781] and in $[Cu(OH)(benzotriazole)]$ (**364**)[782] in which an unusual long-bonded bridging OH^- anion occurs. In both structures the bridging axial ligand cants the axial direction to give a buckled linear chain. A similar structure occurs in $[Cu(OH_2)_2(O_2CPh)_2]\cdot H_2O$ (**365**),[783] where the bridging $(O_2CPh)^-$ buckles the $[Cu(OH_2)_4]$ chain to enable the OH_2 groups to act as an unusual short-bonded bridging ligand.



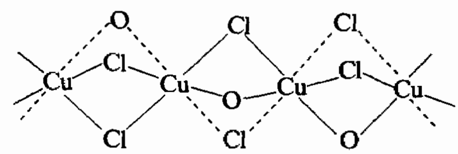
$[Cu_3Cl_6(C_6H_7NO)_2(OH_2)_2]$ **(359)**[772]



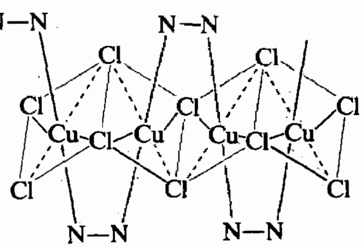
$[Cu(3\text{-pic})(1,1\text{-}N_3)(1,3\text{-}N_3)]$ **(360)**[773]



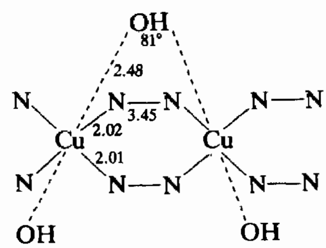
(ipa)$[CuCl_3]$ **(361)**[779]



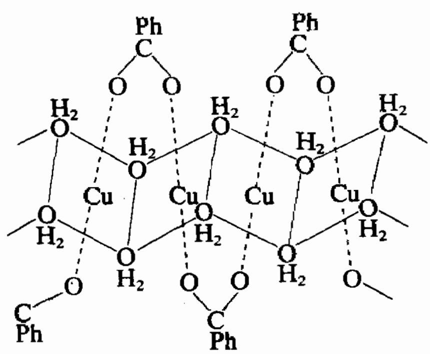
$[CuCl_2(TMSO)]$ **(362)**[780]



$[CuCl_2(1,2,4\text{-triazole})]$ **(363)**[781]



[Cu(OH)(benzotriazole)] **(364)**[782]

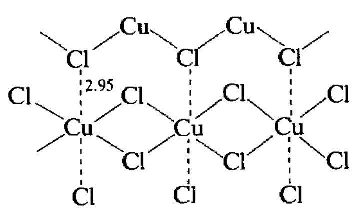


$[Cu(OH_2)_2(O_2CPh)_2]\cdot H_2O$ **(365)**[783]

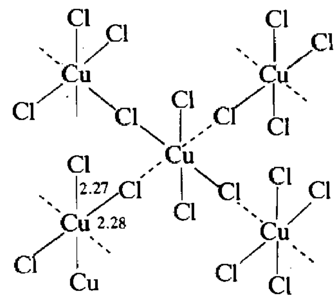
53.4.2.8 Two-dimensional layers

These generally arise (Figure 19.7) through the presence of bridging halide, hydroxide and oxyanions, with the association ranging from the formation of strong Cu—L—Cu bridges, long/short, Cu···L—Cu bridges or less strongly with long/long Cu···L···Cu bridges. Long/long interactions, at the longer distances of 2.8–3.3 Å may approach very closely to being little more than van der Waal attractions or hydrogen bonding. The majority of layer and three-dimensional structures involve the copper(II) ion in a six-coordinate environment with an elongated rhombic or tetragonal octahedral environment, but occasionally square pyramidal (4 + 1) or trigonal bipyramidal environments occur, primarily as CuO_5 chromophores.

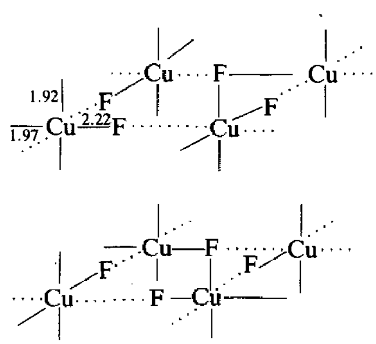
Anhydrous $CuCl_2$ has a distorted CdI_2 structure with the $CuCl_6$ **(366)**[784] environment distorted to give an elongated tetragonal octahedral stereochemistry, with the elongation axes aligned (ferrodistortive) such that chains of $[CuCl_2]_\infty$ (**366**)[784] are displaced slightly so that the coplanar $CuCl_4$ chromophores form two additional long Cu—Cl contacts at 2.95 Å to give an infinite layer structure. Halide ion layer structures involve an alternating alignment of the CuX_4X_2 chromophores (antiferrodistortive) in the plane of the layer, as in $(dienH_3)[CuCl_4]Cl$ (**367**),[785] with the space filling $[dienH_3]^+$ cations and the additional free chloride ions physically separating the layers. In $K_2[CuF_4]$ (**368**)[535] the same type of antiferrodistortive layer structures occur, but with the direction of the distortions in adjacent layers reversed, and the layers only separated by the K^+ cations. In CuF_2 (**369**)[786] a more distorted layering is present based upon a rutile lattice and the coplanar CuF_4 units are twisted out of the layer planes with respect to each other.



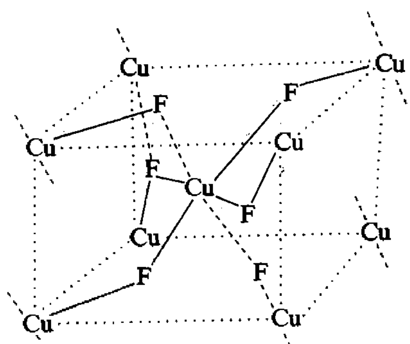
$[CuCl_2]$ (**366**)[784]



$[dienH_3][CuCl_4]Cl$ (**367**)[785]



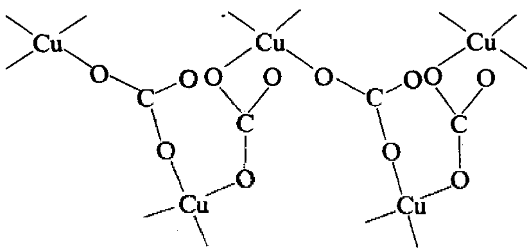
$K_2[CuF_4]$ (**368**)[535]



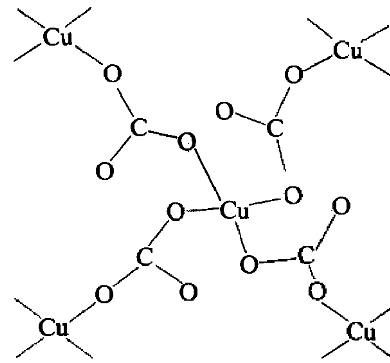
CuF_2 (**369**)[786]

Linear chains of copper(II) ions may be linked into sheets by bridging organic ligands as in $[(CuCl_2)_3(1,4\text{-oxathiane})_2]$,[787] where buckled $CuCl_2Cu$ chains are linked by bridging dioxane molecules into sheets (*cf.* **346**). The greatest potential for forming layered and three-dimensional structures probably arises with oxyanions, especially if the OH^- anion is also present. The bridging potential of the OH^- anion has already been recognized in the two-coordinate and three-coordinate bridging structures of (**263**) and (**323**), respectively. The ability of oxyanions to be involved in coordination numbers of one to twelve is reviewed in Chapter 15.5. In copper(II) oxyanion complexes these high coordination numbers and bridging roles are brought out in anhydrous complexes and Cu^{II}:oxyanion ratios greater than 1:2 and can be further increased with trigonal planar oxyanions, such as $(CO_3)^{2-}$, $(NO_3)^-$, $(NO_2)^-$, $(O_2CMe)^-$ and $(O_2CH)^-$ anions, if off-axis coordination is involved. The most simple oxyanion layer structure is that of $K_2[Cu(CO_3)_2]$ (**370**),[788] in which coplanar CuO_4 chromophores are bridged by $(CO_3)^{2-}$ anions whose planes are at *ca.* 90° to the CuO_4 planes, but even here two of the three $(CO_3)^{2-}$ oxygen atoms are involved in off-axis bonding at 2.80 Å to give a bicapped square pyramidal $CuO_4O'_2$ chromophore (see **231**) to produce a slight tetrahedral twist to the CuO_4 chromophore. In $Na_2[Cu(CO_3)_2]$ (**371**)[789] a slightly different layer structure is involved: coplanar CuO_4 chromophores are present with bridged $(CO_3)^{2-}$ oxyanions, but with the planes of the CuO_4 and $(CO_3)^{2-}$ units nearly coplanar to produce a slightly puckered layer. The layers are separated by Na^+ cations, and are stacked in such a way that each CuO_4 unit involves an additional long Cu—O distance of 2.77 Å, relative to 1.90 and 1.95 Å in the plane, to give a square pyramidal CuO_4O' chromophore and a three-dimensional lattice. In $[Cu(OH)(IO_3)]$ (**372**)[790] there are chains of $CuO_2O'_2O''_2$ chromphores involving short OH^- bridges, short-bridging $(O_2IO)^-$ anions and long single iodate oxygen bridges between the chains to give a layer structure involving a four-coordinate $(IO_3)^-$ anion, involving two short and two long

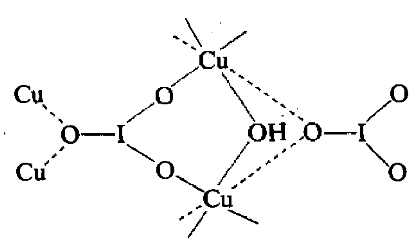
Cu—O distances. In $[Cu_2(OH)_3(ONO_2)]$ (**373**)[791] the mixed hydroxy-bridged and monodentate nitrato-bridged layers are linked by hydrogen bonding of the uncoordinated nitrate oxygen atoms to hydroxide hydrogen atoms of the adjacent layers. In the corrugated sheet structure of $[Cu(ONO_2)_2(O_2NMe)]$ (**374**)[792] bidentate bridging nitrato groups link the CuO_4 chromophores, but each of these also involves a terminal fifth ligand Cu—O distance of 2.31 Å, from a nitromethane oxygen, to give a square pyramidal CuO_4O' chromophore, in which an off-axis nitrate distance of 2.75 Å increases the coordination to a $(4+1+1^*)$ type. In $[Cu(O_2NO)_2(MeCN)_2]$[793] a similar puckered sheet structure is present involving short, intermediate and off-axis Cu—O distances, with the sheets separated by the *trans* Cu—NCMe ligands above and below each Cu atom. In $(PhCH_2NH_3)_2[Cu(C_2O_4)_2]$ (**375**),[794] aligned rhombic coplanar $[Cu(C_2O_4)_2]^{2-}$ anions are linked by long Cu—O distances to terminal oxalate oxygens to give a $CuO_2O'_2O''_2$ chromophore and an infinite layer structure.



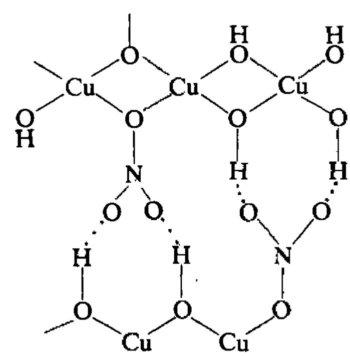
$K_2[Cu(CO_3)_2]$ (**370**)[788]



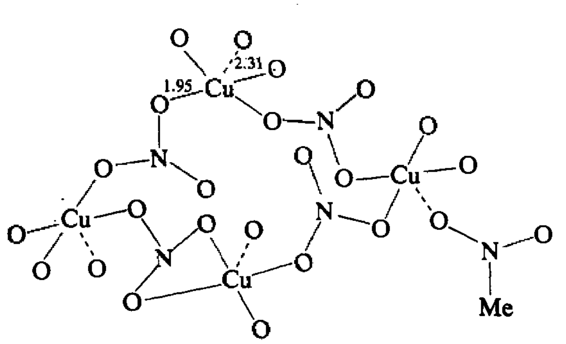
$Na_2[Cu(CO_3)_2]$ (**371**)[789]



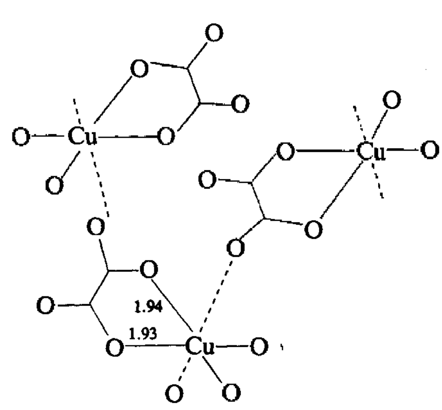
$[Cu(OH)(IO_3)]$ (**372**)[790]



$[Cu_2(OH)_3(ONO_2)]$ (**373**)[791]

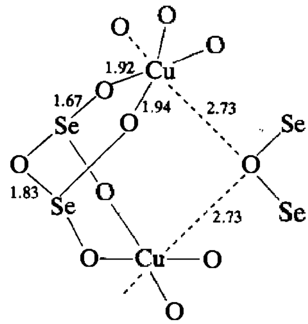


$[Cu(O_2NO)_2(O_2NMe)]$ (**374**)[792]



$[PhCH_2NH_2]_2[Cu(C_2O_4)_2]$ (**375**)[794]

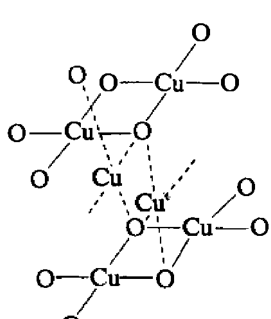
In $[Cu(Se_2O_5)]$ (**376**)[795] the unusual three-dimensional structure of the four-coordinate $(Se_2O_5)^{2-}$ anions (Chapter 15.5) links the rhombic octahedral $CuO_2O'_2O''_2$ chromophore into zigzag chains, with a 90° misaligned principal axis, which are cross-linked into sheets.



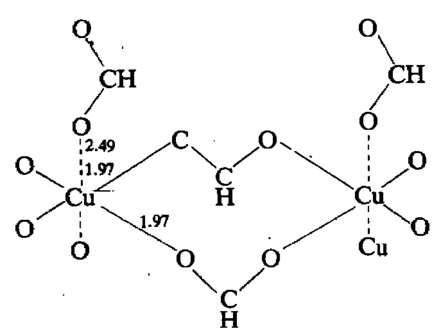
$[Cu(Se_2O_5)]$ **(376)**[795]

53.4.2.9 *Three-dimensional structures*

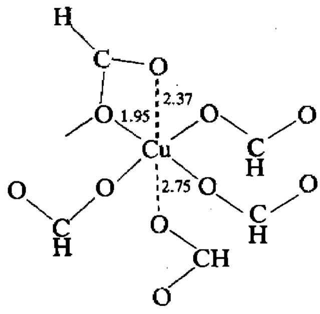
The most simple three-dimensional structure of copper(II) is that of [CuO] **(377)**,[796] which has a distorted PdO-type structure (ref. 10, Figure 12.4b) with two interpenetrating linear chains of planar CuO_4 chromophores sharing common tetrahedral O atoms. While independent linear chains of symmetrically bridging formate anions (*anti–anti*) occur in $(NH_2Me_2)[Cu(O_2CH)_3]$ **(378)**[797] to form an infinite lattice of centrosymmetric elongated rhombic octahedral CuO_6 chromophores, a less symmetrical CuO_6 chromophore occurs in anhydrous α-$[Cu(O_2CH)_2]$ **(379)**,[570] in which two formate anions bridge to separate Cu atoms, but one is also involved in out-of-plane chelation to produce a restricted elongation of 2.37 Å compared to one of 2.78 Å in the *trans* Cu—O position. In anhydrous $[Cu(CO_3)]$ **(380)**[798] sheets of coplanar CuO_4 chains are linked into coplanar sheets by bidentate $(O_2CO)^{2-}$ bridges with the sheets stacked, such that there is a short out-of-plane Cu—O distance of 2.25 Å, which results in the Cu atom being lifted out of the plane ($\rho = 0.48$ Å) to give a square pyramidal CuO_4O' chromophore. In the sublimed form of anhydrous $[Cu(NO_3)_2]$ **(381)**[799] linear chains of bidentate nitrate bridges occur in two dimensions to give a layer structure, but *trans* pairs of bridging nitrate groups are involved in the interlayer direction at 2.68 Å. These oxygens are further linked to a Cu atom in an adjacent layer at 2.43 Å to yield an unsymmetrical elongated rhombic octahedral CuO_6 chromophore. In anhydrous $[Cu(O_2SO_2)]$ **(382)**,[800] bridging five-coordinate $(SO_4)^{2-}$ anions (see Chapter 15.5) are present to yield an elongated rhombic octahedral $CuO_4O'_2$ chromophore, linking six-coordinate $(SO_4)^{2-}$ anions (Chapter 15.5) into an infinite lattice, with chains of Cu—Cu atoms linked at 3.3 Å. CuO_5 chromophores with a trigonal bipyramidal stereochemistry and a one-, two- or three-dimensional bridged structure are much less common, but they occur in $[CuGaInO_4]$ **(222)**.[503] Table 39 summarizes some examples of oxyanion structures involving CuO_n chromophores, their stereochemistry, the coordination number of the oxyanion (see Chapter 15.5) and their lattice type. It is then of interest that the proposed structure for $[Cu(O_2ClO_2)_2]$ (Chapter 15.5, Figure 4) has a six-coordinate ($4+2^*$) structure,[423] with an unusually short Cu—Cu distance of 3.01 Å, compared to 3.3 Å in $[CuSO_4]$ **(382)**.[800]



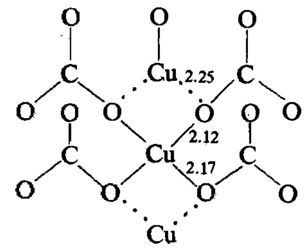
[CuO] **(377)**[796]



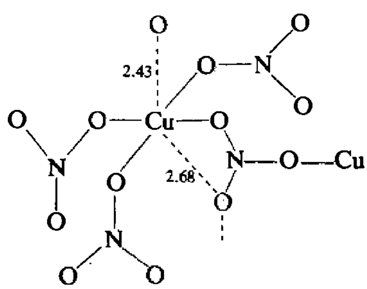
$[NH_2Me_2][Cu(O_2CH)_3]$ **(378)**[797]



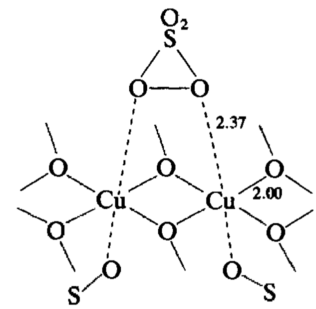
α-$[Cu(O_2CH)_2]$ (**379**)[700]



$\rho = 0.48$ $[Cu(CO_3)]$ (**380**)[798]



α-$[Cu(O_2NO)_2]$ (**381**)[799]



$[Cu(O_2SO_2)]$ (**382**)[800]

Table 39 Selection of Coordinated Oxyanions and Anhydrous Transition Metal Oxyanion Salts[a]

Complex	*Chromophore*	*Coordination no.*	*Stereochemistry*[c]	*Oxyanion coordination no.*	*Type of lattice*	*Ref.*
$[Cu(O_2PEt_2)]$	CuO_4	4	CTd	II	Chains	496
$[Cu(tsglyo)_2]$[b]	CuO_4O'	5	SBP	III	Chains	801
$[Cu(O_2PF_2)_2]$	$CuO_4O'_2$	6	ERO	III	Sheet	802
$[Cu(Se_2O_5)]$ (**376**)	$CuO_4O'_2$	6	ERO	III	Sheet	795
$[Cu(ClO_4)_2]$	CuO_4	4	SP	II	Sheet	423
$[Cu(CO_3)]$ (**380**)	$CuO_4O'_2$	5	SBP	V	Sheet	798
$[Cu(NO_3)_2]$ (**381**)	$CuO_4O'_2$	6	ERO	III	Three dimensional	799
$[Cu(O_2CH)_2]$ (**379**)	CuO_4O'	6	ERO	III	Three dimensional	569
$[Cu(SO_4)]$ (**382**)	$CuO_4O'_2$	6	ERO	VI	Three dimensional	800
$[CuGaInO_4]$ (**222**)	$CuO_2O'_3$	5	TB	—	Three dimensional	503
$[Cu_3(PO_4)_2]$	$CuO_4O'_2$	6	ERO	IX	Three dimensional	803
$[Cu_3(TeO_6)]$	$CuO_2O'_2$	6	ERO	XVIII	Three dimensional	804
$[Cu_3WO_6]$	CuO_2O_3	5		XV	Three dimensional	805

[a] For a discussion of oxyanion coordination numbers see Chapter 15.5, structures I–IV. [b] tsglyo = *N*-tosylglycinate. [c] CTd = compressed tetrahedral; SBP = square-based pyramidal; ERO = elongated rhombic octahedral; TB = trigonal bipyramidal; LB = long bipyramidal; SP = square planar.

53.4.2.10 Summary of the stereochemistries of polynuclear copper(II) complexes

For the polynuclear complexes of the copper(II) ion, as summarized in the molecular structures (**256**)–(**382**), Tables 28 to 34 and Figure 19, the following generalization may be made:

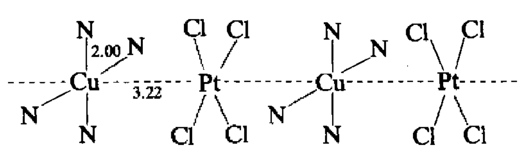
(a) the mononuclear chromophore stereochemistries are still recognizable with elongated rhombic ≈ square pyramidal > square coplanar > compressed tetrahedral > trigonal bipyramidal;

(b) The number of bridging groups varies: $2 > 4 \gg 1 \approx 3$;

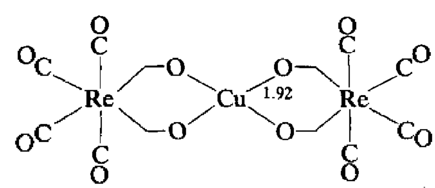
(c) in molecular polynuclear structures: dinuclear > tetranuclear > trinuclear, pentanuclear and hexanuclear structures;
(d) in infinite structures, chain, sheet and infinite lattices all occur with comparable frequency;
(e) the types of distortion observed with mononuclear complexes (see Section 53.4.2.1) are still recognizable in polynuclear structures, but the extent of the distortions are less due to the restrictions of the bridging ligands limiting the plasticity effect;
(f) due to the presence of rigid bridging ligands fluxional behaviour is generally absent, but fluxional linear chains occur in $Cs[CuCl_3]$ (**181**) and $[Cu(NH_3)_2Br_2]$ (**234**) and a fluxional three-dimensional lattice occurs in $K_2Pb[Cu(NO_2)_6]$ (**177**) and $Cs_2[PbCu(NO_2)_6]$ (**250–252**); and
(g) the Cartesian axes of the local molecular chromophore of the copper(II) ions may be found to be equally aligned or misaligned.

53.4.3 Mixed Metal Complexes of Copper(II)

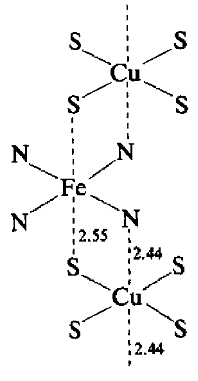
These are not very well characterized for copper(II) but some examples are listed in Table 40. They include $[Cu(NH_3)_4PtCl_4]$ (**383**),[806] Millon's salt, which involves an infinite chain structure of alternate planar CuN_4 and $PtCl_4$ chromophores with a Cu—Pt distance of 3.22 Å, with the Cu—N and Pt—Cl directions displaced by *ca.* 26° about the Cu—Pt direction. In general four-, five- and six-coordinate geometries occur for both metals with the copper(II) ion exhibiting the normal mononuclear static structures of Figure 19. Thus in meta-Zeunerite[807] an elongated tetragonal CuO_4O_2' chromophore is present, while in $[CuHg(OH)_2(ONO_2)_2(OH_2)_2]$[810] the same chromophore occurs with single oxygen nitrate bridging ligands generating an infinite sheet structure. A trinuclear Re_2Cu unit occurs in $[\{Re\text{-}cis\text{-}(OC)_4\}_2(MeCO)_2Cu]$ (**384**)[811] and a tetranuclear Cu_2Fe_2 unit in $[Cu_2Fe_2C_{138}H_{102}N_{17}S_8Cl_8]$ (**385**),[813] with a coplanar CuN_4 chromophore in the former and a CuS_4N_2 chromophore in the latter.



$[Cu(NH_3)_4][PtCl_4]$ (**383**)[806]



$[\{Re\text{-}cis\text{-}(OC)_4\}_2(MeCO)_2Cu$ (**384**)[811]



$[Cu_2Fe_2C_{138}H_{102}N_{17}S_8Cl_8]$ (**385**)[813]

53.4.4 Electronic Properties of Copper(II) Complexes

53.4.4.1 Introduction

The chemistry of the copper(II) ion differs from that of the copper(I) ion in that while the latter has a closed shell configuration, $(Ar)3d,$[10] and forms diamagnetic and colourless complexes,[10,17,27] the former has an incomplete *d* shell configuration, $(Ar)3d,$[9] and its

Table 40 Copper(II) Mixed Metal Complexes

Complex	*Chromophore*		*Geometry*[c]	*Bond lengths* (Å)	*Comments*	*Ref.*
$[Pt(NH_3)_4CuCl_4]$(Becton's salt) (**383**)	PtN_4	$CuCl_4$	SP/EO	Pt—N, 2.03; Cu—Cl, 2.27, 2.30, 3.26	Layered structure	806
$[Cu(NH_3)_4PtCl_4]$(Millon's salt)	CuN_4	$PtCl_4$	SP/SP	Pt—Cl, 2.298; Cu—N, 2.00	Linear chains	806
$[Cu(UO_2)(AsO_4)]\cdot 8H_2O$(meta-zeunerite)	CuO_4O_2	UO_2O_4	EO/O	U—O, 1.78, 1.94, 2.18; Cu—O, 2.14, 2.57	Linear chains	807, 808
$[IrCl(PPh_3)_2(\mu\text{-dppn})(\mu\text{-NO})CuCl](PF_6)_2$[a]	IrN_3P_2Cl	CuN_3Cl	O/RC	Cu—Cl, 2.15; N, 1.98–2.01	Dinuclear	809
$[CuHg(OH)_2(ONO_2)_2(OH_2)_2]$	CuO_4O_2'	HgO_4O_2'	SBP/SBP	—	—	810
$[\{Re\text{-}cis\text{-}(OC)_4\}_2(MeCo)_2Cu]$ (**384**)	ReC_4C_2'	CuO_4	O/SP	Cu—O, 1.92	Trinuclear	811
$[\{Cu(apoxa)\}_3Co](ClO_4)_2\cdot 4H_2O$[b]	CuN_4	CoO_6	SP/O	—	Tetranuclear	812
$[CuFe_2C_{138}H_{102}N_{17}S_8Cl_8]$ (**385**)	CuS_4	FeN_4S_2	RC/O	Cu—S, 2.28	Tetranuclear	813

[a] dppn = 3,6-di(2-pyridyl)pyridazine. [b] apoxa = *N,N'*-bis(aminoalkyl)oxamide. [c] SP = square planar; EO = elongated octahedral; O = octahedral; RC = rhombic coplanar; SBP = square-based pyramidal.

complexes are predominantly paramagnetic and almost always highly coloured.[10,17,22] As the detailed electronic behaviour of the copper(II) ion is determined by its stereochemical environment,[47,48] the electronic properties are just as variable as the stereochemical environments described in Section 53.4.2. Consequently, an extensive literature exists on the magnetic properties,[22,583,584] ESR spectra,[814–816] electronic spectra,[47,817] and redox properties,[818,819] of copper(II) complexes and attempts to relate these to the underlying copper(II) stereochemistry.[47,48] In many cases an attempt is made to use the electronic properties to predict the local copper(II) environment, a process that is unreliable, especially if incomplete electronic data are used,[820,821] but can produce useful correlations for closely related series of complexes.[822,823]

The following sections (53.4.4.2–6) attempt to describe the electronic properties of simple mononuclear complexes of the copper(II) ion,[47,48] to show how these are related to the different stereochemistries of the copper(II) ion and how these properties are modified by the formation of polynuclear complexes.[17,30] Particular emphasis is placed on the appearance of the different types of electronic property and how they may be used to provide qualitative evidence for the different types of copper–copper interactions, and hence for possible polynuclear structure formation, particularly in the solid state. While the main emphasis will be on the electronic properties in the solid state, where X-ray evidence may be obtained for a single magnetic species,[10] the measurement of the electronic properties in solution will also be described, although in solution a mixture of complex species may be present in equilibrium and complicate the interpretation of the electronic properties.[584,816,817,824]

The copper(II) ion has an (Ar)$3d^9$ outer electron configuration.[47,48] The effective single electron present has an orbital angular momentum quantum number $l = 2$, and as there is only one effective unpaired electron, the total orbital angular momentum $L = 2$. The spin multiplicity is given by $r = 2S + 1$, where S is the total spin angular momentum, in this case 1/2, so $r = 2$. Together, these give rise to a ^2D spectroscopic ground state for the copper(II) ion. As there is only one unpaired electron, there are no Russell–Saunders terms of higher energy.[817] The way in which the ^2D term splits in an octahedral or tetrahedral crystal field may be understood using the appropriate Orgel diagram (Figure 26a).[817,825,826] The levels in the octahedral symmetry are further split in an elongated tetragonal octahedral crystal field (D_{4h} symmetry) and the sense of this splitting is understandable when the origin of the symmetry labels is appreciated.[826] These may be understood by considering the way in which the d orbitals of the copper(II) ion are split in crystal fields of different symmetry (Figures 26a and 27a and b). In an octahedral crystal field the $d_{x^2-y^2}$ and d_{z^2} orbitals are destabilized relative to the d_{xz}, d_{yz} and d_{xy} orbitals by the crystal-field splitting parameter, Δ. In an elongated tetragonal octahedral stereochemistry, these levels are further split with the $d_{x^2-y^2}$ and d_{xy} levels further destabilized relative to the octahedral levels, and the d_{z^2}, d_{xz} and d_{yz} levels stabilized. For the copper(II) ion with a d^9 configuration, this yields a one-electron orbital configuration in D_{4h} symmetry of d_{xz}^2, d_{yx}^2, d_{xy}^2, $d_{z^2}^2$, $d_{x^2-y^2}^1$ or e_g^4, b_{2g}^2, a_{1g}^2, b_{1g}^1, using the symmetry representations of the d orbitals in D_{4h} symmetry. These configurations then represent the ground state of the copper(II) ion in this stereochemistry, but as there is only one unpaired electron present the symmetry of the state is the same as the symmetry of the one-electron orbital in which it is contained, namely, in this case, b_{1g}. Hence the spectroscopic state is $^2B_{1g}$, using a capital letter to distinguish the spectroscopic state from the one-electron orbital level. The equivalence of the spectroscopic states derived from the Orgel diagrams[825] and the one-electron orbital configurations for both the ground states and the excited states are shown in Figures 26(a) and (b). From Figure 26 it can be seen that the ground state of the copper(II) ion in an elongated tetragonal octahedral crystal field of D_{4h} symmetry may be equally well described as a single electron in a $d_{x^2-y^2}$ or b_{1g} level or by a $^2B_{1g}$ spectroscopic state. The labels for the excited states may be understood similarly. As the symmetry labels vary with the molecular point groups of the different crystal fields,[827] the d orbital description is preferred and will be used hereafter.

The one-electron orbital sequences of the main stereochemistries of the copper(II) ion described in Figure 19.1 may be derived by a corresponding method and are shown in Figures 27(a) and (b). Crystal-field calculations cannot give the precise energies or even the ordering of these levels,[828–832] for example they cannot determine whether the d_{z^2} orbital lies above or below the d_{xy}, d_{xz} or d_{yz} levels in a square coplanar stereochemistry, but crystal-field calculations can specify which of the five d orbitals has the highest energy and which, therefore, will contain the odd electron of the d^9 configuration; these are summarized in Table 41. The vast majority of copper(II) complexes (see previous section) give rise to orbitally degenerate

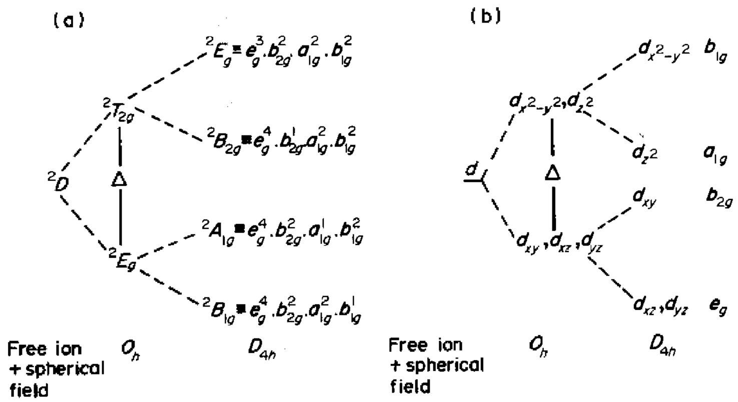


Figure 26 The relationship between the spectroscopic states and the one-electron energy levels for the copper(II) ion in an elongated tetragonal octahedral crystal field

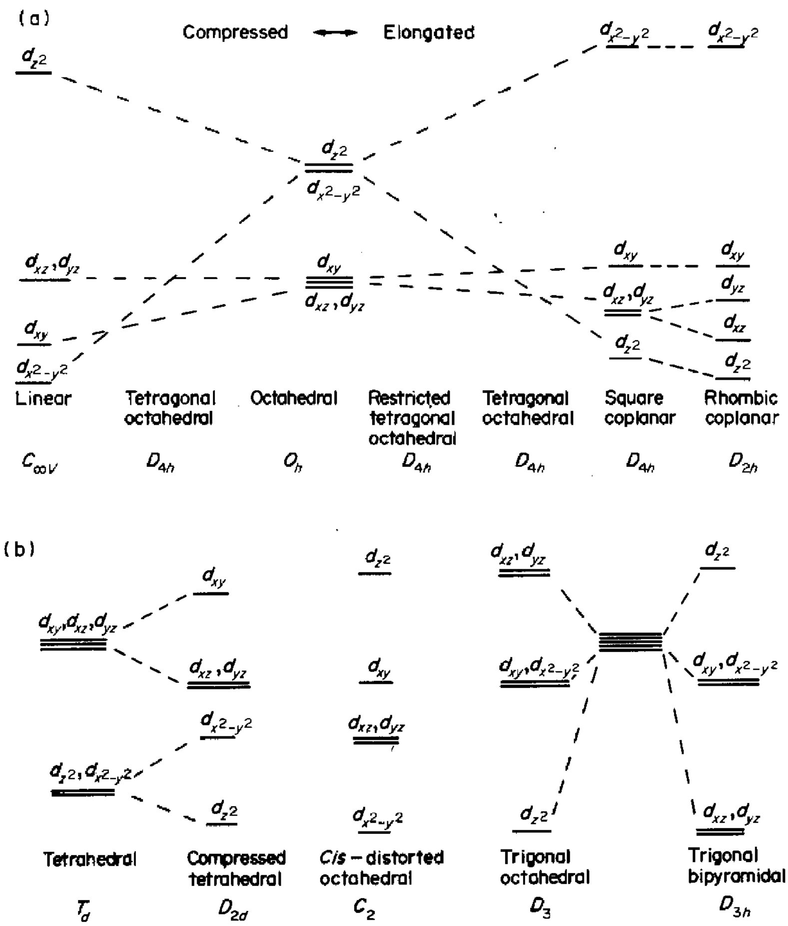


Figure 27 (a) The splitting of the one-electron energy levels of the copper(II) ion in crystal fields of axial and rhombic symmetry; (b) The splitting of the one-electron energy levels of the copper(II) ion in crystal fields of tetrahedral, *cis*-distorted octahedral, trigonal octahedral and trigonal bipyramidal symmetry

ground states[48] involving a *static* form of distortion, *i.e.* square coplanar. The majority also involve a $d_{x^2-y^2}$ ground state, but a number involve either a d_{z^2} or d_{xy} ground state. The degenerate ground state configurations shown in 4 and 5 of Table 41, are uncommon and usually involve some form of dynamic or pseudo-dynamic Jahn–Teller effect,[396,397] which removes the orbital degeneracy of the ground state (see Section 53.4.5).

The magnetic and electron spin resonance (ESR) properties of copper(II) complexes are

Table 41 The One-electron Orbital Ground States for the Known Stereochemistries of the Copper(II) Ion[a]

1. $d^1_{x^2-y^2}$	Elongated tetragonal octahedral
	Elongated rhombic octahedral
	Square coplanar
	Square-based pyramidal
	Compressed tetragonal octahedral
	Square coplanar
2. $d^1_{z^2}$	Linear
	Trigonal bipyramidal
	Cis-distorted octahedral
3. d^1_{xy}	Compressed tetrahedral
	Square coplanar — $Cu(acac)_2$-type
4. $d^2_{z^2}, d^1_{x^2-y^2}$ or $d^1_{z^2}, d^2_{x^2-y^2}$ [b]	Octahedral
5. d^2_{xz}, d^1_{yz} or d^1_{xz}, d^2_{yz} [b]	Trigonal octahedral
	Elongated tetrahedral
6. $d^2_{xy}d^2_{xz}d^1_{yz}$ [b]	Tetrahedral

[a] Figure 1; see text for notation. [b] These configurations are orbitally degenerate. In 5 and 6 this orbital degeneracy is removed by spin–orbit coupling, but it is not removed by this mechanism in 4 (see Section 53.4.5).

mainly determined by the electronic configuration of the ground state, and only marginally by the electronic configuration of the excited states.[47,48] On the other hand the energies of the electronic spectra are primarily determined by the energy differences (*ca.* 7–29 000 cm^{-1}) between the ground state and the excited states, although a precise knowledge of the ground and excited state configurations is necessary to understand the selection rules which govern the transitions between these levels.[47] The following sections attempt to show the connection between the electronic properties of the copper(II) ion and the stereochemistry of its complexes.

53.4.4.2 Magnetic properties

When the individual copper(II) ions are physically well separated from each other (>5 Å), the effective magnetic moment is given by the spin-only value, $\mu_{so} = \sqrt{4S(S+1)}$, of 1.73 BM. In practice the experimental values at room temperature lie in the range 1.8–2.00 BM;[583,584,833–840] some typical values are given in Table 42. These all lie appreciably above the spin-only value of 1.73 BM, but as the electronic ground states are nondegenerate, this cannot arise from inherent orbital angular momentum in the ground state, but arises due to mixing in of some orbital angular momentum from excited states *via* spin–orbit coupling. The extent of the mixing-in is given by the expression $\mu_{eff} = (1 - 4r^2\lambda/\Delta E)\mu_{so}$, where ΔE is the energy separation of the ground state from the excited state which is being mixed in, and r is the combined orbital and spin–orbit reduction factor (see Section 53.4.4).[833] Consequently, although the observed magnetic moments are consistent with the presence of a single unpaired electron, they yield no stereochemical information.

Table 42 Some Representative Room Temperature Magnetic Moments for Copper(II) Complexes of Various Stereochemistries

Stereochemistry	*Complex*	μ_{eff} (BM)
Octahedral	$K_2Pb[Cu(NO_2)_6]$ (**177**)	1.94
Trigonal octahedral	$[Cu(en)_3](SO_4)$ (**178**)	1.91
Elongated tetragonal octahedral	$[Cu(NH_3)_4(NO_2)_2]$ (**174**)	1.81
Square coplanar	$Na_4[Cu(NH_3)_4][Ag(S_2O_3)_2]_2 \cdot OH_2$ (**176**)	1.90
Rhombic coplanar	$[Cu(3\text{-Meacac})_2]$ (**207**)	1.91
Square-based pyramidal	$[Cu(NH_3)_4(OH_2)](SO_4)$ (**219**)	1.87
Trigonal bipyramidal	$[Cu(NH_3)_2Ag(NCS)_3]$ (**223**)	1.83
	$[Co(NH_3)_6][CuCl_5]$ (**221**)	1.85
Compressed tetragonal octahedral	$Rb_2Pb[Cu(NO_2)_6]$ (**233**)	1.94
Cis-distorted octahedral	$[Cu(bipy)_2(ONO)](NO_3)$ (**253**)	1.89
Compressed tetrahedral	$Cs_2[CuCl_4]$ (**175**)	1.92
Seven coordinate	$[Cu(py)_3(O_2NO)_2]$ (**244**)	1.97
Eight coordinate	$Ca[Cu(O_2CMe)_4] \cdot 6H_2O$ (**246**)	1.94
Nine coordinate	$Ca[Cu(2\text{-cpa})_4(OH_2)] \cdot 4H_2O$ (**248**)	—

More structural information may be obtained from measurements of the bulk magnetic susceptibility of copper(II) complexes by recording the variation of the magnetic susceptibility (χ_M) with the absolute temperature (T).[833] For normal dilute copper(II) systems, the Curie behaviour[583,584] applies and the variation of χ_M against T is shown in Figure 28(a), and against $1/T$ in Figure 28(b); the former is a hyperbolic function and the latter, for $Ca[Cu(O_2CMe)_4]\cdot 6H_2O$ (**246**), is a straight line through the origin. The value of such plots is their use for identifying the presence of magnetic interactions in *non*-magnetically dilute systems. If such magnetic interactions are weak, the behaviour is still paramagnetic and the measured susceptibility is still independent of the magnetic field H, but the χ_M *vs.* $1/T$ plot does not pass through the origin; this is the Curie–Weiss relationship (Figure 28b, ----), with $\chi_M = C/(T - \theta)$, where C and θ are the Curie and Weiss constants, respectively. Unfortunately, it is not possible to relate the Weiss constant to any simple structural features and the practice has developed of ignoring the θ constant and evaluating the magnetic moments as $\mu_{eff} = 2.84\sqrt{\chi_M T}$, as listed in Table 42.

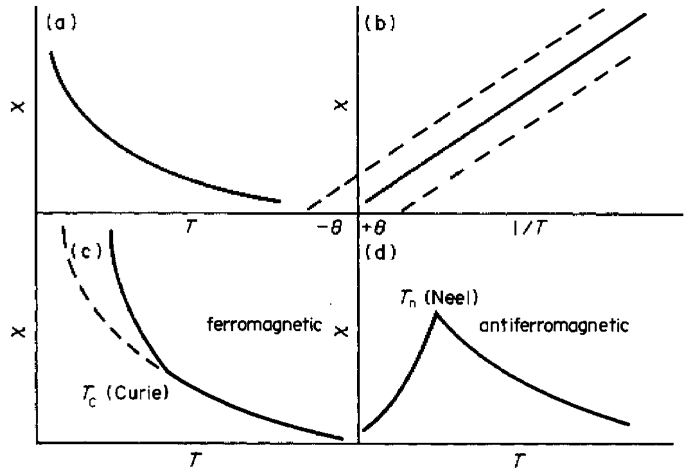


Figure 28 The temperature variable magnetic properties of copper(II) complexes: (a) paramagnetic, χ *vs.* T; (b) paramagnetic, χ *vs.* $1/T$; (c) ferromagnetic, χ *vs.* T; and (d) antiferromagnetic, χ *vs.* T

In a number of copper(II) systems the paramagnetism is more complicated and they are both temperature and field dependent. Two important cases are relevant to copper(II) complexes: these are antiferromagnetism and ferromagnetism. In both types of magnetism the Curie or Curie–Weiss law is obeyed down to a certain temperature, but below this temperature the χ *vs.* T plot shows a deviation from the simple Curie law. For ferromagnetic systems (Figure 28c) below the Curie temperature T_C the observed susceptibility rises more rapidly than predicted for the simple Curie behaviour with decreasing temperature (Figure 28a) and the value of μ_{eff} may be higher than the μ_{so} value at the lower temperature.[834] For antiferromagnetic systems below the Neel temperature T_N the observed susceptibility increases less than predicted with decreasing temperature (Figure 28d) and μ_{eff} decreases with decreasing temperature and falls well below the μ_{so} value. Thus in $[Cu(O_2CMe)_2(OH_2)]_2$ (**316**),[682–684] μ_{so} falls from 1.4 at 298 K to 0.4 BM at low temperature. This behaviour of antiferromagnetic and ferromagnetic copper(II) systems below their Curie and Neel temperatures, respectively, is due to the interaction of the single unpaired electrons on the separate copper(II) ions, the magnitude of which must be comparable to that of thermal energy kT (*ca.* 200 cm^{-1}). In the former the magnetic interaction results in a spin-pairing process (Figure 29a), while in the latter the magnetic interactions result in a parallel spin alignment of the original unpaired electrons (Figure 29b). For most copper(II) systems the magnetic interactions increase with decreasing separation of the copper(II) ions. In normal paramagnetic copper(II) complexes the magnetic interaction is very much less than the thermal energy kT and the magnetic separation $2J$ will be less than 20 cm^{-1}. Any magnetic interaction will only be apparent at near absolute zero.[583,584] For larger interactions the precise mechanism of the interaction is not thought to involve direct Cu—Cu bonding,[836] but is believed to occur *via* a super-exchange mechanism through the filled orbitals on diamagnetic bridging atoms between the copper centres, such as O^{2-}, S^{2-}, Cl^- and OH^-

anions.[835–838] However, the precise mechanism of this exchange pathway is not completely understood, but is believed to occur through a short-bonded, σ-bonding pathway by an appropriate orbital overlap of the unpaired spin on the copper(II) ion *d* orbitals, with the filled *s*, *p* or *d* orbitals (or hybrid orbitals) of the bridging atom (Figure 29c). The orbital containing the single unpaired electron is no longer entirely localized on the copper atom, but in an antibonding delocalized orbital encompassing both the copper(II) ion and the ligand atom.[839,840] The spins of the two copper(II) ions can then interact through these two delocalized 'magnetic orbitals' to yield two types of exchange interaction, kinetic and potential exchange.[836] *Kinetic exchange* arises when the 'magnetic orbital' overlap is nonorthogonal and results in antiparallel spin coupling, *i.e.* antiferromagnetism, between the two copper(II) ions, which can be considered to involve incipient bond formation. *Potential exchange* arises when the 'magnetic orbital' overlap is orthogonal, resulting in parallel spin coupling, *i.e.* ferromagnetism, between the two copper(II) ions. The orthogonal overlap may be considered as a discontinuity in the exchange pathway that blocks the transmission of the antiferromagnetic spin information between the two copper(II) ions. In general the kinetic exchange (antiferromagnetism) is stronger than the potential exchange (ferromagnetism) and both types of exchange occur together in a Cu—L—Cu bridged system. But as long as there is any nonorthogonal pathway present, the kinetic exchange will predominate and the overall interaction will be antiferromagnetic. The occurrence of a nonorthogonal pathway will be determined by the relative symmetry of the *d* orbital occupied by the unpaired electron on the copper(II) ions and the symmetry of the bridging atom filled orbital. The geometry of the bridging ligand will determine the orientation of the bridging orbitals and the symmetry of the copper(II) *d* orbitals will be determined by the stereochemistry of the CuL_n chromophore (Figures 26 and 27 and Table 41). In general the bridging ligands are monatomic, such as Cl^- or Br^-, or nearly so, *e.g.* OH^-, or polyatomic, such as N_3^- or $(C_2O_4)^{2-}$, *etc.* (see Table 43).[839–863] The stereochemistries of the local CuL_n chromophores are no different from those summarized in Figure 19.1 and their combination into polynuclear copper(II) structures are as shown in Figures 19.2–19.7. For the dinuclear series (Figure 19.2) the structures have been further classified into types I–IV, according to the number of bridging ligands present. As most magnetic information is available on dinuclear copper(II) systems, this account will concentrate on these systems.

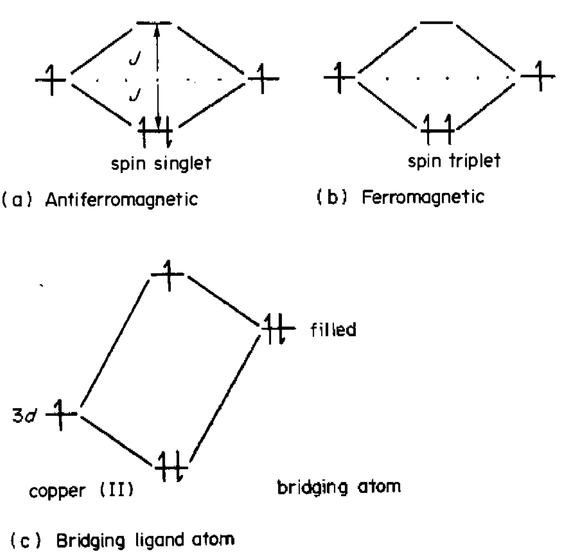


Figure 29 Magnetic interaction of separate copper(II) ions (a) antiferromagnetic and (b) ferromagnetic

Dimeric copper(II) complexes[839,840,864] can range from normal paramagnetic ($\mu_{eff} = \mu_{so}$) to ferromagnetic ($\mu_{eff} > \mu_{so}$ and $2J = +0–200\ cm^{-1}$), to antiferromagnetic but still paramagnetic ($\mu_{eff} < \mu_{so}$ and $2J = -0–300\ cm^{-1}$), to strongly antiferromagnetic ($2J > 300\ cm^{-1}$) and diamagnetic. For pronounced exchange behaviour there must generally be at least one continuous short σ-bonding pathway involved between the bridging ligand and the two copper(II) ions

(Figure 30a).[835–840,864] For antiferromagnetic systems monobridging Cu—X—Cu chromophores generally only involve weak interactions, while CuX_2Cu systems are generally more strongly antiferromagnetic. Thus, with the single CuClCu and $CuCl_2Cu$ systems[839–847] the $2J$ values are restricted to +2 to $-10\,cm^{-1}$, but vary with the Cu—Cl—Cu angle θ, and hence the Cu—Cu separation (Table 43a). For doubly bridged $Cu(OH)_2Cu$ systems (Figure 30b) a more extensive interaction is involved, with $2J$ values from +172 to $-509\,cm^{-1}$, and is clearly a function of the Cu—(OH)—Cu angle (Table 43b).[848–861,864] For the planar chromophores[839] of Figure 30(a) and (b) and for the square pyramidal chromophores of Figure 30(c), the effect of the location of the copper(II) unpaired electron in the $d_{x^2-y^2}$ (or d_{xy}) orbital is a significant factor. This is nicely illustrated for a series of $[MM(fsa)_2en(OH_2)_2]^{n+}$ cations (**386**), where the $[(fsa)_2en]^{4-}$ anion is *N,N'*-(1-hydroxy-2-carboxybenzilidene)ethylenediamine (Figure 31).[840,865] For the Cu/VO_2 complex the unpaired electron on the copper(II) cation is in a d_{xy} orbital and can overlap with the *p* orbital of the bridging O atom to form an asymmetric magnetic orbital (A'') with respect to the mirror plane (yz) of the dimer (C_s symmetry), whereas the unpaired electron on the VO_2^+ cation is in a $d_{x^2-y^2}$ orbital and can form a symmetric magnetic orbital (A'), which is orthogonal to the magnetic orbital on the copper(II) ion and hence the exchange interaction is ferromagnetic, $2J = +116$. In the Cu/Cu complex (Figure 31b) both of the magnetic orbitals are antisymmetric and nonorthogonal with the bridging oxygen *p* orbital and in this case the exchange is antiferromagnetic, $2J = -650\,cm^{-1}$. In the corresponding Cu/Cr complex (Figure 31c), which has near C_{2v} symmetry, the magnetic orbitals are again antisymmetric and symmetric, respectively, with respect to the mirror plane, and again ferromagnetism is observed, with $2J = +120\,cm^{-1}$.

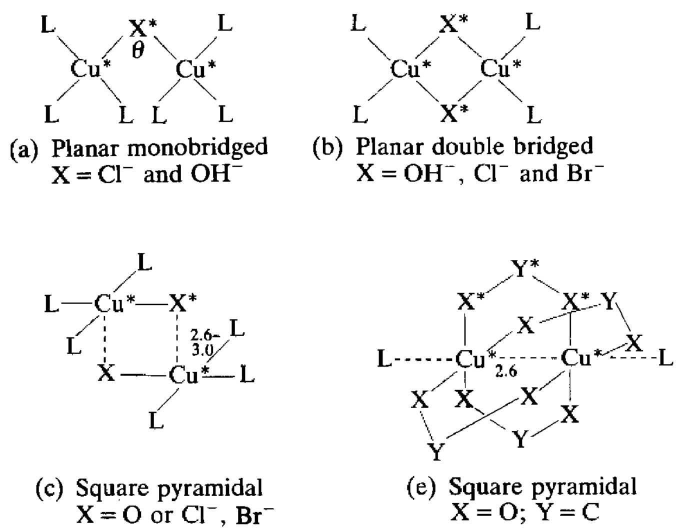


Figure 30 The main types of dimeric copper(II) structures of magnetic interest. The asterisks label the atom pathway involving short σ bonds

In the case of the bridging Cu_2X_2 units[839] (Table 43b) the cross-over points ($2J = 0$) between ferro- and antiferro-magnetic behaviour do not involve a Cu—X—Cu angle of exactly 90°, but of 97°, 103° and 104°, for $X = OH^-$, N_3^- and Cl^-. In the case of the bridging $Cu_2(N_3)_2$ unit[866] as in (**387**), the bridging involves a 1,1-N_3 end-on bridging role (see also **267**) and produces a ferromagnetic ground state with $2J = +70\,cm^{-1}$ for a θ value of 103.6°. For nonplanar Cu_2O_2 structures, as in the roof-top stereochemistry of $[Cu(MeNH_2)_2(OH)(O_2SO_2)]_2{\cdot}H_2O$ (**271**)[617] with a roof angle of 132.9° only weak antiferromagnetism, $2J = -7.9\,cm^{-1}$, occurs, which is believed to arise from an accidental near degeneracy of the magnetic orbitals of the copper(II) ion.[867] In the sideways overlap of the two parallel, but not coplanar, CuL_4 chromophores (Figure 30c) the long Cu—L distances (see **283** to **293**) lengthen the direct σ-bonding pathways and hence reduce the direct antiferromagnetic interactions to less than $-100\,cm^{-1}$ (Table 43b and refs. 868–871).[868] With monatomic bridging atoms, such as the halide ions, the Cu—Cu separation varies from 3.0 to 4.6 Å. With larger polyatom bridging groups, such as $(CN)^-$ (**388**),[871] $(N_3)^-$ (**297**)[654] and (**298**),[655] $(NCO)^-$ (**299**)[656] or $(C_2O_4)^{2-}$ (**300**),[627] the Cu—Cu separation is increased still further (>5.0 Å) and in general the antiferromagnetism is less than

Table 43 The Magnetic Behaviour of Mono-μ-bridged (CuXCu) and Di-μ-bridged (CuX_2Cu) Systems

(*a*) $X = Cl^-$	*Cu—Cl$_b$* (Å)	*Cu—Cl$'_b$* (Å)	*Cu—Cu* (Å)	*Cu—Cl$_b$—Cu* (°)	*J* (cm^{-1})	*Ref.*
Mono-μ-chloro-bridged						
$[Cu(DMSO)_2Cl_2]_2$ [a]	2.072(2)	2.290(2)	4.757(2)	144.6(1)	−6.1	724–842
$[Cu(dmaep)Cl_2]_2$ [b]	2.785(2)	2.300(2)	4.263(2)	113.58(5)	+1.58	727, 841
Di-μ-chloro-bridged						
$[Cu(py)_2Cl_2]_n$	3.026(2)	2.299(2)	3.87	88.48(5)	−9.2	843, 747
$[Cu(4\text{-}Etpy)_2Cl_2]_2$	3.21	2.28	4.00	91.9	−6.7	845, 846
$[Cu(thiazole)_2Cl_2]_2$	2.998(1)	2.322(1)	3.853(4)	91.89(2)	−3.8	847

(*b*) $X = OH^-$	*Cu—Cu* (Å)	*Cu—O* (Å)	*Cu—O—Cu* (°)	$2J$ (cm^{-1})	*g*	*θ* (K)	*Ref.*
$[Cu(bipy)(OH)]_2(NO_3)_2$	2.85	1.920–1.923	95.6	+172	2.10	−0.45	848
$[Cu(bipy)(OH)]_2(ClO_4)_2$	2.87	1.92	96.6	+93	2.22	−0.5	834, 849
$[Cu(bipy)(OH)]_2(SO_4)\cdot 5H_2O$	2.89	1.92–1.95	97.0	+49	2.20	0.10	602, 851
α-$[Cu(dmaep)(OH)]_2(ClO_4)_2$ [b]	2.94	1.936–1.947	98.45	−2.4	2.08	—	855, 856
$[Cu(eaep)(OH)]_2(ClO_4)_2$ [c]	2.92	1.895–1.930	98.8	−130	2.04	—	601, 857, 85
β-$[Cu(dmaep)(OH)]_2(ClO_4)_2$ [b]	2.94	1.900–1.919	100.4	−200	2.03	—	852, 600
$[Cu(tmen)(OH)]_2(ClO_4)_2$ [d]	2.97	1.897–1.931	102.3	−360	2.09	—	849, 859
$[Cu(tmen)(OH)]_2Br_2$ [d] (**263**)	3.00	1.902	104.1	−509	2.0	—	598, 861

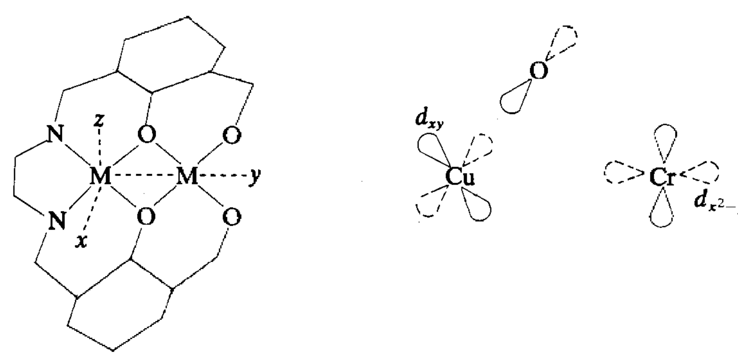
(*c*) $X = (C_2O_4)^{2-}$	*Cu—Cu* (Å)	$2J$ (cm^{-1})	*Ref.*
$[Cu_2(Et_5dien)_2(C_2O_4)](BPh_4)_2$ (**392**)	5.41	−37.4	862
$[Cu_2(tmen)_2(OH_2)_2(C_2O_4)](ClO_4)_2\cdot 1.25H_2O$ (**389**)	5.16	−385.4	863
$[Cu(dien)(C_2O_4)Cu(OH_2)_2(tmen)](ClO_4)_2$ (**390**)	4.63–5.84	−75.5	863
$[Cu_2(tmen)_2(2\text{-}Meim)_2(C_2O_4)](ClO_4)_2$ (**391**)	5.43	−13.8	863

[a] DMSO = dimethyl sulfoxide. [b] dmaep = 2-(2-dimethylaminoethyl)pyridine. [c] eaep = 2-(2-ethylaminoethyl)pyridine. [d] tmen = *N,N,N′,* tetramethylenediamine.

C_s point group

$A^1 d_{x^2-y^2}, d_{z^2}, d_{xy} M$

$A^{11} d_{yz}, d_{xz}$



(a) Cu/VO (b) Cu/Cu (c) Cu/Cr

Cu/VO		Cu/Cu		Cu/Cr	
Cu^{II}	VO^{2+}	Cu^{II}	Cu^{II}	d_{xy}	$d_{x^2-y^2}$
d^9	d^1	d^9	d^9	Cu^{II}	Cr^{III}
ground state $d'_{xy}(A^{11})$	$d_{x^2-y^2}(A^1)$	$d_{xy}(A^1)$	$d_{xy}(A^1)$	d^9	d^3
overlap $\langle d_{xy} \mid P_\sigma \rangle$	$\langle d_{x^2-y^2} \mid P_\pi \rangle$	$\langle d_{xy} \mid P_\sigma \rangle$	$\langle d_{xy} \mid P_\sigma \rangle$	$d_{xy}(A_2)$	$d_{x^2-y^2} d_{xz} d_{yz}$
					$a_1 b_2 a_2$
				$\langle d_{xy} \mid P_\sigma \rangle$	$\langle d_{x^2-y^2} \mid P_\sigma \rangle$

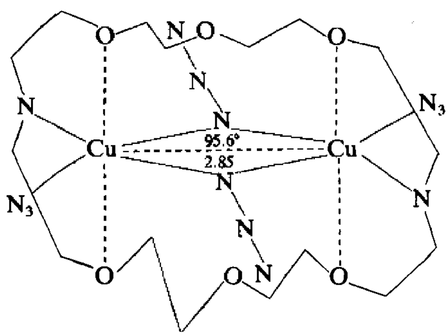
Overlap zero ∴ ferro, $2J = +116\ cm^{-1}$

Overlap non-zero ∴ antiferro, $2J = -650\ cm^{-1}$

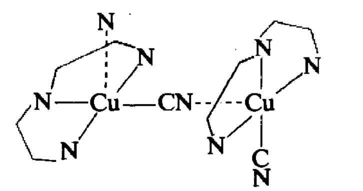
Overlap zero ∴ ferro, $2J = +120\ cm^{-1}$

Figure 31 The molecular structure of $[MM'(fsa)_2en]^+$ cation (**386**)[840]

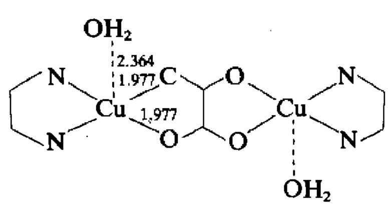
$-100\ cm^{-1}$. In addition bridging polyatomic anions can generate misalignment[871,872] of the local molecular axes of the two separate copper(II) environments in the dimer. With larger polyatomic anions, such as the $(C_2O_4)^{2-}$ anion (Table 43c), the physical separation can increase still further to >6.0 Å, but the antiferromagnetic interaction is not necessarily reduced.[873,874] In the three structures (**389**)–(**391**)[863] the axial elongations of the Cu chromophore are either square pyramidal or elongated rhombic octahedral. They are clearly defined and locate the unpaired electron on each copper(II) ion in the equatorial plane. Where the planar $(C_2O_4)^{2-}$ anion is coplanar with the $d_{x^2-y^2}$ (or d_{xy}) orbitals as in (**389**), with short Cu—O bond distances, significant antiferromagnetism occurs, namely $2J = -385.4\ cm^{-1}$. Where the plane of the oxalate anion is not coplanar with one of the two copper(II) equatorial planes and also involves a long Cu—O distance, as in (**390**), there is a significant reduction in the antiferromagnetism to $-75.4\ cm^{-1}$. When the plane of the oxalate anion is at 90° to both of the copper(II) equatorial planes and both involve one long Cu—O distance, as in (**391**), the antiferromagnetism is still further reduced to $-13.8\ cm^{-1}$. In the distorted trigonal bipyramidal CuN_3O_2 chromophores of $[Cu_2(Et_2dien)_2(C_2O_4)](BPh_4)_2$ (**392**),[863] with an approximate d_{z^2} ground state, the low antiferromagnetism, $2J = -37.4\ cm^{-1}$, is difficult to understand, but can be rationalized if an approximate $d_{x^2-y^2}$ ground state is involved.



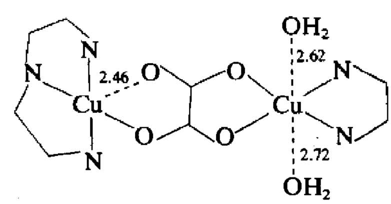
$[Cu_2(N_3)_2(C_{16}H_{34}N_2O_6)(N_3)_2]$ (**387**)[866]



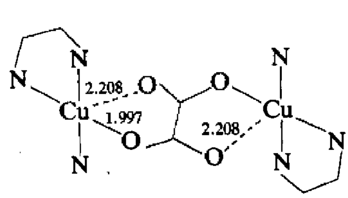
$[Cu(terpy)(CN)](NO_3)$ (**388**)[871]



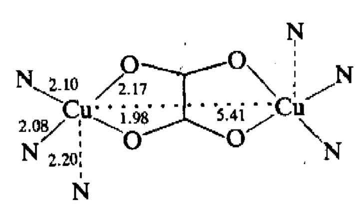
$[Cu_2(tmen)_2(C_2O_4)(OH_2)_2](ClO_4)_2 \cdot 1.25H_2O$ (**389**)[863]



$[Cu(dien)(C_2O_4)Cu(OH_2)(tmen)](ClO_4)_2$ (**390**)[863]



$[Cu_2(tmen)_2(2\text{-Meim})_2(C_2O_4)](ClO_4)_2$ (**391**)[863]



$[Cu_2(Et_5dien)_2(C_2O_4)](BPh_4)_2$ (**392**)[863]

The best known example of antiferromagnetism in a copper(II) structure is in $[Cu(O_2CMe)_2(OH_2)_2]$ (**316**; Figure 30e);[682–684] the μ_{so} is reduced to *ca.* 1.4 BM, with a $2J$ value of *ca.* $300\ cm^{-1}$, but over a range of ligands (Table 34[685,686,687]) the Cu—Cu distances only vary from 2.58 to 2.89 Å and $2J = -400$ to $-200\ cm^{-1}$.[875] In these acetate-type dimers the nature of the exchange coupling has been extensively discussed,[585,875] and has equally been accounted for on different occasions, in terms of direct metal–metal bonding or super-exchange *via* the acetate bridging groups.[583–587] Neither description of the bonding has remained predominant, but the best recent calculations[877] suggest that both types of coupling are actually present at the same time. Whichever it is, these dimers are remarkably stable and generate rigid copper(II) structures (**316**) unsuitable for any kinetic involvement in a redox process,[682–684] but it is then relevant that the acetate bridging is retained, in part, in the structure of anhydrous $[Cu(O_2CMe)]$ (**103**).[222] A wider range of antiferromagnetic behaviour is observed (Tables 43 and 44) in the planar CuL_n chromophores bridged by planar polyatomic anions, which must bridge through a σ-bonding pathway to account for the strong antiferromagnetism observed (Table 44), which ultimately gives rise to diamagnetism. Thus while the strong antiferromagnetic behaviour of these diamagnetic species is reasonably well understood, the same cannot be said for the occurrence of ferromagnetism in copper(II) complexes, which according to the above, requires a clearly orthogonal exchange pathway before the ferromagnetism is 'revealed' (Table 45). Equally complicated[882] is the behaviour of the higher polynuclear copper(II) complexes, from the tetranuclear Cu_4O_4 complexes (**331**)[712] and (**332**),[716] in which strongly coupled dimers are linked by weaker dimer–dimer exchange interactions[880–884] into infinite chain structures as in $[Cu(O_2PR_2)_2]$ (**213**) complexes[484] where different exchange coupling constants are involved along and between the chains.[883] Neither is the observation of ferromagnetism in the biologically relevant mixed oxidation state clusters of $Tl_2[Cu^{II}_6Cu^{I}_8$(D-pen)] (Figure 16a) easy to rationalize in terms of the simple exchange mechanism described above.[391,392] With one-, two- and three-dimensional lattices (Figure 19.7, 19.8 and 19.9) the presence of a σ-bonding pathway can lead to one-, two- or three-dimensional magnetism,[864] but increasingly examples are being found of linear ferromagnetic systems that are at present difficult to understand.[762,782] These must await a better understanding of the relationship between the magnetic exchange properties and these extended coordinated copper(II) environments.

Table 44 Bridging Polyatomic Anions Involving a Planar/Planar Dimer Leading to Strong Antiferromagnetism

Complex	*Cu—Cu* (Å)	*Cu—O* (Å)	*2J* (cm^{-1})	μ_{eff}	*Ref.*
$[Cu(C_2O_4)]\cdot1/3H_2O$	5.14	1.96	−291	Paramagnetic	878
$[Cu_2[S_2C_2\{N(CH_2)_2OH\}_2](OSO_3)_2]\cdot H_2O$ (**345**)	5.67	—	−594	Paramagnetic	756
$[Cu_2$(glycylglycine thioxamide$)_2]$	5.61	—	−630	—	879
$[Cu_2(N_3)_2(C_{18}H_{38}N_2S_4)(N_3)_2$	5.14	2.0	—	Diamagnetic	669
$[Cu(N_3)C_{43}H_{49}N_{10}O][BF_4]_2$[a]	—	—	−600	—	866
$[Cu(tmen)(OH)]_2Br_2$	3.00	1.90	−509	—	598, 861
$[Cu_2(tmen)_2(OH_2)_2(C_2O_4)](ClO_4)_2\cdot1.5H_2O$	5.16	—	−385.4	—	863

[a] Square-based pyramidal.

Table 45 Polynuclear Copper(II) Systems Involving Ferromagnetic Behaviour

Complex	*Cu—Cu* (Å)	*Cu—X* (Å)	*Cu—X—Cu* (°)	*2J* (cm^{-1})	*Ref.*
$[Cu(bipy)(OH)]_2(NO_3)_2$	2.85	1.92	95.6	+172	834, 848
$[Cu_2(N_3)_2(C_{16}H_{34}N_2O_6)(N_3)_2]$ (**387**)	2.85	1.99	103.6	+70	866
$Tl_5[Cu^{II}_6Cu^{I}_8$(D-pen$)_{12}Cl]\cdot nH_2O$[a]	6.6–6.9	—	—	*ca.* +6.0	391
$Tl_5[Cu^{II}_6Cu^{I}_8\{SC(CH_2NH_2)_2\}_{12}Cl]\cdot3.5H_2O$	6.5–6.83	—	—	*ca.* +5.0	393, 394
$[Cu_4L_4]\cdot9MeOH$	3.12–3.41	2.00	104.4	+28	880
$[Cu(DMGH)Cl_2]_2$	3.44	2.70	88.0	+6.3	881
$[CuVO(fsa)_2en]$[b]	2.99[c]	1.91–1.94	98–99	+116	840

[a] See Figure 16(a). [b] See Figure 31. [c] Cu—V.

53.4.4.3 *Electron spin resonance spectroscopy*

The copper(II) ion, with a d^9 configuration, has an effective spin of $s = 1/2$ and associated spin angular momentum $m_s = +1/2$, leading to a doubly degenerate spin state in the absence of a magnetic field.[47,48] In a magnetic field this degeneracy is removed and the energy difference between these two states is given by $E = h\nu = g\beta H$, where h is Plancks constant, ν is the frequency, g is the Lande splitting factor (equal to 2.0023 for the free electron), β is the electronic Bohr magneton and H is the magnetic field.[583,584,814–816] For normal fields (*ca.* 3500 G) the resonance frequency is in the X-band microwave region (10^4 MHz), and hence the absorption is performed using microwave optics.[814–816]

For the free copper(II) ion there is also an interaction with the magnetic field due to the orbital angular momentum L of the electron, and the total interaction becomes $E = (2.0023S + L)H$. The orbital degeneracy is removed by the crystal field and the orbital angular momentum is said to be 'quenched' for the ground states of copper(II) complexes.[294,884–886] Spin–orbit coupling mixes into the ground state some orbital angular momentum from certain excited states,[47] the extent of which is reflected in the modifications to the Lande splitting factor g. Table 46 lists some examples of the way the g factors are modified. In the octahedral case the g factor is isotropic and increased above the free ion value of 2.0023 by the factor $6r_2\lambda/\Delta$, where Δ is the crystal field splitting energy (Figure 26). The free ion value of λ is -0.829 kK and r measures the combined reduction of the orbital angular momentum and the spin–orbit coupling constant from their free ion values to those in the actual complex. It is influenced by such factors as covalent bonding and electron delocalization from the ligand atom to the copper(II) ion.[47,48] Typical values for isotropic g factors are given in Table 47. In axial copper(II) ion environments the g factors are anisotropic ($g_z = g_\parallel$ and $g_x, g_y = g_\perp$), as the effect of mixing-in is no longer isotropic. The expressions are given in Table 46 and the energies involved are those of Figures 26 and 27. In axial systems the g factors are different depending on whether a $d_{x^2-y^2}$ or a d_{z^2} ground state is present, $g_\parallel \gg g_\perp > 2.0$ and $g_\perp \approx g_\parallel > 2.0$, respectively (Table 46).

Table 46 The Theoretical Expressions for the g Values for a Copper(II) Ion in Different Liquid Fields

(1) Cubic

$$g_i = 2 - \frac{4r^2\lambda}{E_{d_{xy}, d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}, d_{z^2}}}$$

(2) Axial

(a) Elongated — $d_{x^2-y^2}$ (or d_{xy}) ground state

$$g_\perp = 2 - \frac{2r^2\lambda}{E_{d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}}}, \quad g_\parallel = 2 - \frac{8r^2\lambda}{E_{d_{xz} \rightarrow d_{x^2-y^2}}} \qquad g_\parallel \gg g_\perp > 2.0$$

(b) Compressed — d_{z^2} ground state

$$g_\perp = 2 - \frac{6r^2\lambda}{E_{d_{xz}, d_{yz} \rightarrow d_{z^2}}}, \quad g_\parallel = 2.0 \qquad g_\perp \gg g_\parallel = 2.0$$

Table 47 Typical g Factors for Copper(II) Complexes

(1) Isotropic	g_i		
$K_2Pb[Cu(NO_2)_6]$	2.10		
$[Cu(en)_3](SO_4)$	2.13		
(2) Axial (a) elongated	(i) $d_{x^2-y^2}$ ground state		
	$g_\perp$	$g_\parallel$	
$Ca[CuSi_4O_{10}]$	2.054	2.326	
$[Cu(NH_3)_4(NO_2)_2]$	2.052	2.234	
	(ii) d_{xy} ground state		
$Cs_2[CuCl_4]$	2.103	2.384	
$Ca[Cu(MeCO_2)_4]\cdot 6H_2O$	2.070	2.360	
(b) compressed — d_{z^2} ground state			
$[Cu(NH_3)_2Ag(SCN)_3]$	2.004	2.207	
(3) Rhombic (a) elongated	(i) $d_{x^2-y^2}$ ground state		
	g_1	g_2	g_3
$Ba_2[Cu(HCO_2)_6]\cdot 4H_2O$	2.078	2.109	2.383
$[Cu(dien)_2]Br_2\cdot H_2O$	2.045	2.097	2.213
	(ii) d_{xy} ground state		
$[Cu(3\text{-}Meacac)_2]$	2.057	2.061	2.255
$[Cu(H_2edta)\cdot H_2O]$	2.058	2.069	2.341
(b) compressed — d_{z^2} ground state			
$[Cu(dien)_2](NO_3)_2$	2.03	2.13	2.16
$[Cu(bipy)_2(ONO)](NO_3)$	2.029	2.170	2.205

In practice, the ESR spectra of copper(II) complexes are displayed as first derivative absorption curves and the general line shapes observed are illustrated in Figure 32. The two axial spectra (b and c) are clearly recognized and may be used as criteria for distinguishing a $d_{x^2-y^2}$ and d_{z^2} ground state, respectively, as shown by the numerical g factors for $[Cu(NH_3)_4(NO_2)_2]$ (**174**; $g_\parallel \gg g_\perp > 2.0$)[570] and $[Cu(NH_3)_2Ag(SCN)_3]$ (**223**; $g_\perp \gg g_\parallel \approx 2.0$; Table 47).[504] Complex (**223**) has a lowest g value of 2.0023, compared with the lowest g factor of 2.056, for (**174**). It must be emphasized that such a simple interpretation of the ESR spectra only applies if all the tetragonal axes of the local copper(II) ion environments are aligned parallel in the unit cell. For a rhombic local molecular environment the g factor expressions are more involved[47] and three g factors are observed if all the molecular axes are aligned parallel, as in $Ba_2[Cu(HCO_2)_6]\cdot 4H_2O$ (**191**; Table 47).[443] In rhombic systems a d_{z^2} ground state also results in a numerically lowest g factor below 2.03 (see $[Cu(bipy)_2(ONO)](NO_3)$ (**253**); Table 47),[546] but it is never quite as low as in the axial systems. Consequently, a d_{z^2} ground state is not as clearly recognized in a rhombic system as is an axial one.

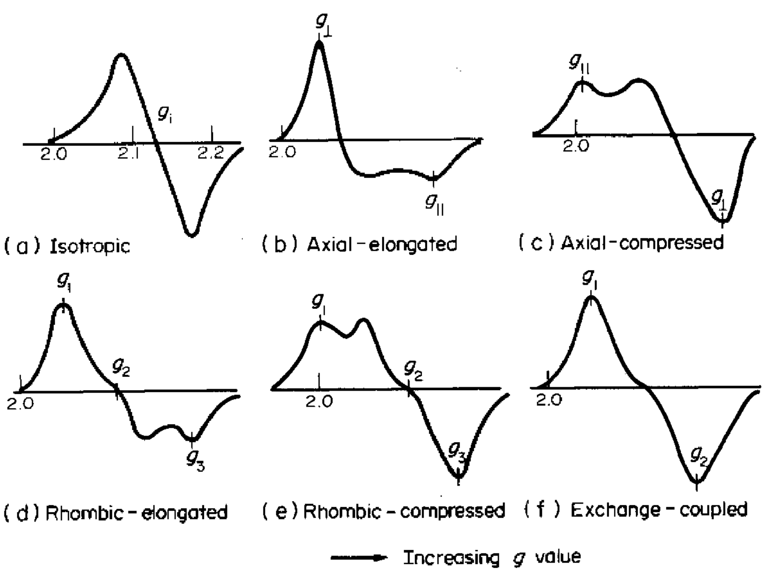


Figure 32 The different types of ESR spectra obtained from polycrystalline samples of copper(II) complexes (first derivative absorption curves)[47,48]

Owing to the approximations made in analyzing the ESR spectra of polycrystalline samples (Figure 32) more accurate crystal g factors may be obtained from the measurement of the single-crystal ESR spectra.[47] In addition the directions of the crystal g factors are determined and may be used to relate the individual g factors to the local molecular directions of the CuL_6 chromophore if the latter are aligned in the unit cell.[396,432] Three situations arise, as illustrated in Figure 33(a), (b) and (c). In (a) the local molecular axes are aligned parallel, a situation that is referred to as ferrodistortive ordering.[432] In this case the crystal g values equate with the local molecular g values as exchange narrowing[47] is said to occur, and the g values relate to the local stereochemistry. For misaligned CuL_6 chromophores ($2\gamma < 90°$; Figure 33b) exchange broadening occurs and results in a near isotropic signal, as in Figure 32(f), which yields no useful g value information. For the special value of $2\gamma = 90°$, total misalignment occurs and is referred to as antiferrodistortive ordering (Figure 33b), An axial ESR spectrum is observed, that is 'reversed' in type,[47] with $g_\perp > g_\parallel > 2.0$, but with the lowest g value significantly above 2.00, as occurs in an aligned system with a d_{z^2} ground state. This numerical relationship is illustrated schematically in Figure 34, and by the numerical g values for $K_2[CuF_4]$ and $Ba_2[CuF_6]$ (Table 48).[887,888]

For copper(II) complexes involving large ligands and anions, the physical separation of the copper(II) ions may exceed 5 Å and the g values may display evidence for copper nuclear hyperfine splitting, $2I+1$, for ^{63}Cu and ^{65}Cu $I = 3/2$,[814–816,884–886] and each g value is split into four lines, separated by the nuclear hyperfine splitting constant A. For the elongated tetragonal octahedral stereochemistry $A_\parallel > A_\perp$, and for concentrated copper(II) complexes only the $A_\parallel$ value is observed in practice,[889] as in $[Cu(phen)_3](ClO_4)_2$ (**196**; Figure 35).[448] If the copper(II)

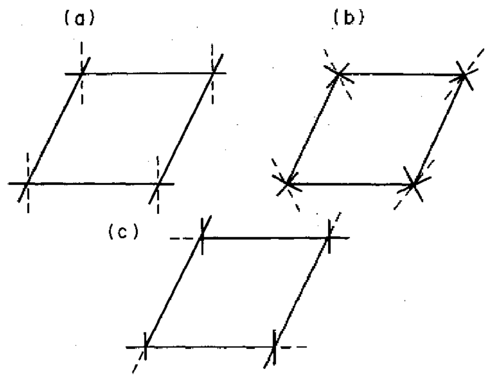


Figure 33 Exchange coupling between crystallographic Cu centres; the types of crystallographic CuL_6 chromophore orientations: (a) aligned (ferrodistortive order; $2\gamma = 0°$); (b) misaligned ($2\gamma = 45°$); (c) 90° misaligned (antiferrodistortive order; $2\gamma = 90°$) (where 2γ = angle between the elongation axes)

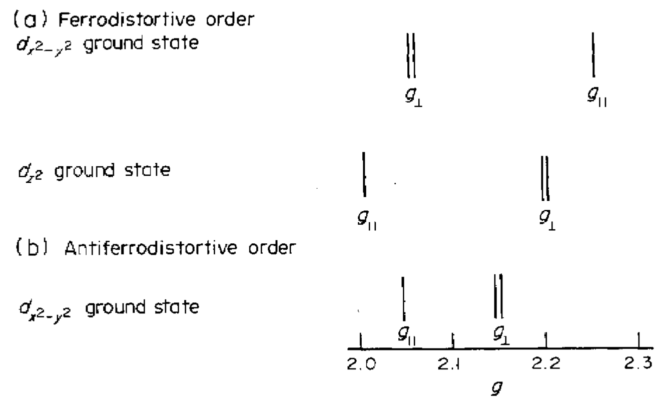


Figure 34 ESR spectra for axial environment involving (a) ferrodistortive order and (b) antiferrodistortive order[396]

Table 48 The g Values for $K_2[CuF_4]$ and $Ba_2[CuF_6]$

	$K_2[CuF_4]$[887]	$Ba_2[CuF_6]$[888]
Ferrodistortive	2.09, 2.28, 2.28	2.05, 2.20, 2.36

ions are further separated by dilution in a diamagnetic host lattice, such as a zinc(II) complex, or the ESR spectrum is measured in solution, even more nuclear hyperfine splitting is revealed as set out systematically in Figure 36.[396] For nitrogen ligands the nitrogen hyperfine splitting constant I_N equals one and the number of lines is given for n ligands as $2nI_N + 1$, and if all are resolved the spectrum may yield information on the number of nitrogen ligands coordinated to the copper(II) ion, as shown for $[Cu(phen)_3](ClO_4)_2$ (**196**; Figure 35b),[890] in which type of spectrum proton hyperfine structure may also be observed. By using double resonance techniques, such as ENDOR spectroscopy,[891] even more detail may be revealed, especially if single-crystal rotation data are recorded (see ref. 891), and especially on copper(II)-doped systems. Unfortunately, the major limitation of copper(II)-doped systems is that the precise stereochemistry of the copper(II) ion is unknown. In zinc(II) host lattices in particular it is rarely justified to assume that the CuL_n environment equates with the ZnL_n environment.[396,397,432] It is most likely to do so for the extreme static four-coordinate stereochemistry of rhombic coplanar, but it is unlikely to do so for four-coordinate tetrahedral and certainly not for any of the five- or six-coordinate stereochemistries,[514] as in the latter the zinc(II) ion has a spherically symmetrical $t_{2g}^6 e_g^4$ electronic configuration (see Figure 18).

Most ESR instruments use the fixed frequency of 9500 MHz (X-band frequency),[886] but a number of ESR spectra are measured at 3500 MHz (Q-band frequency),[892] which, in the case of misaligned concentrated copper(II) complexes, can resolve the local molecular g values of

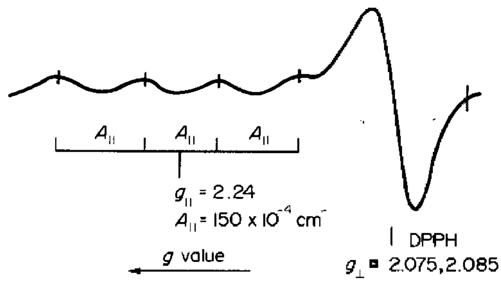


Figure 35 The ESR spectrum of $[Cu(phen)_3](ClO_4)_2$ (**196**) measured as a polycrystalline sample[889]

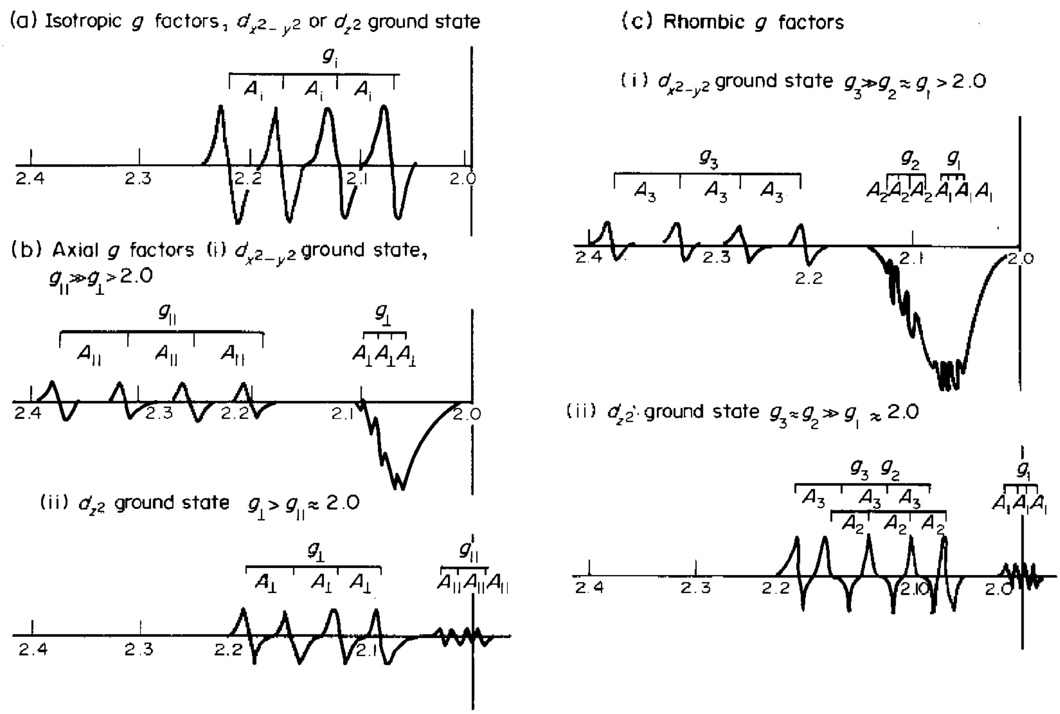


Figure 36 Polycrystalline ESR spectra of dilute copper(II)-doped zinc(II) systems

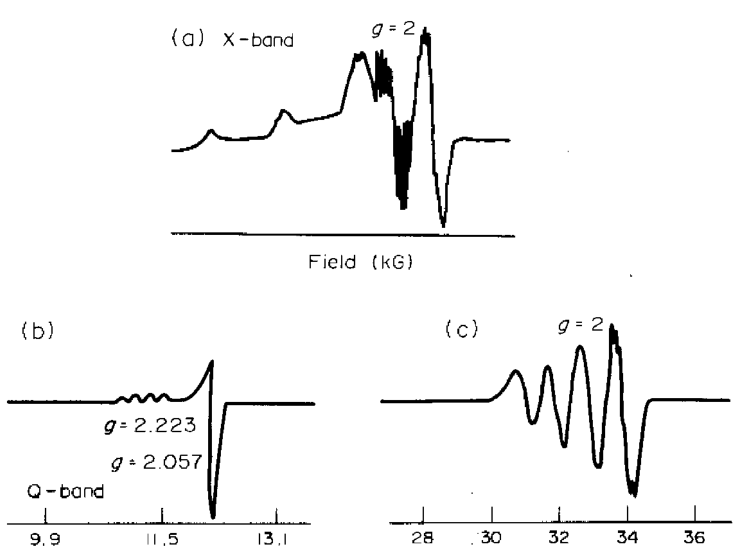


Figure 37 The ESR spectrum of a copper(II) complex measured at (a) X-band and (b) Q-band frequency, showing the resolution of the g values of the local molecular Cu chromophore in (b) and (c) in solution[294]

the misaligned chromophores,[893] which are merged by exchange coupling (Figure 33 and 34), when measured at X-band frequency (Figure 37, but see ref. 894).

In copper(II) coordination chemistry one of the most important applications of ESR spectra has been their use for 'fingerprinting' to distinguish, in a series of copper(II) complexes CuL_nX_2 of unknown crystal structure, involving the same ligand L, the electronic ground state of the copper(II) ion.[47,48] This enables the separation of the complexes into the two groups of stereochemistries of Table 41 (1) and (2) associated with these two alternate ground states. This approach has been particularly valuable in distinguishing the two alternate five-coordinate geometries of square and trigonal bipyramidal,[396,397] but in any series of complexes CuL_4X_2 only about 50% have their local molecular axes aligned and yield a definitive ESR spectrum, which only arises for ferromagnetic ordering (Figure 33a). The remainder are misaligned and only yield a broad isotropic ESR spectrum, due most probably to the presence of misalignment (Figure 33b), which contains no information on the electronic ground state. Even this simplistic approach is complicated by the observation of an axial 'reversed' type ESR spectrum, $g_\perp > g_\parallel > 2.0$, associated with the presence of antiferrodistortive ordering (Figure 33c). In this 'fingerprint' use of ESR spectra,[822] the spectra are most conveniently (and quickly) determined in the solid state as polycrystalline samples and the g values obtained are the crystal g values, associated with an ultimate crystal structure determination. Additional information may be obtained by dissolving the complex in solution, but in this case, for copper(II) complexes, the structure may be significantly different from that present in the solid state. In solution the ESR spectrum will in any case appear different: due to the increase in copper–copper separation copper hyperfine splitting will be revealed (Figure 36), and due to rapid tumbling in solution the anisotropic g and A values will be averaged to give single isotropic g and A values, which contain little structural information (Figure 37c). More useful structural information may be obtainable from the correlation of the g values with the tetragonality of the CuL_6 chromophore of a closely related series of complexes, such as the $[Cu(NH_3)_n]X_2$ complexes (Figure 38a).[354,396,895] Similarly, the correlation of the g value with corresponding A values, where they can be measured, has provided a very useful means of distinguishing CuO_4, CuS_4 and CuN_2O_2 chromophores (Figure 38b),[896,897] that has found extensive application in biological systems (Section 53.4.8).[898] A particularly useful correlation is that the $A_\parallel$ value of a compressed tetrahedral CuL_4 chromophore is significantly lower than that of a square coplanar chromophore (Table 49).

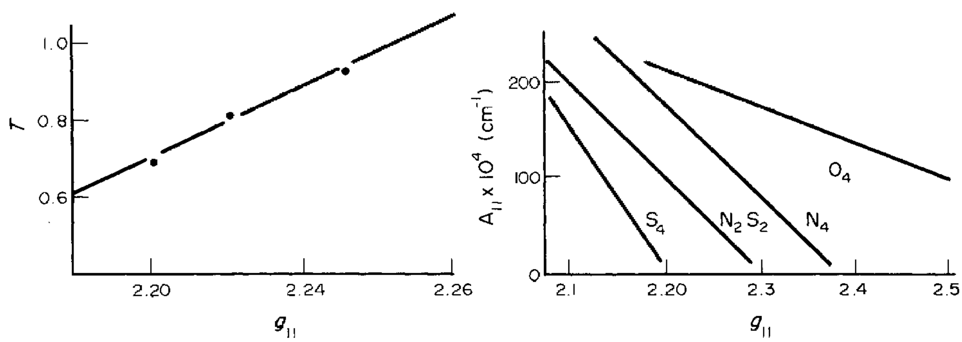


Figure 38 Correlation of g values with (a) tetragonality (T) for $[Cu(NH_3)_4]X_2$; (b) with $A_\parallel$ values ($\times 10^{-4}$ cm^{-1}) of complexes tetrahedral CuL_4 chromophores[896]

A second major application of the ESR spectra of mononuclear copper(II) complexes has been in distinguishing the vast majority of complexes that involve a static stereochemistry from those involving a temperature variable one (Section 53.4.2.1x). In general the g values associated with a static structure will be nontemperature variable,[505] while those associated with a temperature variable structure will themselves vary with temperature. Historically, this temperature variability was first observed in the ESR spectrum of copper(II)-doped $K_2[Zn(OH_2)_6](SO_4)_2$ (Figure 39a)[909] and yielded the characteristic variation of the g values and A values (Figure 39b and c). The g_3 value increases with decreasing temperature, g_2 decreases and g_1 is virtually temperature invariant. The corresponding change with temperature of the Cu—O distances of the concentrated copper(II) complex $K_2[Cu(OD_2)_6](SO_4)_2$ (**393**; Figure 39d) has been determined recently, using powder profile analysis of neutron diffraction

Table 49 Some g and A Values for Various Copper(II) Stereochemistries

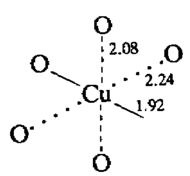
Stereochemistry	*Chromophore*	*Complex*	$g_\perp$	$A_\perp \times 10^4$ (cm^{-1})	$g_\parallel$	$A_\parallel \times 10^4$ (cm^{-1})			*Ref.*
Elongated rhombic octahedral	CuO_6	$[(Zn)Cu(OH_2)_6][SiF_6]$	2.10	<30	2.46	110			899
	CuN_6	$[(Zn)Cu(phen)_3](NO_3)_2 \cdot 2H_2O$	2.064	<7	2.273	160			900
Square coplanar	$CuCl_4$	$K_2[Pd(Cu)Cl_4]$	—	34.5	—	164			901
	CuO_2N_2	$[Cu(8\text{-hydroxyquinolinate})_2]$	2.047	29.0	2.21	206			902
	CuN_4	$[Cu(NH_3)_4][PtCl_4]$	2.051	28.0	2.217	211			903
Compressed tetrahedral	$CuCl_4$	$Cs_2[Zn(Cu)Cl_4]$	2.09	25.0	2.446	48.5			904
	CuN_4	$[Cu(bipyam)_2](ClO_4)_2$	2.064	—	2.244	145			905
Square-based pyramidal	CuO_5	$[Cu(apy)_5](ClO_4)_2$	2.079	35.0	2.4	126			906
Trigonal bipyramidal	CuN_4N	$[Cu(Zn)(tren)(NH_3)](ClO_4)_2$	2.176	110	2.029	84			499
Cis-distorted octahedral	CuN_4O_2	$[Cu(Zn)(bipy)_2(ONO)](NO_3)$	2.197, 2.165	106, 92	2.025	*ca.* 10			908
			g_1	A_1[a]	g_2	A_2[a]	g_3	A_3[a]	
Seven coordinate	CuN_3O_4	$[Zn(Cu)(py)_3(O_2NO)_2]$	2.028	70	2.189	56	2.251	—	905
Eight coordinate	$CuO_4O'_4$	$Ca[Cd(Cu)(O_2CMe)_4] \cdot 6H_2O$	2.038	50	2.164	25	2.414	102	907

Table 50 The Estimation of g, A, J and r Values from the Half-field Lines of Copper(II) ESR Spectra at 77 K: (a) doped system and (b) frozen solution[824]

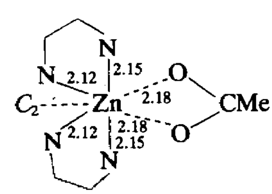
	$g_\perp$	$g_\parallel$	$A_\perp \times 10^4$ (cm^{-1})	$A_\parallel \times 10^4$ (cm^{-1})	J (cm^{-1})	r^a (Å)	r^b (Å)
(*a*) *Solid (doped system)*							
Cu-doped $[Zn(pyNO)_2(O_2NO)_2]_2$	2.040	2.303	10	140	+30	3.46	3.46
Cu-doped $Cu(salim)_2$	2.025	2.265	10	150	—	4.05	4.05
Cu-doped $Cu(Et_2CS_2)_2$	2.020, 2.015	2.07	27, 7	148	+24	3.85	3.59
(*b*) *Frozen solution*							
$Cu(salen)_2$	2.055	2.15	20	205	−20	4.55	3.18
$Cu(DMG)_2$	2.01	2.11	10	175	−20	4.47	3.88
$Cu(\pm\text{-tartrate})_2$	2.06	2.278	30	178	−18	3.77	2.99

[a] From ESR data. [b] From X-ray data.

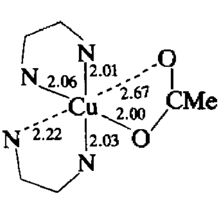
data.[579,910] Even more dramatic changes occur in the powder ESR spectra of $Cs_2Pb[Cu(NO_2)_6]$ (**251**) at different temperatures (Figure 40a and b) from an isotropic g value at 460 K, to a 'reversed' axial spectrum at 298 K, to a normal axial spectrum at 160 K.[432,911] These changes correspond with the variations of stereochemistry from regular octahedral at 460 K, to compressed octahedral at 298 K and elongated rhombic octahedral at 160 K (see molecular structures **250–252**). In the case of the change from the trigonal octahedral stereochemistry of $[Cu(en)_3](SO_4)$ (**178**)[427] at 295 K to the compressed rhombic at 120 K, the ESR spectrum[912] changed from isotropic to 'reversed' axial at 120 K, but required the application of some elegant single-crystal ESR measurements at 120 K to sort out the observation of three separate g values at the low temperature, which were generated by the formation of three separate magnetic domains related by the room temperature three-fold axis (Figure 41a). In the case of the trigonal octahedral CuO_6 chromophore of $[Cu(ompha)_3](ClO_4)_2$ (**179**), the broad isotropic ESR spectrum[913] at 298 K shows clear evidence of copper hyperfine structure at 77 K (Figure 41b). With the two-dimensional structural variation of the *cis*-distorted octahedral structure, as in $[Cu(bipy)_2(ONO)](NO_3)$ (Figure 24b), the temperature variation of the polycrystalline ESR spectrum of the copper(II)-doped $[Zn(phen)_2(O_2CMe)](BF_4)\cdot 2H_2O$ (**394**) (Figure 42a) is marked.[914] At room temperature (——) the spectrum corresponds to an axially compressed octahedral stereochemistry, $g_\perp \gg g_\parallel > 2.0$, but at the temperature of liquid nitrogen (---) it is consistent with an axially elongated tetragonal octahedral stereochemistry, $g_\parallel \gg g_\perp > 2.0$. In the single-crystal ESR spectrum (Figure 42b) temperature variability is only observed in the plane of the Cu, N(2), N(4), O(1) and O(2) atoms and the isotropic room temperature spectrum ($g_\perp = 2.10$ and $A_\perp = 94 \times 10^{-4}\ cm^{-1}$) splits into two clear g values (g_2 and g_1) at the low temperature, a behaviour that is consistent with the formation of an elongated square pyramidal (4 + 1 + 1*) geometry at low temperature, comparable with the room temperature structure of $[Cu(phen)_2(O_2CMe)](BF_4)$ (**395**).[576]



$K_2[Cu(OD_2)_6](SO_4)_2$ (**393**)[910]



$[Zn(phen)_2(O_2CMe)](BF_4)\cdot 2H_2O$ (**394**)[914]



$[Cu(phen)_2(O_2CMe)](BF_4)$ (**395**)[576,1094]

In practice, the marked temperature variability of the ESR spectra of these temperature variable copper(II) structures has proved a useful criterion of their fluxional stereochemistry,[396] which has then been confirmed by low temperature X-ray crystallography (Chapter 53.4.2.1x).

In polynuclear copper(II) complexes the most important application of the measurement of ESR spectra is in the identification of Cu—Cu dipolar interaction,[814,824,884,885] as this generates a zero-field splitting parameter, D. In copper(II) dinuclear complexes D is generally less than $0.04\ cm^{-1}$ and while it does not significantly change the numerical value of the g and A factors (Table 50),[824] it does affect the appearance of the ESR spectra. Additional transitions arise associated with the $\Delta M = \pm 2$ values, compared with the $\Delta M = \pm 1$ values in mononuclear complexes. In X-band spectra (Figure 43) the latter are associated with fields of *ca.* 3000 gauss, while the former generate an absorption at the 'half-field' values of *ca.* 1500 gauss and the presence of this 'half-field' band is a useful criterion for dipolar interaction from the presence of some dinuclear (or polynuclear) complex formation. Figure 43 illustrates[915,916] the effect of the zero-field splitting on the g values and the consequent appearance of the ESR spectrum of a polycrystalline sample, in which the spectrum can be spread over a magnetic field of 0–6000 gauss. Figure 44 shows the actual appearance of the polycrystalline ESR spectrum[917–920]

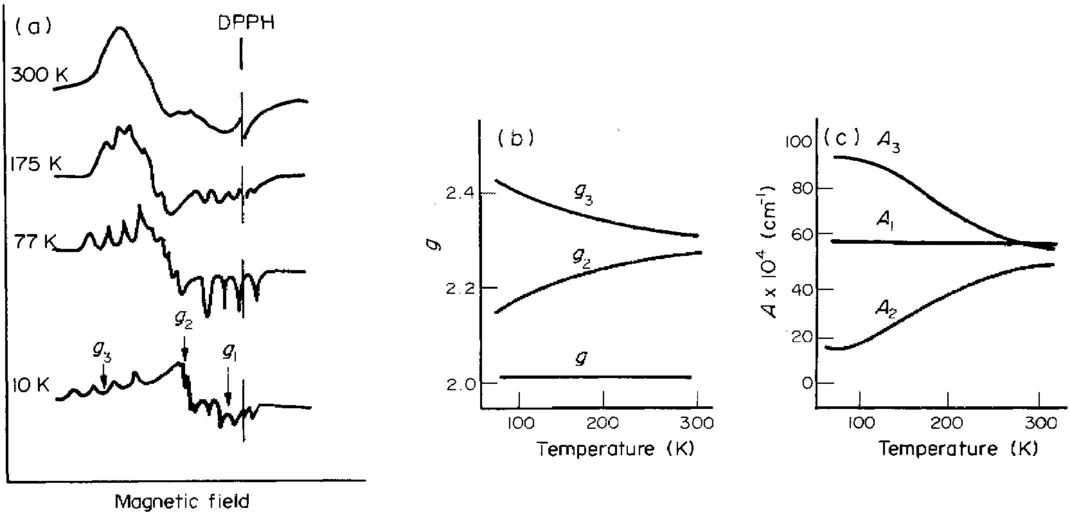


Figure 39 Copper-doped $K_2[Zn(OH_2)_6](SO_4)_2$: the temperature variation of (a) the polycrystalline ESR spectra; (b) the g factors; and (c) the A factors[909]

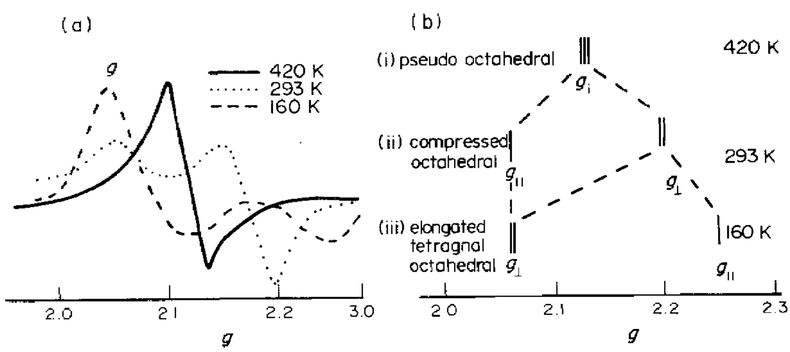


Figure 40 Temperature variation of the ESR spectrum of $Cs_2[PbCu(NO_2)_6]$ (a) polycrystalline sample; (b) schematic diagram[432,911]

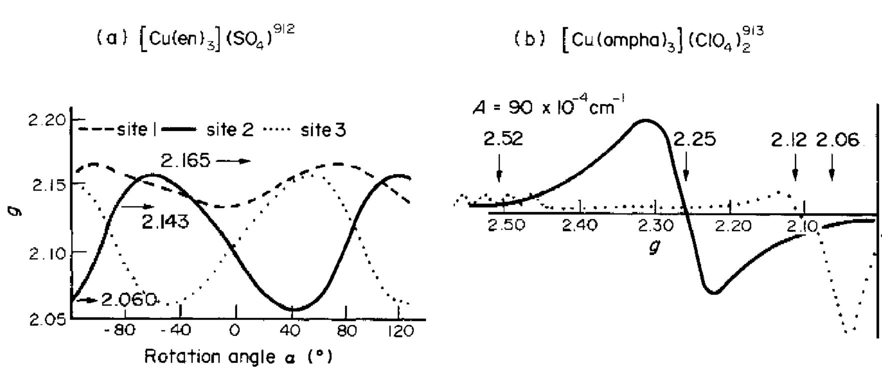


Figure 41 The single-crystal ESR spectrum of $[Cu(en)_3](SO_4)$ at 140 K and the polycrystalline ESR spectrum of $[Cu(ompha)_3](ClO_4)_2$ at 298 (——) and 77 (···) K[912,913]

of (a) $[Cu(O_2CMe)_2(OH_2)]_2$ **(316)**[682–684] and (b) $[Cu(O_2CCH_2CN)_2]$,[918] at 298 and 77 K. In many of these spectra of dinuclear copper(II) complexes, there is usually a weak peak at *ca.* 3000 gauss that is associated with the presence of a small amount of a copper(II) monomer (see Figure 44a and b). The resolution in these concentrated copper(II) systems is significantly increased by recording the spectra[918] at low temperature (Figure 44a and b), and in the latter case this revealed the presence of copper nuclear hyperfine splitting on the 'half-field' band at

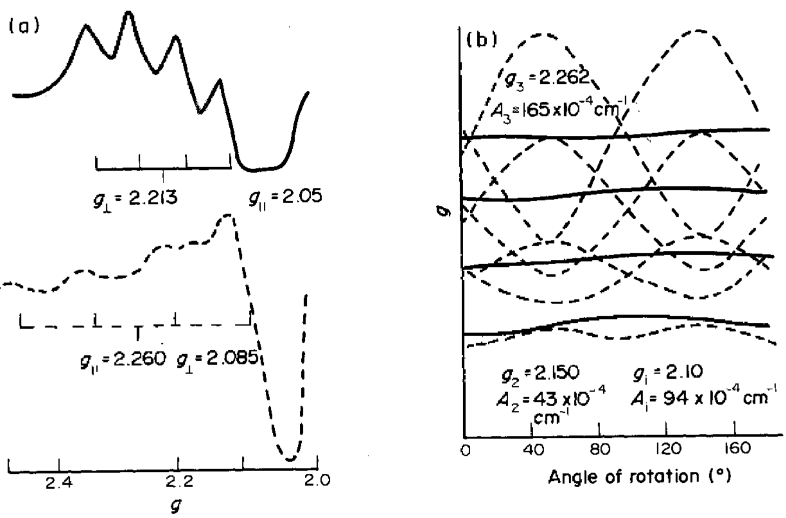


Figure 42 ESR spectra of copper(II)-doped $[Zn(phen)_2(O_2CMe)](BF_4)\cdot 2H_2O$[394] (a) polycrystalline sample, and (b) single-crystal sample; (——) room temperature; (– – –) liquid nitrogen temperature[914]

ca. 1500 gauss. The appearance of the copper hyperfine coupling can be further enhanced by recording the ESR spectrum of these dinuclear copper(II) complexes diluted in a diamagnetic host lattice, such as the dinuclear zinc(II) complex,[824] as in $[Zn(pyridine\ N\text{-oxide})_2(ONO_2)_2]$ (**396** and **397**; Figure 45). There is still uncertainty concerning the actual structure of the copper(II) species in these doped systems, but their particular values is that by the use of an elegant curve-fitting procedure,[824] it is possible to evaluate not only the *g*, *A* and *J* values, but also the Cu—Cu separations, *r*, which can then be compared with those obtained by X-ray crystallography. Table 50 shows that there is excellent agreement where the CuO_5 and ZnO_5 chromophores are of comparable geometry[824,921,922] but this situation is not always the case (see Section 53.4.5).[514] It is also noteworthy that the $2J$ values of $30\,cm^{-1}$ indicate weakly ferromagnetic behaviour[923] for this dilute system, whereas in the pure copper(II) complex this ferromagnetic behaviour has been questioned.[924] However the behaviour in the dilute and concentrated complexes do not necessarily have to be the same. The importance of the above type of estimation of the Cu—Cu separation from zero-field splitting parameters is not restricted to the solid state, as they can also be carried out in solution (or frozen solution) (Table 50), where they yield unique *r* values that are not available by any other technique (but see EXAFS spectroscopy, Section 53.4.4.7).

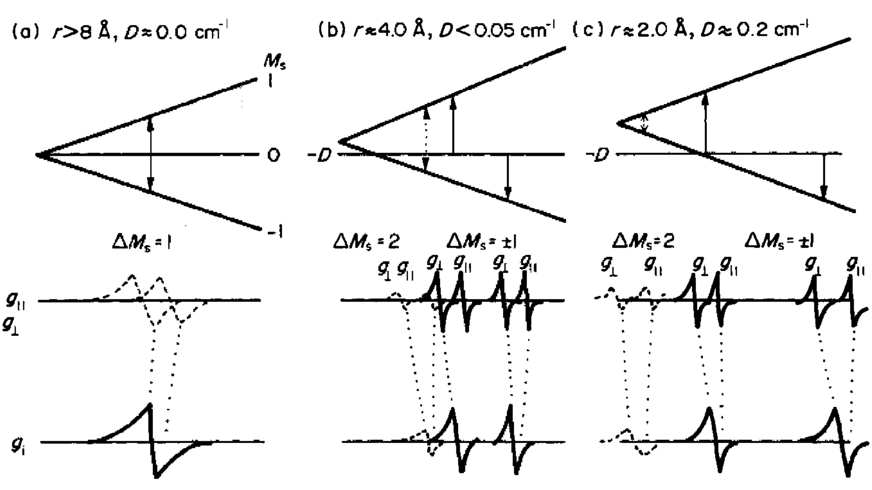


Figure 43 Dinuclear copper(II) complexes: the effect of zero field splitting on the isotropic *g* value for (a) large Cu—Cu separation, $r > 7$ Å, $D = 0.0\,cm^{-1}$; (b) intermediate, $r = 4$ Å, $D < 0.05\,cm^{-1}$, (c) small, $r < 3.0$ Å, $D = 0.2\,cm^{-1}$[824]

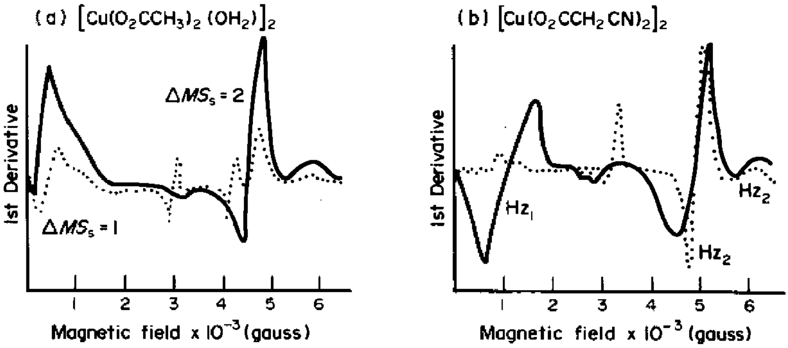


Figure 44 The polycrystalline ESR spectra (first derivative) of (a) $[Cu(O_2CMe)_2(OH_2)]_2$ (**316**)[682–684] and (b) $[Cu(O_2CCH_2CN)_2]$[918] at room temperature (——) and at 77 K (– – –)

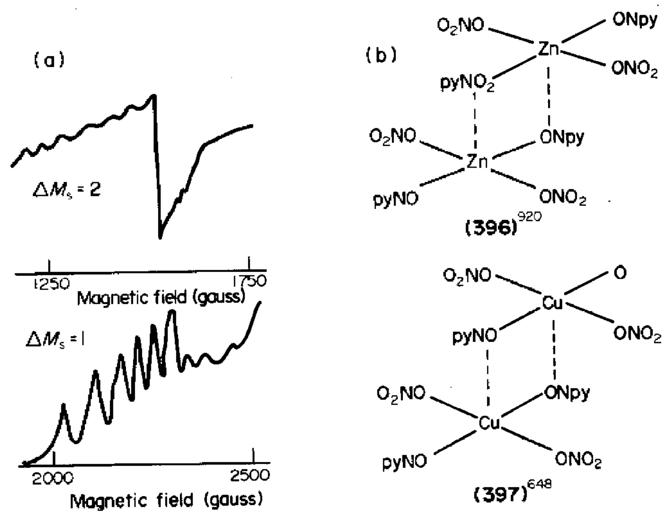
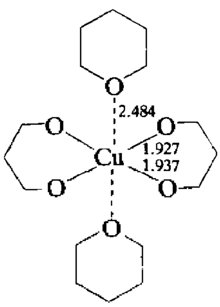


Figure 45 The copper(II)-doped $[Zn(pyNO)_2(O_2NO)_2]_2$ system: (a) ESR spectrum (77 K),[824] and (b) the molecular structures of the Zn^{II} and Cu^{II} complexes

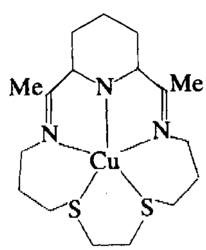
In favourable situations it is possible to obtain evidence for zero-field splitting from the nuclear hyperfine splitting patterns observed on the $\Delta M_s = 1$ transitions of a copper(II) complex, particularly the $g_{\parallel}$ or $g_{\perp}$ factors (Table 51). These can range from cofacial dicopper porphyrin complexes,[926] to [*N,N'*-ethylenebis(salicylideneiminato)copper(II)] dimers,[927] to sulfato-bridged dimers[928] and dinuclear Cu_2,[890] CuNi and Cu/Ni_2 systems.[929] Clear evidence for this type of dipolar interaction has been well demonstrated in a series of single-crystal ESR spectral measurements on $Rb_2[Cu(OH_2)_6](SO_4)_2$[930] and $[Cu(mbtfac)_2(dioxane)_2]\cdot 2dioxane$ (**398**),[931] where mbtfac = *p*-methoxybenzoyltrifluoroacetonate anion. The splittings observed range from the four lines normally associated with ^{63}Cu, $I = 3/2$, to a maximum of nine lines with the magnetic field parallel to the short crystallographic axis (Figure 46a). Likewise the observation of eight copper hyperfine lines (Figure 46b) on the nearly isotropic ESR spectrum of $[Cu(N_3S_2)(NCS)](BPh_4)$ (**399**) has been used to suggest a dimeric structure for the $[Cu(N_3S_2)(NCS)]^+$ cation,[932] and that of only four lines on the near isotropic spectrum of $[Cu(N_3S_2)](BPh_4)_2$, to suggest a normal monomeric structure for the $[Cu(N_3S_2)]^{2+}$ cation.[932,933] Even more intriguing has been the observation of eight hyperfine lines on the isotropic g value for the mixed valence $[Cu^ICu^{II}(L^9)](ClO_4)_3$ (**167**) complex (see Section 53.3.7) in dichloromethane solution (Table 52).[243,388,934–936] This implies that the single d electron is sensitive to the presence of the second copper(I) atom, presumably by dipolar interaction, but does not necessarily imply that the two copper atoms are in equivalent environments, as required for class II Robin and Day behaviour.[360] What is particularly interesting about this ESR spectrum is that at 77 K the CH_2Cl_2 solution spectrum reverts to a normal (frozen) type spectrum (Figure 36b) associated with an isolated elongated rhombic octahedral copper(II) environment. It is difficult to understand why the dipolar Cu–Cu interaction should be so temperature dependent; it suggests that there may be a definite change of structure in solution at the lower temperature. A near degenerate potential energy well system has been suggested to account for this temperature variability (see Figure 71, Section 53.4.5).[934–937]

Table 51 The Estimation of *g*, *J* and *D* Values from the $\Delta M_s = \pm 1$ and ± 2 lines in the ESR Spectra of Copper(II) Systems[824]

	$g_\perp$	$g_\parallel$	$A_\parallel \times 10^4$ (cm^{-1})	*D* (cm^{-1})	*J* (cm^{-1})	*Temperature* (K)	*Ref.*
$\Delta M_s = \pm 2$							
$[Cu(O_2CCH_2CN)_2]_2$	2.08	2.40	—	0.39	310	77	918
$[Cu_2(Me_5dien)_2(N_3)_2](BPh_4)_2$	2.104	2.19	—	0.159	—	—	925
[Cu(diporphyrin)]	—	—	—	0.042	—	77	926
$\Delta M_s = \pm 1$							
[Cu(salen)]	2.03	2.34	104	0.036	20	77	927
$[Pt(dpe)(3,5\text{-}Me_2pz)_2]$	2.08	2.32	227	0.030	—	298	928
Cu-doped$[Ni_2A^4B^3]$	2.057	2.140	—	0.0025	−12.2	77	890
$[Cu(mbtfac)_2(diox)_2]$	2.073	2.327	155	—	—	—	930



$[Cu(mbtfac)_2(dioxane)_2]\cdot 2dioxane$ **(398)**[931]



$[Cu(N_3S_2)(NCS)](BPh_4)$ **(399)**[932]

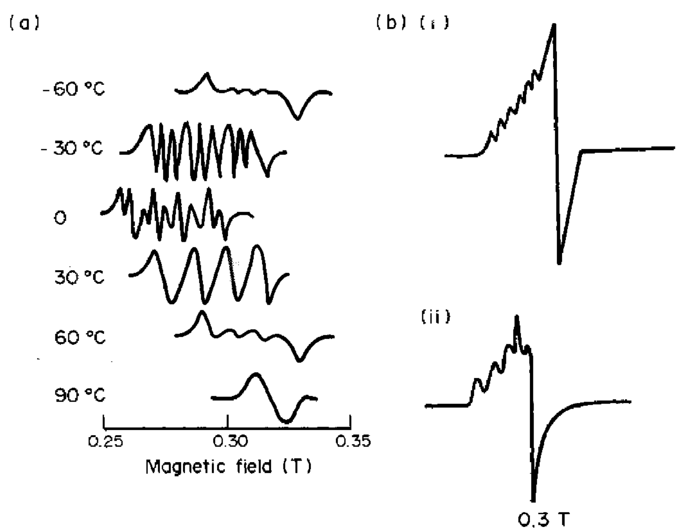


Figure 46 (a) The single-crystal ESR spectra of $[Cu(mbtfac)_2(dioxane)_2]\cdot$dioxane[931] and (b) the polycrystalline ESR spectra of (i) $[Cu(N_3S_2)(NCS)](BPh_4)$ and (ii) $[Cu(N_3S_2)](BPh_4)_2$[932]

Table 52 The ESR Spectral Data for $[Cu^ICu^{II}(L^9)](ClO_4)$ in CH_2Cl_2 Solution[243]

	Temperature (K)	g_{av}	$g_\perp$	$g_\parallel$	$A_{av} \times 10^4$ (cm^{-1})	$A_\parallel$($\times 10^{-4}$ cm^{-1})
Solid	15	2.085	—	—	—	—
Solution	298	2.169	—	—	46	—
Solution	82	—	2.228	2.080	—	187

53.4.4.4 Electronic spectroscopy

Complexes of the copper(II) ion are in general coloured,[13,17,22] the origin of this colour is normally the maximum of four electronic transitions between the ground state and the excited states of the crystal-field levels shown in Figures 26, and 27(a) and (b).[17,47,817,938,939] These transitions occur in the range 4.0–30.0 kK (kK = 1000 cm^{-1}). In the range 4.0–3.0 kK, five types of transitions may be observed (Figure 47):[817] (i) pure *d–d* transitions; (ii) charge-transfer transitions; (iii) internal ligand transitions; (iv) combination and overtone vibrations of the ligands;[297] and (v) intervalence charge transfer transitions.[360]

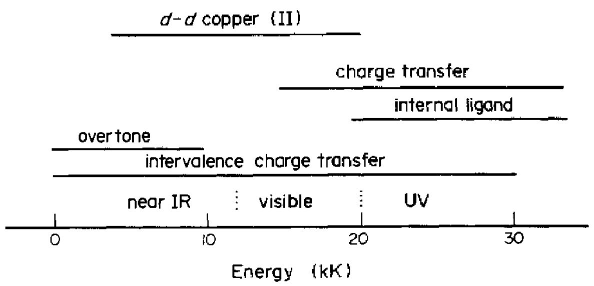


Figure 47 The copper(II) energy ranges, 4–30.0 kK, of the four types of transition

In copper(II) complexes (i) tends to occur below 20 kK, (ii) and (iii) above 20–30 kK, (iv) below 10 kK and (v) over the full range 4–30 kK.[47,48,817] Type (iv) and (v) spectra tend to be sharp relative to (i) and are generally distinguishable from types (i) and (ii). Type (ii) and (iii) spectra tend to be much more intense than (i) and if they are of low enough energy, they may well mask the less intense *d–d* transitions;[817] this frequently occurs when sulfur ligands are present.[940] In general only the *d–d* spectra are simply related to the underlying CuL_n chromophore stereochemistry present, although MLCT and LMCF bands may show some dependence on the copper(II) stereochemistry as well.[941–943]. Most copper(II) *d–d* spectra show only a single broad band (half-width *ca.* 5000 cm^{-1}), with only occasionally resolution into a shoulder or two bands and only rarely evidence of the two further partially resolved levels, notwithstanding the possible occurrence of up to four transitions as predicted from Figures 27(a) and (b).[47,48,897]

The spectra may be measured in three ways: in solution,[817] as reflectance spectra[944] and as polarized single-crystal spectra.[47,354] The solution spectra yield accurate extinction coefficient data, but there is always an uncertainty with copper(II) complexes regarding the actual species present in solution and the possibility of more than one species in equilibrium. The reflectance and single-crystal spectra clearly relate to the crystal structure in the solid state, but neither yields accurate extinction coefficients.[47,354] The large half-widths of all these spectra make it very difficult to determine the positions of the underlying transition (maximum four). In solution Gaussian analyses of the spectra were used in the classic paper on the electronic spectra of $[Cu(acac)_2]$ in various donor solvents (Figure 48),[945] but is rarely used in view of the large half-widths and low extinction coefficients in the *d–d* transition involved (10–200 cm^{-1} mol^{-1}).[946] Gaussian analysis of copper(II) electronic reflectance spectra is even less justified as the problem is compounded by nonlinear extinction coefficients,[468] but approximate relative extinction coefficients may be obtained by the use of the Kortuum-type analysis.[944] The most accurate method of obtaining the resolution of a copper(II) electronic spectrum into its components is by the measurement of the polarized single-crystal electronic spectrum (Figure 49)[47,48,817] recorded in the three mutually perpendicular directions determined by the crystal indices.[835b,947] In crystals where the local molecular axes are aligned (ferrodistortive order) resolution into two to four bands may be obtained, and by relating the polarization direction to the local molecular directions of the CuL_n chromophore under favourable circumstances it is then possible to obtain tentative information on the absolute assignment of the electronic spectra from the polarized single-crystal measurements.[48] However, in most cases it is in practice difficult to distinguish the intensity gaining mechanism involved (electronic or vibronic) and the final assignment reduces, at best, to a choice between two alternative one-electron orbital sequences.[47] Thus in the case of the square or rhombic coplanar copper(II) stereochemistry alternative assignments have placed the d_{z^2} orbital above[948] and below[949] the component of the octahedral t_{2g} level (Figure 27a). However a recent consensus prefers the latter assignment.[489] For the above reason, despite an abundant literature on copper(II) polarized single-crystal spectra in the period 1965–1975,[47,354,817] very few polarized spectra have been published in the past 10 years (but see Figure 50).[948,950–955,478] It is then of interest that despite the vibronic origin of the intensity of many copper(II) spectra,[956] there is generally no evidence for vibronic structure in even the polarized single-crystal spectra at room temperature and only limited appearance in the low temperature spectra.[952,953] The resolution of the electronic reflectance spectra can be improved by recording the spectra at low temperature, but usually with a shift in band maximum to lower energy by *ca.* 200 cm^{-1}.[505,939] At helium temperature (6 K) the reflectance spectra[505,939] usually give an indication of the bands resolved in the polarized single-crystal spectra (Table 53).[957]

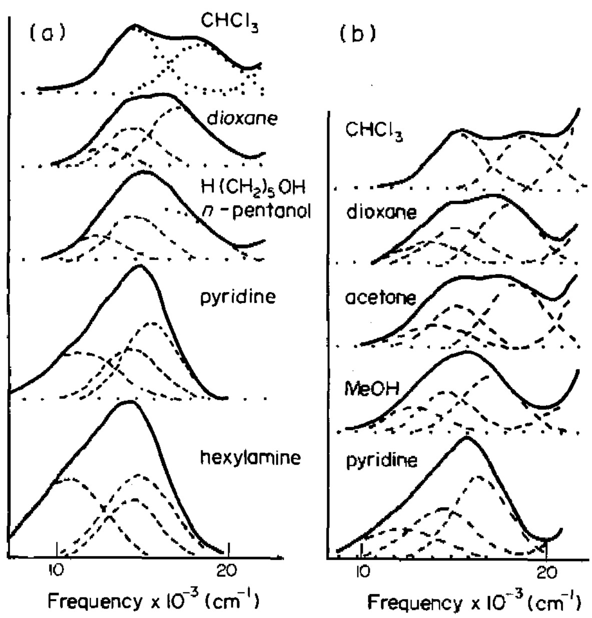


Figure 48 Gaussian analysis of the electronic spectra of [Cu(acac)$_2$] in different donor solvents (a) Cu(acac)$_2$; (b) Cu(3-Etacac)$_2$[945]

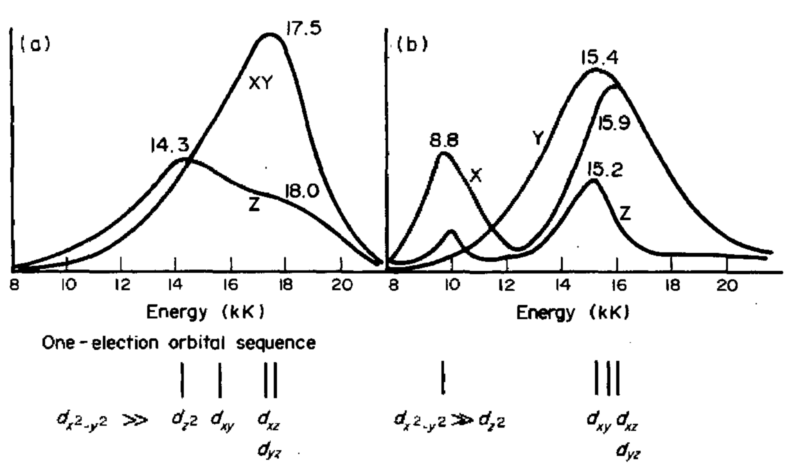


Figure 49 The assignment of the polarized single-crystal electronic spectra of (a) [Cu(NH$_3$)$_4$(NO$_2$)$_2$] (**174**)[456] and (b) [Cu(dien)$_2$]Br$_2$·H$_2$O (**194**)[446]

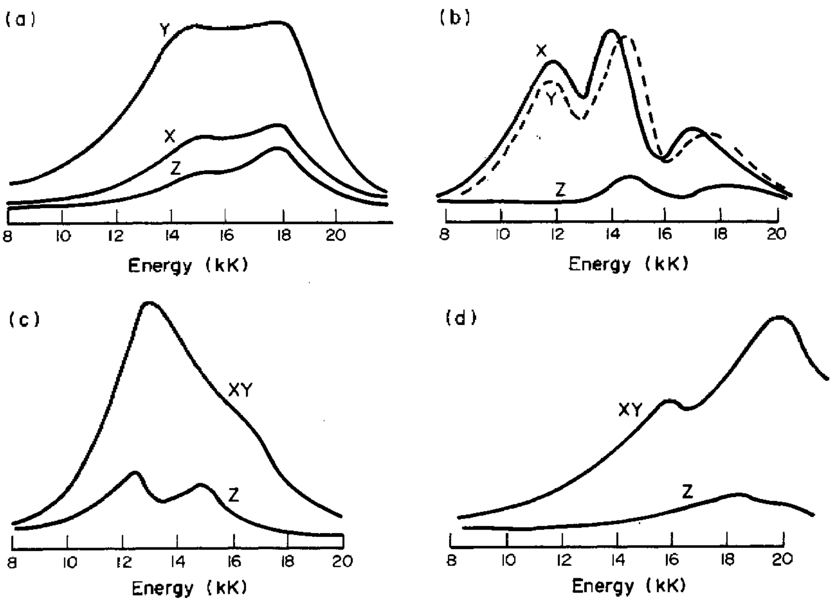


Figure 50 The polarized single-crystal electronic spectra of (a) $[Cu(Bzacac)_2]$;[948] (b) $(nmph)_2[CuCl_4]$;[925] (c) $[Cu(phen)_2(OH_2)](NO_3)_2$[955] and (d) $Cs_2[Cu(succinimide)_4]\cdot 2H_2O$[956]

Table 53 Copper(II) Electronic Spectra of $[Cu(bipy)_2(NH_3)](BF_4)_2$ and $[Cu(bipy)_2Cl]Cl\cdot 6H_2O$ as Reflectance Spectra[505] and Polarized Single-crystal (PSC) Spectra[957]

	$[Cu(bipy)_2(NH_3)](BF_4)_2$ [b]	$[Cu(bipy)_2Cl]Cl\cdot 6H_2O$ [b]
Reflectance spectra		
298 K	12.3	12.0
77 K	11.6 13.0	
6 K	11.45 13.2 15.5(sh)	10.9 12.8 15.5(sh)
PSC spectra [a]	10.8 11.6 13.4 15.8	11.3 12.7

[a] At 298 K. [b] Units are kK.

The problem in determining the band position and one-electron energy levels of a copper(II) ion in its complexes is further compounded by the variation of contributions to the precise energies observed with: (i) the types of ligand present, namely Cl, O, N, as these determine the value of Δ_{oct} according to the position of the ligand in the spectrochemical series;[13] (ii) the particular CuL_n coordination number (n) and the geometry it may assume (Section 53.4.2, Figure 19.1); (iii) geometry—for a given geometry the distortion may involve significant differences in the bond lengths (tetragonality, $R_L - R_S = 0.5$ Å) and bond angles (25°), both of which must affect the electronic energies; and (iv) geometry—for a given geometry defined in terms of short (R_S) and long (R_L) Cu—L distances, additional off-axis ligands, such as the unsymmetrically bidentate nitrate and acetate oxyanions (Chapter 15.5) may increase the effective coordination number from five to seven, as in $[Cu(py)_3(O_2NO)_2]$ (**244**)[556] and from four to eight, as in $Ca[Cu(O_2CMe)_4]\cdot 4H_2O$ (**246**).[563,564] In these complexes the off-axis ligands must contribute to the precise energies of the d–d transitions and to the observed electronic spectra.

For the above reasons, while the electronic spectra of the copper(II) ion in its complexes displays a wealth of variety (Figure 51),[48] on an absolute scale they provide little positive information on the underlying copper(II) stereochemistry that is present. Nevertheless, for a closely related series of ligands the average energies of the copper(II) d–d transitions increase in the sequence restricted tetragonal octahedral, elongated tetragonal octahedral, square or rhombic coplanar (Figure 27a).[822] This general increase in average electronic energy is illustrated for the CuO_{6-4} and CuN_{6-4} chromophores in the electronic reflectance spectra of Figure 51(a) and (b). Thus within these restricted ranges of ligand donors, it is then possible to establish a correlation between the range of energies of the d–d transitions of a CuN_x

chromophore and the different stereochemistries present. This is set out in Figure 52;[822] it may then be appropriate to use the correlations of Figures 27(a), 51(a) and 52 to predict an assignment of the one-electron orbital sequences for the series of stereochemistries involved, which may then be used to choose between the alternative assignment of the polarized single-crystal spectra (Figures 49–51).[950] In this respect the latter only provide more accurate band positions, but not necessarily an absolute assignment. Treated in this way the electronic reflectance spectra may be used to substantiate the crystal-field splitting sequences of Figures 26 and 27, and as set out in Table 54. With the number of unknown parameters involved (i–iv above), it is not too surprising that little absolute information is available from the electronic spectra of copper(II) ions which enables the local chromophore stereochemistry to be predicted. Consequently, it is not too surprising that many literature reports of the electronic spectra of copper(II) complexes either ignore any structural information that might be tentatively extracted from the spectra or make rather exaggerated claims concerning the stereochemistry present. A middle course should be possible,[822] such as in the nice series of complexes[958] of alkyl thiocarboxylate copper(II) amine adducts, which are green (**400**), violet and blue. The electronic spectra alone, especially if measured into the near IR (Figure 53), are strongly suggestive of the well known dimeric acetate structure of the green form, the rhombic coplanar structure of the violet form and square pyramidal structure of the blue form, although the increase in coordination number from five to seven by off-axis bonding of the acetate groups of the blue form could not be recognized. This type of correlation is even better if a combination of the electronic properties and stereochemistry is used. It has already been established that for the $[Cu(NH_3)_{4-5}]X_2$ series of complexes[895] the observed tetragonality (T) varies linearly with the $g_{\parallel}$ value (Figure 38a). A similar correlation may be observed for the tetragonality (T) and the electronic energy of the d–d bond maximum (Figure 54a), and between the energies E and the $g_{\parallel}$ values (Figure 54b), and this lends confidence to the prediction of stereochemistry for a *related* series of copper(II) complexes.[822]

Table 54 The Approximate One-electron Orbital Sequences of the Copper(II) Ion in Complexes as a Function of Their Static Stereochemistry[47]

Elongated rhombic octahedral
$d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{xy} \approx d_{yz}$
Square-based pyramidal
$d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{xz}, d_{yz}$
Compressed tetrahedral
$d_{xy} > d_{xz} \approx d_{yz} > d_{x^2-y^2} > d_{z^2}$
Trigonal bipyramidal
$d_{z^2} > d_{xy} = d_{x^2-y^2} > d_{xz} = d_{yz}$
Square coplanar
$d_{x^2-y^2} > d_{xy} > d_{xz} \approx d_{yz} > d_{z^2}$

From Figure 47 it can be seen that charge-transfer bands can occur in the visible–UV region of the electromagnetic spectrum.[940,941] These may be either ligand to copper (LMCT), or copper to ligand (MLCT), or internal ligand–ligand transitions. In general they are electronically allowed ($\varepsilon > 10^3$) and consequently much more intense than the d–d transitions ($\varepsilon > 10^3$). They are generally assigned (Table 55) using extended Hückel-type molecular orbital calculations for the ligands,[959] particularly for sulfur-containing ligands,[940,941] and relate to the unpaired electron on the copper(II) ion. In these assignments the geometry associated with the unpaired d electron is almost irrelevant, as the major concern appears to be with a fingerprint-type characterization of the charge-transfer bands to identify the type of sulfur ligand present (Table 55).

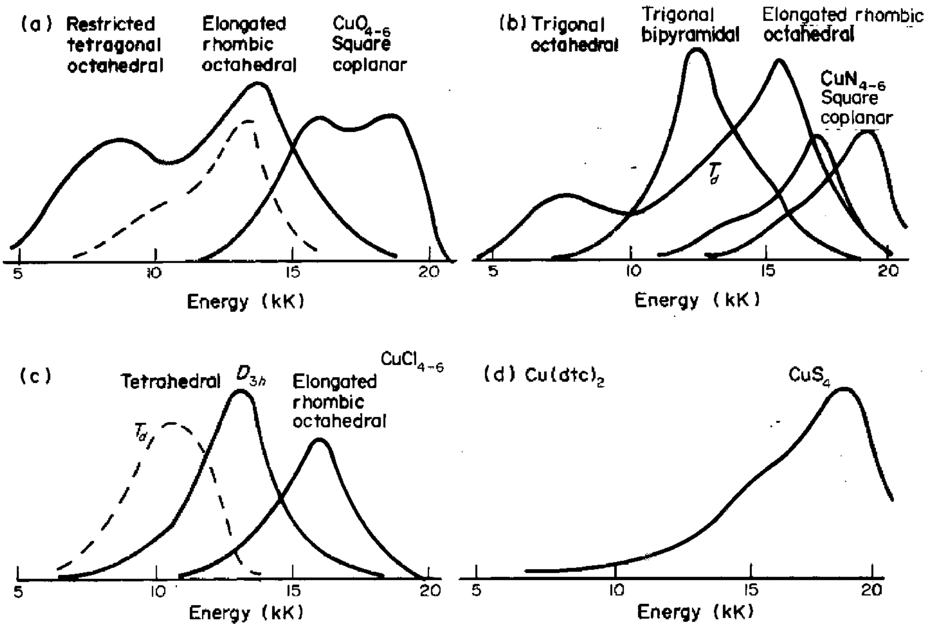


Figure 51 The electronic reflectance spectra of the CuL_n chromophore: (a) L = O; (b) L = N; (c) L = Cl^-; (d) L = S[48]

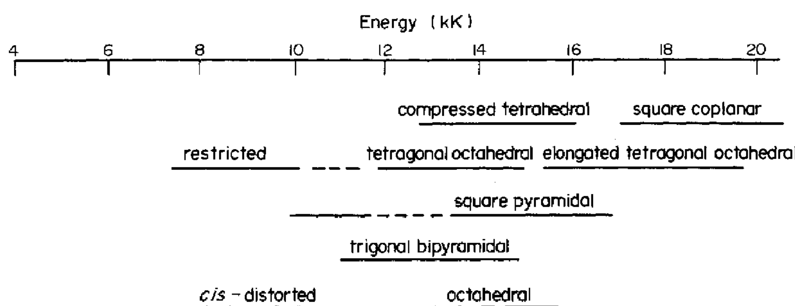


Figure 52 A correlation of the range of energies for the *d–d* transitions for the CuN_x chromophore for different stereochemistries[822]

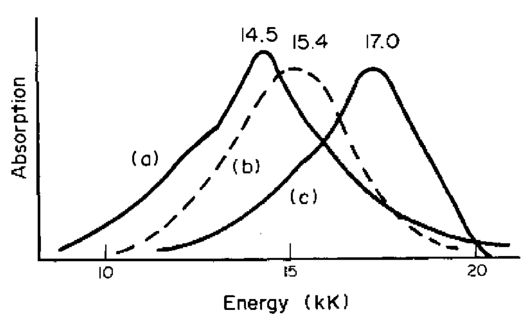


Figure 53 The electronic reflectance spectra of a series of $[Cu(RSCH_2CO_2)_2(amine)_x]$: (a) green; (b) blue; and (c) violet-blue[958]

Relatively little use has been made of the techniques of optical activity[960–962] and magnetic circular dichroism[963] of copper(II) complexes. The absolute configuration[964] of $(-)_{589}$-$[Cu(1\text{-}pn)_3]Br_2{\cdot}H_2O$ has been determined by X-ray crystallography and the absolute configuration denoted as $\Delta(\lambda\lambda\lambda)$. The circular dichroism of the $[Cu(NH_3)_4]^{2+}$ cation and $[Cu(tren)(NH_3)](ClO_4)$ (**224**) have been determined (Figure 55a and b),[965] and using magnetic dipole selection rules, the absorption spectrum is shown to be consistent with the one-electron orbital sequence $d_{z^2} < d_{xy}$, $d_{x^2-y^2} < d_{xz}$, d_{yz}. The natural circular dichroism of the $[Cu(OH_2)_6]^{2+}$ cation in a chiral lattice has been reported.[966]

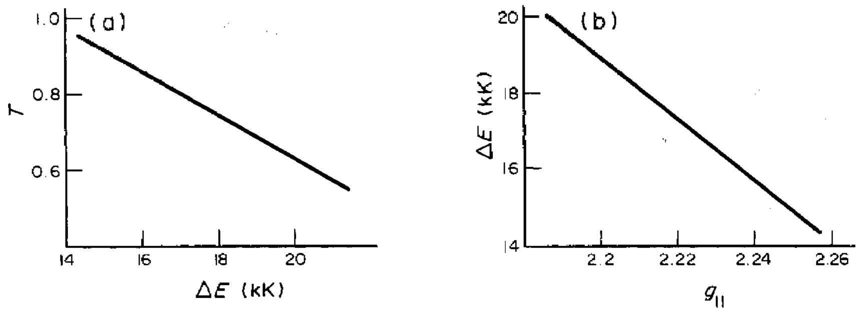
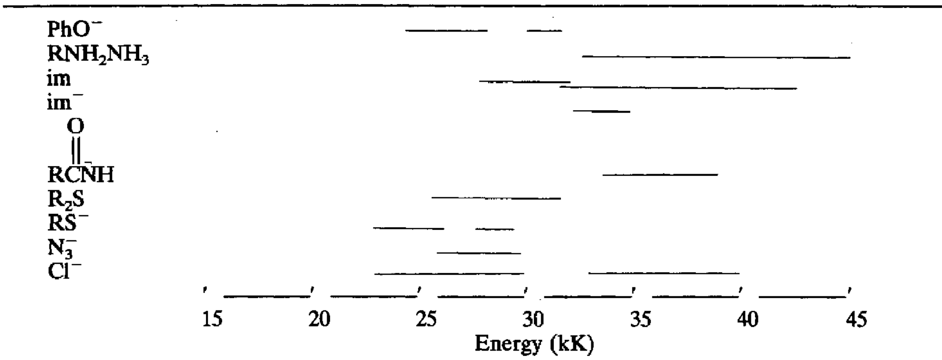
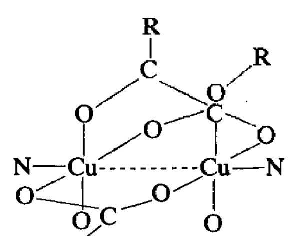


Figure 54 $[Cu(NH_3)_{4-5}X_2]$ complexes: the correlation of (a) the tetragonality (T) and the electronic energy E, and (b) ΔE_{max} *vs.* $g_{\parallel}$ values

Table 55 Identification of the Energy of the LM or MLCT Bands with the Type of Ligand Present[1203]





R = isopropylthio

$[Cu_2(RSCH_2CO_2)_4(amine)_2]$ **(400)**[958]

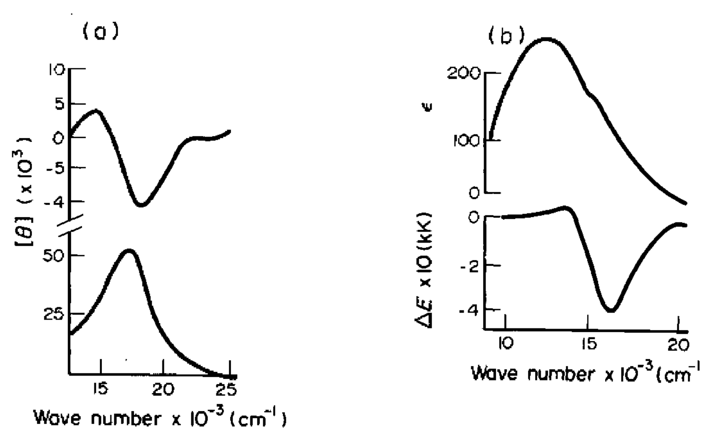


Figure 55 Absorption and circular dichroism spectra of (a) $[Cu(NH_3)_4]^{2+}$ cation in solution,[963] and (b) $[Cu(tren)(NH_3)](ClO_4)_2$ as a single crystal[961]

53.4.4.5 Kinetic and redox properties

The general question of the kinetic and mechanistic properties of copper(II) complexes in solution are of importance in ligand substitution reactions for the preparation of complexes,[22,27] in their redox reactions [copper(I)/(II)/(III)][818,819] and for the role of copper in biological systems (Section 53.4.8).[25–29] A number of texts[967,968] and sections in inorganic chemistry textbooks[17,20,21] give a general introduction to these topics, but with surprisingly little reference to examples of copper(I)/(II)/(III) systems. This is primarily due to the general lack of stability of copper complexes relative to chromium(III) and cobalt(III) complexes (Chapters 35 and 47) and results in fast reaction kinetics, which are more difficult to measure.[967,968]

The reactions of copper(II) complexes to be considered are of two types: (i) ligand substitution reactions; and (ii) redox reactions, *i.e.* electron transfer involving a change in oxidation state, copper(I)/(II)/(III).

(i) Ligand substitution reactions

The preparation of copper(II) complexes is usually carried out in aqueous or nonaqueous solution; in the former, the reactions involved are of the type shown in equation (12) and the strength of the Cu—ligand bond is then determined by a number of factors.[28] The free energy change, $\Delta G = -RT\ln K = \Delta H - T\Delta S$, relates the enthalpy change ΔH, modified by the entropy term ΔS, to the overall stability constant, K. The stability constants are still determined by the classical methods of ref. 969 and the copper(II) data have been tabulated for an extensive range of ligands[970] and recently updated.[971] Equilibrium constants, enthalpy and entropy values are tabulated, not only for equivalent ligands, but also for nonequivalent ligands, which are becoming particularly relevant in the formation of ternary complexes in biological systems (Section 53.4.8).[25–29] The copper(II) ion is characterized by relatively high step-wise (K_n) and overall (β_n) stability constants relative to other first row transition metal divalent ions (Figure 56a);[28,970] this is associated with the overall *d*-block contraction Mn^{II}–Zn^{II} modified by the appropriate crystal-field stabilization energy (CFSE), the Irvin–Williams series.[972] In general, the overall stability constants for copper(II) are slightly less than those for other metal(II) cations due to the general preference of copper(II) for four-coordinate complexes rather than six-coordinate complexes with six equal Cu—L distances (see Section 53.4.2.1ii). Where definite six-coordinate complexes of copper(II) are formed, as in the $[Cu(OH_2)_6]^{2+}$ cation, notwithstanding a clear elongated rhombic octahedral distortion, the copper(II) ion forms the most stable complex, as indicated in the ΔH values of Figure 56(b), $\Delta H = 520\ \text{kcal mol}^{-1}$ ($2174\ \text{kJ mol}^{-1}$). In general chelate ligands form more stable complexes than monodentate ligands (Table 56a), a difference that was earlier described as the 'chelate effect',[969] but this explanation has been questioned.[28] The correlation of the thermodynamic properties (ΔH and ΔS) with structural factors such as ring size and ring strain for a series of related copper(II) chelate complexes has been reviewed and extended to macrocyclic complexes.[973–975] The correlation between the band maximum of the electronic spectra of a series of elongated rhombic octahedral $[CuN_4X_2]$ complexes and their heats of formation ΔH(aq) (Figure 57) is reasonably linear and the greater strength of the Cu—N bond in macrocyclic complexes of the copper(II) ion has been termed the macrocylic effect.[976] More recently thermodynamic studies have been used to measure the equilibrium properties of copper ligands in mixed metal complexes.[977–979] On the basis of the stability constant data metal ions have been classified as hard and soft Lewis acids, depending on their relative stability with different donor ligand atoms (Table 2; Section 53.4.1).[36,967] In this classification the copper(II) ion is classified as having intermediate class (a) and (b) behaviour, *i.e.* Cl = F, but O, S and N ≫ P (see **177–380** and Section 53.2). An alternative measure of the Lewis acid strength of a $[Cu(OH_2)_6]^{2+}$ cation is its tendency to lose a proton (an inductive effect) according to equation (13).[980] The pK_a value for this equation of 6.8, is lower than any of the other first-row divalent transition metal ions, reflecting its greater Irvin–Williams series stability (Table 57b). This enhanced stability is also associated[981] with the exchange of water by the $[M(OH_2)_6]^{2+}$ ion (equation 14). As shown in Table 57(b), the exchange rate for the copper(II) ion is very much greater[982] than that of the other first-row hexaqua cations, in conflict with its Irvin–William type stability,[972] but consistent with the greater Cu—O bond distances[10] of the most loosely held water, as a result of the Jahn–Teller effect (Section 53.4.5)[15] and the rapid inversion of axes.[982] In general, a dissociative S_N1 type mechanism is predicted from ligand-field activation energies for the copper(II) ion to be significantly more likely than an associative S_N2 type mechanism, but as these estimations are based on regular five-, six- and seven-coordinate geometries,[967] they should not be accepted without question, as the involvement of the characteristically distorted geometries of the copper(II) ion in these coordination numbers, such as (4 + 1 + 1*), (4 + 1* + 1*) and (5 + 1* + 1*), may significantly affect these predictions (see Section 53.4.2.1).

$$[Cu(OH_2)_6]^{2+} + L_n(\text{ligand}) \longrightarrow CuL_n + 6H_2O \tag{12}$$

$$[Cu(OH_2)_6]^{2+} \underset{}{\overset{K_a}{\rightleftharpoons}} [Cu(OH_2)_6(OH)]^+ + H^+ \tag{13}$$

$$[M(OH_2)_6] + O^*H_2 \overset{K_1}{\rightleftharpoons} [M(OH_2)_5(O^*H_2)] + OH_2 \tag{14}$$

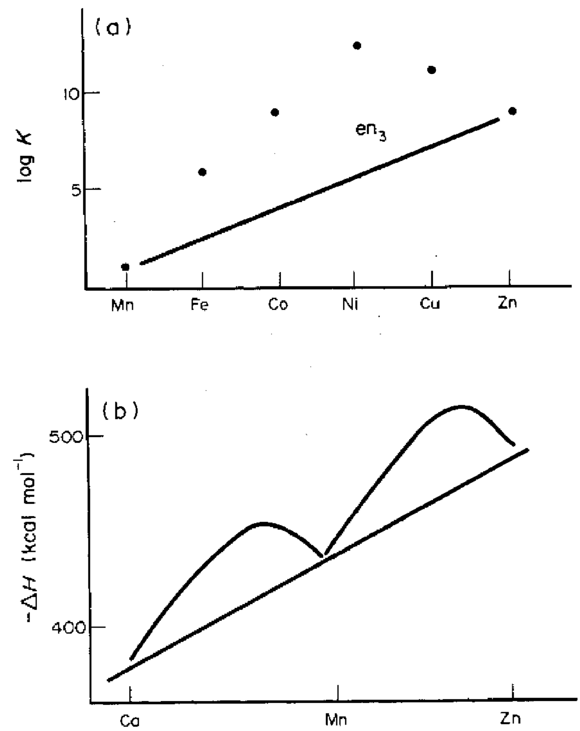


Figure 56 (a) Variation of the overall stability constant log K for M^{2+} ions relative to the $[M^{II}(OH_2)_6]^{2+}$ cation (Irvin–Williams series); (b) variation of ΔH for $[M^{II}(OH_2)_6]^{2+}$ cations (1 kcal = 4.18 kJ)

Table 56 Copper(II) Stability Constant Data (Logarithms)[28]

(a) Stepwise stability constants (k_n)				
	NH_3	*en*	*pn*	*bipy*
k_1	4.2	—	—	—
k_2k_1	3.5, 4.15	10.72, 10.6	9.77	16.8
k_3	2.9	—	—	—
k_4k_3	2.1, 3.5	9.31, 9.1	7.17	6.3
k_5	−0.5	—	—	—
k_6k_3	−2.89	−1.0	—	6.2
(b) Overall stability constants (β_n)				
		3bipy	edta	3en
β_n		5.5	18.8	22.4

Equilibrium studies of $[Cu(chelate)_2]$ complexes are generally determined spectrophotochemically using static and stopped-flow techniques.[967,969] In the substitution[983] of water in the five-coordinate $[Cu(trenMe_6)(OH_2)]^{2+}$ cation by NCO^-, Cl^- or Br^-, the rate is very much slower than that reported for the $[Cu(OH_2)_6]^{2+}$ cation (Table 58), with K values of

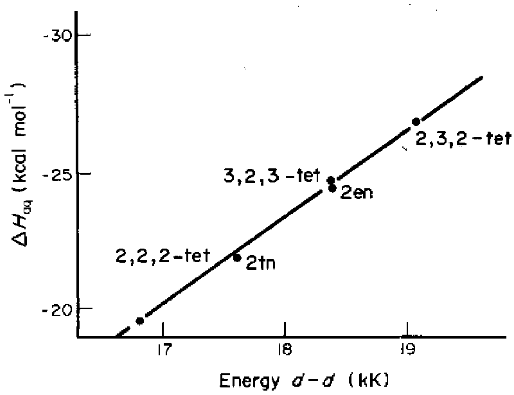


Figure 57 [Cu(*N,N*-chelate)$_2$]X$_2$ complexes; *d–d* maximum *vs.* ΔH_{aq} (1 kcal = 4.18 kJ)[976]

Table 57 $[M^{II}(OH_2)_6]^{2+}$ Cation (a) pK_a Values (Inductive Effects)[980] and (b) Water Exchange Rates (K_1)[981]

	Mn	*Fe*	*Co*	*Ni*	*Cu*	*Zn*
pK_a	0.6	9.5	8.9	10.6	6.8	8.8
K_1(s^{-1})	3×10^7	3×10^6	1×10^6	3×10^4	8×10^9	—

10–100 s^{-1}.[981,983] Dissociation kinetics of [Cu(chelate)$_2$] complexes in acid solution vary with the ring size of the chelate ligand: with six-membered (pm) rings the rates are pH independent, while for five-membered (en) rings the rate constant shows a nonlinear dependence on the H$^+$ concentration, with three alternative pH dependent pathways suggested (Figure 58).[984–986] An even more complicated pH dependence is observed for tridentate polyamines.[985] The kinetics of the ligand exchange reactions with the formation of mixed ligand complexes have been extensively studied (equations 15 and 16).[987]

Table 58 Rate Constant Structural Barriers and Stereochemistry of Some [Cu(chelate)$_2$]$^{2+/1+}$ Cations with Cytochrome c$_2$[1001,1002]

Complex	*Second order rate constant* (M^{-1} s^{-1})	*Self-exchange rate* (M^{-1} s^{-1})	ΔG (kJ mol^{-1})	*Geometry*^{a}	$E°$
(*a*) *chelates*					
[Cu(2,9-dmphen)$_2$]$^{2+}$	1.00×10^6	1.7×10^4	19 }	CT	0.603
[Cu(dipa)$_2$]$^{2+}$	1.62×10^2	6.8×10^2	26 }		0.20
[Cu(nitrophen)$_2$]$^{2+}$	1.57×10^2	8.6×10	32 }		0.257
[Cu(phen)$_2$]$^{2+}$	2.72×10	4.3×10	34 }	T + Td	0.174
[Cu(bipy)$_2$]$^{2+}$	1.39×10	1.4×10^2	30 }		0.12
[Cu(pyim)$_2$]$^{2+}$	1.7	1.2×10	38	P	0.08
(*b*) *O and Cl donors*					
[Cu(OH$_2$)$_6$]$^{2+}$	5.7	5.2	26	ERO	—
[CuCl]$^+$	2.3×10^2	6.6	32	—	—
[CuCl$_2$]	5.6×10^3	20	30	—	—
(*c*)					
[Cu(pdto)]$^{2+}$	1.7×10^4	4.6	36	—	—
[Cu(pmas)]$^{2+}$	1.7×10^3	4.6×10	29	—	—
[Cu(14-ane-S)]$^{2+}$	2.4×10^6	7.6×10^4	11	—	—

^{a} CT = compressed tetragonal; T = tetragonal; Td = tetrahedral; P = planar; ERO = elongated rhombic octahedral.

$$CuA_2 + HB \rightleftharpoons CuAB + HA \quad k_1 \tag{15}$$

$$CuAB + HB \rightleftharpoons CuB_2 + HA \quad k_2 \tag{16}$$

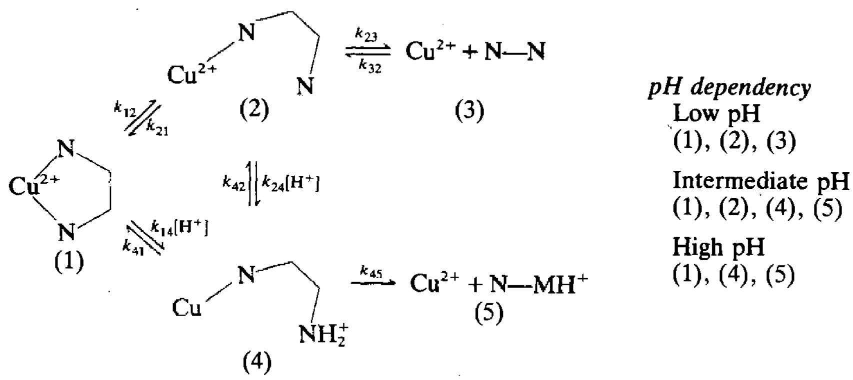


Figure 58 Dissociation pathways, acid dissociation of Cu(chelate) species[984]

Thus [Cu(t-butylsalim)$_2$] has been reacted with N-alkylsalicylidimine using a range of substituents and a variety of aprotic solvents.[987] A complex solvent dependence of the substitution kinetics is found and correlated using two alternative mechanisms, one water dependent (Figure 59a) and the second nonligand dependent (Figure 59b). A comparable two-path pathway has been suggested for reaction (17), where tetren = tetraethylenepentamine.[988] With the increased interest in mixed ligand complexes an extensive literature now exists on these ternary systems.[29] Equally the biological relevance of mixed metal complexes (Section 53.4.8) has resulted in the reporting not only of formation constant data but also of the kinetics and mechanism of the exchange of a metal in a complex by copper(II).[29,989] Thus copper(II) will replace the zinc(II) ion in zinc(II) macrocyclic tetramines, involving 12- to 15-membered macrocyclic rings, with a common two step mechanism (equations 18 and 19) with K_1, the slow rate-determining step.[990] In the case of [Ni(ida)$_2$], where ida = iminodiacetate anion, a different two step process is suggested (equations 20 and 21) with (20) the slow rate-determining step.[991] This last reaction is of interest as it suggests the possible involvement of a dinuclear [Ni(ida)Cu(ida)]$_2$ intermediate species. A dinuclear mixed metal complex has also been postulated in the back solvent extraction of [Ni(8-mercaptoquinolate)$_2$] by copper(II) from a chloroform to an aqueous phase in the pH range 3.7–5.8.[992] The general area of solvent extraction of metal ions by chelate ligands has been reviewed and the kinetics and mechanism of solvent extraction by copper chelates discussed.[993,994] A complete kinetic and mechanistic study has been made of the solvent extraction of [Cu(8-hydroxyquinoline)$_2$] and suggests that the process is diffusion controlled in both the aqueous and organic phases.[995] The formation of copper(II) complexes on ion exchange resins has been reviewed and the industrial importance of these systems in the extraction of copper from low grade ores is emphasized.[996]

$$[\mathrm{Cu(dien)}]^{2+} + \mathrm{tetren} \rightleftharpoons [\mathrm{Cu(tetren)}]^{2+} + \mathrm{dien} \quad (17)$$

$$[\mathrm{ZnL}]^{2+} + \mathrm{MeCO_2H} \overset{K_1}{\rightleftharpoons} [\mathrm{Zn(O_2CMe)}]^{+} + \mathrm{LH}^{+} \quad (18)$$

$$\mathrm{LH}^{+} + [\mathrm{Cu(O_2CMe)}]^{+} \overset{K_2}{\rightleftharpoons} [\mathrm{CuL}]^{2+} + \mathrm{MeCO_2H} \quad (19)$$

$$[\mathrm{Ni(ida)_2}]^{2-} + \mathrm{Cu}^{2+} \rightleftharpoons [\mathrm{Ni(ida)}]^{+} + [\mathrm{Cu(ida)}]^{+} \quad (20)$$

$$[\mathrm{Ni(ida)}]^{-} + \mathrm{Cu}^{2+} \rightleftharpoons \mathrm{Ni}^{2+} + [\mathrm{Cu(ida)}]^{-} \quad (21)$$

The mechanism of the transport of copper(II) complexes through liquid and cell membranes is receiving active attention in view of its biological importance.[997,998]

(ii) *Copper(II) redox reactions*

Like all redox reactions[26,28,967,968] those of copper(II) may be divided into two types: (a) outer sphere mechanisms involving electron (or proton) transfer between coordination shells that remain essentially intact; and (b) inner sphere mechanisms in which the oxidizing and reducing species are connected by a bridging ligand, which is common to both metal ion coordination spheres.[999]

Both types of reaction must obey the Frank–Condon principle,[1000] which states that there must be no movement of the nuclei during the time of electron transfer. Consequently, the

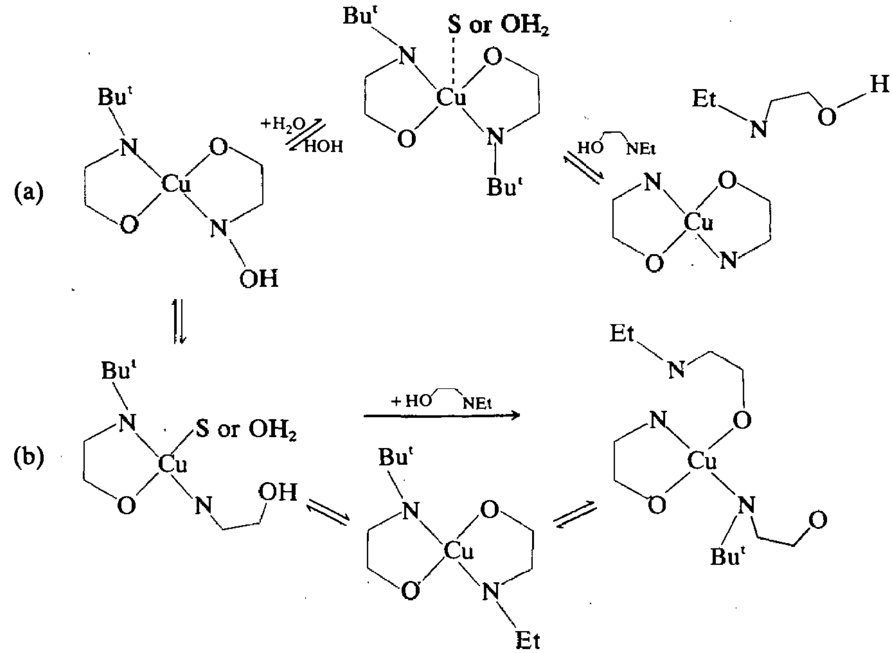


Figure 59 Ligand substitution pathways for [Cu(t-butylsalim)$_2$]: (a) water induced and (b) ligand induced[987]

geometry of the two copper species, [$Cu^{I}L_n$] and [$Cu^{II}L_n$], must be essentially the same before and after the reaction. As the stereochemistry of copper(I) can be summarized as three- < four- > five-coordination (Section 53.3.2.1), while that of copper(II) can be summarized as four- ≈ five- ≈ six-coordination (Section 53.4.2.1), the only coordination number that is common to both oxidation states is that of four coordination.[1001] However, while that of copper(I) may involve a reasonably regular tetrahedral geometry, that of copper(II) always involves a compressed tetrahedral geometry, thus if electron transfer takes place in the ground states of the reactants, the products will both be in excited states after reaction, with higher energies due to geometries that are inconsistent with the respective oxidation states in the ground states. Consequently, both must rearrange their geometry (Figure 60) either before or after the electron transfer process. The former must yield a near regular CuL_4 geometry for both copper(I) and (II) species, which for the latter is inconsistent with the Jahn–Teller theorem (see Section 53.4.5),[15] while in the former, the near regular $Cu^{I}L_4$ chromophore may distort to a compressed tetrahedral $Cu^{I}L_4$ geometry or dissociate into a three-coordinate geometry, plus a free ligand L. With this emphasis on four coordination the kinetics studies of Cu^{I}/Cu^{II} systems have centred on systems[986,1001] with a potential four-coordinate tetrahedral geometry such as $[Cu(bipy)_2]^{2+}$, $[Cu(phen)_2]^{2+}$ and $[Cu(2,9\text{-dmphen}_2]^{2+}$ cations, preferably with a common reducing agent, such as cytochrome (Table 58),[1001,1002] ascorbic acid[1003] 3,5-di-t-butylcatechol or $[Ni^{II}(oximes)_2]$.[1004] In general, the data have been interpreted to suggest a significant 'structural barrier'[1002,986] associated with the change in geometry of the copper(II) ion in its two different oxidation states of 30 ± 10 kJ mol^{-1}, but even here the precise geometry or coordination number of either the copper(II) or copper(I) ions in solution is uncertain, and the best that can be said is that the four-coordinate copper(II) will be favoured by soft ligands,[36] *i.e.* phen, or bulky substituents, *i.e.* dmphen. With more complicated tripod-type ligands containing one or more sulfur ligands the 'structural barrier' is still approximately 30 kJ mol^{-1} and seemingly independent of the donor type, except for CuS_4 (Table 58c).[1001]

A relatively high Cu^{I}/Cu^{II} exchange rate of 5×10^7 mol^{-1} s^{-1} has been observed[1005] in 12 M HCl where [$CuCl_n$] species are present and for the aqueous Cu^{I} species[1006] oxidized by $[Co(NH_3)_5Cl]^{2+}$, A $\times 10^8$ mol^{-1} s^{-1}, but in both cases an inner sphere mechanism probably involving a chloro bridging anion is thought to be present.[999] Thus notwithstanding the extensive literature on inorganic reaction mechanisms of the more stable ML_6 and ML_4 transition metal complexes involving S_N1 and S_N2 type mechanisms and the greater lability of both copper(I) and copper(II) stereochemistries, coupled with their variable coordination

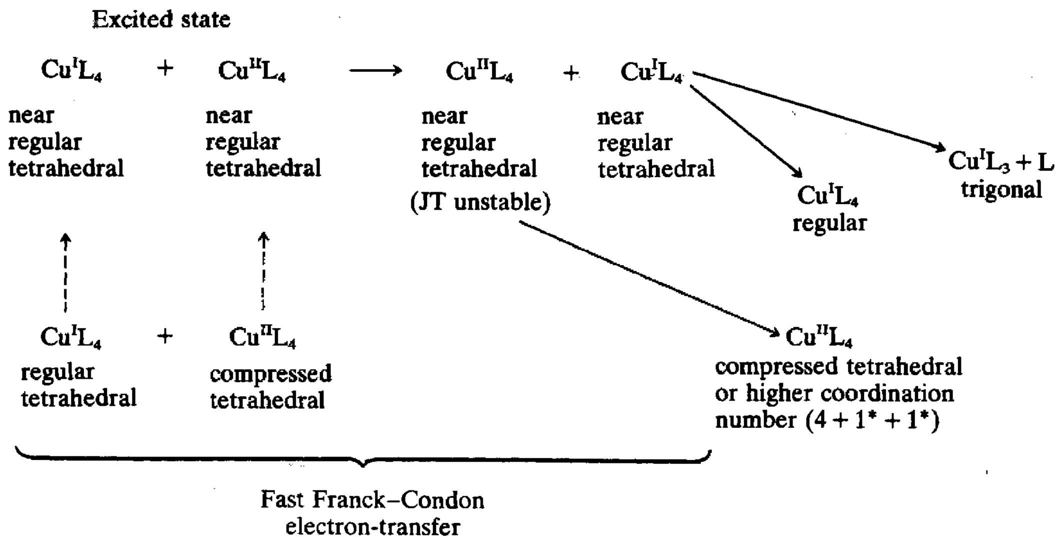


Figure 60 The redox reaction of copper(I)L_4 and copper(II)L_4 species[986]

number (see the plasticity effect in copper(II) systems, Section 53.4.5.1), very little is known about the precise mechanism of the Cu^I/Cu^{II} redox reaction in solution.[986]

Some useful information on these redox processes in solution has been obtained from photoinduced redox and luminescent measurements.[1007,1008] More precise information on the redox properties of the copper(I)/(II) systems can be defined by the standard electrode potential of the process (equation 22).[28,1009] In general, the electrode potentials of Cu^{II}/Cu^I systems are measured by cyclic voltammetry in aqueous solution with the addition of an alkali metal salt ($NaClO_4$) to maintain the ionic strength (Figure 61), from which ΔE and E° values may be obtained, but also the number of electrons transferred and an idea of the reversibility of the electron transfer reaction.[1010] As many copper(II) complexes are not readily soluble in aqueous solution, the measurement of cyclic voltammograms in nonaqueous solution is now commonplace, particularly the use of MeCN as a solvent, with the addition of $(NEt_4)(ClO_4)$ to maintain the ionic strength of the solution.[1011] By definition the Cu^{II}/Cu^I redox process occurs at the surface of the electrode, but as the potentials are measured in solution, these will be influenced by the copper(I) and copper(II) ionization potentials, modified by the respective cation ligand environments, namely their coordination number, stereochemistry and the type of ligand atoms (hard or soft acid behaviour, Table 3). As in the kinetics of redox in solution the E° values are difficult to relate to the coordination number and stereochemistries of the species present, as these are variable and more than one species may be present in solution. Nevertheless, the E° values for various Cu^{II}/Cu^I systems are generally described in terms of the ligands present in the solid state (Figure 62). In general reducing (soft acid) ligands such as CN^-, I^- and phen produce the more positive E° values and stabilize the Cu^I state, as in the addition of KI to Cu^{II} (equation 23), while hard acids like en produce a clear negative E° of -0.35 V, with OH_2 and NH_3 having only just positive potentials of 0.153 and 0.01 V, respectively. For a comparable range of ligands, such as the chelate nitrogen ligands of Table 59(a), there is a reasonable correlation between the log of the second order rate constant and the E° values. There is also a correlation between the suggested stereochemistries of Table 59(a), but in view of the uncertainty of the precise geometry involved in solution, this correlation may be coincidental.

$$Cu^{2+} + e^- \longrightarrow Cu^+ \quad E^\circ \qquad (22)$$

$$Cu^{2+} + 2I^- \rightleftharpoons CuI + I^0 \qquad (23)$$

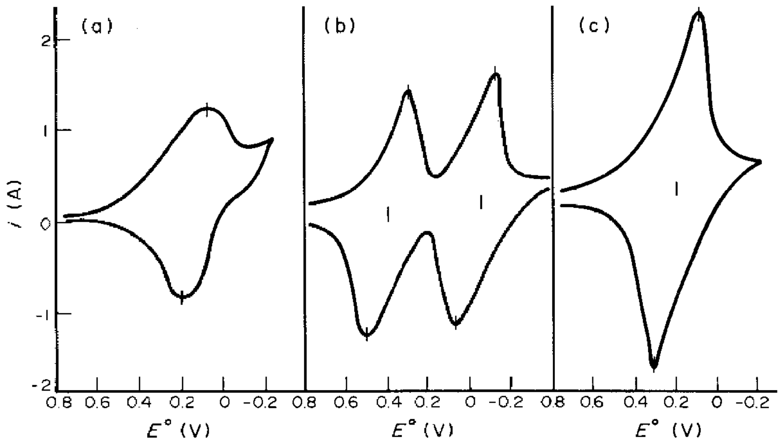


Figure 61 Cyclic voltammograms for $Cu^{II/I}$ systems: (a) one-electron transfer; (b) two-electron transfer at different $E°$ values and (c) at the same $E°$ value

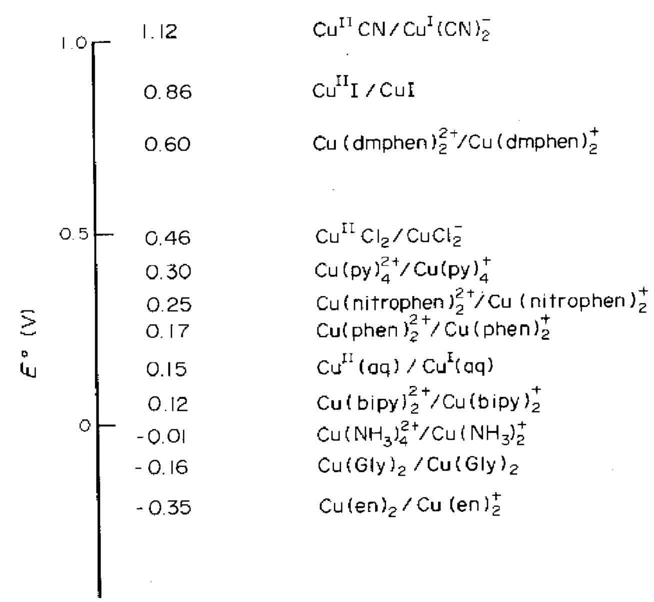


Figure 62 The standard electrode potentials (V) of the $Cu^{II/I}$ system as a function of ligand environment[818]

The relationship between the $E°$ values for the Cu^{II}/Cu^{I} system and the type of ligand present (Figure 62) was first established and extended to copper chelate systems, where it was concluded that nonplanar complexes were easier to reduce than planar complexes and for the latter the ease of reduction was in the order $N_4 < N_2O_2 < N_2S_2$.[818,1012] Later attempts to show any correlation between the redox values and those electronic properties which vary with stereochemistry proved even less successful, but some correlation was observed between $E°$ and $g_{\parallel}$ for a series of $[Cu(P2A\text{-}R)_2]$ complexes, where P2A-R = *N*-alkylpyrrolecarboxaldimine (Figure 63a).[818,1013–1019] A tetrahedral twist of the planar CuN_4 chromophore results in a decrease in $g_{\parallel}$ and an increase in the $E°$ value by 200 mV (Figure 63b). For a limited range of aryl-substituted $[Cu(P2A\text{-}aryl)_2]$ complexes, a positive correlation was obtained between the $E°$ values and the Taft induction factor σ^0 (Figure 63b). A reasonable correlation of $E°$ with the band maximum of the electronic spectrum has also been obtained for a series of elongated rhombic octahedral CuN_2S_2 chromophores in MeCN solution.[1016]

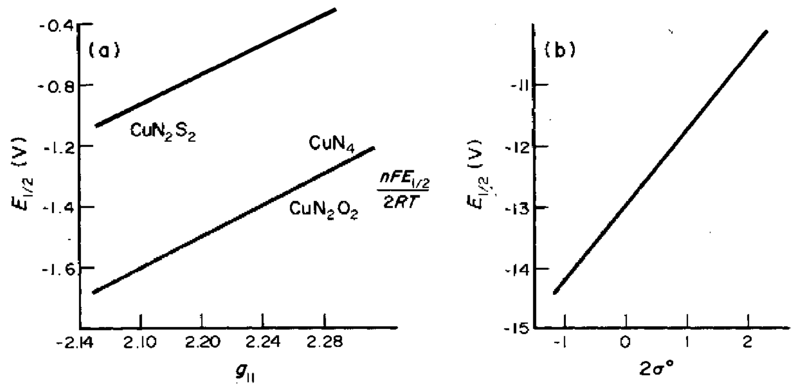


Figure 63 $[Cu(P2A\text{-}R)_2]$ complexes correlation of (a) $E^\circ_{1/2}$ *vs.* $g_{\|}$ and (b) $E^\circ_{1/2}$ and $2\sigma°$, where $\sigma°$ is the Taft induction parameter[1011,1014]

The redox properties of the copper(II) ion in saturated polyaza macrocyclic complexes CuN_4 and CuN_5 have been shown[1020] to vary with the chelate ring size, and the very negative $E°$ values (Figure 62) are consistent with a 'macrocyclic effect', from stability constant measurements.[976]

The redox properties of dinuclear copper(II) complexes have received extensive attention using cyclic voltammetry measurements, and it was recognized in the early literature that the two copper(II) ions could be reduced to copper(I) at the same potential or at different potentials (Section 53.3.7).[30,934,1021,1022] In either case the reduction requires a two electron process and if the $E°$ values are well separated may result in the observation, under favourable circumstances, of a two-peaked cyclic voltammogram (Figure 61b), as in $[Cu_2(isiom)(Mepy)_2(OH)]$ and other systems. Nevertheless care has to be taken that a two-stepped cyclic voltammogram does not arise from a two-stepped reduction of the type shown in equation (24), involving a two electron reduction of Cu^{III} to Cu^I.[1023] Equally, from a copper(II) to copper(I) reduction, plus a single electron reduction of the ligand, although ligand reductions usually fall outside the range +1.0 to −1.0 V, or if two different copper(II) species occur in the same solution but reduce at different potentials, as in the case of the $[Cu(bbdH)Cl]^+$ and $[Cu(bbdH)(MeCN)_x]^{2+}$cations in MeCN solution,[1024] which arise from the plasticity effect[461] when a mixture of species (or isomers) can be generated in the same solution. More frequently, two electron reduction may result in the observation of a single peak in the cyclic voltammogram due to the identical $E°$ values or to two different values that cannot be resolved. The two electron reduction can be recognized in the magnitude of the reduction current, which will be twice that involved in a single electron reduction and generally arises where the two copper(II) centres are completely independent (but have the same geometry) and are physically well separated, as in [Cu(cryptate)].[1025,1026] But a single peak may also arise if the two copper(II) centers are closely connected, as in $[Cu(1,3,5\text{-triketone})_2]$[1027] or in $[Cu_2(C_{20}H_{26}F_{12}N_2O_4)]$[619,1028] **(273–275)**, where controlled electrochemical reduction has enabled the intermediate mixed oxidation state Cu^I/Cu^{II} complex to be isolated. In the latter at room temperature, the ESR spectrum shows a seven line adsorption (Section 53.4.4.3), indicating that the copper(II) environment is influenced by the copper(I) neighbour in the dimer, suggesting a class II Robin and Day behaviour for this mixed oxidation state dimer (Section 53.3.7).[360]

$$[Cu^{III}(Pr^i_2dtc)_2]^- \xrightarrow{+e^-} [Cu^{II}(Pr^i_2dtc)_2]^0 \xrightarrow{+e^-} [Cu^I(Pr^i_2dtc)_2]^+ \qquad (24)$$

In situ photoacoustic spectroscopy has been used to study the redox process on the surface of an electrode using copper metal in alkaline solution.[1029] The $E°$ values of copper(II) Schiff base complexes[1030] absorbed on optically transparent thin-layer electrodes (OTTLE) have been determined in the UV region and the results are consistent with the trends previously established (Figure 62).[1030] The use of the OTTLE technique is attractive as it provides the absorption spectrum of the electrochemically generated species in solution, but still with the uncertainty of the precise species in solution. What is really required is the ability to record the electronic reflectance spectrum of the electrochemically generated species on the electrode surface, in order to correlate the $E°$ values with the copper(II) environment in the solid state.[1031]

53.4.4.6 *Infrared and Raman spectroscopy*[92]

Infrared spectroscopy can give information in three main areas of structural copper(II) chemistry, namely the vibrations of the ligand, of the CuL_n chromophore and of any polyatomic anions present. The former two catagories are well covered in standard text books[297] and that of NH_3 as a ligand to the copper(II) ion in a range of possible stereochemistries has been reviewed (Table 59).[354] In general the ammonia vibrations are not very sensitive to the different stereochemistries present and even the Cu—N vibrations show little systematic variation with stereochemistry (Table 59). However the Cu—L vibrations are frequently split into two or more peaks relative to the vibrations observed in other transition metal complexes. This effect has been discussed in the crystal-field aspects of the vibrational spectra of metal complexes.[1032] The IR and Raman spectra of polyatomic oxyanions as ligands have been dealt with in Chapter 15.5, of polyhalide anions in Section 53.3, and of the halogen-containing anions in Chapter 15.5; no attempt will be made to duplicate these accounts. But there are two areas of copper(II) coordination chemistry involving IR spectroscopy that are unique to copper(II). The first is the IR criteria for semi-coordination of a polyatomic anion in the fifth and sixth axial positions of an otherwise rhombic coplanar CuL_4 chromophore, as in $[Cu(en)_2(FBF_3)_2]$ (**193**), which involves a long Cu—F distance of 2.56 Å compared with a distance of 3.34 Å in $[Cu(pyNO)_4](BF_4)_2$.[468,354] The IR spectrum of the latter (Figure 64a) indicates an ionic $(BF_4)^-$ anion, while in (**193**) the IR spectrum (Figure 64b) indicates that the $(FBF_3)^-$ anion is involved in weak coordination to the copper(II) ion, *i.e.* is semi-coordinated (Section 53.4.2.1ii).[468] In a series of $[Cu(substituted\text{-}en)_2X_2]$ complexes a correlation has been demonstrated between the copper–nitrogen frequency and the highest copper–halogen or –oxygen frequency.[1033] In the $[Cu(en)_2X_2]$ complexes a correlation exists between the maxima of the electronic spectra and the Cu—N frequencies (Figure 65a), while for a series of $[Cu(NH_3)_{4-5}X_2]$ complexes, the maxima of the electronic spectra correlate with the square of the Cu—N frequencies for a range of stereochemistries from square coplanar through elongated rhombic octahedral to square-based pyramidal (Figure 65b).[1033,1034] Together, these correlations suggest that there is a small but positive interaction of semi-coordinate ligands with the copper(II) ion. Much less information is available on the Raman spectra of copper(II) complexes, due to the their colour limiting the excitation energies that are available, but some Raman spectra have been reported.[1035–1037] The second feature associated with the IR spectra of copper(II) complexes is related to the splitting of the Cu—N bands of Table 60 and is associated with fluxional[397] copper(II) stereochemistries and may relate to the underlying state stereochemistries present (see Section 53.4.5, Figure 67 and Table 60).[1038,1039]

Table 59 Some IR Assignments of $[Cu(NH_3)_x]X_2$ Complexes (cm^{-1})[354]

	NH_3 asymmetric deformation	*NH_3 symmetric deformation*	*NH_3 rocking*	*Cu—N stretching*	*N—Cu—N bending*
Hexaammines	1609–1587	1229–1223	732–694	522–510	—
		1150–1087		406–399	
		1085–1013			
Pentaammines	1645–1595	1302–1230	742–716	537–509	246–230
		1272–1087		420–390	
Tetraammines	1635–1590	1300–1240	725–680	460–408	250–232
Diammines	1673–1585	1310–1227	755–700	500–437	268–220
			685–640		

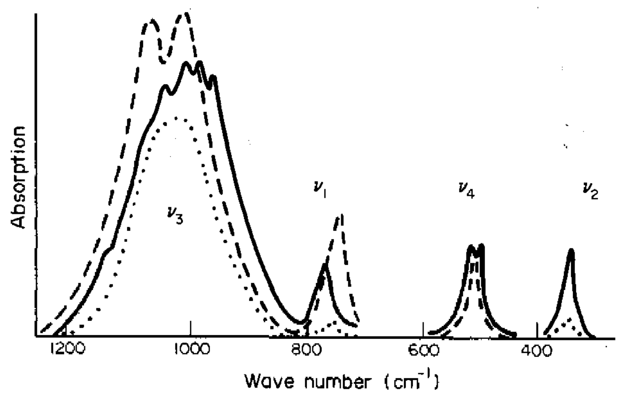


Figure 64 The IR spectrum of the $(BF_4)^-$ anion: (a) $K(BF_4)$, ionic, Td symmetry (·····); (b) $[Cu(en)_2(BF_4)_2]$, semicoordinate C_{3v} symmetry (——); (c) $[Me_3SnBF_4]$, bridging covalent, C_{2v} symmetry (- - - -)

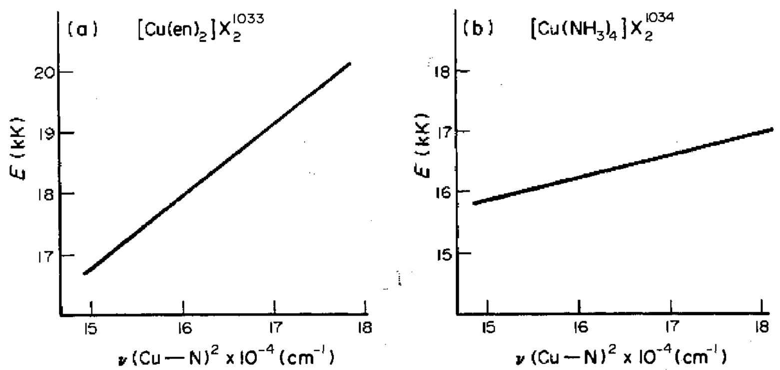


Figure 65 The variation $(Cu—N)_2$ *vs.* band maximum of the *d–d* spectra (a) $[Cu(en)_2]X_2$ and (b) $[Cu(NH_3)_4X_2]$ complexes[1033]

Table 60 Some IR Data (cm^{-1}) for the Series $[M^{II}(NH_3)_6]Cl_2$[1023]

	Mn	*Fe*	*Co*	*Ni*	*Cu*	*Zn*
NH_3 degenerate deformation	1592	1597	1602	1607	1609	1596
NH_3 symmetric deformation	1134	1151	1163	1175	1087,1229	1145
NH_3 rocking	617	641	654	650	732	645
M—N stretching	307	321	327	334	406, 430	300

53.4.4.7 EXAFS spectroscopy

The current availability of synchrotron radiation sources has resulted in the increasing availability of copper–ligand bond-length data (but not bond-angle data) from systems that are not available as single-crystals and hence accessible to single-crystal X-ray crystallographic techniques.[1043–1045] These are polycrystalline samples, surface absorbed species and, more recently, biological systems. EXAFS spectra at the K-edge absorption,[1040–1042] which is associated with the $1s \rightarrow 4p$ transition, have been suggested to distinguish the Cu^I and Cu^{II} oxidation states, but as the shift in band position only involves 1–2 eV on 935 eV, the spectra may not be totally convincing at present as a criterion for these oxidation states. The technique of EXAFS spectroscopy readily provides data on the short copper–ligand distances with low resolution data,[1043–1046] but it has become clear that only high resolution data, including back-scattering from light atoms as far out as 4.0 Å, is required to obtain accurate long copper–ligand distances and the correct number of ligands. Thus, while the EXAFS spectrum of $[Cu(OH_2)_4(OSO_3)]\cdot H_2O$ (**439**) yielded four Cu—O distances of 1.95 Å, compared with the crystallographic values of 1.97 Å, the spectra failed to yield any evidence for the two long

Cu—O distances of 2.4 Å. Nevertheless, the technique does yield a reasonable Cu—O distance of 1.95–2.00 Å in the linear chains of $[Cu(C_6O_4Br_2)]$ and $[Cu(C_2O_4)(H_2O)]$, and in the Cu—S distances of 2.22–2.61 Å in $[Mn_{0.87}Cu_{0.26}PS_3]$.[1047–1050] This technique has yielded novel data on the environment of the Cu^{2+} cation adsorbed on the surface of the synthetic zeolite $[Zr(PO_4H)_2(H_2O)_4]$ involving four Cu—O distances of 1.92–1.97 Å,[1051] but then reports five equivalent Cu—N distances of 2.06 Å in $[Cu(NH_3)_5](BF_4)_2$[1052] when other techniques suggest a square pyramidal CuN_5 chromophore, as in $K[Cu(NH_3)_5](PF_6)_3$ (**218**).[449] It is equally interesting that the EXAFS spectrum of $[CuCl_2(OH_2)_2]$ (**192**) (see Chapter 15.5, Table 6) predicts, correctly, both the long and short Cu—Cl distance in (**192**), and in polycrystalline $[Cu(ClO_4)_2]$ predicts very reasonable Cu—O and Cu—Cl distances, which then require a very short Cu—Cu separation of 3.0 Å (see Figure 4, Chapter 15.5).[402,1053] EXAFS spectra have been reported for copper(I), (II) and (III) carboxylates involving short metal–metal distances,[1054] and the Cu—Cu and Ni—Cu distances in $[NiCu(C_2O_4)_2(H_2O)_4]$ have been used to rationalize the antiferromagnetic properties.[1055] It is then of interest that the EXAFS spectra of $K_2Pb[Cu(NO_2)_6]$ (**177**) and $[Cu(en)_3](SO_4)_2$ (**178**) indicate two short Cu—N distances of *ca.* 2.00 and 2.4 Å, suggesting that these relate to the underlying static geometry of these fluxional chromophores,[397] as the lifetimes of these spectra, 10^{-18} s, are extremely short (see Section 53.4.5.2).[1056,1057]

EXAFS spectroscopy has been used to examine the adsorption of CO_n on $Cu/ZnO/Al_2O_3$ shift catalysts,[1058] of the $[Cu(en)_2]^{2+}$ cation on zeolites,[1059] the bond length of iodine absorbed on the Cu[111] and Cu[100] faces of Cu metal,[1060] and to determine the metal–metal distance in Ru—Cu clusters.[1061] More recently the use of polarized X-ray absorption spectroscopy of oriented single-crystal samples has suggested that this technique may yield angular data as well as copper–ligand distances in the not too distant future.[1062] Nevertheless, some caution should be exercised in accepting the long Cu—L distances suggested for copper(II) structures by EXAFS spectroscopy until more convincing examples of its ability to predict both short and long Cu—L distances on model complexes of known crystal structure have been obtained, such as the data for $CuCl_2{\cdot}2H_2O$ above (Chapter 15.5).[1053]

At the end of this section on the relationship between the electronic properties and the stereochemistry of complexes of the copper(II) ion, it is worth summarizing the most useful physical techniques which offer a criterion for the presence of a polynuclear copper(II) complex rather than a mononuclear complex. These are: (i) magnetic susceptibility measurements down to near absolute zero, for the determination of *O* or *J* values; (ii) ESR spectra of magnetically dilute systems, in the solid state or in solution, to obtain hyperfine data; and (iii) cyclic voltammetry to show evidence for a one-step reduction process in a Cu_2 species.

In general, electronic spectra, IR, Raman and EXAFS spectra relate to the mononuclear CuL_n geometry and give no evidence for the presence of a polynuclear structure.

53.4.5 The Jahn–Teller Theorem

The above account of copper(II) stereochemistry and electronic properties (Sections 53.4 and 53.4.4) establishes the uniqueness of the regular octahedral (and trigonal octahedral) stereochemistries and the novel temperature variability of this stereochemistry (Sections 53.4.2.1i and x) and the corresponding ESR spectra.[396–397] In order to understand these properties it is necessary to examine the Jahn–Teller theorem[15] in a little more detail, as the consequences of this theorem extend beyond the above two topics and will cover the following: (i) temperature variable (fluxional) copper(II) pseudo stereochemistries;[397] (ii) non temperature variable, static copper(II) stereochemistries;[396] (iii) the plasticity effect and varying tetragonal distortions;[456] (iv) the second order Jahn–Teller effect;[1063–1065] and (v) the cooperative[432] and noncooperative[514] Jahn–Teller effects.[1063,1065] For this reason the application of the Jahn–Teller theorem to the coordination chemistry of the copper(II) ion will be described[461,1066–1072] and extended to the above topics.[461,540,1066–1072]

The Jahn–Teller theorem requires that any nonlinear system with an electronically degenerate ground state will undergo a distortion of its nuclear framework in order to remove the degeneracy.[15,1067,1072] The form of the distortion can be any of the non totally symmetric normal modes of vibration of the octahedral chromophore CuL_6 whose representations are contained in the direct product of the ground-state representation for the appropriate point group. In the present case, the representation of the ground state is e_g in the O_h point group. The direct product, $e_g \times e_g$, reduces to $a_{1g} + a_{2g} + e_g$. As the a_{1g} mode is totally symmetric and there is no a_{2g} mode, only the components of the e_g mode are shown in Figure 66, I and II. The extrema of these vibrations are of the same form as the static distortions commonly found in six-coordinate copper(II) complexes. The elongated tetragonally distorted octahedron, (Figure 66, III) and the elongated rhombically distorted octahedron (IV) result from having the odd electron in the $d_{x^2-y^2}$ orbital. The compressed structures V and VI result from having the odd electron in the d_{z^2} orbital. Calculations suggest that the elongated structures are energetically more favourable, consistent with their more frequent occurrence.[1129] It must be emphasized that although the Jahn–Teller theorem may account for the types of distortion observed in copper(II) complexes, it cannot determine the magnitude of the distortion.

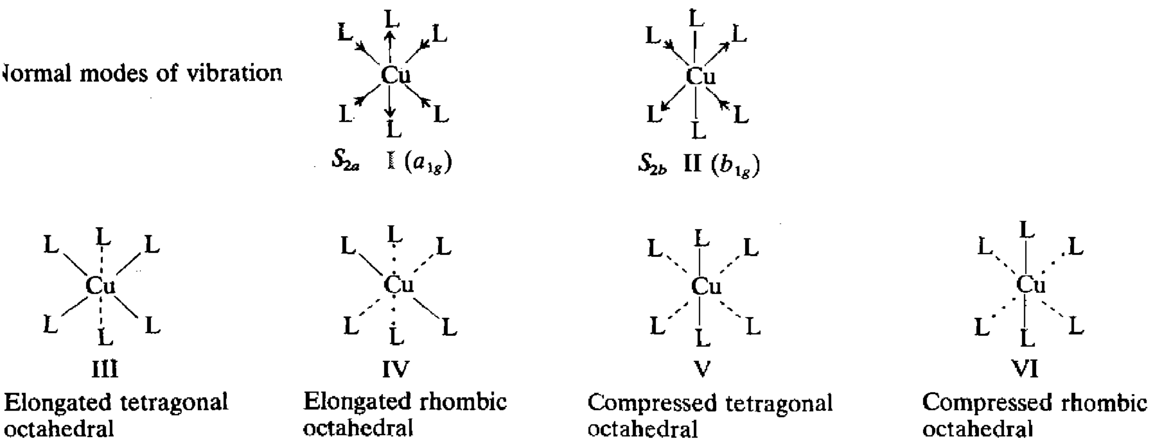


Figure 66 The form of the tetragonal and rhombic distortion of an octahedral chromophore CuL_6. Bond lengths are represented ——<– – –<· · ·

The regular octahedral CuN_6 chromophore in $K_2Pb[Cu(NO_2)_6]$ **(177)**[426] would seem to conflict with the predictions of the Jahn–Teller theorem as the copper(II) ion 'appears' to be spherically symmetrical.[47,48] This is well illustrated in the variation of the unit cell parameters (Table 61) of the series of isostructural complexes $K_2Pb[M^{II}(NO_2)_6]$, $M^{II} = Fe^{II}$, Co^{II}, Ni^{II} and Cu^{II}.[1073] There is a systematic increase in the a values from the spherically symmetrical ions, iron(II) and nickel(II) (in a one-electron orbital configuration sense) to the non spherically symmetrical copper(II) ion. This is consistent with the systematic filling of the ligand-repelling e_g orbital level. The regular CuN_6 chromophore present in $[Cu(en)_3](SO_4)$ **(178)**[427] is also in conflict with the predictions of the Jahn–Teller theorem.[15]

Table 61 The Unit Cell Parameters $\bar{a}$(Å) for the Series of Complexes $K_2[PbM^{II}(NO_2)_6]$[1073]

	Fe	*Co*	*Ni*	*Cu*
$\bar{a}$	10.31	10.40	10.55	10.65
$\bar{a}$	10.36	10.51	10.60	10.70
One-electron orbital configuration	$t_{2g}^6e_g^0$	$t_{2g}^6e_g^1$	$t_{2g}^6e_g^2$	$t_{2g}^6e_g^3$

Qualitatively, the electronic properties of the d^9 configuration of the copper(II) ion in an orbitally degenerate electronic ground state can no longer involve separately defined electronic and vibrational energies (the Born–Oppenheimer approximation), but a vibronic potential energy surface, as in Figure 67, is required.[540] The even mode of vibration of e_g symmetry, made up of two displacement coordinates, S_{2a} and S_{2b} (Figure 67b), is the only mode that can couple with the electronically degenerate ground state of E_g symmetry, of energy E^0, in a cubic system and remove the orbital degeneracy. The energy surfaces which arise from this coupling, E^- and E^+, take the form shown in Figure 67(a), and this is known as the 'Mexican hat' model. The surface E^- involves a potential energy minimum E_{JT}, the Jahn–Teller stabilization energy, relative to E^0 at a distance R_{JT}, the Jahn–Teller radius, from the origin. If only first-order coupling terms are involved, the potential energy well has full cylindrical symmetry, but if strong Jahn–Teller coupling and higher order terms are involved, the lower energ surface is warped (Figure 67c). If the sign of the coupling constant is negative (Figure 68a) minima occur in the potential surface for $\theta = 0$, 120 and 240° and these values correspond, a equilibrium, to three equivalent elongated tetragonal octahedral distortions, C_{3v} symmetry along the three orthogonal z, x and y axes, respectively (Figure 68a, points I, II and III). I crystals, lattice-packing effects and cooperative Jahn–Teller effects (see later) may further war the potential energy surface such that the strict C_{3v} symmetry is removed. Figure 68 illustrate the three different situations that can arise; three elongated tetragonal octahedral stereochem istries are involved: type (a), where all three wells are of equal energy, type (b), where tw wells are of equal energy and type (c), where one low energy well occurs.

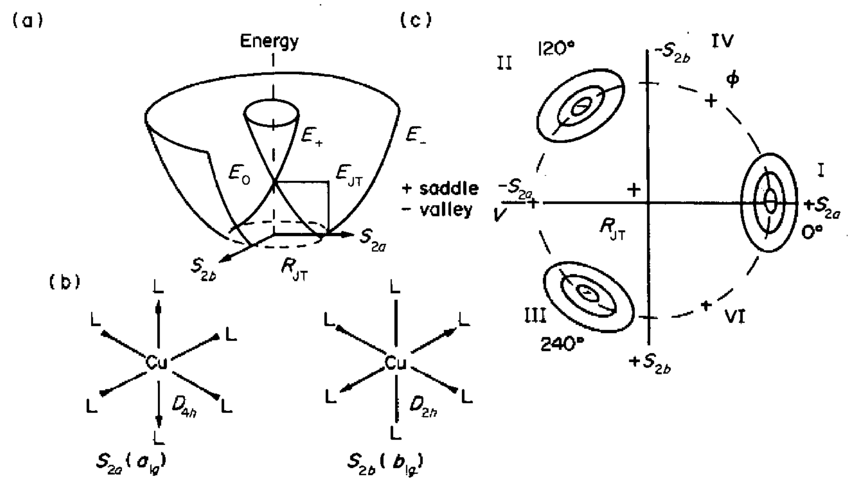


Figure 67 (a) The adiabatic potential energy surfaces (Mexican hat); (b) the normal coordinates S_{2a} and S_{2b}; (c) th projection of the potential energy surface (a) warped by the inclusion of higher order terms viewed down the princip axes of (a), with R_{JT} = radius of the minimum potential[432]

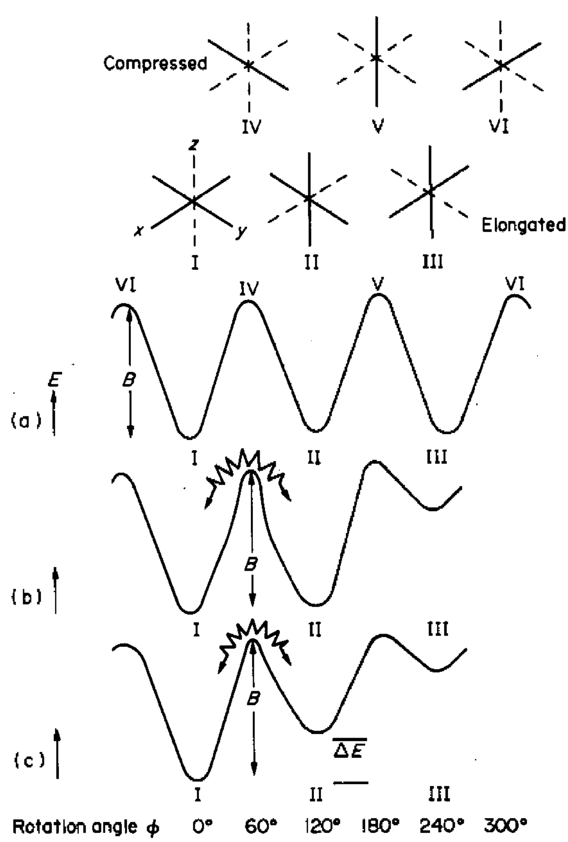


Figure 68 The circular cross-section of the warped potential energy surface (a) three wells of equal energy; (b) tw wells of equal energy; (c) one low energy well

If all three wells[540] are of equal energy (Figure 68a), and if $B <$ thermal energy kT (*ca.* 200 cm^{-1}), at any one copper site a three-dimensional dynamic interconversion of the elongation axes occurs with equal thermal population of wells I, II and III. Consequently, the crystallographically determined structure will be octahedral, but is better described as a pseudo-octahedral stereochemistry in view of the three-dimensional dynamic behaviour involved. Figure 68(b) depicts a situation in which well III is of considerably higher energy than wells I and II, which are of approximately equal energy and hence approximately equally occupied. If $B <$ thermal energy (kT), then the two 90° misaligned CuL_6 chromophores are thermally accessible and at any one copper site a two-dimensional dynamic interconversion of the elongation axes occurs. The crystallographically determined CuL_6 stereochemistry will appear compressed octahedral, but is better described as a pseudo-compressed stereochemistry,[396,397] in view of the two-dimensional dynamic behaviour involved. If the potential energies of wells I and II are significantly different (Figure 68c), and if $B <$ thermal energy (kT), then the observed structure will be elongated rhombic octahedral, but the observed tetragonality T will be high ($T = 0.90$) and temperature variable (T = mean in-plane Cu—L bond distance/mean out-of-plane Cu—L bond distance).[465] If B is larger than the thermal energy (kT), the elongated tetragonal or rhombic octahedral structure of well I (Figure 68c), predominates and the static non temperature variable elongated rhombic octahedral stereochemistry occurs, as found for the majority of elongated rhombic octahedral complexes of the copper(II) ion, with tetragonalities in the region $T = 0.75$–0.85.[456]

In order to understand the predominance of the static elongated rhombic octahedral stereochemistry for the six-coordinate copper(II) ion rather than the compressed rhombic and regular octahedral (or trigonal) stereochemistry, it is necessary to look more closely at the origin of the vibronic coupling associated with the Jahn–Teller effect.[1064,1065,1074] In the dynamic Jahn–Teller effect (Figure 69) only the components of the e_g mode of vibration (a_{1g} and b_{1g} in D_{4h} symmetry) can couple with the electronically degenerate E_g ground state of a copper(II) ion in a regular octahedral stereochemistry CuL_6 (Figure 69, A). If the a_{1g} mode alone is involved (Figure 69) the O_h symmetry is lowered to D_{4h}, with an elongated distortion, B, having a $^2B_{1g}$ ground state, for a positive coupling (+) and with a compressed tetragonal distortion, C, having a $^2A_{1g}$ ground state, for a negative coupling (−). From Figure 67c both of these situations can be seen to correspond to an energy lowering relative to E^0, but $(+)a_{1g}$ coupling corresponds to a lower energy (well I of Figure 68a) relative to the saddle-point V for $(-)a_{1g}$ coupling. If the b_{1g} mode alone is involved, with both positive (+) and negative (−) coupling, the O_h symmetry is lowered to D_{2h} with elongated rhombic octahedral distortions, D and E, both with an approximate $^2B_{1g}$ ground state. In general a linear combination of a_{1g} and b_{1g} modes will produce an elongated rhombic octahedral distortion except at $\theta = 60$, 120, 240 and 270°, where a tetragonal distortion occurs (Figures 67c and 68a).

In all four distortions of Figure 69 B–E the magnitude of the distortion will generally be small, *i.e.* tetragonalities T of 0.98 and 1.02, all of which remove the orbital degeneracy of the regular octahedral CuL_6 chromophores of Figure 69 B–E. To account for the more distorted geometries found in real complexes, with $T = 0.9$–0.8, two further operations must then occur.[1064,1065,1067]

(a) $4s + 3d_{z^2}$ mixing: in the D_{4h} point group the $4s$ and $3d_{z^2}$ orbitals transform as a_{1g} and may mix. This will significantly lower the energy of the $^2B_{1g}$ ground state by lowering the energy of the a_{1g} level (Figure 70a), a lowering of the energy of the d_{z^2} level that corresponds to an increase in the observed elongation and a decrease of T from 0.98 to 0.80. This gain in energy does not arise in the compressed tetragonal octahedral stereochemistry (Figure 70b) as, although the mixing may occur, the gain in energy is less as there is only one electron in the d_{z^2} orbital. In addition the mixing can only force the d_{z^2} and $d_{x^2-y^2}$ levels together, back towards an octahedral geometry with orbital degeneracy and violation of the Jahn–Teller (first order) effect.

(b) Second order Jahn–Teller effect:[1063–1067] in the D_{4h} point group the near degenerate $d_z{}^2$ and $d_{x^2-y^2}$ levels transform as a_{1g} and b_{1g} respectively, and may be connected by matrix elements of the type $|\langle\Gamma_g|\,H_q\,|\Gamma_e\rangle|^2/\Delta E$. As long as r_g and r_e differ in symmetry, they may be connected by vibrations of the appropriate symmetry to produce a nonzero matrix element. If H_{aq} transforms as b_{1g}, mixing of the d_{x^2} and $d_{x^2-y^2}$ levels will occur, *i.e.* vibronic coupling, and distortion of the chromophore of D_{4h} symmetry will occur along the x or y axes (Figure 69, F and G). In both cases the distortion must be at 90° to the z axis of the D_{4h} point group, and will involve a lowering of symmetry to D_{2h}.

Taken together, (a) accounts for the predominant occurrence of the elongated rather than

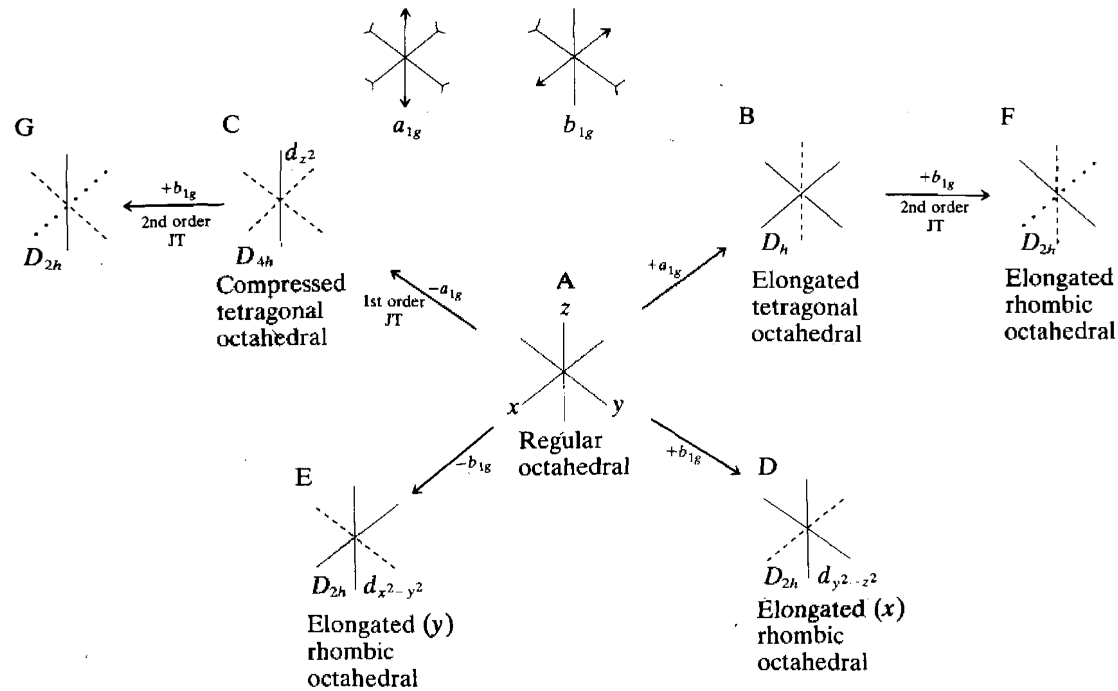


Figure 69 Vibronic coupling for octahedral copper(II) (a) dynamic Jahn–Teller effect (a_{1g} and $\pm b_{1g}$); (b) pseudo Jahn–Teller effect ($+b_{1g}$)

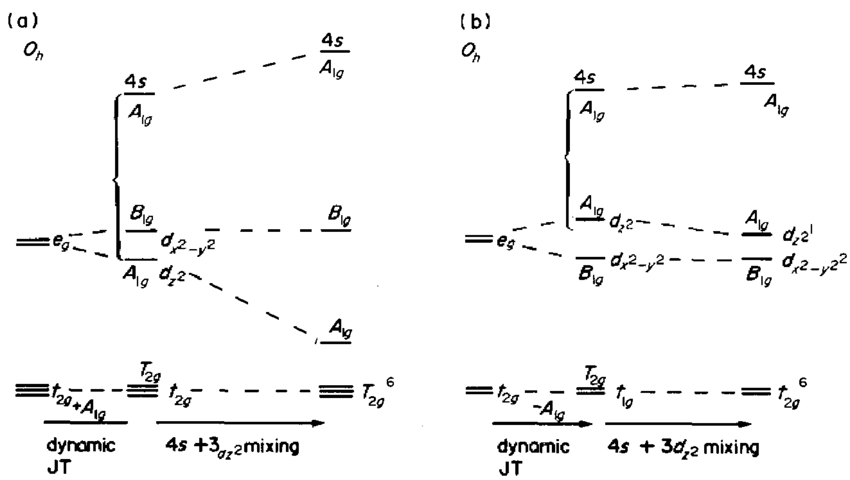


Figure 70 The effect of $4s + 3d_{z^2}$ mixing on the six-coordinate copper(II) chromophore, D_{4h}: (a) elongated tetragonal octahedral; (b) compressed tetragonal octahedral[1074]

the compressed octahedral stereochemistry[1075] and (b) for the general occurrence of rhombic rather than tetragonal octahedral geometries, in both the elongated and (more limited) compressed stereochemistries of the copper(II) ion with six equivalent ligands (Section 53.4.2.1ii).

The adiabatic potential energy surface of Figures 67 and 68 only applies strictly to six-coordinate complexes of the copper(II) ion with six equivalent ligands. With nonequivalent ligands, as in a *trans*- or *cis*-CuL_4X_2 chromophores, the general behaviour of Figure 68 can still be applied, except that the regular six-coordinate geometry of Figure 68(a) can never arise and hence the genuine dynamic Jahn–Teller effect (Figure 69, A–E) cannot apply. Nevertheless, the general features of Figure 68(b) and (c) can still occur as in Figure 71(a), (b) and (c).[461,1066] Two potential energy surfaces are still involved, which are split at the origin by 2Δ due to the small differences in the bond lengths and bond angles in a CuL_4X_2 chromophore. For a *trans*-CuL_4X_2 structure, approximately D_{4h} symmetry is still appropriate with an elongated or compressed geometry, generating $^2B_1$ and $^2A_1$ ground states, respectively (Figure 71a and b). In both cases $4s + 3d_{z^2}$ mixing can still apply [(a) above] and stabilizes the former; it combines with the second-order vibronic coupling for a single vibrational mode of b_1 symmetry [(b) above] with the formation of a two well system (Figure 71a and b) with a $^2B_1$ ground state of D_{4h} symmetry distorting *via* the $(+)b_1$ mode to a D_{2h} symmetry (Figure 71a, wells I and II) but retaining the predominant elongation along the z axis. For equal energies of wells I and II (Figure 71a), the thermal populations will be equal and the averaged structure will be elongated tetragonal octahedral; for many real lattices wells I and II will not be of equal energy, and one will predominate, as in Figure 71(c). The population of well I will be greater than that of well II, and an elongated rhombic octahedral CuL_4X_2 chromophore of D_{2h} symmetry will be observed, with the extent of the in-plane rhombic component along x or y restricted by lattice-packing forces, or in-plane chelate ligands, to be less than the z axis elongation (Figure 69, F) as the latter is so large (Figure 70a).

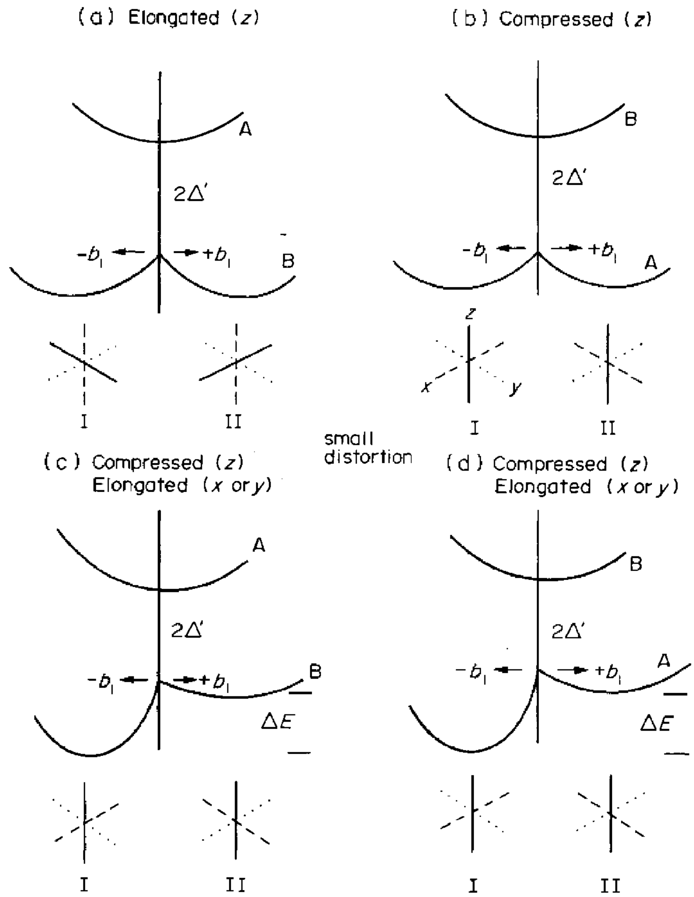


Figure 71 Adiabatic potential energy surface for a pseudo Jahn–Teller *trans* and *cis* CuL_4X_2 chromophore: equivalent and near-equivalent wells (a) elongated (D_{4h} and C_2); (b) compressed (D_{4h} and C_2); and (c) and (d) nonequivalent wells D_{2h} and D_2

In the case of a compressed *trans*-CuL_4X_2 chromophore of D_{4h} symmetry ($^2A_{1g}$ ground state), $4s + 3d_z$ mixing (Figure 70b) cannot significantly change the z-axial compression, and for a single vibrational mode of b_1 symmetry (x or y axis), a two-well system is formed (Figure 71b; $^2A_1$ ground state). For equal thermal populations of wells I and II, a pseudo-compressed octahedral structure is observed. In lattices of low symmetry the energies of wells I and II are not equal and well I predominates to give a compressed rhombic octahedral $CuL_2L_2X_2$ chrompkore with a slight elongation along the x or y axes (Figure 71b wells I or II, respectively). If the in-plane elongation is sufficiently large, a change from a compressed ($^2A_1$) to an elongated ($^2B_1$) stereochemistry will occur, with the elongation along the x or y axes and a rotation of 90° of the principal axis from z to x (or y) (Figure 72a). For a *cis*-CuL_4X_2 chromophore even D_{4h} symmetry is no longer possible, but is reduced to C_2 symmetry. The elongated and compressed distortions still arise (Figure 72b) giving C_2 symmetry with equal thermal populations of wells I and II (Figure 71a and b). For the elongated *cis*-CuL_4X_2 chromophore in lattices of low symmetry the energies of wells I and II are not equal and significant in-plane distortion along the x or y axes will occur (Figure 71d), but the dominant

z-axis distortion to maintain the $^2B_1$ ground state is still retained. For the compressed cis-CuL_4X_2 chromophore, with small in-plane distortion from C_2 symmetry along the x or y axes (Figure 72b), the overall compressed six-coordinate geometry is retained (Figure 71d), but for strong b_1 coupling, the distortion axis (x or y) may become the dominant elongation axis to give a change of elongation axis by 90° ($z > x$) and of the ground state from $^1A_1$ to $^2B_1$ (Figure 71c). The adiabatic potential energy surfaces of Figures 67, 68 and 71 emphasize the importance of vibronic coupling in determining the crystallographically 'observed' stereochemistry of the copper(II) ion, the importance of the a_{1g} and b_{1g} octahedral modes of vibration in the dynamic or first-order Jahn–Teller effect[1067] and equally the importance of the b_1 symmetry mode in the second-order Jahn–Teller effect.[1063–1067] Both effects use the coupling of a CuL_6 chromophore geometry to a particular mode of vibration of the CuL_n chromophore, which then determines the direction of the distortion of the nuclear framework, until constrained by the lattice-packing forces or by the presence of chelate ligands in six-coordinate complexes of the copper(II) ion (Section 53.4.2.1ii).

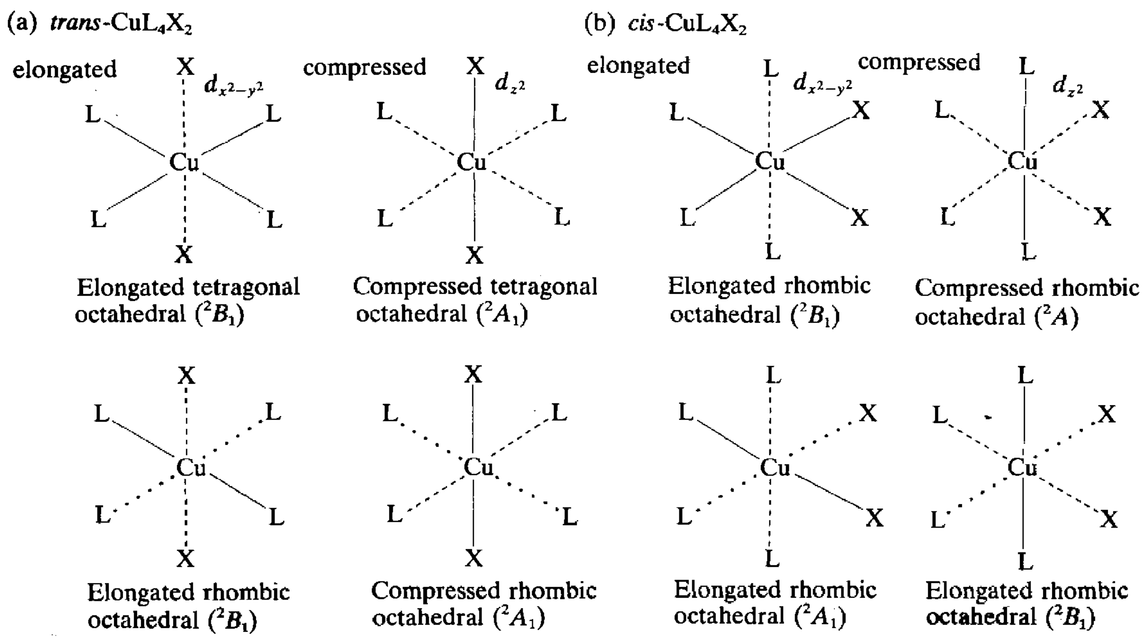
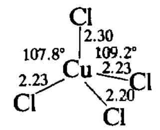


Figure 72 Connection between elongated and compressed (a) *trans* CuL_4X_2 and (b) *cis* CuL_4X_2 octahedral chromophores (—— short, – – – intermediate, · · · long)

The nonoccurrence of the regular tetrahedral CuL_4 chromophore has generally been associated with spin–orbit coupling removing the degeneracy of the $^2T_2$ ground state of the copper(II) ion.[1076] It has recently been suggested that the tetrahedral copper(II) ion may also be associated with a first-order Jahn–Teller effect involving the direct product $t_2 \times t_2 = a_1 + e + t_2$, of which only the e and t_2 modes will remove the triple orbital degeneracy of the T_2 term.[1077,1078] For the majority of tetrahedral copper(II) species the compressed tetrahedral stereochemistry (Figure 17 and **175**)[212–217] suggests that the $T_2 \times E$ coupling operates (S_4 axis), but the trigonal distortion $T_2 \times T_2$ is also possible as in $(Me_3NH)_3[Cu_2Cl_7]$ (**401**).[1079] Both senses of distortion produce a nondegenerate ground state, a d_{xy} orbital of B_2 symmetry for the E mode. The first order $T_2 \times E$ coupling produces an adiabatic potential energy surface involving three potential wells (Figure 73a) which relate to the three possible conformations of the compressed tetrahedron, compressed along the x, y, and z directions.[1077] The ground state $^2T_2$ is split by $3E_{JT}$ and the tetragonal distortion lowers the ground state by $2E_{JT}$ (Figure 73d). As the ground state wave function $e^4t_2^5$ involves the d_{xz}, d_{yz} and d_{xy} orbitals, which are linearly independent, there are no possible inter-well transfers, as in the octahedral CuL_6 chromophore (Figure 67a).[1077,1080] Even a small distortion of the potential surface by lattice effects will produce a single low energy potential well, which will correspond to a static stereochemistry of compressed tetrahedral geometry or trigonal geometry. Consequently the tetrahedral e mode of vibration connects the regular tetrahedral geometry to the compressed tetrahedral geometry and ultimately to the square coplanar stereochemistry by a first-order Jahn–Teller effect, just as the octahedral a_{1g} mode (D_{4h} symmetry) connects the CuL_6 chromophore to a square coplanar CuL_4 chromophore.



$(Me_3NH)_3[Cu_2Cl_7]$ (**401**)[1079]

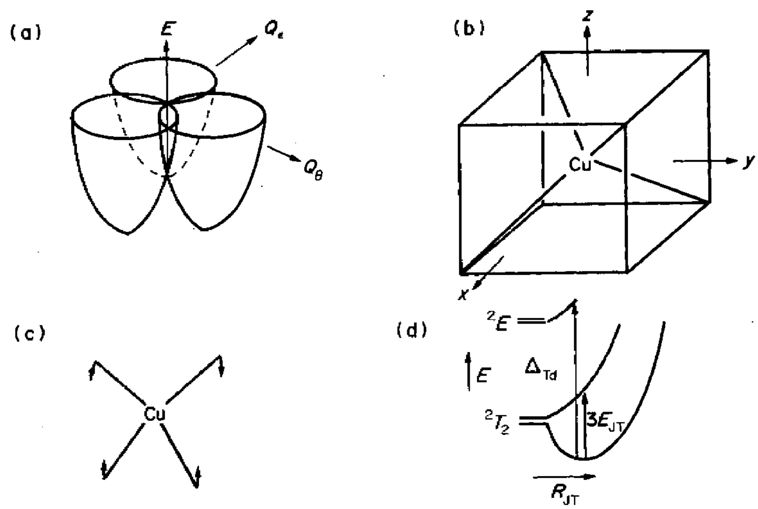


Figure 73 The adiabatic potential energy surface for an orbitally triply degenerate $^2T_2$ ground state tetrahedral stereochemistry[1077]

The five-coordinate CuL_5 chromophore rarely involves a regular trigonal bipyramidal or square pyramidal geometry (Section 53.4.2.1v), but generally involves a square pyramidal distorted trigonal bipyramidal or a trigonally distorted square pyramid (Figure 21b). Their sense of distortion may be connected by the Berry twist mechanism (which retains a C_2 axis of symmetry; Figure 74a) and involves a dominant mode of vibration of e' symmetry.[507] In these distorted intermediate geometries of approximately C_{2v} symmetry an A_1 ground state is appropriate (Figure 3c) and second-order Jahn–Teller coupling ensures that the mode of distortion follows the form of the e' modes of the parent D_{3h} point group (Figure 74b).[1077,1081,1082]

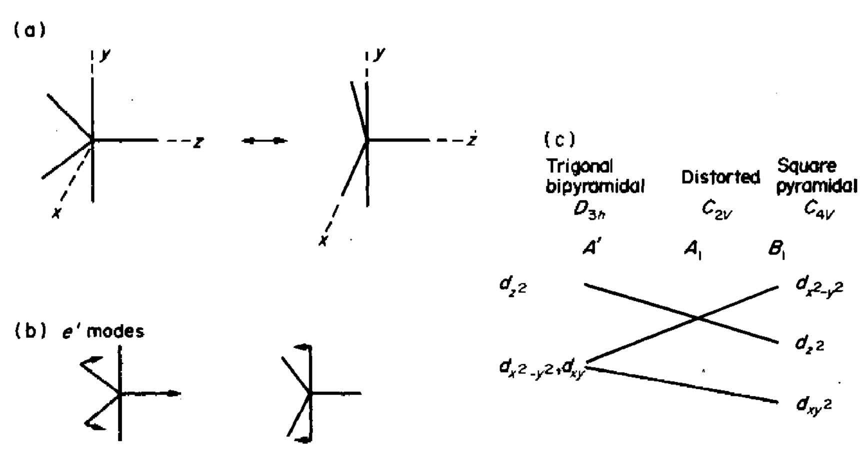


Figure 74 (a) The Berry-twist mechanism connecting a trigonal bipyramidal and square pyramidal geometry; (b) e' modes of vibration; (c) correlation of one-electron energy levels $D_{3h} \rightarrow C_{4v}$

Thus while the Jahn–Teller theorem is generally invoked to account for the distorted octahedral geometries of the copper(II) ion, in terms of the first-order vibronic coupling the extension of the coupling to some second-order effects also allows some rationalization of the tetrahedral and five-coordinate geometries of the copper(II) ion.[1063–1067]

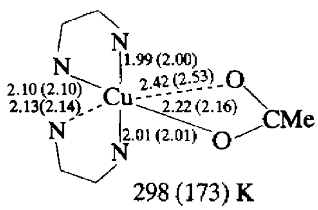
Nevertheless, the ability of the pseudo Jahn–Teller effect[1067] to account for the structure and electronic properties (see later) of the six-coordinate copper(II) complexes has been questioned[1083] on the basis that the effect is an order of magnitude too small to account for the distortions involved, 0.4–1.0 Å. However, an exactly comparable potential energy diagram to that of Figure 67 has been proposed using the approach of near degenerate nonrigid molecules (see Figure 5, ref. 902). As it is impossible at present to distinguish between these two alternative approaches, this chapter retains the more unifying approach of the pseudo Jahn–Teller effect.[1067]

53.4.5.1 The 'observation' of the Jahn–Teller effect

The major value of the 'Mexican hat' model for six-coordinate copper(II) complexes, involving six equivalent or nonequivalent ligands, is that it accounts for the mixture of non temperature variable (static) and temperature variable (fluxional) structures that is observed.[396] It predicts[540] that the former may involve bond-length changes of the order of the Jahn–Teller radius, R_{JT} (Figure 67a), namely 0.1–0.4 Å, which are available from a comparison of room temperature and low temperature crystal structures (Figure 24 and b; Section 53.4.2.1x).[540] It also predicts that low temperature crystallographic data can yield numerical data on the energy separation ΔE of the lowest energy wells of Figure 68, as listed in Table 62(a), all within thermal energy limits, namely 200 cm^{-1}. Thus the three diagrams of Figure 68(a) describe the genuine dynamic Jahn–Teller systems, such as $K_2Pb[Cu(NO_2)_6$ **(177)**[462] and $[Cu(en)_3](SO_4)$ **(178)**,[427] which all involve high symmetry chromophores (O_h or D_3) and involve six equivalent ligands. Figure 68(b) accounts for the occurrence of the compressed tetragonal or rhombic octahedral copper(II) complexes,[397] as in $Cs_2Pb[Cu(NO_2)_6]$ **(251)**[532] and $Rb_2Pb[Cu(NO_3)_6]$ **(233)**,[531] and Figure 68(c) accounts for the existence of (i) fluxional elongated rhombic octahedral copper(II) complexes,[397] as in $(NH_4)_2[Cu(OH_2)_6](SO_4)_2$ **(202)**[457,458] and $[Cu(dien)_2]Br_2{\cdot}H_2O$ **(194)**,[446] and (ii) the static elongated rhombic octahedral complexes, as in $Cs_2[Cu(OH_2)_6](SO_4)_2$ **(184)**,[435] which dominate this stereochemistry for the copper(II) ion. The pseudo dynamic Jahn–Teller effect[1067] and the second-order Jahn–Teller effect,[1065] then explain (Figure 70a and b) why the elongated rhombic octahedral stereochemistry far outweighs the number of compressed rhombic octahedral complexes, even for six equivalent ligands. The pseudo Jahn–Teller effect as described in Figure 71(a)–(d) then accounts for the stereochemistry of the wide range of six-coordinate copper(II) complexes involving nonequivalent ligands, CuL_4X_2, with both *trans*- and *cis*-octahedral geometries. Figure 71(a) accounts for the large number of static elongated octahedral complexes with a *trans*-CuL_4X_2 chromophore, tetragonal (D_{4h}) as in $[Cu(NH_3)_4(NO_2)_2]$ **(174)**[570] and rhombic (D_{2h}) as in $[Cu(en)_2(FBF_3)](BF_4)$ **(193)**.[445] In **(193)** the in-plane rhombic distortion is only small (*ca.* 0.1 Å) and never overrides the predominant *z*-axis elongation, and hence a ^2B ground state always applies.[554] It also accounts for the restricted elongation of the *cis*-CuL_4X_2 chromophore of $[Cu(hfacac)_2(bipy)]$ **(197)**[449] and of $[Cu(phen)_2(NCS)_2]$ **(198)**,[450] with C_2 symmetry but clear $d_{x^2-y^2}$ ground states ($^2B_{1g}$). Figure 71(b) accounts for the compressed tetragonal octahedral stereochemistry with a *trans*-CuL_4X_2 chromophore and near D_{4h} symmetry of $[Cu(dien)_2](NO_3)$ **(235)**[537] and $[Cu(methoxyacetate)_2(OH_2)_2]$ **(237)**,[541] both with ^2A ground states. It also accounts for the strict C_2 symmetry of the compressed rhombic octahedral stereochemistry with a *cis*-CuL_4X_2 chromophore and ^2A ground state of $[Cu(phen)_2(O_2CMe)](ClO_4){\cdot}2H_2O$ **(239)**[243] and the near C_2 symmetry of $[Cu(bipy)_2(ONO)](NO_3)$ **(253)**[546] and $[Cu(phen)_2(O_2CMe)](ClO_4)$ **(402)**,[404,1084] both with ^2A ground states (Figure 71c). Figure 71(d) then accounts for the very rhombic in-plane distortion of b_1 symmetry in the *trans*-CuL_4X_2 chromophore of $[Cu(dien)_2]Br_2{\cdot}H_2O$ **(194)**,[446] and in the distorted *cis*-CuL_4O_2 chromophore of $[Cu(bipy)_2(ONO)BF]$ **(241)**.[547] In the structures of **(194)** and **(241)** the in-plane distortion of b_1 symmetry is so large that the ground state changes from ^2A to ^2B with the elongation in the *x* direction. In the near high symmetry structures above, the axial elongations along *z* and the in-plane rhombic distortions along *x* or *y* are restricted by the 'bite' or the chelate ligands present and for $\Delta E < kT$, Figure 68(a) and (b) predicts that these structures will be temperature variable. The observation of the pseudo octahedral and pseudo compressed octahedral stereochemistries for the copper(II) ion then arises as an artifact of fluxional behaviour (Figure 68a) for CuL_6 chromophores and Figure 71(b) for the CuL_4X_2 chromophores. The three independent wells of Figure 73(a) then account for the nonregular tetrahedral structure of the four-coordinate CuL_4 chromophore, such as $[CuCl_4]^{2-}$ in $Cs_2[CuCl_4]$ (**175**)[483] and the CuN_4 chromophore of $[Cu(bipyam)_2](ClO_4)_2$ (**214**),[485] both with a clear compressed tetrahedral stereochemistry, which is non temperature variable. The Berry twist type mechanism (second-order Jahn–Teller effect; Figure 74)[1065] then accounts for the infrequent occurrence of the regular trigonal bipyramidal or square pyramidal copper(II) stereochemistries (Section 53.4.2.1v) and the frequent occurrence of the trigonally distorted five-coordinate copper(II) stereochemistries.[396]

Table 62 (a) Crystallographically and (b) ESR determined ΔE Values for Fluxional Copper(II) System

	$\Delta E(cm^{-1})$	*Ref.*
(*a*) *Crystallographic*		
$[Cu(bipy)_2(ONO)](NO_3)$	74	576
$[Cu(phen)_2(O_2CMe)](ClO_4)$	125	1084
$(NH_4)_2[Cu(OH_2)_6](SO_4)_2$	160	578
(*b*) *ESR spectra* (*dilute*)		
$K_2[Cu(Zn)(OH_2)_6](SO_4)_2$	168	578
$[Cu(Zn)(phen)_2(O_2CMe)](ClO_4)\cdot 2H_2O$	132	914



$[Cu(phen)_2(O_2CMe)](ClO_4)$ (**402**)[404,1084]

The adiabatic potential energy surfaces of Figure 67(a) may be used to understand the relationship between the observed copper(II) stereochemistry (both static and fluxional) and certain of the electronic properties of the copper(II) ion. For static stereochemistries, the relationship is as set out in Section 53.4.4.4, but for the fluxional systems the relationship is going to be dependent on the relative lifetimes of the ground state and excited state configurations involved in their measurement (Table 63).[1057] X-ray diffraction has an interaction time of 10^{-18} s, but is averaged over vibrational motion, so the structure is time averaged (~1 s); ESR spectroscopy has an interaction time of 10^{-9} s, and is also averaged by vibrational motion, while electronic spectroscopy has an interaction time of 10^{-15} s and is *not* time averaged, but reflects the extreme static configuration of the molecular vibration. Consequently, the X-ray and ESR techniques provide averaged structural data in these fluxional systems, while electronic spectroscopy relates to the underlying static stereochemistry. It is anticipated that EXAFS spectroscopy, with an interaction time of 10^{-15} s, will also yield bond distances that relate to the underlying static structure of these fluxional chromophores.[1043, 1044]

Table 63 Time Scales for Structural Techniques[1057]

Physical techniques	*Approximate time scale*(*s*)
X-Ray diffraction	10^{-18}
UV spectra	10^{-15}
Visible spectra	10^{-14}
IR–Raman spectra	10^{-13}
ESR spectra	10^{-8}
EXAFS	10^{-15}

Thus the structures of Figure 19 may be reclassified as temperature variable (pseudo) structures and non temperature variable (static) structures (Table 64) in which the former only arise as an artifact of the Jahn–Teller effect and only the latter can be considered as genuine static stereochemistries of the copper(II) ion with electronic properties (Section 53.4.4.4) simply related to their copper(II) stereochemistry. The pseudo structures of Table 64 are then characterized by temperature variable crystal structures (Section 53.4.2.1x) and typified by non spherically symmetrical thermal parameters[540,1085] whose magnitude is lower along a Cu—L direction than at right angles to this direction (Table 65a). This information is also present in the thermal parameters of low symmetry CuL_6 chromophores, if the thermal parameters are expressed as Cu—L parameters $\Delta U^{1/2}$ (Cu—ligand, Å; Table 65b). The ESR spectra of static CuL_n chromophores have been described in Section 53.4.4.3. Pseudo stereochemistries are related to the averaged room temperature structure, but at low temperature may change to the g values associated with the underlying static stereochemistries (see Figures 39–42). Historically, it was the temperature variability of the g values of fluxional copper(II) complexes that first suggested the possible temperature variable stereochemistry of the copper(II) ion.[909] The data for copper(II)-doped $K_2[Zn(OH_2)_6](SO_4)_2$ complexes[909] yielded the first approximate parameters for a potential energy surface for the fluxional $[Cu(OH_2)_6]^{2+}$ cation (Figure 75), a result that has been confirmed by the recent low-temperature structure of $K_2[Cu(OD_2)_6](SO_4)_2$ **(393)**.[910]

Table 64 Subdivision of the Copper(II) Stereochemistries into their Temperature Variable and Non Temperature Variable Types

Geometry	*Complex*	*Ref.*
(*a*) *Temperature variable* (*pseudo*)		
Pseudo octahedral	$K_2Pb[Cu(NO_2)_6]$ **(177)**	426
Pseudo trigonal octahedral	$[Cu(en)_3](SO_4)$ **(178)**	427
Elongated tetragonal octahedral	$(NH_4)_2[Cu(OH_2)_6](SO_4)_2$ **(254)**	578
Elongated rhombic octahedral	$Ba_2[Cu(OH_2)_2(O_2CH)_4](HCO_2)_2{\cdot}2H_2O$ **(191)**	443
Pseudo compressed tetragonal octahedral	$Rb_2Pb[Cu(NO_2)_6]$ **(233)**	531
Pseudo compressed rhombic octahedral	$[Cu(dien)_2](NO_3)_2$ **(235)**	537
Pseudo *cis*-distorted octahedral	$[Cu(bipy)_2(ONO)](NO_3)$ **(253)**	546
(*b*) *Non temperature variable* (*static*)		
Linear	$CuCl_2$(gaseous) **(242)**	546
Trigonal bipyramidal	$[Cu(NH_3)_2Ag(NCS)_3]$ **(223)**	504
Square-based pyramidal	$K[Cu(NH_3)_5](PF_6)_3$ **(221)**	499
Square coplanar	$Ca[CuSi_4O_{10}]$ **(205)**	474
Rhombic coplanar	$[Cu(3\text{-Meacac})_2]$ **(207)**	477
Eight coordinate	$Ca_2[Cu(MeCO_2)_4]_4{\cdot}6H_2O$ **(246)**	563, 564
Compressed tetrahedral	$Cs_2[CuCl_4]$ **(175)**	483
Distorted square pyramidal	$[Cu(dien)(O_2CH)](HCO_2)$ **(347)**	758
Asymmetrical *cis*-distorted	$[Cu(bipy)_2(ONO)](BF_4)$ **(241)**	547

The electronic spectra of copper(II) complexes involving static stereochemistries may be assigned using the energy level diagrams of Figures 26 and 27(a) and (b) with some help from polarized single-crystal spectra where these are available (Figures 49 and 50).[47] The electronic energies of the fluxional CuL_6 chromophore can be interpreted using a cross-section of the warped Mexican hat potential energy surface (Figure 67a)[540] involving a low energy transition $\psi(d_{x^2-y^2}) - \psi^+(d_{z^2})$ of $4E_{JT}$ and a high energy transition, $\psi^-(d_{x^2-y^2}) - T_{2g}(d_{xz}, d_{yz}, d_{xy})$ of $\Delta + 2E_{JT}$ (Figure 76a). These transitions are no different from the one-electron energy level descriptions, except that a vibronic coupling description is used and enables the value of R_{JT} to be calculated.[540,1067] Table 66 summarizes some structural and spectroscopic data for copper(II) systems involving six equivalent ligands, which suggest that R_{JT} lies in the range 0.25–0.35 Å. The appearance of the electronic reflectance spectra of fluxional and static copper(II) systems do not differ significantly (Figure 77a). The three-dimensional dynamic systems such as cubic $K_2Pb[Cu(NO_2)_6]$ **(177)** show no polarization effects[1073] and the trigonal $[Cu(en)_3](SO_4)$ **(178)** only shows a change of intensity with polarization (Figure 77b).[1086] The reason for this insensitivity of the electronic spectra to fluxional effects lies in the very short time scale (10^{-15} s)[1057] involved in electronic transitions which relate to the underlying static distorted stereochemistry of a fluxional CuL_6 chromophore and not to the time averaged structure as

Table 65(a) Comparison of the Nitrogen Atom Thermal Motion for $M^I_2M^{II}[M(NO_2)_6]$ Systems, Root-mean-square Displacements (Å)[540]

		U_{11}	U_{22}	U_{33}
(i) Non Jahn–Teller complexes				
$K_2Pb[Ni(NO_2)_6]$	N(1)	0.130	0.133	0.115[a]
$K_2Sr[Ni(NO_2)_6]$	N(2)	0.120	0.122	0.110[a]
(ii) Static Jahn–Teller complexes				
$K_2Sr[Cu(NO_2)_6]$	N(1)	0.141	0.144	0.119[a]
	N(2)	0.113[a]	0.121	0.138
	N(3)	0.130	0.111[a]	0.129
(iii) Dynamic Jahn–Teller complexes (cubic)				
$K_2Pb[Cu(NO_2)_6]$	N(1)	0.170	0.164	0.182[a]
(iv) Pseudo compressed Jahn–Teller complexes				
$K_2Pb[Cu(NO_2)_6]$[b]	N(1)	0.17	0.17	0.11[a]
	N(2)	0.15	0.16[a]	0.15
	N(3)	0.18[a]	0.11	0.25
$Rb_2Pb[Cu(NO_2)_6]$	N(1)	0.148	0.152	0.128[a]
	N(2)	0.182	0.190[a]	0.141
	N(3)	0.199[a]	0.151	0.144

[a] Displacement along the M—N bond. [b] At 276 K.

Table 65(b) $\Delta U^{1/2}$ (Cu—ligand; Å) for CuL_6 Chromophores Along the Cu—ligand Bond Directions[540]

	Type	L(1)	L(2)	L(3)
$[Cu(en)_3](SO_4)_2$	(a)	0.176	0.176	0.176
$K_2Pb[Cu(NO_2)_6]$	(a)	0.144	0.144	0.144
$Rb_2Pb[Cu(NO_2)_6]$	(b)	0.062 (static)	0.145	0.147
$[Cu(dien)_2](NO_3)_2$	(b)	0.248	0.062 (static)	0.186
$[Cu(methoxyacetate)_2(OH_2)_2]$	(b)	0.098[a]	0.093[a]	0.048[a]
		0.042[b]	0.041[b]	0.025[b]
$(NH_4)_2[Cu(OH_2)_6](SO_4)_2$	(c)	0.126[a]	0.122[a]	0.062[a]
		0.141[c]	0.132[c]	0.107[c]
		0.123[d]	0.122[d]	0.106[d]
$[Cu(HBpz_3)_2]$ I	(c)	0.15	0.12	0.7
II	—	0.04	0.7	<0.0

[a] At 298 K. [b] At 125 K. [c] At 203 K. [d] At 123 K.

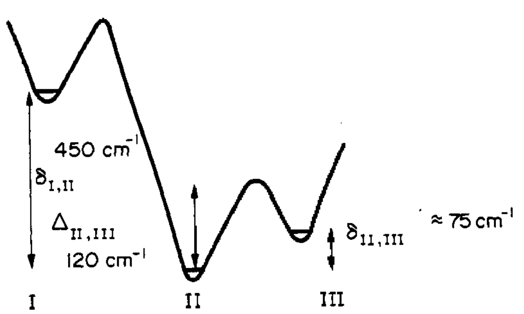


Figure 75 Circular cross-section of the potential energy surface associated with the three Jahn–Teller wells I–III in copper-doped $K_2[Zn(OH_2)_6](SO_4)_2$[909]

determined by X-ray crystallographic and ESR techniques. This insensitivity of the electronic spectra of copper(II) complexes has been a major factor in recognizing the occurrence of fluxional copper(II) systems.[397] Thus the 'sameness' of the electronic spectra of the three complexes of Figure 77(a) suggests essentially the same CuN_6 chromophore stereochemistry, modified by slight differences due to the different crystal lattices. Crystallographically, $K_2Pb[Cu(NO_2)_6]$ (**177**)[426] has an octahedral CuN_6 structure, $Rb_2Pb[Cu(NO_2)_6]$ (**233**)[531] has a compressed rhombic octahedral structure and $K_2Ba[Cu(NO_2)_6]$ (**182**)[433] an elongated rhombic octahedral structure, which belies the fluxional properties of the first two complexes.

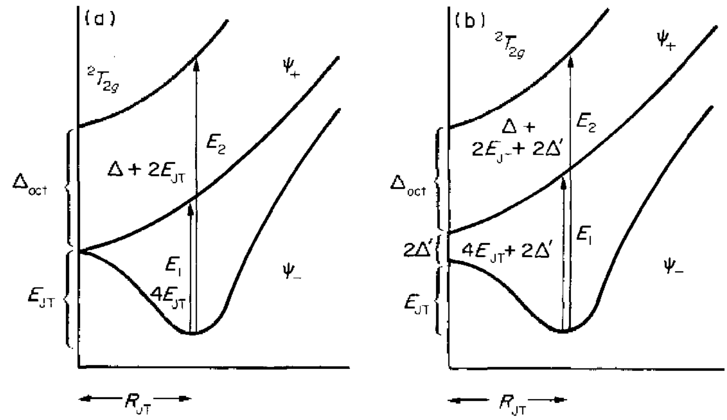


Figure 76 A section through the potential energy surfaces of the Mexican hat for: (a) equivalent ligands and; (b) nonequivalent ligands[540]

Table 66 Structural and Spectroscopic Data for Some Copper(II) Complexes Involving Six Equivalent Ligands, Room-temperature[540]

	d_0(Å)	R_{JT}(Å)	E_{JT}(kK)	E_2(kK)
(a) Pseudo (3D)				
$[Cu(en)_3](SO_4)$	2.150	0.358	2.18	15.7
$K_2Pb[Cu(NO_2)_6]$	2.111	0.333	1.75	16.5
(b) Pseudo (2D)				
$Rb_2Pb[Cu(NO_2)_6]$	2.136	0.252	1.92	15.7
$Cs_2Pb[Cu(NO_2)_6]$	2.171	0.343	1.92	16.3
(c) Static				
$K_2Ca[Cu(NO_2)_6]$	2.138	0.303	1.98	16.5
$K_2Sr[Cu(NO_2)_6]$	2.127	0.318	1.90	16.5
$K_2Ba[Cu(NO_2)_6]$	2.132	0.308	1.92	16.55

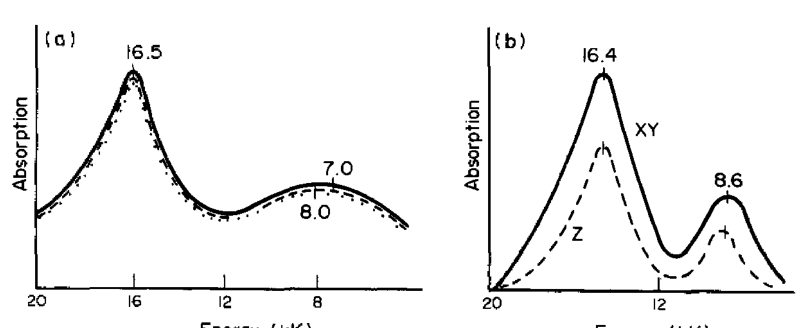
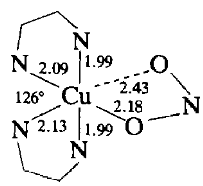


Figure 77 (a) The electronic reflectance spectra of (i) $K_2Pb[Cu(NO_2)_6]$—three-dimensional dynamic (——), (ii) $Rb_2Pb[Cu(NO_2)_6]$—two dimensional dynamic (– – –), and (iii) $K_2Ba[Cu(NO_2)_6]$—static (· · ·); (b) the polarized single-crystal electronic spectra of $[Cu(en)_3](SO_4)$[1086]

The electronic spectra of fluxional copper(II) complexes involving nonequivalent ligands and the potential energy surface of Figure 67(a) can be similarly interpreted, (Figure 76b), but due to the additional splitting of E^0 by $2\Delta'$ it is not possible to evaluate E_{JT}. Nevertheless, the electronic spectra of these fluxional pseudo Jahn–Teller systems show the same insensitivity to the anions present. In a series $[Cu(bipy)_2(ONO)]X$ complexes, $X = (NO_3)^-$ (**253**), $(BF_4)^-$ (**241**)[547] and $(PF_6)^-$ (**403**),[396] the electronic spectra (Figure 78a),[908,1087] consist of two broad peaks of comparable energy and intensity, despite the clear difference in in-plane geometry in (**253**), (**241**) and (**403**), $\Delta O = ([Cu—O(2)] - [Cu—O(1)]) = 0.090$, 0.346 and 0.251 Å, respectively (Figure 24b). The comparable electronic spectra of (**253**) and (**241**), with bands at *ca.* 9500 and 15 000 cm^{-1}, suggest a closely comparable underlying static CuN_4O_2 chromophore stereochemistry, which is substantiated in the Cu—O(2) *vs.* Cu—O(1) plot of Figure 78(b). The low temperature data for (**253**) clearly give a linear correlation and the data for (**241**) lie on this correlation, suggesting that (**253**) and (**241**) exhibit different degrees of fluxional behaviour, but with the same underlying static CuN_4O_2 chromophore stereochemistry.[397]



$[Cu(bipy)_2(ONO)](PF_6)$ (**403**)[396]

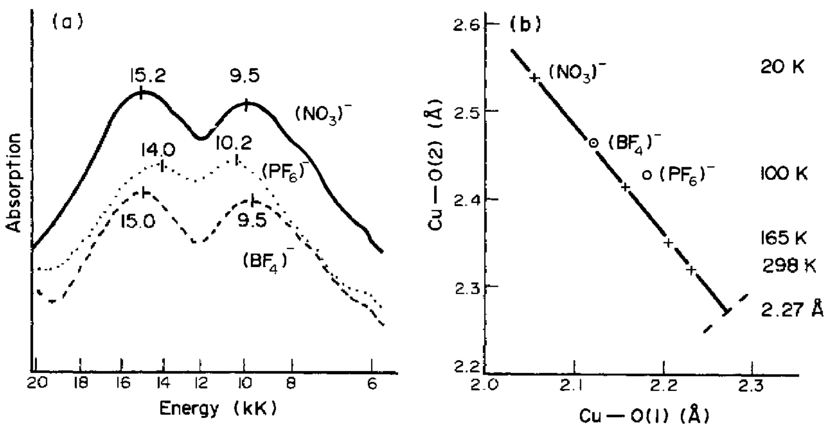
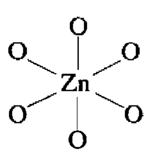


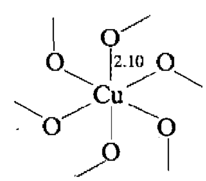
Figure 78 $[Cu(bipy)_2(ONO)](Y)$ complexes: (a) electronic reflectance spectra;[900] (b) Cu—O(1) *vs.* Cu—O(2) (+ refers to $[NO_3]$ at different temperatures)

In discussing the electronic properties of copper(II) complexes the previous sections have involved concentrated copper(II) complexes, rather than those of the copper(II) complexes diluted into a diamagnetic host lattice. In order to determine whether or not the electronic properties of pure copper(II) complexes are determined by the presence of near neighbour copper(II) ions, it is desirable to examine the properties of copper(II) ions diluted in an isomorphous diamagnetic host lattice such as the corresponding zinc(II) complex.[396,397] In such studies the electronic properties will be either influenced by the presence of adjacent ions, *i.e.* the cooperative Jahn–Teller effect,[432] and the electronic properties will change with the percentage of Cu^{II} present and a phase change may occur, or the electronic properties will not be influenced by adjacent ions, *i.e.* the noncooperative Jahn–Teller effect.[514,1087] In general three factors will be involved: (i) the magnetic dilution of the individual copper(II) ion; (ii) the relative structure of the CuL_n chromophore and the ZnL_n host lattice environment; and (iii) the nature of the lattice present,[540] namely class I, hard lattices, ionic or covalent,[432] or class II, soft lattices, molecular.[396]

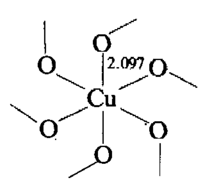
For class I behaviour at low dilution the CuL_6 environment is forced by the strong lattice vibrations present to assume the high symmetry of the local lattice, as in NaCl,[1088] MgO[1089] or $Ca(OH)_2$ (Table 67a).[1090] With increasing concentration of Cu^{2+} a phase transition occurs (due to the limited solubility of the Cu^{2+} ion in the high symmetry environment) to lower symmetry, as in $CuCl_2$ (**366**)[784] and CuO (**377**).[788] For lower symmetry environments in class I such as $Ba_2[Zn(WO_6]$ (**404**)[1091] a phase transition occurs at 20% copper(II) substitution, above which there is a gradual shift in the electronic energy levels to higher energy with increasing copper(II) concentration (Figure 79a and b). In class II behaviour, a high symmetry host lattice, such as $[Zn(pyNO)_6](BF_4)_2$ (**405**),[1092] may also constrain the $[Cu(PyNO)_6]^{2+}$-doped cation to have a pseudo trigonal octahedral stereochemistry, against the tendency of the CuO_6 chromophore to distort, as in $[Cu(pyNO)_6](NO_3)_2$ (**406**).[1093,1094] This lattice effect, the 'cooperative Jahn–Teller Effect',[432] may be retained through increasing copper(II) concentrations up to 100% Cu with no change of phase and accounts for the occurrence of the cubic $K_2[PbCu(NO_2)_6]$ (**177**)[426] and trigonal $[Cu(en)_3](SO_4)$ (**178**)[427] complexes. In (**177**)[426] the long Pb—O distance of 2.77 Å for the PbO_{12} chromophore contributes to the retention of a cubic lattice, and hydrogen bonding of the trigonal sulfate anion in (**178**)[427] contributes to the retention of a trigonal lattice with the formation of a fluxional pseudo octahedral CuN_6 chromophore in both complexes. This situation even applies to the lower C_2 symmetry of the two-dimensional fluxional CuN_4O_2 chromophore of $[Cu(phen)_2(O_2CMe)](BF_4)\cdot 2H_2O$ (**239**)[243] and in the corresponding $[Zn(phen)_2(O_2CMe)](BF_4)\cdot 2H_2O$ (**394**),[914] where hydrogen bonding between the acetate oxygen atoms and the water molecules may also help to retain the C_2 symmetry of the copper(II) lattice against its tendency to distort to a (4 + 1 + 1*) structure, as in $[Cu(phen)_2(O_2CCH_2](BF_4)$ (**395**) and $[Cu(bipy)_2O_2CH)](BF_4)$ (**408**).



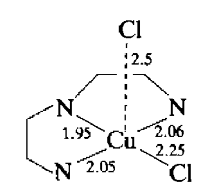
$Ba_2[Zn(WO_6)]$ (**404**)[1091]



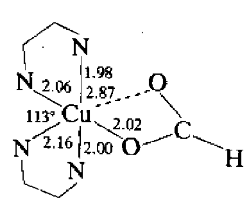
$[Zn(pyNO)_6](BF_4)_2$ (**405**)[1092]



$[Cu(pyNO)_6](NO_3)_2\cdot 2H_2O$ (**406**)[1093]



$[Cu(terpy)Cl_2]$ (**407**)[1267]



$[Cu(bipy)_2(O_2CH)](BF_4)$ (**408**)[548]

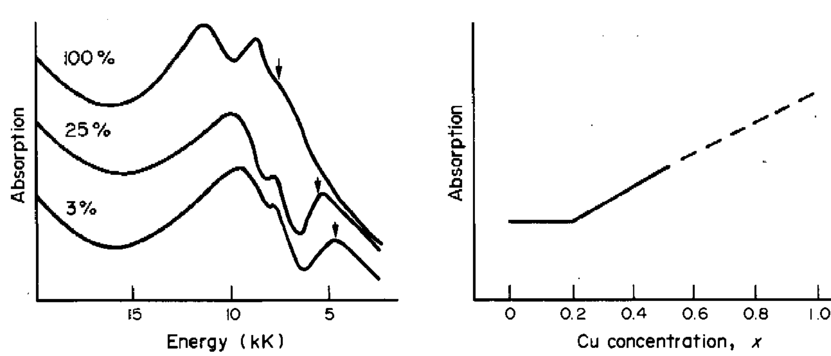


Figure 79 The electronic reflectance spectra[1091] of 1–100% $Ba_2[Zn(Cu)WO_6]$: (a) variation with composition; (b) variation of the $d_{z^2} \leftarrow d_{x^2-y^2}$ transition (↓), $4E_{JT}$, with composition x

This general feature of both class I and class II behaviour of the copper(II) ion, *i.e.* the ability to exist in a high symmetry environment against the prediction of both the first- and second-order Jahn–Teller effects, is the best single piece of evidence for the cooperative Jahn–Teller effect and has recently been reviewed.[432] It is generally responsible for the whole range of fluxional copper(II) stereochemistries and of the temperature variable ESR spectra of

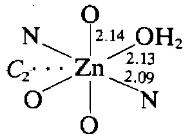
Table 67 Class I and Class II Lattice Behaviour for Concentrated Copper(II) Ions and $[Cu(ligand)_6]^{2+}$ Complexes Diluted in a Host Lattice[540]

	Class I	Class II	
High symmetry Cubic or trigonal	Hard	Soft	High symmetry Cubic (O_h), trigonal (D_3) or monoclinic(C_2)
e.g. NaCl, MgO, *etc.*	Cu^{2+} sites	$[Cu(ligand)_n]^{2+}$	*e.g.* $K_2Pb[Cu(NO_2)_6]$ (O_h) $[Cu(pyNO_6]X_2$, (D_3) $[Cu(phen)_2(O_2CMe)](ClO_4)\cdot 2H_2O$ (C_2)
	(*a*) *Equivalent ligands*		
(i) Low dilution: no local CuL_6 e_g mode			(i) Low dilution: local CuL_6 chromophore dominates
(ii) High concentration: whole lattice distorts (phase change) to a low symmetry CuL_6 static environment, *e.g.* $CuCl_2$, CuO			(ii) High concentration: local CuL_6 chromophore domination retained
	(*b*) *Nonequivalent ligands*		
Only low symmetry lattice formed (i) Low dilution: CuL_n–ZnL_n (ii) High concentration: ↓ Phase change CuL_n distorts away from ZnL_n geometry to static distorted CuL_n, *i.e.* Ba_2CuWO_6 Cooperative Jahn–Teller effect[432]		No phase change ↓	Only low symmetry lattice formed Low and high dilution give distorted CuL_6 independent of concentration, *i.e.* $Cu/[Zn(bipy)_2(ONO)](NO_3)$ $Cu/[Zn(dien)_2]Br_2\cdot H_2O$ Noncooperative Jahn–Teller effect[514]

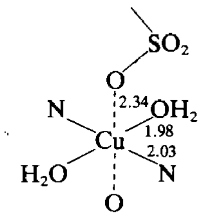
these complexes. In concentrated copper(II) compounds it is responsible for the general feature of exchange narrowing[47] of the ESR spectra of 'ferrodistortive' CuL_n chromophores and of exchange coupled misaligned antiferrodistortive systems (Figure 33a and c), which have generally complicated the relationship between the ESR spectra and stereochemistry of copper(II) complexes.[47,48,396,397,432,816]

The behaviour[540] of class II copper(II) complexes involving nonequivalent ligands (Table 67b) is more complicated for two reasons. First, the corresponding zinc(II) and copper(II) complexes may simply not exist,[1095] as in $[Zn(3\text{-pyridine sulfate})_2(OH_2)_2]\cdot 2H_2O$ (**409**) and $[Cu(3\text{-pyridine sulfate})_2(OH_2)]\cdot H_2O$ (**410**); where they do exist, as in $[Zn(methoxyacetate)_2(OH_2)_2]$ (**411**)[397] and $[Cu(methoxyacetate)_2(OH_2)]$ (**237**),[541] the space groups may not be isomorphous, *Fdd*2 and *P*2/*n* respectively, and the MO_6 chromophores can not be isostructural. In complex (**411**)[397] the two waters occupy *cis* positions, while in the copper complex they occupy *trans* positions. Secondly, even where the corresponding zinc(II) and copper(II) complexes do exist with the same space group, the ZnL_6 and CuL_6 chromophores are not generally isostructural due to the differences of their d^{10} and d^9 electronic configurations, respectively. Even in low symmetry the ZnN_4O_2 chromophore of $[Zn(bipy)_2(ONO)](NO_3)$ (**412**)[547] is less distorted than the CuN_4O_2 chromophore of (**253**).[546] In these systems the copper complexes can be diluted [514] over the full range of 1–100% in the zinc complex[1096] and the electronic spectra do not vary over the whole range of concentration. This is best seen in the constancy of the electronic reflectance spectra (Figure 80a and b). Thus, notwithstanding the more nearly octahedral structure of the ZnN_4O_2 chromophore of (**253**),[546] this suggests that the structure of the CuN_4O_2 chromophore is the same in the concentrated copper(II) complex, and in the 1% copper(II)-doped zinc(II) complex. In general[397] the local molecular geometry of a CuL_6 chromophore doped in the corresponding ZnL_6 chromophore corresponds with that of the pure CuL_6 complex. This situation has recently been established for the $Cs_2(Cu)[ZnCl_4]$ (**413**) systems.[931]

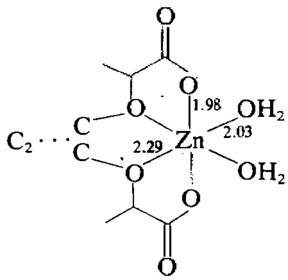
In these molecular type lattices the structure of the CuN_4O_2 chromophore is independent of the structure of the host lattice, and the effect is referred to as the noncooperative Jahn–Teller effect.[514] It applies to the vast majority of low symmetry copper(II) complexes involving organic type ligands, but even here cooperative effects that influence the ESR properties, such



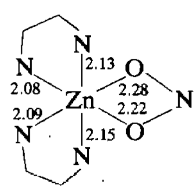
$[Zn(3\text{-}pySO_3)_2(OH_2)_2]\cdot 2H_2O$ **(409)**[1095]



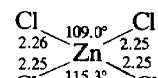
$[Cu(3\text{-}pySO_3)_2(OH_2)_2]\cdot H_2O$ **(410)**[1095]



$[Zn(methoxyacetate)_2(OH_2)_2]$ **(411)**[397]



$[Zn(bipy)_2(ONO)](NO_3)$ **(412)**[547]



$Cs_2(Cu)[ZnCl_4]$ **(413)**[1096]

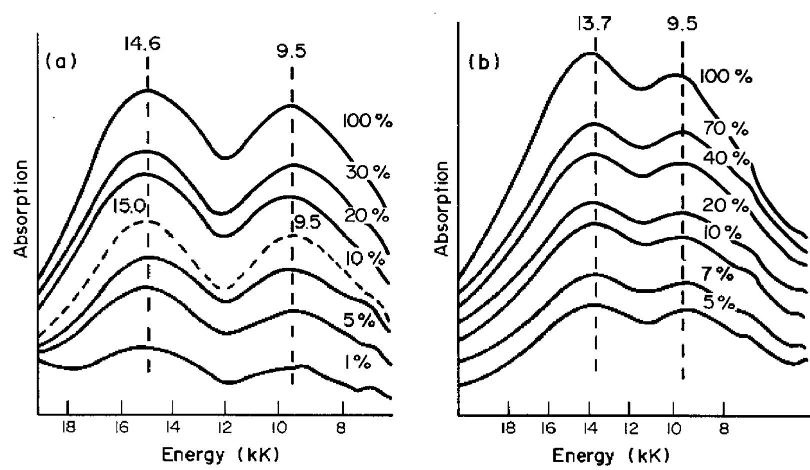
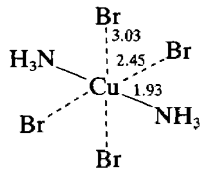


Figure 80 The electronic reflectance spectra of 1–100% copper-doped $[Zn(bipy)_2(ONO)](NO_3)$ (——) and $[Cu(bipy)_2(ONO)](BF_4)$ (- - -);[1087] and (b) the electronic reflectance spectra of 5–100% copper-doped $[Zn(phen)_2(O_2CMe)](BF_4)\cdot 2H_2O$

as exchange coupling, will only disappear with very bulky ligands, as in $[Cu(phen)_3](ClO_4)_2$ **(196)**,[448] which displays copper nuclear hyperfine structure, $A_{\parallel} = 160 \times 10^{-4}\ cm^{-1}$, even in the concentrated complex (Figure 35).[957] In these dilute class II copper(II) systems[540] the more accurate g and A values determined in the <10% copper(II)-doped zinc(II) complex may be associated with the crystallographically determined CuN_4O_2 chromophore geometry of the 100% copper(II) complex.[514]

The connection between the Jahn–Teller effect (first and second order) and the vibrational modes of the CuL_n nuclear framework (Figure 24) has already been used to link a range of distorted stereochemistries of the copper(II) ion and summarized in the plasticity effect (Figure 20a)[416] or the mutual influence of ligands (Figure 20b).[463] The continuously variable tetragonality (Figure 20a)[459] of the elongated tetragonal octahedral stereochemistry accounts for the most common examples of isomerism in copper(II) complexes such as the two forms of I and II $[Cu(HBpz_3)_2$ **(199)**.[451] Less common is the occurrence of the same compound with two different stereochemistries such as the elongated rhombic octahedral structure of α-$[Cu(NH_3)_2Br_2]$ **(414)**[1097] and the compressed tetragonal octahedral structure of β-$[Cu(NH_3)_2Br_2]$ **(234)**.[536] As the former involves a pseudo copper (II) stereochemistry, the latter is an artifact of the fluxional behaviour and these two structures are not genuine static structural isomers as the β form may be converted to the α form by the application of pressure.[1098–1100] Less extreme changes in stereochemistry of a copper(II) chromophore can occur through a change in temperature, which can result in a significant change in colour, thermochroism,[1104–1104] although the actual structural change is only associated with small changes in conformation of the ligands or hydrogen bonding effects.



α-$[Cu(NH_3)_2Br_2]$ **(414)**[1097]

The term distortion isomer may be extended slightly to include:[1102] (a) anion distortion isomers, such as $M^IM^{II}[Cu(NO_2)_6]$ (**250–252**) and $R_2[CuCl_4]$ (**175**, **187** and **206**); and (b) cation distortion isomers, such as $[Cu(dien)(bipyam)]X_2$ (**227**)[514] and $[Cu(bipy)_2Cl]X$ (**225**).[505] By varying the cations in (a) and the anions in (b) a wide range of complexes containing the same anion (a) or cation (b) may be prepared, but each with a significant range of CuL_6 stereochemistries (Table 68). Examples of anion distortion isomers have already been given for the $M^IM^{II}[Cu(NO_2)_6]$ series (Table 68a) in the pseudo octahedral structure of $K_2Pb[Cu(NO_2)_6]$ (**177**),[426] in the pseudo compressed octahedral structure of $Rb_2[PbCu(NO_2)_6]$ (**233**)[531] and in the static stereochemistry of $K_2Ba[Cu(NO_2)_6]$ (**182**).[433] The effect of both temperature and pressure will change the pseudo structure of (**177**),[1102] while that of temperature yields the three forms (**250**), (**251**) and (**252**) of $Cs_2[PbCu(NO_2)_6]$. Cation distortion isomers also occur with static stereochemistries as in the compressed tetrahedral to square coplanar stereochemistries of the $[CuCl_4]^{4-}$ anion.[175,476,483] The static compressed tetrahedral stereochemistry of the $CuCl_4$ chromophore of $Cs_2[CuCl_4]$ (**175**)[483] has the alternative static square coplanar geometry in (modphma)$[CuCl_4]$ (**206**).[476] Examples of cation distortion isomers having different geometries have been described in the compressed rhombic octahedral CuN_6 chromophore of $[Cu(dien)_2](NO_3)_2$ (**235**)[537] and in the elongated rhombic octahedral chromophore of $[Cu(dien)_2]Br_2{\cdot}H_2O$ (**194**).[446] Examples of cation distortion isomers involving only small changes in a basic static geometry are in the CuN_5 chromophores of the $[Cu(dien)(bipyam)]X_2$ (**227**)[505] series (Table 68b).[396,1105,1106] Bond-length changes up to 0.2 Å and bond-angle changes of up to 25° can be involved in these essentially static structures. Within these series of static distortion isomers there is then a significant change in the energies of the electronic reflection spectra (Figure 81a–c),[1107] although this is less than the changes in energy observed for a change in coordination number of the $[Cu(NH_3)_x]X_y$ chromophores of (Figure 81d).[895] Nevertheless, the differences in the electronic spectra do suggest a 'criterion of stereochemistry' *within* these series of anion or cation distortion isomers involving the same set of ligands.[822] The sense of the changes in energy of the electronic spectra from one distortion isomer to the next can then be used to suggest an assignment of the underlying electronic transition, even in the absence of polarized single-crystal electronic spectra (Section 53.4.4.5). In these series of anion or cation distortion isomers, the separate structures may be looked upon as points along the structural pathway[1085,1108] connecting the extreme regular structures and essentially mapping the route of the vibrational distortion along the pathway.[396,461,1109] This concept of a structural pathway may be extended to include geometries that involve a change in coordination number, as in the dissociative S_N1 and associative S_N2 processes of chemical reaction mechanisms.[967,1108] This is shown for the $CuCl_n$ chromophore in Figure 82, for which a range of coordination numbers from two to six are available.[461,489] Figure 83, then, shows a plot of the changes in electronic energies round this structural pathway, which are clearly a function of the coordination number, the geometry and of the distortion present.[489] Unfortunately, it is not possible to construct a structural pathway for every type of copper ligand as copper complexes with the required range of coordination numbers for equivalent ligands and differing geometries are not formed. However it is possible for complexes with nonequivalent ligands to keep one section of the coordinating ligands the same and to vary the remainder and in this way to develop a series of related complexes with a sufficient range of coordination numbers and geometries. This has been demonstrated for the $[Cu(bipy)_2X]Y$ (**225**) complexes;[396,505,1105,1106,1110,1111] as in Figure 84, the stereochemistries range from four- to six-coordinate, but without a rhombic coplanar geometry, as the coplanar arrangement of the bipy rings of the $[Cu(bipy)_2]^{2+}$ cation cannot occur because of the static interaction of the

Table 68 X-ray Crystallographic Data for Some Cation Distortion Isomers[a]

(*a*) $M^I_2M^{II}[Cu(NO_2)_6]$

	K_2Ca	K_2Sr	K_2Ba
Cu—N(1)	2.313	2.310	2.311
Cu—N(2)	2.052	2.041	2.048
Cu—N(3)	2.050	2.029	2.038

(*b*) $[Cu(dien)(bipyam)]X_2$ *complexes* (**227**)[514]

	$(NO_3)^-$	$(ClO_4)^-\cdot 0.5H_2O$	$Cl^-\cdot H_2O$
Cu—N(1)	2.032(19)	2.026(5)	1.990(12)
Cu—N(2)	2.039(18)	2.023(4)	2.013(12)
Cu—N(3)	2.071(18)	2.052(5)	2.020(12)
Cu—N(4)	1.991(19)	1.993(4)	1.998(11)
Cu—N(5)	2.150(19)	2.170(3)	2.126(11)
N(1)—Cu—N(3)(3)	135.5(7)	151.9(1)	159.1(5)
N(2)—Cu—N(4)(4)	172.0(8)	167.9(1)	162.9(1)

(*c*) $[Cu(bipy)_2Cl]X$ *complexes* (**225**)[396]

	$(ClO_4)^-$ [1105,1106]	$0.5(S_5O_6)^{2-}\cdot 3H_2O$ [1105,1106]	$(PF_6)^-$ [505]
Cu—N(1)	1.993	1.998	1.996
Cu—N(2)	1.991	2.089	2.105
Cu—N(3)	2.076	1.988	2.005
Cu—N(4)	2.136	2.105	2.108
Cu—Cl	2.263	2.293	2.344
N(2)—Cu—Cl	137.1	130.1	115.7
N(4)—Cu—Cl	126.4	122.1	120.5
N(2)—Cu—N(4)	96.5	107.3	123.8

[a] Bond lengths in Å, bond angles in degrees.

2,9-hydrogen atoms.[820] The link between the five- and six-coordinate geometries is extended by (4 + 1 + 1*) type structures (**203**) and (**204**) involving a *cis* bonding of the oxyanions present.[470] The structural pathway is complicated by the fluxional properties of the *cis* distorted octahedral geometry of $[Cu(bipy)_2(ONO)]^+$ cation, but once identified, by low temperature crystallography or ESR spectroscopy, causes little confusion.[397] The correlation of the stereochemistry with the energies of the electronic spectra involves some ambiguities, but with the help of the ESR spectra to determine the electronic ground state, most of these are resolved (Figure 85). From a spectroscopic point of view the major attraction of the structural pathway is that it offers a background against which the observed ESR and electronic spectra may be rationalized (Figure 85) and used to establish an 'electronic criterion of stereochemistry' for a *limited* range of complexes.[517,820,822] The ESR spectra can be used to identify the electronic ground state, $d_{x^2-y^2}$ or d_{z^2} (Figures 26 and 27), and the presence of fluxional systems (from the observation of temperature variability), and the electronic spectra can be used for determining the range of excited state energies (Figure 85).

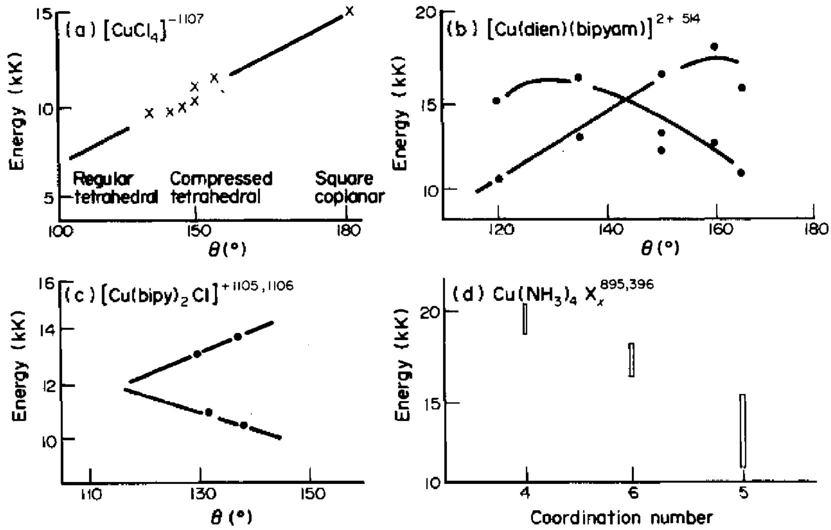


Figure 81 The correlation of the structure and electronic energy levels of series of anion and cation distortion isomers

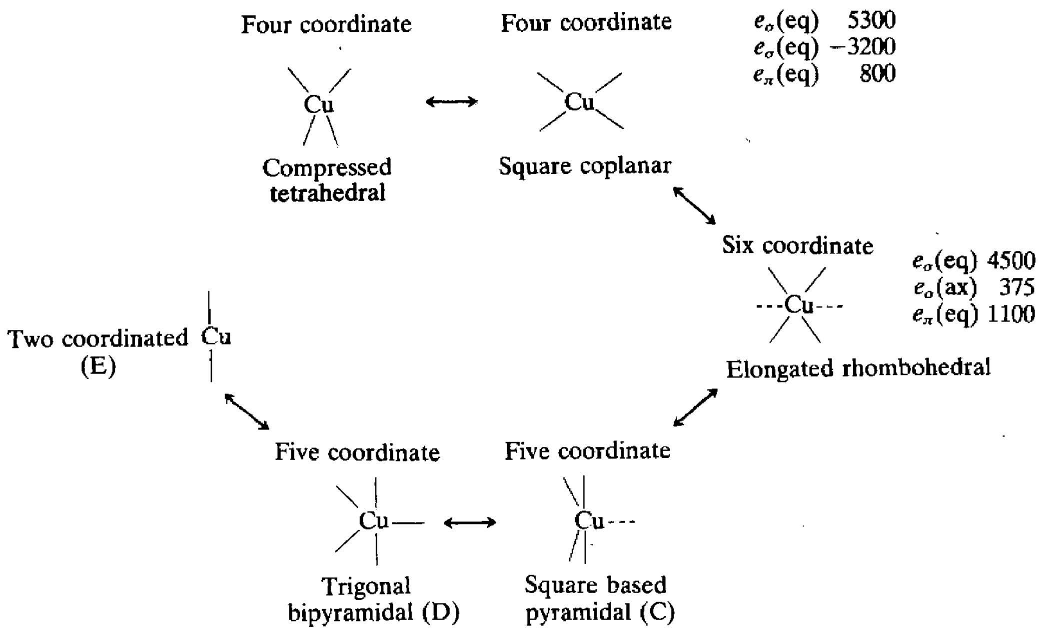


Figure 82 Structural pathway for the $CuCl_{4-6}$ system and some calculated AOM coefficients[1085,1108]

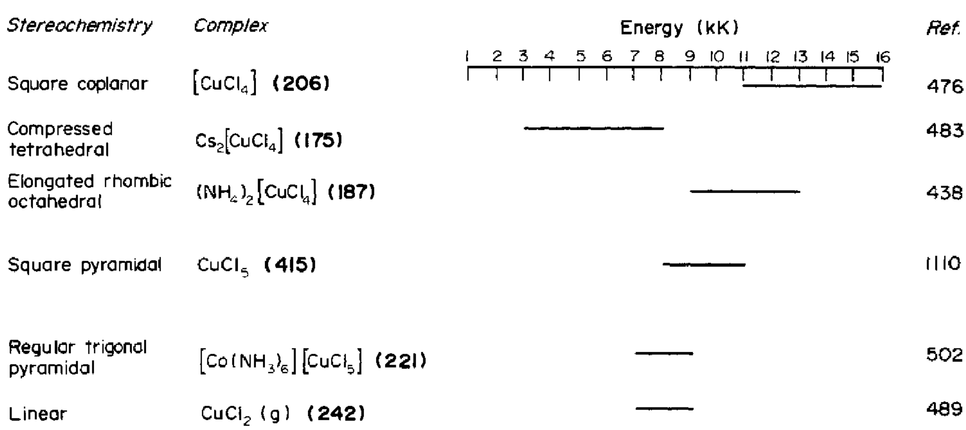
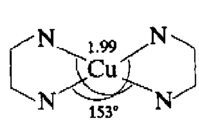
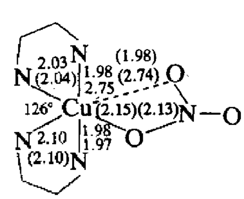


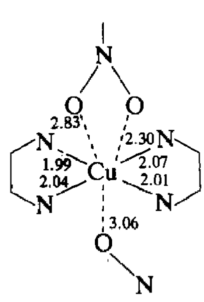
Figure 83 The electronic energies of a $CuCl_n$ chromophore structural pathway[461,489,1108]



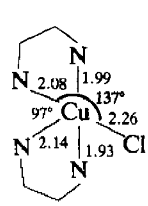
$[Cu(bipy)_2](PF_6)_2$ **(415)**[494]



$[Cu(bipy)_2(O_2NO)](PF_6)$ **(416)**[1110]



$[Cu(bipy)_2(O_2NO)](NO_3)\cdot H_2O$ **(417)**[1111]



$[Cu(bipy)_2Cl](ClO_4)$ **(418)**[1105]

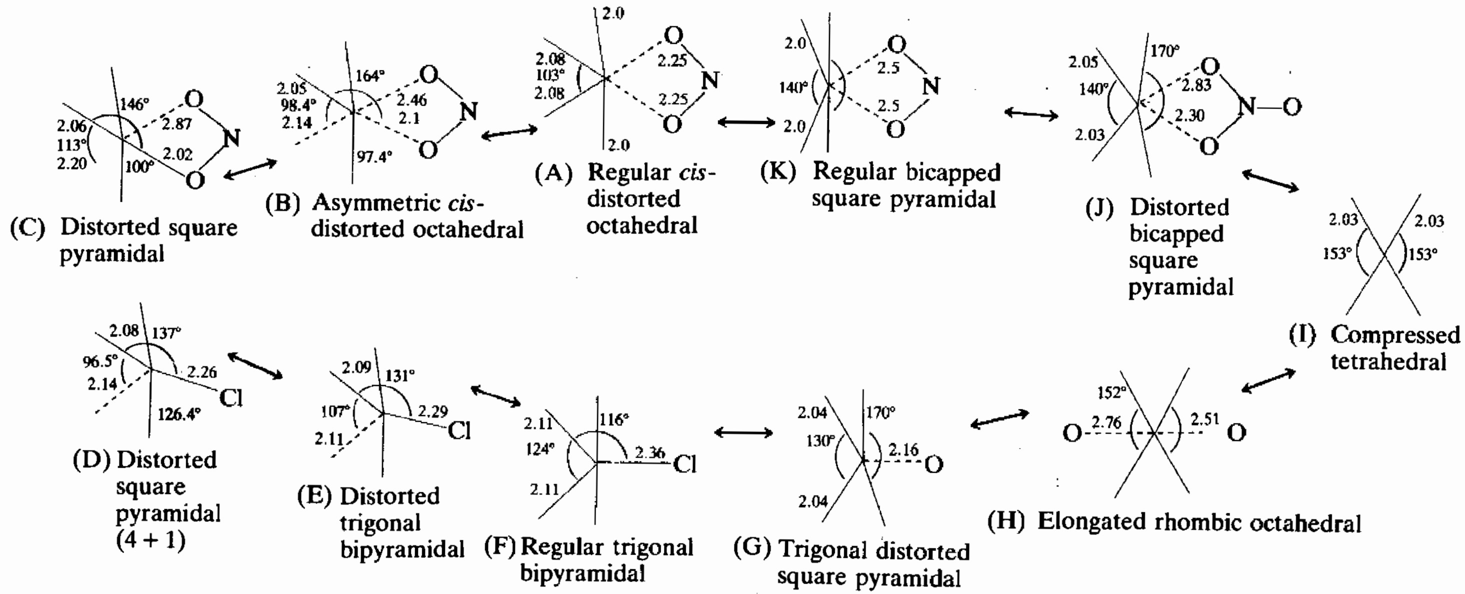


Figure 84 [Cu(bipy)$_2$X]Y complexes—structural pathway[505,1105,1106]

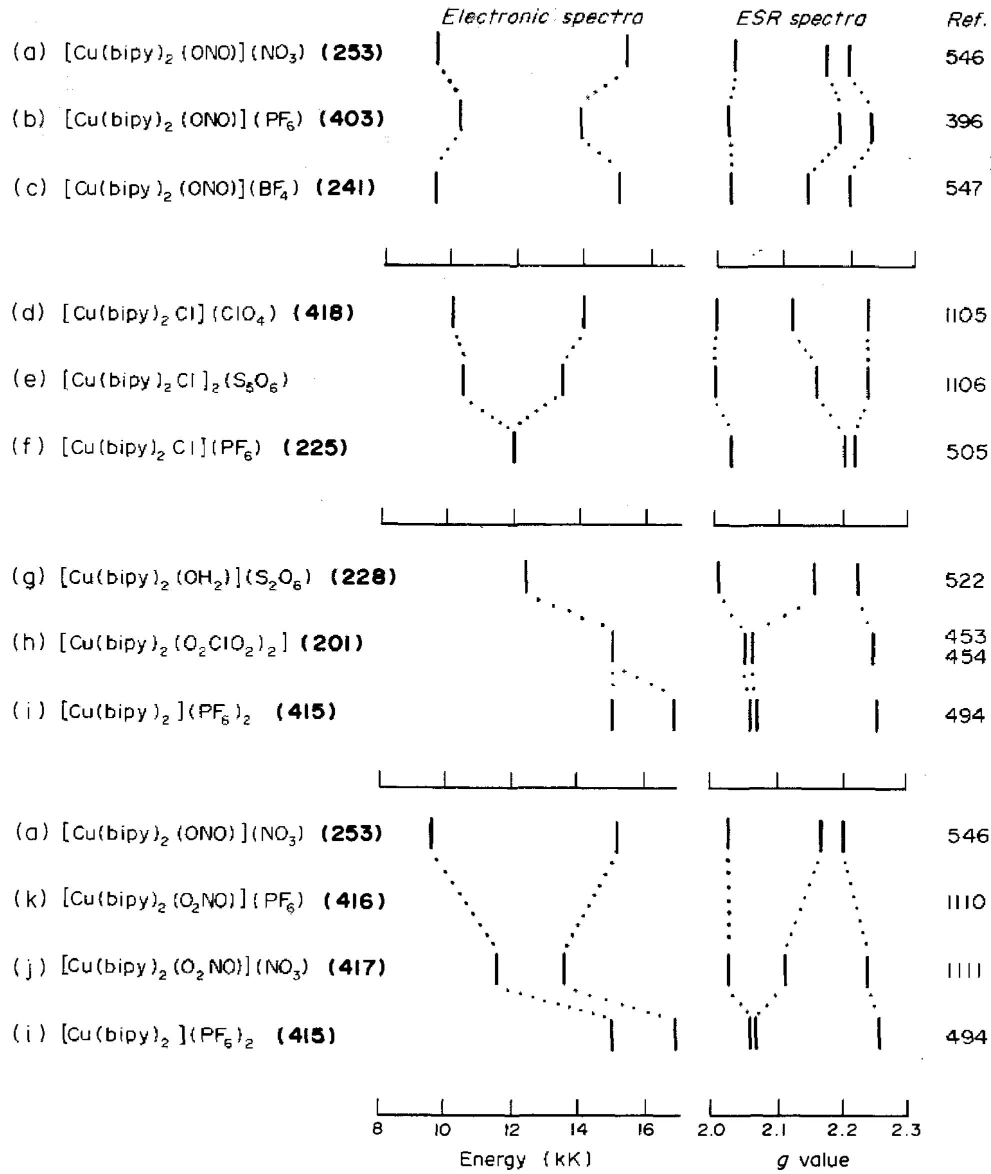


Figure 85 Correlation of electronic spectral energies and g values for $[Cu(bipy)_2X]Y$ complexes in a structural pathway (see Figure 84)[396]

While the structural pathway may be used to rationalize the structures and electronic properties of a series of copper(II) complexes, it is dependent upon the data available. It does not explain why, with water or ammonia as ligands to copper(II), five- and six-coordination predominate, with no tetrahedral four-coordinate species known and the square coplanar known only for the ammonia ligand.[895] Equally, it is not clear why the square pyramidal geometry is known for $K[Cu(NH_3)_5](PF_6)_3$ (**218**),[499] but is unknown for the water ligand and why neither ammonia nor water ligands will form a regular trigonal bipyramidal geometry, although the former has been suggested from EXFAS spectroscopy to occur in $[Cu(NH_3)_5](BF_4)_2$,[1052] in contrast to the square pyramidal stereochemistry predicted from the electronic reflectance spectra.[449]

53.4.6 Theoretical Calculations of Energy Levels

From the range of regular and distorted geometries of the copper(II) ion (Figure 19) and the presence of only a single unpaired electron, (Ar)$3d^9$, this might suggest that the calculation of the electronic energy levels of the copper(II) ion in the different CuL_n chromophore geometries would be a relatively simple matter.[830,1112–1117] Unfortunately, while most of the approaches from the crystal field theory,[828–832,1117–1123] through ligand field theory,[1115,1116,1119] to molecular orbital theory[830–832,1115,1118] are generally able to predict the correct ground state for the copper(II) ion in a given stereochemistry (Table 41) and can in most cases predict the correct sequence of excited state levels,[1123] the quantitative estimation of these energy levels leaves a great deal to be desired (Figure 86).[1124] Even when the crystal-field splitting parameter Δ is replaced by the more informative second and fourth order radial distribution functions α_2 and α_4, their calculation involves such large uncertainties that the ratio α_2/α_4 is usually assumed to be *ca.* 3.0.[829] Thus, with different ligand atoms and Cu—L distances, α_2^L and α_4^L, too many unknown parameters are required to assign the copper(II) electronic transitions, especially if these are poorly resolved (see Section 53.4.4.4). The extension of these crystal field calculations to include spin–orbit coupling for the various copper(II) geometries has not simplified the problem.[1117] While the use of various ligand field,[830,832,1125] extended Hückel,[1118,1126] or *ab initio* self-consistent field approaches[1127] has been extensively applied to copper(II) species (Table 69), they at best only yield satisfactory agreement with the observed electronic energies.[1124] The greatest discrepancy has been in calculating the energy levels of the square coplanar CuL_4 chromophore;[1065,1074,1124] these estimate the d_{z^2} orbital (Figure 27a) to lie above the d_{xy}, d_{xz} and d_{yz} levels by *ca.* 5000 cm^{-1}. Even the assignment of the polarized single-crystal spectra,[1124,1136] such as in the [Cu(R-acac)$_2$] systems,[949,1137,1138] have been ambiguous but are now considered[1124] to involve the d_{z^2} level lying below the d_{xy}, d_{xz} and d_{yz} levels (Figure 27a). This discrepancy of 5000 cm^{-1} is now considered [1139] to arise from $4s$–$3d_{z^2}$ mixing (see Section 53.4.5), and introduces a further arbitrary parameter into the calculation.[836,1065,1139]

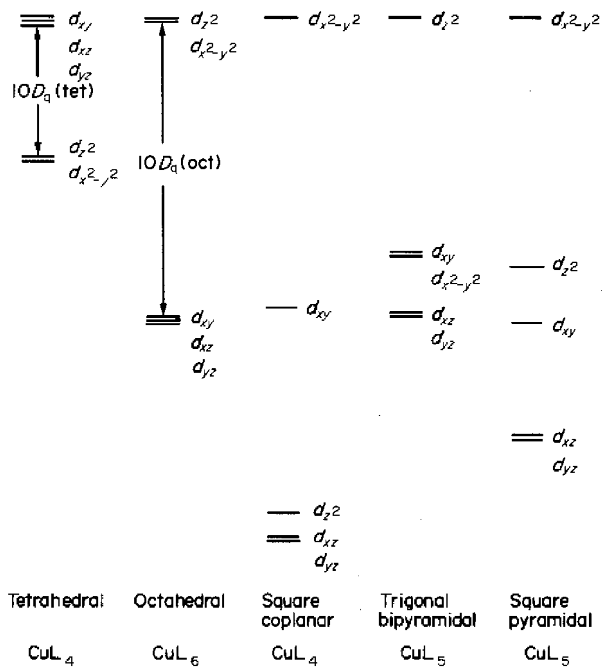


Figure 86 Crystal field levels of regular stereometries in units of D_q

Table 69 Theoretical Calculations of the Electronic Properties of $Cu^{II}X_n$ Chromophores

Chromophore	*Method of calculation*	*Stereochemistry*[a]	*Ref.*
$[CuF_6]^{4-}$	MO–WH	ERO	1128
$[CuCl_6]^{4-}$, $[CuF_6]^{4-}$	LCAO–MO	ERO	1129
$[CuCl_5]^{3-}$	MO	TB	1130
CuF_2	SCF (RHF and UHF), INDO	L	1127
Cu(porphyrin)—CuN_4, CuS_4	Extended Hückel and MO	SP	1131, 1132
Cu(cyclops)—CuN_4X	MO	SBP	1131
Cu(macrocycle)—CuN_4, CuS_4	MO	SP	1133, 1134
[Cu(Et$_2$dtc)$_2$]—CuS_4	HFS–LCAO Extended Hückel	RC	1135

[a] ERO = elongated rhombic octahedral; TB = trigonal bipyramidal; L = linear; SP = square planar; SBP = square-based pyramidal; RC = rhombic coplanar.

In the most recent literature, two hopeful signs have appeared, which attempt to get round this problem. Firstly, the X_α technique[1140] has been shown to provide a reasonable basis for the calculation of the energy levels of the square coplanar CuN_4 chromophore[1141] and of those of the $[CuCl_4]^{2-}$ anion,[1142] as a function of the change from square coplanar to compressed tetrahedral (Figure 82). Unfortunately, this method loses the identity of the *d* orbitals that are familiar to coordination chemistry.[1140] Secondly, the semi-empirical angular overlap method (AOM) has been extensively applied to the simple copper(II) stereochemistries using just the electronic energy levels of copper(II) complexes and the appropriate AOM expression for the different coordination numbers and stereochemistries (Table 70).[20,1124,1143,1144,1065] Unfortunately, the number of parameters required (e_σ, $e_{\pi_\parallel}$ and $e_{\pi_\perp}$) for copper(II) complexes generally exceeds the number of resolved energy levels (maximum four), due to the broadness of the bands and frequent extensive overlap. The use of polarized single-crystal electronic spectra while improving the number of resolved bands, rarely provides a definitive assignment of the electronic energy levels for a particular complex due to the ambiguities in determining the appropriate 'effective symmetry' to be used.[836] Even where good electronic spectral energies are available for isolated complexes,[1124] the insensitivity of the energies to small differences in the values of e_σ and e_π makes the determination of the latter from the electronic spectral transitions alone difficult,[1124] if not impossible.[1145] This situation is further compounded by the complication introduced by the $4s$–$3d_{z^2}$ mixing referred to above. The limitation of the number and accuracy of the electronic energies has been elegantly overcome, by the fitting of the e_σ and e_π parameters to both magnetic susceptibility and ESR experimental data measured by single-crystal techniques and using the CAMMAG programme.[1146] As these two electronic properties are much more sensitive to the low symmetry effects of a copper(II) ion in a complex, they more adequately reflect the precise copper(II) ion environment[835b] and are a better test of the AOM parameters.[1147] This also removes some of the ambiguity associated with the determination of the 'effective symmetry' to be used in the assignment[47] of the polarized single-crystal electronic spectra due to their insensitivity to low-symmetry ligand-field effects.[835b,1148] In practice to increase the amount of experimental data the single-crystal χ and g values along with their directional properties are used to calculate a best fit to the observed electronic energies, with no assumption of the 'effective symmetry' of the copper(II) ion environment or about the direction of χ and g tensors. The method uses the crystallographically determined copper(II) geometry, which is used to resolve the measured crystal χ and g values into their corresponding local molecular χ and g values, if the CuL_n chromophores are misaligned by the space group elements of symmetry (see Figure 33). Applied in this way the AOM approach[836,1146–1149] has been used to determine e_σ and e_π values for a significant number of first-row transition metal ions from chromium to nickel and while the original expectation that the AOM would yield e_σ and e_π values that are transferable from one metal to another has not been realized,[1143–1147] the range of e_σ and e_π values has been established.[835b,1147] Nevertheless, in ref. 1147 there are only a few values for copper(II) complexes, despite the wealth of magnetic, ESR and spectral data available.[832,836,47,48] The problem arises from $4s$–$3d_{z^2}$ mixing referred to earlier, which cannot be measured experimentally.[836,1065,1139] This problem has been nicely bypassed (but not overcome) in the more recent application of the CAMMAG program by associating a negative e_σ bonding role with the special 'voids' of the square coplanar, square pyramidal and elongated tetragonal octahedral stereochemistries of the copper(II) ion.[1148,1150] Figure 87 summarizes the e_σ and e_π values for a range of distorted copper(II) complexes, the e_σ(eq) values range from 5000–6500 cm^{-1} and the e_σ(ax) from +1000 to $-3500\ cm^{-1}$, with the latter consistent with the increasing tetragonal distortion from restricted tetragonal octahedral, to square coplanar. More recently the AOM approach has been applied to a series of $CuCl_{4-6}$ chromophores from four-coordinate square coplanar to elongated tetragonal octahedral, following the structural pathway of Figure 82(b), and mirroring the variation of the change of the electronic energies along the pathways of Figure 81(a), as shown in Figure 88.[1148] This correlation demonstrates, for the first time, that this modified AOM approach can be used to mirror the changes of e_σ and e_π coefficients along the structural pathway of a series of CuL_n geometries and equally establishes that the total bonding content $\Sigma_1^n\,[e_\sigma(\text{eq}) + e_\sigma(\text{ax}) + e_\pi(\text{ax})]$ is approximately constant at $23\,000 \pm 1000\ cm^{-1}$ (Figure 88). It will be of interest to discover if the AOM approach can be used to mirror the change in electronic energies along the structural pathway from compressed tetrahedral to square coplanar (Figure 82a) and from square pyramidal to trigonal pyramidal (Figure 82d). If so, then a significant advance will have been made in describing the e_σ and e_π bonding function of the Cl^- anion as a ligand, and as a function of the stereochemistry of the copper(II) ion,

Table 70 Angular Overlap Method (AOM) d-Oribital σ- and π-Interaction Energies for Various Regular Copper(II) Geometries[a]

Chromophore	*Stereochemistry*[b]	d_{z^2} e_σ	d_{z^2} e_π	$d_{x^2-y^2}$ e_σ	$d_{x^2-y^2}$ e_π	d_{xy} e_σ	d_{xy} e_π	d_{xz} e_σ	d_{xz} e_π	d_{yz} e_σ	d_{yz} e_π
MX_4	SP	1	0	3	0	0	4	0	2	0	2
	CTd	0	8/3	0	8/3	4/3	8/9	4/3	8/9	4/4	8/9
MX_5	SBP	2	0	3	0	0	4	0	3	0	3
	TP	11/4	0	9/8	3/2	9/8	3/2	0	7/2	0	7/2
MX_6	ETO	3	0	3	0	0	4	0	4	0	4

[a] Compiled from Table 9.2 ref. 1065. [b] SP = square planar; CTd = compressed tetrahedral; SBP = square-based pyramidal; TP = trigonal pyramidal; ETO = elongated tetragonal octahedral.

namely the structural pathway of Figure 82. In establishing the e_σ and e_π values for the $CuCl_{4-6}$ chromophores of Figure 88, the assignments of the electronic spectra were determined as those which gave the most reasonable variation in the e_σ and e_π values, including the negative e_σ(ax) values. In contrast a comparable attempt to assign the electronic spectrum of $[Cu(imidazole)_4(ONO_2)_2]$ (**419**) unfortunately rejected the most 'reasonable' assignment, as it produced a negative e_σ(ax) value.[1147,1151] The application of this approach to the π-bonding function of the 2,2′-bipyridyl ligand, as in $[Cu(bipy)_2I]$ (**420**) suggests (Figure 89) that is a π donor at N(1), e_π positive, but a π acceptor at N(2), e_π negative, consistent with the shorter Cu—N(1) distance of 2.01 Å relative to a Cu—N(2) distance of 2.03 Å.[1148,1152] It would be nice to think that at last the AOM is yielding separate e_σ and e_π parameters that quantify the σ- and π-bonding function of chelate ligands to the copper(II) ion.

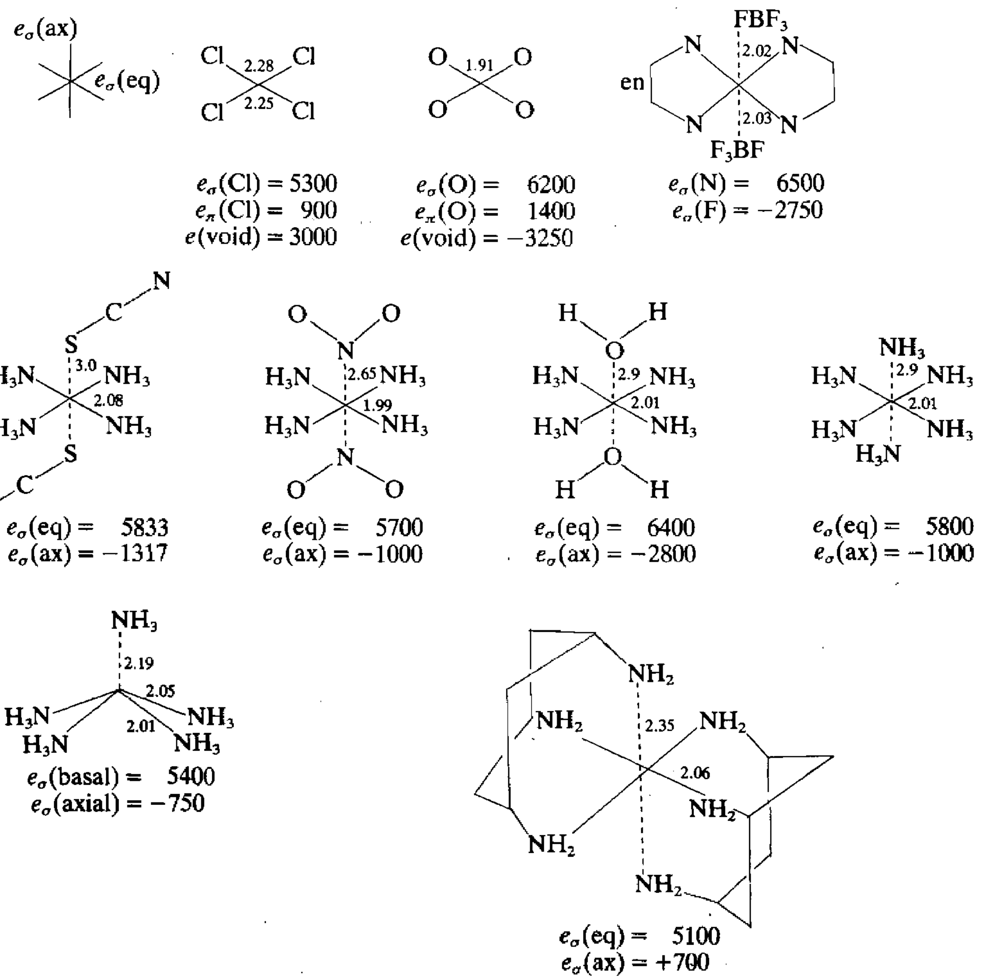


Figure 87 e_σ and e_π AOM coefficient for a number of copper(II) complexes[1148]

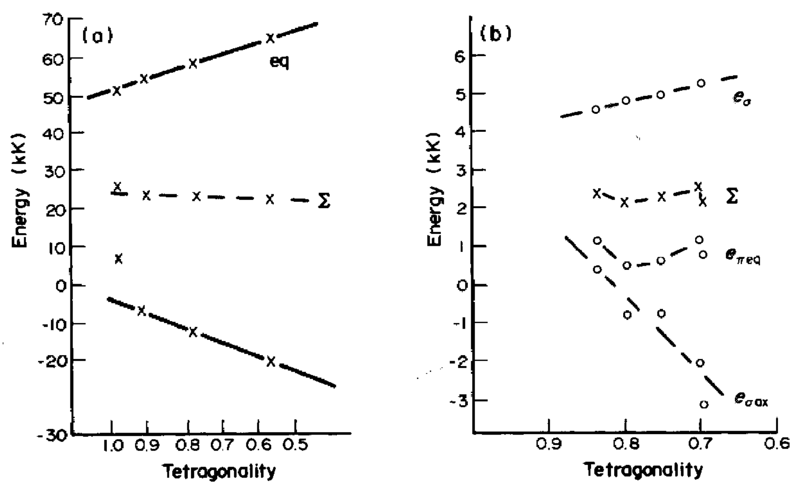


Figure 88 Modified AOM parameters e_σ and e_π against tetragonality (T) for (a) $[Cu(NH_3)_{4-6}]$ and (b) $[CuCl_{4-6}]$ with summations Σ[1148]

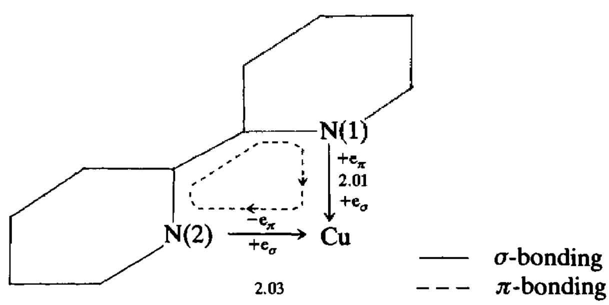
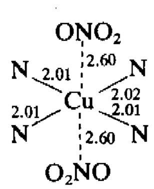
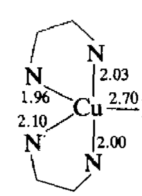


Figure 89 The bonding of the bipy ligand in the trigonal pyramidal CuN_4I chromophore of $[Cu(bipy)_2I]I$[1146]



$[Cu(imidazole)_4(ONO_2)_2]$ **(419)**[1151]



$[Cu(bipy)_2I]I$ **(420)**[1152]

Notwithstanding the limited success of the various approaches to the calculations of the electronic energies of the copper(II) ion (Table 69), these various approaches have been applied to the calculation of other physical data, with, not surprisingly, only limited success. Thus they have been used to calculate the g values using crystal-field calculations,[1121] molecular orbital methods,[1153] extended Hückel,[1135] X_α-type[1140] and simple AOM-type[1154] calculations of which the X_α calculations have been the most successful. By combining the g values with the electronic energies of the d–d transitions of Figure 27, it is possible to obtain values for the combined orbital and spin–orbit reduction factors, r.[47,48] In axial copper(II) complexes these are related through electron delocalization of the metal electrons to the simplified molecular orbital coefficients of the antibonding molecular orbitals given in Table 71 by the expressions: $r_\parallel = \alpha\beta_1$ and $r_\perp = \alpha\beta$, where α measures the in-plane σ bonding, β_1 measures the in-plane π bonding and β the out-of-plane π bonding. Table 72 lists a number of examples of orbital reduction parameters, assuming the above approximation. A number of conclusions may be deduced from this data. Firstly, for purely σ-bonding ligands such as ammonia and ethylenediamine α lies in the range 0.73–0.77 (for a purely covalent bond $\alpha = 0.5$ and for a purely ionic bond $\alpha = 1.0$). Secondly, with these in-plane σ-bonding ligands there is some evidence that in tetragonal octahedral complexes there is some weak out-of-plane π bonding as the β values are less than 1.0. Thirdly, with potentially π bonding in-plane ligands, such as oxygen, as $r_\parallel > r_\perp$ the most significant π bonding is out of the plane. Nevertheless, caution is

Table 71 The Antibonding Molecular Orbitals for an Axial Copper(II) Complex with a $d_{x^2-y^2}$ Ground State

$$\psi_1 = \sigma d_{x^2-y^2} - \sigma_1'[\sigma_x^1 + \sigma_y^2 - \sigma_x^3 - \sigma_y^4]/2$$
$$\psi_2 = \sigma d_{z^2} - \sigma'[2\sigma_z^5 + 2\sigma_z^6 - \sigma_x^1 - \sigma_y^2 - \sigma_x^3 - \sigma_y^4]/\sqrt{12}$$
$$\psi_3 = \beta d_{xy} - \beta_1'[p_y^1 + p_x^2 - p_y^3 - p_x^4]/2$$
$$\psi_4 = \beta d_{xz} - \beta_1'[p_z^1 - p_z^3]/\sqrt{2}$$
$$\psi_5 = \beta d_{yz} - \beta_1'[p_z^2 - p_z^4]/\sqrt{2}$$

advised in applying this over simplified molecular orbital treatment, even with good single-crystal g values and electronic energies, as attempts to extend this approach were not helpful, even for simple copper(II) geometries.[1155] More recently the use of k values has been reintroduced in a slightly different form involving $g = g_0 + n\mu$, where n is an integer and $\mu = k^2\lambda/\text{energy}$, and the g value relation used to confirm the assignment of the electronic spectra.[405,432] Attempts to calculate the variation of the g and A values with the change in geometry from trigonal bipyramidal to square-based pyramidal were more successful.[925] Equally, the calculation of the g values for the $[CuCl_4]^{2-}$ anion from tetrahedral to square coplanar by the $\chi\alpha$ method was remarkably successful,[1142] and it will be interesting to see if this method can be extended to more than monatomic ligands.

Table 72 The Combined Orbital and Spin–Orbit Reduction Parameters and Molecular Oribital Coefficients

Complex	$r_{\parallel}$	$r_{\perp}$	α	β	β'
$Na_4[Cu(NH_3)_4][Cu(S_2O_3)]_2 \cdot H_2O$	0.76	0.78	0.76	1	1
$Na_4[Cu(NH_3)_4][Cu(S_2O_3)]_2 \cdot NH_3$	0.77	0.78	0.77	1	1
$[Cu(NH_3)_4(SCN)_2]$	0.74	0.76	0.74	1	1
$[Cu(NH_3)_4(NO_2)_2]$	0.74	0.73	0.74	1	0.99
$[Cu(en)_2(BF_4)_2]$	0.73–0.75	0.74	0.73–0.75	1	0.98–1.0
$[Cu(en)_2(SCN)_2]$	0.71–0.75	0.71	0.71–0.75	1	0.94–1.0
$Ca[CuSi_2O_{10}]$	0.80	0.72	0.80	1[a]	0.90
$[Cu(3\text{-}Meacac)_2]$	0.77	0.74	0.77	1[a]	0.96
$[Cu(UO_2)_2(AsO_4)_2] \cdot 8H_2O$	0.80	0.78	0.80	1[a]	0.975
$[Cu(HCO_2)_2 \cdot 4H_2O]$	0.77	0.69	0.77	1[a]	0.90
$Ca[Cu(MeCO_2)_4] \cdot 6H_2O$	0.926	0.78	0.926	1[a]	0.84

[a] It may not be justified to assume that $\beta_1 = 1$ in these cases.

During the past few years extensive use has been made of MO calculations to correlate the assignment of the charge-transfer spectra of copper(II) complexes, especially those containing sulfur ligands,[958,959] with the calculated values for these charge-transfer spectra using extended-Hückel-type calculations. As these transitions vary widely from 20 000–50 000 cm^{-1} and are not very sensitive to the stereochemistry of the copper(II) environment (see Section 53.4.4.5) their assignment from MO-type calculations is more successful than for the assignments of the corresponding d–d transitions of the copper(II) ion. Consequently, these calculations are proving useful as probes for identifying the type of metal ligand donor atom, especially for sulfur-type ligands[30,958,959]

An area in which MO orbital calculations have been surprisingly successful is in the calculation of the magnitude of the magnetic interaction in polynuclear copper(II) complexes (Section 53.4.4.3), where antiferromagnetic or ferromagnetic behaviour may be present.[876,877] In $[Cu(O_2CMe)_2]_2$ (**316**),[682] the nature of the Cu—Cu interaction has been debated for 20–30 years,[873–879] but the most recent calculations suggest that the mechanism may be a mixture of direct metal–metal bonding and super-exchange through the acetate bridging ligands (but see ref. 1155 for a note of caution).

53.4.7 Catalytic Copper(II) Systems

Copper and its complexes are outstanding among the transition metal elements as reagents or catalysts in the reaction of organic compounds.[1156] The importance of the copper(II) species in oxygenation reactions has been reviewed (Figure 10; Section 53.3.4).[30] In general they yield relatively unstable copper(II) species, including the only dioxygen copper(II) complex of known crystal structure, $[Cu_4(O_2)_2(OH_2)_4(L^{10})](PF_6)_4$ (**153**).[333] The question of copper-promoted reactions in aromatic chemistry has been reviewed[1156,1157] and also the role of organometallic complexes in organic reactions.[1158] In general the role of the copper is intimately involved and related to the presence of Cu^{I} and Cu^{II} oxidation states,[30] although there is little or no information on the stereochemistry of the various copper(I) or (II) complexes or of the mechanisms of their involvement. Thus in the Wacker process,[1159] involving the industrial oxidation of ethylene to acetaldehyde (equations 25–27) the $Cu^{II} \rightleftharpoons Cu^{I}$ redox process is involved only as an internal redox loop (a ping-pong process), continuously regenerating Cu^{II} from Cu^{I} by the reaction with molecular oxygen, which is so catalytically effective that the process is industrially viable.[1160] Many electron shuttle or ping-pong reactions are known,[1156–1158] with little doubt about the involvement of a copper(I) oxidation state. It is then of interest that the kinetics of the auto-oxidation of the copper/ascorbate/dioxygen reaction in solution, pH = 2–4, has been studied independently and identical rate laws determined,[1161,1162] but the two groups differ in the suggested mechanism of the reaction. The first group involves a copper(I) species,[1160] while the second postulates the involvement of a dinuclear copper(II) dioxygen species $[Cu_2(AsCh)_2(O_2)]^{2+}$.[1160] As dinuclear copper species are well known in copper(I) and copper(II) coordination complexes (Sections 53.3.2.2 and 53.4.2.3, respectively) this does not resolve the question, which is further compounded by the isolation of copper(I) and (II) oxygen and dioxygen species in the solid state (Tables 15 and 73, respectively). The crystallographic characterization of the copper(II) dioxygen Cu_4O_2 species (Figure 11) is then of interest as two distinct types are observed, a μ_4-oxo plus a terminal oxygen ligand, and two symmetrical bridging Cu—O—Cu surface cage species. This further complicates the role of the O_2 species in these dioxygen complexes, both of which involve either a superoxide or peroxide species.[1163] The whole question of the dioxygen complexes of the transition metal ions has been reviewed recently,[1164,1165] and the physical characterization of the O_2 species summarized (Figure 90). While the O—O distances range from 1.25–1.49 Å, with IR frequencies ranging from 1195 to 790 cm^{-1}, the problems of identifying these vibrations by IR, Raman or resonance Raman spectroscopy are not trivial (Section 53.4.4.7),[1203] and X-ray crystallographic data are clearly to be preferred. In view of the difficulty of obtaining good single crystals of these generally unstable complexes, this area of model compound synthesis has a promising future, particularly for low temperature X-ray powder profile analysis.[1165]

$$C_2H_4 + [PdCl_4]^{2-} + H_2O \longrightarrow MeCHO + Pd^0 + 2HCl + 2Cl^- \quad (25)$$

$$Pd^0 + CuCl_2 \longrightarrow [PdCl_4]^{2-} + 2CuCl \quad (26)$$

$$2CuCl + 2HCl + 1/2O_2 \longrightarrow CuCl_2 + H_2O \quad (27)$$

Table 73 Some Solid and Solution State 'Dioxygen' Copper(II) Complexes[a]

Complex	*Colour*	*Visible spectra* (cm^{-1})	*ESR*	μ_{eff}	*IR* (cm^{-1})	*Ref.*
$\{Cu(OH)_2\}_2(OOH)(MeCO_2)]$	Brown	*ca.* 14 000	Silent	Diamagnetic	820	1369
$Cu_2(HBpz_3)_2(O_2)]$	Green	—	—	Paramagnetic	520(Cu—O)	133
$Cu_2(C_{24}H_{40}N_2O_2S_4)(O_2)](BF_4)_2$	Green	*ca.* 15 000	$g = 2.05, 2.22$; $A_{\parallel} = 75 \times 10^{-4}\ cm^{-1}$	Paramagnetic	—	320
$Cu\{HB(3,5\text{-}Me_2pz)_3\}(O_2)]\cdot 1/8Et_2O$	Green	*ca.* 19 000	—	Diamagnetic	—	45, 30(b)
$Cu(N,N\text{-}Et_4en)_2(OH_2)(O_2)](ClO_4)_2$	Blue	15 873	Silent	Diamagnetic	825(O—O)	45, 30(b)
$Cu_4Cl_4L_3O_2]$[b]	Brown	*ca.* 17 000	—	Paramagnetic	—	[c]

[a] See Table 15 for corresponding copper(I) 'dioxygen' complexes. [b] L = py, 4-pic, 2,4-lutidine, bipy. [c] G. Speier, Z. Tyeklar and A. Rockenbauer, Inorg. Chim. Acta, 1982, 66, L69.

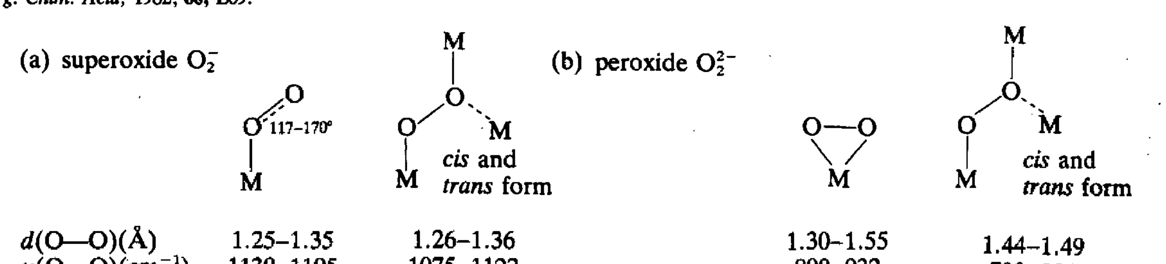
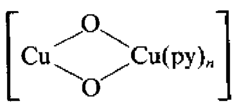
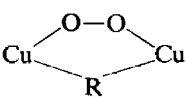


Figure 90 Structural classification of dioxygen complexes.[1164,1165] Vaska classification superoxide I(a) and II(a); peroxide I(b) and II(b)

The question of the role of copper(II) complexes as catalysts has been expanded to look at the role of dinuclear copper(II) complexes themselves, rather than those resulting from the oxygenation of the corresponding copper(I) complexes (Figure 10b) and the oxidation of catechol to *o*-benzoquinone (Figure 91a).[1167] By using a binuclear triketone complex, $[Cu_2(BAA)_2]$ (**421**), a 1:1 addition compound is postulated involving a good steric match (Figure 91b),[1156,1168] and which can be as effective as the 'reactive copper' species in the CuCl·py system involving a postulated system:[172,1169]



The later is effective in oxidizing catechol to muconic acid even under nitrogen (equation 28).[1167] This 'reactive copper' species[172] has been variously formulated as a $[Cu_2O_2]^{2-}$ unit containing a superoxide or peroxide O_2 unit,[1169] which may then involve a postulated unit:[1167]



The unit has an asymmetric dibridging molecular structure (see **306**). Similarly a structural mechanism for the hydroxylation of monophenolic substrates by oxytyrosinase has been postulated[1170] involving this asymmetric dibridged species (Figure 92a) and the postulated pathway of Figure 92(b), I. In the associative ligand substitution I, initial carboxylate approach to a square pyramidal copper(II) centre I(A) is followed by the two-dimensional rotation of the three planar copper ligand bonds to yield coordinated carboxylate structures I(B) and (C). However, as structures II(B) and (C) are difficult to relate to model copper(II) complexes of known crystal structure, the mechanism shown in Figure 92(b) II(A)–(C) is suggested. An initial bicapped CuL_4O_2 chromophore is preferred with asymmetric two-dimensional rotation, resulting in the formation of a more familiar $(4+1^*+1^*)$-type coordination with the carboxylate involved in its more familiar off-axis asymmetric bidentate bonding.[470] These structures are then typical of the fluxional stereochemistries of the $[Cu(chelate)_2(OXO)]Y$-type complexes,[397] which themselves have been characterized as the ultimate 'oxygenation' products of the $[Cu^I(chelate)_2]Y$ complexes (see Section 53.3.8). Until definitive crystallographic data are available on these reactive oxygenated species,[1171] it is nice to see the detailed crystallographic structure determinations of the oxygen insertion reaction (Figure 11b) taken[141] from a copper(I) dinuclear complex I, through to a stable dinuclear hydroxy-bridged species IV to the free phenol V, but implying a possible dinuclear II, $Cu^I_2O_2$ and $Cu^{II}_2O_2$, species, or possibly a mixed $Cu^ICu^{II}O_2$ species. The reactivity of these oxygenated species (Figure 12) has already been probed by the use of their reaction products with CO_2.[328] It is postulated that the μ_4-oxo plus terminal oxygen species (b), is unreactive towards CO_2, but the surface-bridged species (a) readily reacts with CO_2 to form a carbonate complex $[Cu_4Cl_4(CO_3)_2]$ with the postulated structure of Figure 12(c). This bonding role of the carbonate anion as a bridging ligand has already been established in $[\{Cu(L^6)\}_2(\mu\text{-}O_2CO)]$ (**122**)[254] and $[Cu_2(Me_4pn)_2Cl_2(O_2CO)]$ (**280**).[628] In view of the reactivity of these oxygenated products of copper(I) and copper(II) in the oxidation of small organic molecules, it is worth commenting that there is an extensive chemistry of addition compound formation by copper(I) with CO (Figure 7), and ethylene/acetylene (Figure 8), while no such adducts are formed with copper(II). Indeed, the $[Cu\{HB(3,5\text{-}Me_2pz)_3\}(C_2H_4)]$ (**132**)[270] complex is sufficiently coordinatively unsaturated for it to have been used (at 40 °C) as the starting material for a $[Cu^I\{HB(3,5\text{-}Me_2pz)_3\}(O_2)]$ complex, which turns green on standing for a few days at room temperature.[245] The stability may be sufficient to justify low temperature X-ray crystal structure determination by powder profile analysis. Much less information is available on the activation of copper(II) complexes for the oxidation of inorganic systems, but the kinetics of the oxidation of copper(I) by oxygen in acid solution has been reported and also the oxidation of $Na_2(S_2O_3)\cdot 5H_2O$ by oxygen-activated $[Cu(NH_3)_4X_2]$ complexes.[1172]

The catalytic role of copper complexes in the oxidation of organic molecules is not restricted to solution, but can also occur at surfaces, particularly involving ion exchange[1173] on silica gel,[1174] Lind molecular sieves[1175] or ion exchange resins.[1176] The ion exchange of the $[Cu(OH_2)_6]^{2+}$ cation has been most studied,[1177] both at room temperature and after thermal

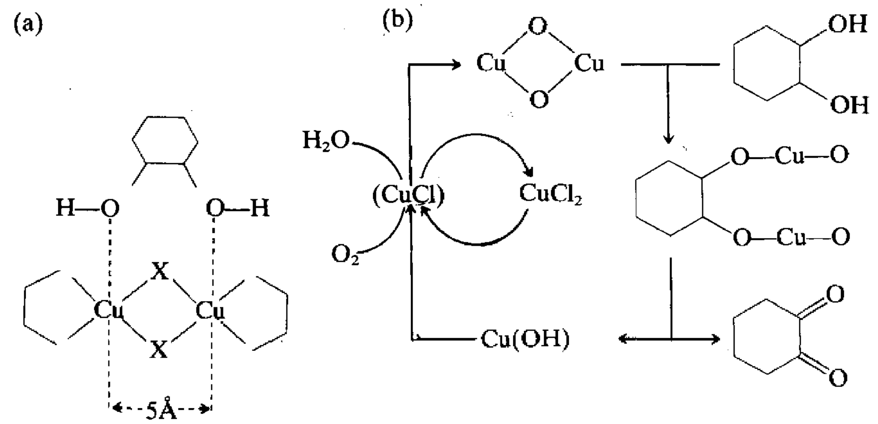


Figure 91 (a) Proposed catechol/copper(II) dimer;[1156,1168] (b) catechol/orthoquinone cycle with copper(I)/(II) ping-pong loop[1167]

$$\text{catechol} + O_2 \text{ (or } N_2) + \text{Cu reagent} \longrightarrow \text{muconic acid} \quad (28)$$

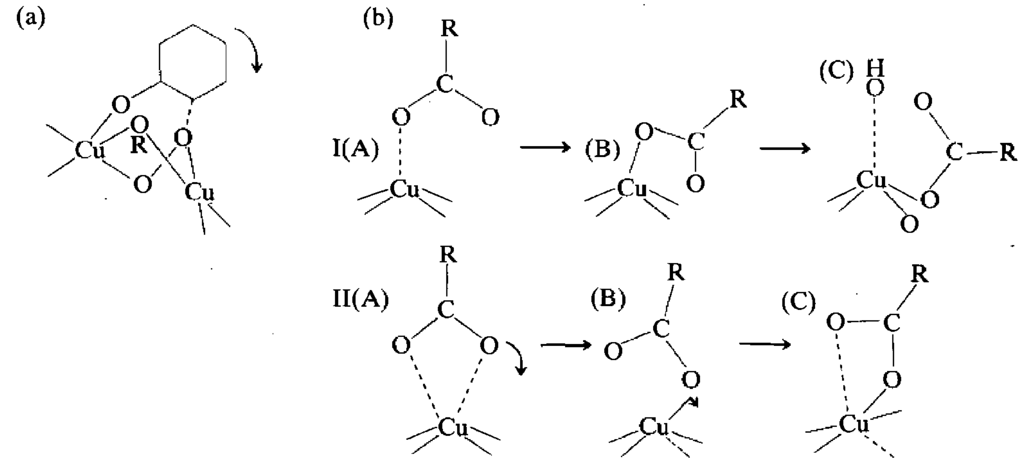
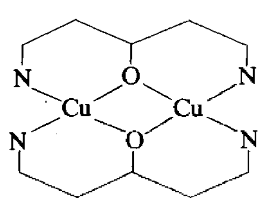


Figure 92 (a) Structural mechanism for the hydroxylation of monophenolic substrates by oxytyrosinase; (b) reaction coordinate diagram for associative ligand substitution at the copper site of tyrosinase



$[Cu_2(BAA)_2]$ (**421**)[1168]

dehydration under vacuum at temperatures up to 1000 °C. The changes have been extensively studied by ESR[1178] and electronic reflectance spectroscopy,[1179] both of which techniques are sensitive to the copper(II) ion environment, but neither of which can yield precise information on the copper(II) ion environment. More recently an elegant series of crystal structure determinations of the $[Cu(OH_2)_6]^{2+}$ cation doped in zeolites has been carried out,[1180,1181] before and after vacuum dehydration at 100–500 °C. The resulting stereochemistries are shown in Figure 93, and suggest that there is extensive reduction to copper(I), even at 350 °C, to a $(Cu^{II}_5)(Cu^{I}_3)Si_{12}Al_{12}O_{48}{\cdot}xH_2O$ species, with novel tetrahedral and trigonal pyramidal CuO_n chromophores, neither of which is commonly observed in normal copper(II) complexes with oxygen ligands (see **213** and **222**). Nevertheless, the trigonal pyramidal $[CuO_5]$ species explains the observed ESR spectra and suggests a d_{z^2} ground state.[1178,1179] Unfortunately, the electronic reflectance spectra of these unique systems were not reported. At higher temperatures the copper environments involve six trigonal CuO_3 chromophores and two Cu atoms on the zeolite surface. Whether or not this set of structure determinations is correct in every detail, it clearly establishes that nature can be much more complex than molecular coordination chemists imagine, that novel copper stereochemistries can be observed in less obvious copper situations and that only by pushing crystallography to the 'limits of credibility' will such interesting results be obtained.[1180] It is then significant that the novel technique of pulsed electron spin-echo modulation analysis[1182] has also confirmed a trigonal bipyramidal $[Cu(OH)_2O_3]$ environment (**422**) in a hydrated copper(II) zeolite.[1182] While the Cu—O distances with Cu—O(ax) ≫ Cu—O(eq) are unexpected (see Section 53.4.2.1v), they are lent some credibility in the light of the above single crystal zeolite results. Unfortunately, this interesting technique involves the same type of curve fitting that is required in EXAFS spectroscopy and leads to uncertainty in the estimation of the all important *long* Cu—L distances. The use of EXAFS spectroscopy has also been applied to obtaining Cu—O distances on adsorbed copper(II) species,[1051,1183] and extended to an interesting series of synthetic zirconium phosphate ion exchange resins.[1184,1185]

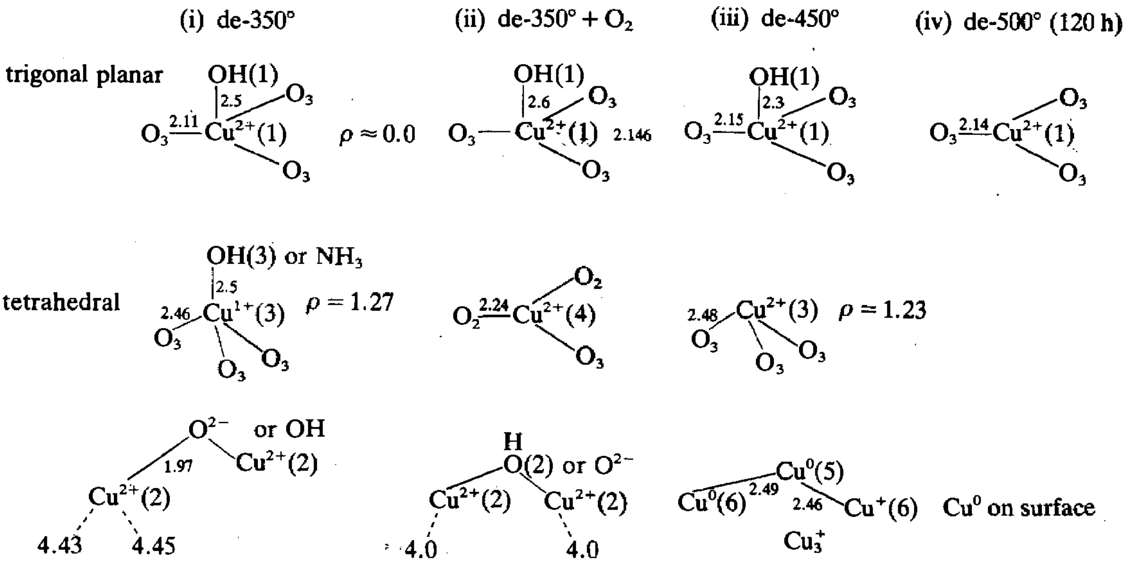
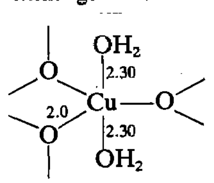


Figure 93 Single-crystal structures of Cu zeolite Cu_8-A, $(Cu^{2+})_5(Cu^+)_3(OH)Si_{12}Al_{12}O_{48}\cdot H_2O$, prepared by ion exchange at 100 °C



Cu zeolite (**422**)[1182]

53.4.8 Biological Copper(II) Systems

The general involvement of the elements[7,8,26–29,1186] in biological systems is well documented and their biological function is now usually included in the majority of recent text books on inorganic chemistry.[17,19–21]

A number of texts are now available on bioinorganic chemistry but ref. 26 provides a useful emphasis and account of the role of transition metal ions in biological systems.[28] A number of texts[24,25] and reviews[1187–1196] on copper proteins are now available and individual chapters on the different functions of the copper proteins are contained in the various volumes of 'Metal Ions in Biological Systems' edited by H. Sigel;[29] in particular, volumes 12 and 13 are almost exclusively devoted to copper. In biological systems copper is the third most abundant transition metal element,[26] with an occurrence of 80–120 mg in a normal human body (70 kg),[26,1197] compared to values of 4–5 g for iron and 1.4–2.3 g for zinc. It generally occurs in the copper(II) oxidation state, but is believed to involve a copper(I) oxidation state in deoxyhemocyanin (Section 53.3.5)[351,352] and the copper(III) oxidation state has been invoked in mechanistic studies (Section 53.5).[26,11]

The function[26] of copper in biological systems (Figure 94) is primarily in redox reactions (equation 29) associated with the reduction of oxygen to water (equation 30) with the transfer of oxygen to a substrate (Figure 10), namely (i) monooxygen insertion — oxygenase, *e.g.* phenol → diphenol, and (ii) dioxygen insertion — dioxygenase, *e.g.* catechol → *o*-quinone. Superoxide dismutase[26] has the specific, but important, role of removing the highly reactive superoxide anion (dismutation) (equation 31) and in these oxygenation reactions the copper is acting as the biological catalyst (enzyme) in the reaction (Section 53.4.7).[188] The second major biological role of copper is in the transport of copper around the human body,[997] controlling its uptake and excretion. This transportation process is essential in controlling the two most important diseases of the human body caused by copper deficiency, namely (i) Wilson's disease,[1198] and (ii) Kroky hair syndrome.[1199] This transportation process controls the upper level of the copper concentration in the human body, above which it acts as a poison.[1200–1202]

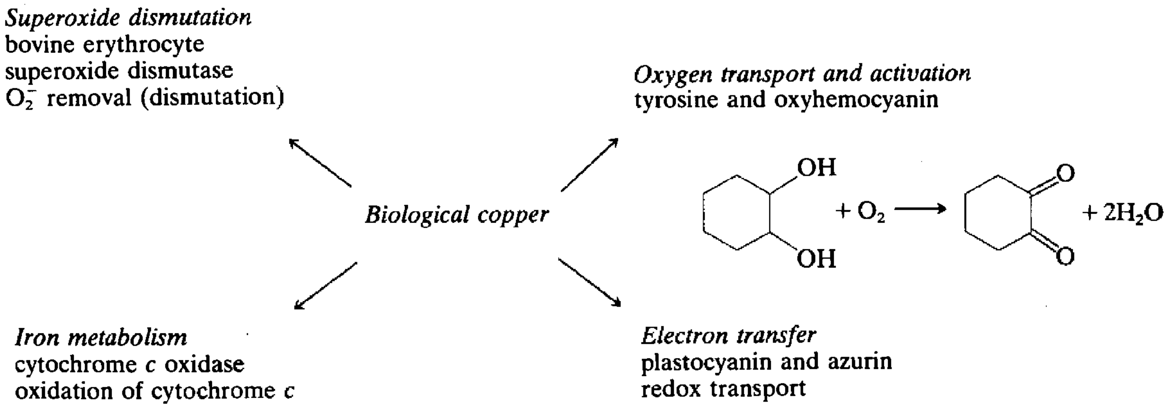


Figure 94 Types of biological copper activity[26]

$$Cu^{I} - e^- \longrightarrow Cu^{II} - e^- \longrightarrow Cu^{III} \quad (29)$$

$$O_2 + 4e^- + 4H^+ \longrightarrow 2H_2O \quad (30)$$

$$2O_2^- \longrightarrow O_2 + O_2^{2-} \quad (31)$$

During the past 10–15 years a great deal of effort has been put into characterizing the biological role of copper using the combined or separate techniques of biology/biochemistry and of coordination chemistry (Section 53.4.8.1).[24–30,1186–1196] Parallel to this has been an equally extensive effort to prepare and characterize a wealth of coordination complexes of the copper(II) ion in an attempt to model the physical and chemical behaviour of the biological copper system (Section 53.4.8.2).[30,1180,1191,1203] These two approaches are outlined in the next two sections.

53.4.8.1 Biological copper(II) types I–III

The biological function of copper has been classified into four types:[26,1203,1189] the first three types (I–III; Figure 95)[1189,1204] are associated with copper proteins containing a single type of copper centre, while type IV[25–30] involves more than one of the type I–III copper environments (Table 74). The copper proteins are generally referred to as the copper 'blue' proteins[1187–1197] as they are frequently associated with an intense blue colouration, which is now known to be characteristic of the type I copper proteins (Figure 95).[30,1203] These blue proteins are usually associated with low molecular weights (for proteins) of approximately 20 000 dalton units as in poplar plastocyanin (21 000-2Cu), azurin (14 000-1Cu) and stellacyanin (16 800-1Cu).[1205] All three proteins are believed to contain essentially the same copper(II) environment, involving a CuN_2S_2 chromophore, the precise structure of which has been determined by single-crystal X-ray crystallography for plastocyanin[353b,1206] to a resolution of 2.7 Å (Figure 96) and azurin to a resolution of 2.5 Å.[1207] The CuN_2S_2 environments are similar and involve a very distorted tetrahedral geometry, with approximately trigonal (C_{3v}) symmetry. The coordination involves two histidine nitrogen ligands at 2.04 Å (Hist-37) and 2.10 Å (Hist-87), a cysteine sulfur ligand at 2.13 Å (Cyst-84) and a methionine sulfur ligand at 2.90 Å (Met-92). It also involves some

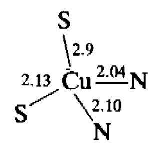
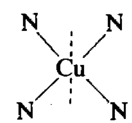
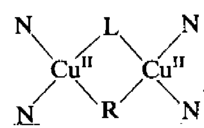
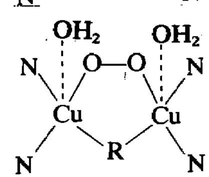
Type and examples	Oxidation state	Structure	Spectra (nm; cm^{-1}; $\varepsilon: M^{-1} cm^{-1}$)	Redox (mV)	g value	ESR A ($10^{-4} cm^{-1}$)	Function
Type I blue	II	 (angles 85–132°)	Cysteine–Cu (CT)	Cu^{II}/Cu^{I}	2.05		Oxidases
1. **Poplar plastocyanin** (21 000 – 2Cu)			559; 17 890		2.23	$A_{\parallel} < 100$	Electron transfer
			606; 16 490	150–700			
2. **Azurin** (14 000 – 1Cu)			749; 13 350		2.26	$A_{\parallel}60$	Not solvent accessible
			ε 3000–6000	370	2.05		
3. **Stellacyanin** (16 800 – 1Cu)			d–d		2.29	$A_{\parallel}31$	
			600; 16 667	300	2.08	$A_{\perp}28$, 84	
			ε 5000–12 000				
Type II non-blue normal	II						
1. **Galactose oxidase** (75 000 – Cu)			630; 15 873		2.08	$A_{\parallel}140$–190	Electron transfer
			ε 100–1000		2.04	$A_{\parallel}185$	Bond F^{-} and inhibit oxidase
Type III proteins		Proposed structure					
1. **Deoxyhemocyanin** (7–8×10^{6} – 2Cu)	I/I	Cu^{I} Cu^{I}	Colourless	350 to 600 Cu^{II}/Cu^{I}	Diamagnetic		Hydroxy monophenols Oxidizing o-diphenols
2. **Met-hemocyanine** or tyrosinase	II/II		670; 14 925		ESR silent		$O_2 \rightarrow 2H_2O$ (catalase) Oxygen bonding
3. Tyrosinase Cu^{II} Cu^{II} (120 000 – 4Cu)	II/II		580; 17 241		ESR silent		Oxygen transport
			345; 28 986				
			ε 10^{3}–2×10^{4}				

Figure 95 Biological copper types I–III physical and chemical characteristics[24–30,1203]

very nontetrahedral angles of 123, 137, 85 and 97°. This geometry is unusual in a number of respects. Firstly, it is virtually unknown in a model mononuclear copper(II) complex, molecular structures (**174**) to (**255**), and in view of the long Cu—S of 2.90 Å, may equally be described as approximately three coordinate, plus a long fourth copper–sulfur ligand distance. As a three-coordinate geometry for a mononuclear copper(II) complex is also unknown, the type I geometry is doubly unique. In view of this novel geometry, the type I copper proteins exhibit some unique electronic properties.[1203,1208] The intense blue colour originates from a broad multiple transition band at 13 000–18 000 cm^{-1} (ε, 3000–6000 $M^{-1}\,cm^{-1}$; Figure 97a), which is associated with sulfur to copper charge transfer from the cysteine ligand and is not *d–d* in origin.[1209] The *d–d* transitions have been identified in the near IR region in the circular dichroism spectrum of plastocyanin.[1208,1209] Polarized single crystal spectra of a film of plastocyanin have been used to suggest an assignment of the intense visible and less intense IR (*d–d*) spectra (Figure 97a).[1209] The ESR spectrum[1203,1209] of plastocyanin (Figure 97b) is consistent with an axial elongated environment $g_{\parallel} \gg g_{\perp} > 2.0$ (Table 41) equivalent to an appropriate $d_{x^2-y^2}$ (or d_{xy}) ground state (Figure 98), but with characteristically low copper hyperfine $A_{\parallel}$ values $< 100 \times 10^{-4}\,cm^{-1}$ (see Figure 38b for tetrahedral $A_{\parallel}$ values). The electronic energy levels of the CuN_2S_2 chromophore of the plastocyanin system has been simulated by crystal- and ligand-field calculations,[1203,1208–1210] and the latter suggest the mixture of energy levels shown in Figure 98. The type I copper(II) proteins are also characterized by relatively positive redox potentials (Figure 62) in the range +180–+700 mV.[818]

Table 74 Multiple-type Copper Enzymes in Blue Oxidases

	No. of types present			*EMF*(mV)		
	I	*II*	*III*	*I*	*II*	*III*
Plus laccase	1	1	1	394	365	434
Ascorbate oxidase	3	1	2	—	—	—
Ceruloplasmin	2	1	1 or 2	490	—	—
Laccase (tree)	1	1	1	—	—	—
Laccase (fungal)	1	1	1	—	—	—

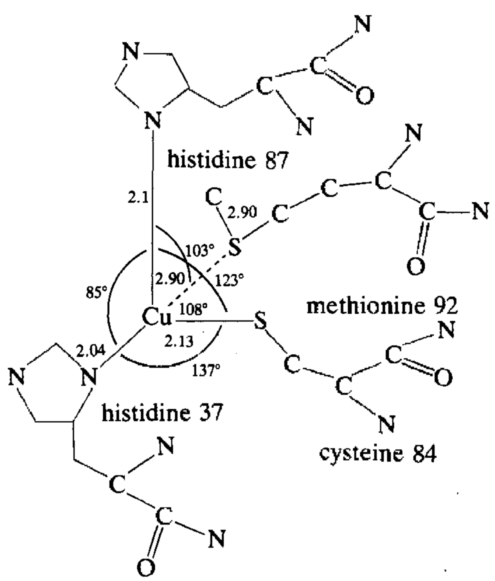


Figure 96 Molecular structure of the type I copper blue site in plastocyanin at pH > 7.0[1207]

The type II copper proteins (Figure 95) are generally referred to as the non-blue or normal copper proteins as,[1203] although they appear blue, this colour is not associated with the high intensity of the type I S → Cu charge transfer, but with the low intensity of a normal copper(II) *d–d* transition (ε = 100–1000 $M^{-1}\,cm^{-1}$).[1203] The type II proteins are generally associated with higher molecular weights than the type I proteins,[1205] thus galactose oxidase has one Cu atom associated with a molecular weight of 75 000 dalton units. While the structure is unknown, it is

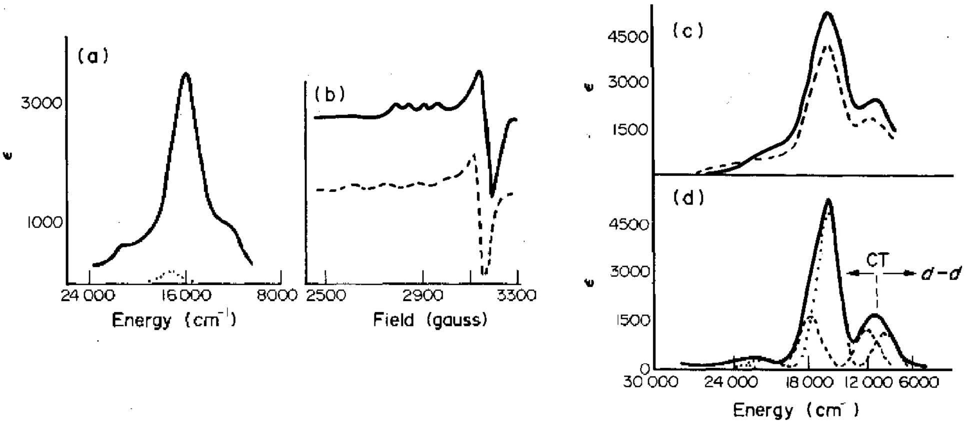


Figure 97 Blue copper protein (a) electronic spectrum; (b) ESR spectrum (—— 'blue' copper; - - - 'normal' copper); (c) plastocyanin polarized single-crystal spectrum; and (d) resolution by Gaussian analysis[1204]

D_{2d}		
$d_{x^2-y^2}$	0	$0.9d_{x^2-y^2}$
d_{xy}	3500	$0.8d_{xy}$
d_{z^2}	9100	$0.6d_{z^2} + 0.3d_{yz}$
d_{xz}	10 000	$0.4d_{yz} + 0.3d_{z^2} + 0.2d_{xz}$
d_{yz}	11400	$0.7d_{xz} + 0.2d_{yz}$

Figure 98 Suggested assignment of the *d–d* spectrum energy levels of the CuN_2S_2 chromophore in plastocyanin (energy values are in cm^{-1})[1203,1209]

believed to involve a normal mononuclear CuN_4X_2 chromophore environment with an elongated rhombic octahedral stereochemistry.[1203] It has (Figure 95) a typical *d–d* band at $16\,000\,cm^{-1}$ ($\varepsilon = 100\,M^{-1}\,cm^{-1}$), and an axial ESR spectrum, $g_\perp = 204$, $g_\parallel = 2.28$, with a normal copper hyperfine value for $A_\parallel$ of $185 \times 10^{-4}\,cm^{-1}$ (Table 49). The function of galactose oxidase is to catalyze the oxidation of galactose to the aldehyde, a process that can be poisoned by addition of ligands such as thiocarbamate, cyanide and fluoride ions.[26,1203,1211] Type II copper protein behaviour also occurs in mixed metal copper proteins such as bovine erthyrocyte superoxide dismutase (SOD, 35 000-2Cu,2Zn)[1203] and cytochrome *c* oxidase (100 000-2Fe,2Cu).[28] The crystal structure of SOD has been determined (Figure 99) and shown to involve a ZnCu dimer with a tetrahedral ZnN_2NO chromophore bridged by one imidazole anion to a square pyramidal CuN_3NO chromophore.[1212] A more recent structure determination is essentially the same but involves a slight tetrahedral distortion of the in-plane CuN_4 chromophore (see Section 53.4.2.1v).[1213] The electronic spectrum and ESR spectral properties are comparable to those of a normal axially elongated copper(II) complex (Figure 95).[1203]

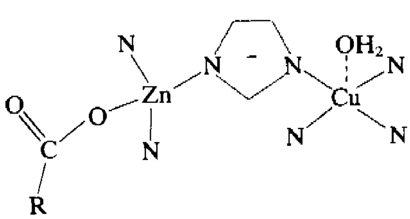
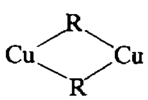


Figure 99 The molecular structure of bovine erythrocyte superoxide dismutase[1212]

The type III copper proteins are probably the most interesting of the non-blue or normal proteins, if only due to their high molecular weights (Figure 95). They are still of unknown crystal structure, but preliminary results have been reported.[1214] They occur[1215] in tyrosinase (119 000-4Cu), Met-hemocyanin ($7–8 \times 10^6$-2Cu), oxyhemocyanin and deoxyhemocyanin (see Figure 16c for the nomenclature used in naming the three hemocyanin proteins). They are all believed to involve dimeric Cu_2 structures,[26,1203] with unsymmetrical bridging ligands (Figure 100), which in the case of the oxy- and deoxy-hemocyanin possibly involve a methoxy- and peroxy-bridging ligand, respectively (Figure 95), bridging two tetragonal octahedral $CuN_2O_2X_2$

chromophores. As deoxyhemocyanin involves two copper(I) ions, a bridging peroxy group is unlikely; the coordination number will more likely be three or four and the protein will be colourless. For the met- and oxy-hemocyanins, $Cu^{I}Cu^{II}$ and $Cu^{II}Cu^{II}$, respectively, the *normal* axial copper(II) environments are predicted to generate *normal* copper(II) *d–d* spectra at 16–17 000 cm^{-1} and *normal* ESR spectra for the single copper(II) environment of the met-hemocyanin. However, the most interesting feature of the oxyhemocyanin is that, like the deoxyhemocyanin ($Cu^{I}Cu^{I}$), it is diamagnetic[1216] despite the presence of two copper(II) ions which must therefore be antiferromagnetically coupled with $-J > 500$ cm^{-1} (see Section 53.4.4.3). As a consequence of this large antiferromagnetic coupling the oxyhemocyanin protein is ESR silent,[1203] notwithstanding the presence of a visible *d–d* spectrum at 16–17 000 cm^{-1}, consistent with the presence of copper(II) ions. As seen in Section 53.4.4.3 the antiferromagnetic coupling is consistent with both a di- and mono-bridged Cu_2 dimer (Figure 100a and b respectively). In the absence of any crystallographic data on di- or mono-oxo-bridged copper(I) or copper(II) species (notwithstanding the structure of (**153**),[333] which is not antiferromagnetically coupled) the evidence for the bonding role of the O_2 bridge must rest very heavily on the spectroscopic evidence. Thus IR and Raman spectroscopy,[1203,1217] resonance Raman spectroscopy,[1218,1219] and EXAFS spectroscopy[290,1220] provide knowledge of the copper atom environment, most of which supports the *dioxo-di-bridge* model of Figure 95 (Table 75). See ref. 1203, for a detailed review of the spectroscopic arguments in support of what is still only a suggestion for the structure of the oxyhemocyanin protein. The met-hemocyanin structures are believed[1221,1222] not to involve an oxygenated bridge, O_2, but to involve a mixed oxidation state $Cu^{I}Cu^{II}$ system (see Section 53.3.7). The probing of these systems with exogenous bridging ligands such as $(N_3)^-$, $(NO_2)^-$ and halide anions produces evidence for intervalence charge-transfer spectra (Figure 101).[1203,1222] As the class II Robin and Day behaviour[360] (Section 53.3.7) is unlikely to be associated with a single short bridging ligand, but always with two short bridging ligands, the structure of the half-met-hemocyanin is most likely to involve a dibridged unit:



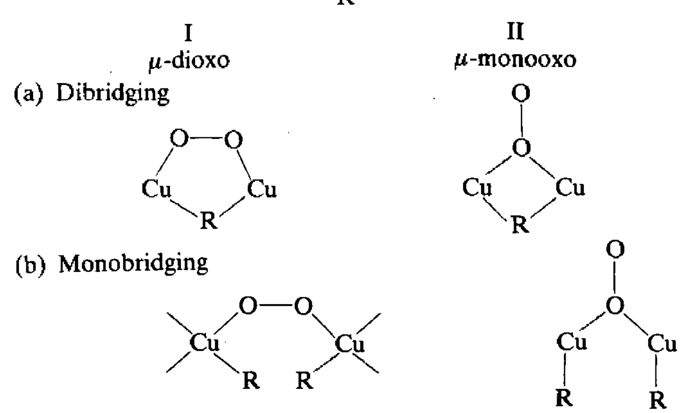
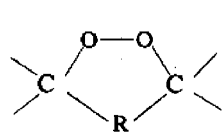


Figure 100 The dinuclear bridging unit in the met- and oxy-hemocyanin: (a) dibridging and (b) monobridging[1203]

Table 75 Spectroscopic Evidence for the  Bridge Unit in Oxyhemocyanin[1217–1221]

Infrared	Cu—N stretches ~280 cm^{-1}		
Raman[30,1203]	50 cm^{-1}		
Resonance Raman[1218,1219]	$^{16}O_2$	~750 cm^{-1}	peroxide
	$^{18}O_2$	~710 cm^{-1}	O_2^{2-}
EXAFS[1222]	Cu—Cu 3.58–3.66 Å		
	Four-coordinate Cu		

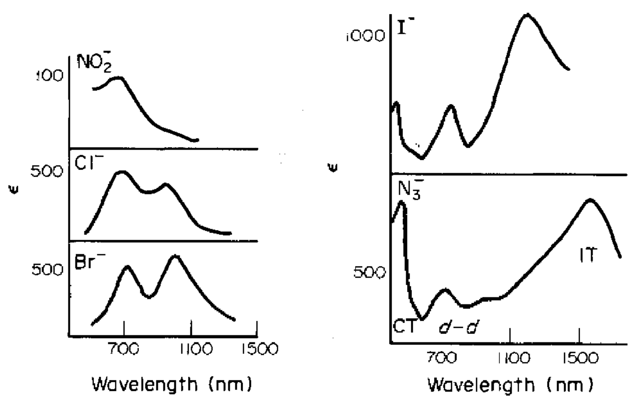


Figure 101 The absorption spectra of half-met-hemocyanin protein plus added bridging ligands: 15 K IT = intervalence charge-transfer spectra[1203]

The multicomponent type IV copper proteins are usually coloured (Figure 95) as they generally contain at least one blue type I copper centre, but as there are usually more than one of each type present, the physical properties of the different types I–III environments are difficult to separate and, for ESR-silent type III centres, difficult to detect.[1203] No crystallographic data are yet available on a type IV copper protein.

53.4.8.2 Model compounds of type I–III biological copper(II)

A wealth of model compounds have been quoted in the literature. Refs. 30 and 898 give excellent up-to-date accounts of the model compound approach to all three types of biological copper. Table 76 lists some examples of complexes that have been suggested as model compounds of the three type I–III biological environments.[1223–1228] The greatest effort has involved the preparation of type I and III structures, as type II structures equate directly with the known mononuclear copper(II)-type stereochemistry.[1203,1234] Biologically relevant ligands such as the amino acids, heterocyclic ligands such as pyrazine and imidazole, and sulfur-containing SR_2 and SR^- ligands have been involved in the simulation of the type I copper centres.[1223–1226] Two-centred macrocyclic ligands have been widely studied to simulate the binuclear type III copper behaviour.[1227–1230] Not surprisingly, the best approaches have involved the synthesis of an extensive range of model complexes involving only small changes in the ligands present, followed by the determination of as wide a range of physical properties as possible, such as magnetism, ESR and electronic spectra, and redox properties, then X-ray structure determination of those complexes whose properties best correspond to those of the appropriate type of biological copper system. Not surprisingly, the majority of these approaches failed to produce electronic properties remotely comparable to the unique properties of the biological system, but in this respect the low $A_{\parallel}$ values ($<70 \times 10^4$ cm^{-1}) of the ESR spectra of the type I biological copper have been the most difficult to simulate (but see **155**). On the other hand, the search for strongly antiferromagnetically coupled Cu_2 dimers has produced a wealth of magnetic and structural data, involving a range of Cu—Cu separations (Table 76c), which must inevitably result in a better understanding of the relationship between structure and exchange coupling and hence of the mechanism of exchange coupling. But equally importantly it has revealed the deficiency in our knowledge of the classical coordination chemistry of copper and has generated an interesting distinction[1203] between the 'extrinsic' and 'intrinsic' active metal sites in biological systems 'that will generate a copper site that is intrinsically different from that of small molecule copper complexes' (ref. 1203, p. 11). However, the biological copper situations are not different from those in small molecule copper complexes as long as we recognize that long copper–ligand distances (semi-coordination) and off-the-z-axis bonding are just as important as short copper–ligand distances.[456,468,470] The flexible biological ligand structures (Figure 96) are only a manifestation of the nonspherical symmetry of the copper(II) ion, which is illustrated in the plasticity effect[416] with faculative ligands and in the fluxional behaviour of temperature variable copper(II) structures.[397] The potential energy diagram that explains the pseudo Jahn–Teller[1067] behaviour is no different from that which describes the temperature variability of the Cu^ICu^{II} Robin and Day class II

Table 76 Mononuclear Model Copper(II) Complexes of Biological Copper Systems

	Chromophore	*Electronic spectra* (cm^{-1})	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel} \times 10^4$ (cm^{-1})	*CT* (cm^{-1})	*Ref.*
(*a*) *Type I*							
[Cu(mercaptoacetylglycyl-L-prolyl-L-histidine)]	$CuSN_2O$	16 950, 14 200	2.296	2.081	75	20 000	1223
[$Cu(S_4N_2C_{17}H_{24})$] (**423**)	CuN_2S_2	12 300	2.132	2.06	160	—	1224
[$Cu(bidhp)Cl_2$] (**424**)	$CuN_2Cl_2S_2$	13 200, 9200	2.19	2.01	—	27 000	1225
[$Cu_2(L^8)Cl_2$]$\cdot 6H_2O$ (**275**)	CuN_2O_2Cl	—	—	—	—	—	622
(*b*) *Type II*							
[$Cu(imidazole)_4(ONO_2)_2$] (**419**)	CuN_4O_2	18 000, 15 400, 12 500	2.23	2.05	—	—	1151
[$Cu(C_{22}H_{21}N_5O_3)$]	CuN_3OO'	15 900	2.23	—	173.6	—	1226
[Cu(salapssal)]	CuN_2O_2S	17 120	2.20	2.05	179.0	31 650	1227
[Cu(bipym)Fe] (**425**)	$FeN_6CuN_2O_4$	—	2.38	2.20	190.0	—	1228

	Cu—Cu (Å)	*Cu—O—Cu* (°)	*2J* (cm^{-1})	*Ref.*
(c) Type III				
$Cu(L)(OEt)_2(NCS)_2$]	3.00	—	—	1230
[$Cu_2(L—Et)(N_3)$](BF_4)	3.615	136.7	Diamagnetic	1231
[$Cu_2(PAP)OH)Cl_3$]$\cdot 1.5H_2O$ (**315**)[a]	—	—	—	681
[$Cu_2(PAP)(OH)(IO_3)_3$]$\cdot 4H_2O$ (**427**)[a]	3.165	114	−335	1232
[$Cu_2(L)(O_2CMe)$]$(PF_6)_3$	3.547	140.2	−80	—
[$Cu_2(L)Cl_2$]$(ClO_4)_2$	4.128	119.9	0	—
$Cu_2(L)(OH)$]$(ClO_4)_2$ (**428**)	3.03	104.8, 99.1	−675	1233
[$Cu(L^8)Cl_2$] (**275**)	3.13	—	—	622

[a] PAP = 1,4-bis(2-pyridylamino)phthalazine.

systems[360] in the biologically relevant [Cu_2(triketone)$_2$] (**421**) complexes.[1168] Consequently it is not understood why it is said (ref. 1203, p. 11) that biological copper systems 'are different', when the local copper(II) environment of the type II and III coppers are 'normal' elongated rhombic or tetragonal octahedral stereochemistries, but both can behave as electron transfer catalysts in air in both biological systems (Figures 94 and 95) and in organic reactions. Is even the type I copper stereochemistry so different (Figure 96)? In general, it is the long Cu—S(methionine) distance of 2.90 Å that is considered unique (Figure 96), but this is known in a model compound [Cu(bidhp)Cl_2] (**424**).[1225,1234] Maybe the unique nature of the type I stereochemistry lies in the shortness of the short Cu—S(cysteine) distance of 2.13 Å, which must be responsible for the low energy charge-transfer bands that characterize the 'blue' proteins, but equally, the type I stereochemistry may represent a near 'half way house' geometry along the structural pathway between a compressed tetrahedral copper(II) geometry and a trigonal planar copper(I) geometry (Figure 102), with the direction of the structural pathway determined by the $\nu_3(T_2)$ mode of vibration of a regular tetrahedron of C_{3v} symmetry, but with the 'extent' of reduction controlled by the reducing properties of the cysteine sulfur ligand. Consequently, the unique type I geometry is determined by the combination of a suitable copper chromophore, a soft mode of vibration and a suitable sulfur ligand redox process, none of which is uniquely biological in origin. The precise geometry of the type I copper CuN_2SS^1 chromophore will then be dependent upon its environment. If then the type I–III geometries of biological copper systems are to be considered as normal small molecule

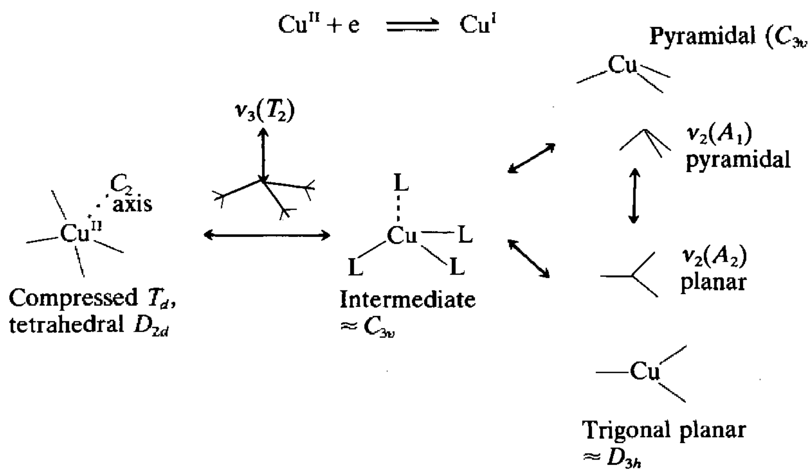
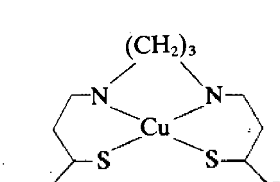
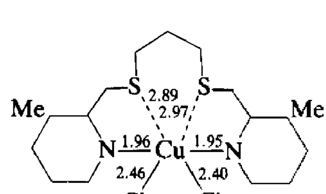


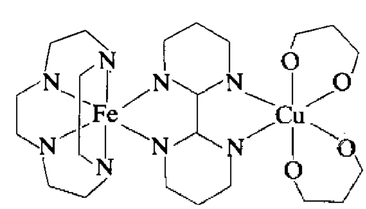
Figure 102 The structural pathway connecting the compressed tetrahedral copper(II) geometry and the trigonal planar copper(I) geometry, and the relationship with the type I copper geometry



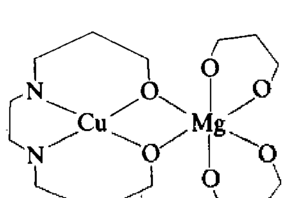
[$Cu(S_4N_2C_{17}H_{24})$] (**423**)[1224]



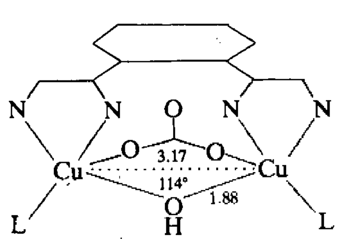
[Cu(bidhp)Cl_2] (**424**)[1225]



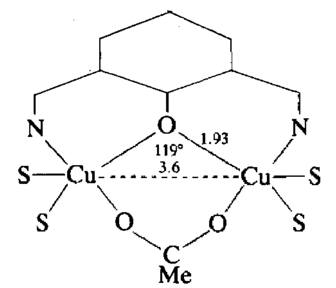
[Fe^{II}(bipym)Cu^{II}] (**425**)[1228]



[$CuN_2O_2MgO_6$] (**426**)[1229]



[Cu_2(PAP)(OH)$(IO_3)_3$]·$4H_2O$ (**427**)[1232]



[Cu_2(L)(OH)]$(ClO_4)_2$ (**428**)[1233] copper complexes, then a bright future is predicted for the 'open minded' synthesis of small molecule copper(I) and copper(II) complexes to simulate the biological copper type I–III systems. At the same time, the question that should be asked is why is the *same* copper(II) ion such a good general purpose catalyst in both biological and classical organic reactions. In this case, it is the flexible copper(I) *and* copper(II) stereochemistries that link these two oxidation states.

53.4.9 Survey of Copper(II) Ligands

The classification of metals and ligands into hard and soft acids and bases (Table 2b) places the copper(II) ion with borderline hard/soft acid behaviour, in contrast to the clearly soft acid behaviour of the copper(I) ion (Section 53.2.6).[36] In practice the cordination chemistry of the copper(II) ion is dominated by nitrogen and oxygen as donor atoms followed by chlorine and then sulfur;[5,22,29] bromine is well characterized, but fluorine is surprisingly limited. Iodine coordinated to copper(II) only exists in the presence of, particularly, nitrogen donor ligands which stabilize the copper(II) ion with respect to reduction (equation 32). The phosphorus atom as a donor is surprisingly uncommon compared to its frequent occurrence in copper(I) coordination chemistry (Sections 53.3.2.1–10); again this is associated with an ability to reduce copper(II) to copper(I). Equally uncommon are ligand donor atoms involving arsenic, antimony and bismuth, and selenium or tellurium.

$$Cu^{2+} + 4X^- \longrightarrow Cu_2X_2 + X_2^0 \quad (32)$$

The following sections summarize the different types of ligands that form complexes with the copper(II) ion, in the order that the ligands are described in Chapters 11 and 12, and are illustrated by Tables 77–82, in which data for molecular structures involving the different ligands are collected. Only in the case of novel ligand bonding roles are additional molecular structures included. The tables can then be used to obtain an overview of the types of complexes formed by a ligand, without giving an exhaustive listing of all the copper(II) complexes formed by a particular ligand.

53.4.9.1 Mercury ligands

No examples of simple Cu—Hg bonds are known.

53.4.9.2 Carbon ligands

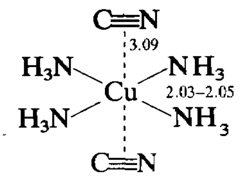
The most common Cu—C bonded systems involve σ-bonded $(CN)^-$ ligands (Table 77)[1235] with none of the extensive alkyl-,[23] alkene- or carbon-monoxide-bonded systems described for the copper(I) ion (Sections 53.3.2.10 and 11). The general chemistry of the cyanide ion as a ligand has been reviewed, with some mention of the Cu^{II}—CN linkage.[1235] The addition of $(CN)^-$ to aqueous copper(II) solutions produces a transient purple colouration, which has been characterized by ESR spectroscopy as the $[Cu(CN)_4]^{2-}$ anion.[1236] The overall formation constant of $[Cu(CN)_4]^{2-}$ has been examined electrochemically and a mechanism for its decomposition suggested, involving the possible formation of a transient dinuclear $[Cu_2(CN)_6]^{2-}$ anion.[1237] The decomposition to copper(I) cyanide and gaseous cyanogen may be represented by equation (33), a reaction that may be prevented if the copper(II) ion is stabilized by complex formation, as in $[Cu(phen)_2CN]^+$ or $[Cu(phen)(CN)_2]$ species.[1238] The former has been characterized in $[Cu(phen)_2(CN)](NO_3)$[1239] and $[Cu(bipy)_2(CN)](NO_3)\cdot 2H_2O$[1240] with trigonal pyramidal CuN_4C chromophores and in the square pyramidal CuN_4C chromophore of [Cu(cyclops)(CN)] (**220**).[501] The monodentate $(CN)^-$ ion as a ligand to the copper(II) ion coordinates *via* the carbon atom, but this does not rule it out as a bridging ligand, as in $[Cu_2([14]\text{-}4,11\text{-diene-}N_4)(CN)](ClO_4)$ (**258**).[589] In both situations the Cu—C,N distances are short (*ca.* 2.10 Å), but the $(CN)^-$ ligand has been characterized as a long-bonded bridging ligand as in $[Cu_2(tren)(CN)_2](BPh_4)_2$,[1241] but at the long second distance of 3.05 Å. A novel long (3.09 Å) semi-coordinate bonding of the $(CN)^-$ triple bond to the copper(II) ion in a $CuN_4(\pi - CN)_2$ chromophore is found in $[Cu(NH_3)_4][Cu_4(CN)_6]$ (**429**).[1242]

Table 77 Carbon Ligands

Complex	*Chromophore*	*Geometry*[a]	*Ref.*
$[Cu(phen)_2(CN)](NO_3)$	CuN_4C	TB	1239
$[Cu(bipy)_2(CN)](NO_3)\cdot 2H_2O$	CuN_4C	TB	1240
[Cu(cyclops)(CN)] (**220**)	CuN_4C	SBP	501
$[Cu_2(14\text{-}4,11\text{-diene-}N_4)_2(CN)](ClO_4)_3$ (**258**)	CuN_4C	SBP	589
$[Cu_2(tren)(CN)_2](BPh_4)_2$	—	SBP	1241

[a] TB = trigonal bipyramidal; SBP = square-based pyramidal.

$$Cu^{2+} + 2CN^- \longrightarrow Cu(CN)_2 \longrightarrow CuCN + 1/2(CN)_2 \quad (33)$$



$[Cu(NH_3)_4][Cu_4(CN)_6]$ (**429**)[1242]

53.4.9.3 Nitrogen ligands

Nitrogen donors are the commonest ligands to the copper(II) ion; they are superior to oxygen and the halides as ligands. Of the σ donor nitrogen ligands, ammonia is the most abundant (Table 78a),[895] readily forming up to four short Cu—N distances (1.95–2.08 Å) and a longer fifth Cu—N distance (2.19 Å) which is responsible for the 'pentaamine effect' in $[Cu(NH_3)_n]X_2$ systems.[1243] While $[Cu(NH_3)_6]X_2$ complexes have been suggested,[1073,1244] there is no unambiguous single-crystal X-ray crystallographic evidence to support the elongated tetragonal octahedral stereochemistry with two semi-coordinated Cu—N distances of *ca.* 2.6 Å, and these are better formulated as pentaammine ammonia adducts, $[Cu(NH_3)_5X_2]\cdot NH_3$.[456] In general the $[Cu(NH_3)_4X_2]$ complexes involve an elongated tetragonal octahedral stereochemistry with semi-coordinated polyatomic anions, X^-, from the familiar $(NO_3)^-$ in $[Cu(NH_3)_4(NO_3)_2]$,[1245] $(BF_4)^-$ and $(ClO_4)^-$ anions to the less familiar linear $(I_4)^{2-}$ and $(I_3)^-$ anions of $[Cu(NH_3)_4(I_4)_2]$ (**430**) and $[Cu(NH_3)_4(I_3)_2]$.[1246]

Table 78 Nitrogen Ligands

	Chromophore	*Stereo-chemistry*[a]	*Ref.*
(*a*) NH_3			
$[Cu(NH_3)_4(NO_2)_2]$ (**174**)	$CuN_4N'_2$	ETO	570
$K[Cu(NH_3)_5(PF_6)_3$ (**218**)	CuN_5	SBP	499
$Na_4[Cu(NH_3)_4][Cu(S_2O_3)_2]_2\cdot OH_2$ (**176**)	CuN_4O_2	ETO	457
$[Cu(NH_3)_4(OH_2)](SO_4)$ (**219**)	CuN_4O	SBP	500
$[Cu(NH_3)_2Ag(NCS)_3]$ (**223**)	$CuN_2N'_3$	TB	504
$[Cu(tren)(NH_3)](ClO_4)_2$ (**224**)	CuN_4N	TB	505
β-$[Cu(NH_3)_2Br_2]$ (**234**)	CuN_2Br_4	ERO	536
α-$[Cu(NH_3)_2Br_2]$ (**414**)	$CuN_2Br_2Br'_2$	ERO	1098
$[Cu(NH_3)_2(C_2O_4)]\cdot 2H_2O$ (**338**)	$CuN_2O_2O'_2$	CRO	738
$[Cu(NH_3)_2(O_2CO)]$ (**351**)	CuN_2O_2O'	SBP	764
$[Cu(NH_3)_4][PtCl_4)]$ (**383**)	CuN_4Pt_2	ETO	806
$[Cu(NH_3)_4][Cu_4(CN)_6]$ (**429**)	$CuN_4(\pi\text{-}CN)_2$	ETO	1242
$[Cu(NH_3)_4(I_4)_2]$ (**430**)	CuN_4I_2	ETO	1246
(*b*) *Substituted* NH_3			
$[Cu_2(cyclohexamine)_4(OH)_2](ClO_4)_2$ (**270**)	CuN_2O_2	SP	616
$[Cu_2(MeNH_2)_4(OH)_2(OH_2)_2](SO_4)\cdot H_2O$ (**271**)	CuN_2O_2O'	SBP	617
$[Cu(O_2CMe)_2]_2(hmta)$ (**357**)	CuO_4N	SBP	770

Table 78 (*continued*)

	Chromophore	Stereo-chemistry[a]	Ref.
(*c*) *Nitro/nitrito*			
$K_2Pb[Cu(NO_2)_6]$ **(177)**	CuN_6	O	426
$K_2Ba[Cu(NO_2)_6]$ **(182)**	$CuN_4N'_2$	ETO	433
$Rb_2Pb[Cu(NO_2)_6]$ **(233)**	$CuN_2N'_4$	CTO	531
$Cs_2Pb[Cu(NO_2)_6]$ **(250)–(252)**	CuN_6	O, CRO, ERO	532, 571, 572
$[Cu(NH_3)_4(NO_2)_2]$ **(174)**	$CuN_4N'_2$	ETO	570
$K_3[Cu(NO_2)_5]I$ **(249[a])**	$CuN_3O_2O_2$	7C	568
$[Cu(bipy)(ONO)_2]$ **(204)**	$CuN_2O_2O'_2$	ERO	472
$[Cu(bipy)_2(ONO)](NO_3)$ **(253)**	$Cu_2N'_2O''_2$	*cis*-O	546
$[Cu(bipy)_2(ONO)](PF_6)$ **(403)**	$CuN_2N'_2O_2$	*cis*-O	396
$[Cu(bipyam)_2(ONO)](NO_2)$ **(240)**	$CuN_2N'_2O_2$	*cis*-O	547
(*d*) *Azide*			
$[Cu_2(Bu^tpy)_4(N_3)_2](ClO_4)_2$ **(267)**	$CuN_2N'_3$	SBP	613
$[Cu_2(Me_5dien)_2(N_3)_2](BPh_4)_2$ **(297)**	$CuN_3N'N''$	SBP	654
$[Cu(Me_4en)(N_3)_2]_2$ **(298)**	$CuN_2N'_2N''$	SBP	655
$[Cu_2(L^F)(N_3)_2(1,3\text{-}N_3)](ClO_4)$ **(303)**	$CuN_3N'N''$	SBP	661
$[Cu_2(ehpdtb)(N_3)](ClO_4)_3$ **(306)**	CuN_2ONN'	SBP	667
$[Cu_2(L^B)(N_3)_2(1,3\text{-}N_3)_2]$ **(307)**	$CuN_2N'N''S_2$	ERO	669
$[Cu_2(LC^1)(pdc)(1,3\text{-}N_3)]$ **(308)**	CuN_3OS_2	ERO	671
$[Cu_2(LC^3)(N_3)_2(N_3)](ClO_4)$ **(311)**	$CuN_3N'_2$	SBP	675
$[Cu_3(2\text{-}bzpy)_2(N_3)(N_3)_5]$ **(325)**	$CuN_2N'_2N''$	SBP	707
$[Cu(3\text{-}pic)(1,1\text{-}N_3)(1,3\text{-}N_3)]$ **(360)**	$CuN_2N'_2N''$	SBP	773
$[Cu(N_3)_2(C_{16}H_{34}N_2O_6)(N_3)_2]$ **(387)**	$CuN_2N'_2O_2$	ERO	866
$[Cu(Et_4dien)Br(N_3)]$ **(435)**	CuN_3BrN'	TB	1265
Nitrogen-type ligands			
(*e*) *Cyanate*			
$[Cu_2(tren)_2(NCO)_2](BPh_4)_2$ **(299)**	CuN_4N'	TB	656
$[Cu(py)_2(NCO)_2]$ **(431)**	$CuN_2N'_2O_2$	ERO	1251
$[Cu(2,4\text{-}lut)_2(NCO)_2]$ **(432)**	CuN_4N'	SBP	1252
(*f*) *Thiocyanate*			
$[Cu(NH_3)_2Ag(NCS)_3]$ **(223)**	$CuN_2N'_3$	TB	504
$[Cu(NH_3)_2(NCS)_2]$ **(433)**	$CuN_2N'_2S_2$	ERO	1253
$[Cu(tren)(NCS)](NCS)$	CuN_4N'	TB	1254
Pyridine-type ligands			
(*g*) *Heterocyclic nitrogen ligands*			
$[Cu(imidazole)_6](NO_3)_2$ **(183)**	$CuN_4N'_2$	ETO	434
$[Cu(imidazole)_4(OH_2)_2]F_2$ **(188)**	CuN_4O_2	RTO	440
$[Cu(pyrazine)_2(O_2NO)_2]$ **(203)**	$CuN_2O_2O'_2$	ERO	472
$[Cu(ttbz)_2(O_2NO_2)_2]$ **(238)**	CuN_2O_4	CTO	542
$[Cu(py)_3(O_2NO)_2]$ **(244)**	$CuN_3O_2O'_2$	7C	555
$[Cu_2(2\text{-}pic)_2Cl_2]$ **(285)**	CuN_2Cl_2Cl'	SBP	633
$[Cu_2(Bu^tpy)_4(N_3)_2](ClO_4)_2$ **(267)**	$CuN_2N'_2$	SP	613
$[Cu_2F_2(mppzH)_4(F_2BF_2)_2]$ **(265)**	$CuN_2F_2F'_2$	ERO	604
$[Cu(4\text{-}Meox)_2Cl_2]_2$ **(284)**	CuN_2Cl_2Cl'	SBP	632
$[Cu_2(dmpz)_2(mpz)_4F_2](BF_4)_2$ **(287)**	CuN_3F_2	SBP	632
$[Cu_2(1\text{-}Meim)_4(O_2CMe)_4]\cdot 6H_2O$ **(290)**	CuN_2O_2O'	SBP	647
$[Cu_3(OH)(pz)_3(Hpz)_2(ONO_2)]\cdot H_2O$ **(324)**	CuN_3OO'	SBP	706
$[Cu(bpim)(im)]_2(NO_3)_4\cdot 3H_2O$ **(329)**	CuN_3N'	RC	593
$[Cu(pyrazine)(O_2NO)_2]$ **(335)**	$CuN_2O_2O'_2$	ERO	728
$[Cu(hfacac)_2(pyrazine)$ **(336)**	CuO_4N_2	ERO	738
$[Cu_3(im)_2(imH)_8](ClO_4)_4$ **(358)**	CuN_4O_2	ERO	771
$[Cu(3\text{-}pic)(1,1\text{-}N_3)(1,3\text{-}N)]$ **(360)**	$CuN_2N'_2N''$	SBP	773
$[CuCl_2(1,2,4\text{-}triazole)]$ **(363)**	$CuCl_4N_2$	ERO	781
$[Cu(OH)(benzotriazole)]$ **(364)**	CuN_4O_2	ERO	782
$[Cu_2(tmen)_2(2\text{-}Meim)_2(C_2O_4)](ClO_4)_2$ **(391)**	$CuN_2N'OO'$	SBP	863
$[Cu(imidazole)_4(ONO_2)_2]$ **(419)**	CuN_2O_2	ERO	1151
$[Cu(bipy)_2I]I$ **(420)**	$CuN_2N'_2I$	TB	1152
Chelate nitrogen ligands			
(*h*) *Ethylenediamine-type ligands*			
$[Cu(en)_3](SO_4)$ **(178)**	CuN_6	TO	427
$[Cu(en)_2(OH_2)Cl]Cl$ **(200)**	CuN_4OCl	ERO	452
$[Cu(N,N\text{-}Et_2en)_2](NO_3)_2$ **(208)**	CuN_4	RC	478
$[Cu(en)_2(F_2BF_2)_2]$ **(193)**	CuN_4F_2	ETO	445

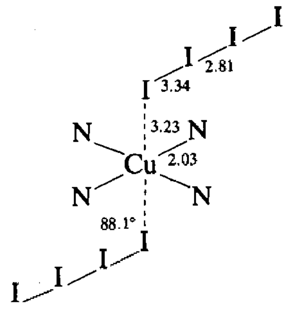
Table 78 (*continued*)

	Chromophore	Stereo-chemistry[a]	Ref.
Chelate nitrogen ligands			
(*h*) *Ethylenediamine-type ligands* (*continued*)			
$[Cu_2(tmen)_2(OH)_2]Br_2$ (**263**)	CuN_2O_2	SP	598
$[Cu_2(Me_4en)_2(N_3)(OH)](ClO_4)_2$ (**276**)	$CuN_2ON'O'$	SBP	623
$[Cu_2(Me_4en)_2(C_2O_4)(OH_2)_2](PF_6)_2 \cdot H_2O$ (**279**)	$CuN_2OO'O''$	SBP	627
$[Cu_2(Me_4pn)_2Cl_2(O_2CO)]$ (**280**)	CuN_2O_2Cl	SBP	628
$[Cu_2(en)_2(OPh)_4] \cdot 2PhOH$ (**289**)	CuN_2O_2O'	SBP	646
$[Cu_2(Me_4en)_2(N_3)_4]$ (**298**)	$CuN_2N'_2N''$	SBP	655
$[Cu(en)Cl_2]$ (**348**)	$CuN_2Cl_2Cl'_2$	ERO	760
$[Cu(en)_2(SeCN)_2]$ (**434**)	CuN_4Se_2	ERO	1257
$[Cu(tmen)(OH_2)(C_2O_4)](ClO_4) \cdot 1.25H_2O$ (**389**)	CuN_2O_2O'	SBP	863
$[Cu(dien)(C_2O_4)Cu(OH_2)(Me_4en)](ClO_4)_2$ (**390**)	CuN_3OO'	SBP	863
	CuN_2O_2O'	SBP	863
$[Cu(tmen)(Meim)(C_2O_4)Cu(2Meim)(tmen)]$-$(ClO_4)$ (**391**)	$CuN_2N'OO'$	SBP	863
Chelate nitrogen type ligands			
(*i*) *Chelate imine-type ligands*			
$[Cu(phen)_3](ClO_4)_2$ (**196**)	$CuN_4N'_2$	ERO	448
$[Cu(hfacac)_2(bipy)]$ (**197**)	$CuO_2O'_2N_2$	ERO	449
$[Cu(phen)_2(NCS)_2]$ (**198**)	$CuN_2N'_2N''_2$	ERO	450
$[Cu(bipy)_2(F_2BF_2)](BF_4)$ (**201**)	CuN_4F_2	ERO	453, 454
$[Cu(bipy)(ONO)_2]$ (**204**)	$CuN_2O_2O'_2$	ERO	472
$[Cu(bipyam)_2](ClO_4)_2$ (**214**)	CuN_4	CTd	485
$[Cu(bipy)_2Cl](PF_6)$ (**225**)	CuN_4Cl	TB	505
$[Cu(bipy)_2(OH_2)](S_2O_6)$ (**228**)	CuN_4O	SBP	522
$[Cu(dien)(bipyam)](X)$ (**227**)	$CuN_3N'_2$	SBP	514
$[Cu(phen)_2(O_2CMe)](BF_4) \cdot 2H_2O$ (**239**)	$CuN_2N'_2O_2$	*cis*-O	543
$[Cu(bipyam)_2(ONO)](NO_2)$ (**240**)	$CuN_2N_2N'_2N''O_2$	*cis*-O	545
$[Cu(bipy)_2(ONO)](BF_4)$ (**241**)	$CuN_2N'_2O_2$	*cis*-O	547
$[Cu(bipy)_2(ONO)](NO_3)$ (**253**)	$CuN_2N'_2O_2$	*cis*-O	546
$[Cu_2(bipy)_4(OH)](ClO_4)_3$ (**257**)	$CuN_2N'_2O$	SBP	588
$[Cu_2(5'\text{-}AMP)(bipy)(OH_2)_2](NO_3) \cdot 6H_2O$ (**278**)	CuN_2O_2O'	SBP	626
$[Cu(DMG)_2]_2$ (**292**)	CuN_4O	SBP	649
$[Cu(bipy)(C_2O_4)] \cdot 2H_2O$ (**349**)	$CuN_2O_2O'_2$	ERO	762
$[Cu(phen)_2(O_2CMe)](BF_4)$ (**408**)	$CuN_2N'_2O_2$	*cis*-O	576
$[Cu(phen)_2(O_2CMe)](ClO_4)$ (**402**)	$CuN_2N'_2O_2$	*cis*-O	404, 1084
$[Cu(bipy)_2(ONO)](PF_6)$ (**403**)	$CuN_2N'_2O_2$	*cis*-O	396
$[Cu(bipy)_2(O_2NO)](PF_6)$ (**416**)	$CuN_2N'_2O_2$	*cis*-O	1110
$[Cu(bipy)_2(O_2NO)](NO_3)$ (**417**)	$CuN_2N'_2O_2O'$	7C	1111
$[Cu(phen)_2](PF_6)_2$	$CuN_2N'_2$	CTd	497
Nitrogen tridentate-type ligands			
(*j*) *Linear ligands*			
$[Cu(dien)_2]Br_2 \cdot H_2O$ (**194**)	$CuN_2N'_2$	ERO	446
$[Cu(dien)(bipyam)]X_2$ (**227**)	$CuN_3N'_2$	SBP	514
$[Cu(dien)_2](NO_3)_2$ (**235**)	$CuN_2N'_4$	CRO	537
$[Cu(Me_5dien)_2(N_3)_2](BPh_4)_2$ (**297**)	$CuN_3N'N''$	SBP	654
$[Cu_2(Et_5dien)_2(C_2O_4)](PF_6)_2 \cdot 2H_2O$ (**300**)	CuN_3OO'	SBP	627
$[Cu(dien)(O_2CH)](HCO_2)$ (**347**)	CuN_3OO'	SBP	758
$[Cu_2(Et_5dien)_2(C_2O_4)](BPh_4)_2$ (**392**)	CuN_3OO'	SBP	862
$[Cu(terpy)_2](NO_3)_2$ (**436**)	$CuN_2N'_4$	CRO	538, 1266
$[Cu(terpy)Cl_2]$ (**407**)	CuN_3ClCl'	SBP	1267
(*k*) *Tripod ligands*			
$[Cu(metri)_2]$ (**180**)	CuN_6	O	429
$[Cu(HBpz_3)_2]$ (**199**)	$CuN_2N'_2N''_2$	ERO	451
$[Cu(tach)_2](NO_3)_2$ (**236**)	$CuN_2N'_4$	CTO	540
$[Cu_2(HBpz_3)_2Cl_2]$ (**264**)	CuN_2Cl_2N'	SBP	603
Tetradentate chelate ligands			
(*l*) *Linear ligands*			
$[Cu(trien)(SCN)]$ (**437**)	CuN_4S	SBP	1268
$[Cu(cyclam)(SPh)_2]$ (**189**)	CuN_4S_2	ETO	441
$[Cu(phthalocyanine)]$ (**210**)	CuN_4	SP	480
$[Cu(cyclops)(CN)]$ (**220**)	CuN_4C	SBP	501

Table 78 (*continued*)

	Chromophore	Stereo chemistry[a]	Ref.
(*m*) *Tripod ligands*			
$[Cu(tren)(NH_3)](ClO_4)_2$ (**224**)	CuN_4N'	TB	505
$[Cu_2(tren)_2(benzidine)](NO_3)_4$ (**262**)	CuN_4N'	SBP	596
$[Cu_2(tren)_2(NCO)_2](BPh_4)_2$ (**299**)	CuN_4N'	TB	656
$[Cu_2(tren)(NCS)](NCS)$	CuN_4N'	TB	1254
μ-$[Cu(biprim)(\mu\text{-}ONO_2)(ONO_2)]$ (**438**)	$CuN_2O_2O'O''$	ERO	1269

[a] ETO = elongated tetragonal octahedral; SBP = square-based pyramidal; TB = trigonal bipyramidal; ERO = elongated rhombic octahedral; CRO = composed rhombic octahedral; SP = square planar; O = octahedral; CTO = compressed tetragonal octahedral; 7C = seven coordinate; *cis*-O = *cis*-octahedral; RC = rhombic coplanar; TO = tetragonal octahedral; CTd = compressed tetrahedral.



$[Cu(NH_3)_4(I_4)_2]$ (**430**)[1246]

Substituted nitrogen donors to copper(II) are much less common (Table 78b).[367,616,617] Anionic nitrogen ligands, such as nitrite (Table 78c),[1247] azide (Table 78d),[773,1249,1250] cyanate (Table 78e)[1248] and thiocyanate (Table 78f)[1248] are all good ligands to the copper(II) ion, but their functions are complicated by their ability to coordinate as ambidentate ligands.[1250] The nitrite ion readily forms hexanitro copper(II) complexes,[1073,1247] but is also equally prolific in the formation of monodentate nitrito coordination, *e.g.* $K_3[Cu(NO_2)_5]I$ (**249**),[568] and asymmetric bidentate nitrito coordination, the latter generally involving off-the-*z*-axis coordination as in $[Cu(bipy)(ONO)_2]$ (**204**).[472] The azide ion[1249] as a ligand to copper(II) (Table 78d) has been well characterized in a surprisingly wide range of structural roles (Figure 103),[773] from monodentate, terminal bridging, 1,1-, 1,1,1- and 1,3-bridging, but is generally restricted to only one or two azide ions per copper(II) ion. The coordination chemistry of the cyanate ligand, $(NCO)^-$, has been reviewed,[1248] but is less well characterized crystallographically than the isoelectronic N_3^- anion, notwithstanding a wealth of preparative and physical properties.[1248] The $(NCO)^-$ anion generally bonds through the nitrogen atom for short Cu—L bonds, but through oxygen for long Cu—L bonds, as in $[Cu(py)_2(NCO)_2]$ (**431**),[1251] but can also bridge as in $[Cu(2,4\text{-lut})_2(NCO)_2]$ (**432**).[1251,1252] The $(NCS)^-$ anion generally short bonds to the copper(II) ion through nitrogen as in $[Cu(NH_3)_2(NCS)_2]$ (**433**)[1253] and

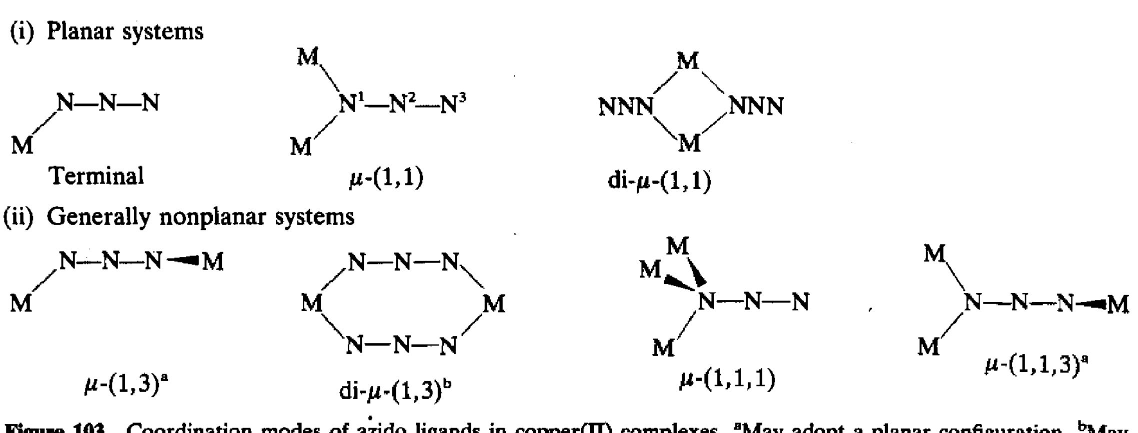
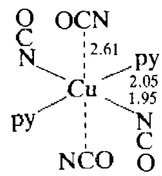
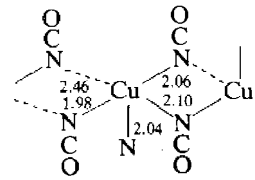


Figure 103 Coordination modes of azido ligands in copper(II) complexes. [a]May adopt a planar configuration. [b]May adopt a planar structure or a form with only the azido groups coplanar[773]

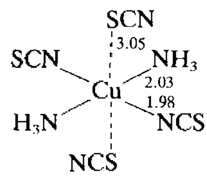
[Cu(tren)(NCS)](NCS),[1254] but is generally long bonded in the axial position through sulfur as in $[Cu(NH_3)_4(SCN)_2]$[1255] and $[Cu(en)_2(SCN)_2]$,[1256] with long Cu—S distances of 3.00 and 3.27 Å, respectively. In the corresponding $[Cu(en)_2(SeCN)_2]$ (**434**) a unique long Cu—Se distance of 3.26 Å is observed.[1257]



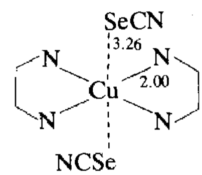
$[Cu(py)_2(NCO)_2]$ (**431**)[1251]



$[Cu(2,4\text{-lut})(NCO)_2]$ (**432**)[1252]

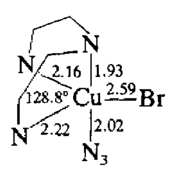


$[Cu(NH_3)_2(NCS)_2]$ (**433**)[1253]

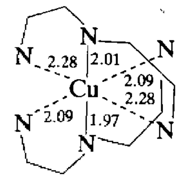


$[Cu(en)_2(SeCN)_2]$ (**434**)[1257]

With the monodentate heterocyclic nitrogen ligands,[1258] a wealth of ligand types are formed (Table 78g) from pyridine, imidazole and pyrazine in Cu:L ratios of 1:1 to 1:6, but with short Cu—N distances, 1.95–2.05 Å, for ratios up to 1:4, from the elongated tetragonal octahedral CuN_4O_2 chromophore of $[Cu(py)_4(O_2CCF_3)_2]$[1259] and $[Cu(imidazole)_4(OH_2)_2]F_2$ (**188**)[440] to the novel seven-coordinate structure of $[Cu(py)_3(O_2NO)_2]$ (**244**).[555] With the increasing biological relevance of these hetercyclic nitrogen ligands when incorporated into polydentate chelate ligands,[1258] it is gratifying to realize that they function as simple nitrogen donors to copper(II). The ethylenediamine molecule represents the simplest type of nitrogen chelate ligand which readily forms mono and bis chelate copper(II) complexes (Table 78h),[1260,1261] but only a limited number of tris chelate complexes, such as $[Cu(en)_3](SO_4)$ (**178**).[427] In general all three types of complexes are six coordinate with an elongated rhombic octahedral chromophore; an odd exception is the square base pyramidal CuN_4O chromophore of $[Cu(en)_2(OH)_2]$-$Cu_2(CN)_2(SCN)_2$.[1260] A range of substituted ethylenediamine ligands are known (Table 78h), which form a series of mixed ligand complexes, but with the complete absence of any tris chelate copper(II) complexes. The substituents increase the bulk of the ethylenediamine ligand and may block adjacent coordinate positions to give coordination numbers lower than six, as in the rhombic coplanar CuN_4 chromophore of $[Cu(N,N\text{-}Et_2\text{-}en)_2](NO_3)_2$ (**208**).[478] Chelate imine type ligands are most extensive with 2,2-bipyridyl,[1262,1263] 1,10-phenanthroline[1263] and 2,2′-bipyridylamine (bipyam) (Table 78i). Mono, bis and tris chelate complexes are formed for all three ligands except a tris chelate for bipyam. Six coordination is the most common, but with *cis*-distorted octahedral the predominant stereochemistry of the $[Cu(chelate)_2X_2]$ complexes,[396,397] in contrast to the elongated rhombic octahedral stereochemistry of the $[Cu(en)_2X_2]$ complexes (Table 78i).[47] In the $[Cu(chelate)_2]X_2$ complexes a compressed tetrahedral geometry was recognized early in $[Cu(bipyam)_2](ClO_4)_2$ (**214**),[485] but only recently in $[Cu(bipy)_2](PF_6)_2$[454] and $[Cu(phen)_2](PF_6)_2$.[526] In the $[Cu(chelate)_2X]Y$ complexes the suggestion[396] of a structural pathway connecting the range of four-, five- and six-coordinate geometries for the bipy complexes[454] can be extended to the phen and bipyam type complexes.[1264] The most simple tridentate chelate ligand, diethylenetriamine, readily forms mono and bis chelate complexes and mixed ligand complexes (Table 78j),[823] in which the CuN_3 chromophore involves an approximately planar conformation, as in $[Cu(dien)(O_2CH)](HCO_2)$ (**347**)[758] and $[Cu(dien)_2]Br_2{\cdot}H_2O$ (**194**).[446] However, in the substituted dien ligands, a bent CuN_3 chromophore is formed as $[Cu(Et_4dien)(N_3)Br]$ (**435**).[1265] The most simple tridentate tripod-type ligands, such as $[Cu(HBpz_3)_2]$ (**199**),[451] are shown in Table 78(j). They generally involve a restricted tetragonal elongation due to the restricted bite of the ligands. With more rigid tridentate chelate ligands such as 2,2′,2″-terapyridyl (terpy), mono and bis tridentate complexes are formed as in the distorted five-coordinate CuN_3Cl_2 chromophore of $[Cu(terpy)Cl_2]$[1266] and six-coordinate compressed rhombic octahedral CuN_6 chromophore of $[Cu(terpy)_2](NO_3)_2$ (**436**).[1267]

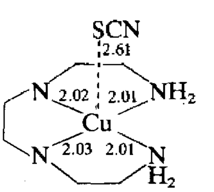


$[Cu(Et_4dien)N_3Br]$ (**435**)[1265]

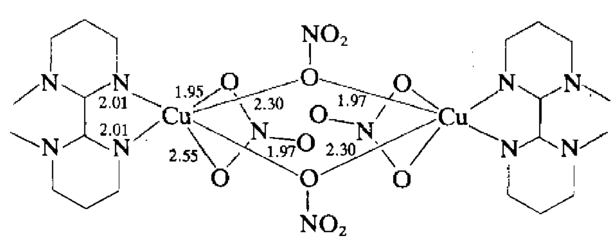


$[Cu(terpy)_2](NO_3)_2$ (**436**)[538,1267]

The most simple tetradentate nitrogen ligand is trien (Table 78k), which in [Cu(trien)(SCN)](NCS) (**437**) involves an essentially planar CuN_4 chromophore,[1268] but with the copper lifted out of the plane to give a square-based pyramidal stereochemistry. With the tripod ligand tren, the CuN_4X chromophore stereochemistry is generally five coordinate with a trigonal bipyramidal stereochemistry [Cu(tren)(NCS)](NCS).[1254] Certain tetradentate chelate ligands, such as phthalocyanine[480] and cyclops[501] (Table 78k), are cyclic and represent the simplest type of macrocyclic ligand that generally constrains the N_4 ligand to be coplanar. With polynuclear heterocyclic ligands, such as 2,2′-bipyrimidinyl (biprim), tetradentate chelate type coordination occurs as in $[Cu(biprim)(\mu\text{-}ONO_2)(O_2NO)]$ (**438**),[1269] which involves a linear chain structure with bridging and asymmetric bidentate nitrate coordination. Polydentate chelate nitrogen ligands with more than four nitrogen donors are not unusual, in view of the stereochemical constraints that such polydentate functions must impose. The ligand ebtd does form a hexadentate copper(II) complex in $[Cu(ebtd)](BF_4)(BF_3OEt)\cdot H_2O$ (**230**),[524] but in the process imposes a most unusual bicapped square pyramidal stereochemistry on the CuN_6 chromophore. Likewise, the CuN_7 chromophore in $[Cu(L^{12})](ClO_4)_2$ (**243**)[554] involves a most unusual seven-coordinate pentagonal bipyramidal stereochemistry. In general with polydentate chelate ligands with more than three donor nitrogens, the preference is to form polynuclear copper(II) complexes as in the molecular structures (**260**), (**261**), (**277**), (**302**), (**303**), (**305**) and (**306**)–(**312**).



[Cu(trien)(SCN)](NCS) (**437**)[1268]



$[Cu(biprim)(\mu\text{-}ONO_2)(O_2NO)]$ (**438**)[1269]

53.4.9.4 *Phosphorus ligands*

Phosphorus ligands are of very limited occurrence in copper(II) chemistry, due to the reducing properties of the phosphorus, but if the copper(II) is stabilized by complex formation they do arise, as in the teraacetate dimers of $[Cu_2(O_2CMe)_4(PPh_3)_2]$ (**317**).[698]

53.4.9.5 *Oxygen ligands*

Oxygen donors to copper(II) are nearly as frequent in occurrence as nitrogen donors (Table 79). They have a lower tendency to form oxygen chelate ligands, compared to the nitrogen chelates (Section 53.4.9.3), but adequately compensate for this limitation in the occurrence of hydrates and oxygen donors in oxyanions (see Chapter 15.5).

The most simple oxygen donor is the water molecule, which predominantly functions as a monodentate ligand notwithstanding the presence of two lone pairs on the oxygen atom. In aqueous solution the copper(II) ion is solvated to give the hexaaqua copper(II) ion, which also occurs in the various Tutton salts[1270] of Table 79(a) and in $[Cu(OH_2)_6](ClO_4)_2$.[1270,1271] In

Table 79 Oxygen as a Ligand

	Chromophore	Stereo-chemistry[c]	Ref.
(a) H_2O			
$[Cu(en)_2(OH_2)Cl]Cl$ (**200**)	CuN_4OCl	ERO	452
$[Cu(NH_3)_4(OH_2)](SO_4)$ (**219**)	CuN_4O	SBP	500
$[Cu_2(succinate)_2(OH_2)_2]$ (**356**)	CuO_4O'	SBP	769
$[Cu(bipy)_2(OH_2)](S_2O_6)$ (**228**)	CuN_4O	SBP	522
$Ca[Cu(2\text{-}cpa)_4(OH_2)]\cdot 3H_2O$ (**248**)	$CuO_4O'_4O''$	9C	567
$[Cu(5'\text{-}AMP)(bipy)(OH_2)]_2(NO_3)_2\cdot 6H_2O$ (**278**)	CuN_2O_2O'	SBP	626
$[Cu_2(Me_4en)_2(C_2O_4)(OH_2)_2](PF_6)_2\cdot 2H_2O$ (**279**)	CuN_2O_2O'	SBP	627
$[Cu(im)_4(OH_2)_2]F_2$ (**188**)	CuN_4O_2	ERO	440
$Ba_2[Cu(OH_2)_2(O_2CH)_4](HCO_2)_2\cdot 2H_2O$ (**191**)	$CuO_2O'_2O'_2$	ERO	443
$[CuCl_2(OH_2)_2]$ (**192**)	$CuO_2Cl_2Cl'_2$	ERO	444
$[Cu(3\text{-}pySO_3)_2(OH_2)_2]$ (**410**)	$CuN_2O_2O'_2$	ERO	1095
$[Cu(methoxyacetate)_2(OH_2)_2]$ (**237**)	$CuO_2O'_2O''_2$	ERO	541
$[Cu(OH_2)_2(O_2NO)_2]\cdot 0.5H_2O$ (**245**)	$CuO_2O'_2O''_2O'''$	7C	558
$[Cu(O_2CH)_2(OH_2)_2]\cdot 2H_2O$ (**339**)	$CuO_4O'_2$	ETO	741
$Li[CuCl_3(OH_2)_2]$ (**352**)	$CuCl_2O_2Cl'$	SBP	765
$[Cu_3Cl_6(C_6H_7NO)_2(OH_2)_2]$ (**359**)	$CuCl_2Cl'_2O_2$	ERO	772
	$CuCl_2O_2Cl'$	SBP	772
$[Cu(OH_2)_3(C_5O_5)]$ (**337**)	$CuO_2O'_2O''_2$	ERO	737
$[Cu(OH_2)_4(O_2SO_2)]\cdot H_2O$ (**439**)	$CuO_4O'_2$	ERO	1272
$Cs_2[Cu(OH_2)_6](SO_4)_2$ (**184**)	$CuO_2O'_2O''_2$	ERO	435
$(NH_4)_2[Cu(OH_2)_6](SO_4)_2$ (**202**)	$CuO_2O'_2O''_2$	ERO	457, 458
$(ND_4)_2[Cu(OD_2)_6](SO_4)_2$	$CuO_2O'_2O''_2$	ERO	910
$[Cu(OH_2)_2(O_2CPh)_2]\cdot H_2O$ (**365**)	$CuO_4O'_2$	ERO	783
$[Cu(tsglyH)_2(4\text{-}Mepy)_2(OH_2)]$	$CuN_2O_2O'_2$	ERO	1276
$[Cu_2(OH_2)_{10}][Cu(OH_2)_6][ZrF_7]_2$ (**440**)	$CuO_4O'_2$	ERO	1274
$[Cu(Hmaleate)(OH_2)_4]$	$CuO_4O'_2$	ETO	1275
(b) Hydroxide ligands			
$Ba_2[Cu(OH)_6]$ (**185**)	$CuO_2O'_2O''_2$	ERO	436
Bidentate			
$[Cu_2(bipy)_4(OH)(ClO_4)_3$ (**257**)	$CuN_2N'_2O$	TB	588
$[Cu_2(tmen)_2(N_3)(OH)](OClO_3)_2$ (**276**)	$CuN_2N'OO'$	SBP	623
$[Cu_2(bpy\text{-}2)_2(OH_2)]_2(PF_6)_2\cdot 2H_2O$ (**288**)	CuN_3OO'	SBP	645
$[Cu_2(p\text{-}XYLpy2)(OH)](BF_4)_3$ (**301**)	$CuNS_2OO'$	SBP	658
$[Cu_2(Me_4en)_2(OH)_2]Br_2$ (**263**)	CuN_2O_2	SP	598
$[Cu_2(cyclohexamine)_4(OH)_2](ClO_4)_2$ (**270**)	CuN_2O_2	SP	616
$[Cu_2(MeNH_2)_4(OH)_2(OH_2)_2](SO_4)\cdot H_2O$ (**271**)	CuN_2O_2O'	SBP	617
$[Cu_2(L^G)(OH)(O_2ClO_2)](ClO_4)_2\cdot CHCl_3$ (**309**)	CuN_3OO'	SBP	673
Tridentate			
$[Cu_3(OH)(pao)_3](SO_4)\cdot 10.5H_2O$ (**322**)	CuN_2O_2	SP	703
$[Cu_3(OH)(pz)_3(Hpz)_2(ONO_2)_2]\cdot H_2O$ (**324**)	CuN_3OO'	SBP	706
$[Cu_3(OH)_3(ONO_2)]$ (**373**)	$CuO_2O'_2$	RC	791
$[Cu(OH)(O_2IO)]$ (**372**)	$CuO_2O'_2O''_2$	ERO	790
$[(CuL)_3(CuLO)(\mu\text{-}OH)]$ (**328**)	CuN_3O_2	TB	710
(c) Alkoxide ligands			
$[Cu(babz)(O_2NO)(HOMe)]NO_3$ (**232**)	$CuN_3OO'O''$	ERO	526
$[Cu(methoxyacetate)_2(OH_2)_2]$ (**237**)	$CuO_2O'_2O''_2$	ERO	541
$[Cu_2(tmhd)_2(OCH_2Ph)_2]$ (**266**)	$CuO_2O'_2$	SP	612
$[Cu_2\{OC_6H_3[CH_2N(CH_2CH_2Py)_2]\text{-}2,6\text{-}(OMe)\}]$ (**277**)	CuN_2O_2N'	SBP	624
$[Cu_2(en)_2(OPh)_4]\cdot 2PhOH$ (**289**)	CuN_2O_2O'	SBP	646
$[Cu_2(N_3py2)_2(OMe)_2(ClO_4)_2$ (**305**)	CuN_2O_2N'	SBP	666
(d) Ether ligands			
$[Cu(p\text{-}NO_2btfa)_2(dioxane)]$ (**346**)	$CuO_4O'_2$	ERO	757
$[Cu(mbtfac)_2(dioxane)_2]\cdot 2$ dioxane (**398**)	$CuO_4O'_2$	ERO	931
$[Cu(pyNO)_6](NO_3)_2\cdot 2H_2O$ (**406**)	CuO_6	TO	1093
$[Cu(pyNO)_6](BF_4)_2$ (**255**)	CuO_6	TO	582
$[Cu(pyNO)_4](BF_4)_2$ (**443**)	CuO_4	SP	1280
$[Cu(Ph_3PO)_2Cl_2]$ (**216**)	CuO_2Cl_2	CT	487
$[Cu_2Br_4(pyNO)_2]$ (**269**)	CuO_2OBr_2	SBP	615
$[Cu_2(pyNO)_2(O_2NO)_2]$ (**291**)	$CuO_2O'_2O''_2O'''$	7C	648
$[Cu(DMSO)_2Cl_2]$ (**334**)	CuO_2Cl_2Cl'	SBP	724
$[CuCl_2(TMSO)]$ (**362**)	$CuCl_2Cl'_2O'_2$	ERO	780

Table 79 (*continued*)

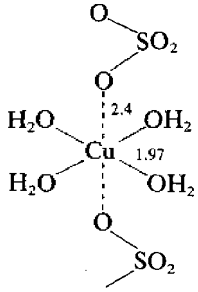
	Chromophore	*Stereo-chemistry*[c]	*Ref.*
(*e*) *Chelate oxygen ligands*			
[Cu(hfacac)$_2$(bipy)] (**197**)	$CuO_2N_2O'_2$	ERO	449
[Cu(3-Meacac)$_2$] (**207**)	CuO_4	RC	480
[Cu(acac)$_2$py] (**444**)	CuO_4N	SBP	1282
[Cu$_2$(tmhd)$_2$(OCH$_2$Ph)$_2$] (**266**)	CuO_2O_2	RC	612
[Cu(*trans*-chd)$_2$Cl$_2$) (**294**)	CuO_2Cl_2Cl	SBP	651
[Cu(mbtfac)$_2$(dioxane)$_2$]·2dioxane (**398**)	$CuO_4O'_2$	ERO	931
[Cu(hfacac)$_2$(pyrazine)] (**336**)	CuO_4N_2	ERO	729
[{Re-*cis*-(OC)$_4$}$_2$(O$_2$CMe)$_2$Cu] (**384**)	CuO_4	RC	811
[Cu(OH$_2$)$_3$(C$_5$O$_5$)] (**337**)	$CuO_2O'_2O''_2$	ERO	737
[Cu(ompha)$_3$](ClO$_4$)$_2$ (**179**)	CuO_6	TO	428
(*f*) *Oxyacids of carbon ligands*			
[Cu$_2$(Me$_4$pn)$_2$Cl$_2$(O$_2$CO)] (**280**)	CuN_2O_2Cl	SBP	628
[Cu(NH$_3$)$_2$(O$_2$CO)] (**351**)	CuN_2O_2O'	SBP	764
K$_2$[Cu(CO$_3$)$_2$] (**370**)	$CuO_4O'_2$	ERO	788
Na$_2$[Cu(CO$_3$)$_2$] (**371**)	$CuO_4O'_2$	ERO	789
[Cu(CO$_3$)] (**380**)	$CuO_2O'_2O'$	SBP	798
[Cu$_2$(Me$_4$en)$_2$(C$_2$O$_4$)(OH$_2$)$_2$](PF$_6$)$_2$·2H$_2$O (**279**)	CuN_2O_2O'	SBP	627
[Cu$_2$(Et$_5$dien)$_2$(C$_2$O$_4$)](BPh$_4$)$_2$ (**392**)	CuN_3OO'	SBP	862
[Cu$_2$(Et$_5$dien)$_2$(C$_2$O$_4$)](PF$_6$)$_2$·2H$_2$O (**300**)	CuN_2OO'	SP	627
[Cu$_2$(tmen)$_2$(OH$_2$)$_2$(C$_2$O$_4$)](ClO$_4$)$_2$·1.25H$_2$O (**389**)	CuN_2O_2O'	SBP	863
[Cu(NH$_3$)$_2$(C$_2$O$_4$)]$_2$·2H$_2$O (**338**)	$CuN_2O_2O'_2$	CRO	738
Na$_2$[Cu(C$_2$O$_4$)$_2$]·2H$_2$O (**343**)	$CuO_4O'_2$	ERO	743
(PhCH$_2$NH$_2$)$_2$[Cu(C$_2$O$_4$)$_2$] (**375**)	$CuO_2O'_2O''_2$	ERO	794
(pnH$_2$)[Cu(C$_2$O$_4$)$_2$] (**344**)	$CuO_4O'_2$	ETO	755
[Cu(biby)(C$_2$O$_4$)]·2H$_2$O (**349**)	$CuN_2O_2O'_2$	ERO	762
[Cu(dien)(C$_2$O$_4$)Cu(OH$_2$)(tmen)](ClO$_4$)$_2$ (**390**)	CuN_3OO'	SBP	863
	$CuN_2O_2O'_2$	ERO	863
[Cu$_2$(tmen)$_2$(2-Meim)$_2$(C$_2$O$_4$)](ClO$_4$)$_2$ (**391**)	CuN_3OO'	SBP	863
[Cu(O$_2$CH)$_2$(OH$_2$)$_2$]·2H$_2$O (**339**)	$CuO_4O'_2$	ETO	741
[Cu(O$_2$CH)(OH)] (**340**)	$CuO_2O'_2$	RC	742
[Cu(dien)(O$_2$CH)](HCO$_2$) (**347**)	$CuN_3OO'O''$	ERO	758
[Cu(methoxyacetate)$_2$(OH$_2$)$_2$] (**237**)	$CuO_2O'_2O''_2$	ERO	541
[Cu(L)(O$_2$CMe)]·2MeOH (**354**)	CuN_2O_2O'	SBP	767
[Cu$_2$(CA)(O$_2$CMe)$_2$] (**355**)	CuN_3OO'	TB	768
[Cu(phen)$_2$(O$_2$CMe)](ClO$_4$) (**402**)	$CuN_2N'_2O_2$	*cis*-O	404, 1084
[Cu(phen)$_2$(O$_2$CMe)](BF$_4$)·2H$_2$O (**239**)	$CuN_2N'_2O_2$	*cis*-O	243
[Cu(phen)$_2$(O$_2$CMe)](BF$_4$) (**395**)	$CuN_2N'_2O$	SBP	576
Ca[Cu(2-cpa)$_4$(OH$_2$)]·3H$_2$O (**248**)	$CuO_4O'_4O''$	9C	567
[Cu$_2$(1-Meim)(O$_2$CMe)$_4$] (**290**)	CuN_2O_2O'	SBP	647
[Cu$_2$(O$_2$CMe)$_4$(OH$_2$)$_2$] (**316**)	CuO_4O'	SBP	682, 684
[Cu(O$_2$CMe)$_2$(PPh$_3$)]$_2$ (**317**)	CuO_4P	SBP	698
[Cu$_2$(RSCH$_2$CO$_2$)$_4$(amine)$_2$] (**400**)	CuO_4N	SBP	958
[Cu$_2$(O$_2$CCCl$_3$)$_4$(tempo)$_2$] (**318**)	CuO_4O'	TB	699
Ca[Cu(O$_2$CMe)$_4$]·6H$_2$O (**246**)	$CuO_4O'_4$	8C	563, 564
[Cu(OH$_2$)$_2$(O$_2$CPh)$_2$]·H$_2$O (**365**)	$CuO_2O'_2O''_2$	ERO	783
[Cu$_2$(succinate)$_2$(OH$_2$)$_2$] (**356**)	CuO_4O'	SBP	769
[NH$_2$Me$_2$][Cu(O$_2$CH)$_3$] (**378**)	$CuO_4O'_2$	ETO	797
α-[Cu(O$_2$CH)$_2$] (**379**)	$CuO_4O'_2$	ETO	569
[Cu(bipy)$_2$(O$_2$CH)](BF$_4$) (**408**)	$CuN_4O'O''$	ERO	548
(*g*) *Nitrite* (*nitrito/nitro*)			
[Cu(O$_2$NO)$_2$(O$_2$NMe)] (**374**)	$Cu_2O_2O'_3$	SBP	792
[Cu(bipy)(ONO)$_2$] (**204**)	$CuN_2O_2O'_2$	ERO	472
[Cu(bipyam)$_2$(ONO)](NO)$_2$ (**240**)	$CuN_2N'_2O_2$	*cis*-O	245
[Cu(bipy)$_2$(ONO)](BF$_4$) (**241**)	$CuN_2N'_2O_2$	*cis*-O	547
[Cu(bipy)$_2$(ONO)](PF$_6$) (**403**)	$CuN_2N'_2O_2$	*cis*-O	396
K$_3$[Cu(NO$_2$)$_5$] I (**249**)	$CuN_3O_2O'_2$	7C	568
K$_3$[Cu(NO$_2$)$_5$] II (**249**)	$CuN_2O_2O'_2$	*cis*-O	568
[Cu(bipy)$_2$(ONO)](NO$_3$) (**253**)	$CuN_2N'_2O_2$	*cis*-O	546
(*h*) *Nitrate*			
[Cu$_2$(OH)$_3$(O$_2$NO$_2$)] (**373**)	$CuO_2O'_2$	RC	791
[Cu(bipy)$_2$(O$_2$NO)](PF$_6$) (**416**)	$CuN_2N'_2O_2$	*cis*-O	1110
[Cu(bipy)$_2$(O$_2$NO)](NO$_3$)·H$_2$O (**417**)	$CuN_2N'_2O_2$	Bd	1111
[Cu(OH$_2$)$_2$(O$_2$NO)$_2$]·0.5H$_2$O (**245**)	$CuO_2O'_2O''_2O'''$	7C	558
[Cu(pyrazine)$_2$(O$_2$NO)$_2$] (**203**)	$CuN_2O_2O'O''$	ERO	526

Table 79 (*continued*)

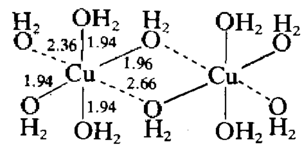
	Chromophore	*Stereo-chemistry*[c]	*Ref.*
(*h*) *Nitrate* (*continued*)			
$[Cu(babz)(O_2NO)(OMe)]$ (**232**)	$CuN_3O'O''O'''$	ERO	526
$[Cu_2(pyNO)_2(O_2NO)_2]$ (**291**)	$CuO_2O'_2O''_2O'''$	7C	648
$[Cu(py)_3(O_2NO)_2]$ (**244**)	$CuN_3O_2O'_2$	7C	556
α-$[Cu(O_2NO)_2]$ (**381**)	$CuO_2O'_2O''_2$	ERO	799
$[Cu(O_2NO)_2(O_2NMe)]$ (**374**)	$CuO_2O'_2O'$	SBP	792
$[Cu(ttbz)_2(O_2NO)_2]$ (**238**)	$CuN_2O_2O'_2$	CTO	542
$[Cu(O_2NO)_2(NCMe)_2]$	$CuN_2O'_2O''_2$	ERO	793
$[Cu(Metaab)(O_2NO)](NO_3)$	CuN_4O_2	BdSBP	525
$[Cu(im)_4(ONO_2)_2]$ (**419**)	CuN_4O_2	ETO	1151
$(AsPh_4)_2[Cu(O_2NO)_4]$ (**247**)	$CuO_4O'_4$	8C	566
$[Cu_2\{N(Me)edtb\}(O_2NO)_3](NO_3)\cdot H_2O$ (**313**)	$CuN_2O_2O'_2$	ERO	679
$[Cu_4(mpz)_4(acmpz)(O_2NO_2)_2]$ (**330**)	CuN_2O_2O'	SBP	710
$[Cu(pyrazine)(O_2NO)_2]$ (**335**)	$CuN_2O_2O'_2$	ERO	728
(*i*) *Oxyacids of phosphorus*			
$K[Cu(O_4P)]$ (**54**)[a]	CuO_4O'	SBP	1285
α-$Na[Cu(O_4P)]$ (**55**)[a]	CuO_4O'	SBP	1286
$[Cu_3(O_4P)_2]$ (**60**)[a]	CuO_4O'	SBP	803
$[Cu(Et_2PO_2)_2]$	CuO_4	CTd	486
$[Cu(5'\text{-}AMP)(bipy)(OH_2)]_2(NO_3)_2\cdot 6H_2O$ (**278**)	CuN_2O_2O'	SBP	626
(*j*) *Oxyacids of sulfur*			
$[Cu_2\{S_2C_2[N(CH_2)_2OH]_2\}(O_2SO_2)]\cdot 2H_2O$ (**345**)	CuO_2NSO'	SBP	756
$[Cu(O_2SO_2)]$ (**382**)	$CuO_4O'_2$	ERO	800
$[Cu(Me_4en)(OSO_3)(OH_2)]\cdot H_2O$ (**22**)[a]	CuN_2O_2	RC	1287
$[Cu(pn)_2(OSO_3)]\cdot H_2O$ (**23**)[a]	CuN_4O_2	ERO	1288
$[Cu(bipy)_2(S_4O_6)]$	CuN_4O_2	ERO	1289
$[Cu(bipy)_2(S_3O_6)]$	CuN_4O_2	ERO	1290
$[Cu(bipy)_2(S_2O_8)]$	CuN_4O_2	ERO	1291
$[Pb_2Cu_5(O_2SeO)_2(UO_2)_6(OH)_6]\cdot 2H_2O$	CuO_4O'	SBP	1292
$[Cu(Se_2O_5)]$ (**376**)	$CuO_2O'_2O''_2$	ERO	795
(*k*) *Perchlorate*			
$[Cu(14\text{-}ane\text{-}S_4)(OClO_3)_2]$ (**190**)	CuS_4O_2	ERO	442
$[Cu_2(tmen)_2(N_3)(OH)(OClO_3)_2]$ (**276**)	CuN_2ONO'	SBP	623
$[Cu_2(L^G)(OH)(O_2ClO_2)](ClO_4)_2\cdot CHCl_3$ (**309**)	CuN_3O_2O'	ERO	673
$[Cu_2(LC^5)(pdc)(OClO_3)](ClO_4)\cdot H_2O$ (**310**)	CuN_2S_2OO'	ERO	674
$[Cu_3(im)_2(imH)_8(O_2ClO_2)_4]$ (**358**)	CuN_4O_2	ETO	771
$[Cu(O_2ClO_2)_2]$[b]	$CuO_4O'_4$	8C	1053
(*l*) *Iodate*			
$[Cu(OH)(O_2IO)]$ (**372**)	$CuO_2O'_2O''_2$	ERO	790

[a] Numbers refer to structures in Chapter 15.5. [b] See Figure 4, Chapter 15.5. [c] 8C = eight coordinate; 9C = nine coordinate; BdSBP = bicapped square based pyramid. For other abbreviations see Table 78.

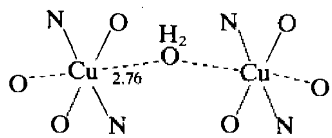
these $[Cu(OH_2)_6]^{2+}$ cations the stereochemistry is generally elongated rhombic octahedral, complicated by the presence of fluxional behaviour (Section 53.4.5).[397] In the presence of nitrogen donors, halide ions and oxyanions, lower hydrates are formed, involving up to four water molecules, *e.g.* $[Cu(en)_2(OH_2)Cl]$ (**200**),[452] $[CuCl_2(OH_2)_2]$ (**192**),[444] $[Cu(OH_2)_2(O_2NO)_2]\cdot 0.5H_2O$ (**245**)[588] and $[Cu(O_2CH)_2(OH_2)_2]\cdot 2H_2O$ (**339**).[741] In the latter tetrahydrate, only two of the water molecules are involved in coordination to the copper(II) ion, at the semi-coordinate distance of 2.36 Å; the remaining two waters are present as lattice waters. The pentahydrates of copper(II) are probably the least common, but, ironically, probably the best known hydrate of copper(II) is $[Cu(OH_2)_4(O_2SO_2)]\cdot H_2O$ (**439**),[1272] which only involves coordination to give a tetrahydrate copper(II) cation, with bridging semi-coordinate $(SO_4)^{2-}$ anions and the fifth water in the lattice. Water as a ligand is uncommon as a semi-coordinate ligand in six-coordinate copper(II), but it does occur in $[Cu(en)_2(OH_2)Cl]Cl$(**200**)[425] and $[Cu(imidazole)_4(OH_2)_2]F_2$ (**188**).[440] It is equally uncommon as the fifth ligand in a square pyramidal or trigonal bipyramidal five-coordinate stereochemistry, but does occur in $[Cu(NH_3)_4(OH_2)](SO_4)$ (**219**)[500] and $[Cu(en)_2(OH_2)][Cu_2(SeCN)(CN)_3]$[1260] for the former and in $[Cu(phen)_2(OH_2)](NO_3)_2$[1273] and $[Cu(bipy)_2(OH_2)](S_2O_6)$ (**228**) for the latter.[522] A bridging role for the water ligand is equally uncommon, but does occur in $[Cu(OH_2)_2(O_2CPh)_2]$ (**365**).[783] In the novel dimeric $\{Cu_2(OH_2)_{10}\}^{4+}$ cation of $[Cu_2(OH_2)_{10}](Cu(OH_2)_6][ZrF_7]_2$ (**440**),[1274] asymmetric Cu—O distances occur, of 1.96 and 2.66 Å, respectively. A comparable asymmetric bridging role occurs in the linear chains of $[Cu(OH_2)_4]^{2n+}$ in $[Cu(OH_2)_4$ (Hmaleate)],[1275] while an almost linear bridging semi-coordinate water ligand occurs in $[Cu(tsglyH)_2(4\text{-}Mepy)_2(OH_2)]$ (**441**).[1276]



$[Cu(OH_2)_4(O_2SO_2)]\cdot H_2O$ (**439**)[1272]



$[Cu_2(OH_2)_{10}][Cu(OH_2)_6][ZrF_7]_2$ (**440**)[1274]



$[Cu(tsglyH)_2(4\text{-}Mepy)_2(OH_2)]$ (**441**)[1276]

In contrast to water as a ligand the OH^- anion (Table 79b) functions less as a monodentate ligand than as a bridging ligand (Figure 104). The only six-coordinate hydroxy complex of known crystal structure is $Ba_2[Cu(OH)_6]$ (**185**),[436] although the $[Cu(OH)_4]^{2-}$ anion almost certainly exists.[1277] The predominant structural role of the OH^- anion is as a single bridging ligand as in $[Cu_2(bipy)_4(OH)](ClO_4)_3$ (**257**)[588] or as a double bridging ligand as in $[Cu(Me_4en)_2(OH)_2](NO_3)_2$ (**263**).[598] In the latter the Cu_2O_2 unit is generally planar and is noteworthy for the formation of a series of magnetic interactions ranging from ferro- to antiferro-magnetic (see Section 53.4.4.2). The OH^- anion may function as a tridentate ligand, utilizing all three of its lone pairs in short Cu—O distances of *ca.* 2.00 Å, as in $[Cu_3(OH)(pao)_3(O_3SO)]\cdot 16.3H_2O$ (**322**),[703] in which the trigonal Cu_3O unit is capped from underneath by a tridentate sulfate anion (**323**), involving longer Cu—O distance of 2.15 Å, to yield an overall square-based pyramidal CuN_2O_2O' chromophore. The Cu_3O_2 unit occurs in a novel copper(II) cryptate, $[Cu_3(OH)_2(C_{18}H_{42}N_6O_3)](ClO_4)_4$ (**442**)[1278] to produce a *cis*-$CuN_2O_2O'_2$ chromophore involving the unusual semi-coordinate ether-type oxygen ligand. The methoxide and phenoxide ligands have been characterized (Table 79c) in a similar bridging role to the hydroxide anion in $[Cu_2(O_6H_3\{CH_2N(CH_2py_2)_2\}\text{-}2,6\text{-}(OMe)]$ (**277**)[624] and $[Cu_2(en)_2(OPh)_2]\cdot 2PhOH\cdot 6H_2O$ (**298**), respectively.[646] The bridging role of the $(OMe)^-$ anion is of interest as it is believed to be present in the type III biological copper systems (see Section 53.4.8).[1203] The diethyl ether group as a ligand in copper(II) coordination chemistry is not well characterized; dioxane occurs as a bridging ligand (Table 79d) at semi-coordinate distances in $[Cu(nibtfac)_2(dioxane)]\cdot 2$ dioxane (**398**),[931] but with two uncoordinated dioxane molecules in the lattice. The weakness of the ether-type oxygen atom as a ligand is demonstrated in the dinuclear complex $[Cu_2(L^G)(OH)(O_2ClO_2)](ClO_4)\cdot CHCl_3$ (**309**)[673] in which two ether oxygen atoms remain uncoordinated, while OH^- and $(O_2ClO_2)^-$ ligands are involved in coordination, the latter at semi-coordinate distances. On the other hand, the ether-type oxygen ligands of $[Cu_3(OH)_2(C_{18}H_{42}N_6O_3)](ClO_4)_4$ (**442**)[1278] are involved in semi-coordinate bonding in this macrocyclic trinuclear complex. The $R_nX{=}O$ group is a much better oxygen ligand than the ether group (Table 79d); pyNO, Ph_3PO, DMSO and TMSO, respectively, form a wealth of complexes with the copper(II) ion.[1279] The six-coordinate CuO_6 chromophore is characterized in $[Cu(pyNO)_6](BF_4)_2$ (**255**) with a regular trigonal octahedral stereochemistry,[582] in conflict with the Jahn–Teller effect (see Section 53.4.5), while a four-coordinate CuO_4 chromophore occurs in $[Cu(pyNO)_4](BF_4)_2$ (**443**) as one of the few clearly square coplanar copper(II) stereochemistries.[1280] In $[Cu(pyNO)_2(O_2NO)_2]$ (**291**)[648] an elongated rhombic octahedral

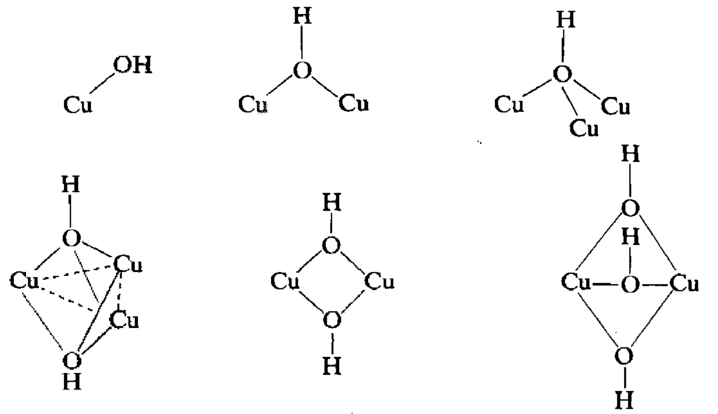
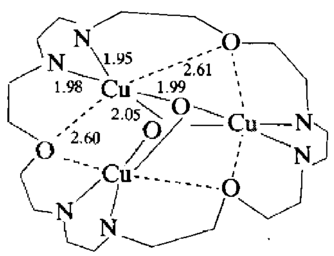
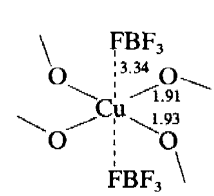


Figure 104 Coordination modes of the hydroxide ion in copper(II) complexes

$CuO_2O'_2O''_2$ chromophore is present, but with the more bulky $Ph_3P{=}O$ ligand a compressed tetrahedral geometry occurs as in $[Cu(Ph_3PO)_2Cl_2]$ (**216**).[487]

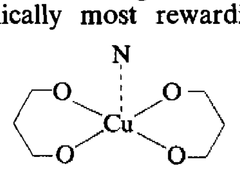


$[Cu_3(OH)_2(C_{18}H_{42}N_6O_3)](ClO_4)_4$ (**442**)[1278]



$[Cu(pyNO)_4](BF_4)_2$ (**443**)[1280]

Chelate oxygen ligands are best represented by the acetonylacetonate-type ligand and its substituted derivatives (Table 79e),[1281] which readily form stable planar six-membered rings to copper(II) as in $[Cu(3\text{-}Meacac)_2]$ (**207**),[480] interest in which stems from the determination of the one-electron *d*-orbital sequence of the rhombic coplanar stereochemistry, which remains the same independent of the substituents present.[948] Higher coordination numbers do occur, as in the five-coordinate $[Cu(acac)_2py]$ (**444**)[1282] and in $[Cu(hfacac)_2(bipy)]$ (**197**),[449] which has a high tetragonality T of 0.9 due to the restricted bite of the out-of-plane chelate ligands and crystallographic C_2 symmetry. CuO_6 chromophores occur in the tris chelate copper(II) complexes, such as $[Cu(ompha)_3](ClO_4)_2$ (**179**),[428] $[Cu(diol)_3](SO_4)$[1283] and $(C_{14}H_{19}N_2)[Cu(hfacac)_3]$.[1284] A most prolific area of copper–oxygen coordination chemistry involves oxyanions as ligands and has been reviewed as a whole in Chapter 15.5 from the point of view of the coordination number of the oxyanion involved. As this section includes a significant coverage of the copper(II) oxyanion coordination chemistry, this will not be repeated, but Table 79(f) to (k) lists the different molecular structures of copper(II) oxyanion complexes included in the present account according to the oxyanion present. While this collection is not exhaustive, it gives an overview of oxyanions as ligands to the copper(II) ion and along with Chapter 15.6 includes most of the significant structural types. Table 79(e)–(i) also indicates the oxyanions of carbon, which were excluded from Chapter 15.6, but included in Chapter 15.5. In addition, significant reviews have been published of the following oxyanions: carbonates,[1293] acetates,[1294] nitrites,[1247] nitrates[473] and perchlorate oxyanions.[1295] Those for the nitrate[473] and nitrite[1247] oxyanions involve an excellent coverage of the coordination chemistry and physical properties of complexes and of the anhydrous salts, as it is in the latter that the most multifunctional bonding roles of oxyanions are found (see Chapter 15.5). The perchlorate review[1295] specifically limits its discussion to the ligand-containing complexes of the perchlorate ion, thus excluding the stereochemically most rewarding area of anhydrous perchlorate chemistry (see Chapter 15.5).[1053]



$[Cu(acac)_2py]$ (**444**)[1282]

53.4.9.6 Sulfur ligands

Copper–sulfur bonds[35] are more common (Table 80) than copper–phosphorus bonds, but are limited to thiocarbamate-type ligands (**209**),[479] (**293**)[650] and dimercaptomalionitrile (**385**).[813] Owing to their reducing properties simple sulfides[1296–1297] as ligands to the copper(II) ion are only observed if the oxidation state is stabilized by, generally, nitrogen chelate ligands as with the macrocyclic ligands, *e.g.* in (**301**), (**307**), (**308**), (**310**), (**423**) and (**424**). Both short (*ca.* 2.30 Å) and long (*ca.* 2.90 Å) Cu—S distances are involved and highlight the shortness of the copper–cysteine bond in the type I biological copper as unusual (Figure 96) and hence probably responsible for the unique properties of the type I copper systems (Section 53.4.8). The thiolate ligand occurs in a semi-coordinate bonding role in $[Cu(cyclam)(SPh)_2]$ (**189**)[441] and the SCN^- anion also bonds in this position in $[Cu(NH_3)_2(NCS)_2]$ (**433**),[1253] $[Cu(en)_2(SCN)_2]$ (**434**)[1256] and [Cu(trien)(SCN)](NCS) (**437**),[1268] all with long Cu—S distances of *ca.* 3.0 Å.

No copper(II) complexes containing short Cu—Se or Cu—Te distance are known, but a long Cu···Se distance of 3.26 Å occurs in $[Cu(en)_2(SeCN)_2]$ (**434**).[1257]

Table 80 Sulfur as a Ligand

	Chromophore	*Stereochemistry*[a]	*Ref.*
$[Cu(diethylthiocarbamate)_2]$ (**209**)	CuS_4	RC	479
$[Cu(diethyldithiocarbamate)_2]_2$ (**293**)	CuS_4S'	SBP	650
$[Fe(p\text{-}Cl_4tpp)]_2[Cu(mnt)_2]_2 \cdot 3C_6H_6$ (**385**)	CuS_4Fe_2	RC	813
$[Cu(cyclam)(SPh)_2]$ (**189**)	CuN_4S_2	ERO	441
$[Cu_2\{S_2C_2[N(CH_2)_2OH]\}(O_2SO_2)] \cdot 2H_2O$ (**345**)	CuO_2NSO'	SBP	756
$[Cu(bipy)_2(thiourea)](ClO_4)_2$	CuN_4S	TB	1307
$[Cu_2(p\text{-}XYLpy2)(OH)](BF_4)_3$ (**301**)	$CuNSOO'$	SBP	658
$[Cu_2(L^B)(N_3)_2(1,3\text{-}N_3)_2]$ (**307**)	$CuN_3N'S_2$	ERO	669
$[Cu_2(LC^1)(pdc)(1,3\text{-}N_3)]$ (**308**)	$CuN_2N'OS_2$	ERO	671
$[Cu_2(LC^5)(pdc)(OClO_3)](ClO_4)_2 \cdot H_2O$ (**310**)	$CuN_2S_2O'_2$	ERO	674
$[Cu(S_4N_2C_{17}H_{24})]$ (**423**)	CuN_2S_2	RC	1224
$[Cu(bidhp)Cl_2]$ (**424**)	$CuN_2Cl_2S_2$	*cis*-O	1225

[a] For abbreviations see Table 78.

53.4.9.7 Halogen ligands

As a group the halide ions are second only to nitrogen and oxygen as ligands to the copper(II) ion, a predominance that is obtained through the widespread coordination of the chloride ion (Table 81b),[489] which is much more extensive than that of the bromide ion and very much more extensive than that of either the fluoride or iodide ion (Table 81a and d, respectively). The fluoride ion is uncommon as a simple monodentate ligand to the copper(II) ion, but does occur in the $[CuF_6]^{4-}$ anion in (**186**).[437] It has been characterized in a dinuclear bridging role, as in $[Cu_2F_2(mppzH)_4(F_2BF_2)_2]$ (**265**).[604] It is also found in a more extensive bridging role in the infinite lattices of $[CuF_2]$ (**369**)[786] and $K_2(CuF_4)$ (**368**).[535] The $(BF_4)^-$ anion may be involved in long Cu—F distances of *ca.* 2.7 Å as a monodentate ligand or as a bidentate bridging ligand, *e.g.* in $[Cu(en)_2(FBF_4)_2]$ (**193**)[445] and $[Cu(bipy)_2(F_2BF_2)](BF_4)$ (**201**).[453,454] Similarly the $(PF_6)^-$ anion is involved as a monodentate ligand with a long Cu—F distance of 2.48 Å in $[Cu(na_2)(OH_2)(FBF_3)](BF_4)$.[1298] The coordination chemistry of the copper(II)–Cl^- systems has been extensively reviewed,[489] and covers most of the simple stereochemistries of the copper(II) ion (Table 81b), *i.e.* compressed tetrahedral (**175**),[483] square coplanar (**206**),[476] elongated rhombic octahedral (**365**),[784] square pyramidal (**217**)[498] and trigonal bipyramidal (**221**),[502] all of which involve a mononuclear $CuCl_n$ chromophore, with $n = 4$–6. Extensive polynuclear complexes are known from dinuclear (**353**),[766] trinuclear (**359**)[772] and tetranuclear (**331**)[711] up to infinite lattices such as $[CuCl_2]$ (**366**).[784] In general, the Cu—Cl distances are *ca.* 2.3 Å (short) and 2.9 Å (long).

While the range of copper(II) complexes involving Cu—Br bonds (Table 81c) is more limited than those for Cu—Cl bonds (Table 81b), the structures tend to be analogous, with short Cu—Br distances of 2.4 Å and long distances of *ca.* 3.0 Å. Simple iodine complexes of the copper(II) ion are unknown, in view of the ready reduction of copper(II) to copper(I) with the liberation of iodine, nevertheless, copper–iodine bonds are formed if the copper(II) ion is stabilized by complex formation, as in $[Cu(bipy)_2I]I$ (**420**),[1299] the structure of which involved the first example of five-coordinate copper(II) stereochemistry.[1300] Semi-coordinate iodide

Table 81 Halides as Ligands

	Chromophore	*Stereochemistry*[a]	*Ref.*
(*a*) *Fluoride*			
$[Cu_2(metgb)F_2](BF_4)_2 \cdot 2H_2O$ (**260**)	CuN_3FO	SBP	594
$[Cu_2F_2(mppzH)_4(F_2BF_2)_2]$ (**265**)	$CuN_2F_2F'_2$	ERO	604
$K_2[CuF_4]$ (**368**)	$CuF_4F'_2$	ETO	535
$[CuF_2]$ (**369**)	$CuF_4F'_2$	ETO	786
$[Cu(en)_2(FBF_3)_2]$ (**193**)	CuN_4F_2	ERO	445
$[Cu(bipy)_2(F_2BF_2)](BF_4)$ (**201**)	CuN_4F_2	ERO	453, 454
(*b*) *Chloride*			
$Cs_2[CuCl_4]$ (**175**)	$CuCl_4$	CTd	483
$(Me_3NH)_3[Cu_2Cl_7]$ (**401**)	$CuCl_4$	TTd	1079
$[Cu(Ph_3PO)_2Cl_2]$ (**216**)	CuO_2Cl_2	CTd	487
$[Cu\{(NPMe_2)_4H\}][CuCl_3]$	$CuNCl_3$	CTd	488
$[Ph_4As]_2[Cu_2Cl_6]$ (**268**)	$CuCl_2Cl_2$	CTd	614
$[Co(en)_3][Cu_2Cl_8]Cl_2 \cdot 2H_2O$ (**283**)	$CuCl_4Cl'$	SBP	631
$[Cu_2(\textit{trans}\text{-chd})_4Cl_4]$ (**294**)	CuO_2Cl_2Cl'	SBP	651
$\{N\text{-(2-amet)pipzH}_3\}[CuCl_5] \cdot 2H_2O$ (**217**)	$CuCl_4Cl'$	SBP	498
$[Cu_2(medpeo)Cl_4]$ (**296**)	$CuCl_4$	CTd	653
	CuN_2OCl_2	SBP	653
$[Co(NH_3)_6][CuCl_5]$ (**221**)	$CuCl_5$	TB	502
$[Cu(bipy)_2Cl](PF_6)$ (**225**)	CuN_2N_2Cl	TB	505
$[Cu_2(p\text{-XYLpy2})Cl_4]$ (**261**)	CuN_3ClCl'	SBP	595
$[Cu_2Cl_2(HBpz_3)_2]$ (**264**)	CuN_2Cl_2N'	SBP	603
$[Cu_2(L)_2Cl_2] \cdot 6H_2O$ (**275**)	CuN_2O_2Cl	SBP	622
$[Cu_2(Me_4pn)_2Cl_2(O_2CO)]$ (**280**)	CuN_2O_2Cl	SBP	628
$[Cu_2(4\text{-meox})_2Cl_2]$ (**284**)	CuN_2Cl_2Cl'	SBP	632
$[Cu(2\text{-pic})_2Cl_2]_2$ (**285**)	CuN_2Cl_2Cl'	SBP	633
$[Cu_2(tet\text{-}b)_2Cl](ClO_4)_3$ (**256**)	CuN_4Cl	TB	587
$[CuCl_2]$ (gas) (**242**)	$CuCl_2$	L	417
$Cs[CuCl_3]$ (**181**)	$CuCl_3Cl'_3$	TO	431
$[CuCl_2]$ (solid) (**366**)	$CuCl_4Cl'_2$	ERO	784
$(NH_4)_2[CuCl_4]$ (**187**)	$CuCl_4Cl'_2$	ETO	438
$Li[CuCl_3(OH_2)_2]$ (**352**)	$CuCl_4Cl'$	SBP	765
$[CuCl_2(OH_2)_2]$ (**192**)	$CuO_2Cl'_2Cl''$	ERO	444
$(NH_4)_2[Cu_2Cl_6]$ (**353**)	$CuCl_2Cl'_2Cl''_2$	ERO	766
$Cs_3[Cu_2Cl_7(OH_2)_2]$ (**314**)	$CuCl_3OCl'_2$	ERO	680
$(ipa)[CuCl_3]$ (**361**)	$CuCl_4Cl'_2$	ETO	779
$[Cu_2(C_{18}H_{14}N_6)Cl_3(OH)] \cdot 1.5H_2O$ (**315**)	CuN_2OClCl'	SBP	681
$(dienH_3)[CuCl_4]Cl$ (**367**)	$CuCl_4Cl'_2$	ERO	785
$[Cu(denc)_2Cl_2]_3$ (**320**)	$CuN_2Cl_2Cl'_2$	ERO	701
	CuN_2Cl_2Cl'	SBP	701
$(Me_3NH)_2[Cu_4Cl_{10}]$ (**326**)	$CuCl_4Cl'_2$	ETO	708
	$CuCl_2Cl'_2$	CTd	708
$[Cu(salen)CuCl_2]_2$ (**327**)	$CuCl_2O_2Cl$	SBP	709
$[Ph(CH_2)_2NH_2(Me)_2]_2[CuCl_4]$ (**206**)	$CuCl_4$	SP	476
$[Cu(DMSO)_2Cl_2]$ (**334**)	CuO_2Cl_2Cl'	SBP	724
$[Cu(TMSO)Cl_2]$ (**362**)	$CuO_2Cl_2Cl'_2$	ERO	780
$[Cu(en)Cl_2]$ (**348**)	$CuN_2Cl_2Cl'_2$	ERO	760
$[CuCl_2(1,2,4\text{-triazole})]$ (**363**)	$CuCl_4N_2$	ETO	781
$[Cu(pyridic)(HCl)]$ (**350**)	CuN_2OClO'	SBP	763
$[Cu_3Cl_6(C_6H_7NO)_2(OH_2)_2]$ (**359**)	$CuCl_2O_2Cl'_2$	ERO	772
$[Cu_4OX_6L_4]$ (**331**)	CuX_3L	CTd	711
(*c*) *Bromide*			
$\beta\text{-}[Cu(NH_3)_2Br_2]$ (**234**)	CuN_2Br_4	CTO	536
$\alpha\text{-}[Cu(NH_3)_2Br_2]$ (**414**)	$CuN_2Br_2Br'_2$	ERO	1098
$[Cu_2Br_4(pyNO)_2]$ (**269**)	CuO_2Br_2Br'	SBP	615
$[Cu_2Br_2(4\text{-meox})_2]$ (**286**)	CuN_2Br_2Br'	SBP	634
$[Cu_2(dmthbp)_2Br_4]$ (**295**)	$CuNSBr_2Br'$	SBP	652
$[CuBr_2]$ (gas) (**242**)	$CuBr_2$	L	417
(*d*) *Iodide*			
$[Cu(im)_4I_2]$ (**445**)	CuN_4I_2	ERO	1301
$[Cu(bipy)_2I]I$ (**420**)	$CuN_2N'_2I$	TB	1153

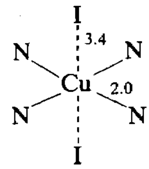
[a] L = linear. TTd = trigonal distorted tetrahedral. For other abbreviations see Table 78.

Table 82 X—Y-type Ligands

	Chromophore	*Stereo-chemistry*[a]	*Ref.*
(*a*) *Bidentate mixed ligands N—O*			
$[Cu(N\text{-Mesalim})_2]$ **(212)**	CuO_2N_2	RC	481, 482
$[Cu_4\{O(CH_2)_4NR_2\}_4L_4]$ **(332)**	$CuNO_2L$	SBP	716
(*b*) *Tridentate mixed ligands*			
$[Cu_2(p\text{-XYLpy}_2)Cl_4]$ **(261)**	CuN_3ClCl'	SBP	595
$[Cu(L^F)(N_3)_2(1,3\text{-}N_3)](ClO_4)$ **(303)**	$CuN_3N'N''$	SBP	661
$[Cu_2(N_3py2)(OMe)_2](ClO_4)_2$ **(305)**	CuN_3O_2	SBP	666
$[(CuL)_3(CuLO)(OH)]$ **(328)**	CuN_3OO'	SBP	710
$[Cu_2(L')Cl_2]\cdot 6H_2O$ **(275)**	$CuN_2OO'Cl'$	SBP	622
$[Cu(bpim)(im)]_2(NO_3)_4\cdot 3H_2O$ **(329)**	CuN_3N	RC	593
$[Cu_2(dana)_2(py_2)]$ **(274)**	CuO_4N	RC	620
$[Cu_4(mpz)_4(acmpz)(ONO_2)_2]$ **(330)**	CuN_2O_2O'	SBP	710
$[Cu(aiba\text{-}nno)_2]$ **(272)**	CuN_2O_2	RC	618
$[Cu_2(O_2CMe)_2(CA)]$ **(355)**	$CuN_2N'OO'$	SBP	768
$Na[Cu_2(Gly\text{-}Gly\text{-}O)_2(im)]\cdot 6H_2O$ **(259)**	$CuN_2N'O$	RC	259
$[Cu(N_3)_2(C_{16}H_{34}N_2O_6)(N_3)_2]$ **(387)**	$CuNN_3'O_2$	ERO	866
$[Cu_2(L^G)(OH)(O_2ClO_2)](ClO_4)_2\cdot CHCl_3$ **(309)**	CuN_3N_2'	SBP	673
$[Cu_2(LC^3)(N_3)_2][\mu\text{-}N_3)]$ **(311)**	CuN_3N_2'	SBP	675
$[Cu_3(OH)(pao)_3](SO_4)\cdot 10.5H_2O$ **(322)**	CuN_2OO'	RC	703
$[Cu_2(L^B)(N_3)_2(1,3\text{-}N_3)_2]$ **(307)**	$CuNS_2N_3'$	ERO	669
$[Cu(S_4N_2C_{17}H_{24})]$ **(423)**	CuN_2S_2	RC	1224
$[Cu_2(LC^1)(pdc)(1,3\text{-}N_3)]$ **(308)**	$CuNN'N''OS_2$	ERO	671
$[Cu(bidhp)Cl_2]$ **(424)**	$CuN_2S_2Cl_2$	*cis*-O	1225
$[Cu_2(LC)(pdc)(OClO_3)](ClO_4)_2\cdot H_2O$ **(310)**	$CuNS_2N'OO'$	ERO	674
$[Cu_3O(dpeo)_3]_2$ **(333)**	CuN_2O_2O'	SBP	723
$[Cu_2\{S_2C_2[N(CH_2)_2OH]_2\}(O_2SO_2)]\cdot 2H_2O$ **(345)**	$CuONSO'$	SBP	756
$[Cu(pyrdic)HCl]$ **(350)**	CuN_2OClO'	SBP	763
(*c*) *Tetradentate mixed donor ligands*			
$[Cu(cyclam)(SPh)_2]$ **(189)**	CuN_4S_2	ERO	441
$[Cu(cyclops)(CN)]$ **(220)**	CuN_4C	SBP	501
$[Cu_2(tet\text{-}b)_2Cl](ClO_4)_3$ **(256)**	CuN_4Cl	TP	587
$[Cu_2(14\text{-}4,11\text{-diene-}N_4)_2(CN)](ClO_4)_3$ **(258)**	CuN_4C	TP	589
$[Cu_2(sal\text{-}m\text{-}pda)_2]$ **(281)**	$CuNON'O'$	RC	629
$[Cu_2(C_{26}H_{34}N_7O_{15})](ClO_4)_3$ **(302)**	CuN_3OO'	SBP	660
$[Cu_2(ephdtb)(N_3)](ClO_4)_3$ **(306)**	$CuN_3N'O$	SBP	667
$[Cu_2\{OC_6H_3[CH_2N(CH_2CH_2py)_2]\text{-}2,6\text{-}(OMe)\}]$ **(277)**	CuN_3OO'	SBP	624
$[Cu_2(metgb)F_2](BF_4)_2\cdot 2H_2O$ **(260)**	CuN_3OF	SBP	594
$[Cu(14\text{-ane-}S_4)(OClO_3)_2]$ **(190)**	CuS_4O_2	ERO	442
$[Cu_2(p\text{-XYLpy2})(OH)](BF_4)_3$ **(301)**	$CuNS_2OO'$	SBP	658
$[Cu_2(ppda)_2(OSO_3)_2]_2\cdot 13H_2O$ **(312)**	CuN_2O_2O'	SBP	678
$[Cu_2(C_{18}H_{14}N_6)Cl_3(OH)]\cdot 1.5H_2O$ **(315)**	CuN_2OClCl'	SBP	68
$[Cu(L^{12})]$ **(215)**	CuN_2S_2	RC	486
$[Cu(phthalocyanine)]$ **(341)**	CuN_4	RC	480
(*d*) *Pentadentate chelate ligands*			
$[Cu(H_2edta)(OH_2)]$ **(195)**	CuN_2O_3O'	ERO	447
$[Cu(cbpo)]$ **(229)**	CuN_2O_3	SBP	523
$[Cu(N_3S_2)(NCS)](BPh_4)$ **(399)**	CuN_3S_2	SBP	932
(*e*) *Hexadentate chelate ligands*			
$[Cu(ebtd)](BF_4)(BF_3OEt)\cdot H_2O$ **(230)**	CuN_4N_2'	Bd SBP	524
$[Cu(Me\text{-taab})(O_2NO)](NO_3)$	CuN_4O_2	Bd SBP	525
$[Cu(phen)_2(O_2NO)](NO_3)$ **(231)**	CuN_4O_2	Bd SBP	526
(*f*) *Heptadentate chelate ligands*			
$[Cu(L^{12})](ClO_4)_2$ **(243)**	$CuN_2N_2'N_3''$	PB	554

[a] BdSBP = bicapped square-based pyramidal. PB = pentagonal bipyramidal. For other abbreviations see Table 78.

occurs in [Cu(imidazole)$_4$I$_2$] (**445**)[1301] with a long Cu—I distance of 3.4 Å compared to a short Cu—I distance of *ca.* 2.7 Å.



[Cu(imidazole)$_4$I$_2$] (**445**)[1301]

53.4.9.8 Hydrogen ligands

There is no X-ray crystallographic evidence that the hydrogen atom can bond to the copper(II) ions.

53.4.9.9 Mixed donor chelate ligands

These form an extensive series of copper(II) complexes ranging from bidentate chelate ligands to hexadentate chelate ligands (Table 82a–e) with the predominant donor atoms N, O and S. Schiff's base N,O donor systems dominate the bidentate chelate ligands,[481,1302] *e.g.* in [Cu(NMesalim)$_2$] (**212**) and the early interest in these systems was concerned with the relationship[1303] between the CuN_2O_2 chromophore geometry, from rhombic coplanar (**212**) to compressed tetrahedral [Cu(*t*-butylsalim)$_2$][1304] and the electronic properties of the copper(II) ion.[1305] With higher chelate ligand denticity the interest has involved the formation of a wider range of copper(II) geometries, but more importantly the formation of polynuclear complexes, where the polydentate ligand may be involved in a bridging function that could hold the copper(II) ions sufficiently close together for antiferromagnetic interaction to occur with the ultimate formation of diamagnetic dimers that are ESR silent (Table 44). Reference 30 gives an excellent up-to-date account of the wealth of structural and magnetic data that is currently available in this continually developing area. With the increasing denticity of the chelate ligands, there is considerable overlap with macrocyclic chemistry,[1298] where the geometry of the macrocyclic ligand, if rigid, as in [Cu(phthalocyanine)] (**210**)[480] imposes its 'own' geometry on the copper(II) ion, namely square coplanar, but with increasing flexibility of the ligand, the 'plasticity' of the copper(II) ion (Section 53.4.5) may also contribute to the final geometry of the copper(II) ion, as determined in the crystalline state.[461,463]

53.5 MIXED COPPER(II)/(III) COMPLEXES

Compared to the copper(I)/(II) mixed oxidation state complexes (see Section 53.3.7) the copper(II)/(III) mixed oxidation states are of extremely limited occurrence and there are no single-crystal X-ray structural data available. The most simple system[1308] is the dark brown Cs:Cu:F phase obtained by fluorination of a CsCl:CuCl mixture at approximately 400 °C. The product is believed to be a mixture at approximately 400 °C of orthorhombic Cs[$Cu^{II}Cu^{III}F_6$] and tetragonal $Cs_2[Cu^{II}_{0.5}Cu^{III}F_6]$. Based on the comparison of the X-ray powder photograph of the former with Cs[$Ni^{II}Ni^{III}F_6$] the CuF_6 chromophore environment involves a regular octahedral environment with a Cu^{III}—F distance of 1.90 Å.[1309] In $Cs_2[Cu^{II}_{0.5}Cu^{III}F_6]$ the CuF_6 octahedral environment involves a Cu—F distance of 1.93 Å. As the d^8 configuration of the CuF_6 chromophore involves a spin-free configuration, the copper(III) environment is predicted to be paramagnetic, but unambiguous data have not been reported due to the presence of the accompanying copper(II) species. A mixed copper oxidation state involving copper(III) has also been suggested for the perovskite $La_3Ba_2[Cu^{II}_{(5-2y)}Cu^{III}_{(1+2x)}O_{(14+y)}]$.[1310]

A more complex example of a $Cu^{II/III}$ system (Figure 105) is present in the trinuclear system $[Cu_3O_p(OH)_{1-p}(\text{ligand})_3]$, where $0 \leq p \leq 1$; ligand = RNC(R')C(R')NO$^-$; R = Et, Pr, Bu or

Ph; and R′ = Me or Ph.[1311] In acid conditions ($HClO_4$) the Cu_3OH unit predominates, but in the base NEt_3, equilibrium deprotonation occurs to the Cu_3O species (equation 34).

$$Cu_3OH \rightleftharpoons Cu_3O + H^+ \quad (34)$$

The yellow-green mixed valence complex $[Cu_3O(Pr^nL')_3](ClO_4)_2 \cdot H_2O$ may be isolated from acetonitrile solution by a nearly reversible electrolytic oxidation (E°_{298} + 0.44 V *vs.* SCE) of the corresponding Cu^{II}_3O species. The complex (Figure 105a) is diamagnetic and has a relatively narrow and intense solvent sensitive intervalence electronic spectrum (Figure 1b). While there is no crystallographic structure available, the near equivalence of the IR and proton NMR spectra of the $Cu^{II}_2Cu^{III}O$ complex and those of the Cu^{II}_3O species of known crystal structures (Figure 105a) suggests a comparable structure and type II Robin and Day behaviour.[360,362,1312] It is then of interest that the Cu^{II}_3OH complex only undergoes electrolytic reduction to yield a $Cu^I_2Cu^{II}_2O$ complex E°_{298} 0.3–0.45 V *vs.* SCE).[1313]

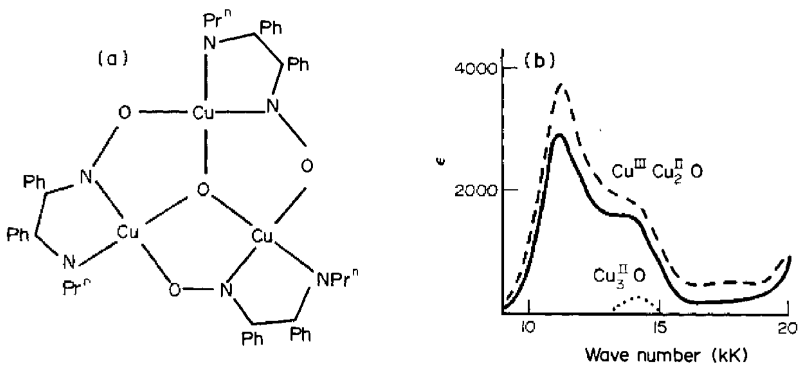


Figure 105 (a) The proposed structure[1313] of $[Cu_3O(Pr^nL')_3](ClO_4)_2 \cdot H_2O$; and (b) the intervalence charge transfer spectra at 11 091 cm^{-1}, sh 13 889 cm^{-1}

53.6 COPPER(III) COMPLEXES

The copper(III) oxidation state is three orders of magnitude less common than that of even copper(I), and crystallographic data are limited to less than 20 compounds or complexes.[5,10,11,17] It is a strong oxidizing agent and due to its ready reduction does not occur in nature,[11] but due to its occurrence as a possible intermediate in redox reactions in biological systems,[11] it has attracted increased interest in the literature, especially in redox/kinetic data.[17] Brief accounts of the chemistry of copper(III) appear in ref. 5 and the various editions of ref. 10 and 17. The chemistry of copper(III) was first reviewed in 1950,[1314] and again in 1981;[11] the latter review forms the best account of the structural chemistry of copper(III) to date, especially the redox/kinetic aspects of copper peptide chemistry, associated with the biological interest in the chemistry of copper(III).

53.6.1 Preparation of Copper(III) Complexes

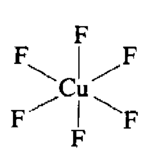
As a higher oxidation state than copper(I) and copper(II) species, copper(III) is prepared by oxidation of the two lower oxidation states (Figure 106). Historically[11] this was first carried out in aqueous solutions using oxidizing agents such as the hypochlorite ion $(ClO)^-$,[1315] chlorine gas Cl_2,[1316] and the persulfate anion $(S_2O_8)^{2-}$,[1317] under alkaline conditions (Figure 106a–e). However as the $[Cu(OH_2)_6]^{3+}$ species is still unknown and the hypothetical $[Cu(OH)_4]^-$ anion is very unstable,[1318] although oxidation occurs, as reflected in the observation of colour changes, characterizing the copper(III) species in solution has proved very difficult. Nevertheless, the use of rather unusual oxidizing oxyanions,[1319] such as the $(TeO_6)^{6-}$ and $(IO_6)^{5-}$ anion, results in the preparation of some relatively stable copper(III) complexes even from aqueous solution, namely $Na_9[Cu(TeO_6)_2] \cdot 16H_2O$ and $Na_7[Cu(IO_6)_2] \cdot 20H_2O$. By using preparative mixtures of $Cu(OH)_2$ and Na/KOH relatively simple compounds of copper(III) such as $NaCuO_2$ and $Ba(CuO_2)_2$ were isolated,[1314,1318,1320] while the use of MCl/Cu_2Cl_2 and fluorine gas as the oxidizing agent proved most successful in the preparation of a range of $M_3[CuF_6]$ copper(III) complexes.[1321,1322] But even the use of the highly electronegative fluorine gas was surpassed by the use of electrolytic oxidation,[1314,1319] especially in aqueous[1323] and nonaqueous organic solvents[11] such as alcohol, acetone, acetonitrile[1324] or sulfur dioxide.[1325] This not only opened up the preparation of copper(III) complexes involving nitrogen and sulfur ligands,[11] but complexes involving ligands such as thiocarbamates,[1326] diphos and diarsine,[1327] which are normally considered highly reducing. Using electrolytic reduction in liquid SO_2 even the novel $[Cu(pyNO)_4](PF_6)_3$ complexes were prepared,[1325] the $Cu(III)N_4$ chromophore of Cu macrocyclic complexes[1328] and polypeptide complexes.[11,1329] The preparation of borane hydride complexes of copper(III) and also of carborane complexes also became possible.[1330,1331]

			Ref.
(a) Hypochlorite			
Cu^{II} + alkaline HClO	$\longrightarrow$	Cu^{III} species + O_2 (First suggested CuO_2) yellow	1315
(b) Chlorine			
$Cu(OH)_2 + KOH + Cl_2$	$\longrightarrow$	Cu_2O_3 red	1316
$+ Ba(OH)_2$	$\longrightarrow$	$BaCuO_2$ red, unstable	1318
(c) Electrochemical oxidation			
$Cu(OH)_2$ + NaOH (12–14 M)	$\longrightarrow$	Yellow ppt.	1322
(d) NaClO or $K_2S_2O_8$ + NaOH + $(TeO_6)^{6-}$	$\longrightarrow$	$Cu/(TeO_6)$ complexes	1317, 1319
or electrochemically or $(IO_6)^{5-}$	$\longrightarrow$	$Cu/(IO_6)$ complexes	
(e) $Cu_2Cl_2 + CsCl + F_2$	$\xrightarrow[400\,^\circ C]{F_2}$	$Cs_3[CuF_6]$	1312

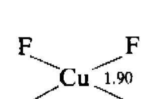
Figure 106 The preparation of copper(III) complexes

53.6.2 Stereochemistry of Copper(III) Complexes

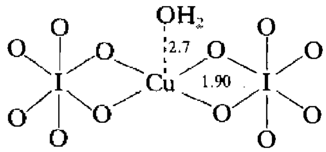
To date all copper(III) complexes of known crystal structure are mononuclear and there are no polynuclear copper(III) complexes of known crystal structure (but see Figure 105). The first structure of a copper(III) complex was that of the pale green $K_3[CuF_6]$ (**446**),[1332] which on the basis of its paramagnetism of $\mu_{eff} = 3.01$ BM was presumed to involve an octahedral CuF_6 anion consistent with its X-ray powder photograph. More recently[1333] the structure of the diamagnetic yellow-green $Cs[CuF_4]$ (**447**) has been determined by X-ray powder photography and shown to be square coplanar with a Cu—F distance of *ca.* 1.9 Å. The first single-crystal X-ray structure of a copper(III) complex was carried out on the first crystal of a copper(III) complex to be isolated, namely $Na_3KH_3[Cu(IO_6)_2]\cdot 14H_2O$ (**448**).[1334] The structure involves a square coplanar CuO_4 chromophore with Cu—O distances of 1.90 Å, but with an additional water molecule at a Cu—O distance of 2.70 Å, a distance that is rather long to be described as square-based pyramidal. In view of the instability of the copper(III) ion in aqueous solution and the number of water molecules and free hydrogen cations in this complex, the structure is remarkably reminiscent of a copper(II) stereochemistry, but its diamagnetism is the best evidence for the presence of a copper(III) ion. However, the recent crystal structure of the green [Cu(macrocycle)] (**449**),[1335] where macrocycle = disodium 7,9,16,18,19,20-hexamethyl-8,17-dioxa-1,2,5,6,10,11,14,15-octaazatricyclo$[13.3.1.1^{6,10}]$icosane-3,4,12,13-tetronato(4 −)-N^2,N^5,N^{11},N^{14}]-α-hydroxocuprate(III), involves a less ambiguous set of crystallographic data for a copper(III) complex, which also involves a square-based pyramidal CuN_4O chromophore. This complex also has a comparable long Cu—O distance of 2.7 Å with the copper lifted out of the N_4 plane and suggests that the structure of (**448**) above is correct.



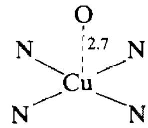
$K_3[CuF_6]$ (**446**)[1332]



$Cs[CuF_4]$ (**447**)[1333]

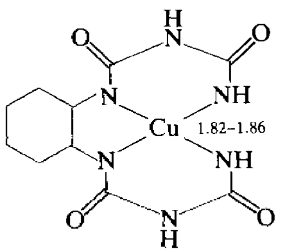


$Na_3KH_3[Cu(IO_6)_2]\cdot14H_2O$ (**448**)[1334]

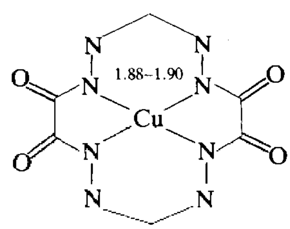


[Cu(macrocycle)] (**449**)[1335]

A number of diamagnetic square coplanar complexes of copper(III) are known involving a CuN_4 chromophore, such as (Bu_4N)[*o*-phenylenebis(biuretato)cuprate(III)]$\cdot CHCl_3$ (**450**)[1336] and the blue $(EtNH_3)[Cu(macro\text{-}N_4)]$ (**451**)[1337] complexes, where macro-N_4 = the macrocyclic ligand 3,10-dimethyl-1,2,4,5,8,9,11,12-octaazatetradecane-6,7,13,14-tetrane. Both complexes are diamagnetic and involve a coplanar CuN_4 chromophore with a short Cu—N distance of 1.82–1.86 and 1.88–1.90 Å, respectively, and neither involves a fifth axial ligand within a 3.0 Å distance.

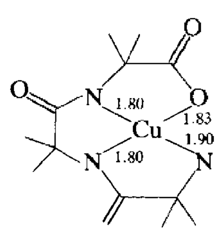


$(Bu^t_4N)[Cu(macro\text{-}N_4)]\cdot CHCl_3$ (**450**)[1336]



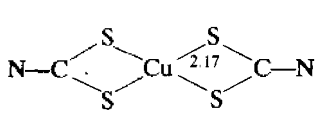
$(EtNH_3)[Cu(macro\text{-}N_4)]$ (**451**)[1337]

The structure of $[Cu(H_{-2}Aib_3)]\cdot2H_2O\cdot1.5NaClO_4$ (**452**)[1338] is important as the first structure of a copper(III) complex of a tripeptide which coordinates in the deprotonated state of the ligand.[11] The structure involves a square planar CuN_3O chromophore with some of the shortest Cu—N distances known, even for copper(II). The closest axial approach is a $(ClO_4)^-$ oxygen atom at a distance of 2.91 Å and the copper(III) ion lies in the plane of the N_3O ligands.

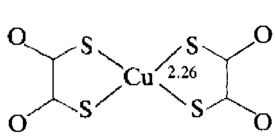


$[Cu(H_{-2}aib_3)]\cdot2H_2O\cdot1.5NaClO_4$ (**452**)[1338]

The largest group of copper(II) complexes of known structure (Table 83) involves coordination by the dithiolate group to yield Cu—S bonds with a planar CuS_4 chromophore.[1339,1344] The Cu—S distances are in the range 2.17–2.26 Å and at the lower range are considerably shorter than the normal Cu^{II}—S distance of 2.3 Å. Mention should be made of the novel copper(III) carborane complex $(Ph_3PMe)[Cu(C_2B_9H_{11})_2]$ (**456**),[1345] the structure of which involves a slipped sandwich $Cu(C_2B_3)_2$ chromophore with four mean Cu—C distances of 2.52 Å and six mean Cu—B distances of 2.21 Å. As this type of copper environment involving six to ten coordination is unusual in copper chemistry, the matter is referred to (ref. 257), but it is worth noting that the corresponding copper(II) and (III) carborane complexes are isostructural.[1346]



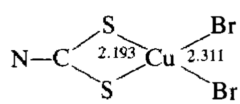
$(Bu^n_4N)[Cu(MNdtc)]$ (**453**)[1339]



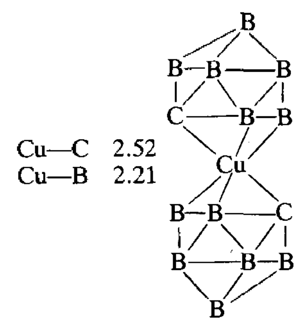
$\{(Ph_3P)_2N\}\{Cu(S_2C_2O_2)_2]$ (**454**)[1343]

Table 83 Some Copper(III) Dithiol Complexes

	Cu—S (Å)	*Ref.*
[CuBu$^n_4${bis(maleonitriledithionate)}] (**453**)	2.17	1339
K[Cu(1,1-dicarboxyethylenedithiol)$_2$·Et$_2$O	2.195	1340
[Cu(*N*-pyrrolidyldithiocarbamato)$_2$](ClO$_4$)	2.20	1341
Cu{*N*,*N*-(Bu^n)$_2$NCS$_2$}$_2$](I$_3$)	2.22	1342
{(Ph$_3$P)$_2$N}[Cu(S$_2$C$_2$O$_2$)$_2$] (**454**)	2.26	1343
[Cu(Bu^n)$_2$dteBr$_2$] (**455**)	2.19	1344



[Cu(Bu^n)$_2$dtcBr$_2$] (**455**)[1344]



(Ph$_3$PMe)[Cu(C$_2$B$_9$H$_{11}$)$_2$] (**456**)[1345]

With so few crystallographic examples it is rather difficult to summarize the stereochemistry of copper(III). Nevertheless, it can be said that O, N, and S sulfur ligands dominate the coordination chemistry of copper(III) with Cu—L distances approximately 0.1 Å shorter than the corresponding copper(II) ligand distance (Figure 107). While the fluoride ion appears to be a reasonable ligand, the chloride and iodide ions are absent as ligands and only one example of the Cu—Br bond has been characterized.[1344] The most common stereochemistries are rhombic coplanar, supplemented occasionally by a relatively long fifth ligand of *ca.* 2.7 Å. With the fluoride as a ligand the predominant geometry is regular octahedral. The tetrahedral or trigonal bipyramidal stereochemistries have not been characterized for the copper(III) ion.

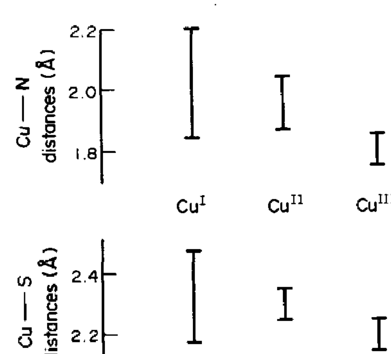


Figure 107 Ranges of Cu—L distances (Å) for Cu^I, Cu^{II} and Cu^{III} complexes

53.6.3 Polynuclear Copper(III) Complexes

There are no clear crystallographic examples of polynuclear copper(III) complexes but the structure of the mixed copper(II)/(III) complex of Figure 105 suggests that these may exist.

53.6.4 Electronic Properties of Copper(III) Complexes

The copper(III) ion with an (Ar)3d^8 configuration generates the spectroscopic states ^3F, ^3P, which split in an octahedral crystal field as shown in Figure 108(a). The magnetic properties of a series of $MM'_2[CuF_6]$ (**446**) complexes give $\mu_{eff} = 2.7–2.9$ BM, consistent with the presence of two free spins in the spin-free $t_{2g}^6 e_g^2$ configuration of the copper(III) ion in an octahedral crystal field.[1321] The electronic reflectance spectra involve spin-forbidden and spin-allowed bands observed in the region 9–20 kK with two charge-transfer bands in the region 30–45 kK.[1347] The spectrum yields a Δ_{oct} value of 14.1 kK appropriate to an M^{III} ion. All other complexes of the copper(III) ion are spin paired and diamagnetic with the spectra dominated by charge transfer spectra, which mask the *d–d* transition.[1348]

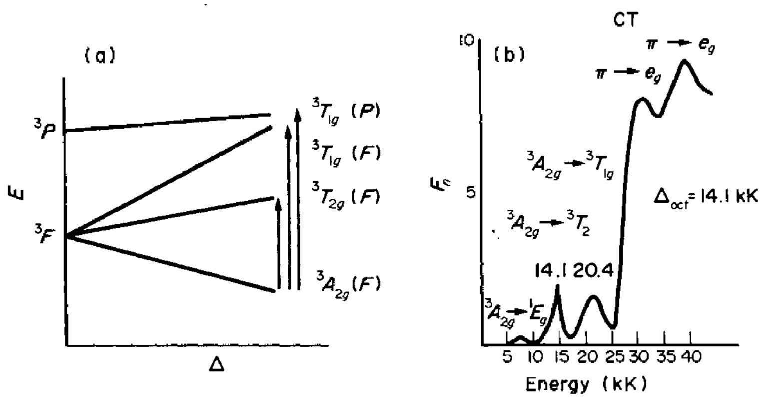


Figure 108 Copper(III) ion (a) Orgel diagram and (b) the electronic spectrum of $[CuF_6]^{3-}$ anion[1347]

Very little IR or Raman spectroscopy of copper(III) complexes have been reported,[297] but recently the spectra of $[Cu^{II,III}(biuret)]$ have been examined by normal coordinate analysis,[1349] and the biuret ligand undergoes little change on oxidation from copper(II) to copper(III), with a general increase in the frequency of the modes of vibration.

The redox properties[1350] of $copper^{II/III}$ couples are relatively low, with $E°$ values in the region 0.57–0.78 V for the $[Cu(R_2dtc)]_2$ systems in acetone solution,.[1350,1351] In copper(II) peptide complexes,[11] the $E°$ values cover a wider range and show an interesting correlation with the ν_{max} of the copper(II) peptide electronic spectrum (Figure 109),[1352] suggesting that the square planar $Cu^{III}L_4$ chromophore is more stable the more square coplanar the copper(II) starting stereochemistry. This implies that the significant crystal field stabilization energy (CFSE) of the square coplanar CuL_4 in the higher oxidation state must make a significant contribution to the thermodynamic stability of the copper(III) peptide complexes (see ref. 11 for a more extensive discussion).[1353] The oxidation–reduction properties of the copper(III/II) couple with macrocyclic ligands also suggests a dependence upon the electronic structure of the two ions involved in the inner-sphere electron transfer pathway.[1354] The photochemistry of copper(III) complexes with macrocyclic ligands also invokes the involvement of a copper(III) macrocyclic intermediate,[1355] while the reaction of the $[Cu^{III}(enio)]^+$ cation with the I^- ion, where enio = *N,N'*-ethylenebis(isonitrosoacetylacetoneimine), suggests an inner-sphere mechanism first order in $[I^-]$.[1356] The ability of photoelectron spectroscopy to distinguish the copper(II) and copper(III) oxidation states has been reported (but see page 574).[1357,1358]

53.6.5 Biological Copper(III) Systems[1359–1362]

At present there is no X-ray crystallographic evidence to support the suggestion that the copper(II)/(III) redox cycle is present in any biological system, nevertheless this possibility should always be considered where a copper(I)/(II) redox cycle is considered.[1359] The presence of copper(III) has been suggested in the active form of galactose oxidase and all its properties are said to support this suggestion, including its ESR spectrum.[1363] As the most likely form of copper(III) in a biological system is rhombic coplanar and diamagnetic, this suggestion has been questioned,[1364] but the final outcome must await X-ray crystallographic evidence.

For the area of copper(III) peptide substrate oxidation and of copper(III) catalysis of O_2 activation,[1365] the reader is referred to ref. 11, pp. 121–123.

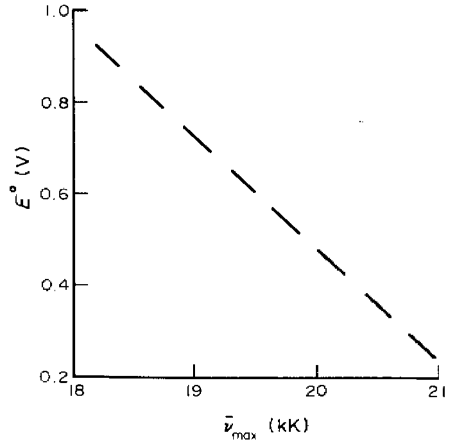


Figure 109 The correlation of the E° values for copper(II/III) complexes with the copper(II) $d-d$ electronic spectra maxima[1352]

53.7 COPPER(IV) COMPLEXES

This is one of the most limited oxidation states of copper and has only been characterized by two or three compounds with the most electronegative ligands, F^- and O^{2-}.[5,10,11,17,21] The best characterized is that of $Cs_2[CuF_6]$,[1366] which is an orange-red solid prepared by high pressure (350 atm) fluorination of $Cs[CuCl]_3$ at 410 °C. The structure probably involves an octahedral $[CuF_6]^{4-}$ anion, as the solid is paramagnetic ($\mu_{eff} = 1.5$ BM), which suggests that it is either a spin-paired complex with a $t_{2g}^6e_g^1$ configuration due to the high oxidation state or it is spin free $t_{2g}^5e_g^2$, with antiferromagnetic coupling of the three unpaired electrons. The copper(IV) oxidation state is also believed to occur[9,1367] in the complex $BaCuO_{2.63}$, which is obtained by heating $BaCuO_2$ in air. The CuO_2 species has been characterized by matrix isolation techniques and is believed to involve an O=Cu=O structure, from IR evidence, and not a peroxide (O_2^{2-}).[1368]

53.8 REFERENCES

1. Gmelin, 'Handbook of Inorganic Chemistry', Springer-Verlag, Berlin, 1955; V. M. Goldschmidt, *J. Chem. Soc., Dalton Trans.*, 1975, 656.
2. D. Mendeleev, *J. Russ. Phys. Chem. Soc.*, 1869, **1**, 60; L. S. Foster, *J. Chem. Educ.*, 1939, **16**, 409.
3. J. W. van Spronsen, 'The Periodic System of the Elements', Elsevier, Amsterdam, 1969.
4. K. L. Loening, *J. Chem. Educ.*, 1984, **61**, 136; *Chem. Br.*, 1984, **20**, 390; P. G. Nelson, *Chem. Br.*, 1985, **21**, 1077.
5. A. Massey, in 'Comprehensive Inorganic Chemistry', ed. J. C. Bailar, H. J. Emeléus, R. S. Nyholm and A. F. Trotman-Dickinson, Pergamon, Oxford, 1973, vol. 3, p. 1.
6. J. R. Partington, 'A Textbook of Inorganic Chemistry', 5th edn., Macmillan, London, 1947, p. 785.
7. D. R. Williams, 'The Metals of Life', Van Nostrand-Reinhold, New York, 1971.
8. D. A. Phipps, 'Metals and Metabolism', Clarendon, Oxford, 1976.
9. H. Gampp and A. D. Zuberbuhler, in 'Metal Ions in Biological Systems', ed. H. Sigel, Dekker, New York, 1981, vol. 12, p. 133.
10. A. F. Wells, 'Structural Inorganic Chemistry', 5th edn., Clarendon, Oxford, 1984; 1st edn., 1945; 2nd edn., 1950; 3rd edn., 1962; 4th edn., 1975.
11. D. W. Margerum and G. D. Owens, in 'Metal Ions in Biological Systems', ed. H. Sigel, Dekker, New York, 1981, vol. 12, p. 75.
12. N. V. Sidgwick, 'Chemical Elements and Their Compounds', Clarendon, Oxford, 1949, vol. 1, p. 103.
13. C. K. Jorgenson, 'Adsorption Spectra and Chemical Bonding', Academic, London, 1962; 'Inorganic Complexes', Academic, London, 1963.
14. J. D. Dunitz and L. E. Orgel, *J. Phys. Chem. Solids*, 1957, **3**, 20.
15. H. A. Jahn and E. Teller, *Proc. R. Soc. London, Ser. A*, 1937, **161**, 220.
16. P. J. Durant and B. Durant, 'An Introduction to Advanced Inorganic Chemistry', Longman, London, 1962.
17. F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry', Wiley Interscience, New York; (a) 1st edn., 1952; (b) 2nd edn., 1960; (c) 3rd edn., 1970; (d) 4th edn., 1980.
18. R. W. G. Wyckoff, 'Crystal Structures', 2nd edn., Interscience, New York, 1965, vol. 1.
19. K. M. Mackay and R. A. Mackay, 'Introduction to Modern Inorganic Chemistry', Intertext Books, London, 3rd edn., 1981.

20. J. E. Huheey, 'Inorganic Chemistry: Principles of Structure and Reactivity', 3rd edn., Harper International, Cambridge, 1983.
21. N. N. Greenwood and A. Earnshaw, 'Chemistry of the Elements', Pergamon, Oxford, 1984.
22. W. E. Hatfield and R. Whyman, *Transition Met. Chem.*, 1969, **47,** 5.
23. F. H. Jardin, *Adv. Inorg. Chem. Radiochem.*, 1975, **17,** 115.
24. J. Peisach, P. Aisen and W. E. Blumberg (eds.), 'The Biochemistry of Copper', Academic, New York, 1966.
25. T. G. Spiro (ed.) 'Copper Proteins', Wiley International, New York, 1981; R. Lontie, 'Copper Proteins and Copper Enzymes', CRC Press, Boca Raton, FL, 1984, vol. I–III.
26. E. Ochiai, 'Bioinorganic Chemistry, An Introduction', Allyn and Bacon, Boston, 1977.
27. A. S. Brill, 'Transition Metals in Biochemistry', Springer-Verlag, Berlin, 1977.
28. (a) M. N. Hughes, 'Inorganic Chemistry of Biological Systems', 2nd edn., Wiley, Chichester, 1981; (b) R. W. Hay, 'Bio-Inorganic Chemistry', Wiley, Chichester, 1984.
29. H. Sigel (ed.), 'Metal Ions in Biological Systems', Dekker, New York, 1973–81, vol. 1–13.
30. K. D. Karlin and J. Zubieta (ed.), (a) 'Copper Coordination Chemistry: Biochemical and Inorganic Perspectives', Adenine Press, New York, 1983; (b) 'Biological and Inorganic Copper Chemistry', Adenine Press, New York, 1986.
31. J. A. Howard, K. F. Preston, R. Sutcliff and B. Mile, *J. Phys. Chem.*, 1983, **87,** 536.
32. D. McIntosh and G. A. Ozin, *J. Am. Chem. Soc.*, 1976, **98,** 3167.
33. P. G. Eller, D. C. Bradley, M. B. Hursthouse and D. W. Meek, *Coord. Chem. Rev.*, 1977, **24,** 1.
34. J. P. Fackler, *Prog. Inorg. Chem.*, 1975, **19,** 55.
35. S. G. Murray and F. R. Hartley, *Chem. Rev.*, 1981, **81,** 365.
36. Ref. 28a, p. 62.
37. D. J. Gulliver, W. Levason and M. Webster, *Inorg. Chim. Acta,* 1981, **52,** 153.
38. R. N. Keller and H. D. Wycoff, *Inorg. Synth.*, 1946, **2,** 1; G. B. Kaufman and R. P. Pinnell, *Inorg. Synth.*, 1960, **6,** 3.
39. I. M. Kolthoff and J. E. Coetzee, *J. Am. Chem. Soc.*, 1957, **79,** 1852.
40. B. J. Hathaway, D. G. Holah and J. D. Postlethwaite, *J. Chem. Soc.*, 1961, 3215.
41. P. Hemmerich and C. Sigwart, *Experientia,* 1963, **19,** 488.
42. A. I. Vogel, 'Textbook of Quantitative Inorganic Analysis', 3rd edn., Longman, 1961.
43. I. Csoregh, P. Kierkegaard and R. Norrestam, *Acta Crystallogr., Sect. B,* 1975, **31,** 314.
44. B. J. Hathaway, unpublished results.
45. J. S. Thompson and J. F. Whitney, *J. Am. Chem. Soc.*, 1983, **105,** 5488; J. S. Thompson, in ref. 898; J. S. Thompson, *J. Am. Chem. Soc.*, 1984, **106,** 4057, 8308.
46. R. J. Gillespie, *J. Chem. Soc.*, 1963, 4672.
47. B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, 1970, **5,** 143.
48. B. J. Hathaway, *Essays Chem.*, 1971, **2,** 61.
49. L. Pauling, 'Nature of the Chemical Bond', 2nd edn., Oxford University Press, 1946.
50. M. R. Truter and K. W. Rutherford, *J. Chem. Soc.*, 1962, 1748.
51. F. A. Cotton and D. M. L. Goodgame, *J. Chem. Soc.*, 1960, 5267; L. M. Engelhardt, C. Pakawatchai and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1985, 125.
52. A. H. Lewin, R. J. Michel, P. Ganis, U. Lepore and G. Avitabile, *Chem. Commun.*, 1971, 1400.
53. (a) D. A. Haitko, (b) P. C. Healy, L. M. Engelhardt, V. A. Patrick and A. H. White, *J. Chem. Soc., Dalton Trans,* 1985, 2541.
54. R. Hamaalainen, M. Ahlgren, U. Turpeinen and T. Raikas, *Cryst. Struct. Commun.*, 1979, **8,** 75.
55. S. K. Hoffmann, P. J. Corvan, P. Singh, C. N. Sethulekshmi, R. M. Metzger and W. E. Hatfield, *J. Am. Chem. Soc.*, 1983, **105,** 4608.
56. P. J. Burke, D. R. McMillin, W. R. Robinson, *Inorg. Chem.*, 1980, **19,** 1211.
57. M. G. B. Drew, T. R. Pearson, B. P. Murphy and S. M. Nelson, *Polyhedron,* 1983, **2,** 269.
58. R. J. Dickman and R. J. Doedens, *Inorg. Chem.*, 1980, **19,** 3112.
59. P. Leoni, M. Pasquali and C. A. Ghilardi, *J. Chem. Soc., Chem. Commun.*, 1983, 240.
60. G. W. Hunt, N. W. Terry, III and E. L. Amma, *Acta Crystallogr., Sect. B,* 1979, **35,** 1235.
61. E. N. Baker and G. E. Norris, *J. Chem. Soc., Dalton Trans.*, 1977, 877.
62. M. M. Olmstead, W. K. Musker and R. M. Kessler, *Transition Met. Chem.*, 1982, **7,** 140.
63. W. K. Musker, M. M. Olmstead, R. M. Kessler, M. B. Murphey, C. H. Neagly, P. B. Roush, N. L. Hill, T. L. Wolford, H. Hope, G. Delker, K. Swanson and B. V. Gorewit, *J. Am. Chem. Soc.*, 1980, **102,** 1225.
64. H. van der Meer, *J. Chem. Soc., Dalton Trans.*, 1973, 1.
65. L. L. Diaddario, Ph.D. Thesis, Wayne State University, 1979.
66. E. R. Dockal, L. L. Diaddario, M. D. Glick and D. B. Rorabacher, *J. Am. Chem. Soc.*, 1977, **99,** 4530.
67. A. P. Gaughan, Z. Dori and J. A. Ibers, *Inorg. Chem.*, 1974, **13,** 1657.
68. S. J. Lippard and K. M. Melmed, *J. Am. Chem. Soc.*, 1967, **89,** 3929.
69. F. Takusagawa, A. Fumagalli, T. F. Koetzle, S. G. Shore, T. Schmitkons, A. V. Fratini, K. W. Morse, C.-Y. Wei and R. Bau, *J. Am. Chem. Soc.*, 1981, **103,** 5165; R. J. Spohas, *Inorg. Chim. Acta,* 1986, **118,** 99.
70. S. L. Lippard and K. M. Melmed, *Inorg. Chem.*, 1969, **8,** 2755.
71. E. W. Ainscough, E. N. Baker, A. M. Brodie, N. G. Larsen and K. L. Brown, *J. Chem. Soc., Dalton Trans.*, 1981, 1746.
72. B. E. Green, C. H. L. Kennard, C. J. Hawkins, G. Smith, B. D. James and A. H. White, *Acta Crystallogr., Sect. B,* 1980, **36,** 2407.
73. G. R. Brubaker, J. N. Brown, M. K. Yoo, T. M. Kutchan and E. A. Mottel, *Inorg. Chem.*, 1979, **18,** 299.
74. J. S. Thompson, J. J. Marks and J. A. Ibers, *J. Am. Chem. Soc.*, 1979, **101,** 4180.
75. P. G. Eller and G. J. Kubas, *J. Am. Chem. Soc.*, 1977, **99,** 4346.
76. J. Bojes, T. Chivers and P. W. Codding, *J. Chem. Soc., Chem. Commun.*, 1981, 1171.
77. A. Pignedoli and G. Peyronel, *Spectrochim. Acta, Ser. A,* 1980, **36,** 885.
78. S. Jeannin, Y. Jeannin and G. Lavigne, *Inorg. Chem.*, 1979, **18,** 3528.
79. F. Cariati, L. Naldini, A. Panzanelli, F. Demartin and M. Manassero, *Inorg. Chim. Acta,* 1983, **69,** 117.

80. G. G. Messmer and G. J. Palenik, *Inorg. Chem.*, 1969, **8**, 2750.
81. W. A. Anderson, A. J. Carty, G. J. Palenik and G. Schreiber, *Can. J. Chem.*, 1971, **49**, 761.
82. M. G. B. Drew, A. H. B. Othman, D. A. Edwards and R. Richards, *Acta Crystallogr., Sect. B*, 1975, **31**, 2695.
83. M. W. Bartlett, Ph.D. Thesis, University of Waterloo, 1970.
84. O. M. A. Salah, M. I. Bruce, P. J. Lohmeyer, C. L. Raston, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1981, 962.
85. (a) B. E. Green, C. H. L. Kennard, G. Smith, B. D. James and A. H. White, *Acta Crystallogr., Sect. C*, 1984, **40**, 426; (b) A. L. Reingold and M. E. Fountain, *J. Crystallogr. Spectrosc. Res.*, 1984 **14**, 549.
86. R. R. Gagne, J. L. Allison and G. C. Lisensky, *Inorg. Chem.*, 1978, **17**, 3563.
87. K. D. Karlin, P. L. Dahlstrom, M. L. Stanford and J. Zubieta, *J. Chem. Soc., Chem. Commun.*, 1979, 465.
88. K. D. Karlin, P. L. Dahlstrom, J. R. Hyde and J. Zubieta, *J. Chem. Soc., Chem. Commun.*, 1980, 906.
89. J. Zubieta, K. D. Karlin and J. C. Hayes, in ref. 30, Fig. 7, p. 101.
90. R. B. Roof, Jr., A. C. Larson and D. T. Cromer, *Acta Crystallogr., Sect. B*, 1968, **24**, 269.
91. R. W. R. Corfield, C. Ceccarelli, M. D. Glick, I. W.-Y. Moy, L. A. Ochrymowycz and D. B. Rorabacher, *J. Am. Chem. Soc.*, 1985, **107**, 2399.
92. M. S. Weininger, G. W. Hunt and E. L. Amma, *J. Chem. Soc., Chem. Commun.*, 1972, 1140.
93. D. Coucouvanis, C. N. Murphy and S. K. Kanodia, *Inorg. Chem.*, 1980, **19**, 2993.
94. P. G. Eller and P. W. R. Corfield, *Chem. Commun.*, 1971, 105.
95. A. H. Lewin, R. J. Michl, P. Ganis and U. Lepore, *J. Chem. Soc., Chem. Commun.*, 1972, 661.
96. K. D. Karlin, Y. Gulteh, J. C. Hayes and J. Zubieta, *Inorg. Chem.*, 1984, **23**, 519.
97. C. Kappenstein and R. P. Hugel, *Inorg. Chem.*, 1978, **17**, 1945.
98. P. C. Healy, C. Pakawatchai and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1983, 1917.
99. P. H. Davis, R. L. Belford and I. C. Paul, *Inorg. Chem.*, 1973, **12**, 213.
100. G. W. Hunt and E. L. Amma, *J. Chem. Soc., Chem. Commun.*, 1973, 869.
101. E. W. Ainscough, A. M. Brodie and K. L. Brown, *J. Chem. Soc., Dalton Trans.*, 1980, 1042.
102. D. A. Haitko, *J. Coord. Chem.*, 1984, **13**, 119.
103. (a) J. V. Dagdigan, V. McKee and C. A. Reed, *Inorg. Chem.*, 1982, **21**, 1332; (b) E. R. Atkinson, D. J. Gardiner, A. R. W. Jackson and E. S. Raper, *Inorg. Chim. Acta*, 1985, **98**, 35; (c) G. A. Bowmaker, G. R. Clark, D. A. Rogers, A. Camus and N. Marsich, *J. Chem. Soc., Dalton Trans.*, 1984, 37.
104. R. J. Restivo, A. Costin, G. Ferguson and A. J. Carty, *Can. J. Chem.*, 1975, **53**, 1949.
105. (a) M. Asplund, S. Jagner and M. Nilsson, *Acta Chem. Scand., Ser. A*, 1983, **37**, 57; (b) N. P. Rath and E. M. Holt, *J. Chem. Soc., Chem. Commun.*, 1986, 665.
106. M. Asplund, S. Jagner and M. Nilsson, *Acta Chem. Scand., Ser. A*, 1984, **38**, 57.
107. T. Sakurai, K. Kobayashi, H. Masuda, S. Tsuboyama and K. Tsuboyama, *Acta Crystallogr., Sect. C*, 1983, **39**, 334.
108. I. D. Brown and J. D. Dunitz, *Acta Crystallogr.*, 1961, **14**, 480.
109. M. J. Schilstra, P. J. M. W. L. Birker, G. C. Verschoor and J. Reedijk, *Inorg. Chem.*, 1982, **21**, 2637.
110. S. A. Koch, R. Fikar, M. Miller and T. O'Sullivan, *Inorg. Chem.*, 1984, **23**, 121.
111. (a) H. A. Henrickson, B. Stoberg and R. Osterberg, *J. Chem. Soc., Chem. Commun.*, 1976, 130; (b) H. Hope, M. M. Olmstead, P. P. Power, J. Sandell and X. Xu, *J. Am. Chem. Soc.*, 1985, **107**, 4337; (c) C. Eaborn, P. B. Hitchcock, J. D. Smith and A. C. Sullivan, *J. Organomet. Chem.*, 1984, **263**, 23; (d) G. Dessy, V. Fares, P. Imperatori and G. O. Morpurgo, *J. Chem. Soc., Dalton Trans.*, 1985, 1285.
112. R. R. Gagne, J. L. Allison, R. S. Gall and C. A. Koval, *J. Am. Chem. Soc.*, 1977, **99**, 7170.
113. M. G. B. Drew, C. Cairns, S. G. McFall and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1980, 2020.
114. M. R. Churchill and F. J. Rotella, *Inorg. Chem.*, 1979, **18**, 166.
115. W. Clegg, S. R. Acott and C. D. Garner, *Acta Crystallogr., Sect. C*, 1984, **40**, 768.
116. T. Ottersen, L. G. Warner and K. Seff, *Inorg. Chem.*, 1974, **13**, 1904.
117. M. Asplund and S. Jagner, *Acta Chem. Scand., Ser. A*, 1984, **38**, 129.
118. M. Bolte and M. Massaux, *Inorg. Chim. Acta*, 1981, **52**, 191.
119. H. Negita, M. Hiura, Y. Kushi, M. Kuramoto and T. Okuda, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 1247.
120. J. A. Campbell, C. L. Raston and A. H. White, *Aust. J. Chem.*, 1977, **30**, 1937.
121. P. C. Healy, C. Pakawatchai, C. L. Ralston, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1983, 1905.
122. M. Asplund and S. Jagner, *Acta Chem. Scand., Ser. A*, 1984, **38**, 297.
123. P. G. Eller and R. R. Ryan, *Acta Crystallogr., Sect. B*, 1977, **33**, 619.
124. P. G. Eller, G. J. Kubas and R. R. Ryan, *Inorg. Chem.*, 1977, **16**, 2454.
125. N. P. Rath, E. M. Holt and K. Tanimura, *J. Chem. Soc., Dalton Trans.*, 1986, 2303.
126. L. M. Engelhardt, R. I. Papasegio and A. H. White, *Aust. J. Chem.*, 1984, **37**, 2207.
127. R. Graziani, G. Bombieri and E. Forsellini, *J. Chem. Soc. (A)*, 1971, 2331.
128. A. Pignedoli and G. Peyronel, *Acta Crystallogr., Sect. B*, 1979, **35**, 2009.
129. M. Pasquali, P. Fiaschi, C. Floriani and A. Gaetani-Manfredotti, *J. Chem. Soc., Chem. Commun.*, 1983, 197.
130. I. G. Dance, P. J. Guerney, A. D. Rae and M. L. Scudder, *Inorg. Chem.*, 1983, **22**, 2883.
131. J. R. Creighton, D. J. Gardiner, A. C. Gorvin, C. Gutteridge, A. R. W. Jackson, E. S. Raper and P. M. A. Sherwood, *Inorg. Chim. Acta*, 1985, **103**, 195.
132. R. H. Lane, N. S. Pantaleo, J. K. Farr, W. M. Coney and M. G. Newton, *J. Am. Chem. Soc.*, 1978, **100**, 1610.
133. C. S. Arcus, J. L. Wilkinson, C. Mealli, T. J. Marks and J. A. Ibers, *J. Am. Chem. Soc.*, 1974, **96**, 7564; 1976, **98**, 711.
134. S. M. Nelson, F. S. Esho and M. G. B. Drew, *J. Chem. Soc., Chem. Commun.*, 1981, 358.
135. R. F. Ziolo, A. P. Gaughan, Z. Dori, C. G. Pierpoint and R. Eisenberg, *Inorg. Chem.*, 1971, **10**, 1289; *J. Am. Chem. Soc.*, 1970, **92**, 738.
136. K. D. Karlin, J. R. Hyde and J. Zubieta, *Inorg. Chim. Acta*, 1982, **66**, L23; M. Asplund and S. Jagner, *Acta Chem. Scand., Ser. A*, 1985, **39**, 47; E. R. Atkinson, E. S. Raper, D. J. Gardiner, H. M. Dawes, M. P. C. Walker and A. R. W. Jackson, *Inorg. Chim. Acta*, 1985, **100**, 285; N. Aoi, Y. Takano, H. Ogino, G. Matsubayashi and T. Tanaka, *J. Chem. Soc., Chem. Commun.*, 1985, 703.

137. S. M. Nelson, ref. 30, p. 358.
138. R. R. Gagne, R. P. Kreh and J. A. Dodge, *J. Am. Chem. Soc.*, 1979, **101**, 6917.
139. T. N. Sorrell and D. L. Jameson, *J. Am. Chem. Soc.*, 1982, **104**, 2053.
140. K. D. Karlin, Y. Gultneh, J. P. Hutchinson and J. Zubieta, *J. Am. Chem. Soc.*, 1982, **104**, 5240.
141. K. D. Karlin, J. C. Hayes, Y. Gultneh, R. W. Cruse, J. W. Mckowen, J. P. Hutchinson and J. Zubieta, *J. Am. Chem. Soc.*, 1984, **106**, 2121; K. D. Karlin, J. C. Hayes, J. P. Hutchinson and J. Zubieta, *Inorg. Chim. Acta*, 1983, **78**, L45.
142. T. N. Sorrell, M. R. Malachowski and D. L. Jameson, *Inorg. Chem.*, 1982, **21**, 3250.
143. T. B. Rauchfuss, S. R. Wilson and D. L. Wrobleski, *J. Am. Chem. Soc.*, 1981, **103**, 6769.
144. R. R. Gagne, R. P. Kreh, J. A. Dodge, R. E. Marsh and M. McCool, *Inorg. Chem.*, 1982, **21**, 254.
145. H. M. J. Hendriks, P. J. M. W. L. Birker, J. van Rijn, G. C. Verschoor and J. Reedijk, *J. Am. Chem. Soc.*, 1982, **104**, 3607.
146. E. S. Raper, *Coord. Chem. Rev.*, 1985, **11**, 115.
147. D. M. Ho and R. Bau, *Inorg. Chem.*, 1983, **22**, 4079.
148. N. Bresciani, N. Marsich, G. Nardin and L. Randaccio, *Inorg. Chim. Acta*, 1974, **10**, L5.
149. G. Nardin, L. Randaccio and E. Zangrando, *J. Chem. Soc., Dalton Trans.*, 1975, 2566.
150. A. Muller and U. Schimanski, *Inorg. Chim. Acta*, 1983, **77**, L187.
151. J. A. Tiethof, J. K. Stalick, P. W. R. Corfield and D. W. Meek, *J. Chem. Soc., Chem. Commun.*, 1972, 1141.
152. A. G. Gash, E. H. Griffith, W. A. Spofford, III and E. L. Amma, *J. Chem. Soc., Chem. Commun.*, 1973, 256.
153. A. Camus, N. Marsich, G. Nardin and L. Randaccio, *J. Organomet. Chem.*, 1973, **60**, C39.
154. J. C. Dyason, P. C. Healy, L. M. Engelhardt, C. Pakawatchai, V. A. Patrick, C. L. Ratson and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1985, 839.
155. J. E. O'Connor, G. A. Janusonis and E. R. Corey, *Chem. Commun.*, 1968, 445.
156. P. F. Rodesiler and E. L. Amma, *J. Chem. Soc., Chem. Commun.*, 1974, 599.
157. M. Berry, W. Clegg, C. D. Garner and I. H. Hillier, *Inorg. Chem.*, 1982, **21**, 1342.
158. F. L. Carter and E. W. Hughes, *Acta Crystallogr.*, 1957, **10**, 801.
159. J. A. J. Jarvis, B. T. Kilboum, R. Pearce and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 1973, 475.
160. K. Wade, in 'Transition Metal Clusters', ed. B. Johnson, Wiley, Chichester, 1980, p. 193.
161. T. Greiser and E. Weiss, *Chem. Ber.*, 1976, **109**, 3142.
162. A. N. Nesmeyanov, Yu. T. Struchkov, N. N. Sedova, V. G. Andrianova, Yu. V. Valgin and V. A. Sazonova, *J. Organomet. Chem.*, 1977, **137**, 217.
163. (a) R. G. Vranka and E. L. Amma, *J. Am. Chem. Soc.*, 1966, **88**, 4270. (b) M. Asplund and S. Jagner, *Acta Chem. Scand., Ser. A*, 1984, **38**, 725.
164. A. M. Manotti-Lanfredi, A. Tiripicchio, A. Camus and N. Marsich, *J. Chem. Soc., Chem. Commun.*, 1983, 1126.
165. G. van Koten and J. G. Noltes, *J. Organomet. Chem.*, 1975, **84**, 129.
166. S. L. Lawton, W. J. Rohrbaugh and G. J. Kokotailo, *Inorg. Chem.*, 1972, **11**, 612.
167. H. Hope and P. P. Power, *Inorg. Chem.*, 1984, **23**, 936.
168. M. R. Churchill and K. L. Kalra, *Inorg. Chem.*, 1974, **13**, 1899.
169. M. R. Churchill B. G. De Boer and S. J. Mendak, *Inorg. Chem.*, 1975, **14**, 2041.
170. J. C. Dyason, P. C. Healy, L. M. Engelhardt, V. A. Patrick, C. L. Raston and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1985, 831.
171. V. Schramm, *Cryst. Struct. Commun.*, 1980, **9**, 1231.
172. G. Davies and M. A. El-Sayed, in ref. 30, p. 281.
173. M. R. Churchill, G. Davies, M. A. El-Sayed, J. P. Hutchinson and M. W. Rupich, *Inorg. Chem.*, 1982, **21**, 995.
174. M. R. Churchill and W. J. Young, *Inorg. Chem.*, 1979, **18**, 1133.
175. P. F. Barron, J. C. Dyson, L. M. Engelhardt, P. C. Healy and A. H. White, *Inorg. Chem.*, 1984, **23**, 3766.
176. F. G. Mann, D. Purdie and A. F. Wells, *J. Chem. Soc.*, 1936, 1503; B.-T. Teo and J. C. Calabrese, *Inorg. Chem.*, 1976, **15**, 2474.
177. R. G. Goel and A. L. Beauchamp, *Inorg. Chem.*, 1983, **22**, 395.
178. J. S. Filippo, Jr., L. E. Zyontz and J. Potenza, *Inorg. Chem.*, 1975, **14**, 1667.
179. R. Hesse, *Ark. Kemi*, 1964, **20**, 481.
180. R. Hesse and U. Aava, *Acta Chem. Scand.*, 1970, **24**, 1355.
181. G. A. Bowmaker, G. R. Clark and D. K. P. Yuen, *J. Chem. Soc., Dalton Trans.*, 1976, 2329; M. Asplund and S. Jagner, *Acta Chem. Scand., Ser. A*, 1984, **38**, 725.
182. E. H. Griffith, G. W. Hunt and E. L. Amma, *J. Chem. Soc., Chem. Commun.*, 1976, 432.
183. G. A. Bowmaker and L. C. Tan, *Aust. J. Chem.*, 1979, **32**, 1443.
184. I. G. Dance and J. C. Calabrese, *Inorg. Chim. Acta*, 1976, **19**, L41; G. A. Bowmaker, G. R. Clark and J. K. Seadon, *Polyhedron*, 1984, **3**, 535.
185. C. P. Huber, M. L. Post and O. Siiman, *Acta Crystallogr., Sect. B*, 1978, **34**, 2629.
186. M. R. Churchill and K. L. Kalra, *Inorg. Chem.*, 1974, **13**, 1427; M. R. Churchill, B. G. De Boer and D. J. Donovan, *Inorg. Chem.*, 1975, **14**, 617.
187. M. Marsich, G. Nardin and L. Randaccio, *J. Am. Chem. Soc.*, 1973, **95**, 4053.
188. P. W. R. Corfield and H. M. M. Shearer, *Acta Crystallogr.*, 1966, **21**, 957.
189. I. G. Dance, *Aust. J. Chem.*, 1978, **31**, 2195.
190. P. Murray-Rust, P. Day and C. K. Prout, *Chem. Commun.*, 1966, 277.
191. S. A. Bezman, M. R. Churchill, J. A. Osborn and J. Wormold, *J. Am. Chem. Soc.*, 1971, **93**, 2063; M. R. Churchill, S. A. Bezman, J. A. Osborn and J. Wormold, *Inorg. Chem.*, 1972, **11**, 1818.
192. D. M. Ho and R. Bau, *Inorg. Chim. Acta*, 1984, **84**, 213.
193. J. M. Guss, R. Mason, K. M. Thomas, G. van Koten and J. G. Noltes, *J. Organomet Chem.*, 1972, **40**, C79.
194. R. W. M. den Hoedt, J. G. Noltes, G. van Koten and A. L. Spek, *J. Chem. Soc., Dalton Trans.*, 1978, 1800.
195. G. Henkel, P. Betz and B. Krebs, *J. Chem. Soc., Chem. Commun.*, 1984; 314; A. Muller, M. Romer, H. Bogge, E. Krickemeyer and D. Bergmann, *J. Chem. Soc., Chem. Commun.*, 1984, 348.
196. J. P. Fackler, Jr. and D. Coucouvanis, *J. Am. Chem. Soc.*, 1966, **88**, 3913; L. E. McCandlish, E. C. Bissell, D. Coucouvanis, J. P. Fackler and K. Knox, *J. Am. Chem. Soc.*, 1968, **90**, 7357.

197. F. J. Hollander and D. Coucouvanis, *J. Am. Chem. Soc.*, 1977, **99**, 6268, 8057.
198. P. Betz, B. Krebs and G. Henkel, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 311.
199. D. M. Adams, 'Inorganic Solids', Wiley, London, 1974, chap. 4.
200. D. T. Cromer, *J. Phys. Chem.*, 1957, **61**, 1388.
201. A. F. Wells 'Models in Structural Inorganic Chemistry', Clarendon, Oxford, 1970.
202. C. I. Branden, *Acta Chem. Scand.*, 1967, **21**, 1000.
203. A. Mosset, M. Abboudi and J. Galy, *Z. Kristallogr.*, 1983, **164**, 181.
204. J. A. Campbell, C. L. Raston and A. H. White, *Aust. J. Chem.*, 1977, **30**, 1937.
205. C. Brink and C. H. MacGillavry, *Acta Crystallogr.*, 1949, **2**, 158.
206. C. K. Prout and P. Murray-Rust, *J. Chem. Soc. (A)*, 1969, 1520.
207. C. J. Simmons, M. Lundeen and K. Seff, *J. Chem. Soc., Chem. Commun.*, 1979, 595; *Inorg. Chem.*, 1979, **18**, 3444.
208. J. C. Barnes and J. D. Paton, *Acta Crystallogr., Sect. B*, 1982, **38**, 3091.
209. G. O. Morpurgo, G. Dessy and V. Fares, *J. Chem. Soc., Dalton Trans.*, 1984, 785.
210. H. Hartung, *Z. Anorg. Allg. Chem.*, 1970, **372**, 150.
211. Y. Kinoshita, I. Matsubara and Y. Saito, *Bull. Chem. Soc. Jpn.*, 1959, **32**, 741.
212. M. Asplund and S. Jagner, *Acta Chem. Scand.*, 1984, **38**, 129.
213. (a) C. Bink, N. F. Binnendijk and J. van der Linde, *Acta Crystallogr.*, 1954, **7**, 176; (b) M. Asplund and S. Jagner, *Acta Chem. Scand., Ser. A*, 1984, **38**, 807.
214. C. Romming and K. Waerdstad, *Chem. Commun.*, 1965, 299.
215. H. Hartl and F. Mahdjour-Hassan-Abadi, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 772.
216. H. Hartl and F. Mahdjour-Hassan-Abadi, *Z. Naturforsch., Teil B*, 1984, **39**, 149.
217. P. M. Boorman, K. A. Kerr, R. A. Kydd, K. J. Moynihan and K. A. Valentine, *J. Chem. Soc., Dalton Trans.*, 1982, 1401.
218. A. Mosset, M. Abboudi and J. Galy, *Z. Kristallogr.*, 1983, **164**, 171.
219. M. Massaux, M.-J. Bernard and M.-J. le Bihan, *Acta Crystallogr., Sect. B.*, 1971, **27**, 2419.
220. P. J. Fisher, N. E. Taylor and M. M. Harding, *J. Chem. Soc.*, 1960, 2303.
221. I. D. Brown and J. D. Dunitz, *Acta Crystallogr.*, 1960, **13**, 28.
222. (a) R. D. Mounts, T. Ogura and Q. Fernando, *Inorg. Chem.*, 1974, **13**, 802; (b) K. Lijima, T. Itoh and S. Shibata, *J. Chem. Soc., Dalton Trans.*, 1985, 2555.
223. M. G. A. Drew, D. A. Edwards and R. Richards, *J. Chem. Soc., Chem. Commun.*, 1973, 124.
224. D. T. Cromer, A. C. Larsen and R. B. Roof, *Acta Crystallogr.*, 1966, **20**, 279.
225. D. T. Cromer, A. C. Allen, A. C. Larsen and R. B. Roof, *Acta Crystallogr.*, 1965, **19**, 192.
226. J. F. Blount, H. C. Freeman, P. Hemmerich and C. Sigwart, *Acta Crystallogr., Sect. B*, 1969, **25**, 1518.
227. Ref. 10, p. 410.
228. Ref. 10, p. 125.
229. D. L. Smith and V. L. Saunders, *Acta Crystallogr., Sect. B*, 1982, **38**, 907.
230. C. L. Raston, B. Walter and A. H. White, *Aust. J. Chem.*, 1979, **32**, 2757.
231. M. Pasquali and C. Floriani, in ref. 30, p. 311.
232. M. I. Bruce, *J. Organomet. Chem.*, 1972, **44**, 209.
233. A. L. Kohl and F. C. Rusenfield, 'Gas Purification', McGraw-Hill, New York, 1960; W. Bracken and R. Vestin, *Acta Chem. Scand., Ser. A*, 1979, **33**, 85.
234. A. F. Scott, L. L. Wilkening and B. Rubin, *Inorg. Chem.*, 1969, **8**, 2533.
235. M. I. Bruce and A. P. P. Ostazewski, *J. Chem. Soc., Chem. Commun.*, 1972, 1124; M. R. Churchill, B. D. DeBoer, F. J. Rotella, O. M. Abu Salah and M. I. Bruce, *Inorg. Chem.*, 1975, **14**, 2051.
236. M. Pasquali, F. Marchetti and C. Floriani, *Inorg. Chem.* 1978, **17**, 1684.
237. M. Pasquali, C. Floriani and A. Gaetani-Manfredotti, *J. Chem. Soc., Chem. Commun.*, 1978, 921; *Inorg. Chem.*, 1980, **19**, 1191.
238. M. Pasquali, C. Floriani and A. Gaetani-Manfredotti, *Inorg. Chem.*, 1981, **20**, 3382.
239. M. Pasquali, C. Floriani, A. Gaetani-Manfredotti and C. Gaustini, *J. Chem. Soc., Chem. Commun.*, 1979, 197; *Inorg. Chem.*, 1980, **19**, 2525.
240. M. Pasquali, C. Floriani, G. Venturi, A. Gaetani-Manfredotti and A. Chiesi-Villa, *J. Am. Chem. Soc.*, 1982, **104**, 4092.
241. Y. Souma, J. Iyoda and H. Sano, *Inorg. Chem.*, 1976, **15**, 968.
242. T. Ogura, *Inorg. Chem.*, 1976, **15**, 2301.
243. R. R. Gagne. C. A. Koval and T. J. Smith, *J. Am. Chem. Soc.*, 1977, **99**, 8367.
244. C. D. Desjardins, D. B. Edwards and J. Passmore, *Can. J. Chem.*, 1979, **57**, 2714.
245. S. Kitagawa and M. Munakata, *Inorg. Chem.*, 1981, **20**, 2261.
246. T. Tsuda, H. Habu, S. Horiguchi and T. Saegusa, *J. Am. Chem. Soc.*, 1974, **96**, 5930.
247. R. L. Geerts, J. C. Huffman, K. Folting, T. H. Lemmen and K. G. Caulton, *J. Am. Chem. Soc.*, 1983, **105**, 3503.
248. M. Pasquali, P. Fiaschi, C. Floriani and P. F. Zanazzi, *J. Chem. Soc., Chem. Commun.*, 1983, 613.
249. J. S. Thompson and J. F. Whitney, *Inorg. Chem.*, 1984, **23**, 2813.
250. G. Doyle, K. A. Eriksen and D. van Engen, *Inorg. Chem.*, 1983, **22**, 2892.
251. D. T. Clark, A. Sgamellotti and F. Tarantelli, *Inorg. Chem.*, 1981, **20**, 2602.
252. J. Marsh, 'Advanced Organic Chemistry: Reactions, Mechanism and Structure', McGraw-Hill, New York, 1968, p. 417; T. Tsuda, M. Miwa and T. Saegusa, *J. Org. Chem.*, 1979, 3734.
253. A. W. Addison, H. M. J. Hendricks, J. Reedijk and L. K. Thompson, *Inorg. Chem.*, 1981, **20**, 103.
254. R. R. Gagne, R. S. Gall, G. C. L. Lisensky, R. E. Marsh and L. M. Speltz, *Inorg. Chem.*, 1979, **18**, 771.
255. R. Guan, H. Hashimoto and T. Yoshida, *Acta Crystallogr., Sect. B*, 1984, **40**, 109.
256. H. W. Quin and J. H. Tsai, *Adv. Inorg. Chem. Radiochem.*, 1968, **12**, 217.
257. G. van Koten and J. G. Noltes, in 'Comprehensive Organometallic Chemistry', ed. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, 1982, vol. 2, p. 709.

258. Ref. 1, 'Organo Copper Compounds', part 2, 1983.
259. D. M. P. Mingos, in 'Comprehensive Organometallic Chemistry', ed. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, 1982, vol. 3, p. 1.
260. L. T. J. Delabaere, D. W. McBride and R. B. Ferguson, *Acta Crystallogr., Sect. B*, 1970, **26**, 515.
261. F. A. Cotton and J. Takats, *J. Am. Chem. Soc.*, 1970, **92**, 2353.
262. R. W. Turner and E. L. Amma, *J. Am. Chem. Soc.*, 1963, **85**, 4046.
263. J. H. van den Hende and W. C. Baird, *J. Am. Chem. Soc.*, 1963, **85**, 1009.
264. N. C. Baenziger, H. L. Haight and J. R. Doyle, *Inorg. Chem.*, 1964, **3**, 1535.
265. R. W. M. ten Hoedt, J. G. Noltes, G. van Koten and A. L. Spek, *J. Chem. Soc., Dalton Trans.*, 1978, 1800.
266. N. C. Baenziger, G. F. Richards and J. R. Doyle, *Inorg. Chem.*, 1964, **3**, 1529.
267. D. Blake, G. Calvin and G. E. Coates, *J. Chem. Soc.*, 1959, 396.
268. M. Pasquali, C. Floriani, A. Gaetini-Manfredotti and A. Chiesi-Villa, *Inorg. Chem.*, 1979, **18**, 3535; *J. Am. Chem. Soc.*, 1978, **100**, 4918.
269. J. S. Thompson and J. F. Whitney, *Acta Crystallogr., Sect. C*, 1984, **40**, 756.
270. J. S. Thompson, R. L. Harlow and J. F. Whitney, *J. Am. Chem. Soc.*, 1983, **105**, 3522.
271. O. M. A. Salah, M. I. Bruce and J. D. Walsh, *Aust. J. Chem.*, 1979, **32**, 1209.
272. S. M. Nelson, in ref. 30, p. 364.
273. M. Pasquali, P. Leoni, C. Floriani and A. Gaetani-Manfredotti, *Inorg. Chem.*, 1982, **21**, 4324.
274. S. M. Nelson, in ref. 30, p. 357.
275. L. Banci, A. Bencini, A. Dei and D. Gatteschi, *Inorg. Chim. Acta*, 1984, **84**, L11.
276. W. Clegg, C. D. Garner and J. R. Nicholson, *Acta Crystallogr., Sect. C*, 1983, **39**, 552.
277. C. Potvin, J. M. Manoli, M. Salis and F. Secheresse, *Inorg. Chim. Acta*, 1984, **83**, L19.
278. W. Clegg, C. D. Garner, J. R. Nicholson and P. R. Raithby, *Acta Crystallogr., Sect. C*, 1983, **39**, 1007.
279. S. R. Acott, C. D. Garner, J. R. Nicholson, and W. Clegg, *J. Chem. Soc., Dalton Trans.*, 1983, 713.
280. (a) S. Bristow, C. D. Garner and W. Clegg, *Inorg. Chim. Acta*, 1983, **76**, L261; (b) P. Nierkegard and B. Nyberg, *Acta Chem. Scand.*, 1965, **19**, 2189.
281. A. Muller, T. K. Hwang and H. Bogge, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 628.
282. R. Doherty, C. R. Hubbard, A. D. Mighell, A. R. Siedle and J. Stewart, *Inorg. Chem.*, 1979, **18**, 2991.
283. F. Cecconi, C. A. Ghilardi, S. Midolini and A. Orlandini, *Angew. Chem. Suppl.*, 1983, 718.
284. L. F. Rhodes, J. C. Huffman and K. G. Caulton, *J. Am. Chem. Soc.*, 1983, **105**, 5137.
285. V. Bel'sky, V. M. Ishchenko, B. M. Bulychev and G. L. Soloveichik, *Polyhedron*, 1984, **3**, 749.
286. M. R. Churchill and S. A. Bezman, *Inorg. Chem.*, 1974, **13**, 1418; V. G. Albano, D. Braga, S. Martinengo, P. Chini, M. Sansoni and D. Strumolo, *J. Chem. Soc., Dalton Trans.*, 1980, 52.
287. L. Carlton, W. E. Lindsell, K. J. McCullough and P. N. Preston, *J. Chem. Soc., Chem. Commun.*, 1983, 216.
288. G. B. Ansell, M. A. Moderick and J. S. Bradley, *Acta Crystallogr., Sect. C*, 1984, **40**, 365.
289. R. R. Gagne, J. L. Allison, C. A. Koval, W. S. Mialki, T. J. Smith and R. A. Walton, *J. Am. Chem. Soc.*, 1980, **102**, 1905; R. A. Walton, *Inorg. Chem.*, 1980, **19**, 1100.
290. S. P. Cramer and K. O. Hodgson, *Prog. Inorg. Chem.*, 1979, **25**, 2; B.-K. Teo, *Acc. Chem. Res.*, 1980, **13**, 412.
291. W. E. Summers and J. E. Bulkowski, in ref. 30, p. 45.
292. M. Sano, T. Maruo and H. Yamatera, *Chem. Phys. Lett.*, 1983, **101**, 211.
293. R. G. Linford, P. G. Hall, C. Johnson and S. S. Hasnain, *SERC Daresbury Lab. Rep.*, 1984, 410E.
294. R. S. Drago, 'Physical Methods in Chemistry', Saunders, Eastbourne, 1977.
295. S. Kitagawa, M. Munakata and N. Miyaji, *Inorg. Chem.*, 1982, **21**, 3842.
296. K. Deguchi, K. Matsushita, T. Fujito, K. Endo and K. Yamamoto, *JEOL News*, 1984, **20A**, 15.
297. K. Nakamoto, 'Infrared and Raman Spectra of Inorganic and Coordination Compounds', 3rd edn., Wiley Interscience, New York, 1978.
298. D. N. Waters and B. Basak, *J. Am. Chem. Soc.*, 1971, **93**, 2733.
299. G. A. Bowmaker, L. D. Brockliss and R. Whiting, *Aust. J. Chem.*, 1973, **26**, 29.
300. G. A. Bowmaker and D. A. Rogers, *J. Chem. Soc., Dalton Trans.*, 1984, 1249.
301. O. Simon, *Inorg. Chem.*, 1981, **20**, 2285.
302. P. Leupin and C. W. Schlapfer, *J. Chem. Soc., Dalton Trans.*, 1983, 1635.
303. D. E. Nikles, A. B. Anderson and F. L. Urbach, in ref. 30, p. 203.
304. M. J. Schugar, in ref. 30, p. 43.
305. D. R. McMillin, R. E. Gamache, Jr., J. R. Kirchoff and A. A. Del Paggio in ref. 30, p. 223; B.-T. Ahn and D. R. McMillin. *Inorg. Chem.*, 1981, **20**, 1427.
306. C. Daul, C. W. Schlapfer, A. Goursot, E. Penigault and J. Weber, *Chem. Phys. Lett.*, 1981, **78**, 304.
307. J. K. Burdett and P. D. Williams, *Inorg. Chem.*, 1980, **19**, 2779.
308. D. M. P. Mingos, *Adv. Organomet. Chem.*, 1977, **15**, 1.
309. P. K. Mehrotra and R. Hoffman, *Inorg. Chem.*, 1978, **17**, 2188.
310. F. A. Cotton and T. E. Haas, *Inorg. Chem.*, 1964, **3**, 10.
311. J. M. Guss, R. Mason, I. Sotoffe, G. van Koten and J. G. Noltes, *J. Chem. Soc., Chem. Commun.*, 1972, 446.
312. M. R. Churchill and K. L. Kalra, *J. Am. Chem. Soc.*, 1973, **95**, 5772.
313. A. Avdeef and J. P. Fackler, *Inorg. Chem.*, 1978, **17**, 2182.
314. K. Wade, in 'Metal–Metal Clusters', ed. B. F. G. Johnson, Wiley, Chichester, 1980, p. 247.
315. A. Ozin, H. Huber, D. McIntosh, S. Mitchell, J. G. Norman, Jr. and L. Noodleman, *J. Am. Chem. Soc.*, 1979, **101**, 3504; E. Miyoshi, H. Tatewaki and T. Nakamura, *Int. J. Quantum Chem.*, 1983, **23**, 1201.
316. T. P. Martin and A. Kakizaki, *J. Chem. Phys.*, 1984, **80**, 3956.
317. P. S. Guimaraes and N. J. Parada, *J. Phys. Chem., Solid State Phys.*, 1984, **17**, 1695.
318. L. Ciavatta, D. Ferri and R. Palombari, *J. Inorg. Nucl. Chem.*, 1980, **42**, 593.
319. M. G. Simmons, C. L. Merrill, L. J. Wilson, L. A. Bottomley and K. M. Kadish, *J. Chem. Soc., Dalton Trans.*, 1980, 1827; C. L. Merrill, L. J. Wilson, T. J. Thamann, T. M. Loehr, N. S. Ferris and W. Woodruff, *J. Chem. Soc., Dalton Trans.*, 1984, 2207.

320. J. E. Bulkowski, P. L. Burk, M.-F. Ludmann and J. A. Osborn, *J. Chem. Soc., Chem. Commun.*, 1977, 498.
321. H. Gampp and A. D. Zuberbuhler, *Chimia*, 1978, **32**, 54; Zuberbuhler, in ref. 30, p. 254.
322. A. E. Martell, *Pure Appl. Chem.*, 1983, **55**, 125; T. G. Spiro, 'Metal Activation of Dioxygen', Wiley Interscience, New York, 1980.
323. M. Munakata, S. Nishibayashi and H. Sakamoto, *J. Chem. Soc., Chem. Commun.*, 1980, 219; ref. 30, p. 473.
324. M. G. Burnett, V. McKee and S. M. Nelson, *J. Chem. Soc., Chem. Commun.*, 1980, 829.
325. K. D. Karlin, P. L. Dahlstrom, S. N. Cozzette, P. M. Scensny and J. J. Zubieta, *J. Chem. Soc., Chem. Commun.*, 1981, 881.
326. H. Praliaud, Y. Kodratoff, G. Coudurier and M. V. Mathieu, *Spectrochim. Acta, Ser. A*, 1974, **30**, 1389.
327. G. Davies, M. A. El-Sayed and R. E. Fasano, *Inorg. Chim. Acta*, 1983, **71**, 95; *Inorg. Chem.*, 1983, **22**, 1257.
328. G. Davis and M. A. El-Sayed in ref. 30, p. 281; A. El-Toukhy, G.-Z. Cai, G. Davies, T. R. Gilbert, K. D. Onan and M. Veidis, *J. Am. Chem. Soc.*, 1984, **106**, 4596.
329. F. R. Hopf, M. M. Rogic and J. F. Wolf, *J. Phys. Chem.*, 1983, **87**, 4681.
330. E. Balogh-Hergovich and G. Speier, *Inorg. Chim. Acta*, 1984, **84**, 129.
331. G. Davis, M. F. El-Shazly, M. W. Rupich, M. R. Churchill and F. Rotella, *J. Chem. Soc., Chem. Commun.*, 1978, 1045; M. R. Churchill and F. J. Rotella, *Inorg. Chem.*, 1979, **18**, 853; G.-Z. Cai, G. Davies, A. El-Toukhy, T. R. Gilbert and M. Henary, *Inorg. Chem.*, 1985, **24**, 1701.
332. G. Davies, A. El-Toukhy, K. D. Onan and M. Veids, *Inorg. Chim. Acta*, 1985, **98**, 85.
333. J. E. Bulkowski and W. E. Summers, in ref. 30, Fig. 8, p. 452.
334. C. Lapinte, H. Rivière and A. Roselli, *J. Chem. Soc., Chem. Commun.*, 1981, 1109.
335. L. Wilputte-Steinert, *J. Mol. Catal.*, 1981, **10**, 151.
336. S. Goldstein and G. Czapski, *J. Am. Chem. Soc.*, 1983, **105**, 7276.
337. R. D. Gray, *J. Am. Chem. Soc.*, 1969, **91**, 56.
338. R. F. Jameson and N. J. Blackburn, *J. Chem. Soc., Dalton Trans.*, 1982, 9.
339. N. Al-Shati, A. G. Lappin and A. G. Sykes, *Inorg. Chem.*, 1981, **20**, 1466.
340. W. Zamudio, A. M. Garcia and E. Spocine, *Transition Met. Chem.*, 1983, **8**, 69.
341. M. T. Garland, E. Spodine and W. Zamudio, *J. Appl. Crystallogr.*, 1981, **14**, 475.
342. B. J. Hathaway, I. M. Procter, R. C. Slade and A. A. G. Tomlinson, *J. Chem. Soc. (A)*, 1969, 2219.
343. J. Salazar, R. Baraona and W. Zamudio, *J. Inorg. Nucl. Chem.*, 1981, **43**, 2881.
344. N. Marsich and A. Camus, *J. Inorg. Nucl. Chem.*, 1977, **39**, 275.
345. T. Ikariya and A. Yamamoto, *J. Organomet. Chem.*, 1974, **72**, 145; R. P. A. Sneeden, in 'Comprehensive Organometallic Chemistry', ed. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, 1982, vol. 4, chap. 50, p. 225.
346. A. Miyashita and A. Yamamoto, *J. Organomet. Chem.*, 1976, **113**, 187.
347. T. Tsuda, Y. Chujo and T. Saegusa, *J. Am. Chem. Soc.*, 1980, **102**, 431.
348. B. Sarkar, in ref. 29, 1981, vol. 12, p. 233.
349. N. Marsich, G. Nardin and L. Randaccio, *Inorg. Chim. Acta*, 1977, **23**, 131; R. F. Jamison, in ref. 29, 1981, vol. 12, p. 1.
350. R. Osterberg, *Coord. Chem. Rev.*, 1974, **12**, 309.
351. T. G. Spiro, G. L. Wollery, J. M. Brown, L. Powers, M. E. Winkler and E. I. Solomon, in ref. 30, p. 23.
352. J. M. Brown, L. Powers, B. Kincaid, J. A. Larrabee and T. G. Spiro, *J. Am. Chem. Soc.*, 1980, **102**, 4210; J. A. Larrabee and T. G. Spiro, *J. Am. Chem. Soc.*, 1980, **102**, 4217.
353. (a) E. J. M. van Schaick, W. G. Schutter, W. P. I. Gaykoma, A. M. H. Schepman and W. G. J. Hol, *Mol. Biol.*, 1982, **158**, 457; W. P. J. Gaykema, W. G. J. Hol, J. M. Vereijken, N. M. Soeter, H. J. Bak and J. J. Beintema, *Nature (London)*, 1984, **309**, 23. (b) H. C. Freeman, in 'Coordination Chemistry-21', ed. J. L. Laurent, Pergamon, Oxford, 1981, p. 29. (c) A. G. Sykes, *Chem. Soc. Rev.*, 1985, **14**, 283.
354. B. J. Hathaway and A. A. G. Tomlinson, *Coord. Chem. Rev.*, 1970, **5**, 1.
355. F. H. Jardine and F. J. Young, *J. Chem. Soc. (A)*, 1971, 2444.
356. F. H. Jardine, A. G. Vohra and F. J. Young, *J. Inorg. Nucl. Chem.*, 1971, **33**, 2941; S. J. Lippard and D. J. Ucko, *Inorg. Chem.*, 1968, **7**, 1051; S. J. Lippard and P. S. Welcker, *Inorg. Chem.*, 1972, **11**, 6.
357. J. G. M. van der Linden and P. J. M. Geurts, *Inorg. Nucl. Chem. Lett.*, 1972, **8**, 903.
358. E. Uhlig, B. Borek and H. Glauer, *Z. Anorg. Allg. Chem.*, 1966, **348**, 189.
359. W. R. McWhinnie and V. Rattanaphani, *Inorg. Chim. Acta*, 1974, **9**, 153.
360. M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 247.
361. P. Day, *Endeavour*, 1970, **20**, 45.
362. P. Day, *Int. Rev. Phys. Chem.*, 1981, **1**, 149.
363. N. S. Hush, 'Mixed Valence Compounds', Reidel, Dordrecht, 1980, p. 151.
364. F. A. Hart, J. Newbery and P. Thornton, *Annu. Rep. Chem. Soc.*, 1980, **77**, 232.
365. R. H. P. Francisco, R. H. de Almeida Santos, J. R. Lechat and A. C. Massabni, *Acta Crystallogr., Sect. B*, 1981, **37**, 232; W. C. Marsh and J. Trotter, *J. Chem. Soc. (A)*, 1971, 1482.
366. A. Ferrari, A. Briabanti and T. Tiripicchio, *Acta Crystallogr.*, 1966, **21**, 605; B. J. Hathaway and F. S. Stephens, *J. Chem. Soc. (A)*, 1970, 884.
367. R. J. Williams, A. C. Larson and D. T. Cromer, *Acta Crystallogr., Sect. B*, 1972, **28**, 858.
368. R. J. Baker, S. C. Nyburg and J. T. Szymanski, *Inorg. Chem.*, 1971, **10**, 138.
369. D. A. Wrobleski, S. R. Wilson and T. B. Rauchfuss, *Inorg. Chem.*, 1982, **21**, 2114.
370. W. E. Marsh, W. E. Hatfield and D. J. Hodgson, *Inorg. Chem.*, 1983, **22**, 2901.
371. E. W. Ainscough, A. M. Brodie, J. M. Husbands, G. J. Gainsford, E. J. Gabe and N. F. Curtis, *J. Chem. Soc., Dalton Trans.*, 1984, 151.
372. C. Kappenstein and U. Schubert, *J. Chem. Soc., Chem. Commun.*, 1980, 1116.
373. J. Garaj, *Inorg. Chem.*, 1969, 304.
374. M. Koman, D. Valigura, E. Durcanska and G. Ondrejovic, *J. Chem. Soc., Chem. Commun.*, 1984, 381.
375. A. W. Addison, *Inorg. Nucl. Chem. Lett.*, 1976, **12**, 899.
376. D. Datta and A. Chakravorty, *Inorg. Chem.*, 1982, **21**, 363.

377. R. L. Lintvedt, G. Ranger and B. A. Schoenfelner, *Inorg. Chem.*, 1984, **23**, 688.
378. J. A. Baglid, H. Weakliem, F. Demelio and P. A. Vaughan, *J. Inorg. Nucl. Chem.*, 1970, **32**, 795, 803.
379. J. Kaiser, G. Brauer, F. A. Schroder, I. F. Taylor and S. E. Rasmussen, *J. Chem. Soc., Dalton Trans.*, 1974, 1490.
380. T. Sakurai, K. Kobayashi, H. Masuda, S. Tsuboyama and K. Tsuboyama, *Acta Crystallogr., Sect. C*, 1983, **39**, 334; P. Kierkegaard and B. Nyberg, *Acta Chem. Scand.*, 1965, **19**, 2189.
381. R. J. Williams, D. T. Cromer and A. C. Larson, *Acta Crystallogr., Sect. B*, 1971, **27**, 1701.
382. D. B. Brown, J. A. Zubieta, P. A. Vella, J. T. Wobleski, T. Watt, W. E. Hatfield and P. Day, *Inorg. Chem.*, 1980, **19**, 1945.
383. C. Sigwart, P. Hemmerich and J. T. Spence, *Inorg. Chem.*, 1968, **7**, 2545.
384. D. B. Brown, J. A. Donner, J. W. Hall, S. R. Wilson, R. B. Wilson, D. J. Hodgson and W. E. Hatfield, *Inorg. Chem.*, 1979, **18**, 2635.
385. D. Gatteschi, C. Meali and L. Sacconi, *Inorg. Chem.*, 1976, **15**, 2774.
386. B. F. Hoskins, N. J. Mcleod and H. A. Schaap, *Aust. J. Chem.*, 1976, **29**, 515.
387. R. R. Gagne, C. A. Koval, T. J. Smith and M. C. Cimolino, *J. Am. Chem. Soc.*, 1979, **101**, 4571.
388. R. R. Gagne, L. M. Henling and T. J. Kistenmacher, *Inorg. Chem.*, 1980, **19**, 1226.
389. K. P. Dancey, P. A. Tasker, R. Price, W. E. Hatfield and D. C. Brower, *J. Chem. Soc., Chem. Commun.*, 1980, 1248.
390. M. M. Olmstead, W. K. Musker and R. M. Kessler, *Inorg. Chem.*, 1981, **20**, 151.
391. P. J. M. W. L. Birker and H. C. Freeman, *J. Chem. Soc., Chem. Commun.*, 1976, 312; *J. Am. Chem. Soc.*, 1977, **99**, 6890.
392. P. J. M. W. L. Birker, *Inorg. Chem.*, 1979, **18**, 3502.
393. H. J. Schugar, C.-C. Ou, J. A. Thich, J. A. Potenxa, T. R. Felthouse, M. S. Haddad, D. N. Hendrickson, W. Furey, Jr. and R. A. Lalancette, *Inorg. Chem.*, 1980, **19**, 543.
394. H. van Kempen, J. A. A. J. Perenboom and P. J. M. W. L. Birker, *Inorg. Chem.*, 1981, **20**, 917.
395. G. F. Kokoszka, J. Baranowski, C. Goldstein, J. Orsini, A. D. Mighell, V. L. Himes and A. R. Siedle, *J. Am. Chem. Soc.*, 1983, **105**, 5627.
396. B. J. Hathaway, *Struct. Bonding (Berlin)*, 1984, **57**, 55.
397. B. J. Hathaway, M. Duggan, A. Murphy, J. Mullane, C. Power, A. Walsh and B. Walsh, *Coord. Chem. Rev.*, 1981, **36**, 267.
398. E. I. Solomon, in ref. 30, Fig. 9, p. 11.
399. R. S. Himmelwright, N. C. Eickman, C. D. Lubien and E. I. Solomon, *J. Am. Chem. Soc.*, 1980, **102**, 5378.
400. Y. Agnus, R. Louis and R. Weiss, *J. Chem. Soc., Chem. Commun.*, 1980, 867.
401. C. C. Addison and B. J. Hathaway, *Proc. Chem. Soc.*, 1957, 19.
402. B. J. Hathaway, *Proc. Chem. Soc.*, 1958, 344.
403. C. C. Addison and B. J. Hathaway, *J. Chem. Soc.*, 1960, 1468.
404. F. Clifford, E. Counihan, W. Fitzgerald, K. Seff, C. Simmons, S. Tyagi and B. J. Hathaway, *J. Chem. Soc., Chem. Commun.*, 1982, 196.
405. B. J. Hathaway and A. Murphy, *Acta Crystallogr., Sect. B*, 1980, **36**, 295.
406. S. Tyagi and B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1983, 199.
407. O. Kennard, F. H. Allen and D. G. Watson, 'Molecular Dimensions', Cambridge Crystal Data Centre, 1970, pp. 1–15.
408. L. Sacconi, *Transition Met. Chem.*, 1986, **4**, 199.
409. R. Stomberg, B. Svensson, A. A. G. Tomlinson, and I. Persodtter, *Acta Chem. Scand., Ser. A.*, 1982, **36**, 579.
410. D. Nicholls, in 'Comprehensive Inorganic Chemistry', ed. J. C. Bailar, H. J. Emeléus, R. S. Nyholm and A. F. Trotman-Dickinson, Pergamon, Oxford, 1973, vol. 3, p. 1109.
411. C. Furlani, *Coord. Chem. Rev.*, 1968, **3**, 141.
412. R. J. Gillespie, *J. Chem. Soc.*, 1963, 4672.
413. G. E. Bacon, 'Neutron Diffraction', 3rd edn., Oxford University Press, London, 1975.
414. A. K. Cheetham and J. C. Taylor, *J. Solid State Chem.*, 1977, **21**, 253.
415. H. Manohar, *Curr. Sci.*, 1983, **52**, 39.
416. SERC Daresbury Laboratory X-Ray Powder Users Group Meeting, September, 1983 and July 1985.
417. J. T. Hougen, G. E. Leroi and T. C. James, *J. Chem. Phys.*, 1961, **34**, 1670; S. P. Ramdall, F. T. Greene and J. L. Margrave, *J. Phys. Chem.*, 1959, **63**, 758.
418. R. E. La Villa and S. H. Bauer, *J. Am. Chem. Soc.*, 1963, **85**, 3597; S. Shibata and K. Iifima, *J. Mol. Struct.*, 1984, **117**, 45.
419. S. Shibata, T. Sasase and M. Ohta, *J. Mol. Struct.*, 1983, **96**, 347.
420. T. Yamaguchi and H. Ohtaki, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 415; A. Musino, G. Paschina, G. Piccaluga and M. Magini, *Inorg. Chem.*, 1983, **22**, 1184; G. Licheri, A. Musino, G. Paschina, G. Piccaluga, G. Pinna and A. F. Sedda, *J. Chem. Phys.*, 1984, **80**, 5308.
421. M. Magini, *Inorg. Chem.*, 1982, **21**, 1535.
422. P. A. Lee, P. H. Citron, P. Eisenberger and B. M. Kincaid, *Rev. Mod. Phys.*, 1981, **53**, 769.
423. J.-L. Pascal, J. Potier, D. J. Jones, J. Roziere and A. Michalowicz, *Inorg. Chem.*, 1984, **23**, 2068.
424. M. S. Co, R. A. Scott and K. O. Hodgson, *J. Am. Chem. Soc.*, 1981, **103**, 986.
425. A. Michalowicz and R. Fourme, *Acta Crystallogr., Sect. C*, 1981, **37**, 307.
426. N. W. Isaacs and C. H. L. Kennard, *J. Chem. Soc. (A)*, 1969, 386; D. L. Cullen and E. C. Lingafelter, *Inorg. Chem.*, 1971, **10**, 1264.
427. D. L. Cullen and E. C. Lingafelter, *Inorg. Chem.*, 1970, **9**, 1858.
428. M. D. Joesten, M. S. Hussain and P. G. Lenhert, *Inorg. Chem.*, 1970, **9**, 151; M. D. Joesten, M. S. Hussain, P. G. Lenhert and J. H. Venable, *J. Am. Chem. Soc.*, 1968, **90**, 5623.
429. R. I. Sheldon, A. J. Jircitano, M. A. Beno, J. M. Williams and K. B. Mertes, *J. Am. Chem. Soc.*, 1983, **105**, 3028.
430. D. Taylor, *Aust. J. Chem.*, 1978, **31**, 713.

431. W. J. Crama, *Acta Crystallogr., Sect. B*, 1981, **37**, 2133; S. Hirotsu, *J. Phys. C*, 1977, **10**, 967; C. J. Krose, J. J. A. Maaskant and G. C. Verschoor, *Acta Crystallogr., Sect. B*, 1974, **30**, 1053.
432. D. Reinen and C. Friebel, *Struct. Bonding (Berlin)*, 1979, **37**, 1.
433. S. Takagi, D. Joesten and P. G. Lenhert, *Acta Crystallogr., Sect. B*, 1975, **31**, 596.
434. D. L. McFadden, A. T. McPhail, P. M. Gross, C. D. Garner and F. E. Maabs, *J. Chem. Soc., Dalton Trans.*, 1975, 263.
435. K. G. Shields and C. H. L. Kennard, *Cryst. Struct. Commun.*, 1972, **1**, 189.
436. E. Dubler, P. Korber and H. R. Oswald, *Acta Crystallogr., Sect. B*, 1973, **29**, 1929.
437. C. Friebel, *Z. Naturforsch., Teil B*, 1974, **296**, 634.
438. R. D. Willett, *J. Chem. Phys.*, 1964, **41**, 2243.
439. M. Bukovska and M. A. Porai-Koshits, *Zh. Strukt. Khim.*, 1961, **7**, 712.
440. W. Vreugdenhil, P. J. M. W. L. Birker, R. W. M. ten Hoedt, G. C. Verschoor and J. Reedijk, *J. Chem. Soc., Dalton Trans.*, 1984, 429.
441. A. W. Addison and E. Sinn, *Inorg. Chem.*, 1983, **22**, 1225.
442. M. D. Glick, D. P. Gavel, L. L. Diaddario and D. B. Rorabacher, *Inorg. Chem.*, 1976, **15**, 1190.
443. R. V. G. Sundara Rao, K. Sundaramma and G. Sivasankara Rao, *Z. Kristallogr.*, 1958, **110**, 231.
444. D. Harker, *Z. Kristallogr.*, 1936, **93**, 136.
445. D. S. Brown, J. D. Lee and B. G. A. Melsom, *Acta Crystallogr., Sect. B*, 1968, **24**, 730.
446. F. S. Stephens, *J. Chem. Soc. (A)*, 1969, 2233.
447. F. S. Stephens, *J. Chem. Soc. (A)*, 1969, 1723.
448. O. P. Anderson, *J. Chem. Soc., Dalton Trans.*, 1973, 1237.
449. M. V. Veidis, G. M. Schreiber, T. E. Gough and G. J. Palenik, *J. Am. Chem. Soc.*, 1969, **91**, 1859.
450. A. Sedov, M. Dunaj-Jurco, M. Kabesova, J. Gazo and J. Garaj, *Inorg. Chim. Acta*, 1982, **64**, L257.
451. A. Murphy, B. J. Hathaway and T. J. King, *J. Chem. Soc., Dalton Trans.*, 1979, 1646.
452. G. Giuseppetti and F. Mazzi, *Rend. Soc. Min. Ital.*, 1955, **11**, 202; R. D. Ball, D. Hall, C. E. F. Rickard and T. N. Waters, *J. Chem. Soc. (A)*, 1967, 1435.
453. H. Nakai, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 1637.
454. J. Foley, D. Kennefick, D. Phelan, S. Tyagi and B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1983, 2333.
455. E. D. McKenzie, *Coord. Chem. Rev.*, 1971, **6**, 187.
456. A. A. G. Tomlinson, B. J. Hathaway, D. E. Billing and P. Nichols, *J. Chem. Soc. (A)*, 1969, 65.
457. H. Montgomery and E. C. Lingafelter, *Acta Crystallogr.*, 1966, **20**, 659.
458. G. M. Brown and R. Chidambaram, *Acta Crystallogr., Sect. B*, 1969, **25**, 676.
459. B. J. Hathaway and P. G. Hodgson, *J. Inorg. Nucl. Chem.*, 1973, **35**, 4071.
460. J. Gazo, *Pure Appl. Chem.*, 1974, **38**, 279.
461. J. Gazo, I. B. Bersuker, J. Garaj, M. Kabesova, J. Kohout, H. Langfelderova, M. Melnik, M. Serator and F. Valach, *Coord. Chem. Rev.*, 1976, **19**, 253.
462. M. Melnik, *Coord. Chem. Rev.*, 1982, **47**, 239.
463. J. Gazo, R. Boca, E. Jona, M. Kabesova, L. Macaskova, J. Sima, P. Pelikan and F. Valach, *Coord. Chem. Rev.*, 1982, **43**, 87.
464. H. B. Burgi, *Inorg. Chem.*, 1973, **2**, 2321.
465. P. Murray-Rust, H. B. Burgi and J. D. Dunitz, *J. Am. Chem. Soc.*, 1975, **97**, 921.
466. J. D. Dunitz, 'X-Ray Analysis and the Structure of Organic Molecules', Cornell University Press, Ithaca, NY, 1979, chap. 7.
467. H. B. Burgi and J. D. Dunitz, *Acc. Chem. Res.*, 1983, **10**, 153.
468. I. M. Procter, B. J. Hathaway and P. Nicholls, *J. Chem. Soc. (A)*, 1968, 1678.
469. R. J. Deeth and M. Gerloch, *Inorg. Chem.*, 1984, 3846.
470. B. J. Hathaway, 'Structure and Bonding', 1973, **14**, 49.
471. A. Santoro, A. D. Mighell and C. W. Reimann, *Acta Crystallogr., Sect. B*, 1970, **26**, 979.
472. F. S. Stephens, *J. Chem. Soc. (A)*, 1969, 2081.
473. C. C. Addison, N. Logan, S. C. Wallwork and C. D. Garner, *Q. Rev. Chem. Soc.*, 1971, **25**, 289.
474. A. Pabst, *Acta Crystallogr.*, 1959, **12**, 733.
475. A. Ferrari, A. Braibanti and A. Tiripicchio, *Acta Crystallogr.*, 1966, **21**, 605; B. Morosin and A. C. Larsen, *Acta Crystallogr., Sect. B*, 1969, **25**, 1417.
476. H. C. Nelson, S. H. Simonsen and G. W. Watt, *J. Chem. Soc., Chem. Commun.*, 1979, 632.
477. J. Robertson and R. Truter, *J. Chem. Soc. (A)*, 1967, 309.
478. A. Walsh and B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1984, 15.
479. M. Bonamico, G. Dessy, A. Mugnoli, A. Vaciago and L. Zambonelli, *Acta Crystallogr.*, 1965, **19**, 886.
480. C. J. Brown, *J. Chem. Soc. (A)*, 1968, 2488.
481. R. H. Holm and M. J. O'Connor, *Prog. Inorg. Chem.*, 1971, **14**, 241.
482. E. C. Lingafelter, B. Morosin and G. L. Simmons, *Acta Crystallogr.*, 1960, **13**, 1025.
483. L. Helmholz and R. F. Kruh, *J. Am. Chem. Soc.*, 1952, **74**, 1176; J. A. McGinnety, *J. Am. Chem. Soc.*, 1972, **94**, 8406.
484. J. S. Haynes, K. W. Oliver, S. J. Rettig, R. C. Thompson and J. Trotter, *Can. J. Chem.*, 1984, **62**, 891.
485. J. E. Johnson, T. A. Beineke and R. A. Jacobson, *J. Chem. Soc. (A)*, 1971, 1371.
486. J. R. Dorfman, R. D. Bereman and M.-H. Whangbo, in ref. 30, p. 75.
487. J. A. Bertrand and A. R. Kalyanaraman, *Inorg. Chim. Acta*, 1971, **5**, 341.
488. J. Trotter and S. H. Whitlow, *J. Chem. Soc. (A)*, 1970, 455.
489. D. W. Smith, *Coord. Chem. Rev.*, 1976, **21**, 93.
490. M. Elder and B. R. Penfold, *J. Chem. Soc. (A)*, 1969, 2556.
491. G. Dessy and V. Fares, *Cryst. Struct. Commun.*, 1979, **8**, 101.
492. C. E. Baxter, O. R. Rodig, R. K. Schlatzer and E. Sinn, *Inorg. Chem.*, 1979, **18**, 1918.
493. C. H. Wie, *Inorg. Chem.*, 1972, **11**, 2315.
494. J. Foley, S. Tyagi and B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1984, 1.

495. R. Cini, P. Colamarino, P. L. Orioli, L. S. Smith, P. R. Newman, H. D. Gillman and P. Nanelli, *Inorg. Chem.*, 1977, **16**, 3223.
496. K. W. Oliver, S. J. Rettig, R. C. Thompson and J. Trotter, *Can. J. Chem.*, 1982, **60**, 2017.
497. K. Amornjarusiri and B. J. Hathaway, unpublished results.
498. L. Antolini, G. Marcotrigiano, L. Menabue and G. C. Pellacani, *J. Am. Chem. Soc.*, 1980, **102**, 1303.
499. M. Duggan, N. Ray, B. J. Hathaway, G. Tomlinson, P. Brint and K. Pelin, *J. Chem. Soc., Dalton Trans.*, 1980, 1342.
500. F. Massi, *Acta Crystallogr.*, 1955, **8**, 137; B. Morosin, *Acta Crystallogr., Sect. B*, 1969, **25**, 19.
501. O. P. Anderson and A. B. Packard, *Inorg. Chem.*, 1980, **19**, 2941.
502. M. Mori, Y. Saito and T. Watanabe, *Bull. Chem. Soc. Jpn.*, 1961, 295; I. Bernal, J. D. Korp, E. O. Schlemper and M. S. Hussain, *Polyhedron*, 1982, **1**, 365.
503. V. A. Roesler and D. Reinen, *Z. Anorg. Allg. Chem.*, 1981, **479**, 119.
504. H. Jin-ling, L. Jien-ming and L. Jia-xi, *Acta Chim. Sinica*, 1966, **32**, 194.
505. S. Tyagi, B. J. Hathaway, S. Kremer, H. Stratemeier and D. Reinen, *J. Chem. Soc., Dalton Trans.*, 1984, 2087.
506. E. L. Muetterties and R. A. Schunn, *Q. Rev. Chem. Soc.*, 1966, **20**, 245; B. F. Hoskins and F. D. Williams, *Coord. Chem. Rev.*, 1972, **9**, 365.
507. S. Berry, *J. Chem. Phys.*, 1960, **32**, 933.
508. A. W. Addison, T. Nageswara Rao, J. Reedijk, J. van Rijn and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1984, 1349.
509. O. P. Anderson and A. B. Packard, *Inorg. Chem.*, 1980, **19**, 2123.
510. D. D. Klaehn, H. Paulus, R. Grewe and H. Elias, *Inorg. Chem.*, 1984, **23**, 483.
511. G. O. Morpurgo, V. Mosini, P. Porta, G. Dessy and V. Fares, *J. Chem. Soc., Dalton Trans.*, 1980, 1272.
512. S. M. Morehouse, A. Polychronopoulou and G. J. B. Williams, *Inorg. Chem.*, 1980, **19**, 3558.
513. N. Ray, Ph.D. Thesis, University College, Cork, 1979; A. G. Tomlinson and B. J. Hathaway, *J. Chem. Soc. (A)*, 1968, 1685.
514. N. Ray, L. Hulett, R. Sheahan and B. J. Hathaway, *Inorg. Nucl. Chem. Lett.*, 1978, **14**, 305; *J. Chem. Soc., Dalton Trans.*, 1981, 1463.
515. B. G. Segal and S. J. Lippard, *Inorg. Chem.*, 1974, **13**, 822.
516. G. Marongiu and M. Cannas, *J. Chem. Soc., Dalton Trans.*, 1979, 41.
517. N. A. Bailey and E. D. McKenzie, *J. Chem. Soc., Dalton Trans.*, 1972, 1566.
518. P. C. Jain and E. C. Lingafelter, *J. Am. Chem. Soc.*, 1967, **89**, 6131.
519. S. Tyagi and B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1981, 2029.
520. A. Sedov, J. Kozisek, M. Kabesova, M. Dunaj-Jurco, J. Gazo and J. Garaj, *Inorg. Chim. Acta*, 1983, **75**, 73.
521. F. S. Stephens, *J. Chem. Soc., Dalton Trans.*, 1972, 1350.
522. W. D. Harrison and B. J. Hathaway, *Acta Crystallogr., Sect. B*, 1979, **35**, 2910.
523. J. Ellis, G. M. Mockler and E. Sinn, *Inorg. Chem.*, 1981, **20**, 1206.
524. P. J. M. W. L. Birker, H. M. J. Hendriks, J. Reedijk and G. C. Verschoor, *Inorg. Chem.*, 1981, **20**, 2408.
525. A. J. Jirocitano, R. I. Sheldon and K. B. Mertes, *J. Am. Chem. Soc.*, 1983, **105**, 3022.
526. K. Amornjarusiri and B. J. Hathaway, unpublished results.
527. K. Takahashi, Y. Nishida and S. Kida, *Polyhedron*, 1984, **3**, 113.
528. E. E. Bernarducci, P. K. Bharadwaj, R. A. Lalancette, K. Krogh-Jespersen, J. A. Potenza and H. J. Schugar, *Inorg. Chem.*, 1983, **22**, 3911.
529. G. J. Kleywegt, W. G. R. Weismeijer, G. J. van Driel, W. L. Driessen, J. Reedijk and J. H. Nordik, *J. Chem. Soc., Dalton Trans.*, 1985, 2177.
530. R. Allman, S. Kremer and D. Kucharzcyk, *Inorg. Chim. Acta*, 1984, **85**, L19.
531. S. Takagi, M. D. Joesten and P. Lenhert, *J. Am. Chem. Soc.*, 1975, **97**, 444.
532. D. Mullen, G. Hegar and D. Reinen, *Solid State Commun.*, 1975, **17**, 1249.
533. K. Knox, *J. Chem. Phys.*, 1959, **30**, 991.
534. H. G. von Schnering, *Z. Anorg. Allg. Chem.*, 1967, **13**, 353.
535. E. Herdtweck and D. Babel, *Z. Anorg. Allg. Chem.*, 1981, **474**, 113; C. Friebel and B. Reinen, *Z. Anorg. Allg. Chem.*, 1974, **407**, 193; E. Herdtweck and D. Babel, *Z. Anorg. Allg. Chem.*, 1981, **474**, 113.
536. F. Hanic and I. Cakajdova, *Acta Crystallogr.*, 1958, **11**, 610.
537. F. S. Stephens, *J. Chem. Soc. (A)*, 1969, 883.
538. R. Allmann, W. Henke and D. Reinen, *Inorg. Chem.*, 1978, **17**, 378.
539. M. I. Arriortua, T. Rojo, J. M. Amigo, G. Germain and J. P. Declercq, *Acta Crystallogr., Sect. B*, 1982, **38**, 1323.
540. J. H. Ammeter, H. B. Burgi, E. Gamp, V. Meyer-Sandrin and W. P. Jensen, *Inorg. Chem.*, 1979, **18**, 733.
541. C. K. Prout, R. A. Armstrong, J. R. Carruthers, J. G. Forrest, P. Murray-Rust and F. J. C. Rossotti, *J. Chem. Soc. (A)*, 1968, 2791.
542. M. F. Belicchi, G. F. Gasparri, C. Pelizzi and P. Tarasconi, *Transition Met. Chem.*, 1985, **10**, 295.
543. F. Clifford, E. Counihan, W. Fitzgerald, K. Seff, C. Simmons, S. Tyagi and B. J. Hathaway, *J. Chem. Soc., Chem. Commun.*, 1982, 196; C. J. Simmons, K. Seff, F. Clifford and B. J. Hathway, *Acta Crystallogr., Sect. C*, 1983, **39**, 1360.
544. C. Escobar and O. Wittke, *Acta Crystallogr., Sect. C*, 1983, **39**, 1643.
545. C. P. Power, B. J. Hathaway and J. P. Fackler, unpublished results.
546. I. M. Procter and F. S. Stephens, *J. Chem. Soc. (A)*, 1969, 1248.
547. A. Walsh, B. Walsh, B. Murphy and B. J. Hathaway, *Acta Crystallogr., Sect. B*, 1981, **37**, 1512.
548. W. Fitzgerald and B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1981, 567.
549. B. J. Hathaway, N. Ray, D. Kennedy, N. O'Brien and B. Murphy, *Acta Crystallogr., Sect. B*, 1980, **36**, 1371.
550. S. Tyagi, B. J. Hathaway and M. Horgan, unpublished results.
551. G. Nardin, L. Randaccio, R. P. Bonomo and E. Rizzarelli, *J. Chem. Soc., Dalton Trans.*, 1980, 369.
552. M. van Meerssche, G. Germain, J. P. Declerq and L. Willputte-Steinert, *Cryst. Struct. Commun.*, 1981, **10**, 47.
553. S. Tyagi and B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1983, 2693.

554. M. G. B. Drew, J. Nelson and S. M. Nelson, *J. Chem., Soc., Dalton Trans.*, 1981, 1685.
555. D. Webster and G. J. Palenik, *J. Am. Chem. Soc.*, 1975, 7565.
556. A. F. Cameron, D. W. Taylor and R. H. Nuttall, *J. Chem. Soc., Dalton Trans.*, 1972, 1603.
557. C. J. O'Connor, R. J. Romananch, D. M. Robertson, E. E. Edouk and F. R. Fronczek, *Inorg. Chem.*, 1983, **22,** 449.
558. B. Morosin, *Acta Crystallogr., Sect. B*, 1970, **26,** 1203.
559. C. V. Goebel and R. J. Doedens, *Inorg. Chem.*, 1971, **10,** 2607.
560. G. Smith, E. J. O'Reilly, C. H. L. Kennard and T. C. W. Mak, *Inorg. Chim. Acta*, 1982, **65,** L219.
561. M.-M. Borel, L. Boniak, F. Busnot and A. Leclaire, *Z. Anorg. Allg. Chem.*, 1979, **455,** 88.
562. M.-M. Borel, F. Busnot and A. Leclaire, *Z. Anorg. Allg. Chem.*, 1979, **449,** 177.
563. D. A. Langs and C. R. Hare, *Chem. Commun.*, 1967, 890.
564. E. A. Klop, A. J. M. Duisenberg and A. L. Spek, *Acta Crystallogr., Sect. C*, 1983, **39,** 1342.
565. B. Sjoberg, R. Osterberg and R. Soderquist, *Acta Crystallogr., Sect. B*, 1973, **29,** 1136.
566. T. J. King and A. Morris, *Inorg. Nucl. Chem. Lett.*, 1974, **10,** 237.
567. G. Smith, E. J. O'Reilly, C. H. L. Kennard and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1985, 243.
568. K. A. Klanderman, W. C. Hamilton and I. Bernal, *Inorg. Chim. Acta*, 1977, **23,** 117.
569. A. F. Cameron, R. H. Nuttall and D. W. Taylor, *Chem. Commun.*, 1970, 865; 1971, 253; A. F. Cameron, K. P. Forrest, D. W. Taylor and R. H. Nuttall, *J. Chem. Soc.*, 1961, 2492.
570. G. A. Barclay and C. H. L. Kennard, *J. Chem. Soc.*, 1961, 3289; N. Burger and H. Fuess, *Solid State Commun.*, 1980, **34,** 699.
571. S. Klein and D. Reinen, *J. Solid State Chem.*, 1978, **25,** 295.
572. S. Klein and D. Reinen, *J. Solid State Chem.*, 1980, **32,** 311.
573. I. Bertini, P. Dapporto, D. Gatteschi and A. Scozzafava, *J. Chem. Soc., Dalton Trans.*, 1979, 1409.
574. V. S. B. Metwa, K. Prout, A. Murphy and B. J. Hathaway, Spring Crystallography Meeting, Royal Society of Chemistry, University of Durham, April 1982.
575. K. Prout, unpublished results.
576. C. Simmons, A. Clearfield, W. Fitzgerald, S. Tyagi and B. J. Hathaway, *J. Chem. Soc., Chem. Commun.*, 1983, 189; C. J. Simmons, A. Clearfield, W. Fitzgerald, S. Tyagi and B. J. Hathaway, *Inorg. Chem.*, 1983, **22,** 2463; W. Fitzgerald and B. J. Hathaway, *Acta Crystallogr., Sect. C*, 1984, **40,** 243.
577. C. J. Simmons, B. J. Hathaway, K. Amornjarusiri, B. D. Santarsiero and A. Clearfield, *J. Am. Chem. Soc.*, 1987, accepted for publication.
578. N. W. Alcock, M. Duggan, A. Murray, S. Tyagi, B. J. Hathaway and A. Hewat, *J. Chem. Soc., Dalton Trans.*, 1984, 7.
579. A. W. Hewat and B. J. Hathaway, *J. Solid State Chem.*, 1984, **51,** 364.
580. M. D. Joesten, S. Tyagi and P. G. Lenhert, *Inorg. Chem.*, 1977, **16,** 2680.
581. A. Murphy, J. Mullane and B. J. Hathaway, *Inorg. Nucl. Chem. Lett.*, 1980, **16,** 129.
582. C. P. Keijzers, R. K. McMullan, J. S. Wood, G. van Kalkeren, R. Srinivasan and E. de Boer, *Inorg. Chem.*, 1982, **21,** 4275.
583. A. Earnshaw, 'An Introduction to Magnetochemistry', Academic, London, 1968.
584. F. E. Mabbs and D. J. Machin, 'Magnetism and Transition Metal Complexes', Chapman and Hall, London, 1973.
585. R. L. Martin, in 'New Pathways in Inorganic Chemistry', ed. E. Ebsworth, D. Maddock and A. Sharpe, Cambridge University Press, Cambridge 1968, chap. 9.
586. V. Casellato, M. Vidali and P. A. Vigato, *Coord. Chem. Rev.*, 1977, **23,** 31.
587. R. A. Bauer, W. R. Robinson and D. W. Margerum, *J. Chem. Soc., Chem. Commun.*, 1973, 289.
588. M. S. Haddad, S. W. Wilson, D. J. Hodgson and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1981, **103,** 384.
589. D. M. Duggan, R. G. Jungst, K. R. Mann, G. D. Stucky and D. N. Hendricksons, *J. Am. Chem. Soc.*, 1974, **96,** 3443.
590. R. Jungst and G. Stucky, *Inorg.Chem.*, 1974, **13,** 2404.
591. A. Riesen, M. Zehnder and T. A. Kaden, *J. Chem. Soc., Chem. Commun.*, 1985, 1336.
592. K. Matsumoto, S. Ooi, Y. Nakao, W. Mori and A. Nakahara, *J. Chem. Soc., Dalton Trans.*, 1981, 2045.
593. G. Kolks and S. J. Lippard, *Acta Crystallogr., Sect. C*, 1984, **40,** 261.
594. J. van Rijn and J. Reedijk, *Recl. Trav. Chim. Pays-Bas*, 1984, **103,** 78.
595. R. D. Karlin, P. L. Dahlstrom, L. T. Dipierro, R. A. Simon and J. Zubieta, *J. Coord. Chem.*, 1981, **11,** 61.
596. T. R. Felthouse, E. N. Duesler, A. T. Christensen and D. N. Hendrickson, *Inorg. Chem.*, 1979, **18,** 245.
597. J. R. Wasson, T. P. Mitchell and W. H. Bernard, *J. Inorg. Nucl. Chem.*, 1968, **30,** 2865.
598. T. P. Mitchell, W. H. Bernard and J. R. Wasson, *Acta Crystallogr., Sect. B*, 1970, **26,** 2096.
599. W. E. Hatfield, T. S. Piper and U. Klabunde, *Inorg. Chem.*, 1963, **2,** 629; D. L. Lewis, K. T. McGregor, W. E. Hatfield and D. J. Hodgson, *Inorg. Chem.*, 1974, **13,** 1013.
600. E. D. Esters, W. E. Hatfield and D. J. Hodgson, *Inorg. Chem.*, 1974, **13,** 1654.
601. D. L. Lewis, W. E. Hatfield and D. J. Hodgson, *Inorg. Chem.*, 1972, **11,** 2216.
602. A. T. Casey, B. F. Hoskins and F. D. Whillans, *Chem. Commun.*, 1970, 904.
603. S. G. N. Roundhill, D. M. Roundhill, D. R. Bloomquist, S. Landee, R. D. Willett, D. Dooley and H. B. Gray, *Inorg. Chem.*, 1979, **18,** 831.
604. W. C. Velthuizen, J. G. Haasnoot, A. J. Kinneging, F. J. Rietmeijer and J. Reedijk, *J. Chem. Soc., Chem. Commun.*, 1983, 1366.
605. D. H. Svedung, *Acta Chem. Scand.*, 1969, **23,** 2865.
606. D. W. Phelps, W. H. Goodman and D. J. Hodgson, *Inorg. Chem.*, 1976, **15,** 2266.
607. M. R. Churchill and J. P. Hutchinson, *Cryst. Struct. Commun.*, 1980, **9,** 1209.
608. E. D. Estes, W. E. Estes, W. E. Hatfield and D. J. Hodgson, *Inorg. Chem.*, 1975, **14,** 106.
609. M. Megnamisi-Belombe and M. A. Novotny, *Inorg. Chem.*, 1980, **19,** 2470.
610. E. Luukkonen and A. Pajunen, *Suom. Kemistil B*, 1973, **46,** 292.
611. P. Singh, D. Y. Jeter, W. E. Hatfield and D. J. Hodgson, *Inorg. Chem.*, 1972, **11,** 1657.

612. H. E. LeMay, Jr., D. J. Hodgson, P. Pruettiangkura and L. J. Theriot, *J. Chem. Soc., Dalton Trans.*, 1979, 781.
613. S. Sikorav, I. Bkouche-Waksman and O. Kahn, *Inorg. Chem.*, 1984, **23**, 490.
614. R. D. Willett and C. Chow, *Acta Crystallogr., Sect. B*, 1974, **30**, 207.
615. A. D. Mighell, C. W. Reimann and A. Santoro, *Chem. Commun.*, 1970, 204.
616. M. F. Charlot, S. Jeannin, Y. Jeannin, O. Kahn, J. Lucrece-Abaul and J. Martin-Frere, *Inorg. Chem.*, 1979, **18**, 1675.
617. Y. Litaka, K. Shimuzu and T. Kwan, *Acta Crystallogr.*, 1966, **20**, 803.
618. M. Mikuriya, T. Harada, H. Okawa and S. Kida, *Inorg. Chim. Acta*, 1983, **75**, 1.
619. J. H. Timmons, J. W. L. Martin, A. E. Martell, P. Rudolf, A. Clearfield, S. J. Loeb and C. J. Willis, *Inorg. Chem.*, 1981, **20**, 181.
620. M. J. Heeg, J. L. Mack, M. D. Glick and R. L. Lintvedt, *Inorg. Chem.*, 1981, **20**, 833; R. L. Lintvedt, M. D. Glick, B. K. Tomlonovic, D. P. Gavel and J. M. Kuszaj, *Inorg. Chem.*, 1976, **15**, 1633.
621. M. D. Glick and R. L. Lintvedt, *Prog. Inorg. Chem.*, 1976, **21**, 233.
622. B. F. Hoskins, N. J. Mcleod and H. A. Scharp, *Aust. J. Chem.*, 1976, **29**, 515.
623. O. Kahn, S. Sikorav, J. Gouteron, S. Jeannin and Y. Jeannin, *Inorg. Chem.*, 1983, **22**, 2877.
624. K. D. Karlin, P. L. Dahlstrom, S. N. Cozzette, P. M. Scensy and J. Zubieta, *J. Chem. Soc., Chem. Commun.*, 1981, 881.
625. T. N. Sorrell, D. L. Jameson and C. J. O'Connor, *Inorg. Chem.*, 1984, **23**, 190.
626. K. Aoki, *J. Am. Chem. Soc.*, 1978, **100**, 7106.
627. J. Sletten, *Acta Chem. Scand., Sect. A*, 1983, **37**, 569.
628. M. R. Churchill, G. Davies, M. A. El-Sayed, M. F. El-Shazly, J. P. Hutchinson, M. W. Rupich and K. O. Watkins, *Inorg. Chem.*, 1979, **18**, 2296.
629. C. A. Bear, J. M. Waters and T. N. Waters, *J. Chem. Soc. (A)*, 1970, 2494.
630. D. J. Hodgson, *Inorg. Chim. Acta*, 1983, **75**, 225.
631. D. J. Hodgson, P. K. Hale and W. E. Hatfield, *Inorg. Chem.*, 1971, **10**, 1061.
632. W. E. Marsh, D. S. Eggleston, W. E. Hatfield and D. J. Hodgson, *Inorg. Chim. Acta*, 1983, **70**, 137.
633. W. E. Marsh, W. E. Hatfield and D. J. Hodgson, *Inorg. Chem.*, 1982, **21**, 2679.
634. W. E. Marsh, T. L. Bowman, W. E. Hatfield and D. J. Hodgson, *Inorg. Chim. Acta*, 1982, **59**, 19.
635. R. W. M. ten Hoedt, J. Reedijk and G. C. Verschoor, *Recl. Trav. Chim. Pays-Bas*, 1981, **100**, 400.
636. F. J. Rietmeijer, R. A. G. de Graaf and J. Reedijk, *Inorg. Chem.*, 1984, **23**, 151.
637. D. D. Swank, G. F. Needham and R. D. Willett, *Inorg. Chem.*, 1979, **18**, 761.
638. R. Sillanpaa, *Inorg. Chim. Acta*, 1984, **82**, 75.
639. M. Megnamisi-Belombe and H. Endres, *Acta Crystallogr., Sect. C*, 1983, **39**, 707.
640. T. Rojo, J. Darriet, J. M. Dance and D. Beltran-Porter, *Inorg. Chim. Acta*, 1982, **64**, L105.
641. W. E. Marsh, K. C. Patel, W. E. Hatfield and D. J. Hodgson, *Inorg. Chem.*, 1983, **22**, 511.
642. S. K. Hoffman, D. K. Towle, W. E. Hatfield, P. Chaudhuri and K. Weidghardt, *Inorg. Chem.*, 1985, **24**, 1307.
643. I. Sotofte and K. Nielsen, *Acta Chem. Scand., Ser. A*, 1981, **35**, 733.
644. R. Sillanpaa, M. Leskela and L. Hiltunen, *Acta Crystallogr., Sect. B*, 1982, **38**, 1591.
645. K. D. Karlin, Y. Gultneh, J. C. Hayes and J. Zubieta, *Inorg. Chem.*, 1984, **23**, 519.
646. F. Calderazzo, F. Marchetti, G. Dell'Amico, G. Pelizzi and A. Colligiani, *J. Chem. Soc., Dalton Trans.*, 1980, 1419.
647. P. Y. Boukari, A. Busnot, F. Busnot, A. Leclaire and M. A. Bernard, *Acta Crystallogr., Sect. B*, 1982, **38**, 2458.
648. S. Scavnicar and B. Matkovic, *Acta Crystallogr., Sect. B*, 1969, **25**, 2046.
649. E. Frasson, R. Bardi and S. Bezzi, *Acta Crystallogr.*, 1959, **12**, 201.
650. M. Bonamico, G. Dessy, A. Mugnoli, A. Vaciago and L. Zambonelli, *Acta Crystallogr.*, 1965, **19**, 886.
651. P. C. Chieh, G. G. Meissmer and G. J. Palenik, *Inorg. Chem.*, 1971, **10**, 133.
652. E. W. Ainscough, E. N. Baker, A. M. Brodie and N. G. Larsen, *J. Chem. Soc., Dalton Trans.*, 1981, 2054.
653. M. Antolovich, D. J. Phillips and A. D. Rae, *J. Chem. Soc., Chem. Commun.*, 1984, 582.
654. T. R. Felthouse and D. N. Hendrickson, *Inorg. Chem.*, 1978, **17**, 444.
655. I. Bkouche-Waksman, S. Sikorav and O. Kahn, *J. Cryst. Struct. Res.*, 1983, **13**, 303.
656. E. J. Laskowski, D. M. Duggan and D. N. Hendrickson, *Inorg. Chem.*, 1975, **14**, 2449.
657. M. S. Haddad, E. N. Duesler and D. N. Hendrickson, *Inorg. Chem.*, 1979, **18**, 141.
658. P. L. Burke, J. Osborn and M.-T. Youinou, *J. Am. Chem. Soc.*, 1981, **103**, 1273.
659. P. L. Burke, J. A. Osborn, M.-T. Youinou, Y. Angus, R. Louis and R. Weiss, *J. Am. Chem. Soc.*, 1981, **103**, 384.
660. V. McKee and J. Smith, *J. Chem. Soc., Chem. Commun.*, 1983, 1465.
661. M. G. B. Drew, M. McCann and S. M. Nelson, *J. Chem. Soc., Chem. Commun.*, 1979, 481.
662. P. K. Coughlin, A. E. Martin, J. C. Dewan, E.-I. Watanabe, J. E. Bulkowski, J.-M. Lehn and S. J. Lippard, *Inorg. Chem.*, 1984, **23**, 1004.
663. P. K. Coughlin, J. C. Dewan, S. J. Lippard, E. Watanabe and J.-M. Lehn, *J. Am. Chem. Soc.*, 1979, **101**, 265.
664. M. G. B. Drew, C. Cairns, A. Lavery and S. M. Nelson, *J. Chem. Soc., Chem. Commun.*, 1980, 1122.
665. M. G. B. Drew, M. McCann and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1981, 1868.
666. K. D. Karlin, J. Shi, J. C. Hayes, J. W. Mckown, J. P. Hutchinson and J. Zubieta, *Inorg. Chim. Acta*, 1984, **91**, L3.
667. V. McKee, J. V. Dagdigan, R. Bau and C. A. Reed, *J. Am. Chem. Soc.*, 1981, **103**, 7000.
668. A. E. Martin, J. E. Bulkowski, K. J. Coskran and E. Sinn, in ref. 30, p. 405.
669. Y. Agnus, R. Louis and R. Weiss, *J. Am. Chem. Soc.*, 1979, **101**, 3381.
670. J. Comarmond, J. M. Lehn, P. L. Plumere, Y. Agnus, R. Louis, R. Weiss, O. Kahn and I. Morgenstern-Badaran, *J. Am. Chem. Soc.*, 1982, **104**, 6330.
671. Y. L. Agnus, in ref. 30, p. 384, Figs. 11 and 12.
672. M. G. B. Drew, J. Nelson, F. Esho, V. McKee and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1982, 1837
673. P. K. Coughlin and S. J. Lippard, *J. Am. Chem. Soc.*, 1981, **103**, 3228; 1984, **106**, 2328.

674. Y. L. Agnus, in ref. 30, p. 381 and ref. 43 therein.
675. J. E. Bulkowski and E. Sinn, in ref. 30, p. 448, Fig. 5.
676. S. J. Lippard, in ref. 30, p. 403, Fig. 6.
677. Y. Agnus, R. Louis and R. Weiss, *J. Am. Chem. Soc.*, 1979, **101**, 3381.
678. Y. Kajikawa, T. Sakurai, N. Azuma, S. Kohno, S. Tsuboyama, K. Kobayashi, K. Mukai and K. Ishizu, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 1454.
679. Von W. Vogt and H. Haas, *Acta Crystallogr., Sect. B*, 1971, **27**, 1528.
680. G. Marongiu and E. C. Lingafelter, *Acta Crystallogr., Sect. B*, 1982, **38**, 620.
681. L. K. Thompson, V. T. Chacko, J. A. Elvidge, A. B. P. Lever and R. V. Parish, *Can. J. Chem.*, 1969, **47**, 4141.
682. J. N. van Niekerk and F. R. L. Schoening, *Acta Crystallogr.*, 1963, **6**, 227.
683. R. Chidambaram and G. M. Brown, *Cryst. Struct. Commun.*, 1972, **1**, 269; G. M. Brown and R. Chidambaram, *Acta Crystallogr., Sect. B*, 1973, **29**, 2393.
684. P. de Meester, S. R. Fletcher and A. C. Skapski, *J. Chem. Soc., Dalton Trans.*, 1973, 2575.
685. M. Kato, H. B. Jonnasen and J. C. Fanning, *Chem. Rev.*, 1964, **64**, 99.
686. R. J. Doedens, *Prog. Inorg. Chem.*, 1976, **21**, 209.
687. M. Melnik, *Coord. Chem. Rev.*, 1982, **42**, 259.
688. B. Morosin, R. C. Hughes and Z. G. Soos, *Acta Crystallogr., Sect. B*, 1975, **31**, 762.
689. V. Rao and H. Manohar, *Inorg. Chim. Acta*, 1979, **34**, L213.
690. Y. B. Yablokov, L. N. Mosina, Y. A. Simonov, L. N. Milkova, A. V. Ablou and V. I. Ivanov, *Zh. Strukt. Khim.*, 1978, **19**, 42.
691. D. M. L. Goodgame and D. F. Marsham, *J. Chem. Soc. (A)*, 1966, 1167.
692. F. Pavelcik and F. Nanic, *J. Cryst. Mol. Struct.*, 1978, **8**, 59.
693. M. M. Borel and A. Leclaire, *Acta Crystallogr., Sect. B*, 1976, **32**, 1275.
694. L. Boniak, M. M. Borel, F. Busnot and A. Leclaire, *Rev. Chim. Miner.*, 1979, **16**, 501.
695. Y. A. Simonov, L. N. Milkovia, A. V. Ablov and T. I. Malinovskii, *Dokl. Akad. Nauk SSSR*, 1976, **229**, 1976.
696. J. A. Moreland and R. J. Doedens, *Inorg. Chem.*, 1978, **17**, 674.
697. J. A. Moreland and R. J. Doedens, *J. Am. Chem. Soc.*, 1975, **97**, 508.
698. R. McCrindle, G. Ferguson, A. J. McAlees and P. J. Roberts, *J. Chem. Soc., Dalton Trans.*, 1981, 1406.
699. L. C. Porter, M. H. Dickman and R. J. Doedens, *Inorg. Chem.*, 1983, **22**, 1964.
700. C. M. Harris, B. F. Hoskins and R. L. Martin, *J. Chem. Soc.*, 1959, 3728.
701. K. D. Onan, M. Veidis, G. Davies, M. A. El-Sayed and A. El-Toukhy, *Inorg. Chim. Acta*, 1984, **81**, 7.
702. H. Muhonen, A. Pajunen and R. Hamalainen, *Acta Crystallogr., Sect. B*, 1980, **36**, 2790.
703. R. Beckett, R. Colton, B. F. Hoskins, R. L. Martin and D. G. Vince, *Aust. J. Chem.*, 1969, **22**, 2527; R. Beckett and B. F. Hoskins, *J. Chem. Soc., Dalton Trans.*, 1972, 291.
704. J. E. Young and R. K. Murmann, *J. Phys. Chem.*, 1963, **67**, 2647; P. F. Ross, R. K. Murmann and E. O. Schlemrer, *Acta Crystallogr., Sect. B*, 1974, **30**, 1120.
705. R. J. Butcher, E. J. O'Connor and E. Sinn, *Inorg. Chem.*, 1981, **20**, 537.
706. F. B. Hulsbergen, R. W. M. ten Hoedt, G. C. Verschoor, J. Reedijk and A. L. Spek, *J. Chem. Soc., Dalton Trans.*, 1983, 539.
707. M. A. S. Goher and T. C. W. Mak, *Inorg. Chim. Acta*, 1985, **99**, 223.
708. R. E. Caputo, M. J. Vukosavovich and R. D. Willett, *Acta Crystallogr., Sect. B*, 1976, **32**, 2516.
709. C. A. Bear, J. M. Waters and T. N. Waters, *J. Chem. Soc., Dalton Trans.*, 1974, 1059.
710. D. Hall and T. N. Waters, *J. Chem. Soc.*, 1960, 2644.
711. R. W. M. ten Hoedt, F. B. Hulsbergen, G. C. Verschoor and J. Reedijk, *Inorg. Chem.*, 1982, **21**, 2369.
712. R. Belford, D. E. Fenton and M. R. Truter, *J. Chem. Soc., Dalton Trans.*, 1972, 2345.
713. J. A. Bertrand and J. A. Kelly, *Inorg. Chem.*, 1982, **8**, 1969; M. E. Lines, A. P. Ginsberg, R. L. Martin and R. E. Sherwood, *J. Chem. Phys.*, 1972, **57**, 1.
714. B. J. Kilbourn and J. D. Dunitz, *Inorg. Chim. Acta*, 1967, **1**, 209.
715. N. S. Gill and M. Stern, *Inorg. Chem.*, 1970, **9**, 1619.
716. R. Mergehenn, L. Merz and W. Haase, *J. Chem. Soc., Dalton Trans.*, 1980, 1703.
717. L. Merz and W. Haase, *J. Chem. Soc., Dalton Trans.*, 1980, 875; R. Mergehenn and W. Haase, *Acta Crystallogr., Sect. B*, 1977, **33**, 1877.
718. B. Jesowska-Trzebiatowska, Z. Olejnik and T. Lis, *J. Chem. Soc., Dalton Trans.*, 1981, 251.
719. L. Walz, H. Paulus, W. Haase, H. Langhof and F. Nepveu, *J. Chem. Soc., Dalton Trans.*, 1983, 657.
720. K. Nieminen, *Acta Chem. Scand., Ser. A*, 1979, **33**, 375.
721. K. Nieminen, *Acta Chem. Scand., Ser. A*, 1977, **31**, 693.
722. M. Ahlgren, U. Turpeinen and R. Hamalainen, *Acta Crystallogr., Sect. B*, 1982, **38**, 429.
723. M. Ahlgren, U. Turpeinen and K. Smolander, *Acta Crystallogr., Sect. B*, 1980, **36**, 1091.
724. R. D. Willett and K. Chang, *Inorg. Chim. Acta*, 1970, **4**, 447.
725. B. K. S. Lundberg, *Acta Chem. Scand.*, 1972, **26**, 3977.
726. G. Bandoli, M. C. Biagini, D. A. Clemente and G. Rizzardi, *Inorg. Chim. Acta*, 1976, **20**, 71.
727. R. A. Bream, E. D. Estes and D. J. Hodgson, *Inorg. Chem.*, 1975, **14**, 1672.
728. A. Santoro, A. D. Mighell and C. W. Reimann, *Acta Crystallogr., Sect. B*, 1970, **26**, 979.
729. R. C. E. Belford, D. E. Fenton and M. R. Truter, *J. Chem. Soc., Dalton Trans.*, 1974, 17.
730. R. C. E. Belford, D. E. Fenton and M. R. Truter, *J. Chem. Soc., Dalton Trans.*, 1972, 2208.
731. D. M. S. Bagguley and J. H. E. Griffiths, *Proc. R. Soc. London, Ser. A*, 1950, **201**, 366; O. G. Holmes and D. S. McClure, *J. Chem. Phys.*, 1957, **26**, 1686.
732. P. C. Healy, C. H. L. Kennard, G. Smith and A. H. White, *Cryst. Struct. Commun.*, 1978, **7**, 565.
733. J.-C. Tedenac and E. Philippot, *J. Inorg. Nucl. Chem.*, 1975, **37**, 846; M. Dunaj-Jurco and M. A. Poraj-Koshits, *Chem. Zvesti*, 1966, **20**, 783.
734. H. Nakai, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 2412.
735. N. Ray, S. Tyagi and B. J. Hathaway, *Acta Crystallogr., Sect. B*, 1982, **38**, 1574.
736. B. Morosin and J. Howatson, *Acta Crystallogr., Sect. B*, 1970, **26**, 2062.

737. M. D. Glick, G. L. Downs and L. F. Dahl, *Inorg. Chem.*, 1964, **3**, 1712.
738. J. Garas, M. Langfelderova, G. Lundgren and J. Gazo, *Collect. Czech. Chem. Commun.*, 1972, **37**, 3181.
739. A. F. Wells, *J. Chem. Soc.*, 1947, 1670.
740. I. Agrell, *Acta Chem. Scand.*, 1967, **21**, 2647; I. Agrell and S. Lamnevik, *Acta Chem. Scand.*, 1968, **22**, 2038; R. Soderquist, *Acta Crystallogr., Sect. B*, 1968, **24**, 450.
741. R. Kiriyama, H. Ibamoto and K. Matsuo, *Acta Crystallogr.*, 1954, **7**, 482.
742. H. Tamura, K. Ogawa, W. Mori and M. Kishita, *Inorg. Chim. Acta*, 1981, **54**, L87.
743. E. C. Lingafelter G. L. Simmons, B. Morosin, G. Scheringer and C. Freiburg, *Acta Crystallogr.*, 1961, **14**, 1222.
744. A. Gleizes, F. Muray and J. Galy, *Inorg. Chem.*, 1980, **19**, 2074; P.Chananont, P. E. Nixon, J. M. Waters and T. N. Waters, *Acta Crystallogr., Sect. B*, 1980, **36**, 2145.
745. J. A. C. van Ooijen, J. Reedijk, E. J. Sonneveld and J. W. Visser, *Transition Met. Chem.*, 1979, **4**, 305.
746. W. E. Marsh, E. J. Valente and D. J. Hodgson, *Inorg. Chim. Acta*, 1981, **51**, 49.
747. B. Morosin, *Acta Crystallogr., Sect. B*, 1975, **31**, 632.
748. D. D. Swank and R. D. Willett, *Inorg. Chem.*, 1980, **19**, 2321.
749. C. K. Prout, J. R. Carruthers and F. J. C. Rossotti, *J. Chem. Soc. (A)*, 1971, 3342.
750. H. Endres, N. Genec and D. Nothe, *Acta Crystallogr., Sect. C*, 1983, **39**, 701.
751. A. C. Villa, A. Gaetani-Manfredotti, M. Nardelli and G. Pelizzi, *J. Cryst. Mol. Struct.*, 1971, **1**, 245.
752. L. Walz, H. Paulus and W. Haase, *J. Chem. Soc., Dalton Trans.*, 1985, 913.
753. S. C. Abrahms and E. Prince, *J. Chem. Phys.*, 1962, **36**, 50.
754. A. Engberg, *Acta Chem. Scand.*, 1970, **24**, 3510.
755. D. R. Bloomquist, J. J. Hansen, C. P. Landee, R. D. Willett and R. Buder, *Inorg. Chem.*, 1981, **20**, 3308.
756. J. J. Girerd, S. Jeannin, Y. Jeannin and O. Kahn, *Inorg. Chem.*, 1978, **17**, 3034.
757. C. J. Evenhuis, M. A. Hitchman, R. G. McDonald, D. M. L. Goodgame, E. Kwistowski, U. Dettloff-Weglikowska, C. Pakawatchai and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1984, 943.
758. G. Davey and F. S. Stephens, *J. Chem. Soc. (A)*, 1971, 103.
759. G. Druhan and B. J. Hathaway, unpublished results.
760. G. Guiseppetti and F. Mazzi, *Rend. Soc. Mineral. Ital.*, 1965, **11**, 202.
761. H. M. Hellis, W. H. Goodman, R. B. Wilson, J. A. Morgan and D. J. Hodgson, *Inorg. Chem.*, 1977, **16**, 2412.
762. W. Fitzgerald, J. Foley, D. McSweeney, N. Ray, D. Sheahan, S. Tyagi, B. J. Hathaway and P. O'Brien, *J. Chem. Soc., Dalton Trans.*, 1982, 1117.
763. C. J. O'Connor, C. L. Klein, R. J. Majeste and L. M. Trefonas, *Inorg. Chem.*, 1982, **21**, 64.
764. M. H. Meyer, P. Singh, W. E. Hatfield and D. J. Hodgson, *Acta Crystallogr., Sect. B*, 1972, **28**, 1607.
765. P. H. Vossos, L. D. Jennings and R. E. Rundle, *J. Chem. Phys.*, 1960, **32**, 1590.
766. R. D. Willett, C. Dwiggins, Jr., R. F. Kruh and R. E. Rundle, *J. Chem. Phys.*, 1963, **38**, 2429; G. O'Bannon and R. D. Willett, *Inorg. Chim. Acta*, 1981, **53**, L131.
767. R. D. Willett and E. Rundle, *J. Chem. Phys.*, 1964, **40**, 838.
768. B. Chiari, W. E. Hatfield, O. Piovesana, T. Tarantelli, L. W. ter Haar and P. F. Zanazzi, *Inorg. Chem.*, 1983, **22**, 1468.
769. B. J. O'Connor and E. N. Maslen, *Acta Crystallogr.*, 1966, **20**, 824.
770. Von J. Pickardt, *Acta Crystallogr., Sect. B*, 1981, **37**, 1753.
771. G. Ivarsson, K. S. Bruno and N. Ingri, *Acta Chem. Scand.*, 1972, **26**, 3005.
772. R. S. Sager and W. H. Watson, *Inorg. Chem.*, 1968, **7**, 2035.
773. M. A. S. Goher and T. C. W. Mak, *Inorg. Chim. Acta*, 1984, **85**, 117.
774. R. Sillanpaa, T. Nortia and L. Hiltunen, *Inorg. Chim., Acta*, 1984, **83**, 111.
775. V. C. Copeland, W. E. Hatfield and D. J. Hodgson, *Inorg. Chem.*, 1973, **12**, 1340.
776. M. M. Olmstead, W. K. Musker, L. W. Ter Haar and W. E. Hatfield, *J. Am. Chem. Soc.*, 1982, **104**, 6627.
777. A. W. Schlueter, R. A. Jacobson and R. E. Rundle, *Inorg. Chem.*, 1966, **5**, 277.
778. T.-I. Li and G. D. Stucky, *Inorg. Chem.*, 1973, **12**, 441.
779. S. A. Roberts, D. R. Bloomquist, R. D. Willett and H. W. Dodgen, *J. Am. Chem. Soc.*, 1981, **103**, 2603.
780. D. W. Swank, C. P. Lande and R. D. Willett, *Phys. Rev., B; Condens. Matter*, 1979, **20**, 2154.
781. J. A. J. Jarvis and A. F. Wells, *Acta Crystallogr.*, 1960, **13**, 1027.
782. I. Sotofte and K. Nielsen, *Acta Chem. Scand., Ser. A*, 1984, **38**, 253.
783. H. Koizumi, K. Osaki and T. Watanabe, *J. Phys. Soc. Jpn.* 1963, **18**, 117.
784. A. F. Wells, *J. Chem. Soc.*, 1947, 1670.
785. G. L. Ferguson and B. Zaslow, *Acta Crystallogr., Sect. B*, 1971, **27**, 849.
786. C. Billy and H. M. Haendler, *J. Am. Chem. Soc.*, 1957, **79**, 1049.
787. J. C. Barnes, J. D. Paton and A. McKissock, *Acta Crystallogr., Sect. C*, 1983, **39**, 547.
788. A. Farrand, A. K. Gregson, B. W. Skelton and A. H. White, *Aust. J. Chem.*, 1980, **33**, 431.
789. P. C. Healy and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1972, 1913.
790. S. Ghose, *Acta Crystallogr.*, 1962, **15**, 1105.
791. B. Bovio and S. Locchi, *J. Crystallogr. Spectrosc. Res.*, 1982, **12**, 507; H. Effenberger, *Z. Kristallogr.*, 1983, **165**, 127.
792. B. Duffin and S. C. Wallwork, *Acta Crystallogr.*, 1966, **20**, 210.
793. B. Duffin, *Acta Crystallogr., Sect. B*, 1968, **24**, 396.
794. B. R. Bloomquist, J. J. Hanse, C. P. Landee and R. D. Willett, *Inorg. Chem.*, 1981, **20**, 3308.
795. G. Meunier, C. Svensson and A. Carpy, *Acta Crystallogr., Sect. B*, 1976, **32**, 2664.
796. S. Asbink and L.-J. Norrby, *Acta Crystallogr., Sect. B*, 1970, **26**, 8.
797. E. Sletton and H. J. Jensen, *Acta Crystallogr. Sect. B*, 1973, **29**, 1752.
798. Von H. Seidel, K. Viswanathan, W. Johannes and H. Ehrardt, *Z. Anorg. Allg. Chem.*, 1974, **410**, 138.
799. S. C. Wallwork and W. E. Addison, *J. Chem. Soc.*, 1965, 2925.
800. B. Rama Rao, *Acta Crystallogr.*, 1961, **14**, 321.
801. L. Antolini, L. Menabue, G. C. Pellacani, G. B. Gavioli, G. Grandi, L. P. Battaglia, A. B. Corradi and G. Marcotrigiano, *J. Chem. Soc., Dalton Trans.*, 1984, 1687.

802. M. J. Begley, M. F. Dove, R. C. Hibbert, N. Logan, M. Nunn and D. B. Sowerby, *J. Chem. Soc., Dalton Trans.*, 1985, 2433.
803. G. L. Shoemaker, J. B. Anderson and E. Kostiner, *Acta Crystallogr., Sect. B*, 1977, **33,** 2969.
804. L. Falck, O. Lindqvist and J. Moret, *Acta Crystallogr., Sect. B*, 1978, **34,** 896.
805. L. Gebert and L. Kihborg, *Acta Chem. Scand.*, 1969, **23,** 221.
806. B. Morosin, P. Fallon and J. S. Vallentine, *Acta Crystallogr., Sect. B*, 1975, **31,** 2220.
807. F. Hannic, *Czech. J. Phys., Sect. B*, 1960, **10,** 169.
808. D. E. Billing, B. J. Hathaway and P. Nicholls, *J. Chem. Soc. (A)*, 1969, 316.
809. A. Tiripicchio, A. M. M. Lanfredi, M. Ghedini and F. Neve, *J. Chem. Soc., Chem. Commun.*, 1983, 97.
810. B. Kamenar, *Acta Crystallogr., Sect. B*, 1969, **25,** 800.
811. P. G. Lenhert, C. M. Lukehart and L. T. Warfield, *Inorg. Chem.*, 1980, **19,** 311.
812. H. Okawa, Y. Kawahara, M. Mikuriya and S. Kida, *Bull. Chem. Soc. Jpn.*, 1980, **53,** 549.
813. C. K. Schauer, K. Akabori, C. M. Elliot and O. P. Anderson, *J. Am. Chem. Soc.*, 1984, **106,** 1127.
814. B. R. McGarvey, in 'Electron Spin Resonance of Transition Metal Complexes', ed. R. L. Carlin, Dekker, New York, 1966, vol. 3, p. 89; D. R. Eaton and K. Zaw, *Coord. Chem. Rev.*, 1971, **7,** 197.
815. B. A. Goodman and J. B. Raynor, *Adv. Inorg. Chem. Radiochem.*, 1970, **13,** 135; J. B. Raynor, *Chem. Br.* 1974, **10,** 254.
816. A. Bencini and D. Gatteschi, *Transition Met. Chem.*, 1982, **8,** 1; I. Bertini, D. Gatteschi and A. Scozzafava, *Coord. Chem. Rev.*, 1979, **29,** 67.
817. A. B. P. Lever, 'Inorganic Electronic Spectroscopy', 2nd edn., Elsevier, New York, 1984; J. Ferguson, *Prog. Inorg. Chem.*, 1970, **12,** 159; N. S. Hush and R. J. M. Hobbs, *Prog. Inorg. Chem.*, 1968, **10,** 259.
818. G. S. Patterson and R. H. Holm, *Bioinorg. Chem.*, 1975, **4,** 257.
819. A. W. Addison, in ref. 30, p. 109.
820. E. D. McKenzie, *J. Chem. Soc. (A)*, 1970, 3095.
821. C. M. Harris and E. D. McKenzie, *J. Chem. Soc. (A)*, 1969, 746.
822. B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1972, 1196.
823. M. J. Bew, B. J. Hathaway and R. J. Fereday, *J. Chem. Soc., Dalton Trans.*, 1972, 1229.
824. T. D. Smith, *Coord. Chem. Rev.*, 1974, **13,** 173.
825. L. E. Orgel, 'Introduction to Transition Metal Chemistry — Ligand Field Theory', Methuen, London, 1960.
826. D. Sutton, 'Electronic Spectra of Transition Metal Ions', McGraw-Hill, London, 1968.
827. F. A. Cotton, 'Chemical Applications of Group Theory', 2nd. edn., Wiley Interscience, New York, 1971.
828. C. J. Ballhausen, *Dan. Mat. Fys. Medd.*, 1954, **4,** 29; C. J. Ballhausen and C. K. Jorgensen, *ibid.*, 1955, **14,** 29.
829. A. L. Companion and M. A. Komarynski, *J. Chem. Educ.*, 1964, **41,** 257.
830. C. J. Ballhausen, 'Introduction to Ligand-Field Theory', McGraw-Hill, New York, 1962.
831. T. M. Dunn, D. S. McClure and R. G. Pearson, 'Some Aspects of Crystal-Field Theory', Harper and Row, New York, 1965.
832. B. N. Figgis, 'Introduction to Ligand Fields', Interscience, New York, 1966.
833. B. N. Figgis and J. Lewis, *Prog. Inorg. Chem.*, 1964, **6,** 37; C. J. O'Connor, *Prog. Inorg. Chem.*, 1982, **29,** 203.
834. K. T. McGregor, N. T. Watkins, D. L. Lewis, R. F. Drake, D. J. Hodgson and W. E. Hatfield, *Inorg. Nucl. Chem. Lett.*, 1973, **9,** 423.
835. J. B. Goodenough, 'Magnetism and the Chemical Bond', R. E. Krieger, Huntingdown, NY, 1963.
836. M. Gerloch, 'Magnetism and Ligand-Field Analysis', Cambridge University Press, Cambridge, 1983; M. Gerloch, *Prog. Inorg. Chem.*, 1979, **26,** 1; R. L. Carlin, 'Magnetochemistry', Springer-Verlag, Berlin, 1986.
837. E. Sinn, *Coord. Chem. Rev.*, 1970, **5,** 313.
838. A. P. Ginsberg, *Inorg. Chim. Acta Rev.*, 1971, 45.
839. W. E. Hatfield, *Comments Inorg. Chem.*, 1981, **1,** 105; D. J. Hodgson, *J. Mol. Catal.*, 1984, **23,** 219; O. Kahn, *Inorg. Chim. Acta*, 1982, **62,** 3; M. Julve, M. Verdaguer, M.-F. Charlot, O. Kahn and R. Claude, *Inorg. Chim. Acta*, 1984, **82,** 5.
840. R. D. Willett, D. Gatteschi and O. Kahn, 'Magneto-Structural Correlations in Exchange Coupled Systems', Reidel, Dordrecht, 1985.
841. N. T. Watkins, D. J. Jeter, W. E. Hatfield and S. M. Horner, *Trans. Faraday Soc.*, 1971, **67,** 2531.
842. W. E. Estes, W. E. Hatfield, J. A. C. van Ooijen and J. Reedijk, *J. Chem. Soc., Dalton Trans.*, 1980, 2121.
843. D. J. Jeter and W. E. Hatfield, *J. Inorg. Nucl. Chem.*, 1972, **11,** 1826.
844. W. Duffy, J. Venneman, D. Strandberg and P. M. Richards, *Phys. Rev. B: Solid State*, 1974, **9,** 2220.
845. V. H. Crawford and W. E. Hatfield, *Inorg. Chem.*, 1977, **16,** 1336.
846. M. Laing and G. Garr, *J. Chem. Soc. (A)*, 1971, 1141.
847. W. E. Estes, D. P. Grave, W. E. Hatfield and D. J. Hodgson, *Inorg. Chem.*, 1978, **17,** 1415.
848. R. J. Majeste and E. A. Meyers, *J. Phys. Chem.*, 1970, **74,** 3497.
849. V. H. Crawford, H. W. Richardson, J. R. Wasson, D. J. Hodgson and W. E. Hatfield, *Inorg. Chem.*, 1976, **15,** 2107.
850. A. T. Casey, *Aust. J. Chem.*, 1972, **25,** 2311.
851. B. F. Hoskins and F. D. Whillans, *J. Chem. Soc., Dalton Trans.*, 1975, 1267.
852. J. A. Barnes, W. E. Hatfield and D. J. Hodgson, *Chem. Commun.*, 1970, 1593.
853. K. T. McGregor, D. J. Hodgson and W. E. Hatfield, *Inorg. Chem.*, 1973, **12,** 731.
854. J. A. Barnes, D. J. Hodgson and W. E. Hatfield, *Inorg. Chem.*, 1972, **11,** 144.
855. D. L. Lewis, W. E. Hatfield and D. J. Hodgson, *Inorg. Chem.*, 1974, **13,** 147.
856. K. T. McGregor, D. J. Hodgson and W. E. Hatfield, *Inorg. Chem.*, 1976, **15,** 421.
857. P. Krahmer, M. Maaser, K. Staiger and E. Uhlig, *Z. Anorg. Allg. Chem.*, 1967, **354,** 242.
858. D. J. Jeter, D. L. Lewis, J. C. Hempel, D. J. Hodgson and W. E. Hatfield, *Inorg. Chem.*, 1972, **11,** 1958.
859. C. Arcus, K. P. Fivizzani and J. Pavkovic, *J. Inorg. Nucl. Chem.*, 1977, **39,** 285.
860. A. T. Casey, B. F. Hoskins and F. D. Whillans, *Chem. Commun.*, 1970, 940.
861. B. J. Cole and W. H. Brumage, *J. Chem. Phys.*, 1970, **53,** 4718.

862. T. R. Felthouse, E. J. Laskowoski and D. N. Hendrickson, *Inorg. Chem.*, 1977, **16**, 1077.
863. M. Julve, M. Verdaguer, A. Gleizes, M. Philoche-Levisalles and O. Kahn, *Inorg. Chem.*, 1984, **23**, 3809.
864. L. V. Interrante, *ACS Symp. Ser.*, 1974, **5**.
865. U. Castellato, P. A. Vigato, D. E. Fenton and M. Vidli, *Chem. Soc. Rev.*, 1979, **8**, 199.
866. Y. Iitaka, K. Shimizu and T. Kwan, *Acta Crystallogr.*, 1966, **20**, 803.
867. M. F. Charlot, O. Kahn, S. Jeannin and Y. Jeannin, *Inorg. Chem.*, 1980, **19**, 1410.
868. W. E. Marsh, K. C. Patel, W. E. Hatfield and D. J. Hodgson, *Inorg. Chem.*, 1983, **22**, 511.
869. J. A. C. van Ooijen and J. Reedijk, *Inorg. Chim. Acta*, 1977, **25**, 131.
870. J. Reedijk and R. W. M. ten Hoedt, *Recl. Trav. Chim. Pays-Bas*, 1982, **101**, 49.
871. E. Coronado, M. Drillon and B. Beltran, *Inorg. Chim. Acta*, 1984, **82**, 13.
872. R. D. Willett and C. P. Landee, *J. Appl. Phys.*, 1981, **52**, 2004.
873. D. J. Hodgson and E. Pederson, *Acta Chem. Scand., Ser. A*, 1982, **36**, 281.
874. J. W. Hall, W. E. Marsh, R. R. Weller and W. E. Hatfield, *Inorg. Chem.*, 1981, **20**, 1033.
875. R. W. Jotham, S. F. A. Kettle and J. A. Marks, *J. Chem. Soc., Dalton Trans.*, 1972, 428; A. E. Hansen and C. J. Ballhausen, *J. Chem. Soc., Faraday Trans.*, 1965, **61**, 631.
876. P. J. Hay, J. C. Thibeault and R. Hoffmann, *J. Am. Chem. Soc.*, 1975, **97**, 4884.
877. P. de Loth, P. Cassoux, J. P. Daudey and J. P. Malrieu, *J. Am. Chem. Soc.*, 1981, **103**, 4007.
878. A. Michalowicz, J. J. Girerd and J. Goulon, *Inorg. Chem.*, 1979, **18**, 3004; J. J. Girerd, O. Kahn and M. Verdaguer, *Inorg. Chem.*, 1980, **19**, 274.
879. J. J. Girerd and O. Kahn, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 385.
880. H. Astheimer, F. Nerveu, L. Waltz and W. Haase, *J. Chem. Soc., Dalton Trans.*, 1985, 315.
881. D. H. Svedung, *Acta Chem. Scand., Ser. A*, 1969, **23**, 2865; M. Megnamisi-Belombe and M. A. Novotny, *Inorg. Chem.*, 1980, **19**, 2470.
882. W. Haase, *J. Mol. Catal.*, 1984, **23**, 331.
883. J. S. Haynes, K. W. Oliver, S. J. Rettig, R. C. Thompson and J. Trotter, *Can. J. Chem.*, 1984, **62**, 891.
884. A. Carrington and A. D. McLachlan, 'Introduction to Magnetic Resonance', Harper, New York, 1967, chaps. 9 and 13.
885. A. Abragam and B. Bleaney, 'Electron Paramagnetic Resonance of Transition Ions', Clarendon, 1970.
886. E. Konig, in 'Physical Methods in Advanced Inorganic Chemistry', ed. H. A. O. Hill and P. Day, Interscience, London, 1968.
887. C. Friebel and D. Reinen, *Z. Anorg. Allg. Chem.*, 1974, **407**, 193; C. Friebel, *Z. Naturforsch., Teil B*, 1974, **29**, 634; D. Reinen, *Solid State Commun.*, 1977, **21**, 137.
888. C. Friebel, V. Propach and D. Reinen, *Z. Naturforsch., Teil B*, 1976, **31**, 1574.
889. B. J. Hathaway, P. G. Hodgson and P. C. Power, *Inorg. Chem.*, 1974, **13**, 2009.
890. E. F. Hasty, T. J. Colburn and D. N. Hendrickson, *Inorg. Chem.*, 1973, **12**, 2414.
891. A. Scheiger and H. H. Gunthard, *Chem. Phys.*, 1978, **32**, 35; S. Kita, M. Hashimoto and M. Iwaizumi, *J. Magn. Reson.*, 1982, **46**, 361; A. Schweger, *Struct. Bonding (Berlin)*, 1982, **51**, 1.
892. Ref. 294, p. 317.
893. A. Bencini, D. Gateschi and C. Zanchini, *J. Am. Chem. Soc.*, 1980, **102**, 5234.
894. B. N. Figgis and R. Leckie, *Aust. J. Chem.* 1981, **34**, 2019.
895. R. J. Dudley, B. J. Hathaway, P. G. Hodgson, J. K. Mulcahy and A. A. G. Tomlinson, *Inorg. Nucl. Chem.*, 1974, **36**, 1947.
896. J. Peisach and W. E. Blumberg, *Arch. Biochem. Biophys.*, 1974, **165**, 691.
897. A. W. Addison, in ref. 30, pp. 109 and 117.
898. K. D. Karlin and Y. Gultneh, *J. Chem. Educ.*, 1985, **62**, 983.
899. V. E. Petrashen, Y. V. Yablokov and R. L. Davidovich, *Phys. Status Solids B*, 1980, **101**, 117; D. K. De, *J. Magn. Reson.*, 1982, **47**, 181; B. Bleaney, K. D. Bowers and D. J. E. Ingram, *Proc. R. Soc. London, Ser. A*, 1955, **228**, 147, and references therein; A. M. Stoneham, *Proc. Phys. Soc.*, 1965, **85**, 107.
900. G. F. Kokoszka, C. W. Reimann, H. C. Allen and G. Gordon, *Inorg. Chem.*, 1967, **6**, 1657.
901. H. C. Allen, G. F. Kokoszka and R. G. Inskeep, *J. Am. Chem. Soc.*, 1964, **86**, 1023.
902. G. Rist, J. Ammeter and H. H. Gunthard, *J. Chem. Phys.*, 1968, **49**, 2210; J. Ammeter, G. Rist and H. H. Gunthard, *J. Chem. Phys.*, 1972, **57**, 3852.
903. H. P. Fritz and H. J. Keller, *Z. Naturforsch., Teil B*, 1965, **206**, 1145; J. B. Raynor, *Z. Naturforsch., Teil B*, 1969, **241**, 775.
904. M. Sharnoff, *J. Chem. Phys.*, 1965, **42**, 3383.
905. G. L. McPherson and C. P. Anderson, *Inorg. Chem.*, 1974, **13**, 677.
906. R. Srinivasan and C. K. Subramanian, *Indian J. Pure Appl. Phys.*, 1970, **8**, 817.
907. R. P. Bonomo and J. R. Pilbrow, *J. Magn. Reson.*, 1981, **45**, 404.
908. W. Fitzgerald, B. Murphy, S. Tyagi, B. Walsh, A. Walsh and B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1981, 2271.
909. B. L. Silver and D. Getz, *J. Chem. Phys.*, 1974, **61**, 638.
910. B. J. Hathaway and A. Hewat, unpublished results.
911. C. Friebel, *Z. Anorg. Allg. Chem.*, 1975, **417**, 197.
912. I. Bertini, P. Dapporto, D. Gatteschi and A. Scozzafava, *J. Chem. Soc., Dalton Trans.*, 1979, 1409.
913. R. C. Koch, M. D. Joesten and J. H. Venable, *J. Chem. Phys.*, 1973, **59**, 6312.
914. W. Fitzgerald, B. J. Hathaway and C. J. Simmons, *J. Chem. Soc., Dalton Trans.*, 1985, 141.
915. G. F. Kokoszka and R. W. Duerst, *Coord. Chem. Rev.*, 1970, **5**, 209.
916. Ref. 294, p. 500.
917. J. Lewis, F. E. Mabbs, L. K. Royston and W. R. Smail, *J. Chem. Soc. (A)*, 1969, 291.
918. J. R. Wasson, C.-I. Shyr and C. Trapp, *Inorg. Chem.*, 1968, **7**, 469.
919. G. Plesch, O. Svajlenova, J. Kratsmar-Smogrovic and M. Kohutova, *Chem. Zvesti*, 1983, **37**, 169.
920. N. F. Albanese and H. M. Haendler, *Polyhedron*, 1983, **2**, 1131.

921. E. Bannister and F. A. Cotton, *J. Chem. Soc.*, 1960, 2276.
922. S. Scavnicar and R. Matkovic, *Chem. Commun.*, 1967, 297.
923. K. T. McGregor, J. A. Barnes and W. E. Hatfield, *J. Am. Chem. Soc.*, 1973, **95,** 7793.
924. R. L. Carlin, R. Burriel, R. M. Cornelise and A. J. van Duyneveldt, *Inorg. Chem.*, 1983, **22,** 831.
925. A. Bencini, I. Bertini, D. Gatteschi and A. Scozzafava, *Inorg. Chem.*, 1978, **11,** 3194.
926. C. K. Chang, *J. Heterocycl. Chem.*, 1977, **14,** 1285.
927. G. O. Carlisle and W. E. Hatfield, *Inorg. Nucl. Chem. Lett.*, 1970, **6,** 633.
928. F. Cariati, G. Micera, A. Scozzafava, G. Minghetti and G. Banditelli, *Inorg. Chem.*, 1982, **21,** 3843.
929. A. Bencini, D. Gatteschi, J. Reedijk and C. Zanchini, *Inorg. Chem.*, 1985, **24,** 207.
930. M. A. Hitchman, *J. Chem. Phys.*, 1978, **68,** 3425.
931. C. J. Evenhuis, M. A. Hitchman, R. G. McDonald, D. M. L. Goodgame, E. Kwiatkowski, U. Dettlaff-Weglikowska, C. Pakawatchai and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1984, 943.
932. M. G. B. Drew, C. Cairns, S. M. Nelson and J. Nelson, *J. Chem. Soc., Dalton Trans.*, 1981, 942; M. G. B. Drew, S. M. Nelson and J. Reedijk, *Inorg. Chim. Acta,* 1982, **64,** L189.
933. T. Izumitani, M. Nakamura, H. Okawa and S. Kida, *Bull. Chem. Soc. Jpn.*, 1982, **55,** 2122.
934. R. C. Long and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1983, **105,** 1513.
935. D. N. Hendrickson, R. C. Long, Y. T. Hwang and H.-R. Chang, in ref. 30(b).
936. M. D. Timen, S. R. Wilson and D. N. Hendrickson, *Inorg. Chem.*, 1985, **24,** 3450.
937. J. H. Ammeter, L. Zoller, J. Bachmann, P. Baltzer, E. Gamp, R. Bucher and E. Deiss, *Helv. Chim. Acta,* 1981, **64,** 1063.
938. W. Manch and W. C. Fernelius, *J. Chem. Educ.*, 1961, **38,** 192.
939. D. Reinen, *Angew. Chem., Int. Ed. Engl.*, 1971, **10,** 901.
940. T. G. Fawcett, E. E. Bernarducci, K. Krogh-Jespersen and H. J. Schugar, *J. Am. Chem. Soc.*, 1980, **102,** 2598; E. Bernarducci, W. F. Schwindinger, J. L. Hughey, K. Krogh-Jesperen and H. J. Schugar, *J. Am. Chem. Soc.*, 1981, **103,** 1686.
941. Y. Nisida and S. Kida, *Coord. Chem. Rev.*, 1979, **21,** 275.
942. H. S. Maslen and T. N. Waters, *Coord. Chem. Rev.*, 1975, **17,** 137.
943. B. D. Bird and P. Day, *J. Chem. Phys.*, 1968, **49,** 392.
944. G. Kortum, 'Reflectance Spectroscopy, Principles Methods and Applications', Springer, Berlin, 1969; E. L. Simmons, *Coord. Chem. Rev.*, 1974, **14,** 181.
945. R. L. Bedford, M. Calvin and G. Belford, *J. Chem. Phys.*, 1957, **26,** 1165.
946. L. L. Funck and T. R. Ortolano, *Inorg. Chem.*, 1968, **7,** 567.
947. C. R. Hare and C. J. Ballhausen, *J. Chem. Phys.*, 1964, **40,** 792.
948. M. A. Hitchman and R. L. Belford, *Inorg. Chem.*, 1971, **10,** 987.
949. B. J. Hathaway, D. E. Billing and R. J. Dudley, *J. Chem. Soc. (A)*, 1970, 1420.
950. M. V. Rajasekharan, C. N. Sethulakshmi, P. T. Manoharan and H. Gudel, *Inorg. Chem.*, 1976, **15,** 2657.
951. R. J. Ford and M. A. Hitchman, *Inorg. Chim. Acta,* 1979, **33,** 241; D. J. Mackey, R. F. McMeeking and M. A. Hitchman, *J. Chem. Soc., Dalton Trans.*, 1979, 299.
952. M. A. Hitchman and P. J. Cassidy, *Inorg. Chem.*, 1979, **18,** 1745; 1978, **17,** 1682.
953. R. J. Deeth, M. A. Hitchman, G. Lehmann and H. Sachs, *Inorg. Chem.*, 1984, **23,** 1310; R. G. McDonald and M. A. Hitchman, *Inorg. Chem.*, 1986, **25,** 3273.
954. M. J. Lindbeck, J. E. Drumheller and K. Emmerson, *J. Solid State Chem.*, 1984, **52,** 180.
955. A. Benchini and D. Gatteschi, *Inorg. Chem.*, 1977, **16,** 1994.
956. M. Cieslak-Golonka, A. Bartecki and S. P. Sinh, *Coord. Chem. Rev.*, 1980, **31,** 251.
957. R. J. Dudley, B. J. Hathaway, P. G. Hodgson, P. C. Power and D. J. Loose, *J. Chem. Soc., Dalton Trans.*, 1974, 1005.
958. A. Ouchi, Y. Sato, Y. Yukawa and T. Takeuchi, *Bull. Chem. Soc. Jpn.*, 1983, **56,** 2241.
959. H. F. Shugar, in ref. 30, p. 43.
960. Y. Saito, *Coord. Chem. Rev.*, 1974, **13,** 305.
961. S. F. Mason, 'Molecular Optical Activity and Chiral Discrimination', Cambridge University Press, Cambridge, 1982.
962. R. Gillard, *Prog. Inorg. Chem.*, 1966, **7,** 215.
963. D. M. Dooley and J. H. Dawson, *Coord. Chem. Rev.*, 1984, **60,** 1.
964. T. Okamoto, K. Matsumoto and H. Kuroya, *Bull. Chem. Soc. Jpn.*, 1970, **43,** 1915.
965. R. Kuroda, S. F. Mason, T. Prosperi, S. Savage and D. E. Tranter, *J. Chem. Soc., Dalton Trans.*, 1981, 2565.
966. K. D. Gailey and R. A. Palmer, *Chem. Phys. Lett.*, 1972, **13,** 76.
967. R. G. Pearson, *J. Am. Chem. Soc.*, 1963, **85,** 3533; *J. Chem. Educ.*, 1968, **45,** 581, 643; F. Basolo and R. G. Pearson, 'Mechanism of Inorganic Reactions', 2nd edn. Wiley, 1967.
968. R. G. Wilkins, 'The Study of the Kinetics and Mechanisms of the Reactions of Coordination Complexes', Allyn and Bacon, London, 1974.
969. F. J. C. Rossotti and H. S. Rossotti, 'The Determination of Stability Constants', McGraw-Hill, London, 1961.
970. J. Bjerrum, G. Schwarzenbach, L. G. Sillen and A. E. Martell (eds.), 'Stability Constants', The Chemical Society, London, 1963 and 1964.
971. A. E. Martell and R. M. Smith, 'Critical Stability Constants' 5th edn., Plenum, New York, 1982; P. Paoletti, Commission on Equilibrium Data, *Pure Appl. Chem.*, 1984, **56,** 491; A. E. Martell and R. M. Smith, 'Critical Stability Constants', Plenun, New York, 1982, p. 5.
972. H. M. N. H. Irving and R. J. P. Williams, *J. Chem. Soc.*, 1953, 3192.
973. R. Barbucci, L. Fabbrizzi and P. Paoletti, *Coord. Chem. Rev.*, 1972, **8,** 31.
974. E. Gallori, E. Martini, M. Micheloni and P. Paoletti, *J. Chem. Soc., Dalton Trans.*, 1980, 1722; B. Wang and C.-S. Chung, *J. Chem. Soc., Dalton Trans.*, 1982, 2565.
975. S. Funahashi, Y. Yamaguchi and M. Tanaka, *Bull. Chem. Soc. Jpn.*, 1984, **57,** 204.
976. L. Fabbrizi, P. Paoletti and A. B. P. Lever, *Inorg. Chem.*, 1976, **15,** 1503; P. Paoletti, L. Fabrizzi and R. Barbucci, *Inorg. Chemm.*, 1973, **12,** 1961; J. D. Carr and J. Vasiliades, *Inorg. Chem.*, 1972, **11,** 2104.

977. L. S. W. L. Sokol, T. D. Fink and D. B. Rorabacher, *Inorg. Chem.*, 1980, **19**, 1263; I. Nagypal and F. Debreczeni, *Inorg. Chim. Acta*, 1984, **81**, 69.
978. S. Funahashi, T. Nisimoto, A. Hioki and M. Tanaka, *Inorg. Chem.*, 1981, **20**, 2648.
979. R. N. Sylva and M. R. Davidson, *J. Chem. Soc., Dalton Trans.*, 1979, 232; G. R. Crayley, I. D. Kelly, P. F. Knowles and K. D. S. Yadav, *J. Chem. Soc., Dalton Trans.*, 1981, 2370.
980. Ref. 26, p. 57, Table 3.6.
981. Ref. 26, p. 58, Table 3.7.
982. D. W. Margerum, G. R. Crayley, D. C. Weatherburn and G. K. Pagenkoff, *ACS Monogr.*, 1978, **174**.
983. J. H. Coates, P. R. Collins and S. F. Lincoln, *Aust. J. Chem.*, 1980, **33**, 1381.
984. P. G. Graham and D. C. Weatherburn, *Aust. J. Chem.*, 1981, **34**, 291; D. C. Weatherburn, *ibid.*, 1983, **36**, 433.
985. S. Siddiqui and R. E. Shepherd, *Inorg. Chem.*, 1983, **22**, 3726; J. D. Carr and V. K. Olson, *Inorg. Chem.*, 1975, **14**, 2168.
986. J. K. Yandel, in ref. 30, p. 157.
987. H. Elias, U. Frohn, G. Giegerich, M. Stenger and K. J. Wannowius, *J. Chem. Soc., Dalton Trans.*, 1982, 577; H. Elias, H. Muth, M. Sahm, H. Volz and K. J. Wannowius, *Inorg. Chim. Acta*, 1983, **68**, 163, and refs. therein.
988. W. Dietzsch, J. Lerchner, J. Reinhold, J. Stach, R. Kirmse, G. Steimecke and E. Hoyer, *J. Inorg. Nucl. Chem.*, 1980, **42**, 509.
989. R. W. Hay and P. Bannerjee, *J. Chem. Soc., Dalton Trans.*, 1980, 2385; M. S. Nair, M. Santappa and P. Natarajan, *J. Chem. Soc., Dalton Trans.*, 1980, 2138 and refs. therein.
990. M. Kodama and E. Kimura, *J. Chem. Soc., Dalton Trans.*, 1980, 2447.
991. R. K. Steinhaus and S. H. Erickson, *Inorg. Chem.*, 1980, **19**, 1913.
992. K. Haraguchi and H. Freiser, *Inorg. Chem.*, 1983, **22**, 653.
993. E. Uhlig, *Coord. Chem. Rev.*, 1982, **43**, 299.
994. D. S. Flett, *Acc. Chem. Res.*, 1977, **10**, 99; S. F. Lincoln, J. H. Coates, B. D. Doddridge, A. M. Hounslow and D. L. Pisaniello, *Inorg. Chem.*, 1983, **22**, 2869.
995. C. A. Flemming and M. J. Nicol, *J. Inorg. Nucl. Chem.*, 1980, **42**, 1327.
996. S. K. Sahni and J. Reedijk, *Coord. Chem. Rev.*, 1984, **59**, 1.
997. B. Sarkar, in ref. 29, vol. 12, p. 33.
998. K. Marauyama, H. Tsukube and T. Araki, *J. Chem. Soc., Chem. Commun.*, 1980, 966.
999. E. J. Laskowski, D. M. Duggan and D. H. Hendrickson, *Inorg. Chem.*, 1975, **14**, 2449.
1000. P. W. Atkins, 'Physical Chemistry', Oxford University Press, Oxford, 1978, p. 591.
1001. K. D. Karlin and J. K. Yandel, *Inorg. Chem.*, 1984, **23**, 1184.
1002. G. S. Yoneda, G. L. Blackmer and R. A. Holwerda, *Inorg. Chem.*, 1977, **16**, 3376; M. A. Augustin and J. K. Yandel, *Inorg. Chem.*, 1979, **18**, 577.
1003. N. Oishi, Y. Nishida, K. Ida and S. Kida, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 2847; Y. Nishida, N. Oishi and S. Kida, *Inorg. Chim. Acta*, 1980, **46**, L69.
1004. A. E. Allan, A. G. Lappin and M. C. M. Laranjeira, *Inorg. Chem.*, 1984, **23**, 477.
1005. K. M. Davies, *Inorg. Chem.*, 1983, **22**, 615.
1006. D. J. Parker and J. H. Espenson, *J. Am. Chem. Soc.*, 1969, **91**, 1968; *J. Chem. Soc., Faraday Trans. 1*, 1972, 78, 3009.
1007. G. Ferraudi and S. Murlidharan, *Coord. Chem. Rev.*, 1981, **36**, 45.
1008. J. A. Deluca, *J. Chem. Educ.*, 1980, **57**, 541.
1009. U. Bertocci and D. R. Turner, in 'Encyclopeadia of the Electrochemistry of the Elements', ed. A. J. Bard, Dekker, New York, vol. 11, chap. 6; L. Meites, G. Mason, P. Zuman, E. B. Rupp and A. Narayanan, 'Inorganic Electrochemistry', CRC Press, Boca Raton, FL, 1981, vol. 2.
1010. P. T. Kissinger and W. R. Heineman, *J. Chem. Educ.*, 1983, **60**, 702; G. A. Mabbott, *ibid.*, 1983, **60**, 697.
1011. A. W. Addison and J. H. Stenhouse, *Inorg. Chem.*, 1978, **17**, 2161.
1012. B. R. James and R. J. P. Williams, *J. Chem. Soc.*, 1961, 2007.
1013. H. Yodoi and A. W. Addison, *Inorg. Chem.*, 1977, **16**, 1341.
1014. A. W. Addison, M. Carpenter, L. K.-M. Lau and M. Wicholas, *Inorg. Chem.*, 1978, **17**, 1545.
1015. P. K. Coughlin and S. J. Lippard, *Inorg. Chem.*, 1984, **23**, 1446.
1016. N. Aoi, G.-E. Matsubayashi, T. Tanaka and K. Nakatsu, *Inorg. Chim. Acta*, 1984, **85**, 123.
1017. D. E. Nikles, M. J. Powers and F. L. Urbach, *Inorg. Chim. Acta*, 1979, **37**, L499.
1018. A. W. Addison, T. N. Rao and E. Sinn, *Inorg. Chem.*, 1984, **23**, 1957.
1019. D. Datta and A. Chakravorty, *Inorg. Chem.*, 1983, **22**, 1085.
1020. L. Fabbrizzi, A. Poggi and P. Zanello, *J. Chem. Soc., Dalton Trans.*, 1984, 1495; 1983, 2191.
1021. P. Zanello, P. A. Vigato and G. A. Mazzocchin, *Transition Met. Chem.*, 1982, **7**, 291.
1022. S. K. Mandel and K. Nag, *J. Chem. Soc., Dalton Trans.*, 1983, 2429; S. Harmalker, S. E. Jones and D. T. Sawyer, *Inorg. Chem.*, 1983, **22**, 2790.
1023. A. R. Hendrickson, R. L. Martin and N. M. Rohde, *Inorg. Chem.*, 1976, **15**, 2115.
1024. M. F. Cabral, J. De O. Cabral, J. van Rijn and J. Reedijk, *Inorg. Chim. Acta*, 1984, **87**, 87.
1025. J. S. Gisselbrecht, M. Gross, A. H. Alberts and J. M. Lehn, *Inorg. Chem.*, 1980, **19**, 1386.
1026. H. Doine, F. Stephens and R. D. Cannon, *Inorg. Chim. Acta*, 1983, **75**, 155.
1027. R. L. Lintvedt and L. S. Kramer, *Inorg. Chem.*, 1983, **22**, 796; D. E. Fenton and R. L. Lintvedt, *J. Am. Chem. Soc.*, 1978, **100**, 6367; S. K. Mandel and K. Nag, *Inorg. Chem.*, 1983, **22**, 2567.
1028. A. W. Addison, *Inorg. Nucl. Chem. Lett.*, 1976, **12**, 899; R. L. Lintvedt, L. S. Kramaer, P. W. Corfield and M. D. Glick, *Inorg. Chem.*, 1983, **22**, 3580.
1029. U. Sanders, H.-H. Strehblow and J. K. Dohrmann, *J. Phys. Chem.*, 1981, **85**, 447.
1030. R. C. Elder, E. A. Blubaugh, W. R. Heineman, P. J. Burke and D. R. McMillan, *Inorg. Chem.*, 1983, **22**, 2777.
1031. C. H. Langford, W. M. Sont and R. D. Burch, *Inorg. Chim. Acta*, 1980, **44**, L73.
1032. D. A. Thornton, *Coord. Chem. Rev.*, 1984, **55**, 113.
1033. A. B. P. Lever and E. Mantovani, *Inorg. Chim. Acta*, 1971, **5**, 429; *Inorg. Chem.*, 1971, **10**, 817.

1034. R. J. Dudley, B. J. Hathaway, P. G. Hodgson, J. K. Mulcahy and A. A. G. Tomlinson, *J. Inorg. Nucl. Chem.*, 1974, **36**, 1947.
1035. M. L. Bansal, V. C. Sahni and A. P. Roy, *J. Phys. Chem. Solids*, 1979, **40**, 109; P. Stein, P. W. Jensen and T. G. Spiro, *Chem. Phys. Lett.*, 1981, **80**, 451.
1036. J. A. Shelnutt, *J. Am. Chem. Soc.*, 1981, **103**, 4275; Y. Mathey, D. R. Greig and D. F. Shriver, *Inorg. Chem.*, 1982, **21**, 3409.
1037. T. G. Spiro, *Acc. Chem. Res.*, 1974, **7**, 339; D. P. Strommen and K. Nakamoto, *J. Chem. Educ.*, 1977, **54**, 474.
1038. Y. Morioka and I. Nakagawa, *Spectrochim. Acta, Ser. A*, 1981, **37**, 437.
1039. K. Akiyama, Y. Morioka and I. Nakagawa, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 1015; S. Ganguly, K. J. Rao and C. N. R. Rao, *Spectrochim. Acta, Sect. A*, 1985, **41**, 307.
1040. U. C. Srivastava and H. L. Nigram, *Coord. Chem. Rev.*, 1972, **9**, 275.
1041. L. Alagna, E. Paparazzo, T. Prosperi and A. A. G. Tomlinson, *J. Chem. Res.*, 1982, 352.
1042. T. Murugesan, P. R. Sarode, J. Gopalakrishnan and C. N. R. Rao, *J. Chem. Soc., Dalton Trans.*, 1980, 837.
1043. B.-K. Teo, in 'EXAFS Spectroscopy, Techniques and Applications', ed. B.-K. Teo and D. C. Joy, Plenum New York, 1981.
1044. K. O. Hodgson (ed.), 'Springer: Proceedings in Physics', vol. 2: 'EXAFS and Near Edge Structure III', Springer, Heidelberg, 1984.
1045. Daresbury Laboratory Users Meeting, March 1981 and July 1985.
1046. J. P. Hunt and H. L. Friedman, *Prog. Inorg. Chem.*, 1983, **30**, 359.
1047. R. W. Joyner, *Chem. Phys. Lett.*, 1980, **72**, 162.
1048. M. Verdaguer, A. Michalowicz, J. J. Girerd, N. Alberding and O. Kahn, *Inorg. Chem.*, 1980, **19**, 3279.
1049. A. Michalowicz, J. J. Girerd and J. Goulon, *Inorg. Chem.*, 1979, **18**, 3004.
1050. Y. Mathey, A. Michalowicz, P. Toffoli and G. Vlaic, *Inorg. Chem.*, 1984, **23**, 897.
1051. L. Alagna and A. A. G. Tomlinson, *J. Chem. Soc., Faraday Trans. 1*, 1982, **78**, 3009.
1052. L. Alagna, T. Prosperi, A. A. G. Tomlinson and G. Vlaic, *J. Chem. Soc., Dalton Trans.*, 1983, 645.
1053. J. L. Pascal, J. Potier, D. J. Jones, J. Roziere and A. Michalowicz, *Inorg. Chem.*, 1985, **24**, 238.
1054. G. Sankar, P. R. Sarode and C. N. R. Rao, *J. Chem. Phys.*, 1983, **76**, 435.
1055. M. Verdaguer, M. Julve, A. Michalowicz and O. Kahn, *Inorg. Chem.*, 1983, **22**, 2624.
1056. C. D. Garner and B. J. Hathaway, unpublished results.
1057. E. L. Mutterties, *Inorg. Chem.*, 1965, **4**, 795; I. Beattie, *Chem. Soc. Rev.*, 1975, **13**, 107.
1058. G. Vlaic. J. C. J. Bart, W. Cavigilo and S. Mobilio, *Chem. Phys. Lett.*, 1980, **76**, 453.
1059. T. I. Morrison, G. K. Shenoy, L. E. Iton, G. D. Stucky and S. L. Suib, *J. Chem. Phys.*, 1982, **76**, 5665.
1060. P. H. Citrin, P. Eisenberg and R. C. Hewitt, *Phys. Rev. Lett.*, 1980, **45**, 1948.
1061. J. H. Sinfelt, G. H. Via and F. W. Lytle. *J. Chem. Phys.*, 1980, **72**, 4832.
1062. J. H. Hahn and K. O. Hodgson, *ACS Symp. Ser.*, 1983, 431; T. A. Smith, J. E. Penner-Hahn, M. A. Berding, S. Doniach and K. O. Hodgson, *J. Am. Chem. Soc.*, 1985, **107**, 5945.
1063. R. P. Pearson, *J. Am. Chem. Soc.*, 1969, **91**, 1252, 4947.
1064. J. K. Burdett, *Inorg. Chem.*, 1975, **14**, 931; 1981, **20**, 1959.
1065. J. K. Burdett, 'Molecular Shapes', Wiley, Interscience, 1980.
1066. I. B. Bersuker, *Coord. Chem. Rev.*, 1976, **14**, 357.
1067. I. B. Bersuker, 'The Jahn–Teller Effect and Vibronic Interactions in Chemistry', Plenum, New York, 1984.
1068. A. D. Liehr and C. J. Ballhausen, *Ann. Phys.*, 1958, **3**, 304.
1069. U. Opik and M. H. L. Pryce, *Proc. R. Soc. London, Ser. A*, 1957, **238**, 425.
1070. M. C. M. O'Brien, *Proc. R. Soc. London, Ser. A*, 1964, **281**, 323.
1071. M. D. Sturge, *Solid State Phys.*, 1967, **20**, 91.
1072. R. Engelman, 'The Jahn–Teller Effect in Molecules and Crystals', Wiley-Interscience, London, 1972.
1073. H. Elliott, B. J. Hathaway and R. C. Slade, *Inorg. Chem.*, 1966, **5**, 669.
1074. M. Gerloch, *Inorg. Chem.*, 1981, **20**, 638.
1075. H. Yamatera, *Acta Chem. Scand.*, 1979, **33**, 107; R. W. Jotham and S. F. A. Kettle, *Inorg. Chim. Acta*, 1971, **5**, 183.
1076. A. D. Liehr, *J. Phys. Chem.*, 1960, **64**, 43.
1077. D. Reinen, *Comments Inorg. Chem.*, 1983, **2**, 227; D. Reinen, C. Friebel and K. P. Retz, *J. Solid State Chem.*, 1972, **4**, 103.
1078. M. Bacci, *Struct. Bonding (Berlin)*, 1983, **55**, 67.
1079. R. M. Clay, P. Murray-Rust and J. Murray-Rust, *J. Chem. Soc., Dalton Trans.*, 1973, 595.
1080. Ref. 885, pp. 790–847, 1085.
1081. D. Reinen and C. Friebel, *Inorg. Chem.*, 1984, **23**, 791.
1082. D. Reinen, *J. Solid State Chem.*, 1979, **27**, 71.
1083. R. Boca, private communication.
1084. C. J. Simmons, K. Seff, N. W. Alcock, W. Fitzgerald and B. J. Hathaway, *Acta Crystallogr., Sect. C*, 1985, **41**, 42.
1085. J. D. Dunitz, 'X-Ray Structure Determination of Organic Molecules', Cornell University Press, London, 1979, chap. 7; K. N. Trueblood, *J. Mol. Struct.*, 1985, **130**, 103.
1086. I. Bertini and D. Gatteschi, *J. Inorg. Nucl. Chem. Lett.*, 1972, **8**, 207.
1087. N. J. Ray, L. Hullett, R. Sheahan and B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1981, 1463.
1088. R. H. Brocherts, A. Kanzaki and H. Abe, *Phys. Rev. B: Solid State*, 1970, **2**, 23.
1089. R. E. Coffman, *J. Chem. Phys.*, 1968, **48**, 609.
1090. R. G. Wilson, F. Holnj and N. E. Hedgecock, *Phys. Rev. B: Solid State*, 1970, **1**, 3609.
1091. H. O. Wellern, Ph.D. Thesis, University of Marburg, 1973.
1092. C. J. O'Connor, E. Sinn and R. L. Carlin, *Inorg. Chem.*, 1977, **16**, 3314.
1093. C. J. O'Connor, E. Sinn, T. L. Fariss and B. S. Deaver, Jr., *J. Phys. Chem.*, 1982, **86**, 2369.
1094. J. P. Keifzers and R. O. Day, *Acta Crystallogr., Sect. C*, 1984, **40**, 404.

1095. B. Walsh and B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1980, 681.
1096. M. Duggan, B. J. Hathaway and J. Mullane, *J. Chem. Soc., Dalton Trans.*, 1980, 690.
1097. F. Hanic, *Acta Crystallogr.*, 1959, **12,** 739.
1098. J. R. Ferraro and G. J. Long, *Acc. Chem. Res.*, 1975, **8,** 171.
1099. F. Valch, B. Koren, P. Sivy and M. Melink, *Struct. Bonding (Berlin)*, 1983, **55,** 101.
1100. M. Serator, H. Langfelderova, J. Gazo and J. Stracelsky, *Inorg. Chim. Acta,* 1978, **30,** 267; B. Papankova, M. Serator, J. Gazo and J. Stracelsky, *Inorg. Chim. Acta,* 1982, **60,** 171; M. D. Joesten, F. D. Strygley and P. Galen-Lenhert, *Inorg. Chem.*, 1983, **22,** 1255; A. H. Ewald and E. Sinn, *Inorg. Chem.*, 1969, **8,** 537; A. Paduan-Filho, F. P. Missell and R. L. Carlin, *Solid State Commun.*, 1981, **37,** 529.
1101. D. R. Bloomquist and R. D. Willett, *Coord. Chem. Rev.*, 1982, **47,** 125 and refs. therein; J. A. Ibers, L. J. Pace, J. Martinsen and B. M. Hoffman, *Struct. Bonding (Berlin)*, 1982, **50,** 1.
1102. L. Fabbrizzi, M. Micheloni and P. Paoletti, *Inorg. Chem.*, 1974, **13,** 3019.
1103. T. J. Lee, T. H. Lu, C.-S. Chung and T. S. Lee, *Acta Crystallogr., Sect. C,* 1984, **40,** 70; *J. Inorg. Nucl. Chem. Lett.*, 1981, **43,** 2333.
1104. L. Menadue, G. C. Pellacani, L. P. Battaglia, A. B. Corradi, F. Sandrolini, A. Motori, R. J. Pylkki and R. D. Willett, *J. Chem. Soc., Dalton Trans.*, 1984, 2187.
1105. W. D. Harrison, D. M. Kennedy and B. J. Hathaway, *Inorg. Nucl. Chem. Lett.*, 1981, **17,** 87.
1106. W. D. Harrison, D. M. Kennedy, M. Power, R. Sheahan and B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1981, 1556; W. D. Harrison, B. J. Hathaway and D. Kennedy, *Acta Crystallogr., Sect. C,* 1979, **35,** 2301.
1107. R. Harlow, W. J. Wells, G. W. Watt and S. H. Simonsen, *Inorg. Chem.*, 1975, **14,** 1468.
1108. H. B. Burgi, *Angew. Chem., Int. Ed. Engl.*, 1975, **14,** 460; H. B. Burgi and J. D. Dunitz, *Acc. Chem. Res.*, 1983, **16,** 153; H. B. Burgi, *Abstr. Am. Crystallogr. Assoc.*, (May 1984), 20.
1109. R. Boca, *Inorg. Chem.*, 1981, **20,** 1618; R. Boca, P. Pelikan, M. Breza and J. Gazo, *Polyhedron,* 1983, **2,** 921.
1110. S. Tyagi and B. J. Hathaway, unpublished results.
1111. R. J. Fereday, P. Hodgson, S. Tyagi and B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1981, 2070.
1112. E. U. Condon and S. H. Shortly, 'The Theory of Atomic Spectra', Cambridge University Press, Cambridge, 1963.
1113. J. S. Griffiths, 'Theory of Transition Metal Ions', Cambridge University Press, Cambridge, 1961.
1114. C. K. Jorgensen, 'Modern Aspects of Ligand-Field Theory', North-Holland, Amsterdam, 1971.
1115. C. K. Ballhausen, 'Molecular Electronic Structures of Transition Metal Complexes', McGraw-Hill, New York, 1979.
1116. M. Gerloch and R. C. Slade, 'Ligand-Field Parameters', Cambridge University Press, Cambridge, 1977.
1117. A. D. Liehr, *Prog. Inorg. Chem.*, 1962, **3,** 281; 1962, **4,** 455; 1963, **5,** 385.
1118. H. B. Gray and C. J. Ballhausen, 'Molecular Orbital Calculation', Benjamin, New York, 1965.
1119. C. A. L. Becker, D. W. Meek and T. M. Dunn, *J. Phys. Chem.*, 1968, **72,** 3588.
1120. D. E. Billing, *J. Chem. Soc. (A)*, 1970, 2099.
1121. D. J. Garner and F. E. Mabbs, *J. Chem. Soc., (A)*, 1970, 1711, 1716.
1122. R. J. Fereday, *J. Chem. Soc. (A)*, 1971, 3035.
1123. R. Krishnamurphy and W. D. Schaap, *J. Chem. Educ.*, 1969, **46,** 779; 1970, **47,** 433; A. L. Companion and D. J. Trevor, *J. Chem. Educ.*, 1975, **52,** 710.
1124. D. W. Smith, *Struct. Bonding, (Berlin)*, 1972, **12,** 49; 1978, **35,** 87.
1125. J. S. Wood and P. T. Green, *Inorg. Chem.*, 1969, **8,** 491; J. S. Wood, *J. Chem. Soc. (A)*, 1969, 1582.
1126. J. R. Roberts, 'Molecular Orbital Calculations', Benjamin, New York, 1962.
1127. P. C. de Mello, M. Hehenberger, S. Larsson and M. Zerner, *J. Am. Chem. Soc.*, 1980, **102,** 1278; S. Larsson, B. O. Roos and E. M. Siegbahn, *Phys. Chem. Lett.*, 1983, **96,** 436.
1128. H. Johanson and C. J. Ballhausen, *Mol. Phys.*, 1966, **10,** 175.
1129. P. Ros, A. van der Avoird and G. C. A. Schuit, *Coord. Chem. Rev.*, 1967, **2,** 77; A. D. Bacon and M. C. Zerner, *Theor. Chim. Acta,* 1979, **53,** 21; L. L. Lohr and W. N. Lipscomb, *Inorg. Chem.*, 1963, **2,** 911; L. L. Lohr, *Inorg. Chem.*, 1967, **6,** 1890.
1130. W. E. Hatfield, H. D. Bedon and S. M. Horner, *Inorg. Chem.*, 1965, **4,** 1181.
1131. B. M. Gimarc and J.-K. Zhu, *Inorg. Chem.*, 1983, **21,** 399.
1132. R. Sheahan and B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1979, 17.
1133. B. K. Coltrain and S. C. Jackels, *Inorg. Chem.*, 1981, **20,** 2032.
1134. T. Yamabe, K. Hori, T. Minato, K. Fukui and Y. Sugiura, *Inorg. Chem.*, 1982, **21,** 2040.
1135. C. P. Keijzers, and H. J. M. de Avoird, *Inorg. Chem.*, 1972, **11,** 1338.
1136. P. J. M. Geurts, P. C. P. Bouten and A. van der Avoird, *J. Chem. Phys.*, 1980, **73,** 1306.
1137. R. L. Belford and G. Belford, *Theor. Chim. Acta,* 1965, **3,** 465.
1138. R. L. Belford, G. Belford and J. W. Carmichael, *J. Chem. Phys.*, 1976, **46,** 4515.
1139. D. W. Smith, *Inorg. Chim. Acta,* 1977, **22,** 1.
1140. K. H. Johnson, *Adv. Quantum Chem.*, 1973, **7,** 143.
1141. D. A. Case and M. Karplus, *J. Am. Chem. Soc.*, 1977, **99,** 6182; S. F. Sontum and D. A. Case, *J. Phys. Chem.*, 1982, **86,** 1596; S. Harris, *Chem. Phys.*, 1982, **67,** 229; A. Bencini and D. Gatteschi, *J. Am. Chem. Soc.*, 1983, **105,** 5535.
1142. S. R. Destardins, K. W. Penfold, S. L. Cohen, R. L. Musselman and E. I. Solomon, *J. Am. Chem. Soc.* 1983, **105,** 4590.
1143. P. Day and C. K. Jorgensen, *J. Chem. Soc.*, 1964, 6226.
1144. C. E. Schaffer, *Struct. Bonding (Berlin)*, 1968, **5,** 68; 1973, **14,** 69; S. E. Harnung and C. E. Schaffer, *Struct. Bonding (Berlin)*, 1972, **12,** 201, 257.
1145. M. Gerloch and I. Morgenstern-Badarau, *J. Chem. Soc., Dalton Trans.*, 1977, 1619.
1146. R. J. Deeth and M. Gerloch, *Inorg. Chem.*, 1984, **24,** 1754.
1147. A. Bencini, C. Benelli and D. Gatteschi, *Coord. Chem. Rev.*, 1984, **60,** 131.
1148. R. J. Deeth and M. Gerloch, *Inorg. Chem.*, 1984, **23,** 3853; 1985, **24,** 4490.

1149. M. Gerloch and R. J. Woolley, *Prog. Inorg. Chem.*, 1984, **31**, 371; D. A. Cruse and M. Gerloch, *J. Chem. Soc., Dalton Trans.*, 1977, 1917; B. N. Figgis, M. Gerloch, J. Lewis and R. C. Slade, *J. Chem. Soc. (A)*, 1968, 2028.
1150. M. Gerloch, J. H. Harding and R. J. Wooley, *Struct. Bonding (Berlin)*, 1981, **46**, 1.
1151. L. Banci, C. Benelli, D. Gatteschi and F. Mani, *Inorg. Chem.*, 1982, **21**, 1130.
1152. G. A. Barclay, B. F. Hoskins and C. H. L. Kennard, *J. Chem. Soc. (A)*, 1966, 1443.
1153. S. Vijaya and P. T. Manoharan, *Inorg. Chem.*, 1981, **20**, 1304.
1154. M. Bacci, *Inorg. Biochem.*, 1980, **13**, 49.
1155. M. Gerloch, *Prog, Inorg. Chem.*, 1979, **26**, 1.
1156. R. G. R. Bacon and H. A. O. Hill, *Q. Rev. Chem. Soc.*, 1965, **19**, 95; R. G. R. Bacon and S. C. Rennison, *J. Chem. Soc. (C)*, 1969, 308.
1157. A. D. Zuberbuhler, *Helv. Chim. Acta*, 1970, **53**, 473.
1158. R. P. A. Sneeden and I. Tkatchenko, in 'Comprehensive Organometallic Chemistry', ed. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, 1982, vol. 8.
1159. In ref. 17, p. 1300.
1160. J. Schmidt, R. Jira, J. Sedlmeier, R. Turringer and H. Kojer, *Angew. Chem., Int. Ed. Engl.* 1962, **1**, 80; ref. 20, p. 660.
1161. R. F. Jameson and N. J. Blackburn, *J. Inorg. Nucl. Chem.*, 1975, **37**, 809; *J. Chem. Soc., Dalton Trans*, 1976, 534.
1162. E. V. Shtamm, A. P. Purmal and Y. I. Skurlatov. *Int. J. Chem. Kinet.*, 1979, **11**, 461; *Russ. J. Phys. Chem. (Engl. Transl.)*, 1974, **48**, 1323; 1977, **51**, 1825.
1163. G. Davis and M. A. El-Sayed, in ref. 30, p. 281.
1164. Ref. 21, p. 719.
1165. M. H. Gubelmann and A. F. William, *Struct. Bonding (Berlin)*, 1983, **55**, 1.
1166. S. Kida, H. Okawa and Y. Nishida, in ref. 30, p. 425.
1167. M. M. Rogic, M. D. Swerdloff and T. R. Demmin, in ref. 30, p. 268.
1168. D. E. Fenton and R. L. Lintvedt, *J. Am. Chem. Soc.*, 1978, **100**, 268, 6367; N. Oishi, Y. Nishida, K. Ida and S. Kida, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 2847.
1169. J. K. Kochi and R. A. Sheldon, 'Metal-Catalyzed Oxidations of Organic Compounds', Academic, New York, 1981, chap. 4.
1170. D. E. Wilcox, A. G. Porras, Y. T. Hwang, K. Lerch, M. E. Winkler and E. I. Solomon, *J. Am. Chem. Soc.*, 1985, **107**, 4015.
1171. M. A. El-Sayed, A. El-Touky and G. Davies, *Inorg. Chem.* 1985, **24**, 3387 and refs. therein.
1172. M. J. Nicol, *S. Afr. J. Chem.*, 1984, **37**, 77; J. J. Byerley, S. A. Fouda and G. L. Rempel, *J. Chem. Soc., Dalton Trans.*, 1975, 1329.
1173. L. Alagna, T. Prosperi and A. A. G. Tomlinson, in 'Ion Exchange Technology', ed. D. Naden and M. Streat, Ellis Horwood, London, 1984, p. 222.
1174. B. J. Hathaway and C. E. Lewis, *J. Chem. Soc. (A)*, 1969, 2295; M. Shimokawabe, N. Takezawa and H. Kobayashi, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 1337.
1175. S. S. Thantry, K. V. Iyer and P. S. Ramanathan, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 585.
1176. P. J. Hoek and J. Reedijk, *J. Inorg. Nucl. Chem.*, 1980, **42**, 1759; S. K. Sahni and J. Reedijk, *Coord. Chem. Rev.*, 1984, **59**, 1.
1177. S. J. Gentry, N. W. Hurst and A. Jones, *J. Chem. Soc., Faraday Trans. 1*, 1979, **75**, 1688; M. Iwamoto, H. Nagano, H. Furukawa and S. Kagawa, *Chem. Lett.*, 1983, 471; A. Maes and A. Cremers, *J. Chem. Soc., Faraday Trans. 1*, 1984, 513.
1178. C.-C. Chao and J. H. Lunsford, *J. Chem. Phys.*, 1972, **57**, 2890; E. F. Vansant and J. H. Lunsford, *J. Phys. Chem.*, 1972, **76**, 2860; R. G. Herman and D. R. Flentge, *J. Phys. Chem.*, 1978, **82**, 720; A. von Zelewsky and J.-M. Bemtgen, *Inorg. Chem.*, 1982, **21**, 1771; J. C. Conesa and J. Soria, *J. Chem. Soc., Faraday Trans. 1*, 1979, 406, 423; G. Martini and L. Burlamacchi, *J. Phys. Chem.*, 1979, **83**, 2505.
1179. D. R. Flentge, J. H. Lunsford, P. A. Jacobs and J. B. Uytterhoeven, *J. Phys. Chem.*, 1975, **79**, 354; A. Maes, R. A. Schoonheydt, A. Cremers and J. B. Uytterhoeven, *J. Phys. Chem.*, 1980, **84**, 2795; J. Texter, D. H. Strome, R. G. Herman and K. Klier, *J. Phys. Chem.*, 1977, **81**, 333.
1180. K. Seff, *Acc. Chem. Res.*, 1976, **9**, 121; H. S. Lee and K. Seff, *J. Phys. Chem.*, 1981, **85**, 397; H. S. Lee, W. V. Cruz and K. Seff, *J. Phys. Chem.*, 1982, **86**, 3562.
1181. I. E. Maxwell and J. J. de Boer, *J. Phys. Chem.*, 1975, **79**, 1874.
1182. T. Ichikawa and L. Evans, *J. Chem. Soc., Faraday Trans. 1*, 1981, **77**, 2567; *J. Am. Chem. Soc.*, 1981, **103**, 5355; M. Narayan and L. Kevan, *J. Phys. C*, 1983, **16**, 361; *J. Chem. Phys.*, 1983, **78**, 3573; D. Suryanarayana, P. A. Narayana and L. Kevan, *Inorg. Chem.*, 1983, **22**, 474.
1183. Ref. 1173, p. 222; L. Alagna and A. A. G. Tomlinson, *J. Chem. Soc., Faraday Trans. 1*, 1982, **78**, 3009.
1184. A. Clearfield and S. P. Pack, *J. Inorg. Nucl. Chem.*, 1980, **42**, 771.
1185. L. Alagna, A. A. G. Tomlinson, C. Ferragina and A. L. Ginestra, *J. Chem. Soc., Dalton Trans.*, 1981, 2376.
1186. R. J. P. Williams, *Endeavour*, 1967, **26**, 96.
1187. E. Frieden, *Sci. Am.*, 1968, **218**, 103.
1188. H. Sigel, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 167; B. L. Vallee and R. J. P. Williams, *Proc. Natl. Acad. Sci. USA*, 1968, **59**, 498; R. J. P. Williams, *Inorg. Chim. Acta*, 1971, **5**, 137.
1189. R. Malkin and B. G. Malmstrom, *Adv. Enzymol.*, 1970, **33**, 177.
1190. H. C. Freeman, *Adv. Protein Chem.*, 1967, **22**, 257.
1191. R. Osterberg, *Coord. Chem. Rev.*, 1974, **12**, 309.
1192. J. A. Fee, *Struct. Bonding (Berlin)*, 1975, **23**, 1.
1193. G. R. Moore and R. J. P. Williams, *Coord. Chem. Rev.*, 1976, **18**, 125.
1194. H. Beinert, *Coord. Chem. Rev.*, 1977, **23**, 119; 1980, **33**, 55.
1195. C. D. Garner and P. M. Harrison, *Chem. Br.*, 1982, **18**, 173.
1196. R. A. Lontie and D. R. Groeseneken, *Top. Curr. Chem.*, 1983, **108**, 1.
1197. E.-I. Ochiai, *J. Chem. Educ.*, 1974, **51**, 235.

1198. S. A. K. Wilson, *Brain,* 1912, **34,** 295.
1199. B. Sarkar, in ref. 997, p. 275.
1200. A. M. Feabane and D. R. Williams, 'The Principles of Bio-Inorganic Chemistry', Monographs for Teachers No 31, The Chemical Society, London, 1977, chap. 1 and 2.
1201. In ref. 7, p. 19.
1202. C. A. Owen, 'Copper Deficiency and Toxicity Acquired and Inherited in Plants, Animals and Man', Noyes, Park Ridge, NJ, 1981.
1203. E. I. Solomon, K. W. Penfield and D. E. Wilcox, *Struct. Bonding (Berlin),* 1983, **53,** 1.
1204. E. I. Solomon, in ref. 30, p. 1.
1205. Ref. 26, Table 9.1, p. 219.
1206. P. M. Colman, H. C. Freeman, J. M. Guss, M. Murata, V. A. Norris, J. A. M. Ramshaw and M. P. Venkatappa, *Nature (London),* 1978, **272,** 319.
1207. G. E. Norris, B. F. Anderson and E. N. Baker, *J. Mol. Biol.,* 1983, **165,** 501; J. M. Guss and C. Freeman, *J. Mol. Biol.,* 1983, **169,** 521.
1208. H. B. Gray and B. G. Malmstrom, *Comments Inorg. Chem.,* 1983, **11,** 203.
1209. E. I. Solomon, J. W. Hare, D. M. Dooley, J. H. Dawson, P. J. Stephens and H. B. Gray, *J. Am. Chem. Soc.,* 1980, **102,** 168; K. W. Penfold, R. R. Gay, R. S. Himmelwright, N. C. Eickman, V. A. Norris, H. C. Freeman and E. I. Solomon, *J. Am. Chem. Soc.,* 1981, **103,** 4382.
1210. G. F. Bryce, *J. Phys. Chem.,* 1966, **70,** 3549; A. S. Brill and G. F. Bryce, *J. Chem. Phys.,* 1968, **48,** 4398.
1211. R. Branden, B. G. Malmstrom and T. Vanngard, *Eur. J. Biochem.,* 1973, **36,** 195; ref. 29, p. 225.
1212. J. S. Richardson, K. A. Thomas, B. H. Rubin and D. C. Richardson, *Proc. Natl. Acad. Sci. USA,* 1975, **72,** 1349.
1213. J. A. Tainer *et al.,* in 'Brookhaven Protein Structure Data Bank', ed. D. C. Richardson and J. S. Richardson, 1980.
1214. K. A. Magnus and W. E. Love, in 'Invertebrate Oxygen-Binding Proteins', ed. J. Lamy and J. Lamy, Dekker, New York, 1981, p. 363.
1215. M. E. Winkler, K. Lerch and E. I. Solomon, *Inorg. Chem.,* 1981, **103,** 7002; R. S. Himmelwright, N. C. Eickman, C. D. Lubien, K. Lerch and E. I. Solomon, *J. Am. Chem. Soc.,* 1980, **102,** 7339.
1216. E. I. Solomon, D. M. Dooley, R. H. Wang, H. B. Gray, M. Cerdonio, F. Mogno and G. L. Romani, *J. Am. Chem. Soc.,* 1976, **98,** 1029; D. M. Dooley, R. A. Scott, J. Ellinghaus, E. I. Solomon and H. B. Gray, *Proc. Natl. Acad. Sci. USA,* 1978, **75,** 3019.
1217. G. A. Ozin, *Prog. Inorg. Chem.,* 1971, **14,** 173.
1218. A. L. Verma and H. J. Bernstein, *J. Chem. Phys.,* 1974, **61,** 2560; H. Beraldo, A. Garner-Suillerot and L. Tosi, *Inorg. Chem.,* 1983, **22,** 4117.
1219. C. D. Lubien, M. E. Winkler, R. J. Thamann, R. A. Scott, M. S. Co, K. O. Hodgson and E. I. Solomon, *J. Am. Chem. Soc.,* 1981, **103,** 7014.
1220. N. J. Blackburn and S. S. Hasnain, in ref. 30(b); S. S. Hasnain, Daresbury Laboratory Report, 1986, P523E.
1221. G. L. Woolery, L. Powers, M. Winkler, E. I. Solomon and T. G. Spiro, *J. Am. Chem. Soc.,* 1984, **106,** 86.
1222. D. E. Wilcox, J. R. Long and E. I. Solomon, *J. Am. Chem. Soc.,* 1984, **106,** 2186; M. S. Co, K. O. Hodgson and T. K. Eccles, *J. Am. Chem. Soc.,* 1981, **103,** 984; R. A. Scott, S. P. Cramer, R. W. Shaw, H. Beinert and H. B. Gray, *Proc. Natl. Acad. Sci. USA,* 1981, **78,** 664; D. M. Dooley and C. E. Cote, *Inorg. Chem.,* 1985, **24,** 3996.
1223. Y. Hirayama and Y. Sugiura, *Biochem. Biophys. Res. Commun.,* 1979, **86,** 40; *Inorg. Chem.,* 1976, **15,** 679; Y. Sugiura, *Inorg. Chem.,* 1978, **17,** 2176.
1224. R. B. Bereman, M. R. Churchill and G. Sheilds, *Inorg. Chem.,* 1979, **18,** 3117.
1225. J. Van Rijn, W. L. Driessen, J. Reedijk and J.-M. Lehn, *Inorg. Chem.,* 1984, **23,** 3584.
1226. R. D. Bereman, G. D. Sheilds, J. R. Dorfman and J. Bordner, *J. Inorg. Biochem.,* 1983, **19,** 75.
1227. T. Sakurai, S. Suzuki and A. Nakahara, *Bull. Chem. Soc. Jpn.,* 1981, **54,** 2313.
1228. R. H. Petty and L. J. Low, *J. Chem. Soc., Chem. Commun.,* 1978, 483.
1229. D. E. Fenton, N. Bresciani-Pahor, M. Calligaris, G. Nardin and L. Randaccio, *J. Chem. Soc., Chem. Commun.,* 1979, 39.
1230. S. M. Nelson, F. Esho, A. Lavery and M. G. B. Drew, *J. Am. Chem. Soc.,* 1983, **105,** 5693.
1231. V. McKee, J. V. Dagdigian, R. Bau and C. A. Reed, *J. Am. Chem. Soc.,* 1981, **103,** 7000.
1232. L. K. Thompson, *Can. J. Chem.,* 1983, **61,** 579; L. K. Thompson, A. W. Hanson, and B. S. Ramaswamy, *Inorg. Chem.,* 1984, **23,** 2459.
1233. Y. Nishida, H. Shimo, H. Maehara and S. Kida, *J. Chem. Soc., Dalton Trans.,* 1985, 1945.
1234. J. Reedijk, P. J. M. W. L. Birker and J. van Rijn, *J. Mol. Catal.,* 1984, **23,** 369.
1235. A. Ludi and H. U. Guldel, *Struct. Bonding (Berlin),* 1973, **14,** 1; B. M. Chadwick and A. G. Sharpe, *Adv. Inorg. Chem. Radiochem.,* 1966, **8,** 84.
1236. A. Longo and T. Buch, *Inorg. Chem.,* 1967, **6,** 556; S. Yoshimura, A. Katagiri, Y. Deguchi and S. Yoshizawa, *Bull. Chem. Soc. Jpn.,* 1980, **53,** 2434; H. Yokoi and A. Hanaki, *Chem. Lett.,* 1984, 481.
1237. A. Katagiri, S. Yoshimura and S. Yoshizawa, *Inorg. Chem.,* 1981, **20,** 1143.
1238. M. Wicholas and T. Wolford, *Inorg. Chem.,* 1974, **13,** 316.
1239. O. P. Anderson, *Inorg. Chem.,* 1975, **14,** 730.
1240. S. Tyagi and B. J. Hathaway, *J. Chem. Soc., Dalton Trans.,* 1983, 199.
1241. D. M. Duggan and D. N. Hendrickson, *Inorg. Chem.,* 1974, **13,** 1911.
1242. Z. Koziskova, M. Dunaj-Jurco and J. Gazo, *Chem. Zvesti,* 1984, **38,** 583.
1243. N. Bjerrum, C. J. Ballhausen and C. K. Jorgensen, *Acta Chem. Scand.,* 1954, **8,** 1275.
1244. T. Distler and P. A. Vaughan, *Inorg. Chem.,* 1967, **6,** 126; M. Badri and J. W. S. Jamieson, *Can. J. Chem.,* 1979, **57,** 1926.
1245. B. Morosin, *Acta Crystallogr., Sect. B,* 1976, **32,** 1237.
1246. K.-F. Tebbe, *Z. Anorg. Allg. Chem.,* 1982, **489,** 93.
1247. M. A. Hitchman and G. L. Rowbottom, *Coord. Chem. Rev.,* 1982, **42,** 55.

1248. A. H. Norbury and A. I. P. Sinha, *Q. Rev. Chem. Soc.*, 1970, **24**, 69; J. Kohout, M. Hvastijova and J. Gazo, *Coord. Chem. Rev.*, 1978, **27**, 141.
1249. Z. Dori and R. F. Ziolo, *Chem. Rev.*, 1973, **73**, 247; K. Matsumoto, S. Ooi, K. Natkatsuka, W. Mori, S. Suzuki, A. Nakahara and Y. Nakao, *J. Chem. Soc., Dalton Trans.*, 1985, 2095.
1250. A. H. Norbury, *Adv. Inorg. Chem. Radiochem.*, 1975, **17**, 232.
1251. F. Valach, M. Dunaj-Jurco and M. Handlovic, *J. Cryst. Mol. Struct.*, 1980, **10**, 61.
1252. M. Hvastijova and J. Kohout, *Z. Chem.*, 1984, **24**, 105.
1253. J. Garaj, *Inorg. Chem.*, 1969, **8**, 304.
1254. P. C. Jain and E. C. Lingafelter, *J. Am. Chem. Soc.*, 1967, **89**, 6131.
1255. M. A. Porai-Koshits, *Zh. Strukt. Khim.*, 1963, **4**, 584.
1256. B. W. Brown and E. C. Lingfafelter, *Acta Crystallogr.*, 1964, **17**, 254.
1257. V. Vrabel, J. Lokaj and J. Garaj, *Collect. Czech. Chem. Commun.*, 1983, **48**, 2893.
1258. J. Reedijk, *Recl. Trav. Chim. Pays-bas*, 1970, **89**, 993; J. Reedijk, J. C. A. Windhorst, N. H. M. van Ham and W. L. Groeneveld, *Recl. Trav. Chim. Pays-bas*, 1971, **90**, 234; P. J. M. W. L. Birker and J. Reedijk, in ref. 30, p. 409.
1259. J. Pradillas, H. W. Chen, F. W. Koknat and J. P. Fackler, *Inorg. Chem.*, 1979, **18**, 3519.
1260. V. Vrabel, J. Garaj and L. Kutschabsky, *Acta Crystallogr., Sect. B*, 1979, **35**, 357.
1261. W. M. Reiff, H. Wong, B. Dockum, T. Brennan and C. Cheng, *Inorg. Chim. Acta*, 1978, **30**, 69; I. M. Procter, B. J. Hathaway and P. G. Hodgson, *J. Inorg. Nucl. Chem.*, 1982, **34**, 3689.
1262. W. R. McWhinnie and J. D. Miller, *Adv. Inorg. Chem. Radiochem.*, 1967, **12**, 135.
1263. E. D. McKenzie, *Coord. Chem. Rev.*, 1971, **6**, 187.
1264. K. Amornjarusiri and B. J. Hathaway, unpublished results.
1265. R. F. Ziolo, M. Allen, D. D. Titus, H. B. Gray and Z. Dori, *Inorg. Chem.*, 1972, **11**, 3044.
1266. M. Mathew and G. J. Palenik, *J. Coord. Chem.*, 1971, **1**, 243; R. Allmann, W. Henke and D. Reinen, *Inorg. Chem.*, 1978, **17**, 378.
1267. W. Henke, S. Kremer and D. Reinen, *Inorg. Chem.*, 1983, **22**, 2858.
1268. G. Marongue, E. C. Lingafelter and P. Paolotti, *Inorg. Chem.*, 1969, **8**, 2763.
1269. G. De Munno and G. Bruno, *Acta Crystallogr., Sect. C*, 1984, **40**, 2030.
1270. F. E. Mabbs and J. K. Porter, *J. Inorg. Nucl. Chem.*, 1973, **3**, 3219; M. A. Hitchman and T. D. Waite, *Inorg. Chem.*, 1976, **15**, 2150.
1271. N. V. Mani and S. Ramaseshan, *Z. Kristallogr.*, 1961, **115**, 97.
1272. C. A. Beever and H. Lipson, *Proc. R. Soc. London, Ser. A*, 1934, **146**, 570; J. N. Varghese and E. N. Maslen, *Acta Crystallogr., Sect. B*, 1985, **41**, 184.
1273. H. Nakai and Y. Deguchi, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 2557.
1274. J. Fisher and R. Weiss, *Acta Crystallogr., Sect. B*, 1973, **29**, 1963.
1275. C. K. Prout, J. R. Carruthers and F. J. C. Rossotti, *J. Chem. Soc. (A)*, 1971, 3342.
1276. L. P. Battaglia, A. B. Corradi and L. Menabue, *Inorg. Chem.*, 1983, **22**, 3251.
1277. K.-E. Falk, E. Ivanova, B. Roos and T. Vanngard, *Inorg. Chem.*, 1970, **9**, 556.
1278. J. Comarmond, B. Dietrich, J.-M. Lehn and R. Louis, *J. Chem. Soc., Chem. Commun.*, 1985, 74.
1279. W. H. Watson, *Inorg. Chem.*, 1969, **8**, 1879.
1280. D. S. Brown, J. D. Lee and B. G. A. Melson, *Chem. Commun.*, 1968, 852.
1281. D. W. Thompson, *Struct. Bonding (Berlin)*, 1971, **9**, 27; D. P. Graddon, *Coord. Chem. Rev.*, 1969, **4**, 1.
1282. S. Ooi and Q. Fernando, *Chem. Commun.*, 1967, 532.
1283. B.-M. Anti, B. K. S. Lundberg and N. Ingri, *Acta Chem. Scanda.*, 1972, **26**, 3984.
1284. M. R. Truter and B. L. Vickery, *J. Chem. Soc., Dalton Trans.*, 1972, 395.
1285. G. L. Shoemaker, E. Kostiner and J. B. Anderson, *Z. Crystallogr.*, 1980, **152**, 317.
1286. M. Quarton and A. W. Kolsi, *Acta Crystallogr., Sect. C*, 1983, **39**, 664.
1287. J. C. Dewan and S. Lippard, *Inorg. Chem.*, 1980, **19**, 2079.
1288. J. Balvich, K. P. Fivizzani, S. P. Pavkovic and J. N. Brown, *Inorg. Chem.*, 1976, **15**, 71.
1289. W. D. Harrison and B. J. Hathaway, *Acta Crystallogr., Sect. B*, 1978, **34**, 2843.
1290. M. B. Ferrari, G. G. Fava and C. Pelizzi *J. Chem. Soc., Chem. Commun.*, 1977, 8.
1291. W. D. Harrison and B. J. Hathaway, *Acta Crystallogr., Sect. B*, 1980, **36**, 1069.
1292. D. Grinderow and F. Cesbron, *Acta Crystallogr., Sect. C*, 1983, **39**, 824.
1293. D. A. Palmer and R. van Eldik, *Chem. Rev.*, 1983, **83**, 651.
1294. C. Oldham, *Prog. Inorg. Chem.*, 1968, **10**, 223.
1295. M. R. Rosenthal, *J. Chem. Educ.*, 1973, **50**, 331; 'Perchoric Acid and Percholates', A. A. Schilts, G. F. Smith Chemical Co., Columbus, OH, 1979; N. M. N. Gowda, S. B. Naikar and G. K. N. Reddy, *Adv. Inorg. Chem. Radiochem.*, 1984, **28**, 255; J. L. Pascal, J. Potier, D. J. Jones, J. Roziere and A. Michalowicz, *Inorg. Chem.*, 1984, **23**, 2068; J. L. Pascal, J. Potier and C. S. Zhang, *J. Chem. Soc., Dalton Trans.*, 1985, 297.
1296. A. C. Braithwaite, C. E. F. Rickworth and T. N. Waters, *Inorg. Chim. Acta*, 1978, **26**, 63.
1297. A. W. Addison and E. Sinn, *Inorg. Chem.*, 1983, **22**, 1225; M. D. Glick, D. P. Gravel, L. L. Diaddario and D. B. Rorabacher, *Inorg. Chem.*, 1976, **15**, 1190.
1298. B. L. Kindberg, E. H. Griffith and E. L. Amma, *J. Chem. Soc., Chem. Commun.*, 1977, 461; O. P. Anderson, C. M. Perkins and K. K. Brito, *Inorg. Chem.*, 1983, **22**, 1267.
1299. C. M. Harris, T. N. Lockyer and H. Waterman, *Nature (London)*, 1961, **192**, 424.
1300. G. A. Barclay and C. H. L. Kennard, *Nature (London)*, 1961, **192**, 425; B. J. Hathaway and A. Murphy, *Acta Crystallogr., Sect. B*, 1980, **36**, 295; T. W. Hambley, C. L. Raston and A. H. White, *Aust. J. Chem.*, 1977, **30**, 1965.
1301. F. Akhtar, D. M. L. Goodgame, G. W. Raynor-Canham and A. C. Shapski, *Chem. Commun.*, 1968, 1389.
1302. E. Sinn and C. M. Harris, *Coord. Chem. Rev.*, 1969, **4**, 391.
1303. R. H. Holm and M. J. O'Connor, *Prog. Inorg. Chem.*, 1971, **14**, 241.
1304. T. P. Cheeseman, D. Hall and T. N. Waters, *J. Chem. Soc. (A)*, 1966, 685.
1305. S. M. Nelson, *Pure Appl. Chem.*, 1980, **52**, 2461.

1306. R. J. Dudley, R. J. Fereday, B. J. Hathaway and P. G. Hodgson, *J. Chem. Soc. (A)*, 1972, 1341.
1307. M. B. Ferrari, A. B. Corradi, G. G. Fava, C. G. Palmieri, M. Nardelli and C. Pelizzi, *Acta Crystallogr., Sect. B*, 1972, **29**, 1808.
1308. R. Hoppe and G. Wingefeld, *Z. Anorg. Allg. Chem.*, 1984, **519**, 189.
1309. T. Fleischer and R. Hoppe, *J. Fluorine Chem.*, 1982, **19**, 529.
1310. L. Er-Rakho, C. Michel, J. Provost and B. Raveau, *J. Solid State Chem.*, 1981, **37**, 151.
1311. D. Datta and A. Chakravorty, *Inorg. Chem.*, 1983, **22**, 1611; D. Datta, P. K. Mascharak and A. Chakravorty, *Inorg. Chem.*, 1981, **20**, 1673.
1312. D. Datta, P. K. Mascharak and A. Chakravorty, *Inorg. Chim. Acta*, 1978, **27**, L95.
1313. D. Datts and A. Chakravorty, *Inorg. Chem.*, 1982, **27**, 363.
1314. R. Scholder and V. Voelskow, *Z. Anorg. Chem.*, 1951, **266**, 256.
1315. L. Thenard, *Ann. Chim. Phys.*, 1818, **9**, 51; E. T. Gray. Jr., R. W. Taylor and D. W. Margerum, *Inorg. Chem.*, 1977, **16**, 3047.
1316. M. Kruger, *Pogg. Ann.*, 1844, **62**, 477.
1317. B. Brauner and B. Kuzma, *Ber. Dtsch. Keram. Ges.*, 1907, **40**, 3362.
1318. M. W. Lister, *Can. J. Chem.*, 1953, **31**, 638.
1319. C. Malaprade, *C. R. Hebd. Seances Acad. Sci.*, 1937, **204**, 979; 1940, **210**, 504; L. Malatesta, *Gazz. Chim. Ital.*, 1941, **467**, 580; G. Beck, *Mikrochim. Acta*, 1951, **38**, 152; D. D. Upreti, R. Mishra and R. P. Agarwal, *Inorg. Chim. Acta*, 1980, **45**, L221.
1320. K. Wahl and W. Klemm, *Z. Anorg. Chem.*, 1952, **270**, 69; J. S. Magee, Jr. and R. H. Wood, *Can. J. Chem.*, 1965, **43**, 1234.
1321. W. Klemm and E. Huss, *Z. Anorg. Allg. Chem.*, 1949, **258**, 221.
1322. R. Hoppe and G. Wingefeld, *Z. Anorg. Allg. Chem.* 1984, **519**, 195.
1323. L. Fabbrizzi and A. Poggi, *J. Chem. Soc., Chem. Commun.*, 1980, 646.
1324. D. C. Olson and J. Vasilevskis, *Inorg. Chem.*, 1971, **10**, 463.
1325. P. R. Sharp and A. J. Bard, *Inorg. Chem.*, 1983, **22**, 3462.
1326. B. B. Kaul and K. B. Pandeya, *J. Inorg. Nucl. Chem.*, 1981, **43**, 1942.
1327. L. F. Warren and M. A. Bennett, *Inorg. Chem.*, 1976, **15**, 3126.
1328. C. B. Castellani, L. Fabrizzi, M. Licchelli, A. Perotti and A. Poggi, *J. Chem. Soc., Chem. Commun.*, 1984, 806; J. J. Bour and J. J. Steggerda, *Chem. Commun.*, 1967, 85.
1329. T. Sakurai, J.-I. Hongo, A. Nakahara and Y. Nakao, *Inorg. Chim. Acta*, 1980, **46**, 205; Y. Sulfab and N. Al-Shatti, *Inorg. Chim. Acta*, 1984, **87**, L23.
1330. D. E. Hyatt, J. L. Little, J. T. Morgan, F. R. Schoter and L. J. Todd, *J. Am. Chem. Soc.*, 1967, **86**, 3347.
1331. M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Piling, A. D. Pitts, M. Reintjes, L. F. Warren. Jr. and P. A. Wegner, *J. Am. Chem. Soc.*, 1968, **90**, 879; L. F. Warren, Jr. and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1968, **90**, 4823.
1332. R. Hoppe, *Angew. Chem.*, 1950, **62**, 339.
1333. T. Fleischer and R. Hoppe, *Z. Anorg. Allg. Chem.*, 1982, **492**, 76.
1334. I. Hadinec, L. Jensovsky, A. Linek and V. Synecek, *Naturwissenschaften*, 1960, **47**, 377.
1335. J. F. Boas, J. R. Pilbrow, G. J. Troup, C. Morre and T. D. Smith, *J. Chem. Soc. (A)*, 1969, 965; G. R. Clark, B. W. Skelton and T. N. Waters, *J. Chem. Soc., Chem. Commun.*, 1972, 1163; G. R. Clark, B. W. Skelton and T. N. Waters, *J. Chem. Soc., Dalton Trans.*, 1976, 1528.
1336. P. J. M. W. L. Birker, *Inorg. Chem.*, 1977, **16**, 2478.
1337. K. J. Oliver and T. N. Waters, *J. Chem. Soc., Chem. Commun.*, 1982, 1111.
1338. L. L. Diaddario, W. R. Robinson and D. W. Margerum, *J. Am. Chem. Soc.*, 1983, **22**, 1021.
1339. J. D. Forrester, A. Zalkin and D. H. Templeton, *Inorg. Chem.*, 1964, **3**, 1507.
1340. D. Coucouvanis, F. J. Hollander and M. L. Caffery, *Inorg. Chem.*, 1976, **15**, 1853.
1341. K. L. Brown, *Cryst. Struct. Commun.*, 1979, **8**, 157.
1342. J. G. Wijnhoven, T. E. M. van der Hark and P. T. Beurskens, *J. Cryst. Mol. Struct. Commun.*, 1979, **8**, 157.
1343. M. G. Kanatzidis, N. C. Baenziger and D. Coucouvanis, *Inorg. Chem.*, 1985, **24**, 2680.
1344. P. T. Beurskens, J. A. Cras and J. J. Steggerda, *Inorg. Chem.*, 1968, **7**, 810.
1345. R. M. Wing, *J. Am. Chem. Soc.*, 1968, **90**, 4828.
1346. R. M. Wing, *J. Am. Chem. Soc.*, 1967, **89**, 5599.
1347. G. C. Allen and K. D. Warren, *Struct. Bonding (Berlin)*, 1971, **9**, 49; G. C. Allen and K. D. Warren, *Inorg. Chem.*, 1969, **8**, 1895.
1348. A. Balikungeri and M. Pelletier, *Inorg. Chim. Acta*, 1978, **29**, 141.
1349. T. J. Thamann and T. M. Loehr, *Spectrochim. Acta, Part A*, 1980, **36**, 751.
1350. F. P. Bossu, K. L. Chellappa and D. W. Margerum, *J. Am. Chem. Soc.*, 1977, **99**, 2195.
1351. A. R. Hendrickson, R. L. Martin and N. M. Rohde, *Inorg. Chem.*, 1976, **15**, 2115.
1352. J. M. Anast and D. W. Margerum, *Inorg. Chem.*, 1981, **20**, 2319.
1353. T. A. Neubecker, S. T. Kirksey, Jr., H. L. Chellappa and D. W. Margerum, *Inorg. Chem.*, 1979, **18**, 444; S. T. Kirksey, Jr., T. A. Neubecker and D. W. Margerum, *J. Am. Chem. Soc.*, 1979, **101**, 1631; A. G. Lappin, M. P. Youngblood and D. W. Margerum, *J. Am. Chem. Soc.*, 1980, **19**, 407; L. J. Kirschenbaum and D. Meyerstein, *Inorg. Chem.*, 1980, **19**, 1373; J. S. Rybka, J. L. Kurtz, T. A. Neubecker and D. W. Margerum, *J. Am. Chem. Soc.*, 1980, **19**, 2791; M. P. Youngblood and D. W. Margerum, *Inorg. Chem.*, 1980, **19**, 3068; J. M. T. Raycheba and D. W. Margerum, *Inorg. Chem.*, 1981, **20**, 45; G. D. Owens and D. W. Margerum, *J. Am. Chem. Soc.*, 1981, **20**, 1446; J. S. Rybka and D. W. Margerum, *Inorg. Chem.*, 1981, **20**, 1453; C. A. Koval and D. W. Margerum., *Inorg. Chem.*, **20**, 2311; A. W. Hamburg and D. W. Margerum, *Inorg. Chem.*, 1983, **22**, 3884; D. W. Margerum, in ref. 30(b).
1354. K. Kumar, F. P. Rotzinger and J. F. Endicott, *J. Am. Chem. Soc.*, 1983, **105**, 7064.
1355. S. Muralidharan and G. Ferraudi, *Inorg. Chem.*, 1981, **20**, 2306.
1356. N. I. Al-Shatti, M. A. Hussein and Y. Sulfab, *Transition Met. Chem.*, 1984, **9**, 31.
1357. W. E. Keyes, W. E. Swartz, Jr. and T. M. Loehr, *Inorg. Chem.*, 1978, **17**, 3316.

1358. D. G. Brown and U. Weser, *Inorg. Chem.*, 1980, **19,** 264.
1359. G. I. Rozovskii, A. K. Misyavichyus and A. Yu. Prokopchik, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1972, **17,** 219.
1360. M. Anbar, *Adv. Chem. Ser.*, 1965, **49,** 126.
1361. D. W. Margerum, in 'Oxidase and Related Redox Systems', ed. T. E. King, H. S. Mason and M. Morrison, Pergamon, Oxford, 1982, pp. 193.
1362. *Chem. Eng. News,* 1975, Dec. 8, p. 26; *ibid.*, 1976, Jan. 26, p. 23.
1363. G. A. Hamilton, P. K. Adolf, J. deJersey, G. C. DuBois, G. R. Dyrkacz and R. D. Libby, *J. Am. Chem. Soc.*, 1978, **100,** 1899; G. A. Hamilton, R. D. Libby and C. R. Hartzell, *Biochem. Biophys. Res. Commun.*, 1973, **55,** 333; G. R. Dyrkacz, R. D. Libby and G. A. Hamilton, *J. Am. Chem. Soc.*, 1976, **98,** 626.
1364. R. D. Bereman, M. J. Ettinger, D. J. Kosman and R. J. Kurland, *Adv. Chem. Ser.*, 1977, **162,** 263; D. J. Kosman, M. J. Ettinger, R. S. Giordano and R. D. Bereman, *Biochemistry,* 1977, **16,** 1597; R. D. Bereman and D. J. Kosman, *J. Am. Chem. Soc.*, 1977, **99,** 7322.
1365. S. T. Kirksey, Jr. and D. W. Margerum, *Inorg. Chem.*, 1979, **18,** 966; J. M. T. Raycheba and D. W. Margerum, *Inorg. Chem.*, 1981, **20,** 45.
1366. W. Harnischmacher and R. Hopper, *Angew. Chem., Int. Ed. Engl.*, 1973, **12,** 582.
1367. M. Arjomand and D. J. Machin, *J. Chem. Soc., Dalton Trans,* 1975, 1061.
1368. V. E. Bondybey and J. H. English, *J. Phys. Chem.*, 1984, **88,** 2247; D. McIntosh and G. A. Ozin, *Inorg. Chem.*, 1977, **16,** 59.
1369. E.-I. Ochiai, *Inorg. Nucl. Chem. Lett.*, 1973, **9,** 987.

54
Silver

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The coordination chemistry of silver has historically been centred on the reaction of silver(I) ions with N-donor ligands and halides. However, an extensive chemistry now exists for P- and S-donor ligands, whilst for O-donor ligands only weak complexes are generally formed and they have been studied in much less detail. Based on the reactivity and stability of its coordination complexes, the silver(I) ion has been characterized as a class B or 'soft' acid, for which the following stability order is observed: $N \ll P > As > Sb$; $O \ll S \sim Se \sim Te$; $F < Cl < Br < I$. Comparative studies between ligands with these donor atoms allowed the relative stability of silver bonds to be determined as $P > S > N > O$.

A large amount of structural data for silver complexes has been accumulated. The linear $[H_3N—Ag—NH_3]^+$ ion was established in 1934 and for many years two-coordination was believed to be characteristic of the Ag^I ion. With further development of silver chemistry, a wide range of geometries was realized, and especially in solution the silver(I) ion was often found to adopt a tetrahedral arrangement. For example, in liquid ammonia Raman spectroscopic studies have shown that the linear $[Ag(NH_3)_2]^+$ ion becomes further solvated to yield the tetrahedral ion $[Ag(NH_3)_4]^+$. For pyridine, a tetrahedral complex $[Ag(py)_4]ClO_4$ has recently been isolated and its X-ray crystal structure determined. The complex was thermally unstable and on standing at room temperature readily lost 2 mol of pyridine. With imidazole, another structural aspect of silver chemistry becomes highlighted, that of cluster formation. In bis(imidazole)silver(I) nitrate, an isolated linearly coordinated cation is present. Investigations on the perchlorate salt, however, suggested a different arrangement and an X-ray crystal structure determination revealed the presence of a planar $(Ag^+)_6$ cluster, in which three radiating pairs of Ag^+ ions were disposed on the corners of an equilateral triangle. In this system both three- and five-coordinate Ag^I ions were present.

Rather complex silver coordination is also exemplified by P- and S-donor ligands and a coordination number of two is rarely observed. With phosphines, a number of structural types have been found including tetrameric cubane and stair-type complexes. Steric requirements were found to play a dominant role in these structural variations. With thiols and metallothio anion ligands, recent attention has been focussed on the clusters generated by their reaction with silver(I) ions. Novel ring systems have been found where the silver ion was either three- or four-coordinate. Much future work is necessary to consolidate a systematic understanding of the factors determining the geometries of complex species in the solid state and in solution.

Both the Ag^{II} and Ag^{III} ions are readily accessible, although in aqueous solution these high oxidation states are thermodynamically and kinetically unstable and to achieve even limited stability requires the presence of N heterocycles, N macrocycles or biguanides. The preparation of these Ag^{II} and Ag^{III} complexes can be carried out by either electrochemical or chemical oxidations. Traditionally, $S_2O_8^{2-}$ has been a convenient oxidant, and with neutral ligands precipitation of red insoluble $S_2O_8^{2-}$ salts occurs. A number of other oxidants have been used, such as ozone, PbO_2 or $NOClO_4$.

In non-aqueous solvents, it is possible to alter the relative stability of the oxidation states of silver such that with some N_4 macrocycles the silver(I) complexes are unstable and will actually disproportionate to produce the corresponding silver(II) complexes.

One application of these high oxidation state silver complexes has been as oxidants in organic syntheses. In particular, decarboxylations often proceed in high yield with Ag^{II} complexes or with $S_2O_8^{2-}$ in the presence of an Ag^I salt.

Based on the limited structural data available, Ag^{II} and Ag^{III} complexes appear to commonly adopt a square planar arrangement with four N-donor atoms. Some six-coordinate complexes have also been identified. The Ag^{II} ion is paramagnetic ($4d^9$) and is readily detected by ESR spectroscopy. ESR spectra of N-heterocyclic Ag^{II} complexes in frozen aqueous solution have also been interpreted in terms of square planar geometry and showed that little or no structural change occurred on dissolution. Considering the stability observed with N-donor ligands for Ag^{II} and Ag^{III}, it seems that these ions have more class A or 'hard' acid characteristics.

The photographic industry continues to dominate in the industrial applications of silver complexes, especially in relation to halogen compounds, and a vast amount of literature each year is concerned with this field. Photographic applications of coordination complexes are covered separately in Chapter 59 and will not be dealt with in depth here.

Biological and medicinal aspects of silver chemistry are covered in Chapter 62 but a number of features will be outlined here. Silver salts are powerful bacteriocides and it has been known for many years that storing water in silver vessels prevents spoilage. Silver nitrate is highly corrosive and can be applied locally to remove warts or cauterize wounds. In many states in the USA, a 1% $AgNO_3$ solution is dropped into the eyes of newborn infants to prevent ophthalmia neonatorum. Silver sulfadiazine has been found effective as a topical application to prevent infections in serious burns victims.

Since much research work on silver complexes has been biased towards N-donor ligands, a large proportion of this chapter has been devoted to that field with broader coverage given to P-, S- and O-donor ligands. Several volumes of the Gmelin series were recently published (1972–1976) on the coordination chemistry of N-, O-, P- and S-donor ligands. These constitute the only substantial reviews of silver chemistry and exhaustively cover the European literature in particular. Owing to limitations of space, the references given here are to the more frequently cited periodicals and review journals and preference has been given to those published in English before January 1984.

54.1 SILVER(I) COMPOUNDS

51.1.1 Group IV Ligands

54.1.1.1 Cyanides and fulminates

(i) Cyanides

An important method for the extraction of silver from silver ores was by cyanidation, in which the ores were leached with a dilute solution of sodium cyanide. The silver was then recovered from the solution by treatment with zinc. Silver has also been precipitated from cyanide solutions by electrolysis and such solutions are employed as the electrolyte in silver plating.

The complex species present in aqueous solutions containing an excess of cyanide are $Ag(CN)_2^-$, $Ag(CN)_3^{2-}$ and $Ag(CN)_4^{3-}$. Thermodynamic data for these species are collected in Table 1.[1,2]

Crystal data are available for the salts $KAg(CN)_2$[3,4] and $K_3Ag(CN)_4$.[5] These salts were isolated by evaporation at room temperature of aqueous solutions containing KCN and AgCN in appropriate molar ratios. $K_3Ag(CN)_4$ was anhydrous (not hydrated as originally proposed)[6] and isomorphous with the corresponding copper salt. The dicyanoargentate(I) ion was found to be linear, with an Ag—C distance of 213 pm. $KAg(CN)_2$ has UV absorption bands at 236 and 270 nm.[7]

IR spectroscopy has been used to study complex formation in solution and the absorption of complex cyano anions on 200–400 mesh Dowex-A-1 anion exchange resin.[8] To complement these studies the Raman spectra have been obtained for solid $KAg(CN)_2$ and for the complex

Table 1 Some Thermodynamic Data for Complex Silver Cyanides[1,2]

	log K[a]	*log K*[b]	$\Delta H^{\circ b}$ (kJ mol^{-1})	$\Delta S^{\circ b}$ (J K^{-1} mol^{-1})
$Ag(CN)_2^-/Ag\cdot(CN^-)^2$	20.0	20.48	−138	−71, (−67)[2]
$Ag(CN)_3^{2-}/Ag\cdot(CN^-)^3$	20.3 (30 °C)	21.4	−140	−54, (−46)[2]
$Ag(CN)_4^{3-}/Ag\cdot(CN^-)^4$	20.8 (30 °C)	—	—	—
$Ag(OH)(CN)^-/Ag\cdot(OH^-)\cdot(CN^-)$	12.7	13.2	—	—
$Ag^+\cdot CN^-/AgCN$ (s)	−15.4	−15.66	—	—

[a] 25 °C, $I = 1.0$. [b] 25 °C, $I = 0$.

Table 2 Characteristic Vibrational Bands for (a) Silver(I) Cyanides

	Raman[9] (cm^{-1})	*Infrared*[8] (cm^{-1})
$Ag(CN)_2^-$	γ 2139_{sym}	γ 2135_{asym}
$Ag(CN)_3^{2-}$	γ 2108_{sym}	
	γ 2108_{asym}	γ 2105_{asym}
$Ag(CN)_4^{3-}$	γ 2097_{sym}	
	γ 2094_{asym}	γ 2092_{asym}

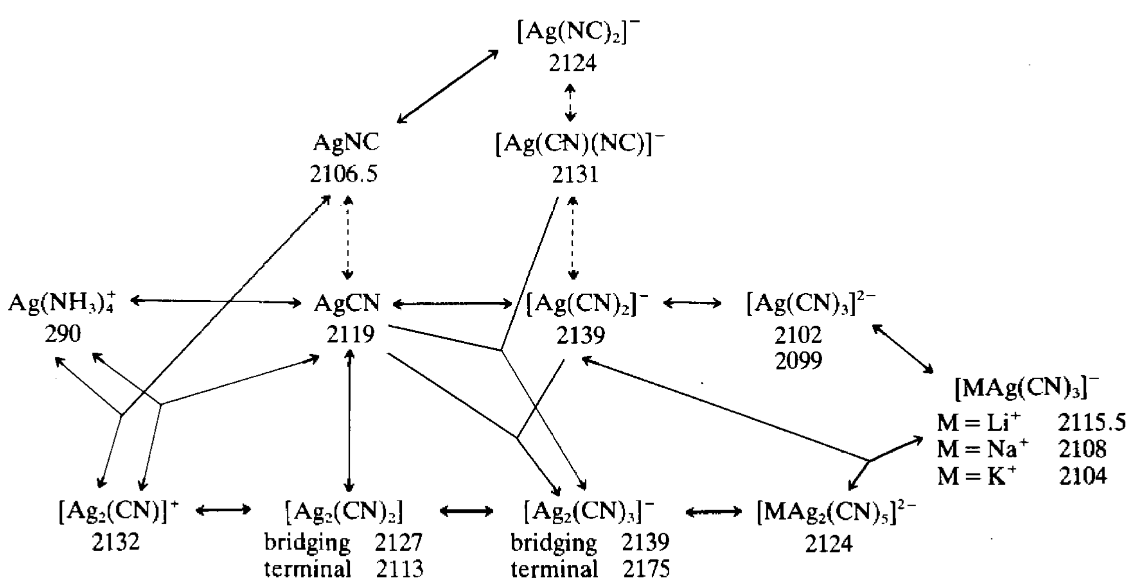
(b) For Solid $KAg(CN)_2$

$\gamma_1 (A)$	$\gamma_2 (A)$	$\gamma_3 (B)$	$\gamma_4 (B)$	$\gamma_5 (A)$	$\gamma_6 (A)$	$\gamma_6 (B)$	$\gamma_7 (A)$	$\gamma_7 (B)$	*Ref.*
2145.5	360	—	—	250	328	—	142	—	10
2148	—	2139.5	392	252	—	311	—	147	11
—	360	2140	390	250	—	310	—	107	12

species in solution at various CN^- to Ag^I molar ratios.[9,10] Spectral data are presented in Table 2.[8–12]

More recently, Raman spectroscopy has been used to analyze the equilibria between Ag^+ and CN^- in liquid ammonia.[13] The factors affecting linkage isomerism, ion aggregation and ion pairing of the following species were discussed: AgCN, AgNC, $Ag(CN)_2^-$, $Ag(CN)(NC)^-$, $Ag(NC)_2^-$, $Ag(CN)_3^{2-}$, $Ag_2(CN)^+$, $Ag_2(CN)_2$, $Ag_2(CN)_3^-$, $MAg_2(CN)_5^{2-}$ ($M = Na^+, K^+$) and $MAg(CN)_3^-$ ($M = Li^+$, Na^+ or K^+). The equilibria and characteristic CN^- absorption for these silver(I) cyano species are summarized in Scheme 1. In the horizontal direction the scheme shows a change in the ratio of cyanide to silver in both mono- and bi-nuclear complexes. Compounds which lie on a vertical axis are in general linkage isomers (the exception is $Ag_2(CN)_2$ which is the dimer of AgCN). Compounds in the bottom row are formed by joining together a pair of mononuclear complexes. Finally, $MAg(CN)_3^-$ is a heterobinuclear complex, or ion pair, formed from $Ag(CN)_3^{2-}$ and an alkali metal cation.

The solubility of silver cyanide in anhydrous HF at 20 °C was at least 3.2 M; it was less soluble in wet HF and virtually insoluble in the aqueous acid. On the basis of IR and ^1H NMR spectroscopy it was proposed that the equilibria described by equations (1) and (2) occurred. It was estimated that there was ~40% each of $(HCN)_2Ag^+$ and Ag^+ and 20% $HCNAg^+$ in



Scheme 1 Raman absorption bands (cm^{-1}) used to characterize species involved in equilibria between CN^- and Ag^I in liquid ammonia[13]

solution.[14] Transition metal complexes of HCN and related ligands were recently reviewed.[15]

$$AgCN + HF \longrightarrow HCNAg^+ + F^- \quad (1)$$

$$2HCNAg^+ \longrightarrow (HCN)_2Ag^+ + Ag^+ \quad (2)$$

(*ii*) *Fulminates*

Silver fulminate was recognized by Gay–Lussac[16] to have the same composition as silver cyanate, thus providing the first example of isomerism. Two polymorphs of silver fulminate are known and their structures have been determined.[17] Silver fulminate is regarded as a poor detonator due to its dangerous sensitivity; this may depend on the presence or absence of the second form.[17]

The preparation of a non-explosive and thermally stable fulminate complex, $Et_4N^+[Ag(CNO)_2]^-$, has been described and ^{14}N NMR and IR spectra have been recorded ($\delta = +164$ p.p.m. in CH_2Cl_2, *cf.* NO_3^-,[18] $2\gamma_s CNO = 2294$, $\gamma_{as} CNO = 2119$, $\gamma_s CNO = 1144\ cm^{-1}$).[19]

54.1.2 Nitrogen Ligands

54.1.2.1 Ammonia and amines

(*i*) *Ammonia*

Classical methods of group analysis and separation take advantage of the stability of the $[Ag(NH_3)_2]^+$ ion to separate silver from mercury. Treatment of a precipitate containing AgCl with dilute ammonia leads to the reaction in equation (3) bringing the silver into solution. To confirm the presence of Ag^+, nitric acid must then be added to cause reprecipitation of AgCl. In aqueous ammonia, the diammine was the highest species formed, and thermodynamic data for its formation are collected in Table 3.[20–23]

$$AgCl(s) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) + Cl^-(aq) \quad (3)$$

Where equilibrium constants have been expressed in concentration terms, it has been found that significant variations can occur depending on the concentration and kind of ionic medium employed. Recently, these variations were investigated for the Ag^+/NH_3 system where it was discovered that the formation constants were generally lower in NO_3^- media than in ClO_4^-.[22,23] The variation was interpreted in terms of interactions occurring between oppositely charged ions in solution.

In liquid ammonia, Raman spectroscopy indicated that the major species present was the tetraammine.[24] This was based on the observation that the band assigned as $\gamma(N—Ag—N)_{sym}$ at $370\ cm^{-1}$ in aqueous solutions was absent in liquid ammonia, whilst a new band occurred at $290\ cm^{-1}$. Also, whilst no tetraammine salts have been isolated from aqueous solution, recrystallization of $[Ag(NH_3)_2]ClO_4$ from liquid ammonia yielded $[Ag(NH_3)_4]ClO_4$.

Crystal structural data are available for $[Ag(NH_3)_2]_2SO_4$,[25] $[Ag(NH_3)_2]NO_3$ (room temperature[26] and 223 K[27]) and $[Ag(NH_3)_2][Ag(ONO)_2]$.[28] For the latter complex, the linear $[H_3N—Ag—NH_3]^+$ units had Ag—N bond lengths of 211 pm, a little longer than that found in

Table 3 Some Thermodynamic Data for the Formation of Silver(I) Ammines at 25 °C

Medium	*log* β_1	*log* β_2	$\Delta H\beta_2$ (kJ mol^{-1})	$\Delta S\beta_2$ (J K^{-1} mol^{-1})	*Ref.*
$I = 0$	3.31 ± 0.06	7.22 ± 0.01	−56.1 ± 0.4	−49.8 ± 21	20, 21
1 M $LiNO_2$	3.22	7.21	—	—	22
1 M $NaNO_3$	3.28	7.25	—	—	22
1 M KNO_3	3.27	7.24	—	—	22
1 M $NaClO_4$	3.36	7.38	—	—	22
3 M $NaClO_4$	3.62	7.93	−59.3	−47.0	23

Table 4 Observed Frequencies (cm^{-1}) in Raman Spectra of Saturated Aqueous Solutions of Diammine Silver(I) Complexes[30]

$[Ag(NH_3)_2]NO_3$	$[Ag(NH_3)_2]ClO_4$	*Assignment*
3373	—	$\gamma(NH_3)$ asym
3287	3293	$\gamma(NH_3)$ sym
3195	3203	$2\delta(NH_3)$ deg
1658	1658	$\delta(NH_3)$ deg
1624	1634	$\delta(NH_3)$ deg
1224	1223	$\delta(NH_3)$ sym
372	369	γ(NAgN) sym
1399 (γ_3)	1107 (γ_3)	
1048 (γ_1)	934 (γ_1)	NO_3^- or ClO_4^-
715 (γ_4)	629 (γ_4)	bands
—	460 (γ_2)	

the earlier studies (189 pm). In aqueous solution, an X-ray diffraction study of diammine silver(I) nitrate showed that the Ag—N bond was even longer at 222 ± 2 pm.[29]

IR and Raman studies of some diammine silver(I) salts and their deuterated derivatives have been reported.[30,31] Characteristic absorption bands are given in Tables 4 and 5.

A ^1H and ^2H NMR study of single crystals of $[Ag(NH_3)_2][Ag(ONO)_2]$ has been reported.[32] Rapid reorientational motions of the ammine groups around their C_3 axes were found. The orientations of the C_3 axes within the crystal corresponded with the Ag—N bond directions of the $[H_3N—Ag—NH_3]^+$ unit. The deuterium quadrupole coupling constant was determined and found to be identical to that of solid ND_3. It was concluded that the electronic configuration and the geometric structure of ammonia were changed only very slightly upon coordination to silver ions.

The explosive nature of silver ammine salts (fulminating silver) has been thoroughly investigated. Neither the solid, precipitated during the addition of ammonia to a solution of a silver(I) salt, nor the silver salt ammine complex, formed when the precipitate was redissolved, was sensitive to even the most severe initiators of explosions. Tests have been performed on a range of concentrations and temperatures and for both fresh and aged solutions. Dried whole solutions were not sensitive to mechanical shock unless they were dried at 95 °C or higher; then some darkening occurred and the solids would explode if initiated with shocks greater than 100 kg cm^{-1} drop weight. An extremely sensitive and violently explosive precipitate separated from ammoniacal silver solutions at pH values above 12.9. Such a precipitate could not be formed by addition of ammonia alone to a dissolved silver salt, but did form when KOH was added to the Ag–NH_3 complex solution, or when silver oxide was dissolved in ammonia with or without decantation. The explosive species was given as Ag_3N_4. It was noticed that both ammonium carbonate and acetate completely inhibited NH_3–Ag–oxide explosions.[33]

Tollens' reagent, which is based on $Ag(NH_3)_2^+$, can be used to test for the presence of aldehydes. The weakly oxidizing system converts aldehydes to carboxylates and if the reaction is slow and the walls of the vessel are clean, then a silver mirror can often be observed, otherwise a grey or black precipitate results. No oxidation of ketones occurs, except with α-hydroxy ketones, and on the basis of its reaction with sugars, they can be categorized as

Table 5 Observed Frequencies (cm^{-1}) in the IR Spectra of some Diammine Silver(I) Salts and their Deuterated Analogues[31]

$[Ag(NH_3)_2]NO_3$	$[Ag(ND_3)_2]NO_3$	$[Ag(NH_3)_2]_2SO_4$	$[Ag(ND_3)_2]_2SO_4$	*Assignment*
3320	2465	3320	2450	NH_3 str (asym)
3270	2375	3230	2380	
3180	2320	3150	2290	NH_3 str (sym)
1624	1177	1642	1196	NH_3 def
1602	1167	1626	1185	
1246	953	1236	937	NH_3 bend
1214	932	1222	930	NH_3 bend
660	495	740	548	NH_3 rock
610	479	703	517	

reducing or non-reducing. Reducing sugars contain hemiacetal or hemiketal groups and exist in equilibrium with non-cyclic aldehydes or α-hydroxy ketones. On the other hand, a negative test is found for non-reducing sugars, since these carbohydrates contain acetals or ketals, which do not exist in equilibrium with aldehydes or α-hydroxy ketones.[34]

(*ii*) *Aliphatic monodentate amines*

In aqueous solution, silver does not appear to bind more than two monodentate amine ligands, which are predicted to give linear or almost linear structures, similar to that found for ammonia.

Table 6 Some Thermodynamic Data for Silver Complexes of Primary Amines

Amine	pK_a	$\log \beta_1$	$\log \beta_2$	$-\Delta H°\beta_2$ (kJ mol^{-1})	$-\Delta S°\beta_2$ (J K^{-1} mol^{-1})	*Ref.*
Methyl	[a] 10.644 ± 0.005	3.06 ± 0.03	6.78 ± 0.05			35
	[b] 10.666 ± 0.002	3.07 ± 0.02	6.89 ± 0.01	49.04 ± 0.2	32.6 ± 0.2	36
Ethyl	[a] 10.662 ± 0.004	3.44 ± 0.03	7.34 ± 0.05			35
	[c] 10.98 ± 0.01	3.46 ± 0.06	7.57 ± 0.02			37
	[b] 10.636 ± 0.008	3.46 ± 0.03	7.36 ± 0.03	52.34 ± 0.1	34.6 ± 0.1	36
n-Propyl	[c] 10.92 ± 0.01	3.47 ± 0.03	7.54 ± 0.01			37
	[b] 10.564 ± 0.004	3.45 ± 0.01	7.44 ± 0.02	53.22 ± 0.04	36.1 ± 0.1	36
Isopropyl	[a] 10.623 ± 0.008	3.64 ± 0.06	7.77 ± 0.04	59.83		35,44
n-Butyl	[c] 10.93 ± 0.02	3.50 ± 0.1	7.60 ± 0.05			37
	[b] 10.639 ± 0.003	3.43 ± 0.03	7.48 ± 0.03	52.59 ± 0.2	33.3 ± 0.2	36
s-Butyl	[a] 10.559 ± 0.003	3.65 ± 0.06	7.77 ± 0.03			35
t-Butyl	[a] 10.663 ± 0.01	3.69 ± 0.06	7.87 ± 0.03	57.45		35, 44
n-Pentyl	[c] 10.93 ± 0.06	3.55 ± 0.09	7.70 ± 0.03			37
	[b] 10.597 ± 0.007	3.57 ± 0.02	7.50 ± 0.03	51.63 ± 0.1	22.2 ± 0.1	36
n-Hexyl	[b] 10.630 ± 0.001	3.54 ± 0.02	7.56 ± 0.02	53.05 ± 0.4	33.3 ± 0.4	36
Cyclopropyl	[a] 9.064 ± 0.01	3.10 ± 0.08	6.43 ± 0.05			35
Cyclopentyl	[a] 10.625 ± 0.003	3.61 ± 0.06	7.83 ± 0.04	65.48		35, 44
Cyclohexyl	[a] 10.617 ± 0.006	3.72 ± 0.08	8.02 ± 0.05	62.17		35, 44

[a] $I = 0.1$, $T = 25$ °C. [b] $I = 0$, $T = 25$ °C. [c] $I = 0.05$, $T = 20$ °C.

The effect of increasing the chain length on the stability of the silver amine complex has been investigated. Thermodynamic data are collected in Table 6.[35–37,44] In general, there was an increase in stability as methyl groups were substituted in the hydrocarbon chain. For *n*-butyl- and *n*-pentyl-amine complexes, however, there may have been some hydrophobic interaction between the two ends of the hydrocarbon chain, since the increase in stability over the methylamine complex was not as large as expected.[36] Secondary and tertiary amine complexes were generally less stable than their primary amine analogues (Table 7).[38–44]

Table 7 Some Thermodynamic Data for Silver Complexes of Secondary and Tertiary Amines

Amine	*Medium*	*Log* β_1	*Log* β_2	$\Delta H°\beta_2$ (kJ mol^{-1})	$\Delta S°\beta_2$ (J K^{-1} mol^{-1})	*Ref.*
Dimethylamine	20 °C, $I = 1.09$	2.23	4.55	—	—	38
	25 °C	—	—	−41	−33	39
Diethylamine	25 °C, $I \rightarrow 0$	—	6.38	−44.56	−27	39
	—	3.06	6.36	—	—	40
Diisopropylamine	25 °C, $I = 0.1$	3.41	6.73	—	—	44
	Acetone, 0.1 M $NaClO_4$	—	10.05 ± 0.13	—	—	41
Dibutylamine	Acetone, 0.1 M $NaClO_4$	—	10.18 ± 0.05	—	—	41
Diisobutylamine	Acetone, 0.1 M $NaClO_4$	—	8.83 ± 0.13	—	—	41
Diallylamine	Acetone, 0.1 M $NaClO_4$	—	8.96 ● 0.05	—	—	41
Trimethylamine	15 °C, $I \approx 0.1$	—	3.31	—	—	42
Triethylamine	25 °C, $I = 0.4$ ($C_6H_{15}N{\cdot}HNO_3$)	2.6	4.8	−78.7	−21	43
Tributylamine	50 mol % ethanol	2.22	3.82	—	—	40

(iii) *Ethylenediamine and aliphatic polyamines*

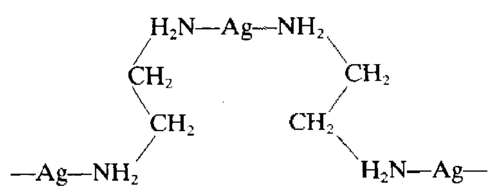
Studies on bidentate and higher dentate amine ligands have indicated that complex formation with silver(I) was rather more complicated than for monodentate amines. Polynuclear, protonated and even hydroxo complexes have been postulated to occur in solution.

The silver(I) ethylenediamine system has been thoroughly investigated and thermodynamic data for complex formation are given in Table 8.[45,46] The maximum coordination number of the silver(I) in these complexes was claimed to be two, although two molecules of ethylenediamine are coordinated. However, the stability constants, β_2, of $[Ag(NH_3)_2]^+$ and $[Ag(en)_2]^+$ were almost the same. A linear arrangement could not be achieved with ethylenediamine forming a chelate ring and could only occur if the ethylenediamines acted as monodentate ligands. This explained the stability constants found. However, when only one N of ethylenediamine coordinates, the other amino group must be able to add a proton or another Ag^+. This led to a variety of species not found for simple monodentate amines.

Table 8 Thermodynamic Data for Silver(I) Ethylenediamine Complexes

	Log β	ΔH° (kJ mol^{-1})	ΔS° (J K^{-1} mol^{-1})	*Ref.*
$AgHen^{2+}/Ag^+.H^+.en$	2.34	−25.4	−41	45
$AgH_2en_2^{3+}/Ag^+.(H^+)^2.(en)^2$	4.90	−50.8	−77	45
$AgH(en)_2^{2+}/Ag^+.(H^+).(en)^2$	6.47	−56.9	−66	45
$Ag(en)_2^+/Ag^+.(en)^2$	7.64	−52.5	−30	45
		−55.2 ± 1.3	−39 ± 5	46
$Ag_2(en)_2^{2+}/(Ag^+)^2.(en)^2$	13.15	−97.1	−74	45
		−107.8 ± 2.7	−109 ± 9	46

The crystal structure of $[Ag(en)]ClO_4$ has been determined.[47] In solution, it has been suggested that the 1:1 complex may exist as a hydrated chelate with some strain within the five-membered chelate ring.[46] In the solid state, however, the complex formed infinite chains (**1**) with a bridging ethylenediamine between the silver atoms.[47]



(1)

Recently the stability of silver(I) complexes of *N*-methyl-substituted 4-methyldiethylenetriamines has been investigated by potentiometric pH and pAg measurements. Besides mononuclear complexes, polynuclear and protonated complexes were formed. Evidence of hydroxo complexes was also presented.[48]

(iv) *Aromatic amines*

Silver(I) complexes with aromatic amines have been less studied than their aliphatic amine analogues, and in general are much less stable (Table 9).[49–52]

Once again, 1:2 linear complexes are expected, although it has been predicted that aromatic amines may also form 2:1 complexes because of the possibility that a second silver ion could coordinate with the aromatic nucleus.[49]

Complexation with racemic 2,3-di(4-aminophenyl)butane (L) gave $Ag(L)_3NO_3$, which was claimed to be six-coordinate with the silver bound to the six donor atoms.[53] By comparison, the *meso* stereoisomer gave only a 1:1 complex $AgNO_3$.

(v) *Aziridines, piperidines and quinuclidines*

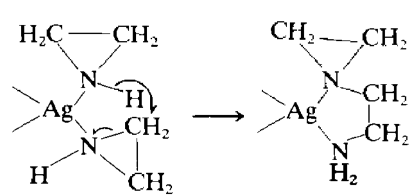
Addition of an excess of anhydrous aziridine to silver chloride resulted in dissolution and the formation of a colourless solution. Attempts to isolate a complex were unsuccessful and addition of water, ethanol or ether caused reprecipitation of silver chloride.

Table 9 Some Stability Constant Data for Silver(I) Complexes with Aromatic Amines

Amine	*Medium*	pK_a	$Log\ \beta_1$	$Log\ \beta_2$	*Ref.*
Aniline	25 °C, 1 M KNO_3	4.62	1.44	—	49
	17 °C, $I \approx 0.2$	—	—	3.47	50
	50 mol % EtOH	—	1.38	2.88	51
	25 °C, 59 wt % EtOH–H_2O	—	—	3.0 ± 0.05	52
2-Toluidine	25 °C, 1 M KNO_3	4.43	1.51	—	49
	25 °C, 59 wt % EtCH–H_2O	—	—	3.65 ± 0.05	52
3-Toluidine	25 °C, 1 M KNO_3	4.71	1.47	—	49
	25 °C, 59 wt % EtOH–H_2O	—	—	3.4 ± 0.05	52
4-Toluidine	25 °C, 1 M KNO_3	5.12	1.57	—	49
	25 °C, 59 wt % EtOH–H_2O	—	—	3.9 ± 0.05	52
2-Bromoaniline	25 °C, 59 wt % EtOH–H_2O	—	—	2.8 ± 0.05	52
3-Bromoaniline	25 °C, 59 wt % EtOH–H_2O	—	—	2.8 ± 0.05	52
4-Bromoaniline	25 °C, 59 wt % EtOH–H_2O	—	—	2.75 ± 0.05	52
2-Chloroaniline	25 °C, EtOH	—	—	1.71	51
3-Chloroaniline	25 °C, EtOH	—	—	2.13	51
4-Chloroaniline	25 °C, EtOH	—	—	2.65	51
4-Iodoaniline	25 °C, EtOH	—	—	2.50	51
2-Nitroaniline	25 °C, 59 wt % EtOH–H_2O	—	—	1.9	52
3-Nitroaniline	25 °C, 59 wt % EtOH–H_2O	—	—	1.7	52
4-Nitroaniline	25 °C, 59 wt % EtOH–H_2O	—	—	1.7	52
2,4-Dimethylaniline	96% EtOH	—	2.37	3.70 ($\log \beta_3 = 4.07$)	51
2,6-Dimethylaniline	25 °C, 1 M KNO_3	4.1	1.62	—	49
3,5-Dimethylaniline	25 °C, 1 M KNO_3	4.9	1.63	—	49
N-Methylaniline	25 °C, 1 M KNO_3	4.78	1.0		49
	25 °C, $I < 0.01$	—	1.38	1.74	51

With silver nitrate, colourless sheets could be precipitated by the addition of anhydrous ether to an aziridine solution. It was noticed that on standing for a few days in aqueous solution the salt decomposed and deposited metallic silver. The formation constants in aqueous solution were determined at 16.5 °C ($I = 1.0$ M $NaNO_3$): $\log \beta_1 = 2.40$, $\log \beta_2 = 5.40$.[54]

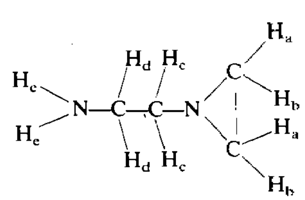
In the presence of a range of metal ions, including Ag^I, aziridine was found to dimerize to 1-(2-aminoethyl)aziridine (equation 4). A bis complex of this ligand was isolated as the silver nitrate salt. Characteristic ^1H NMR spectral data are given in Table 10.[55]



(4)

The stability of silver(I) salts of piperidine and alkylpiperidines has been reported.[56] Formation constants ($\log \beta_2$) were in the range 3.8–7.7 (Table 11).

Table 10 ^1H NMR Spectral Data for 1-(2-Aminoethyl)aziridine and its Silver(I) Complex (p.p.m.)[55]



	Solvent	$\delta(H_a)$	$\delta(H_b)$	$\delta(H_c)$	$\delta(H_d)$	$\delta(H_e)$
$Ag(L)_2NO_3$	D_2O	−1.43	−1.85	−2.38	−2.94	—
L	D_2O	−1.32	−1.73	−2.32	−2.77	—
	Neat	−1.04	−1.59	−2.14	−2.72	−1.42

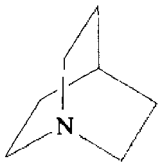
Reference: internal DSS (for D_2O) or TMS; $T = 37$ °C

Table 11 Formation Constants of some Silver(I) Salts of Piperidine and Alkylpiperidines (25 °C, $I = 0.5$ M KNO_3)[56]

Ligand	*Log* β_1	*Log* β_2
Piperidine	3.12 ± 0.1	6.43 ± 0.01
2-Methylpiperidine	3.450 ± 0.005	6.942 ± 0.004
3-Methylpiperidine	3.04 ± 0.01	6.427 ± 0.004
4-Methylpiperidine	3.20 ± 0.01	6.50 ± 0.01
2,6-Dimethylpiperidine	3.96 ± 0.04	7.71 ± 0.03
N-Methylpiperidine	2.64 ± 0.02	3.8 ± 0.1
N-Ethylpiperidine	3.12 ± 0.02	5.20 ± 0.06
2-Ethylpiperidine	3.84 ± 0.06	7.36 ± 0.02
2-Propylpiperidine	4.0 ± 0.1	7.52 ± 0.01
Quinuclidine (DMSO, $I = 0.1$)[58]	2.1	3.6

The crystal structure of the complex between silver iodide and piperidine has been determined.[57] The colourless crystals were prepared by warming silver iodide with sufficient piperidine to allow the silver iodide to dissolve and then allowing the resulting solution to cool. The structure consisted of tetrahedral clusters of iodide ions with the silver atoms embedded into the faces of the tetrahedron. The $(AgI)_4$ clusters were separated by the piperidine molecules which were bound to the silver *via* the N atom. The Ag—N bond lengths were 232.9 pm, while the Ag—I distances were 285.3, 293.6 and 294.2 pm.

The first metal complex of quinuclidine (**2**) was reported in 1966.[58] $Ag(quinuclidine)_2NO_3$ was isolated as a white solid after reaction of quinuclidine and silver nitrate in acetonitrile for several days. The formation constants were determined in DMSO (Table 11). The complex melted with decomposition at 158 °C.



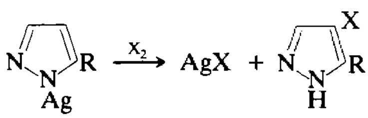
(**2**)

54.1.2.2 N-heterocyclic ligands

(*i*) *Pyrazoles and imidazoles*

Complexes containing the uninegative pyrazolide ion have been known since 1889 when the formation of an insoluble silver pyrazolide salt Ag(pz) was reported.[59] The structure has never been established but it was probably polymeric. Some substituted pyrazolide derivatives were also prepared at that time.

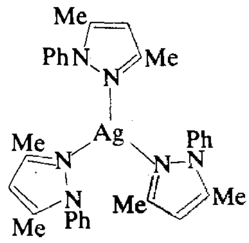
A stepwise halogenation of pyrazole and substituted pyrazoles has been carried out *via* their silver salts. Thus silver pyrazolide yields 4-halopyrazoles and 5-methylpyrazole gave 4-halo-5-methylpyrazole (equation 5).[60,61]



(5)

The silver complex (4-*i*-C_3F_7pz)Ag was found to be soluble in acetone where it was tetrameric. In general, silver pyrazolides were found to be remarkably insensitive to light.[62]

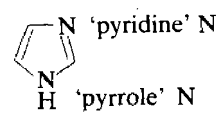
The crystal structure of tris(1-phenyl-3,5-dimethylpyrazole)silver(I) nitrate (**3**) has been determined.[63] The Ag^+ ion sat at the centre of a triangle of 3 Ns from the pyrazole rings and the Ag—N bond lengths were about 224 pm. The nitrate groups were situated between the silver ions in the crystal lattice but the separations were of the order of 550–700 pm—too far for any significant interaction.



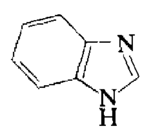
(3)

Poly(1-pyrazolyl)borates are dealt with in Section 54.1.2.6.

A large number of imidazole (**4**) and benzimidazole (**5**) silver(I) complexes have been prepared.[64] Early reports predicted that the site of complex formation of the imidazole molecule would be the 'pyridine' nitrogen rather than the 'pyrrole' nitrogen. However, the crystal structure of bis(imidazole)silver nitrate showed that the two pyrrole nitrogens were bound in almost linear arrangement (Ag—N 212.0, 213.2 pm, N—Ag—N, 172°).[65]

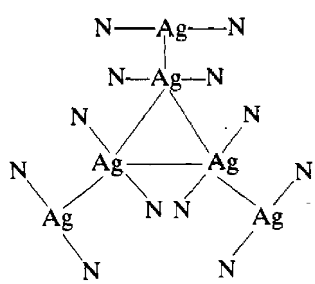


(4)



(5)

The crystal structure of bis(imidazole)silver(I) perchlorate has recently been determined.[66] The structure revealed the presence of a planar $(Ag^+)_6$ cluster (**6**), in which three radiating pairs of Ag^+ ions 305.1 pm apart were disposed on the corners of an equilateral triangle, the inner Ag^+ ions being 349.3 pm apart. Each silver ion was linearly coordinated to two imidazole rings which were planar. The Ag—N distances were somewhat shorter than in the nitrate salt (Ag—N = 207.5 and 208.9 pm).



(6)

Exposure to ^{60}Co γ-rays at 77 K resulted in electron addition to a group of three equivalent silver atoms. ESR spectra showed no indication of delocalization on to the remaining three Ag^+ ions in the cluster.

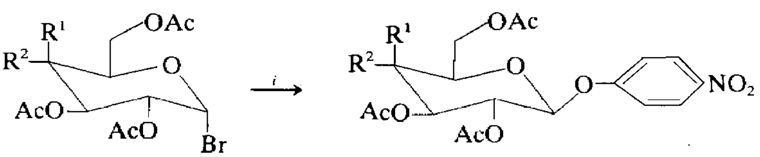
Stability constant measurements have shown that imidazoles form some of the most stable complexes of all N-heterocyclic ligands. Some thermodynamic data are given in Table 12.

Table 12 Some Thermodynamic Data for the Formation of Silver(I) Imidazole Complexes

		$Log\ K_1$	$Log\ K_2$	$\Delta H\beta_2$ (kJ mol^{-1})	$\Delta S\beta_2$ (J K^{-1} mol^{-1})	*Ref.*
Imidazole	$I = 0.1$, 0 °C	3.52	7.88	25 ± 7	9 ± 25	67
	$I = 1.0$, 25 °C	3.05	6.88	−65.7 ± 0.8	−88 ± 4	68
1-Methylimidazole	$I = 1.0$, 25 °C	3.00	6.89	−65.3 ± 0.8	−88 ± 4	68
2-Methylimidazole	$I = 1.0$, r.t.	3.11	6.98	—	—	64
2-Ethyl-4-methylimidazole	$I = 1.0$, r.t.	3.64	7.74	—	—	64

The acidity of the hydrogen bound at the pyrrole nitrogen is very weak; it is perhaps surprising therefore that silver imidazolates have been known since 1877.[64] Silver(I) imidazolate has been prepared by dissolving equimolar amounts of $AgNO_3$ and imidazole in distilled water. NaOH solution was then added dropwise until a pH of approximately 10 was reached. The precipitate formed was filtered, washed with ethanol and dried at room temperature under vacuum. To obtain $Ag(imidazole)_2NO_3$, the white precipitate formed on adding $AgNO_3$ to imidazole was dissolved by adding HNO_3 to give a pH of 5.5 or 4.[69] Colourless crystals were deposited on slow evaporation. The IR spectrum of Ag(imidazolate) showed that the N—H stretching band normally appearing at 3150–3400 cm^{-1} for imidazole complexes was missing as expected.[68]

Silver imidazolate together with mercury(II) chloride or zinc(II) chloride has proved to an efficient promoting system for glycosidations. For example, 1,2-*trans*-linked aryl glucosides have been prepared from fully acetylated glycopyranosyl bromides in almost quantitative yield (equation 6).[70]



(6)

i, Ag(imidazolate), $ZnCl_2$, CH_2Cl_2, 40 °C, 48 h, $HOC_6H_4NO_2$-*p*

(*ii*) *Pyridines, pyrimidines and pyrazines*

Stability constant measurements on the silver(I) pyridine system were made by Bjerrum as early as 1941, although they were not published until 1972.[71] It was found when determining the stability constants of the relatively weak pyridine complexes that an important cause of error in glass electrode measurements was the strong activity-decreasing effect of pyridine on its complex ions as well as on pyridine itself. This salting-in effect gave rise to inflated values for the maximum ligand number, which Bjerrum concluded was two.[71] More recently, the formation constants have been optimized using the chemical shifts of the three different types of carbon atom observed in the ^{13}C NMR spectrum.[72] Since the exchange rates for bound and free pyridine molecules were fast on the NMR timescale, single, sharp resonances were obtained at 152.85 ± 0.04 (*ortho*), 126.70 ± 0.02 (*meta*) and 140.54 ± 0.05 (*para*). Thermodynamic data are summarized in Table 13.[72,73,81–85]

Silver nitrate is very soluble in water-free pyridine. The solid isolated from pyridine was temperature dependent wih maximum solvation occurring at low temperatures. Thus below −25 °C, $Ag(py)_2NO_3{\cdot}4py$ was reported to be the stable solid.[74] From aqueous pyridine, the bis

Table 13 Some Thermodynamic Data for Silver(I) Pyridine Derivatives

Amine	*Medium*	*pK*	*Log* β_1	*Log* β_2	$\Delta H\beta_2$ (kJ mol^{-1})	$\Delta S\beta_2$ (J K^{-1} mol^{-1})	*Ref.*
Pyridine	25 °C, $I = 0$	—	1.96	4.17	—	—	72
		—	2.05	4.10	−47.03	−79.1	73
	25 °C, 96% EtOH, 0.1 M $NaClO_4$	5.17	2.20	4.50			81
2-Methylpyridine		5.97	2.45	4.93			81
3-Methylpyridine		5.68	2.40	4.82			81
4-Methylpyridine		6.02	2.45	4.91			81
2-Ethylpyridine		5.97	2.49	4.92			81
2,4,6-Trimethylpyridine		7.59	2.86	5.76			81
2-Aminopyridine	25 °C, $I = 0.61$	6.96	2.38	4.79			82
3-Aminopyridine		6.26	2.21	4.41			82
3-Cyanopyridine	25 °C, $I \approx 0.02$	—	—	3.28	−12.3	−21.6	83
4-Cyanopyridine	25 °C, $I \approx 0.03$	—	—	2.94	−12.0	−16.0	83
Pyridine-2-carboxylate	20 °C, $I = 0.1$	—	3.40	5.0	—	—	84
6-Methylpyridine-2-carboxylate		—	3.85	7.0	—	—	84
Pyridine-3-carboxylic acid, methyl ester	25 °C, $I = 0.02$	—	—	2.85	−31.2	−49.83	85

pyridyl complex was obtained with three to four weakly bound water molecules which were lost when the salt was dried.[71]

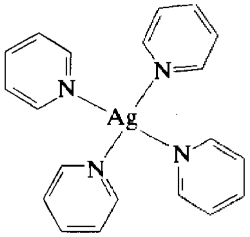
It has recently been reported that $[Ag(py)_4]ClO_4$ can be obtained by recrystallizing $[Ag(py)_2]ClO_4$ from a 5:1 chloroform–pyridine mixture.[75] The complex readily lost pyridine and satisfactory analysis could not be obtained. ^{14}N NQR transition frequencies found for these two salts are given in Table 14.

Table 14 NQR Transition Frequencies (kHz) for Coordinated Pyridine at 77 K[75]

	ν_+ (±1)	ν_+ (±2)	ν_0 (±1)
$[Ag(py)_2]ClO_4$	2275	1901	374
	2227	1711	516
$[Ag(py)_4]ClO_4$	2638	2137	501
	3130	(2460)^a	670
	2638	(2045)^a	593

^{a} Calculated

The crystal structures of $Ag(py)_2NO_3{\cdot}H_2O$[85] and $[Ag(py)_4]ClO_4$[76] have been determined. In the first, silver adopted a distorted octahedral arrangement where the nitrato groups were not only chelated as bidentate ligands but also bridged between two silver ions. Two Ag—O bond lengths were 282 pm, the other two were 291 pm. The Ag—N bond lengths were 216 pm and the py—Ag—py bond angle was 173°. The water molecule was not coordinated. In the more recent structure (**7**) the unstable $[Ag(py)_4]ClO_4$ salt was characterized at 260 K. The coordination geometry was close to tetrahedral and the Ag—N bond lengths were 232.2 pm.[76]



(**7**)

The Raman spectrum of pyridine adsorbed on a silver electrode under potentiostatic control in potassium chloride electrolyte medium was reported in 1974.[77] This study opened up a new field of scientific enquiry, which has rapidly grown in the last several years. The intensity of the Raman spectrum of pyridine was enhanced by at least five to six orders of magnitude over what could be expected from the scattering cross section of the isolated molecule.[78,79] This enhanced scattering intensity allowed the observation of a surface Raman spectrum of a monolayer of adsorbed species and led to the name 'surface-enhanced Raman scattering' (SERS). The reason for the enhancement is still uncertain, but it is believed that the effect of electrochemical etching on the silver surface produces a local periodic potential which interacts with the pyridine molecule to produce a much greater degree of polarizability than would be present in pyridine itself.[80]

The complexes of silver(I) ions with substituted pyridines are well known and some representative thermodynamic data for their formation are included in Table 13.[81–85] Several attempts have been made to correlate the stability of the silver complexes with the basicity of the substituted pyridines.[81,82] In general, a linear relationship between the logarithm of the formation constants and the pK_a of the free bases was found to exist.

For amino- and cyano-pyridines, it has been found that coordination to silver primarily occurred through the pyridyl N atom.[82,83] IR spectral evidence has been used to show that this was not the case for substituted 2-amino-[85] or 2-cyano-pyridines, however. Some cyano stretching frequencies for silver complexes are collected in Table 15.[86,87]

Silver(I) complexes can also be obtained when the pyridyl N becomes quaternized, if the aliphatic group contains an amine. Thermodynamic data for silver complexes with ligands of the type $C_5H_5N^+(CH_2)_nNH$ (n = 2–5) are given in Table 16.[88,89]

Table 15 Some IR Spectral Data (cm^{-1}) for Silver(I) Complexes of Cyanopyridines

Complex	*Nitrile stretch*	*C—C and C—N stretch*	*Ring breathing*	*Ref.*
Ag(2-cyanopyridine)$_2$ClO$_4$	2250	1587, 1558, 1467, 1430	980, 1040	86
Ag(2-cyano-4-methylpyridine)$_2$ClO$_4$	2242	1610, 1475, 1459	980, 1040	87
Ag(2-cyano-6-methylpyridine)$_2$ClO$_4$	2249	1600, 1468, 1460, 1453	1013[a]	87
Ag(2-cyano-4-nitropyridine)$_2$ClO$_4$	2271		[b]	87
Ag(2-cyano-4-nitropyridine)ClO$_4$	2277	1605, 1588, 1538, 1465	1007, 1043	87
Ag(2-cyano-4-chloropyridine)$_2$ClO$_4$	2275		[b]	87
Ag(2-cyano-4-chloropyridine)ClO$_4$	2273	1580, 1551, 1476, 1463	926, 1009	87
Ag(3-cyanopyridine)$_2$ClO$_4$	2235	1595, 1567, 1475, 1418	1025, 1075	86
Ag(3-cyanopyridine)$_3$ClO$_4$	2240, 2247	1595, 1567, 1475, 1417	1028, 1082[c]	86
Ag(4-cyanopyridine)$_2$ClO$_4$	2240	1600, 1541, 1497, 1416	1060, 1085	86

[a] Masked by strong ClO_4^- absorption. [b] Complex dissociated to the 1:1 complex. [c] 3:1 complex.

Table 16 Thermodynamic Data for some Silver(I) Complexes of ω-Aminoalkylpyridinium Complexes[88,89]

$C_5H_5N^+(CH_2)_nNH_2$	$Log\ \beta_1$	$Log\ \beta_2$	$-\Delta H\beta_2$ (kJ mol^{-1})	$-\Delta S\beta_2$ (J K^{-1} mol^{-1})
$n=2$	2.08	4.46	46.4 ± 0.17	70.3
3	3.91	6.01	53.93 ± 0.04	65.7
4	3.24	6.61	56.36 ± 0.17	62.3
5	3.49	7.22	56.57 ± 0.08	51.5

The reaction of silver(I) ions with pyridine-2-carboxylate (picolinate) (L) yields a white water-insoluble compound, initially assigned the structure Ag(L).[90] The addition of a strong oxidant converted this into the red Ag^{II} complex $Ag(L)_2$. Elemental analysis of the white solid, however, indicated that the assignment as a simple 1:1 complex was incorrect.[91,92] Further, when $AgNO_3$ or $AgClO_4$ was used as a starting material it was discovered that some anion was retained. This was detected by both physical and chemical methods. Thus, X-ray photoelectron spectroscopy (ESCA) showed two peaks in the nitrogen 1*s* region centred at 405.5 and 400.5 eV. The position of the higher energy peak which was approximately one-fifth the intensity of the lower energy peak, was attributed to the nitrate ion. When $AgClO_4$ was used as starting material the white precipitate could be shown by ESCA to contain perchlorate ions.[91] In addition, when the sample prepared from $AgNO_3$ was treated with 2,2′-bipyridine, then some $Ag(bipy)_2NO_3{\cdot}2H_2O$ was obtained in low yield.[92] It was concluded that the simple 1:1 formula was inappropriate and the exact composition, which may contain AgL·HL and $Ag(HL)_2NO_3$, depended upon the reaction conditions. IR data for species obtained at pH 3–4 and pH 7 are summarized in Table 17.[92]

The crystal structure of silver(I) pyridine-2-carboxylate monohydrate has been determined.[93] Each Ag atom was coordinated by two N atoms (Ag—N = 220.7(3) pm) and two carboxylic O atoms (Ag—O = 252.4(4) pm). The H atoms of the CO_2H groups were located on centres of symmetry making symmetrical hydrogen bonds between non-coordinated carboxylate O atoms. Thus the H atoms were equally shared by the CO_2H groups and there was no distinct molecule of silver(I) picolinate.

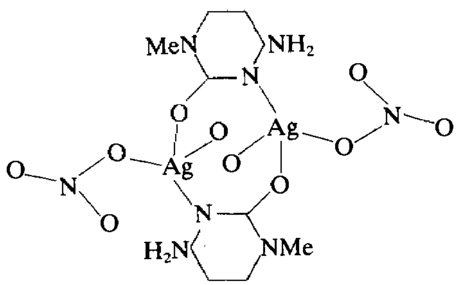
Little is known about the chemistry of silver(I) complexes of unsubstituted pyrimidine; however, an extensive range of substituted pyrimidine complexes have been investigated due to their use in the preparation of nucleic acid constituents.[85,94] In these reactions, which lead to the formation of glycosides, silver salts of uracils or thymines are treated with poly-*O*-

Table 17 Some IR Spectral Data (cm^{-1}) for 'Silver(I) Pyridine-2-carboxylate'[92]

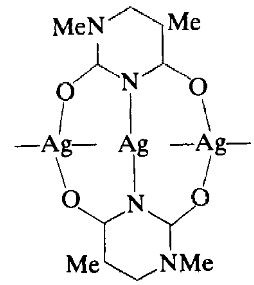
	ν(C—O)	*ν(C—O)*	*ν(C—H)*
pH 3–4	1589s	1682s	2200–2600mw, br
pH 7	1561s, 1579s, 1604ms		

acylglycosyl halides. In addition, it is well established that Ag^I has one of the highest propensities for binding at base (purine or pyrimidine) sites over phosphate groups in its strong interaction with nucleic acids and polynucleotides.[95]

Crystal structures of 1-methylcytosine[95] and 1-methylthymine[96] complexes have been determined as aids to the understanding of Ag^I binding to polynucleotides. In (1-methylcytosine)silver(I) nitrate, a centrosymmetric dimer was present in which the N heterocycles were bridged by two Ag^+ ions. Within these dimers, there were two strong metal–ligand bonds, (Ag—N = 222.5, Ag—O = 236.7 pm) and an eight-membered ring (**8**) resulted.



(**8**)



(**9**)

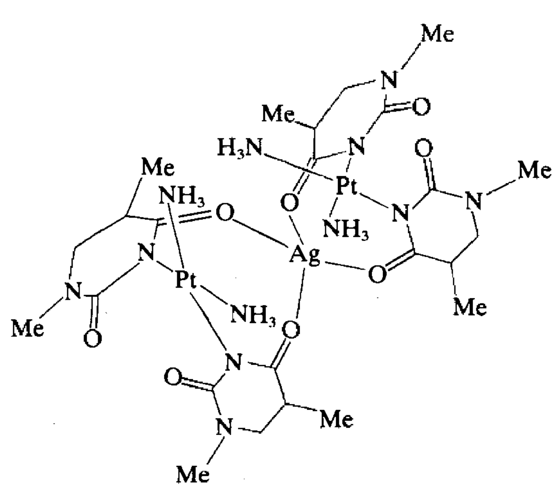
In (1-methylthymine)silver(I), one half of the silver atoms had linear coordination (N—Ag—N angle of 180°) and were strongly bound to the N atoms of the deprotonated ligands (Ag—N = 208.1 pm). The resulting planar $Ag(L)_2^-$ units (**9**) were connected by the remaining silver atoms, which were tetrahedrally surrounded with oxygen atoms from two $Ag(L)_2^-$ units (Ag—O = 233.3 and 251.2 pm).

These structures, together with potentiometric measurements, allowed proposals to be made as to the probable mode of interaction between Ag^+ ions and polyuridine (polyU). For $pH < 6$, $Ag_2(polyU)_2$ was considered the predominant species, whilst for $pH > 6$, $Ag(polyU)_2^-$ became increasingly important. Equilibrium constants were calculated for these 2:2 and 2:1 complexes as $\log \beta_{22} = 12.1$ and $\log \beta_{12} = 9.3$. $Ag(polyU)_2^-$ was considered to have linear coordination while $Ag_2(polyU)_2$ was predicted to have, in addition to the N coordination, links through the O-4 atoms.

Metal binding of the N-3 position of either 1-methylthymine or 1-methyluracil monoanion facilitates binding of additional metals through exocyclic oxygens of these ligands.

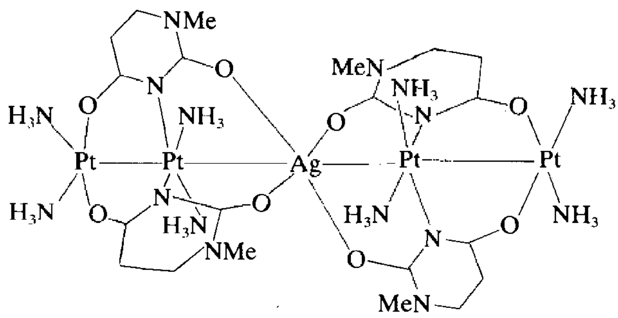
Recently, heteronuclear complexes containing *cis*-$Pt(NH_3)_2^{2+}$, Ag(I) and either 1-methylthymine[97] or 1-methyluracil[98] have been isolated. These studies were initiated due to the interest in the binding of platinum(II) antitumour agents to DNA.

In Ag[*cis*-$Pt(NH_3)_2$(1-methylthymine)$_2$]$_2NO_3 \cdot 5H_2O$, the molecular cation (**10**) consisted of two units connected by a silver cation *via* the exocyclic O-4 atoms. The Ag—O bond distances were in the range 235.3–256.3 pm.[97]



(**10**)

For $[(NH_3)_8Pt_4(1\text{-methyluracil})_4Ag]^{5+}$ (**11**), the molecular cation showed crystallographic centrosymmetry with Ag being at the inversion centre. The silver atom thus had square planar coordination with four O-2 oxygens of 1-methyluracil ligands, two from each platinum dimer. The Ag—O bond distances in this case were 243 and 235 pm, and the Pt—Ag separation was 278.7 pm.



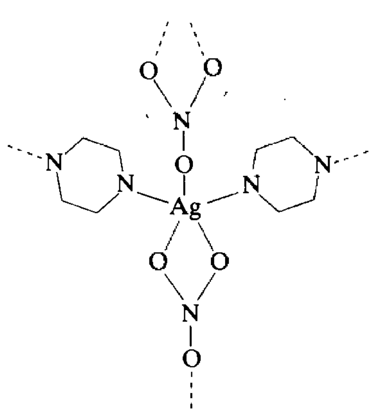
(11)

Silver(I) complexes of pyrazine were first reported in 1895.[99] Since then there have been numerous reports on the preparation and properties of pyrazine complexes of silver(I).[85] Thermodynamic data for some of these complexes are given in Table 18.

Table 18 Thermodynamic Data for the Formation of some Silver(I) Pyrazine Complexes (0.1 M KNO_3, 25 °C)[100]

	Log β_1	*Log* β_2	$\Delta H\beta_2$ (kJ mol^{-1})	$\Delta S\beta_2$ (J K^{-1} mol^{-1})
Pyrazine	1.38	2.41	-33.9 ± 0.2	-67.4 ± 0.4
2-Methylpyrazine	1.65 ± 0.01	2.76 ± 0.02	-36.8 ± 0.2	-70.7 ± 0.4
2,5-Dimethylpyrazine	1.96 ± 0.01	3.13 ± 0.03	-40.0 ± 0.2	-67.8 ± 0.8
2,6-Dimethylpyrazine	1.95 ± 0.02	3.46 ± 0.10	-31.8 ± 0.3	-46.9 ± 0.8
2-Chloropyrazine	0.96 ± 0.01	1.53 ± 0.05	-32.1 ± 0.3	-76.1 ± 0.8
2-Aminopyrazine	1.81 ± 0.02	3.50 ± 0.01	—	—

The structure of $Ag(pyrazine)NO_3$ (**12**) has been determined.[101] The 1:1 complex consisted of approximately planar kinked chains of the type $[\text{—Ag—NC}_4\text{H}_4\text{N—}]_n$, with symmetric Ag—N distances of 221.3 ± 1.4 pm and N—Ag—N′ angles of $159.2 \pm 0.9°$. Looking down a chain, the pyrazine rings were alternatively canted in opposite directions with a dihedral angle between the ring plane and the N—Ag—N′ plane of roughly 14°. The next nearest neighbours were nitrate oxygen atoms (Ag—O = 272.0 ± 2.1, 294.3 ± 1.7 pm) and were beyond that expected for weak Ag—O bonds (~250 pm).



(12)

It has been argued that in complexes in which pyrazine is bound through only one of its nitrogen atoms, then the low local symmetry experienced by the pyrazine moiety would allow for a band to appear in the IR spectrum at 950–1000 cm^{-1}. This band should be absent in bridged polymers of long chain length but may be weak in others of shorter chain length. For Ag(pyrazine)NO_3, which is known to contain bridging pyrazine molecules, a medium weak band is present at 990 cm^{-1}. Other bands were present at 1420vs, 1320s, 1162s, 1120s, 1080vs, 990m and 805s cm^{-1}.[102]

It has been observed that when an aqueous solution of pyrazine was added to an excess of silver nitrate solution, a precipitate of shiny white platelets formed immediately. If the order was reversed, however, and silver nitrate was added to an excess of pyrazine, the precipitate was formed only very slowly and after cooling. In each case, the precipitate was found to be Ag(pyrazine)NO_3 and the solubility product was determined as 2.3×10^{-4}.[103]

(*iii*) *2,2′-Bipyridine, 1,10-phenanthroline, 2,2′,2-terpyridine and related species*

Silver(I) complexes of bipy, phen, terpy and their derivatives have usually only been isolated as intermediates in the preparation of the silver(II) salts. Few studies have dealt solely with the silver(I) species. Despite this, considerable information concerning their properties is available.[104]

Thermodynamic data for the formation of $[Ag(bipy)_2]^+$ and $[Ag(phen)_2]^+$ and some derivatives are given in Table 19.[104–108] Stability data in acetonitrile and ethanol have also been determined.[109]

IR spectral data for $[Ag(bipy)_2]ClO_4$ and $[Ag(phen)_2]ClO_4$ are tabulated in Table 20.[92,110,111]

X-Ray photoelectron spectroscopy (ESCA) studies on silver(I) complexes have shown that the silver $3d_{3/2,5/2}$ binding energies are insensitive to the nature of the central environment and therefore not useful for distinguishing between Ag^I and Ag^{II} salts.[92] However, the peaks for the Ag^{II} complexes were generally significantly broader. Table 21 presents the binding energies found for $Ag(bipy)_2NO_3{\cdot}2H_2O$ and $Ag(phen)_2NO_3{\cdot}H_2O$.

The presence of methyl substituents on bipy or phen can cause marked changes in the stereochemistry adopted by the central metal ion due to steric constraints. With 4,6,4′,6′-tetramethyl-2,2′-bipyridine, only bis-ligand silver(I) complexes have been obtained and these were proposed to be tetrahedral. No silver(II) complexes could be isolated and this was claimed to be due to the inability of the molecule to adapt a planar configuration about the silver(II) ion.[112]

In contrast, monochelated complexes have been obtained for 2-methylphen and 2,9-dimethylphen.[113,114] It was considered that these could be either trigonal coplanar monomeric species or dimeric, with the anionic ligand acting as the bridging unit. Molecular weight determinations were prevented due to low solubility.

With terpy, compounds of the type Ag(terpy)X have been prepared and cannot be tetrahedral for steric reasons, in that terpy cannot span three corners of a tetrahedron. It has been argued that more likely only two of the N atoms are coordinated and that a distorted linear structure is adapted.[115] However, if this was the case the central N group would necessarily be within bonding distance. The other alternative was that they were three-coordinate. Addition reactions with neutral ligands such as H_2O, pyridine or phosphines would then yield distorted square planar structures.[115]

Table 19 Some Thermodynamic Data for the Formation of Silver(I) Complexes of Bipy, Phen and their Derivatives

Ligand	*Medium*	*Log β_1*	*Log β_2*	$\Delta H\beta_2$	$\Delta S\beta_2$	*Ref.*
bipy	0.1 M KNO_3, 35 °C	3.03	6.67	—	—	106
	50% EtOH, 25 °C	3.70	7.22	−49.120	−26.5	105
phen	$I = 0.1$, 25 °C	5.02	7.05	—	—	107
5-Methylphen	0.1 M KNO_3, 25 °C	7.30	13.39	—	—	108
2,9-Dimethylphen	0.1 M KNO_3, 50% EtOH	6.34 ± 0.06	13.93 ± 0.01	—	—	104
4,7-Dimethylphen	0.1 M KNO_3, 50% EtOH, 25 °C	5.76	11.07	—	—	104
5,6-Dimethylphen	0.1 M KNO_3, 50% EtOH, 25 °C	5.51	10.67	—	—	104
5-Phenylphen	0.1 M KNO_3, 50% EtOH	4.99	10.14	—	—	104
4,7-Diphenylphen	0.1 M KNO_3, 50% EtOH, 25 °C	5.13	10.02	—	—	108
5-Chlorophen	0.1 M KNO_3, 25 °C	4.70	11.04	—	—	108
5-Bromophen	0.1 M KNO_3, 25 °C	5.30	11.77	—	—	108

Table 20 IR Spectral Data for $[Ag(bipy)_2]ClO_4$,[110] $[Ag(phen)_2]ClO_4$[111] and $[Ag(bipy)_2]NO_3 \cdot 2H_2O$[92]

$[Ag(bipy)_2]ClO_4$	$[Ag(phen)_2]ClO_4$	$[Ag(bipy)_2]NO_3 \cdot 2H_2O$
2684w		
2551w		
2141w		
	1622	1635w, br
	1593	1593m
1587s		1586m
	1575	1575mw
1562w		1566m
	1515s	
	1500	
	1433s	
	1350	
1312m	1339	
1244w	1222	
1190m		
1155m	1143s	
1070m		
1000m	987	
	961	
	860	
	850	
807m	840s	
	770	
757s	764s	
725m	726s	
	720	
669w		
	610	

Table 21 Silver 3*d* and Nitrogen 1*s* Binding Energies (eV) for Silver(I) Complexes of bipy and phen[92]

	$Ag\ 3d_{3/2}$	$Ag\ 3d_{5/2}$	$N\ 1s$	
$[Ag(bipy)_2]NO_3 \cdot 2H_2O$	374.1	368.1	406.2	399.3
$[Ag(phen)_2]NO_3 \cdot H_2O$	374.1	368.1	406.3	399.6

Referenced to carbon 1*s* line of graphite at 284.0 eV.

54.1.2.3 Nitrosyls and related ligands

(i) Nitrosyls, dinitrogen, hydrazine and hydroxylamine

Little is known of the silver(I) chemistry of the title ligands.[116] Hydrazine and hydroxylamine are sufficiently strong reducing agents that simple salts of Ag^I are unstable and decomposition readily occurs.

The reduction of silver(I) ions by hydrazine was characterized by a long induction period where a 1:1 complex formed ($\log K_1 \approx 3.2$).[117] The nature of the complex was not established. Several hydrazinates of silver have been identified and the preparation of $Ag_2SO_4 \cdot 3N_2H_4$ was reported in 1932.[116] The rate of the reduction to metallic silver was found to be influenced by pH and composition of the solution phase. Hydrazine complexes of transition metal ions in general have been reviewed.[118,119]

With hydroxylamine, the stability constant ($\log K_1$) with silver(I) ions was determined to be 1.85. Attempts to measure the formation constants of higher complexes were thwarted due to the rate of the redox reaction being too high. An estimate of $\log \beta_2 < 3$ was made, however.[120]

(ii) Azo and azomethine dyestuffs

The use of azo salts for the complexometric and colorimetric determination of metal ions has been well established. For silver(I), complexes from a wide range of reagents have been investigated but only in a few cases have their spectra or stability constants been determined. Many of the original studies were done prior to 1900, although a recent review is available.[121]

54.1.2.4 *Mono- and di-alkylamides, imido and nitrido ligands*

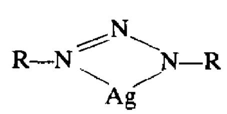
General reviews of transition metal complexes of alkoxides, dialkylamides[122] and nitrides[123] showed that the main focus of attention was on the earlier transition metal elements, in particular, the Ti, V and Cr triads.

There has been little systematic study of silver(I) with these ligands, or indeed, with the copper triad as a whole. Cu^I and Au^I dialkylamides have been reported, although no mention was made of analogous Ag^I complexes.[122] The explosive Ag_3N has been known for some time[123] and '$AgNI_2$' was reported in 1893.[124]

54.1.2.5 *Triazenes, sulfur diimines, azides, cyanates, thiocyanates, selenocyanates and tellurocyanates*

(i) Triazenes

Addition of bispyridylsilver(I) acetate to a methanolic solution of either diazoaminobenzene or its 4,4′-dimethyl derivative gave lemon-yellow needles of the corresponding silver salt.[125] The compounds were only slightly soluble, except in warm nitrobenzene. MW measurements in pyridine suggested that the complexes were monomeric, although it was claimed that this may have been caused by the strong donor properties of that solvent.[126] The compounds were not sufficiently soluble in non-coordinating solvents to verify this proposal. The anticipated structure for these compounds involved a four-membered ring (**13**).



(**13**)

(ii) Sulfur diimines and related ligands

Organic sulfides react with chloramines to give a variety of compounds including sulfur diimides (Scheme 2).[127,128] In solution and especially in the solid phase, it was proposed that the molecule dimerized and was held together by electrostatic attractions. Ebullioscopic MW determinations of the diethyl derivative were intermediate between that required for monomer and dimer.[128]

$$R_2S + NH_2Cl \longrightarrow [R_2S{-}NH_2]^+Cl \longrightarrow R_2S{=}NH \xrightarrow{NH_2Cl}$$

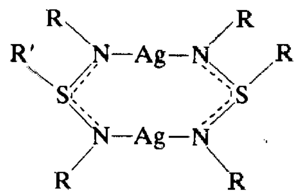
$$[R_2S(NH)NH_2]^+Cl^- \xrightarrow{NaOEt} R_2S(NH)_2 \text{ and } [R_2S(NH)_2]_2$$

Scheme 2

Reaction of the diethyl derivative (L) with $AgClO_4$, Ag_2SO_4 and $AgNO_3$ produced $Ag_3(L)ClO_4{\cdot}H_2O$, $Ag_3(L)HSO_4{\cdot}2H_2O$ and $Ag_3(L)NO_3$ respectively; the crystal structure of the latter has been determined.[129]

The structure was best described as consisting of SAg_3N tetrahedra with central N atoms linked to form double layers with four common corners. The nitrate ions were positioned between these layers.

Treatment of RN=S=NR with a Grignard (R′MgX) or alkyllithium reagent (LiR′) gave an *S,N,N′*-trisubstituted sulfur diimino complex of Li or Mg. Reaction of these with AgI produced complexes thought to have a bridged structure (**14**).[130]



(14)

(*iii*) *Azides*

Silver azide can be readily prepared by precipitation from aqueous solutions containing silver and azide ions. Recrystallization from aqueous ammonia affords colourless plates and needles. It was found to be potentially explosive and often detonated when subjected to shock.[131]

In solutions containing an excess of azide ions, the diazido anion $Ag(N_3)_2^-$ was proposed to account for the increase in solubility. No structural information is available of isolated salts or from solution studies. Table 22 gives stability constants ($\log \beta_2$) for the anion in a range of solvents.[132,133] Significant increases in stability were found in the non-aqueous solvents as compared to water, a result similar to that found for other anionic species AgX_2^- (see Section 54.1.7).

Table 22 Stability Constants ($\log \beta_2$) for $Ag(N_3)_2^-$ in Different Solvents

	Water	*DMF*	*DMSO*	*HMPT*	*Ref.*
25 °C, $I = 0.005–0.01$	4.2	11.9	7.0	11.4	132
$I = 0.1$	—	—	8.0	—	133

(*iv*) *Cyanates*

The cyanate ion forms complexes with a wide range of metal ions although its coordination behaviour has not been studied as widely as that of the thiocyanate ion.[134] A ^{14}N NMR study of the NCO group in a range of metal complexes showed that N bonding was more common than O bonding, *i.e.* they should be regarded as isocyanates.[135] All the isocyanates studied gave chemical shifts to high field of the free ion and conversely, alkyl or aryl cyanates gave rise to large low-field shifts.

The diisocyanatoargenate(I) ion, $Ag(NCO)_2^-$, was found to give a chemical shift value, δ(NCO), of $\sim +42$ p.p.m.[135] Based on this and IR data[136,137] it was proposed that N bonding was present as was found in the crystal structure of the N-bridged polymer AgNCO.[138]

Owing to the rapid decomposition of the cyanate ion in water, the use of aprotic solvents was necessary for the preparation of the $Ag(NCO)_2^-$ ion. Since alkali cyanates are poorly soluble in aprotic solvents, the cyanate salts used were the tetraethylammonium, tetramethylammonium and tetraphenylarsonium cyanates. Either dry acetone or acetonitrile could be used as solvent as silver isocyanate was reasonably soluble in both. Once prepared the silver salts were found to be light- and moisture-sensitive.[136,137]

The crystal structure of the tetramethylammonium salt of $Ag(NCO)_2^-$ has been determined.[139] The anion was approximately linear (N—Ag—N bond angle 177.2°) and the Ag—N bond lengths were 201.5 and 206.8 pm.

(*v*) *Thiocyanates, selenocyanates and tellurocyanates*

In aqueous solution, thiocyanato complexes of the type $Ag_m(SCN)_{(2m+2)}^{(m+2)-}$ have been inferred from solubility and potentiometric data. For high concentrations of thiocyanate the complex having $m = 1$ was predicted to be the most abundant. Thermodynamic data are collected in Table 23.[140,141]

Crystal data are available for $NH_4Ag(SCN)_2$[142] and $KAg(SCN)_2$.[143] The symmetry of the ammonium salt was monoclinic, belonging to space group $P2_1/n$. The unit cell contained four molecules. The crystal was found to be built up of AgSCN molecules, NH_4^+ ions and SCN^- ions

Table 23 Some Thermodynamic Data for Complex Silver Thiocyanates[140,141]

	Log K^a	Log K^b	ΔH ($kJ\,mol^{-1}$)
$Ag(SCN)/Ag.SCN^-$	4.59	4.75	—
$Ag(SCN)_2^-/Ag.(SCN^-)^2$	8.29	8.23	—
$Ag(SCN)_3^{2-}/Ag.(SCN^-)^3$	10.06	9.45	—
$Ag(SCN)_4^{3-}/Ag.(SCN^-)^4$	11.26	9.67	−117

^{a} 25 °C, $I = 4$ ($NaClO_4$). ^{b} 25 °C, $I \rightarrow 0$.

and not, as expected, by a linear $Ag(SCN)_2^-$ ion. The silver atom coordinated four sulfur atoms in a very distorted tetrahedron. The Ag—S distances were 247.4 ± 2.0 pm within the AgSCN molecule, 265.4 ± 1.9, 263.0 ± 2.7 and 274.2 ± 2.9 pm from one AgSCN molecule to the three surrounding SCN^- ions.[142]

An IR and Raman spectroscopy study of $NH_4Ag(SCN)_2$ has been interpreted in terms of a superposition of the spectra of the SCN^- ion and the AgSCN molecule, in agreement with the above structural data.[144]

In aqueous solution it was found that the binding of the sulfur atoms to the silver nucleus was not strong enough to give the complexes a character of independent units which could be detected by spectroscopic means. The displacements observed in the CN stretching vibration were directly dependent upon the amount of silver present per thiocyanate group.[144]

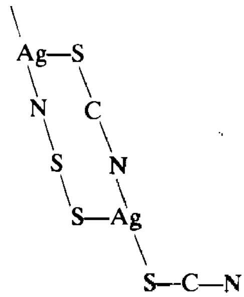
The nature of thiocyanato complexes of silver in non-aqueous solvents has recently been reassessed.[145] IR and Raman spectra were used to show that when Ag^+ was complexed by SCN^-, the species present and the equilibrium steps involved were solvent specific. Characteristic absorption bands are summarized in Table 24. In pyridine, complexation passed through $[Ag_2(SCN)]^+$ and AgSCN to $[Ag(SCN)_2]^-$, such that even when the $[SCN^-]_T/[Ag^+]_T$ ratio was 0.059, 50% was present as the linear $[Ag(SCN)_2]^-$ ion.

Table 24 Characteristic Absorption Bands (cm^{-1}) for Silver(I) Thiocyanato Complexes[145]

Raman	*IR*	*Assignment*
2106 ± 2	2104 ± 2	Bridged SCN, *e.g.* $[Ag_2(SCN)^+]$
2093 ± 4	2086 ± 4	$\gamma_{sym}(CN)$; $\gamma_{asym}(CN)$ in $[Ag(SCN)_2]^-$
2077 ± 3	2074 ± 4	Either AgSCN or terminal SCN in bridged complexes
2057 ± 3	2054 ± 4	Free SCN^-
—	2116	Observed in hmpa solution; doubly bridged complex or tetrahedral species

Only AgSCN and $[Ag(SCN)_2]^-$ were identified in THF, DMSO and acetone, and only $[Ag(SCN)_2]^-$ was found in propylene carbonate. Solutions in DMF and DMA at high $[SCN^-]/[Ag^+]$ ratios contained a small proportion of the SCN^- as the bridged complex $[Ag_2(SCN)_3]^-$, but in trimethyl phosphate the SCN^- was approximately equally distributed between $[Ag_2(SCN)_3]^-$ and $[Ag(SCN)_2]^-$. The Raman spectra of thiocyanatosilver(I) complexes in HMPA could not be obtained due to deposition of silver metal on the cell walls. IR spectra in HMPA were found to differ from those in all the other solvents; no linear $[Ag(SCN)_2]^-$ complex could be detected. One possible explanation was that due to the powerful donor and solvating properties of HMPA a tetrahedral complex of the type $[Ag(SCN)_2(HMPA)_2]^-$ was produced. An alternative explanation for the observed bands at 2118, 2105 and 2080 cm^{-1} was that a multinuclear complex such as (**15**) occurred, containing two SCN bridges between the Ag^+ centres. Such a complex was predicted to require two frequencies (symmetric and asymmetric) due to the bridging ligands (2118 and 2105 cm^{-1}) and one due to the terminal ligand (2080 cm^{-1}).[145]

Complexes related to $CoHg(SCN)_4$, the well-known calibrant used in magnetic susceptibility measurements, have recently been prepared containing silver(I).[146,147a] In the presence of a number of Lewis bases octahedral adducts such as $Co[Ag(SCN)_2]\cdot 2DMF$ were obtained. Magnetic moments indicated the presence of high-spin cobalt(II). With nickel(II), two types of complex



(15)

were isolated. In one, zigzag thiocyanate bridges gave rise to polymeric structures, whilst the other consisted of ion pairs of the type $[NiL_x][Ag(SCN)_2]_2$ (where x was 3, 4 or 6).

The interaction of silver ions with $[Co(NH_3)_5NCS]^{2+}$ was first reported in 1899 to give a stable silver adduct $[Co(NH_3)_5NCSAg]^{3+}$.[147b] More recently similar adducts have been prepared as part of studies on the silver ion-assisted aquations of this and other related complexes and UV and IR data were reported.[147c]

The selenocyanate ion is much less stable than the thiocyanate ion. However, silver selenocyanate complexes are in general more stable than the corresponding thiocyanates.[148] Complex species of the type $[Ag(SeCN)_n]^{1-n}$ and $[Ag_n(SeCN)]^{n-1}$ ($n = 1$–4) have been predicted from potentiometric and solubility studies in aqueous solution.

Colourless crystals of $KAg(SeCN)_2$ separated from aqueous solutions as regular cubes in addition to crystals of $K_3Ag(SeCN)_4$ and finely acicular colourless crystals of $K_2Ag(SeCN)_3$. The latter salt was more readily prepared from alcoholic and acetone solutions.

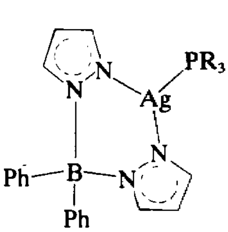
To obtain the higher complexes such as $Ag(SeCN)_4^{3-}$ it was often necessary to introduce non-aqueous solvents. For example, in aqueous solution the most abundant high complex was found to be $Ag(SeCN)_3^{2-}$; however, on addition of acetone, the complex $Ag(SeCN)_4^{3-}$ became prevalent. A similar effect was observed in methanol. Formation constants in mixed methanol–water systems have been determined and in 74% MeOH $\log \beta_3$ and $\log \beta_4$ were 14.60 and 15.13 respectively.[149]

Tellurocyanate complexes of silver(I) have not been reported.

54.1.2.6 Poly(pyrazolyl)borates

The first silver(I) poly(pyrazolyl)borate complexes were reported in 1975.[150] Since then, a number of silver complexes of the type $Ag(L)(R_nB(pz)_{4-n})$ have been isolated and characterized.[151,152] They were prepared by the reaction of the poly(pyrazolyl)borate anions with silver(I) salts, usually the nitrate, in the presence of donor ligands, L, and were isolated as white, thermally stable compounds. In most cases they were either insoluble, or at best only sparingly soluble, in common organic solvents.

The crystal structure of $[Ag\{P(C_6H_4Me\text{-}p)_3\}\{BPh_2(pz)_2\}]$ (**16**) has been determined.[153] The silver atom was pseudo-three-coordinate with the $BPh_2(pz)_2$ ligand attached *via* one normal (219.4 pm) and one long (241.1 pm) Ag—N bond; the P—Ag—N bond angle was 160°.



(**16**)

The ^1H NMR spectrum of this complex showed no inequivalence of the pyrazolyl protons between −60 and 20 °C. This was interpreted in terms of the molecule being fluxional with either (a) a rocking motion of the R_3PAg moiety between the two nitrogens or (b) a complete dissociation and reassociation of the pyrazolyl nitrogens, occurring rapidly, even at lower temperatures, making the two pyrazolyl groups equivalent.[153]

54.1.2.7 Nitriles

Acetonitrile interacts with the d^{10} metal ions Cu^{I} and Ag^{I} to form solvated species of marked stability. This stability has been used in potentiometry where the |Ag|, 0.01 M $AgNO_3$ couple in acetonitrile has been recommended as a reversible reference electrode.[154]

A variety of techniques have suggested that in acetonitrile the linear $Ag(MeCN)_2^+$ ion forms. The complexes $AgNO_3{\cdot}MeCN$ and $AgNO_3{\cdot}2MeCN$ have been isolated from silver nitrate solutions in acetonitrile and their IR and Raman spectra have been reported.[155,156a] $Ag(MeCN)_4ClO_4$ was isolated as colourless needle-shaped crystals on dissolving AgCl in MeCN. It was unstable at room temperature and an X-ray crystal structure performed at 240 K, to avoid decomposition, showed discrete tetrahedral ions, $Ag(MeCN)_4^+$, with Ag—N bond lengths between 218 and 233 pm.[156b]

At room temperature, Raman spectroscopy has been used to study the solvation of $AgNO_3$ in H_2O–MeCN mixtures.[157] Solvation numbers were found to vary with Ag^+ concentration, being near four in the dilute concentrations range (<0.05 M), about two in the moderate concentration range (~0.05–5.0 M) and decreasing to about one at higher concentrations (>5.0 M).[157] The formation constants of the mono- and bis-acetonitrile complexes were determined to be 0.41($\log \beta_1$) and 0.78($\log \beta_2$) in water–acetonitrile mixtures.[158]

In the presence of $AgBF_4$, *N*-alkyl derivatives of nitriles have been prepared by reaction with alkyl bromides. The first step was believed to involve the formation of species such as $[Ag(RCN)_4]BF_4$.[159]

Dinitriles of the type $NC(CH_2)_nCN$, where $n = 2$, 3 or 4, react with silver(I) salts to form bis(dinitrile) silver(I) complexes.[160–163] With silver nitrate a range of stoichiometries were found. For example, if dichloromethane was added to a hot solution of silver nitrate in succinonitrile, $2AgNO_3{\cdot}(CN)_2C_2H_4$ was obtained, whereas addition of benzene gave $AgNO_3{\cdot}(CN)_2C_2H_4$.[160] In the case of glutaronitrile $3.75AgNO_3{\cdot}(CN)_2C_3H_6$ formed when dichloromethane was added to $AgNO_3$ dissolved in the dinitrile.[162]

The structure of $2AgNO_3$·succinonitrile revealed the presence of complex cations, $[AgNC(CH_2)_2CNAg]^{2+}$, and ionic nitrate ions.[161] The Ag—N distances were 197 pm and the C—N bond distance was close to that expected for a triple bond (112 pm). In $AgClO_4$·2(adiponitrile) the structure was in the form of a two-dimensional polymer with the adiponitrile acting as a bridge between silver ions. The silver ion was tetrahedrally coordinated by four N atoms with Ag—N distances of ~228 pm.[163]

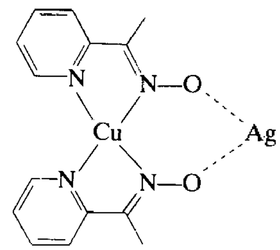
Silver tricyanomethide, $AgC(CN)_3$, has been prepared by precipitation from a mixture of solutions of $AgNO_3$ and $KC(CN)_3$.[164] Flat needles could be obtained by recrystallization from dilute ammonia solution. The X-ray structure was undertaken to determine whether a planar three-coordinate species was formed. The results suggested that a distorted layer arrangement existed with three non-equivalent Ag—N bond lengths of between 211 and 226 pm.

54.1.2.8 Oximes

Little information is available concerning the reaction of oximes with silver(I) salts.[165] *syn*-Phenyl-2-pyridylketoxime (*syn*-PhC(=NOH)C_5H_5N; HPPK) has been reported to react with silver nitrate in ethanol–water to form $Ag(HPPK)_2NO_3$ (white salt, m.p. 190–191 °C). On the basis of IR and electronic spectra it was concluded that the structure was linear with only the pyridyl N atoms being bound to the Ag^+ ion.[166]

Reaction of the bis(pyridine-2-aldoxime) copper salt with silver ions has been reported to lead to a heterobinuclear species being produced. The perchlorate salt could be isolated from neutral solution and the OH stretch of the intramolecularly H-bonded species of the starting material at 1600 cm^{-1} was not observed. The most likely structure was given as (**17**). The dissociation constant for equation (7) was determined as $2.2 \pm 0.3 \times 10^{-3}$ dm^3 mol^{-1}.[167]

$$\underset{(\mathbf{17})}{Ag\{Cu(C_6H_5N_2O)_2\}} \longrightarrow Ag^+ + Cu(C_6H_5N_2O)_2 \qquad (7)$$



(17)

A range of substituted 4-hydroxyimine-5-pyrazolone silver(I) complexes have been studied. Their properties have been reviewed.[165]

An unusual class of compounds containing silver(I), an organic anion and a 2,6-dioximino-cyclohexanone in a 1:1:1 mole ratio has been reported to exist in the solid state. No structural assignment was made and the compounds were found to be completely dissociated in solution.[168]

54.1.3 Phosphorus, Arsenic, Antimony and Bismuth Ligands

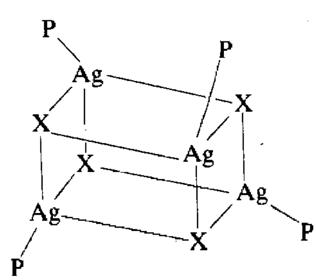
54.1.3.1 Phosphines

(*i*) *Monodentate phosphines*

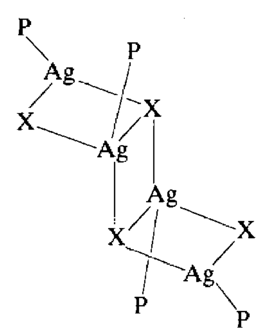
A variety of silver(I) complexes of phosphines are known. For triaryl and mixed alkyl–aryl tertiary phosphines, stoichiometries of from 1:1 to 1:4 have been reported, whereas with trialkylphosphines most of the isolated complexes were of 1:1 stoichiometry.[169]

Among these, halide and pseudohalide complexes of the general formula AgP_nX (where X = halide or pseudohalide, P = phosphine and n = 1–4) have been studied in detail.

For the 1:1 complexes with X = halide, a number of crystal structure determinations have shown that tetrameric $[AgXPR_3]_4$ units (R = Et or Ph) are formed where the arrangement could be either 'cubane-like' or a chair form (**18a** and **18b**). Some relevant bond distances are summarized in Table 25.[170–177]



(**18a**) cubane



(**18b**) chair

The observed stereochemical variation (equation 8) was ascribed to the increasing intramolecular repulsive interactions, X · · · X for example, when bulkier phosphines and heavier halides were introduced. Based on measurements of molecular species in solution, it was further proposed that a step involving dissociation into two dimeric molecules may occur for extremely bulky ligands.[174]

$$\underset{\text{(cubane)}}{M_4X_4P_4} \rightleftharpoons \underset{\text{(distorted cubane)}}{M_4X_4P_4} \rightleftharpoons \underset{\text{(chair)}}{M_4X_4P_4} \qquad (8)$$

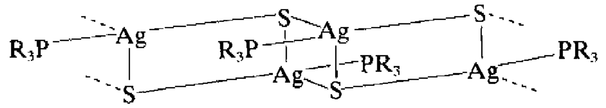
The structure of $Ag(SCN)(PPr^n_3)$ was found to contain zigzag polymeric —Ag—SCN—Ag—SCN chains,[178] cross-linked in pairs by Ag—S bonds to form double chains having a stair-step

Table 25 Distances (pm) in some Silver Halide (or Pseudohalide) Phosphines (for Ag—X and X—X, the maximum and minimum values are given if available)

Compound	*Ag—P*	*Ag—X*	*Ag—X (mean value)*	*X—X*	*Ref.*
$[AgCl(PEt_3)]_4$	239.0(0.2)	282.1(0.2)	265	392.6(0.3)	170
$[AgCl(PPh_3)]_4$	237.6(0.3)	276.1(0.3)	265	403.3(0.3)	171
	238.8(0.3)	253.2(0.3)		365.2(0.5)	
$[AgBr(PEt_3)]_4$[a]	240.2(0.5)	289.7(0.5)	273	420.1(0.3)	170
		242.2(0.7)			
$[AgBr(PPh_3)]_4$	241.5(0.5)	296.2(0.1)	280	420.0(0.1)	172
	242.9(0.2)	267.7(0.1)		396.4(0.2)	
$[AgI(PEt_3)]_4$	243.8(0.2)	291.9(0.1)	291.1	476.8(0.1)	173
		291.8(0.1)		472.3(0.1)	
$[AgI(PPh_3)]_4$	245.9(0.4)				
cubane	246.2(0.5)	303.8(0.2)	291	480.3(0.2)	174
	245.6(0.5)	283.7(0.2)		440.0(0.2)	
	245.5(0.5)				
$1.5CH_2Cl_2$[b]	243.0(0.3)	299.5(0.1)	292	476.3(0.1)	174
chair form	245.4(0.3)	272.4(0.1)		450.5(0.1)	174
$[AgCl(PPh_2py)]_4$	239.6(0.5)	264.6(0.5)	270.5	—	175
	238.7(0.5)	253.8(0.5)			
$[AgSCN(PPh_3)_2]_2$	248	Ag—N 235	Ag—S 258	—	176
$[AgCl(PPh_3)_2]_2$	247.2(0.2)	274.1(0.2)	267	371.0(0.2)	177
	246.7(0.2)	259.6(0.2)			
$[AgBr(PPh_3)_2]_2{\cdot}CHCl_3$	251.3(0.7)	274.2(0.4)	274.2	403.0(0.6)	172
	247.9(0.6)				
$AgCl(PPh_3)_3$	255.2(0.1)				
	255.6(0.1)	255.2(0.1)	255.2	—	187
	252.0(0.1)				

[a] Ag has a three-fold disordered position around the three-fold axis, P and X do not. [b] Ag is three-coordinate.

configuration (**19**). IR data on this and other thiocyanato phosphine complexes are collected in Table 26.[179,180]



(**19**) R = Pr

Stable 1:1 complexes of the type $R_3PAg(OClO_3)$ have been isolated using bulky phosphines such as PBu^t_3, PCy_3 (Cy = cyclohexyl) and $P(o\text{-}MeC_6H_4)_3$ as well as with the less bulky triphenylphosphine and *para*-substituted triarylphosphines.[181] On the basis of molecular weight measurements and also their IR spectra, it was concluded that they had linear two-coordinate monomeric structures in which the perchlorate ion was coordinated to the silver in both the solid state and in dichloromethane solution.[181]

Table 26 IR Data for Some Silver Thiocyanate Phosphine Complexes (cm^{-1})

	ν(CN)	*ν(CS)*	*ν(NCS)*	*Ref.*
$AgSCN(PEt_2Ph)$	2128vs, 2075sh	—	450m, 441m	179
$AgSCN(PPr^i_3)$	2111s	738m	475s	180
$AgSCN(PBu^n_3)$	2108vs, 2068sh	—	454w, 444w	179
$AgSCN(PPr^n_3)$	2090	—	—	180
$AgSCN(PMe_3)$	2100s, 2050sh	757m	456w, 447w	179
$AgSCN(PPh_3)_2$	2092vs, 2050sh	—	484m	179
$AgSCN(PCy_3)_2$	2090	732w	462s	180
$AgSCN(PEt_2Ph)_2$	2083s	—	494m	179
$AgSCN(PEtPh_2)_3$	2074vs	—	—	179

For Bu^t_3P complexes of the type Bu^t_3PAgX, where $X = Cl^-$, Br^-, I^-, CN^-, SCN^-, OAc^- and NO_3^-, ^1H and ^{31}P NMR and IR spectra as well as conductance measurements showed that the complexes were non-ionic. Molecular weight measurements in 1,2-dichloroethane or chloroform, suggested that for $X = Cl^-$, OAc^- or NO_3^- the species were monomeric, whereas the bromo complex was a dimer.[182]

Reactions of (1,8-naphthalenedicarboxylato)disilver(I) with phosphines yielded products containing R_3PAg^+ units, where R = phenyl or *p*-tolyl.[183] The crystal structure of the complex containing triphenylphosphine was determined and an Ag_4O_8 core was found in which the coordination geometry of each of the four silver ions was different. In each case the silver ions were bound to one phosphine and the Ag—P distances were in the range 234.1–237.8 pm. Variable temperature ^{31}P NMR spectra showed that whilst the four Ph_3PAg units were equivalent, this was not due to intermolecular exchange, since the Ag—P bond did not dissociate at low temperatures on the NMR timescale. It was argued that changes in the coordination of the oxygen atoms could result in a symmetric central Ag_4O_8 core and that such a process would only involve a waving of the naphthalene moieties above and below the Ag_4 unit. This would then result in equivalent Ph_3PAg units.[183]

For the 1:2 complexes $AgXP_2$, structural determinations have shown that in general the complexes are dimeric. From the bond distances in Table 25 it can be seen that the Ag—P distances are relatively constant and unaffected by the nature of X. This is in contrast to that observed for AgXP-type complexes.

Trimesitylphosphine has been described as the bulkiest known phosphine.[184] When this was treated with silver(I) hexafluorophosphate in CH_2Cl_2 in the dark, a 1:2 adduct was obtained in 70% yield as a white crystalline solid. The crystal structure of this, the first 1:2 cationic adduct with phosphines, has been determined.[185] In the cations, the Ag—P distance was 246.1 pm, a little larger than expected, possibly due to the intermolecular overcrowding between mesityl groups on opposing ligands. The P—Ag—P moiety was essentially linear (179.4°).

Some 1:2 complexes have also been reported for Bu^t_3P.[182] Spectral data and conductance measurements suggested that for $Bu^t_3P_2AgX$ with $X = ClO_4^-$, BF_4^-, PF_6^- and NO_3^-, the complexes contained the linear cation $[P—Ag—P]^+$.

A notable characteristic in the ^{31}P NMR spectra of $[(tol)_3P]_2AgL$ complexes was the variation in magnitude of the Ag—^{31}P coupling constants (Table 27). Thus values from 380 to 470 Hz were observed in compounds for which conductivity studies did not indicate an appreciable extent of dissociation (equation 9).

$$\{(tol)_3P\}_2AgL \rightleftharpoons \{(tol)_3P\}_2Ag^+ + L^- \qquad (9)$$

The values of the Ag—P coupling constant were correlated with the percent *s* character in the Ag—P bond and also with the magnitude of the P—Ag—P bond angle.[186]

For 1:3 complexes of the type $AgXP_3$, the only solid state structure yet determined is for $AgCl(PPh_3)_3$.[187] This was monomeric and had a distorted tetrahedral arrangement around the central silver ion (Table 25).

No structural determinations of 1:4 $AgXP_4$ complexes are available although they have been detected by ^{31}P NMR in solution.[186] It was proposed that they would be tetrahedral with the halide ion not coordinated and that elimination of a phosphine group to yield $AgX(PR_3)_3$ would readily occur.

Table 27 Coupling Constants for some Silver Phosphine Complexes (Hz)

Compound	$J(^{107}Ag–P)$	*Ref.*
$[(tol)_3P]_2AgF$	450	186
$[(tol)_3P]_2AgCl$	378	186
$[(tol)_3P]_2AgCN$	278	186
$[(tol)_3P]_2AgNO_3$	470	186
$[(tol)_3P]_2AgPF_6$	496	186
$(Bu^t_3P)_2AgClO_4$	442	182
$(Bu^t_3P)_2AgBF_4$	444	182
$(Bu^t_3P)_2AgPF_6$	437	182
$(Bu^t_3P)_2AgNO_3$	442	182

Table 28 Bond Lengths (pm) for some Silver(I) Disphosphine Complexes

Complex	*Ag—P*	*Ag—X*	*Ag—X (mean value)*	*X—X*	*Ref.*
$[AgCl(PSP)]_2$[a]	248.1(0.4)	265.6(0.4)	265.0	378.6(0.8)	188
	246.1(0.4)	264.3(0.4)			
$[AgI(PSP)]_2$	246.1(0.2)	291.1(0.1)	289.5	432.3(0.1)	189
	246.1(0.2)	287.9(0.1)			
$[AgCl(PC_5P)]_2$[b]	247.2(0.3)	266.4(0.4)			
	249.2(0.3)	271.8(0.3)	268.1	376.9(0.4)	190
	249.3(0.4)	267.8(0.3)			
	249.9(0.4)	266.3(0.3)			
AgCl(P · · · P)[c]	245.5(0.1)	251.2(0.1)	251.2	—	191
	241.2(0.1)				
$[AgDPM(NO_3)]_2$[d]	243.6(0.2)				192
	241.7(0.2)				
$[Ag_4(DPM)_4(NO_3)_2](PF_6)_2$	241.1(0.3)				192
	239.0(0.3)				
	245.6(0.3)				
	245.5(0.3)				

[a] PSP = $Ph_2PCH_2CH_2SCH_2CH_2PPh_2$. [b] $PC_5P = Ph_2P(CH_2)_5PPh_2$. [c] Ag is three-coordinate; (P · · · P) = 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene. [d] DPM = bis(diphenylphosphino)methane.

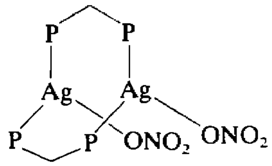
(*ii*) *Diphosphines*

Most of the diphosphine complexes of silver known are of the type $AgXP_2$, where X is a halide and P_2 is a diphosphine. In general, they adopt dimeric structures in the solid state, with the exception of the silver chloride complex of 2,11-bis(diphenylphosphinomethyl)benzo[*c*]-phenanthrene which is monomeric.

From the bond distances in Table 28,[188–192] it can be seen that the Ag—P distances remain relatively constant, whilst the Ag—X distance varies depending on the halide. This was also the case with 1:2 silver complexes with monodentate phosphines.

Reaction of $AgNO_3$ with an equimolar quantity of bis(diphenylphosphino)methane in methanol afforded the complex $[Ag(DPM)NO_3]_2$. The product was an air-stable, colourless crystalline material, soluble in polar solvents such as MeOH, MeCN, DMF and DMSO, although insoluble in water. Solid samples and solutions of the compound showed no sensitivity to light. Metathesis with excess $K[PF_6]$ in MeOH at room temperature led to the tetranuclear complex $[Ag_4(DPM)_4(NO_3)_2](PF_6)_2$. It had similar properties to the bimetallic complex in that it was also light- and air-stable.[192]

The doubly bridged complexes were structurally characterized by single-crystal X-ray methods and found to contain M_2P_4 core structures in the previously unknown *syn* conformation (**20**). The $Ag_2(DPM)_2$ framework in these compounds was quite flexible, exhibiting folding angles from 138° to 152° in the solid state. In addition, the nitrate ligands in $[Ag(DPM)NO_3]_2$ were found to be labile, dissociating in solution with the formation of planar dicationic species $[Ag_2(DPM)_2]^{2+}$. The ability of the $[Ag_2(DPM)_2]^{2+}$ unit to fold along the Ag—Ag axis allowed the close approach of two of these units to produce an enclosed central cavity. In $[Ag_4(DPM)_4(NO_3)_2]^{2+}$, this cavity was occupied by two nitrate anions.[192]



(**20**)

54.1.3.2 Phosphites

The reaction of phosphorus-donor ligands with silver(I) ions has traditionally been centred on tertiary arylphosphines. The synthesis of complexes with tertiary phosphites has often been hampered by the fact that many of them melt below room temperature.[169,186] Insoluble, crystalline complexes have been prepared, but in general these are ionic and of the type $[Ag\{P(OR)_3\}_4]^+X^-$.

With triethyl phosphite, ^{31}P NMR has been used in an attempt to characterize the interaction with silver(I) ions. At −100 °C, in 80:20 dichloromethane–toluene mixture, the predominant species was the cationic complex $[Ag\{P(OEt)_3\}_4]^+X^-$. For a range of anions including Cl^-, Br^-, I^-, SCN^-, NO_3^- and ClO_4^-, the coupling constant, $J(^{107}Ag—P)$ was 341 ± 1 Hz and the chemical shift δ was found to be 153 ± 0.1 p.p.m., relative to an internal capillary containing PEt_3. When the temperature was allowed to warm up to 25 °C it was found that, because of the kinetic lability of the silver phosphorus bond, the ^{31}P NMR spectra could not provide useful information concerning the composition of the solution. The temperature dependence of the chemical shift for the complexes was taken as evidence for significant dissociation of the ligand. Species such as AgL_3X, AgL_2X, $AgL_3^+X^-$ and $Ag_2L^+X^-$ were proposed to exist in solution.[186] Conductivity measurements were also used as further evidence that dissociation had occurred.

$^{31}P-[^{107}Ag, {}^1H]$ magnetic triple resonance experiments have also been applied to the study of the complex ions $[(EtO)_3P]_nAg^+$ (n = 1–4), made by dissolving silver thiocyanate or nitrate and triethyl phosphite in dichloromethane at −80 °C. Table 29 gives the NMR parameters obtained and shows the trends in silver shielding as n changes. As found earlier, when $n = 4$ then the silver is fully coordinated by the phosphite ligands and the NMR parameters were almost independent of counter ion.[193]

Slow addition of silver perchlorate to a large excess of trimethyl phosphite gave rise to a mildly exothermic reaction from which $[AgL_4]ClO_4$ could be obtained. It should be pointed out that if the $AgClO_4$ was added too rapidly, then the reaction mixture burst into flames.

Use of silver nitrate and only a small excess of trimethyl phosphite also gave rise to an exothermic reaction; in this case AgL_2NO_3 was isolated.[195] The low conductivity of this complex in acetone and its IR spectrum in the nitrate region suggested the presence of coordinated nitrate. In acetone, it was found to be monomeric and only poorly conducting. The structure was expected to contain a bidentate nitrate. In acetonitrile, dissociation was evident due to the 10-fold increase in molar conductivity.

The crystal structure of $[Ag\{P(OMe)_3\}_2NO_3]_2$ has been determined.[195] In the crystalline state, the structure consisted of a centrosymmetric dimer (**21**) containing a bridged nitrate. The bridging occurred *via* only one oxygen and this was equidistant from both silver atoms (Ag—O distances were 245.6 and 245.4 pm). The Ag—Ag separation was 409.5 pm, while the Ag—P bond lengths were 241.1 and 241.2 pm.

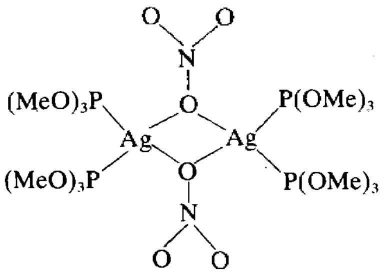
The ^1H NMR spectrum of $[Ag\{P(OMe)_3\}_4]BPh_4$ has been recorded.[196] It comprised a doublet $[^3J(P—H) = 11.5\ Hz]$ which was fully resolved. The appearance of intraligand phosphorus–hydrogen coupling in the spectrum was attributed to very rapid ligand exchange.

Deprotonated secondary phosphites $[(RO)_2PO]^-$ may act as ambidentate ligands (**22**) and (**23**). Examples of both bonding modes are known. The IR spectrum of silver diethyl phosphite (Nujol mull) was found to bear a striking resemblance to that of triethyl phosphite and showed no bands attributable to a P—H or P=O group.[197] By way of contrast, a ^{31}P NMR spectrum of $AgP(O)(OEt)_2$ in diethylamine gave a single resonance at 104.2 p.p.m.[198] It was claimed that

Table 29 ^{31}P and ^{107}Ag NMR Parameters of $[\{(EtO)_3P\}_nAg]^+X^-$ ($X = SCN^-$ or NO_3^- [a] in CH_2Cl_2 solution at −80 °C)[193]

n	$\delta(^{107}Ag)$ [b]		$J(^{107}Ag-^{31}P)$ [c]		$\delta(^{31}P)$ [d]	
	SCN^-	NO_3^-	SCN^-	NO_3^-	SCN^-	NO_3^-
1	−350	−904	794.1	1059.0	130.5	125.2
2	−191	−593	535.3	689.4	132.0	126.8
3	−33	−212	402.2	454.1	132.4	132.8
4	1	0	341.8	340.8	130.8	130.9

[a] In solution there was rapid equilibrium between Ag—X and Ag^+X^-, and for any particular value of n the parameters listed are an average. [b] In p.p.m. relative to $[(EtO)_3P]_4Ag^+NO_3^-$, selected as the most stable and least susceptible to effects of concentration and temperature. [c] In Hz; possibly this coupling constant is negative. [d] In p.p.m. relative to high frequency of 85% H_3PO_4.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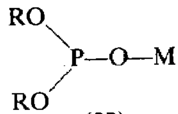
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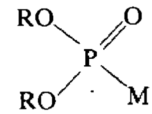

(23)

for an O-bonded complex the resonance should have occurred above 130 p.p.m., relative to 85% H_3PO_4. At 233 K, the silver ligand bond was kinetically stable on the NMR timescale, and the ^{31}P NMR spectrum consisted of two doublets due to spin–spin coupling with ^{107}Ag and ^{109}Ag (both $I = \frac{1}{2}$), consistent with their natural abundance and gyromagnetic ratio. The size of the coupling constant [$J(^{107}Ag—^{31}P) = 954$ Hz] indicated a one-bond coupling and was believed to be the largest reported for $J(^{107}Ag—^{31}P)$.

The ligand properties of the related phosphonites $P(OR)_2R'$ and phosphinites $P(OR)R'_2$ have attracted little attention.[199,200] Reaction with silver chloride generally produced 1:1 complexes of the type AgClL, whilst with silver nitrate, complex cations of the type AgL_4^+ were generated. The products were characterized by elemental analysis, ^1H and ^{31}P NMR spectroscopy and conductivity measurements.

54.1.3.3 Arsenic, antimony and bismuth ligands

Silver iodide derivatives of trialkyl-phosphines and -arsines were prepared in 1937 for comparison with their copper(I) iodide analogues.[201] The preparations involved shaking the ligands with silver iodide dissolved in concentrated aqueous KI. The products were found to be tetramers and of similar structure to the Cu^I complexes. The Pr^n_3As silver complex was isomorphous with $[CuI{\cdot}AsEt_3]_4$. Molecular weight determinations in a range of organic solvents showed that partial dissociation occurred in solution.

Ligand exchange reactions have been used to prepare mercury(II) trialkylarsine complexes.[202] Reaction of $AgNO_3{\cdot}AsMe_3$ with mercury halides gave the mercury arsine and silver halide (equations 10 and 11). The silver nitrate complex was not characterized.

$$AgNO_3{\cdot}AsMe_3 + HgCl_2 \longrightarrow [HgCl{\cdot}AsMe_3]NO_3 + AgCl \qquad (10)$$

$$[HgCl{\cdot}AsMe_3]^+ + AgNO_3{\cdot}AsMe_3 \longrightarrow [Hg(AsMe_3)_2]^{2+} + AgCl \qquad (11)$$

Silver salts of triphenylarsine and triphenylstibine have also been prepared. When silver trifluoroacetate was added to a methanol–water solution of triphenylarsine, a change due to complexation was observed in the UV spectrum. The trifluoroacetate was assumed to be completely dissociated and a 1:1 complex with the arsine formed. The stability constant at 25 °C was determined as $\log \beta_1 = 5.7$–5.8.[203]

Derivatives of $AsPh_3$ and $SbPh_3$ with AgSCN[179] and AgOAc[204] had different stoichiometry. Regardless of the mole ratio used in the preparations, the only products obtained with AgSCN were the 1:2 complexes $AgSCN{\cdot}2XPh_3$ (X = As, Sb).[179] These were assumed to be dimeric by comparison with the analogous phosphine complex X = P (see Section 54.1.3.1). 1:3 complexes were isolated with AgOAc from refluxing acetonitrile.[204] Attempts to prepare a triphenylbismuth complex were unsuccessful, a black solid insoluble in nitric acid being formed. In solution, the complexes $AgOAc{\cdot}3XPh_3$ (X = As, Sb) were found to be partially dissociated, as evidenced by conductivity and molecular weight measurements.[204]

An X-ray structure analysis of the complex formed from the normally chelating ligand, *o*-allylphenyldimethylarsine, and silver nitrate showed that it contained two silver atoms bridged by the ligand. One silver atom was coordinated to the arsenic (Ag—As ≈ 249 pm) and the other to the alkene. These two silver atoms were also bridged by a doubly bidentate nitrato group with four similar Ag—O bond lengths (Ag—O = 254–273 pm). A second bridging nitrate completed the chain-like structure, forming two asymmetric bidentate linkages with two

Table 30 Some Formation Constants for Silver(I) Complexes with Ligands Containing As

R in $RC_6H_4As(CH_2CO_2H)_2$	*Log* K_{AgL^-}	*Log* K_{AgHL}	*Log* $K_{AgH_2L^+}$	*Ref.*
H[a]	6.13	5.126	4.643	207
o-OMe[a]	6.14	4.67	4.540	207
m-OMe[a]	6.20	4.804	4.556	207
p-OMe[a]	6.36	5.495	4.759	207
o-Cl[a]	5.20	4.13	4.045	207
p-Cl[a]	5.96	4.958	4.466	207
o-SMe[b]	5.14	7.88 (log β_{Ag_2L})	4.64 (log $\beta_{AgH_2L^+}$)	212

[a] 20 °C, $I = 0.1$. [b] 25 °C, $I = 0.1$.

Ag—O distances (285, 281 pm) significantly longer than the other two (243, 235 pm). The silver atom was six-coordinate since a long bond (290 pm) linked an oxygen atom of a neighbouring chain.[205]

The preparation of a range of substituted bis(carboxymethyl)phenylarsines of general formula $RC_6H_4As(CH_2CO_2H)_2$ has been reported and their interaction with Ag^I ions in aqueous solution studied.[206,207] The complex species AgL^-, AgL and AgH_2L^+ were proposed and their formation constants were determined. Table 30 gives some representative examples.

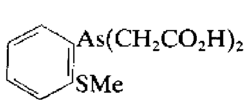
A number of di- and tri-arsine ligands have been reacted with Ag^I ions. When silver nitrate was treated with *o*-phenylenebisdimethylarsine, a non-conducting complex of the type $(AgNO_3)_2L$ was formed. The IR spectrum indicated monodentate nitrato groups and the complex was assigned a dimeric structure with a single bridging ligand.[208] Previously, complexes of the type $[AgL_2][AgX_2]$ ($X = Cl^-$, Br^-, I^-, NO_2^-) and $[AgL_2]Y$ ($Y = NO_3^-$, ClO_4^-) had been obtained with this ligand.[209]

Reaction of (triars)AgBr (triars = bis(*o*-dimethylarsinophenyl)methylarsine) with the carbonyl anions $Mn(CO)_5^-$, $Fe(CO)_4^{2-}$ and $Co(CO)_4^-$ in THF gave complexes of the type (triars)Ag—$Co(CO)_4$.[210] The crystal structure of the complex with an Ag—Co bond has been determined.[211] The silver atom had a distorted tetrahedral arrangement with three Ag—As bonds (262–272 pm) and an Ag—O bond (266 pm). The tetrahedral starting material was prepared by reaction of the triarsine with AgBr in ethanol.[210]

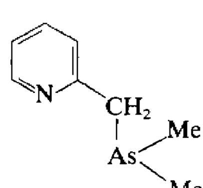
Other arsenic-containing ligands reported include mixed donor species with S[212] or N[213,214] as the other donor atom. The ligand bis(carboxymethyl)(*o*-methylthiophenyl)arsine (**24**) contains S and As donors in a position suitable for chelation. Formation constants for its complexes with Ag^I are given in Table 30. The silver complexes of the *m* and *p* derivatives were insoluble under the conditions used and no data could be collected.[212]

The bidentate ligands (**25**) and (**26**) have been reacted with silver(I) salts. Reaction of $AgCl_2^-$ with (**25**) in alcohol gave a colourless solution when heated for 1 h on a water bath, in the absence of air. After filtering the hot solution, colourless rods deposited when crystallization was induced by cooling and scratching.[213] The product obtained was formulated as $[AgL_2][AgCl_2]$ and was found to be light sensitive.

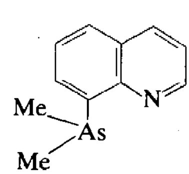
Colourless bis-chelated silver(I) cations containing (**26**) have been isolated by the addition of large anions, such as ClO_4^-, PF_6^- and BPh_4^-. The complexes were univalent electrolytes in solution.[214]



(**24**)



(**25**)



(**26**)

54.1.4 Oxygen Ligands

54.1.4.1 Aqua species

Most compounds of silver are practically insoluble in water and when isolated are invariably anhydrous, suggesting a low affinity of silver for oxygen.[215] Those salts which were readily soluble included the fluoride, nitrate, chlorate and perchlorate, of which the latter was actually hygroscopic. In aqueous solution, reports of the hydration number vary considerably, with most early reports favouring a value of 2. On the other hand, an NMR method gave a smaller value (0.7)[216] and conductivity[217] and compressibility[218] measurements gave values of 3–4. It has been claimed[219a] that this was perhaps a reflection that the techniques employed were unsuitable and that the probable value was 4, with the aqua complex adopting a tetrahedral structure. This was recently confirmed by an extended X-ray absorption fine structure (EXAFS) study, performed on concentrated aqueous silver perchlorate and nitrate solutions. Data collected on solutions between 3 and 9 M were consistent with the coordination of four water molecules each bound to the Ag^+ ion, with Ag—O distances of 231–236 pm.[219b] These distances were slightly smaller than those predicted earlier by X-ray diffraction studies,[29] but significantly longer than those obtained for the diammine silver(I) ion (222 pm), indicating that the water molecules were not so strongly held.

Solvation in non-aqueous solvents has been described as comparable to that of the potassium ion (ionic radii, 126 pm Ag^+, 133 pm K^+).[220]

The hydrolytic behaviour of Ag^I in solution has been critically reviewed by Baes and Mesmer.[221] The addition of alkali to Ag^+ solutions produces a dark brown precipitate, Ag_2O, which is more soluble in highly alkaline solutions than in water. Even under these conditions, only the mononuclear species AgOH and $Ag(OH)_2^-$ are produced and claims of polynuclear species have not been substantiated. At 25 °C and $I = 0$, the equilibrium constants for the formation of AgOH and $Ag(OH)_2^-$ were determined to be $-12.0 \pm 3(\log \beta_1)$ and $-24.0 \pm 0.1(\log \beta_2)$.[221]

54.1.4.2 *Dioxygen, peroxides and superoxides*

The gas-phase oxidation of ethylene to ethylene oxide over a supported silver catalyst was discovered in 1933 and is a commercially important industrial process. Using either air or oxygen, the ethylene oxide is produced with 75% selectivity at elevated temperatures (*ca.* 250 °C). Low yields of epoxides are obtained with propylene and higher alkenes so that other metal-based catalysts are used. A silver–dioxygen complex of ethylene has been implicated as the active reagent.[222]

To gain more insight into silver–dioxygen species, a matrix isolation study involving cocondensation of Ag atoms with $^{16}O_2$ and $^{18}O_2$ was initiated. Two products were obtained, $Ag^+(O_2^-)$ and $Ag^+(O_4^-)$.[223]

Unlike $Au^+(O_2^-)$, which was green,[224] both $Ag^+(O_2^-)$ and $Ag^+(O_4^-)$ were colourless, although weak absorptions at 275 and 290 nm respectively were observed in their UV spectra. $Ag^+(O_2^-)$ was formulated as a 'side-on'-bonded superoxo molecular species and this was supported by IR spectra. $Ag^+(O_4^-)$ was described as a tetraoxygen species rather than a bis(dioxygen) complex. Neither copper nor gold gave a secondary reaction to produce a related $M^+(O_4^-)$ complex.[223]

54.1.4.3 *Alcohols and alkoxides*

In 1930, it was reported that silver nitrate had a high solubility in a variety of solvents. For example, at 25 °C 100 cm^3 of ethylene glycol and phenol dissolved 53.9 and 82 g of the salt respectively. Monohydric alcohols, esters and ketones were found to be poor solvents. From the results of potentiometric measurements, the existence of complexes between $AgNO_3$ and the solvent molecules was deduced.

A compound, $AgNO_3 \cdot 2PhOH$, was isolated as white crystalline cubes from phenol, although its limits of stable existence were narrow; a metastable m.p. at 7.6 °C necessitated supercooling to −30 °C before the compound could be obtained.[225]

The reactions of alcohols related to phenolphthalein and fluorescein with Ag^I ions have been investigated for their application as colorimetric reagents in determining trace amounts of silver.[226] A simple, rapid and sensitive method was found which used 2,4,5,7-tetrabromofluorescein and 1,10-phenanthroline. A ternary complex was formed with a deep pink colour (λ_{max} 550 nm) in the presence of silver(I) ions and the two reagents. No significant colour change was observed in the absence of the diimine.[227]

A recent review suggested that alkoxy derivatives of the later transition metals had increased in interest since 1975, with several reports of Rh, Ru, Pd and Pt complexes. However, no Ag^I complexes were included.[228]

54.1.4.4 β-Ketoenolates

The silver(I) salt of 2,4-pentanedione (acetylacetone; A) has been prepared by mixing equimolar quantities of approximately 1 M solutions of $AgNO_3$ and NaA dissolved in oxygen-free water. The creamy white silver complex precipitated immediately. It was first prepared in 1893[229] and when pure could be kept for a few days with only moderate darkening. Decomposition was more rapid when the compound was exposed to oxygen, water or organic solvents, or if it was heated, when liberation of silver occurred. Some characteristic IR absorption frequencies are given in Table 31 and for comparison, those due to the starting material, NaA.[230]

Table 31 Some Characteristic IR Absorptions of Silver(I) Acetylacetonate (cm^{-1})[230]

AgA	*NaA*
1612	1604
1508	1508
1464	1462
1414	1408
(1366)	(1360)
1232	1228
—	(1193)
1008	1108
905	906
764	763
—	650

The stability of some silver β-diketone complexes has been determined by pH titrations at 30 °C in 75% dioxane.[231] For most of the complexes studied, a linear relationship existed between the dissociation constant of the β-diketone (pK_d) and the stability constant ($\log K_1$) (Table 32).

In 1975, it was reported that while lanthanide shift reagents could not be used directly to simplify the NMR spectra of alkenes, when coupled with silver salts substantial shifts could be induced.[232] Since then, a number of studies have reported the use of both chiral and achiral lanthanide(III)–silver(I) binuclear shift reagents,[233–237] where the ligands were generally fluorinated β-diketones.

In order for the shifts to be induced in the NMR spectrum of different substrates, two equilibria (equations 12 and 13) were proposed to exist. In one, the substrate S coordinated to

Table 32 Stability Constants ($\log K_1$) of some Silver(I) Complexes of β-Diketone in 75% Dioxane at 30 °C[231]

Ligand	*Formula*	*Acid dissociation constant*	*Stability constant*
2,4-Pentadione	$MeCOCH_2COMe$	12.65	9.72
1-(2-Furyl)-1,3-butanedione	$C_4H_3OCOCH_2COMe$	12.10	7.61
1-Acetyl-2-cycloheptanone	$MeCOC_7H_{11}O$	14.10	6.67
1-Acetyl-2-cyclohexanone	$MeCOC_6H_9O$	13.80	6.52
1,3-Diphenyl-1,3-propanedione	$PhCOCH_2COPh$	13.75	6.07
1-(2-Furyl)-3-phenyl-1,3-propanedione	$C_4H_3OCOCH_2COPh$	13.00	5.74
3-Phenyl-2,4-pentanedione	MeCOCHPhCOMe	12.60	5.44
1-Phenyl-1,3-butanedione	$PhCOCH_2COMe$	12.85	5.43
1-(2-Thienyl)-1,3-butanedione	$C_4H_3SCOCH_2COMe$	12.25	5.19
1-Acetyl-2-cyclopentanedione	$MeCOC_5H_7O$	11.60	4.22

a silver β-diketonate, Ag(β-dik). This was then further associated with a lanthanide chelate, Ln(β-dik)$_3$, to form *in situ* a tetrakis complex. The tetrakis chelate ion pair was believed to be the active shift reagent complex.[237]

$$Ag(\beta\text{-dik}) + S \rightleftharpoons Ag(\beta\text{-dik})(S) \tag{12}$$

$$Ln(\beta\text{-dik})_3 + Ag(\beta\text{-dik})(S) \rightleftharpoons Ln(\beta\text{-dik})_4Ag(S) \tag{13}$$

54.1.4.5 Thiosulfates

The process of fixation of photographic negatives involves the dissolution of silver halides in thiosulfate solution. In fact, photography could not have become a commercial success without Herschel's discovery in 1839 that unexposed silver halide could be washed away with thiosulfate before the image was exposed to light.[238] Up to that stage, unexposed silver halide in the recorded image darkened upon repeated exposure to light and hence photographic images were not permanent.

From studies of the reaction between silver and thiosulfate ions, a large number of complex ions have been suggested to exist in solution. The available thermodynamic data for these species are collected in Table 33.[239,240]

Table 33 Some Thermodynamic Data for Thiosulfate Silver(I) Complexes[239,240]

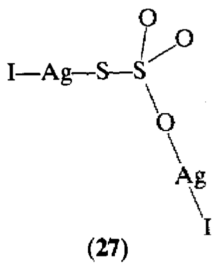
	log K[a]	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})
$Ag(S_2O_3)/Ag^+.S_2O_3^{2-}$	7.36		
$Ag(S_2O_3)_2^{3-}/Ag^+.(S_2O_3^{2-})^2$	13.46[b,239]	−79.71[239]	−9.6[239]
	12.72		
$Ag(S_2O_3)_3^{5-}/Ag^+.(S_2O_3^{2-})^3$	13.15		
$Ag_2(S_2O_3)_4^{6-}/(Ag^+)^2.(S_2O_3^{2-})^4$	26.3		
$Ag_3(S_2O_3)_5^{7-}/(Ag^+)^3.(S_2O_3^{2-})^5$	39.8		
$Ag_6(S_2O_3)_8^{10-}/(Ag^+)^6.(S_2O_3^{2-})^8$	78.6		
$Ag_9(S_2O_3)_{11}^{13-}/(Ag^+)^9.(S_2O_3^{2-})^{11}$	116.3		

[a] 25 °C, $I = 4.0$, unless indicated otherwise. [b] 20 °C, $I = 0$.

A wide variety of salts have been isolated from solution; however, it has been claimed that obtaining pure products is beset with difficulties and this perhaps explains some of the divergent formulations based on analytical data.[241]

Structural data are available for $NaAgS_2O_3 \cdot H_2O$,[242] $(NH_4)_7[Ag(S_2O_3)_4] \cdot 2NH_4Cl$[243] and $Na_4[Ni(NH_3)_4][Ag(S_2O_3)_2]_2 \cdot NH_3$.[244] In $NaAgS_2O_3 \cdot H_2O$, the two independent Ag^+ ions have similar tetrahedral coordination sites binding to one water molecule and three terminal S atoms with Ag—O = 262 and 275 pm and Ag—S between 248 and 265 pm. Each coordinated S belongs to three Ag coordination polyhedra, giving a polymeric structure containing double layers parallel to [010]; these are held together by Na^+ ions which have distorted octahedral coordination with Na—O = 229–277 pm.[242] In the $[Ag(S_2O_3)_4]^{7-}$ anion, the thiosulfate group again behaved as a monodentate ligand bound to silver *via* the terminal sulfur atom. The arrangement of $S_2O_3^{2-}$ groups around the silver was approximately tetrahedral with Ag—S bond distances approximately 258 pm.

On the basis of IR results it has been claimed that the thiosulfate group may also act as a bidentate ligand bonding through both the terminal S atom and an O atom. One such case was $(NH_4)_2Ag_2(I)_2(S_2O_3)$ (**27**).[245] Characteristic absorption bands for thiosulfato silver(I) complexes are given in Table 34.[246]



(27)

Table 34 Characteristic Absorption Bands (cm^{-1}) for Thiosulfato Silver(I) Complexes

	γ_1	γ_2	γ_4	γ_5	Ref.
$Na[Ag(S_2O_3)]\cdot H_2O$	1020	635	1170	527	240
$Na_3[Ag(S_2O_3)_2]\cdot 2H_2O$	1035	670	1162	543	240
$(NH_4)_3[Ag(S_2O_3)_2]$	1005	640	1160	535, 528	240
$Ba_3[Ag(S_2O_3)_2]_2$	1010	650	1185, 1150	550, 520	240
$Na_4[Ni(NH_3)_4][Ag(S_2O_3)_2]_2\cdot NH_3$	1010	650	1180, 1145, 1120	550, 530	244

54.1.4.6 Carboxylates and oxalates

(i) Carboxylates

Silver(I) carboxylates have been obtained by the addition of equivalent amounts of freshly prepared silver oxide to aqueous solutions of the appropriate acid.[247] Their degradation by halogens provides a convenient method for the preparation of alkyl halides (Hunsdiecker reaction) or esters (Simonini reaction).[248] Equations (14)–(18) have been proposed to account for the products obtained and were the result of extensive studies.

$$RCO_2Ag + X_2 \longrightarrow RCO_2X + AgX \quad (14)$$

$$RCO_2X \longrightarrow RCO_2\cdot + X\cdot \quad (15)$$

$$RCO_2\cdot \longrightarrow R\cdot + CO_2 \quad (16)$$

$$R\cdot + RCO_2X \longrightarrow RX + RCO_2\cdot \quad (17)$$

$$RX + RCO_2Ag \longrightarrow RCO_2R + AgX \quad (18)$$

Limited structural information is available for silver(I) carboxylates, despite their extensive use as catalysts in the manufacture of urethane polymers. This is in part due to their frequent insoluble and light-sensitive nature making chemical characterization of the complexes difficult. Dimeric structures have been reported for the perfluorobutyrate[249] and trifluoroacetate complexes.[250] In each case two-fold symmetry was crystallographically imposed. The Ag—O bond lengths were 223–224 pm, and in the more accurate determination of the trifluoroacetate, the Ag—Ag separation was found to be 297 pm. A dimeric structure was also found for the silver(I) complex of 3-hydroxy-4-phenyl-2,2,3-trimethylhexane carboxylate.[251] In the asymmetric crystal unit the Ag···Ag separations were 277.8 and 283.4 pm.

The asymmetric stretching frequency for 24 silver carboxylates [$\nu_{as}(CO_2^-)$] was observed to correlate with the Taft substituent constant σ^*. IR absorption data could be used to predict σ^* values with a standard deviation of 0.1.[252]

The ^{19}F NMR spectrum of single crystals of silver trifluoroacetate showed a single resonance at room temperature due to rapid rotation of the CF_3 moiety. Cooling to 40 K gave the rigid lattice spectrum which consisted of the six lines expected for the two types of dimer present in the unit cell.[250]

Complex ions of the type $Ag(O_2CR)_2^-$ and $Ag_2(O_2CR)^+$ have been proposed to exist in solution, based on measurements of solubility in water and in mixed solvents. Some thermodynamic data for silver carboxylates are given in Table 35.[253,254]

Table 35 Some Thermodynamic Data for Silver(I) Carboxylates (25 °C, $I = 0$)

	Log K	$\Delta H°$ (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})	Ref.
$AgOAc/Ag^+.OAc^-$	0.73	4	25	253
$Ag(OAc)_2^-/Ag^+.(OAc^-)^2$	0.64	4	25	
$Ag_2(OAc)^+/(Ag^+)^2.(OAc^-)$	1.14			
$Ag(O_2CCH_2Cl)/Ag^+.(O_2CCH_2Cl^-)$	0.64			253
$Ag(O_2CCH_2Cl)_2^-/Ag^+.(O_2CCH_2Cl^-)^2$	0.7 ± 0.2			
$Ag(O_2CPh)/Ag^+.(O_2CPh^-)$	0.53[a]			254
$Ag(O_2CPh)_2^-/Ag^+.(O_2CPh^-)^2$	0.62			

[a] $I = 1$.

The products of the reactions between silver(I) carboxylates and triphenylphosphine were colourless, diamagnetic solids, stable at room temperature to oxygen and not significantly light sensitive. Reaction with triphenylphosphine was also found useful as a method of solubilizing silver carboxylates.

Three types of monocarboxylato silver complexes have been obtained from these reactions. In the first, three triphenylphosphine molecules were present together with a unidentate carboxylato group. The second contained two triphenylphosphines and a bidentate carboxylate group. From studies of their ^{1}H NMR and IR spectra and solution molecular weights it was claimed that the silver atoms were four-coordinate in both cases.[255,256] The stoichiometry of these complexes was found to be pK_a dependent. All the acids formed complexes of the type $[Ag(O_2CR)(PPh_3)_3]$ but only those with $pK_a > 3.9$ formed complexes of the type $[Ag(O_2CR)(PPh_3)_2]$. Table 36 gives some IR CO_2^- stretching data. It can be seen that for the tris(triphenylphosphine) complexes, the differences between ν_8 (asym) and ν_3 (sym) carboxylate stretching frequencies are significantly larger than for the bis-ligand complexes. This supported the proposal of chelated carboxylate groups.

The third type of complex found was $[Ag(O_2CMe)(PPh_3)]_4$. This was prepared by reaction of silver acetate with an equimolar amount of PPh_3 in toluene at reflux, followed by filtration of the hot solution and recrystallization by slow evaporation of the same solvent. The X-ray crystal structure determination showed a centrosymmetric tetramer with two independent Ag atoms having different environments. One was bound to one PPh_3 (Ag—P = 237.6 pm) and two O atoms (Ag—O = 224.1 and 226.0 pm) while the other was bound to a PPh_3 (Ag—P = 235.4 pm) and three O atoms (Ag—O = 222.6, 232.0 and 247.5 pm). The shortest Ag—Ag separation was 312.2 pm.[257]

Recently the use of mixed lanthanide silver complexes as NMR shift reagents has been assessed. In the original experiments[232,233] silver(I) carboxylates such as AgO_2CCF_3 and $AgO_2CC_3F_7$ were used, although later studies showed that larger shifts could be induced with silver β-diketonates (see Section 54.1.4.4).

(*ii*) *Oxalates*

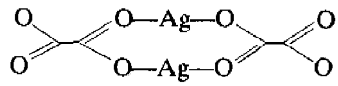
Silver oxalate is a colourless, crystalline substance which on heating undergoes an exothermic decomposition. The reaction begins at a little over 100 °C and easily becomes explosive. It was noticed quite early that samples prepared in the presence of an excess of oxalate were less stable thermally than those prepared using stoichiometric amounts of oxalate and silver ions. The thermal decomposition of silver oxalate into silver and CO_2 has subsequently been studied under varying conditions of preparation, decomposition environment and preirradiation.[258,259]

The crystal structure of silver oxalate may be considered to be made up of a series of chains held together in sheets by Ag—O crosslinks (**28**). Ag—O bond lengths were 217–230 pm and between chains the Ag—O separation was 258–261 pm.[260]

Mechanical treatment of silver(I) oxalate with Cu^{II} has recently been shown to cause the copper ions to dissolve in the silver(I) oxalate to form a dilute solution of Cu^{II} ions detectable

Table 36 Infrared CO_2^- Stretching Data (cm^{-1}) for Silver Carboxylates[255]

Complex	ν_8	ν_3	$\Delta\nu$ $\nu_8 - \nu_3$	$\Delta\nu$ (*sodium salt*)	*Mode of coordination* (*uni- or bi-dentate*)	pK_a *of parent acid*
$[Ag(O_2CMe)(PPh_3)_3]$	1570	1380	190	164	uni	4.76
$[Ag(O_2CMe)(PPh)_3)_2]$	1530	1390	140	164	bi	4.76
$[Ag(O_2CPh)(PPh_3)_3]$	1525	1360	165	140	uni	4.18
$[Ag_2(O_2CPh)(PPh_3)_2]$	1530	1400	130	140	bi	4.18
$[Ag(O_2CC_6H_4Me\text{-}m)(PPh_3)_3]$	1530	1360	170	150	uni	4.27
$[Ag(O_2CC_6H_4Me\text{-}m)(PPh_3)_2]$	1480	1360	120	150	bi	4.27
$[Ag(O_2CC_6H_4Me\text{-}o)(PPh_3)_3]$	1550	1360	190	145	uni	3.91
$[Ag(O_2CC_6H_4Me\text{-}o)(PPh_3)_2]$	1510	1355	155	145	bi	3.91
$[Ag(O_2CCH_2Cl)(PPh_3)_3]$	1600	1340	260	185	uni	2.87
$[Ag(O_2CCHCl_2)(PPh_3)_3]$	1625	1320	305	235	uni	1.48
$[Ag(O_2CCCl_3)(PPh_3)_3]$	1660	1295	365	295	uni	0.70
$[Ag(O_2CC_6H_4OH\text{-}o)(PPh_3)_3]$	1590	1405	185	160	uni	3.00



(28)

by ESR.[261] More prolonged treatment of silver(I) oxalate brought about decomposition analogous to that of thermal decomposition and which was accelerated by the Cu^{II}.[262]

A voltammetric study of complex formation between silver(I) and oxalate ions was performed at a rotating platinum electrode.[263] From half-wave potential measurements the formula of the complex was found to be $AgC_2O_4^-$. Preliminary paper electrophoresis studies with saturated sodium oxalate as the supporting electrolyte gave definite indications of a negatively charged complex also. However, due to the very low solubility of $Ag_2C_2O_4$ and the low stability of the negatively charged complex, no quantitative data were obtained. From the voltammetric study the instability constant ($\log K$) for the negatively charged complex was determined as -2.41 (hence $\log \beta_1 = 2.41$).[263]

54.1.4.7 Aliphatic and aromatic hydroxy acids

There are only scant reports of the reaction of silver ions with aliphatic or aromatic hydroxy acids and only a few stability constants have been reported.[264] In general only weak complexes were formed and typical examples include reactions with ascorbic or tartaric acids.

With ascorbic acid, silver was reduced to metallic silver although at room temperature the reaction was slow enough for a measurement of the instability constant ($K_1 = 2.2 \pm 0.2 \times 10^{-4}$ hence $\log \beta_1 = 3.66 \pm 0.04$).[265]

Reaction of disodium tartrate with silver nitrate at pH 5.6 was followed by the change in the absorption spectrum at 216–250 nm. Two complex ions were proposed, $Ag(C_4H_4O_6)^-$ and $Ag(C_4H_4O_6)_2^{3-}$, with formation constants $\log \beta_1 = 2.29$ and $\log \beta_2 = 4.21$ respectively.[266]

In relation to carbohydrate chemistry, the Koenigs–Knorr synthesis of glycosides involves the treatment of glycosyl halides with an alcohol or phenol in the presence of a heavy metal salt.[267] Karrer[268] discovered that reaction of silver salts of hydroxy acids could also be used and use of these reagents has been extended more recently.[269] Numerous variations and improvements on the original method have now been reported, and silver oxide, silver carbonate or silver trifluoromethanesulfonate have since become the accepted standard reagents.[267]

54.1.4.8 DMSO and DMF

(*i*) *DMSO*

DMSO solvates of $AgNO_3$ and $AgClO_4$ have been reported. $Ag(DMSO)NO_3$ was obtained by evaporation of the excess DMSO in vacuum from DMSO solutions of $AgNO_3$. $[Ag(DMSO)_2]ClO_4$ was isolated by evaporation of acetone and DMSO in vacuum from acetone solutions containing anhydrous $AgClO_4$ and DMSO. It was very unstable and on rubbing or scratching exploded with extreme violence. Their IR spectra indicated that the DMSO was coordinated *via* the O atom. Characteristic bands for the SO stretch and CH_3 rock were reported for $Ag(DMSO)NO_3$ at 1018vs and 949 cm^{-1}, and for $Ag(DMSO)_2ClO_4$ at 1020vs and 950s cm^{-1} respectively.[270]

The stability of DMSO solvates of $AgClO_4$ have been measured in a range of solvents.[271] Formation constants are presented in Table 37. In general, the complexes were found to be more stable than the corresponding DMF species (see Section 54.1.4.8.ii).

The crystal structure of $[Ag(DMSO)_2]ClO_4$ has been determined.[272] The structure was built up of infinite chains of silver atoms joined by doubly bridging DMSO oxygens. Each silver was also coordinated to a perchlorate ion giving an overall distorted trigonal bipyramidal structure. The Ag—O bond distances ranged from 236 to 274 pm. A general review of transition metal complexes of sulfoxides was recently published and this summarized the sparse literature dealing with silver(I).[273]

Table 37 Formation Constants for DMSO Adducts of $AgClO_4$[271]

Solvent	*Log* β_1	*Log* β_2	*Log* β_3	*Log* β_4
Nitroethane	—	4.8 ± 0.1	5.0 ± 0.2	6.40 ± 0.10
Acetone	1.2 ± 0.2	2.41 ± 0.10	2.48 ± 0.10	3.40 ± 0.10
Sulfolane[a]	1.74 ± 0.15	2.48 ± 0.15	3.24 ± 0.15	—

[a] 1,1-Dioxo-1-thiocyclopentane.

(*ii*) *DMF*

The formal reduction potential of silver ion in DMF was found to be $+0.579 \pm 0.004$ V *vs.* SCE. The values of the stability constants of the DMF complexes of silver(I) in various solvents are given in Table 38. It was observed that the complexes were most stable in nitroethane.[274]

Table 38 Stability Constants of DMF Complexes of Silver(I) in Various Solvents[274]

Solvent	*Log* β_1	*Log* β_2	*Log* β_3	*Log* β_4
Nitroethane	1.7 ± 0.2	2.7 ± 0.2	3.0 ± 0.2	2.42 ± 0.15
Sulfolane	1.3 ± 0.2	1.7 ± 0.2	—	—
Acetone	0.5 ± 0.1	1.24 ± 0.05	—	—
2-Butanol	0.36 ± 0.05	0.3 ± 0.1	—	—
Methanol	-0.36 ± 0.02	-0.7 ± 0.1	—	—

1:1 adducts of DMF with $AgBF_4$ and $AgClO_4$ have been isolated from 2-nitropropane. Their ^1H NMR spectra show close similarity to those of DMF–Lewis acid or DMF–protonating acid spectra. Coordination was proposed to exist *via* the carbonyl O atom.[275] Proton shifts are presented in Table 39.

Table 39 ^1H NMR Shifts of Silver(I) Adducts with DMF in 2-Nitropropane[275]

Adduct	cis-*Methyl*[a]	trans-*Methyl*	*CHO*[b]
$AgBF_4 \cdot DMF$	94	87	488
$AgClO_4 \cdot DMF$	96	90	490
DMF	102	94	474

[a] Shifts in Hz upfield from second peak in 2-nitropropane septet. *Cis* and *trans* are with respect to the aldehyde proton. [b] Shifts in Hz downfield from internal TMS.

The addition of absolute benzene to solutions of silver nitrate in DMF gave a fine white precipitate with the composition $AgNO_3 \cdot 2DMF$.[276] The adduct was hygroscopic and photosensitive. The IR spectrum showed a series of strong bands (Table 40) and indicated that coordination occurred *via* the O atom. The adduct melted at 210 ± 2 °C after which decomposition occurred in the liquid phase. Further heating to 500 °C eventually led to metallic silver being produced.

Table 40 Infrared Spectral Data for $AgNO_3 \cdot 2DMF$ (cm^{-1})[276]

$AgNO_3 \cdot 2DMF$	*Possible assignment*
1610vs	ν(C=O)[a]
1325vs	
1120	ν(CN)
1025w	
815s	Anionic NO_3^-
730s	
670s	δ(N—C=O)

[a] For pure DMF ν(C=O) occurred at 1680 cm^{-1}.

(iii) Other amides and N-*oxides*

Reaction of $AgClO_4$ with *N,N*-dimethylacetamide (DMA) in excess DMA followed by addition of ether gave $Ag(ClO_4)\cdot DMA\cdot H_2O$. The white crystals decomposed at 92 °C. An IR spectrum showed that the $\nu(C{=}O)$ band, originally at $1662\ cm^{-1}$ for free DMA, was shifted to $1628\ cm^{-1}$. This shift of $34\ cm^{-1}$ on coordination indicated a decrease in the stretching force constant and was taken as evidence of coordination through the O rather than N atom.[277]

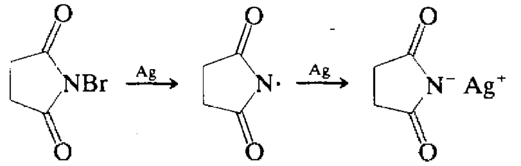
In contrast, it was reported that at least small amounts of a complex of Ag^+ linked to the nitrogen existed in aqueous solutions of the system $AgNO_3$—DMA.[278] This conclusion was reached on the basis of the lowering of the activation parameters for the barrier to rotation about the amide N—C bond (Table 41).[279]

Table 41 Activation Parameters for Rotation About Amide N—C Bond[279]

	T_c (K)	A (s^{-1})	E_a ($kJ\ mol^{-1}$)	$\Delta H\ddagger$ ($kJ\ mol^{-1}$)	$\Delta S\ddagger$ ($J\ mol^{-1}\ K^{-1}$)
Ag^+-DMA-d^3	337	4×10^{13}	79.5 ± 2.9	77.0 ± 2.9	±5.9
DMA-d^3	336	8×10^{13}	87.9 ± 3.8	84.9 ± 3.8	±11.3

A 1:2 adduct, $AgNO_3\cdot 2DMA$, has also been isolated.[276] The white crystalline precipitate was obtained by the addition of benzene to a solution of silver nitrate in DMA. It has a melting point of 200 ± 2 °C.

Metallic silver was found to react with NBS and provided a convenient high yield route to the silver salt of succinimide (equation 19).[280] Spin trapping experiments were performed to show that nitrogen-centred radicals were intermediates in the reaction.



(19)

The coordination chemistry of aromatic amine *N*-oxides and dioxides has been the subject of numerous studies in recent years.[281–283]

The basicity of the aromatic amine *N*-oxide can be substantially varied by the introduction of substituents on the aromatic ring. IR spectra of free *N*-oxides display a prominent band between 1200 and $1300\ cm^{-1}$, attributable to the nitrogen–oxygen stretching frequency $\nu(NO)$. The more activating the substituent, the lower the energy of the absorption. Upon coordination, $\nu(NO)$ is decreased by up to $60\ cm^{-1}$. IR data for pyrazole and pyridine derivatives are given in Table 42.[281–286]

Table 42 IR Spectral Data for some Silver(I) Complexes with *N*-oxides

	$\nu(NO)$ (cm^{-1})	*Ref.*
Pyrazine N-*oxides*		
$Ag(pz\ 1\text{-oxide})_2NO_3$	1310	284
$Ag(L)NO_3$		
L = 3-methylpyrazine 1-oxide	1254	284
2,5-dimethylpyrazine 1-oxide	1320, 1310, 1288	284
2-chloro-3-methylpyrazine 1-oxide	1303	284
2-chloro-3-methylpyrazine 4-oxide	1310	284
Pyridine N-*oxides*		
$Ag(py\ 1\text{-oxide})_2ClO_4\cdot(py\ 1\text{-oxide})$	1210, 1238	281
$Ag(L)_2ClO_4$		
L = 4-methylpyridine 1-oxide	1203	281
4-methoxypyridine 1-oxide	1199	285
2-ethylpyridine 1-oxide	1197	281
4-chloropyridine 1-oxide	1225	285
2-cyanopyridine 1-oxide	1210, 1220	286
4-cyanopyridine 1-oxide	1239	286

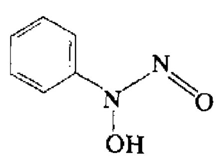
Reaction of $AgClO_4$ with *N*-oxides in acetone, methanol or ethanol often resulted in salts containing more than one mole of ligand. Bridging structures were proposed to occur, based on the IR spectral shifts.[286] The analysis of the silver perchlorate complex with 2,2′-bipyridyl 1,1-dioxide indicated two moles of ligand per mole of silver. In this case it was considered that the complex was monomeric and that each ligand was bound to the silver ion by only one oxygen giving rise to a linear, two-coordinate arrangement.[287]

54.1.4.9 Hydroxamates, cupferron and related oxygen ligands

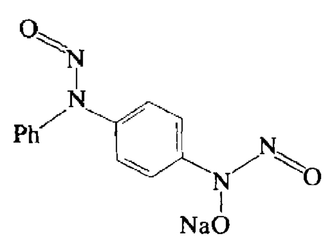
The complexing capacity of hydroxamic acids was predicted by Werner in 1908, who also indicated the metals most likely to form stable complexes.[288] Since then, the formation of poorly soluble and intensely coloured hydroxamates has been used for analytical determinations for a number of metal ions, such as Fe^{3+}, Mo^{5+}, V^{5+} *etc.* A recent general review of transition metal complexes of hydroxamic acids included the few known examples of silver(I) complexes.[289]

The rearrangement of hydroxamic acids or their esters to isocyanates was discovered in 1872 by Lossen and is now known as the Lossen rearrangement.[290] During attempts to determine the mechanism of this rearrangement, a variety of silver hydroxamates were prepared and their decomposition to isocyanates observed.[291] In each case, the sodium or potassium salt of an ester of the hydroxamic acid was dissolved in ether–alcohol solution and then treated with aqueous silver nitrate. The ether layer often turned yellow before precipitation occurred in the aqueous phase. Decomposition temperatures of the silver salts were generally greater than 100 °C at which stage the isocyanate was formed. The hydroxamic acids investigated were diphenylacetylhydroxamic acid, triphenylacetylhydroxamic acid, pyromucylhydroxamic acid and thenoylhydroxamic acid.

Cupferron (**29**), as the name suggests, has been applied to the analytical determination of copper and iron. In neutral solution, a white 1:1 complex with Ag^I has been obtained which reacted with MeI to give the methyl ether.[292] Reaction of the related ligand (**30**) with silver nitrate in aqueous methanol gave a red precipitate which on further reaction with MeI gave the methyl ether in a reaction analogous to that for cupferron.[293]



(**29**)



(**30**)

54.1.5 Sulfur Ligands

54.1.5.1 Thiolates

The coordination chemistry of the thiolate group has been widely investigated where it was part of a polydentate ligand. Fewer studies involving monothiolates have been carried out to determine the coordination characteristics intrinsic to the RS^- group.[294,295]

Compounds of the type AgSR have been known and used for a long time. Early studies with primary alkanethiolates showed that the yellow solids were thermally stable and generally insoluble in common organic solvents. Some interesting early examples include $AgSC_3H_7$ and $AgSCF_3$.

Characterization of the essential oils of onion and garlic was aided by the isolation of silver derivatives. The salts containing *n*-propanethiol and allyl thiol were both insoluble and could not be recrystallized.[296]

When silver fluoride and CS_2 were heated in an autoclave at 140 °C then $AgSCF_3$ was formed in 70–80% yield (equation 20).[297] The trifluoromethanethiol group formed could be transferred intact by further reactions.[298]

$$3AgF + CS_2 \longrightarrow Ag_2S + AgSCF_3 \qquad (20)$$

Until recently, little structural information has been available for silver thiolates. Based on molecular weight measurements it was suggested that for $[AgSR]_n$ when R was a tertiary alkyl then $n = 8$, while when R was a secondary alkyl then $n = 12$. For primary alkanethiolates which were generally insoluble, unreliable high molecular weights were obtained, indicative of non-molecular structures.

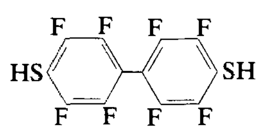
The crystal structures of several silver thiolates have now been reported and, in general, the Ag—S distances were between 240 and 280 pm.[299–302] If longer distances (*e.g.* 330 pm) or secondary bonding were included in the interpretation, then molecular cycles and a variety of molecular cages could be recognized. These included $[Ag_4(SR)_6]^{2-}$, $[Ag_5(SR)_6]^{-}$, $[Ag_5(SR)_7]^{2-}$ [300] and $[Ag_6(SR)_8]_n^{2n-}$ ($n = 1, 2$).[301] A one-dimensional non-molecular structure was confirmed in only one compound.[302]

The structure of (3-methylpentane-3-thiolato)silver(I) was found to consist of cores of chains, which were approximately linear. Each chain contained two separate strands, with alternating silver atoms and double bridged thiolate ligands, which were intertwined. Of interest was the unprecedented absence of any silver–sulfur bonding between chains.[302]

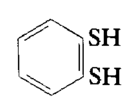
For benzenethiol, crystallization equilibria (equation 21) exist in non-aqueous solvents, such that pale yellow $(Me_4N)[Ag_6(SPh)_8]$ as well as colourless $(AgSPh)_n$ and yellow $(Me_4N)_2[Ag_5(SPh)_7]$ can be isolated.[301] Far IR spectral data are available for the latter compound and also for $AgSBu^t$ and $(Et_4N)[Ag_5(SBu^t)_7]$.[303]

$$(AgSPh)_n(S) \underset{}{\overset{PhS^-}{\rightleftharpoons}} [Ag_6(SPh)_8]^{2-} \overset{PhS^-}{\rightleftharpoons} [Ag_5(SPh)_7]^{2-} \qquad (21)$$

The dithiols (**31**) and (**32**) were found to react with a variety of heavy metal ions to form precipitates of the corresponding metal mercaptides.[304,305] Characteristic IR data for these complexes are given in Table 43.



(**31**)



(**32**)

Recently the crystal structures of two 1,1-dithiolate cluster anions have been reported. The first, $[Ag_6\{S_2C{=}C(CN)_2\}_6]^{4-}$, contained a cube of eight Ag^I atoms,[306] while the second,

Table 43 IR Spectral Data for Silver(I) Dithiolates (cm^{-1})

$AgSC_6F_4C_6F_4SAg$ [304]	$(AgSC_6H_4SAg)_n$ [305]
1632w	1630
1485sh	
1474sh	1475vs
1469s	
1460s	
1440m	
	1390vs
1369w	
	1350vw
1232w	
	1100vs
	1010s
980m	
949m	
895m	
	810ms
760w	
719s	
598w	
	540vs
	500vs
	490s
432w	

$[Ag_6\{S_2C{=}C(CN)_2\}_6]^{6-}$, contained an Ag octahedron.[307] Both could be formed from acetonitrile solutions of bis(benzyltriethylammonium)-2,2-dicyanoethane-1,1-dithiolate and $AgNO_3$. They can be readily distinguished by their IR spectra. $[Ag_8\{S_2C{=}C(CN)_2\}_6]^{4-}$ has a characteristic absorption at 910–920 cm^{-1} whilst in $[Ag_6\{S_2C{=}C(CN)_2\}_6]^{6-}$ the corresponding band occurs between 930 and 945 cm^{-1}. The latter compound was found to be structurally identical to the neutral molecule $[Ag^I_6(S_2CNPr_2)_6]$.[308]

54.1.5.2 Thioethers

Dialkyl and diaryl thioethers generally react with silver(I) salts to form 1:1 complexes.[309,310] Few data are available for these adducts; however, on the basis of formation constants they appear to have relatively high stability (Table 44).[311,312]

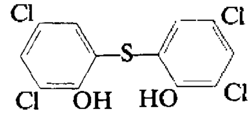
Table 44 Formation Constants for some 1:1 Silver(I) Thioether Complexes

		Log β_1	*Log* β_2	*Ref.*
Tetrahydrothiophene	50% aq EtOH, 25 °C, 1 M $NaClO_4$	3.51	—	311
2,2′-Thioethanol	1 M aq KNO_3, 20 °C	3.60	6.06	312
	1 M $NaNO_3$, 25 °C	3.43		311
Bithionol	Ethanol–water, 25 °C, 1 M $NaClO_4$	4.55	7.10	314

The IR spectra of the compounds $Me_2S{\cdot}AgNO_3$, $Et_2S{\cdot}AgNO_3$ and $Pr^n_2S{\cdot}AgNO_3$ indicated that the nitrate anion retained its D_{3h} symmetry in the compounds, *i.e.* was ionic.[313] The broad intense γ_3 band at 1370 cm^{-1} was not split, γ_2 was at 819 cm^{-1}, and there was no indication of absorption by the nitrate in the 1030 cm^{-1} region. The sulfur atoms may serve as bridges between silver atoms.[313]

With bidentate thioethers such as $RS(CH_2)_nSR$ ($n = 2$–5), *cis*-R′SHC=CHSR′ and *o*-$C_6H_4(SMe)_2$, silver(I) forms 1:2 chelate complexes involving tetrahedral Ag^I. The stabilities in aqueous solution of some of these complexes in which $R = CH_2CH_2OH$ have been measured.[312]

Silver forms a 1:2 complex with bithionol (**33**), a commercial bacteriostat.[314] The formation constants are given in Table 44.

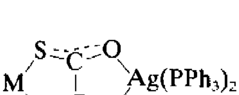


(**33**)

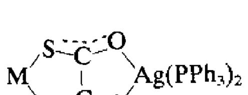
54.1.5.3 Metallothio anions as ligands

One area of silver chemistry that has received much recent attention is the synthesis of multinuclear aggregates.[315] Anionic metal dithiolato complexes such as $K_nM(S_2C_2O_2)_2$ were found to form adducts with silver(I) phosphines. In these complexes, the inert cations (K^+) that accompanied the metallothio anions could be readily substituted by coordinatively unsaturated silver phosphines $Ag(PR_3)_2^+$. For dithiooxalto complexes this led to the isolation of a remarkable range of linkage isomers (**34**)–(**37**).[316,317]

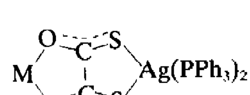
Spectral data used to characterize these structural types are given in Table 45. The type of isomer obtained for the dithiooxalates depended on the kinetic inertness of the original complex and occasionally the resulting products were not the energetically most stable species.



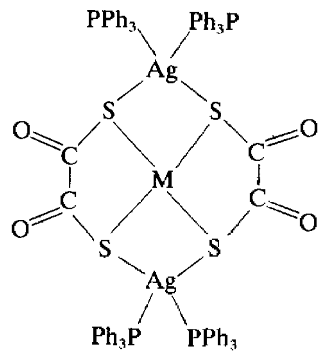
(**34**) M = Co^{III}, Cr^{III}



(**35**) M = $Cu(PPh_3)_2$, $Ag(PPh_3)_2$



(**36**) M = Al^{III}, Fe^{III}, Cr^{III}, Rh^{III}



(37) M = Ni^{II}

In such cases slow rearrangements to the thermodynamically favoured form occurred. With kinetically labile complexes, the bridging mode adopted by the dithiooxalate ligand was a reflection of the thermodynamic stability of $M—S_2C_2O_2$ *vs.* $(R_3P)_2—Ag—S_2C_2O_2$ interactions.

Table 45 Some Properties of Polynuclear Dithiolate Complexes Containing Silver Phosphines

Complex	*Colour*	μ_{eff}^{corr} (BM)	*ν(C=O) stretch* (cm^{-1})	*ν(C—C) and ν(C—S)*	*ν(M—S)*	*Ref.*
$Cr(S_2C_2O_2)_3[Ag(PPh_3)_2]_3$	Light brown	3.86	1622m, 1440s, 1572s	862br	325s, 370s	315
$Co(S_2C_2O_2)_3[Ag(PPh_3)_2]_3$	Light brown	Diamagnetic	1608w, 1530s	1081sh	343m	315
$Cr(O_2C_2S_2)_3[Ag(PPh_3)_2]_3$	Light brown	3.95	1370s	1120w	375s, br	315
$Fe(O_2C_2S_2)_3[Ag(PPh_3)_2]_3$	Black	5.81	1380	—	314s, br	315
$Ni(S_2C_2O_2)_2[Ag(PPh_3)_2]_2$	Red	Diamagnetic	1653s, 1628s	1034s	345s	315
			ν(C≡N) stretch (cm^{-1})			
$Ni(mnt)_2[Ag(PPh_3)_2]_2$[a]	Orange-red	—	2202s	1495s, 1146s	355s	318
$Ni(mnt)_2[Ag(Ptol_3)_2]_2$	Orange-red	—	2200s	1492s, 1146s	—	318
$Ni(i\text{-}mnt)_2[Ag(PPh_3)_2]_2$[b]	Green	—	2210s	1445vs, 924sh, 914m, 879m	380, 288	318
$Ni(i\text{-}mnt)_2[Ag(Ptol_3)_2]_2$	Green	—	2200s	1485vs, 933m, 922sh, 878m	—	318

[a] MNT = 1,2-dicyano-1,2-ethylenedithiolate. [b] i-MNT = 1,1-dicyano-2,2-ethylenedithiolate.

The majority of these metal species have been found for Ni^{II} dithiolates.[318] The ^{31}P NMR spectra for various substituted phosphine complexes of the type $[(R_3P)_2Ag]_2Ni(mnt)_2$ (where mnt = 1,2-dicyano-1,2-ethylenedithiolate) have been examined.[319] The magnitudes of the Ag—P coupling constants observed were in the order $PPh_3 < PEtPh_2 < PEt_2Ph = PEt_3$ (Table 46). This increase in J_{Ag-P} was interpreted as a consequence of reduced steric strain which allowed the P—Ag—P bond angle to open as the *s* character of the P—Ag bond increased from PPh_3 to PEt_3. An alternative explanation was based on the increase in basicity of the phosphine as alkyl groups were successively introduced.

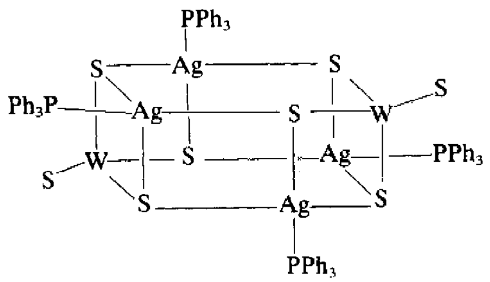
An unusual cage structure with two six-membered rings was formed by reaction of thiometalates with silver salts. Extraction of an aqueous solution of either $(NH_4)_2WS_4$[320] or

Table 46 Coupling Constants for some Silver Phosphine Complexes (Hz)[319]

Compound	*J(^{107}Ag–P)* (*^{108}Ag–P*)
$\{(PPh_3)_2Ag\}_2L$[a]	394 (451)
$\{(PEtPh_2)_2Ag\}_2L$	413 (475)
$\{(PEt_2Ph)_2Ag\}_2L$	426 (489)
$\{(PEt_3)_2Ag\}_2L$	426 (489)

[a] L = $Ni(mnt)_2$

$(NH_4)_2MoS_4$[321] with a solution of Ph_3P and $AgNO_3$ in dichloromethane gave crystals of $[M_2S_8Ag_4](PPh_3)_4$ (M = W, Mo). The complexes were isostructural and contained a system of SAg_2S_2M rings which were connected with metal–sulfur bonds (**38**). All the metal atoms were tetrahedrally coordinated and the WS_4^{2-} or MoS_4^{2-} ions could be considered as terdentate ligands where the terminal MS bonds were significantly shorter. The Ag—S and Ag—P bond lengths were in the ranges 254–265 pm and 240–244 pm respectively.



(**38**)

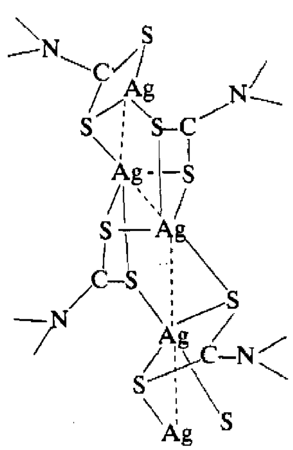
54.1.5.4 Mono- and di-thiocarbamates

The preparation and properties of some silver(I) complexes of dialkyldithiocarbamates were reported in 1959.[322] The complexes $Ag(R_2dtc)$ were polymeric in solution as well as in the solid state.

The crystal structures of the diethyl-[323,324] and di-*n*-propyl-dithiocarbamates[325] have been determined. The α-forms of the diethyldithiocarbamate and the di-*n*-propyldithiocarbamate contain discrete hexameric molecules. In $[Ag(Pr_2dtc)]_6$, the silver atoms form a somewhat distorted octahedron with six comparatively short and six longer edges. The short edges correspond to metal–metal distances which are comparable or somewhat longer than those in the metallic phase of silver. The long edges form two centrosymmetrically related triangles in the silver octahedron. Outside the other six faces of the octahedron, one dithiocarbamato ligand is situated, linked to the silver atoms of the face by silver–sulfur coordination.

One of the sulfur atoms is linked to one silver atom while the other is linked to two. The silver coordination is three-fold but not planar, the metal atoms being situated 'inside' the plane of the coordinating sulfur atoms.[325]

In the α-modifications of silver(I) diethyldithiocarbamate irregular hexamers are linked in chains by weak bonds only (Ag—S = 299 pm). Two of the six silver atoms have four-fold coordination, the others three-fold. Two ligands coordinate to only two metal atoms, the others to four. Five short metal–metal distances occur in each of the hexamers.[323] In the β-modification, which is a true high polymer, all the silver atoms have four-fold coordination and all the ligands are linked to three metal atoms, (**39**). There are only two short metal–metal distances per six silver atoms. Crystals of the β-form were obtained from CS_2 solutions cooled to −40 °C. Ag—S bond lengths were in the range 251–274 pm.[324]



(**39**)

The use of silver diethyldithiocarbamate has been recommended for the determination of arsenic and antimony.[327] One disadvantage, however, was that the red colour developed during the test varied markedly in intensity and wavelength depending on the reagent. Thus between different batches, the wavelength of maximum absorption could vary between 520 and 550 nm. The reagent containing a small excess of silver had higher sensitivity to arsenic and was found to absorb at longer wavelengths than did the complex containing a slight excess of free ligand.[326]

54.1.5.5 1,2-Dithiolenes

A recent review on transition metal complexes of 1,2-dithiolenes summarizes the virtually non-existent literature dealing with silver complexes.[328] Only one general report exists for their production, which gave complexes of the type $[AgL_n(ClO_4)]$ [where $n = 1$, 2 and L = various thioethers, $C_2H_2(SH)_2$, $C_6H_4(SH)_2$, *o*-$MeC_6H_3(SH)_2$, maleonitriledithiolate (mnt^{2-}) and toluene 3,4-dithiolate (tdt^{2-})].[329] An early report claimed the existence of an ESR-detectable $Ag(mnt)_2^{2-}$ species; however, this could not be obtained free from impurities[330]

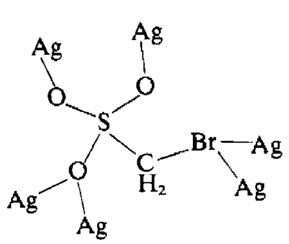
54.1.5.6 Other S-containing ligands

(i) Sulfonates and sulfonamides

In 1958, some water-soluble sulfonated aromatic ethers, sulfides and selenides were prepared and the stability constants of their complexes with silver ions determined. The coordinating capacity of sodium benzenesulfonate was found to be negligible ($\log K = -0.04$) compared with that of the ligands containing the additional donor atoms such as S or Se. The *p*-MeO derivative also had a very small stability constant ($\log K_1 = -0.12$), and so for both these ligands coordination through the sulfonate group only was predicted and the sulfonate group was shown to be a very poor donor for silver(I) ions.[331]

More recently, the crystal structures of several silver sulfonates have been determined: those containing methanesulfonate,[332] bromomethanesulfonate[333] and pyridinesulfonate.[334] In the first of these, no distinct molecule of the silver salt was found in the unit cell. The silver atom was five-coordinate with a very distorted trigonal bipyramidal arrangement. Ag—O bond distances were in the range 234–263 pm. Each silver was bound to five different methanesulfonates.[332]

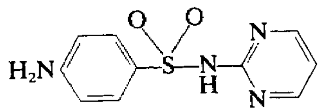
Slow evaporation of an aqueous solution containing stoichiometric amounts of Ag_2O and bromomethanesulfonic acid led to the precipitation of crystals of the silver salt. Each ligand was found to coordinate four silver atoms by means of its three sulfonic O atoms and a further two by means of the Br atom (**40**). Thus each silver atom was octahedrally surrounded by four O atoms (Ag—O = 235.4 and 248.6 pm) and by two Br atoms in axial positions (Ag—Br = 297 pm).[333]



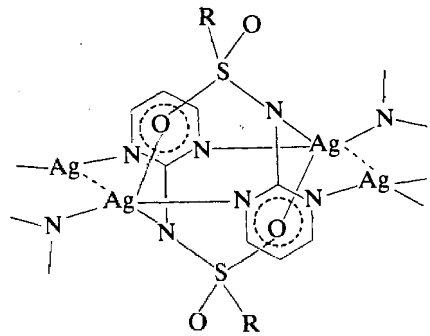
(**40**)

Sulfonamides have been extensively used in medicine for their antibacterial properties. Silver sulfadiazene (*N*-pyrimidin-2-ylsulfanilamide, **41**), when applied topically, has proved effective in preventing infections in burns victims.[335,336]

The mode of antibacterial action appeared to involve interaction with DNA, thus binding the silver.[337] Silver sulfadiazine solutions were not light sensitive and unlike silver nitrate did not remove chloride from body fluids.[336]



(41)



(42) R = $C_6H_4NH_2$-*p*

The structure of silver sulfadiazine has been the subject of some controversy which for the solid state has now been settled by X-ray crystal structure determinations.[338,339] The silver was not coordinated to the amine N to give linear two-fold coordination. Instead, the nitrogen atoms of the pyrimidine ring were found to coordinate to two different silver atoms to form polymeric chains extending through the crystal. Each silver in this chain was also coordinated to an oxygen from a sulfonyl group (Ag—O ≈ 254 pm). A second identical chain was joined to the first chain by coordination of an imido nitrogen and in addition the silver atoms in one chain were only 292 pm from a symmetry-related silver atom in the second. The coordination about the silver was described as a distorted trigonal bipyramid (**42**).[339]

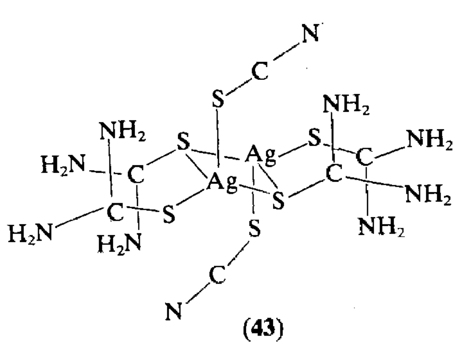
(*ii*) *Thiocarboxylic acid amides, including thiourea*

The preparation and structural investigation of silver(I) thiourea complexes have been the subject of numerous reports.[340] In solution, the formation of stable, mononuclear complexes containing up to four thiourea groups has been proposed and the associated thermodynamic data are collected in Table 47.[341,342]

Table 47 Thermodynamic Data for the Formation of Silver(I) Thiourea Complexes

Temperature (°C)	*Medium*	*Log* β_1	*Log* β_2	*Log* β_3	*Log* β_4	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})	*Ref.*
15	0.5 KNO_3	7.17	11.01	13.43	14.40	−100	−78.2	341
25	$I \rightarrow O$, pH 6.8	7.30	10.60	12.80	13.72	−143	−213	342

Crystal structure data are available for $Ag(tu)_2Cl$,[343] $Ag(tu)_3ClO_4$[344] and $Ag(tu)_2SCN$.[345] In the latter compound the Ag atoms were coordinated by two thiourea S atoms (Ag—S = 248.2 and 246.2 pm) and one S of a thiocyanate ligand (Ag—S = 260.8 pm). The three S atoms formed an almost planar arrangement with the central Ag atom. A fourth sulfur atom was much more weakly bound (Ag—S = 311.1 pm) and completed a highly distorted tetrahedron. In addition, it acted as a bridge to the second half of the centrosymmetric dimer (**43**).



(43)

Polymeric thiourea complexes have also been isolated. For example, $[Ag_2(tu)_3(NO_3)_2]_n$ was

Table 48 Characteristic IR Absorption Bands (cm^{-1}) of Thiourea and $[Ag_2(tu)_3]^{2+}$ [346]

tu	$[Ag_2(tu)_3]^{2+}$	*Assignment*
	3450sh,br	
3260s, br	3300s, br	γ(N—H)
1630sh, 1588s	1625s, 1600s	NH_2 def
1468s	1513w, 1485m	γ(C—N)
1433s, 1396w	1430w, 1410w, 1388s	γ(C=S)
1091s	1094m	ρ-NH_2
735sh, 727sh, 721s	729m, 703m	Mostly C=S, some C—N

precipitated from a solution of thiourea in nitric acid by adding an aqueous silver nitrate solution. IR spectra were interpreted in terms of silver–sulfur bonding only. Characteristic IR absorption bands are given in Table 48.[346]

Attempts have been made to deprotonate the coordinated thiourea group. Upon contact of $Ag(tu)_3NO_3$ with ammonia, the initially white complex became grey and turned black following complete removal of the solvent. The products obtained (ammonium nitrate, silver sulfide, thiourea and cyanamide)were rationalized by equations (22) and (23).[347]

$$Ag(tu)_3NO_3 + 2NH_3 \longrightarrow [Ag(NH_3)(tuH)] + NH_4NO_3 + 2tu \qquad (22)$$

$$2[Ag(NH_3)(tuH)] \longrightarrow Ag_2S + tu + N{\equiv}CNH_2 + 2NH_3 \qquad (23)$$

A wide range of substituted thiourea derivatives of silver(I) have been studied.[340] The crystal structure of tris(*N*-methylthiourea) silver(I) chloride has been determined and the central silver atom was tetrahedrally coordinated to three S atoms (Ag—S = 252 pm) and one Cl atom (Ag—Cl = 265 pm).[348]

Thioacetamide is a well-known reagent which has been used in both qualitative and quantitative analysis. Its reaction with silver ions has been used for its determination.[349]

In the titration of thioacetamide with silver nitrate in distilled water and in slightly acidic or basic solution, a black precipitate of silver sulfide formed. The other products of the reaction were ammonium nitrate and acetic acid. Two reaction pathways have been suggested for the course of this reaction, Scheme 3 and equation (24).[349,350] In the presence of 0.1 M HNO_3, the reaction proceeded similarly. However, in 0.5 M or more concentrated HNO_3 solutions a different reaction took place. Under these conditions a light, pearly precipitate was formed and a silver thioacetamide complex was obtained.

$$Me{-}\overset{\overset{\Large S}{\|}}{C}{-}NH_2 + 2H_2O + 2Ag^+ \rightarrow Ag_2S + Me{-}\overset{\overset{\Large O}{\|}}{C}{-}OH + NH_4^+ + H^+ \qquad (24)$$

Reaction of 2-thioamidopyridine (L) with silver perchlorate in polar solvents, or by means of the halide complexes $K[AgX_2]$ in aqueous ethanol, resulted in the fleeting yellow precipitate which formed first being rapidly reduced to a mixture of colloidal silver and silver sulfide, a

$$Me\overset{\overset{\Large S}{\|}}{C}NH_2 + 2AgNO_3 \longrightarrow Ag_2S + MeCN + 2HNO_3$$

$$MeCN + 2H_2O \longrightarrow NH_4OAc$$

$$NH_4OAc + 2HNO_3 \longrightarrow AcOH + NH_4NO_3 + HNO_3$$

Scheme 3

result similar to that observed with thioacetamide. However, by allowing the ligand to react with $AgClO_4$ in benzene then the yellow complex $[AgL]ClO_4{\cdot}2H_2O$ was isolated. The water could be removed by drying at 100 °C. Conductance measurements in DMF showed that the complex was a uniunivalent electrolyte. The substance absorbed at 367 nm in the visible spectrum. Evidence for sulfur bonding was given by the shifts observed in its IR spectrum.[351,352] Silver halide solvates of *N,N*-dimethylthioformamide (DMTF) have been prepared by dissolving the silver salts in DMTF under nitrogen at 50 °C and cooling the saturated solution to 0 °C. For the iodide it was necessary to aid crystallization by the addition of a small quantity of absolute diethyl ether. AgCl·2DMTF and AgBr·2DMTF were found to be isomorphous. The silver atom was tetrahedrally surrounded by three sulfur atoms (Ag—S bonds ranging from 250 to 281 pm) and one halide atom (Ag—Cl = 254, Ag—Br = 266 pm) forming a chain-like structure.

The silver atom in AgI·DMTF was at the centre of a distorted tetrahedron of three iodide ions (Ag—I = 280–296 pm) and one sulfur atom (Ag—S = 252 pm). The structure was described as band-like.[353]

The IR and NMR spectra of the solvates in solution show only slight shifts from the free ligand. The dissociation constants, log *K*, calculated in DMTF from conductivity measurements, were found to be −2.17 (AgCl·2DMTF), −2.28 (AgBr·2DMTF), and −2.85 (AgI·DMTF).[354]

54.1.6 Selenium and Tellurium Ligands

Few studies have been made on silver complexes of selenium- or tellurium-containing ligands.[335] It was noted in 1951 that Me_2Te in acetone reacted with AgI in concentrated aqueous KI to give $AgI(TeMe_2)_2$ and $(AgI)_2TeMe_2$.[356] These were unstable and smelt strongly of Me_2Te. Me_2Se gave a colourless compound, $(AgI)_2SeMe_2$, which rapidly decomposed in air, while SMe_2 and OEt_2 showed no signs of reacting at all under these conditions. From this and other observations it has been concluded that with Ag^+ the stability order is Te > Se > S ≫ O.[357]

A wide range of ligands of the type $RXCH_2CO_2H$ where R = alkyl, alkenyl or aryl and X = S, Se or Te have been reacted with silver ions and thermodynamic data for some representative examples are given in Table 49.[358,359] The silver–selenium complexes were found to be more stable than their silver–sulfur analogues as a result of both larger favourable enthalpy and smaller unfavourable entropy changes.

Ligands of the type $X(CH_2CH_2CO_2H)_2$ (X = O, S, Se or Te) were synthesized and their reactions with silver(I) ions studied. Thermodynamic data for their formation are also given in

Table 49 Thermodynamic Data for the Formation of Selected Silver(I) Complexes with Ligands Containing Group VI Elements

R	*X*	*Medium* *I*	*T* (°C)	*Log* β_1	*Log* β_2	$\Delta H\beta_2$ (kJ mol^{-1})	$T\Delta S$ (kJ mol^{-1})	*Ref.*
$RXCH_2CO_2H$								
Bu^n	S	0.2	25	3.92	6.70	−58.5	−16.1	358
	Se	0.2	25	4.58	8.01	−59.6	−13.5	358
$CH_2{=}CH(CH_2)_2$	S	0.2	25	4.77	7.02	−126.1	−25.6	358
	Se	0.2	25	5.16	7.96	−155.5	−110	358
						$\Delta H\beta_1$ (KJ mol^{-1})	$\Delta S\beta_1$ (J K^{-1} mol^{-1})	
Ph	O	0.1	25	0.92	—	(*I* = 0.2) −4.48	−2.5	359
	S	0.1	25.1	2.77	4.8	−22.2	−21.3	359
	Se	0.1	25	3.62	6.1	−28.8	−27.2	359
m-ClC_6H_4	Se	0.1	25	3.33	5.6	−28.9	−33.0	359
p-ClC_6H_4	Se	0.1	24.9	3.44	5.9	−28.7	−30.5	359
p-MeC_6H_4	Se	0.1	25	3.73	6.5	−30.7	−31.8	359
$X(CH_2CH_2CO_2H)_2$					*Log K* (AgH_2L)	ΔH (AgH_2L) (kJ mol^{-1})	ΔS (AgH_2L) (J K^{-1} mol^{-1})	
—	S	0.2	25		3.18	−22 ± 2	−4 ± 2	357
—	Se	0.2	25		4.05	−30 ± 5	−7 ± 5	357
—	Te	0.2	25		5.03	−32 ± 5	−4 ± 5	357

Table 49.[357] It was assumed that in all of these cases bonding was primarily through the Group VI donor atom with minimal chelation through the carboxyl groups. This was supported by the apparent absence of a silver complex for $X = CH_2$.

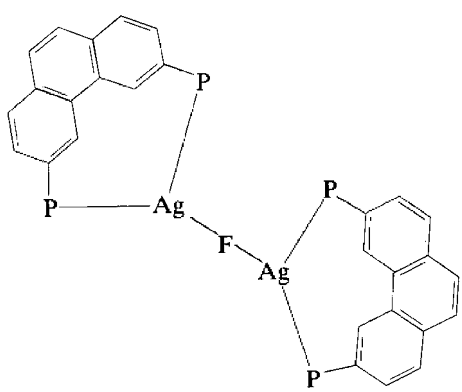
54.1.7 Halides

Silver(I) halides are undoubtedly the best known of all silver(I) salts and the ability of the silver ion to form sparingly soluble precipitates with halide ions has been applied to their quantitative determination for many years.

Conventional photographic emulsions contain face-centred cubic AgBr and AgCl and may contain up to 10 wt % hexagonal AgI. Their primary sensitivity to light, which is in the order AgBr > AgCl > AgI, is magnified up to 10^{11} times when the emulsions are developed (see Photographic Applications, Chapter 59).

Complex ions of the type AgX_2^- and AgX_3^{2-} have been described for chloride, bromide and iodide and their relative stability was found to be $I^- > Br^- > Cl^-$.[360] The effect of this complex ion formation on solubility can be readily assessed from the observation that in 1 M HCl, AgCl becomes ~100 times more soluble than in pure water.

Complex halides containing fluoride, however, do not appear to be as common, although they are known for silver(II).[361] Recently, the first example of a fluoro-bridged dinuclear silver(I) complex was reported.[362] Attempts to crystallize a BF_4^- salt of the silver(I) diphosphine complex $Ag(diphos)^+$ (diphos = 2,11-bis(diphenyl phosphinomethyl)benzo[*c*]-phenanthrene) resulted in a few colourless crystals being deposited. On solving the crystal structure it became evident that the complex was actually $[(diphos)Ag—F—Ag(diphos)]BF_4$ (**44**). It was suggested that decomposition of a BF_4^- ion had occurred in solution and generated some F^- ion. The Ag—F bond distances were ~255 pm and the Ag—F—Ag bond angle was 158.6.[362]



(**44**)

The stability constants for AgX_2^- species (where $X = Cl^-$, Br^- or I^-) have been determined for a range of solvents (Table 50).[363–365] The table shows that in all cases higher stability was found in a non-aqueous solvent than occurred in water.

Table 50 Stability Constants ($\log \beta_2$) for the Formation of the Complex Silver Halide Anions AgX_2^- in Various Solvents

Solvent	*Conditions*	$AgCl_2^-$	$AgBr_2^-$	AgI_2^-	*Ref.*
DMSO	$I = 0.1$, 23 °C	11.9	11.7	13.1	363
MeCN	$I = 0.1$, 23 °C	12.6	13.4	14.6	363
MeOH	1 M $LiClO_4$, 23 °C	8.0	10.9	14.8	363
Acetone	0.1 M $LiClO_4$, 23 °C	16.7	19.7	22.2	363
Nitroethane	1 M $LiClO_4$, 23 °C	22.2	22.5	23.5	363
Water	25 °C	5.4	7.6	11.2	364
DMF	$I = 0.005–0.01$, 25 °C	16.3	16.6	17.8	364
Sulfolane	30 °C	19.8	19.7	—	365

A large number of complexes containing the AgX_2^- anion (where $X = Br^-$ or I^-) have been isolated,[360] although in some cases they may not contain a linear AgX_2^- anion. For example, a complex described as $[Rhpy_4Br_2Ag]Br_2$ was reported in 1935 to be isolated from *trans*-$[Rhpy_4Br_2]^+$ salts by treatment with $AgNO_3$, followed by HBr.[366a] Although this could perhaps be reformulated as *trans*-$[Rhpy_4Br_2]^+AgBr_2^-$, it is also possible that it is similar to intermediates more recently observed in studies of silver ion-induced aquation of $[Co(NH_3)_5X]^{2+}$ salts.[366b]

A series of compounds of the type $[M(en)_2][AgX_2]_2$ have been prepared (where M = Co, Ni, Cu, Pd and Pt and $X = Br^-$ and/or I^-].[367]

The orange crystals of the Ni^{II} salts with $X = Br^-$ and I^- were isomorphous and were also isomorphous with the I^- salts where $M = Pd^{II}$ and Pt^{II}.[368] The crystal structure revealed square planar $Ni(en)_2^{2+}$ ions and chains of $[AgX_2]_n^{n-}$ ions. The silver ion was not linearly coordinated, but instead had a distorted tetrahedral structure where four halogen atoms were coordinated. These tetrahedra were linked by the sharing of edges. Weak interactions of two halides for the nickel ion were observed with Ni—Br ≈ 336 pm and Ni—I ≈ 351 pm. Average bond lengths reported were 272 pm for Ag—Br and 287 pm for Ag—I.[368] The square planar nature of the Ni^{II} ion had earlier been predicted on the basis of the diamagnetism and diffuse reflectance spectra of the complexes.[367]

A linear AgX_2^- anion was reported in the complex $[(Bu_2^nNCS_2)_2Au][AgBr_2]$.[369] The gold ion was square planar with four sulfur atoms coordinated (Au—S ≈ 232–236 pm) whilst the $AgBr_2^-$ ion was linear with AgBr = 245 pm. The anion was near the sulfur of the cation with the shortest contact Ag···S = 316 pm.

Compounds of general composition M_2AgX_3 have been known for over 150 years.[370] Crystal structure data have been reported for K_2CuCl_3 (isomorphous with Cs_2AgCl_3 and Cs_2AgI_3)[371] and K_2AgI_3[372,373] (approximately isomorphous with Rb_2AgI_3[374] and $(NH_4)_2AgI_3$). In these compounds the silver was tetrahedrally coordinated to four halogen atoms, but in these cases the tetrahedra shared corners to generate AgI_3^{2-} chains.

A claim for the only example of trigonal coordination of silver in an AgX_3^{2-} ion was made for $[PMePh_3]_2AgI_3$.[375] Attempts to prepare other trigonal AgX_3^{2-} ions in compounds of the type $[cation]_2AgX_3$ (where cation NEt_4^+, NPr_4^+, $AsPh_4^+$, PPh_4^+ and $N(PPh_3)_2^+$) were unsuccessful. Reaction of the appropriate halide with AgX in a 2:1 mol ratio resulted in the formation of either compounds of different stoichiometry, *e.g.* $[NEt_4][Ag_2Cl_3]$, $[NPr_4]_3[AgBr_4]$, $[PPh_4][AgBr_2]$ and $[N(PPh_3)_2][AgCl_2]$, or compounds of the desired stoichiometry, *e.g.* $[NPr_4]_2[AgI_3]$ whose far-IR spectra contained too many bands to be due to mononuclear, planar AgX_3^{2-} species. For $[PMePh_3]_2[AgI_3]$ the far-IR spectrum showed a strong ν(Ag—I) band at 133 cm^{-1} which was assigned to the asymmetric Ag—I stretching mode.[375] Previous assignments[376] of some AgI_3^{2-} compounds as C_{3v} pyramidal or C_s pyramidal were questioned since their Raman spectra could be satisfactorily analyzed in terms of infinite polymeric structures.[375]

The crystal structure of the analogous Cu^I complex, $[PMePh_3]_2[CuI_3]$, showed that the anion was not perfectly symmetrical and that significant differences occurred in the Cu—I bond lengths. The ^{127}I NQR spectrum detected these differences and was consistent with the presence of three crystallographically inequivalent iodine atoms. For $[PMePh_3]_2[AgI_3]$, once again a number of resonances were observed in the ^{127}I NQR spectra and these were claimed to be due to chemically similar but crystallographically inequivalent iodine atoms in an isolated AgI_3^{2-} anion.[375]

In solution, a band in the UV at ~252 nm was tentatively attributed to the AgI_3^{2-} anion. Bands due to other anionic and cationic silver iodide species were also assigned.[377]

The existence of $AgCl_3^{2-}$ was recently reassessed and the value of $\log \beta_3$ in water was determined as 5.65 ± 0.03 at 25 °C.[378] A review of older values was made and they were compared to that obtained from a study of the solubility product of AgCl in water–ethanol mixtures.

Solids with high ionic conductivity have been prepared from KI and AgI *e.g.* KAg_4I_5. The rubidium salt was isostructural with this and had somewhat better handling properties, being less sensitive to the effects of moisture, which caused decomposition to AgI and M_2AgI_3. $RbAg_4I_5$ was found to have the highest temperature specific electrolytic conductivity, 0.27 $(\Omega\ cm)^{-1}$ of any solid measured. This and other iodide-based solid electrolytes were recently reviewed.[379]

Cationic silver halide species have been known for a long time.[360] To account for the solubility of silver halides in aqueous silver(I) salts, complex ions such as Ag_2X^+ and Ag_3X^{2+} were proposed. Stability constants for these species ($X = Cl^-$, Br^- and I^-) are given in Table

Table 51 Stability Constants (Log β) of Cationic Silver Halide Complexes Ag_2X^+ and Ag_3X^{2+} in Various solvents at 24 °C[380]

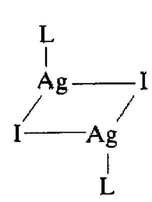
Cation	*DMSO* $I = 0.5$	*MeCN* $I = 1$	*Acetone* $I = 0.5$	*Water*
Ag_2Cl^+	7.73	—	—	5.04
Ag_3Cl^{2+}	7.32	—	—	5.48
Ag_2Br^+	8.23	—	—	9.70
Ag_2I^+	10.40	10.04	—	13.20
Ag_3I^{2+}	10.61	9.11	18.96	14.10

51[380] allowing comparisons to be made between the stability of species obtained by dissolving a silver halide in excess halide or excess silver ion. In general, it can be seen that the cationic complexes are less stable than the analogous anionic complexes in the same solvent.

Neutral adducts of silver halides with phosphines have been discussed earlier under Section 54.1.3.1. 1:1 adducts were found to be tetrameric and adopted either a (pseudo)-'cubane' or 'chair' ('step') type structure.

Until recently, only two reports existed for 1:1 adducts of silver halides with amines, namely AgI·piperidine[57] and AgI·morpholine.[381] The first had a tetrameric cubane structure whilst the second was described as a stair polymer adduct. The range has now been extended to include 2- and 3-methylpyridine, quinoline and triethylamine.[382] In each case the adduct was obtained by recrystallization of silver(I) iodide from neat base. The colourless crystals were found to lose base readily on exposure to the atmosphere and structural data were collected from crystals mounted in argon-filled capillaries, containing mother liquor.

The triethylamine complex was found to be isomorphous with the tetrameric triethylphosphine analogue and had a pseudo-cubane structure. The remaining three had stair polymeric structures (**45**) with the 2- and 3-methylpyridine complexes being quite similar, although the quinoline derivative exhibited significant differences. Ag—N bond lengths were in the range 232–235 pm and Ag—I bond lengths were 283–296 pm. It was concluded that the commonly held belief of linear, two-fold coordination for Ag^I was questionable since for halide complexes at least they were actually rare.[382]



L = 2- or 3-methylpyridine
or quinoline

(**45**)

54.1.8 Hydrides

The existence of a stoichiometric solid silver hydride remains doubtful, but evidence has been obtained for a gaseous silver hydride (AgH).[383,384] Silver hydride species have been postulated in the reaction mechanism of oxidations involving gaseous hydrogen with silver salts present as catalysts.[385]

Several complex hydrides have been prepared, such as $AgBH_4$; these were all thermally unstable.[383] More stable complexes were obtained with substituted boranes when isolated as phosphine derivatives.[386–388]

Reaction of tris(triphenylphosphine)silver(I) nitrate or tris(methyldiphenylphosphine)-silver(I) nitrate with KH_3BCO_2R (R = H, Et) produced complexes containing silver–hydrogen–boron bridges. Characteristic IR data are given in Table 52.[386–388] Pertinent features supporting monodentate coordination were the position and number of peaks in the terminal and stretching region, in particular the strong 1060 cm^{-1} absorption assigned as a BH_3 deformation band. The separation between terminal and bridging B—H stretching modes, generally found to be >200 cm^{-1}, further supported monodentate coordination. The carbonyl

Table 52 IR Absorption Data (cm^{-1}) for some Silver(I) Complex Hydrides

Complex	*<1000*	*1000–1300*	*1300–1500*	*γ(C=O) 1500–1700*	*$γ_{bridge}$(B—H) 1900–2200*	*$γ_{term}$(B—H) 2200–2500*	*Ref.*
$(Ph_3P)_2AgBH_4$	—	1110s	1380m	—	2000s 1965s	2355s 2260w 2210w	388
$(MePh_2P)_3AgBH_4$	—	1070s	—	—	2050s	2300s	388
$(Ph_3P)_3AgHBH_2CO_2H$	770w ?	1230m 1130ms 1050vs	—	1660s	2100s	2330s	387
$(Ph_3P)_3AgHBH_2CO_2Et$	820w	1140–1150s 1050vs	—	1640vs	2080s	2350sh 2290s	386, 387
$(MePh_2P)_3AgHBH_2CO_2Et$	805m	1230m 1120–1130s 1045vs	—	1660s	2130s	2320s 2270	388
KH_3BCO_2Et	905m	1220m 1190m 1110s 1030m	1450w 1380w	1630s	—	2320s	
KBH_4		1110vs				2260vs	

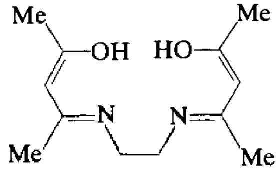
absorption bands were all present in the 1640–1660 cm^{-1} range, consistent with the lack of coordination by the oxygen sites. In solution, conductivity, molecular weight and NMR data suggested that a phosphine dissociated from the single-hydrogen-bridged complex and a doubly bridged complex then formed. The reverse process, involving formation of the singly bridged species, could be obtained by addition of an excess of phosphine.

54.1.9 Mixed Donor Ligands

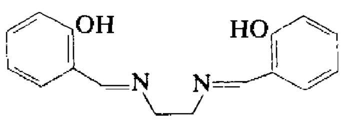
54.1.9.1 Open polydentate species

(*i*) *Schiff base ligands*

Schiff base complexes of transition metal ions have occupied a central role in the development of coordination chemistry. In particular, the tetradentate ligands acacenH_2 (**46**) and salenH_2 (**47**), prepared from ethylenediamine and acetylacetone or salicylaldehyde, have been thoroughly investigated since their discoveries in 1889 and 1931.[389] Most of these studies have dealt with divalent metal ions such as Co^{II}, Ni^{II} or Cu^{II} and there are relatively few reports concerning silver(I) complexes.[390]



(**46**)



(**47**)

In 1962, it was reported that when silver nitrate was added to a warm aqueous solution of acacenH_2, a finely divided colourless compound immediately precipitated. If instead the solution was heated on a water bath, then an uncharacterized dark brown substance formed. Analytical data and conductivity measurements suggested that the former complex was Ag_2(acacenH_2)$(NO_3)_2$.[391] The decomposition observed was most likely caused by hydrolysis, since many Schiff base ligands hydrolyze rapidly in water.

Formation constants for 1:1 and 2:1 Ag^I complexes with ethylenediamine Schiff bases of the type $RCH{=}NCH_2CH_2N{=}CHR$, have been reported (Table 53).[392] Based on the higher stability of the pyridyl derivative, it was claimed that the pyridyl N participated in the coordination.

Schiff base metal complexes have been shown to act as ligands.[393,394] When the calculated quantity of silver perchlorate in ethanolic solution was added to a chloroform solution of

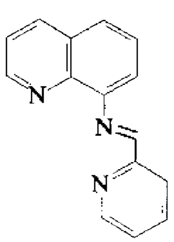
Table 53 Formation Constants for some Silver(I) Schiff Base Complexes in Methanol at 20 °C, $I = 0.1$[392]

Ligand $RCH{=}NCH_2CH_2N{=}CHR$	*Log β_1*	*Log β_2*
R = Ph	6.48	8.36
2-furyl	6.70	8.95
2-thienyl	7.54	9.42
2-pyridyl	9.78	11.00

Cu(salen), then a red precipitate of $\{Cu(salen)\}_2AgClO_4 \cdot 2H_2O$ formed. The structure was thought to be similar to that found with $NaClO_4$,[395] where the silver atom would be six-coordinate. Four oxygen atoms from the complex ligands, Cu(salen), and two from the bidentate perchlorate ion would make up a distorted octahedral arrangement.

A terdentate Schiff base ligand 8-(2-pyridylmethyleneamino)quinoline (**48**; pmg) was reacted with silver(I) for comparison to the structurally similar ligand, 2,2′,2″-terpyridyl. It was found that complexes of the type $Ag(pmg)ClO_4$ and $[Ag(pmg)L]ClO_4$, where L = py or PPh_3, could be isolated. No firm conclusions could be made concerning the structure of these complexes. However, the existence of the cationic species $Ag(pmg)^+$ was demonstrated and its coordination unsaturation established with respect to addition of monodentate ligands, py and PPh_3. Similar results were obtained with 2,2′,2″-terpyridyl.[115]

Reaction of the Schiff base ligand *N,N′*-bis(*o*-diphenylphosphinobenzylidene)(ethylenediamine (**49**; en=P_2) with $AgBF_4$ produced a pale yellow salt. The IR spectrum of this complex showed strong bands due to the imino and BF_4^- group (ν(C=N) 1653 cm^{-1}, $\nu(BF_4^-)$ 1080 cm^{-1}). The crystal structure of the Cu^I analogue was reported and the copper ion was found to adopt a severely distorted tetrahedral geometry. This strain was manifested in its reactivity since both the copper and silver complex reacted with *t*-butyl isocyanide. In the case of silver(I) a five-coordinate adduct was obtained, $[Ag(en{=}P_2)(Bu^tNC)]BF_4$.[396]



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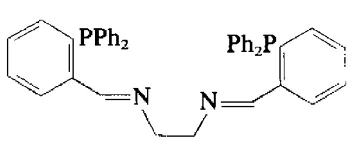

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54.1.9.2 Amino acids, proteins and peptides

(*i*) *Amino acids*

The reaction of silver(I) ions with amino acids has received considerable attention.[397] A number of studies have attempted to analyze the effects of substituents on the stability of the silver(I) complexes. When a series of ω-amino acids $NH_3^+(CH_2)_nCO_2$ ($n = 1$–5) were examined, it was found that lengthening of the aliphatic side chain increased the overall stability of the complex.[398,399]

When side chains containing alkenic groups were introduced, it was found that the stability was generally higher than in amino acids having fully saturated side chains. Interaction of the silver ion with the alkene was proposed to account for this increase in stability.[400] Thermodynamic data for the formation of some silver(I) amino acid complexes are collected in Table 54.[398–404,411]

The crystal structures of Ag(Gly)[69] and $Ag(HGly)NO_3$[405] have been determined. For the latter compound, the silver ions bridged centrosymmetrically related carboxyl groups to form dimers of glycine. The actual composition was best represented as $(\overset{+}{N}H_3CH_2CO_2^-Ag^+)_2(NO_3^-)_2$. Below −55 °C the compound was found to be ferroelectric. It was the first crystal containing either silver or the nitrate ion in which ferroelectricity was observed.[406]

The IR spectra of partially deuterated Ag(Gly) and Ag(Ala) have been recorded. Changes occurring when the amine group was deuterated are collected in Table 55.[407]

Table 54 Thermodynamic Data for the Formation of some Silver(I) Amino Acid Complexes

Ligand	*Medium*	*Log* β_1	*Log* β_2	$\Delta H\beta_2$ (kJ mol^{-1})	$\Delta S\beta_2$ (J K^{-1} mol^{-1})	*Ref.*
$\overset{+}{N}H_3(CH_2)_nCO_2^-$	0.5 M KNO_3, 25 °C					
n = 1	(0.05 M KNO_3, 25 °C)	3.15 (3.22)	6.56 (6.75)	—	—	398 (399)
n = 2		3.33 (3.44)	7.12 (7.25)	—	—	398 (399)
n = 3		3.46 (3.47)	7.20 (7.24)	—	—	398 (399)
n = 4		3.56 (3.50)	7.35 (7.41)	—	—	398 (399)
n = 5		3.59 (3.62)	7.54 (7.54)	—	—	398 (399)
$RCH(NH_2)CO_2H$	*I* = 0.1, 25 °C					
R = $CH_2{=}CH_2$		4.22	7.38	—	—	400
$CH_2{=}CH(CH_2)_2$		3.81	6.74	—	—	400
$CH_2{=}CH(CH_2)_3$		3.34	6.41	—	—	400
$CH_3(CH_2)_2$	(norvaline)	3.08	6.27	—	—	400
$CH_3(CH_2)_3$	(norleucine)	3.21	6.71	—	—	400
Glycine	20 °C	4.0	7.26			401
	I = 0.01, 25 °C	3.44	6.81	−33.7 ± 2.5	−47 ± 8	402
	I = 0.1, 25 °C	3.01	6.22	—	—	400
Alanine	25 °C	3.64	7.21	—	—	403
	I = 0.6, 25 °C	3.60	7.06	—	—	404
Serine	*I* = 0.6, 25 °C	3.40	6.67	—	—	404
β-Phenyl-α-alanine	*I* = 0.6, 25 °C	5.30	7.83	—	—	404
L-Methionine	*I* = 0.6, 25 °C	6.45	—	—	—	404
	0.1 M KNO_3, 25 °C	5.22	—	—	—	411
Asparagine	*I* = 0.6, 25 °C	3.30	6.45	—	—	404
S-Methyl-L-cysteine	0.1 M KNO_3, 25 °C	5.42	9.62	—	—	411
L-Ethionine	0.1 M KNO_3, 25 °C	—	9.66	—	—	411

When sulfur atoms are introduced into the amino acids, the formation of silver–sulfur bonds appears to be of critical importance. The involvement of the other two donor centres, *i.e.* NH_2 and CO_2^-, however, then becomes less clear. It was discovered that reaction of silver nitrate with either Cu^{II}[408] or Co^{II}[409] salts of *S*-methyl-L-cysteine gave rise to adducts, where the silver ions were proposed to bind only to the sulfur atoms. NMR spectroscopy has been used to study the binding sites in a range of sulfur-containing α-amino acids.[410,411]

For *S*-methyl-L-cysteine solutions containing a 1:1 mole ratio of silver(I) ions, variation of the pH from 2 to 9 made no difference to the chemical shift of the *S*-Me protons. This suggested that the ligand was bound entirely through the sulfur since the shift did not depend on the deprotonation of the carboxyl ($pK_1 = 2.14$) or, apparently, the amine ($pK_2 = 9.22$) groups. For 1:2 Ag^I to ligand ratios, a shift in the *S*-Me protons was observed above pH 4.5, until at pH > 9 it reached a constant value of only about 0.13 p.p.m. in comparison to the *S*-Me group of the free ligand. This was interpreted in terms of amine group complexation and loss of one of the sulfur atoms from the coordination sphere. Similar results were obtained for L-methionine and L-ethionine, suggesting that coordination occurred primarily through the S atoms.[411]

Table 55 IR Spectral Data (cm^{-1}) for Partially Deuterated Silver Amino Acid Complexes[407]

		ν_{as}	ν_s	δ	γ	*Twist*	*Swing*
Amino group							
glycine	NH_2	3256	3170	1640	1154	1171	638
	ND_2	2344	2340	1195	944	891	482
alanine	NH_2	3237	3153	1616	1262	1169	659
	ND_2	2426	2327	1201	937	892	513
Carboxylate							
	Amine group:						
glycine	Not deuterated	1601	1391	682	591	—	564
	Deuterated	1582	1392	703	597	—	571
alanine	Not deuterated	1581	1406	770	692	—	574
	Deuterated	1584	1404	770	670	—	573

(ii) Proteins and peptides

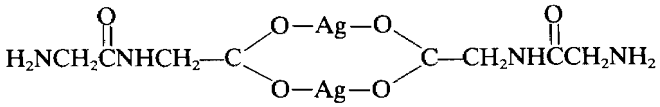
A knowledge of the structure of proteins has long been recognized as fundamental to an understanding of their chemical and biological functions. One technique for the successful determination of the X-ray crystal structure of proteins was initiated by Perutz in 1954 and involved the isomorphous replacement of heavy atoms into the protein crystal.[412] The development of this technique was recently reviewed.[413]

Silver nitrate has been found to react with cysteine, as in hemoglobin,[412] or more often with histidine, as in myoglobin, trypsin and carboxypeptidase A.[414] In most cases the reaction was similar to that for Hg^{2+}.

Silver ions cause strong quenching of protein fluorescence by at least two distinct mechanisms: collisional quenching and energy transfer to Ag^+–mercaptide absorption bands.[415] The effect was studied in detail for both sulfhydryl and non-sulfhydryl proteins and had a number of practical applications including the determination of SH groups and as a probe of binding sites.

Another approach to the study of proteins has been the reaction of silver ions with simpler model compounds, for example di- and tri-peptides.[416] The reaction with glycylglycine was first studied in 1951 and the formation constants for 1:1 and 1:2 complexes were determined.[403] Thermodynamic parameters for these reactions have since been measured ($\log\beta_1 = 2.90$, $\log\beta_2 = 5.65$, $\Delta H\beta_2 = -56.9 \pm 0.8\ \mathrm{kJ\ mol^{-1}}$, $\Delta S\beta_2 = -80.5 \pm 3\ \mathrm{J\ K^{-1}\ mol^{-1}}$).[416]

The crystal structure of $Ag(HGly–Gly)NO_3$ has been determined.[69] At pH 6 the complex formed showed that each Ag^I ion was coordinated by the O (carboxyl) atoms of two different ligands, but both oxygen atoms of each carboxylate group were involved in metal binding **(50)**. In the eight-membered ring generated, the Ag—O bond lengths were 219 pm.[69]



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Recently the structures of silver(I) complexes with cyclo-(glycyl-L-histidyl), cyclo-(L-methionyl-L-histidyl) and cyclo-(L-histidyl-L-histidyl) were examined using ^1H and ^{13}C NMR spectroscopy. The NMR measurements suggested that the silver ion was bound to the sulfur atom of the thioether and to the nitrogen atom of imidazole groups in these cyclic peptides, but not to their amide groups.[417]

54.1.9.3 Complexones

The ability of polyaminocarboxylic acids to form stable, water-soluble chelates over a wide pH range accounts for their diversity of uses. Ethylenediaminetetraacetic acid, H_4EDTA, has played a central role in this development and stimulated interest in other complexones with a view to finding ligands with increased affinity and selectivity for metal ions.

There have been few studies dealing solely with the reaction of silver(I) ions and complexones to form complexes.[418] Generally these complexes are less stable than those with other transition metal ions and formation constants for silver often bear close similarity to those of alkaline earth cations. Based on this, methods have been devised where silver electrodes can be used in the titration of metal ions, particularly alkaline earths, with H_4EDTA,[419] diethylenetriaminepentaacetic acid (H_5DTPA)[420] or ethyleneglycol bis(2-aminoethyl ether)-*N,N'*-tetraacetic acid (H_4EGTA).[421] In the presence of suitable masking agents selective titration of calcium in the presence of magnesium could be achieved since the $\log K$ of silver–EGTA was intermediate between the values for calcium and magnesium ($\log K$ in 0.05 M borate buffer: Ag^+, 6.0; Ca^{2+}, 9.0; Mg^{2+}, 4.4).[421] Formation constants for silver(I) ions with various complexones are given in Table 56.[418–425]

Characterization of complexes has generally been based on solution studies, for example using NMR spectroscopy (^1H,[426] ^{13}C,[427] ^{15}N[428]) since few reports have dealt with isolated complexes.[422]

Two salts of H_4EDTA have been prepared, Ag_2H_2EDTA and Ag_4EDTA. Upon addition of a solution of $AgNO_3$ to a solution of Na_2H_2EDTA under vigorous stirring, a heavy white

Table 56 Formation Constants for some Complexes of Silver(I) Ions with Complexones

Complexone[a]	*Conditions*	$Log\ K^{Ag\cdot L}_{AgL}$	$Log\ K^{Ag\cdot HL}_{AgHL}$	$Log\ K^{AgHL\cdot H}_{AgH_2L}$	*Ref.*
NTA	25 °C, $I = 0.1$	5.35	6.80	—	418
HEDTA	25 °C, $I = 0.1$	6.63	5.82	4.96	418
CyDTA	25 °C, $I = 0.1$	8.39	6.90	5.13	418
DTPA	25 °C, $I = 0.1$	8.72	7.86	5.07	418
		8.61			
EGTA	25 °C, $I = 0.1$	7.04	7.64		418
	0.05 M borate			6.18	
	buffer	6.0	—	—	421
	0.1 M KNO_3	6.9	—	—	421
EDTA	25 °C, $I = 0.1$	7.3	—	—	419
		7.28	3.36		422
TTHA	$I = 0.1$	8.7	8.9	$Log\ K^{Ag_2\cdot L}_{Ag_2L} = 14.0$	423
PIDA	20 °C, $I = 0.1$	6.09	—	—	424
CyDA	20 °C, $I = 0.1$	4.94	—	—	425

[a] NTA = nitrilotriacetic acid, HEDTA = hydroxy-2-ethylenediaminetriacetic acid, CyDTA = *trans*-1,2-diaminocyclohexane-*N,N,N′,N′*-tetraacetic acid, DTPA = diethylenetriaminepentaacetic acid, EGTA = ethyleneglycolbis(2-aminoethyl)-*N,N′*-tetraacetic acid, EDTA = ethylenediaminetetraacetic acid, TTHA = triethylenetetraminetetraacetic acid, PIDA = *N*-(2-pyridylmethyl)iminodiacetic acid, CyDA = cyclohexyliminodiacetic acid.

precipitate immediately appeared. In pure water, the pH after saturation with the salt was 4.0–4.3 from which the solubility was calculated as $1.4–1.5 \times 10^{-3}$ M.

The Ag_4EDTA salt was obtained by adding $AgNO_3$ to Ag $EDTA^{3-}$ or $EDTA^{4-}$, keeping the pH of the solution above 8. The precipitate was silk white and appeared as fine needles under a microscope (×200). Its solubility was calculated to be between 1.9 and 2.8×10^{-4} M.[422]

NMR studies of Ag^I with CyDTA indicated a high degree of ionic character for the ligand–metal bond since no coupling to ^1H, ^{13}C or ^{15}N was observed and the spectra were similar to that found for the free ligand.[426–428] Table 57 gives some chemical shift data.

Table 57 Chemical Shift Data for the Silver(I) Cydta Complex, $[Ag(CyDTA)]^{3-}$, in Solution[426–428]

^1H, 28 °C	$\delta_{acetone}$ [a]	$\delta(AB)$[b]	$J(AB)$	$\delta(methine)$	
	3.03	0.48	17.4	2.56	
	3.07	0.27	15.5		
^{13}C, 7 °C	$\delta(CO_2^-)$[c]	$\delta(CH)$	$\delta(CH_2\ eq)$	$\delta(CH_2\ ax)$	δ(*cyclohexane ring* CH_2)
pH 10.7	181.3 (×2)	61.4 (×2)	58.5 (×2)	54.3 (×2)	26.4 (×2)
	180.3 (×2)				24.6 (×2)
^{15}N, 22 °C	δ[d]				
	−345.2				

[a] Chemical shift of pattern relative to sodium 3-(trimethylsilyl)-1-propanesulfonate. [b] Relative chemical shift of two AB protons. [c] Relative to external (capillary) TMS standard. [d] Relative to $Me^{15}NO_2$ at $\delta = 0$.

The ^{13}C shifts were not significantly pH dependent above pH 9, and selective relaxation experiments revealed no uncoordinated carboxylates at pH 12.5. The complex in solution was therefore formulated as a hexadentate species $Ag^I(CyDTA)^{3-}$.

54.1.9.4 Bidentate N—O, N—S, etc.

(*i*) *8-Hydroxyquinoline*

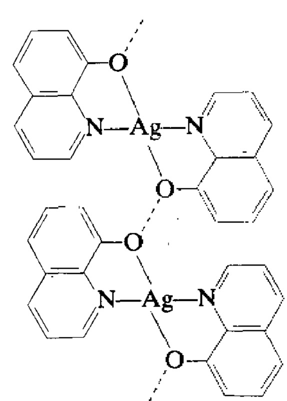
The reaction of 8-hydroxyquinoline with silver(I) ions to give metal chelates is well established.[429,430] Complexes of the type AgOx·HOx and $Ag(HOx)_2^+$ have been isolated, with formation constants (log K, 20 °C, $I=0.1$) of 5.20 [AgL/Ag·L$^-$] and 9.56 [AgL_2^-/Ag·$(L^-)^2$].[431] Resolution of optical isomers has been achieved with α-bromo-d-camphorsulfonate.[429,432] In 2 N H_2SO_4 $[\alpha]_D^{20} = +39.1°$ whilst in $CHCl_3$ containing 10% pyridine $[\alpha]_D^{20} = +43.3°$.[432]

A yellow and a green form of AgOx·HOx have been reported and it was proposed that the temperature of the solutions determined which product was obtained.[430] Several explanations have been given for the difference in colour, for example, the green form contained silver(II)[433] or contained some free metallic silver.[430]

Both complexes are diamagnetic and attempts to remove one of the ligands to leave a 1:1 complex resulted in total disruption of the structure:[434] no compound of the type AgOx has been identified. IR spectra of the yellow and green compounds, run as KBr pellets in the 4000–200 cm^{-1} region, differed significantly only by the appearance of a weak band at *ca.* 2580 cm^{-1} for the yellow form. By analogy with a uranium complex, this was interpreted in terms of a monodentate ligand and the existence of an N^+–H–O^- hydrogen-bonded system.[91] The fourth coordination site of the tetrahedral species would be occupied by a solvent molecule.

X-Ray photoelectron spectroscopy of the yellow form showed only one peak in the N 1*s* region, centred at 399.9 eV. This was regarded as not being inconsistent with the formation of some AgOx·HOx·S (S = solvent), since a small amount of positively charged nitrogen present would have gone undetected in the presence of the large peak due to neutral nitrogen.

The crystal structure of a pyridine solvate of bis(8-hydroxyquinoline)silver(I) has been reported.[435] The silver atom was bound to both ligands through the phenolic oxygens and the ring nitrogen atoms in a distorted tetrahedral arrangement. The Ag—O bond lengths were 245.1 pm and 250.5 pm; in contrast, the Ag–N distances were not significantly different (214.5, 215.5 pm; **51**). The distance between O-1 in one molecule and atom O′-1 in an adjacent molecule was 245.7 pm indicating that the phenolic hydrogen was contained between the two oxygen atoms forming a strong hydrogen bond. The pyridine molecule appeared to be held in the lattice by van der Waals forces only, and was subject to considerable thermal motion.[435]



(51)

(ii) Thiosemicarbazides, thiosemicarbazones and related N,S ligands

Thiosemicarbazides (TSC) and thiosemicarbazones generally react with transition metal ions to form chelate complexes by bonding through both the sulfur and the hydrazinic nitrogen atoms. With silver(I) however, they appear to behave as monodentate ligands and bond through the sulfur atom only.[436]

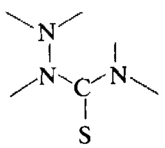
Thermodynamic data for the formation of $Ag(TSC)_3^+$ are given in Table 58.[437] Based on the similarity of the stability of this complex and the analogous thiourea complex, the ligand was proposed to be monodentate. The IR spectra of $[Ag_2(TSC)_3](NO_3)_2$[438] and of Ag(TSC)Cl[439] were also interpreted in terms of silver–sulfur bonding only.

For the free ligand, the hydrazinic N lies *trans* to the S atom (**52a**), whereas to form chelated complexes a *cis* arrangement (**52b**) must be present. The only structures of complexes known so far in the *trans* configuration are polymeric silver(I) complexes.[436]

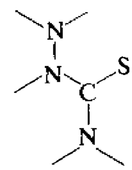
The X-ray crystal structure of colourless, orthorhombic needles of Ag(TSC)Cl (**53**) revealed two distinct types of silver atom.[440] Both had tetrahedral stereochemistry, although their

Table 58 Thermodynamic Data for the Formation of some Silver(I) Complexes with Potentially Bidentate N,S Ligands

Ligand	*Conditions*	*Log* β_2	*Log* β_3	ΔH ($kJ\ mol^{-1}$)	ΔS ($J\ K^{-1}\ mol^{-1}$)	*Ref.*
TSC	30 °C, $I = 0.1$ M	10.56	12.49	-113 ± 1	-134 ± 4	437
Acetone thiosemicarbazone	25 °C, pH = 5, 40% EtOH	—	13.2	—	—	442
Glyoxal dithiosemicarbazone	pH 1.1	log $\beta_1 = 23.6$		—	—	443

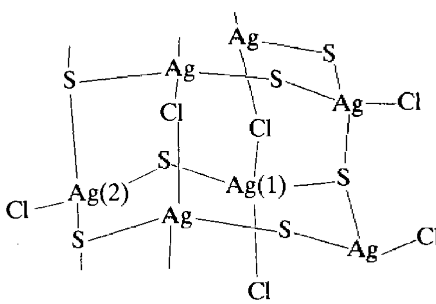


(52a)



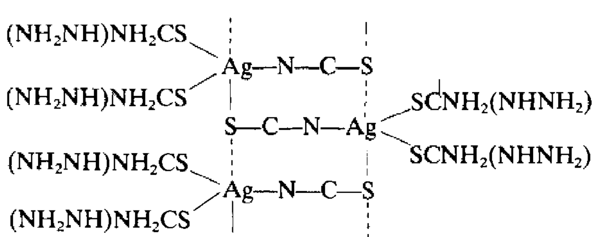
(52b)

environments were different. One silver atom was bound to two S atoms and two Cl atoms, with one of the Ag—Cl bonds longer than the other (275 *cf.* 265 pm). The other silver atom was coordinated to three S atoms and one Cl atom, with one of the Ag—S bonds markedly longer than the other (277 *cf.* 248 and 251 pm).



(53)

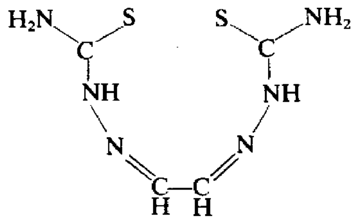
X-Ray data are also available for $Ag_2Br_2(TSC)_3$ and a bridged thiocyanate complex, $[AgNCS(TSC)_2]_n$.[441] In the latter complex (**54**) the silver stereochemistry was considered unusual in that two S atoms from two TSC molecules and one N and one S from two different NCS groups made up the nearest neighbours in a distorted trigonal pyramid. The NCS groups linked the silver atoms, although the Ag—S bond was relatively weak (299 pm). There were three longer contacts to two N atoms and an S, which completed the coordination polyhedron of a distorted pentagonal bipyramid.[441]



(54)

Thiosemicarbazones have been known for some time to exhibit a range of biological activity, including action against smallpox and certain kinds of tumour. This activity has frequently been thought to be due to their ability to chelate metal ions.[436] It is perhaps surprisingly therefore that virtually no thermodynamic data are available for thiosemicarbazones.[442]

Table 58 gives the formation constants for silver(I) complexes of acetone thiosemicarbazone and glyoxal dithiosemicarbazone (**55**).[443] In the latter case, the ligand was found to be suitable for the photometric determination of silver at pH 1:1, in the presence of EDTA. The effective molar absorptivity was 43 000 $cm^2\ mmol^{-1}$ at 335 nm.[443]



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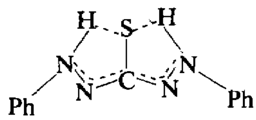
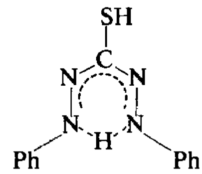


(**56a**) thione



(**56b**) thiol

The reactions of silver(I) with 1,5-diphenyl thiocarbazone (**56**; dithizone = H_2Dz) by comparison to thiosemicarbazones have been thoroughly investigated.[442,444] Dithizone has for many years been used as a colorimetric reagent for trace metal ions. Its metal complexes are of two types, the so-called 'primary' and 'secondary' dithizonates. Primary dithizonates are generally formed at low pHs where the ligand becomes mono depronated ($pK_1 \approx 4.5$) but retains the NH proton. Secondary dithizonates are formed in the presence of an excess of metal and/or at higher pH values where the ligand becomes fully deprotonated. Since it has been estimated that for free dithizone $pK_2 > 15$, the second proton obviously becomes labilized in the presence of metal ions.

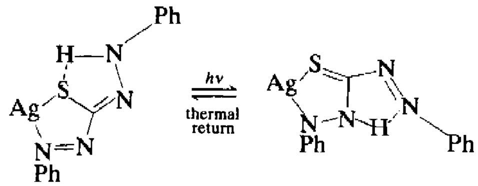
Primary and secondary silver(I) complexes have been readily prepared by extraction of silver nitrate into a chloroform solution of dithizone. For the secondary complex an excess of silver nitrate was necessary.[445] IR spectral data for both complexes are recorded in Table 59.[446] The primary complex Ag(HDz) has been reported in hydrated[445] and anhydrous[446] orange-red forms. The secondary complex Ag_2Dz was an anhydrous brown solid.

Silver was one of several metals found to give a photochromic primary complex. In THF it was normally yellow ($\lambda_{max} \approx 470$ nm). Activation at 450 nm, *i.e.* in the region containing the normal visible absorption band, generated a violet solution with λ_{max} in the 570–620 nm

Table 59 Principal IR Bands and Far-IR Spectral Data (cm^{-1}) for Dithizone (H_2Dz) and its Primary (AgHDz) and Secondary (Ag_2Dz) Complexes[446]

Assignment	H_2Dz	*AgHDz*	Ag_2Dz
ν(NH)		3218m	
ν(C=C) ring	1593m	1600m	1582m
	1562vw	1563vw	1562w
δ(NH)	1520sh	1520vs	
	—	1510vs	1511vw
ν(CN) + δ(NH)	1500vs	1500sh	
		1413sh	
δ(NH)	1440vs	1431m	
ν(NPh)	1320s	1358vs	1318s
		1309m	1309s
	1250s	1262s	1260vs
ν(CS)	889s	856vw	870sh
	546m	549m	557m
	524sh	526s	537s
	509m	508m	522sh
	498vs	493s	497m
			462w
	442m	447w	
	438sh		
	426sh	417w	419sh
		356vw	
		326vw	323vw
	300s	304vw	304vw
	283w	280m	280vw
	265w		
	247sh	243m	245m
	222m	227m	226m
	190m		
Ring deformations	157w	157w	
	150w	150m	149mw

range.[445] After 40–60 seconds at 10 °C this activated form returned to the normal form. At higher temperatures the rate increased markedly, such that at 25 °C the return time was 2–5 seconds. The photochromic effect was rationalized for the Hg^{II} complex in terms of a rearrangement involving the breaking of a hydrogen bond and IR data supported this proposal. When deuterated, the return rate for the mercury complex was slowed down three-fold.[447] An analogous change was proposed for the primary silver complex (equation 25). Further support for a change in hydrogen bonding was provided by the observation that no photochromism occurred with secondary dithizonates.[444]



(25)

The extraction constant for primary silver(I) dithizonate, from aqueous solution to a range of organic solvents, has been found to lie in the range $\log K = 5.8–8.94$.[442,444] It was concluded that changing the solvents did not achieve any worthwhile improvement in separability of silver from other metal ions compared to what could be achieved by addition of suitable masking agents. Carbon tetrachloride was the preferred extractive solvent ($\lambda_{max} = 463$ nm).[444]

A novel use of ultrasonics for the collection of silver has been reported.[448] When solid dithizone was added to an aqueous solution containing trace acounts of silver and irradiated by ultrasonics for 15 minutes, 98% of the silver was collected on the solid dithizone powder which could then be filtered off. In the absence of ultrasonic irradiation less than 40% collection occurred.

A number of substituted dithizone ligands have been prepared although few have major advantages over the original ligand in analytical applications.[444]

54.1.10 Multidentate Macrocyclic Ligands

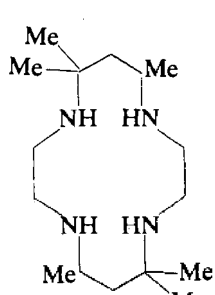
54.1.10.1 Planar macrocycles

(i) Porphyrins

Although a number of silver(I) porphyrins have been isolated,[436] they have not been extensively studied since they tend to disproportionate readily into the corresponding silver(II) complexes (Section 54.2.6.1.i).

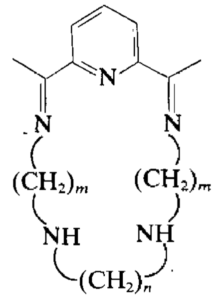
54.1.10.2 Other polyaza macrocycles

Reaction of silver(I) with macrocyclic tetraaza ligands has been found to be a facile process for forming silver(II) complexes.[450,451] Metallic silver was a by-product in each of these reactions. In dry acetonitrile, however, no disproportionation occurred and with (**57**) a white silver(I) complex precipitated. The necessity for water to be present for disproportionation was shown by the fact that if this complex was then added to water or aqueous methanol solutions, disproportionation then readily occurred.[451]



(57)

Macrocyclic N_5 complexes have been prepared from 2,6-diacetylpyridine and an appropriate tetramine using template methods. The crystal structures of two silver(I) complexes containing the ligands 3,2,3-N_5 (**58**) and 2,3,2-N_5 (**59**) have been determined.[452,453]

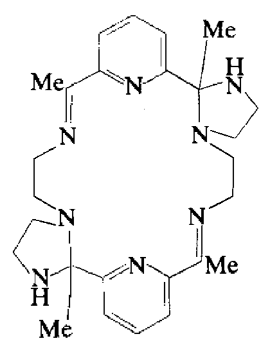


(**58**) $m = 3,\ n = 2$ (3,2,3-N_5)

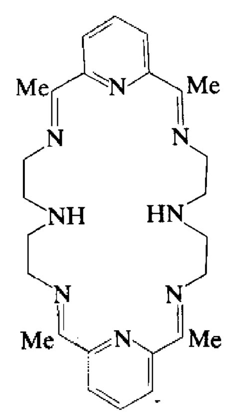
(**59**) $m = 2,\ n = 3$ (2,3,2-N_5)

In [Ag(3,2,3-N_5)]ClO_4 there were two cations of similar geometries in the unit cell. Ag—N bond lengths were in the range 237–255 pm.[452] In the dimeric complex [Ag(2,3,2-N_5)$]_2(ClO_4)_2$, two near planar [Ag(2,3,2-N_5)$]^+$ cations were associated in a face to face fashion such that each Ag^I ion interacted with an N of the other macrocycle. The Ag—Ag separation was 317.7 pm, which may have represented a weak Ag···Ag bond.[453]

A novel reversible ring expansion of the macrocycle (**60**) to (**61**) has been discovered. On treatment of [Sr (**60**) $(ClO_4)_2$] with $AgClO_4$ in refluxing methanol over a period of 30 minutes, the fluorescent yellow colour deepened and small yellow crystals separated in 80% yield on cooling. The ^1H NMR spectrum of the complex in CD_3CN unequivocally established that the macrocycle was in the (**61**) form. The product, [Ag_2 (**61**)]$(ClO_x)_2$, contained two four-coordinate silver atoms. The reverse process was achieved by treatment of this complex with an excess of $BaBr_2$ in refluxing MeOH. This gave AgBr along with the complex [Ba (**60**)$(ClO_4)_2$], which was shown to be identical in properties to an authentic sample prepared *via* a template method.[454]



(**60**)



(**61**)

54.1.10.3 Multicomponent ligands

(i) Crown ethers

A significant development in the attempt to understand cation selectivity of ligands was the synthesis of over 50 polyethers, having ring sizes ranging from 9 (3 oxygens) to 30 (10 oxygens).[455] Since the initial observations that these compounds showed marked selectivity toward certain alkali metal ions, a number of other cations, including Ag^+, have been found to be strongly complexed in both water and less polar solvents.

Table 60 The Formation Constants of Silver(I) with some Crown Ethers

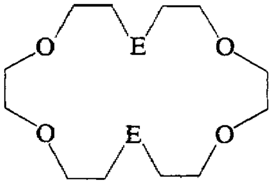
Crown ether	*Medium*	*Log β*	*ΔH* (kJ mol^{-1})	*ΔS* (J K^{-1} mol^{-1})	*Ref.*
15C5		0.94	−13.5 ± 0.1	−27.2	457
18C6		1.50 ± 0.03	−9.08 ± 0.4	−1.7	457
	25 °C, H_2O	1.6			456
DC18C6					
isomer A: *cis-syn-cis*	25 °C, H_2O	2.36 ± 0.11	0.3 ± 0.004	46	457
		2.3			456
isomer B: *cis-anti-cis*	25 °C, H_2O	1.59	−8.74	1.3	457
		1.8			462
C18C6	25 °C, H_2O	1.7–1.9			456
DB18C6		1.4			458

A comprehensive review of synthetic macrocycles gave detailed tabulations of preparations, effects of binding sites and thermodynamic data known up to 1973.[456] Table 60 gives thermodynamic data for the formation of silver(I) crown ethers in aqueous solution and includes several more recent figures.[457,458]

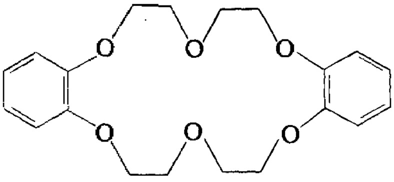
The complexing power of crown ethers for Ag^+ has also been investigated by solvent extraction studies.[459–461] Extraction of silver picrate into either benzene or chloroform solution was compared in the presence of a range of crown ethers. In all cases, the Ag^+ ion was more extractable into benzene than chloroform and this was thought to be due to the strong interaction of the Ag^+ ion with the π electrons of the benzene molecules. The ion pair complex formation constants ($\log K$) for extraction of silver picrate into benzene by crown ethers, defined by equation (26), are as follows: 12C4, 2.22; 15C5, 4.71; B15C5, 3.59; 18C6, 4.70; DB18C6, 3.82; DB24C8, 3.35 (12C4 = 12-crown-4, DB18C6 = dibenzo-18-crown-6, *etc.*).[461]

$$(\text{Ag picrate})_{\text{organic}} + (\text{crown ether})_{\text{organic}} \rightleftharpoons (\text{Ag(crown ether)picrate})_{\text{organic}} \quad (26)$$

The effect of substituting S or N for O on the metal-binding properties of 18C6 (**62**) and DB18C6 (**63**) has been studied.[462] The replacement of two ether donors by thioethers significantly enhanced the coordinating ability of 18C6. Replacement of these S atoms by N further enhanced this effect. Unfortunately, the data were not obtained in the same solvent (K^+: methanol; Ag^+: water) making valid comparisons difficult. The same donor order (*i.e.* N > S > O) was claimed to exist for Ag^+ with acyclic ligands.[463]



(**62**) E = O; 18C6

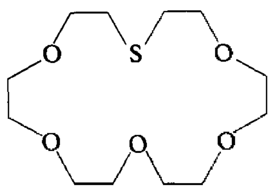


(**63**) DB18C6

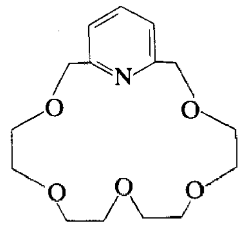
The increase in affinity for Ag^+ by the introduction of sulfur into the macrocyclic ring was the subject of an extensive study. As much as four orders of magnitude increase in the formation constants could be achieved.[464]

In addition to the above studies, the effect of substituting sulfur, aza nitrogen and pyridyl nitrogen in crown ether rings has recently been investigated. The reactions of the ligands (**64**)–(**69**) in methanol at 25 °C were studied by titration calorimetry. Thermodynamic data for those reactions, where measurable heat was obtained, are recorded in Table 61.[465–467] The ligand which gave the greatest selectivity for Ag^+ over Na^+ and K^+ was found to be thia-18-crown-6 (T18C6, **64**).[467]

The crystal structures of two isomeric 15-membered ring macrocycles containing the donor groups ON_2S_2 (**70**) and OS_2N_2 (**71**) have been determined as their silver thiocyanate salts.[468,469] In the first, the coordination sphere around the Ag^I ion embedded in the cavity was approximately square pyramidal, with a weak interaction between the Ag^+ ion and the O atom (Ag—O 288.3 pm). In the second, a square pyramidal structure was again obtained, although in this case there was no interaction with the O atom (Ag—O 371.9 pm).



(64) T18C6



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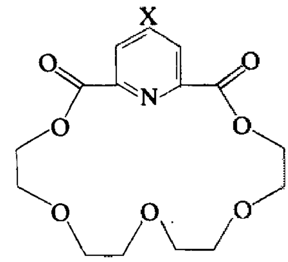
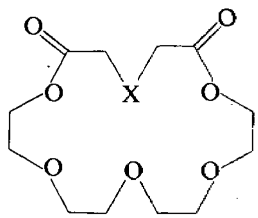
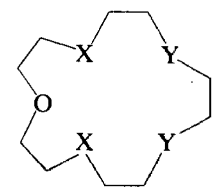


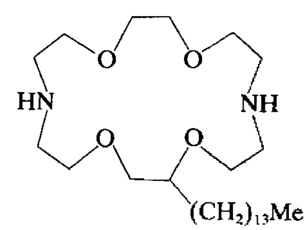
(66) X = H
(67) X = Cl



(68) X = O
(69) X = S



(70) X = N, Y = S
(71) X = S, Y = N



(72)

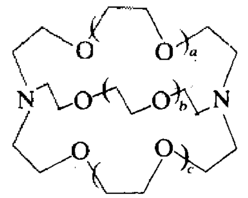
Table 61 Thermodynamic Data for the Reaction of some Macrocyclic Ligands with Silver(I) in Methanol at 25 °C

Ligand	*Log K*	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})	*Ref.*
(64) = T18C6	>5.5	-51.5 ± 0.8		466
(65)	>5.5	-34.9		465
(66; X = H)	4.88 ± 0.05	-32.8 ± 0.1	-16.4	465
(67; X = Cl)	3.76 ± 0.02	-33.6 ± 0.3	-40.7	465
(68; X = O)	2.50 ± 0.07	-6.40	26.4	467
(69; X = S)	3.05 ± 0.05	-29.2 ± 0.3	-39.4	467
15C5	3.62 ± 0.01	-27.5 ± 0.2	-23.0	466
18C6	4.58 ± 0.03	-38.3 ± 0.5	-40.7	466
21C7	2.46 ± 0.04	-28.9 ± 0.3	-49.1	466

Crown ethers with an alkane chain readily form micelles with critical micelle concentrations (CMCs) ranging between 10^{-5} and 10^{-3} M. The crown ether surfactant **(72)** was found to bind Ag^+ ions ($\log \beta \approx 8$) strongly and formed a relatively large micellar aggregate (MW = 6.3×10^6). A variety of sensitizers, when solubilized in aqueous solutions containing the silver complex, were shown to be oxidatively bleached, with simultaneous formation of Ag^0. Under visible light irradiation, rapid bleaching of cyanine dyes was observed and a stable absorption band with $\lambda_{max} = 415$ nm detected. This band was attributed to monatomic silver atoms stabilized within the macrocycle. The photoinduced reduction to Ag^0 was also performed with a number of other chromophores, including $Ru(bipy)_3^{2+}$.[470]

(*ii*) *Cryptands*

Shortly after the discovery of crown ethers (Section 54.1.10.3.i), the preparation of macropolycyclic complexing agents **(73)–(75)** containing three polyether strands joined by two bridgehead nitrogens was reported.[471,472] These ligands were collectively termed [2]cryptands, where the [2] indicated that they were bicyclic ligands. Species containing three and four macrocyclic rings are also known. Cryptands were found to have the ability to accommodate metal ions of suitable sizes and form inclusion complexes, called cryptates. The observed stability constants were very high, exceeding values of comparable crown polyethers by two or more orders of magnitude.[473] This was thought to be due to more effective chelation, since the



(**73**) $a = 1$, $b = c = 0$, C[2.1.1]
(**74**) $a = b = 1$, $c = 0$, C[2.2.1]
(**75**) $a = b = c = 1$, C[2.2.2]

metal ion became embedded in a three-dimensional cavity created by the bi- or tri-cyclic cagelike molecules.

The stability and selectivity patterns of cryptands were found to be markedly solvent dependent and stability constants of Ag[2]cryptates in a range of solvents are presented in Table 62.[474–478] Thermodynamic data for their formation in water are given in Table 63.[476]

Table 62 Stability Constants (Log K) for Silver [2]Cryptates in Various Solvents at 25 °C

	Water	*MeOH*	*EtOH*	*MeCN*	*Propylene carbonate*	*N-Methyl propionamide*	*DMF*	*DMSO*
$Ag(2.1.1)^+$	8.52[474]	10.6[475]	9.70[475]	7.7[475]	14.4[475]	7.6[475]	8.60[475]	6.1[475]
	11.13[476]	10.61[476]					8.62[476]	
$Ag(2.2.1)^+$	10.60[474]	13.3[478]	13.8[475]	9.7[478]	18.5[475]	10.4[475]	12.4[475]	8.2[478]
	11.82[476]	14.64[476]		11.2[475]			12.43[476]	9.6[475]
$Ag(2.2.2)^+$	9.6[477]	12.20[476]		8.9[475]	16.29[476]	9.1[475]	10.0[475]	7.15[475]
			11.5[475]	8.92[476]				7.2[478]
	9.85[474]	12.3[478]		9.3[478]	16.3[475]		10.03[476]	7.3[476]

Table 63 Thermodynamic Data for the Formation of Silver [2]Cryptates in Water at 25 °C[476]

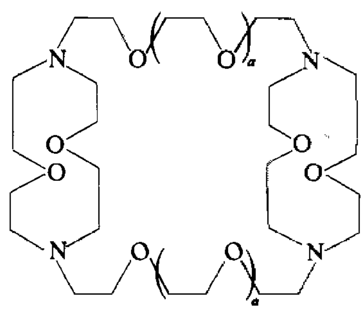
	Log K	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})
$Ag(2.1.1)^+$	11.13	−71.5	−25
$Ag(2.2.1)^+$	11.82	−51.0	54
$Ag(2.2.2)^+$	9.6	−53.6	5

The data obtained for [2.2.2]cryptand in acetonitrile solutions were further investigated.[479,480] Silver ions are strongly solvated by acetonitrile and a competition was found to exist between complexation of the ligand and the solvent. This was claimed to be predominantly responsible for the lower stability of $Ag[2.2.2]^+$ in acetonitrile than in water and for the rapid decrease in the stability constant at low mole fraction of acetonitrile (x_{MeCN}). This phenomenon was then studied by determining the rate of formation and dissociation of $Ag[2.2.2]^+$ in acetonitrile–water mixtures.[481]

The dissociation rate constant was found to be almost independent of solvent composition and the rapid decrease in the stability constant near $x_{MeCN} = 0$ was therefore due to the variation in the formation rate constant. The constant value of k_d, suggested that in the transition state the Ag^I ion was bound to the [2.2.2] nitrogen atoms in a manner similar to that usually found with other nitrogen donors, for example, acetonitrile.[481]

Slow evaporation of a methanol–butanol solution of the [3]cryptand (**76**) and of silver nitrate yielded crystals with stoichiometry (**76**)–$3AgNO_3$. The crystal structure revealed that two of the silver atoms were located inside the molecular cavity of the [3]cryptand with an Ag—Ag separation of 388 pm. These silver ions were bound to five heteroatoms of the ligand and to an oxygen atom of a nitrate ion. The third silver ion was located outside the ligand and was bound to all three nitrate anions, forming an $[Ag(NO_3)_3]^{2-}$ unit. The two sections were connected by bridging oxygen atoms from the nitrato group forming chains.[482]

^1H and ^{13}C NMR spectroscopy have been used to study successive formation of mononuclear and dinuclear complexes with [3]cryptands.[483] A heteronuclear (Ag^+, Pb^{2+}) complex of (**77**) was described. In the ^{13}C spectra, significant differences were observed for the carbon atoms adjacent to the bridgehead nitrogen atoms, such that the dinuclear silver complex and dinuclear lead complex could be readily distinguished from the heteronuclear species. The fact



(76) $a = 0$
(77) $a = 1$

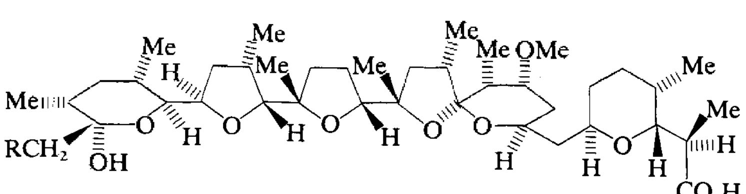
that three distinct C—N resonances were observed for this complex indicated that the intramolecular cation exchange process was slow on the NMR timescale.[483]

54.1.11 Naturally Occurring Ligands

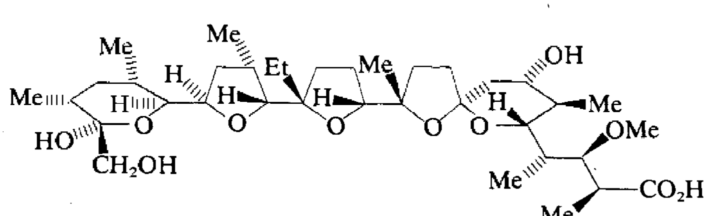
54.1.11.1 Polyether antibiotics

Since the discovery in 1964 that the antibiotic valinomycin exhibited alkali cation specificity in rat liver mitochondria, a new area of research has developed, based not only on biological systems but also on model systems such as crown ethers.[484] The ability of neutral compounds to form lipid-soluble alkali and alkaline earth complexes was observed in 1951. The structure of the corresponding ligand, the anion of the antibiotic nigericin (**78**), was characterized as its silver salt in 1968.[485,486] Silver was used as a heavy atom crystallographically, since the Ag^+ cation had a radius between that of Na^+ and K^+, which were the two alkali cations with which nigericin was most active.

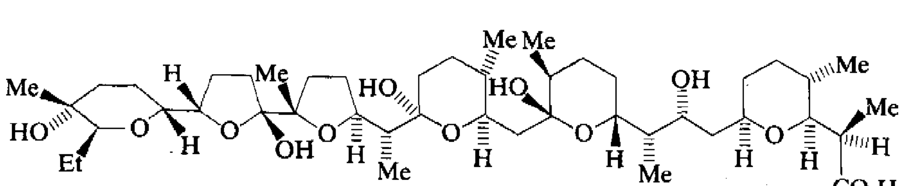
The structure and absolute configuration of a series of similar compounds, grisorixin (**79**),[487] monensin (**80**),[488] X-206 (**81**),[489], X-537A (**82**)[490] and lysocellin (**83**),[491] all antibiotics of the nigericin group, were then elucidated within a short period, again as their silver salts.



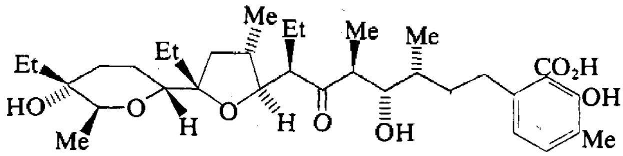
(**78**) R = OH
(**79**) R = H



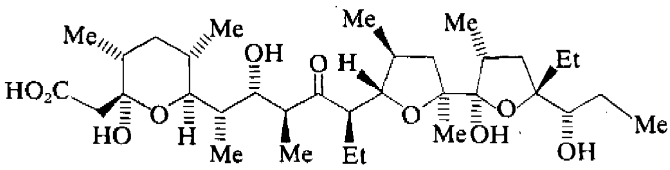
(**80**)



(**81**)

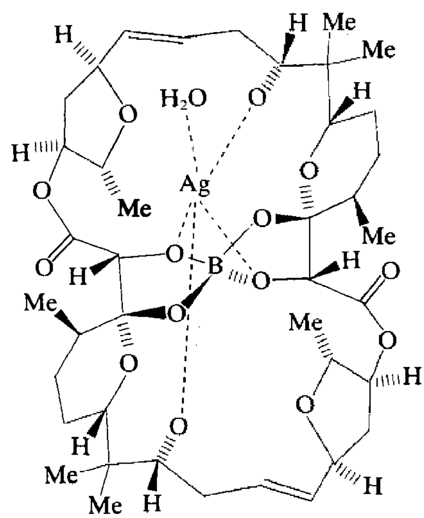


(82)



(83)

A boron-containing antibiotic has also been studied using this technique.[492] Aplasmomycin (84) appears related to boromycin, which was the first well-defined boron-containing organic compound to be found in nature.[493]



(84)

Values of the stability constant of silver(I) monensin in a range of non-aqueous solvents have recently been determined ($\log K$, 25 °C):[494] MeOH, 8.1 ± 0.1; propylene carbonate, 15.0 ± 0.1; DMF, 9.94 ± 0.05; MeCN, 8.6 ± 0.1; DMSO, 5.37 ± 0.05. The value of K increased by 10 orders of magnitude on going from DMSO to propylene carbonate. For the aprotic solvents, K was observed to increase in the same order in which the solvation of the free silver ion decreased. The formation rates were practically diffusion controlled ($\sim 10^{10}\,M^{-1}\,s^{-1}$) in methanol, acetonitrile and DMF.

54.2 SILVER(II) COMPOUNDS

54.2.1 Heterocyclic Nitrogen Ligands

A general method for preparing silver(II) complexes with heterocyclic N donors is to precipitate the peroxodisulfate from water as a sparingly soluble, yellow to dark red crystalline powder.[495,496] This is achieved by oxidation of a silver(I) salt solution with potassium persulfate in the presence of an excess of the appropriate ligand. Complexes of other anions have been subsequently prepared by double decomposition. PbO_2, BaO_2, CaO_2 and O_3 have also sufficed as oxidants in the case of heterocyclic ligands, due to the lowering of the Ag^I/Ag^{II} oxidation potential brought about by coordination. Alternatively, anodic oxidation techniques may be used.[497]

The properties of the N-heterocyclic complexes of silver(II) have recently been reviewed and it was found that in most complexes square planar coordination occurs about the central ion although higher coordination numbers are known.[496]

54.2.1.1 Pyridine and pyridinecarboxylates

Silver(II) pyridine salts have been prepared by both chemical[498] and electrochemical[499] oxidation. $[Ag(py)_4]X_2$ ($X = \frac{1}{2}S_2O_8^{2-}$ or NO_3^-) salts are orange or orange-red crystals depending on the anion. Silver(II) ions are rather unstable due to their powerful oxidizing nature in solution. However, it has been observed that when strongly acidified with non-reducing acids aqueous solutions of Ag^{II} are fairly stable.

The equilibria in acids between free and complexed ligand and $silver^{II}$ may be described either by equations (27) and (28) or by equations (28) and (29), where L = py.

$$Ag^{2+}(aq) + 4HL^+ \rightleftharpoons [AgL_4]^{2+} + 4H^+ \qquad (27)$$

$$L + H^+ \rightleftharpoons HL^+ \qquad (28)$$

$$Ag^{2+}(aq) + 4L \rightleftharpoons [AgL_4]^{2+} \qquad (29)$$

No stability constants for equations (27) and (29) are available, although an estimate for $\log \beta_4$ of 27 has been made.[499] The equilibrium between silver(II) and protons competing for N donors was predicted to be set up fairly quickly, just as for copper(II), and the tacit assumption in early work that silver(II) was kinetically inert in nitric acid media was incorrect.

The persulfate salt is only sparingly soluble in water but dissolves in nitric acid without reduction. However, dissociation or partial dissociation of the ligands occurs on dissolution. Consequently all results collected in this medium should be treated with suspicion. This includes electronic and electron spin resonance spectra.[496]

No structural data are available for silver(II) pyridine salts. Based on the evidence[500] of ease of doping at all levels of the silver and copper persulfate complexes into the cadmium species, isomorphism was assumed. X-Ray powder photographs have since shown this not to be the case.[499]

Electron spin resonance studies of silver(II) pyridine complexes have proved to be extremely useful in determining the nature of the species in solution. Since natural silver has two isotopes, ^{107}Ag and ^{109}Ag, in approximately the same abundance, both of spin $I = \frac{1}{2}$, and since their nuclear magnetic moments differ by less than 15%, interpretation of spectra is often considered in terms of a single nucleus. The forms of the hyperfine splitting patterns for 1N, *cis* and *trans* 2N, 3N and 4N, would be expected to be quite different and hence the number of pyridines can be readily assessed from well-resolved spectra. Spin Hamilton parameters obtained from both solid and frozen solution spectra are collected in Table 64.[497,499,501–510]

Secondary-ion mass spectrometry (SIMS) has been applied to the study of some silver complexes.[511] For $[Ag(py)_4]S_2O_8$ however, although the spectrum obtained was rich in fragment ions, no AgL_n species could be detected. Doubly charged species are not commonly observed in SIMS analyses and the reduced form of the intact cation, *i.e.* $[Ag(py)_4]^+$, was apparently not sufficiently stable in the gas phase.

Peroxydisulfate oxidations have also been used to prepare a variety of pyridine mono- and di-carboxylic acid silver(II) complexes.[496] All these compounds were orange-red in colour and sparingly soluble to insoluble in most solvents, including water.

For the neutral 1:2 monocarboxylic acid complexes, their IR absorption spectra showed a shift of the free CO_2H group from $\sim1700\,cm^{-1}$ to $\sim1630\,cm^{-1}$ on coordination. This was indicative of coordination of the carboxylate group. Far-IR spectral data indicated that pyridyl N atoms were also involved in the bonding to the central Ag^{II} ion.[512]

No single crystal X-ray structure determinations have been reported for the monocarboxylates. The 2-carboxylate (picolinate) was claimed to be isomorphous with the copper(II) analogue however, which had square planar stereochemistry. On the basis of X-ray powder data, polymeric square planar structures were proposed for the 3-carboxylate (nicotinate) and 4-carboxylate (isonicotinate).

Magnetic susceptibility measurements for the 2- and 4-carboxylates were found to obey

Table 64 Spin Hamiltonian Parameters Obtained from ESR Studies of N-heterocyclic Complexes of Ag^{II}

Complex	*Medium*	$g_\perp$ or g_1	g_2	$g_\parallel$ or g_3	$A_\parallel^{Ag}$	$A_\perp^{Ag}$	$A_\parallel^{N}$	$A_\perp^{N}$	*Ref.*
$[Ag(py)_4]S_2O_8$	Solid	2.044	2.089	2.158					501
		2.049	2.098	2.148					502
		2.048	2.100	2.150					499
	Diluted with $Cd(py)_4S_2O_8$	2.04		2.18	34	22	17	22	503, 504, 505
		2.06		2.16					506
		2.042		2.204	18.0	34.5	21.0	19.6	499
trans-$Ag(py)_2(NO_3)_2$	Frozen HNO_3 solution	2.050		2.178					507
	Solid	2.035	2.062	2.187					507
Ag(py) on zeolite		2.036		2.193	54	72	18	24	508
cis-$Ag(phen)(NO_3)_2$	Frozen HNO_3 solution	2.048		2.214	34.0	23.5	23.5	20.5	499
$Ag(bipy)_2S_2O_8$[a]	Solid	2.032		2.164					502
	Ag solution	2.045		2.129					497
	Frozen HNO_3 solution	2.047		2.210	42.2	26.0	30.1	21.1	509
	Solid, 77 K	2.047		2.184					509
$[Ag(4\text{-Me-py})_4]S_2O_8 \cdot 2H_2O$	Solid	2.044	2.100	2.130					499
		2.046		2.168					502
$[Ag(phen)_2]S_2O_8$	Solid	2.04		2.18					510

[a] Examination of N hyperfine structure suggests partial dissociation to $Ag(bipy)(NO_3)_2$.

Curie–Weiss behaviour from 309 to 83 K with a Weiss constant $\theta \leq 10$ K. The 3-carboxylate was studied in the range 275–4.2 K and the data were interpreted in terms of an antiferromagnetic interaction between silver ions using the Ising linear chain model. This gave an exchange energy of $J = -30.8 \pm 1.0\ \text{cm}^{-1}$ and $g = 2.5 \pm 0.02$ which was somewhat smaller than the experimentally determined $\langle g \rangle$ of 2.08.[513]

The oxidative effects of silver(II) complexes of pyridine carboxylates have been studied for a variety of substrates. With α-amino acids, a rapid reaction occurred at 70 °C in aqueous solution with bis(pyridyl-2-carboxylato)silver(II).[514] The product was the next lower homologous aldehyde and yields were generally greater than 80%. Other substrates included primary and secondary amines, alcohols, monosaccharide derivatives, alkenes, arylalkanes and arylalkanols.[90] Only minor differences were detected in efficiencies when 2-, 3- or 4-mono-, or 2,3-di-carboxylates were used as the oxidant.

Silver(II) complexes of the following pyridinedicarboxylic acids have been isolated following peroxydisulfate oxidations of their silver(I) salts: 2,3-quinolinic, 2,5-isocinchomeronic, 2,6-dipicolinic, 3,4-cinchomeronic and 2,4-lutidinic acids.[496] The complexes have generally been assigned structures of the type $Ag(LH)_2$ and IR data confirm the presence of free and coordinated carboxylate groups. The magnetic moments reported for the dicarboxylates at room temperature were in the range 1.74–1.80 BM with the 2,6 derivative giving the lowest value. Curie–Weiss behaviour with $\theta \leq 10$ K was found for all except the 2,6 derivative which had $\theta = 0$ K. This suggested a structural difference for this complex.[515]

The crystal structures of the 2,3-[516] and 2,6-dicarboxylates[517] have been determined. In the former, the silver atom lay on a centre of symmetry and was strongly bound to the 2-carboxyl group (Ag—O 213.1 pm) and to the nitrogen atom (Ag—N 212 pm). The overall structure was a tetragonally distorted octahedron, since stacking occurred and weak interactions existed between the silver atom and the ketonic group of the 3-carboxylic acid (Ag—O 298 pm).[516]

In the latter monohydrate complex, a highly distorted octahedral structure was revealed, containing two different ligands coordinated to the silver. One was described as dianionic (dipic) whilst the other a neutral ligand ($dipicH_2$). The formula was therefore best represented by $Ag(dipic)(dipicH_2)\cdot H_2O$.[517] For the dianionic ligand, the silver atom formed bonds to the two negatively charged (and crystallographically equivalent) oxygen atoms (Ag—O 221 pm) and also to the nitrogen (Ag—N 209 pm). With the neutral ligand, the silver atom was less strongly bonded to the two ketonic oxygen atoms (Ag—O 253 pm) and the nitrogen (Ag—N 221 pm). The two ligands were approximately planar and intersected at 83.4°. The complex molecule was assigned C_2 symmetry.

The X-ray photoelectron spectra of pyridine dicarboxylates have been investigated and binding energies for the silver $3d_{3/2}$ and $3d_{5/2}$ electrons are given in Table 65.[92] It was found that the complex $Ag(dipic)(dipicH_2)\cdot 4H_2O$ gave the lowest silver 3*d* binding energies, an observation said to be consistent with an increase in coordination number relative to the other complexes. It was argued that this higher coordination number would result in an enhanced build-up of negative charge at the silver centre resulting in a decrease in the binding energies.[92]

Table 65 X-Ray Photoelectron Data on 3*d* Binding Energies for Silver(II) Pyridinedicarboxylates[92]

Substitution positions	*Complex*	$3d_{3/2}$[a]	$3d_{5/2}$
2,3-	$[Ag(quinH)_2]\cdot 2H_2O$	373.6	367.6
2,4-	$[Ag(lutH)_2]\cdot 2H_2O$	374.1	368.2
2,5-	$[Ag(isocinchH)_2]$	375.1	369.0
2,6-	$[Ag(dipic)(dipicH_2)\cdot 4H_2O$	372.9	366.9
3,4-	$[Ag(cinchH)_2]\cdot H_2O$	374.5	368.5

[a] Carbon 1*s* binding energy at 284.0 eV was used as a reference in each case.

54.2.1.2 Pyrazine and pyrazine carboxylates

A dark red-brown precipitate of $Ag(pyrazine)_2S_2O_8$ was obtained by peroxydisulfate oxidation of Ag^I solutions containing pyrazine at 0–5 °C. In a related experiment, the 2-carboxylate derivative was obtained. Both reactions proceeded *via* the oxidation of white silver(I) precipitates and were essentially quantitative. It was found necessary to store the samples of 0–5 °C, since at room temperature, decomposition occurred after a few days.[518]

Reaction with pyrazine-2,3-dicarboxylic acid led only to the isolation of a mixed oxidation state complex of stoichiometry $Ag^{II}Ag^{I}_{2}\{pyz\text{-}2,3\text{-}(CO_2)\}_2$. No stoichiometric product could be isolated with the ligand, pyrazine-2,3,5-tricarboxylic acid. Although a dark brown solid containing Ag^{II} was formed after about 10 minutes, longer reaction times led to decomposition of the ligand.

The structure of the pyrazine complex was suggested to contain polymeric square planar cations with bridging pyrazines and the magnetic properties (300–80 K) were interpreted in terms of an antiferromagnetic exchange interaction. A Curie–Weiss constant of 84 K was calculated. At room temperature, the magnetic moment was found to be 1.61 BM.

The 2-carboxylic acid derivative had normal magnetic behaviour ($\mu = 1.81$ BM at 295 K). A diffuse reflectance spectrum was characteristic of square planar complexes and an IR spectrum showed the presence of covalently bound carboxylate groups.

Examination of $Ag^{II}Ag^{I}_{2}\{pyz\text{-}2,3\text{-}CO_2)_2\}_2$ X-ray powder patterns showed that the complex was not a mixture of silver(I) species but a discrete silver(I)–silver(II) mixed oxidation state complex.[518] A polymeric structure was again proposed and this was supported by ESR, NMR and IR data.[496]

54.2.1.3 2,2′-Bipyridyl and 1,10-phenanthroline

Mono and bis 2,2′-bipyridyl and 1,10-phenanthroline complexes of silver(II) have been isolated as red-brown crystals by either peroxydisulfate, anodic or ozone oxidation techniques.[497,519] No tris-chelated species have been substantiated,[497] although it is worth noting that a 2,2′,2″-terpyridyl bis complex has been isolated and claimed to be a six-coordinate species.[520]

The redox potential for $Ag(bipy)_2^{2+}/Ag(bipy)_2^{+}$ has been reported as 1.453 V[521] while that of the corresponding 1,10-phenanthroline couple was 65 mV less.[522]

The magnetic moments for solid silver(II) N-heterocyclic complexes are generally close to 1.8 BM suggesting quenched orbital angular momentum and spin-only paramagnetism (Table 66).[496,497,500,523–525]

Table 66 Bulk Magnetic Susceptibilities and Effective Magnetic Moments of Ag^{II} Complexes at ~298 K

	μ_{eff} (BM)	*Ref.*
$Ag(py)_2S_2O_8$	1.71–1.78	500, 523
$[Ag(bipy)_2]X_2$		
$X = \frac{1}{2}S_2O_8^{2-}$	1.82	500
NO_3^-	2.12	497
ClO_4^-	2.29	523
$[Ag(bipy)_2]S_2O_8 \cdot H_2O$	1.94	524
$[Ag(phen)_2]S_2O_8$	1.84	524
$[Ag(terpy)_2]S_2O_8 \cdot 3H_2O$	1.87	525

Crystal structure data are available for $Ag(bipy)_2(NO_3)_2 \cdot H_2O$[526] and $Ag(bipy)(NO_3)_2$.[527] In the former case two bridging nitrate groups at 278 and 282 pm make up an essentially octahedral arrangement around the Ag^{II} ion. One of the bipyridyl ligands was planar and the other non-planar. Nitrate bridging was also a feature in the latter complex.

The electronic spectrum of aqueous $Ag(bipy)_2^{2+}$ solutions in the visible region shows a maximum at 455 nm with $\varepsilon_{max} \approx 2000\ dm^3\ mol^{-1}\ cm^{-1}$.[528]

A spectrophotometric study of an aqueous solution of silver(II) containing nitric acid and an excess of 2,2′-bipyridine was consistent with the existence of only two complexes related by the equilibrium shown in equation (30). At 25 °C, K_h for this equilibrium was determined as $3.3 \pm 0.5 \times 10^{-3}$. From the variation with temperature the enthalpy and entropy for the reaction were calculated to be $11.5 \pm 2.6\ kJ\ mol^{-1}$ and $-9 \pm 10\ J\ K^{-1}\ mol^{-1}$ respectively.[528]

$$[Ag(bipy)_2]^{2+} + H^+ \rightleftharpoons [Ag(bipy)]^{2+} + Hbipy^+ \qquad (30)$$

The kinetics of the oxidation of hydrogen peroxide by $Ag(bipy)_2^{2+}$ were investigated in aqueous nitric acid medium.[529] The reactive species was found to be $Ag(bipy)^{2+}$, present in equilibrium with $Ag(bipy)_2^{2+}$. It was claimed that this was not necessarily due to the freeing of coordination sites but may be due to the difference in redox reactivity.

The use of nitric acid as a solvent for ESR spectra once again highlights the problem of dissociation or partial dissociation of the heterocyclic N ligands. Thus, dissolution of $[Ag(bipy)_2]S_2O_8$ in a minimum quantity of concentrated nitric acid produced spectra which, on the basis of the observed nitrogen hyperfine structure, can only be assigned to *cis*-$Ag(bipy)X_2$-type species.[499]

The ESR spectra of polycrystalline samples of $Ag(bipy)_2^{2+}$ and $Ag(phen)_2^{2+}$ show axial or rhombic g tensor symmetry. No silver or nitrogen hyperfine structure could be resolved.

Secondary-ion mass spectrometry (SIMS) of $[Ag(bipy)_2]^{2+}$ yields a spectrum identical to that of the silver(I) complex, showing peaks attributable to $(L+H)^+$, Ag^+ and AgL^+. This suggested facile reduction occurred to the unipositive cation.[530]

54.2.2 Oxygen Ligands

54.2.2.1 Aqua species

It has been known for some time that Ag^{2+} ions could be stabilized by the use of strongly acidic conditions.[531] Studies in perchloric, sulfuric and phosphoric acids have emphasized the importance of silver(II)–solvent complexes and the role of kinetic factors in determining the lifetime of Ag^{II} with regard to its reduction by water.[532,533]

A number of striking similarities were observed in the kinetics of Ag^{II} decomposition in these mineral acids. (1) The rate laws showed second order dependence on Ag^{II} and inverse first order dependence on Ag^{I} concentration. (2) Arrhenius activation energies were all about $46\ kJ\ mol^{-1}$. (3) Measured rate constants taken under similar conditions of temperature and ionic strength were comparable from one medium to another.

On this basis it was proposed that in each case the disproportion of Ag^{II} (equation 31) was the critical reaction step since it would be independent of the nature and charge of the solvent ligand. The detailed mechanism then involved reactions of Ag^{3+} species (equations 32 and 33).[532,533]

$$2Ag^{2+} \underset{}{\overset{K}{\rightleftharpoons}} Ag^+ + Ag^{3+} \quad \text{rapid} \tag{31}$$

$$Ag^{3+} + H_2O \overset{K}{\rightleftharpoons} AgO^+ + 2H^+ \quad \text{rapid} \tag{32}$$

$$AgO^+ \xrightarrow{k} Ag^+ + \tfrac{1}{2}O_2 \quad \text{rate-determining} \tag{33}$$

Using pulse radiolysis techniques, the reaction of Ag^+ ions with OH· radicals has been studied.[534] Formation of silver(II) species were believed to proceed *via* OH· radical addition, shown by equation (34). Subsequently depending on the pH of the solution, hydrolysis equilibria were established for which the pK values of the reactions given by equations (35) and (36) were calculated as 5.35 and 8.35 respectively.[534]

$$Ag^+ + OH\cdot \longrightarrow Ag(OH)^+ \tag{34}$$

$$AgOH^+ + H^+(aq) \rightleftharpoons Ag^{2+} + H_2O \tag{35}$$

$$Ag(OH)_2 \rightleftharpoons AgOH^+ + OH^- \tag{36}$$

54.2.2.2 Carboxylates

The persulfate ion $S_2O_8^{2-}$, with or without various transition metal ions, is a particularly effective oxidant, especially for the decarboxylation of carboxylic acids.[535] In the presence of silver(I), persulfate oxidation to silver(II) readily occurs and for aliphatic carboxylic acids the decarboxylation mechanism given in Scheme 4 has been established. The aliphatic radicals produced may then disproportionate, abstract hydrogen or be further oxidized to an alcohol. In the presence of N heterocycles in acidic media, the alkyl radical generated can also be used for homolytic alkylation reactions.[536] With arylacetic acids, coupled 1,2-diarylethanes have been produced, often in high yield.[537] In all of these cases it is anticipated that Ag^{II} carboxylates are intermediates; however, none have been isolated.

$$\begin{aligned} Ag^I + S_2O_8^{2-} &\longrightarrow Ag^{II} + SO_4^{\cdot-} + SO_4^{2-} \\ Ag^I + SO_4^{\cdot-} &\longrightarrow Ag^{II} + SO_4^{2-} \\ Ag^{II} + RCO_2H &\longrightarrow Ag^I + RCO_2\cdot + H^+ \\ RCO_2\cdot &\longrightarrow R\cdot + CO_2 \end{aligned}$$

Scheme 4

54.2.3 Sulfur Ligands

54.2.3.1 Mono- and di-thiocarbamates

In 1959, it was reported that on mixing silver(I) *N,N*-dialkyl dithiocarbamates with the corresponding thiuram disulfide, dissolved in benzene or chloroform, the solution immediately turned blue.[538,539] ESR spectra of these solutions showed the formation of paramagnetic d^9 Ag^{II} complexes. The reaction was explained by the equilibrium expressed in equation (37).

$$(R_2N\overset{\overset{\displaystyle S}{\|}}{C}S)_2 + Ag^I \longrightarrow (R_2NCS_2)_2Ag^{II} \qquad (37)$$

When these experiments were repeated, in the absence of air, it was discovered that the intensity of the ESR signal due to the Ag^{II} species almost doubled.[539] Reexamination of the reaction for $R = Bu^n$ showed that further oxidation to a red, diamagnetic Ag^{III} complex occurred in air or with excess thiuram disulfide and this accounted for the decrease in signal intensity.[540] Values of spin Hamiltonian parameters for some silver(II) complexes are given in Table 67.[539–542]

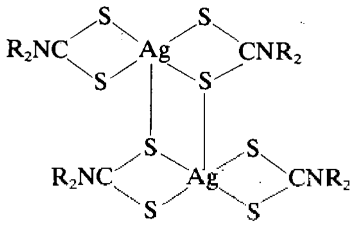
Table 67 Spin Hamiltonian Values for some Silver(II) *N,N*-Dialkyldithiocarbamate Complexes

							Ref.
		$\langle g \rangle$		$\langle A \rangle$ ($\times 10^{-4}$ cm^{-1})			
$[Pr^i_2NCS_2]_2Ag$		2.019		27			539
$[Bu^n_2NCS_2]_2Ag$		2.022		28			540
	$g_\parallel$		$g_\perp$	$A_\parallel$ ($\times 10^{-4}$ cm^{-1})	$A_\perp$ ($\times 10^{-4}$ cm^{-1})		
$[Pr^i_2NCS_2]_2Ag$	2.035		2.011	37	24		541
	g_x	g_y	g_z	A_x ($\times 10^{-4}$ cm^{-1})	A_y ($\times 10$ cm^{-1})	A_z ($\times 10^{-4}$ cm^{-1})	
$[(Pr^i_2NCS_2)_2Ag]_2$ doped into Zn complex	2.0087	2.0156	2.0456	12.5	13.2	17.7	542
$[Pr^i_2NCS_2]_2Ag$ doped into Zn complex	2.0094	2.0157	2.0493	21.1	22.6	33.5	542

A kinetic study of the oxidation of some hexameric silver(I) dialkyl dithiocarbamate complexes by thiuram disulfides to the silver(II) complexes has been reported.[543] Although a 100-fold excess of the thiuram disulfide was used, the formation of the Ag^{III} complex reported earlier was not considered.

ESR spectra obtained from magnetically dilute samples of the silver(II) complexes doped into the corresponding dimeric zinc complex could be attributed to both homo- (Ag,Ag) and hetero- (Ag,Zn) dinuclear species. In the Ag,Ag dimer the *g* values were almost equal to those for the Ag,Zn dimer; however, the hyperfine coupling constants *A* were only about half. From this it was concluded that the structures of these two species were very similar.[542]

By analogy to the zinc structure, the coordination sphere around the silver(II) ion was anticipated to contain four sulfur atoms from two dialkyl dithiocarbamates in a square planar arrangement. Dimerization would occur by interaction *via* two Ag—S bridges (**85**).[538]



(**85**)

Polarized optical absorption measurements have been made for the bis(*N*,*N*-diethyldithiocarbamato)silver(II) complex also diluted in the zinc complex.[544] Two spin-allowed transitions were observed: $^2A_2 \rightarrow {}^2B_1$ (625 nm) and $^2A_2 \rightarrow {}^2B_2$ (425 nm).

54.2.4 Halogens

AgF_2 has been prepared by fluorination of AgCl at 200 °C. It was an amorphous, black solid, which was very hygroscopic and reacted vigorously with water. Complex fluorides of the type $MAg^{II}F_6$ (where M^{IV} = Sn, Pb, Zr or Hf) have been prepared by fluorination of Ag_2SO_4–A_2MX_2 mixtures at 480 °C.[545] Evidence for an elongated tetragonal $Ag^{II}F_6$ group came from an electronic and ESR study of these complexes.[546] The distortions where M^{IV} = Zr or Hf were much greater than where M^{IV} = Sn or Pb and substantial exchange between Ag^{II} sites was indicated in the former compounds.[545,546] In this respect, the colours of the compounds were noteworthy (Zr, Hf, blue-violet; Sn, Pb, light blue).

Other complex Ag^{II} fluorides prepared were A^IAgF_3 (A^I = K, Rb or Cs) which had a similar structure to $KCuF_3$, blue-violet K_2AgF_4[547] and $CsAgM^{III}F_6$ (M^{III} = Tl, In or Sc).[548] The latter compounds were shown to have the cubic $RbNiCrF_6$ structure and had complex magnetic properties.

High oxidation state silver halide complexes of chloride, bromide and iodide tend to be even more unstable with respect to reduction and have not been studied in detail.[549]

54.2.5 Mixed Donor Ligands

54.2.5.1 Amino acids

The silver(II)-catalyzed decarboxylation of carboxylic acids was noted in Section 54.2.2.2. The oxidation of amino acids is thought to occur by a similar process.

In a recent kinetic study, Ag^{II}, generated from Ag^I by reaction with OH· radicals, was treated with glycine. Transient spectra, kinetics and product analysis indicated that the mechanism involved two steps. The first step was formation of an Ag^{II} complex. The second step was an electron transfer from the carboxyl group to the Ag^{II} within the complex. Formaldehyde was found to be the main product obtained. Oxidation of α-phenylglycine gave benzaldehyde.

The possible participation of Ag^{III} as an oxidant was discounted on the basis of the kinetic data. The observed complexations and oxidations occurred at timescales shorter than those required for the formation of Ag^{III}.[550]

54.2.6 Multidentate Macrocyclic Ligands

54.2.6.1 Planar macrocycles

(*i*) *Porphyrins*

It has been known for some time that silver(I) porphyrins are generally unstable toward disproportionation to the silver(II) complex, sometimes with deposition of a silver mirror.[551]

For example, when silver acetate in pyridine was added to free *meso*-tetraphenylporphyrin (H_2TPP), a green disilver(I) complex rapidly formed, requiring only slight warming. Vigorous boiling of the salt slowly converted it to a reddish-orange monosilver(II) complex. Owing to the greater instability of the disilver(I) complex in acetic acid solution, only the silver(II) complex could be isolated from this solvent. Silver(III) porphyrins have been produced by both electrochemical and redox reactions.

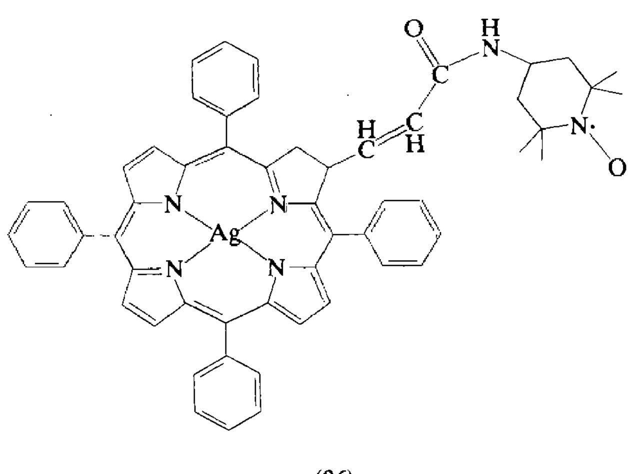
Studies on silver(II) porphyrins have largely been centred on synthetic porphyrins, such as H_2TPP and octaethylporphyrin, H_2OEP. However, a range of complexes based on heme derivatives have also been described.[552] Some of these latter complexes have been characterized by IR spectroscopy.[553]

It has been found that whereas Cu^{II} porphyrins luminesce, the Ag^{II} complexes do not. By an examination of electronic absorption spectra, emission spectra, redox potentials and near-IR absorption data, it was proposed that this could be rationalized on the basis of the energy of the b_{1g} ($d_{x^2-y^2}$) orbital. Extended Hückel molecular orbital calculations predicted that the d–π^* transition would be above the lowest (π, π^*) levels for Cu^{II} but below them in the Ag^{II} complexes. The near-IR absorptions found for Ag^{II} were attributed to CT transitions.[554]

Complexing silver with TPP or OEP caused small but noticeable chemical shifts in the binding energy of the Ag, C and N peaks.[555] Weak N 1*s* satellites have also been observed in the X-ray photoelectron spectra.[556]

Recently, ESR spectroscopy has been used to study silver(II) porphyrins. Aggregation in metalloporphyrins, in tetrachloroethane (TCE) and 2-methyltetrahydrofuran (MTHF) has been studied at 77 K.[557] In MTHF a well-resolved signal due to monomeric Ag^{II} mesoporphyrin(IX) dimethyl ester (MPD) was observed. In TCE, however, additional signals on the monomer spectrum and a $g = 4$ signal with a partially resolved structure were found when the gain was increased. The $g = 4$ signal was ascribed to the $\Delta M_s = 2$ transition of the dimeric $[Ag^{II}MPD]_2$. In an equimolar molar mixture of Cu^{II}MPD and Ag^{II}MPD a heterodinuclear complex was formed.

ESR spectroscopy has also been used to study spin-labelled silver porphyrins such as (**86**).[558,559] The isotropic exchange coupling constant J was found to be greater for the *trans* isomer than for the *cis* isomer (34.8 G *cf.* ~20 G). For the *trans* isomer, it was proposed that the interaction was possibly due to overlap of metal orbitals with porphyrin orbitals providing a direct pathway to the point of attachment of the vinyl group to the porphyrin and on through the vinyl group to the nitroxyl ring. The ENDOR result for AgTPP indicated that the metal–porphyrin interaction was a combination of both σ and π effects.[560] Similarly the silver–nitroxyl interaction was believed to be due to a mixture of both σ and π effects. The geometry of the molecules would prevent intramolecular metal–nitroxyl collisions and the spectra were concentration independent indicating that intermolecular collisions also did not contribute significantly.



(**86**)

The enhanced resolution of ENDOR over ESR allowed a more detailed analysis of the spectrum of AgTPP. It was found that the nominally d-like odd electron had ≤38% 4d character.[560]

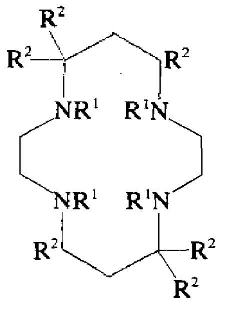
(ii) Phthalocyanines

Silver(II) phthalocyanine has been obtained by the action of silver nitrate on dilithium phthalocyanine in absolute alcohol at room temperature, or by the action of silver sulfate upon lead phthalocyanine in boiling 1-chloronaphthalene.[496,561] ESR studies confirmed the presence of the paramagnetic d^9 Ag^{II} ion, and for a frozen solution in 1-chloronaphthalene showed well-resolved nitrogen hyperfine lines. In the undiluted solid at room temperature, only a broad resonance was observed at $g \approx 2.016$. This may have been caused by aggregation.[562]

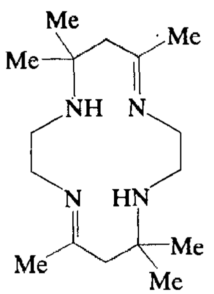
Silver(I) phthalocycinines have not been substantiated.[561]

54.2.6.2 Macrocyclic Polyaza Ligands

Addition of silver(I) perchlorate or nitrate to an aqueous suspension or 50% methanolic solution of *meso*-Me_6[14]ane (**87**), a completely saturated macrocycle, resulted in disproportionation of the initially formed silver(I) complex to elemental silver and a silver(II) complex with the ligand.[450] Later, a variety of macrocyclic complexes were similarly prepared, in which the nature of the peripheral substituents and ligand saturation were varied as in (**87**)–(**90**).[451] All of these silver(II) complexes were yellow to orange and had IR spectra similar to their nickel analogues. Magnetic moments were in the range 1.9–2.1 BM as expected for monomeric d^9 complexes (Table 68). The complexes were exceptionally stable even in reducing solvents such as ethanol which only after some time led to silver mirrors being deposited.



(**87**) $R^1 = H, R^2 = Me$
(**88**) $R^1 = H, R^2 = H$
(**89**) $R^1 = Me, R^2 = H$



(**90**)

Table 68 Spectral, Magnetic and Electrochemical Data for Silver(II) Tetraaza Macrocycles[451]

Complex	μ_{eff} [a] (BM)	λ_{max} [b] (nm)	$g_{\parallel}$ [c]	$g_{\perp}$ [c]	*Anodic wave*[e] (V)	*Cathodic wave*[e] (V)
(**87**)	2.2	348 (2.7) 280 (3.6)	2.11	2.05_8 [d]	0.617 (1)	−0.283 (2)
(**88**)	1.95	342 (13.3) 275sh (3)	2.09_5	2.03_8	0.71 (1)	—
(**89**)	1.81	382 (8.6) 300 (2)	1.99_7	2.07	0.96 (1)	f
(**90**)	1.96	338 (6.2) 300 (6.2)	—	—	0.63 (1)	−0.37 (2)

[a] Faraday measurements. [b] 10^{-3} M in complex, 10^{-1} M Et_4NClO_4 in MeCN; molar extinction coefficient, ε, $\times 10^{-3}$ in parentheses. [c] Polycrystalline samples at room temperature unless otherwise noted. [d] ~5% doped in corresponding Ni^{II} complex. [e] Rotating Pt working electrode, |Ag| 0.1 M Ag^+ in MeCN reference electrode, 10^{-3} M complex, 10^{-1} M Et_4NClO_4; number of electrons given in parentheses. [f] Very poorly defined two-electron wave.

ESR spectra of the Ag^{II} complexes were found to be typical of a d^9 axial system. In each case $g_{\parallel}$ and $g_{\perp}$ were well resolved although resolution of nitrogen hyperfine structure could not be achieved.

Electrochemical data obtained for these complexes are also given in Table 68. In each case a one-electron quasi-reversible anodic wave was observed between 0.7 and 0.9 V which suggested that Ag^{III} complexes might be obtained either by electrochemical or perhaps by chemical oxidation. This was confirmed by isolation of $Ag(\mathbf{87})(ClO_4)_3$ by controlled potential oxidation and more easily by reaction with $NOClO_4$ in acetonitrile. It was found that when the silver(II) complexes of (**87**) and (**88**) were dissolved in nitric acid, diamagnetic species were produced suggesting oxidation had occurred.

The crystal structure of Ag(*meso*-Me_6[14]ane)$(NO_3)_2$ was found to contain a square planar arrangement of N atoms from the macrocycle at Ag—N distances of approximately 216 pm. Axial interactions with nitrate oxygens resulted in distorted octahedral coordination in which the Ag—O distance was 280.7 pm.[563]

54.3 SILVER(III) COMPOUNDS

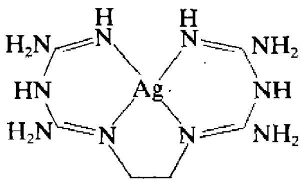
54.3.1 Nitrogen Ligands

54.3.1.1 Biguanides

A number of well-defined crystalline complexes of silver(III) have been described.[496] In particular, biguanides, substituted biguanides, ethylenebis(biguanide) and piperazine dibiguanide have been found to complex and stabilize silver(III).

The piperazine dibiguanide silver(III) complexes prepared were $[Ag^{III}(\text{pipz bigH})_2]X_3$ where $X = OH^-$, NO_3^- or $\frac{2}{3}SO_4^{2-}\cdot\frac{1}{2}H_2O$.[564] These compounds were red to red-brown and were sparingly soluble in water but insoluble in alcohol, chloroform, acetone, ether, DMF and diacetone alcohol. The biguanide and substituted biguanide silver(III) complexes had the general formula $[Ag(\text{bigH})_2]X_3$ and $[Ag(\text{MebigH})_2]X_3$ where $X = NO_3^-$, OH^-, $\frac{2}{3}SO_4^{2-}$ or mixed anions.[565] The complexes were generally isolated in a hydrated form.

The first preparation of a silver(III) biguanide was as a result of attempts to prepare a silver(II) derivative of ethylenebis(biguanide) (**91**).[566] Oxidation of a silver(I) salt by sodium peroxydisulfate in the presence of the ligand, however, gave the red silver(III) derivative instead.



(**91**)

Crystal structure data are available for three salts of this complex: the nitrate,[567] perchlorate,[568] and sulfate hydrogen sulfate hydrate.[569] In these salts, the organic ligand acts as a tetradentate ligand coordinated through four nitrogen atoms and wrapping itself around the silver ion, to give a slightly distorted square planar configuration. The Ag—N bond lengths were approximately equal at ~197–203 pm. In the latter salt, coordination around silver was completed by two oxygen atoms belonging to SO_4^{2-} and HSO_4^- groups, which were on opposite sides of the square plane at rather long distances of 293–294 pm. One interesting feature of this compound was the presence of the strongly hydrogen-bonded species $[O_3SO—H—OSO_3]^{3-}$, with OHO separation 251 pm and bond angle 168°.[569]

The kinetics of the oxidation of $Ag(\text{enbisbig})^+$ to Ag^{III} by excess $S_2O_8^{2-}$ were shown to consist of two consecutive reactions, each being first order with respect to $[Ag(\text{enbisbig})^+]$ and $[S_2O_8^{2-}]$.[570] It was argued that the oxidation of the silver(I) complex occurred in one-electron steps, the silver(III) complex being formed by the reactions given in equations (38) and (39), where X may be $S_2O_8^{2-}$ or both SO_4^- and SO_4^{2-}. The activation energies for these reactions were 54.8 ± 3 kJ mol^{-1} and 59.8 ± 16 kJ mol^{-1}; the corresponding values for $\log_{10} A$ were 7.7 and 9.6.

$$Ag(\text{enbisbig})^+ + S_2O_8^{2-} \longrightarrow Ag(\text{enbisbig})^{2+} + X \quad (38)$$

$$Ag(\text{enbisbig})^{2+} + S_2O_8^{2-} \longrightarrow Ag(\text{enbisbig})^{3+} + X \quad (39)$$

Photoelectron spectroscopy of $Ag(\text{enbisbig})(ClO_4)_3$ gave binding energy chemical shifts for

Ag^{III} as 377.3 eV ($3d_{3/2}$) and 371.4 eV ($3d_{5/2}$) which were some 3.0 eV larger than for Ag^{I} or Ag^{II} complexes, indicative of the +3 oxidation state.[571]

54.3.2 Oxygen Ligands

54.3.2.1 Aqua species

The simplest species containing silver(III) is $Ag(OH)_4^-$, which in 1.2 M NaOH at 25 °C was stable for about 2 hours. The yellow solution gave a single broad absorption band in the UV region with $\lambda_{max} \approx 270$ mm. Preparation of the ion generally involved anodic oxidation of silver metal in basic media.[572,573]

The stability of $Ag(OH)_4^-$ was found to be very dependent on base strength. In 0.1 M OH^{-1}, the ion had a half-life of less than 30 minutes and when a solution at 30 °C was rapidly brought to pH 11, decomposition occurred within 1 or 2 seconds. The products of decomposition in base were solid AgO and oxygen. A kinetic study of the acid-initiated reduction has been reported.[573]

54.3.3 Multidentate Macrocyclic Ligands

54.3.3.1 Planar macrocycles

(i) Porphyrins

Oxidation of Ag^{II}OEP (OEP = octaethylporphyrin) in chloroform with iron(III) perchlorate gave a quantitative conversion to [Ag^{III}OEP]ClO_4.[574] The colour of the solution changed from a bright red to a brownish red. The qualitative electronic excitation spectrum of the Ag^{III} complex was quite similar to that for Ag^{II}OEP.[496] Values of λ_{max} and ε (in parentheses) obtained for [Ag^{III}OEP]ClO_4 were 552 nm (25 000), 576 nm (9800) and 404 nm (131 000).

Based on the similarity of the spectra it was proposed that oxidation had not occurred at the porphyrin ring but rather at the silver ion. The sample was found to be diamagnetic, as expected for a d^8 square planar configuration. Cyclic voltametry with Ag^{II}OEP also confirmed that the oxidation occurred at the central metal and the measured Ag^{III}OEP/Ag^{II}OEP couple was 0.44 V.[574]

Photoelectron spectroscopy of a sample of [Ag^{III}OEP]ClO_4 mixed with a small amount of Ag^{II}OEP showed marked shifts of ~3 eV in the binding energies of the silver $3d_{3/2}$ and $3d_{5/2}$ electrons for the Ag^{III} complex.[555] These occurred at 377.1 and 371.0 eV for the Ag^{III} complex. Comparable shifts have also been reported for Ag^{III} biguanides.[496]

54.3.3.2 Macrocyclic tetraaza ligands

Macrocyclic tetraaza ligand complexes of silver have been found for oxidation states +1, +2 and +3. In the presence of water, the silver(I) complexes generally disproportionate to silver(II) depositing silver metal. Some of the silver(II) species obtained have been oxidized, both chemically ($NOClO_4 \cdot H_2O$ in acetonitrile) and electrochemically, to silver(III) complexes of substantial stability.[496]

Me_6[14]1,4,8,11-N_4-ane (**87**) and [14]1,4,8,11-N_4-ane (**88**) gave violet Ag^{III} complexes in aqueous solution which slowly turned yellow. The solutions initially showed no ESR signal but these were found to grow with time, as the violet colour disappeared. The spectra finally obtained corresponded to those of the Ag^{II} complexes. The hexamethyl derivative was quite stable both in the solid state and in dry, purified acetonitrile. On the other hand, the unsubstituted ligand complex was very unstable in the solid state and in solution, excepting pure acetonitrile containing concentrated perchloric acid.[451]

The silver(II) complexes of (**87**) and (**88**) were found to be oxidized by concentrated nitric acid to orange silver(III) complexes. NMR spectra were obtained for these diamagnetic Ag^{III} complexes and were compared to the Ni^{II} analogues. Addition of concentrated HCl led to red-orange needles being formed. These were claimed to contain $[Ag(L)Cl_2]^+$; however, they could not be fully characterized.

54.4 REFERENCES

1. R. M. Smith and A. E. Martell, 'Critical Stability Constants', Plenum, New York, 1977, vol. 4.
2. R. M. Izatt, M. D. Johnston, G. D. Watt and J. J. Christensen, *Inorg. Chem.*, 1967, **6,** 132.
3. J. L. Hoard, *Z. Kristallogr.*, 1933, **84,** 231.
4. E. Staritzky, *Anal. Chem.*, 1956, **28,** 419.
5. E. Staritzky and F. H. Ellinger, *Anal. Chem.*, 1956, **28,** 423.
6. M. Bassett and A. S. Corbet, *J. Chem. Soc.*, 1924, **125,** 1660.
7. F. Gallais, *Bull. Soc. Chim. Fr.*, 1945, **12,** 657.
8. L. H. Jones and R. A. Penneman, *J. Chem. Phys.*, 1954, **22,** 965.
9. G. W. Chantry and R. A. Plane, *J. Chem. Phys.*, 1960, **33,** 736.
10. T. M. Loehr and T. V. Long, II, *J. Chem. Phys.*, 1970, **53,** 4182.
11. G. L. Bottger, *Spectrochim. Acta, Part A*, 1968, **24,** 1821.
12. L. H. Jones, *J. Chem. Phys.*, 1957, **26,** 1578.
13. P. Gans, J. B. Gill, M. Griffin and P. C. Cahill, *J. Chem. Soc., Dalton Trans.*, 1981, 968.
14. M. F. A. Dove and J. G. Hallett, *J. Chem. Soc. (A)*, 1969, 2781.
15. B. Corain, *Coord. Chem. Rev.*, 1982, **47,** 165.
16. J. L. Gay-Lussac, *Ann. Chim. Phys.*, 1824, **27,** 199., in an editorial footnote to a paper by F. Wohler.
17. D. Britton and J. D. Dunitz, *Acta Crystallogr.*, 1965, **19,** 662.
18. W. Becker and W. Beck, *Z. Naturforsch., Teil B*, 1970, **25,** 101.
19. W. Beck, P. Swoboda, K. Felol and E. Schuierer, *Chem. Ber.*, 1970, **103,** 3591.
20. R. Näsänen, *Acta Chem. Scand.*, 1947, **1,** 763.
21. W. V. Smith, U. L. J. Brown and K. S. Pitzer, *J. Am. Chem. Soc.*, 1937, **57,** 1213.
22. M. Maeda, G. Nakagawa and G. Biedermann, *J. Phys. Chem.*, 1983, **87,** 121.
23. M. Maeda, R. Arnek and G. Biedermann, *J. Inorg. Nucl. Chem.*, 1979, **41,** 343.
24. P. Gans and J. B. Gill, *J. Chem. Soc., Dalton Trans.*, 1976, 779.
25. R. B. Corey and R. W. G. Wycoff, *Z. Kristallogr.*, 1934, **87,** 264.
26. R. B. Corey and K. Pestrecov, *Z. Kristallogr.*, 1934, **89,** 528.
27. T. Yamaguchi and O. Lindqvist, *Acta Chem. Scand., Ser. A*, 1983, **37,** 685.
28. H. M. Maurer and A. Weiss, *Z. Kristallogr.*, 1978, **146,** 227.
29. M. Maeda, Y. Maegawa, T. Yamaguchi and H. Ohtaki, *Bull. Chem. Soc. Jpn.*, 1979, **52,** 2545.
30. M. G. Miles, J. H. Patterson, C. W. Hobbs, M. J. Hopper, J. Overend and R. S. Tobias, *Inorg. Chem.*, 1968, **7,** 1721.
31. A. L. Geddes and G. L. Bottger, *Inorg. Chem.*, 1969, **8,** 802.
32. H. M. Mauer and A. Weiss, *J. Chem. Phys.*, 1978, **69,** 4046.
33. E. A. MacWilliam and M. J. Hazard, *Photogr. Sci. Eng.*, 1977, **21,** 221.
34. T. W. Solomons, 'Organic Chemistry', 2nd edn., Wiley, New York, 1980, p. 740.
35. R. D. Hancock, *J. Chem. Soc., Dalton Trans.*, 1980, 416.
36. L. D. Hansen and D. J. Temer, *Inorg. Chem.*, 1971, **10,** 1439.
37. D. J. Alner, R. C. Lansbury and A. G. Smeath, *J. Chem. Soc. (A)*, 1968, 417.
38. H. S. Harned and B. B. Owen, *J. Am. Chem. Soc.*, 1930, **52,** 5079.
39. W. S. Fyfe, *J. Chem. Soc.*, 1955, 1347.
40. R. Kleim (ed.), 'Gmelins Handbuch der Anorganischen Chemie', Springer Verlag, Berlin, 1975, no. 61, part B6, p. 47.
41. K. K. Mead, D. L. Maricle and C. A. Streuli, *Anal. Chem.*, 1965, **37,** 237.
42. H. T. S. Britton and W. G. Williams, *J. Chem. Soc.*, 1935, 796.
43. J. Bjerrum, *Chem. Rev.*, 1950, **46,** 381.
44. R. D. Hancock, B. S. Nakani and F. Marsicano, *Inorg. Chem.*, 1983, **22,** 2531.
45. L. C. Van Poucke, *Talanta,* 1976, **23,** 161.
46. B. Magyar and G. Schwarzenbach, *Acta Chem. Scand., Ser. A*, 1978, **32,** 943.
47. E. Bang, *Acta Chem. Scand., Ser. A*, 1978, **32,** 555.
48. J. Yperman, J. Mullens, J. P. François and L. C. Van Poucke, *Inorg. Chem.*, 1983, **22,** 1361.
49. C. Golumbic, *J. Am. Chem. Soc.*, 1952, **74,** 5777.
50. H. T. S. Britton and W. G. Williams, *J. Chem. Soc.*, 1934, 96.
51. See ref. 40, part B6, p. 50.
52. W. S. Fyfe, *J. Chem. Soc.*, 1952, 2018.
53. N. P. Marulb, J. F. Allen, G. T. Cochran and R. A. Lloyd, *Inorg. Chem.*, 1974, **13,** 115.
54. T. B. Jackson and J. O. Edwards, *J. Am. Chem. Soc.*, 1961, **83,** 355.
55. H. P. Fritz and G. Hierl, *Z. Naturforsch., Teil B*, 1971, **26,** 476.
56. M.-J. Blais and G. Berthon, *Bull. Chem. Soc. Fr.*, 1973, 2969.
57. G. B. Ansell, *J. Chem. Soc. (B)*, 1971, 443.
58. H. M. Hilliard and J. T. Yoke, III, *Inorg. Chem.*, 1966, **5,** 57.
59. E. Buchner, *Chem. Ber.*, 1889, **22,** 842.
60. H. Reimlinger, A. Noels, J. Jadot and A. Van Overstraeten, *Chem. Ber.*, 1970, **103,** 1942.
61. H. Reimlinger, A. Noels and J. Jadot, *Chem. Ber.*, 1970, **103,** 1949.
62. W. Mahler, quoted in S. Trofimenko, *Chem. Rev.*, 1972, **72,** 497.
63. R. H. P. Francisco, Y. P. Mascarehnas and J. R. Lechat, *Acta Crystallogr., Sect. B*, 1979, **35,** 177.
64. See ref. 40, part B6, p. 136.
65. C.-J. Antti and B. K. S. Lundberg, *Acta Chem. Scand.*, 1971, **25,** 1758.
66. G. W. Eastland, M. A. Mazid, D. R. Russell and M. C. R. Symons, *J. Chem. Soc., Dalton Trans.*, 1980, 1682.

67. S. P. Datta and A. K. Grzybowski, *J. Chem. Soc. (A)*, 1966, 1059.
68. J. E. Bauman, Jr. and J. C. Wang, *Inorg. Chem.*, 1964, **3**, 368.
69. C. B. Acland and H. C. Freeman, *Chem. Commun.*, 1971, 1016.
70. P. J. Garegg, H. Hultberg, C. Ortega and B. Samuelsson, *Acta Chem. Scand., Ser. B*, 1982, **36**, 513.
71. J. Bjerrum, *Acta Chem. Scand.*, 1972, **26**, 2734.
72. D. K. Lavallee and J. D. Doi, *Inorg. Chem.*, 1981, **20**, 3345.
73. R. M. Izatt, D. Eatough, R. L. Snow and J. J. Christensen, *J. Phys. Chem.*, 1968, **72**, 1208.
74. L. Kahlenberg and R. K. Brewer, *J. Phys. Chem.*, 1908, **12**, 283.
75. G. V. Rubenacker and T. L. Brown, *Inorg. Chem.*, 1980, **19**, 392.
76. K. Nilsson and A. Oskarsson, *Acta Chem. Scand., Ser. A*, 1982, **36**, 605.
77. M. Fleischmann, P. J. Hendra and A. J. McQuillan, *Chem. Phys. Lett.*, 1974, **26**, 163.
78. D. L. Jeanmaine and R. P. Van Duyne, *J. Electroanal. Chem.*, 1977, **84**, 1.
79. M. G. Albrecht and J. A. Creighton, *J. Am. Chem. Soc.*, 1977, **99**, 5215.
80. R. L. Burke, J. R. Lombardi and L. A. Sanchez, *Adv. Chem. Ser.*, 1982, **201**, 69.
81. M. Molina and T. Tabak, *J. Inorg. Nucl. Chem.*, 1972, **34**, 2985.
82. M. S. Sun and D. G. Brewer, *Can. J. Chem.*, 1967, **45**, 2729.
83. R. K. Murmann and F. Basolo, *J. Am. Chem. Soc.*, 1955, **77**, 3484.
84. G. Anderegg, *Helv. Chim. Acta*, 1960, **43**, 414.
85. See ref. 40, part B6, p. 84.
86. F. Farha, Jr. and R. T. Iwamoto, *Inorg. Chem.*, 1965, **4**, 844.
87. L. El-Sayed and R. O. Ragsdale, *J. Inorg. Nucl. Chem.*, 1968, **30**, 651.
88. L. C. van Poucke, H. F. de Brabander and Z. Eeckhaut, *Bull. Soc. Chim. Belg.*, 1969, **78**, 131.
89. L. C. van Poucke, G. F. Thiers and Z. Eeckhaut, *Bull. Soc. Chim. Belg.*, 1972, **81**, 357.
90. J. A. Azoo, R. G. R. Bacon and K. K. Gupta, *J. Chem. Soc. (C)*, 1970, 1975.
91. A. D. Baker, M. Brisk and A. Storch, *J. Inorg. Nucl. Chem.*, 1974, **36**, 1755.
92. D. P. Murtha and R. A. Walton, *Inorg. Chem.*, 1973, **12**, 368.
93. J.-P. Deloume, R. Faure and H. Loiseleur, *Acta Crystallogr., Sect. B*, 1977, **33**, 2709.
94. J. P. Scannell and F. W. Allen, *J. Org. Chem.*, 1960, **25**, 2143.
95. T. J. Kistenmacher, M. Rossi and L. G. Marzilli, *Inorg. Chem.*, 1979, **18**, 240.
96. F. Guay and A. L. Beauchamp, *J. Am. Chem. Soc.*, 1979, **101**, 6260.
97. B. Lippert and D. Neugebauer, *Inorg. Chim. Acta*, 1980, **46**, 171.
98. B. Lippert and D. Neugebauer, *Inorg. Chem.*, 1982, **21**, 451.
99. C. Stoehr, *J. Prakt. Chem.*, 1895, **51**, 449.
100. K. Houngbossa, O. Enea and G. Berthon, *Thermochim. Acta*, 1974, **10**, 415.
101. R. G. Vranka and E. L. Amma, *Inorg. Chem.*, 1966, **5**, 1020.
102. H. D. Stidham and J. A. Chandler, *J. Inorg. Nucl. Chem.*, 1965, **27**, 397.
103. J. G. Schmidt and R. F. Trimble, *J. Phys. Chem.*, 1962, **66**, 1063.
104. See ref. 40, part B6, p. 118.
105. S. Cabani and E. Scrocco, *J. Inorg. Nucl. Chem.*, 1958, **8**, 332.
106. C. Luca, *Bull. Soc. Chim. Fr.*, 1967, 2556.
107. J. M. Dale and C. V. Banks, *Inorg. Chem.*, 1963, **2**, 591.
108. Y. Bokra, *Bull. Soc. Chim. Fr.*, 1974, 1267.
109. W. J. Peard and R. T. Pflaum, *J. Am. Chem. Soc.*, 1958, **80**, 1593.
110. B. Martin, W. R. McWhinnie and G. Waind, *J. Inorg. Nucl. Chem.*, 1961, **23**, 207.
111. A. A. Schilt and R. C. Taylor, *J. Inorg. Nucl. Chem.*, 1959, **9**, 211.
112. J. R. Hall, M. R. Litzow and R. A. Plowman, *Aust. J. Chem.*, 1970, **23**, 1125.
113. E. W. Ainscough and R. A. Plowman, *Aust. J. Chem.*, 1970, **23**, 699.
114. J. R. Hall, R. A. Plowman and H. S. Preston, *Aust. J. Chem.* 1965, **18**, 1345.
115. C. M. Harris and T. N. Lockyer, *Aust. J. Chem.*, 1970, **23**, 1125.
116. See ref. 40, part B6, p. 35.
117. R. J. Hodges and W. F. Pickering, *Aust. J. Chem.*, 1966, **19**, 981.
118. F. Bottomley, *Q. Rev., Chem. Soc.*, 1970, **24**, 617.
119. J. R. Dilworth, *Coord. Chem. Rev.*, 1976, **21**, 29.
120. I. Szilard, *Acta Chem. Scand.*, 1963, **17**, 2674.
121. See ref. 40, part B6, p. 285.
122. D. C. Bradley, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 259.
123. W. P. Griffith, *Coord. Chem. Rev.*, 1972, **8**, 369.
124. J. Szuhay, *Chem. Ber.*, 1893, **26**, 1933.
125. F. P. Dwyer, *J. Am. Chem. Soc.*, 1941, **63**, 78.
126. C. M. Harris, B. F. Hoskins and R. L. Martin, *J. Chem. Soc.*, 1959, 3728.
127. R. Appel, H. W. Fehlhaber, D. Hänssgen and R. Schöllhorn, *Chem. Ber.*, 1966, **99**, 3108.
128. J. A. Cogliano and G. L. Braude, *J. Org. Chem.*, 1964, **29**, 1397.
129. D. Hass and G. Bergerhoff, *Acta Crystallogr., Sect. B*, 1974, **30**, 1361.
130. J. Kuyper, P. C. Keijzer and K. Vrieze, *J. Organomet. Chem.*, 1976, **116**, 1.
131. B. L. Evans, A. D. Yoffe and P. Gray, *Chem. Rev.*, 1959, 515.
132. R. Alexander, E. C. F. Ko, Y. C. Mac and A. J. Parker, *J. Am. Chem. Soc.*, 1967, **89**, 3707.
133. M. Le Démézet, C. Madec and M. L'Her, *Bull. Chim. Soc. Fr.*, 1970, 365.
134. A. H. Norbury and A. I. P. Sinha, *Q. Rev., Chem. Soc.*, 1970, **24**, 69.
135. K. F. Chew, W. Derbyshire, N. Logan, A. H. Norbury and A. I. P. Sinha, *Chem. Commun.*, 1970, 1708.
136. A. H. Norbury and A. I. P. Sinha, *J. Inorg. Nucl. Chem.*, 1971, **33**, 2638.
137. T. Austad, J. Songstad and K. Ase, *Acta Chem. Scand.*, 1971, **25**, 1136.
138. D. Britton and J. D. Dunitz, *Acta Crystallogr.*, 1965, **18**, 424.
139. K. Aarflot and K. Ase, *Acta Chem. Scand., Ser. A*, 1974, **28**, 137.

140. I. Leden and R. Nilsson, *Z. Naturforsch, Teil A,* 1955, **10,** 67.
141. W. Jaenicke, *Z. Naturforsch., Teil A,* 1949, **4,** 363.
142. I. Linqvist and B. Strandberg, Acta Crystallogr., 1957, **10,** 173.
143. H. Chateau, A. de Cugnac and B. Cerisy, *C.R. Hebd. Seances Acad. Sci.,* 1962, **255,** 1727.
144. P. O. Kinell and B. Strandberg, *Acta Chem. Scand.,* 1959, **13,** 1607.
145. P. Gans, J. B. Gill and D. P. Fearnley, *J. Chem. Soc., Dalton Trans,* 1981, 1708.
146. P. P. Singh and S. P. Yadav, *J. Inorg. Nucl. Chem.,* 1978, **40,** 1881.
147. (a) P. P. Singh, S. A. Khan and J. P. Pandey, *Can. J. Chem.,* 1979, **57,** 3061; (b) A. Werner and H. Müller, *Z. Anorg. Allg. Chem.,* 1899, **22,** 91; (c) G. C. Lalor and H. Miller, *J. Inorg. Nucl. Chem.,* 1975, **37,** 307.
148. A. M. Golub and V. V. Skopenko, *Russ. Chem. Rev. (Engl. Transl.),* 1965, **34,** 901.
149. A. M. Golub and V. V. Skopenko, *Russ. J. Inorg. Chem. (Engl. Transl.),* 1961, **6,** 61.
150. O. M. Abu Salah and M. I. Bruce, *J. Organomet. Chem.,* 1975, **87,** C15.
151. O. M. Abu Salah, G. S. Ashby, M. I. Bruce, E. A. Pederzolli and J. D. Walsh, *Aust. J. Chem.,* 1979, **32,** 1613.
152. M. I. Bruce and J. D. Walsh, *Aust. J. Chem.,* 1979, **32,** 2753.
153. M. I. Bruce, J. D. Walsh, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.,* 1981, 956.
154. H. L. Yeager and B. Kratochvil, *J. Phys. Chem.,* 1969, **73,** 1963.
155. G. J. Janz, M. J. Trait and J. Meier, *J. Phys. Chem.,* 1967, **71,** 963.
156. (a) C. B. Baddiel, M. J. Trait and G. J. Janz, *J. Phys. Chem.,* 1965, **69,** 3634; (b) K. Nilsson and A. Oskarsson, *Acta Chem. Scand., Ser. A,* 1984, **38,** 79.
157. B. G. Oliver and G. J. Janz, *J. Phys. Chem.,* 1970, **74,** 3819.
158. K. M. Stelting and S. E. Manahan, *Anal. Chem.,* 1974, **46,** 592.
159. H. Meerwein, V. Hederich and K. Wunderlich, *Arch Pharm. (Weinheim, Ger.),* 1958, **291,** 541.
160. M. Kubota, D. L. Johnston and I. Matsubara, *Inorg. Chem.,* 1966, **5,** 386.
161. T. Nomura and Y. Saito, *Bull. Chem. Soc. Jpn.,* 1966, **39,** 1468.
162. M. Kubota and D. L. Johnston, *J. Am. Chem. Soc.,* 1966, **88,** 2451.
163. D. M. Barnhart, C. N. Caughan and M.-U. Haque, *Inorg. Chem.,* 1969, **8,** 2768.
164. J. Konnert and D. Britton, *Inorg. Chem.,* 1966, **5,** 1193.
165. See ref. 40, part B6, p. 304.
166. D. Malone and B. Sen, *J. Inorg. Nucl. Chem.,* 1973, **35,** 2114.
167. C. H. Liu and C. F. Liu, *J. Am. Chem. Soc.,* 1961, **83,** 4167.
168. A. F. Ferris and O. L. Salerni, *Inorg. Chem.,* 1964, **3,** 1721.
169. See ref. 40, part B7, 1976, p. 199.
170. M. R. Churchill, J. Donahue and F. J. Rotella, *Inorg. Chem.,* 1976, **15,** 2752.
171. B.-K. Teo and J. C. Calabrese, *Inorg. Chem.,* 1976, **15,** 2467.
172. B.-K. Teo and J. C. Calabrese, *J. Chem. Soc., Chem. Commun.,* 1976, 185.
173. M. R. Churchill and B. C. DeBoer, *Inorg. Chem.,* 1975, **14,** 2502.
174. B.-K. Teo and J. C. Calabrese, *Inorg. Chem.,* 1975, **15,** 2474.
175. Y. Inogushi, B. Milewski-Mahrla, D. Neugebauer, P. G. Jones and H. Schmidbaur, *Chem. Ber.,* 1983, **116,** 1487.
176. J. Howatson and B. Morosin, *Cryst. Struct. Commun.,* 1973, **2,** 51.
177. A. Cassel, *Acta Crystallogr., Sect B,* 1979, **35,** 174.
178. C. Panattoni and E. Frasson, *Acta Crystallogr.,* 1963, **16,** 1258.
179. J. L. Cox and J. Howatson, *Inorg. Chem.,* 1973, **12,** 1205.
180. C. Pecile, G. Giacometti, A. Turco and G. Semerano, *Atti Acad. Naz. Lincei, Cl. Sci. Fis., Mat. Nat., Rend.,* 1960, **28,** 189.
181. T. G. M. Dikhoff and R. G. Goel, *Inorg. Chim. Acta,* 1980, **44,** L72.
182. R. G. Goel and P. Pilon, *Inorg. Chem.,* 1978, **17,** 2876.
183. A. F. M. J. van der Ploeg, G. van Koten and A. L. Spek, *Inorg. Chem.,* 1979, **18,** 1052.
184. E. C. Alyea, S. A. Dias and S. Stevens, *Inorg. Chim. Acta,* 1980, **44,** L203.
185. E. C. Alyea, G. Ferguson and A. Somogyvari, *Inorg. Chem.,* 1982, **21,** 1369.
186. E. L. Muetterties and C. W. Alegranti, *J. Am. Chem. Soc.,* 1972, **94,** 6386.
187. A. Cassel, *Acta Crystallogr., Sect. B,* 1981, **37,** 229.
188. K. Aurvillius, A. Cassel and L. Falth, *Chem. Scr.,* 1974, **5,** 9.
189. A. Cassel, *Acta Crystallogr., Sect. B,* 1975, **31,** 1194.
190. A. Cassel, *Acta Crystallogr., Sect. B,* 1976, **32,** 2521.
191. M. Barrow, H. B. Burgi, M. Camalli, F. Caruso, E. Fischer, L. M. Venanzi and L. Zambonelli, *Inorg. Chem.,* 1983, **22,** 2356.
192. D. M. Ho and R. Bau, *Inorg. Chem.,* 1983, **22,** 4073.
193. I. J. Colquhoun and W. McFarlane, *J. Chem. Soc., Chem. Commun.,* 1980, 145.
194. K. J. Coskran, T. J. Huttemann and J. G. Verkade, *Adv. Chem. Ser.,* 1966, **62,** 590.
195. J. H. Meiners, J. C. Clardy and J. G. Verkade, *Inorg. Chem.,* 1975, **14,** 632.
196. D. A. Couch and S. D. Robinson, *Inorg. Chim. Acta,* 1974, **9,** 39.
197. T. D. Smith, *J. Inorg. Nucl. Chem.,* 1960, **15,** 95.
198. P.-P. Winkler and P. Peringer, *Transition Met. Chem.,* 1982, **7,** 313.
199. D. A. Couch and S. D. Robinson, *Inorg. Chem.,* 1974, **13,** 456.
200. D. A. Couch and S. D. Robinson, *J. Chem. Soc., Dalton Trans.,* 1974, 1309.
201. F. G. Mann, A. F. Wells and D. Purdie, *J. Chem. Soc.,* 1937, 1828.
202. P. L. Goggin, R. J. Goodfellow, S. R. Haddock and J. G. Eary, *J. Chem. Soc., Dalton Trans.,* 1972, 647.
203. D. C. Olson and J. Bjerrum, *Acta Chem. Scand.,* 1966, **20,** 143.
204. D. A. Edwards and M. Longley, *J. Inorg. Nucl. Chem.,* 1978, **40,** 1599.
205. M. K. Cooper, R. S. Nyholm, P. W. Carreck and M. McPartlin, *J. Chem. Soc., Chem. Commun.,* 1974, 343.
206. L. D. Pettit and A. Royston, *J. Chem. Soc. (A),* 1969, 1570.
207. G. J. Ford, P. Gans, L. D. Pettit and C. Sherrington, *J. Chem. Soc., Dalton Trans.,* 1972, 1763.
208. W. Levason and C. A. McAuliffe, *Inorg. Chim. Acta,* 1974, **8,** 25.

209. J. Lewis, R. S. Nyholm and D. J. Phillips, *J. Chem. Soc.*, 1962, 2177.
210. A. S. Kasenally, R. S. Nyholm and M. H. B. Stiddard, *J. Chem. Soc.*, 1965, 5343.
211. T. L. Blundell and H. M. Powell, *J. Chem. Soc. (A)*, 1971, 1685.
212. G. J. Ford, L. D. Pettit and C. Sherrington, *J. Inorg. Nucl. Chem.*, 1971, **33,** 4119.
213. H. A. Goodwin and F. Lions, *J. Am. Chem. Soc.*, 1959, **81,** 311.
214. G. A. Barclay, M. A. Collard, C. M. Harris and J. V. Kingston, *J. Inorg. Nucl. Chem.*, 1969, **31,** 3509.
215. See ref. 40, part B6, p. 6.
216. J. W. Akitt, *J. Chem. Soc., Dalton Trans.*, 1974, 175.
217. N. I. Gusev, *Russ. J. Phys. Chem. (Engl. Transl.)*, 1973, **47,** 1309.
218. D. S. Allam and W. H. Lee, *J. Chem. Soc.*, 1966, 5.
219. (a) R. D. Brown and M. C. R. Symons, *J. Chem. Soc., Dalton Trans.*, 1976, 426; (b) T. Yamaguchi, G. Johansson, B. Holmberg, M. Maeda and H. Ohtaki, *Acta Chem. Scand., Ser. A*, 1984, **38,** 437.
220. J. Burgess, 'Metal Ions in Solution', Ellis Horwood, Chichester, 1978, p. 149.
221. C. F. Baes, Jr. and R. E. Mesmer, 'The Hydrolysis of Cations', Wiley-Interscience, New York, 1976, p. 274.
222. P. A. Kilty and W. M. H. Sachtler, *Catal. Rev.*, 1974, **10,** 1.
223. D. McIntosh and G. A. Ozin, *Inorg. Chem.*, 1977, **16,** 59.
224. D. McIntosh and G. A. Ozin, Inorg. Chem., 1976, **15,** 2869.
225. C. R. Bailey, *J. Chem. Soc.*, 1930, 1534.
226. See ref. 40, part B6, p. 206.
227. M. T. El-Ghamry and R. W. Frei, *Anal. Chem.*, 1968, **40,** 1986.
228. R. C. Mehrotra, *Adv. Inorg. Chem. Radiochem.*, 1983, **26,** 269.
229. J. V. Nef, *Liebigs Ann. Chem.*, 1893, **277,** 68.
230. R. West and R. Riley, *J. Inorg. Nucl. Chem.*, 1958, **5,** 295.
231. V. V. Sukhan, E. Uhlemann and L. Wolf, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1967, **12,** 233.
232. D. F. Evans, J. N. Tucker and G. C. De Villardi, *J. Chem. Soc., Chem. Commun.*, 1975, 205.
233. A. Dambska and A. Janowski, *Org. Magn. Reson.*, 1980, **13,** 122.
234. T. J. Wenzel, T. C. Bettes, J. E. Sadlowski and R. E. Sievers, *J. Am. Chem. Soc.*, 1980, **102,** 5903.
235. T. J. Wenzel and R. E. Sievers, *Anal. Chem.*, 1980, **53,** 393.
236. T. J. Wenzel and R. E. Sievers, *J. Am. Chem. Soc.*, 1982, **104,** 382.
237. T. J. Wenzel and R. E. Sievers, *Anal. Chem.*, 1982, **54,** 1602.
238. 'Kirk–Othmer Encyclopedia of Chemical Technology', 3rd edn., Wiley-Interscience, New York, 1982, vol. 17, p. 611.
239. H. Chateau, B. Hervier and P. Pouradier, *J. Phys. Chem.*, 1957, **61,** 250.
240. R. O. Nilsson, *Ark. Kemi,* 1958, **12,** 219, 337.
241. A. K. Dey, *J. Inorg. Nucl. Chem.*, 1958, **6,** 71.
242. L. Cavalca, A. Mangia, C. Palmieri and G. Pelizzi, *Inorg. Chim. Acta,* 1970, **4,** 299.
243. F. Bigoli, A. Tiripicchio and M. Tiripicchio-Camellini, *Acta Crystallogr., Sect. B,* 1972, **28,** 2079.
244. R. Stomberg, I.-G. Svensson and A. A. G. Tomlinson, *Acta Chem. Scand., Ser. B,* 1973, **27,** 1192.
245. G. A. Newman, *Chem. Ind. (London)*, 1968, 514.
246. G. A. Newman, *J. Mol. Struct.*, 1970, **5,** 61.
247. J. Catterick and P. Thornton, *Adv. Inorg. Chem. Radiochem.*, 1977, **20,** 291.
248. N. J. Bunce and N. G. Murray, *Tetrahedron,* 1971, **27,** 5323.
249. A. E. Blakeslee and J. L. Hoard, *J. Am. Chem. Soc.*, 1965, **78,** 3029.
250. R. G. Griffin, J. D. Ellet, Jr., M. Mehring, J. G. Bullitt and J. S. Waugh, *J. Chem. Phys.*, 1972, **57,** 2147.
251. P. Goggan and A. T. McPhail, *J. Chem. Soc., Chem. Commun.*, 1972, 91.
252. C. Pascual and W. Simon, *Helv. Chim. Acta,* 1966, **49,** 1344.
253. F. H. MacDougall and L. E. Topol, *J. Phys. Chem.*, 1952, **56,** 1090.
254. D. G. Vartak and R. S. Shetiya, *J. Inorg. Nucl. Chem.*, 1967, **29,** 1261.
255. C. Oldham and W. F. Sanford, *J. Chem. Soc., Dalton Trans.*, 1977, 2068.
256. D. A. Edwards and M. Longley, *J. Inorg. Nucl. Chem.*, 1978, **40,** 1599.
257. E. T. Blues, M. G. B. Drew and B. Femi-Onadeko, *Acta Crystallogr., Sect. B,* 1977, **33,** 3965.
258. See ref. 40, part B5, pp. 148, 186.
259. A. G. Leiga, *J. Phys. Chem.*, 1966, **70,** 3254, 3260.
260. R. L. Griffith, *J. Chem. Phys.*, 1943, **11,** 499.
261. I. Ebert, E. Winkler and H. Jost, *Z. Chem.*, 1980, **20,** 271.
262. E. Winkler, H. Jost and G. Heinicke, *Z. Chem.*, 1979, **19,** 426.
263. S. H. Cohen, R. T. Iwamoto and J. Kleinberg, *J. Am. Chem. Soc.*, 1960, **82,** 1844.
264. A. E. Martell and R. M. Smith, 'Critical Stability Constants', Plenum, New York, 1977, vol. 3.
265. R. I. Noveselov, Z. A. Muzykantova and B. V. Ptitsyn, *Russ. J. Inorg. Chem. (Engl. Trans.)*, 1964, **9,** 1399.
266. B. Kuznik and M. Czakis-Sulikowska, *Zesz. Nauk. Politech. Lodz., Chem.*, 1967, **18,** 101 (*Chem. Abstr.*, 1968, **69,** 92 514w).
267. L. Hough and A. C. Richardson, in 'Comprehensive Organic Chemistry', ed. D. H. R. Barton and W. D. Ollis, Pergamon, Oxford, 1979, vol. 5, p. 714.
268. P. Karrer, *Chem. Ber.*, 1917, **50,** 833.
269. G. Wulff and G. Röhle, *Chem. Ber.*, 1972, **105,** 1122.
270. S. Ahrland and N.-O. Björk, *Acta Chem. Scand., Ser. A,* 1974, **28,** 823.
271. D. C. Luehrs, R. W. Nicholas and D. A. Hamm, *J. Electroanal. Chem. Interfacial Electrochem.*, 1971, **29,** 417.
272. N.-O. Björk and A. Cassel, *Acta Chem. Scand., Ser. A,* 1976, **30,** 235.
273. J. A. Davies, *Adv. Inorg. Chem. Radiochem.*, 1981, **24,** 115.
274. D. C. Luehrs, *J. Inorg. Nucl. Chem.*, 1971, **33,** 2701.
275. S. J. Kuhn and J. S. McIntyre, *Can. J. Chem.*, 1965, **43,** 995.
276. V. P. Komarov and I. S. Shaplygin, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1982, **27,** 1685.
277. W. E. Bull, S. K. Madan and J. E. Willis, *Inorg. Chem.*, 1963, **2,** 303.

278. P. A. Temussi and F. Quadrifoglio, *Chem. Commun.*, 1968, 844.
279. P. A. Temussi, T. Tancredi and F. Quadrifoglio, *J. Phys. Chem.*, 1969, **73**, 4227.
280. O. E. Edwards, D. H. Paskovich and A. H. Reddoch, *Can. J. Chem.*, 1973, **51**, 978.
281. R. G. Harvey, J. H. Nelson and R. O. Ragsdale, *Coord. Chem. Rev.*, 1968, **3**, 375.
282. N. M. Karayannis, L. L. Pytlewski and C. M. Mikulski., *Coord. Chem. Rev.*, 1973, **11**, 93.
283. N. M. Karayannis, A. N. Speca, D. E. Chasan and L. L. Pytlewski, *Coord. Chem. Rev.*, 1976, **20**, 37.
284. P. J. Huffman and J. E. House, Jr., *J. Inorg. Nucl. Chem.*, 1974, **36**, 2618.
285. L. C. Nathan and R. O. Ragsdale, *Inorg. Chim. Acta*, 1974, **10**, 177.
286. L. C. Nathan, J. H. Nelson, G. L. Rich and R. O. Ragsdale, *Inorg. Chem.*, 1969, **8**, 1494.
287. S. K. Madan and W. E. Bull, *J. Inorg. Nucl. Chem.*, 1964, **26**, 2211.
288. A. Werner, *Chem. Ber.*, 1908, **41**, 1062.
289. B. Chatterjee, *Coord. Chem. Rev.*, 1978, **26**, 281.
290. W. Lossen, *Liebigs Ann. Chem.*, 1872, **161**, 347.
291. L. W. Jones and C. D. Hurd, *J. Am. Chem. Soc.*, 1921, **43**, 2422.
292. M. J. Danzig, R. F. Martel and S. R. Riccitiello, *J. Org. Chem.*, 1961, **26**, 3327.
293. M. J. Danzig, S. R. Riccitiello, *J. Org. Chem.*, 1962, **27**, 686.
294. B. R. Hollebone and R. S. Nyholm, *J. Chem. Soc.* (*A*), 1971, 332.
295. A. Akerstrom, *Acta Chem. Scand.*, 1964, **18**, 1308.
296. F. Challenger and D. Greenwood, *Biochem. J.* 1949, **44**, 87.
297. H. J. Emeléus and D. E. MacDuffie, *J. Chem. Soc.*, 1961, 2597.
298. R. B. King and A. Efraty, *Inorg. Chem.*, 1971, **10**, 1376.
299. I. G. Dance, L. J. Fitzpatrick and M. L. Scudder, *Inorg. Chem.*, 1984, **23**, 2276.
300. I. G. Dance, *Aust. J. Chem.*, 1978, **31**, 2195.
301. I. G. Dance, *Inorg. Chem.*, 1981, **20**, 1487.
302. I. G. Dance, L. J. Fitzpatrick, A. D. Rae and M. L. Scudder, *Inorg. Chem.*, 1983, **22**, 3785.
303. G. A. Bowmaker and L.-C. Tan, *Aust. J. Chem.*, 1979, **32**, 1443.
304. K. Langille and M. E. Peach, *Can. J. Chem.*, 1970, **48**, 1474.
305. G. N. Schrauzer and H. Prakash, *Inorg. Chem.*, 1975, **14**, 1200.
306. P. J. M. W. L. Birker and G. C. Verschoor, *J. Chem. Soc., Chem. Commun.*, 1981, 322.
307. H. Dietrich, W. Storck and G. Manecke, *J. Chem. Soc., Chem. Commun.*, 1982, 1036.
308. R. Hesse and L. Nilson, *Acta Chem. Scand.*, 1969, **23**, 825.
309. See ref. 40, part B7, p. 10.
310. S. G. Murray and F. R. Hartley, *Chem. Rev.*, 1981, 365.
311. H. Sigel, V. M. Rheinberger and B. E. Fischer, *Inorg. Chem.*, 1979, **18**, 3334.
312. M. Widmer and G. Schwarzenbach, *Chimia*, 1970, **24**, 447.
313. M. Kubota, D. H. Johnston and I. Matsubara, *Inorg. Chem.*, 1966, **5**, 386.
314. A. G. Fogg, A. Gray and D. T. Burns, *Anal. Chim. Acta*, 1970, **51**, 265.
315. D. Coucouvanis, in 'Transition Metal Chemistry—Current Problems of General Biological and Catalytic Relevance', ed. A. Müller and E. Diemann, Verlag Chemie, Weinheim, 1981, pp. 59–89.
316. D. Coucouvanis and D. Piltingsrud, *J. Am. Chem. Soc.*, 1973, **95**, 5556.
317. F. J. Hollander and D. Coucouvanis, *Inorg. Chem.*, 1974, **13**, 2381.
318. M. L. Caffery and D. Coucouvanis, *J. Inorg. Nucl. Chem.*, 1975, **37**, 2081.
319. F. J. Hollander, Y. H. Ip and D. Coucouvanis, *Inorg. Chem.*, 1976, **15**, 2230.
320. A. Müller, H. Bögge and E. Königer-Ahlborn, *J. Chem. Soc., Chem. Commun.*, 1978, 739.
321. A. Müller, H. Bögge, E. Königer-Ahlborn and W. Hellmann, *Inorg, Chem.*, 1979, **18**, 2301.
322. S. Akerstrom, *Ark. Kemi*, 1959, 14, 387.
323. H. Yamaguchi, A. Kido, T. Uechi and K. Yasukouchi, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 1271.
324. H. Anacker-Eickhoff, R. Hesse, P. Jennische and A. Wahlberg, *Acta Chem. Scand., Ser. A*, 1982, **36**, 251.
325. R. Hesse and L. Nilson, *Acta Chem. Scand.*, 1969, **23**, 825.
326. Analytical Methods Committee, *Analyst* (*London*), 1975, **100**, 54.
327. R. H. Merry and B. A. Zarcinar, *Analyst* (*London*), 1980, **105**, 558.
328. R. P. Burns and C. A. McAuliffe, *Adv. Inorg. Chem. Radiochem.*, 1979, **22**, 303.
329. R. Heber and E. Hoyer, *J. Prakt. Chem.*, 1976, **318**, 19.
330. R. Williams, E. Billig, J. H. Waters and H. B. Gray, *J. Am. Chem. Soc.*, 1966, **88**, 43.
331. S. Ahrland, J. Chatt, N. R. Davies and A. A. Williams, *J. Chem. Soc.*, 1958, 264.
332. F. Charbonnier, R. Faure and H. Loiseleur, *Acta Crystallogr., Sect. B*, 1977, **33**, 2824.
333. F. Charbonnier, R. Faure and H. Loiseleur, *Acta Crystallogr., Sect B*, 1978, **34**, 3598.
334. F. Charbonnier, R. Faure and H. Loiseleur, *Cryst. Struct. Commun.*, 1981, **10**, 1129.
335. M. Wruble, *J. Am. Pharm. Assoc. Sci. Ed.*, 1943, **32**, 80.
336. C. L. Fos, Jr., *Arch. Surg.*, 1968, 184.
337. H. S. Rosenkranz and S. Rosenkranz, *Antimicrob. Agents Chemother.*, 1972, **2**, 373.
338. D. S. Cook and M. F. Turner, *J. Chem. Soc., Perkin Trans. 2*, 1975, 1021.
339. N. C. Baenziger and A. W. Struss, *Inorg. Chem.*, 1976, **15**, 1807.
340. See ref. 40, part B7, p. 128.
341. G. Berthon and C. Luca, *Bull. Soc. Chim. Fr.*, 1969, 432.
342. A. Bellomo, D. De Marco and A. De Robertis, *Talanta*, 1973, **20**, 1225.
343. E. A. Vizzini, I. F. Taylor and E. L. Amma, *Inorg. Chem.*, 1968, **7**, 1351.
344. M. R. Udupa and B. Krebs, *Inorg. Chim. Acta*, 1973, **7**, 271.
345. M. R. Udupa, G. Henkel and B. Krebs, *Inorg. Chim. Acta*, 1976, **18**, 173.
346. W. I. Stephen and A. Townshend, *J. Chem. Soc.* (*A*), 1966, 166.
347. G. W. Watt and J. S. Thompson, Jr., *J. Inorg. Nucl. Chem.*, 1971, **33**, 1319.
348. T. C. Lee and E. L. Amma, *J. Cryst. Mol. Struct.*, 1972, **2**, 125.
349. M. K. Papay, K. Toth, V. Izvekov and E. Pungor, *Anal. Chim. Acta*, 1973, **64**, 409.

350. D. Rosenthal and T. I. Taylor, *J. Am. Chem. Soc.*, 1960, **82**, 4169.
351. G. J. Sutton, *Aust. J. Chem.*, 1966, **19**, 2059.
352. G. J. Sutton, *Aust. J. Chem.*, 1969, **19**, 2475.
353. See ref. 40, part B7, pp. 121, 122.
354. K. Danksagmuller, G. Gritzner and V. Gutmann, *Inorg. Chim. Acta*, 1976, **18**, 269.
355. See ref. 40, part B7, pp. 191, 198.
356. G. E. Coates, *J. Chem. Soc.*, 1951, 2003.
357. D. K. Laing and L. A. Pettit, *J. Chem. Soc., Dalton Trans.*, 1975, 2297.
358. D. S. Barnes, G. J. Ford, L. D. Pettit and C. Sherrington, *J. Chem. Soc. (A)*, 1971, 2883.
359. D. Barnes, P. G. Laye and L. D. Pettit, *J. Chem. Soc. (A)*, 1969, 2073.
360. See ref. 40, part B1, p. 466; part B2, pp. 141, 383.
361. G. C. Allen, R. F. McMeeking, R. Hoppe and B. Muller, *J. Chem. Soc., Chem. Commun.*, 1972, 291.
362. M. Camalli, F. Caruso and L. Zambonelli, *Inorg. Chim. Acta*, 1982, **61**, 195.
363. D. C. Luehrs, R. T. Iwamoto and J. Kleinberg, *Inorg. Chem.*, 1966, **5**, 201.
364. R. Alexander, E. C. F. Ko, Y. C. Mac and A. J. Parker, *J. Am. Chem. Soc.*, 1967, **78**, 3703.
365. R. L. Benoit, A. L. Beauchamp and M. Deneux, *J. Phys. Chem.*, 1969, **73**, 3268.
366. (a) P. Poulenc, *Ann. Chim. (Paris)*, 1935, 4, 651; (b) G. C. Lalor and D. S. Rustad, *J. Inorg. Nucl. Chem.*, 1969, **31**, 3219.
367. A. B. P. Lever, J. Lewis and R. S. Nyholm, *J. Chem. Soc.*, 1963, 2552.
368. R. Stomberg, *Acta Chem. Scand.*, 1969, **23**, 3498.
369. J. A. Cras, J. H. Noordik, P. T. Beurskens and A. M. Verhoeven, *J. Cryst. Mol. Struct.*, 1971, **1**, 155.
370. P. Boullary, *Ann. Chim. (Paris)*, II, 1827, **34**, 377.
371. C. Brink and C. H. MacGillaury, *Acta Crystallogr.*, 1949, **2**, 158.
372. C. Brink and H. A. S. Kroese, *Acta Crystallogr.*, 1952, **5**, 433.
373. M. M. Thackeray and J. Coetzer, *Acta Crystallogr., Sect. B*, 1975, **31**, 2339.
374. I. D. Brown, H. E. Howard-Lock and M. Natarajan, *Can. J. Chem.*, 1977, **55**, 1511.
375. G. A. Bowmaker, G. R. Clark, D. A. Rogers, A. Camus and N. Marsich, *J. Chem. Soc., Dalton Trans.*, 1984, 37.
376. L. A. Bustos and J. G. Contreras, *J. Onorg. Nucl. Chem.*, 1980, **42**, 1293.
377. D. J. Greenslade and M. C. R. Symons, *J. Chem. Soc., Faraday Trans.*, 1966, **62**, 307.
378. J. I. Kim and H. Duschner, *J. Inorg. Nucl. Chem.*, 1977, **39**, 471.
379. S. Geller, *Acc. Chem. Res.*, 1978, **11**, 87.
380. D. C. Luehrs and K. Abate, *J. Inorg. Nucl. Chem.*, 1968, **30**, 549.
381. G. B. Ansell, *J. Chem. Soc., Perkin Trans. 2*, 1976, 104.
382. P. C. Healy, N. K. Mills and A. H. White, *Aust. J. Chem.*, 1983, **36**, 1851.
383. See ref. 40, part B1, p. 18.
384. N. R. Thompson, in 'Comprehensive Inorganic Chemistry', ed. J. C. Bailar, Jr., H. J. Emeléus, R. S. Nyholm and A. F. Trotman-Dickenson, Pergamon, Oxford, 1973, vol. 3, p. 93.
385. A. H. Webster and J. Halpern, *J. Phys. Chem.*, 1957, **61**, 1245.
386. J. C. Bommer and K. W. Morse, *J. Am. Chem. Soc.*, 1974, **96**, 6222.
387. J. C. Bommer and K. W. Morse, *Inorg. Chem.*, 1979, **18**, 531.
388. J. C. Bommer and K. W. Morse, *Inorg. Chem.*, 1980, **19**, 587.
389. R. H. Holm, G. W. Everett and A. Chakravorty, *Prog. Inorg. Chem.*, 1966, **7**, 83.
390. See ref. 40, part B6, p. 279.
391. K. V. Astakhov and I. E. Bukolov, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1962, **7**, 1077.
392. E. Hoyer and V. V. Skopenko, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1966, **11**, 436.
393. E. Sinn and C. M. Harris, *Coord. Chem. Rev.*, 1969, **4**, 391.
394. M. D. Hobday and T. D. Smith, *Coord. Chem. Rev.*, 1973, **9**, 311.
395. G. H. W. Milburn, M. R. Truter and B. L. Vickery, *Chem. Commun.*, 1968, 1188.
396. J. C. Jeffrey, T. B. Rauchfoss and P. A. Tucker, *Inorg. Chem.*, 1980, **19**, 3306.
397. See ref. 40, part B6, p. 233.
398. G. F. Thiers, L. C. Van Poucke and M. A. Herman, *J. Inorg. Nucl. Chem.*, 1968, **30**, 1543.
399. D. J. Alner, R. C. Lansbury and A. G. Smeeth, *J. Chem. Soc. (A)*, 1968, 417.
400. M. Israeli and L. D. Pettit, *J. Inorg. Nucl. Chem.*, 1975, **37**, 999.
401. D. J. Alner, *J. Chem. Soc.*, 1962, 3282.
402. S. P. Datta and A. K. Grzybowski, *J. Chem. Soc.*, 1959, 1091.
403. C. B. Monk, *Trans. Faraday Soc.* 1951, **47**, 292.
404. Yu. M. Azizov, A. Kh. Miftakhova and V. F. Toropova, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1967, **12**, 345.
405, J. K. Mohana Rao and M. A. Viswamitra, *Acta Crystallogr., Sect. B*, 1972, **28**, 1484.
406. R. Pepinsky, Y. Okaya, D. P. Eastman and T. Mitsui, *Phys. Rev.*, 1957, **107**, 1538.
407. B. Dupuy, C. Castinel and C. Garrigou-Lagrange, *Spectrochim. Acta, Part A*, 1969, **25**, 571.
408. S. E. Livingstone and J. D. Nolan, *Inorg. Chem.*, 1968, **7**, 1447.
409. C. A. McAuliffe, *Inorg. Chem.*, 1973, **12**, 1699.
410. D. F. S. Natusch and L. J. Porter, *J. Chem. Soc. (A)*, 1971, 2527.
411. L. D. Pettit, K. F. Siddiqui, H. Kozlowski and T. Kowalik, *Inorg. Chim. Acta*, 1981, **55**, 87.
412. D. W. Green, V. M. Ingram and M. F. Perutz, *Proc. R. Soc. London, Ser. A*, 1954, **225**, 287.
413. B. W. Mathews, in 'The Proteins', ed. H. Neurath, R. L. Hill and C.-L. Boeder, Academic, New York, 1977, vol. III, p. 404.
414. T. L. Blundell and J. A. Jenkins, *Chem. Soc. Rev.*, 1977, **6**, 139.
415. R. F. Chen, *Arch. Biochem. Biophys.*, 1973, **158**, 605.
416. See ref. 40, part B6, p. 265.
417. Y. Kojima, T. Yamashita, Y. Ishino, T. Hirashima and T. Miwa, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 3841.
418. M. Machtinger, M. Sloim-Bombard and B. Tremillon, *Anal. Chim. Acta*, 1979, **107**, 349.

419. J. S. Fritz and B. B. Garralda, *Anal. Chem.*, 1964, **36,** 737.
420. E. D. Olsen and F. S. Adamo, *Anal. Chem.*, 1967, **39,** 81.
421. I. E. Lichtenstein, E. Coppola and D. A. Aikens, *Anal. Chem.*, 1972, **44,** 1681.
422. G. A. Rechnitz and Z. Lin, *Anal. Chem.*, 1967, **39,** 1406.
423. A. Ringbom and L. Harju, *Anal. Chim. Acta,* 1972, **59,** 49.
424. H. Irving and J. J. R. F. da Silva, *J. Chem. Soc.*, 1963, 1144.
425. H. Irving and J. J. R. F. da Silva, *J. Chem. Soc.*, 1963, 3308.
426. R. J. Day and C. N. Reilley, *Anal. Chem.*, 1965, **37,** 1326.
427. O. W. Howarth, P. Moore and N. Winterton, *J. Chem. Soc., Dalton Trans.*, 1975, 360.
428. E. H. Curzon, N. Herron and P. Moore, *J. Chem. Soc., Dalton Trans.*, 1980, 721.
429. F. Hein and H. Regler, *Chem. Ber.*, 1936, **69,** 1692.
430. B. P. Block, J. C. Bailar, Jr. and D. W. Pearce, *J. Am. Chem. Soc.*, 1951, **73,** 4971.
431. J. Hala, *J. Inorg. Nucl. Chem.*, 1965, **27,** 2659.
432. F. Hein and K.-H. Vogt, *Chem. Ber.*, 1965, **98,** 1691.
433. S. L. Tzinberg, *Zavod. Lab.*, 1937, *6,* 499 (*Chem. Abstr.*, 1937, **31,** 7786).
434. W. W. Wendlandt and J. H. Van Tassel, *Science,* 1958, **127,** 242.
435. J. E. Fleming and H. Lynton, *Can. J. Chem.*, 1968, **46,** 471.
436. M. J. M. Campbell, *Coord. Chem. Rev.*, 1975, **15,** 279.
437. S. O. Ajayi and D. R. Goddard, *J. Chem. Soc., Dalton Trans.*, 1973, 1751.
438. W. I. Stephen and A. Townshend, *J. Chem. Soc.* (*A*), 1966, 166.
439. G. R. Burns, *Inorg. Chem.*, 1968, 277.
440. G. F. Gasparri, A. Mangia, A. Musatti and M. Nardelli, *Acta Crystallogr., Sect. B,* 1968, **24,** 367.
441. L. Calzolari Capacchi, G. Fava Gasparri, M. Ferrari and M. Nardelli, *Chem. Commun.*, 1968, 910.
442. See ref. 40, part B6, p. 282; part B7, p. 171.
443. B. W. Dudesinsky and J. Svec, *Anal. Chim. Acta,* 1971, **55,** 115.
444. H. M. N. H. Irving, 'Dithizone—Analytical Sciences Monograph', Chemical Society, London, 1977.
445. L. S. Meriwether, E. C. Breitner and C. L. Sloan, *J. Am. Chem. Soc.*, 1965, **87,** 4441.
446. A. C. Fabretti and G. Peyronel, *J. Inorg. Nucl. Chem.*, 1975, **37,** 603.
447. L. S. Meriwether, E. C. Breitner and N. B. Colthup, *J. Am. Chem. Soc.*, 1965, **87,** 4448.
448. K. Fukuda and A. Mizvike, *Anal. Chim. Acta,* 1970, **51,** 77.
449. See ref. 40, part B7, p. 301.
450. M. O. Kestner and A. L. Allred, *J. Am. Chem. Soc.*, 1972, **94,** 7189.
451. E. K. Barefield and M. T. Mocella, *Inorg. Chem.*, 1973, **12,** 2829.
452. S. M. Nelson, S. G. McFall, M. G. B. Drew, A. H. Othman and N. B. Mason, *J. Chem. Soc., Chem. Commun.*, 1977, 167.
453. S. M. Nelson, S. G. McFall, M. G. B. Drew and A. H. Othman, *J. Chem. Soc., Chem. Commun.*, 1977, 370.
454. M. G. B. Drew, J. Nelson and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1981, 1678.
455. C. J. Pedersen, *J. Am. Chem. Soc.*, 1967, **89,** 7017.
456. J. J. Christensen, D. J. Eatough and R. M. Izatt, *Chem. Rev.*, 1974, 351.
457. R. M. Izatt, R. E. Terry, B. L. Haymore, L. D. Hansen, N. K. Dalley, A. G. Avondet and J. J. Christensen, *J. Am. Chem. Soc.*, 1976, **98,** 7620.
458. E. Shchori, N. Nae and J. Jagur-Grodzinski, *J. Chem. Soc., Dalton Trans.*, 1957, 2381.
459. Y. Takeda and H. Gotō, *Bull. Chem. Soc. Jpn.*, 1979, **52,** 1920.
460. Y. Takeda and F. Takahashi, *Bull. Chem. Soc. Jpn.*, 1980, **53,** 1167.
461. Y. Takeda, M. Nemoto and S. Fujiwara, *Bull. Chem. Soc. Jpn.*, 1982, **55,** 3438.
462. H. K. Frensdorff, *J. Am. Chem. Soc.*, 1971, **93,** 600.
463. J. R. Lotz, B. P. Block and W. C. Fernelius, *J. Phys. Chem.*, 1959, **63,** 541.
464. R. M. Izatt, R. E. Terry, L. D. Hansen, A. G. Avondet, J. S. Bradshaw, N. K. Dalley, T. E. Jensen, J. J. Christensen and B. L. Haymore, *Inorg. Chim. Acta,* 1978, **30,** 1.
465. J. S. Bradshaw, G. E. Mass, J. D. Lamb, R. M. Izatt and J. J. Christensen, *J. Am. Chem. Soc.*, 1980, **102,** 467.
466. J. D. Lamb, R. M. Izatt, C. S. Swain and J. J. Christensen, *J. Am. Chem. Soc.*, 1980, **102,** 479.
467. J. D. Lamb, R. M. Izatt, C. S. Swain, J. S. Bradshaw and J. J. Christensen, *J. Am. Chem. Soc.*, 1980, **102,** 479.
468. R. Louis, D. Pélissard and R. Weiss, *Acta Crystallogr., Sect. B,* 1976, **32,** 1480.
469. R. Louis, Y. Agnus and R. Weiss, *Acta Crystallogr., Sect. B,* 1977, **33,** 1418.
470. M. Gratzel, K. Kalyanasundaran and J. Kim, *Struct. Bonding* (*Berlin*), 1982, **49,** 37.
471. B. Dietrich, J.-M. Lehn and J.-P. Sauvage, *Tetrahedron Lett.*, 1969, 2885.
472. B. Dietrich, J.-M. Lehn and J.-P. Sauvage, *Tetrahedron Lett.*, 1969, 2889.
473. W. Burgermeister and R. Winkler-Oswatitsch, *Top. Curr. Chem.*, 1977, **69,** 91.
474. F. Arnaud-Neu, B. Spiess and M. Schwing-Weill, *Helv. Chim. Acta,* 1977, **60,** 2633.
475. B. G. Cox, J. Garcia-Rosas and H. Schneider, *J. Am. Chem. Soc.*, 1981, **103,** 1384.
476. J. Gutnecht, H. Schneider and J. Stroka, *Inorg. Chem.*, 1978, **17,** 3326.
477. G. Anderegg, *Helv. Chim. Acta,* 1975, **58,** 1218.
478. M.-F. Lejaille, M.-H. Livertoux, C. Guidon and J. Bessière, *Bull. Soc. Chim. Fr., Part 1,* 1978, 373.
479. B. G. Cox, C. Guminski and H. Schneider, *J. Am. Chem. Soc.*, 1982, **104,** 3789.
480. B. G. Cox, P. Firman, D. Gudlin and H. Schneider, *J. Phys. Chem.*, 1982, **86,** 4988.
481. B. G. Cox, C. Guminski, P. Firman and H. Schneider, *J. Phys. Chem.*, 1983, **87,** 1357.
482. R. Weist and R. Weiss, *J. Chem. Soc., Chem. Commun.*, 1973, 678.
483. J.-M. Lehn and J. Simon, *Helv. Chim. Acta,* 1977, **60,** 141.
484. W. Simon, W. E. Morf and P. C. Meier, *Struct. Bonding* (*Berlin*), 1973, **16,** 113.
485. L. K. Steinrauf, M. Pinkerton, J. W. Chamberlin, *Biochem. Biophys. Res. Commun.*, 1968, **33,** 29.
486. T. Kubota, S. Matsutani, M. Shiro and H. Koyama, *Chem. Commun.*, 1968, 1541.
487. M. Alleaume and D. Mickel, *Chem. Commun.*, 1970, 1422.
488. A. Agtarap, J. N. Chamberlin, M. Pinkerton and L. Steinrauf, *J. Am. Chem. Soc.*, 1967, **89,** 5737.

489. J. F. Blount and J. W. Westley, *Chem. Commun.*, 1971, 927.
490. C. A. Maier and I. C. Paul, *Chem. Commun.*, 1971, 181.
491. M. Koenuma, H. Kinashi, N. Ōtake, S. Sato and Y. Saito, *Acta Crystallogr., Sect. B*, 1976, **32**, 1267.
492. H. Nakamura, Y. Iitaka, T. Kitahara, T. Okazaki and Y. Okami, *J. Antibiot.*, 1977, **30**, 714.
493. R. Hütter, W. Keller-Schierlien, F. Knüsell, V. Prelog, G. C. Rodgers, Jr., P. Suter, G. Vogel, W. Voser and H. Zähner, *Helv. Chim. Acta*, 1967, **50**, 1533.
494. J. Garcia-Rosas, H. Schneider and B. G. Cox, *J. Phys. Chem.*, 1983, **87**, 5467.
495. J. A. McMillan, *Chem. Rev.*, 1962, 65.
496. H. N. Po, *Coord. Chem. Rev.*, 1976, **20**, 171.
497. W. P. Thorpe and J. K. Kochi, *J. Inorg. Nucl. Chem.*, 1971, **33**, 3958.
498. G. A. Barbieri, *Gazz. Chim. Ital.*, 1912, **42**, 7.
499. J. C. Evans, R. D. Gillard, R. J. Lancashire and P. H. Morgan, *J. Chem. Soc., Dalton Trans.*, 1980, 1277.
500. N. Perakis and L. Capatos, *J. Phys. Radium*, 1938, **9**, 27.
501. T. S. Johnson and H. G. Hecht, *J. Mol. Spectrosc.*, 1965, **17**, 98.
502. J. A. McMillan and B. Smaller, *J. Chem. Phys.*, 1961, **35**, 1698.
503. T. Buch, *J. Chem. Phys.*, 1965, **43**, 761.
504. H. M. Gijsman, H. J. Gerritsen and J. van der Handel, *Physica*, 1954, **20**, 15.
505. H. G. Hecht and J. B. Frazier, III, *J. Inorg. Nucl. Chem.*, 1967, **29**, 613.
506. N. S. Garif'yano, B. M. Kozyrev and E. I. Semenova, *Dokl. Akad. Nauk SSSR*, 1962, **147**, 365.
507. T. Halpern, W. D. Phillips and J. A. McMillan, *J. Chem. Phys.*, 1970, **52**, 5548.
508. N. Kanzaki and I. Yasumori, *J. Phys. Chem.*, 1978, **82**, 2351.
509. T. Halpern, S. M. McKoskey and J. A. McMillan, *J. Chem. Phys.*, 1970, **52**, 3526.
510. K. D. Bowers, *Proc. Phys. Soc. (London), Sect. A*, 1953, **66**, 666.
511. J. L. Pierce, K. L. Busch, R. G. Cooks and R. A. Walton, *Inorg. Chem.*, 1983, **22**, 2492.
512. A. Kleinstein and G. A. Webb, *J. Inorg. Nucl. Chem.*, 1971, **33**, 405.
513. R. P. Eckberg and W. E. Hatfield, *Inorg. Chem.*, 1975, **14**, 1205.
514. T. G. Clarke, N. A. Hampson, J. B. Lee, J. R. Morley and B. Scanlon, *J. Chem. Soc. (C)*, 1970, 815.
515. G. N. A. Fowles, R. W. Mathews and R. A. Walton, *J. Chem. Soc. (A)*, 1968, 1108.
516. M. G. B. Drew, R. W. Mathews and R. A. Walton, *J. Chem. Soc. (A)*, 1971, 2959.
517. M. G. B. Drew, R. W. Mathews and R. A. Walton, *J. Chem. Soc. (A)*, 1970, 1405.
518. R. W. Mathews and R. A. Walton, *Inorg. Chem.*, 1971, **10**, 1433.
519. G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 1930, 2594.
520. D. P. Murtha and R. A. Walton, *Inorg. Nucl. Chem. Lett.*, 1975, **11**, 301.
521. E. Scrocco and G. Marmami, *R.C. Accad. Lincei*, 1954, **16**, 637.
522. E. Scrocco and M. Reagazzini, *R.C. Accad. Lincei*, 1954, **16**, 489.
523. S. Sugden, *J. Chem. Soc.*, 1932, 161.
524. G. T. Morgan and S. Sugden, *Nature (London)*, 1931, **128**, 31.
525. D. P. Murtha and R. A. Walton, *Inorg. Nucl. Chem. Lett.*, 1973, **9**, 819.
526. J. L. Atwood, M. L. Simms and D. A. Zatko, *Cryst. Struct. Commun.*, 1973, **2**, 279.
527. G. W. Bushnell and M. A. Khan, *Can. J. Chem.*, 1972, **50**, 315.
528. M. P. Heyward and C. F. Wells, *J. Chem. Soc., Dalton Trans.*, 1981, 431.
529. M. P. Heyward and C. F. Wells, *J. Chem. Soc., Dalton Trans.*, 1981, 1863.
530. J. L. Pierce, K. L. Busch. R. G. Cooks and R. A. Walton, *Inorg. Chem.*, 1983, **22**, 2492.
531. E. Mentast, C. Baiocchi and J. S. Coe, *Coord. Chem. Rev.*, 1984, **54**, 131.
532. J. B. Kirwin, F. D. Peat, P. J. Proll and L. H. Sutcliffe, *J. Phys. Chem.*, 1963, **67**, 1617.
533. G. A. Rechnitz and S. B. Zamochnick, *Talanta*, 1965, **12**, 479.
534. K.-D. Asmus, M. Bonifacic, P. Toffel, P. O'Neill, D. Schulte-Frohlinde and S. Steenken, *J. Chem. Soc., Faraday Trans. 1*, 1978, **74**, 1820.
535. D. A. House, *Chem. Rev.*, 1962, **62**, 185.
536. M. Fiorentino, L. Testaferri, M. Tiecco and L. Troisi, *J. Chem. Soc., Perkin Trans. 2*, 1977, 87.
537. W. E. Fristad and J. A. Klang, *Tetrahedron Lett.*, 1983, **24**, 2219.
538. See ref. 40, part B7, p. 317.
539. T. Vänngard and S. Åkerstrom, *Nature (London)*, 1959, **184**, 183.
540. T. J. Bergendahl and E. M. Bergendahl, *Inorg. Chem.*, 1972, **11**, 639.
541. B. R. McGarvey, *J. Phys. Chem.*, 1967, **71**, 51.
542. J. G. M. Van Rens and E. DeBoer, *Chem. Phys. Lett.*, 1975, **31**, 377.
543. H. Kita, S. Miyake, K. Tanaka and T. Tanaka, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 3532.
544. M. V. Rajasekharan, C. N. Sethulakshmi, P. T. Manoharan and H. Gudel, *Inorg. Chem.*, 1976, **15**, 2657.
545. B. Muller and R. Hoppe, *Z. Anorg. Allg. Chem.*, 1972, **392**, 37.
546. G. C. Allen, R. F. McMeeking, R. Hoppe and B. Muller, *J. Chem. Soc., Chem. Commun.*, 1972, 291.
547. R.-H. Odenthal and R. Hoppe, *Monatsh. Chem.*, 1971, **102**, 1340.
548. B. Muller and R. Hoppe, *Z. Anorg. Allg. Chem.*, 1973, **395**, 239.
549. See ref. 40, part B1 p. 494; part B2 p. 433.
550. A. Kumar and P. Neta, *J. Am. Chem. Soc.*, 1980, **102**, 7284.
551. G. D. Dorough, J. R. Miller and F. M. Huennekens, *J. Am. Chem. Soc.*, 1951, **73**, 4315.
552. See ref. 40, part B7, p. 301.
553. L. J. Boucher and J. J. Katz, *J. Am. Chem. Soc.*, 1967, **89**, 1340.
554. A. Antipas, D. Dolphin, M. Gouterman and E. C. Johnson, *J. Am. Chem. Soc.*, 1978, **100**, 7705.
555. D. Karweik, N. Winograd, D. G. Davis and K. M. Kadish, *J. Am. Chem. Soc.*, 1974, **96**, 591.
556. S. Muralidharan and R. G. Hayes, *J. Am. Chem. Soc.*, 1980, **102**, 5106.
557. S. Konishi, M. Hoshino and M. Imamura, *J. Phys. Chem.*, 1983, **86**, 4888.
558. K. M. More, S. S. Eaton and G. R. Eaton, *J. Am. Chem. Soc.*, 1981, **103**, 1087.
559. R. Damoder, K. M. More, G. R. Eaton and S. S. Eaton, *Inorg. Chem.*, 1983, **22**, 3738.

560. T. G. Brown and B. M. Hoffman, *Mol. Phys.*, 1980, **39**, 1073.
561. A. B. P. Lever, *Adv. Inorg. Chem. Radiochem.*, 1965, **7**, 27.
562. A. MacCragh and W. S. Koski, *J. Am. Chem. Soc.*, 1963, **85**, 2375.
563. K. B. Mertes, *Inorg. Chem.*, 1978, **17**, 49.
564. S. N. Poddar and N. G. Podder, *J. Indian Chem. Soc.*, 1970, **47**, 39.
565. D. Sen, *J. Chem. Soc. (A)*, 1969, 1304.
566. P. Ray, *Chem. Rev.*, 1961, **61**, 313.
567. N. R. Kunchur, *Nature (London)*, 1968, **217**, 539.
568. M. L. Simms, J. L. Atwood and D. A. Zatko, *J. Chem. Soc., Chem. Commun.*, 1973, 46.
569. L. Coghi and G. Pelizzi, *Acta Crystallogr., Sect. B*, 1975, **31**, 131.
570. J. D. Miller, *J. Chem. Soc. (A)*, 1968, 1778.
571. D. A. Zatko and J. W. Prather, II, *J. Electron Spectrosc. Relat. Phenom.*, 1973, **2**, 190.
572. G. L. Cohen and G. Atkinson, *J. Electrochem. Soc.*, 1968, **115**, 1236.
573. L. J. Kirschenbaum, J. H. Ambrus and G. Atkinson, *Inorg. Chem.*, 1973, **12**, 2832.
574. J.-H. Furhop, K. M. Kadish and D. G. Davis, *J. Am. Chem. Soc.*, 1973, **95**, 5140.

55
Gold

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55.1 INTRODUCTION

This article will cover coordination complexes of gold in all oxidation states. It will include descriptions of metal–gold-bonded complexes, but will exclude most organometallic chemistry. A general account of gold chemistry, giving references to recent reviews, a brief survey of the properties of gold complexes in each accessible oxidation state, and a general survey of bonding in gold complexes are given first. Some of these aspects will be treated in a more specific way in the main part of the text, which is systematized according to oxidation states of gold and ligand types.

55.2 REVIEWS OF GOLD CHEMISTRY

Gold chemists are fortunate in the number of reviews which have been published, including three recent monographs.[1–3] Some recent reviews are listed in Table 1, and readers wishing more detailed accounts of specific aspects of gold chemistry than can be given in this chapter are referred to these reviews.

The most active aspects of the coordination chemistry of gold, besides the organometallic chemistry[1,2,15–21] which will not be treated here, appear to be studies of gold compounds in unusual oxidation states and stereochemistries,[4,7] the bioinorganic chemistry of gold with especial reference to the treatment of rheumatoid arthritis (chrysotherapy),[9–14] and the synthesis and properties of gold clusters and other complexes with gold–metal bonds.[2,4,24] This work has been greatly assisted by the applications of spectroscopic techniques[2,23] and particularly by the routine determination of structures by X-ray crystallography.[7]

Table 1 Recent Reviews of Gold Chemistry

Title	*Ref.*
Gold: Organic Compounds	1
The Chemistry of Gold	2
Gold Usage	3
Compounds of Gold in Unusual Oxidation States	4
Gold Chemistry Today	5
Is Gold Chemistry a Topical Field of Study?	6
X-Ray Structural Investigations of Gold Compounds. A Compilation of Reference Data	7
Gold: Inorganic Chemistry	8
Platinum, Gold and Other Metal Chemotherapeutic Agents: Chemistry and Biochemistry	9
Bioinorganic Chemistry of Gold Coordination Compounds	10
The Mammalian Biochemistry of Gold: An Inorganic Perspective of Chrysotherapy	11
Immunopharmacology of Gold	12
The Biological Chemistry of Gold	13
The Chemistry of Gold Drugs Used in the Treatment of Rheumatoid Arthritis	14
Organogold Chemistry	15
Gold: Organometallic Chemistry	16
The Organic Chemistry of Gold	17
Reactivity and Mechanism in Organogold Chemistry	18
Organic Complexes of Univalent Gold	19
The Oxidation–Reduction Reactions of Gold Complexes	20
Organogold Chemistry	21
Gold: Electrochemistry	22
Gold and Mössbauer Spectroscopy	23
Preparation and Properties of Gold Cluster Compounds	24

55.3 A SURVEY OF OXIDATION STATES IN GOLD COMPLEXES

The complexes of gold are most readily classified according to the oxidation state of gold. This section will give a very brief summary of the oxidation states found for gold, to serve as an introduction to the more detailed treatment which follows.

55.3.1 Oxidation State –I[4,25]

The alloy CsAu has been known to have non-metallic properties for many years.[26] It has also been recognized that gold could act as a pseudohalogen, based on the high electron affinity of gold (2.31 eV, *cf.* 3.06 eV for iodine).[27] CsAu has the CsCl lattice structure and recent studies have shown that the compound is essentially ionic Cs^+Au^-. The evidence includes studies by Mössbauer and ESCA spectroscopies on the solid and conductivity studies on the melt (m.p. 590 °C).[4] In addition, CsAu exists in the gas phase at high temperature and the dissociation energy of 460 kJ mol^{-1} is very similar to that for CsCl (444 kJ mol^{-1}).[26] Theoretical studies[27] suggest that these CsAu species are also very largely ionic, Cs^+Au^-. There is a steady trend towards less ionic character, and therefore more metallic character, in the series of alloys MAu (M = Cs, Rb, K, Na).

Of greater interest to the coordination chemist is the observation that solvated electrons in liquid ammonia can reduce gold to Au^-, characterized by an absorption band at 278 nm ($\varepsilon = 5 \times 10^4$).[30] Electrochemical studies show that Au^- is stable in liquid ammonia and the anodic wave in the cyclic voltammogram, corresponding to oxidation of Au^{-I} to Au^0, occurs at −2.15 V.[31] These solutions have not been studied by coordination chemists, but they have great potential for synthesis of gold complexes in low oxidation states. Au^- has the electron configuration $[Xe]4f^{14}5d^{10}6s^2$ and is isoelectronic with Hg^0.

55.3.2 Oxidation State 0

Gold(0) is most important for the elemental state. In the gas phase, gold exists largely as Au_2 molecules with D_0^0(AuAu) 221 kJ mol^{-1} and r(AuAu) 250 pm.[32]

Atomic gold is highly reactive and a number of complexes have been trapped by matrix isolation at low temperatures. For example, the complexes AuO_2, AuCO, $Au(CO)_2$, AuC_2H_4, $Au(C_2H_4)_2$, AuC_2H_2 and AuC_6H_6 have been prepared by condensing Au atoms with the appropriate reagent in noble or inert hydrocarbon matrices and have been characterized spectroscopically.[33–37] The complexes with CO, C_2H_4 and C_6H_6 are the normal π complexes[33–37] but $Au(C_2H_2)$, formed from Au atoms and acetylene, can exist as σ-bonded radical species Au—CH=CH$^\bullet$ or Au—$\dot{C}$=CH_2, as determined by ESR studies.[34,37]

There are also a great number of gold complexes in which gold–gold or gold–metal bonds are present, in which the formal oxidation state of gold may be considered to be zero or fractional values close to zero. These complexes will be discussed in Sections 55.21–55.23.

Reports on the extraction of metallic gold from ores[38] or from laboratory residues[39] have been published.

55.3.3 Oxidation State +I

Au^I and Au^{III} are the most common oxidation states in coordination complexes of gold. Gold(I) has the electron configuration $[Xe]4f^{14}5d^{10}$, and it can form linear, trigonal planar or tetrahedral complexes in which the hybridization at gold can be considered to be *sp* (linear), sp^2 (trigonal planar) or sp^3 (tetrahedral) respectively, using the 6*s* and one or more of the 6*p* orbitals of gold in bonding. This picture is oversimplified since the 5*d* orbitals of gold are involved in bonding to some extent. Gold(I) has a much stronger tendency to form linear complexes than does copper(I) or silver(I), and the reasons for this have been discussed.[2,40–42] A claim of square planar Au^I in $KAu(CN)_2$bipy has been disproved;[43] the complex contains linear $[Au(CN)_2]^-$ ions.

Gold(I) is a very soft metal ion as can be seen from the standard potentials and stability constants given in Table 2, referring to the reactions of equations (1) and (2).

$$[AuL_2]^+ + e^- \longrightarrow Au + 2L \qquad \pi^0_{1,0} \tag{1}$$

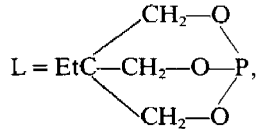
$$[Au(OH_2)_2]^+ + 2L \rightleftharpoons [AuL_2]^+ + 2H_2O \qquad K = \beta_2 \tag{2}$$

Table 2 Standard Electrode Potentials at 25 °C, and Stability Constants for Gold(I) Complexes in Aqueous Solution[22,44]

Ligand, L	$\pi^0_{1,0}$	*log* β_2
H_2O	+1.83[a]	0
Cl^-	+1.154	11
Br^-	+0.959	15
SCN^-	+0.662	20
I^-	+0.578	21
NH_3	+0.563	21
$S{=}C(NH_2)_2$	+0.380	24
$Se{=}C(NH_2)_2$	+0.20	27
$S_2O_3^{2-}$	+0.153	28
CN^-	−0.48	39

[a] This value is estimated and is used to calculate the values for log β_2. Others have estimated $\pi^0_{1,0}$ for the gold(I) aqua complex in the range 1.67–2.12 V.

A more extensive series of stability constants has been determined in acetonitrile solution, where disproportionation of gold(I) does not cause major problems.[45–48] The stability constants follow the following series: *anionic complexes* $[AuX_2]^-$: $CNO^- < CNS^- \sim Cl^- < Br^- < I^- \ll CN^-$; *cationic complexes* $[AuL_2]^+$: $Ph_3PO < Me_2S < py < AsPh_3 < NH_3 \ll PPh_3$ and $ArNC < MeNC \sim PPh_3 < PPh_2Me < PPhMe_2$; *neutral complexes* [*AuXL*]: $Me_2O \sim cod \ll Me_2S < Me_2Se < SbPh_3 < ArNC \sim AsPh_3 < Me_2Te < MeNC \sim PPh_3 < PPh_2Me < PPhMe_2$.

In the titration of $[Au(MeCN)_2]^+$ with the ligand  it was found that the stability constants followed the series $K_1 \gg K_2 \gg K_3 > K_4$ and with $K_4 = 6.6\,M^{-1}$ in acetonitrile at 25 °C.[47] The data again show that Au^I is a soft metal ion and the trend in stability constants shows clearly the preference of Au^I for coordination number two.

In complexes with ambidentate ligands, gold(I) almost invariably bonds to the softer end of the ligand, as is clearly expected from the above discussion. For example, the ligands NCO^-, $S_2O_3^{2-}$ and SO_3^{2-} bond through N or S rather than O.[49–52] Similarly, SCN^- normally bonds through S rather than N, though the equilibrium between the N- and S-bonded forms in [AuL(NCS)] depends on the nature of the ligand, L.[52,53] An example of a trigonal planar complex with S-bonded thiocyanate is shown in Figure 1.[54]

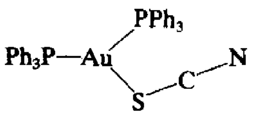


Figure 1 The structure of $[Au(SCN)(PPh_3)_2]$

55.3.4 Oxidation State +II[4]

From the ionization energies given in Table 3, it can be seen that more energy is needed to give Au^{2+} from atomic gold, than to give either Cu^{2+} or Ag^{2+} from the neutral atoms, but that the M^{3+} state is reached more easily for Au than for Ag or Cu. Hence the +II oxidation state is less common for gold than for either Cu or Ag. There is a strong tendency for disproportionation to give Au^I and Au^{III}. The electron configuration of Au^{2+} is $[Xe]4f^{14}5d^9$, and ESR spectroscopy is a useful technique for studying mononuclear gold(II) complexes which are paramagnetic.

Table 3 Ionization Energies ($kJ\,mol^{-1}$) of Cu, Ag and Au

Element	*1st*	*2nd*	*3rd*
Cu	745	1958	3554
Ag	731	2074	3361
Au	890	1980	2943

Many complexes whose empirical formulae suggest the presence of Au^{II} are not paramagnetic. The majority of such complexes are really mixed oxidation state Au^I–Au^{III} complexes but there are also many binuclear gold(II) complexes with Au—Au bonds.[2,4] Examples include '$AuCl_2$', which contains equal numbers of linear Au^I and square planar Au^{III} centres in the $[Au_4Cl_8]$ molecules,[55] and $[Au_2I_2\{\mu\text{-}(CH_2)_2PMe_2\}_2]$[56] respectively. The structures of these molecules are given in Figure 2.

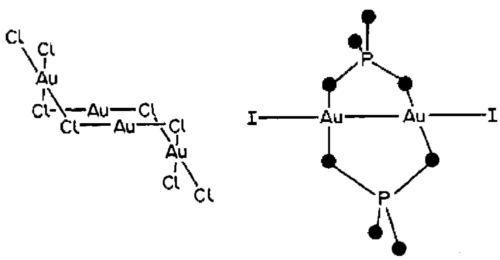


Figure 2 The structures of a gold(I)–gold(III) complex, $[Au_4Cl_8]$, and a gold(II) complex, $[Au_2I_2\{\mu\text{-}(CH_2)_2PMe_2\}_2]$

55.3.5 Oxidation State +III

The electron configuration of Au^{3+} is $[Xe]4f^{14}5d^8$, and all known gold(III) complexes are diamagnetic with the low-spin configuration. The vast majority of complexes are square planar, but complexes with coordination number five and six are also known. These have distorted square pyramidal and tetragonally distorted octahedral structures respectively.[2]

Gold(III) is a very soft metal ion as can be seen from the electrode potentials and stability constants given in Table 4. The potentials $\pi^0_{3,0}$ and $\pi^0_{3,1}$ refer to the reactions of equations (3) and (4) respectively, and β_4 is the stability constant for equation (5). Although gold(III) forms many more complexes with hard ligands, such as oxygen donors, than does gold(I), it has been argued that gold(III) displays the higher selectivity for soft ligands.[44] There is no doubt that both Au^I and Au^{III} are soft metal ions.

$$[AuL_4]^{3+} + 3e^- \longrightarrow Au + 4L \qquad \pi^0_{3,0} \tag{3}$$

$$[AuL_4]^{3+} + 2e^- \longrightarrow [AuL_2]^+ + 2L \qquad \pi^0_{3,1} \tag{4}$$

$$[Au(OH_2)_4]^{3+} + 4L \rightleftharpoons [AuL_4]^{3+} + 4H_2O \qquad K = \beta_4 \tag{5}$$

Table 4 Standard Electrode Potentials at 25 °C and Stability Constants for Gold(III) Complexes in Aqueous Solution[22,44]

Ligand	$\pi^0_{3,0}$	*log* β_4	$\pi^0_{3,1}$
H_2O	(+1.52)[a]	0	(+1.4)
Cl^-	+1.00	26	+0.93
Br^-	+0.85	34	+0.81
SCN^-	+0.64	45	+0.62
I^-	+0.56	49	+0.56
NH_3	+0.32	60	+0.21
CN^-	(−0.10)	82	(+0.1)

[a] This value is estimated and is used to calculate the values for log β_4. The value $\pi^0_{3,0} = +1.50$ is also commonly quoted.[22,44]

Of the two common oxidation states +I and +III, gold(III) is favoured with hard ligands and gold(I) with soft ligands. This can be seen by study of the equilibrium constants, K, for the disproportionation reaction of equation (6), for which the values (L, K) are: H_2O, 10^{10}; Cl^-, 5×10^7; Br^-, 10^5; SCN^-, 2.1; CN^-, $\sim 10^{-25}$.

$$3[AuL_2]^+ \overset{K}{\rightleftharpoons} [AuL_4]^+ + 2Au + 2L \tag{6}$$

55.3.6 Oxidation State +IV

There are no well-characterized gold(IV) complexes. An oxide, AuO_2, has been reported and its electrochemistry has been studied,[22] but it is very improbable that it contains gold(IV).

Organogold(IV) complexes have been suggested as reaction intermediates. Thus the decomposition of $[AuMe_4]^-$ is catalyzed by oxygen (equations 7 and 8). It is suggested that an electron transfer reaction gives $[AuMe_4]$ and O_2^-, and that the gold(IV) species then undergoes reductive elimination of ethane to give $[AuMe_2]$. The gold(II) intermediate $[AuMe_2]$ then decomposes to C_2H_6 and Au or, in the presence of PPh_3, disproportionates to gold(I) and gold(III).[57]

$$[AuMe_4]^- \xrightarrow{O_2} 2C_2H_6 + Au \tag{7}$$

$$2[AuMe_4]^- + 2PPh_3 \xrightarrow{O_2} 2C_2H_6 + [AuMe(PPh_3)] + [AuMe_3(PPh_3)] \tag{8}$$

55.3.7 Oxidation State +V

The electron configuration of Au^{5+} is $[Xe]4f^{14}5d^6$, and all complexes have the expected low-spin octahedral stereochemistry. Only fluoride complexes have been prepared, and AuF_5 and $[AuF_6]^-$ are very powerful oxidizing agents.[58] Attempts have been made to prepare $[AuF_6]$, but these have not been successful and it remains to be seen if gold(VI) complexes will ever be accessible.

55.4 BONDING IN GOLD COMPLEXES

It is intended to give some general comments on bonding in gold complexes here, but it would not be appropriate to give a comprehensive coverage. Bonding in specific classes of compounds will be discussed in the main body of the text.

55.4.1 The Significance of Relativity[40]

Gold's position in the Periodic Table is such that relativistic effects are at a maximum, and it has been argued convincingly that many of the anomalous properties of Au, when compared to Ag and Cu, may be ascribed to such effects. The relativistic effect is to strongly stabilize the 6*s* level, to stabilize the 6*p* levels to a lesser extent and to destabilize the 5*d* levels of gold. The effects are as follows:

(1) The relativistic contraction of the Au 6*s* shell explains the shorter and stronger covalent bonds formed by Au compared to Ag.[40] For example, it has been calculated that ~1 eV of the total bonding energy of the Au_2 molecule of 2.34 eV and ~46% of the dissociation energy of AuH are due to relativistic effects.[40,60] The common occurrence of Au—Au bonds in cluster complexes can be attributed to this effect. It also accounts for the high ionization energy and electron affinity of gold, which in turn are responsible for the nobility of gold and the ability of gold to form Au^- respectively.

(2) The relativistic effect is responsible for the large $6s \rightarrow 6p$ energy separation in gold, which is partly responsible[2] for the tendency of gold(I) to form linear complexes with coordination number two.

(3) The stabilization of the 6*s* and destabilization of the 5*d* levels by the relativistic effect leads to a particularly low $5d \rightarrow 6s$ separation for gold. In turn, this makes the 5*d* levels of suitable energy for bonding. It is not yet clear how significant 5*d*–6*s* hybridization is in the bonding of gold(I) complexes,[2] but the effect is certainly helpful in stabilizing the higher oxidation states +III and +V for gold with respect to copper and silver.[40]

Clearly, relativistic effects must be included in MO calculations of gold complexes.

55.4.2 Bonding in Gold(I) Complexes

The involvement of 5*d* orbitals in bonding in gold(I) complexes has for many years been considered as a major cause of the high tendency of Au^I to form linear complexes. The argument is (according to the VB method most commonly quoted) that mixing of the closely spaced $5d_{z^2}$ and 6*s* orbitals on gold gives the orbitals ψ_1 and ψ_2 of Figure 3. The electron pair then occupies ψ_1 (rather than $5d_{z^2}$), where lobes are concentrated in the *xy* plane away from the ligands. Further hybridization of ψ_2 with $6p_z$ then gives two orbitals with lobes directed along the *z* axis, suitable for accepting electron pairs from two ligands.[41,42]

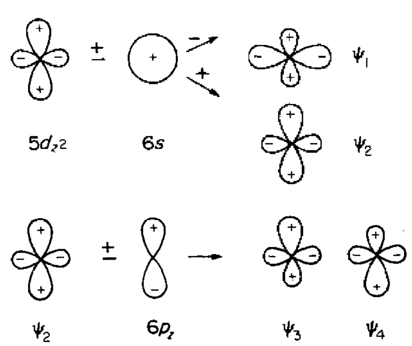


Figure 3 Proposed hybridization of $5d_{z^2}$ and 6*s* orbitals in linear gold(I) complexes

There have been several theoretical studies of bonding in gold(I) complexes, but agreement between different groups is far from perfect. Most recent studies indicate that 5*d* involvement in bonding is significant and also indicate that there is very little involvement of the 6*p* orbitals.[35,40,59,61–65] For example, in $[AuMe(PH_3)]$ the Au—P bond is calculated to involve

~35% Au $5d$ character but very little Au $6p$ character and similar results are found for the ions $[AuX_2]^-$ (X = CN, Cl, F).[62,63] The old assumption of $6s$–$6p_z$ hybridization in linear gold(I) complexes thus appears doubtful, based on these theoretical studies.

Early studies of ^{197}Au Mössbauer spectra of gold(I) complexes were interpreted in terms of *sp* hybridization of gold(I), with little involvement of $5d$ orbitals.[66] This interpretation is still used in most papers on ^{197}Au Mössbauer spectra,[23,67,68] but the existing data are also consistent with the *d–s* hybridization scheme predicted from MO calculations.[62]

Detailed studies of the electronic and MCD spectra of gold(I) complexes such as $[AuCl_2]^-$, $[Au(CN)_2]^-$, $[Au(CNEt)_2]^+$, [Au(CN)(MeNC)] and $[Au\{P(OMe)_3\}]^+$ have been interpreted in terms of a splitting of the $5d$ levels of gold to give σ (d_{z^2}), π (d_{xz}, d_{yz}) and δ (d_{xy}, $d_{x^2-y^2}$) levels with the ordering $\sigma > \delta > \pi$, as expected from crystal field theory. The σ level is destabilized by σ bonding and the π level is stabilized by π back-bonding, in the cases with π-acceptor ligands, compared to the non-bonding σ orbitals of gold.[69–72] The data were therefore interpreted in terms of *sp* hybridization at gold with little involvement of $5d$ orbitals. In contrast, a study of the UV photoelectron spectra of $[AuMe(PMe_3)]$ indicated that the $5d_\pi$ and $5d_\delta$ levels were coincident and that the $5d_\sigma$ level ($5d_{z^2}$) was stabilized by σ bonding. This must be due to involvement of $5d_{z^2}$ in bonding,[63] and a qualitative MO diagram is given in Figure 4. It will be clear from this account that a definitive description of bonding in linear gold(I) complexes is still awaited.

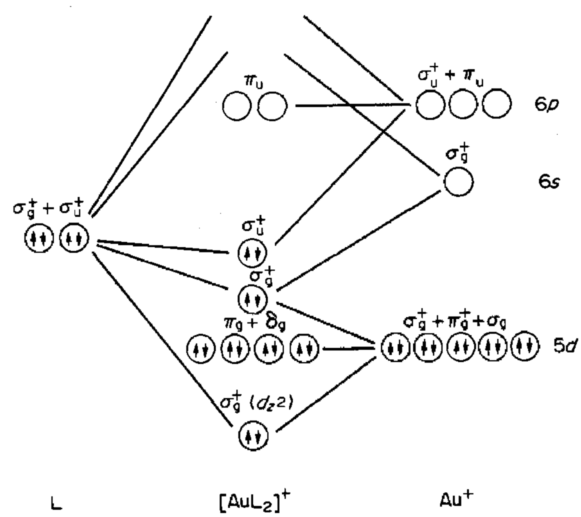


Figure 4 A qualitative MO correlation diagram for a linear complex $[AuL_2]^+$, applicable to $[AuMe(PMe_3)]$

The techniques of ^{197}Au Mössbauer spectroscopy,[23,66–68,73–77] NQR spectroscopy[78,79] and X-ray photoelectron spectroscopy[80–82] have all been very useful in investigating structure and bonding in gold(I) complexes, and in distinguishing between gold(I) and other oxidation states of gold.

55.4.3 Bonding in Gold(III) Complexes

Calculations on square planar gold(III) complexes are generally consistent with the idea of $5d_{x^2-y^2}6s$–$6p_x6p_y$ hybridization of gold(III), and with the sequence of energy levels $d_{x^2-y^2} > d_{xy} > d_{xz}, d_{yz} > d_{z^2}$ as is common for square planar complexes.[83–86] There is a need for new calculations using more powerful MO methods and including relativistic effects, in order to give quantitative predictions which can be tested experimentally.

A number of physical techniques including ^{197}Au Mössbauer,[23,73] NQR,[87,88] UV-visible absorption and MCD spectroscopies[88–92] and UV and X-ray photoelectron spectroscopies[93–95] have been used to probe the electronic structures of specific gold(III) complexes.

55.4.4 The *trans* Influence in Gold Complexes

The *trans* influence of a ligand is the ability of a ligand to weaken the bond *trans* to itself in a complex. Gold(I) and gold(III) complexes are, in the simplest treatment, considered to use *sp* and dsp^2 hybrid orbitals in forming linear and square planar complexes respectively. A good σ donor, L, tends to concentrate gold 6*s* character in the AuL bond and the *trans* bond must then overlap with an orbital of low *s* character. A weaker and more ionic bond is then formed.

The *trans* influence can be measured by many techniques, including bond lengths from X-ray structures, bond stretching force constants from vibrational spectroscopy, or from ^{197}Au Mössbauer or NQR parameters.

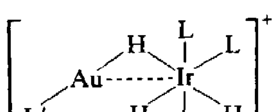
Tables 5 and 6 contain Au—Cl bond lengths in a variety of linear gold(I) and square planar gold(III) complexes. It can be seen that the *trans* influence follows rougly the series C donors (alkyl, aryl) > P donors (phosphines, phosphites) ~ S donors (thiols) > Cl^- > CO > O donors, although the range of bond lengths is not great. The series appears to hold for both gold(I) and gold(III), and it is consistent with similar series deduced from NQR and ^{197}Au Mössbauer measurements[2,23,73,78] and from vibrational spectra.[2,121–137] Some typical gold–halogen stretching frequencies are given in Table 7, and they are self-explanatory. For linear gold(I) complexes, it has been suggested that the parameter $\sigma = 0.5(IS/8 + QS/22.37)$, derived from isomer shifts (IS) and quadrupole splittings (QS) from the ^{197}Au Mössbauer spectra of complexes $[AuL_2]^+$, can give a measure of the donor ability of the ligands L. In addition, an additivity model operates so that isomer shifts and quadrupole splittings in linear gold(I) complexes, $[AuLL']^+$, can be estimated.[73] This σ parameter appears to be better in this sense than the partial quadrupole splitting, which is satisfactory for other Mössbauer nuclei.[23] A list of σ parameters is given in Table 8.

Table 5 Gold–Chloride Bond Distances (pm) in Some Linear Gold(I) Complexes

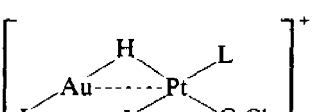
Complex	trans *atom*	*r(AuCl)*	*Ref.*
[AuCl(piperidine)]	N	225.6(8)	96
[AuCl(CO)]	CO	226.1(6)	97
$[AuCl\{P(OPh)_3\}]$	P	227.3(5)	98
$[AuCl_2]^-$	Cl	228.1(2)	7, 99
$[AuCl(PCl_3)]$	P	229	100
$[AuCl(PPh_3)]$	P	227.9(3)	101
$[Au_2Cl_2(\mu\text{-dppm})]$	P	228.8(1)	102
$[(ClAuPPh_2CH_2)_3CMe]$	P	229.2	103
$[Au_3Cl_2(\mu\text{-dppm})_2]^+$	P	229.5 (mean)	104
$[Au_2Cl_2(\mu\text{-PhSCH}_2CH_2SPh)]$	S	231 (mean)	105
$[AuCl\{C(NMe_2)Ph\}]$	C	229.5(10)	106

55.5 HYDRIDE COMPLEXES OF GOLD(I)

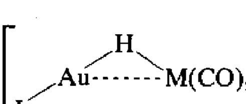
Gaseous AuH has been known to exist at high temperatures for many years, and its spectroscopic and bonding properties have been studied in detail.[40,60,138,139] No simple gold hydrides of the formula [AuHL] are known, but some complexes with bridging hydrides are known. These are formed by displacement of THF from $[Au(THF)(PR_3)]^+$ or Cl^- from $[AuCl(PPh_3)]$ by nucleophilic metal hydrides, *mer*-$[IrH_3(PPh_3)_3]$, *trans*-$[PtH(C_6Cl_5)(PEt_3)_2]$ or $[MH(CO)_5]^-$, where M = Cr or W. The products have structures (**1**)–(**3**) and the structures of (**1a**) and (**3a**) have been confirmed by X-ray crystallography.[140,141] Since the Au—H bond is strong,[40,139] there is reason to believe that many more hydrido complexes should be prepared.



(**1a**) L = PPh_3, L′ = PPh_3
(**1b**) L = PPh_3, L′ = PEt_3



(**2**) L = PEt_3



(**3a**) L = PPh_3, M = Cr
(**3b**) L = PPh_3, M = W

Table 6 Gold–Chloride Bond Distances (pm) in Some Square Planar Gold(III) Complexes

Complex	trans *atom*	*r(AuCl)*	*Ref.*
$[Au(SeO_3)Cl]_n$	O	225.0(5)	107
	Cl	227.7(7)	107
$[AuCl(terpy)]^{2+}$	N	227	108
$[AuCl_3L^1]$[a]	N	227	109
	Cl	228	109
$[AuCl_3L^2]$[b]	N	225.9(7)	110
	Cl	227.6(8)	110
$[AuCl_3(NH_3)]$	N	227.7(5)	119
	Cl	228.5(5)	
$[AuCl_3L^3]$[c]	N	227	120
	Cl	227	
$[Au_2Cl_6]$	μ-Cl	224	111
$[AuCl_4]^-$	Cl	227(1)	7, 112
$[Au_4Cl_8]$	μ-Cl	225(2)	55
$[AuCl_3L^4]$[d]	Cl	227.4	113
	S	230.5	
cis-$[AuCl_2Ph(SPr_2)]$	S	227(1)	114
	C	238(1)	
$[AuCl_3(PPh_3)]$	Cl	227.5	115
	P	235	115
$[Au_2Cl_2\{\mu\text{-}(CH_2)_2PEt_2\}_2]$	Au	235.9	116
$[Au_2Cl_2(\mu\text{-}CH_2)\{\mu\text{-}(CH_2)_2PMe_2\}_2]$	C	238(1)	117
cis-$[AuCl(C_6F_5)_2(PPh_3)]$	C	238	118
$[AuCl(C_6F_5)_3]^-$	C	230.7(10)	104

[a] L^1 = 7-methyl-4-azafluorene, [b] L^2 = PRAZEPAM. [c] L^3 = 4,4′-azotoluene. [d] L^4 = thianthrene.

Table 7 Gold–Halogen Stretching Frequencies (cm^{-1}) for some Complexes [AuXL] and $[AuX_3L]$

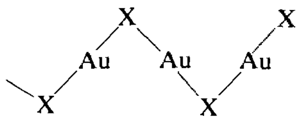
L in [AuXL]	*ν(AuCl)*	*ν(AuBr)*	*ν(AuI)*	*Ref.*
Ph_3PS	349			121
Ph_3P	329–333	229–234	187	121–125
Ph_3As	328–338	232–235	190	121, 123–125
Ph_3Sb	333	250	—	123
$(MeO)_3P$	326	—	—	126
Me_2S	325	229–234	—	127, 128
Me_3As	317	210	155	124, 129
Me_3P	311	205–206	164	124, 129
L in [AuX₃L]	*ν(AuCl) trans L*	*ν(AuBr) trans L*	*ν(AuI) trans L*	
Ph_3P	312	202	—	134
Ph_3As	302	215	—	121
Me_2S	313	202	—	127
Ph^-	289	182	162	132

55.6 HALIDE COMPLEXES OF GOLD(I)

The syntheses,[142–145] reactions,[2,146,147] spectroscopic properties[148–150] and structures[7,145] of the gold(I) halides AuCl, AuBr and AuI have been studied thoroughly. They are all coordination polymers (**4**) with bridging halide ligands, X, and linear coordination about gold(I). In AuCl the AuClAu angle is ~93° while in AuI the corresponding AuIAu angle is 72°; AuBr exists in two forms, one isostructural with AuCl and the other with AuI. Gold(I) fluoride is not known and is expected to be unstable with respect to disproportionation to gold and AuF_3.

Table 8 The σ Parameters[73,74] Derived from ^{197}Au Mössbauer Spectra of Linear Complexes $[AuL_2]^+$

Ligand	*IS* (mm s^{-1})	*QS* (mm s^{-1})	σ
Cl^-	1.72	6.13	0.23
Ph_3PS	2.46	6.82	0.31
N_3^-	2.61	6.84	0.32
C_5H_5N	3.19	7.32	0.36
Me_2S	3.43	7.56	0.38
$AsPh_3$	3.98	8.45	0.44
$C_5H_{10}NH$	4.04	7.88	0.43
CN^-	4.30	10.12	0.50
$PMePh_2$	4.75	9.69	0.51
PPh_3	5.06	9.43	0.53
PMe_2Ph	5.48	10.15	0.57



(**4**) X = Cl, Br, I

The complexes $[AuX_2]^-$ are colourless when X = Cl or Br, but yellow when X = I. The complex ions with X = Cl or Br can be prepared by reduction of $[AuX_4]^-$ in absolute ethanol[155] and, when X = I, by reaction of $[AuBr_2]^-$ with excess iodide.[155] They can be isolated as salts with bulky cations.[155,156]

The complex ions $[AuCl_2]^-$ and $[AuBr_2]^-$ disproportionate in aqueous solution[155,157] according to equation (6) for L = Cl^- or Br^-, but $[AuI_2]^-$ does not.[146] However, the complex ions are stabilized in the presence of excess halide, and calculations[158,159] indicate that soluble gold in sea water is present as ions such as $[AuCl_2]^-$, $[AuClBr]^-$ and $[AuCl(OH)]^-$.

The vibrational spectra,[79,155,160] ^{197}Au Mössbauer spectra[73,74,78] and NQR spectra[78,79] of $[AuCl_2]^-$ and the bromo and iodo analogues have been studied. The NQR study indicated that the AuCl bonds in $[AuCl_2]^-$ have ~68% ionic character,[78,79] but theoretical studies indicate greater covalent character.[62,64]

X-Ray structural studies have proved that the ions $[AuX_2]^-$ have linear structures as expected, for example in the complexes $[Au(C_5H_5N)_2][AuCl_2]$ and $[Au(S_2CNBu_2)_2]$-$[AuBr_2]$.[7,156] There are also many structures on mixed oxidation state complexes containing mixtures of $[AuX_2]^-$ and $[AuX_4]^-$ ions, which will be discussed again in Section 55.12.1. Typical examples are $Cs_2[AuCl_2][AuCl_4]$,[161,162] $Rb_3[AuCl_2]_2[AuCl_4]$,[163] $Rb_2[AuBr_2][AuBr_4]$[163] and $K_2[AuI_2][AuI_4]$.[164] Several others are also known and they are usually prepared by controlled thermolysis of the corresponding gold(III) complexes.

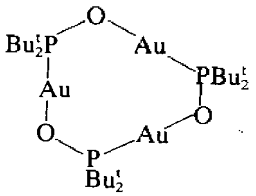
There are a great number of gold(I) complexes with both halide and other ligands, and these will be treated in the following sections.

55.7 COMPLEXES OF GOLD(I) WITH OXYGEN DONOR LIGANDS

The only simple oxo complex of gold(I) appears to be CsAuO, which is isostructural with KAgO and therefore contains $Au_4O_4^{4-}$ units.[7,167] Most other complexes contain a tertiary phosphine ligand on gold(I), and all are reactive compounds since gold(I) has little affinity for oxygen donors.

A common synthetic method is that of equation (9), where X = $MeCO_2$,[168] $PhSO_3$,[169] NO_3[170] or ClO_4,[171] and relies on the precipitation of silver chloride. A variation of this method is the synthesis of the ring complex (**5**), by the reaction (10).[172] In other cases, the synthesis may involve mercury(II) salts or sodium salts (equations 11 and 12).[173,174] Another useful synthetic method involves reaction of alkyl- or aryl-gold(I) complexes with carboxylic acids or acid anhydrides (equations 13–15).[176,177]

$$[AuCl(PPh_3)] + AgX \longrightarrow [AuX(PPh_3)] + AgCl \qquad (9)$$



(5)

$$3[AuCl(PBu^t_2Cl)] + 3Ag_2O \longrightarrow [AuPBu^t_2O]_3 + 6AgCl \quad (10)$$

$$2[AuCl(PPh_3)] + Hg\{ON(CF_3)_2\}_2 \longrightarrow 2[Au\{ON(CF_3)_2\}(PPh_3)] + HgCl_2 \quad (11)$$

$$[AuCl(PMe_3)] + NaOSiMe_3 \longrightarrow [Au(OSiMe_3)(PMe_3)] \quad (12)$$

$$[AuPh(PPh_3)] + MeCO_2H \longrightarrow [Au(O_2CMe)(PPh_3)] + C_6H_6 \quad (13)$$

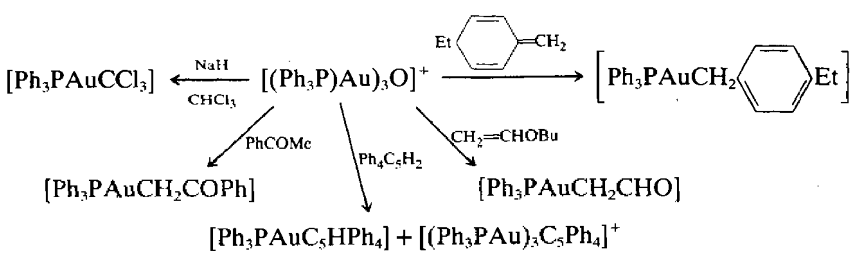
$$[AuPh(PPh_3)] + (CF_3CO)_2O \longrightarrow [Au(O_2CCF_3)(PPh_3)] + CF_3COPh \quad (14)$$

$$[AuMe(PPh_3)] + (CF_3)_2CO{\cdot}H_2O \longrightarrow [(CF_3)_2C(OAuPPh_3)_2] \quad (15)$$

The tris(triphenylphosphinegold) oxonium ion is a particularly significant oxo complex, prepared most conveniently by reaction (16)[178,180] and which crystallizes in dimeric units.[179]

$$[AuCl(PPh_3)] \xrightarrow[NaBF_4]{Ag_2O} [(Ph_3PAu)_3O]^+[BF_4]^- \quad (16)$$

In all these complexes with Au—O bonds, the oxygen donor is easily displaced by other ligands and this gives them a very useful role in synthesis. Some typical reactions of $[(Ph_3PAu)_3O]^+$ are shown in Scheme 1.



Scheme 1

55.8 COMPLEXES OF GOLD(I) WITH SULFUR AND SELENIUM DONOR LIGANDS

55.8.1 Complexes with Sulfide and Selenide Ligands

The simple sulfide Au_2S is a very insoluble, luminescent compound whose coordination chemistry is unknown.[184,185] Better characterized complexes can be prepared with tertiary phosphine–gold(I) units (equation 17; R = Me, Et, Ph).[186–188] In $[S(AuPPh_3)_2]$, each gold(I) centre has linear stereochemistry with angle AuSAu = 88.7(1)°.[188]

$$2[AuCl(PR_3)] + Na_2S \longrightarrow [S(AuPR_3)_2] + 2NaCl \quad (17)$$

Both S^{2-} and Se^{2-} derivatives of formula $[X(AuPPh_3)_3]^+$ are known (equation 18; X = S or Se).[186–189] The structures are similar,[188,189] and the dimeric unit with short Au · · · Au contacts found in the selenide derivative is shown in Figure 5.[188] A similar complex $[Au\{S(AuPPh_3)_2\}_2]^+[Me_3SnCl_2]^-$ is formed by reaction of $[AuCl(PP_3)]$ with $S(SnMe_3)_2$.[190]

$$3[AuCl(PPh_3)] + Se(SiMe_3)_2 \longrightarrow [Se(AuPPh_3)_3]^+Cl^- + 2Me_3SiCl \quad (18)$$

There are also interesting complexes with sulfide bridging between gold(I) and tungsten(VI),

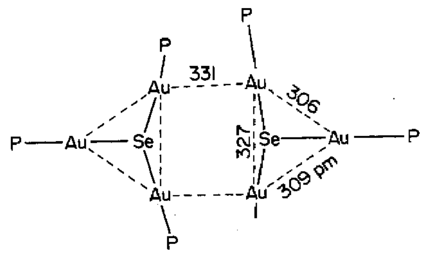
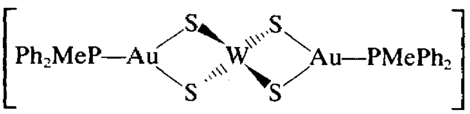
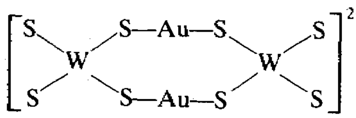


Figure 5 The dimer units in the structure of $[Se(AuPPh_3)_3]^+$. Phenyl groups are omitted

as in (**6**) and (**7**) with trigonal and linear stereochemistry at gold respectively,[191,192] and in $[Au_2BaSnS_4]$, chains of $[SnS_4]^{4-}$ tetrahedra are similarly linked by linear S—Au—S bridges.[193]



(**6**)



(**7**)

55.8.2 Complexes with Sulfite and Thiosulfate Ligands

The complex $Na_3[Au(SO_3)_2]$ is formed by reduction of $[Au(SO_3)_4]^{5-}$ by alkaline sulfite solution, and is thought to contain linear gold(I) with S-bonded sulfite ligands.[51,194–196] These gold sulfite complexes are important in electroplating applications, giving more desirable gold deposits than the traditional cyanide solutions, and a useful derivative is $Na_4Au(SO_3)_2(NO_2)$ whose structure is not known.[51]

The thiosulfate derivative $Na_3[Au(S_2O_3)_2]\cdot 2H_2O$ contains S-bonded thiosulfate ligands and the stereochemistry at gold(I) is linear.[49,50] The complex may be formed from gold(III) solutions by treatment with thiosulfate (equation 19), and the reaction involves initial substitution to give $[Au(S_2O_3)_3(OH_2)]^{3-}$ followed by reduction of gold(III) to gold(I) by excess thiosulfate.[197]

$$[Au(NH_3)_4]^{3+} + 4S_2O_3^{2-} + 4H^+ \longrightarrow [Au(S_2O_3)_2]^{3-} + S_4O_6^{2-} + 4NH_4^+ \qquad (19)$$

55.8.3 Thiocyanate and Selenocyanate Complexes

The simplest derivatives are the linear complexes $[Au(SCN)_2]^-$,[198] $[Au(SCN)(PPh_3)]$[52,53,199,200] and $[Au(SeCN)(PPh_3)]$, which may be prepared according to equations (20) and (21).

$$[AuCl(PPh_3)] + AgSCN \longrightarrow [Au(SCN)(PPh_3)] + AgCl \qquad (20)$$

$$[AuCl(PPh_3)] + NaSeCN \longrightarrow [Au(SeCN)(PPh_3)] + NaCl \qquad (21)$$

In selenocyanates, the ligand is always Se-bonded, but for thiocyanates some N-bonded isomer along with the major S-bonded species can be detected.[53] For [Au(SCN)L] the abundance of N-bonded isomer depended on L as $L = P(OPh)_3 > PMe_3 > PPh_3 > AsPh_3 > S(CH_2Ph)_2$. With bidentate phosphine ligands, bridged complexes [NCSAuL⌒LAuSCN] with L⌒L = $Ph_2PCH_2CH_2PPh_2$ or $Ph_2PC{\equiv}CPPh_2$ are known.[199,201]

Thiocyanate complexes of gold(I) with higher coordination numbers are known. Thus, the tricyclohexylphosphine complex $[Au(PCy_3)_2][SCN]$ is ionic with linear gold(I)[202] but $[Au(SCN)(PPh_3)_2]$[199] has trigonal planar stereochemistry, with S-bonded thiocyanate.[54] The difference is due to the greater steric hindrance of tricyclohexylphosphine. Even a four-coordinate gold(I) complex $[Au(SCN)(PPh_3)_3]$ can be prepared by crystallization in the presence of a large excess of PPh_3, and has distorted tetrahedral stereochemistry with a very long AuS bond distance of 279.1(3) pm.[203]

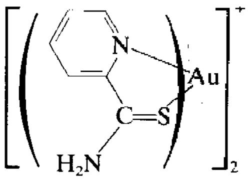
Complexes with thiocyanate bridging between Au^I—Au^I, Au^I—Au^{III} or Au^I—Pd^{II} centres can be prepared, for example according to equation (22).[204,205]

$$2[Au(SCN)(C_6F_5)]^- + [Pd(C_6F_5)_2(SC_4H_8)_2] \xrightarrow{-2SC_4H_8} [\{(C_6F_5)Au(\mu\text{-}SCN)\}_2Pd(C_6F_5)_2]^{2-} \quad (22)$$

55.8.4 Complexes with Thiourea, Triphenylphosphine Sulfide and Related Ligands

Thiourea gives a very stable water-soluble gold(I) complex $[Au\{S{=}C(NH_2)_2\}_2]^+$, which is useful in the extraction of gold from its ores.[206] There is no tendency to add a third thiourea ligand or for gold to interact with the counter ion in solid complexes.[207,208] Derivatives such as $[Au\{S{=}C(NHMe)_2\}_2]^+$ and $[Au\{S{=}\overline{CNHCH_2CH_2NH}\}_2]^+$ are known, and the structure of the latter has confirmed a distorted linear structure with $r(AuS) = 228$ ppm and angle $SAuS = 167.1°$.[209,210]

Other molecules containing C=S linkages, for example thioamides, $RC({=}S)NH_2$, or thiohydroxamic acid derivatives, such as $PhC({=}S)N(Ph)OH$, form stable complexes with gold(I).[211,212] The complex ion formed from 2-thioamidopyridine is thought to contain tetrahedral gold(I) with structure (**8**). Similarly, complexes derived from $Ph_3P{=}S$ such as $[AuCl(SPPh_3)]$ are stable complexes.[214,215]



(**8**)

55.8.5 Complexes with Thioether Ligands

Complexes of formula $[AuCl(SR_2)]$ are usually prepared by reaction of $[AuCl_4]^-$ with the corresponding dialkyl sulfide (equation 23).

$$[AuCl_4]^- + 2R_2S + H_2O \longrightarrow [AuCl(SR_2)] + R_2SO + 2H^+ + 3Cl^- \quad (23)$$

Mechanistic studies show that the first step involves substitution to give $[AuCl_3(SR_2)]$ and then attack by further ligand SR_2 leads to reduction. However, it is not clear whether the second thioether attacks at gold, at halogen or at coordinated OH groups.[216–218] One suggested sequence of reactions is given in equations (24)–(26), and involves a chlorine atom transfer from gold to sulfur in the redox step.[216]

$$[AuCl_4]^- + SR_2 \longrightarrow [AuCl_3(SR_2)] + Cl^- \quad (24)$$

$$[AuCl_3(SR_2)] + SR_2 \longrightarrow [AuCl(SR_2)] + [R_2SCl]^+Cl^- \quad (25)$$

$$[R_2SCl]^+Cl^- + H_2O \longrightarrow R_2SO + 2HCl \quad (26)$$

Alternatively, the complexes can be prepared by direct addition of the thioether or selenoether to AuCl (equation 27).[219]

$$AuCl + SeMe_2 \longrightarrow [AuCl(SeMe_2)] \quad (27)$$

With bidentate ligands the only complexes isolated are of formula $[ClAuS(R)(CH_2)_nS(R)AuCl]$, with bridging thioether ligands. Complexes are known with R = Me, $n = 2, 3$; R = Et, $n = 2$; and R = Ph, $n = 2, 5, 8, 10$.[105,219,220,221]

The vibrational spectra and NMR spectra of many thioether complexes have been reported,[121,127,128,222] and the molecular structure of $[ClAuS(Ph)CH_2CH_2S(Ph)AuCl]$ has been determined.[105] This molecule packs so that there are short intermolecular Au^I—Au^I contacts, between the otherwise linear gold(I) centres. The stability constants for formation of [AuClL] follow the series $L = Me_2Te > Me_2Se > Me_2S$.[48]

Thioether ligands are easily displaced from gold(I) by tertiary phosphine and other good ligands for gold(I), and the complexes $[AuCl(SR_2)]$ are therefore useful synthetic intermediates. For syntheses in organic solvents the complexes $[AuCl(SR_2)]$, with R = Me or Et, or [AuCl(tetrahydrothiophene)] are often used but for syntheses in aqueous solution the water-soluble derivative with $R = CH_2CH_2OH$ is preferred. This method involves treatment of $[AuCl_4]^-$ with R_2S to give $[AuCl(SR_2)]$, followed by *in situ* displacement of SR_2 by other ligands.[223–227]

55.8.6 Thiolate Derivatives

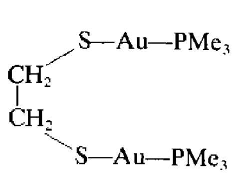
Gold(I) thiolates have important applications in gold coating and in the treatment of rheumatoid arthritis. There has been intensive research on these complexes, and excellent reviews have been published.[9–14] The reader is referred to Chapter 62.2 for a review of medicinal applications.

Complexes $(AuSR)_n$ may be prepared by reaction of RSH with $[AuCl_4]^-$ or with $[AuCl\{S(CH_2CH_2OH)_2\}]$ or by reaction of $[AuCl(AsPh_3)]$ with Me_3SiSR.[223,228] Complexes are known with a very wide range of alkyl or aryl groups, R, including terpene dithiolate, 2,3-dimercaptopropanol (BAL), thiovanol and other complex thiolates.[229–232] The polymeric gold(I) thiolates may be insoluble solids or liquids. The 'liquid golds' may be painted on to pottery *etc.* and then pyrolyzed to give decorative gold films.

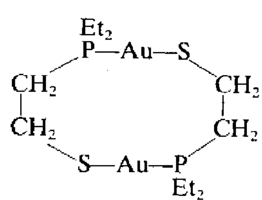
A second important class of complexes contains both thiolate and tertiary phosphine ligands. These are prepared by reactions such as those of equations (28) or (29).[187,228,233–236] Bridged complexes (**9**) and (**10**) may be prepared either from dithiols or from tertiary phosphine thiol derivatives, respectively.[187,237] The structure of the large ring complex (**10**) has been determined.[238]

$$[AuCl(PMe_3)] + RSH + Et_3N \longrightarrow [Au(SR)(PMe_3)] + Et_3NHCl \qquad (28)$$

$$[AuMe(PMe_2Ph)] + PhSH \longrightarrow [Au(SPh)(PMe_2Ph)] + CH_4 \qquad (29)$$



(**9**)



(**10**)

A complex with bridging thiolate ligand has been prepared (equation 30).[239]

$$Me_3Sn(\mu\text{-}SR)Cr(CO)_5 + [AuCl(PPh_3)] \longrightarrow [Ph_3PAu(\mu\text{-}SR)Cr(CO)_5] + Me_3SnCl \qquad (30)$$

The complexes which have been used in chrysotherapy (the treatment of rheumatoid arthritis by gold drugs) are given in Table 9. Of these, (**11**), (**12**) and (**18**) are the most important. Complexes (**11**) and (**12**) were for many years dominant, but they must be administered parenterally, and the new drug (**18**) is unique in that it is therapeutically beneficial when administered orally.[9–14,240]

Complex (**18**) is a crystalline solid, whose structure has been determined (Figure 6).[241] The coordination at gold(I) is almost linear: angle SAuP = 173.6°, with r(AuS) = 229 pm and r(AuP) = 226 pm. The NMR and ^{197}Au Mössbauer spectra have been studied, and samples of (**18**) labelled with ^{195}Au, ^{32}P and ^{35}S have been prepared.[242–245]

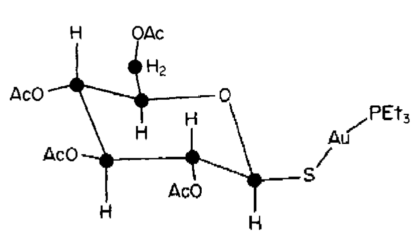
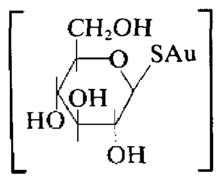
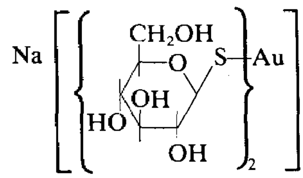
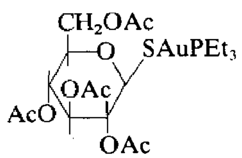
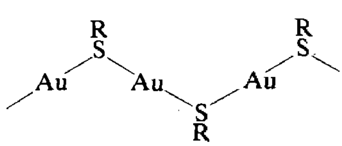


Figure 6 The structure of the gold drug, 'Ridaura'

Table 9 Gold(I) Complexes used in Chrysotherapy

Number	*Formula*	*Name (trade name)*
(11)	$Na_2^+[AuSCH(CO_2^-)CH_2CO_2^-]$	Gold(I) sodium thiomalate (Myochrysin)
(12)		Gold(I) thioglucose (Solganol)
(13)	$[AuSCH_2CH(NH_3^+)CO_2^-]$	L-Cysteinatogold(I)
(14)		Sodium gold(I) thioglucose
(15)	$Na[Au(S_2O_3)_2]$	Sodium gold(I) thiosulfate (Sanochrysin, Aurothion)
(16)	$Na^+[AuSCH_2CH(OH)CH_2SO_3^-]$	Sodium gold(I) thiopropanol-sulfonate (Allochrysine)
(17)	$[AuCl(PEt_3)]$	Chloro(triethylphosphine)gold(I) (S, K and F 36 914)
(18)		(*S*)-2,3,4,5-Tetraacetyl-1-*β*-*O*-thioglucose(triethylphosphine) gold(I) (Auranofin, Ridaura)
(19)	$AuSCH_2CONHPh$	Gold(I) thioglycoanilid (Lauron)

The structures of (**11**) and (**12**) have been investigated by EXAFS, and shown to contain approximately linear gold(I) centres with $r(AuS) = 229–237$ pm.[246,247] The structures are therefore thiolate-bridged polymers (**20**). The ^{197}Au Mössbauer and electronic spectra are fully consistent with this structure.[248–250] In solution, the linear AuS_2 coordination is maintained and it is thought that cyclic oligomers $(AuSR)_n$ (*e.g.* $n = 6$) exist, but the degree of oligomerization is dependent on pH and ionic strength.[246,247,251]



(**20**)

The biochemistry and medicinal chemistry of the gold(I) thiolates used in chrysotherapy have been thoroughly reviewed elsewhere[9–14,240] and this account will deal only with stability and ligand exchange reactions of the gold(I) thiolates of interest to coordination chemists.

Complex (**18**) is decomposed in acid solution, but the nature of the products is dependent on the solvent. In aqueous media the primary reaction is de-O-acetylation and the Au—S bond remains intact.[262] However, in aqueous methanol, reaction occurs to give $[AuCl(PEt_3)]$ and the μ-thiolate $[RS(AuPEt_3)_2]^+$, with R = tetraacetylthioglucose.[263] *In vivo,* the triethylphosphine ligand of (**18**) is displaced from gold and oxidized to Et_3PO.[264,265] Under these conditions, it is probable that (**18**) will behave in a similar way to (**11**) and (**12**) in the body, and the unique property of (**18**) is probably the lipid solubility which leads to effective transport in the body after being administered orally.[252]

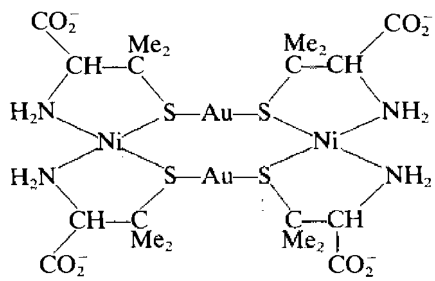
Although the mechanism of action of gold drugs is still unclear,[9–14] there is general agreement that interaction of the gold(I) centres with thiol groups of proteins and enzymes is of key significance. Studies of model systems have shown that exchange reactions occur readily by an associative mechanism, for which the simplest representation is given in equation (31), and the exchange of thiol groups has been fully confirmed *in vivo* by appropriate labelling studies.[9–14,266,267]

$$\mathrm{AuSR + R'SH \rightleftharpoons [R'S{-}Au{-}SR]^- + H^+} \quad \updownarrow \quad \mathrm{R'SAu + RSH} \tag{31}$$

The equilibrium (31) has been studied in detail with RSH = L-cysteine and is expressed in equation (32). The true equilibrium constant K is 2.1×10^{-3} for formation of $[Au(Cys)_2]^-$ (cys = L-cysteine), but formation of this species is almost complete in basic solution.[267]

$$[\mathrm{Au(Cys)}]_s \rightleftharpoons [\mathrm{Au(Cys)}]_{aq} \underset{K}{\overset{\mathrm{CysH}}{\rightleftharpoons}} [\mathrm{Au(Cys)_2}]^- + \mathrm{H}^+ \tag{32}$$

No structure determinations on simple bis(thiolato)gold(I) complexes have yet been reported, but they are assumed to have linear stereochemistry as in $[Au(S_2O_3)_2]^{3-}$ and in the complex D-penicillamine derivative $Na[Au^I_2Ni^{II}_2(pen)_4]$, of structure (**21**).[268,269,270]



(**21**)

In at least some cases, the equilibria are more complex than shown in equations (31) and (32), since the polymeric $(AuSR)_n$ may add thiolate to give oligomeric species, such as $[Au_4(SR)_7]^{3-}$ and other $[Au(SR)_n]^{(1-n)-}$ species with $1 < n < 2$.[251,271,272]

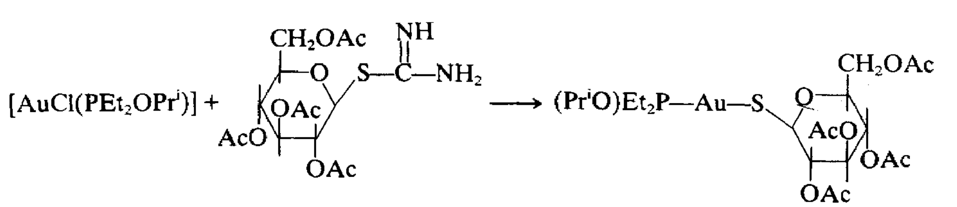
Similar thiolate exchange reactions have been shown to occur in complex (**18**),[244,264,273] and displacement of chloride (and phosphine) from $[AuCl(PEt_3)]$ was also established (equation 33).[264,265] The gold(I) thiolate can displace weakly bonded ligands from gold to give μ-thiolate derivatives (equation 34).[265]

$$[\mathrm{AuCl(PEt_3)}] + \mathrm{RSH} \rightleftharpoons [\mathrm{Au(SR)(PEt_3)}] + \mathrm{HCl} \tag{33}$$

$$[\mathrm{Au(NO_3)(PEt_3)}] + [\mathrm{Au(SR)(PEt_3)}] \rightleftharpoons [\mathrm{RS(AuPEt_3)_2}]^+\mathrm{NO_3^-} \tag{34}$$

These thiolate exchange reactions are thought to lead to incorporation of gold(I) to thiolate functions in proteins and enzymes, and thence to interfere with the inflammatory process. Thiols such as 2,3-dimercaptopropanol (BAL), *N*-acetylcysteine and penicillamine have also been used in the treatment of gold toxicity. Protein-bound gold is mobilized by complexation to the added thiol and can then be excreted.[250,273]

There is still intense interest in developing better gold thiolate drugs and new modifications of the complexes are being sought (equation 35).[274]



(35)

Toxicity of gold may in part be due to reactions with disulfide groups in proteins according to equations (36) and (37).[275,276]

$$\mathrm{3RSSR + 10AuBr_4^- + 18H_2O \longrightarrow 6RSO_3^- + 10Au^0 + 40Br^- + 36H^+} \tag{36}$$

$$\mathrm{RSSR \xrightarrow[H_2O]{AuBr_4^-} 2ROH + 2SO_4^{2-}} \tag{37}$$

55.8.7 Complexes with Unsaturated Thiolate Ligands

Some complexes with particularly interesting structures are formed from gold(I) and *N,N*-dialkyldithiocarbamates and *O,O'*-diisopropyldithiophosphate,[277-279] and probably also for dithiophosphinates, prepared according to equation (38).[280] These form dimeric units with approximately linear SAuS linkages, but the dimers are further associated into chains by intermolecular Au···Au contacts as shown in Figure 7. When it is considered that the Au—Au distance in metallic gold is 276.8 pm, it is clear that the intramolecular and intermolecular Au—Au distances in these complexes of 276–310 pm and 305–340 pm respectively must involve some bonding interaction,[7] and this has been confirmed by Raman spectroscopy.[281]

$$H[AuCl_4] + 3Na[S_2PEt_2] \longrightarrow [AuS_2PEt_2]_2 + (Et_2PS_2)_2 + 3NaCl + HCl \quad (38)$$

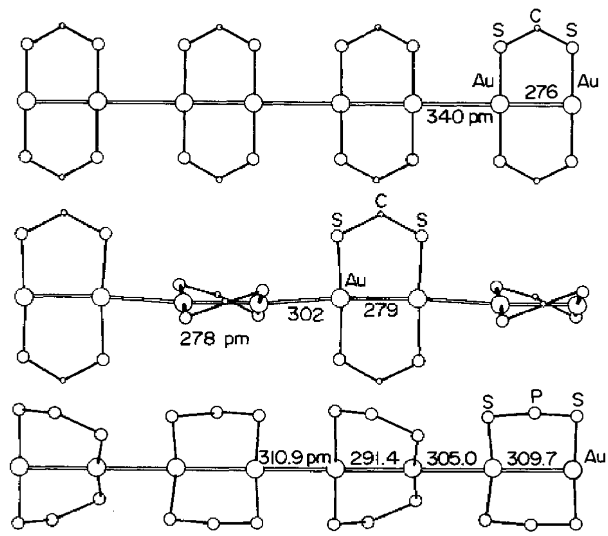
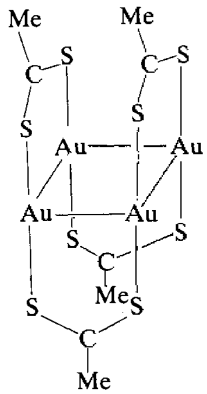


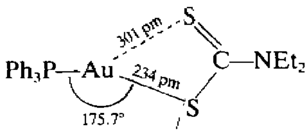
Figure 7 The structures of: top, AuS_2CNPr_2; middle, AuS_2CNBu_2; bottom, $AuS_2P(OPr^i)_2$. Dialkylamino and alkoxy groups are omitted. After ref. 7.

A related complex is the dithioacetate $[(AuS_2CMe)_4]$ prepared from $Na[AuCl_4]$ and $MeCS_2H$. This forms a tetrameric unit (**22**) in which all four Au—Au bond distances are 301 pm.[282]

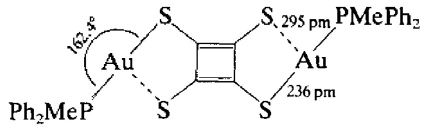


(**22**)

There are many derivatives with tertiary phosphine ligands of formula $[Ph_3PAuX]$, where X = SC(=S)OMe, SC(=S)NMe$_2$, SP(=S)F$_2$, SP(=S)(OPr^i)$_2$, SeC(=O)NR$_2$ and SC(=O)NR$_2$, and $[Ph_3PAuX\frown XAuPPh_3]$ where X⌢X = SC(CN)=C(CN)S or C_4S_4.[200,283-287] In the dithiocarbamate and tetrathiosquarate derivatives (**23**) and (**24**) the gold(I) centres are approximately linear with a weak interaction with the second sulfur atom of the ligand.[285,286]



(23)



(24)

In thiocarbamates or sulfinates, prepared according to equations (39) or (40), the ligand is S-bonded to gold(I).[284,288,289]

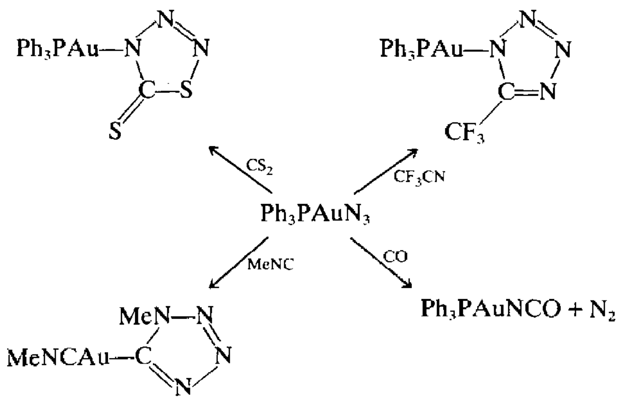
$$[AuCl(PPh_3)] + AgSO_2Ph \longrightarrow [Au(SO_2Ph)(PPh_3)] + AgCl \quad (39)$$

$$[AuMe(PMe_3)] + SO_2 \longrightarrow [Au(SO_2Me)(PMe_3)] \quad (40)$$

55.9 COMPLEXES OF GOLD(I) WITH NITROGEN DONOR LIGANDS

55.9.1 Azide and Isocyanate Complexes

The azide complexes $[Au(N_3)_2]^-$ and $[Au(N_3)(PPh_3)]$ are readily prepared,[290–292] and ^{14}N NMR studies indicate the presence of covalent Au—N bonds.[293] The complex $[Au(N_3)(PPh_3)_3]$ is also known.[294] Both $[Au(N_3)_2]^-$ and $Au(N_3)(PPh_3)]$ undergo 1,3-dipolar cycloaddition reactions with unsaturated reagents, as illustrated in Scheme 2, but CO reacts to give isocyanatogold(I) derivatives.[290,291,294]



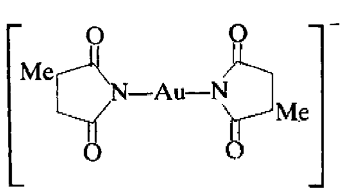
Scheme 2

Isocyanatogold(I) complexes, including bridged complexes such as [OCN—AuPPh$_2$CH$_2$CH$_2$PPh$_2$Au—NCO], can be prepared by metathesis or by reaction of azidogold complexes with CO (Scheme 2, equation 41).[294,295]

$$[Au(N_3)_4]^- + CO \longrightarrow [Au(NCO)_2]^- + N_2 \quad (41)$$

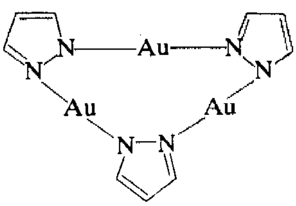
55.9.2 Complexes with Anionic Nitrogen Donor Ligands

The complex (**25**), prepared from $[AuCl_4]^-$ and *N*-methylhydantoin in aqueous solution, contains linear gold(I) centres with r(AuN) = 194 pm.[296] The Au—N bonds are easily cleaved by thiols.

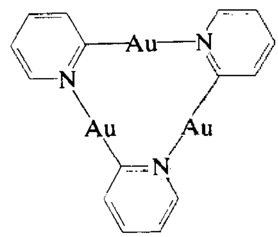


(**25**)

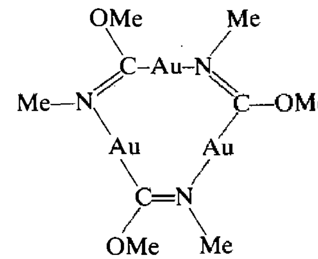
Derivatives of simple amides are the volatile $[Au\{N(SiMe_3)_2\}(PMe_3)]$ and the particularly significant tetrakis(triphenylphosphinegold)ammonium ion $[N(AuPPh_3)_4]^+$.[174,297] There are also interesting cyclic derivatives, such as (**26**)–(**28**), prepared from pyrazoles, 2-pyridyllithium or isocyanide precursors respectively.[298–301]



(**26**)

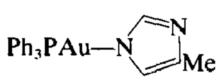


(**27**)

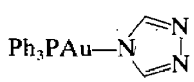


(**28**)

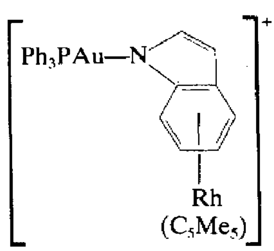
Finally, there are a considerable number of complexes of formula $[AuX(PPh_3)]$, with X = imidazolyl and similar derivatives, *e.g.* (**29**) and (**30**),[302–304] as well as the more complex products (**31**) and (**32**), which have been characterized crystallographically.



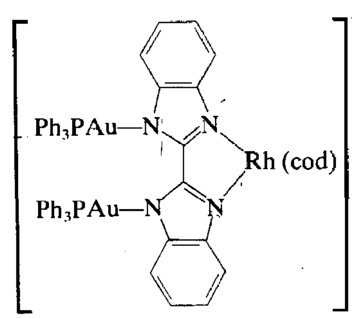
(**29**)



(**30**)



(**31**)



(**32**)

55.9.3 Complexes with Amines, Nitriles and Related Ligands

These ligands give simple linear gold(I) complexes, such as $[Au(MeCN)_2]^+$, $[Au(NH_3)_2]^+$ and $[AuCl(NH_3)]$.[307–310] In [AuCl(piperidine)], with $r(AuN) = 207$ pm, the molecules associate into tetramers through weak intermolecular Au · · · Au interactions.[96]

Diamines can bridge between gold(I) centres, as in $[ClAuNH_2CH_2CH_2NH_2AuC_6F_5]$.[311,312]

55.9.4 Complexes with Pyridine and Other Heterocyclic Ligands

The complexes AuX(py) have recently been shown to be $[Au(py)_2]^+[AuX_2]^-$ (X = Cl, I) and there are intermolecular Au · · · Au contacts as shown in Figure 8.[313]

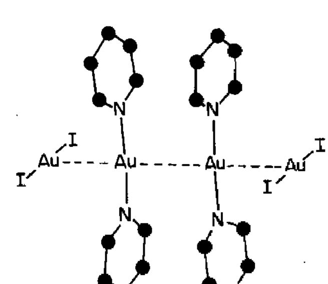
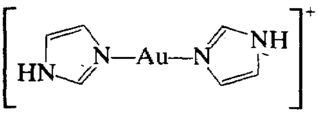
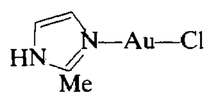
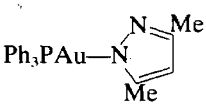


Figure 8 The structure of $[Au(py)_2][AuI_2]$

There are also many interesting complexes derived from pyrazoles and imidazoles, such as (33)–(35).

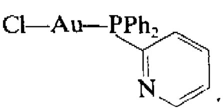

(33)

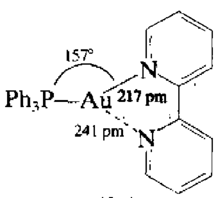

(34)


(35)

In the complexes $[AuL_2]^+$ the ligands L are bonded through the pyridine nitrogen when L = 3- or 4-cyanopyridine, but through the nitrile function when L = 2-cyanopyridine.[317]

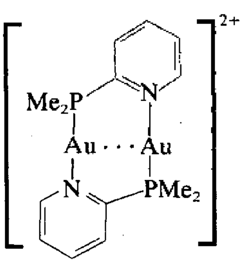
There are some interesting structures in gold complexes derived from bidentate ligands.[318–322] For example, in complex (36), derived from 2-diphenylphosphinopyridine, only the phosphorus atom is coordinated whereas in the 2,2′-bipyridine complex (37), both nitrogen atoms coordinate and the stereochemistry of gold(I) is between linear and trigonal planar.[318–321]


(36)



(37)

The ligand 2-dimethylphosphinopyridine forms a binuclear gold(I) complex (38), with a remarkably short Au···Au distance of 277.6(1) pm, clearly indicating a bonding interaction.[323]


(38)

55.10 COMPLEXES OF GOLD(I) WITH PHOSPHORUS, ARSENIC AND ANTIMONY DONOR LIGANDS

55.10.1 Complexes with Phosphide, Arsenide or Antimonide

The compound Au_2P_3 is not a gold(III) complex, but contains linear gold(I) centres linking P_6 rings, and $Au_7P_{10}I$ is $Au^I_7(P_{10})^{6-}I^-$ and contains both trigonal planar AuP_3 centres and also linear gold(I) centres.[32]

In the arsenide and antimonide derivatives Na_2AuAs or Na_2AuSb there are zigzag $(AuX)_n^{2n-}$ chains, with structures like the gold(I) halides (4), while $AuSb_2$ has metallic properties and has the cubic fluorite structure.[325–327]

The diphenylphosphide and diphenylarsenide derivatives $[(AuPPh_2)_n]$ and $[(AuAsPh_2)_n]$ are formed according to equation (42), and are presumed to have structure (4) where $X = PPh_2$.[236]

$$[AuMe(PMe_2Ph)] + Ph_2PH \longrightarrow [(AuPPh_2)_n] + CH_4 + PMe_2Ph \quad (42)$$

55.10.2 Linear Gold(I) Complexes with Monodentate Phosphine, Arsine or Stibine Ligands

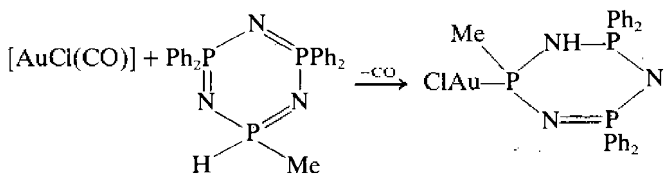
These complexes are stable and easily prepared, and so are very commonly used in gold(I) chemistry. The usual synthetic method involves reaction of $[AuCl_4]^-$ with the tertiary phosphine, arsine or stibine (equation 43; Y = P, As or Sb, R = alkyl or aryl). The phosphine acts as both reducing agent and ligand in these reactions, and the mechanism has been studied in detail.[328]

$$[AuCl_4]^- + 2R_3Y \longrightarrow [AuCl(YR_3)] + R_3YCl_2 + Cl^- \qquad (43)$$

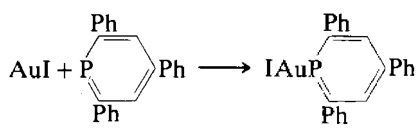
In other syntheses, a weakly bound ligand L is displaced from [AuClL] (L = Me_2S, CO, alkene) by the new ligand, or direct combination of the gold(I) halide with the ligand is used (equations 44–46).[329–331]

Alkyl phosphite complexes can be prepared by alcoholysis of chlorophosphine complexes (equation 47).[274,332]

$$[AuCl(SMe_2)] + Bu^t_3P \longrightarrow [AuCl(Bu^t_3P)] + Me_2S \qquad (44)$$



(45)



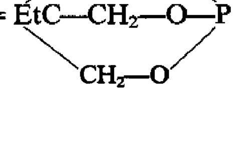
(46)

$$[AuCl(PCl_3)] + 3MeOH \longrightarrow [AuCl\{P(OMe)_3\}] + 3HCl \qquad (47)$$

A great number of complexes [AuXL] are known including derivatives with L = PMe_3, $AsMe_3$,[129] PPh_3,[333] $AsPh_3$, $SbPh_3$,[328] PMe_nPh_{3-n}, PBu^t_3, $P(cyclohexyl)_3$[334] and $P(CH_2SiMe_3)_3$.[335] Structure determinations on $[AuCl(PCl_3)]$,[100] $[AuCl(PPh_3)]$,[101] $[AuBr(AsPh_3)]$[336] and $[AuCl\{P(OPh)_3\}]$[98] confirm the expected linear structures, and detailed studies of vibrational spectra[121–137] and ^{197}Au Mössbauer spectra[23] have been completed. Studies of vibrational spectra of complexes $[AuCl(Ph_2PC{\equiv}CPh)]$ and $[Au_2Cl_2(\mu\text{-}Ph_2PCCPPh_2)]$ indicate that d_π–d_π back-bonding from gold to phosphorus is very weak in these complexes, and other spectroscopic studies are certainly consistent with this view.[337–339]

55.10.3 Complexes of Gold(I) with Excess Phosphine, Arsine or Stibine Ligands

It has long been known that complexes $[AuX(PR_3)]$ (X = halide, R = alkyl or aryl) could interact with excess phosphine to give complexes $AuX(PR_3)_2$, $AuX(PR_3)_3$ or $AuX(PR_3)_4$ but only recently has a good understanding of the system been obtained.[340–346]

A careful study of the system [AuXL] with excess L studied by UV-visible spectroscopy and conductivity indicated the equilibria of equation (48) were significant (X = Cl, Br, I and L = PPh_3). No interaction was observed with the weaker ligands $AsPh_3$ or $SbPh_3$, and the ionization of $[AuXL_2]$ to $[AuL_2]^+X^-$ was only significant for X = Cl, not for X = Br or I.[342] Similar observations were made using the ligands *m*-diphenylphosphinobenzenesulfonate and 2-phenylphosphindoline. For the latter ligand (L) the complex $[AuIL_2]$ was found to be undissociated and non-conducting in dichloromethane solution.[343,344] Preparative and stability constant studies with phosphite ligands, L, showed that complexes up to $[AuL_4]^+$ could be formed.[345] For example with L = 

, the equilibria of equation (49) were

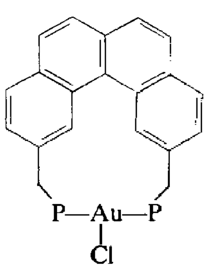
observed, with $K_1 \gg K_2 \gg K_3 > K_4 = 6.6\,M^{-1}$ in acetonitrile solution at 25 °C.[346]

$$[AuXL] \overset{L}{\rightleftharpoons} [AuXL_2] \rightleftharpoons [AuL_2]^+X^- \overset{L}{\rightleftharpoons} [AuL_3]^+X^- \tag{48}$$

$$[Au(MeCN)_2]^+ \underset{K_1}{\overset{L}{\rightleftharpoons}} [AuL(MeCN)]^+ \underset{K_2}{\overset{L}{\rightleftharpoons}} [AuL_2]^+ \underset{K_3}{\overset{L}{\rightleftharpoons}} [AuL_3]^+ \underset{K_4}{\overset{L}{\rightleftharpoons}} [AuL_4]^+ \tag{49}$$

The factors influencing the coordination number for gold(I) are complex and the use of ^{31}P NMR studies in solution and ^{197}Au Mössbauer spectroscopy and X-ray crystallography on solid samples has been vital in studying this problem. In solution studies, the simplest systems use non-coordinating anions such as ClO_4^-, BF_4^- or PF_6^-. Under these conditions, complexes $[AuL_2]^+$, $[AuL_3]^+$ and $[AuL_4]^+$ have been detected using ^{31}P NMR spectroscopy. Exchange of free and coordinated phosphine is fast on the NMR time scale at room temperature but can be slowed at low temperatures. The maximum coordination number is dependent on the bulk of the phosphine used. Thus, when L = P(cyclohexyl)$_3$ only $[AuL_2]^+$ is observed, when L = PBu_3 or P(4-tolyl)$_3$ both $[AuL_2]^+$ and $[AuL_3]^+$ are detected, and when L = PEt_3 or $P(OEt)_3$ $[AuL_2]^+$, $[AuL_3]^+$ and $[AuL_4]^+$ are observed.

In solution studies in which [AuClL] is treated with excess L, the first complex formed is $[AuL_2]^+Cl^-$ with no evidence for $[AuClL_2]$, when L = PEt_3 or P(4-tolyl)$_3$.[348,350] However, in the solid state the situation is different. Thus, both $[AuCl(PPh_3)_2]$ and $[AuCl(PPh_3)_3]$ contain coordinated chloride and have distorted trigonal planar and tetrahedral stereochemistries respectively.[351,352] Complexes $[AuSCN(PPh_3)_2]$ and $[AuSnCl_3(PMe_2Ph)_2]$ are also trigonal planar.[54,353] If the anion is non-coordinating or if the phosphine ligand is very bulky, the linear $[AuL_2]^+$ structure is also observed in the solid state, as in $[Au(PMePh_2)_2][PF_6]$ and $[Au\{P(cyclohexyl)_3\}_2]SCN$ respectively.[354,355] In the 2,11-bis(diphenylphosphinomethyl)benzo-[*c*]phenanthrene derivative (**39**), gold(I) has approximately T-shaped stereochemistry with an almost linear PAuP skeleton and a very long Au—Cl bond.[356]



(**39**)

When three tertiary phosphines are present, complexes may be trigonal planar with non-coordinated anion as in $[Au(PPh_3)_3]^+X^-$ ($X = B_9H_{19}S$, BPh_4 or NO_3) or distorted tetrahedral as in $[AuCl(PPh_3)_3]$ or $[AuSCN(PPh_3)_3]$.[203,357–360]

In complexes with four tertiary phosphines or stibines, the complexes may be regular or distorted tetrahedral $[AuL_4]^+$, as in $[Au(PMePh_2)_4][PF_6]$ or $[Au(SbPh_3)_4][Au(C_6F_5)_2]$.[361,362] However, salts of $Au(PPh_3)_4BPh_4$ may contain mixtures of tetrahedral and trigonal planar gold(I) centres or, in the $CHCl_3$ solvate, essentially trigonal planar gold(I) with one PPh_3 ligand interacting only very weakly with gold. It is probable that steric effects are again important here.[363]

The above discussion has been based largely on structures derived from X-ray studies, but ^{197}Au Mössbauer spectroscopy is also very useful in distinguishing between linear, trigonal and tetrahedral stereochemistry in these complexes. For example a sample analyzing as $Au(AsPh_3)_3ClO_4$ was shown to contain a mixture of $[AuL_2]^+$ and $[AuL_4]^+$ rather than $[AuL_3]^+$ centres by ^{197}Au Mössbauer spectroscopy.[347,364]

There are interesting trends in bond lengths in tertiary phosphine complexes (Table 10). The Au—P and AuCl bond lengths increase dramatically in $[AuCl(PPh_3)_n]$ as n increases from 1 to 3, and there is a similar trend in r(AuP) for the complexes $[Au(PPh_3)_n]^+$ with $n = 2$–4. This increase in bond length is due to a decrease in s character of the hybrid orbitals used by gold in the Au—P bonds, as the hybridization changes from sp to sp^2 and sp^3 in the linear, trigonal and tetrahedral complexes, and also due to steric effects in complexes with higher coordination numbers.

Table 10 Bond Lengths (pm) and Angles (°) in Some Tertiary Phosphine Gold(I) Complexes

Complex	*r(AuP)*	*r(AuX)*	∠*(PAuP)*	*Ref.*
$[AuCl(PPh_3)]$	223.5(3)	227.9(3)		351
$[AuCl(PPh_3)_2]$	232.3–233.9	250.0(4)	132.1(1)	351
$[AuCl(PPh_3)_2]$	223.0–231.3	252.6(10)	136.4(3)	351
$[AuCl(PPh_3)_3]$	239.5–243.1	271.0(2)	116.1–119.6	352
$[Au(SCN)(PPh_3)_2]$	234.6–234.9	246.8(4)	127.8(1)	54
$[Au(SCN)(PPh_3)_3]$	238.4–241.3	279.1(3)	113.8–122.3	203
$[Au(PPh_3)_2][TCNQ]$	228.6(3)	—	180	351
$[Au(PPh_3)_3]^+$	238.2 (mean)		120 (mean)	357–360
$[Au(PPh_3)_4][BPh_4]$	260, 261			363
$[Au(PMePh_2)_2][PF_6]$	231.6(4)		180	353
$[Au(PMePh_2)_4]^+$	244.9		109	362
$[Au(PCy_3)_2][SCN]$	229.5–231.6		180	354

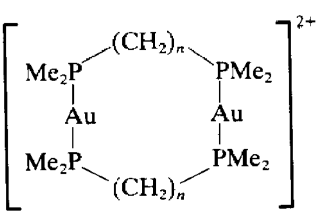
55.10.4 Complexes with Bidentate and Tridentate Ligands

The most common complexes have these ligands bridging between linear gold(I) centres, giving complexes such as [ClAuL⌒LAuCl] where L⌒L = $Ph_2PCH_2PPh_2$, $Ph_2PCH_2CH_2PPh_2$, $Ph_2AsCH_2CH_2AsPh_2$, 2,2′-bis(diethylphosphino)biphenyl, $Bu^t_2POPBu^t_2$ or $Ph_2PNRPPh_2$ (R = H or Me).[102,365–369] Similarly, the tridentate ligand $MeC(CH_2PPh_2)_3$ give a trigold(I) complex $MeC(CH_2PPh_2AuCl)_3$, in which two of the linear gold(I) centres are only 309 pm apart.[103]

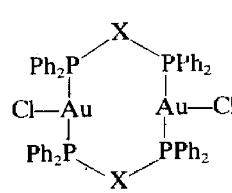
With higher ligand to gold ratios a number of different structural forms have been observed. The simplest complexes are binuclear bridged complexes (**40**) with linear gold(I) centres,[370] but with different UV-visible absorption spectra from mononuclear $[AuL_2]^+$ derivatives.

It is also possible for the anion to coordinate in similar complexes to give three-coordinate gold(I) centres in (**41**)[371–373] in which the diphosphines bridge between gold(I) centres, or in (**39**) and (**42**) in which the diphosphines chelate.[356,374] In the binuclear complex (**41a**) the AuAu separation is only 296 pm.[371]

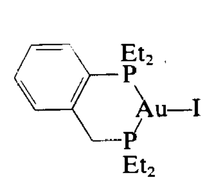
Coordination number four is observed either in chelate complexes, such as (**43**) and (**44**), or in bridged complexes, such as [IAu(μ-$Ph_2PC{\equiv}CPPh_2)_3AuI$].[375–378]



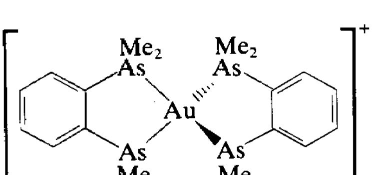
(**40a**) *n* = 1
(**40b**) *n* = 2
(**40c**) *n* = 3



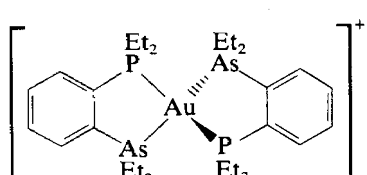
(**41a**) X = CH_2
(**41b**) X = NH



(**42**)



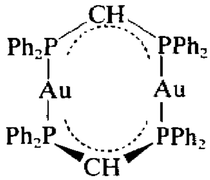
(**43**)



(**44**)

Complexes (**41**) can be deprotonated with strong bases to give the bis(diphenylphosphino)methanide or amide derivatives (**45**) and (**46**), and (**45**) has a remarkably short Au ··· Au contact of 288.8(3) pm.[372,379,380]

Bis(diphenylphosphino)methane also gives the trinuclear complex (**47**), in which there are two linear ClAuP and one linear AuP_2^+ unit, with short gold–gold contacts.[104]



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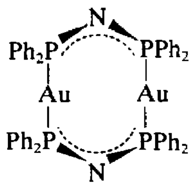

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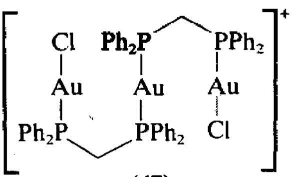


(47)

55.11 COMPLEXES OF GOLD(I) CARBON DONOR LIGANDS[1]

An earlier review treated the organometallic derivatives, including alkyl, aryl, vinyl, alkynyl, carbonyl, carbene, alkene and alkyne complexes,[16] and these will not be treated here (see Table 1 for other books and reviews on organogold chemistry). Two important articles dealing with [AuCl(CO)], including its structure and catalytic properties, have been published recently.[97,381]

55.11.1 Cyanide and Fulminate Complexes[1,2]

The complex $[Au(CN)_2]^-$ is of great commercial significance, since its ready formation from gold, cyanide and oxidizing agents is exploited in the extraction of gold from its ores and because solutions of $[Au(CN)_2]^-$ are often used in gold electroplating applications. The mechanisms involved in these processes have been studied and AuCN is considered a probable intermediate in both systems.[382–386]

Both the cyanide, $[Au(CN)_2]^-$, and fulminate, $[Au(CNO)_2]^-$, ions contain linear gold(I) centres.[387,388] A report that $KAu(CN)_2$(2,2′-bipyridyl) contains square planar gold(I) has been disproved; the bipy ligand is not coordinated to gold and the complex contains linear $[Au(CN)_2]^-$ ions.[389,390] AuCN is polymeric with a linear $(\text{—Au—CN—})_n\text{Au—}$ chain structure.[391]

The neutral cyanide complexes formed according to equations (50) and (51) have been shown to contain linear gold(I) centres,[392,393] and there are also anionic complexes such as $[Au(C_6F_5)(CN)]^-$.[394]

$$[Au(CN)_2]^- + MeI \longrightarrow [Au(CN)(MeNC)] + I^- \quad (50)$$

$$[Au(O_2CMe)(PPh_3)] + HCN \longrightarrow [Au(CN)(PPh_3)] + MeCO_2H \quad (51)$$

The ion $[Au(CN)_2]^-$ has been subjected to exhaustive theoretical and spectroscopic studies.[62,71,85,395–397] In ^{197}Au Mössbauer studies, the sign of the electric field gradient was shown to be negative and the Mössbauer parameters are strongly affected by pressure.[62,398–400]

55.11.2 Isocyanide Complexes

Alkyl and aryl isocyanides are good ligands for gold(I) and many complexes are known. They can be prepared by reaction of the isocyanide with $[AuCl_4]^-$ to give first $[AuCl_3(RNC)]$, which is reduced by excess isocyanide to give [AuCl(RNC)].[401–403] However, the preferred route is to displace SR_2 from the complexes $[AuX(SR_2)]$ (equations 52 and 53).[404–407]

$$[AuCl(SMe_2)] + MeNC \longrightarrow [AuCl(MeNC)] + SMe_2 \quad (52)$$

$$[AuC_6F_5(SC_4H_8)] + PhNC \longrightarrow [AuC_6F_5(PhNC)] + SC_4H_8 \quad (53)$$

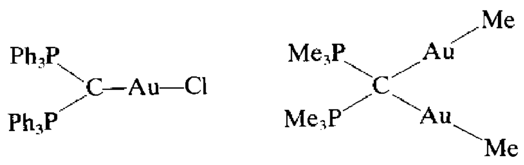
Addition of excess isocyanide ligand gives the ionic $[Au(RNC)_2]^+$ and there is some evidence for $[Au(RNC)_4]^+$ also, but more work is needed to characterize complexes with higher coordination number.[402,403,405,408]

Spectroscopic studies, including vibrational spectroscopy, UV-visible absorption and MCD spectroscopy and ^{197}Au Mössbauer spectroscopy, suggest that isocyanides act largely as σ donors to gold(I) with very little d_π–p_π back-bonding.[69,404,408] It is this polarization R—

$N{\equiv}C^{\delta+}{-}Au^{\delta-}$ which makes the isocyanide ligands susceptible to nucleophilic attack and has led to formation of carbene complexes, iminoalkyl complexes and catalytic conversion of isocyanides to formamidines using alkyl or aryl isocyanide complexes of gold(I).[301,402–407,409–415] A review of this significant work has been published.[16]

55.11.3 Carbodiphosphorane Complexes

Two remarkable complexes (**48**) and (**49**) have been synthesized directly from the carbodiphosphoranes, which are good ligands for gold(I).[416,417]



(**48**) (**49**)

55.12 COMPLEXES OF GOLD(II)[4]

55.12.1 Apparent Gold(II) Complexes

It has long been realized that many complexes which, from the empirical formulae, appear to be gold(II) complexes are really mixed oxidation state gold(I)-gold(III) complexes. Some early examples were the demonstration that $CsAuCl_3$ is $Cs_2[AuCl_2][AuCl_4]$, $AuCl_2S(CH_2Ph)_2$ is $[AuCl\{S(CH_2Ph)_2\}][AuCl_3\{S(CH_2Ph)_2\}]$ and AuCl(DMG) is $[Au(DMG)_2][AuCl_2]$ (DMG = dimethylglyoximate).[418–420] A beautiful recent example is the demonstration that $AuCl_2$ is really Au_4Cl_8 with equal numbers of gold(I) and gold(III) centres (Figure 2).[55] A number of other well-characterized examples are given in Table 11.

Table 11 Some Apparent Gold(II) Complexes

Formula	*Best formulation*	*Ref.*
AuO	$Au^IAu^{III}O_2$	422
AuS	$Au^IAu^{III}S_2$	423
AuSe	$Au^IAu^{III}Se_2$	424
$CsAuCl_3$	$Cs_2[AuCl_2][AuCl_4]$	99, 162
$RbAuBr_3$	$Rb_2[AuBr_2][AuBr_4]$	163
$KAuI_3$	$K_2[AuI_2][AuI_4]$	164
$Rb_3Au_3Cl_8$	$Rb_3[AuCl_2]_2[AuCl_4]$	163
$Rb_2AgAu_3I_8$	$Rb_2Ag[AuI_2]_2[AuI_4]$	165
$K_5Au_5(CN)_{10}I_2$	$K_5[Au(CN)_2]_4[Au(CN)_2I_2]$	425
$Au_2Cl_4(CO)$	$[Cl_3Au^{III}(\mu\text{-}Cl)Au^ICO]$	381
$Au_2Cl_4(MeCCMe)_2$	$[Au(MeCCMe)_2][AuCl_4]$	426
$Au(mnt)PPh_3$[a]	$[Au(PPh_3)_2][Au(mnt)_2]$	427
$Au(dtc)Br$[b]	$[Au(dtc)_2][AuBr_2]$	156

[a] mnt = maleonitriledithiolate. [b] dtc = *N,N*-dibutyldithiocarbamate.

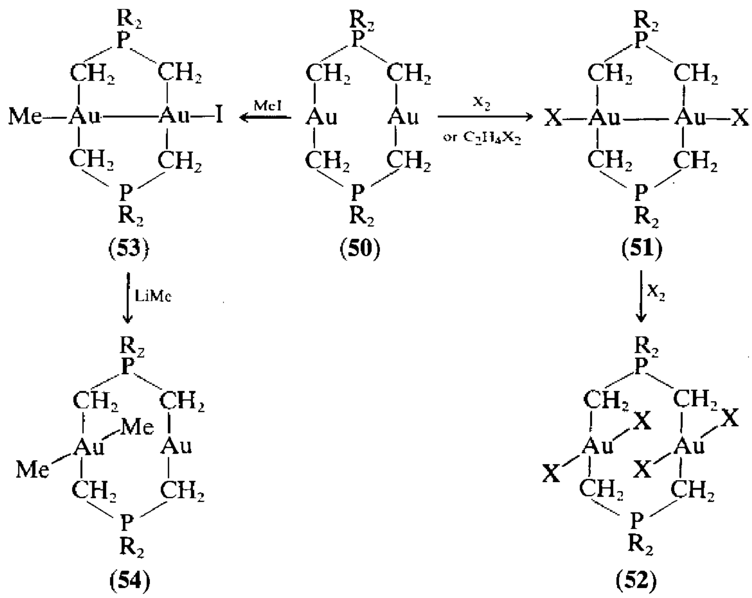
It will be clear from Table 11 that mixed oxidation state complexes need not contain equal numbers of Au^I and Au^{III} centres, and fractional oxidation states between I and III may be observed.[163,165,300,425] The mixed oxidation state complexes can, in many cases, be distinguished from true Au^{II} complexes by ^{197}Au Mössbauer spectroscopy or by ESCA.[4,23,428–429]

Another problem which can arise is the crystallization in the same lattice of $[AuBr_2]^-$ and Br_3^-, or of Au^II and I_3^-. Clearly it will be difficult to assign oxidation states without application of X-ray structure determination, ^{197}Au Mössbauer or ESCA.[166,430]

In the structure of $Cs_2[AuCl_2][AuCl_4]$ there is association between the ions giving each gold atom a very distorted octahedral stereochemistry. At very high pressure the longer interionic $Au \cdots Cl$ distances contract until all gold centres have approximately octahedral stereochemistry, and the system may then become a true gold(II) system. Similar observations have been made on $AuX_2\{S(CH_2Ph)_2\}$ (X = Cl or Br).[431–433]

55.12.2 Binuclear Gold(II) Complexes[4,434]

The formation and reactions of some binuclear gold(II) ylide complexes are shown in Scheme 3. Oxidation of complexes (**50**) with halogens or with ethylene dihalides gives the gold(II) complexes (**51**), in which the gold centres have square planar stereochemistry including formation of a gold–gold bond. The complexes are therefore diamagnetic. A typical structure is given in Figure 2. Further oxidation with halogens occurs with cleavage of the Au—Au bond to give (**52**).[56,434–438]

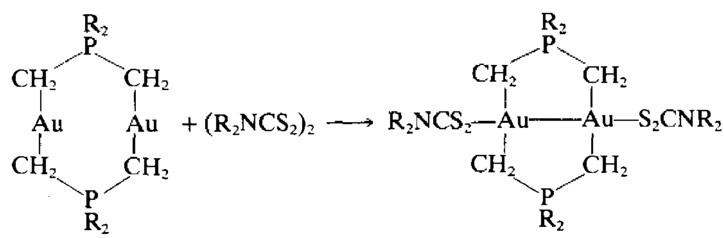


X = Cl, Br, I
R = Me, Et, Bu^t, Ph

Scheme 3

Oxidation of (**50**) with methyl iodide gives (**53**), a methyl gold(II) complex which is very photosensitive. A long-distance *trans* influence is observed in (**53**; R = Me), since r(AuI) = 289.4 pm compared to r(AuI) = 269.9 pm in (**51**; X = I, R = Me).[56] Treatment of (**53**) with methyllithium gives (**54**), which is now a mixed oxidation state complex with both linear gold(I) and square planar gold(III) centres.[435] The reaction illustrates that the gold(I)–gold(III) or binuclear gold(II) complexes may have very similar energies.

Some further examples in which binuclear gold(I) complexes can be oxidized to give binuclear gold(II) complexes are given in equations (54), (55; R = Et, Pr, Bu) and (56; X = CH_2, CMe_2 or NMe).[369,372,441,442a]



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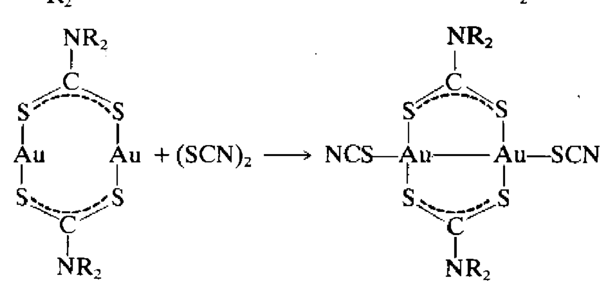

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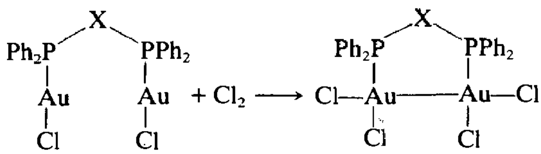
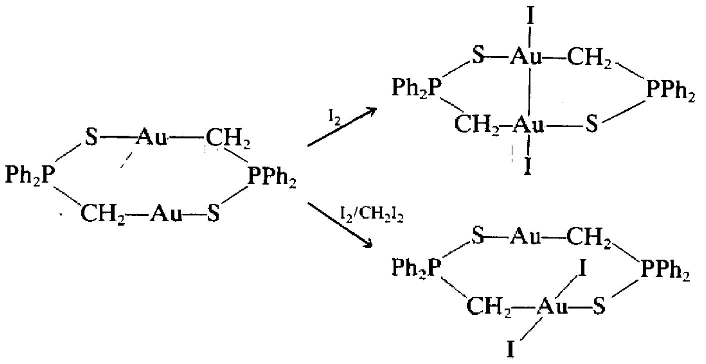


(56)

The gold(II) complex of equation (55)[441] and related species are unstable with respect to disproportionation to the known complexes $[Au(dtc)_2]^+[Au(SCN)_2]^-$.

Remarkably, oxidative addition to $[Au_2\{\mu\text{-}CH_2P(S)Ph_2\}_2]$ may give either a gold(II)-gold(II) or a gold(I)–gold(III) complex as shown in equation (56a).[442b]

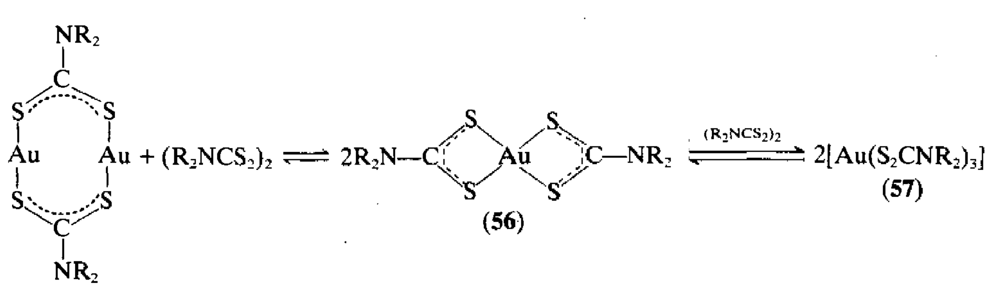


(56a)

55.12.3 Mononuclear Gold(II) Complexes

The first evidence for mononuclear gold(II) complexes was obtained during a study of the reaction (57).

The major species present were (**55**) and (**57**), but the gold(II) complex (**56**) could be detected by ESR at its very low equilibrium concentration.[443] Since the only naturally occurring isotope of gold, ^{197}Au, has $I = \frac{3}{2}$, the ESR spectrum contains four lines of equal intensity due to coupling with the ^{197}Au nucleus. When $R = Pr^i$, the complex has g 2.040 and $A(^{197}Au)$ $28 \times 10^{-4}\ cm^{-1}$. It is thought that the odd electron is in the σ^* $(5d_{x^2-y^2})$ orbital of gold, but is undoubtedly delocalized over the dithiocarbamate ligands, The complexes $[Au(S_2CNR_2)_2]$ can be cocrystallized with the stable diamagnetic complexes $[Ni(S_2CNR_2)_2]$, and a similar diselenocarbamate $[Au(Se_2CNEt_2)_2]$ has been detected by ESR during decomposition of $[AuSe_2CNEt_2]$.[444–446]



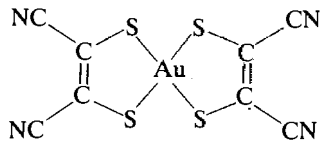
(55)

(56)

(57)

(57)

The first isolated gold(II) complex was the maleonitriledithiolate derivative $(Bu_4N)_2[Au\{S_2C_2(CN)_2\}_2]$, obtained by reduction of the corresponding gold(III) complex with sodium borohydride.[447] The complex is green, air-sensitive and has the square planar structure (**58**). This same complex can be obtained in a comproportionation reaction between $AuCl\{S(CH_2Ph)_2\}\cdot AuCl_3\{S(CH_2Ph)_2\}$ and $Li_2[S_2C_2(CN)_2]$.[448] The anion can be cocrystallized with $(Bu_4N)_2[M\{S_2C_2(CN)_2\}_2]$ (M = Ni, Pd or Pt) and detailed ESR studies suggest that the odd electron in the gold complex is in a largely ligand-based MO.[449] There is also good evidence for the mixed ligand complex $[Au(S_2CNEt_2)\{S_2C_2(CN)_2\}]^-$, formed by reduction of the gold(III) derivative.[450]



(58)

The gold(II) complex $[Au\{S_2C_2(CF_3)_2\}_2]$ forms a charge transfer complex with tetrathiafulvalene, which gives one of the very few examples of a spin-Peierls transition, in which a system of 1D antiferromagnetic $S = \frac{1}{2}$ Heisenberg chains becomes progressively dimerized as a result of magnetoelastic coupling with the 3D lattice phonons. As a result its magnetic properties have been studied in very great detail.[451–454]

There are two other significant gold(II) complexes. The phthalocyanine complex of gold(II) was prepared by reaction of AuBr with 1,3-diiminoisoindoline at 250 °C and was characterized by its ESR spectrum,[455] while the carborane derivative $(Et_4N)_2[Au(B_9C_2H_{11})_2]$, which is a blue-green solid, has the magnetic moment $\mu_{eff} = 1.79$ BM expected for a mononuclear gold(II) complex.[456]

55.12.4 Gold(II) Complexes as Reaction Intermediates

The first evidence for gold(II) was obtained from a study of the Fe^{II}-catalyzed exchange of chloride with $[AuCl_4]^-$. The first step was thought to involve formation of a labile gold(II) complex formed according to equation (58).[457]

$$Fe^{2+} + [AuCl_4]^- \longrightarrow Fe^{3+} + [AuCl_4]^{2-} \quad (58)$$

Many other redox reactions involving gold(I)–gold(III) interconversions are thought to involve gold(II) intermediates,[57,458,459] but only in one case have they been sufficiently long-lived to enable direct detection by ESR.[443]

55.13 HALIDE COMPLEXES OF GOLD(III)

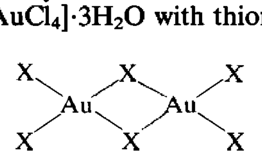
55.13.1 Fluoride Complexes

The parent $[(AuF_3)_n]$ is best prepared by reaction of Au or $[Au_2Cl_6]$ with fluorine. It has a unique fluorine-bridged helical chain structure.[460,461] Tetrafluoroaurates(III) can be prepared directly from $[(AuF_3)_n]$ (equation 59), by reaction of BrF_3 with gold in the presence of KCl or Ag to give $K[AuF_4]$ or $Ag[AuF_4]$ respectively, or by reaction of $[AuCl_4]^-$ salts with F_2 or BrF_3.[462,463] All these fluoride complexes are hydrolyzed by water and react with benzene to give fluorinated derivatives.[460] Complexes $[AuF_3{\cdot}SeF_4]$ and $[AuF_3{\cdot}BrF_3]$ are known and are thought to contain a bridging fluoride ligand.

$$NOF + AuF_3 \longrightarrow [NO]^+[AuF_4]^- \quad (59)$$

55.13.2 Chloride and Bromide Complexes

The parent halides $[Au_2X_6]$ (X = Cl, Br) have structure (**59**), with square planar gold(III).[464,465] They can be prepared by direct combination of the elements, and $[Au_2Cl_6]$ can also be prepared by reaction of $H[AuCl_4]{\cdot}3H_2O$ with thionyl chloride.[466–468]



(59) X = Cl or Br

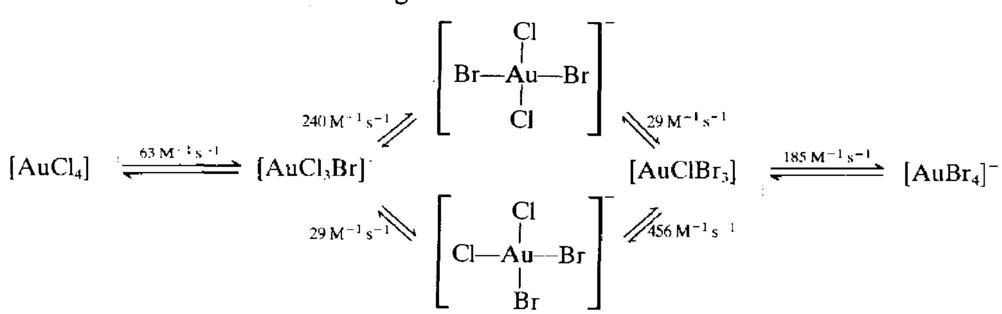
The acids $H[AuCl_4]$ and $H[AuBr_4]$ are prepared by oxidation of gold in the presence of HCl or HBr. The oxidant can be concentrated HNO_3, Cl_2 or Br_2, and many others or electrochemical oxidation can be effected.[469,470] The acids can be crystallized in hydrated forms, and give many salts such as $Na[AuCl_4]\cdot 2H_2O$, $K[AuCl_4]$ and $K[AuBr_4]\cdot 2H_2O$.

The ions $[AuCl_4]^-$ and $[AuBr_4]^-$ have regular square planar stereochemistry both in the solid state and in solution,[7,471–473] and their spectroscopic properties have been studied exhaustively.[83–90]

There have been claims that association of $[AuX_4]^-$ with added halide or pseudohalide can occur to give spectroscopically observed complexes with coordination number five or six.[478,480] However, these claims have not been confirmed and, in some cases, have been disproved.[481,482] For example, $[AuBr_4]^-$ reacts with Br^- to give no $[AuBr_6]^{3-}$ but $[AuBr_2]^-$ and Br_3^-, which then reacts with solvent, and $[AuCl_4]^-$ with Br^- gives not $[AuCl_4Br]^-$ but $[AuCl_nBr_{4-n}]^-$. The equilibrium constant for equation (60) is given by $\log K = 7.3 \pm 0.3$, the bromide complex being more stable for the soft gold(III) centre.[481,483]

$$[AuCl_4]^- + 4Br^- \rightleftharpoons [AuBr_4]^- + 4Cl^- \quad (60)$$

Although there is little evidence for long-lived five-coordinate complexes derived from $[AuCl_4]^-$ or $[AuBr_4]^-$, there is no doubt that ligand substitution reactions involve short-lived five-coordinate intermediates. For substitution of ligands Y^- (NO_2^-, N_3^-, Br^-, I^-, SCN^-) for Cl^- in $[AuCl_4]^-$ the rates were shown to follow the rate law $-d/dt[AuCl_4^-] = \{k_1 + k_2[Y^-]\}[AuCl_4^-]$. The k_1 term corresponds to the usual associative displacement by solvent, while the k_2 term corresponds to direct displacement of Cl^- by Y^-. Gold(III) displays a very high discriminating power for soft entering ligands, indicating that bond formation is important in the transition state.[481,484] The rates are also dependent on the *trans* effect of the *trans* ligand and on the nature of the leaving group.[481,484–486] For the substitution of bromide for chloride in $[AuCl_4]^-$, the k_1 term is very small and the magnitudes of the second-order rate constants k_2 for the consecutive substitution reactions leading to $[AuBr_4]^-$ are given in equation (61).[481] The effect on the rate constants of the large *trans* effect of Br^- over Cl^- is obvious.



(61)

The catalytic effect of iron(II) on the substitution reactions of $[AuCl_4]^-$ is well known. Larger amounts of iron(II) can reduce $[AuCl_4]^-$ to $[AuCl_2]^-$ and the reaction proceeds in two one-electron steps.[487,488] However, with reducing agents such as $[PtCl_4]^{2-}$ or $[PtCl_2(2,2'$-bipyridine)], the reduction of $[AuCl_4]^-$ occurs in one two-electron step with Cl atom transfer.[488,489] The reduction of $[AuCl_4]^-$ by ligands like phosphines, arsines, stibines, thioethers and thiourea is also thought to involve one two-electron reduction step, again with Cl atom transfer, as discussed in previous sections.[490,491]

Complexes of formula $AuCl_3\cdot XCl_4$, where X = S, Se or Te, can be prepared (equation 62). These complexes contain distorted square planar $AuCl_4$ coordination with a bridging chloride $[Cl_3AuClXCl_3]$, but in solution they ionize to give $[XCl_3][AuCl_4]$.[492–495]

$$Au_2Cl_6 + 2SCl_2 + 2Cl_2 \longrightarrow 2AuCl_3\cdot SCl_4 \quad (62)$$

An important reaction of gold(III) chloride[496,497] and, under some conditions, of $H[AuCl_4]$[498] is the ability to metallate aromatic compounds to give arylgold(III) complexes. The reader is referred to an earlier review for details.[16]

55.13.3 Iodide Complexes

Gold(III) iodide complexes may be easily reduced to gold(I) in many cases. For example, the equilibrium constant for equation (63) in aqueous solution is $200\,M^{-1}$, corresponding to about

25% conversion to $[AuI_4]^-$ in saturated iodine solution.[482,499]

$$[AuI_2]^- + I_2 \rightleftharpoons [AuI_4]^- \quad (63)$$

Pure $Et_4N[AuI_4]$ can be prepared by reaction of $Et_4N[AuCl_4]$ with anhydrous liquid HI, but it is of limited stability.[482] There are more stable derivatives such as *trans*-$[AuI_2\{C(NHC_6H_4Me)_2\}_2]^+$ and *trans*-$[AuI_2(CN)_2]^-$, formed by iodine oxidation of the corresponding gold(I) complexes.[500]

55.14 HYDRIDE COMPLEXES OF GOLD(III)

There are no well-characterized hydrides of gold(III), though there is evidence for formation of AuH_3, $Li[AuH_4]$, $Au(BH_4)_3$ and $Au(AlH_4)_3$ at −120 °C. They decompose on warming to hydrogen and metallic gold.[501]

55.15 COMPLEXES OF GOLD(III) WITH OXYGEN DONOR LIGANDS

There is no evidence for the simple aqua ion $[Au(OH_2)_4]^{3+}$, but mixed chloro-aqua and chloro-hydroxo complexes are formed by hydrolysis of $[AuCl_4]^-$ (equations 64 and 65).[502–504]

$$[AuCl_4]^- + H_2O \rightleftharpoons [Au(OH_2)Cl_3] + Cl^- \quad (64)$$

$$[Au(OH_2)Cl_3] \rightleftharpoons H^+ + [Au(OH)Cl_3]^- \quad (65)$$

Gold(III) oxide, Au_2O_3, contains square planar gold(III) with bridging oxo ligands, and the compounds AuOCl and $Au_2O(SeO_3)_2$ are also polymeric with bridging oxo ligands.[107,505,506] Little is known about their coordination chemistry.[507–509]

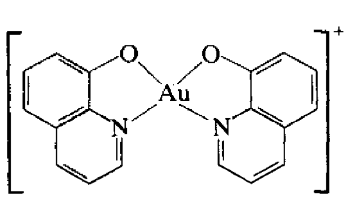
The compound $[Au(SO_3F)_3]$ has been prepared and is a powerful acceptor for SO_3F^-. Thus complexes of $[Au(SO_3F)_4]^-$ with cations K^+, Br_3^+, Br_5^+, $[I(SO_3F)_2]^+$ and $[Br(SO_3F)_2]^+$ have been prepared. $H[Au(SO_3F)_4]$ is a strong acid when dissolved in HSO_3F. Complexes can be prepared by several methods, for example as shown in equation (65a).[510–512]

$$KCl + AuCl_3 + 4BrSO_3F \longrightarrow K[Au(SO_3F)_4] + 2Cl_2 + 2Br_2 \quad (65a)$$

Nitrato complexes, with monodentate nitrate, are very similar to the fluorosulfates. Thus $Au(NO_3)_3$ and the better characterized salts of $[Au(NO_3)_4]^-$ are known. For example reaction of gold with N_2O_5 gives $[NO_2]^+[Au(NO_3)_4]^-$, and the structure of $K[Au(NO_3)_4]$ has been determined.[513–515]

In the complex oxides $MAuO_2$ (M = K or Rb) there are infinite chains with square planar gold(III) centres linked by μ_2-oxo ligands, while M_3AuO_3 are properly formulated $M_6[Au_2O_6]$ in which the anion is isostructural with $[Au_2Cl_6]$.[516,517]

As well as complexes containing only oxygen donors, there are several gold(III) complexes with mixed O,N donors. These are typically prepared by substitution of $[AuCl_4]^-$ with the appropriate ligand. Some examples are **(60)**–**(63)**.[518,519]



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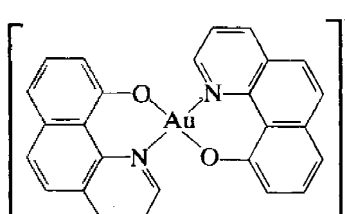

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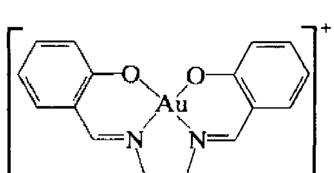

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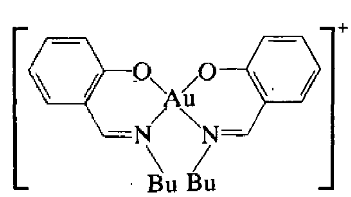


(63)

55.16 COMPLEXES OF GOLD(III) WITH SULFUR, SELENIUM AND TELLURIUM DONOR LIGANDS

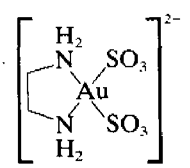
55.16.1 Sulfide, Selenide and Telluride Complexes

The complexes Au_2X_3 (X = S, Se or Te) are known but their structures are uncertain.[520] In AuSeBr all gold(III) centres have square planar coordination, but some have $AuSe_4$ and some $AuSe_2Br_2$ structures.[521] In $AuTe_2X$ (X = Cl or I), there are polymeric $[Au(Te_2)]_n^+X^-$ units with ditelluride, Te_2^{2-}, ligands bridging between square planar gold(III) centres. The compounds exhibit metallic conductivity.[522–524]

55.16.2 Sulfite and Selenite Complexes

Reaction of Na_2SO_3 with $[Au(OH)_4]^-$ gives $[Au(SO_3)_4]^{5-}$ and the salt $Na_5[Au(SO_3)_4]\cdot 5H_2O$ has been isolated.[51] This contains S-bonded sulfite, and can be reduced by excess sulfite to $[Au(SO_3)_2]^{3-}$. Selenite complexes of gold(III) are O-bonded, however.[525]

The structure of $[Au(SO_3)_2(NH_2CH_2NH_2)]^{2-}$ has been determined and shown to be (**64**) with S-bonded sulfite.[526]

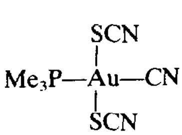


(**64**),

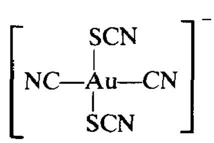
55.16.3 Thiocyanate Complexes

Most thiocyanato complexes of gold(III) are S-bonded. These include $[Au(SCN)_4]^-$ and the complexes (**65**)–(**67**), which are formed by oxidative addition of thiocyanogen to the corresponding gold(I) complex.[295,527–529]

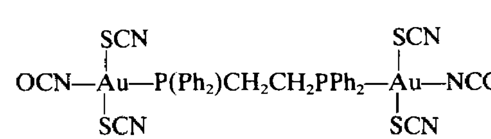
An apparent exception is seen in the products from reaction of $[Au(SCN)_4]^-$ with $(Et_2NCH_2CH_2)_2NCS_2^-$, which are thought to exist as an equilibrium mixture of isomers as shown in equation (66).



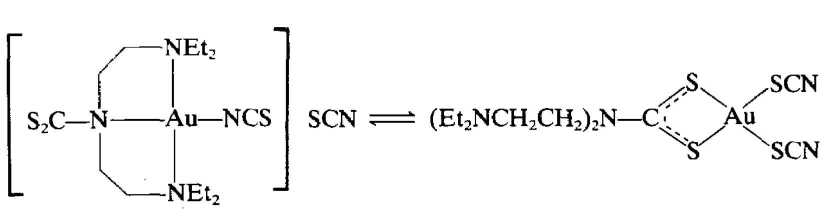
(**65**)



(**66**)



(**67**)

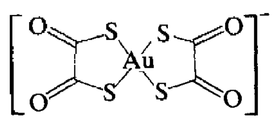
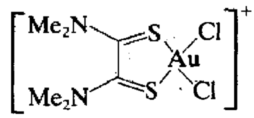


(66)

Many organometallic derivatives are known, including complexes with bridging thiocyanate ligands.[530,531]

55.16.4 Complexes with Ligands Having C = S Groups

There are a considerable number of complexes of thioketones, thioamides, thioacids and thiourea, some examples being (**68**) and (**69**).[532,536]

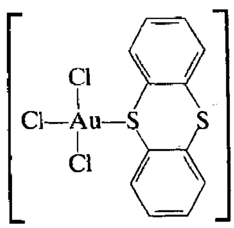
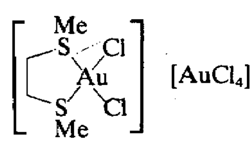
(68) (69)

In some cases easy reduction to gold(I) may occur and in others the gold(III) centre may catalyze hydrolysis of the ligand.[537–539]

55.16.5 Complexes with Thioether Ligands

Complexes $[AuCl_3(SR_2)]$ and $[AuBr_3(SR_2)]$ are numerous. They are usually prepared by oxidation of the gold(I) complex $[AuCl(SR_2)]$ or $[AuBr(SR_2)]$ with the required halogen. These are also formed as intermediates in the reaction of excess thioethers with $[AuCl_4]^-$ or $[Au_2Cl_6]$ to give $[AuCl(SR_2)]$, and the redox reactions between gold(I) and gold(III) are particularly easy in these derivatives.[219–222,227] The IR and NMR spectra of the complexes have been analyzed,[121,127,134,222] and the molecular structure of $[AuCl_3(\text{thianthrene})]$ **(70)** has been determined.[113]

The bidentate ligand $MeSCH_2CH_2SMe$ forms a chelate derivative of gold(III) **(71)**, but the structures of $AuCl_3{\cdot}L$ where $L = MeSe(CH_2)_3SeMe$ or $Se(CH_2CH_2)_2Se$ are not known.[219,540,541]

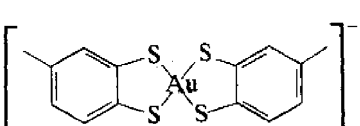
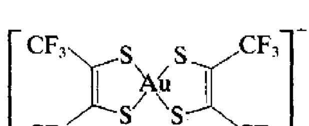
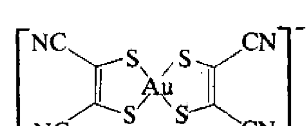
(70) (71)

55.16.6 Dithiolate and Dithiocarbamate Complexes

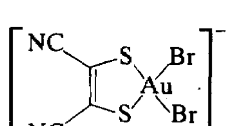
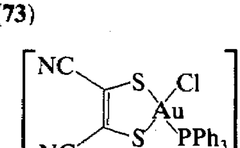
1,2-Dithiols give several stable square planar gold(III) complexes. Some complexes of biochemical interest are those derived from 2,3-dimercaptopropanol (BAL),[230] dimercaptosuccinic acid[249] and penicillamine.[542] These are thought to have structures similar to that of the toluenedithiolate derivative **(72)**.[543] They can be prepared by reaction of $[AuCl_4]^-$ with the dithiol and base or by oxidation of gold in the presence of the dithiol.

Also significant are the alkene dithiolate derivatives such as **(73)** and **(74)**, prepared according to equations (67) and (68).[544,545]

Using the mild transfer agent $Me_2SnS_2C_2(CN)_2$, it is possible to prepare complexes such as **(75)** and **(76)** with only one dithiolate ligand.[287]

(72) (73) (74)

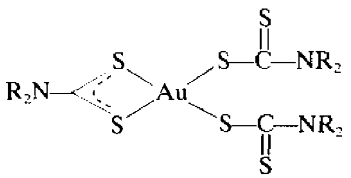
(75) (76)

$$[AuCl(PPh_3)] + \begin{matrix} CF_3\text{—}C\text{—}S \\ \| \quad | \\ CF_3\text{—}C\text{—}S \end{matrix} \longrightarrow [PClPh_3][Au\{S_2C_2(CF_3)_2\}_2] \tag{67}$$

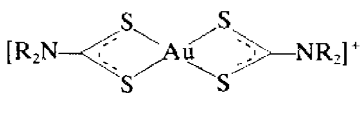
$$[AuCl_3(PPh_3)] + Na_2S_2C_2(CN)_2 \xrightarrow{PPh_3} [Au(PPh_3)_2][Au\{S_2C_2(CN)_2\}_2] \tag{68}$$

Dithiocarbamate and related complexes of gold(III) have been studied in great detail. There are two types of derivatives of general structures (**77**) and (**78**), having AuS_4 coordination. Complexes (**77**) are formed by oxidative addition of $(R_2NCS_2)_2$ to the gold(I) dithiocarbamate, while (**78**) can be formed by halogen oxidation of gold(I) dithiocarbamate. Both reactions involve gold(II) intermediates as discussed in Section 5.12.2.[156,546–552]

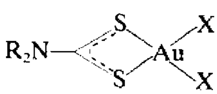
Oxidation of gold(I) dithiocarbamates with excess halogen, X_2, gives the complexes (**79**; X = Cl or Br).[533,554]



(**77**)



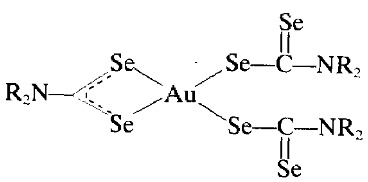
(**78**)



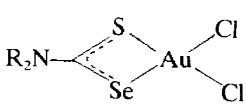
(**79**)

Diselenocarbamate and thioselenocarbamate complexes such as (**80**) and (**81**) can be prepared in similar ways,[555–557] and the dithiophosphinate $[Au\{SP(S)Ph_2\}_3]$ is clearly related.[558,559]

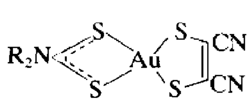
Finally, the mixed ligand complexes with both dithiocarbamate and 1,2-dithiolate ligands should be mentioned. Both neutral and ionic isomers (**82**) and (**83**) have been characterized.[560–562]



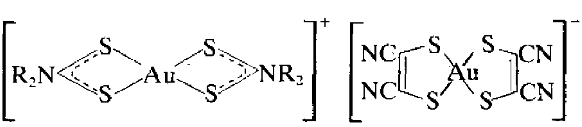
(**80**)



(**81**)



(**82**)



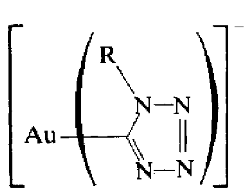
(**83**)

There are interesting addition compounds of $[AuBr_2(S_2CNBu_2)]$ with *trans*-stilbene and *trans*-azobenzene,[563] the electrical resistivity of $[Au(S_2CNR_2)_2][TCNQ]$ has been studied,[564] and the mechanism of decomposition of gold(III) dithiocarbamates has been investigated using photoelectron spectroscopy.[565]

55.17 COMPLEXES OF GOLD(III) WITH NITROGEN DONOR LIGANDS

55.17.1 Azide Complexes

The complex ion $[Au(N_3)_4]^-$ reacts with alkyl isocyanides according to equation (69),[291] and with CO to give $[Au(NCO)_2]^-$.[294] Azide-bridged complexes such as $[Au_2(\mu\text{-}N_3)_2Me_4]$ are also known. The ligand field and charge transfer bands in the UV-visible spectra of $[Au(N_3)_4]^-$ have been assigned and the structure determined.[567]

$[Au(N_3)_4]^- + 4RNC \longrightarrow$  (69)

55.17.2 Ammine Complexes

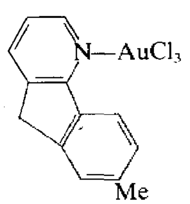
The complex ion $[Au(NH_3)_4]^{3+}$ has been well characterized.[310,568] The complex is a weak acid with pK_a 7.5, but the hydrolysis product $[Au(NH_3)_3(OH_2)]^{3+}$ is a strong acid with pK_a −0.7; the primary species in solution is thus $[Au(NH_3)_3(OH)]^{2+}$. A formation constant for $[Au(NH_3)_4]^{3+}$, $\beta_4 \approx 10^{46}$, has been estimated.[569]

The substitution of bromide for ammonia in $[Au(NH_3)_4]^{3+}$ occurs in a stepwise fashion to give $[AuBr(NH_3)_3]^{2+}$, *trans*-$[AuBr_2(NH_3)_2]^+$, $[AuBr_3(NH_3)]$ and $[AuBr_4]^-$, and the corresponding second-order rate constants follow the sequence $k_1 < k_2 \gg k_3 < k_4$. As a result the complex *trans*-$[AuBr_2(NH_3)_2]Br$ can be isolated from partially reacted mixtures.[570] The complex $[AuCl_3(NH_3)]$ has been isolated in a different way by pyrolysis of $NH_4[AuCl_4]$, and its structure has been determined.[119]

55.17.3 Complexes with Other Monodentate Nitrogen Donor Ligands

There is a very extensive range of complexes $[AuCl_3L]$, which are easily prepared by reaction of either $[AuCl_4]^-$ or $[Au_2Cl_6]$ with the corresponding nitrogen donor ligand L. Bromo derivatives $[AuBr_3L]$ are prepared similarly. Complexes with L = pyridine are most commonly studied and the cationic $[AuCl_2L_2]^+$ may be prepared by further displacement of chloride by pyridine or its derivatives.[571–573] The vibrational spectra, electronic spectra and mechanisms of substitution of pyridine for chloride (and the reverse reaction) have been studied.[92,574–580]

Similar complexes $[AuCl_3L]$ are known for L = RCN,[573,581] pyrazoles[582] and nicotinic acid.[583] More complex examples include the azafluorene and diazepine derivatives **(84)**–**(86)**.[109,110,584]



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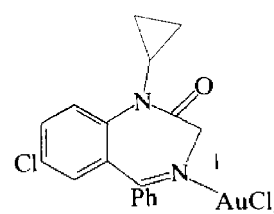

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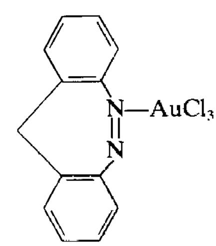
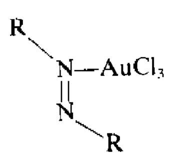


(86)

The complexes $[AuCl_3(RN{=}NR)]$ (**87**; R = Ph or 4-toly) decompose on heating to give 2-chloroazobenzene or 2-chloroazotoluene, and it is proposed that an intermediate (**88**) is formed.[120,572,585,586] This complex (**88**) can be isolated by metathesis from the corresponding mercury(II) complex.[587,588]



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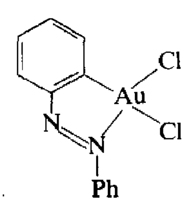


(88)

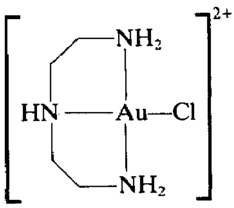
55.17.4 Complexes with Diamine and Triamine Ligands

The NH protons of diamine and triamine complexes of gold(III) are acidic, as shown by the data in Table 12. The acidity increases with the degree of substitution at nitrogen, and the trend is attributed primarily to steric effects.[589–591]

The amido ligand has a higher *trans* influence than the amine ligand as can be seen from the Au—Cl bond lengths of 227 pm and 233 pm in the related dien and (dienH) derivatives (**89**) and (**90**) respectively.[592] However, it has not yet been shown that the longer Au—Cl bond length in (**90**), and in related derivatives of $(Et_4dien\text{-}H) = (Et_2NCH_2CH_2)_2N^-$, leads to greater lability of the Au—Cl bond towards ligand substitution.[590–599]

Table 12 pK_a Values of Amine Complexes of Gold(III)

Complex	pK_a	*Ref.*
$[Au(NH_3)_4]^{3+}$	7.48	569
$[Au(en)_2]^{3+}$	6.3	589, 590
$[Au(dien)OH]^{2+}$	5.8	590
$[Au(dien)Br]^{2+}$	4.5	590
$[Au(dien)Cl]^{2+}$	4.0	590
$[Au(Et_4dien)Cl]^{2+}$	2.2	591



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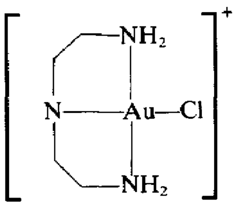


(90)

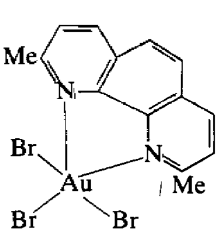
The chelate ligands in these complexes can be displaced from gold in acidic solution, and the reactions involve a stepwise sequence in which each nitrogen is displaced from gold and then protonated, thus preventing the back reaction.[595,599,600]

The ion $[Au(en)_2]^{3+}$ associates with chloride in solution, and in the solid state the ion $[AuCl_2(en)_2]^+$ is found to have distorted octahedral stereochemistry.[600–602] On reaction with chlorine, $[Au(en)_2]^{3+}$ gives the chloroamine derivative $[AuCl_2(HClNCH_2CH_2NHCl)]Cl$ by reaction at the ethylenediamine ligand.[603,604]

55.17.5 Complexes with Other Polydentate Nitrogen Donor Ligands

The complexes of gold(III) with 2,2′-bipyridine, 1,10-phenanthroline and related ligands have been much studied.[605–608] In solution, complexes such as $[AuCl_2(bipy)]Cl$ or $[AuBr_2(phen)]Br$ were characterized, but it was suggested that the neutral complexes such as $[AuBr_3(phen)]$ were present in the solid state. However, it is now thought that the square planar forms persist in the solid state.[609,610] There is evidence for association of $[AuCl_2(bipy)]^+$ and $[AuCl_2(5\text{-nitrophen})]^+$ with chloride in solution, prior to the displacement of the chelate ligands from gold by excess chloride.[611–612]

The formation of five-coordinate gold(III) has been demonstrated clearly in the complexes of 2,9-dimethyl-1,10-phenanthroline and 2,2′-biquinoline, which have the distorted square pyramidal structures (**91**) and (**92**). However, the structures of the ligands prevent square planar coordination, so that these examples are atypical.[613–615] However, a related organometallic derivative, $[AuCl(C_4Ph_4)(phen)]$, is known and has a similar distorted square pyramidal structure.[616]



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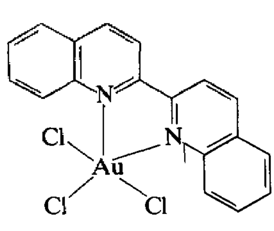
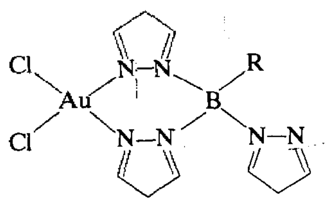


(92)

In gold(III) complexes with tripyrazolylborate or tripyrazolylmethane and related ligands, only two nitrogen atoms coordinate giving complexes such as (**93**) and (**94**) with square planar stereochemistry.[617–619]

In the 2,2′,2″-terpyridyl complex $[AuCl(terpy)]Cl_2{\cdot}H_2O$, one chloride and the water molecule coordinate very weakly to the square planar $[AuCl(terpy)]^{2+}$ ion.[108]



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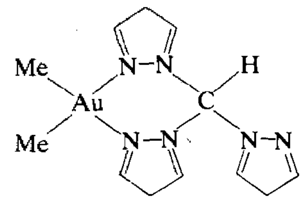
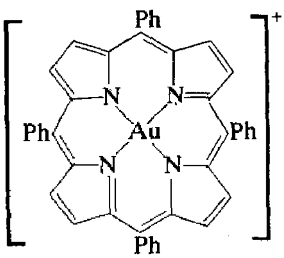


(94)

There are several porphyrin derivatives of gold(III) such as the tetraphenylporphyrinatogold(III) cation, $[Au(TPP)]^+$ (**95**), which forms a square pyramidal complex [AuCl(TPP)] with chloride.[620–622] Reduction of the latter complex gives the phlorin derivative (**96**).[623]

The macrocyclic complexes (**97**) and (**98**) have been prepared by template synthesis.[624–626]



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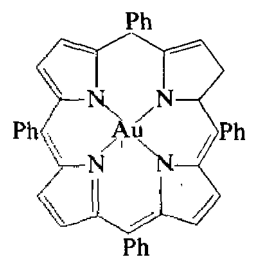

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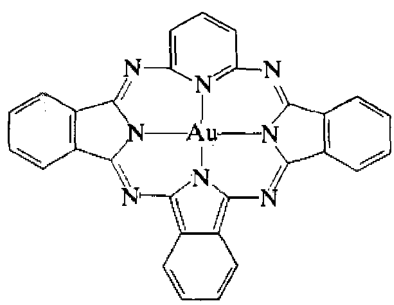

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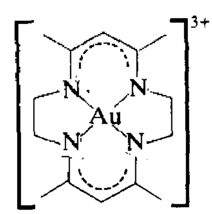


(98)

55.18 COMPLEXES OF GOLD(III) WITH PHOSPHINE, ARSINE AND STIBINE LIGANDS

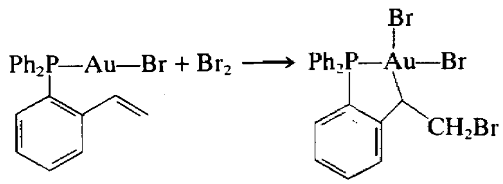
Complexes $[AuX_3(PR_3)]$ are usually prepared by oxidation of the gold(I) derivative $[AuX(PR_3)]$ with the corresponding halogen. Mixed halogen complexes can be prepared in a similar way as in equation (70).[329,627]

$$[AuCl(PEt_3)] + I_2 \longrightarrow [AuClI_2(PEt_3)] \qquad (70)$$

These complexes have sharp melting points and were long considered to be pure compounds, but NMR studies show that they contain all possible combinations and isomers of formula $[AuX_nY_{3-n}(PR_3)]$.[628,629]

The complexes $[AuCl_3(PPh_3)]$ and $[AuMe_3(PPh_3)]$ have distorted square planar stereochemistry, and the electronic structure of $[AuMe_3(PMe_3)]$ has been studied by photoelectron spectroscopy.[93,95,115]

Halogen oxidation of gold(I) complexes can also give products involving reaction of phosphine substituents or give binuclear gold(III) complexes (equations 71 and 72).[369,630]



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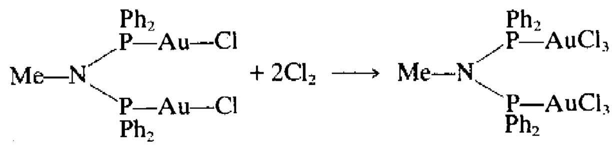


(72)

Oxidation of the tetrahedral derivatives $[Au(L\frown L)_2]^+$, where $L\frown L = o\text{-}C_6H_4(AsMe_2)_2$ or $o\text{-}C_6H_4(PMe_2)_2$, gives gold(III) complexes based on $[Au(L\frown L)_2]^{3+}$. However, this square planar unit binds to added halides to give $[AuX(L\frown L)_2]^{2+}$, presumed to have square pyramidal structure, or $[AuX_2(L\frown L)_2]^+$, with tetragonally distorted octahedral structure.[631–633] The axial bonds to halogens are weak, and the attraction may be primarily electrostatic in origin, as in the amine complexes discussed earlier. In the neutral complex $[Au(C_6F_5)_3\{o\text{-}C_6H_4(AsMe_2)_2\}]$, only one of the arsenic centres is coordinated and the stereochemistry is distorted square planar.[635]

55.19 COMPLEXES OF GOLD(III) WITH CARBON DONOR LIGANDS

Organometallic derivatives have been reviewed elsewhere.[1,2,15–21,635]

55.19.1 Cyanide complexes

The $[Au(CN)_4]^-$ has square planar stereochmistry as determined for the acid $H[Au(CN)_4]\cdot 2H_2O$ and the salt $K[Au(CN)_4]\cdot H_2O$.[636,637] The ions $[Au(CN)_2X_2]^-$ (X = Cl, Br, I) have *trans* stereochemistry and are formed by oxidation of $[Au(CN)_2]^-$ with the corresponding halogen.[638–642] The oxidation of $[Au(CN)_2]^-$ by I_3^- is much faster than by I_2 and a single step *trans* oxidative addition has been suggested.[643] The electronic spectra of these complexes and of *trans*-$[Au(CN)_2BrCl]^-$ have been assigned.[664]

A number of organometallic derivatives $[AuR_2(CN)_2]^-$, R = aryl, have *cis* stereochemistry.[645]

55.19.2 Isocyanide Complexes

Isocyanide complexes, such as $[AuCl_3(PhNC)]$, may be prepared by reaction of the isocyanide with $H[AuCl_4]$ or by chlorine oxidation of $[AuCl(PhNC)]$.[646] Organometallic derivatives have been prepared in a similar way; for example, $[Au(C_6F_5)(PhNC)]$ with bromine gives $[AuBr_2(C_6F_5)(PhNC)]$.[406]

55.20 COMPLEXES OF GOLD(V)

The first pure gold(V) complex to be prepared was $[Xe_2F_{11}][AuF_6]$, formed by reaction of AuF_3 with fluorine and XeF_2.[58] The $[AuF_6]^-$ ion is approximately octahedral with r(AuF) 186 pm.[647]

A number of other salts of $[AuF_6]^-$, including those with the cations K^+, Cs^+, NO^+, O_2^+, $[BrF_6]^+$, $[IF_6]^+$, XeF^+, $Xe_2F_3^+$, $[XeF_5]$ and KrF^+, have since been prepared.[648–656] The simplest synthesis involves fluorine oxidation of $M[AuF_4]$ to give $M[AuF_6]$, with M = K, Cs or NO.[4]

Spectroscopic studies confirm the presence of $[AuF_6]^-$ in most of the above salts, but in $[KrF][AuF_6]$ it seems that there is significant interaction between the ions through a bridging fluoride.[651,653–655] This complex is prepared by reaction of gold in liquid HF with KrF_2.[650,651]

Thermal decomposition of [KrF][AuF_6] or [O_2][AuF_6] gives the parent fluoride AuF_5, which is a fluoride-bridged polymer in the solid state.[648,650,651,654] However, in the gas phase AuF_5 exists as a mixture of dimer [Au_2F_{10}] and trimer [Au_3F_{15}] with approximately octahedral stereochemistry at each gold centre.[657]

55.21 COMPLEXES WITH GOLD–GOLD BONDS

55.21.1 Gold–Gold Bonding in Gold(I) Complexes

In linear gold(I) complexes, the molecules often pack so that short intermolecular AuAu contacts are observed. Such AuAu contacts are typically in the region 275–340 pm. For comparison the AuAu distances in metallic gold, gaseous Au_2 molecules and binuclear gold(II) complexes are 288.4 pm, 250 pm and *ca.* 260 pm respectively. A detailed review of the structures of gold(I) complexes with apparent intermolecular AuAu bonding has been published,[7] and many examples were given in Sections 55.6–55.11.

The intermolecular bonding forces between linear gold(I) centres are not directional in nature. Thus such contacts can involve pairs of gold(I) centres (*e.g.* complex **38**), linear chains of gold(I) centres (*e.g.* Figures 7 and 8), squares of gold(I) centres (*e.g.* complex **72**) or infinite two dimensional arrays of gold(I) centres (*e.g.* MeNCAuCN).[2,7] A bonding picture which can explain these data is outlined below. The linear gold(I) complexes are assumed to use the $6s$–$5d_{z^2}$ hybrid ψ_2 (Figure 3) and $6p_z$ orbital to interact with the ligands along the molecular z axis. The remaining filled $5d_{z^2}$–$6s$ hybrid orbital, and vacant $6p_x$ and $6p_y$ orbitals are then available to interact in the xy plane, forming the weaker intermolecular AuAu bonding interactions. The orbitals are expected to give maximum overlap with AuAuAu angles of 180° or 90°, as is observed experimentally, but any such angles are allowed. In the limiting case, with strong Au—$(Au)_n$—Au chains as in Figures 7 and 8, the hybridization at gold may become close to dsp^2 giving approximately square planar gold centres.

55.21.2 Electron-deficient Gold(I) Complexes

The majority of these compounds are organometallic derivatives and so they will not be dicussed in detail.[1,2,15–21] The chief interest here is in the gold–gold bonding interactions which are observed in such complexes. For example; in the 10-membered ring (2,4,5-$Me_3C_6H_2Au)_5$, Au · · · Au distances of 269–271 pm are observed and in the ferrocene derivative [$Fe(C_5H_5)\{C_5H_4(AuPPh_3)_2\}]^+$ the Au · · · Au distance is 277 pm (Figure 9).[658,659] Similar short Au · · · M distances are observed in the μ-hydrido derivatives (**1a**) and (**3a**) [*e.g.* r(Au · · · Ir) = 276.5 pm in (**1a**)].[140,141] In both classes of compounds the AuCAu or AuHIr interactions are best regarded as closed three-centre two-electron bonds leading to both AuC and AuAu or AuH and AuIr bonding interactions respectively.

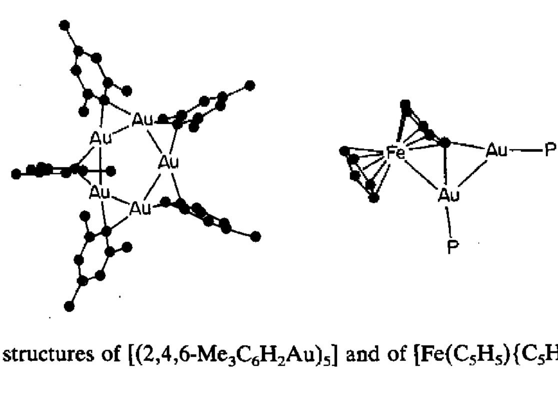
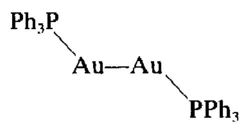


Figure 9 The structures of [(2,4,6-$Me_3C_6H_2Au)_5$] and of [$Fe(C_5H_5)\{C_5H_4(AuPPh_3)_2\}]^+$

55.21.3 Gold Cluster Complexes

This section will review an extensive class of compounds containing two or more gold atoms in which the average oxidation state of gold is less than one. Several fine reviews on aspects of this topic are available,[4,24,660,661] including articles on bonding,[662–665] structure,[7] X-ray photoelectron spectra[21,666,667] and Mössbauer spectra.[23,24] Au_8 clusters have found application as labels in electron microscopy studies.[668] Emphasis here will be placed on syntheses, structures and reactions of the complexes. It will be seen that many of the structures are based on tetrahedra or centred icosahedra of gold atoms, and there is now a logical rationalization of these observations[662–665]

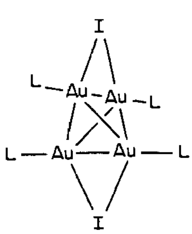
The simplest complex is the binuclear $[Au_2(PPh_3)_2]$, prepared by reaction of $[AuI(PPh_3)]$ with sodium naphthalide, $NaC_{10}H_8$. It is isoelectronic with Hg_2Cl_2 but, curiously, has the *trans* bent structure (**99**) with $r(AuAu) = 276$ pm and angle AuAuP = 129°, rather than the expected linear structure.[664]

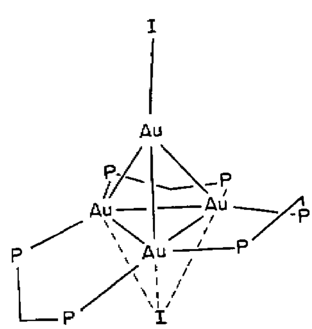


(**99**)

A trinuclear cluster $\{Au(Ph_3C_5POMe)\}_3$ is formed by reaction of methoxide with [AuCl(2,4,6-triphenylphosphabenzene)] and is thought to contain a triangle of gold atoms.[669]

Two tetrahedral Au_4 clusters, (**100**) and (**101**), have been characterized.[670,671] Complex (**100**) is prepared by reaction of $[Au_9(PPh_3)_8]^{3+}$ with iodide ion. This reaction is fairly typical of syntheses in which a higher gold cluster is treated with ligands to give cleavage into smaller clusters. Complex (**101**) contains one terminal iodide and another triply bridging iodide which is bound only very weakly below the plane containing the Au_3P_6 atoms. Complex (**100**) may be considered a 54-electron cluster (counting I as a one-electron ligand)[665] or a 58-electron cluster (counting I as a three-electron ligand),[670] while (**101**) is a 56-electron cluster (considered as $Au_4(dppm)_3I^+$) or a 62-electron cluster (considered as $Au_4(dppm)_3I(\mu_3\text{-}I)$ with μ_3-I as a five-electron ligand) and typifies the difficulties of rationalizing structures in terms of conventional electron counting methods.

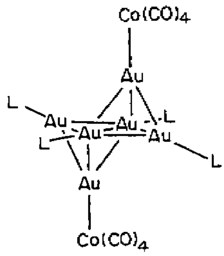




(**100**) (**101**)

The complex $[Au_5(\mu\text{-}Ph_2PCH_2PPh_2)_3(\mu_3\text{-}Ph_2PCHPPh_2)]$ $(NO_3)_2$ is closely related to (**101**) but it contains an extra gold(I) atom with linear PAuC coordination which interacts with the cluster. It can be prepared by reaction of atomic gold with $Ph_2PCH_2PPh_2$ and NH_4NO_3 or by reaction of $[Au_9(PPh_3)_8]^{3+}$ with $Ph_2PCH_2PPh_2$.[24,672]

Three different structural forms have been established for $[Au_6L_6]^{2+}$ clusters. The first such complex was the distorted octahedral $[Au_6\{P(4\text{-}MeC_6H_4)_3\}_6]^{2+}$ ion, isolated as the BPh_4^- salt in minute yield. More recently the neutral $[Au_6(PPh_3)_4\{Co(CO)_4\}_2]$ (**102**) was prepared by reaction of $[Au_8(PPh_3)_7]^{2+}$ with $[Co(CO)_4]^-$, and $[Au_6(Ph_2PCH_2CH_2CH_2PPh_2)_4]^{2+}$ (**103**) was prepared by reaction of $[Au_9(PPh_3)_8]^{3+}$ with the bidentate ligand.[675,676] The edge-shared tetrahedral structure found for (**102**) is also seen in $[Au_6(PPh_3)_6](NO_3)_2$ (**104**).[663,677] It is clear from these structures, from low temperature ^{31}P NMR studies and from theoretical calculations[663,665] that the energy differences between the distorted octahedral, edge-shared tetrahedral and bis(edge-capped) tetrahedral structures are very small.



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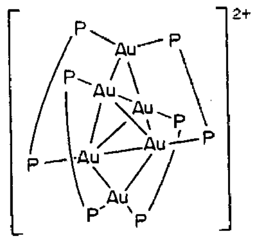

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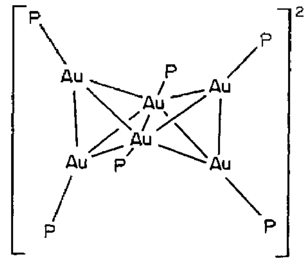
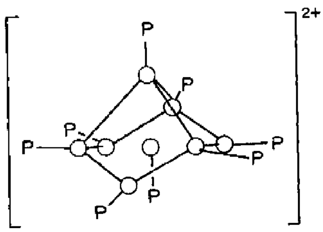


(104)

An Au_7 cluster $[Au_7(PPh_3)_7]^{n+}$ has been partially characterized but details are not available.[661]

Most of the larger gold clusters with 8–13 gold atoms can be considered to be derived structurally from a centred icosahedral Au_{13} cluster by removal of some of the peripheral gold atoms, and a centred Au_6 chair can be identified. The Au_8 clusters so far identified are $[Au_8(PPh_3)_8]^{2+}$ synthesized and characterized as both the alizarinsulfonate or hexafluorophosphate salt, and the $[Au_8(PPh_3)_7]^{2+}$ ion with structures (**105**) and (**106**) respectively.[678–680] In the latter complex the central gold atom is not bound to a triphenylphosphine ligand and so is exposed.



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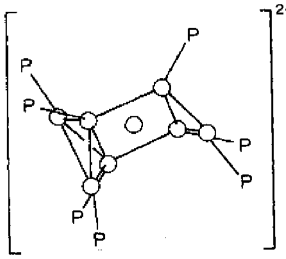


(106)

The complex $[Au_8L_8]^{2+}$ ($L = PPh_3$) is prepared by the reaction of equation (73), as determined by monitoring the reaction using ^{31}P NMR spectroscopy. In addition $[Au_8L_7]^{2+}$ has been shown to be an intermediate in this reaction (equation 74), and the reactions can be reversed by addition of $[Au(NO_3)L]$ (equation 75).[680]

$$[Au_9L_8]^{3+} + 2L \longrightarrow [Au_8L_8]^{2+} + [AuL_2]^+ \quad (73)$$

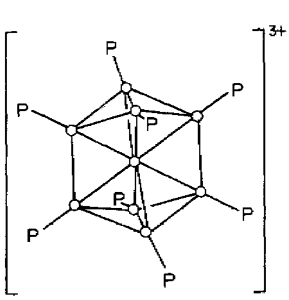
$$[Au_9L_8]^{3+} + L \longrightarrow [Au_8L_7]^{2+} + [AuL_2]^+ \quad (74)$$

$$[Au_8L_7]^{2+} + [AuL]^+ \longrightarrow [Au_9L_8]^{3+} \quad (75)$$

Au_9 clusters may be formed by reduction of $[Au(NO_3)L]$ (L = triarylphosphine) by sodium borohydride in ethanal, when $[Au_9L_8]^{3+}(NO_3^-)_3$ is formed. The structures of the derivatives $[Au_9\{P(4\text{-}MeC_6H_4)_3\}_8]^{3+}$ (**107**), as the PF_6^- salt, and $[Au_9\{P(4\text{-}MeOC_6H_4)_3\}_8]^{3+}$ (**108**) are quite different. Complex (**107**) is based on the centred icosahedral structure with a rectangle of four peripheral Au atoms missing, while (**108**) has a centred crown structure.[682] The ^{31}P NMR spectrum for (**107**) contains only one resonance in solution even at low temperature showing that the complex is fluxional,[686,687] and calculations suggest a very low activation energy to conversion between different structures.[685] However, the solid state ^{31}P NMR spectrum shows two ^{31}P environments in the $[Au_9(PPh_3)_8]^{3+}$ ion.[687]

The neutral Au_9 cluster $[Au_9\{P(C_6H_{11})_3\}_5(SCN)_3]$ has structure (**109**), again based on the centred icosahedron but with different gold atoms missing compared to (**107**). It was prepared by reduction of $[Au(SCN)\{P(C_6H_{11})_3\}]$ with borohydride.[688]

Finally, reduction of $[Au_9(PPh_3)_8]^{3+}$ gives $[Au_9(PPh_3)_8]^+$, with a centred cubane structure (**110**). In mixtures of $[Au_9(PPh_3)_8]^{3+}$ and $[Au_9(PPh_3)_8]^+$ there is some paramagnetic $[Au_9(PPh_3)_8]^{2+}$ present in equilibrium ($K_{eq} = 4.7$) and it can be detected by ESR spectroscopy.[689] The first gold clusters isolated had the formula $[Au_{11}X_3L_7]$.[660] They can be prepared by reduction of $[AuXL]$ (X = halide or thiocyanate) with $Na[BH_4]$ or $[Ti(PhMe)_2]$ or by gold atom reactions with $[AuXL]$.[664,690–692] The structures of $[Au_{11}(SCN)_3(PPh_3)_7]$, $[Au_{11}I_3\{P(4\text{-}ClC_6H_4)_3\}_7]$, $[Au_{11}I_3\{P(4\text{-}FC_6H_4)_3\}_7]$ and $[Au_{11}I_3(PPh_3)_7]$ have been determined.



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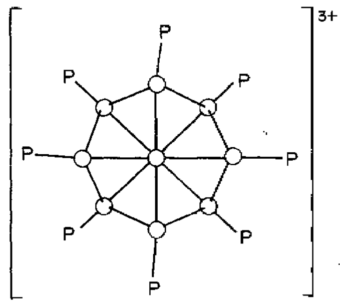

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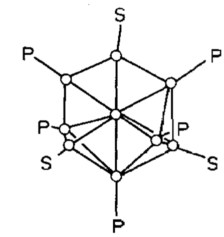
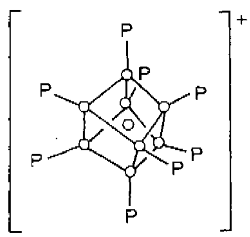


(109)

All are based on a centred icosahedron of gold atoms with two atoms missing, and each peripheral gold is bound to either a phosphine or a halide or thiocyanate ligand.[693–696] A typical skeletal structure for the $[Au_{11}X_3L_7]$ structure is (**111**). Some closely related derivatives of formula $[Au_{11}X_2L_8]^+$ are also known.[692]



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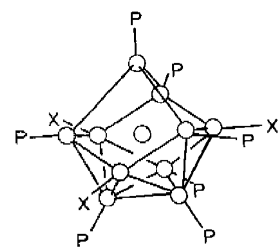
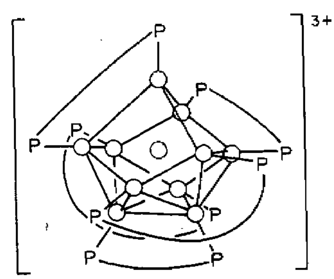


(111)

Reaction of $[Au_{11}(SCN)_3\{P(4\text{-}ClC_6H_4)_3\}_7]$ with $Ph_2PCH_2CH_2CH_2PPh_2$ gave the Au_{11} cluster $[Au_{11}(Ph_2PCH_2CH_2CH_2PPh_2)_5]^{3+}(SCN^-)_3$. This has a skeletal structure based on the centred icosahedron but with one triangle of atoms replaced by a single gold atom at the periphery. The geometry, (**112**), may be affected by constraints from the chelating ligands.[24] The complex $[Au_{11}(PMe_2Ph)_{10}]^{3+}$ is also known.[698]

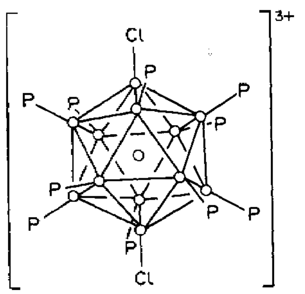


(112)

The largest gold clusters which have been characterized crystallographically are the Au_{13} clusters $[Au_{13}(PMe_2Ph)_{10}Cl_2]^{3+}$ and $[Au_{13}(Ph_2PCH_2PPh_2)_6]^{5+}$, which were prepared by reduction of the appropriate phosphine–gold(I) precursors. They have the structures (**113**) and (**114**), each based on a centred icosahedron of gold atoms.[698,699] This structure is considered the parent of the structures found for many of the Au_8–Au_{11} clusters, which have different numbers of gold atoms missing from the periphery.

The largest cluster claimed is the remarkable $[Au_{55}Cl_6(PPh_3)_{12}]$, isolated on reduction of $[AuCl(PPh_3)]$ with diborane. A reasonable structure, based on analytical, molecular weight and Mössbauer spectral data, appears to be a small section of a gold metal lattice surrounded by ligands.

The theoretical treatment of bonding and structure of gold clusters has met with considerable success. For the higher gold clusters, the best predictions are that, for a cluster $[Au_xL_{x-1}]^{n+}$ in which the peripheral gold atoms define a closed spherical polyhedron, there will be a closed shell electron configuration when $12x + 6$ electrons are present. The structures of complexes



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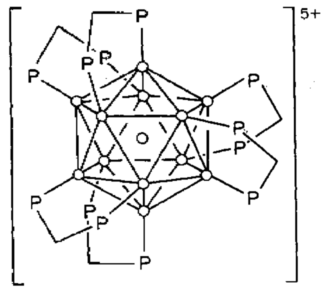


(114)

$[Au_8L_8]^{2+}$ (102 valence electrons), $[Au_9L_8]^{+}$ (114 valence electrons), $[Au_{11}L_{10}]^{3+}$ (138 valence electrons) and $[Au_{13}L_{12}]^{5+}$ (162 valence electrons) fall into this class.[685]

On the other hand, if the peripheral gold atoms have a ring or torus structure for $[Au_xL_{x-1}]^{n+}$, the number of valence electrons for a filled shell should be $12x+4$. The complexes $[Au_8L_7]^{2+}$ (100 valence electrons) and $[Au_9L_8]^{3+}$ (112 valence electrons) fall into this class.[663,685]

In general, the theoretical predictions are upheld although the energy differences between structures are small as a result of the bonding between peripheral gold atoms being weak.[685]

Much of the systematics of synthesis of gold clusters can be understood in terms of steric effects. For example, to prepare the clusters $[Au_{13}L_{12}]^{5+}$, the ligands must be small.[24,663] With larger ligands L, there is not room for the 12 peripheral LAu units in the icosahedral structure, and so smaller clusters with two or more of the LAu units missing are formed. Many of the structures rely on having some small anionic ligands (halide or thiocyanate) to assist in packing. The quantitative aspects of predictions based on steric effects have been aided by calculations of Kitaigorodski packing coefficients or of cluster cone angles.[24,698]

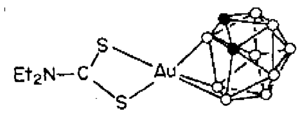
55.22 COMPLEXES WITH GOLD–MAIN GROUP METAL BONDS

55.22.1 Complexes with Gold–Boron Bonds

The simplest complex is $[Au(BPh_2)(PPh_3)]$, prepared according to equation (76).[701] There is also a very reactive complex derived from $[B_5H_8]^-$, thought to be $[Au(B_5H_8)(PPh_3)]$.[702]

$$2[AuCl(PPh_3)] + [Co(BPh_2)_2(PP)_2] \longrightarrow 2[Au(BPh_2)(PPh_3) + [CoCl_2(PP)_2] \qquad (76)$$

A more extensive and better characterized series of complexes is derived from carboranes. Thus $[C_2B_4H_7]^-$ gives $[Au(\mu\text{-}C_2B_4H_7)(PPh_3)]$,[703] $[C_2B_9H_{11}]^{2-}$ gives the isomeric complexes $[Au(S_2CNEt_2)(C_2B_9H_{11})]$ and $[Au(S_2CNEt_2)_2][Au(C_2B_9H_{11})_2]$, and $[C_2B_9H_{10}py]^-$ gives $[Au(C_2B_9H_{10}py)(PPh_3)]$.[456,704–707] The gold(III) carborane derivatives have an interesting 'slipped' structure as typified by **(115)**.[704–706]



(115)

55.22.2 Complexes with Gold–Group IV Metal Bonds

The complexes $[Au(MPh_3)(PPh_3)]$ (M = Si or Ge) can be prepared according to equation (77) and the germanium derivative is the more stable.[708–710] The germanium complex reacts with further $LiGePh_3$ to give the $[Au(GePh_3)_2]^-$ ion, and all the complexes are reactive towards cleavage of the Au—Ge bonds.[709,710]

$$[AuCl(PPh_3)] + [Mn(CO)_5]^- \longrightarrow [Au\{Mn(CO)_5\}(PPh_3)] \qquad (77)$$

A number of complexes with $SnCl_3^-$ ligands are known, and this ligand stabilizes complexes in higher coordination numbers than two for gold(I).[23] The known derivatives include $[Au(SnCl_3)(PPh_3)_2]$, $[Au(SnCl_3)(PPh_3)_3]$ and $[Au(SnCl_3)\{P(CH_2SiMe_3)_3\}_2]$, and the distorted trigonal structure expected for $[Au(SnCl_3)L_2]$ derivatives has been confirmed for $[Au(SnCl_3)(PMe_2Ph)_2]$.[711–714]

55.23 COMPLEXES WITH GOLD-TRANSITION METAL BONDS

It is difficult to draw sharp boundaries between compounds containing simple Au—M bonds, compounds containing a gold atom bound to two or more transition elements, and compounds containing two or more gold atoms and one or more transition metal atoms. Thus compounds with gold–transition metal bonds may be found in Sections 55.21.2, 55.21.3 and in the following sections.

55.23.1 Compounds Containing Linear LAuM Bonds

These were the first gold–metal-bonded complexes to be isolated and many examples are known.[715] They are usually prepared by reaction of the appropriate metal carbonyl anion with a gold(I) complex [AuClL], as in equation (77). Some typical examples are given in Table 13.

Alternative synthetic methods involve use of the transition metal hydride or trialkyltin derivative (equations 78 and 79).[716,718,721]

Table 13 Some Linear Gold–Metal-bonded Complexes

Complex	*M*	*Ref.*
$[Ph_3PAuM(CO)_6]$	V, Nb, Ta	716, 717
$[Ph_3PAuM(CO)_5(PPh_3)]$	V, Nb, Ta	716
$[Ph_3PAuM(CO)_3(\eta\text{-}C_5H_5)]$	Cr, Mo, W	718, 719
$[Et_4N][Au\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$	Mo	720
$[Ph_3PAuM(CO)_5]$	Mn, Re	715, 721–723
$[(PhO)_3PAuMn(CO)_5]$	Mn	724
$[Ph_3PAuMn(CO)_4\{P(OPh)_3\}]$	Mn	724, 725
$[Et_4N][Au\{Mn(CO)_5\}_2]$	Mn	720
$[Ph_3PAuFe(CO)_3(NO)]$	Fe	726
$[Me_3PAuFe(CO)_3(NO)]$	Fe	726
$[Ph_3PAuFe(CO)_3(\eta\text{-}C_3H_5)]$	Fe	727
$[Et_4N][Au\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$	Fe	720
$[Ph_3PAuRu(CO)_4(MMe_3)]$	Si, Ge	728, 729
$[Ph_3PAuCo(CO)_4]$	Co	730–735
$[Ph_3PAuCo(CO)_3(PPh_3)]$	Co	732, 733
$[Et_4N][Au\{Co(CO)_4\}_2]$	Co	720, 738
$[Ph_3PAuM(PF_3)_4]$	Rh, Ir	736
$[Ph_3PAuIr(CO)_3(PPh_3)]$	Ir	737

$$[AuCl(PPh_3)] + [HMo(CO)_3(\eta\text{-}C_5H_5)] \xrightarrow{-HCl} [Au\{Mo(CO)_3(\eta\text{-}C_5H_5)\}(PPh_3)] \quad (78)$$

$$[AuCl(PPh_3)] + [Ph_3SnV(CO)_6] \xrightarrow{-Ph_3SnCl} [Au\{V(CO)_6\}(PPh_3)] \quad (79)$$

In these complexes, the gold–metal bonds are apparently weak and polar and, in many cases, the metal carbonyl anion can be displaced by donor ligands (equation 80)[716,726,732,733] as well as by halogens and similar reagents.[721]

$$[Ph_3PAuTa(CO)_6] + 2Ph_3P \longrightarrow [Au(PPh_3)_3][Ta(CO)_6] \quad (80)$$

The structures of several complexes have been determined.[7,725,727,730,731,738] From the structure of $[Ph_3PAuFe(CO)_3(\eta\text{-}C_3H_5)]$, it has been suggested that the FeAu bond is best considered as a donor–acceptor Fe→Au bond.[727]

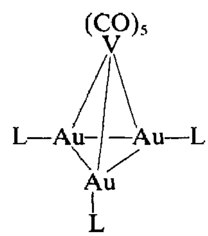
55.23.2 Compounds with $M(AuPR_3)_n$ Units ($n = 2$ or 3)

These complexes are related to those of Section 55.23.1, but have the added feature of Au···Au bonding between the gold atoms. They are usually prepared from the metal carbonyl anion with $[AuCl(PR_3)]$ and some examples are given in Table 14.

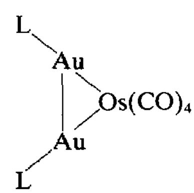
Table 14 Some Complexes with $M(AuPR_3)_n$ Units ($n = 2$ or 3)

Complex	*M*	*Ref.*
$(Ph_3PAu)_3V(CO)_5$	V	739, 740
$(Ph_3PAu)_3M(CO)_4$	Mn, Re	741
$MeC\{CH_2AsMe_2AuMn(CO)_5\}_3$	Mn	742
$(Ph_3PAu)_2M(CO)_4$	Fe, Ru, Os	715, 728, 743–745
$(3,3'\text{-}C_6H_4PPh_2)_2Au_2Fe(CO)_4$	Fe	746
$\{(\mu\text{-dppm})Au_2Fe(CO)_4\}_2$	Fe	747
$\{(\mu\text{-dppe})Au_2Fe(CO)_4\}_2$	Fe	747

The structures of $[(Ph_3PAu)_3V(CO)_5]$ (**116**) and of $[(Ph_3PAu)_2Os(CO)_4]$ (**117**) show the presence of an approximate tetrahedron and triangle of metal atoms respectively.[740,744] Thus AuAu bonding as well as AuV and AuOs bonding is significant. The AuAu bonds are thought to arise in much the same way as the intermolecular AuAu bonds between linear gold(I) centres and between peripheral gold atoms in gold clusters, that is primarily through interaction of filled *d* orbitals on gold with empty $6p_x$ and $6p_y$ orbitals.[747]



(**116**)

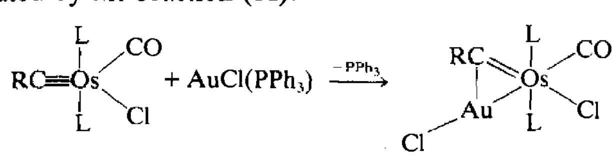


(**117**)

In $[\{(\mu\text{-dppe})Au_2Fe(CO)_4\}_2]$ the two Au_2Fe triangles are similar to those in $[(Ph_3PAu)_2M(CO)_4]$ (M = Fe or Os) and are well separated. However, in $[\{(\mu\text{-dppm})Au_2Fe(CO)_4\}_2]$ there are additional AuAu bonding interactions and the four gold atoms form a distorted rhombus.[744,745,747]

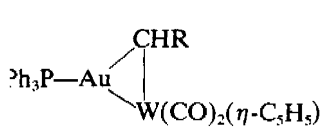
55.23.3 Compounds with AuMC Rings

Metal carbene and carbyne complexes can act as donors analogous to alkenes and alkynes. When gold is the acceptor such interactions can lead to dimetallacyclopropanes or dimetallacyclopropenes, as illustrated by the reaction (81).[748]

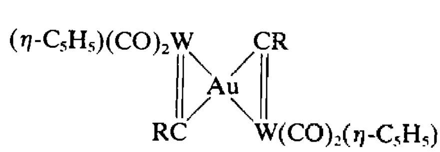


(81)

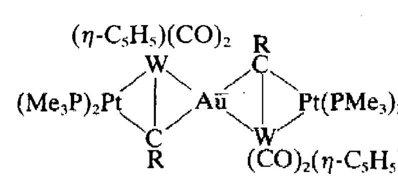
In analogous syntheses, the anionic metal carbene precursor $[(\mu\text{-}C_5H_5)(CO)_2W(\mu\text{-}CHR)W(CO)_5]^-$ gives (**118**), and using carbyne complexes the derivatives (**119**) and (**120**) can be built up in a stepwise manner (R = 4-tolyl).[749,750]



(**118**)



(**119**)



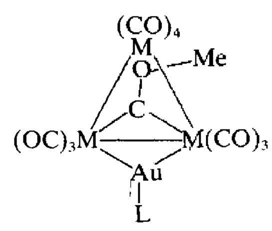
(**120**)

55.23.4 Gold–Metal Mixed Clusters

There has been rapidly growing interest in this area for several reasons. Firstly, a number of new types of complex with gold doubly, triply or quadruply bridging between transition metals have been discovered. Secondly, it has been pointed out that the H atom and LAu unit are approximately isolobal (H using 1*s* and LAu mostly 6*s* in bonding) and that neither has significant steric effects. Thus it was suggested that, when LAu and H derivatives of a given cluster are known, the X-ray structure of the LAu derivative may serve as a guide to the position of H in the corresponding hydride cluster.[751] In practice, this prediction has been useful in many complexes containing only one gold centre. However, when two or more gold atoms are present, gold–gold bonding often occurs and the structures are generally not related to the hydride cluster structures.

The synthetic methods used involve reaction of a cluster anion with [AuClL], elimination of methane between a cluster hydride and [AuMeL] or addition of LAu^+ units to metal–metal bonds. The emphasis here will be on structure and reactions of the complexes. Some examples of mixed gold clusters are given in Table 15, where it can be seen that most work has been on derivatives of clusters of iron, ruthenium and osmium.

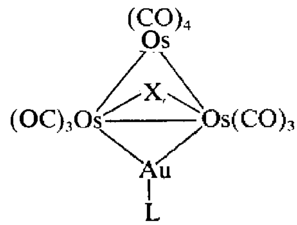
The complexes $[M_3(CO)_{10}(\mu_2\text{-COMe})(\mu_2\text{-AuPPh}_3)]$ (M = Fe, Ru) have structure (**121**), and are formed according to equation (82). They give a good example of complexes in which the hydride and LAu derivatives of the cluster are isostructural.[752,757]



(**121**)

$$[M_3(CO)_{10}(\mu_2\text{-COMe})(\mu_2\text{-H})] + MeAuPPh_3 \xrightarrow{-CH_4} [M_3(CO)_{10}(\mu_2\text{-COMe})(\mu_2\text{-AuPPh}_3)] \quad (82)$$

Another extensive series of complexes is of general formula $[Os_3(CO)_{10}(\mu_2\text{-X})(\mu_2\text{-AuPR}_3)]$ of structure (**122**), with X = H, Cl, SCN, NCO and $AuPR_3$.[761–766] These complexes can be prepared in a number of ways as illustrated by equations (83)–(85).[762–765] Again they are isostructural with the corresponding hydrides.



(**122**)

$$[Os_3H(CO)_{11}]^- + AuCl(PEt_3) \longrightarrow [Os_3H(CO)_{10}(AuPEt_3)] \quad (83)$$

$$[Os_3(CO)_{12}] + AuCl(PPh_3) \longrightarrow [Os_3(CO)_{10}Cl(AuPPh_3)] \quad (84)$$

$$[Os_3(CO)_{12}] + [AuCl(PEt_3)] \xrightarrow{N_3^-} [Os_3(CO)_{11}(NCO)(AuPEt_3)] \xrightarrow{-CO} [Os_3(CO)_{10}(NCO)(AuPEt_3)] \quad (85)$$

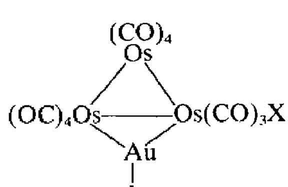
The related complexes $[Os_3(CO)_{11}X(AuPR_3)]$ are thought to have structure (**123**),[762,763,765,766] while the remarkable compound $[\{Os_3(\mu\text{-H})(CO)_{10}\}_2(\mu_4\text{-Au})]^-$, prepared as the $[N(PPh_3)_2]^+$ salt by reaction of (**122**; X = H) with $[N(PPh_3)_2]Cl$, has structure (**124**). This complex has square planar gold(I) bridging between the two Os_3 clusters.[767] The interaction between gold

Table 15 Some Mixed Clusters Containing One or More Gold Atoms

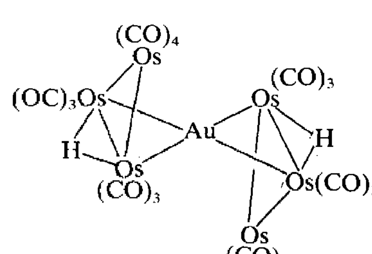
Complex	*Ref.*
$[Fe(CO)_{10}(\mu_2\text{-}COMe)(\mu_2\text{-}AuPPh_3)]$	754
$[Fe_3(CO)_9(\mu_3\text{-}S)(\mu_2\text{-}AuPPh_3)(\mu_3\text{-}AuPPh_3)]$[a]	785
$[Fe_3(CO)_9(\mu_3HC{=}NBu^t)(\mu_2\text{-}AuPPh_3)]$	753
$[Fe_4H(CO)_{12}C(\mu_2\text{-}AuPEt_3)]$	754
$[Fe_4(CO)_{12}C(\mu_3\text{-}AuPEt_3)_2]$[a]	754
$[Fe_5(CO)_{14}C(\mu_4\text{-}AuPEt_3)(\mu_2\text{-}AuPEt_3)]$	755
$[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}COMe)(CO)_9(\mu_2\text{-}AuPPh_3)]$	756, 757
$[Ru_3(\mu_2\text{-}COMe)(CO)_{10}(\mu_2\text{-}AuPPh_3)]$	752, 757
$[Ru_3(\mu_3\text{-}COMe)(CO)_9(\mu_2\text{-}AuPPh_3)_2(\mu_3\text{-}AuPPh_3)]$[a]	756, 757
$[Ru_3(\mu\text{-}H)(\mu_3\text{-}COMe)(CO)_9(\mu_2\text{-}AuPPh_3)_2]$[a]	758
$[Ru_3(\mu_3\text{-}S)(CO)_9(\mu_2\text{-}AuPPh_3)_2]$[a]	758
$[Ru_3(\mu_3\text{-}S)(CO)_8(PPh_3)(\mu_2\text{-}AuPPh_3)_2]$[a]	758
$[Ru_3(\mu_3\text{-}S)(\mu\text{-}H)(CO)_9(\mu_2\text{-}AuPPh_3)]$	758
$[Ru_3(\mu_3\text{-}PPh)(\mu\text{-}H)(CO)_9(\mu_2\text{-}AuPMe_2Ph)]$	759
$[Ru_3(CO)_9(\mu_3\text{-}CCBu^t)(\mu_2\text{-}AuPPh_3)]$	760
$[Os_3(\mu\text{-}H)(CO)_{10}(\mu_2\text{-}AuPPh_3)]$	761, 762
$[Os_3H(CO)_{11}(AuPPh_3)]$	762
$[Os_3(CO)_{10}(\mu_2\text{-}AuPEt_3)_2]$	762
$[Os_3(CO)_{11}(AuPR_3)_2]$	762, 763
$[Os_3(\mu\text{-}Cl)(CO)_{10}(\mu_2\text{-}AuPPh_3)]$	764
$[Os_3(\mu\text{-}NCO)(CO)_{10}(\mu_2\text{-}AuPPh_3)]$	765, 766
$[Os_3(\mu\text{-}SCN)(CO)_{10}(\mu_2\text{-}AuPPh_3)]$	761
$[Os_3(NCO)(CO)_{11}(\mu_2\text{-}AuPPh_3)]$	765, 766
$[\{Os_3(\mu\text{-}H)(CO)_{10}\}_2(\mu_4\text{-}Au)]^-$	767
$[Os_3(CO)_8(PPh_3)(\mu_3\text{-}NHC_5H_4N)(\mu_2\text{-}AuPPh_3)]$	768
$[Ru_4(\mu\text{-}H)_3(CO)_{12}(\mu_2\text{-}AuPPh_3)]$	769, 770, 772
$[Ru_4(\mu\text{-}H)_2(CO)_{12}(\mu_2\text{-}AuPPh_3)_2]$[a]	769, 771
$[Ru_4(\mu\text{-}H)(CO)_{12}(\mu_2\text{-}AuPPh_3)_2(\mu_3\text{-}AuPPh_3)]$[a]	756, 769
$[Ru_4(\mu\text{-}H)_2(CO)_{12}(\mu_2\text{-}AuPPh_3)(\mu_2\text{-}CuPPh_3)]$[a]	771
$[Ru_4(\mu\text{-}H)_2(CO)_{12}(\mu_2\text{-}AuPPh_3)(\mu_2\text{-}AgPPh_3)]$[a]	771
$[Os_4(\mu\text{-}H)(CO)_{13}(\mu_2\text{-}AuPEt_3)]$	770
$[Os_4(\mu\text{-}H)_3(CO)_{12}(\mu_2\text{-}AuPEt_3)]$	770, 773
$[Os_4(\mu\text{-}H)_2(CO)_{12}(\mu_2\text{-}AuPPh_3)_2]$[a]	773
$[Ru_5C(CO)_{15}(\mu_2\text{-}AuPPh_3)Cl]$	774
$[Ru_5C(CO)_{14}(\mu_2\text{-}AuPPh_3)(\mu\text{-}Br)]$	774
$[Ru_5C(CO)_{13}(PPh_3)(\mu_2\text{-}AuPPh_3)(\mu\text{-}I)]$	775
$[Os_5(\mu\text{-}H)(CO)_{15}(AuPR_3)]$	770
$[Os_5C(CO)_{14}(\mu_2\text{-}AuPPh_3)_2]$	776
$[Ru_6C(CO)_{16}(\mu_2\text{-}AuPMePh_2)_2]$	777
$[Ru_5WC(CO)_{17}(\mu_2\text{-}AuPEt_3)_2]$[a]	777
$[Ru_6C(CO)_{15}(NO)(\mu_3\text{-}AuPPh_3)]$	778
$[Os_8(CO)_{22}(\mu_3\text{-}AuPPh_3)_2]$	779
$[Os_{10}C(CO)_{24}(\mu_2\text{-}AuPPh_3)]$	780
$[Rh_2(\mu\text{-}CO)_2(\mu\text{-}C_5Me_5)_2(\mu_2\text{-}AuCl)]$	781
$[FeCo_3(CO)_{12}(\mu_3\text{-}AuPPh_3)]$	751
$[CoRu_3(CO)_{13}(\mu_3\text{-}AuPPh_3)]$	782, 783
$[CoRu_3(\mu\text{-}H)(CO)_{12}(\mu_2\text{-}AuPPh_3)(\mu_3\text{-}AuPPh_3)]$[a]	782, 783
$[CoRu_3(CO)_{12}(\mu_2\text{-}AuPPh_3)_2(\mu_3\text{-}AuPPh_3)]$[a]	782, 783
$[Co_3Ru(CO)_{12}(\mu_3\text{-}AuPPh_3)]$	784
$[Co_2Ru_2(CO)_{12}(\mu_2\text{-}AuPPh_3)(\mu_3\text{-}AuPPh_3)]$[a]	785

[a] An oversimplified formulation since AuAu bonding is also present; see text.

and each Os_3 cluster is best considered a three-centre two-electron bond, but it is interesting that the Os_4Au unit has the eclipsed planar configuration.

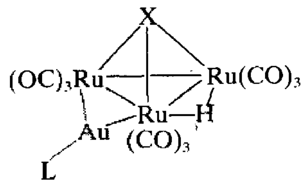


(123)

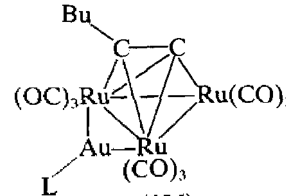


(124)

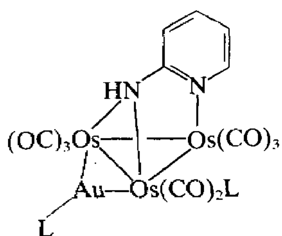
Other trinuclear complexes in which the H and LAu derivatives are isostructural are (**125**; X = S or PPh),[758,759] (**126**)[760] and (**127**),[768] but $[Fe_3(CO)_9(\mu_3\text{-HC}=NBu^t)(\mu_2\text{-AuPPh}_3)]$ of structure (**128**) provides an exception. The hydride analogue has a structure with hydride bridging a different edge of the Fe_3 triangle.[753]



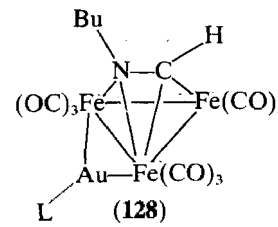
(**125**)



(**126**)

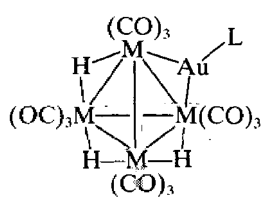


(**127**)

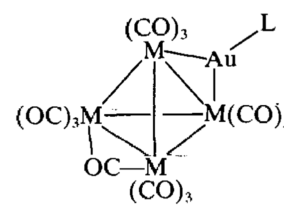


(**128**)

The higher clusters with one μ_2-AuL group also appear to be isostructural with the cluster hydrides in most cases. Examples include $[M_4H_3(CO)_{12}(AuPEt_3)]$ (**129**; M = Ru or Os) and $[Os_4H(CO)_{13}(AuPEt_3)]$ (**130**).[769,770,772]

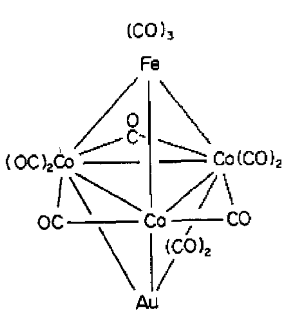


(**129**)

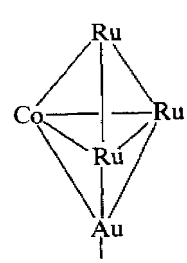


(**130**)

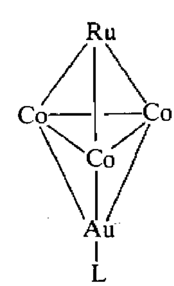
Triply bridging AuL groups are found in several clusters. The first example to be characterized was $[FeCo_3(CO)_9(\mu_2\text{-CO})_3(\mu_3\text{-AuPPh}_3)]$ (**131**) which is isostructural with the corresponding hydride.[751] Similar derivatives are $[CoRu_3(CO)_{10}(\mu_2\text{-CO})_3(\mu_3\text{-AuPPh}_3)]$ and $[Co_3Ru(CO)_9(\mu_2\text{-CO})_3(\mu_3\text{-AuPPh}_3)$ whose skeletal structures are shown as (**132**) and (**133**).[783,784]



(131)

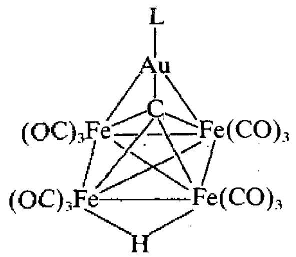


(**132**)

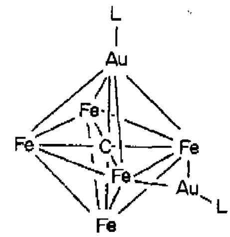


(**133**)

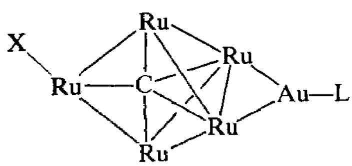
Metal cluster carbides have given some very interesting gold derivatives including $[Fe_4H(CO)_{12}C(\mu_3\text{-AuPEt}_3)]$, in which gold binds to the carbide and two iron atoms as shown in (**134**), and $[Fe_5(CO)_{14}C(AuPPh_3)_2]$ in which one gold binds to the carbide and four iron atoms, as shown by the skeletal structure (**135**). Ru_5 derivatives have been prepared by oxidative addition of $[Ph_3AuX]$ to $[Ru_5C(CO)_{15}]$ to give $[Ru_5C(CO)_{15}X(\mu_2\text{-}AuPP_3)]$ and then, by loss of CO, $[Ru_5C(CO)_4(\mu\text{-}X)(\mu_2\text{-}AuPPh_3)]$ of skeletal structures (**136**) and (**137**).[774,775]



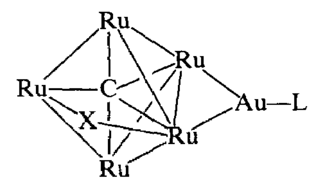
(**134**)



(**135**)



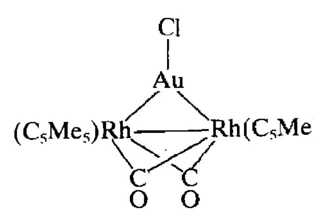
(**136**)



(**137**)

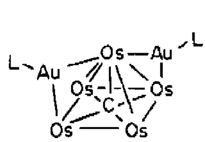
In (**136**) and (**137**) gold is not bound to the carbide, and this is also the case in $[Ru_6C(CO)_{15}(NO)(\mu_3\text{-}AuPPh_3)]$, where gold bridges between three ruthenium atoms on a face of the centred octahedron of Ru atoms, and in the highest nuclearity mixed cluster $[Os_{10}C(CO)_{24}(\mu_2\text{-}AuPPh_3)]$.[778,780]

Finally, in this section on clusters with one gold atom, the unusual complex $[Rh_2(\mu\text{-}CO)_2(C_5Me_5)_2(\mu_2\text{-}AuCl)]$ is prepared by addition of the AuCl unit from $[AuCl(CO)]$ to the Rh=Rh double bond of $[Rh_2(CO)_2(C_5Me_5)_2]$, and is thought to have structure (**138**).[781]

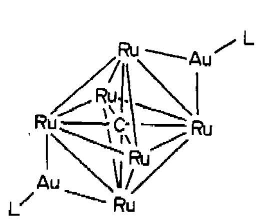


(**138**)

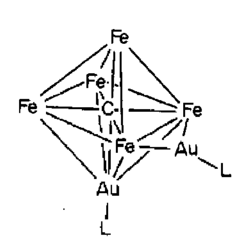
When two or more LAu units are present in a cluster, they are sometimes not bonded to each other. Examples include (**122**) with X = $AuPPh_3$, (**135**) and the carbide clusters $[Os_5C(CO)_{14}(AuPPh_3)_2]$ and $[Ru_6C(CO)_{16}(AuPMePh_2)_2]$ with skeletal structures (**139**) and (**140**). However, in the closely related complexes $[Fe_5C(CO)_{14}(AuPPh_3)_2]$ and $[Ru_5WC(CO)_{17}(AuPEt_3)_2]$ the gold atoms occupy adjacent bridging positions and, at least in the latter case, AuAu interactions are significant (the skeletal structures are **141** and **142**). Variable temperature NMR studies indicate that the Ru_6C derivative is fluxional and that, in solution, isomer (**140**) is in equilibrium with an isomer with structure analogous to (**142**).[776,777]



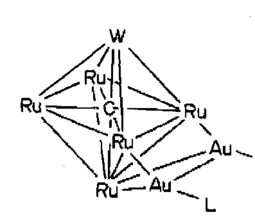
(**139**)



(**140**)

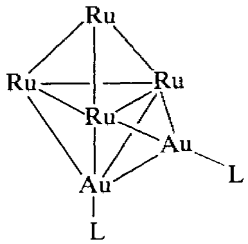


(**141**)

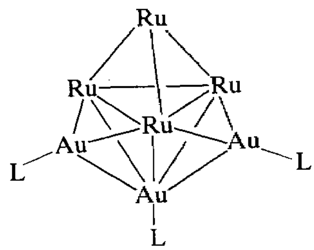


(**142**)

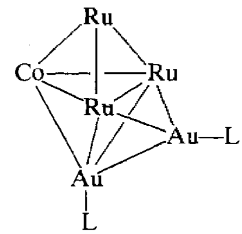
Particularly interesting is the series of complexes $[Ru_4H_n(CO)_{12}(AuPPh_3)_{4-n}]$, $[CoRu_3H_n(CO)_{12}(AuPPh_3)_{3-n}]$ and $[Co_nRu_{4-n}(CO)_{12}(AuPPh_3)_{4-n}]$, containing different numbers of AuL units.[756,769,771,782,785] The skeletal structures of the Ru_4 series are (**129**), (**143**) and (**144**), those of the $CoRu_3$ series are (**132**), (**145**) and (**146**), and those of Co_nRu_{3-n} series are (**133**), (**147**) and (**146**). The way in which the clusters are built up is as follows. The first gold bridges an edge (the Ru_4 series) or a face (the $CoRu_3$ and Co_nRu_{4-n} series) of the cluster according to the isolobal analogy with the H derivative. However, the next gold caps an AuM_3 or AuM_2 face, so as to give Au—Au as well as AuM_2 bonding. The third gold then caps another AuM_2 face in a similar way. Thus a compact structure consisting of face-sharing tetrahedra, with as many adjacent gold centres as possible is built up.



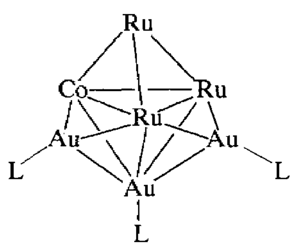
(**143**)



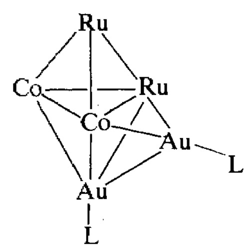
(**144**)



(**145**)

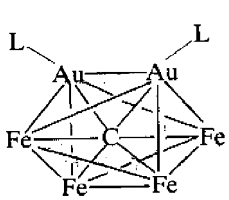


(**146**)

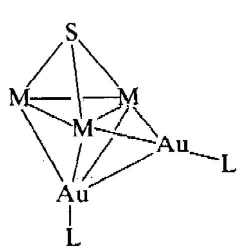


(**147**)

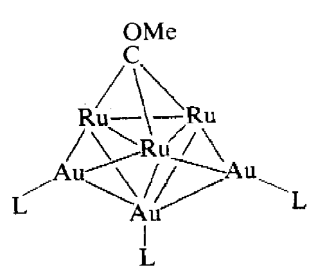
Another pair of complexes which fit and extend this pattern are $[Fe_4C(\mu\text{-}H)(CO)_{12}(AuPPh_3)]$ and $[Fe_4C(CO)_{12}(AuPPh_3)_2]$, with structures (**134**) and (**148**). In (**148**) the Au_2Fe_4 atoms make a distorted octahedron, so that the μ_2-$AuPPh_3$ centre in (**134**) moves over to cap the Fe_3C face, to maximize AuAu and FeAu bonding.[754] Further examples are the related complexes $[Fe_3(CO)_9(\mu_3\text{-}S)(AuPPh_3)_2]$ and $[Ru_3(CO)_8(PPh_3)(\mu_3\text{-}S)(AuPPh_3)_2]$ which have the skeletal structure (**149**; M = Fe or Ru)[758,785] and $[Ru_3(CO)_9(\mu_3\text{-}COMe)(AuPPh_3)_3]$ (**150**).[756]



(**148**)

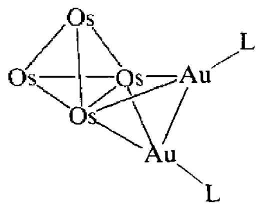


(**149**)

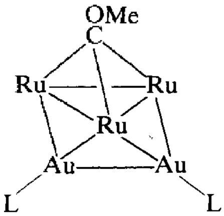


(**150**)

However, there are exceptions to these empirical rules. For example, $[Os_4H_2(CO)_{12}(AuPPh_3)_2]$ has the structure (**151**), described as two tetrahedra sharing a common edge, and $[Ru_3H(\mu_3\text{-}COMe)(CO)_9(AuPPh_3)_2]$ has structure (**152**), in which the Ru_3Au_2 atoms form a distorted square pyramid. Several of these complexes are fluxional, with exchange of non-equivalent Au centres being fast on the NMR timescale. Examples are (**149**; M = Ru) and (**150**) where only one signal is observed for the Ph_3PAu units in the ^{31}P NMR spectrum.[758] Evidently the energy differences between isomers are small and opening of Au—M and/or AuAu bonds can lead to rapid rearrangements of the cluster skeletons.[757]



(151)



(152)

At this stage the field of mixed AuM clusters is in a state of flux with very rapid advances in the synthesis and structure of new clusters, and the general pattern of structures, fluxionality and bonding only beginning to emerge. Further advances are expected in these areas.

55.24 REFERENCES

1. H. Schmidbaur, 'Gold-Organic Compounds', Gmelin Handbook, Springer-Verlag, Berlin, 1980.
2. R. J. Puddephatt, 'The Chemistry of Gold', Elsevier, Amsterdam, 1978.
3. W. S. Rapson and T. Groenewald, 'Gold Usage', Academic, London, 1978.
4. H. Schmidbaur and K. C. Dash, *Adv. Inorg. Chem. Radiochem.*, 1982, **25,** 239.
5. R. J. Puddephatt, *Endeavour, New Ser.*, 1979, **3,** 78.
6. H. Schmidbaur, *Angew. Chem., Int. Ed. Engl.*, 1976, **15,** 728.
7. P. G. Jones, *Gold Bull.*, 1981, **14,** 102; 1981, **14,** 159; 1983, **16,** 114.
8. B. F. G. Johnson and R. Davis, in 'Comprehensive Inorganic Chemistry', ed. J. C. Bailar, H. J. Emeléus, R. Nyholm and A. F. Trotman-Dickenson, Pergamon, Oxford, 1973.
9. S. J. Lippard (ed.), 'Platinum, Gold and Other Metal Chemotherapeutic Agents: Chemistry and Biochemistry', American Chemical Society, Washington, DC, 1983 (*ACS Symp. Ser.*, **209**).
10. 'Bioinorganic Chemistry of Gold Coordination Compounds', ed. B. M. Sutton and R. G. Franz, Smith, Kline and French, Philadelphia, 1983.
11. C. F. Shaw, III, *Inorg. Perspect. Biol. Med.*, 1979, **2,** 287.
12. A. J. Lewis and D. T. Walz, *Prog. Med. Chem.*, 1982, **19,** 1.
13. P. J. Sadler, *Struct. Bonding (Berlin)*, 1976, **29,** 171.
14. D. H. Brown and W. E. Smith, *Chem. Soc. Rev.*, 1980, **9,** 217.
15. B. Armer and H. Schmidbaur, *Angew. Chem., Int. Ed. Engl.*, 1970, **9,** 101.
16. R. J. Puddephatt in 'Comprehensive Organometallic Chemistry', ed. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, 1982, chap. 15.
17. G. K. Anderson, *Adv. Organomet. Chem.*, 1982, **20,** 39.
18. R. J. Puddephatt, *Gold Bull.*, 1977, **10,** 108.
19. K. I. Grandberg, *Russ. Chem. Rev. (Engl. Tranl.)*, 1982, **51,** 249.
20. V. P. Dyadchenko, *Russ. Chem. Rev. (Engl. Transl.)*, 1982, **51,** 265.
21. A. N. Nesmeyanov, E. G. Perevalova, K. I. Grandberg and D. A. Lemenovskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1974, 1124.
22. G. M. Schmid and M. E. Curley-Fiorino, in 'Encyclopedia of Electrochemistry of the Elements', ed. A. J. Bard, Dekker, New York, 1975, vol. IV, chap. IV-3.
23. R. V. Parish, *Gold Bull.*, 1982, **15,** 51.
24. J. J. Steggerda, J. J. Bour and J. W. A. van der Velden, *Recl. Trav. Chim. Pays-Bas*, 1982, **101,** 164.
25. J. J. Lagowski, *Gold Bull.*, 1983, **16,** 8.
26. A. H. Sommer, *Nature (London)*, 1943, **152,** 215.
27. E. C. Coffey, J. Lewis and R. S. Nyholm, *J. Chem. Soc.*, 1964, 1741.
28. B. Busse and K. G. Weil, *Angew. Chem., Int. Ed. Engl.*, 1979, **18,** 629.
29. H. Gollisch, *J. Phys. B*, 1982, **15,** 2569.
30. W. J. Peer and J. J. Lagowski, *J. Am. Chem. Soc.*, 1978, **100,** 6260.
31. T. H. Teherani, W. J. Peer, J. J. Lagowski and A. J. Bard, *J. Electrochem. Soc.*, 1978, **125,** 1717.
32. J. Kordis, K. A. Gingerich and R. J. Seyse, *J. Chem. Phys.*, 1974, **61,** 5114.
33. G. A. Ozin, *Acc. Chem. Res.*, 1977, **10,** 21; D. McIntosh and G. A. Ozin, *Inorg. Chem.*, 1976, **15,** 2869.
34. P. H. Kasai, *J. Chem. Soc.*, 1983, **105,** 6704.
35. G. A. Ozin, D. F. McIntosh, W. J. Power and R. P. Messmer, *Inorg. Chem.*, 1981, **20,** 1782; D. F. McIntosh, G. A. Ozin and R. P. Messmer, *Inorg. Chem.*, 1980, **19,** 3321.
36. A. J. Buck, B. Mile and J. A. Joward, *J. Am. Chem. Soc.*, 1983, **105,** 3381.
37. J. H. B. Chenier, J. A. Howard, B. Mile and R. Sutcliffe, *J. Am. Chem. Soc.*, 1983, **105,** 788.
38. M. I. Brittan, *Am. Sci.*, 1974, **62,** 402.
39. C. F. Shaw, III and R. S. Tobias, *J. Chem. Educ.*, 1972, **49,** 286.
40. P. Pyykkö and J. P. Desclaux, *Acc. Chem. Res.*, 1979, **12,** 276.
41. R. S. Nyholm, *Proc. Chem. Soc., London*, 1961, 273; L. E. Orgel, *J. Chem. Soc.*, 1958, 4186.
42. C. K. Jørgensen and J. Pouradier, *J. Chim. Phys. Phys. Chim. Biol.*, 1970, **67,** 124.
43. P. G. Jones, W. Clegg and G. M. Sheldrick, *Acta Crystallogr., Sect. B*, 1980, **36,** 141.
44. L. H. Skibsted and J. Bjerrum, *Acta Chem. Scand., Ser. A*, 1977, **31,** 155.

45. A. D. Goolsby and D. T. Sawyer, *Anal. Chem.*, 1968, **40**, 1978.
46. R. Roulet, N. Q. Lan, W. R. Mason and G. P. Fenske, Jr., *Helv. Chim. Acta*, 1973, **56**, 2405.
47. G. P. Fenske and W. R. Mason, *Inorg. Chem.*, 1974, **13**, 1783.
48. R. Roulet and R. Favez, *Chimia*, 1975, **29**, 346.
49. R. F. Baggio and S. Baggio, *J. Inorg. Nucl. Chem.*, 1973, **35**, 3191.
50. H. Ruben, A. Zalkin, M. O. Faltens and D. H. Templeton, *Inorg. Chem.*, 1974, **13**, 1836.
51. P. C. Hydes and H. Middleton, *Gold Bull.*, 1979, **12**, 90.
52. J. L. Burmeister and N. J. DeStefano, *Inorg. Chem.*, 1971, **10**, 998.
53. J. L. Burmeister and J. B. Melpolder, *J. Chem. Soc., Chem. Commun.*, 1973, 613; J. B. Melpolder and J. L. Burmeister, *Inorg. Chim. Acta*, 1981, **49**, 115.
54. J. A. Muir, M. M. Muir and S. Arias, *Acta Crystallogr., Sect. B*, 1982, **38**, 1318.
55. D. B. Dell'Amico, F. Calderazzo, F. Marchetti and S. Mertino, *J. Chem. Soc., Dalton Trans.*, 1982, 2257.
56. J. P. Fackler, Jr. and J. D. Basil, in 'Inorganic Chemistry Toward the 21st Century', ed. M. H. Chisholm, American Chemical Society, Washington, DC, 1983, p. 201 (*ACS Symp. Ser.*, **211**); *Organometallics*, 1982, **1**, 871.
57. S. Komiya, T. A. Albright, R. Hoffman and J. K. Kochi, *J. Am. Chem. Soc.*, 1977, **99**, 8440.
58. K. Leary and N. Bartlett, *J. Chem. Soc., Chem. Commun.*, 1972, 903.
59. J. P. Desclaux and P. Pyykkö, *Chem. Phys. Lett.*, 1976, **39**, 300.
60. Y. S. Lee, W. C. Ermler, K. S. Pitzer and A. D. McLean, *J. Chem. Phys.*, 1979, **70**, 288.
61. T. Ziegler and A. Runk, *Inorg. Chem.*, 1979, **18**, 1558.
62. D. Guenzburger and D. E. Ellis, *Phys. Rev. B*, 1980, **22**, 4203.
63. G. M. Bancroft, T. Chan, R. J. Puddephatt and J. S. Tse, *Inorg. Chem.*, 1982, **21**, 2946.
64. H. Zwanziger, J. Reinhold and E. Hoyer, *Z. Chem.*, 1974, **14**, 489.
65. P. Pyykkö, *Adv. Quantum Chem.*, 1978, **11**, 353.
66. P. G. Jones, A. G. Maddock, M. J. Mays, M. M. Muir and A. F. Williams, *J. Chem. Soc., Dalton Trans.*, 1977, 1434.
67. C. A. McAuliffe, R. V. Parish and P. D. Randall, *J. Chem. Soc., Dalton Trans.*, 1977, 1426.
68. K. Moss, R. V. Parish, A. Laguna, M. Laguna and R. Uson, *J. Chem. Soc., Dalton Trans.*, 1983, 2071.
69. S. K. Chastian and W. R. Mason, *Inorg. Chem.*, 1982, **21**, 3717.
70. M. E. Koutek and W. R. Mason, *Inorg. Chem.*, 1980, **19**, 648.
71. W. R. Mason, *J. Am. Chem. Soc.*, 1976, **98**, 5182.
72. W. R. Mason, *J. Am. Chem. Soc.*, 1973, **95**, 3573.
73. T. K. Sham, R. E. Watson and M. L. Perlman, in 'Mössbauer Spectroscopy and its Chemical Applications', American Chemical Society, Washington, DC, 1981, p. 39 (*Adv. Chem. Ser.*, **194**).
74. T. K. Sham, R. E. Watson and M. L. Perlman, *Phys. Rev. B*, 1980, **21**, 1457.
75. M. O. Faltens and D. A. Shirley, *J. Chem. Phys.*, 1970, **53**, 4249.
76. H. D. Bartimik, W. Potzel, R. L. Mössbauer and G. Kaindl, *Z. Phys.*, 1970, **240**, 1.
77. A. Johnson and R. J. Puddephatt, *J. Chem. Soc., Dalton Trans.*, 1978, 980.
78. P. G. Jones and A. F. Williams, *J. Chem. Soc., Dalton Trans.*, 1977, 1430.
79. G. A. Bowmaker and R. Whiting, *Aust. J. Chem.*, 1976, **29**, 1407.
80. A. McNeillie, D. H. Brown, W. E. Smith, M. Gibson and L. Watson, *J. Chem. Soc., Dalton Trans.*, 1980, 767.
81. P. M. T. M. van Attekum, J. W. A. van der Velden and J. M. Trooster, *Inorg. Chem.*, 1980, **19**, 701.
82. H. Schmidbaur, J. R. Mandl, F. E. Wagner, D. F. van der Vondel and G. P. van der Kelen, *J. Chem. Soc., Chem. Commun.*, 1976, 170.
83. H. Basch and H. B. Gray, *Inorg. Chem.*, 1967, **6**, 365.
84. W. R. Mason and H. B. Gray, *J. Am. Chem. Soc.*, 1968, **90**, 5721.
85. H. Zwanziger, J. Reinhold and E. Hoyer, *Z. Chem.*, 1975, **15**, 69; J. Reinhold, H. Zwanziger, E. Hoyer and C. Zwanziger, *Z. Chem.*, 1974, **14**, 314.
86. D. H. Brown and W. E. Smith, *J. Chem. Soc., Dalton Trans.*, 1976, 848.
87. K. B. Dillon and T. C. Waddington, *Inorg. Nucl. Chem. Lett.*, 1978, **14**, 415.
88. H. Ito, J. Fujita and K. Saito, *Bull. Chem. Soc. Jpn.*, 1967, **40**, 2584.
89. A. J. McCaffrey, P. N. Schatz and P. J. Stephens, *J. Am. Chem. Soc.*, 1968, **90**, 5730.
90. W. R. Mason and H. B. Gray, *Inorg. Chem.*, 1968, **7**, 55.
91. H.-H. Schmidtke and D. Garthoff, *J. Am. Chem. Soc.*, 1967, **89**, 1317.
92. D. H. Brown, G. C. McKinlay and W. E. Smith, *Inorg. Chim. Acta*, 1979, **32**, 117.
93. J. Stein, J. P. Fackler, Jr., C. Paparizos and H. W. Chen, *J. Am. Chem. Soc.*, 1981, **103**, 2192.
94. J. Behan, R. A. W. Johnstone and R. J. Puddephatt, *J. Chem. Soc., Chem. Commun.*, 1978, 444.
95. G. M. Bancroft, T. C. S. Chan and R. J. Puddephatt, *Inorg. Chem.*, 1983, **22**, 2133.
96. J. J. Guy, P. G. Jones, M. J. Mays and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1977, 8.
97. P. G. Jones, *Z. Naturforsch., Teil B*, 1982, **37**, 823.
98. P. B. Hitchcock and P. L. Pye, *J. Chem. Soc., Dalton Trans.*, 1977, 1457.
99. J. C. M. T. Eijndhoven and G. C. Verschoor, *Mater. Res. Bull.*, 1974, **9**, 1667.
100. G. J. Arai, *Recl. Trav. Chim. Pays-Bas*, 1962, **81**, 307. Bond lengths corrected in ref. 7.
101. N. C. Baenziger, W. E. Bennett and D. M. Soboroff, *Acta Crystallogr., Sect. B*, 1976, **32**, 962.
102. H. Schmidbaur, A. Wohlleben, F. Wagner, O. Orama and G. Huttner, *Chem. Ber.*, 1977, **110**, 1748.
103. M. K. Cooper, K. Henrick, M. McPartlin and J. L. Latten, *Inorg. Chim. Acta*, 1982, **65**, L185.
104. R. Uson, A. Laguna, M. Laguna, E. Fernandez, M. D. Villacampa, P. G. Jones and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1983, 1679.
105. M. G. B. Drew and M. J. Riedl, *J. Chem. Soc., Dalton Trans.*, 1973, 52.
106. U. Schubert, K. Ackermann and R. Aumann, *Cryst. Struct. Commun.*, 1982, **11**, 591.
107. P. G. Jones, M. Kraushaar, E. Schwarzmann and G. M. Sheldrick, *Z. Naturforsch., Teil B*, 1982, **37**, 941.
108. L. S. Hollis and S. J. Lippard, *J. Am. Chem. Soc.*, 1983, **105**, 4293.

109. L. G. Kuz'mina, Yu. T. Struchkov, L. P. Grigor'eva, Z. I. Ezhkova, V. A. Belonosov, A. K. Molodkin, V. G. Pleshakov and B. E. Zaitsev, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1982, **27**, 695.
110. G. Minghetti, C. Foddai, F. Cariati, M. L. Ganadu and B. M. Manassero, *Inorg. Chim. Acta*, 1982, **64**, L235.
111. E. S. Clark, D. H. Templeton and C. H. MacGillavry, *Acta Crystallogr.*, 1958, **11**, 284.
112. P. G. Jones, J. J. Guy and G. M. Sheldrick, *Acta Crystallogr., Sect. B*, 1975, **31**, 2687; P. G. Jones and G. M. Sheldrick, *Acta Crystallogr., Sect. B*, 1978, **34**, 1353.
113. N. W. Alcock, K. P. Ang, K. F. Mok and S. F. Tan, *Acta Crystallogr., Sect. B*, 1978, **34**, 3364.
114. M. McPartlin and A. J. Markwell, *J. Organomet. Chem.*, 1973, **57**, C25.
115. G. Bandoli, D. A. Clemente, G. Marangoni and L. Cattalini, *J. Chem. Soc., Dalton Trans.*, 1973, 886.
116. H. Schmidbaur, J. R. Mandl, A. Frank and G. Huttner, *Chem. Ber.*, 1976, **109**, 466.
117. P. Jandik, U. Schubert and H. Schmidbaur, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 73.
118. R. W. Baker and P. J. Pauling, *Chem. Commun.*, 1969, 745.
119. J. Strähle, J. Gelinek and M. Kolmel, *Z. Anorg. Allg. Chem.*, 1979, **456**, 241.
120. D. B. Dell'Amico, F. Calderazzo, F. Marchetti and S. Merlino, *Gazz. Chim. Ital.*, 1978, **108**, 627.
121. D. R. Williamson and M. C. Baird, *J. Inorg. Nucl. Chem.*, 1972, **34**, 3393.
122. J. M. Meyer and A. L. Allred, *J. Inorg. Nucl. Chem.*, 1968, **30**, 1328.
123. A. D. Westland, *Can. J. Chem.*, 1969, **47**, 4135.
124. G. E. Coates and C. Parkin, *J. Chem. Soc.*, 1963, 421.
125. A. G. Jones and D. B. Powell, *Spectrochim. Acta, Part A*, 1974, **30**, 563; 1974, **30**, 1001.
126. H. Schmidbaur and R. Franke, *Chem. Ber.*, 1972, **105**, 2985.
127. E. A. Allen and W. Wilkinson, *Spectrochim. Acta, Part A*, 1972, **28**, 2257.
128. P. L. Goggin, R. J. Goodfellow, S. R. Haddock, F. J. S. Reed, J. G. Smith and K. M. Thomas, *J. Chem. Soc., Dalton Trans.*, 1972, 1904.
129. D. A. Duddell, P. L. Goggin, R. J. Goodfellow, M. G. Norton and J. G. Smith, *J. Chem. Soc. (A)*, 1970, 545.
130. C. F. Shaw and R. S. Tobias, *Inorg. Chem.*, 1973, **12**, 965.
131. L. Cattalini, R. J. H. Clark, A. Orio and C. K. Poon, *Inorg. Chim. Acta*, 1968, **2**, 62.
132. P. Braunstein and R. J. H. Clark, *Inorg. Chem.*, 1974, **13**, 2224.
133. K. S. Liddle and C. Parkin, *J. Chem. Soc., Chem. Commun.*, 1972, 26.
134. T. Boschi, B. Crociani, L. Cattalini and G. Marangoni, *J. Chem. Soc. (A)*, 1970, 2408; W. M. Scovell and R. S. Tobias, *Inorg. Chem.*, 1970, **9**, 945.
135. H. Hagnauer, G. C. Stocco and R. S. Tobias, *J. Organomet. Chem.*, 1972, **46**, 179.
136. S. W. Krauhs, G. C. Stocco and R. S. Tobias, *Inorg. Chem.*, 1971, **10**, 1365; G. C. Stocco and R. S. Tobias, *J. Am. Chem. Soc.*, 1971, **93**, 5057.
137. A. Shiotani and H. Schmidbaur, *Chem. Ber.*, 1971, **104**, 2838.
138. U. Ringstrom, *Nature (London)*, 1963, **198**, 981; *Ark. Fys.*, 1964, **27**, 227.
139. A. Kant and K. A. Moon, *High Temp. Sci.*, 1979, **11**, 55.
140. H. Lehner, D. Matt, P. S. Pregosin and L. M. Venanzi, *J. Am. Chem. Soc.*, 1982, **104**, 6825.
141. M. Green, A. G. Orpen, I. D. Salter and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1982, 813.
142. M. N. Zyryanov, G. A. Khlevnikova and V. A. Krenev, *Zh. Neorg. Khim.*, 1973, **18**, 918.
143. M. N. Zyryanov and G. A. Khlebnikova, *Tsevtn. Metall.*, 1972, **45**, 22 (*Chem. Abstr.*, 1972, **77**, 106 193).
144. M. N. Zyryanov and G. A. Khlebnikova, *Tsvetn. Metall.*, 1973, **16**, 112 (*Chem. Abstr.*, 1974, **80**, 16 969).
145. E. M. W. Janssen, J. C. W. Folmer and G. A. Wiegers, *J. Less-Common Met.*, 1974, **38**, 71.
146. A. Hakansson and L. Johansson, *Chem. Scr.*, 1975, **7**, 201.
147. E. M. W. Janssen, F. Pohlmann and G. A. Wiegers, *J. Less-Common Met.*, 1976, **45**, 261.
148. P. Machmer, M. Read and P. Cornil, *C.R. Hebd. Seances Acad. Sci., Ser. A*, 1966, **262**, 650.
149. D. Breitinger and H. Leuchtenstern, *Z. Naturforsch., Teil B*, 1974, **29**, 806.
150. D. Breitinger and K. Koehler, *Inorg. Nucl. Chem. Lett.*, 1972, **8**, 957.
151. J. Strähle and K.-P. Lörcher, *Z. Naturforsch., Teil B*, 1974, **29**, 266.
152. A. Weiss and A. Weiss, *Z. Naturforsch., Teil B*, 1956, **11**, 604.
153. E. M. W. Janssen and G. A. Wiegers, *J. Less-Common Met.*, 1978, **57**, P47.
154. H. Jagodzinski, *Z. Kristallogr.*, 1959, **112**, 80.
155. P. Braunstein and R. J. H. Clark, *J. Chem. Soc., Dalton Trans.*, 1973, 1845.
156. P. T. Beurskens, H. J. A. Blaauw, J. A. Cras and J. J. Steggerda, *Inorg. Chem.*, 1968, **7**, 805.
157. K. S. Ivanova and B. P. Matseevski, *Latv. PSR Zinat. Akad. Vestis, Kim. Ser.*, 1979, 495.
158. B. I. Peshchevitskii, G. N. Anoshin and A. M. Erenburg, *Khim. Resur. Morei Okeanov*, 1970, 141.
159. B. I. Peshchevitskii, G. N. Anoshin and A. M. Erenburg, *Dokl. Akad. Nauk SSSR*, 1965, **162**, 915.
160. E. J. Baran, *Spectrosc. Lett.*, 1975, **8**, 151.
161. J. C. M. Tindemans-van Eijndhoven and G. C. Verschoor, *Mater. Res. Bull.*, 1974, **9**, 1667.
162. H. J. Berthold and W. Ludwig, *Z. Naturforsch., Teil B*, 1980, **35**, 970.
163. J. Strähle, J. Gelinek and M. Kölmel, *Z. Anorg. Allg. Chem.*, 1979, **456**, 241.
164. J. Strähle, J. Gelinek, M. Kölmel and A.-M. Nemecek, *Z. Naturforsch., Teil B*, 1979, **34**, 1047.
165. W. Werner and J. Strähle, *Z. Naturforsch., Teil B*, 1979, **34**, 952.
166. W. Stoeger and A. Rabenau, *Z. Naturforsch., Teil B*, 1979, **34**, 685.
167. H.-D. Wasel-Nielen and R. Hoppe, *Z. Anorg. Allg. Chem.*, 1968, **359**, 36.
168. D. I. Nichols and A. S. Charleston, *J. Chem. Soc. (A)*, 1969, 2581; M. I. Bruce, J. K. Walton, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1983, 809.
169. M. J. Mays and J. Bailey, *J. Chem. Soc., Dalton Trans.*, 1977, 578.
170. L. Malatesta, L. Naldini, G. Simonetta and F. Cariati, *Coord. Chem. Rev.*, 1966, **1**, 255.
171. R. Uson, P. Royo, A. Laguna and J. Garcia, *Rev. Acad. Cienc. Exactas, Fis-Quim. Nat. Zaragoza*, 1973, **28**, 67.
172. H. Schmidbaur, A. A. M. Aly and U. Schubert, *Angew. Chem.*, 1978, **90**, 905.
173. B. L. Booth, R. N. Haszeldine and R. G. G. Holmes, *J. Chem. Soc., Dalton Trans.*, 1982, 523.
174. H. Schmidbaur and A. Shiotani, *J. Am. Chem. Soc.*, 1970, **92**, 7003.
175. H. Schmidbaur, J. Adlkofer and A. Shiotani, *Chem. Ber.*, 1972, **105**, 3389.

176. E. G. Perevalova, T. V. Baukova, E. I. Gorynov and K. I. Grandberg, *Izv, Akad. Nauk SSSR, Ser. Khim.*, 1970, 2148.
177. C. M. Mitchell and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1972, 102.
178. A. N. Nesmeyanov, K. I. Grandberg, V. P. Dyadchenko, D. A. Lemenovskii and E. G. Perevalova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1974, 740.
179. A. N. Nesmeyanov, E. G. Perevalova, Yu. T. Struchkov, M. Yu. Antipin, K. I. Grandberg and V. P. Dyadchenko, *J. Organomet. Chem.*, 1980, **201**, 343.
180. G. Banditelli, A. L. Bandini, F. Bonati, R. G. Goel and G. Minghetti, *Gazz. Chim. Ital.*, 1982, **112**, 539.
181. A. N. Nesmeyanov, E. G. Perevalova, K. I. Grandberg and D. A. Lemenovskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1974, 1124.
182. E. G. Perevalova, E. I. Smyslova and K. I. Grandberg, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 2836.
183. V. I. Rozenberg, R. I. Gorbacheva, E. I. Smyslova, K. I. Grandberg, V. A. Nikanorov, Y. G. Bundel and O. A. Reutov, *Dokl. Akad. Nauk SSSR,* 1975, **225**, 1082.
184. V. Belous and V. I. Tolstobrov, *Dokl. Akad. Nauk SSSR,* 1979, **245**, 598.
185. A. de Cugnac-Pailliotet and J. Pouradier, *C.R. Hebd. Seances Acad. Sci., Ser. C,* 1972, **275**, 551.
186. C. Kowala and J. M. Swan, *Aust. J. Chem.*, 1966, **19**, 547.
187. H. Schmidbaur, R. Franke and J. Eberlein, *Chem.-Ztg.*, 1975, **99**, 91.
188. C. Lensch, P. G. Jones and G. M. Sheldrick, *Z. Naturforsch., Teil B,* 1982, **37**, 944.
189. P. G. Jones, G. M. Sheldrick and E. Hädicke, *Acta Crystallogr., Sect. B,* 1980, **36**, 2777.
190. P. G. Jones, C. Lensch and G. M. Sheldrick, *Z. Naturforsch., Teil B,* 1982, **37**, 141.
191. J. C. Huffman, R. S. Roth and A. R. Siedle, *J. Am. Chem. Soc.*, 1976, **98**, 4340.
192. A. Müller, H. Dornfeld, G. Henkel, B. Krebs and M. P. A. Viegers, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 52.
193. C. L. Teske, *Z. Anorg. Allg. Chem.*, 1978, **445**, 193.
194. J. Socha, S. Safarzynski and T. Zak, *J. Less-Common Met.*, 1975, **43**, 283.
195. N. P. Finkelstein and R. D. Hancock, *Gold Bull.*, 1974, **7**, 72.
196. A. Ya. Fridman and E. V. Shemyakina, *Koord. Khim.*, 1978, **4**, 1507.
197. G. Nord, L. H. Skibsted and A. S. Khalonin, *Acta Chem. Scand., Ser. A,* 1975, **29**, 505.
198. C. J. Hawkins, O. Moensted and J. Bjerrum, *Acta Chem. Scand.*, 1970, **24**, 1059.
199. F. Cariati, D. Galizzioli and L. Naldini, *Chim. Ind.* (*Milan*), 1970, **52**, 995.
200. M. G. King and G. P. McQuillan, *J. Chem. Soc.* (*A*), 1967, 898.
201. A. J. Carty and A. Efraty, *Inorg. Chem.*, 1969, **8**, 543.
202. J. A. Muir, M. M. Muir and E. Lorca, *Acta Crystallogr., Sect. B,* 1980, **36**, 931.
203. J. A. Muir, M. M. Muir, S. Arias, C. F. Campana and S. K. Dwight, *Acta Crystallogr., Sect. B,* 1982, **38**, 2047.
204. R. Uson, A. Laguna and V. Perez, *Synth. React. Inorg. Metal-Org. Chem.*, 1981, **11**, 361.
205. R. Uson, J. Fornies, A. Laguna and J. I. Valenzuela, *Synth. React. Inorg. Metal-Org. Chem.*, 1982, **12**, 935.
206. A. S. Chernyak, *Zh. Prikl. Khim.*, 1979, **52**, 724; V. P. Kazakov, A. I. Lapshin and B. I. Peschevitskii, *Zh. Neorg. Khim.*, 1964, **9**, 1299.
207. G. Marcotrigiano, R. Battistuzzi and G. Peyronel, *Inorg. Nucl. Chem. Lett.*, 1972, **8**, 399.
208. G. Marcotrigiano, G. Peyronel and R. Battistuzzi, *J. Chromatogr.*, 1972, **65**, 425.
209. G. Marcotrigiano, R. Battistuzzi and P. Morini, *Inorg. Nucl. Chem. Lett.*, 1974, **10**, 641.
210. P. G. Jones, J. J. Guy and G. M. Sheldrick, *Acta Crystallogr., Sect. B,* 1976, **32**, 3321.
211. R. Dietzel and P. Thomas, *Z. Anorg. Allg. Chem.*, 1971, **381**, 214.
212. A. J. Aarts, H. O. Desseyn and M. A. Herman, *Transition Met. Chem.*, 1980, **5**, 10.
213. G. J. Sutton, *Aust. J. Chem.*, 1966, **19**, 2059; 1969, **22**, 2475.
214. R. A. Potts and A. L. Allred, *J. Inorg. Nucl. Chem.*, 1966, **28**, 1479.
215. I. M. Keen, *J. Chem. Soc.*, 1965, 5751.
216. G. Annibale, L. Canovese, L. Cattalini and G. Natile, *J. Chem. Soc., Dalton Trans.*, 1980, 1017.
217. B. S. Maritz and R. van Eldik, *Inorg. Chim. Acta,* 1976, **17**, 21; 1976, **20**, 43.
218. D. de Filippo, F. Devillanova and C. Preti, *Inorg. Chim. Acta,* 1971, **5**, 103.
219. K. C. Dash and H. Schmidbaur, *Chem. Ber.*, 1973, **106**, 1221.
220. C. A. McAuliffe, R. V. Parish and P. D. Randall, *J. Chem. Soc., Dalton Trans.*, 1979, 1730.
221. G. W. A. Fowles, D. A. Rice and M. J. Riedl, *J. Less-Common Met.*, 1973, **32**, 379.
222. F. Coletta, R. Ettorre and A. Gambaro, *Inorg. Nucl. Chem. Lett.*, 1972, **8**, 667.
223. H. M. Fitch, *Belg. Pat.* 621 886 (1963) (*Chem. Abstr.*, 1963, **59**, P9897).
224. R. Uson, A. Laguna, J. Vicente, J. Garcia, P. G. Jones and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1981, 655.
225. L. G. Vaughan, *US Pat.* 3 661 959 (1972) (*Chem. Abstr.*, 1972, **77**, 101 904).
226. R. Uson, A. Laguna, M. Laguna and A. Uson, *Inorg. Chim. Acta,* 1983, **73**, 63.
227. R. Uson, A. Laguna and B. Bergareche, *J. Organomet. Chem.*, 1980, **184**, 411.
228. E. W. Abel and C. R. Jenkins, *J. Organomet. Chem.*, 1968, **14**, 285; L. F. Larkworthy and D. Sattari, *J. Inorg. Nucl. Chem.*, 1980, **42**, 551.
229. V. P. Komarov and V. B. Lazarev, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1978, **23**, 1026.
230. D. H. Brown, G. C. McKinlay and W. E. Smith, *J. Inorg. Biochem.*, 1979, **10**, 275.
231. V. P. Komarov, V. B. Lazarev and I. S. Shaplygin, *Zh. Neorg. Khim.*, 1980, **25**, 746.
232. R. G. Lichtenthaler and F. Voegtle, *Chem. Ber.*, 1973, **106**, 1319.
233. E. G. Perevalova, D. A. Lemenovskii, K. I. Grandberg and A. N. Nesmeyanov, *Dokl. Akad. Nauk SSSR,* 1972, **203**, 1320.
234. G. E. Coates, C. Kowala and J. M. Swan, *Aust. J. Chem.*, 1966, **19**, 539.
235. W. Beck and S. Tadros, *Z. Anorg. Allg. Chem.*, 1970, **375**, 231.
236. R. J. Puddephatt and P. J. Thompson, *J. Organomet. Chem.*, 1976, **117**, 395; A. Johnson and R. J. Puddephatt, *J. Chem. Soc., Dalton Trans.*, 1975, 115.

237. E. R. McGusty and B. M. Sutton, *Chem. Abstr.*, 1974, **80**, 100 212; B. M. Sutton and J. Weinstock, *Chem. Abstr.*, 1976, **84**, 31 242.
238. W. S. Crane and H. Beall, *Inorg. Chim. Acta*, 1978, **31**, L469.
239. W. Ehrl and H. Vahrenkamp, *Chem. Ber.*, 1970, **103**, 3563.
240. A. Lorber and T. M. Simon, *Gold Bull.*, 1979, **12**, 149.
241. D. T. Hill and B. M. Sutton, *Cryst. Struct. Commun.*, 1980, **9**, 679.
242. M. T. Razi, P. J. Sadler, D. T. Hill and B. M. Sutton, *J. Chem. Soc., Dalton Trans.*, 1983, 1331.
243. D. T. Hill, B. M. Sutton, A. A. Isab, T. Razi, P. J. Sadler, J. M. Trooster and G. H. M. Calis, *Inorg. Chem.*, 1983, **22**, 2936.
244. P. J. Sadler, *J. Rheum. Suppl.*, 1982, **8**, 71.
245. D. T. Hill, B. M. Sutton, S. H. Levinson and J. Meier, *J. Labelled Compd. Radiopharm.*, 1983, **20**, 363.
246. M. A. Mazid, M. T. Razi, P. J. Sadler, G. N. Greaves, S. J. Gurman, M. H. J. Koch and J. C. Phillips, *J. Chem. Soc., Chem. Commun.*, 1980, 1261.
247. R. C. Elder, M. K. Eidsness, M. J. Heeg, K. G. Tepperman, C. F. Shaw, III and N. Schaeffer, in ref. 9, p. 385.
248. K. Brown, R. V. Parish and C. A. McAuliffe, *J. Am. Chem. Soc.*, 1981, **103**, 4943.
249. G. H. M. Calis, J. M. Trooster, M. T. Razi and P. J. Sadler, *J. Inorg. Biochem.*, 1982, **17**, 139.
250. D. H. Brown, G. McKinlay and W. E. Smith, *J. Chem. Soc., Dalton Trans.*, 1977, 1874.
251. A. A. Isab and P. J. Sadler, *J. Chem. Soc., Dalton Trans.*, 1981, 1657.
252. B. M. Sutton, in ref. 9, p. 355.
253. C. F. Shaw, III, in 'Trace Elements in the Pathogenesis and Treatment of Inflammation', ed. K. D. Rainsford, K. Brune and M. W. Whitehouse, Birkhauser Verlag, Basel, 1981.
254. P. J. Sadler, *Chem. Br.*, 1982, 12.
255. C. F. Shaw, III, H. O. Thompson, P. Witkiewicz, R. W. Satre and K. Siegesmund, *Toxicol. Appl. Pharmacol.*, 1981, **61**, 349.
256. H. O. Thompson, J. Blaszak, C. J. Knudtson and C. F. Shaw, III, *Bioinorg. Chem.*, 1978, **9**, 375.
257. D. T. Walz, M. J. diMartino and D. E. Griswold, *J. Rheumatol.*, 1982, **9**, 54.
258. D. T. Walz, M. J. diMartino and D. E. Griswold, *J. Rheumatol.*, 1982, **9**, 32.
259. S. T. Crooke, *J. Rheumatol.*, 1982, **9**, 61.
260. D. T. Walz, *Prog. Med. Chem.*, 1982, **19**, 1.
261. C. F. Shaw, III, *Inflammatory Dis. Copper*, 1981, 267.
262. J. Hempel and Y. Miduriya, in ref. 10, p. 37.
263. I. C. P. Smith, A. Joyce, H. Jarrell, B. M. Sutton and D. T. Hill, in ref. 10, p. 47.
264. N. A. Malik, G. Otiko, M. T. Razi and P. J. Sadler, in ref. 10, p. 82.
265. C. F. Shaw, III, in ref. 10, p. 98.
266. C. F. Shaw, III, in 'Inorganic Chemistry in Biology and Medicine', ed. A. E. Martell, American Chemical Society, Washington, DC, 1980, p. 349 (*ACS Symp. Ser.*, **140**).
267. C. F. Shaw, III, G. Schmitz, H. O. Thompson and P. Witkiewicz, *J. Inorg. Biochem.*, 1979, **10**, 317.
268. P. J. M. W. L. Birker and G. C. Verschoor, *Inorg. Chem.*, 1982, **21**, 990.
269. G. A. Bowmaker and B. C. Dobson, *J. Chem. Soc., Dalton Trans.*, 1981, 267.
270. E. H. Griffith, G. W. Hunt and E. L. Amma, *J. Chem. Soc., Chem. Commun.*, 1976, 432.
271. A. A. Isab and P. J. Sadler, *J. Chem. Soc., Dalton Trans.*, 1982, 135.
272. C. F. Shaw, III, J. Eldridge and M. P. Cancro, *J. Inorg. Biochem.*, 1981, **14**, 267.
273. N. Schaeffer, C. F. Shaw, H. O. Thompson and R. W. Satre, *Arthritis Rheum.*, 1980, **23**, 165.
274. F. Owings, E. L. Anderson, W. W. Holl and L. B. Killmer, Jr., *Tetrahedron Lett.*, 1982, **23**, 3245.
275. C. F. Shaw, III, M. P. Cancro, P. L. Witkiewicz and J. E. Eldridge, *Inorg. Chem.*, 1980, **19**, 3198.
276. P. L. Witkiewicz and C. F. Shaw, III, *J. Chem. Soc., Chem. Commun.*, 1981, 1111.
277. R. Hesse and P. Jennische, *Acta Chem. Scand.*, 1972, **26**, 3855.
278. P. Jennische, H. Anacker-Eickhoff and A. Wahlberg, *Acta Crystallogr., Sect. A*, 1975, **31**, S143.
279. S. L. Lawton, W. J. Rohrbaugh and G. T. Kokotailo, *Inorg. Chem.*, 1972, **11**, 2227.
280. W. Kuchen and H. Mayatapek, *Chem. Ber.*, 1968, **101**, 3454.
281. T. G. Spiro and F. J. Farrell, *Inorg. Chem.*, 1971, **10**, 1606.
282. O. Piovesana and P. F. Zanuzzi, *Angew, Chem., Int. Ed. Engl.*, 1980, **92**, 561; K. C. Lee and F. Aubke, *Inorg. Chem.*, 1980, **19**, 119.
283. F. Cariati, M. L. Ganadu, L. Naldini and S. Seneci, *Gazz. Chim. Ital.*, 1979, **109**, 181; W. Kuchen and H. Mayatapek, *Chem. Ber.*, 1968, **101**, 3454.
284. F. W. Pijpers, A. H. Dix and J. G. M. van der Linden, *Inorg. Chim. Acta*, 1974, **11**, 41; H. C. Brinkhoff, A. G. Matthijssen and C. G. Oomes, *Inorg. Nucl. Chem. Lett.*, 1971, **7**, 87.
285. J. G. Wijnhoven, W. P. J. H. Bosman and P. T. Beurskens, *J. Cryst. Mol. Struct.*, 1972, **2**, 7.
286. P. G. Jones, G. M. Sheldrick, M. George, A. Fuegner, F. Goetzfried and W. Beck, *Chem. Ber.*, 1971, **114**, 1413.
287. R. Uson, J. Vicente and J. Oro, *Inorg. Chim. Acta*, 1981, **52**, 29; F. N. Tebbe and E. L. Muetterties, *Inorg. Chem.*, 1970, **9**, 629.
288. M. J. Mays and J. Bailey, *J. Chem. Soc., Dalton Trans.*, 1977, 578.
289. A. Johnson and R. J. Puddephatt, *J. Chem. Soc., Dalton Trans.*, 1977, 1384.
290. R. F. Ziolo, J. A. Thich and Z. Dori, *Inorg. Chem.*, 1972, **11**, 626.
291. W. Beck, K. Burger and W. P. Fehlhammer, *Chem. Ber.*, 1971, **104**, 1816.
292. W. Beck, M. Bauder, W. P. Fehlhammer, P. Poellman and H. Schaechl, *Inorg. Nucl. Chem. Lett.*, 1968, **4**, 143.
293. W. Beck, W. Becker, K. F. Chew, W. Derbyshire, N. Logan, D. M. Revitt and D. B. Sowerby, *J. Chem. Soc., Dalton Trans.*, 1972, 245.
294. W. Beck, W. P. Fehlhammer, P. Poellman and H. Schaechl, *Chem. Ber.*, 1969, **102**, 1976.
295. J. L. Burmeister and E. T. Weleski, *Synth. React. Inorg. Metal-Org. Chem.*, 1972, **2**, 295.
296. N. A. Malik, P. J. Sadler, S. Neidle and G. L. Taylor, *J. Chem. Soc., Chem. Commun.*, 1978, 711.
297. E. G. Perevalova, E. I. Smyslova, V. P. Dyadchenko, K. I. Grandberg and A. N. Nesmeyanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 1455.

298. F. Bonati and G. Minghetti, *J. Chem. Soc., Chem. Commun.*, 1974, 88; G. Minghetti, G. Banditelli and F. Bonati, *Inorg. Chem.*, 1979, **18,** 658.
299. L. G. Vaughan, *J. Am. Chem. Soc.*, 1970, **92,** 730.
300. A. L. Balch and D. J. Doonan, *J. Organomet. Chem.*, 1977, **131,** 137.
301. A. Tiripicchio, M. T. Camellini and G. Minghetti, *J. Organomet. Chem.*, 1979, **171,** 399.
302. F. Bonati, A. Burini, M. Felici and B. R. Pietroni, *Gazz. Chim. Ital.*, 1983, **113,** 105.
303. F. Bonati, M. Felici, B. R. Pietroni and A. Burini, *Gazz. Chim. Ital.*, 1982, **112,** 5.
304. R. L. Kieft, W. M. Peterson, G. L. Blundell, S. Horton, R. A. Henry and H. B. Jonassen, *Inorg. Chem.*, 1976, **15,** 1721.
305. R. Uson, L. A. Oro, J. Gimeno, M. A. Ciriano, J. A. Cabeza, A. Tiripicchio and M. T. Camellini, *J. Chem. Soc., Dalton Trans.*, 1983, 323.
306. A. Tiripicchio, M. T. Camellini, R. Uson, L. A. Oro and J. A. Cabeza, *J. Organomet. Chem.*, 1983, **244,** 165.
307. G. Bergerhoff, *Z. Anorg. Allg. Chem.*, 1964, **327,** 139.
308. A. P. Zuur and W. L. Groeneveld, *Recl. Trav. Chim. Pays-Bas*, 1967, **86,** 1089.
309. M. E. Diemer, *J. Am. Chem. Soc.*, 1913, **35,** 553.
310. L. H. Skibsted and J. Bjerrum, *Acta Chem. Scand., Ser. A*, 1974, **28,** 764.
311. K. Brodersen and T. Kahlert, *Z. Anorg. Allg. Chem.*, 1967, **355,** 323.
312. R. Uson, A. Laguna and M. D. Villacampa, *Inorg. Chim. Acta*, 1984, **81,** 25.
313. H. N. Adams, W. Hiller and J. Strahle, *Z. Anorg. Allg. Chem.*, 1982, **485,** 81.
314. K. C. Dash, H. Schmidbaur and A. Schmidpeter, *Inorg. Chim. Acta*, 1980, **46,** 167.
315. D. Leonesi, A. Lorenzotti, A. Cingolani and F. Bonati, *Gazz. Chim. Ital.*, 1981, **111,** 483; F. Bonati, M. Felici, B. R. Pietroni and A. Burini, *Gazz. Chim. Ital.*, 1982, **112,** 5.
316. J. R. Lechat, R. H. de A. Santos, G. Banditelli and F. Bonati, *Cryst. Struct. Commun.*, 1982, **11,** 471; G. Banditelli, A. L. Bandini, G. Minghetti and F. Bonati, *Can. J. Chem.*, 1981, **59,** 1241.
317. F. Farha and R. T. Iwamoto, *Inorg. Chem.*, 1965, **4,** 844.
318. W. Clegg, *Acta Crystallogr., Sect. B*, 1976, **32,** 2712.
319. N. W. Alcock, P. Moore, P. A. Lampe and K. F. Mok, *J. Chem. Soc., Dalton Trans.*, 1982, 207.
320. H. G. Ang, W. E. Kow and K. F. Mok, *Inorg. Nucl. Chem. Lett.*, 1972, **8,** 829.
321. H. Schmidbaur and Y. Inoguchi, *Z. Naturforsch., Teil B*, 1980, **35,** 1329.
322. G. A. Barclay, M. A. Collard, C. M. Harris and J. V. Kingston, *J. Inorg. Nucl. Chem.*, 1969, **31,** 3509.
323. Y. Inoguchi, B. Milewski-Mahrla and H. Schmidbaur, *Chem. Ber.*, 1982, **115,** 3085.
324. W. Jeitschko and M. H. Moller, *Acta Crystallogr., Sect. B*, 1979, **35,** 573.
325. C. Mues and H.-U. Schuster, *Z. Naturforsch., Teil B*, 1980, **35,** 1055.
326. W. D. Johnston, R. C. Miller and D. H. Damon, *J. Less-Common Met.*, 1965, **8,** 272.
327. C. E. Myers, T. J. Conti and N. F. Marley, *J. Less-Common Met.*, 1976, **48,** 213.
328. R. Roulet, N. Q. Lan, W. R. Mason and G. P. Fenske, *Helv. Chim. Acta*, 1973, **56,** 2405.
329. G. Banditelli, A. L. Bandini, F. Bonati, R. G. Goel and G. Minghetti, *Gazz. Chim. Ital.*, 1982, **112,** 539.
330. K. C. Dash, A. Schmidpeter and H. Schmidbaur, *Z. Naturforsch., Teil B*, 1980, **35,** 1286.
331. K. C. Dash, J. Eberlein and H. Schmidbaur, *Synth. React. Inorg. Metal-Org. Chem.*, 1973, **3,** 375.
332. H. Schmidbaur and R. Franke, *Chem. Ber.*, 1972, **105,** 2985.
333. L. Malatesta, L. Naldini, G. Simonetta and F. Cariati, *Coord. Chem. Rev.*, 1966, **1,** 255.
334. J. Bailey, *J. Inorg. Nucl. Chem.*, 1973, **35,** 1921.
335. A. T. T. Hsieh, J. D. Ruddick and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1972, 1966.
336. F. W. B. Einstein and R. Restivo, *Acta Crystallogr., Sect. B*, 1975, **31,** 624.
337. A. J. Carty and A. Efraty, *Chem. Commun.*, 1968, 1559.
338. R. B. King and A. Efraty, *Inorg. Chim. Acta*, 1970, **4,** 319.
339. J. S. Charlton and D. I. Nichols, *J. Chem. Soc. (A)*, 1970, 1484.
340. I. Collamati, *Ric. Sci., Parte 2 Sez. A*, 1964, **6,** 363.
341. J. M. Meyer and A. L. Allred, *J. Inorg. Nucl. Chem.*, 1968, **30,** 1328.
342. A. D. Westland, *Can. J. Chem.*, 1969, **47,** 4135.
343. C. J. Hawkins, O. Moensted and J. Bjerrum, *Acta Chem. Scand.*, 1970, **24,** 1059.
344. J. W. Collier, A. R. Fox, I. G. Hinton and F. G. Mann, *J. Chem. Soc.*, 1964, 1819.
345. D. A. Couch and S. D. Robinson, *Chem. Commun.*, 1971, 1508; *Inorg. Chim. Acta*, 1974, **9,** 39; *Inorg. Chem.*, 1974, **13,** 456.
346. G. P. Fenske and W. R. Mason, *Inorg. Chem.*, 1974, **13,** 1783.
347. R. V. Parish, O. Parry and C. A. McAuliffe, *J. Chem. Soc., Dalton Trans.*, 1981, **10,** 2098.
348. M. J. Mays and P. A. Vergano, *J. Chem. Soc., Dalton Trans.*, 1979, 1112.
349. C. B. Colburn, W. E. Hill, C. A. McAuliffe and R. V. Parish, *J. Chem. Soc., Chem. Commun.*, 1979, 218.
350. E. L. Muetterties and C. W. Allegranti, *J. Am. Chem. Soc.*, 1970, **92,** 4114.
351. N. C. Baenziger, K. M. Dittemore and J. R. Doyle, *Inorg. Chem.*, 1974, **13,** 805; M. Khan, C. Oldham and D. G. Tuck, *Can. J. Chem.*, 1981, **59,** 2714.
352. P. G. Jones, G. M. Sheldrick, J. A. Muir, M. M. Muir and L. B. Pulgar, *J. Chem. Soc., Dalton Trans.*, 1982, 2123.
353. W. Clegg, *Acta Crystallogr., Sect. B*, 1978, **34,** 278.
354. J. J. Guy, P. G. Jones and G. M. Sheldrick, *Acta Crystallogr., Sect. B*, 1976, **32,** 1937.
355. J. A. Muir, M. M. Muir and E. Lorca, *Acta Crystallogr., Sect. B*, 1980, **36,** 931.
356. M. Barrow, H. B. Bürgi, D. K. Johnson and L. M. Venanzi, *J. Am. Chem. Soc.*, 1976, **98,** 2356.
357. L. J. Guggenberger, *J. Organomet. Chem.*, 1974, **81,** 271.
358. P. T. Beurskens, R. Pet, J. H. Noordik, J. W. A. van der Velden and J. J. Bour, *Cryst. Struct. Commun.*, 1982, **11,** 1039.
359. F. Klanberg, E. L. Muetterties and L. G. Guggenberger, *Inorg. Chem.*, 1968, **7,** 2272.
360. P. G. Jones, *Acta Crystallogr., Sect. B*, 1980, **36,** 3105.
361. P. G. Jones, *Z. Naturforsch., Teil B*, 1982, **37,** 937.

362. R. C. Elder, E. H. Kellerzeiher, M. Onady and R. R. Whittle, *J. Chem. Soc., Chem. Commun.*, 1981, 900.
363. P. G. Jones, *J. Chem. Soc., Chem. Commun.*, 1980, 1031.
364. K. Moss, R. V. Parish, A. Laguna, M. Laguna and R. Uson, *J. Chem. Soc., Dalton Trans.*, 1983, 2071.
365. R. Uson, A. Laguna and J. Vicente, *J. Organomet. Chem.*, 1976, **104**, 401.
366. S. S. Sandhu and R. S. Sandhu, *Indian J. Chem.*, 1971, **9**, 482.
367. D. W. Allen, F. G. Mann and I. T. Millar, *Chem. Ind. (London)*, 1966, 196.
368. D. W. Allen, I. T. Millar, F. G. Mann, R. M. Canadine and J. Walker, *J. Chem. Soc. (A)*, 1969, 1097.
369. H. Schmidbaur and F. E. Wagner, *Chem. Ber.*, 1979, **112**, 496.
370. W. Ludwig and W. Meyer, *Helv. Chim. Acta*, 1982, **65**, 934.
371. H. Schmidbaur, A. Wohlleben, U. Schubert, A. Frank and G. Huttner, *Chem. Ber.*, 1977, **110**, 2751.
372. H. Schmidbaur, S. Schattnerer, K. C. Dash and A. A. M. Aly, *Z. Naturforsch., Teil B*, 1983, **38**, 62; H. Schmidbaur and J. R. Mandl, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 640
373. H. Schmidbaur and A. A. M. Aly, *Angew. Chem.*, 1980, **92**, 66.
374. M. Davies and F. G. Mann, *J. Chem. Soc.*, 1974, 3791.
375. R. S. Nyholm, *Nature (London)*, 1951, **168**, 705.
376. W. Cochran, F. A. Hart and F. G. Mann, *J. Chem. Soc.*, 1957, 2816.
377. R. Uson, A. Laguna, J. Vicente, J. Garcia, P. G. Jones and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1981, 655.
378. A. J. Carty and A. Efraty, *Inorg. Chem.*, 1969, **8**, 543.
379. H. Schmidbaur, J. R. Mandl, J. M. Bassett, G. Blaschke and B. Zimmer-Gasser, *Chem. Ber.*, 1981, **114**, 433.
380. C. E. Briant, K. P. Hall and D. M. P. Mingos, *J. Organomet. Chem.*, 1982, **229**, C5.
381. F. Calderazzo and D. B. dell'Amico, *Inorg. Chem.*, 1982, **21**, 3639.
382. I. A. Kokovskii and G. F. Cherkasov, *Izv. Vyssh. Uchebn. Zaved. Tsvetn. Metall.*, 1974, **17**, 87.
383. H. H. Law, *Precious Met.*, 1982, **6**, 169.
384. E. H. Cho, S. N. Dixon and C. H. Pitt, *Metall. Trans. B*, 1979, **10**, 185.
385. A. S. Bychkov, O. M. Petrukhin, V. A. Zarinskii, Yu. A. Zolotov, L. V. Bakhtinova and G. G. Shanina, *Zh. Anal. Khim.*, 1976, **31**, 2114.
386. J. A. Harrison and J. Thompson, *Electrochim. Acta*, 1973, **18**, 829.
387. A. Rosenzweig and D. T. Cromer, *Acta Crystallogr.*, 1959, **12**, 709; L. E. Zyontz, S. C. Abrahams and J. L. Bernstein, *Acta Crystallogr., Sect. A*, 1981, **37**, C154; S. C. Abrahams, J. L. Bernstein, R. Liminga and E. T. Eisenmann, *J. Chem. Phys.*, 1980, **73**, 4585.
388. U. Nagel, K. Peters, H. G. von Schnering and W. Beck, *J. Organomet. Chem.*, 1980, **185**, 427.
389. H. J. Dothie, F. J. Llewellyn, W. Wardlaw and A. J. E. Welch, *J. Chem. Soc.*, 1939, 426.
390. P. G. Jones, W. Clegg and G. M. Sheldrick, *Acta Crystallogr., Sect. B*, 1980, **36**, 141.
391. H. Zhdanov and E. Shugam, *Acta Physicochem. URSS*, 1945, **20**, 253.
392. S. Esperås, *Acta Chem. Scand., Ser. A*, 1976, **30**, 527.
393. P. L. Bellon, M. Manassero and M. Sansoni, *Ric. Sci.*, 1969, **39**, 173.
394. R. Uson, A. Laguna, J. Garcia and M. Laguna, *Inorg. Chim. Acta*, 1979, **37**, 201.
395. B. M. Chadwick and S. G. Frankiss, *J. Mol. Struct.*, 1976, **31**, 1.
396. L. H. Jones, *J. Chem. Phys.*, 1965, **43**, 594.
397. L. H. Jones, *Inorg. Chem.*, 1963, **2**, 777.
398. H. Prosser, G. Wortman, K. Syassen and W. B. Holzapfel, *Z. Phys. B*, 1976, **24**, 7.
399. L. Pfeiffer, R. S. Raghavan, C. P. Lichtenwalner and K. W. West, *Phys. Rev. Lett.*, 1973, **30**, 635.
400. W. Potzel and G. L. Perlow, *Phys. Rev. Lett.*, 1972, **29**, 910.
401. A. Sacco and M. Freni, *Gazz. Chim. Ital.*, 1956, **86**, 195.
402. J. E. Parks and A. L. Balch, *J. Organomet. Chem.*, 1974, **71**, 453.
403. J. A. McCleverty and M. M. M. da Mota, *J. Chem. Soc., Dalton Trans.*, 1973, 2571.
404. L. G. Vaughan and W. A. Sheppard, *J. Am. Chem. Soc.*, 1969, **91**, 6151.
405. F. Bonati and G. Minghetti, *Gazz. Chim. Ital.*, 1973, **103**, 373.
406. R. Uson, A. Laguna, J. Vicente, J. Garcia, B. Bergareche and P. Brun, *Inorg. Chim. Acta*, 1978, **28**, 237.
407. R. Uson, A. Laguna, J. Vicente, J. Garcia and B. Bergareche, *J. Organomet. Chem.*, 1979, **173**, 349.
408. J. Browning, P. L. Goggin and R. J. Goodfellow, *J. Chem. Res. (S)*, 1978, 328.
409. G. Minghetti, L. Baratto and F. Bonati, *J. Organomet. Chem.*, 1975, **102**, 397.
410. G. Minghetti and F. Bonati, *J. Organomet. Chem.*, 1973, **54**, C62.
411. G. Minghetti and F. Bonati, *Inorg. Chem.*, 1974, **13**, 1600.
412. G. Minghetti and F. Bonati, *Gazz. Chim. Ital.*, 1972, **102**, 205.
413. G. Minghetti and F. Bonati, *Angew. Chem., Int. Ed. Engl.*, 1972, **11**, 429.
414. F. Bonati and G. Minghetti, *J. Organomet. Chem.*, 1973, **59**, 403.
415. K. Bartel and W. P. Fehlhammer, *Angew. Chem., Int. Ed. Engl.*, 1974, **13**, 599.
416. H. Schmidbaur, C. E. Zybill, G. Muller and C. Krügger, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 729.
417. H. Schmidbaur and O. Gasser, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 502.
418. N. Elliot and L. Pauling, *J. Am. Chem. Soc.*, 1938, **60**, 1846.
419. F. H. Brain, C. S. Gibson, J. A. J. Jarvis, R. F. Phillips, H. M. Powell and A. Tyabji, *J. Chem. Soc.*, 1952, 3686.
420. R. E. Rundle, *J. Am. Chem. Soc.*, 1954, **76**, 3101.
421. F. Coletta, R. Ettorre and A. Gambaro, *Inorg. Nucl. Chem. Lett.*, 1972, **8**, 667.
422. G. Krüss, *Liebigs Ann. Chem.*, 1887, **237**, 296.
423. T. J. Bergendahl, *J. Chem. Educ.*, 1975, **52**, 731.
424. A. Rabenau and H. Schulz, *J. Less-Common Met.*, 1976, **48**, 89; J. E. Cretier and G. A. Wiegers, *Mater. Res. Bull*, 1973, **8**, 1427.
425. C. Bertinotti and A. Bertinotti, *Acta Crystallogr., Sect. B*, 1972, **28**, 2635.
426. R. Hüttel and H. Forkl, *Chem. Ber.*, 1972, **105**, 1664.
427. T. J. Bergendahl and J. H. Waters, *Inorg. Chem.*, 1975, **14**, 2556.

428. H. Schmidbaur, J. R. Mandl, F. E. Wagner, D. F. van de Vondel and G. P. van der Kelen, *J. Chem. Soc., Chem. Commun.*, 1976, 170; D. F. van de Vondel, G. P. van der Kelen, H. Schmidbaur, A. Wohlleben and F. E. Wagner, *Phys. Scr.*, 1977, **16**, 364.
429. T. P. A. Viegers, J. M. Trooster, P. Bouten and T. P. Rit, *J. Chem. Soc., Dalton Trans.*, 1977, 2074.
430. P. Gütlich, B. Lehnis, K. Römhild and J. Strähle, *Z. Naturforsch., Teil B*, 1982, **37**, 550.
431. W. Denner, H. Schulz and H. d'Amour, *Acta Crystallogr., Sect. A*, 1979, **35**, 360.
432. L. V. Interrante and F. P. Bundy, *J. Inorg. Nucl. Chem.*, 1977, **39**, 1333.
433. R. Keller, J. Fenner and W. B. Holzapfel, *Mater. Res. Bull*, 1974, **9**, 1363.
434. H. Schmidbaur, *Acc. Chem. Res.*, 1975, **8**, 62.
435. H. Schmidbaur and R. Franke, *Inorg. Chim. Acta*, 1975, **13**, 85.
436. H. Schmidbaur and P. Jandik, *Inorg. Chim. Acta*, 1983, **74**, 97.
437. H. Schmidbaur and R. Franke, *Inorg. Chim. Acta*, 1975, **13**, 79; J. P. Fackler, Jr., H. H. Murray and J. D. Basil, *Organometallics*, 1984.
438. H. Schmidbaur, J. R. Mandl, A. Frank, G. Huttner, V. Bejenke and W. Richter, *Chem. Ber.*, 1976, **109**, 466.
439. H. Schmidbaur, J. R. Mandl, A. Frank and G. Huttner, *Chem. Ber.*, 1977, **110**, 2236.
440. H. Schmidbaur and J. R. Mandl, *Naturwissenschaften*, 1976, **63**, 585.
441. D. C. Calabro, B. A. Harrison, G. T. Palmer, M. K. Moguel, R. L. Rebbert and J. L. Burmeister, *Inorg. Chem.*, 1981, **20**, 4311.
442. (a) H. Schmidbaur, A. Wohlleben, F. E. Wagner, D. F. van de Vondel and G. P. van der Kelen, *Chem. Ber.*, 1977, **110**, 2758; (b) A. M. Mazany and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, 1984, **106**, 801.
443. T. Vanngard and S. Akerstrom, *Nature (London)*, 1959, **184**, 183.
444. T. J. Bergendahl and E. M. Bergendahl, *Inorg. Chem.*, 1972, **11**, 638.
445. J. G. M. van Rens, M. P. A. Viegers and E. de Boer, *Chem. Phys. Lett.*, 1974, **28**, 104.
446. R. Kirmse, B. Lorenz, W. Windsch and E. Hoyer, *Z. Anorg. Allg. Chem.*, 1971, **384**, 160.
447. J. H. Waters and H. B. Gray, *J. Am. Chem. Soc.*, 1965, **87**, 3534.
448. J. H. Waters, T. J. Bergendahl and S. R. Lewis, *Chem. Commun.*, 1971, 834.
449. R. L. Schlupp and A. H. Maki, *Inorg. Chem.*, 1974, **13**, 44.
450. J. G. M. van der Linden and H. G. J. van de Roer, *Inorg. Chim. Acta*, 1971, **5**, 254.
451. I. S. Jacobs, J. W. Bray, H. R. Hart, L. V. Interrante, J. S. Kasper and G. D. Watkins, *Phys. Rev. B*, 1976, **14**, 3036.
452. I. S. Jacobs, H. R. Hart, L. V. Interrante, J. W. Bray, J. S. Kasper, G. D. Watkins, D. E. Prober, W. E. Wolf and J. C. Bonner, *Physica B + C (Amsterdam)*, 1977, **86–88**, 655.
453. J. A. Northby, H. A. Groenendijk, L. J. de Jongh, J. C. Bonner, I. S. Jacobs and L. V. Interrante, *Phys. Rev. B*, 1982, **25**, 3215.
454. J. A. Northby, F. J. A. M. Greidanus, W. J. Huiskamp, L. J. de Jongh, I. S. Jacobs and L. V. Interrante, *J. Appl. Phys.*, 1982, **53**, 8032.
455. A. MacCragh and W. S. Koski, *J. Am. Chem. Soc.*, 1965, **87**, 2496.
456. I. F. Warren and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1968, **90**, 4823.
457. R. L. Rich and H. Taube, *J. Phys. Chem.*, 1954, **58**, 6.
458. A. Johnson and R. J. Puddephatt, *J. Chem. Soc., Dalton Trans.*, 1976, 1360; 1975, 115.
459. R. Kaptein, P. W. N. M. van Leevwen and R. Huis, *J. Chem. Soc., Chem. Commun.*, 1975, 568.
460. L. B. Asprey, F. H. Kruse, K. H. Jack and R. Maitland, *Inorg. Chem.*, 1964, **3**, 602.
461. F. W. B. Einstein, P. R. Rao, J. Trotter and N. Bartlett, *J. Chem. Soc. (A)*, 1967, 478; A. J. Edwards and G. R. Jones, *J. Chem. Soc. (A)*, 1969, 1936.
462. A. G. Sharpe, *J. Chem. Soc.*, 1949, 2901; 1950, 2907.
463. R. Hope and W. Klemm, *Z. Anorg. Allg. Chem.*, 1952, **268**, 364; N. Bartlett and P. L. Robinson, *J. Chem. Soc.*, 1961, 3417.
464. E. S. Clark, D. H. Templeton and C. H. MacGillavry, *Acta Crystallogr.*, 1958, **11**, 284.
465. K. P. Lorcher and J. Strahle, *Z. Naturforsch., Teil B*, 1975, **30**, 662.
466. T. Mundorf and K. Dehnicke, *Z. Naturforsch., Teil B*, 1973, **28**, 506.
467. J. R. Partington and A. L. Whynes, *J. Chem. Soc.*, 1949, 3135.
468. D. B. Dell'Amico and F. Calderazzo, *Gazz. Chim. Ital.*, 1973, **103**, 1099.
469. I. A. Kokovskiy and V. V. Gubaylovskiy, *Russ. Metall. (Engl. Transl.)*, 1978, 50.
470. G. D. Christian, M. Chateau-Gosselin and G. J. Patriarche, *Anal. Chim. Acta*, 1979, **107**, 83.
471. P. G. Jones and G. M. Sheldrick, *Acta Crystallogr., Sect. B*, 1978, **34**, 1353.
472. J. Strahle and H. Barnigshausen, *Z. Kristallogr.*, 1971, **134**, 471.
473. H. Ohtaki and M. Maeda, *Chem. Abstr.*, 1977, **86**, 181 120.
474. P. L. Goggin and J. Mink, *J. Chem. Soc., Dalton Trans.*, 1974, 1479.
475. Y. M. Bosworth and R. J. H. Clark, *Chem. Phys. Lett.*, 1974, **28**, 611.
476. A. Gangopadhyay and A. Chakravorty, *J. Chem. Phys.*, 1961, **35**, 2206.
477. R. W. Schwartz, *Inorg. Chem.*, 1977, **16**, 836.
478. C. M. Harris and I. H. Reece, *Nature (London)*, 1958, **182**, 1665.
479. A. J. Hall and D. P. N. Satchell, *J. Chem. Soc., Chem. Commun.*, 1976, 163.
480. A. J. Hall and D. P. N. Satchell, *J. Chem. Soc., Dalton Trans.*, 1977, 1404.
481. L. I. Elding and A. B. Gröning, *Acta Chem. Scand., Ser. A*, 1978, **32**, 867.
482. J. L. Ryan, *Inorg. Chem.*, 1969, **8**, 2058.
483. B. I. Peshchevitskii and V. I. Belevantsev, *Zh. Neorg. Khim.*, 1969, **14**, 2393.
484. L. Cattalini, A. Orio and M. L. Tobe, *J. Am. Chem. Soc.*, 1967, **89**, 3130.
485. G. Patel and R. S. Satchell, *Inorg. Chim. Acta*, 1981, **54**, L97.
486. B. I. Peshchevitskii and G. I. Shamovskaya, *Koord. Khim.*, 1980, **6**, 1657.
487. N. S. Ivanova and B. P. Matseevskii, *Latv. PSR Zinat. Akad. Vestis, Kim. Ser.*, 1979, 537.
488. K. G. Moodley and M. J. Nicol, *J. Chem. Soc., Dalton Trans.*, 1977, 993.
489. A. Peloso, *Coord. Chem. Rev.*, 1975, **16**, 95.

490. E. V. Makotchenko, B. I. Peshchevitskii and R. I. Novoselov, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1978, 44.
491. B. S. Maritz and R. van Eldik, *Inorg. Chim. Acta*, 1976, **20**, 43.
492. A. Finch, P. N. Gates, T. H. Page and K. B. Dillon, *J. Chem. Soc., Dalton Trans.*, 1983, 1837.
493. Z. A. Fokina, N. I. Timoschenko, V. F. Lapko and S. V. Volkov, *Ukr. Khim. Zh.* (*Russ. Ed.*), 1982, **48**, 1014.
494. Z. A. Fokina, S. I. Kuznetsov, E. V. Bryukhova and N. I. Timoschenko, *Koord. Khim.*, 1977, **3**, 1235.
495. Z. A. Fokina, S. I. Kuznetsov, N. I. Timoschenko and E. V. Bryukhova, *Russ. J. Phys. Chem.* (*Engl. Transl.*), 1979, **53**, 75.
496. M. S. Kharasch and H. S. Isbell, *J. Am. Chem. Soc.*, 1931, **53**, 3053.
497. P. W. J. de Graaf, J. Boersma and G. J. M. van der Kerk, *J. Organomet. Chem.*, 1976, **105**, 399.
498. G. V. Nizova and G. P. Saul'pin, *React. Kinet. Catal. Lett.*, 1982, **20**, 69.
499. A. Hakansson and L. Johansson, *Chem. Scr.*, 1975, **7**, 201.
500. L. Manojlovic-Muir, *J. Organomet. Chem.*, 1974, **73**, C45.
501. E. Wiberg and H. Neumaier, *Inorg. Nucl. Chem. Lett.*, 1965, **1**, 35.
502. L. Carlsson and G. Lundgren, *Acta Chem. Scand.*, 1967, **21**, 819.
503. B. I. Peshchevitskii, V. I. Belevantsev and N. V. Kurbatova, *Zh. Neorg. Khim.*, 1971, **16**, 1898.
504. V. I. Dubinskii, V. M. Shul'man and B. I. Peshchevitskii, *Zh. Neorg. Khim.*, 1968, **13**, 54.
505. P. G. Jones, H. Rumpel, E. Schwarzmann and G. M. Sheldrick, *Acta Crystallogr., Sect. B*, 1979, **35**, 1435.
506. P. G. Jones, G. M. Sheldrick, E. Schwarzmann and A. Vielmaeder, *Z. Naturforsch., Teil B*, 1983, **38**, 10.
507. E. Schwarzmann, E. Schulze and J. Mohn, *Z. Naturforsch., Teil B*, 1974, **29**, 561; S. Kagawa and M. Goto, *Kinzoku Sankabutsu*, 1978, 28.
508. S. J. Ashcroft and E. Schwarzmann, *J. Chem. Soc., Faraday Trans. 1*, 1972, **68**, 1360.
509. J. P. Hoare, *Electrochim. Acta*, 1966, **11**, 203.
510. W. M. Johnson, R. Dev and G. H. Cady, *Inorg. Chem.*, 1972, **11**, 2260.
511. K. C. Lee and F. Aubke, *Inorg. Chem.*, 1979, **18**, 389.
512. K. C. Lee and F. Aubke, *Inorg. Chem.*, 1980, **19**, 119.
513. B. O. Field and C. J. Hardy, *J. Chem. Soc.*, 1964, 4428.
514. C. C. Addison, G. S. Brownlee and N. Logan, *J. Chem. Soc., Dalton Trans.*, 1972, 1440.
515. C. D. Garner and S. C. Wallwork, *J. Chem. Soc.* (*A*), 1970, 3092.
516. H. D. Wasel-Nielen and R. Hoppe, *Z. Anorg. Allg. Chem.*, 1970, **375**, 43.
517. H. Klassen and R. Hoppe, *Naturwissenschaften*, 1976, **63**, 387.
518. S. Yamada and K. Yamanouchi, *Bull. Chem. Soc. Jpn.*, 1970, **43**, 1744.
519. T. Inazu, *Bull. Chem. Soc. Jpn.*, 1966, **39**, 1065.
520. F. H. Howie and C. R. Veale, *J. Inorg. Nucl. Chem.*, 1966, **28**, 1149.
521. D. Mootz, A. Rabenau, H. Wunderlich and G. Rosenstein, *J. Solid State Chem.*, 1973, **6**, 583.
522. A. Rabenau, H. Rau and G. Rosenstein, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 145.
523. A. Rabenau and H. Rau, *Inorg. Synth.*, 1973, **14**, 160.
524. H. M. Haendler, D. Mootz, A. Rabenau and G. Rosenstein, *J. Solid State Chem.*, 1974, **10**, 175.
525. P. G. Jones, E. Schwarzmann, G. M. Sheldrick and H. Timpe, *Z. Naturforsch., Teil B*, 1981, **36**, 1050.
526. A. Dunand and R. Gerdil, *Acta Crystallogr., Sect. B*, 1975, **31**, 370.
527. J. B. Melpolder and J. L. Burmeister, *Synth. React. Inorg. Metal-Org. Chem.*, 1981, **11**, 167.
528. J. B. Melpolder and J. L. Burmeister, *Inorg. Chem.*, 1972, **11**, 911.
529. H. Schmidtke, *Ber. Bunsenges. Phys. Chem.*, 1967, **71**, 1138.
530. R. Uson, J. Fornies, A. Laguna and J. I. Valenzuela, *Synth. React. Inorg. Metal-Org. Chem.*, 1982, **12**, 935.
531. W. M. Scovell, G. C. Stocco and R. S. Tobias, *Inorg. Chem.*, 1970, **9**, 2682.
532. A. T. Pilipenko, O. P. Ryabushko and G. Matsibura, *Zh. Anal. Khim.*, 1979, **34**, 1088.
533. G. C. Pellacani, *Inorg. Chim. Acta*, 1975, **12**, L3.
534. A. C. Fabretti, G. C. Franchini, G. C. Pellacani and G. Peyronel, *Inorg. Nucl. Chem. Lett.*, 1976, **12**, 163.
535. A. C. Fabretti, G. C. Pellacani, G. Peyronel and B. Scapinelli, *J. Inorg. Nucl. Chem.*, 1974, **36**, 1067.
536. A. R. Latham, V. C. Mascall and H. B. Gray, *Inorg. Chem.*, 1965, **4**, 788.
537. V. M. Shulman, Z. A. Savel'eva and R. I. Novoselov, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1973, **18**, 376.
538. J. V. Micallet and D. P. N. Satchell, *Inorg. Chim. Acta*, 1982, **64**, L187; *J. Chem. Soc., Perkin Trans. 2*, 1982, 971.
539. A. J. Hall and D. P. N. Satchell, *Chem. Ind.* (*London*), 1976, 373; *J. Chem. Soc., Perkin Trans. 2*, 1976, 1278.
540. E. E. Aynsley, N. N. Greenwood and J. B. Leach, *Chem. Ind.* (*London*), 1966, 379.
541. P. J. Hendra and N. Sadasivan, *J. Chem. Soc.*, 1965, 2063.
542. D. H. Brown, G. C. McKinley and W. E. Smith, *J. Chem. Soc., Dalton Trans.*, 1978, 199.
543. M. A. Mazid, M. T. Razi and P. J. Sadler, *Inorg. Chem.*, 1981, **20**, 2872.
544. J. H. Enemark and J. A. Ibers, *Inorg. Chem.*, 1968, **7**, 2636.
545. T. J. Bergendahl and J. H. Waters, *Inorg. Chem.*, 1975, **14**, 2556.
546. J. H. Noordik, *Cryst. Struct. Commun.*, 1973, **2**, 81.
547. T. Takiguchi, M. Abe, K. Kurosaki, E. Asada and M. Nakagome, *Kogyo Kagaku Zasshi*, 1967, **70**, 1182.
548. J. G. M. van der Linden, *Recl. Trav. Chim. Pays-Bas*, 1971, **90**, 1027.
549. J. G. M. van der Linden and W. P. M. Nijssen, *Z. Anorg. Allg. Chem.*, 1972, **392**, 93.
550. J. A. Cras, J. H. Noordik, P. T. Beurskens and A. M. Verhoeven, *J. Cryst. Mol. Struct.*, 1971, **1**, 155.
551. P. T. Beurskens, J. A. Cras, T. W. Hummelink and J. G. M. van der Linden, *Recl. Trav. Chim. Pays-Bas*, 1970, **89**, 984.
552. P. T. Beurskens, J. A. Cras and J. G. M. van der Linden, *Inorg. Chem.*, 1970, **9**, 475.
553. P. T. Beurskens, J. A. Cras and J. J. Steggerda, *Inorg. Chem.*, 1968, **7**, 810.
554. H. J. A. Blaauw, R. J. F. Nivard and G. J. M. van der Kerk, *J. Organomet. Chem.*, 1964, **2**, 236.
555. B. Lorenz, R. Kirmse and E. Hoyer, *Z. Anorg. Allg. Chem.*, 1970, **378**, 144.
556. R. Kirmse, B. Lorenz and W. Windsch, *Z. Anorg. Allg. Chem.*, 1971, **384**, 160.
557. N. Sonoda and T. Tanaka, *J. Inorg. Nucl. Chem.*, 1973, **35**, 1145.

558. V. V. K. Rao and A. Mueller, *Z. Chem.*, 1970, **10**, 197.
559. A. Mueller, V. V. K. Rao and G. Klinksiek, *Chem. Ber.*, 1971, **104**, 1892.
560. J. G. M. van der Linden, *J. Inorg. Nucl. Chem.*, 1972, **34**, 1645.
561. J. H. Noordik and P. T. Beurskens, *J. Cryst. Mol. Struct.*, 1971, **1**, 339.
562. J. H. Noordik, T. W. Hummelink and J. G. M. van der Linden, *J. Coord. Chem.*, 1973, **2**, 185.
563. F. T. H. M. Wijnhoven, W. P. Bosman, J. Willemse and J. A. Cras, *Recl. Trav. Chim. Pays-Bas*, 1979, **98**, 492.
564. Y. Yamamoto, F. Kato and T. Tanaka, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 1072.
565. P. M. T. M. van Attekum and J. M. Trooster, *J. Chem. Soc., Dalton Trans.*, 1980, 201.
566. W. Beck, W. P. Fehlhammer, P. Pollman and R. S. Tobias, *Inorg. Chim. Acta*, 1968, **2**, 467.
567. H. H. Schmidtke and D. Garthoff, *J. Am. Chem. Soc.*, 1967, **89**, 1317; W. Beck and H. Noth, *Chem. Ber.*, 1984, **117**, 419.
568. M. Weishaupt and J. Straehle, *Z. Naturforsch., Teil B*, 1976, **31**, 554.
569. L. H. Skibsted and J. Bjerrum, *Acta Chem. Scand.*, 1974, **28**, 740.
570. L. H. Skibsted, *Acta Chem. Scand., Ser. A*, 1979, **33**, 113; 1983, **37**, 613.
571. C. S. Gibson and W. M. Colles, *J. Chem. Soc.*, 1931, 2407.
572. P. K. Monaghan and R. J. Puddephatt, *Inorg. Chim. Acta*, 1975, **15**, 231.
573. D. B. Dell'Amico and F. Calderazzo, *Gazz. Chim. Ital.*, 1973, **103**, 1099.
574. L. Cattalini, R. J. H. Clark, A. Orio and C. K. Poon, *Inorg. Chim. Acta*, 1968, **2**, 62.
575. L. Cattalini, M. Nicolini and A. Orio, *Inorg. Chem.*, 1966, **5**, 1674.
576. L. Cattalini, A. Doni and A. Orio, *Inorg. Chem.*, 1967, **6**, 280.
577. L. Cattalini, A. Orio and M. L. Tobe, *Inorg. Chem.*, 1967, **6**, 75.
578. L. Cattalini and M. L. Tobe, *Inorg. Chem.*, 1966, **5**, 1145.
579. L. Cattalini, G. Marangoni and M. Martelli, *Inorg. Chem.*, 1968, **7**, 1145.
580. L. Cattalini, V. Ricevuto, A. Orio and M. L. Tobe, *Inorg. Chem.*, 1968, **7**, 51.
581. M. S. Kharasch and T. M. Beck, *J. Am. Chem. Soc.*, 1934, **56**, 2057.
582. V. A. Belonozov, N. I. Ushakova, Ya. V. Salyn, V. G. Pleshakov, B. E. Zaitsev, V. I. Zelenov, A. M. El'bert and A. K. Molodkin, *Zh. Neorg. Khim.*, 1981, **26**, 963.
583. M. A. S. Goher, *Bull. Soc. Chim. Fr.*, 1982, 262.
584. R. J. Dubois, J. Hagimassy, A. C. Noble and F. D. Popp, *J. Heterocycl. Chem.*, 1966, **3**, 377.
585. R. Huttel and A. Konietzny, *Chem. Ber.*, 1973, **106**, 2098.
586. D. B. Dell'Amico, F. Calderazzo, F. Marchetti and S. Merlino, *Gazz. Chim. Ital.*, 1978, **108**, 627.
587. J. Vicente, M. T. Chicote and M. D. Bermúdez, *Inorg. Chim. Acta*, 1982, **63**, 35.
588. J. Vicente and M. T. Chicote, *Inorg. Chim. Acta*, 1981, **54**, L259.
589. B. P. Block and J. C. Bailar, *J. Am. Chem. Soc.*, 1951, **73**, 4722.
590. W. H. Baddley, F. Basolo, H. B. Gray, C. Nolting and A. J. Poe, *Inorg. Chem.*, 1963, **2**, 921.
591. C. F. Weick and F. Basolo, *Inorg. Chem.*, 1966, **5**, 576.
592. G. Nardin, L. Randaccio, G. Annibale, G. Natile and B. Pitteri, *J. Chem. Soc., Dalton Trans.*, 1980, 220.
593. M. J. Blandamer, J. Burgess, S. J. Hamshere and P. Wellings, *Transition Met. Chem.*, 1979, **4**, 161.
594. R. D. Alexander and P. N. Holper, *Transition Met. Chem.*, 1980, **5**, 108.
595. G. Annibale, G. Natile and L. Cattalini, *J. Chem. Soc., Dalton Trans.*, 1976, 1547.
596. B. I. Peshchevitskii and G. I. Shamovskaya, *Zh. Neorg. Khim.*, 1972, **17**, 2648.
597. W. H. Baddley and F. Basolo, *Inorg. Chem.*, 1964, **3**, 1087.
598. D. L. Fant and C. F. Weick, *Inorg. Chem.*, 1973, **12**, 1864.
599. G. Annibale, G. Natile, B. Pitteri and L. Cattalini, *J. Chem. Soc., Dalton Trans.*, 1978, 728.
600. G. Annibale, L. Cattalini and G. Natile, *J. Chem. Soc., Dalton Trans.*, 1975, 188.
601. L. Kh. Minacheva, G. G. Sadikov, V. G. Sakharova, A. Sh. Gladkaya and M. A. Porai-Koshits, *Koord. Khim.*, 1983, **9**, 566.
602. K. Brodersen and T. Kahlert, *Z. Anorg. Allg. Chem.*, 1967, **355**, 323.
603. Yu. N. Kukushkin and L. I. Zorina, *Zh. Neorg. Khim.*, 1967, **12**, 568.
604. A. A. Grinberg and Y. S. Varshavskii, *Dokl. Akad. Nauk SSSR*, 1965, **163**, 646.
605. C. M. Harris, *J. Chem. Soc.*, 1959, 682.
606. C. M. Harris and T. N. Lockyer, *J. Chem. Soc.*, 1959, 3083.
607. R. C. Conrad and J. V. Rund, *Inorg. Chem.*, 1972, **11**, 129.
608. G. A. Barclay, C. M. Harris and J. V. Kingston, *Chem. Ind. (London)*, 1965, 227.
609. A. A. McConnell, D. H. Brown and W. E. Smith, *Spectrochim. Acta, Part A*, 1982, **38**, 265, 737.
610. T. Mundorf and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1974, **408**, 146.
611. G. Annibale, L. Cattalini, A. A. El-Awady and G. Natile, *J. Chem. Soc., Dalton Trans.*, 1974, 802.
612. G. Annibale, G. Natile and L. Cattalini, *J. Chem. Soc., Dalton Trans.*, 1976, 285.
613. W. T. Robinson and E. Sinn, *J. Chem. Soc., Dalton Trans.*, 1975, 726.
614. R. J. Charlton, C. M. Harris, H. Patil and N. C. Stephenson, *Inorg. Nucl. Chem. Lett.*, 1966, **2**, 409.
615. V. Kumar, M. M. Hao and N. Ahmad, *Indian J. Chem., Sect. A*, 1979, **17**, 305.
616. R. Uson, J. Vicente, M. T. Chicote, P. G. Jones and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1983, 1131.
617. N. F. Borkett and M. I. Bruce, *Inorg. Chim. Acta*, 1975, **12**, L33.
618. A. J. Canty, N. J. Minchin, P. C. Healy and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1982, 1795.
619. A. J. Canty, N. J. Minchin, J. M. Patrick and A. H. White, *Aust. J. Chem.*, 1983, **36**, 1107.
620. R. Timkovich and A. Tulinsky, *Inorg. Chem.*, 1977, **16**, 962.
621. A. MacCragh and W. S. Koski, *J. Chem. Soc.*, 1965, **87**, 2496.
622. E. B. Fleischer and A. Laszlo, *Inorg. Nucl. Chem. Lett.*, 1969, **5**, 373.
623. H. Sugimoto, *J. Chem. Soc., Dalton Trans.*, 1982, 1169.
624. P. Bamfield and P. A. Mack, *J. Chem. Soc. (C)*, 1968, 1961.
625. J. H. Kim and G. W. Everett, Jr., *Inorg. Chem.*, 1979, **18**, 3145.
626. J. H. Kim and G. W. Everett, Jr., *Inorg. Chem.*, 1981, **20**, 853.
627. F. G. Mann and D. Purdie, *J. Chem. Soc.*, 1940, 1235.

628. B. T. Heaton and R. J. Kelsey, *Inorg. Nucl. Chem. Lett.*, 1975, **11**, 363.
629. R. J. Puddephatt and P. J. Thompson, *J. Chem. Soc., Dalton Trans.*, 1975, 810.
630. M. A. Bennett, K. Hoskins, W. R. Kneen, R. S. Nyholm, P. B. Hitchock, R. Mason, G. B. Robertson and A. D. C. Towl, *J. Am. Chem. Soc.*, 1971, **93**, 4591.
631. C. M. Harris and R. S. Nyholm, *J. Chem. Soc.*, 1957, 63.
632. L. F. Warren and M. A. Bennett, *Inorg. Chem.*, 1976, **15**, 3126.
633. V. F. Duckworth and N. C. Stephenson, *Inorg. Chem.*, 1969, **8**, 1661.
634. R. Uson, A. Laguna, M. Laguna, E. Fernandez, P. G. Jones and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1982, 1971.
635. H. Schmidbaur, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 907.
636. R. A. Penneman and R. R. Ryan, *Acta Crystallogr., Sect. B*, 1972, **28**, 1629.
637. C. Bertinotti and A. Bertinotti, *Acta Crystallogr., Sect. B*, 1970, **26**, 422.
638. L. H. Jones, *Inorg. Chem.*, 1964, **3**, 1581.
639. L. H. Jones, *Inorg. Chem.*, 1965, **4**, 1472.
640. J. M. Smith, L. H. Jones, I. K. Kressin and R. A. Penneman, *Inorg. Chem.*, 1965, **4**, 369.
641. L. Cattalini, A. Orio and M. L. Tobe, *Inorg. Chem.*, 1967, **6**, 75.
642. C. Bertinotti and A. Bertinotti, *C.R. Hebd. Seances Acad. Sci., Ser. B*, 1971, **273**, 33.
643. M. H. Ford-Smith, J. J. Habeeb and J. H. Rawsthorne, *J. Chem. Soc., Dalton Trans.*, 1972, 2116.
644. H. Isci and W. R. Mason, *Inorg. Chem.*, 1983, **22**, 2266.
645. J. Vicente, M. T. Chicote, A. Arcas, M. Artigao and R. Jimenez, *J. Organomet. Chem.*, 1983, **247**, 123.
646. L. Malatesta and F. Bonati, 'Isocyanide Complexes of Metals', Wiley, New York, 1969.
647. K. Leary, A. Zalkin and N. Bartlett, *J. Chem. Soc., Chem. Commun.*, 1973, 131; *Inorg. Chem.*, 1974, **13**, 775.
648. N. Bartlett and K. Leary, *Rev. Chim. Miner.*, 1976, **13**, 82.
649. G. Kaindl, K. Leary and N. Bartlett, *J. Chem. Phys.*, 1973, **59**, 5050.
650. V. B. Sokolov, V. N. Prusakov, A. V. Ryzhkov, Yu. V. Drobyshevskii and S. S. Khoroshev, *Dokl. Akad. Nauk SSSR*, 1976, **229**, 884.
651. J. H. Holloway and G. J. Schrobilgen, *J. Chem. Soc., Chem. Commun.*, 1975, 623.
652. M. J. Vasile, T. J. Richardson, F. A. Stevie and W. E. Falconer, *J. Chem. Soc., Dalton Trans.*, 1976, 351.
653. J. E. Griffiths and W. A. Sunder, *Spectrochim. Acta, Part A*, 1979, **35**, 1329.
654. V. B. Sokolov, V. G. Tsinoev and A. V. Ryzhkov, *Teor. Eksp. Khim.*, 1980, **16**, 345.
655. W. A. Sunder, A. L. Wayda, D. Distefano, W. E. Falconer and J. E. Griffiths, *J. Fluorine Chem.*, 1979, **14**, 299.
656. A. J. Edwards, W. E. Falconer, J. E. Griffiths, W. A. Sunder and M. J. Vasile, *J. Chem. Soc., Dalton Trans.*, 1974, 1129.
657. J. Brunvoll, A. A. Ischenko, A. A. Ivanov, G. V. Romanov, V. B. Sokolov, V. P. Spiridinov and T. G. Strand, *Acta Chem. Scand., Ser. A*, 1982, **36**, 705.
658. S. Gambarotta, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Chem. Soc., Chem. Commun.*, 1983, 1304.
659. A. N. Nesmeyanov, E. G. Perevalova, K. I. Grandberg, D. A. Lemenovskii, T. V. Baukova and O. B. Afanassova, *J. Organomet. Chem.*, 1974, **65**, 131.
660. L. Malatesta, *Gold Bull.*, 1975, **8**, 48.
661. (a) J. M. M. Smits, P. T. Beurskens and J. J. Steggerda, *J. Cryst. Spectrosc. Res.*, 1983, **13**, 381; (b) J. W. A. van der Velden, P. T. Beurskens, J. J. Bour, W. P. Bosman, J. H. Noordik, M. Kolenbrander and J. A. K. M. Buskes, *Inorg. Chem.*, 1984, **23**, 146.
662. D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.*, 1976, 1163.
663. D. M. P. Mingos, *Philos. Trans. R. Soc. London, Ser. A*, 1982, **308**, 75.
664. D. M. P. Mingos, *Pure Appl. Chem.*, 1980, **52**, 705.
665. D. G. Evans and D. M. P. Mingos, *J. Organomet. Chem.*, 1983, **232**, 171.
666. P. M. T. M. van Attekum, J. W. A. van der Velden and J. M. Trooster, *Inorg. Chem.*, 1980, **19**, 701.
667. C. Battistoni, G. Mattogno, R. Zanoni and L. Maldini, *J. Electron Spectrosc. Relat. Phenom.*, 1982, **28**, 23.
668. J. S. Wall, J. F. Hainfeld, P. A. Bartlett and S. J. Singer, *Ultramicroscopy*, 1982, **8**, 397.
669. H. Kanter and K. Dimroth, *Tetrahedron Lett.*, 1975, 545.
670. F. Demartin, M. Manassero, L. Nalkini, R. Ruggeri and M, Sansoni, *J. Chem. Soc., Chem. Commun.*, 1981, 222.
671. J. W. A. van der Velden, J. J. Bour, R. Pet, W. P. Bosman and J. H. Noordik, *Inorg. Chem.*, 1983.
672. J. W. A. van der Velden, J. J. Bour, F. A. Vollenbroek, P. T. Beurskens and J. M. M. Smits, *J. Chem. Soc., Chem. Commun.*, 1979, 1162.
673. P. L. Bellon, M. Manassero, L. Naldini and M. Sansoni, *J. Chem. Soc., Chem. Commun.*, 1972, 1035.
674. P. L. Bellon, M. Manassero and M. Sansoni, *J. Chem. Soc., Dalton Trans.*, 1973, 2423.
675. J. W. A. van der Velden, J. J. Bour, B. F. Otterloo, W. P. Bosman and J. H. Noordik, *J. Chem. Soc., Chem. Commun.*, 1981, 583.
676. J. W. A. van der Velden, J. J. Bour, J. J. Steggerda, P. T. Beurskens, M. Rosenboom and J. H. Noordik, *Inorg. Chem.*, 1982, **21**, 4321.
677. C. E. Briant, K. P. Hall and D. M. P. Mingos, *J. Organomet. Chem.*, 1983, **254**, C18.
678. M. Manassero, L. Naldini and M. Sansoni, *J. Chem. Soc., Chem. Commun.*, 1979, 385.
679. F. A. Vollenbroek, W. P. Bosman, J. J. Bour, J. H. Noordik and P. T. Beurskens, *J. Chem. Soc., Chem. Commun.*, 1979, 387.
680. J. W. A. van der Velden, J. J. Bour, W. P. Bosman and J. H. Noordik, *Inorg. Chem.*, 1983, **22**, 1913.
681. J. W. A. van der Velden, J. J. Bour, W. P. Bosman and J. H. Noordik, *J. Chem. Soc., Chem. Commun.*, 1981, 1218.
682. P. L. Bellon, F. Cariati, M. Manassero, L. Naldini and M. Sansoni, *Chem. Commun.*, 1971, 1423.
683. F. Cariati and L. Naldini, *J. Chem. Soc., Dalton Trans.*, 1972, 2286.
684. J. M. M. Smits, P. T. Beurskens, J. J. Bour and F. A. Vollenbroek, *J. Cryst. Spectrosc. Res.*, 1983, **13**, 365.
685. K. P. Hall, B. R. C. Theobald, D. I. Gilmour, D. M. P. Mingos and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 1982, 528.

686. F. A. Vollenbroek, J. P. van den Berg, J. W. A. van der Velden and J. J. Bour, *Inorg. Chem.*, 1980, **19**, 2685.
687. D. W. Diesveld, E. M. Menger, H. T. Edzes and W. S. Veeman, *J. Am. Chem. Soc.*, 1980, **102**, 7935.
688. M. K. Cooper, G. R. Dennis, K. Henrick and M. McPartlin, *Inorg. Chim. Acta*, 1980, **45**, L151.
689. J. G. M. van der Linden, M. L. H. Paulissen and J. E. J. Schmitz, *J. Am. Chem. Soc.*, 1983, **105**, 1903.
690. F. Cariati and L. Naldini, *Inorg. Chim. Acta*, 1971, **5**, 172.
691. F. A. Vollenbroek, P. C. P. Bouten, J. M. Trooster, J. P. van den Berg and J. J. Bour, *Inorg. Chem.*, 1978, **17**, 1345.
692. F. A. Vollenbroek, J. J. Bour and J. W. A. van der Velden, *Recl. Trav. Chim. Pays-Bas*, 1980, **99**, 137.
693. V. G. Albano, P. L. Bellon, M. Manassero and M. Sansoni, *Chem. Commun.*, 1970, 1210.
694. M. McPartlin, R. Mason and L. Malatesta, *Chem. Commun.*, 1969, 334.
695. P. Bellon, M. Manassero and M. Sansoni, *J. Chem. Soc., Dalton Trans.*, 1972, 1481.
696. J. M. M. Smits, P. T. Beurskens, J. W. A. van der Velden and J. J. Bour, *J. Cryst. Spectrosc. Res.*, 1983, **13**, 373.
697. J. M. M. Smits, J. J. Bour, F. A. Vollenbroek and P. T. Beurskens, *J. Cryst. Spectrosc. Res.*, 1983, **13**, 355.
698. C. E. Briant, B. R. C. Theopald, J. W. White, L. K. Bell, D. M. P. Mingos and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 1981, 201.
699. J. W. A. van der Velden, F. A. Vollenbroek, J. J. Bour, P. T. Beurskens, J. M. M. Smits and W. P. Bosman, *Recl. Trav. Chim. Pays-Bas*, 1981, **100**, 148.
700. G. Schmid, R. Pfeil, R. Boese, F. Bandermann, S. Meyer, G. H. M. Calis and J. W. A. van der Velden, *Chem. Ber.*, 1981, **114**, 3634.
701. G. Schmid and H. Nöth, *Chem. Ber.*, 1967, **100**, 2899.
702. N. N. Greenwood and J. Staves, *J. Chem. Soc., Dalton Trans.*, 1978, 1144.
703. C. P. Magee, L. G. Sneddon, D. C. Beer and R. N. Grimes, *J. Organomet. Chem.*, 1975, **86**, 159.
704. H. M. Colquhoun, T. J. Greenhough and M. G. H. Wallbridge, *J. Chem. Soc., Chem. Commun.*, 1976, 1019.
705. H. M. Colquhoun, T. J. Greenhough and M. G. H. Wallbridge, *Acta Crystallogr., Sect. B*, 1977, **33**, 3604.
706. H. M. Colquhoun, T. J. Greenhough and M. G. H. Wallbridge, *J. Chem. Soc., Dalton Trans.*, 1978, 303.
707. H. M. Colquhoun, T. J. Greenhough and M. G. H. Wallbridge, *J. Chem. Soc., Dalton Trans.*, 1979, 619.
708. M. C. Baird, *J. Inorg. Nucl. Chem.*, 1967, **29**, 367.
709. F. Glockling and K. A. Hooton, *J. Chem. Soc.*, 1962, 2658.
710. F. Glockling and M. D. Wilbey, *J. Chem. Soc. (A)*, 1968, 2168.
711. W. Clegg, *Acta Crystallogr., Sect. B*, 1978, **34**, 278.
712. R. V. Parish and P. J. Rowbotham, *J. Chem. Soc., Dalton Trans.*, 1973, 37.
713. J. A. Dilts and M. P. Johnson, *Inorg. Chem.*, 1966, **5**, 2079.
714. A. T. T. Hsieh, J. D. Ruddick and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1972, 1966.
715. C. E. Coffey, J. Lewis and R. S. Nyholm, *J. Chem. Soc.*, 1964, 1741.
716. A. Davison and J. E. Ellis, *J. Organomet. Chem.*, 1972, **36**, 113.
717. A. S. Kasenally, R. S. Nyholm, R. J. O'Brien and M. H. B. Stiddard, *Nature (London)*, 1964, **204**, 871.
718. R. J. Haines, R. S. Nyholm and M. H. B. Stiddard, *J. Chem. Soc. (A)*, 1968, 46.
719. J. B. Wilford and H. M. Powell, *J. Chem. Soc. (A)*, 1969, 8.
720. P. Braunstein and J. Dehand, *J. Organomet. Chem.*, 1975, **88**, C24.
721. E. W. Abel and G. V. Huston, *J. Inorg. Nucl. Chem.*, 1968, **30**, 2339.
722. L. M. Bower and M. H. B. Stiddard, *J. Chem. Soc. (A)*, 1968, 706.
723. W. A. G. Graham, *Inorg. Chem.*, 1968, **7**, 315.
724. A. S. Kasenally, J. Lewis, A. R. Manning, J. R. Miller, R. S. Nyholm and M. H. B. Stiddard, *J. Chem. Soc.*, 1965, 3407.
725. K. A. I. F. M. Mannan, *Acta Crystallogr.*, 1967, **23**, 649.
726. M. Casey and A. R. Manning, *J. Chem. Soc. (A)*, 1971, 2989.
727. F. E. Simon and J. W. Lauher, *Inorg. Chem.*, 1980, **19**, 2338.
728. S. A. R. Knox and F. G. A. Stone, *J. Chem. Soc. (A)*, 1969, 2559.
729. S. A. R. Knox and F. G. A. Stone, *J. Chem. Soc. (A)*, 1971, 2874.
730. T. L. Blundell and H. M. Powell, *J. Chem. Soc. (A)*, 1971, 1685.
731. B. T. Kilbourn, T. L. Blundell and H. M. Powell, *J. Chem. Soc., Chem. Commun.*, 1965, 444.
732. D. A. Brown and R. T. Sane, *Curr. Sci.*, 1972, **41**, 877.
733. R. T. Sane and P. R. Kulkarni, *Curr. Sci.*, 1974, **43**, 42.
734. S. Breitschaft and F. Basolo, *J. Am. Chem. Soc.*, 1966, **88**, 2702.
735. A. Davison, W. McFarlane, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, 1962, 3653.
736. M. A. Bennett and D. J. Patmore, *Inorg. Chem.*, 1971, **10**, 2387.
737. J. P. Collman, F. D. Vastine and W. R. Roper, *J. Am. Chem. Soc.*, 1966, **88**, 5035.
738. R. Uson, A. Laguna, M. Laguna, P. G. Jones and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1981, 366.
739. J. E. Ellis and M. C. Palazzotto, *J. Am. Chem. Soc.*, 1976, **98**, 8264.
740. J. E. Ellis, *J. Am. Chem. Soc.*, 1981, **103**, 6106.
741. J. E. Ellis and R. A. Faltynek, *J. Chem. Soc., Chem. Commun.*, 1975, 966.
742. A. S. Kasenally, R. S. Nyholm and M. H. B. Stiddard, *J. Am. Chem. Soc.*, 1964, **86**, 1884.
743. R. D. George, S. A. R. Knox and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1973, 972.
744. B. F. G. Johnson, J. Lewis, P. R. Raithby and A. Sanders, *J. Organomet. Chem.*, 1984, **260**, C29.
745. J. W. Lauher and K. Wald, unpublished results.
746. B. Chiswell and L. M. Venanzi, *J. Chem. Soc. (A)*, 1966, 901.
747. C. E. Briant, K. P. Hall and D. M. P. Mingos, *J. Chem. Soc., Chem. Commun.*, 1983, 843.
748. G. R. Clark, C. M. Cochrane, W. R. Roper and L. J. Wright, *J. Organomet. Chem.*, 1980, **199**, C35.
749. G. A. Carriedo, D. Hodgson, J. A. K. Howard, K. Marsden, F. G. A. Stone, M. J. Went and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1982, 1006.
750. M. R. Awang, G. A. Carriedo, J. A. K. Howard, K. A. Mead, I. Moore, C. M. Nunn and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1983, 964.
751. J. W. Lauher and K. Wald, *J. Am. Chem. Soc.*, 1981, **103**, 7648.

752. M. Green, K. A. Mead, R. M. Mills, I. D. Salter, F. G. A. Stone and P. Woodward, *J. Chem. Soc., Chem., Commun.*, 1982, 51.
753. M. I. Bruce and B. K. Nicholson, *J. Organomet. Chem.*, 1983, **250**, 627.
754. B. F. G. Johnson, D. A. Kaner, J. Lewis, P. R. Raithby and M. J. Rosales, *J. Organomet. Chem.*, 1982, **231**, C59.
755. B. F. G. Johnson, D. A. Kaner, J. Lewis and M. J. Rosales, *J. Organomet. Chem.*, 1982, **238**, C73.
756. L. W. Bateman, M. Green, J. A. K. Howard, K. A. Mead, R. M. Mills, I. D. Salter, F. G. A. Stone and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1982, 773.
757. L. W. Bateman, M. Green, K. A. Mead, R. M. Mills, I. D. Salter, F. G. A. Stone and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1983, 2599.
758. L. J. Farrugia, M. J. Freeman, M. Green, A. G. Orpen, F. G. A. Stone and I. D. Salter, *J. Organomet. Chem.*, 1983, **249**, 273.
759. M. J. Mays, P. R. Raithby, P. L. Taylor and K. Henrick, *J. Organomet. Chem.*, 1982, **224**, C45.
760. P. Braunstein, G. Predieri, A. Tiripicchio and E. Sappa, *Inorg. Chim. Acta*, 1982, **63**, 113.
761. L. J. Farrugia, J. A. K. Howard, P. Mitrprachachon, J. L. Spencer, F. G. A. Stone and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1978, 260.
762. B. F. G. Johnson, D. A. Kaner, J. Lewis and P. R. Raithby, *J. Organomet. Chem.*, 1981, **215**, C33; K. Burgess, B. F. G. Johnson, D. A. Kaner, J. Lewis, P. R. Raithby and S. N. A. B. Syed-Mustaffa, *J. Chem. Soc., Chem. Commun.*, 1983, 455.
763. J. A. K. Howard, L. Farrugia, C. Foster, F. G. A. Stone and P. Woodward, *Eur. Cryst. Meeting*, 1980, **6**, 73.
764. C. W. Bradford, W. van Bronswijk, R. J. H. Clark and R. S. Nyholm, *J. Chem. Soc. (A)*, 1970, 2889.
765. K. Burgess, B. F. G. Johnson and J. Lewis, *J. Organomet. Chem.*, 1983, **247**, C42.
766. K. Burgess, B. F. G. Johnson and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1983, 1179.
767. B. F. G. Johnson, D. A. Kaner, J. Lewis and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1981, 753.
768. K. Burgess, B. F. G. Johnson, J. Lewis and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 1983, 1661.
769. M. I. Bruce and B. K. Nicholson, *J. Organomet. Chem.*, 1983, **252**, 243.
770. B. F. G. Johnson, D. A. Kaner, J. Lewis, P. R. Raithby and M. J. Taylor, *J. Chem. Soc., Chem. Commun.*, 1982, 314.
771. M. J. Freeman, M. Green, A. G. Orpen, I. D. Salter and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1983, 1332.
772. I. D. Salter and F. G. A. Stone, *J. Organomet. Chem.*, 1984, **260**, C71.
773. B. F. G. Johnson, D. A. Kaner, J. Lewis, P. R. Raithby and M. J. Taylor, *Polyhedron*, 1982, **1**, 105.
774. B. F. G. Johnson, J. Lewis, J. N. Nicholls, J. Puga and K. H. Whitmire, *J. Chem. Soc., Dalton Trans.*, 1983, 787.
775. A. G. Cowie, B. F. G. Johnson, J. Lewis, J. N. Nicholls, P. R. Raithby and M. J. Rosales, *J. Chem. Soc., Dalton Trans.*, 1983, 2311.
776. B. F. G. Johnson, J. Lewis, W. J. H. Nelson, J. N. Nicholls, J. Puga, P. R. Raithby, M. J. Rosales, M. Schröder and M. D. Vargas, *J. Chem. Soc., Dalton Trans.*, 1983, 2447.
777. S. R. Bunkhall, H. D. Holden, B. F. G. Johnson, J. Lewis, G. N. Pain, P. R. Raithby and M. J. Taylor, *J. Chem. Soc., Chem. Commun.*, 1984, 25.
778. B. F. G. Johnson, J. Lewis, W. J. H. Nelson, J. Puga, D. Braga, M. McPartlin and W. Clegg, *J. Organomet. Chem.*, 1983, **243**, C13.
779. B. F. G. Johnson, J. Lewis, W. J. H. Nelson, P. R. Raithby and M. D. Vargas, *J. Chem. Soc., Chem. Commun.*, 1983, 608.
780. B. F. G. Johnson and J. Lewis, *Philos. Trans. R. Soc. London*, 1982, **308**, 5.
781. W. A. Herrmann, C. Bauer and J. Weichmann, *J. Organomet. Chem.*, 1983, **243**, C21.
782. M. I. Bruce and B. K. Nicholson, *J. Chem. Soc., Chem. Commun.*, 1982, 1141.
783. M. I. Bruce and B. K. Nicholson, *Organometallics*, 1984, **3**, 101.
784. P. Braunstein, J. Rose, Y. Dusausoy and J.-P. Mangeot, *C.R. Hebd. Seances Acad. Sci.*, 1982, **294**, II, 967.
785. E. Roland, K. Fischer and H. Vahrenkamp, *Angew. Chem. Int. Ed. Engl.*, 1983, **22**, 326.

56.1
Zinc and Cadmium

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56.1.1 INTRODUCTION

This survey is in two parts, the first dealing with the coordination chemistry of zinc and cadmium, particularly the recent rapidly growing activity in the stuctural investigation of complexes of these elements with a wide range of ligands, and the second, with the biological aspects of zinc and cadmium chemistry. We begin with an account of the application of physical techniques to the study of the coordination chemistry of zinc and cadmium and then focus mainly on the structural features of their complexes, classified according to ligand.

The coordination chemistry of zinc and cadmium in both the non-biological and biological areas has been the subject of intensive research; every reference cannot be cited and selection has had to be severe. Priority is given mainly to work of the last 10 years but frequent references to reviews are provided in the text, both to those which are mainly comprehensive listings of papers and to those which deal critically with a particular topic leading back into earlier work. Wherever possible references have been chosen with the latter feature in mind, particularly where several reports on one topic have appeared at about the same time.

The general chemistry of the two elements has recently been surveyed in detail by Aylett[1] and the well-established main features of the chemistry, particularly structural features, are described in standard texts.[2] Earlier work and particular aspects are also well documented;[3,4] more detailed coverage of earlier work is also available[4–6] and earlier work has been periodically reviewed.[7] Structural work on inorganic systems is particularly well described and correlated by Wells.[8] Recent developments in the coordination chemistry of these elements is comprehensively surveyed in refs. 9–15 and 1468b–j and a similar coverage of recent aspects of reactivity and mechanism is to be found in refs. 16–22. It is not practicable to cover in detail the large volume of work which has been carried out on the determination of the stability constants of zinc and cadmium complexes* with a large range of ligands but a selection of these are to be found[23,24a] and selected thermodynamic information is also available.[25,1468i] Procedures for the determination of stability constants are well documented[26a] and critical surveys[26b] of the computer programmes which are so much a part of such studies are now available. Detailed information on sources of data from recent studies in this area are to be found in listings of references.[9–15,1468c–h] A very large number of preparations have been reported, but in general unless several techniques are used in the study of the products to give convergent structural information they will not be surveyed here but listings and references to them are readily available.[9–15,1468a–h]

We shall first explore some of the important structural features of zinc and cadmium complexes and, to anticipate our findings a little, we shall find a rich variety of stereochemistry for each of these elements. One of their most striking features is their stereochemical flexibility; each is willing to submit readily to the structural demands of the ligand, but they often do so in different ways. In the second part of this survey we shall see how this ready variation of stereochemistry is put to good use in the active site environment—and probably function—of the supremely important zinc metalloenzymes, enzymes which are capable of dramatic catalysis of a wide range of reactions.

56.1.2 THE APPLICATION OF PHYSICAL TECHNIQUES TO THE STUDY OF COORDINATION AT ZINC AND CADMIUM

56.1.2.1 NMR, NQR and Related Topics

A fairly recent development in zinc and cadmium chemistry has been the use of NMR to study the coordination environment of these metals; ^{111}Cd, ^{113}Cd and ^{67}Zn nuclei have been

* A structure–reactivity relationship which predicts formation constants of complexes with organic ligands has been put forward.[24b]

studied and, of course, much information has been obtained by studying the NMR of nuclei in ligands. The following studies serve to illustrate these developments; additional information is available in sections on ligands and in the biochemical section.

Several studies have now been made on the high-resolution NMR of ^{111}Cd (natural abundance = 12.8%, $I = \frac{1}{2}$) and ^{113}Cd (natural abundance = 12.3%, $I = \frac{1}{2}$); the ^{113}Cd (13.31 MHz at 1.4 T) NMR spectra of aqueous solutions of cadmium(II) salts in the presence and absence of many uni- and bi-dentate complexing agents have been reported.[27,28] A large non-linear variation in chemical shift with concentration in the 0.1–5 mol l^{-1} range for the free halide salts shows formation of both mono- and poly-halogeno complexes. Cadmium sulfate, perchlorate and nitrate show linear relationships depending much less on concentration, suggesting little association, although the results for nitrate in these studies are in contrast with previous Raman results which showed considerable coordinated nitrate. In the presence of a wide variety of organic and inorganic ligands, the shifts produced are essentially linear, and we may now conclude that: (i) ligands binding through oxygen (sulfate, nitrate, nitrite, acetate, formate) cause increased shielding of the cadmium nucleus; (ii) those binding through nitrogen (ammonia, pyridine, azide, ethylenediamine) produce a marked deshielding; (iii) ligands in which binding *via* sulfur seems probable (thiourea, thiocyanate) cause very large deshielding. Many of the nitrogen ligands also produce line broadening, which stems from an apparently slower dissociation rate of these complexes. The chemical shifts, or the broadening, may be used for the titrimetric determination of binding constants.

Similar results are found in ^{111}Cd (16.31 MHz at 1.807 T) NMR studies;[29] large non-linear chemical shifts with concentration of cadmium chloride solutions were observed, while the nitrate, sulfate and perchlorate show much smaller linear shifts, consistent with the formation of stable chlorocadmium complexes even at low concentration.

Colton has reported ^{111}Cd NMR data for a comprehensive selection of tetrahalocadmate(II) ions,[30] and has also investigated the equilibria established in solutions containing cadmium and several different halides ions. Colton has also investigated a range of $[CdX_2(PBu_3)_2]$ and $[Cd_2X_4(PBu_3)_3]$ complexes, together with mixed cadmium–mercury phosphine complexes.[31] The formation of edtaH_4 complexes has been studied by ^{113}Cd NMR, and a series of solution equilibria were proposed to account for the results.[32] Biochemical applications of ^{113}Cd NMR include the study of cadmium-substituted horse-liver alcohol dehydrogenase[33] and cadmium-substituted carbonic anhydrase (see Section 56.1.13.2 *et seq.*).[34,1466d,1468c–h]

Promising results are being obtained from the application of magic angle spinning techniques to the ^{113}Cd NMR study of solid cadmium compounds[35–37] and further development of this method is yielding interesting results. Using FT methods, millimolar concentrations of Cd can be studied by ^{113}Cd NMR.[35] The range of chemical shifts found for a variety of organic and inorganic complexes was *ca.* 640 p.p.m. [relative to $Cd(ClO_4)_2$] and is consistent with the ^{113}Cd chemical shifts being dominated by the paramagnetic contribution to the shielding constant. The range of ^{113}Cd chemical shifts spanned by the organocadmium compounds reported is in excess of 300 p.p.m., *i.e.* about 15 times that of the ^{13}C range, the order of which, in increasing shielding, is $CdMe_2$ < MeCdEt < $CdEt_2$ < $CdPr^n_2$ < $CdBu^n_2$ < $CdPh_2$. This trend is not observed in dialkylmercury compounds, where the *n*-propyl and ethyl shieldings are reversed. Cd–C and Cd–H coupling constants are reported. Alkyl group exchange in the system shown in equation (1) has been demonstrated. The rate of exchange is slow on the NMR timescale ($<4.5 \times 10^2\ s^{-1}$). ^{113}Cd organometallic chemical shifts are very sensitive to the Lewis basicity of the solvent. T_1 measurements indicate that for aqueous solutions of $Cd(ClO_4)_2$ and $CdCl_2$, the intermolecular dipole–dipole contribution to relaxation is significant, while the mechanism of relaxation for $CdBr_2$ and CdI_2 is unclear; the mechanism of relaxation in the CdR_2 systems is predominantly spin rotation. Further examples of the use of Cd NMR are given under the appropriate ligands.

$$CdMe_2 + CdEt_2 \rightleftharpoons 2Cd(Et)(Me) \qquad (1)$$

A full description of the application of Fourier transform NMR methods to ^{67}Zn (natural abundance, 4.12%, $I = \frac{5}{2}$, resonance at 4.81 MHz at 1.807 T) appeared in 1974.[39] The dependence of the chemical shift on concentration for solutions of Zn halides is strongly non-linear, higher frequencies being observed with increasing concentration, an effect partly ascribed to the change of stereochemistry from octahedral to tetrahedral on passing along the series from $[Zn(H_2O)_6]^{2+}$ to $[ZnX_4]^{2-}$. No shift with concentration was found for the ClO_4^-, NO_3^-, and SO_4^{2-} salts. For the halides, an anomalous shift to higher frequency was observed on substitution of D_2O as solvent, whereas no shift was observed for the salts containing non-coordinating anions. Similar results were obtained from ^{199}Hg studies. The halides show an increasing chemical shift with increasing temperature and line widths are sensitive to concentration, pH, temperature and the nature of the anion. Two slightly earlier reports,[40,41] by the same group, on the concentration dependence of the chemical shift pointed out that this behaviour resembles that found for analogous cadmium systems and is attributable also to the formation of mono- and poly-halogeno complexes, even at low concentrations.

Recently ^{67}Zn NMR studies of imidazole and carboxylate complexes[30] and the thermolysin–zinc complex[42] have been described and ^{113}Cd NMR studies of a wide range of complexes have been reported;[43–53] ^{113}Cd NMR data for pyridine adducts of Cd^{II} β-diketonates show the influence of the sulfur and nitrogen donors on the chemical shift.[54] Cadmium NMR studies on cadmium fluoride have also been reported.[55] A ^{113}Cd NMR study of ^{113}Cd-enriched phosphine oxide complexes has been reported[43] and a multinuclear NMR investigation (^{31}P and ^{113}Cd) of cadmium dithiophosphate complexes has been described.[47]

A number of multinuclear NMR studies (^{1}H, ^{13}C, ^{57}Zn, ^{113}Cd and ^{77}Se) of the $[ML_4]^{2-}$ (M = Cd or Zn; HL = RSH) and $[ML_2]^{2-}$ (M = Zn or Cd; H_2L = chelating dithiol) species, including the mixed ligand complexes $[Cd(SPh)_n(SePh)_{4-n}]^{2-}$, have been reported.[44–46] A ^{113}Cd NMR study of $[Cd_{10}(SCH_2CH_2OH)_{16}]^{4+}$ has been reported.[56]

Ligand nuclei have been the subject of many studies, for example, ^{35}Cl NMR has been used as a probe of chelated zinc(II) environments.[57] Molar relaxivity is suitable for characterizing the zinc environment in terms of the quadrupolar relaxation of ^{35}Cl nuclei that it can produce in 0.5 M NaCl. Bidentate chelation (glycinate, glutamate, succinate) increases its effectiveness in producing ^{35}Cl relaxation. Terdentate chelation (iminodiacetate, aspartate) can either increase or decrease the amount of relaxation caused by zinc. The least relaxation is produced when the ligand atoms have a formal negative charge and a large acidity constant. In some instances, zinc chelated by four ligand atoms (nitrilotriacetate) is effective for ^{35}Cl relaxation, and therefore such chelation does not represent a coordinatively saturated environment a point of significance in terms of zinc function in metalloenzymes (see Section 56.1.14.1.1). Molar relaxivities for 1:1 and 2:1 chelates usually differ and it is possible to derive formation constants which are consistent with literature values. In a number of systems, hydrolysis reactions are readily identified. Data are readily available.[9–15,1468c–h]

A wide range of pyridine complexes have been investigated. The ^{13}C NMR chemical shifts of the ligand carbon atoms in such complexes have been correlated with the polarizing ability of the metal ion[58] and a good correlation between the calculated pK_a value of the ligand and δ was observed. A multinuclear NMR study (^{13}C and ^{15}N) of ^{13}CN-enriched cyano complexes has been reported {$[Zn(CN)_4]^{2-}$, $J_{C,N}$ 8.9 Hz, $\delta(^{13}C)$ −19.0, $\delta(^{15}N)$ −101.4; $[Cd(CN)_4]^{2-}$, $J_{C,N}$ 7.7 Hz, $\delta(^{13}C)$ −16.5, $\delta(^{15}N)$ −97.8; $\delta(^{13}C)$ with respect to KCN, $\delta(^{15}N)$ with respect to $NaNO_3$}.[59] Recent developments have been reviewed.[9–15,1468c–i]

Measurements of ^{1}H NMR of zinc and cadmium complexes, both in solution and of crystals, have been made. A broad-line ^{1}H NMR study of $[Zn(OH_2)_6][ClO_4]_2$ over the 4.2–363 K temperature range confirms the basic octahedral symmetry of the cation, although some reorientation of the water molecules does occur.[60]

A ^{1}H NMR study of hydrated zinc acetate has been made, and a comparison with the corresponding cadmium species reveals that the geometry of the crystal is dictated by the number of water molecules and the anion, rather than by the cation.[61]

The rotational motion of the ammonium ions in ammonium trifluorozincate has been studied over the temperature range 298–1 K by ^{1}H NMR methods.[62] Halogen NQR studies of $[MX_4]^{2-}$ and $[MX_3]^-$ salts (M = Cd or Zn; X = Cl, Br or I) have been reported.[63]

The lattice dynamics of $[Zn(H_2O)_6]$ $[ClO_4]_2$ have been investigated by ^{1}H NMR (4.2–363 K) and vibrational spectroscopic methods;[64,65] monitoring of the IR-active vibrational modes of the coordinated water revealed phase transitions at 284, 256.5 and 233 K. A ^{1}H NMR study has also revealed that the water–perchlorate hydrogen-bonding interaction in $[M(H_2O)_6][ClO_4]_2$ (M = Zn or Cd) is significantly weaker for the cadmium compound.[66] The interconversion of the isomers of cadmium complexes of the imines $RC(S)CHR'CH{=}NRPr^i$ has been followed by ^{1}H NMR over the temperature range −50 to 60 °C.[67] ^{19}F NMR has not been neglected, for instance, the magnetic screening of the ^{19}F nuclei in the complexes $ZnF_2{\cdot}xH_2O$ (x = 4, 7 or 10) and ZnF(OH) has been calculated from ^{19}F NMR studies.[68]

A considerable number of NQR studies have been made on zinc and cadmium complexes, for example, the ^{35}Cl, ^{81}Br and ^{127}I NQR spectra of a number of CdX_2–polyether complexes have been reported and indicate that the compounds are dimeric in solution, with symmetrical halogen bridges between the metal atoms.[69] A number of amino acids and peptide complexes of cadmium(II) have been investigated by ^{14}N NQR spectroscopy.[70]

The cadmium(II)–pyridine system has been quite extensively studied,[71,72] and the ^{14}N NQR spectra of the complexes $[Cd_2(py)_3(NO_3)_4]$, $[Cd(py)_2Cl_2]$ and $[Cd(py)_3(NO_3)_2]$[73] have been reported. ^{14}N NQR data on the $Zn(ClO_4)_2$ complex with hexamethylenetetramine have been obtained.[74] The ^{14}N NQR spectra of the complexes $[Zn(py)_4(NO_3)_2]$, $[Zn(py)_3(NO_3)_2]$ and $[Zn(py)_2X_2]$ (X = Cl, Br, I, NCS or NO_3) have been reported.[75] Non-coordinated cations in some zinc complex salts have also been studied, *e.g.* the Raman and ^{87}Rb NMR spectra of $Rb_2[ZnCl_4]$[76,77] and $Rb_2[ZnBr_4]$[78–80] have been reported. High-resolution solid state ^{13}C NMR spectra $[Me_4N]_2[ZnCl_4]$[81] and ^{35}Cl NQR spectra of $K_2[ZnCl_4]$[82] have also been reported. The tetrahedral complexes $[MX_2L_2]$ (M = Zn or Cd; L = pyridine or substituted pyridine; X = halide) have been studied by halogen NQR and ^{13}C NMR methods.[83]

Recent developments have been the subject of several reviews.[9–15,1468c–h] There is no doubt that ^{13}C NMR provides a powerful tool for investigating the coordination of organic ligands and their acid–base behaviour.[1469a–e]

56.1.2.2 X-Ray Diffraction, Photoelectron Spectroscopy, Vibrational Spectroscopy and EXAFS

In recent years the technique of X-ray scattering on solutions of metal complexes has yielded interesting results on coordination geometries and metal–ligand distances;[1469i,j] a most interesting finding is that metal–ligand distances of the complexes often differ from those found in the solid state and instances of this are pointed out under the various ligand headings. A recent illustration of the application of this technique combined with Raman spectroscopy is provided in the study of zinc–en complexes in aqueous solution; $[Zn(en)_2]^{2+}$ and $[Zn(en)_3]^{2+}$ have the expected tetrahedral and octahedral geometries respectively.[84a]*

A considerable number of studies of photoelectron spectra of zinc, cadmium (and mercury) compounds[84b] have been described; as we shall see below the results are often not without controversy. The He^I photoelectron spectra of the zinc dihalides have been recently described and comparison with mercury is interesting here.[85a] In contrast to previous work, the $3d$ ionizations are well characterized. The fine structure can be interpreted only on the basis of weak crystal field effects, and there is no evidence for covalency on the part of the inner $3d$ electrons. Preliminary results on Zn dialkyls lead to the same conclusion.[85b] In contrast,[86] the photoelectron spectra of $HgMe_2$, CNHgMe and $Hg(CN)_2$ show an orbital energy sequence ($\delta > \pi > \sigma$) which is opposite to that deduced for the Zn compounds ($\sigma > \pi > \delta$). Preferential stabilization of the π (d) level on substitution of Me by CN in $HgMe_2$ and MeHgCN is attributed to back-donation of electron density from $d\pi$ orbitals to the antibonding π^* orbitals of the cyanide. This was regarded as the first direct evidence for $d\pi$–π^* back-bonding in compounds involving formally d^{10} cations of the B sub-group elements. Again, the results of a photoelectron study[87] of Zn, Cd and Hg halides (except the fluorides) differed from those of a previous report. Much larger chemical shifts are observed for the inner $3d$ metal orbitals, and analysis of the results leads to a larger electronegativity for Hg than for Zn, contrary to the previous result, but in agreement with the Pauling scale. A reinterpretation of the Allred–Rochow electronegativity values for these elements using more accurate screening constant values gives an order of $Zn \leq Cd < Hg$, in agreement with these spectroscopic results and the Pauling scale.

It is interesting to compare these findings with those of a slightly earlier study in which the photoelectron spectra of gaseous zinc, cadmium and mercury halides were investigated.[88–90] Assuming a linear molecule, a simple MO scheme was assigned, and the valence structure appears to be $\sigma_g^2\sigma_u^2\pi_u^4\pi_g^4$. Spin–orbit splitting of the π_g and π_u orbitals is observed, with the π_g splittings generally being greater than those of the π_u orbitals, and the iodide splittings exceeding those of the bromides. It is notable that the π_u molecular orbital has metal contribution, whereas the π_g does not. There is a striking discontinuity in the energies of most of the molecular orbitals on going from cadmium to mercury ($Zn > Cd > Hg$), in common with the trends observed for several other properties of compounds of Group IIB. An order of electronegativity may be deduced which is in agreement with the Allred–Rochow scale ($Zn > Hg$) but at variance with the Pauling scale.

Photoelectron spectra of ZnF_2 in the vapour phase have been recorded using pseudomolecular beam techniques, and it is proposed that the valence shell configuration is:

$$\mathrm{Zn} \quad (\pi_g)^4(\delta_g)^4(\sigma_g)^2 \qquad \mathrm{F} \quad (\sigma_g)^2(\pi_u)^2(\sigma_u)^2(\pi_g)^4$$

* Related and important studies are to be found under the appropriate ligands and are surveyed in recent reviews.[1468c–h]

This differs from the configuration assigned to the other Group IIB dihalides, but closely resembles those of the IIA dihalides.[91] The photoelectron spectrum of CdF_2 was also recorded with results very similar to those reported for ZnF_2.[91a]

Photoelectron spectroscopy studies have not been confined only to halides.[91b] The X-ray photoelectron spectra of the phosphides, sulfides and oxides of Zn show[92] that incomplete screening of the $(n+1)$-s and -p electrons through the nd shells leads to non-systematic changes of orbital energies and valence electron radii in the first, second and third row elements. Interaction of the metal 3d state with the 3sp of the bonded element considerably affects the valence bands of the compounds, and thus should be taken into account when considering the electronic structure of Zn compounds.[1468c] IR and X-ray photoelectron studies have been reported on the oxygen-bonded hydroxylamide derivatives $MX_2(ONH_2Me)_2$ (M = Zn or C; X = Cl or Br) and $MCl_2(ONH_2OH)_2$.[93,94] The X-ray photoelectron spectra of a series of metal chelates of edta (including Zn)[95] show a nearly linear relationship between the chemical shifts of the N(1s) electron binding energies and the charge on the N atoms of the chelates, calculated using Pauling electronegatives. Further information is available.[1468c–g]

The photoelectron spectra of the complexes $[NR_4]_2[ZnX_4]$ (X = Cl, Br, NCO, NCS or NCSe) have been reported.[96] A decrease in binding energy is noted on increasing the R chain length in the tetraalkylammonium ion, while the trend in binding energies associated with X follows the spectrochemical series. In a related area the ionization spectra of $ZnCl_2$ and $CdCl_2$ have been determined, and compared with the calculated ionization potentials.[97] The spectra consist of three groups of energies; the first is due to the metal outer valence s orbitals and the chlorine p orbitals, the second to the metal d orbitals, and the third to the chlorine inner s orbitals.

A large number of IR and some Raman studies of zinc and cadmium complexes with various ligands have been made and some of these are described under the appropriate ligand. The following studies show features of interest and earlier work is well documented in them. The complete vibrational spectra of $K_2M(CN)_4$ (M = Zn, Cd or Hg) and $[Zn(NH_3)_4]I_2$ have been reported.[98–101] An IR study of $K_2M(CN)_4$ and $M(CN)_2$ up to pressures of 30 kbar[102] shows a lowering of the symmetry of the $[M(CN)_4]^{2+}$ ion to D_{2d} through compression when M = Zn or Cd, while either D_2 or C_{3v} symmetry must be considered when M = Hg. The symmetry of $Zn(CN)_2$ is also lowered, whereas $M(CN)_2$ (M = Cd or Hg) are converted into highly symmetric forms. The behaviour of CdF_2 under high pressure has also been studied using Raman spectroscopy.[103] A study of the vibrational spectra of ZnFX, CdF_2 and CdFX (X = Cl or Br) has been made; for the latter the mixed halo species were prepared by mixing equimolar amounts of CdF_2 and CdX_2 in the vapour phase. The fluorohalides were characterized as molecular species for the first time,[104] and further developments have been surveyed.[1468c–h]

Cadmium complexes have not been neglected in these and other physical studies. For example, an electron diffraction study of $CdBr_2$ has been made, and it was concluded that the equilibrium structure corresponds to a linear Br—Cd—Br molecule, with a Cd—Br distance of 2.372 Å and a Br—Br distance of 4.694 Å.[105] Raman and IR spectroscopic studies of $CdCl_2$ have also been reported.[106] The Cd^{2+}—en system is of interest, and a detailed study of the vibrational spectra (IR and Raman) of $[Cd(en)(NO_2)_2]$ and its deuterated derivative has been reported.[107]

The relatively recent technique of quantitative Raman spectroscopy has been applied[108a] to the determination of the equilibrium constants for the reactions in equation (2). The advantages of the technique include the direct proportionality of the signal obtained for a single complex species in a complicated equilibrium to the concentration of the species; this is particularly advantageous in cases of mixed complex formation, where most methods give only indirect evidence for the existence of mixed species, and where very complicated relationships exist between measurable quantities and the total concentration of reactants. The results obtained (K_0–K_3 = 5.3, 8.5, 5, 0.45) agree well with previous values obtained from polarographic and potentiometric studies.

$$[CdI_{3-n}Br_{n+1}]^{2-} + I^- \rightleftharpoons [CdBr_nI_{4-n}]^{2-} + Br^- \quad n = 0\text{–}3 \tag{2}$$

The thermochemistry of complexing of gaseous transition metal ions, including Zn and Cd, with Group V and Group VI ligands has been reviewed.[108b] Gaseous cluster ions including Zn_2 and Cd_2 have been reviewed.[1468b]

EXAFS studies are few in this area; an interesting one on solutions of $ZnBr_2$ in EtOAc has indicated that quasi-solid clusters, resembling the crystal environment, persist even in dilute (0.05 M) solution.[109] Biological applications are important.[1463,1466g,h]

Theoretical studies in this area are not very numerous but *ab initio* molecular orbital calculations[110] on the binding of H_2S and $[HS]^-$ to Zn^{II} suggest that sulfur binding is less favoured than the binding of H_2O, OH^- and NH_3, and also allow an assessment of the effect of coordination on the acidity of H_2S.

Ab initio MO calculations have also been reported for the species $[Zn(OH_2)_6]^{2+}$, $[Zn(OH)_2]$ and $[Zn(OH)_4]^{2-}$.[111,112] The hexaaquazinc(II) ion was calculated to possess regular octahedral symmetry, while in the other species the Zn—O bond angles and bond lengths were calculated to be a function of the number of hydroxy groups bonded to the metal. Of particular interest, as we shall see, to the functions of zinc in biochemical systems is its flexibility in coordination number and geometry,[1469a–d] and in this connection a theoretical study of five-coordination in complexes of stoichiometry bis(unidentate ligand)(terdentate ligand)metal is intriguing.[113] Minimization of the repulsive energy terms shows that neither trigonal bipyramidal nor square pyramidal is the expected stereochemistry; this arises simply from the relative rigidity of the chelate rings and is quite distinct from any other steric interaction in the molecule.

Recent developments have been surveyed.[1468c–h]

56.1.3 HYDRIDE AND RELATED LIGANDS

A convenient and economical synthesis of ZnH_2 has been reported.[114] The 1:1 reaction of NaH with $ZnCl_2$ or the 2:1 reaction of LiH with $ZnBr_2$ or NaH with ZnI_2 produces only the alkali metal halide and ZnH_2. The reaction of KH with $ZnCl_2$ in various molar ratios yields initially ZnH_2 and KCl, although the KCl reacts further with $ZnCl_2$ to yield KZn_2Cl_5. The ZnH_2 prepared by this method is more thermally stable and reactive than that prepared by reaction of $LiAlH_4$ with Zn alkyls. The reaction[115] of ZnX_2 (X = Cl or Br) with AlH_3 produces a complex hydride of composition H_3Zn_2X, while reaction with ZnI_2 produces a complex $ZnI_2 \cdot AlH_3$. Reaction of CdI_2 to give HCdBr is slow. Little structural characterization is possible because of product insolubility. IR studies of the alkali metal borohydrozincates $Li_2Zn(BH_4)_4$, $NaZn(BH_4)_3 \cdot Et_2O$, $K_2Zn_3(BH_4)_8$, $MZn(BH_4)_3$ (M = Na or Rb), $Cs_nZn(BH_4)_{2+n}$ and several hydrates and etherates have been reported.[116] Bonding is postulated to resemble that in borohydroaluminates and covalent borohydrides.

Complex zinc hydrides of composition $M_nZn_mH_{2m+n}$ (M = Li, Na or K) may be synthesized by reaction of the appropriate $M_nZn_mR_{2m+n}$ alkyl with either $LiAlH_4$, $NaAlH_4$ or AlH_3.[117] Thus, the reaction of Li_2ZnMe_4 with $LiAlH_4$ produces Li_2ZnH_4, which is also the product of the reactions of $LiZnR_2H$ (R = Me, Bu^s) and $LiZn_2Me_4H$ with $LiAlH_4$. The reaction of $LiAlH_4$ with $LiZnMe_3$ produces $LiZnH_3$. In contrast to the reaction of $Zn(Bu^s)_2$ with KH, which yields K_2ZnH_4 directly, KH and $ZnMe_2$ react in a 1:1 ratio to produce $KZnMe_2H$. Reaction of this with a further mole of $ZnMe_2$ gives the complex KZn_2Me_4H, which, like its lithium and sodium analogues, decomposes when attempts are made to isolate it. The complexes MZn_2H_5 may be prepared by the reduction of either $MZnMe_2H$ (M = K or Na) or MZn_2Me_4H (M = K) with AlH_3, while reaction of $MZnMe_2H$ (M = K or Na) with $MAlH_4$ (M = K or Na) gives the $MZnH_3$ complexes. Structural data are generally difficult to obtain because of the insolubility of the hydrides. Borohydride complexes are well established; the adduct $[(Cp)_2Nb(CO)H \cdot Zn(BH_4)_2]$[118] involves hydrogen-bridged Nb and Zn (Nb—H—Zn = 107°) and direct Nb—Zn bonding [r(Nb—Zn) = 2.829Å]. Each $[BH_4]^-$ fragment is bidentate with respect to the zinc. Several syntheses have been described for $MgZnH_4$.[119]

56.1.4 NITROGEN LIGANDS

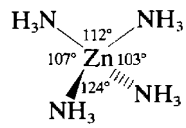
56.1.4.1 Ammonia, Hydroxylamine, Hydrazine and Azide

A wide variety of zinc and cadmium complexes are formed from these ligands and in some cases, *e.g.* that of ammonia and the ammine complexes, they have a long history.[2,3,6,8] They have been widely studied both in the solid state and in solution.[6,23,24] Here attention is drawn to some recent developments.[9–15,1468c–h]

Detailed Raman and IR studies on the ions $[M(NH_3)_4]^{2+}$ and $[M(NH_3)_6]^{2+}$ (M = Zn or Cd), including ^{15}N labelling, have been used in the calculation of force constants for the M—N bonds in those complexes. The force constant increases with decreasing coordination number and decreases from zinc to cadmium.[120,121]

A number of structures in solution, of ammine and related complexes, have been determined by X-ray diffraction techniques, supported by the use of Raman spectroscopy. A study on aqueous solutions containing zinc(II) or cadmium(II) chlorides and ammonia at various mole ratios revealed the tetrahedral species $[Zn(NH_3)_4]^{2+}$ and $[Zn(NH_3)_3Cl]^+$, which were characterized[122] with $r(Zn—N) = 2.03$ Å, and $r(Zn—N) = 2.00$ Å and $r(Zn—Cl) = 2.30$ Å, respectively. No species of higher coordination number could be observed. For $CdCl_2$, (with $NH_3/Cd = 9.9$) the octahedral hexaammine complex was present [$r(Cd—N) = 2.37$ Å].[123] The same approach has been used to study $[Zn(en)_2]^{2+}$ and $[Zn(en)_3]^{2+}$,[124] which have tetrahedral and octahedral stereochemistries with $r(Zn—N)$ at 2.131 and 2.276 Å, respectively. Interestingly the Zn—N distance in the tetraammine complex is shorter than that in $[Zn(en)_2]^{2+}$.

A crystal structural analysis of $[Zn(NH_3)_4]I_2$ has been reported; the near-tetrahedral cation closely resembles that found in the corresponding triiodide salt reported earlier,[125] with Zn—N distances in the range 1.997–2.030 Å.[126] The crystal structure of $[Zn(NH_3)_4][I_3]_2$(**1**) shows the metal to be in a tetrahedral N_4 environment, and the triiodide ion to be nearly linear.[127]



(**1**)

The complexes $[M(NH_3)_4][ReO_4]_2$ (M = Zn or Cd) have been described[128,129] and investigated spectroscopically and thermogravimetrically. Thermal decomposition of these salts leads to the novel species $[M(NH_3)_2(ReO_4)_2]$, containing monodentate oxygen donor perrhenate ions. The crystal structure of $[Zn(NH_3)_2Cl_2]$ shows the metal to be in a near-tetrahedral N_2Cl_2 environment [(Zn—N) = 2.024 Å and (Zn—Cl) = 2.273 Å].[130]

There is considerable interest in zinc–ammine complexes as host molecules and several structural studies have been made; the clathrate complex $[Zn(NH_3)_4][Ni(CN)_4]·0.1PhOH·H_2O$ has been described.[131]

The compounds $M(NH_3)_2Ni(CN)_4$ (M = Zn or Cd), which consist of two-dimensional polymeric sheets of tetracyanonickelate ions bridged by coordinating diamminemetal(II) cations, function as host lattices for clathration of small aromatic molecules such as thiophene, furan, pyrrole or pyridine; IR studies indicate the presence of hydrogen bonding between the host lattice ammonia and the aromatic guest molecules.[132,133] A crystal structure determination of the related clathrate $Cd(en)Ni(CN)_4(pyrrole)_2$ has been reported.[134] Similarly, the complex $Cd(py)_2Ni(CN)_4$ consists of polymeric $[Cd—Ni(CN)_4]_x$ layers held together by Cd-bound pyridine.[135]

Raman spectral studies of solutions of metal nitrates in liquid ammonia show a coordination number of four for zinc and mercury, but six for cadmium.[136] Dissolution of $ZnCl_2$ and $InCl_3$ in a 1:2 ratio in liquid HCN yields $[Zn(NCH)_6][InCl_4]_2$ with HCN coordination *via* nitrogen.[137] A Raman study of the compounds $[Cd(NH_3)_6]X_2$ (X = Cl, Br or I) has been reported.[138] Structural determinations of $A_2Zn(NH_2)_4$ (A = Rb or K) reveal monomeric tetrahedral anions.[139]

Hydroxylamine (L) complexes of the formula MX_2L_2 (M = Zn, X = Cl, Br or $\frac{1}{2}SO_4$; M = Cd, X = Cl or Br) have been prepared. An interesting difference is found between zinc and cadmium; depending on the method of preparation, the ligand is bound to zinc either *via* nitrogen or *via* oxygen as its *N*-oxide; coordination to cadmium is exclusively as the *N*-oxide.[140] In complexes of the stoichiometry $MX_2(MeONH_2)_2$ (M = Zn, X = Cl; M = Cd, X = Cl, Br or I), bonding is *via* nitrogen.[141]

Stability constant measurements for the aqueous Zn^{2+}-azide system indicate that four mononuclear complexes of moderate stability are formed, whereas for mercury, maximum coordination of only two azide ligands is observed.[142,143] Complexation of Cd^{2+} in aqueous NO_3^-–N_3^- yields the mixed species $[Cd(NO_3)(N_3)_n]^{(n-1)-}$ ($n = 1$–4).[144] Crystallographic structural determinations of $A_2Zn(N_3)_4$ (A = K or Cs) have been reported; the former exhibits isolated $Zn(N_3)_4^{2-}$ tetrahedra with linear azide (N—N = 1.18 Å).[145,146] Thermal decomposition of the above compounds yields nitrogen and Zn_3N_2 as the main products.[147] A new α modification of $Zn(N_3)_2$ has been obtained by the use of an ethereal solution of HN_3.[148] The compounds ML_2X_2 and $ZnLCl_2$ (M = Zn or Cd; X = halide or pseudohalide; L = MeNHOH or $MeONH_2$),[149] $[M(N_2H_4)_3(NO_3)_2]$ (M = Zn or Cd), $[Cd(N_2H_4)_2(NO_3)_2]$ and $[Zn(N_2H_4)_2(N_3)_2]$,[150] which are of interest as primary explosives, have been described.

Formation constants for $[Cd(N_3)_n]^{(n-2)-}$ have also been measured ($n = 1$–5).[151] For Zn^{II} or

Hg^{II}, only four or two complexes may be formed, respectively. Hydrazines and substituted hydrazines are the subject of a number of recent studies, for example, the reaction of CdF_2 with 80% hydrazine yields only the oxyfluoride $(N_2H_5)_2(CdOF_2)$, but reaction with anhydrous N_2H_4 yields the adducts $CdF_2{\cdot}2N_2H_4$ and $CdF_2{\cdot}3N_2H_4$, which are postulated to contain double and triple hydrazine bridges.[152]

Reaction of hydrated CdC_2O_4 with hydrazine yields $Cd(C_2O_4)(N_2H_4){\cdot}0.5H_2O$ which may be converted into $Cd(C_2O_4)(N_2H_4)_2$. In both cases, hydrazine acts as a bridging ligand; in the former the oxalate is ionic, while in the latter it is bidentate.[153]

N-Acylhydrazine (L) derivatives of the stoichiometry MX_2L_2 (M = Zn or Cd; X = NCS, NO_2, NCO or $\frac{1}{2}SO_4$; L = formyl-, benzoyl- or nitrobenzoyl-hydrazine) have been prepared; the ligand is N,O-chelate bonded in all cases.[154–157]

The complexes $ML_2{\cdot}nH_2O$ (M = Zn or Cd; H_2L = diformyl- or diacetyl-hydrazine) have also been synthesized, and are dimeric or polymeric with the quadridentate hydrazine acting as a bridging ligand.[158,159] A normal coordinate analysis of diformylhydrazine and its zinc complex with deprotonated ligand has been reported.[160]

Malonic acid dihydrazide (L) complexes of the stoichiometry $MLSO_4{\cdot}xH_2O$ (M = Zn or Cd) have been synthesized; a structure determination of $ZnLSO_4{\cdot}3H_2O$ reveals an $[(H_2O)_2ZnL_2Zn(H_2O)_2](SO_4)_2{\cdot}2H_2O$ dimer in which the ligand is quadridentate and bridging.[161,162]

The preparation and spectroscopic characterization of the complex $Zn[(NSiMe_3)_2]_2L$ (L = pyridine) have been reported.[163]

The molecular structure determination of bis(dicyandiamide)—CdI_2 shows the Cd to be tetrahedrally coordinated by the two nitrilic N atoms of the organic ligands (Cd—N = 2.22 Å, Cd—I = 2.73 Å).[164] The structure thus differs from di-μ-chloro(dicyandiamide)Cd,[165] which is polymeric with the organic molecules bridging adjacent Cd atoms through nitrilic and guanidic nitrogen. Recent work in this area is the subject of several reviews.[9–15,1468c–h]

56.1.4.2 Amines

56.1.4.2.1 Monofunctional amines

In general, the literature contains fewer references to complexes formed from monofunctional amines than to those formed from ammonia itself or from multidentate amines. However, some clarification of earlier studies is to be found in recent reports, *e.g.* the complexes $[Cd(PhNH_2)X_2]$ (X = Cl or Br), and their deuterated derivatives, have been reinvestigated and shown to be octahedral.[166] This latter study clarified some of the confusion present in the earlier literature concerning these compounds. Another aniline complex, $3CdCl_2{\cdot}4L$, has been studied and it has been shown that there are two types of octahedral environment in which the cadmium atoms are found, one comprising a $\{CdCl_6\}$ unit and the other a $\{CdCl_4N_2\}$ unit.[167]

The IR spectra (3500–150 cm^{-1}) of $Zn(aniline)_2X_2$ (X = Cl, Br or I) have been assigned with the help of ^{15}N labelling; ν(Zn—N) stretching frequencies occur in the range 450–350 cm^{-1}.[168]

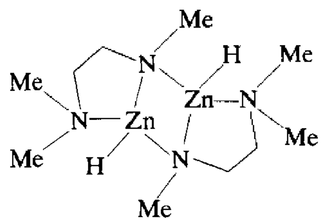
The *in situ* alcoholysis of the easily prepared compound $Ph_3P{=}NSiMe_3$ in the presence of anhydrous halides of zinc and cadmium leads to the formation of a range of complexes of triphenylphosphinimine $Ph_3P{=}NH$(L),[169] including $[ZnX_2L]_2$ (X = Cl, Br or I), $[CdCl_2L]_2$, $[CdI_2L_2]_2{\cdot}(CHCl_3)_2$ and $[Cd_2Br_4L_3]$. The presence of an intense P=N absorption in the region 1106–1118 cm^{-1} of the IR spectrum confirms the ligand to be a two-electron nitrogen donor ($Ph_3P{=}\ddot{N}H$). The dimeric complexes are all *trans* halogen-bridged structures. The 2:1 complex with CdI_2 involves two types of phosphinimine ligands (as evidenced by two different N—H stretching frequencies). This is shown in its structure,[170] which involves two $\{CdI_2L_2\}$ units linked by N—H···I hydrogen bonds. The 3:2 complex with $CdBr_2$ is believed to have a polymeric structure in which $[CdBr_2L_2]$ and $[CdBr_2L]$ units are linked *via* halogen bridges.

56.1.4.2.2 Polyfunctional amines

A very large volume of work on 1,2-diaminoethane and related complexes exists and their properties are well documented. There are several features of interest in recent studies.[9–15,1468c–h]

The stability constants for the formation of Zn—en complexes in DMF have been determined, and the complex ions formed shown to be more stable than the corresponding species in an aqueous environment.[171]

The ternary complexes formed between Zn^{II} and the ligands en, 1,2-pn, gly, $Me_2N(CH_2)_2NH_2$ and $MeNH(CH_2)_2NHMe$ have been investigated[172,173] and an interesting crystal structure of a hydrido-en complex has appeared; X-ray and neutron diffraction studies[174] of the hydrido complex $HZn(MeNCH_2CH_2NMe_2)$ show the compound to be dimeric; it has the structure shown in (**2**). Each zinc atom has a terminal hydride bonded to it, and is also bonded to three nitrogen atoms, to give an N_3H environment.



(**2**)

An X-ray spectroscopic study of aqueous solutions of cadmium–en complexes has shown that, like their zinc(II) counterparts, the ions $[Cd(en)_2]^{2+}$ and $[Cd(en)_3]^{2+}$, respectively, involve a tetrahedral and an octahedral geometry at the metal atom.[175]

Much of the interest in the en complexes has centred upon the ability of $[Cd(en)]^{2+}$ salts to form clathrate compounds. The compounds $[Cd(en)][Pd(CN)_4]$ and $[Cd(NH_3)_2][Pd(CN)_4]$ each accept two guest molecules of phenol, benzene or thiophene[175,176] and the thermal decomposition of these species, and of the related complex $[Cd(en)][Ni(CN)_4]\cdot C_6H_6$ has been studied.[176,177] The compound $[Cd(en)Cd(CN)_4]\cdot 2C_6H_6$ is of interest, since the en ligand has been shown to be bridging, although on heating to 100 °C it loses benzene to form $[Cd(en)][Cd(CN)_4]$.[178]

The structure determination of Zn(en)(NCS)Cl reveals monomeric tetrahedral zinc coordinated to thiocyanate *via* nitrogen.[179] A structure determination of $Cd(en)(NO_2)_2$ reveals a polymer containing cadmium in a seven-coordinate pentagonal prismatic environment; the en functions as a bridging ligand, as does one of the nitrites.[180]

A series of complexes of the type $ML(SCN)_x\ (ClO_4)_{2-x}$ (M = Zn, Cd, or Hg; $x = 1$ or 2) has been prepared where L is en and its tetramethyl derivative, diethylenetriamine and its pentamethyl derivative, triethylenetetramine and its hexamethyl derivative, and bis(ethylenediamine). The complexes are either monomeric with four-, five- or six-coordinate metal, or polymeric containing bridging thiocyanate; the perchlorate is always ionic. The thiocyanate is generally bonded through nitrogen to zinc and cadmium (and through sulfur to mercury).[181]

The molecular structure determination of $L_2Zn(NCS)(C_2O_4)_{\frac{1}{2}}$ (L = en or pn) shows it to consist of $L_2Zn(C_2O_4)ZnL_2$ dimers, with octahedral coordination about the Zn and a *gauche* configuration for the LZn ring.[182,183]

Ethylenediamine is known to react with zinc, cadmium and mercury halides to give complexes possessing a polymeric chain structure with the ethylenediamine acting as a bidentate bridging ligand, and it has been reported[184] to react with $Hg(SCN)_2$ and $M(CN)_2$ (M = Zn, Cd or Hg) to give 1:1 and 1:2 complexes containing monomeric structures with the ethylenediamine acting as a bidentate chelating ligand. Reaction of the more basic *N,N*-diethylethylenediamine, not only with mercuric halides and pseudohalides, but also with zinc and cadmium thiocyanates, gives monomeric, tetrahedral 1:1 complexes.[185]

The crystal structure of (ethylenediamine)zinc benzohydroxamate hydrate has been reported.[188] The two benzohydroxamate ions and an ethylenediamine form a distorted octahedron about the zinc. The asymmetric unit also contains a water molecule and a benzohydroxamic acid molecule.

The mixed ethylenediamine complexes $[Zn(en)_2NO_2]X$ ($X = NO_2$ or Br), containing bidentate nitrite, have been reported, as well as the complex $[Zn(en)_2NO_2]ClO_4$ which is polymeric and contains nitrite bridging through both nitrogen and oxygen.[189]

The preparation of some mixed ethylenediamine–oxalate or other ligand complexes of cadmium(II) has been reported.[190–192] The reaction of a mixture of cadmium oxalate and CdX_2 (X = Cl, Br, I or SCN) with ethylenediamine gives the complexes $Cd(en)X(C_2O_4)_{0.5}$. The cadmium is octahedrally coordinated by ethylenediamine, X and three oxygen atoms (two from bidentate oxalate, one from bridging oxalate). The *cis* octahedral complexes $Cd(en)_2(NCS)Cl$ and $Cd(en)_2BrI$ have also been reported, as well as the complexes $Cd(en)_2XX'$ ($X = NO_3$ or ClO_4; $X' = Br$ or $\frac{1}{2}C_2O_4$), which contain bridging bromide and oxalate groups. The nitrite complexes $Cd(en)_2NO_2(ClO_4)$ and $CdenINO_2$ have also been prepared, as well as the tris complex $Cd(en)_3X(ClO_4)$ ($X = I$ or NO_3).

Salts of the type $[H_2L][ZnX_4]$ ($X = Cl$ or Br; $H_2L = HN^+(CH_2CH_2)_3N^+H$) have been prepared and show interesting behaviour on thermal decomposition.[191] Heating to 423 K results in elimination of HX to form the ZnX_3LH complex, in which the HL molecule now also occupies a position in a deformed tetrahedral coordination sphere.

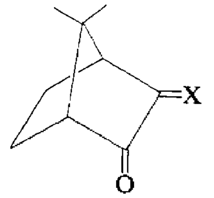
Mixed ligand complexes of Zn^{2+} with en and monoethanolamine (mea) in H_2O–MeOH systems have been investigated.[192] At <20% MeOH, the presence of the complexes $[Zn(en)_n\text{—}(mea)_{3-n}]^{2+}$ ($n = 0$–3) and the complexes $[Zn(en)_2]^{2+}$ and $[Zn(mea)_2]^{2+}$ is indicated. At >20% MeOH, only the tris complexes ($n = 0$ or 3) are found. Stability constants for mixed complexes of Zn^{2+} with en and glycine in mixed aqueous solutions of methanol, dioxane, acetonitrile and DMF have been determined.[193] In general, the stability constants increase with increasing composition of the co-solvent in the order $H_2O < MeOH < MeCN < DMF <$ dioxane.

The crystal structures of dichloro(TMEDA)zinc and dibromo(TMEDA)cadmium have been reported.[194,195] In the former complex, the geometry about the zinc is distorted tetrahedral with average Zn—Cl and Zn—N distances of 2.21 and 2.08 Å, respectively. In the latter complex, each cadmium is octahedrally coordinated by two pairs of bromine atoms (average Cd—Br distance = 2.75 and 2.84 Å) and a pair of nitrogen atoms in a *cis* configuration (average Cd—N distance = 2.46 Å). Bromine atoms provide bridges, resulting in a chain-like structure.

The chelating behaviour of 1,2-diamines towards Cu, Ni and Zn when the stereochemical relationship between the two amino groups is restricted has been studied.[196] Alicyclic *trans* diamines gave 1:1 complexes more stable than those formed with the *cis* isomers. The stability of the metal chelates with 3,3-dimethyl-1,2-diaminobutane is comparable to that of the *trans* isomers. The difference in stability of the *trans* and *cis* diamine complexes increased in the order Cu > Zn > Ni, and both the stereochemical requirements of the ligands and differences in the coordination geometry of the metal are thought to be responsible. Little difference in stability was observed for 1:2 complexes, except in the case of Ni.

The formation of 1,2-pn and 1,3-pn complexes of zinc has been studied, and the simple 1:1 and 1:2 complexes, as well as a 1:1:1 ternary species, have been detected in solution; 1,2-pn, which gives a five-membered chelate ring, is a better ligand for Zn^{II} than 1,3-pn.[197] The polarographic reduction of a number of Zn^{II}–1,3-pn complexes in a range of solvents has also been investigated.[198] The reaction of (**3a**) with 1,3-pn in the presence of Zn^{2+} ions results in the formation of $[ZnL_2]^{2+}$ (L = **3b**) rather than the expected macrocycle.[199] The clathrate complexes $[Cd(\pm\text{-}1,2\text{-pn})][Ni(CN)_4]\cdot 1.5L$ (L = pyrrole, thiophene or benzene) have been prepared, as have $[Cd(\pm\text{-}1,2\text{-pn})][Cd(CN)_4]\cdot 1.5PhH$ and $[Cd(\pm\text{-}1,2\text{-pn})][Hg(CN)_4]\cdot 1.5PhH$.[200] Further clathrate complexes of the type $\{[CdL_n][Ni(CN)_4]\cdot G\}$ ($L = H_2NCH_2CH_2OH$; $n = 1$ or 2; G = benzene, thiophene or pyrrole) have been prepared[201] and structurally characterized.[202]

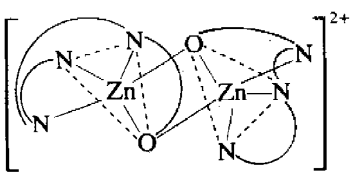
Studies[203] on the complexation of Zn^{2+} with 1,3,5-*cis,cis*-triaminocyclohexane (L) show that the $[ZnL]^{2+}$ complex formed is less stable than that formed with analogous linear triamines such as 3,3′-diaminodipropylamine;[204] in the presence of excess ligand, only the $[ZnL(OH)]^+$ complex is formed in both cases. In contrast, a significant macrocyclic effect is evident in the large stability constant observed for the $[ZnL]^{2+}$ complex containing the cyclic triamine 1,4,7-triazacyclononane.[205] Derivatives of the type $[ZnL](ClO_4)_2\cdot H_2O$ have been prepared where L is the macrocyclic diimine 5,12-dimethyl- or 5,12-diethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene.[206,207]



(**3**) **a**; X = O
b; $X = N(CH_2)_3NH_2$

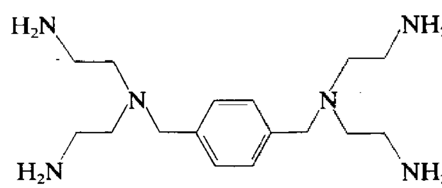
The chemistry of five-coordinate zinc with ligands of this class has been a subject of interest. The crystal structure of μ-oxalato-bis[di-(3-aminopropyl)amine]zinc bis(perchlorate) has been determined.[208] The oxalate group is bridging and bichelate, bound in such a way as to complete a five-membered, rather than a four-membered, ring. Coordination of the three amine nitrogens completes a distorted trigonal bipyramidal coordination about the zinc. Apical sites are occupied by one oxygen of the oxalate and by the tertiary nitrogen of the amine ligand. Zinc complexes with the potentially tridentate ligands [$(MeNH)_3CR$] (R = H, Me or Et) have been described,[209] as have the complex ions $[ZnL]^{2+}$ (L = tach, 1,5,9-triazanonane or $(H_2NCH_2)_3CMe$).[210] In the latter cases it has been shown that the rigidity of the ligand plays an important role in coordination, and this is reflected in the thermodynamics of complex formation. The tripod-like ligand $(Et_2NCH_2CH_2)_2N(CH_2CH_2OH)$ has been shown to give dimeric, five-coordinate complexes as in the cation (**4**) of the compound $[Zn_2L_2][ClO_4]_2$.[211]

The chelating properties of the triamine $H_2N(CH_2)_2NH(CH_2)_4NH_2$ (L) towards Cu, Ni and Zn have been investigated.[212] Five complexes having the formulae ML^{2+}, ML_2^{2+}, MHL^{3+}, $M(HL)_2^{4+}$ and $[MHL_2]^{3+}$ are common to all three metals. In addition, Cu and Zn form the hydroxo complexes $[Cu(OH)L]^+$, $[Zn(OH)L]^+$ and $[Zn(OH)_2L]$. With regard to the simple complex ML^{2+}, the amine acts as a bidentate chelate towards Ni and Zn, and in a terdentate manner towards Cu^{2+}; the latter contains both five-membered and seven-membered chelate rings. The ML_2^{2+} complexes contain only five-membered rings, with both amine ligands acting in a bidentate manner.



(**4**)

The ligand 1,4-bis[bis(2-aminoethyl)aminomethyl]benzene hexahydrochloride[213] (**5**) provides two terdentate moieties separated by a rigid bridge, and so offers the possibility of synthesizing binuclear complexes. Formation constants have been measured for interaction with several cations, including zinc(II), and indicate that $[Zn_2L]$ formation occurs.



(**5**)

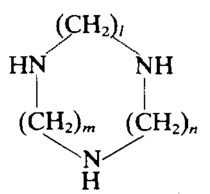
The molecular structure determination of bis(diethylenetriamine)$ZnBr_2 \cdot H_2O$ shows it to contain discrete monomeric $[Zn(dien)_2]^{2+}$ cations.[214] Coordination about the zinc is approximately octahedral with bonds to the secondary nitrogens (2.13 Å) being shorter than the others (2.25 Å).

Complexation of Ni, Cu and Zn in aqueous solution by the tripod-like 1,1,1-tris(aminomethyl)ethane (L) has been investigated.[215] Evidence is presented for the formation of $M(HL)^{3+}$, ML^{2+} and ML_2^{2+} cations, as well as the hydroxo species $[Cu(OH)L]^+$, $[Zn(OH)L]^+$ and $[Zn(OH)_2L]$.

Zn complexes with the cyclic triamines (**6**) have also been investigated.[216] Formation of the 1:1 complex occurs in a single step, but with some of the larger ligands loss of a proton occurs before any noticeable metal–ligand interaction occurs. Some hydrolysis of the $[ZnL]^{2+}$ complexes is observed; the stability increases as the ring size decreases, in agreement with predictions from molecular models.

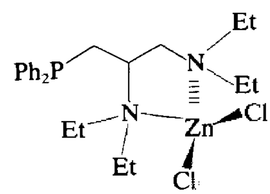
[Bis(2-dimethylaminoethyl)methylamine]$Cd(NCS)_2$ contains five-coordinate cadmium in a square pyramidal environment; the apical position is occupied by N-bonded thiocyanate (Cd—N = 2.18 Å) while the basal positions are occupied by the amine (Cd—N = 2.34–2.37 Å) and the second thiocyanate (Cd—N = 2.21 Å) ligands.[217]

The interaction of Cd^{2+} with $MeNH(CH_2)_3NH_2$,[218] dien, $H_2N(CH_2)_2NH(CH_2)_3NH_2$ or



(6)

$H_2N(CH_2)_3NH(CH_2)_3NH_2$[219] has been investigated and, in each case, a 1:1 complex was formed; {Cd(dien)Cl_2} exists as polymeric chains of octahedral units connected by halide bridges, whereas the complexes with the other ligands contain dimeric species.[219] A structural analysis of an N_2P, potentially terdentate ligand complex [ZnLCl_2] (**7**) (L = $Et_2NCH_2CH(NEt_2)CH_2PPh_2$) has shown the metal to be in a distorted N_2Cl_2 environment, with a pendant non-coordinated phosphine.[220]



(7)

Hexamethylenetetramine is a potentially tetradentate ligand, and a number of groups have investigated its coordination behaviour.[221–224] A range of interesting complexes with zinc and cadmium have been characterized, including [ML_2X_2] (X = OAc[221] or SCN[222]), [ML(SO_4)][222] (M = Zn or Cd) and $3CdI_2{\cdot}2L{\cdot}4H_2O$,[224] in which the amine acts as a terminal monodentate or bridging bidentate ligand. A structural analysis of $3CdI_2{\cdot}2L{\cdot}4H_2O$ has shown the compound to consist of Cd_3I_x clusters bridged by the ligand.[224]

The thermodynamics of complex formation of several linear aliphatic tetramines with zinc have been reported as part of a study to determine the effect of ring size on these thermodynamic functions. Previous results[225] on the $[Zn(2,2,2\text{-tet})]^{2+}$ complex assign it a tetrahedral configuration on the basis of a very large entropy of complexation. However, zinc complexes with 2,3,2-tet and 3,2,3-tet exhibit a higher enthalpy but a lower entropy of formation, and favour either octahedral or square pyramidal geometry.[226] The complex $[Zn(3,2,3\text{-tet})]^{2+}$ may be transformed into the species $[Zn(OH)(3,2,3\text{-tet})]^{+}$ and the thermodynamic functions associated with this reaction are in accord with simple deprotonation of a coordinated water molecule in square pyramidal or octahedral geometry.

Complexes $ZnL(ClO_4)_2$ and $ZnLCl(ClO_4)$ (L = tetramethylcyclam) have been isolated.[227] The latter contains the five-coordinate $ZnLCl^+$ cation for which NMR results indicate a square pyramidal configuration with the chlorine in the apical position and all four methyl groups on the same side of the plane.

Complexation[228] of Zn^{2+} with the quadridentate 1,5-diazacyclooctane-*N,N'*-diacetic acid (H_2L) leads to formation of the trigonal prismatic [Zn(L)H_2O] species. The hydrolysis constant of the coordinated H_2O ($pK_a = 8.6$) is much lower than that of the coordinated H_2O in the octahedral complex formed by ethylenediaminediacetate ($pK_a = 10.5$). This increased acidity of coordinated H_2O with decreasing coordination number has also been previously noted in the $[Zn(Me_6tren)H_2O]^{2+}$ cation,[229] and has been attributed in part to the hydrophobic environment provided by the Me groups. This finding has important implications for the role of the $\geq ZnOH_2$ species in the zinc metalloenzyme, carbonic anhydrase (see Section 56.1.14.1.1).

A series of five-coordinate cadmium and mercury complexes with the tripod-like tetramines tris(2-aminoethyl)amine (tren) and tris(2-dimethylaminoethyl) amine (Me_6tren) have been prepared.[230] A complete X-ray structural analysis showed that the compound $Cd_2(Me_6tren)I_4$ consists of the five-coordinate cation$[CdIMe_6tren]^+$ and the unusual dinuclear anion $Cd_2I_6^{2-}$. The cation is a slightly distorted trigonal bipyramid, whereas the anion is formed by edge sharing between pairs of CdI_4 tetrahedra.[231] Comparison with mercury is interesting here; the molecular structure of the $[HgBr_6]^{4-}$ anion in Tl_4HgBr_6 has been described.[232] IR and conductivity data show that the complexes M_2trenI_4 (M = Cd or Hg), $Hg_2Me_6trenI_4$ and $Hg_2trenBr_4$ possess the same structure, as do the related complexes $[CdClL]BPh_4$ (L = tren or Me_6tren), $[HgClMe_6tren]ClO_4$ and $[HgSCNMe_6tren]BPh_4$.

The compounds $Hg_3(Me_6tren)_2X_6$ (X = Cl or Br) have been formulated on the basis of IR and conductivity data as $[HgXMe_6tren]_2HgX_4$. The complexes $Cd(Me_6tren)X_2$ (X = Cl or Br) show the presence of uncoordinated NMe_2 groups in the IR and are assigned a five-coordinate structure where the tetramine acts as a terdentate ligand. In contrast, $CdBr_2$tren is best formulated as [CdBrtren]Br, with the tetramine acting as a quadridentate ligand. The complex $Hg(SCN)_2$tren also has this structure. The complexes $Cd(ClO_4)L{\cdot}nH_2O$ (L = tren or Me_6tren) have also been prepared. Where $n = 1$, the complexes are best formulated as $[Cd(H_2O)L](ClO_4)_2$, containing bound water in the five-coordinate cation. Where $n = 0$, the IR shows the presence of both coordinated and ionic perchlorate (which is easily displaced in solution) and the complex is then formulated as $[CdLClO_4]ClO_4$. The related nitrate complex $CdL(NO_3)_2$ also contains both ionic and coordinated nitrate.

The open-chain potentially quinquedentate ligand 1,11-bis(dimethylamino)-3,6,9-trimethyl-3,6,9-triazaundecane (Me_7tetren) forms the complex $[Zn(Me_7tetren)]$ $(ClO_4)_2$. On the basis of IR, conductivity and electronic spectral studies of isomorphous Ni and Co complexes, the compound is postulated to have distorted trigonal bipyramidal symmetry. The complexes $[Zn(Me_7tetren)NCS]BPh_4$ and $Zn(Me_7tetren)(NCS)_2$ were also prepared. The former is postulated to be still five-coordinate, while the latter is pseudooctahedral, with the amine acting in a quadridentate manner in both cases.[233] A ^{129}I Mössbauer study[234] of the purportedly five-coordinate $[ZnN(CH_2CH_2NMe)_3I]I$ shows the two iodine atoms to be equivalent. Accidental equivalence is unlikely, and a structural revision may be necessary.

An interesting radical–ligand complex $[ZnL]^+$ has been prepared [L = radical anion of glyoxalbis(*N*-*t*-butylamine)], generated by an electrolytic method within an ESR cavity. This species forms further complexes with ligands X^- (X = Cl, Br, I, NCS, NCO or N_3) in both 1:1 and 1:2 (except I) stoichiometries, and with en in a 1:1 stoichiometry.[235]

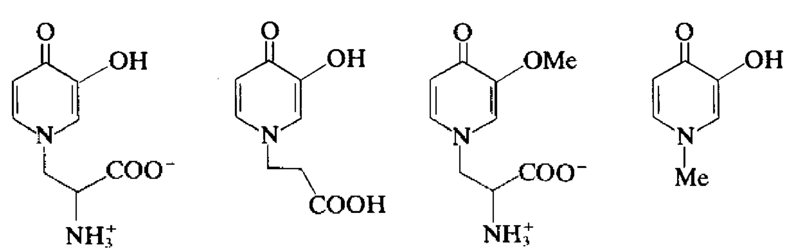
Comprehensive surveys of work in these areas are available.[9–15,1468c–h]

56.1.4.3 Amino Acids

Complexing of zinc and cadmium by amino acids, both natural and otherwise, and of polypeptides, has been the subject of study for many years because of the importance of zinc–protein systems and the physiological effect of cadmium compounds (see Section 56.1.14).

A number of reviews are available in this area; several complexes with amino acids are covered in recent general reviews on ligands of biological importance.[236,237] The coordination chemistry of L-cysteine and D-penicillamine[238] and glutathione[239] has been reviewed.

Some of the complexes have important practical applications, for instance the chelating properties of the amino acid mimosine (**8**; α-amino-β-(3-hydroxy-4-oxo-1,4-dihydropyridin-1-yl)propanoic acid) have been implicated in its inhibition of various metalloenzymes, and hence in its biological activities such as the defleecing of sheep. In this context, formation constants have been measured[240] for Zn^{II} and Cd^{II} with mimosine (**8**) and related compounds (**9–11**). These derivatives formed monomeric complexes, in which metal binding by the hydroxypyridine group was favoured relative to the amino acid group. With mimosine, dimeric complexes were major species. Consideration of a blood plasma model indicates that mimosine binds zinc (and copper) more strongly than do simpler amino acids, in accordance with the suggestion that mimosine exerts its biological action by depleting copper and zinc levels in blood plasma.

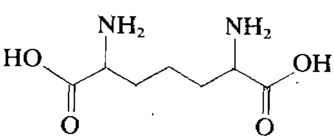


(**8**) (**9**) (**10**) (**11**)

Biological significance can sometimes arise in rather unexpected ways; the thermal properties of chelate polymers of 2,6-diaminopimelic acid (dap; **12**) and 4,4′-diamino-3,3′-dicarboxybiphenyl (bbdc; **13**) with Zn^{II} have been compared[241] with those of non-polymeric divalent metal chelates with amino acids. This confirms the expected enhancement of thermal stability when coordination polymerization occurs, these results possibly being relevant to the thermal stability of certain bacterial spores which contain dap. Zn^{II} complexes of dap are more thermally stable than those of bbdc, possibly because the latter chelate cannot pack as well, due to the intermolecular repulsions of the biphenyl groups.

There are a large number of preparative, structural and physical investigations in the area of amino acid complexes of zinc and cadmium and interesting structural features are often observed.

Complexes studied recently in the solid state include [Zn(*N*-acetyl-DL-leucinate)$_2$L$_2$] (L = H_2O, pyridine, 3-methylpyridine or 4-methylpyridine) which involves bidentate coordination of the amino acid *via* the carboxylate group,[242] $ZnL_2{\cdot}2H_2O$ (HL = glutamine, histidine[243] or *N*-acetyl-DL-tryptophan[244]) and [Cd(L-Phe)$_2$]$\cdot n$H$_2$O.[245] The L-phenylalanine ligand in the complex of Cd^{II} is bidentate coordinating *via* NH_2 and CO_2^- groups in the complex dihydrate, and terdentate in the anhydrous complex, the second oxygen of the carboxylate being linked to another Cd^{II}. Although the use of *N*-acetyl-DL-valine (AcValH)[246] introduces the possibility of coordination *via* the peptide group (**14**), the complexes [Zn(AcVal)$_2$] and [Zn(AcVal)$_2$L$_2$] (L = pyridine, 3- and 4-methylpyridine or 1,10-phenanthroline) probably involve coordination via only the carboxylate group.



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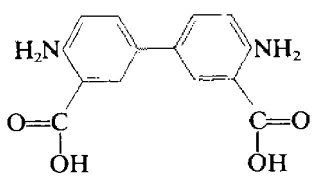

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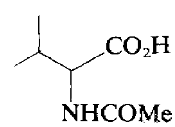


(14)

Most studies of zinc complexes of amino acids have concentrated upon naturally occurring ligands, but some other amino acids have been investigated. Complexes with 3- and 4-aminobenzoic acids have been reported[247,248] and a crystal structure of [ZnL$_2$]$\cdot$1.5H$_2$O (HL = 4-aminobenzoic acid) has shown that the compound is polymeric, with the metal in a distorted N_2O_2 environment.[248]

This is in contrast with the crystal structure of the complex [CdL$_2$(H$_2$O)$_3$] (HL = 4-aminobenzoic acid); here the metal is in a seven-coordinate N_2O_5 environment, with the ligand acting as a bridge to form a polymeric one-dimensional structure.[249]

Determinations of the crystal structures of [Cd(Gly)$_2$X$_2$] (X = Cl or Br) have shown the two compounds to be isomorphous and to involve an octahedral environment about the metal; the amino group is hydrogen bonded to a carbonyl group and a halide ion.[250]

Circular dichroism studies of the [ZnL$_n$(phen)$_2$]$^{(2-n)+}$ (HL = chiral amino acid) systems have been reported.[251] A molecular structure determination of Cd glutamate dihydrate shows the Cd to be coordinated in a square pyramidal fashion by the two oxygens and two nitrogens of the glutamate and the water molecule.[252] The IR spectrum of [Zn-(glycineglycinate)X]$\cdot$H$_2$O has been assigned.[253]

A very large number of amino acid complexes of zinc and cadmium have been described. Among the most recent are complexes of zinc with histidine,[254–256,258] threonine,[258] tyrosine,[257] glutamic acid,[259] DL-nor-leucine,[260] aspartic acid[261] and tryptophan[262] have been described.

Cadmium complexes with glycine,[263,49] histidine,[263] alanine,[264,266] DL-norleucine,[263] valine[269] and numerous other amino acids[267,268] have been reported. A study of the interaction of dipeptides with cadmium ions has also been described.[269]

Rather earlier but still recent studies include those of zinc complexes with glycine,[270,273] alanine,[272,274] β-alanine,[272] norleucine,[271] phenylalanine,[272] proline,[275] methionine,[270] serine,[274] histidine,[271] asparagine,[276] adrenaline,[277] noradrenaline,[277] terizidone,[278] *S*-ethyl-L-cysteine,[279] *S,S′*-methylenebis(L-cysteine),[280] ornithine, lysine, 2,4-diaminobutyric acid and 2,3-diaminopropionic acid.[281]

Cadmium complexes with glycine,[271–273,282–284] alanine,[272,284] norleucine,[271] phenylalanine,[272] proline,[285] serine,[286] histidine,[271] asparagine,[276] leucine, tyrosine, norvaline, arginine, and tryptophan,[286] valine,[287] ornithine,[288] lysine,[289] glycylglycine,[290] 4-aminohippuric acid,[291] terizidone,[278] *S*-ethyl-L-cysteine[279] and a number of other peptides[292,293] have been described.

Solution studies include those on Zn^{II} complexes with L-hydroxyproline,[294] glutamate,[295] glycine,[296] glycine/histamine, glycine/L-histidine,[297] L-histidine/histamine[298] and *N,N'*-dimethylglycine(HA)/2,2'-bipyridine[299] mixed ligands. In the last case, complexes $[Zn(bipy)A]^+$ and $[Zn(bipy)A_2]$ were characterized. Mixed ligand complexes of *O*-phospho-DL-serine, Zn^{II} and L (L = histamine, 1,10-phenanthroline or 2,2'-bipyridine) have been studied to model substrate, enzyme and metal ternary complex formation in the phosphoserine phosphohydrolyase-catalyzed hydrolysis of *O*-phosphoserine in the biosynthesis of serine.[300] Complexes of Cd^{II} include those of L-hydroxyproline,[301] DL-serine,[302] glycine,[303] aspartic acid (as the protonated complexes)[304] and citrulline.[305] Stability constants reported include those for histidine and its derivatives, histamine, glycylhistamine, aspartic and glutamic acids, aspargine, glutamine, glycine, cysteine and alanine[306–317] with Group IIB metals as a whole.

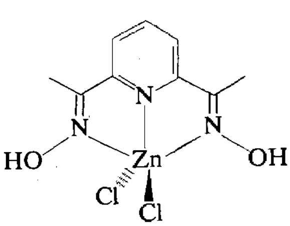
Reactions with peptides perhaps provide better models for the interaction of zinc ions with proteins, and complexes with *N*-acetylglycine,[273] *N*-benzoylglycine,[273] *N*-benzoylglycyl-L-leucine,[292] *cyclo*-(L-histidyl-L-histidyl),[318] *N*-benzoyl-L-leucine[293] and *N*-benzoyl-L-phenylalanine[293] have been described. Complexes of Zn^{II} and Cd^{II} with *N*-benzoylcysteine involve $M(HL)_2$ stoichiometry, with coordination occurring *via* a deprotonated thiol group and carboxyl oxygen, as shown by IR spectroscopy.[319] This is an active area, actively reviewed.[9–15,1468c–h]

56.1.4.4 Schiff Bases, Hydrazones and Oximes

Schiff bases, especially multidentate ones, are powerful ligands for metal ions and zinc and cadmium complexes are well represented in this area. The findings of structural studies are interesting in that the ligand can control the stereochemistry of the complex and provide us with numerous examples of unusual geometry about the central metal ion, thus serving to illustrate the coordination flexibility of these ions.

A recent example of this is a crystal structural analysis of the zinc complex of the imine derived from 2-pyridinealdehyde and *cis,cis,cis*-1,3,5-triaminocyclohexane which shows the metal to be in a trigonal prismatic environment (Zn—*N* (pyridine), 2.211–2.282 Å; Zn—*N* (imine), 2.142–2.167 Å).[320]

Again, a crystal structure of the complex $[ZnLCl_2]\cdot H_2O$ (L = 2,6-diacetylpyridine dioxime) (**15**) has shown the metal to be in a distorted trigonal bipyramidal N_3Cl_2 environment (Zn—Cl, 2.233, 2.244 Å; Zn—N (pyridine), 2.063 Å; Zn—N (oxime), 2.238, 2.246 Å).[321]

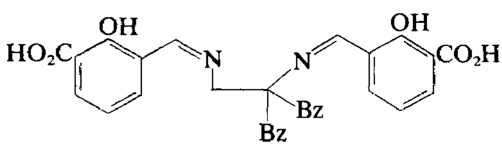


(**15**)

Schiff bases formed from salicylaldehyde and amines, the salicylideneimines, have received a good deal of attention as ligands and form a widely investigated group of anionic N,O donors; a number of Group IIB complexes of these ligands have been described. Zinc complexes with the imines derived from the condensation of salicylaldehyde with amino acids,[322] sulfa drugs (sulfofurazole, sulfaphenazole or sulfamethoxypyradizine)[323] or aminoarenes[324] have been investigated. Related ligands have been prepared by the condensation of 2-hydroxyacetophenone with sulfa drugs,[323] 3-carboxysalicylaldehyde with 1,1-dibenzylethylenediamine (**16**)[325] or 2-hydroxynaphthaldehyde with 2-aminobenzylalcohol (**17**),[326] and all have been shown to form zinc complexes.

4-Amino-2,6-di-*tert*-butylphenol reacts normally with salicylaldehydes to form Schiff bases, and complexes of the type $[ZnL_2]$(HL = **18**) have been isolated, and shown to generate radical species on treatment with PbO_2.[327] In contrast, reaction with bis(diketonato)zinc(II) complexes leads not to the Schiff bases, but to the monoiminoquinone complexes (**19**).[326]

A crystal structure of the complex (**20**) has been reported[329] and it is seen that the complex possesses a distorted C_2 symmetry, with a *trans* arrangement of the ligands.



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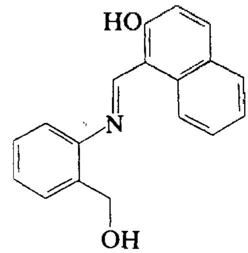

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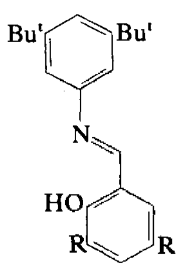

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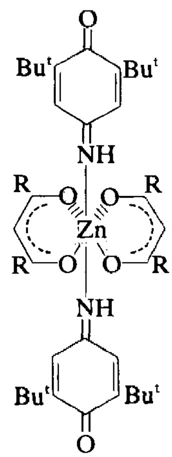

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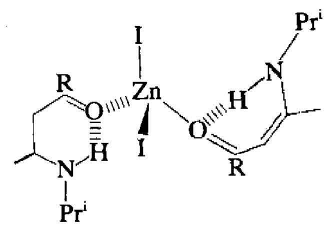
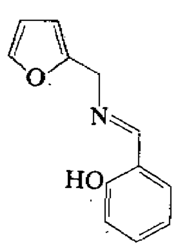


(20)

The Schiff base from 2-aminomethylfuran and salicylaldehyde forms a zinc(II) complex which has been shown, by ^{1}H NMR and IR spectroscopy, to contain the ligand in the form (**21**), rather than as a 2-furylimine (**22**).[330] The complex $[Zn_2L_2]$ (H_2L = **23**) has been described and considered to have the structure (**24**).[331]



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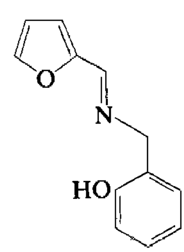

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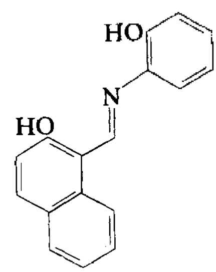

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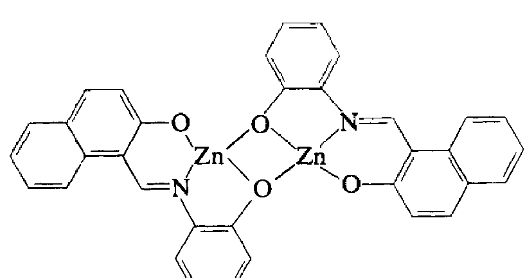
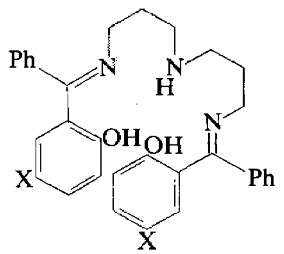
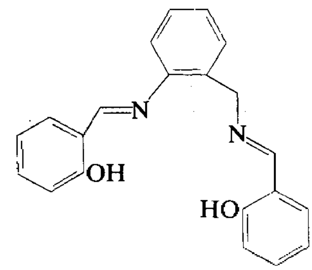


(24)

The complex $[ZnL]\cdot H_2O$ of the quinquedentate Schiff base (**25**; H_2L) has been prepared; the zinc environment is a distorted trigonal bipyramid (Zn—O = 1.95 Å; Zn—N = 2.11–2.16 Å)[332] and IR and NMR studies on the ZnL_2 complex of the quadridentate Schiff base (**26**; H_2L) indicate a tetrahedral rather than a planar configuration.[333]



(25) X = Cl or Me



(26)

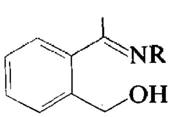
A study of the electronic transitions in salicylaldimine complexes of Zn, Cd and Cu has been reported.[334] Except in cases of profound alteration in coordination, the positions of the UV bands are not sensitive to coordination changes on going from the solid to solution. Evidence for chloroform–oxygen hydrogen bonding is presented. A band previously assigned to a σ–d charge-transfer transition in Cu complexes has been found to be an n–π^* ligand absorption.

In fact, several reports have appeared on the spectroscopic features of complexes of zinc and cadmium with Schiff bases. The electronic absorption spectra of various salicylaldimine complexes of zinc have been determined[335] to clarify assignments made previously for similar copper(II) complexes. A band at *ca.* 41 000 cm^{-1} has been reassigned as an n–π^* transition of the oxygen lone pair, rather than the σ–$3d$ transition proposed earlier.

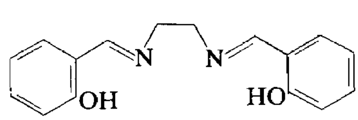
The IR spectra of ^{15}N-labelled complexes of *N-p*-tolylsalicylaldimines with zinc, copper and cobalt have yielded assignments of the metal–ligand stretching frequency and certain ligand vibrations.[336] The ν(M—N) values are metal-ion dependent in the order Co < Cu > Zn as expected from crystal field theory. Substituent-induced shifts are related to the residual polar effects of salicylaldimine substitution and to the inductive effects of *N*-aryl substitutents.

A variable temperature ^1H NMR study of the complexes ZnL_2 (HL = **27a** or **27b**) in solution has indicated that they are dynamic, interconverting between the Λ and Δ enantiomers.[337]

A charge-transfer complex [ZnLQ] (H_2L = **28**; Q = *p*-chloranil) has been characterized, and a weak π–π^* interaction between the ZnL and Q moieties demonstrated.[338] A related complex, [ZnL] (H_2L = **29**), is formed from the template condensation of HCN tetramer, $H_2N(NC)C{=}C(CN)NH_2$ with salicylaldehyde in the presence of $ZnCl_2$.[339] In the absence of the zinc salt, unsymmetrical mono-Schiff bases are obtained.



(27) **a**; R = Me
b; R = $CHMe_2$



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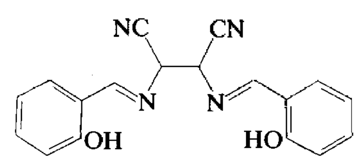
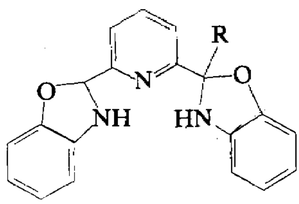


(29)

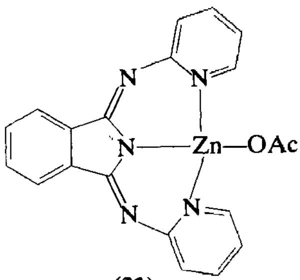
Template and 'capping' reactions feature in recent work. A number of sterically hindered H_2O and N_4 ligands have been prepared in which a quadridentate Schiff base is capped by condensation of salicylaldehyde or pyrrole-2-carbaldehyde with a series of bis(8-aminonaphthyl)alkyl ethers. These ligands combine the versatility of the Schiff base with the protective features well known for certain model porphyrin systems, and appear to be of some interest. The zinc(II) complex and other transition metal complexes have been prepared.[340]

But surprises are sometimes found; reaction of $Cd(OAc)_2$ with the ligands (**30a**, H_2L; **30b**, H_2L') in acetone–DMF results in ring opening to yield polymeric complexes of the stoichiometry $[Cd_4L_2(OAc)_4](DMF)(H_2O)$ and $[Cd_3L'_2(OAc)_2(DMF)_2]$ in which the ligand is bound in the form of its deprotonated Schiff base. The former contains a cubane-like Cd_4O_4 core, while both complexes contain two seven-coordinate cadmium atoms in a distorted pentagonal bipyramidal geometry.[341]

Again, the template condensation of ethylenediamine or phenylenediamine with 2,6-diformylpyridine might be expected to give 2 + 2 N_6 donor macrocycles, but with a range of metals only open-chain complexes were obtained; a crystal structure of the product obtained from the reaction with phenylenediamine in the presence of a cadmium template reveals that a 2 + 1 bisimino ligand is formed, which acts as the basal N_5 donor set in a pentagonal pyramidal complex in which a monodentate phenylenediamine group occupies the axial



(30) a; R = Me
b; R = H

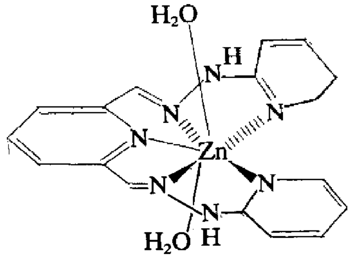


(31)

position.[342] $Zn(OAc)_2$ has been used as a template in the condensation of *o*-phthalonitrile and 2-aminopyridine and gives the complex (**31**) containing an isoindoline ligand.

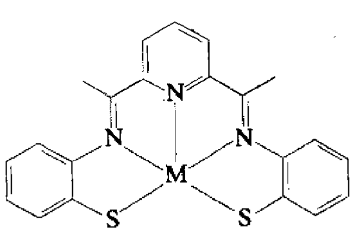
Also containing adjacent OH and CHO groups is pyridoxal, and zinc complexes of Schiff bases derived from histidine and pyridoxal have been investigated as models for the reactions of vitamin B_6 analogues.[343]

2,6-Dicarbonyl pyridine derivatives and their Schiff bases are fruitful sources of polydentate ligands and again there are some interesting structural surprises. A molecular structure determination of the cobalt analogue of the diaqua(2,6-diacetylpyridine bis-2-pyridylhydrazone)zinc cation (**32**) shows the metal to be pentagonal bipyramidally coordinated by five nitrogens and two water molecules.[344] An unusual rearrangement of the zinc complex occurs on deprotonation to give the zinc complex (**33**), is shown in equation (3). Each zinc is surrounded by six N atoms in a distorted octahedral configuration, with the py groups unusually acting in a bridging manner. Reaction of Zn or Cd acetate with the potentially quinquedentate ligand 2,6-bis(2-methyl-2-benzothiazolinyl)pyridine under basic conditions results in rearrangement to produce complexes of the deprotonated tautomeric Schiff base (**34**).[345] The complexes are five-coordinate and contain the Schiff base in a novel helical configuration. The sulfur atoms may be alkylated with MeI or the bridging α,α'-dibromo-*o*-xylene or 1,4-diiodobutane to give complexes as such as (**35**), which appear to be seven-coordinate, approaching a pentagonal bipyramid.



(32)

$$[Zn(H_2L)(H_2O)_2]Cl_2 \xrightarrow{-2H^+} \underset{(\mathbf{33})}{Zn_2L_2(H_2O)_2} \qquad (3)$$



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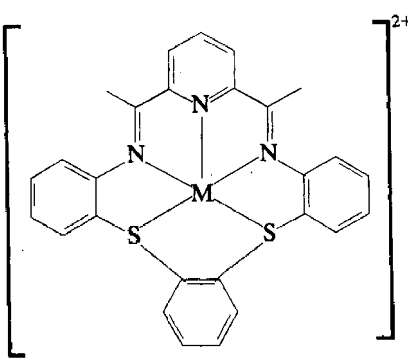


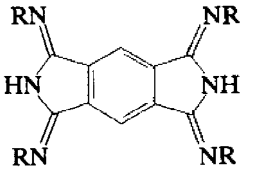
(35)

The first pentagonal bipyramidal complex of zinc, $ZnLCl_2{\cdot}3H_2O$, was reported in 1973, where L is the planar five-coordinate 2,6-diacetylpyridinebis(semicarbazone).[346] The crystal structure determination shows the complex to contain the $[LZnCl(H_2O)]^+$ cation, with three N- and two O-donor atoms forming a slightly distorted planar pentagon around the metal ion and the chlorine and water in axial positions.

Structural surprises are not confined to 2,6-DAP derivatives though; zinc and cadmium complexes have been obtained with the quadridentate thioiminato Schiff base *N,N'*-ethylenebis(monothioacetonimine);[347] uv and visible spectra indicate planar geometry, rather than the tetrahedral geometry observed for the salicylaldimine complexes.

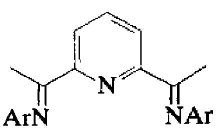
A review[348] on metal complexes of oximes and hydroxylamine contains information on Zn, Cd and Hg complexes of these ligands, and oximes and dioximes have continued to attract attention as ligands in recent years. Attempts have been made to quantify the contributions of oxime deprotonation and oxime–oximato hydrogen bonding to the stability of metal oxime complexes. Thus a range of complexes, including those of zinc(II), of the diamine dioxime ligand 4,4,9,9-tetramethyl-5,8-diazadodecane-2,11-dione dioxime (H_2dddo) and its *O*-methyl ester (Hddmo) have been studied potentiometrically.[349] H_2dddo coordinates in the oxime–oximato form $[Zn(Hdddo)]^+$, and the hydrogen bonding has been studied for $[Zn(Hdddo)]ClO_4$. Hddmo gives the complexes $[Zn(Hddmo)_2]^{2+}$ and $[Zn(Hddmo)(ddmo)]^+$.

Zinc complexes of a number of bulky polydentate ligands (**36**) which are structurally related to phthalocyanines have been reported by Gagne.[350]



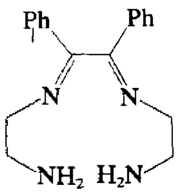
(**36**)

Zinc and cadmium nitrato complexes of the 2,6-diacetylpyridine derivatives (**37**) have been prepared, and reveal a variety of nitrate bonding modes.[351]

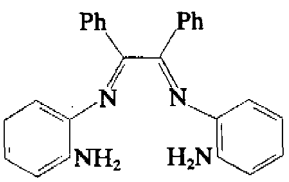


(**37**)

The diimines (**38**) and (**39**) formed by the condensation of benzil with en or 1,2-diaminobenzene, respectively, have been shown to form the tetrahedral complexes [CdL].[352]



(**38**)



(**39**)

For useful surveys of this area, see refs. 9–15 and 1468c–h.

56.1.4.5 Amides, Imides and Hydrazides

These ligands coordinate readily to zinc and cadmium[1468j] and several studies have been made in this area.[9–15,1468c–h]

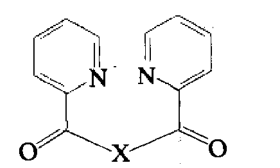
Preparation of the complexes CdX_2L_2 (X = Cl, Br, I or SCN; L = acetamide) has been reported. IR evidence indicates bridging halide ligands, with L coordination *via* O and N.[353]

The crystal structure of dichlorobis(*N,N*-dimethylacetamide)zinc shows zinc tetrahedrally coordinated by the two ligand oxygens (Zn—O = 1.96, 1.98 Å) and two chlorines (Zn—Cl = 2.21, 2.22 Å).[354] The 2:1 complexes of *N,N*-dimethyl- and *N,N*-diethyl-acetamide with ZnX_2 (X = halide) have also been investigated, and the ligands shown to coordinate to the metal *via* the oxygen atom of the amide grouping, again giving a tetrahedral ZnO_2X_2 unit.[355,356]

The malonamide (L) complex $[CdCl_2L_2]\cdot MeOH$ has been prepared in which the coordination about the metal is octahedral, with the malonamide acting as a bidentate N_2 donor and the chlorine atoms mutually *cis*.[357] This compound differs from the related, but five-coordinate, zinc complexes which have also been described.[358,359] The complexes $[Cd(tmu)X_2]$ (X = Cl, Br or I) have been reported and, like the zinc complexes, the ligand has been shown to be coordinated through oxygen.[360]

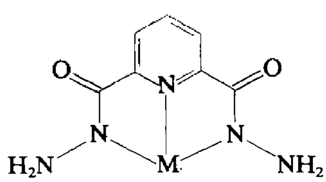
An analysis of the vibrational spectra of the oxamide complexes, $K_2[ZnL_2]$ {L = $(CONH_2)_2$ or $(COND_2)_2$} has been presented.[361]

Much of the interest in amides as ligands has centred around the factors that control the alternative binding modes adopted by these compounds. Binding of Zn^{II} enhances amide deprotonation of *N,N*-bis (2′-pyridinecarboxamide)-1,2-benzene (**40**; LH_2) to give planar $[ZnL\cdot H_2O]$, having maximum electronic delocalization. Coordination of the amide oxygens is hindered by the resulting decrease in the chelating ability of the ligand.[362] Zn^{II} and Cd^{II} complexes with 2,6-dipicolinic acid hydrazide involve a tridentate ligand, with two deprotonated amide nitrogens and a pyridine nitrogen acting as a donor. The amide oxygen atoms are sterically unable to coordinate (**41**). The resulting complex may be cyclized by treating with β-diketones.[363]



X = —NH(*o*-C_6H_4)NH—

(40)

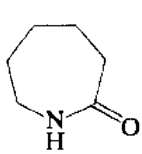


(41)

The ligand *N*-(2-pyridyl)acetamide forms octahedral complexes $[ML_2X_2]$ (X = Cl, Br or I; M = Zn or Cd) that involve the carbonyl oxygen and heterocyclic nitrogen donors,[364] while thermochemical measurements have been carried out on these compounds.[365] IR and Raman studies on the complex $[CdLX_2]$ (X = Cl or Br; L = *N,N′*-dimethyl-l-ethylimidazole-4,5-dicarboxamide) show the ligand to be oxygen-bonded.[366]

In the complexes $[ZnL_2X_2]$, $[ZnL_8I_2]$, $[ZnL_4(NCS)_2]$ (L = **42**; X = Cl or Br), $[ZnL_2X_2]$ and $[ZnL_3(NCS)_2]$ (L = **43**; X = Cl, Br or I) the lactams are coordinated to the metal through the amide oxygen atom.[367]

A number of complexes incorporating saccharin have been described, including $[ZnL_2(H_2O)_4]$ (HL = saccharin) (**44**)[365,369] in which the ligand is thought to act as a monodentate N donor.



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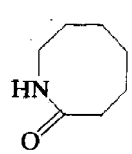
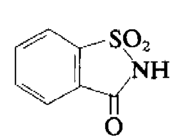


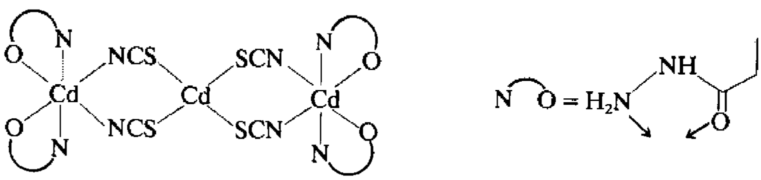
(43)



(44)

A large number of hydrazide complexes are known, and the interaction of a range of ligands of the type $RCONHNR_2$ with zinc and cadmium has been investigated. The hydrazide ligands are thought to act as bidentate N,O donors in the complexes $[CdL_2(SCN)_2]$ and $[CdL_2][(NO_3)_2]$ (L = $RCONHNH_2$; R = Et, Pr^n, *n*-C_5H_{11} or *n*-C_7H_{15})[370] but as monodentate N donors in $[ML_nCl_2]$ (L = $Pr^iCH_2CONHNH_2$; M = Zn or Cd; *n* = 1 or 2).[371] The latter ligand is thought to coordinate to the metal in the iminol form $Pr^iCH_2C(OH){=}NNH_2$.[371] Other complexes which have been described include $CdL_3(SO_4)$, $CdL_3Cl_2\cdot H_2O$ (L = $C_6H_{13}CONHNH_2$)[372] and $ZnL_3(S_2O_6)$ (L = $PhCONHNH_2$).[373] The crystal structure of $[CdL_2(NCS)(SCN)]$ (L = $PhCONHNH_2$) shows the metal to be in a distorted octahedral environment, with the hydrazide acting as a bidentate N,O donor, and one N-bonded and one S-bonded thiocyanate ligand.[374]

The dihydrazides (L) of oxalic and malonic acid have been used as ligands in the complexes [ZnAL]X (X = Cl, NO_3 or $\frac{1}{2}SO_4$; A = deprotonated glycine, serine or methionine).[375] In these complexes, the most probable mode of coordination of the hydrazide ligand is *via* the carbonyl oxygen and amino nitrogen, and an example of this mode is to be seen in a crystal structural analysis of the complex $[L_2Cd(NCS)_2Cd(SCN)_2CdL_2]$ (L = propionic acid hydrazide) which has the structure (**45**).[376]



(**45**)

56.1.4.6 Iminodiacetic Acid and Related Polydentate Ligands

The edta complexes of zinc and cadmium are well documented and we focus here on some of the structural variants based on iminodiacetic acid.

Among the archetypal derivatives a structure determination of $K_2Zn[NH(CH_2CO_2)_2]_2$ reveals discrete anions in which the terdentate ligands give the zinc an octahedral configuration (Zn—N = 2.16 Å; Zn—O = 2.03, 2.12 Å)[377] and the molecular structure determination of the complex $Zn(HL)_2{\cdot}4H_2O$ (H_2L = iminodiacetic acid) shows the HL ligand to be bidentate, coordinating only through the oxygen, and forming bridges between zinc atoms.[378]

Further iminodiethanoate complexes investigated recently have included $(H_2NCOCH_2)N(CH_2CO_2H)_2$ and $(H_2NCOCH_2CH_2)N(CH_2CO_2H)_2$,[379] $(HO_2CCH(OH)CH_2)N(CH_2CO_2H)_2$,[380] DL-$(HO_2CCH_2)_2NCH_2CH(CO_2H)N(CH_2CO_2H)_2$,[381] H_4edta,[382] $(MeO_2CCH_2)_2NCH_2CH_2N(CH_2CO_2Me)_2$[383] and $\{(HO_2CCH_2)_2NCH_2CH_2NHCH_2CH_2NHCH_2CH_2\}_2NH$.[384]

A number of tetraacetate ligands have been compared with edta, and formation constants discussed in terms of structural features in the ligands. Thus, constants for the formation of the 1:1 complexes of ethylenebis(*N,N'*-(2,6-dicarboxy)piperidine) with Zn^{II} and Cd^{II} are lower than those with edta due to the steric effects of the piperidine ring.[385] The influence of the $CH_2C{\equiv}CCH_2$ structure on the chelating properties of 1,4-aminobutyne-2-tetraacetate has also been assessed.[386] Another development in the study of edta has involved the preparation of simple derivatives, such as the tetraamide. This ligand is probably O-bonded *via* the amide function, but on deprotonation the donor atom changes to the amidate nitrogen.[387] Equilibria in acidic solutions of edta complexes of Zn^{II} and Cd^{II} involve the formation of mono- and poly-protonated complexes.[388]

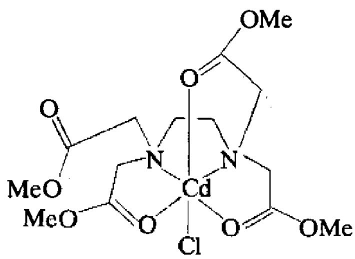
The formation of 1:1 complexes between ethylenediamine-*N,N'*-diacetic acid (edda) and Zn^{II} or Cd^{II} have been studied by calorimetric (ΔH) and potentiometric techniques.[389] Earlier studies had omitted to allow for protonation reactions of the ethanoato groups in the ligand. Thermodynamic parameters for edda lie between those of nitrilotriacetate and triethylenetetramine. Edda appears to undergo a slow metal-ion-catalyzed hydrolysis in aqueous acid solution.

Amide deprotonation is normally observed in copper(II), nickel(II) or cobalt(II) complexes of amides, but it has now been demonstrated that $[Zn(LH)_2]^{2-}$ (H_3L = $H_2NCOCH_2N(CH_2CO_2H)_2$) may be further deprotonated, and that the equilibria in Scheme 1 are established. The ability of the d^{10} zinc(II) ion to promote such equilibria suggests that a major requirement for deprotonation of an amide is a positively charged centre, since the d^{10} ion cannot show ligand field effects.[390]

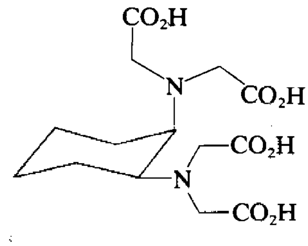
$$[Zn(HL)_2]^{2-} \rightleftharpoons [ZnL(HL)]^{3-} + H^+$$
$$[ZnL(HL)]^{3-} \rightleftharpoons [ZnL_2]^{4-} + H^+$$

Scheme 1

The cadmium complex $[CdLCl]Cl \cdot H_2O$ (L = tetramethyl ethylenediaminetetraacetate) has been prepared and it is proposed that the complex has the octahedral structure (**46**).[391]



(**46**)

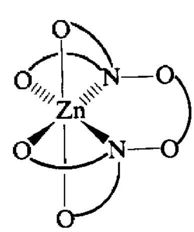


(**46a**)

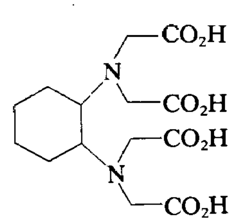
Interaction of Zn^{2+} and Cd^{2+} with the chelating agents ethylenedinitrilotetraacetic acid and 1,2-*trans*-cyclohexylenedinitrilotetraacetic acid (H_4L) (**46a**) shows evidence for the formation of dinuclear $[M_2L]$ species, in addition to mononuclear $[ML]^{2-}$ and $[MHL]^-$ ions.[392] Evidence for similar dinuclear species is obtained from studies of other polychelate agents such as diethylenetriaminepentaacetic acid (H_5L),[393] triethylenetetraaminehexaacetic acid (H_6L)[394] and ethylenediamine-*N,N'*-diacetic acid (H_2L),[395] and the binuclear complex $Zn_2(edta) \cdot H_2O$ has been characterized.[396]

NMR studies have been widely used in studying the complexing of ligands of this type to zinc and cadmium. For example the cadmium complex of *cis*-1,2-cyclohexanediaminetetraacetic acid[397] has been investigated by NMR methods; the complex is octahedral, and there is no evidence for the penetration of water into the inner coordination sphere of the metal.[50] An NMR study of the zinc complex of the ligand $\{(HO_2CCH_2)_2NHCH_2CH_2OCH_2\}_2$ has shown that the ether oxygen atoms are not coordinated to the metal, i.e. the configuration (**47**) is adopted.[398]

The natural abundance ^{15}N NMR spectrum of $[CdL]^{2-}$ (H_4L = **48**) has been reported and satellite peaks due to coupling of ^{15}N to the ^{111}Cd and ^{113}Cd nuclei have been detected.[399]



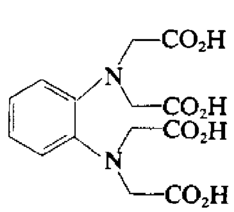
(**47**)



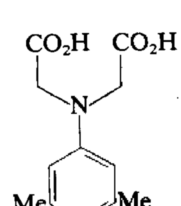
(**48**)

Related ligands which have been studied include (**49**),[400] $(HO_2CCH_2)_2NCH_2CH(CO_2H)$-$N(CH_2CO_2H)_2$,[401] (**50**),[402] (**51**),[402] ethylenediaminedisuccinic acid,[403] $\{(HO_2CCH_2)_2NCH_2CH_2\}_2$-$NCH_2CO_2H$,[404] $\{(HO_2CCH_2)_2NCH_2CH_2\}_2NCH_2CH_2OCH{=}CH_2$[405] and $(HO_2CCH_2)_3N$.[406]

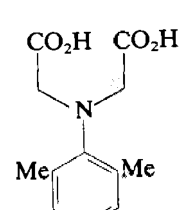
The phosphorus analogue of H_4edta, $(HO_2CCH_2)_2PCH_2CH_2P(CH_2CO_2H)_2$, has been shown



(**49**)



(**50**)



(**51**)

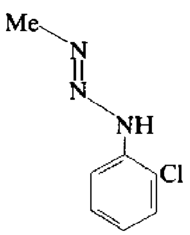
to form zinc and cadmium complexes resembling those of H_4edta itself.[407] Comprehensive surveys of this area are available.[9-15,1468c-h]

56.1.4.7 Azo Compounds

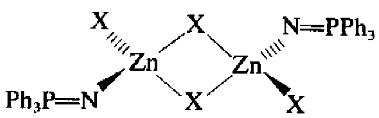
There have been few recent studies in this area. The complex $[ZnL_2(bipy)]$(HL = **52**) has been reported, and shown to adopt a pseudooctahedral configuration, in which the metal interacts with the *ortho* chloro substituent.[408]

Stability constant determinations for complexes of Zn and Cd with various chelating azobenzenes show that zinc forms the stronger complexes.[409]

Related to azo compounds are compounds containing the ⩾P—N— group; alcoholysis of $Ph_3P{=}NSiMe_3$ in the presence of ZnX_2 (X = halide) results in the formation of $Ph_3P{=}NH$ complexes, which are thought to have the halide-bridged structure (**53**).[410]

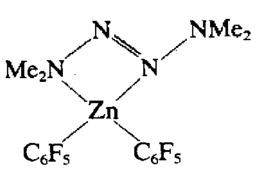


(**52**)



(**53**)

The molecular structure of bis(perfluorophenyl)(tetramethyltetrazene)zinc (**54**) shows tetrahedral coordination about the zinc,[411] with the N_4 system of the tetrazene in a *trans* configuration bonded to the zinc *via* N—1 and N—3 (Zn—N = 2.13, 2.25 Å). NMR data are consistent with a rapid equilibrium in solution (equation 4).



(**54**)

$$\text{TMT}^* + \text{TMTZnR}_2 \rightleftharpoons \text{TMT} + \text{TMT}^*\text{ZnR}_2 \qquad (4)$$

Further phosphorus–nitrogen systems are considered under 'Heterocycles' (Section 56.1.4.8) and have been surveyed.[9-15,1468c-h]

56.1.4.8 Heterocycles

56.1.4.8.1 Imidazole, pyrazole and related species

Many of the biologically active zinc metalloproteins contain a zinc(II) ion bound to one or more imidazole ligands of the amino acid residue histidine. For this reason a large number of studies over an extended period have been carried out on zinc and cadmium complexes of imidazole, substituted imidazoles, histidine and related ligands. There has also been much recent activity in this field; much structural information is available.

A structural determination of $\{Zn(imidazole)_4\}(ClO_4)_2$ shows the zinc to be approximately tetrahedrally coordinated (Zn—N = 1.99, 2.00 Å).[412] The compound $\{CdCl_2(imidazole)\}$ is polymeric; the Cd atoms are linked into infinite chains by double chlorine bridges, while two such chains running parallel to one another are themselves linked by bridging chlorine atoms.

Coordination about cadmium is octahedral (Cd—Cl = 2.67 Å, Cd—N = 2.24 Å).[413] The structure of {Cd(imidazole)}$_3$}(SO_4)·H_2O is also polymeric. Cadmium exhibits octahedral coordination, being bonded to three nitrogens, a water molecule and two oxygens from sulfate, which links the coordination polyhedra in infinite chains (Cd—N = 2.26 Å).[414] {Cd(imidazole)}$_6$(HCO_2)$_2$ has been prepared; the uncoordinated formate is stabilized by unusually strong hydrogen bonding to the imidazole ligands.[415]

The complexes CdL_nX_2 (n = 2, X = Cl, NO_3, OAc, Br or I; n = 4, X = SCN, L = 2-benzylimidazole) have been prepared; thiocyanate is S-bonded.[416]

A good deal of spectroscopic information is also available.

Metal isotope labelling techniques have been used to clarify the M—N bond assignments in the octahedral [Zn(HIm)$_6$]Cl_2 and pseudotetrahedral [Zn(HIm)$_2$$X_2$] complexes (X = Br, I, NO_3, NCS; HIm = imidazole).[417] Much lower frequencies (208 cm^{-1}) are observed for the octahedral complexes as compared to the tetrahedral (255, 239 cm^{-1}). A comparison with other N-bonded species shows that the frequency is governed by both the mass of the ligand L and the strength of the M—L bond.

Solution equilibria have also been the subject of several studies. For example, the gross stability constants (β_n; n = 1–5) of imidazole complexes with the M^{II} ions of Cu, Ni, Cd, Zn and Co have been determined; the following order of stability was found: Cu > Ni > Cd > Zn > Co.[418]

The stepwise formation constants for the displacement of H_2O from $[Cd(H_2O)_6]^{2+}$ by imidazole have been measured.[419] On the basis of enthalpy changes, a change in coordination from octahedral to tetrahedral and then back again is postulated at certain steps (Scheme 2).

$$[Cd(H_2O)_5im]^{2+} \rightleftharpoons [Cd(H_2O)_4(im)_2]^{2+}$$
$$[Cd(im)_4]^{2+} \rightleftharpoons [Cd(im)_5H_2O]^{2+}$$

Scheme 2

A potentiometric study of the formation of cadmium–imidazole complexes has been reported and a number of species, including $[CdL]^{2+}$, $[CdL_2]^{2+}$, $[CdL_3]^{2+}$, $[CdL_4]^{2+}$ and $[Cd(OH)L]^+$, have been characterized.[420]

Imidazole complexes are widely studied as models for zinc-containing enzymes, and the complexes [ZnL_n] (n = 1–4) have been characterized in aqueous solution.[259] A number of ternary complexes with imidazole and carboxylate ligands have been studied,[30,421–425] and, in particular, the Cd^{2+}–HIm–malonate[424] and Cd^{2+}–HIm–succinate[425] systems have been well characterized. Crystal structural analyses of the complexes [Zn(O_2CMe)$_2$(HIm)$_2$] and [Zn(O_2CEt)$_2$(HIm)$_2$] have been reported; in each case the metal is in a near-tetrahedral N_2O_2 environment with monodentate carboxylate groups bonded to the metal (Zn—N, 1.987–2.010 Å; Zn—O, 1.947–1.987 Å; Zn—O (non-bonded), 2.645 Å).[426]

These results are comparable to those obtained from the structural analysis of [Zn(OAc)$_2$$L_2$] (L = *N*-ethylimidazole) which has also been reported (Zn—N, 2.031, 2.010 Å; Zn—O, 1.944, 1.976 Å; Zn—O (non-bonded) 2.850, 2.862 Å).[422]

The *N*-vinylimidazole complexes [ZnL_4]X_2 (X = NO_3, BF_4 or ClO_4) are tetrahedral, whereas [CdL_6]X_2 are octahedral; the complex [CdL_3(NO_3)$_2$] has also been described.[427]

A series of zinc and cadmium complexes of *N*-ethyl- and *N*-propyl-imidazole have been described; the 1:1 complexes [ML_2X_2] (M = Zn or Cd; L = *N*-alkylimidazole; X = halide) are monomeric tetrahedral species, whereas [(MLX_2)$_2$] (M = Zn or Cd; L = *N*-alkylimidazole; X = halide) are halide-bridged dimers.[428]

An IR spectroscopic study of the imidazole complexes [Zn(HIm)$_6$][NO_3]$_2$, [Zn(HIm)$_4$(NO_3)$_2$] and [Zn(HIm)$_4$][ClO_4]$_2$ and their deuterated analogues has been made.[429]

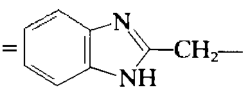
The crystal structure of [Cd(GlyGly)(Im)Cl] has been reported[72] and shown to involve dimeric units with a distorted octahedral geometry about each metal atom; this complex has also been studied in a ^{13}C NMR investigation of a range of nucleoside and peptide complexes of cadmium(II).[430]

Treatment of [Zn(acac)$_2$] with a mixture of imidazole and tetramethylimidazole results in the formation of [Zn(Im)$_2$] and a determination of the crystal structure of this compound has revealed that it consists of tetrahedral {ZnN_4} units, connected by bridging imidazole groups.[431]

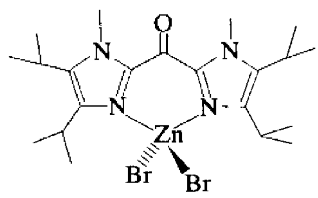
Complexes with 1,2-dimethylbenzimidazole have been described, and there is evidence that the ligand may act as both a monodentate and a bidentate N donor.[432] The ligand (**55**) is prepared by the condensation of 1,2-diaminobenzene with diethylenetetraminepentaacetic acid, and a crystal structure of the complex $[Zn_2LCl_4(H_2O)_2]$ has been reported.[433]

A crystal structural analysis of the bisimidazolyl ketone complex (**56**) has been made, and the metal shown to be in an approximately tetrahedral environment.[434]

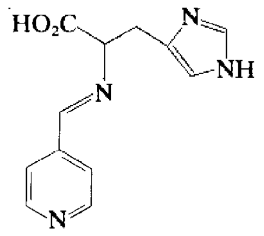
The Schiff base formed in the condensation of histidine with pyridoxal has the structure (**57**) and has been shown to form a range of zinc complexes.[261]

$\{R_2N(CH_2)_2\}_2NR$ where R = 

(**55**)



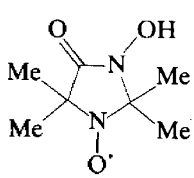
(**56**)



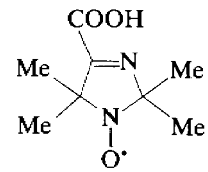
(**57**)

Imidazoline-oxyl complexes have been studied, and the ligand in $[ZnL_2]$ (HL = **58**) has been shown to be coordinated *via* the oxygen atom of the carbonyl group and a deprotonated hydroxy group.[435]

A crystal structural analysis of the complex $[ZnL_2(H_2O)_2]$ (HL = **59**) has been reported, and the metal shown to be coordinated to two water molecules, the carboxylate group and the imino nitrogens of the imidazole residues, to give an $N_2O_2O'_2$ environment.[436]



(**58**)



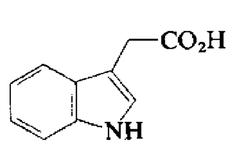
(**59**)

Earlier, an ESR investigation of complexes formed between Zn, Cd and Hg and several paramagnetic imidazolin-1-oxyl free radicals had been reported.[437] For a given ligand, the changes in the ^{14}N hyperfine splittings can be correlated with the formation constants, and the following order of stability is observed: Hg > Cd > Zn.

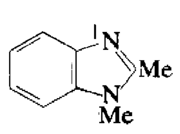
An ^{15}N NMR study of the complexation of 1-methylimidazole-$^{15}N_2$ with $Zn(NO_3)_2$ and $Cd(NO_3)_2$ has been made.[438]

Complexes of 3-indoleacetic acid (**60**) and 1,2-dimethylbenzimidazole (**61**) have been described.[439,440]

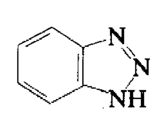
Crystal structures of the benzotriazole complexes $[Zn(HL)Cl_2]$ and $[Zn_2L_4]$ (HL = benzotriazole **62**) have been reported; the former compound has the metal in a tetrahedral N_2Cl_2 environment (Zn—N, 2.014, 2.034 Å; Zn—Cl, 2.241, 2.235 Å) and the latter is a polymeric species.[441] The complex $[H_2L]_2[ZnCl_4]$ (HL = **62**) has also been described; it is isostructural with the tetrachlorocobaltate(II) analogue, which has previously been structurally characterized.[441] The synthesis and powder diffraction pattern for $[ZnL_2Cl_2]$ (L = **62**) have also been reported.[442] Complexes of the type MX_2L_2 (M = Zn, X = Cl, Br, I or SCN; M = Cd, X = Cl; L = allyl or 3,5-dimethylpyrazole) have been synthesized; where L is 3,5-dimethylpyrazole, cadmium also forms the complexes ($CdBr_2L_3$ and CdI_2L_4. When L is allylpyrazole, alkene coordination is not observed; thiocyanate is N-bonded.[443,444]



(**60**)



(**61**)



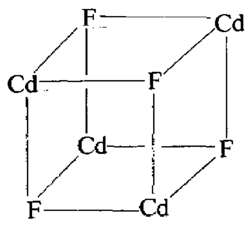
(**62**)

The enthalpies of chelation of Zn^{2+} with $[H_nB(pz)_{4-n}]^-$ (n = 0—2; pz = pyrazolyl) in both acetonitrile and water have been measured; when n = 2, the complex is four-coordinate, but six-coordinate when $n = 0$ or 1. The substantially decreased enthalpy of complexation on going from $n = 1$ to $n = 0$ is attributed to coordination competition from the uncomplexed pyrazole ring.[445]

3,5-Dimethylpyrazole (L) has been shown to react with $Cd(BF_4)_2$ to give CdL_2F_2 containing a linear fluoride-bridged chain structure with L completing an octahedral coordination for the Cd.[446]

The reaction of 5-methylpyrazole with cadmium tetrafluoroborate gives a complex which is formulated as the tetrameric species $[Cd_4F_4L_{12}][BF_4]_4$.[447] It is thought that the fluoride ion is generated by the (possibly metal-assisted) hydrolysis of tetrafluoroborate, and that a heterocubane Cd_4F_4 cluster core (**63**) is formed.

A crystal structure of the complex $[ZnL_2Br_2]$ (L = benzoylaziridine) has shown the metal to be in a tetrahedral N_2Br_2 environment (**64**).[448]



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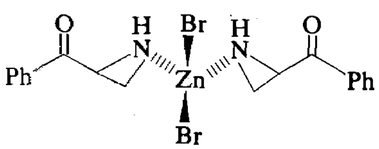


(**64**)

Zinc complexes with imidazole,[449] 1,2-dimethylimidazole,[450] (**61**),[451] 1,2,4-triazole,[452] 5-cyanotetrazole,[453] benzimidazole,[454] 4-amino-1,2,4-triazole[455] and 2-amino-5-phenyl-1,3,4-oxadiazole[456] have been reported. A crystal structure of $[ZnL_2(SCN)_2]$ (L = 1,2,4-triazole) shows it to consist of $\{ZnN_6\}$ octahedra linked by a 2,4-bridging triazole group.[457] The five-coordinate benzotriazole complexes $[ZnL_3X_2]$ ($X = N_3$ or NCO) and the octahedral species $[ZnL_4(NCS)_2]$ have been described.[458] The octahedral complex $[Zn(HL)_2(H_2O)_2]Cl_2 \cdot 2H_2O$ (HL = 2-hydrazino-6-methyl-4(3*H*)-pyrimidone) has also been described; one of the chloride ions is hydrogen-bonded to the ring NH and the zinc atom is coordinated to a ring nitrogen and the terminal NH_2 group.[459]

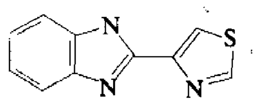
Benzoxazole (L) derivatives of the stoichiometry $M(XCN)_2L_2$ (M = Zn or Cd; X = S or Se) and Cd(NCSe)L have been prepared; the former are pseudotetrahedral while the latter is polymeric. The ligand is N-bonded in all cases.[460] Benzoxazole-2-thione (L) forms the similar MX_2L_2 complexes (M = Zn, Cd, Hg; X = Cl, Br, I) and CdI_2L; coordination is through nitrogen, and not sulfur or oxygen.[461]

Isoxazole (L) complexes of stoichiometry $CdLX_2$ (X = Cl, Br, I or NCS) have been prepared.[462] IR evidence indicates them to be tetrahedral, dimeric, anion-bridged complexes, with N coordination.

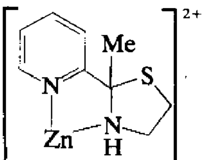
Zinc, cadmium and mercury complexes of isoxazole (L) and several of its derivatives of the stoichiometries MLX_2 and ML_2X_2 (X = Cl, Br, I or SCN) have been prepared. In general, the former are polymeric containing either isoxazole bridging through nitrogen and oxygen or bridging halide, while the latter are either monomeric and tetrahedral, with isoxazole bound through oxygen in the case of zinc, or polymeric and octahedral containing bridging isoxazole.[463,464]

Complexes of the stoichiometry $[ML_3][ClO_4]_2$ [L = thiabendazole (**65**)] contain the metal in an octahedral coordination with the chelating ligand coordinated *via* the nitrogens of the imidazole and thiazole rings.[465]

The complex $[ZnL][ClO_4]_2$ (**66**) has been reported.[466]



(**65**)

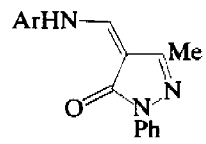


(**66**)

N-Acetylpyrazole reacts with zinc ions to form a tris complex, and the salt $[ZnL_3][BF_4]_2$

(L = *N*-acetylpyrazole) has been isolated.[467] The ligand is coordinated to the metal through nitrogen and the acetyl oxygen atom, and the acetyl group is found to exist as the enol tautomer. A similar mode of bonding is adopted in the tris(*N*-carbamoylpyrazole)zinc(II) ion, which has also been isolated as its BF_4 salt.[468]

The 2:1 complexes ZnL_2 (LH = **67**) have been investigated by multinuclear (^{15}N, ^{13}C and ^{1}H) NMR techniques:[469] complex formation causes considerable change of the π-electron structure in the merocyanin part of the ligand.



(67)

56.1.4.8.2 Pyridines and related species

There is a large body of information on complexes of pyridine, substituted pyridines and ligands containing pyridine rings and other donor atoms. Complexes with pyridine and its derivatives have been reviewed.[470,9–15,1468c–h]

The structure of deca-μ-ethanoatodioxobis(pyridine)heptazinc(II) involves seven zinc atoms, bridged by ethanoate groups, in a heptameric centrosymmetrical unit. In each of the two half-units, a central oxygen is surrounded tetrahedrally by four zinc atoms (one of which is common to both). Five of the six edges of this tetrahedron of zinc atoms are bridged by ethanoate groups, the remaining one being open. The structure thus contains three types of zinc; Zn(1) lies on the centre of symmetry in an octahedral environment, Zn(3) is coordinated to three oxygen atoms from ethanoate and the pyridine nitrogen, whilst Zn(2) and Zn(4) are tetrahedrally coordinated by oxygen atoms. The EPR spectrum of the copper-doped crystal has been measured.[471]

ν(Cd—N) and ν(Cd—X) stretching frequencies have been assigned in the far IR ($\geq 30\ cm^{-1}$) and low-frequency Raman spectra of $[Cd(py)X_2]$ (X = Cl or Br).[472] The results support a structure for this common stoichiometry comprising double-strand halogen-bridged polymeric chains, in which the Cd^{II} is bound by one pyridine ligand, two bicoordinate halogens and three tricoordinate halogens. Complexes[473,474] and formation constant data for a number of substituted pyridines and quinolines have been reported. Zinc complexes of nicotinamides have attracted particular attention[475] and the crystal structures of dichloro- and diiodo-bis(*N,N*-diethylnicotinamide)zinc(II) have been published.[476]

Detailed measurements have been made of the low-frequency Raman spectra of $[Zn(py)_2X_2]$ (X = Cl or Br) and of the far-IR spectra of the complex where X = Cl at liquid nitrogen temperature. It is found that skeletal molecular vibrations couple with lattice vibrations in the crystal, except for the Zn—X stretching vibrations. Force constant calculations indicate the Zn—N bond to be stronger in the bromide, while the Zn—Cl bond is stronger than the Zn—Br bond.[477]

A more refined structure determination of $ZnCl_2Py_2$ has been reported (Zn—N = 2.05 Å, Zn—Cl = 2.22, 2.23 Å).[478] The Raman Zn—Cl stretching frequencies in a series of $ZnCl_2L_2$ (L = pyridine and its substituted derivatives) have been shown to depend significantly on pressure in the range 0–12 kbar; it appears that Zn—Cl π bonding is more sensitive to pressure than the σ-bond component.[479,480] A comparison of calculated vibrational frequencies for the pyridine ring in MX_2py_2 complexes (M = Zn, Cd or Hg; X = Cl, Br or I) reveals that only in the case of zinc do the frequencies depend on the halogen substituent.[481]

Iodine and bromine NQR studies on the complexes MX_2L_2 (M = Zn, Cd or Hg; L = nitrogen heterocycle) show that the covalency of the M—L bond decreases in the order Cd > Zn > Hg.[482] NMR, X-ray photoelectron studies and extended Hückel calculations on $HgCl_2py_2$ indicate a moderate amount of electron transfer to the metal from pyridine relative to $ZnCl_2py_2$; filled mercury *d* orbitals do not participate in bonding.[483]

Quinoline complexes have not been so widely studied as those with pyridine ligands, but a few compounds have been described. The reaction of $[ZnL_2(H_2O)]$ (HL = 1-chloro-2,4-pentanedione) with quinoline gives the five-coordinate species $[ZnL_2(quin)]$.[484] Similar reactions occur with isoquinoline, quinaldine and 4-methylpyridine. The complexes

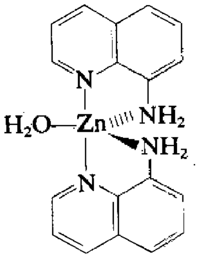
$[Zn(amq)X_2]$ (X = Cl, Br or I) and $[Zn(amq)_2][ClO_4]_2$ are tetrahedral, in contrast to some other zinc(II)–amq complexes which have been described.[485]

A ^{13}C NMR investigation of the ligands 8-HO-quin, 4-Me-8-HO-quin and the complex $[ZnL_2]$ (HL = 4-Me-8-HO-quin) in DMSO-d_6 has demonstrated the complex to have a weakly ionic Zn—O interaction, with most of the negative charge localized on the oxygen.[486]

The complex $[ZnL_2(NCS)_2]$ (L = benzoquinoline) has been prepared and the NCS ligands have been shown to be N bonded, in contrast to those in the corresponding Hg^{II} or Cd^{II} complexes.[487]

The complexes $[ZnL_2Q_2]$ (HL = $PhCO_2H$; Q = quin or isoquinoline) have also been reported and shown to have octahedral coordination at the zinc(II) atom, with a bidentate carboxylate group.[488]

The complexes $[Cd(amq)]X_2$ (X = Cl, Br or I) and $[Cd(amq)_2](ClO_4)_2$[485] have been described, as has $[Cd(amq)_2(SCN)_2]$.[487] In the latter compound the thiocyanate is S-coordinated, in contrast to the corresponding zinc complex in which it is N-bonded to the metal. The crystal structure of $[ZnL_2(H_2O)][ZnCl_4]$ (L = 8-aminoquinoline) has revealed the metal to be in a trigonal bipyramidal environment (**68**).[489]

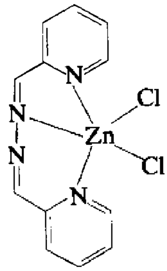


(68)

The complexes $[Zn(4\text{-vinylpyridine})_2X_2]$ (X = Cl, Br or NCS) and $[Zn(2\text{-vinylpyridine})_2X_2]$ (X = Br or I) have been prepared. The crystal structure of the chloro complex shows it to be tetrahedral.[490]

N-Substituted derivatives of 2-[(*N*-acetyl)amino]pyridine (L) react with $ZnCl_2$ to yield $ZnLCl_2$ derivatives in which the ligand is chelate bound *via* pyridine N and amide O atoms.[491]

A structure determination of $[ZnLCl_2]$ (**69**; L = 2-pyridinaldazine, a ligand unusual in its variability of chelation) shows the ligand to be terdentate; the zinc coordination is midway between trigonal bipyramidal and square pyramidal (Zn—N = 2.15–2.17 Å).[492]



(69)

Zinc complexes of several polymeric N-donor ligands have been reported. Poly-(1-vinyl-2-pyrrolidinone) of various molecular weights forms the complex $[ZnCl_2(C_6H_9NO)]_{100}$.[493] Complexes with the polyvinylpyridines poly(2-pyridylethylene) and poly(4-pyridylethylene) have also been prepared.[494]

Metal complexes of several zinc, cadmium and mercury salts with 2-, 3- and 4-cyanopyridine have been reported.[495] In none of the complexes was cyanide coordination observed. Zinc halides react with 3- and 4-cyanopyridine, but not with 2-cyanopyridine, to give 1:2 complexes which are assigned a monomeric tetrahedral structure on the basis of IR evidence. The cadmium halides also form 1:2 complexes with all the cyanopyridines, except cadmium chloride, which reacts with 2-cyanopyridine to give a 1:1 complex. The former contain octahedrally coordinated cadmium with halogen bridges, while the latter contains a dimeric, tetrahedrally coordinated cadmium. Zinc thiocyanate yields a monomeric tetrahedral 1:2 complex with 4-cyanopyridine, but does not react with the 2- and 3-derivatives. Cadmium thiocyanate gives 1:2 complexes with 2- and 3-cyanopyridine which are assigned a polymeric octahedral structure containing M—SCN—M bridges. Zinc sulfate reacts with 4-cyanopyridine to give a 1:2 complex considered to have octahedrally coordinated zinc in a polymeric structure involving chelating sulfate. The 4-cyanopyridine *N*-oxide complex, $ZnL_2(NCS)_2$ is by contrast apparently monomeric with tetrahedral O_2N_2 coordination.[495a]

The involvement of zinc in nicotinamide-based hydride-transfer reactions has led to numerous studies of Group IIB complexes of pyridine carboxylic acid derivatives. Cadmium complexes of 2-pyridinecarboxylic acid,[496] 3-pyridinecarboxylic acid[497] and 3-pyridinecarboxamide[498] have been reported. The crystal structure of $[Cd(HCO_2)_2L_2(H_2O)_2]$ (L = 3-pyridinecarboxamide) has also been described; the metal is in an octahedral environment in which the amide acts as a monodentate N donor.[498]

A range of binary and ternary complexes of nicotinic acid and nicotinamide have been described[499,500] and crystal structural analyses of $[CdL_2(H_2O)_2(HCO_2)_2]$ (L = nicotinamide)[501] and $[CdL_2(H_2O)_2(OAc)_2]$ (L = *N,N*-diethylnicotinamide)[502] have been reported. Both complexes are octahedral, with the amides coordinated to the metal through nitrogen (Cd—OAc 2.281 Å; Cd—N 2.376 Å; Cd—OH 2.299 Å).

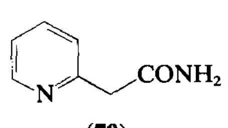
The structure determination of di-μ-(*N,N*-diethylnicotinamide) tetraisothiocyanatodizinc also shows zinc tetrahedrally coordinated with *N,N*-diethylnicotinamide molecules bridging through both nitrogen and oxygen.[503]

The vibrational spectra of $[ZnL_2L'_2]$ (LH = 2-pyridinecarboxylic acid *N*-oxide; L′ = H_2O or D_2O) indicate coordination through the *N*-oxide oxygen and the carboxylate group.[504] In contrast, the complexes with 3-pyridinecarboxylic acid *N*-oxide and pyridine-4-carboxylic acid *N*-oxide are polymeric multinuclear species.[505] Crystal structures of $[ZnL_4(NCS)_2]$ (L = 3-pyridine-*N,N*-diethylcarboxamide)[506] and $[ZnL_2(H_2O)_2(HCO_2)_2]$ (L = 3-pyridinecarboxamide)[507] have been reported.

The crystal structure of $[ZnL_2(H_2O)_2][NO_3]_2$ (L = **70**) shows that the metal is in an octahedral environment, bidentate 2-pyridylacetamide ligands bonding through the ring N and amide O atoms, the water molecules occupying axial sites.[508]

Complexes with pyridine aldehydes and ketones are of interest and the ligand bis(2-pyridyl) ketone has been the subject of several investigations. The type of coordination adopted with this compound appears to depend upon the counterion, since $[ZnL(N_3)_2]$ is four-coordinate whilst $[ZnL_2(NCE)_2]$ (E = S or O) are six-coordinate with the ketone acting as an N_2 donor in each case.[468] Of the complexes $[ZnLX_2]$ (X = Cl, Br or I), only the iodide ionizes in DMF, apparently indicating that the halide ions are strongly coordinated.[509] 3-Pyridinealdehyde is also of interest as a ligand and complexes with the parent compound[510] and its thiosemicarbohydrazone[511] have been reported. The condensation of 2-pyridinealdehyde with tach and 2-pyridinealdehyde or 2-acetylpyridine with 1,1,1-tris(aminomethyl)ethane, results in the formation of tridentate ligands (L) which form the corresponding $[ZnL]^{2+}$ complexes. These complexes have been shown to be chiral, undergoing rapid racemization in solution.[512]

The reaction of $Zn(O_2CMe)_2 \cdot nH_2O$ with **(71)** in BzOH results in the formation of monomeric five-coordinate complexes.[513]



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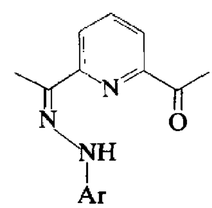


(71)

Zinc complexes of pyridine aldehydes are sometimes regarded as models for the activated complex formed in the reduction of acetaldehyde by NADH in the presence of the zinc-containing alcohol dehydrogenase enzymes (see Section 56.1.14.1) and complexes with 2- and 4-pyridinealdehydes have been studied.[514,515] Nicotinic acid,[509,516] nicotinamide,[509,517] isonicotinamide[509] and 2-aminonicotinic acid[518] have been investigated as ligands, and it is now evident that these compounds normally act as monodentate ligands, coordinating to the metal through the ring nitrogen atom. A crystal structural analysis of the complex $[ZnL_2(acac)_2]$ (L = nicotinic acid) has zinc coordinated in this way.[516]

Crystal structures have also been reported for the complexes $[Zn(dien)L]^{2+}$ (L = bis(2-pyridyl)amine), in which the five-coordinate zinc atom adopts a trigonal bipyramidal configuration,[519] and $[Zn(3\text{-}O_3Spy)_2(H_2O)_4]$, in which the two 3-pyridinesulfonic acid ligands adopt the axial positions of an octahedral $\{ZnO_4N_2\}$ unit.[520] The reaction of $ZnEt_2$ with $LiAlH_4$ in ether results in the formation of a moderately stable form of ZnH_2, which reacts with pyridine to give complexes containing coordinated 1,4-dihydropyridines. The complexes $[L_2ZnL'_2]$ (HL = 1,4-dihydropyridine; $L'_2 = (py)_2$ or TMEN) have been characterized and used for the reduction of carbonyl compounds.[521,522]

The compounds $[CdL_2I_2]$ and $[CdLX_2]$ (X = Cl or Br; L = bis(2-pyridyl)ketone) are all monomeric non-electrolytes in which the ligand acts as an N_2 donor.[509] Complexes of (**71**; Ar = Ph or 2-thienyl) have been reported.[513]

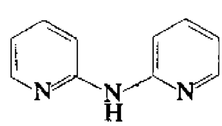
The complex $[ZnL_3]Cl_2{\cdot}EtOH$ (L = **72**) forms a two-dimensional network, held together by —NH · · · Cl hydrogen bonding, and with bidentate N_2-donor ligands (Zn—N (average), 2.179 Å).[523]

The terdentate ligand β-(2-pyridyl)alanine forms zinc complexes with a considerable degree of enantioselectivity.[524] Zinc complexes of 2-pyridyl azo compounds,[525] oximes[526] and sulfonamides[527] have also been described.

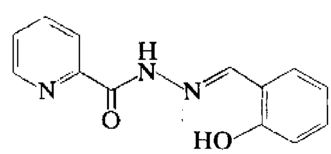
The crystal structure of bis[2-thiobenzaldimino)2,6-diacetylpyridine] zinc has been determined as a five-coordinate complex with the ligand donor atoms describing an approximate trigonal bipyramid.[528] The overall configuration of the ligand is decidedly helical, however, resulting from steric interactions between the methyl groups and the protons of the aromatic rings.

Di-2-pyridyl ketone complexes to Zn^{2+} in an *N,N*-chelate fashion, while the keto group is present in the form of the geminal diol. In basic solution, this latter group is ionized, leading to *N,O*-coordination by the ligand.[529]

The reaction of picolinoylhydrazide with salicylaldehyde results in the formation of the ligand (**73**), which may act as a bi-, ter- or quater-dentate donor, and a number of zinc complexes of this ligand have been prepared.[530]



(**72**)

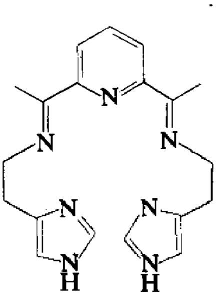


(**73**)

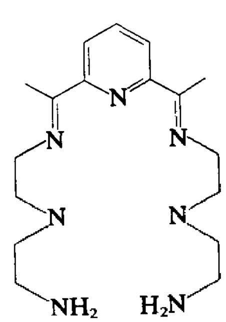
A crystal structure of $[ZnL][ClO_4]_2$ (L = **74**) has been reported, and the ligand shown to be quinquedentate.[531] The related ligand (**75**) forms a pentagonal bipyramidal zinc complex $[ZnL][ClO_4]_2$, which is obtained by a metal exchange reaction of $[BaL][ClO_4]_2$ with $Zn[ClO_4]_2$.[532]

The reaction of [NiL] (H_2L = **76a**) with ammonium persulfate, pyruvic acid and $AgNO_3$ gives (**76b**) which acts as an N_2O_2 donor to a number of transition metals. The complexes [ZnL] (H_2L = **76a** or **76b**) have been prepared, and their electronic spectra reported.[533]

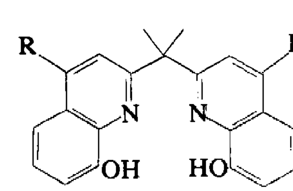
Derivatives of the stoichiometry $ZnL_4(NCS)_2$, $CdL(NCS)_2(DMF)$ and $CdL_2(NCS)_2$ (L = acridine) have been prepared; the first two contain hexacoordinated metal ions, while the third contains N,S-bridging thiocyanate.[534]



(**74**)

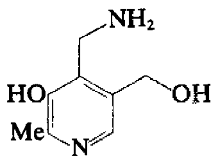


(**75**)



(**76**) **a**; R = H
b; R = O_2CMe

Zinc complexes of a range of pyridone defleecing agents have been described.[535] A number of pyridoxamine(77) complexes have been reported[536,537] and a crystal structural analysis of the complex $ZnL_2(OH_2)_2$ (78) (HL = 77) has been performed.[537]



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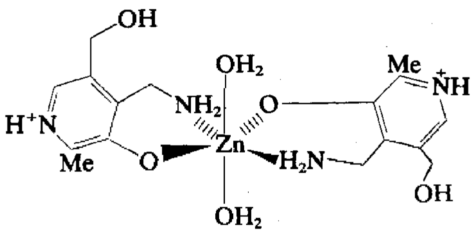


(78)

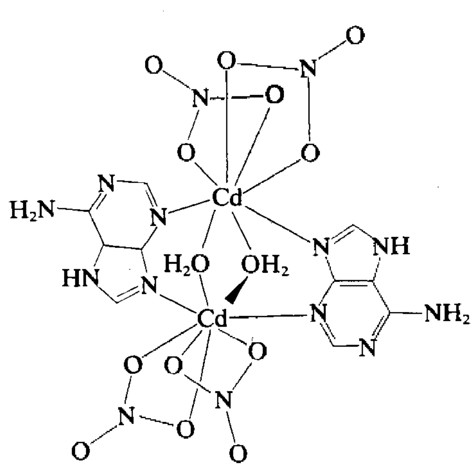
A zinc complex of the carcinostatic antibiotic streptonigrin has been described.[538]

In a rather different area of heterocyclic ligand chemistry compounds of the stoichiometry $Zn(NO_3)_2L$ and Zn_2Cl_4L have been isolated from the reaction of ZnX_2 (X = NO_3 or Cl) with the hexameric dimethylaminophosphazene $N_6P_6(NMe_2)_{12}$.[539] The complex contains $[ZnLX]^+$ cations possessing a distorted trigonal bipyramidal geometry involving coordination of four of the six ring N atoms. Coordination is found to localize the π electrons on nitrogen, weaken the ring bonds, and strengthen the exocyclic P—N bonds.

56.1.4.8.3 Purine bases

The interaction of nucleosides and nucleotides with zinc(II) ions is of obvious biological significance and much work has been done to elucidate the nature of the interaction. Complexes formed between ATP and Zn^{2+} are of particular importance, since the presence of this metal ion accelerates the hydrolysis of the polyphosphate, thus the complexes provide models for ATP transport and biological phosphate transfer and are of possible relevance to DNA and RNA polymerases. A crystal structure of $[Zn(H_2ATP)(bipy)]_2 \cdot 4H_2O$ has been reported, in which the zinc ions are in $\{ZnO_4N_2\}$ octahedra, with two bridging —OPO— units.[540] The adenine complex $[ZnL][ClO_4] \cdot EtOH \cdot H_2O$ (HL = adenine) has been prepared, by the reaction of $Zn[ClO_4]_2$ with adenine in ethanolic triethyl orthoformate, and the method is claimed to be advantageous over those involving aqueous conditions.[541,542] Zinc(II) nucleoside complexes have been investigated by ^{13}C NMR[543] and, in aqueous NaCl, by ^{35}Cl NQR spectroscopy.[544] Zinc complexes with 2-hydrazino-3-methylquinoxaline[545] and 9-methylhypoxanthine[546] have also been described.

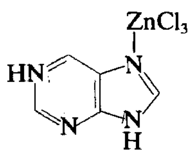
A crystal structural analysis of the dimeric adenine complex $[\{LCd(NO_3)_2(H_2O)\}_2][NO_3]_2$ (L = adenine) has been reported, and the compound shown to have the structure (79); the Cd—Cd distance is 3.616 Å, which indicates that there is little significant metal–metal interaction.[547]



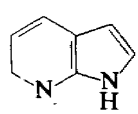
(79)

The complex $[(HL)ZnCl_3]$ (L = purine) has been shown to possess the tetrahedral structure (**80**) (Zn—Cl, 2.226–2.254 Å; Zn—N, 2.054 Å).[548] The interaction of 7-azaindole (**81**) with zinc chloride has been investigated, and the products $[ZnL_2Cl_2]$ (Zn—Cl, 2.231, 2.212 Å; Zn—N, 2.063, 2.038 Å) and $[LH]_2[ZnCl_4]$ have been structurally characterized.[548] Complexes of zinc with cytosine,[549] adenosine triphosphate[550–552] and other purines[553] have been investigated, and a crystal structure of the complex $[\{Zn(bipy)(H_2ATP)\}_2]\cdot 4H_2O$[551] has been described.

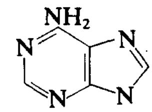
A number of zinc and cadmium complexes of adenine (**82**),[554,555] adenine *N*-oxide,[556] guanine,[557] inosine,[558] cytidine[559] and other nucleosides[560] have been studied. The structure of (9-methyladenine)$ZnCl_2$ is polymeric; each zinc ion is tetrahedrally coordinated to two chlorine atoms (Zn—Cl = 2.22 Å), and to N-1 and N-7 of neighbouring adenine moieties (Zn—N = 2.05 Å).[561] A structural study of the related cadmium complex, $CdCl_2(DMSO)L$ (L = 9-methyladenine), has shown the complex to form a one-dimensional polymer.[562]



(**80**)



(**81**)



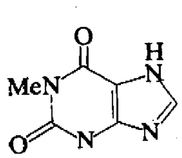
(**82**)

The compounds $Na_2ZnL\cdot 2H_2O$ and $Na_2Cd_3L_2\cdot 6H_2O$ (where L = ATP) have been prepared,[563] and coordination *via* the nitrogen base and phosphate group established. Formation constants have been determined for the ternary complex of Zn^{II}, ATP and 1,10-phenanthroline.[564] Ternary complexes usually involve metal-bridged ligands, but in some cases a ternary complex results from an aromatic ring-stacking between two suitable ligands, with a metal bound to only one of them. However, a particularly enhanced stability of the ternary complex results when stacking and bridging occur. In this context, it is important that ligand–ligand interactions were observed, (*e.g.* by electronic or ^{1}H NMR spectroscopy). This has allowed the intramolecular equilibrium constant for the equilibrium between triphosphate, Zn,L-tryptophanate, 2,2′-bipyridine or 1,10-phenanthroline to be determined by ^{1}H NMR. The percentages of the stacked isomers decrease in the order $[Zn(phen)(ATP)]^{2-}$, $[Zn(bipy)(ATP)]^{2-}$, $[Zn(bipy)(IPT)]^{4-}$, $[Zn(bipy)(UTP)]^{2-}$ (IPT = inosine 5′-triphosphate, UTP = uridine 5′-phosphate). This series is the same as the sequence of stabilities for the metal-free adducts $[(phen)(ATP)]^{4-} > [(bipy)(ATP)]^{4-} \approx [(bipy)(IPP)]^{4-}$. These series reflects the decreasing size of the aromatic-ring systems forming the stacks.[565]

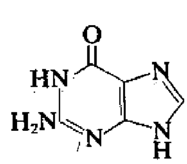
The formation of $[Cd(ATP)]^{2-}$ complexes has been studied by ^{1}H NMR, and it has been shown that there is a marked tendency to form dimeric intermolecularly ion-bridged structures.[550]

Much coordination chemistry has been carried out with simple pyrimidines and the nucleic acid bases. The crystal structure[566] of tetrakis(l-methyl-pyrimidine-2-thione)zinc(II) perchlorate bis(propanone) demonstrates unidentate coordination by the non-methylated (N-3) nitrogen atom, with r(Zn—N) at 2.058 and 2.060 Å. The structure of dichlorobis(1-methylcytosine)cadmium(II)[567] involves two Cd—Cl bonds (2.497 and 2.485 Å) and two Cd—N(3) bonds (2.281 and 2.296 Å) with approximately tetrahedral stereochemistry.

A structure determination of $CdL(H_2O)_5\cdot 3H_2O$ (L = guanosine-5′-phosphate) reveals a cadmium ion octahedrally coordinated by five water molecules and the N-7 of the purine ring system (Cd—N = 2.37 Å; Cd—O = 2.24–2.34 Å).[568] Similarly, a structure determination of $CdL_2(H_2O)_4$ (L = 8-azahypoxanthinato) reveals octahedral cadmium bonded to N-7 of the purine anions and to four water molecules.[569] Theophylline (**83**) is frequently used as a substitute for guanine (**84**) in model systems, and the complexes $[CdL_2(RNH_2)_2(H_2O)_2]$ (L = **83**) have been described.[570]



(**83**)



(**84**)

The zinc(II) complex with methyl-5-nitrosobarbituric acid has been reported.[571] as have formation constants for mixed ligand complexes of Zn^{II} and Cd^{II} involving cytosine[572] and 2-aminopyrimidine[573] respectively.

As we have seen, complexes with adenine and 9-methyladenine (to block the nitrogen atom utilized in binding ribose or deoxyribose groups in nucleic acids) have been much studied; $[Zn(9\text{-Mead})X_2]$ is tetrahedral, but $[Cd(9\text{-Mead})X_2]$ (X = Cl or Br) is octahedral with halide bridges. The zinc complex is isomorphous with the corresponding chloride, of known structure, and probably involves Zn—N interactions with N-1 and N-7 atoms in the purine ring.[574] Adenine complexes $[M(Had)_2X_2]$ (X = Cl, Br, NO_3 or ClO_4), and those with deprotonated ligand, have also been reported.[575,576]

The structure determination of bis(5,5′-diethylbarbiturato)bis(picoline)zinc shows zinc tetrahedrally bonded to the deprotonated nitrogen atoms of the barbital anions (Zn—N = 1.99, 2.01 Å) and to the nitrogen atoms of the picoline ligands (Zn—N = 2.07, 2.10 Å). The molecules are linked by N—H · · · O hydrogen bonds.[577]

Stability constants for formation of $[ML_3]^{2+}$ complexes (L = flavoquinone derivatives; M = Zn or Cd) have been measured; the ligand is N,O-chelate bonded, and the complexes of zinc are the more stable.[578]

The metal complexes of riboflavin-5′-phosphate (flavin mononucleotide, FMN) have been studied. $Zn(FMN)\cdot 2H_2O$ shows some perturbation of the IR bands of the phosphate group, suggesting that metal binding occurs at the phosphate group.[579] Reviews are available.[9–15,1468c–h,1470]

56.1.4.8.4 Bipyridyls and o-phenanthrolines

Complexes of these ligands have long been studied. Some recent extensions of the well-documented earlier work are now described.[9–15,1468c–h]

^1H NMR studies of solutions of $[Zn(bipy)]^{2+}$ and $[Zn(phen)]^{2+}$ have been reported. These complexes show little tendency, unlike the free ligands, to stack in solution.[580]

The electrolysis of alkyl or aryl halides in MeCN–benzene at a zinc electrode in the presence of bipy results in the formation of complexes of the type [RZnX(bipy)] (R = Me, CF_3, Et, $CH_2{=}CHCH_2$, Ph, C_6F_5 or Bz; X = halide). This provides a route to arylzinc complexes, since aryl halides do not normally react with metallic zinc. Oxidation of [RZnX] in the presence of RX and $[R_4N]X$ had resulted in the formation of $[R_4N]RZnX_2$ and these are the first examples of compounds containing the $RZnX_2^-$ anion.[581]

A study of the photophysical behaviour of the N-donor ligands phen and bipy in the complex cations $[Zn(phen)_2(H_2O)_2]^{2+}$ and $[Zn(bipy)_3]^{2+}$ shows that they have larger fluorescence yields and smaller phosphorescence yields than the free molecules. The fluorescence yields of both complexes were higher than those of corresponding mono-bidentate complexes; this change is attributed to ligand–ligand interaction leading to delocalization of the excited singlet state.[582] The luminescence spectrum of $[Zn(bipy)_3]^{2+}$ at 77 K has been reported,[583] and is of particular interest since it had been claimed that anomalies in the fluorescence and vibrational spectra of aqueous solutions of bipy are due to the leaching of Zn^{2+} ions from the glassware to give a highly fluorescent zinc–bipy complex.[584] The anomalies had previously been interpreted[585] as evidence for the formation of a covalent hydrate of the diimine; such species must now be regarded as hypothetical in the absence of any further evidence for their existence.

The factors that control the stability of ternary complexes involving bipy or phen have been studied. The methyl resonances of $[Me_3Si(CH_2)_nSO_3]^-$ (n = 2 or 3) are shifted upfield by $[Zn(bipy)]^{2+}$ or by $[Zn(phen)]^{2+}$, while Zn^{2+} caused no shift at all. This has been attributed[586] to a hydrophobic interaction between the trimethylsilyl group and the heterocyclic aromatic ring system. The effect of varying the π-acceptor properties of the bipyridine ligand on the ternary complex with pyrocatecholate (pyro) and zinc(II) has also been studied.[587] For the equilibrium of equation (5) [dpx = 2,2′-dipyridylamine (dpa), 2,2′-dipyridylmethane (dpm) or 2,2′-dipyridyl ketone (dpk)], the formation constants decrease in the series dpk > dpm > dpa. Thus, the enhanced stability of ternary complexes containing an O donor and a heteroaromatic N base is dependent on the π-acceptor properties of the latter ligand.

$$[M(pyro)_2]^{2-} + [M(dpx)_2]^{2+} \rightleftharpoons 2[M(dpx)(pyro)] \quad (5)$$

Zinc and cadmium complexes with 4,4′-bipyridine have been prepared.[588] The system

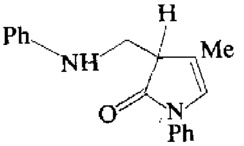
$[Zn(phen)_3]^{2+}$–AMP has been studied, and shown to possess strongly Pfeiffer-active optical activity.[589]

A combined crystallographic and ^{113}Cd NMR study of the complex $[Cd(bipy)_2(NO_3)_2]\cdot\frac{1}{2}H_2O$ in the solid state and in solution has been described; the crystal structure reveals two crystallographically and chemically distinct octahedral environments for the metal. In one case, the metal has two monodentate O-donor nitrate ions coordinated (Cd—N, 2.33–2.43 Å; Cd—O, 2.41–2.435 Å), and in the other it is coordinated to one monodentate nitrate ion and to one water molecule (Cd—N, 2.34–2.39 Å; Cd—ONO_2, 2.43 Å; Cd—OH_2, 2.246 Å). The solid state ^{113}Cd NMR investigations also indicated the presence of two metal sites.[51]

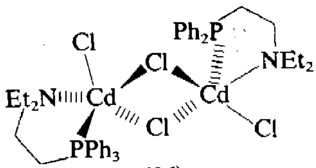
The complex $[ZnL_2(phen)]$(HL = **85**) has been shown to be a homogeneous catalyst for the oxidation of cumene.[590]

56.1.5 PHOSPHORUS LIGANDS

The phosphorus ligand coordination chemistry of zinc and cadmium is not extensive. The 'simple' complexes formed from the interaction of zinc and cadmium halides with tertiary phosphines have proved controversial, and a number of relevant studies have appeared.[9–15,1468c–h] The complexes $M_2L_2X_4$ (M = Zn or Cd; L = $P(cych)_3$; X = Cl, Br or I) are readily prepared, and form halogen-bonded dimers of C_{2h} symmetry.[591] In contrast, the previously reported compounds $[ZnX_2(PR_3)_2]$ have been shown to be $[ZnX_2(PR_3)OPR_3]$ (R = Cy; X = Cl, Br or I).[591] An intensive ^{31}P and ^{113}Cd NMR study of cadmium tri-*n*-butylphosphine and tricyclohexylphosphine complexes has been reported.[51] Cadmium triphenylphosphine complexes have also been studied in solution by NMR methods.[592] Complexes with $(HO)_2P(O)CH_2CH_2P(O)(OH)_2$,[593] MePhP(O)OH,[594] $(HOCH_2CH_2)_2NCH_2P(O)(OH)_2$,[595] $Et_2NCH_2CH_2PPh_2$[596] and HMPA[597] have been described. The complex $[CdL_2Cl_2]$ (L = HMPA) is tetrahedral (Cd—Cl, 2.399 Å; Cd—O, 2.179 Å) with monodentate O-donor ligands;[597] $[ClLCd(\mu\text{-}Cl)]_2$ (L = $Et_2NCH_2CH_2PPh_2$) is a chloro-bridged dimer (**86**)[596] while $[Zn(PhMePO_2)(dioxane)]_n$ is polymeric, with a repeat distance (Zn—Zn) of 4.614 Å.[594]

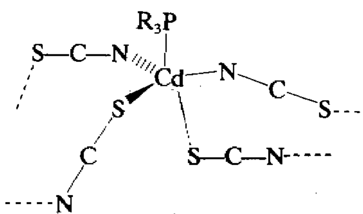


(**85**)

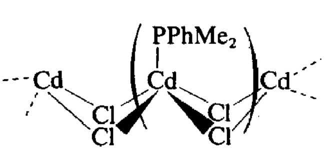


(**86**)

A number of complexes $[CdX_2(R_3P)_2]$ (X = Cl, Br or I) have been prepared by the reaction of R_3P with CdX_2, and are thought to have a pseudotetrahedral C_{2v} skeletal symmetry. Investigation by ^{31}P NMR spectroscopy has established that the complexes undergo fast phosphine exchange at room temperature, but the limiting low temperature spectra correspond to the frozen out species, and show satellites due to coupling to ^{111}Cd and ^{113}Cd nuclei ($I = \frac{1}{2}$).[598] In contrast, $[Cd(PR_3)(SCN)_2]$ is fluxional even at 183 K, and a polymeric trigonal bipyramidal structure is proposed.[599] This has been confirmed by a crystal structural analysis of $[(m\text{-}tol_3P)Cd(SCN)_2]$ (**87**).[599] The five-coordinate complex $\{CdCl_2(PhMe_2P)\}_n$ has been reported, and shown to have the structure (**88**).[600]



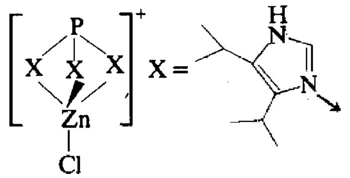
(**87**)



(**88**)

The reactions of $[Cd(DMSO)_6]^{2+}$ with R_3N, R_3P and R_3As parallel those of $[Zn(DMSO)_6]^{2+}$, and a number of complexes with these ligands have been prepared.[601]

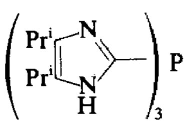
Tetrahedral species $[ZnX_2L_2]$ (X = Cl, Br or I; L = Et_3P or Et_2PhP) have been included in a general study on compounds with these ligands, involving IR, and ^1H, ^{13}C and ^{31}P NMR spectroscopic measurements.[602] A crystal structure of the complex [ZnLCl]Cl·2DMF (**89**) has been reported;[603] the ligand acts as an N_3 donor, and the metal is in a pseudotetrahedral N_3Cl environment.



(**89**)

Zinc in a trigonal prismatic configuration has been found in the fluoroborotris(2-aldoximino-6-pyridyl)phosphine zinc complex cation.[604] As in the analogous d^7 Co^{II} and d^8 Ni^{II} complexes, the clathrochelate zinc cation possesses approximate C_{3v} symmetry. The immediate environment of zinc consists of six nitrogen atoms which define a slightly tapered trigonal prism. Distortion from C_{3v} symmetry is probably caused by the encapsulated metal ion being larger than the cavity of the free unperturbed anion.

Complexes of the phosphine (**90**) have been investigated[605] as models for the active site of carbonic anhydrase enzymes (see Section 56.1.14.1).



(**90**)

56.1.6 OXYGEN LIGANDS

56.1.6.1 Hydroxide and Water

The simple chemistry of coordinated hydroxide and water is well documented. Here we consider some recent work in this area.

Studies have been reported of the complex equilibria present in electrolytically produced supersaturated solutions of Zn^{2+} in aqueous KOH. Light-scattering and NMR techniques indicate the excess zinc to be present as a solute, rather than a colloid, and the predominant species appears to be the $[Zn(OH)_4]^{2-}$ ion.[606] However, Raman and potentiometric studies indicate that initially, quasi-colloidal particles, based on $Zn(OH)_2$ and molecules of solvation, are present.[607] These particles undergo a first-order decay to yield a solution containing the species $[Zn(OH)_2(H_2O)_2]$, $[Zn(OH)_3H_2O]^-$ and $[Zn(OH)_4]^{2-}$, the actual constitution depending on the concentration. The non-colloidal zinc species are tetrahedral, rather than planar or octahedral. Stability constants for the ions $[Zn(OH)_n]^{(n-2)-}$ ($n = 1$–3) have been reported.[608]

A zincate species, (Na_2ZnO_2), has been characterized in the solid phase of the NaOH—ZnO system.[609] Among the related structures recently determined are potassium zincate, $K_2Zn_6O_7$,[610] which involves three-coordinate zinc, and the mineral bayldonite,[611] $(Cu,Zn)_3Pb(AsO_4)_2(OH)_2$, which involves partial substitution of copper by zinc. Its structure consists of two different interconnected sheets, a lead arsenate and a copper octahedral sheet. The latter sheet is formed from three crystallographically distinct $\{CuO_4(OH)_2\}$ octahedra. One of these, the Cu-2 octahedron, is subject to less distortion than the other two, and appears to be the likely site for zinc substitution. Indeed, this Cu-2 site in bayldonite is very similar to the octahedral $\{ZnO_4(OH)_2\}$ group in adamite, $Zn_2AsO_4(OH)$.[612]

An X-ray diffraction study of aqueous $Zn(NO_3)_2$ has been reported, and, as expected, a coordination number of six, almost independent of concentration, was found;[613] however, it is interesting that although the $[Zn(H_2O)_6]^{2+}$ ion persists at most concentrations of aqueous solutions of zinc salts, the total hydration number is concentration dependent, and a study of aqueous zinc sulfate has revealed that the total number of water molecules associated with the $Zn(SO_4)$ decreases linearly with $\log[ZnSO_4]$.[614a] More recent studies confirm octahedral coordination in $[Zn(OH_2)_6]^{2+}$,[614b] but concentration dependence of hydration was not observed.[614c,d] A Raman study of $[Zn(H_2O)_6]MF_6$ (M = Si or Ti) has been reported, and the symmetrical Zn—O stretching frequency has been unequivocally identified.[615] Variable-temperature Raman studies on the species $[M(H_2O)_6]^{2+}$ (M = Zn or Mg) are consistent with stronger binding of water to zinc.[616] NMR studies of M^{2+} (M = Zn, Cd or Hg) in water and methanol suggest that the covalancy of the metal–oxygen interaction increases in the series Hg < Cd < Zn.[617] Raman studies of $Zn(ClO_4)_2$ solutions in aqueous $HClO_4$ indicate a change from octahedral to tetrahedral hydrate coordination as the acid concentration is increased.[618]

X-Ray diffraction measurements carried out on aqueous solutions of $Cd(ClO_4)_2$ show the hydrated Cd^{2+} to be coordinated to six water molecules (Cd—O = 2.31 Å), while similar measurements on an aqueous solution of Na_2CdI_4, supported also by Raman measurements, confirm the tetrahedral configuration of the $[CdI_4]^{2-}$ ion (Cd—I = 2.79 Å).[619]

The Raman spectra of zinc chlorate solutions show chlorate coordination in the species $[Zn(aq)ClO_3]^+$.[620]

The enthalpy of solution of $Zn(ClO_4)_2$ has been measured,[621] while hydrolysis of this compound results in the formation of $[Zn_4(OH)_4]^{4+}$ and $[Zn_2(OH)]^{3+}$.[622] Stability constants have been determined for the species $[Zn(OH)_n]^{(n-2)-}$ (n = 1–4).[623]

Glassy solutions of ZnX_2 (X = halide) in water have also been studied by Raman spectroscopy and the results indicate the presence of the tetrahedral ions, $[ZnX_{4-n}(H_2O)_n]^{(2-n)-}$.[624,625]

A redetermination of the molecular structure of $Zn(NO_3)_2 \cdot 2H_2O$ shows the zinc to be at the centre of a distorted octahedron of four nitrate oxygens and two water molecules (Zn—O = 2.04–2.17 Å). The octahedra are linked by common nitrate groups.[626] The basic nitrate $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ has been reported.[627]

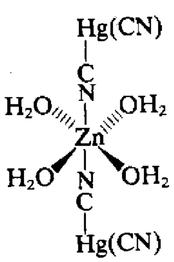
The structure of $NaZn_2(OH)(H_2O)(MoO_4)_2$ contains octahedrally coordinated zinc atoms linked to each other by double oxygen bridges. The edge-shared octahedra form chains parallel to the *b* axis which are connected to each other through tetrahedral molybdate groups (Zn—O = 2.12 Å).[628] $K_2Zn_2(MoO_4)_3$ similarly contains edge-shared ZnO_6 octahedra.[629]

A redetermination[630] of the molecular structure of $Zn_3(PO_4)_2 \cdot 4H_2O$ shows it to consist of irregular $ZnO_2(H_2O)_4$ octahedra, ZnO_4 tetrahedra and PO_4 tetrahedra which share corners and edges (octahedral Zn—O = 2.10 Å, tetrahedral Zn—O = 1.96 Å). Similarly, a molecular structure determination of $Zn_2KH(PO_4)_2 \cdot 2.5H_2O$ shows two distinct Zn atoms, one octahedrally coordinated by three water molecules and three phosphate oxygens (Zn—O = 2.11 Å) and one tetrahedrally coordinated by phosphate oxygens (Zn—O = 1.94 Å).[631]

$Zn[Pb(IO_3)_6] \cdot 6H_2O$ contains zinc octahedrally surrounded by four water molecules and two iodate oxygens (Zn—O = 2.04–2.21 Å).[632]

Crystal data for the methanesulfonates $Cd(MeSO_3)_2 \cdot 2H_2O$ and $Zn(MeSO_3)_2 \cdot 4H_2O$ have been reported.[633,634]

A neutron diffraction examination of $Hg_2Zn(CN)_4(H_2O)_4 \cdot 3H_2O$ reveals structure (**91**).[635] A neutron diffraction study of $K_2[Zn(H_2O)_6](SO_4)_2$ has also been reported.[636]



(**91**)

In $Cd_2(OH)_2(SO_4)$, the metal is in a highly distorted CdO_6 environment,[637] whereas in $Cd(BrO_3)_2 \cdot 2H_2O$ the metal is in a seven-coordinate CdO_7 environment.[638]

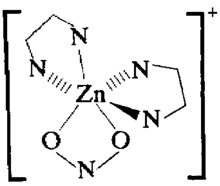
The methanesulfonic acid complex, $[Cd(MeSO_3)_2]$, has been prepared by the reaction of $CdCl_2$ with $MeSO_3H$[639] and a crystal structure of $Cd(O_3SCH_2SO_3) \cdot 3H_2O$ has shown the metal to be seven coordinate, in a distorted pentagonal bipyramidal environment.[640]

A structure determination of β-$Cd_2(OH)_2SO_4$ reveals layers of highly distorted CdO_6 octahedra linked by edge and corner sharing and joined by SO_4^{2-} ions.[641]

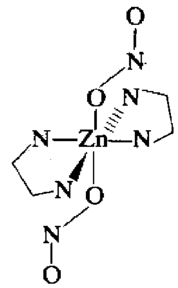
56.1.6.2 Oxyanions

Considerable structural variation is found in complexes in which the ligands are oxyanions and their derivatives.[9–15,1468c–h]

The crystal structures of the nitrito complexes $[Zn(en)_2(NO_2)][NO_2]$ and $[Zn(tmen)_2(NO_2)_2]$ have been described.[642] In $[Zn(en)_2(NO_2)][NO_2]$ (**92**) the coordinated nitrite acts as a chelating O_2 donor (Zn—O, 2.240 Å), whereas in $[Zn(tmen)_2(NO_2)_2]$ (**93**) it acts as a monodentate O donor (Zn—O, 2.221 Å).



(**92**)



(**93**)

The complex dinitratobis(antipyrine)zinc has been shown crystallographically to contain zinc octahedrally coordinated by the oxygens of two antipyrine molecules (Zn—O = 1.93 Å) and four oxygens belonging to one symmetric and one unsymmetric bidentate nitrate groups (Zn—O = 2.03–2.52 Å).[643]

The coordination of Cd^{2+} by nitrite ion in aqueous solution has been studied by Raman spectroscopy,[644] and cumulative formation constants have been derived (β_1–β_4 = 61.6, 993, 2390, 1899). Bidentate O chelation is postulated, except in the third and fourth complexes where unidentate nitrite is also present. This is in contrast to Zn, which forms $Zn(NO_2)_2$ as its highest complex in aqueous solution.

The crystal structure determination of $Cd(NO_3)_2·2H_2O$ shows Cd to be surrounded by seven O atoms (Cd—O = 2.30–2.59 Å) belonging to four nitrate and two H_2O molecules.[645] Five form a distorted pyramid with Cd approximately in the centre of the base, and the other two are on either side of the base. The polyhedra are linked by common nitrate groups to form layers held together by hydrogen bonding. The trihydrate has previously been shown to contain eight-coordinate Cd.[646]

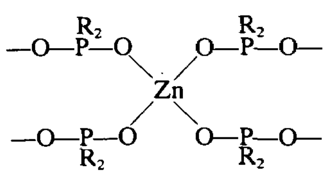
Complexes of stoichiometry $ZnLX_2$ (X = NO_2 or NO_3) have been isolated from the reaction of zinc nitrite or nitrate with 1,2-dimorpholinoethane and 1,2-dipiperidinoethane.[647] The complexes contain zinc in a distorted octahedron of two ligand nitrogens and two bidentate O-bonded nitrite or nitrate anions. The nitrite complexes show greater stability than the nitrates.

The $[Zn(NO_3)_4]^{2-}$ ion similarly contains eight-coordinate zinc with approximate dodecahedral symmetry (Zn—O = 2.06, 2.58 Å).[648]

Crystallographic data on $Cd(PO_3)_2$ have also been reported,[649] while the structure of $(NH_4)Cd(PO_3OH)(OH)$ contains polymeric layers of CdO_6 octahedra (Cd—O = 2.31 Å).[650]

$CdBa(PO_3)_4$ contains infinite (PO_3) chains; cadmium is octahedrally coordinated (Cd—O = 2.24–2.32 Å).[651,652] $Cd_3(P_3O_9)_2·14H_2O$ contains discrete cyclic trimetaphosphate anions; cadmium is again octahedrally coordinated by four phosphate oxygens and two water molecules (Cd—O = 2.23–2.33 Å).[653] In the related $Ba_2Zn(P_3O_9)_2·10H_2O$, zinc is octahedrally coordinated by four water molecules and two phosphate oxygens (Zn—O = 2.03–2.08 Å); barium is eight coordinate.[654] The compound $Zn_5(P_3O_{10})_2·17H_2O$ contains discrete linear tripolyphosphate anions. Zinc coordination is of three types: (a) octahedral, consisting of four phosphate oxygens and two water molecules, (b) tetrahedral, consisting of four phosphate oxygens and (c) octahedral, consisting of two phosphate oxygens and four water molecules (Zn—O = 1.93–2.08 Å).[655,656] In contrast, the zinc in $Zn_2HP_3O_{10}·6H_2O$ possesses either octahedral coordination consisting of four phosphate oxygens and two water molecules or tetrahedral coordination by four phosphate oxygens (Zn—O = 1.92–2.18 Å).[657]

Polymeric zinc phosphinates of the stoichiometry $Zn(OPR_2O)_2$, which may be soluble or insoluble depending on the R group, have been prepared. The insoluble derivatives have structure (**94**), while either structure (**95**) or (**96**) may be true for the soluble polymers.[658]



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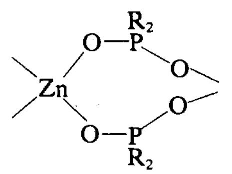

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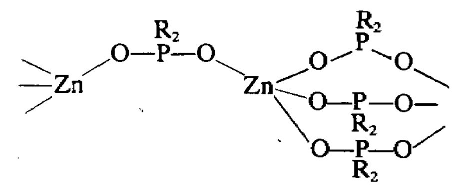
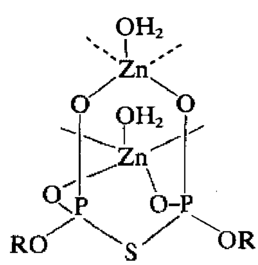


(96)

Zinc halides react with the anions $[P(CHCOCH_2R)O(OEt)_2]^-$ ($R = \overline{NCH_2CH_2OCH_2CH_2}$ or $\overline{N(CH_2)_4CH_2}$) to yield the complexes ZnLX (X = Cl, Br or I) which are dimeric and bridged by the oxygen atom of the carboxy group. The NO_3X donor set thus confers a trigonal bipyramidal coordination on each zinc atom.[659] $ZnCl_2$ reacts with 2-aminoethylphosphonic acid (H_2L) to yield $Zn(HL)_2$ in which zinc is tetrahedrally coordinated.[660] The complex $Zn(OHCH_2PO_3)$ is polymeric, containing distorted ZnO_6 octahedra connected by bridging phosphate ions.[661]

The stable phase in the $Zn_3(PO_4)_2$–$Zn_3(VO_4)_2$ system has the composition $Zn_3P_{1.5}V_{0.5}O_8$. The structure consists of sheets parallel to *(100)* formed of chains containing rings of corner-shared $(Zn\text{-}1)O_4$ and $(V,P)O_4$ tetrahedra; the $(Zn\text{-}2)O_4$ groups form chains parallel to the *b* axis through corner sharing (Zn—O = 1.95, 1.96 Å).[662]

Zinc chloride has been shown to react with triethylthiophosphate to produce the alkyl pyrothiophosphate (L) complex $ZnL(OH_2)$ which probably has the polymeric structure (**97**). On the other hand, reaction with tri-*n*-butylthiophosphate results in formation of the pyrothiophosphate (L) complex $Zn_2L(H_2O)_6$, presumed to have structure (**98**). IR evidence suggests the presence of P—S—P rather than P—O—P linkages.[663]



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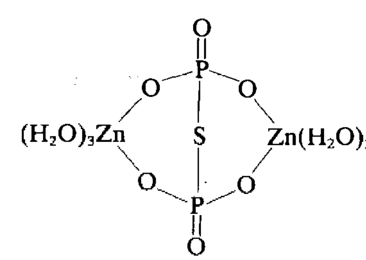


(98)

The complex $Cd_2(PO_4)F$ contains octahedrally coordinated Cd bonded to four O and two F atoms (Cd—O = 2.26 Å; Cd—F = 2.27, 2.46 Å); the fluorine atoms are *cis*.[664]

The X-ray diffraction pattern of $Zn_{1.5}V_{1.5}O_4$ (prepared by reduction of $Zn_2V_2O_3$) indicates a spinel structure with zinc occupying tetrahedral sites.[665] The complexes $M_3V_{10}O_{28}\cdot nH_2O$ (M = Zn or Cd) have been prepared by reaction of the metal acetate with V_2O_5.[666,667]

X-Ray diffraction studies of aqueous $CdSO_4$ solutions have clearly demonstrated the formation of *O*-sulfato complexes.[668–670] These are of the general form $[Cd(H_2O)_{6-n}(OSO_3)_n]^{(2-2n)+}$, and appear to be the major species present in concentrated solutions. These results are fully in accord with tensimetric studies of the cadmium and magnesium sulfate aqueous systems, which indicate an increased interionic attraction at elevated temperatures.[671] In contrast, X-ray diffraction studies on cadmium perchlorate solutions show no evidence for the coordination of the perchlorate ion to the metal, the only cationic species present being $[Cd(H_2O)_6]^{2+}$(Cd—O, 2.292 Å, *cf.* Cd—O, 2.292 Å in solid $[Cd(H_2O)_6][ClO_4]_2$).[670]

The crystal structure of $Cd(SO_4)$ has been redetermined.[672] The cadmium atom in $Cd(SO_4)$ is in a very distorted CdO_4 tetrahedron, with the O—Cd—O angles varying from 88.1 to 142.7. In contrast, the structure of $Cd_2(NH_4)_2(SO_4)_3$ contains two inequivalent octahedral sites for Cd^{2+}, and is essentially isostructural with $K_2Mg(SO_4)_3$. It is found that Mn^{2+} may be preferentially incorporated (82%) into the site with the shorter average cation—oxygen distance.[673]

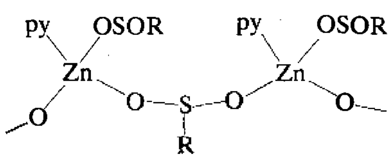
The preparation and thermal analysis of several basic Cd sulfates have been reported.[674] The thiosulfates $A_2[Cd(S_2O_3)_2]$ (A = Rb or NH_4) have been prepared; spectroscopic evidence indicates bidentate coordination through O and S.[675]

The species $MZnSO_4Cl$ (M = Rb or Tl) is polymeric, the anion consisting of infinite layers of the composition $[ZnSO_4Cl]_n^{n-}$; zinc is surrounded by an O_3Cl donor set, forming a distorted tetrahedron (Zn—O = 1.94–1.97 Å; Zn—Cl 2.19 Å).[676]

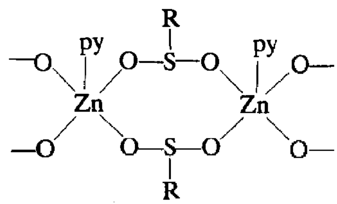
Anhydrous $Zn(SO_3F)_2$ reacts with py to give a complex $[Zn(py)_4(SO_3F)_2]$ having a tetragonally distorted octahedral structure containing unidentate fluorosulfate;[677] by comparison with a series of complexes, $Cu(py)_4X_2$, the fluorosulfate anion may be said to have greater coordinating strength than ClO_4^-, BF_4^- and NO_3^-, but less than $CF_3CO_2^-$ or (*p*-tolyl sulfate)$^-$. Extensive dissociation to give the $[Zn(py)_4L_2]^{2+}$ cation (L = solvent) occurs in solution.

The organosulfinato complexes $(RSO_2)Zn(OH_2)_2$ react with bipy according to equation (6) (R = Ph or *p*-MeC_6H_4). In the case of the bis(bipyridyl) derivatives, both O-bonded and S-bonded linkage isomers are formed.[678] The hydrated sulfinate also reacts with py to give the derivatives $[(RSO_2)_2Zn(py)]$ (R = Ph or *p*-MeC_6H_4).[679] The polymeric structures (**99**) and (**100**) are postulated for the two 1:1 complexes.

$$(RSO_2)_2Zn(OH_2)_2 \xrightarrow[-2H_2O]{+L} (RSO_2)_2ZnL \underset{-L}{\overset{+L}{\rightleftharpoons}} (RSO_2)_2ZnL_2 \underset{-L}{\overset{+L}{\rightleftharpoons}} [ZnL_3][RSO_2]_2 \quad L = \text{bipy} \quad (6)$$



(**99**) R = Ph



(**100**) R = *p*-MeC_6H_4

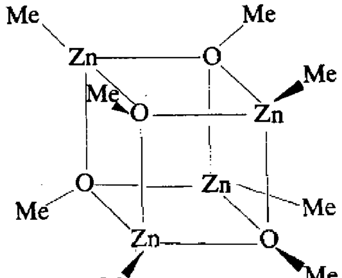
The properties of the complexes $Zn[CrO_4]$ and $Zn[CrO_4]\cdot 3.5Zn(OH)_2\cdot H_2O$ have been investigated; their reduction by CO (formed *in situ* from the decomposition of zinc oxalate) leads to the formation of species containing catalytically active Cr^V and Cr^{III} centres.[680,681]

PPh_4^+ salts of the $[Zn(MoOS_3)_2]^{2-}$ anion have been obtained by reaction of PPh_4Cl with Cs_2MoOS_3 and $ZnSO_4$. The zinc is postulated to be coordinated by four sulfur atoms in a square planar environment.[682]

The zinc atom in $Na_2ZnSi_3O_8$ possess highly distorted tetrahedral coordination (Zn—O = 1.94 Å).[683]

56.1.6.3 Alcohols, Ethers, Ketones, *S*-, *N*- and *P*-Oxides

A number of interesting modes of coordination are found with simple organic molecules as ligands, *e.g.* a crystal structure determination of the tetrameric methylzinc(II) derivative $\{MeZn(OMe)\}_4$[684] shows the structure to be as in (**101**). Closely related to this is the structure of the polymerization catalyst $Zn(OMe)_2(EtZnOMe)_6$ (**102**).[685] The centrosymmetric complex consists of two enantiomorphic distorted cubes which share a corner; the zinc atoms occupy the corners of a tetrahedron and oxygen atoms the corners of an interpenetrating, but smaller, tetrahedron (Zn—O = 2.06 Å).



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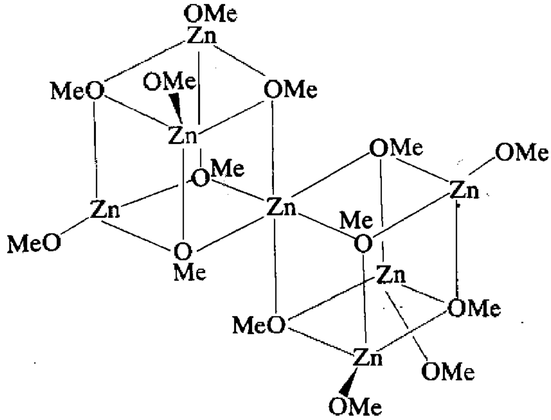
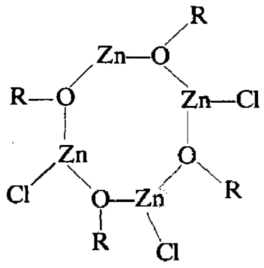


(102)

The molecular structure of chloro (2-diethylaminoethoxo)zinc (**103**) shows it to contain an eight-membered non-planar Zn_4O_4 ring, with Zn—O = 1.96 and 1.92 Å, and Zn—Cl = 2.21 Å.[686] The bromo derivative is similar.



(**103**) $R = (CH_2)_2NEt_2$

Depending on the molar ratio of reactants, the reaction of NaOMe with $ZnCl_2$ in MeOH produces the following complex ions: $Zn(OMe)_4^{2-}$, $Zn(OMe)_3MeOH^-$, $ZnCl(OMe)_2^-$ and $Zn_2Cl_4(OMe)_2^{2-}$. The last is postulated to have methoxide bridges; analogous reactions occur with sodium isopropoxide.[687]

Mass spectroscopic investigations of the species MeZnOR (R = Me, Et or Bu^t) show that all form oligomers in the gaseous state having either six or seven monomer units.[688]

The structure of ZnL_3SO_4 (L = glycol) reveals discrete $[ZnL_3]^{2+}$ cations in which zinc is octahedrally surrounded by six glycol oxygens (Zn—O = 2.09 Å).[689]

The 1:2 complex of tetraethyleneglycol dimethyl ether with cadmium chloride has been shown to be a tetramer.[690]

The complex $[(CF_3)_2Cd(glyme)]$ has been prepared by metathesis of $(CF_3)_2Hg$ with $[CdMe_2]$ in glyme, and has been shown to be a useful intermediate for the preparation of other trifluoromethyl compounds (*e.g.* R_4Ge, R_2Sn and R_3P).[691]

Formation constants for the species $[M(OAc)_n]^{(2-n)+}$ (M = Zn or Cd; n = 1–3) have been determined; in addition, zinc forms a tetraacetato complex.[692,693] Stability constants for complexation of Zn^{2+} and Cd^{2+} by other carboxylic[694,695] and hydroxycarboxylic acids[696-699] have been reported.

A particularly well-studied ligand is L-3,4-dihydroxyphenylalanine (L-DOPA); this may coordinate like alaninate or a pyrocatechol;[700] Zn^{II} appears to favour binding to L-DOPA as to pyrocatechols.[701] Formation constants have been measured for the ternary complexes Zn^{II}: dopamine: alanine/pyrocatechol[702] and Zn^{II}: L-DOPA:L (L = penicillamine, L-alanine, glycine, 2,2′-bipyridine, citric acid, tartaric acid or sulfosalicylic acid).[703]

The complex of vitamin B_6 (pyridoxine) with $CdCl_2$, $[CdLCl_2]$, involves infinite chains of chloro-bridged Cd^{II}. The ligand is bidentate through two oxygen donors and bridges *via* the third, so that each Cd atom is bound in a $CdCl_3O_3$ environment.[704]

X-Ray structural determinations of the complexes MX_2L (M = Cd, X = I; M = Hg, X = Cl; L = pyridine *N*-oxide)[705] show the Cd complex to be composed of infinite chains of [CdI] units alternately bridged through two I atoms and two O atoms. The Cd coordination is trigonal bipyramidal (Cd—O = 2.28, 2.38 Å; Cd—I = 2.72–2.96 Å). Zinc forms the complex ZnL_2I_2, which is monomeric and tetrahedral (Zn—I = 2.57 Å; Zn—O = 1.99 Å).

Salts of $[ZnL_6]^{2+}$ (L = pyridine *N*-oxide) have recently been shown to undergo facile solid state reactions with alkali metal halides, an observation to be taken into account when recording the IR spectra of these and related compounds.[706] A crystal structure of the complex $[ZnL_6][ClO_4]_2$ (L = 4-methylpyridine *N*-oxide) has been reported.[707] The metal is in a near-octahedral O_6 environment, with an average Zn—O distance of 2.114 Å.

The complex with isonicotinate *N*-oxide $[Zn(N\text{-isonicO})_2(OH_2)_2]\cdot 4H_2O$ is polymeric, the ligand bridging adjacent zinc ions and coordinating *via* the *N*-oxide group and a carboxylate oxygen, while the species $[(N\text{-isonicO})_2Zn(OH_2)Zn(N\text{-isonicO})_2]_n$ involves bridging water molecules in addition, the zinc being five-coordinate.[708] The analogous cadmium complex has a polynuclear structure.[709]

8-Hydroxyquinoline *N*-oxide (LH) is usually deprotonated in its complexes, but a series of compounds, including $[Zn(LH)_4(OH_2)_2][ClO_4]_2\cdot 2H_2O$, have been described. The environment of the zinc is octahedral with the ligand coordinating only through the phenolic hydroxyl group.[710]

Reaction of $Zn(ClO_4)_2$ with 2-picolinic acid *N*-oxide (HL) yields ZnL_2 in which the ligand is

O,O-chelate bonded *via* *N*-oxide and carboxylate oxygens.[711] In contrast, nicotinic acid *N*-oxide (HL) forms $ZnL_2{\cdot}5H_2O$, which is best described as a hexacoordinated, linear, polynuclear complex of the type $[ZnL_2(OH_2)_2]_n{\cdot}3nH_2O$, probably involving ZnL_2Zn bridges. The ligand is bound through the *N*-oxide and carboxyl oxygens.[712]

2-Pyridylcarbinol *N*-oxide (HL) reacts with $Zn(ClO_4)_2$ to yield $Zn(HL)_4(ClO_4)_2$; IR studies indicate a six-coordinate structure involving two bidentate and two unidentate ligands.[713]

Zinc–oxygen and zinc–nitrogen stretching frequencies have been assigned in the IR spectra of $[ZnL_nCl_2]$ (L = 2-pyrrolidone; $n = 2$ or 3) and $[Zn(R\text{-sal})_2L_2$ (R-sal = substituted salicylaldehyde; L = H_2O or pyridine).[714]

CdX_2 (X = ClO_4 or BF_4) reacts with 1-methyl-2-pyridone (L) to yield CdL_6X_2, while zinc yields only tetracoordinate ZnL_4X_2 complexes; the ligand is bound *via* oxygen in both cases.[715]

The reactions of zinc and cadmium with thiomorpholin-3-one (L) and thiazolidine-2-thione (L^1) result in the complexes $ML_4(NO_3)_2$, ML_2SO_4, $ML^1_4(NO_3)_2$, $ZnL^1_2SO_4$ and $CdL^1_4SO_4$; except in the last case, IR evidence indicates coordinated sulfate, while nitrate is ionic in all cases. L is coordinated *via* oxygen and L^1 *via* nitrogen.[716]

Crystal structural analyses of the complexes $[ZnBr_2(Ph_3PO)_2]$ Zn—O, 1.965, 1.970 Å; Zn—Br, 2.354, 2.357 Å) and $[ZnCl_2(Ph_3PO)_2]$ (Zn—O, 1.967 Å; Zn—Cl, 2.187 Å) have been reported; both complexes show near-tetrahedral geometries about the metal.[717] Another group had reported the crystal structure of the complex $[ZnCl_2(OPPh_3)_2]$ again finding the metal to be in a near tetrahedral O_2Cl_2 environment.[718]

The structure of $[Zn\{H_3\overset{+}{N}CH_2(Me)P(O)\bar{O}\}Cl_2]$ has also been reported, and the compound forms polymeric —P—O—Zn—O—P— chains, with the metal in a pseudotetrahedral O_2Cl_2 environment (Zn—O, 1.95 Å, Zn—Cl, 2.24 Å).[719]

The vibrational spectra of zinc halide complexes (X = Cl, Br or I) with Me_3PO confirm the presence of the C_{2v} ZnX_2O_2 skeletal structure.[720] Complexes $[Zn(R_3PO)_4][BF_4]_2$ have been prepared[721] for R = Me, $HOCH_2$, Et, Pr, CMe_2H or Bu, while complexes with trimorpholinophosphine oxide (morpo) and chlorodimorpholinophosphine oxide (cdmpo) include $[Zn(morpo)_3][ClO_4]_2{\cdot}H_2O$, $[Zn(morpo)_2][PF_6]_2{\cdot}2H_2O$ and $[Zn(cdmpo)_2X_2]$ (X = NO_3 or ClO_4) where the ligand probably coordinates by the oxide group and a morpholine N atom.[722]

The complex CdL_3Cl_2 [L = $PO(NH_2)_3$] is hexacoordinate, with the ligand N,O-chelate bound.[723] In the complex $ZnL_2(NO_3)_2$ (L = *N*,*N*-dimethyldiphenylphosphinamide), the ligand is bound *via* the phosphoryl oxygen; the nitrates are symmetrical and bidentate.[724]

A determination of the structure of $[ZnL_2][ClO_4]_2$ [L = *o*-phenylenebis(dimethylarsine oxide)] reveals $(ZnL_2)_2^{4+}$ cations; coordination about each zinc is approximately trigonal bipyramidal.[725]

Complexes of tri-4-tolylphosphate (ttp) include $[Zn(ttp)_2Cl_2]$ (monomeric) and $[(ttp)_3M(ttp)_2M(ttp)_3][ClO_4]_2$ (M = Cd or Zn).[726] Studies on IR data (and electronic spectra for transition metal species) indicate that ttp is a ligand almost as strong as the triorganophosphine oxides, and is significantly stronger than trimethylphosphate. The increased donor strength of ttp probably reflects inductive and steric effects. The complexing of Cd^{II} by diethylenetriamine-*N*,*N*,*N*′,*N*″,*N*″-pentamethylphosphonic acid[727] and Zn^{II} and Cd^{II} by methyl diphenyl phosphate[728] have also been reported.

$Zn(ClO_4)_2$ forms the complex $[ZnL_3][ClO_4]_2$ (L = diethyl acetylphosphonate) in which the ligand is bidentate through phosphoryl and acetyl oxygen atoms,[729] and the complex $[ZnL_4(ClO_4)][ClO_4]$ (L = methyl methylphenylphosphinate).[730]

Complexes of nicotinamide (L) and its *N*,*N*-diethyl derivative of the stoichiometry MX_2L_2 (M = Zn, X = Cl, NCS or NCSe; M = Cd, X = NCS or NCSe), MX_2L (M = Zn, X = NCS; M = Cd, X = I) and MX_2L_4 (M = Zn, X = NCS; M = Cd, X = Cl, Br or I) have been prepared. In the first two types, L is bidentate and N,O-bonded; thiocyanate is N-bonded in all cases.[731–733]

The crystal structure of $[Zn(DMSO)_6][ClO_4]_2$ has been reported; the metal is in an octahedral ZnO_6 environment, with an average Zn—O distance of 2.110 Å. Complementary solution studies reveal the persistence of the $[Zn(DMSO)_6]^{2+}$ cation in DMSO solution, with Zn—O distances of 2.127 Å.[734]

The electrochemical behaviour of zinc(II) in DMSO has been investigated ($E^{\ominus}$ Zn/Zn^{2+}, −1.806 V, *cf* −1.562 V in water).[735]

The pseudooctahedral complexes $Cd(O_2SR)_2L$ (L = bipy, *o*-phen) and $Cd(O_2SR)_2L_2$ (L = bipy, en) may also be obtained; the former contain bidentate sulfinate and the latter monodentate, O-bonded in all cases. Complexes of the stoichiometry $Cd(O_2SR)_2L_3$ (L = bipy or en) are best formulated as $[CdL_3][O_2SR]_2$.[736,737]

The structure of $Cd(NCS)_2(urea)_2$ contains infinite chains of cadmium atoms bridged by thiocyanate; urea completes a distorted octahedral configuration.[738] Crystallographic data on $[CdI_2CX(NH_2)_2]$ (X = O or S) have also been reported.[739] Metal acetates react with urea (L) to yield $M(OAc)_2L_2$ (M = Zn, Cd or Hg); the complexes are six-coordinate, containing bidentate acetate.[740] $Zn(ClO_4)_2$ and $Zn(NO_3)_2$ react with urea and *N*-phenylurea respectively to yield ZnL_6X_2 complexes; the complex $[Zn(urea)_4(H_2O)_2][ClO_4]_2$ was also isolated.[741,742]

The reactions of $CdCl_2$ and $SbCl_5$ and organic nitro compounds in non-aqueous solvents lead to formation of $[Cd(RNO_2)_n][SbCl_6]_2$ (R = Me, $n = 4$; R = Ph, $n = 3$; R = α-naphthyl, $n = 2$) containing unidentate ($n = 4$) or bidentate ($n = 2$ or 3) nitro groups.[743]

56.1.6.4 Diketones and Related Ligands

β-Diketones have long been studied as ligands for zinc and, to a lesser extent, cadmium, and here again some unusual structural features are found and intriguing differences between cadmium and zinc are to be seen.[9–15,1468c–h]

An electron diffraction study of $[Zn(acac)_2]$ has recently been reported. The Zn—O distances of 1.942 ± 0.006 Å correlate reasonably well with those determined from an X-ray structural study of the crystalline solid (Zn—O, 1.999 Å) and are shorter than those observed in the solid state structure of the monohydrate (Zn—O, 2.02 Å).[744]

An intensive study of the vibrational (IR) spectrum of $Zn(acac)_2$ and its ^{18}O, ^{68}Zn and ^{64}Zn labelled derivatives has also been made, and the bands assigned on the basis of the isotopic shifts assuming C_{4v} localized symmetry.[745]

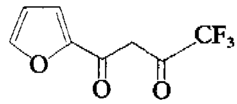
Ethalpies of formation of metal pentane-2,4-dionates (including Zn^{II}) have been measured directly.[746]

Powder EPR spectra for Mn^{II}-doped compounds $[M(acac)_2(bipy)]$ (M = Zn or Cd), $[Zn(acac)_2(phen)]$ and $[Cd(acac)_2(phen)H_2O)]$[747] indicate that distortions from octahedral symmetry were greater for the bipyridine adduct than for the phenanthroline adduct, and greater for Cd than for Zn. IR measurements confirm that all the compounds are tris-bidentate, except for $[Cd(acac)_2(phen)(H_2O)]$ which probably has coordinated water and a free carbonyl group.

The fluorescence and phosphorescence yields of various β-diketones are found to be enhanced by coordination to Zn^{2+}, Al^{3+} and Be^{2+} in an increasing order. This is ascribed to a ligand–ligand interaction in the excited and ground state, in the case of Zn, most probably arising through both Coulomb exchange and dipole–dipole interaction.[748]

The molecular structure of $KCd(acac)_3 \cdot H_2O$ contains discrete $[Cd(acac)_3]^-$ anions in which the coordination is a good approximation to trigonal prismatic stereochemistry (Cd—O = 2.24–2.33 Å).[749] In contrast, the structure of (*catena*-di-μ-acetylacetonato)Cd consists of linear chains of Cd atoms bridged by one oxygen atom of each ligand (Cd—O = 2.28, 2.35 Å). The remaining two sites in the octahedral coordination are occupied by non-bridging oxygens (Cd—O = 2.22–2.25 Å).[750]

A determination of the crystal structure of $[NH_4][CdL_3]$ (HL = **104**) has shown the ligand to be bidentate, with the geometry of the anion again distorted towards a trigonal prism.[751]



(104)

Adducts of the type $Zn(hfa)_2L$ (hfa = hexafluoroacac; L = phen or bipy) have been prepared; IR studies indicate an octahedral configuration.[752] The interaction of $Zn(hfa)_2$ with pyridine in the gas phase under chemical-ion mass spectroscopic conditions shows the presence of ions of the type $[Zn(hfa)(py)_2]^+$, $[Zn(hfa)(py)_3]^+$ and $[Zn(hfa)_2(py)_2]$; the first two stoichiometries are unknown in the solid state.[753]

The reaction of $[Zn(acac)_2]$ with aza heterocycles has been shown to result in the formation of five-coordinate species $[Zn(acac)_2L]$ (L = quinoline, isoquinoline or morpholine).[754]

Further examples of the rare β-diketone (as opposed to β-diketonate ligand have been found, and the complexes $[Zn(acacH)_3][InCl_4]$ and $[Zn(MeCOCH_2CO_2Et)_3][InCl_4]$ have been described.[755]

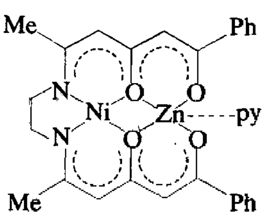
Zinc chelates of the stoichiometry ZnL_2 have been prepared from various substituted monothio-β-diketones RC(SH)═$CHCOCF_3$(HL).[756] The mass spectra of ZnL_2 complexes of the monothio-β-diketones RC(SH)═CHCOPh (R = Me or Ph) have been reported.[757] The most interesting feature is the loss of H_2S, which does not occur with the free ligands, or with metal complexes of fluorinated β-ketones.[758]

The thermodynamics of complex formation between the chelates ML_2 (M = Zn or Hg; HL = RC(SH)═$CHCOCF_3$, R = Me or Ph) and py and bipy have been investigated.[759] Zinc forms 1:1 complexes with both ligands, the bipy being bidentate. Mercury gives a 1:1 complex with py, but only an extremely unstable adduct is formed with bipy.

The molecular structure determination of bis(*O*-ethylthioacetoacetato)zinc[760] shows the metal to be at the centre of a deformed tetrahedron, with Zn—S = 2.25 Å and Zn—O = 2.01 Å. The molecular structure of the related complex bis(*O*-ethylthioacetothioacetato)zinc, in which the bonding is totally *via* sulfur, has also been determined.[761] Coordination is approximately tetrahedral, with Zn—S = 2.30 Å. In both complexes, the bond distances in the chelate ring indicate aromatic character, with a lone pair on the ethoxy oxygen being involved in delocalization.

The complexes ZnL_2 (HL = nicotinylacetone or 4,4,4-trifluoronicotinylacetone) have been prepared. Substitution of a methyl group in the acac ring by a pyridyl ring strengthens the C═O and M—O bonds and weakens the C═C bond of the chelate ring, while further trifluoromethyl substitution increases the C═O and C═C bond strengths and decreases the M—O bond strength.[762,763]

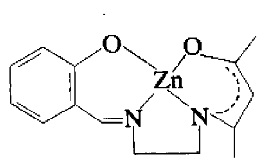
The heteronuclear chelate complex (**105**) has been prepared and its molecular structure determined. The N_2O_2 site is occupied by planar Ni, while the O_2O_2 site is occupied by Zn. Coordinated py completes the five coordination for the zinc. The Zn—O distances average 1.95 Å to the terminal oxygens and 2.09 Å to the bridging oxygens; the zinc is displaced from the least-squares basal plane by 0.32 Å towards the py. Cu, UO_2 or VO may be used in place of zinc.[764]



(**105**)

A fuller account of the structural determination of this heteronuclear chelate complex has appeared.[765] In addition, a paper on the general preparation of the binuclear complexes NiML where M = Zn, Cu, Co^{II}, Fe^{III}, Mn^{II} and VO^{II} has appeared; in all cases, Ni occupies the N_2O_2 site and M occupies the O_2O_2 site.[766]

The cocondensation of Zn^{2+} with ethylenediamine, salicylaldehyde and acetylacetone has been shown to lead to the complex (**106**).[767]



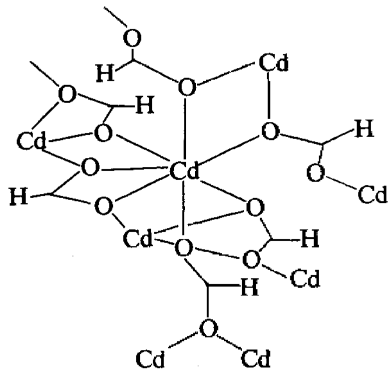
(**106**)

56.1.6.5 Carboxylates and Related Species

With few other ligand classes do zinc and cadmium form such a structurally varied series of complexes.[767b] Multinuclear complexes and intriguing geometries abound.

The crystal structure of cadmium(II) formate dihydrate has been determined[768] and consists of a three-dimensional polymer with each cadmium octahedrally coordinated. In a two-dimensional plane, the formates bridge in an *anti,anti* configuration, while in the perpendicular plane, the bridging is in a *syn,anti* manner. Water molecules occupy the remaining coordination positions, and the polymer is further strengthened by hydrogen bonds between water and formate. The compound is isomorphous with magnesium, zinc, manganese and copper formate dihydrates.

There has in fact been much interest in the cadmium–formate system, and a crystal structure of anhydrous $Cd(HCO_2)_2$ has been reported. The formate ion acts as a bridging ligand, and the metal ion here is seven-coordinate (**107**).[769] The complexes $NaCd(HCO_2)_3$,[770] $KCd(HCO_2)_3$,[771] $K_3Cd(HCO_2)_5$,[771] $[NH_4]Cd(HCO_2)_3$,[772,773] $CdBa(HCO_2)_4{\cdot}2H_2O$[772] and $LiCd(HCO_2)_3$[773] have been characterized as components of the appropriate $Cd(HCO_2)_2$–$M(HCO_2)_x$ systems. The formation of mixed acetate–formate complexes has also been investigated.[774]



(107)

A Raman and IR spectroscopic study of $Zn(OAc)_2$ and $Zn(OAc)_2{\cdot}2H_2O$ has been described; in the latter compound the metal is in an octahedral environment, with *trans* diaxial water ligands and bidentate chelating acetate groups, and in the former compound the metal is in a pseudotetrahedral environment.[775]

A further determination of the crystal structure of $Zn(O_2CMe)_2$ has shown the metal to be in $\{ZnO_4\}$ tetrahedra, which are connected by bridging ethanoate groups.[776]

Mass spectral studies[777] on the well-known basic zinc carboxylates $Zn_4O(RCO_2)_6$ (R = Me, Et or Pr^n) show the presence of tetrametallic molecular ions $[Zn_4O(RCO_2)_6]^+$ which decompose *via* initial loss of a ligand radical followed by elimination of the even-electron species $Zn(RCO_2)_2$ and $(RCO_2)_2O$. The trimetallic cation $[Zn_3O(RCO_2)_3]^+$ and the doubly charged cation $[Zn_4O(RCO_2)_4]^{2+}$ are observed in considerable abundance.

It has been proposed that the higher zinc carboxylates exhibit an enantiomeric polymorphism on the basis of the X-ray diffraction characteristics of the materials at elevated temperatures.[778]

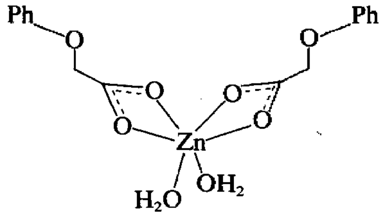
Electrical conductivity studies on molten zinc carboxylates of even-numbered chain length from C_6 to C_{18} are consistent with a small concentration of relatively mobile Zn^{2+} ions.[779]

An IR study of the complexes $Cd(OAc)_2{\cdot}2H_2O$ and $Cd(OAc)_2{\cdot}2D_2O$ has been made, and a full analysis of the spectrum reported.[780] A spectroscopic study of the solvation of $Cd(OAc)_2$ in alcoholic solvents has also been made.[781] The IR spectra of Zn^{II} monoiodoethanoate show a chelating carboxylate group rather than a bridging group, as found in a range of divalent metal iodoethanoates.[782]

The structure determination of cadmium cyanoacetate shows the cadmium to be coordinated to one nitrogen and five oxygen atoms in a distorted octahedral geometry.[783] Each of the two independent cyanoacetate ligands coordinates to three symmetry-related cadmium atoms to give a three-dimensional polymeric lattice. One ligand coordinates through two oxygen atoms, one of them bridging, while the other coordinates through two oxygen atoms and the nitrogen atom. In common with many other acetates, the metal atom is not chelated, with the ligands acting as bridging molecules.

Crystal structures of the isostructural complexes $[Zn(OH_2)_2L_2]$ (LH = phenoxyacetic acid or 4-chlorophenoxyacetic acid) have been reported, and the metal has been shown to be in a distorted octahedral O_6 environment (**108**).[784]

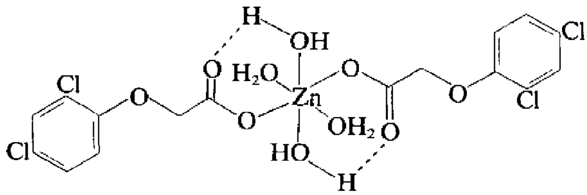
Crystal structures of the related complexes tetraaquabis(2,4-dichlorophenoxyacetato)zinc(II) and diaquabis(2,4-dichlorophenoxyacetato)zinc(II) have been reported, in which two distinct metal environments occur. In the $[Zn(H_2O)_4L_2]$ (HL = 2,4-dichlorophenoxyacetic acid) molecule (**109**) the metal is in an octahedral O_6 environment, with a *trans* diaxial arrangement of



(108)

monodentate carboxylate groups (Zn—OH_2, 2.098 Å; Zn—O, 2.071, 2.121 Å) and hydrogen bonding between coordinated water molecules and uncoordinated oxygens of the carboxylates in the same molecule.

In [Zn$(OH_2)_2L_2$] the metal is in a tetrahedral environment (**110**) (Zn—OH_2, 2.002 Å; Zn—O, 1.915, 1.956 Å).[785]



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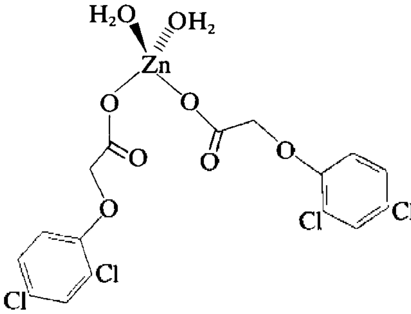
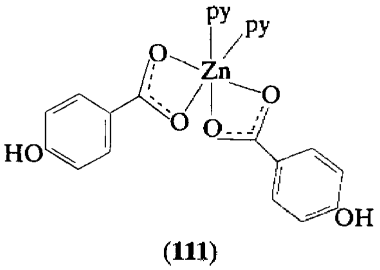


(110)

The crystal structure of $CdL_2(py)_3$·py (LH = 4-hydroxybenzoic acid) has been reported, and the metal shown to be in an octahedral environment;[786,787] one of the carboxylate anions is bidentate, but the other is monodentate and hydrogen-bonded to one of the pyridine molecules. The remaining three pyridine molecules are coordinated to the metal.

A crystal structural analysis of $Zn(py)_2L_2$·2py (LH = 4-hydroxybenzoic acid) has shown the metal to be in a tetrahedral O_2N_2 environment (**111**).[788]



(111)

The crystal structures of several other carboxylato complexes have been reported. The structure of zinc *o*-ethoxybenzoate monohydrate is polymeric with distorted tetrahedral coordination of each zinc by three carboxylato oxygens and one water molecule.[789] Bis(2-chlorobenzoato)zinc is also a polymer; each zinc is bonded in a tetrahedral fashion to four oxygens from four different ligands to form a chain-like structure (Zn—O = 1.91–1.94 Å).[790] The complex μ_3-hydroxo-tri-μ-(2-chlorobenzoato)dizinc·$2H_2O$ again consists of polymeric chains, and contains two independent zinc atoms; one has an unusual trigonal bipyramidal environment, while the other is octahedrally coordinated.[791] The structure of [(*S*-malato)Zn$(H_2O)_2$]·H_2O likewise consists of polymeric chains. An α-carboxy oxygen and the hydroxyl oxygen complete a five-membered chelate ring with the zinc, while coordination of the β-carboxy group creates in addition a six-membered chelate ring; a distorted octahedral zinc configuration is completed by two water molecules and a bridging β-carboxylate oxygen from a neighbouring malate group (Zn—O = 2.05–2.15 Å).[792] Zinc lactate trihydrate contains zinc in a distorted octahedral configuration of four oxygens from two lactate ligands and two water molecules (Zn—O = 2.11 Å).[793a]

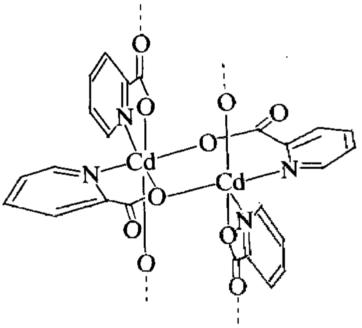
An example of a high coordination number for cadmium is found in aquabis(4-aminobenzoato)cadmium(II),[793b] which involves seven-coordinate cadmium, with two chelating carboxylate groups, a water molecule and axial positions filled by amino groups from ligands bound to the neighbouring metal centres.[794]

The crystal structure of bis(2-methylimidazole)-μ-oxalatozinc(II)·$\frac{1}{2}H_2O$ involves tetradentate oxalate bridges between the zinc atoms, with the two imidazoles *cis* coordinated.[795] Zinc(II) cyanoethanoate involves a polymeric, octahedral structure with bridging or chelating carboxylate groups and an N-bonded cyano group.[796] On reaction with 2,2′-bipyridine or pyridine, the octahedral complexes $[Zn(O_2CCH_2CN)_2(bipy)]$ or $(Zn(O_2CCH_2CN)_2(py)_2]$ are formed, respectively. These contain bidentate carboxylate groups, but no metal–cyano interactions.

In the complex $ZnL_2·2H_2O$ (HL = 2,2,5,5-tetramethyl-3-imidazoline-3-oxo-1-oxyl-4-carboxylic acid), L^- acts as a bidentate ligand *via* carboxylate and oxo oxygen donors. When the 3-oxo group is not present, the ligand is bidentate through the carboxylate and imino groups.[797]

The crystal structures of several further polymeric carboxylato–cadmium complexes have been determined. Anhydrous bis(2-pyridinecarboxylato)cadmium (**112**) has a centrosymmetric dimeric structure with a distorted octahedral coordination about each cadmium, which is chelated by two orthogonal picolinato groups.[798] A sixth coordination position is occupied by the non-chelating oxygen atoms of the non-bridging picolinato group of a neighbouring dimer, thus conferring a polymeric $[Cd(C_5H_4NCO_2)_2]_{2n}$ structure on the complex.

The structure of (pyrazine-2,3-dicarboxylato)zinc dihydrate is also polymeric, but each zinc is coordinated in a distorted octahedral manner by three carboxylato oxygens, one nitrogen and two water molecules.[799]



(112)

The enthalpy and entropy of complex formation between Zn^{II} and picolinate and dipicolinate anions in aqueous solution have been determined by calorimetry and from formation constant data. The greater stability of the dipicolinate complex compared to the picolinate complex reflects an entropy effect, and $\Delta H^{\ominus}$ is actually less favourable. These anions are well known to have a low basicity to H^+ compared to their complexing ability to metals. In the present case, this probably reflects the coplanarity of the carboxylate anions and the pyridine ring, so that the oxygen atoms are in a favourable position to coordinate.[800]

A spectroscopic (IR, electronic and X-ray) study of anhydrous zinc oxalate has been reported; it is suggested that a polymeric structure containing tetradentate oxalate and octahedral zinc ions is adopted.[801] Complexes with a number of other polycarboxylic acids, including malonic,[802–804] succinic,[802–805] maleic,[802] malic[802] and citric acids[802] have also been described. Crystal structures of $[Zn(H_2O)L]$ (H_2L = malonic acid, $CH_2(CO_2H)_2$)[804] and $[Cd(H_2O)_2L]$ (H_2L = succinic acid, $(HO_2CCH_2)_2$)[805] have been reported. In the former compound the metal is in an octahedral D_{4h} environment, and a sheet-type polymer is formed, whereas in the latter compound the metal is in an approximately pentagonal bipyramidal environment, with succinate ions bridging adjacent metal centres. The complexes $[ML_2]$ (M = Zn or Cd; HL = pentamethyl cyclopentadienepentacarboxylate) are air-stable and readily prepared from HL.[806] The ligand is thought to be coordinated to the metals *via* the carbonyl oxygen atoms.

The oxalato complexes $[M(C_2O_4)L_2]$ (M = Zn or Cd; L = substituted pyridines or 4-toluidine) are also polymeric with bridging oxalato groups.[807]

It has been reported that the anhydrous oxalate $K_2[Zn(C_2O_4)_2]$ may easily be prepared by thermal dehydration of $K_2[Zn(C_2O_4)_2]·5H_2O$.[808] Further heating yields ZnO and $K_2C_2O_4$.IR studies indicate that both the hydrated and anhydrous complexes again have polymeric octahedral structures analogous to $K_2[Mn(C_2O_4)_2]$; the water is loosely held and dehydration readily occurs. On the other hand, the molecular structure of $ZnC_2O_4 \cdot H_2O \cdot MeOH$ is monomeric[809] and contains zinc at the centre of a deformed octahedron of six oxygen atoms, with oxalate acting as a quadridentate ligand.

The complexation of Ag^+, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} by unsaturated derivatives of malonic ($RCH(CO_2H)_2$), acetic (RCH_2CO_2H) and iminodiacetic ($RN(CH_2CO_2H)_2$) acids ($R = CH_2{=}CH(CH_2)_n$, $n = 1$–3) has been investigated.[810] Only in the case of Ag^+ was chelate formation involving the alkenic bond observed; similar results were obtained for unsaturated derivatives of various α-amino acids.[811] Preparative and crystallographic data for the malonato complexes $[ZnCH_2(CO_2)_2] \cdot 2H_2O$ and $[ZnHO_2CCH_2CO_2]_2 \cdot 2H_2O$ have also been reported.[812]

A molecular structure determination of Cd malonate monohydrate shows each malonate ligand chelated to three symmetry-related Cd atoms, with two of the oxygen atoms also in bridging positions.[813] The lattice formed is polymeric and further strengthened by hydrogen bonding *via* coordinated water. The Cd is seven-coordinate with nearly pentagonal bipyramidal geometry (Cd—O = 2.27–2.50 Å).

The structure of cadmium(II) maleate dihydrate contains two cadmium atoms and two maleate ligands, both pairs of which are chemically distinct.[814] One cadmium is six-coordinate through four water molecules and two bridging maleate ligands, while the other is eight-coordinate, in a distorted dodecahedral geometry, through four chelated carboxy groups from the two maleate ligands. The maleate ligands link the cadmium atoms into a three-dimensional polymer which is further strengthened by hydrogen bonding.

The thermal decomposition of $Zn(HL)_2$ (H_2L = maleic acid) takes place at 423–503 K to yield maleic acid and ZnL, providing an example of an ion-exchange reaction occurring in the solid state.[815]

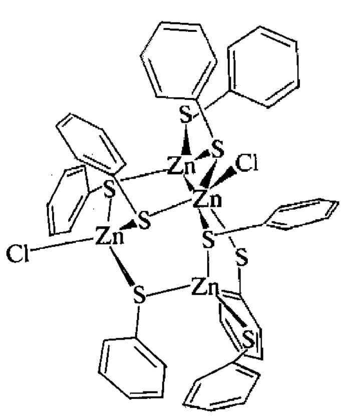
The molecular structure determination of zinc lactate trihydrate also shows zinc to be the centre of an octahedron consisting of four lactate oxygens and two water molecules (Zn—O = 2.11 Å).[816a]

56.1.7 SULFUR LIGANDS

56.1.7.1 Thiols and Thioethers

Very beautiful complexes are obtainable using sulfur-containing ligands. The reactivity of the metal ion–sulfur bond has been reviewed.[816b]

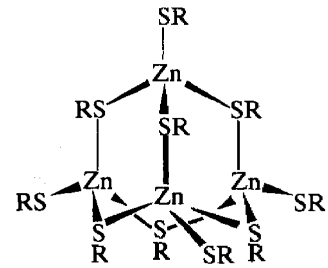
It is now well established that thiophenol reacts with zinc salts to give zinc–sulfur clusters, and a further example, $[Me_4N]_2[(\mu\text{-}SPh)_6(ZnSPh)_2(ZnCl)_2]$, has been characterized crystallographically. The admantane-like structure observed in $[(\mu\text{-}SPh)_6(ZnSPh)_4]^{2-}$ is seen to persist in the anion **(113)**.[817]



(113)

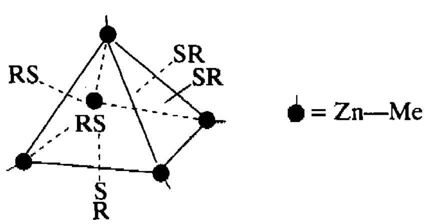
There is an interesting preparative feature in the chemistry of these compounds: the electrochemical oxidation of anodic zinc or cadmium in acetonitrile solutions containing RSH or R_2S_2 provides an excellent route to the polymeric $M(SR)_2$ compounds;[818] this is in contrast to the behaviour when Et_3N is also present in the solution, when the isolated product is the cubane species, $[Et_3NH]_2[Zn_4(SR)_{10}]$.[819] A crystal structure of $[Et_3NH]_2[Zn_4(SPh)_{10}]$, prepared by this method, has been described; it is confirmed that the anion in this compound adopts the adamantane-like structure (**114**), with little evidence for metal–metal bonding, Zn—Zn, 3.98 Å; Zn–S(bridging), 2.371 Å; Zn–S(terminal) 2.291 Å.[819] The same anion geometry is observed in the crystal structure of the complex $[Me_4N]_2[Fe_4(SPh)_{10}]\cdot C_3H_7CN$.[820]

The $[Zn_4(SPh)_{10}]^{2-}$ cluster anion has also been prepared by the reaction of NaSPh with $ZnCl_2$, and ^1H NMR studies have revealed a rapid SPh(bridging)–SPh(terminal) interconversion, which is thought to occur *via* opening of the cluster by successive breaking of two bridging Zn—S bonds.[820] A rapid metal exchange reaction in the mixed-metal clusters $[M_{4-n}Zn_n(SPh)_{10}]^{2-}$ (M = Cd, Co or Fe) and $[Co_{4-n}Cd_n(SPh)_{10}]^{2-}$ was also detected.



(**114**)

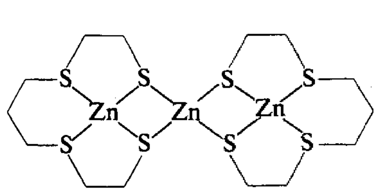
A crystal structural analysis of the pentanuclear cluster $[(MeZn)_5(Bu^tS)_5]$ (**115**) has also been reported; once again there is little evidence for direct Zn—Zn or S—S interactions.[821] The structure is clearly based upon a square pyramid of zinc atoms. Further work in this area is surveyed in references 1468c–h.



(**115**)

The novel species obtained from the reaction of zinc(II) salts with thiophenol have been further investigated and complexes of formula $[Zn_4(SPh)_8(ROH)]$ have been isolated from the interaction of $Zn[CO_3]$ and PhSH in ROH.[822] A crystallographic study of these species has shown that they should be formulated *catena*-(μ-SPh){(μ-SPh)$_6$Zn$_4$(ROH)(SPh)} and that they form one-dimensional polymeric crystals with one intercluster bridging PhS unit. A crystal structure of the complex $[Me_4N][ClZn_4(\mu\text{-}SPh)_{12}(ZnSPh)_4]$, formed from $Zn(NO_3)_2$, PhSH, Pr_3N and $[Me_4N]Cl$, has also been reported.[823]

The reaction of zinc ethanoate with 1,4,8,11-tetrathiaundecane gives the trimetallic complex (**116**) which transmetallates on treatment with $[Ni(H_2O)_6]^{2+}$.

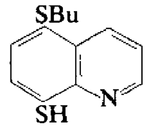


(**116**)

Some interesting polynuclear complexes of zinc(II) have been characterized in another system: 2-pyridinethiolate (pySH) reacts with $ZnCl_2$ in the presence of sodium hydroxide to give $[Zn(pyS)_2]$.[824] A large excess of base leads, however, to the formation of oxohexakis-μ-[2(1*H*)-pyridinethionato]tetrazinc(II) $[L_6Zn_4O]$, involving N,S coordination of the ligand.

Similar complexes were prepared for L = 2-thiazolidinethiolate, 5-methyl-2-thiazolidinethiolate and 1-methyl-4-imidazolethiolate. The following chlorozinc complexes have also been prepared: $[(pyS)_3Zn_2Cl]$, $[(pyS)_4Zn_3Cl_2]$ and [(pyS)ZnCl]. The last compound is probably polymeric.[825]

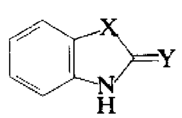
The crystal and molecular structure of ZnL_2 (HL = 5-butylthio-8-thioloquinoline **(117)** has been reported; the metal is more conventionally coordinated here in a distorted tetrahedral N_2S_2 environment.[826]



(117)

The crystal structure of *catena*-bis[μ-(*N*-methylpiperidinium-4-thiolato)]cadmium(II) perchlorate dihydrate[827] involves infinite chains of cadmium atoms, each of them tetrahedrally coordinated to four sulfur atoms of four different *N*-methylpiperidinium-4-thiolato groups. Each sulfur atom bridges two consecutive cadmium atoms, r(Cd—S) = 2.548 Å.

Cadmium(II) complexes with 1-amino-2-mercapto-5-trifluoromethyl-1,3,4-triazole,[828] 1-benzyl-2-ethyl-5-mercapto-1,3,4-triazole,[829] 3-amino-2-mercaptoquinazol-4-one,[830] 2-thiouracil[831] and 4,6-dimethyl-2(1*H*)-pyrimidinethione[832,833] have been reported. With the latter ligand (HL), the complexes $\{Cd(HL)_2X_2\}$ (X = Cl, Br, I or TFA), $[Cd(HL)_3][ClO_4]_2 \cdot 2H_2O$ and CdL_2 have been prepared; the $[Cd(HL)_2X_2]$ compounds are polymeric, with a halogen-bridged structure, and differ from the corresponding zinc(II) and mercury(II) complexes, which are tetrahedral monomers.[832] The complexes $[CdL_2Cl_2]$ with the thiolo and selenide ligands (L) **(118a–e)** have been reported.[834]



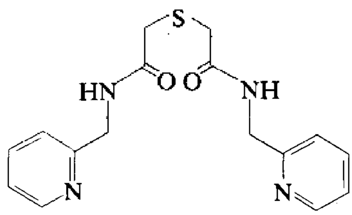
		Y	X
(118)	**a**;	S	NH
	b;	S	S
	c;	Se	NH
	d;	Se	O
	e;	Se	S

Cadmium(II) complexes with a number of thiolodicarboxylic acids[835] and thioethers have been described; the ligands employed include: $HO_2CCH_2SSCH_2CO_2H$ and $HO_2CCH_2CH_2SSCH_2CH_2CO_2H$,[836] Me_2S and MeSSMe,[837] **(119)**[838] and $HO_2CCH_2CH(CO_2H)SCH(CO_2H)CH_2CO_2H$.[839] The complex $[CdLCl_2]$ (L = **119**) has the interesting feature of planar geometry at the metal.[838]

A crystal structural analysis of the complex $[NEt_4][CdL_3]$ (HL = benzothiazole-2(3*H*)-thione) **(120)** has been reported; the anion possesses strict C_3 symmetry with the ligand acting as a bidentate N,S donor (Cd—S, 2.667 Å; Cd—N, 2.47 Å).[840]

The reaction of $ZnCl_2$ with 4-thiolo-1-methylpiperidinium chloride (H_2LCl) results in the formation of $[ZnLCl_2]_2 \cdot H_2O$ which has been shown by a crystal structural analysis to have the zwitterionic structure **(121)**.[841]

We should note in passing that in many cases of ligands having thiolo with other donor atoms, *e.g.* N, it is not always clear how the ligand is coordinated, but for $[ZnL_4][NO_3]_2 \cdot H_2O$ (L = 1-methyl-2-thioloimidazole),[829] $[ZnL_2]$ (HL = **122**),[830] $[Zn(HL)_2X_2]$ and $[ZnL_2] \cdot LH$ (HL = 2-thiolo-4,6-dimethylpyrimidine; X = Cl, Br or I)[832] it has been demonstrated that the metal is present in $\{ZnS_4\}$, $\{ZnN_2S_2\}$ and $\{ZnN_2X_2\}$ polyhedra respectively.



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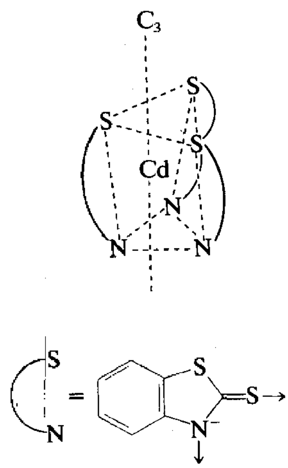

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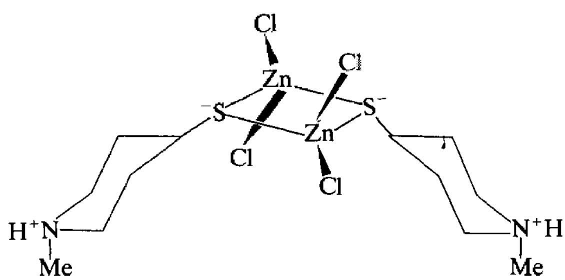

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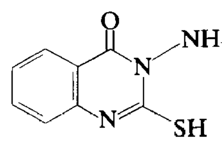


(122)

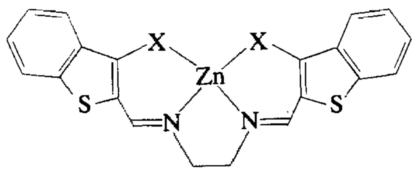
The following complexes with 1,4,6-trimethylpyrimidine-2-thione (L) and 1-methylpyrimidine-2-thione (L′) have also been characterized:[842,843] $[ZnL_3]X_2$ (X = I, ClO_4 or BF_4); $[ML_2X_2]$ (M = Zn or Cd; X = Cl or Br); $[ZnL'_2X_2]$ (X = Cl, Br or I); $[CdL'_2X_2]$ (X = Br or I) and $[CdL'Cl_2]$. The 1:3 complexes involve bidentate ligands (with four-membered chelate rings), while 1:2 complexes result from the presence of anions of greater coordinating power. The 1-methyl derivative, while a weaker ligand, shows greater variety in its coordination pattern. The IR spectra of the 1:2 complexes show metal–halogen stretching frequencies in between those usually observed for tetrahedral and octahedral halogen-bridged compounds. This is interpreted in terms of M—N, M—X and long M—S bonds. However, the crystal structure of tetrakis (1-methylpyrimidine-2-thione)zinc(II) perchlorate shows that the zinc is tetrahedrally coordinated by nitrogen atoms of four ligands. So in this case the sulfur atoms are not coordinated to zinc, the *r*(Zn—S) distances being 3.206 and 3.255 Å.[844] The complexes $[ML_2Cl_2]$ (M = Zn or Cd; L = 2-thiouracil) are probably pseudotetrahedral, with ν(Zn—Cl) at (319 or 337) and 287 cm^{-1} and ν(Zn—S) at 215 cm^{-1}.[831]

Studies on ligands containing the thioether group received fresh impetus from the finding that one of the ligands to copper in the electron-transfer protein, plastocyanin, is a thioether group. Naturally occurring species are L-methionine and *S*-methyl-L-cysteine, while biotin contains a reduced thiophene group. Formation constants for metal:thioether interactions have been measured by observing the decrease in the intensity of the visible spectrum of a Cu—thioether complex resulting from the addition of a competing metal ion. In this way, constants have been determined[845] for Zn^{II} and Cd^{II} with 2,2′-thiodiethanol ($HOCH_2CH_2SCH_2CH_2OH$), tetrahydrothiophene and diethyl sulfide. Data have also been reported for biotin[846] with enthalpies and entropies of complex formation for the thiophene-2-carboxylate ion.[847] Interestingly, comparison of data for the last named ligand with those for ethylthioacetate and phenylthioacetate suggest that aromatic sulfur donors have a greater tendency to form bonds with these metals than do aliphatic sulfur donors. Recent surveys of work in this field are available.[1468c–h]

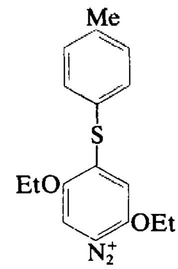
Other measurements on Zn^{II} and Cd^{II} complexes include formation constants for aliphatic thioethers,[848] and calorimetry with dithiodiacetate, 3,3'-thiodipropionate[849] and phenylthioacetate.[850]

The Schiff base complex (**123**) forms a 1:1 complex with *p*-chloranil, which has been intensively investigated.[851] There is evidence for both a $\pi-\pi^*$ interaction of the aromatic rings with the complex, and a local donor–acceptor interaction of the metal with the chloro substituent.

A zinc complex of the diazonium cation (**124**) has been reported, and is claimed to be useful as a high-speed light-sensitive compound.[852]



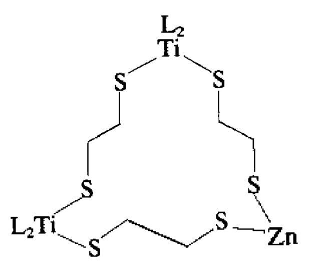
(**123**) X = O, S or Se



(**124**)

Dithiolato complexes of zinc and cadmium, $[NEt_4]_2MX_2$ where X is the dianion of cyclopentadienedithiocarboxylic acid, have been reported.[853,854]

The reaction of $(\pi\text{-Cp})_2TiCl_2$ with $ZnCl_2$ and ethane-1,2-dithiol has been shown to yield the novel complex (**125**).[855]



L = π-Cp
(**125**)

The complexes ZnX_2L_2 [X = Cl, Br or I;L = [3,5-diphenyl-Δ^4-(1,3,4-thiadiazoline)-2-ylidene]-*p*-methoxythioacetophenone or -*p*-methoxyacetophenone] have been isolated.[856] On the basis of IR evidence the metal is believed to be trigonal bipyramidally coordinated with the ligand acting in a bidentate manner. The complexes are thus best formulated as $[ZnL_2X]X$.

56.1.7.2 Thioacids, Thioamides and Related Species

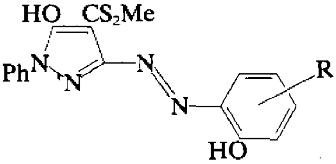
We have seen that physical measurements are indispensable in examining zinc and cadmium coordination and this is no less true in the study of sulfur coordination. Whereas IR, NMR and X-ray investigations dominate this scene other, less direct, techniques have been used.

For example, dipole moment measurements on 2:1 zinc chelates of fluorinated monothiodiketones $RC(SH){=}CHCOCF_3$ are consistent with a tetrahedral configuration in solution.[857] Detailed mass spectral studies on these chelates have also been reported,[858,859] as have mass spectral studies on a variety of zinc, cadmium and mercury thiooxinates.[860] The crystal structure determination of $Cd(thiooxinate)_2$ reveals cadmium in a distorted N_2S_2 tetrahedral configuration.[861] $Tris(thiocarbonohydrazide)Cd(ClO_4)_2$ contains cadmium octahedrally coordinated by the N,S-chelating ligand (Cd—N = 2.47–2.49 Å; Cd—S = 2.59–2.62 Å); a 2:1 derivative can also be isolated in which cadmium is tetrahedrally coordinated, although four perchlorate interactions yield a polyhedral coordination intermediate between a dodecahedron and a square antiprism.[862,863]

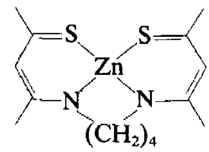
In a cadmium thiodiacetate hydrate, the ligand is terdentate, coordinated *via* sulfur as well as two oxygens (Cd—O = 2.28 Å; Cd—S = 2.66 Å); a distorted octahedral coordination is completed by bonds to a water molecule and to two adjacent ligands.[864] A structure determination of bis(thiobenzoato)Zn$(H_2O)_2$ reveals a tetrahedral zinc environment consisting of two water molecules and two monothiobenzoato groups bonding as unidentate ligands through sulfur (Zn—S = 2.28 Å).[865] Complexes of the stoichiometry bis(monothiobenzoato)M$(py)_2$ (M = Zn or Cd) have also been prepared; the monothiobenzoate is proposed to be bidentate.[866] ^{1}H NMR studies on the complexes ML_2 (M = Zn or Hg; HL = 2-amino-1-cyclopentene-1-dithiocarboxylic acid) support the exclusive use of sulfur atoms by the ligand in metal bonding,[867] while NMR studies of the complexes $[(C_2H_5)_4N]_2ZnL_2$ (H_2L = cyclopentadienedithiocarboxylic acid) show a reduction in the aromaticity of the five-membered ring on coordination.[868]

The pyrazolone derivatives (**126**) give intensely coloured complexes with zinc(II) ions and have been advocated as reagents for the colorimetric determination of the metal.[869]

The molecular structure of tetramethylenebis(thioacetylacetoniminato)zinc (**127**) has been determined.[870] The tetramethylene chain is folded to give pseudotetrahedral symmetry about the zinc, with Zn—S = 2.28 Å and Zn—N = 2.00 Å.



(**126**)



(**127**)

The molecular structure of triaquazinc thiodiglycolate ($^{-2}O_2CCH_2SCH_2CO_2^{2-}$) shows that the zinc has a distorted octahedral environment, being weakly bonded to a sulfur atom (2.60 Å) and five oxygens, one from each of two carboxy groups (2.03, 2.10 Å) and three mutually *cis* water molecules (2.02–2.10 Å). The two five-membered rings are significantly non-planar, and extensive hydrogen bonding exists.[871]

A complete IR and normal coordinate analysis (including metal isotope data) have been carried out on the thiocarbonato complexes $A_2M(CS_3)_2M(CS_3)_2$ (M = Ni or Zn; A = PPh_4^+, NMe_4^+, or $AsPh_4^+$).[872]

The complex bis(ethylxanthato)(py) Zn contains zinc in a trigonal plane composed of the pyridine and a pair of sulfur atoms from the xanthate ligands (Zn—N = 2.03 Å; Zn—S = 2.29 Å).[873] In contrast, the xanthate ligands in bis(ethylxanthato)(1,10-phen)Cd are bidentate, thus conferring a pseudooctahedral configuration on the metal (Cd—N = 2.38 Å; Cd—S = 2.64, 2.72 Å).[874] Zinc chelates of the stoichiometry ZnL_2 have been isolated (HL = several Schiff bases derived from *S*-methyldithiocarbazate).[875]

The complexes $Zn(NH_3)_3S_2O_3\cdot H_2O$ and $Cd(NH_3)_3S_2O_3$ have been prepared; thiosulfate is unidentate and sulfur-bound.[876] In addition, the mixed thiosulfates $3Rb_2S_2O_3\cdot CdS_2O_3\cdot 3H_2O$ and $Rb_2Cd(S_2O_3)_2$ have been isolated; thiosulfate in the former is unidentate and sulfur-bound, whereas it acts as a chelate in the latter.[877]

IR studies of metal xanthates[878] and dithizonates,[879] including complexes of Zn, Cd and Hg, have been reported.

The complexes MX_2L_2 (M = Zn, X = Cl, Br or I; M = Cd, X = Cl) and HgX_2L (X = Cl, Br, SCN, NO_3 or $\frac{1}{2}SO_4$) have been isolated, where L is the sterically hindered ligand 2-imino-4-oxo-1,3-thiazolidine.[880] All complexes are formulated as monomeric tetrahedral; with Zn, ligand coordination is *via* the ring N atom, but in the Cd complexes coordination *via* sulfur is observed. The ligand is bound *via* both N and S in the Hg complexes. The SCN is unidentate and S-bonded; nitrate is unidentate, whereas sulfate is bidentate.

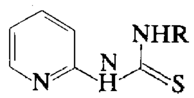
The trithiocarbonato complex anions $[M(CS_3)_2]^{2-}$ (M = Zn or Cd) have been isolated as their tetraphenyl-phosphonium and -arsonium salts.[881] The trithiocarbonate is bidentate and forms four-membered chelate rings.

Stepwise stability constants for complexation between Zn^{2+} and Cd^{2+} and the acids $X(CH_2CH_2CO_2H)_2$ (X = O, S, Se or Te), $Se(CH_2CO_2H)_2$, $X(CH(Me)CO_2H)_2$ (X = S or Se) and $HO_2CCH_2SCH_2CH_2CO_2H$ have been measured.[882] The structures of benzeneselenic acid complexes of zinc, cadmium and mercury have been investigated by IR spectroscopy; the bonding of the areneseleninato ligand depends on the water content of the compound. The hydrated complexes are always of the O,O-type; the anhydrous complexes are mainly O,O bound in the case of zinc, while the cadmium and mercury derivatives contain unidentate ligands bound *via* oxygen and selenium respectively.[883]

Many studies have been made on thiourea, thiocarbazides and thiocarbamates. For example, recent work on complexes of thiourea and its derivatives has included the measurement of formation constants for interaction with Zn^{II} [884] and Cd^{II}.[884,885] Enthalpies of formation for cadmium complexes with thiosemicarbazide (L) and its 4-methyl derivative[886] have been determined, and entropy changes calculated for successive complexation (using literature values for formation constants). The variations in these functions have been interpreted in a model postulating coordination number changes from six in $[Cd(H_2O)_6]^{2+}$ to four in $[CdL(H_2O)_2]^{2+}$ and $[CdL_2]^{2+}$ and back to six in $[CdL_3]^{2+}$. In all cases, the ligand is bidentate. Complexes with thiosemicarbazides and related ligands include the $Zn(O_2CMe)_2$–thiosemicarbazide complex,[887] octahedral $[ZnL_2X_2]$ (L = ethyl methyl ketone thiosemicarbazone; X = Cl, Br, I or NO_3) with bridging X and bidentate, bonded ligand, and tetrahedral $[ZnL_2][ClO_4]_2$,[888] and $ZnLCl_2{\cdot}H_2O$ (L = ethylacetoacetate semicarbazone).[889]

The thiourea ligands in $[Cd(O_2CMe)_2(tu)_2]$ and $[Cd(tu)_n][ClO_4]$ (n = 4 or 6) are bonded through their sulfur atom; the former complex has a tetrahedral S_2O_4 arrangement, with a more distant interaction with two other oxygen atoms giving the metal atom a bicapped tetrahedral geometry,[890] whilst in the latter two complexes the perchlorate counterion is hydrogen-bonded to the amino groups of the ligand.[891]

Complexes of the chelating thioureas (**128**; R = Me, Ph, $PhCH_2$, *o*- and *p*-tolyl) have also been reported,[892] for example those of stoichiometry ML_2X_2 (M = Zn, X = ClO_4; M = Cd or Hg, X = Cl). No perchlorate coordination was observed in the zinc complexes, and IR evidence indicated ligand coordination *via* the sulfur and heterocyclic nitrogen. The Cd and Hg complexes are non-electrolytes; coordination to the Hg is postulated to resemble that in the Zn complex, while it is believed that Cd is coordinated *via* the sulfur and the NH group to the heterocyclic ring.

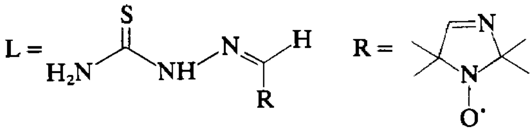


(**128**) R = Me, Ph, $PhCH_2$, *o*- and *p*-tolyl

The molecular structure of bis(ethylenethiourea)zinc thiosulfate has been determined.[893] Zinc is tetrahedrally surrounded by three sulfur atoms (two from ethylenethiourea, one from thiosulfate; Zn—S = 2.32 Å) and one oxygen from the thiosulfate (Zn—O = 2.02 Å). The thiosulfate groups behave as bridging ligands.

Both 1:1 and 2:1 complexes of *N,N*-diethyl- and *N,N*-dimethyl-thiourea with zinc, cadmium and mercury halides have been prepared. The 2:1 complexes are either monomeric and tetrahedral or polymeric and halogen-bridged with octahedral metal coordination; the 1:1 complexes also possess a polymeric, halogen-bridged structure, but with tetrahedral metal coordination.[894,895]

The complexes $ML_2(S_2O_3)$ (M = Zn, Cd or Hg; L = ethylenethiourea) contain bidentate, chelating $S_2O_3^{2-}$.[896a] Paramagnetic imidazoline oxyl complexes $[ML_2]$ (M = Zn or Cd; HL = **129**) show an unusual electron exchange phenomenon between the two ligands.[896b]



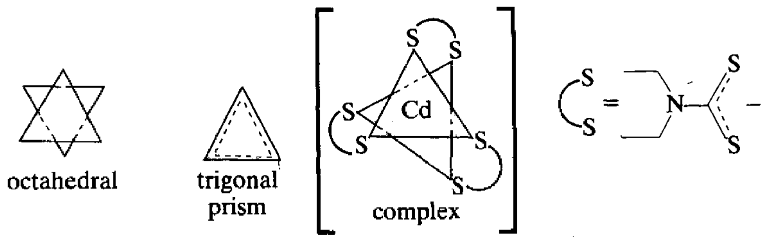
(**129**)

Dithiomalonamide (L) and its dimethyl and diphenyl derivatives form complexes of the stoichiometry $ZnLX_2$ and $ZnL_2(ClO_4)_2$ (X = Cl, Br or I). Both contain tetrahedrally coordinated zinc; the dimethyl ligand is N,S-chelate-bonded while the others are S,S-bonded.[897] The complexes $[ML_3][ClO_4]_2$ have also been prepared and do not contain coordinated perchlorate. The complexes ZnL (H_2L = dithiooxamide, *N,N*-dimethyl- and *N,N*-dicyclohexyl-dithiooxamide) have been isolated,[898] and consist of linear chains containing four-coordinate zinc.

With *N,N*-dimethyl- and *N,N*-dicyclohexyl-dithiooxamide, Zn, Cd and Hg form the non-electrolyte MLX_2 (X = Cl, Br or I) and electrolyte ML_2X_2 and ML_3X_2 ($X = ClO_4$) complexes.[899] IR studies show that all the complexes are S,N-coordinated; for the $ZnLX_2$ complexes, a tetrahedral coordination is indicated, while the analogous Cd complexes contain a halide-bridged octahedral structure.

The reaction of dithiooxamide and its tetramethyl and tetraethyl derivatives with zinc, cadmium and mercury halides leads to complexes of stoichiometry MLX_2 (M = Zn, Cd or Hg; X = Cl, Br or I).[900,901] M—S bonding is involved; IR spectra show that the zinc and mercury complexes are four-coordinate, while the cadmium complexes are octahedral with halogen bridges.

A crystal structure determination of the complex $[NBu_4][CdL_3]$ (**130**) ($HL = Et_2NCS_2H$) has shown the metal to be in a geometry intermediate between octahedral and trigonal prismatic, with each dithiocarbamate acting as a non-symmetrical S_2 chelate (Cd—S, 2.655–2.755 Å).[902]



(**130**)

A detailed study of the reactions of $[CdL_2]$ ($HL = Et_2NCS_2H$) with halogens, and of the reactions of iodo derivatives with Lewis bases has been described.[902]

A crystal structural analysis of the complex $2CdCl_2{\cdot}L_n$ has been described ($L = Bu_2NSCCH_2O(CH_2)_2OCH_2CSNBu_2$), and the metal shown to exist in two separate environments, one trigonal bipyramidal and one octahedral.[903]

In the thioamide complexes $[ML_2X_2]$ (M = Zn or Cd; L = 2-thioacetamidothiazole; X = Cl or Br) the ligand is thought, on the basis of multinuclear NMR studies, to act as a monodentate donor through the ring nitrogen atom.[904]

The crystal structure of the first monomeric thiocarbamate complex, bis(cyclopentamethylenethiocarbamato)bis(piperidine)zinc, was described in 1973.[905] The coordination geometry about the zinc is approximately tetrahedral, consisting of sulfurs of the two thiocarbamate ligands (Zn—S = 2.29, 2.31 Å) and nitrogens of two piperidine ligands. Hydrogen bonding of the uncoordinated thiocarbamate oxygen with the proton of the coordinated piperidine occurs.

Solution studies on the compounds $[Bu_4N][M(R_2NCS_2)_3]$ (M = Zn or Cd; R = Me or Et) show the zinc complex (unlike the cadmium complex) to be some 90% dissociated into the neutral bis complex and the free ligand anion. This is in accord with the structure of the solid complex,[907] which shows that only one dithiocarbamato group is bidentate, the other two being formally unidentate.

Reactions of dithiocarbamate complexes have been the subject of several recent reports. For instance, reaction of $[ZnI_2(TMTD)]$ (TMTD = tetramethylthiuram disulfide) with two equivalents of Ph_3P yields the dithiocarbamate salt $[Ph_3PC(S)NMe_2][ZnI_2(S_2CNMe_2)]$, whereas reaction with three equivalents yields the salt $[Ph_3PC(S)NMe_2][ZnI_3(PPh_3)]$.[908] The anions $[ZnX_2(S_2CNMe_2)]^-$ were also prepared by the reaction of $[Bu^n_4N][S_2CNMe_2]$ with ZnX_2, and addition of a further mole of $[Bu^n_4N][S_2CNMe]$ yields the neutral $[Zn(S_2CNMe_2)_2]$. Further reaction of the latter with $[Bu^n_4N][S_2CNMe_2]$ yields $[Bu^n_4N][Zn(S_2CNMe_2)_3]$.

^1H NMR spectra of some dithiocarbazo complexes of zinc, ZnL_2 ($HL = R^1R^2NNHCSSH$, have been determined,[909] and indicate pseudotetrahedral geometry with chelation by sulfur only.

A ^1H NMR investigation of the configuration of Zn^{II} $R^1R^2C{=}NNHCS_2Me$ and $R^1R^2C{=}NNHCSNH_2$ complexes in solution has been made and the configuration shown to depend upon the nature of the two R groups; with R^1 = Ar and R^2 = H, only one conformer, with the aldehydic hydrogen *syn* to the N—N bond, was present, but a mixture of *syn* and *anti* conformers was present with the compounds derived from ketones.[910] The formation of cadmium(II) complexes of the ligands $R^1R^2C{=}NNHCS_2Me$ and $R^1R^2C{=}NNHCSNH_2$ have been studied by ^1H NMR and the behaviour found shown to be similar to that of the corresponding zinc complexes.[910]

The complexes $CdLX_2$ (X = Cl, Br or NCS) and $CdL_2(ClO_4)_2$ (L = EtMeC=NNHCSNH$_2$] have also been investigated and have been shown to contain tetrahedral cadmium(II).[911]

Bis(thiosemicarbazide)$CdSO_4$ is polymeric, with sulfate acting as bridging ligand (Cd—O = 2.41—2.52 Å). Octahedral configuration about the cadmium is completed by the bidentate N,S-chelating thiosemicarbazide (Cd—S = 2.54 Å, Cd—N = 2.37 Å); both *cis* and *trans* configurations of the two chelate rings are observed.[912]

NMR studies of thiosemicarbazone (L) complexes of the stoichiometry $ZnLCl_2$ and ZnL_2Cl_2 have been used to evaluate the conformer structure in solution and the possibility for rotation of the C—NH_2 bond.[913]

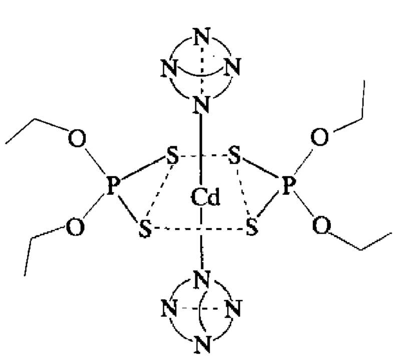
Compounds of the stoichiometry ML_2X_2 (M = Zn or Cd, X = SCN, OAc; M = Hg, X = SCN, CN or BF_4) have been isolated, where L is either thiomorpholin-3-one (L^1) or thiazolidine-2-thione (L^2).[914] In the case of mercury CN and SCN derivatives with both ligands, a pseudotetrahedral geometry is postulated containing S-bonded SCN; L is coordinated *via* S and L^2 *via* N. The zinc–SCN complexes are also tetrahedral but with N-bonded SCN, O-bonded ligand in the case of L^1, and N-bonded ligand in the case of L^2. The cadmium–SCN complexes are polymeric octahedral, with bridging SCN groups and ligand coordination the same as in the case of zinc. IR evidence indicates unidentate coordination of the acetate and tetrafluoroborate groups, while the coordination characteristics of the ligands are the same as found for the SCN complexes.

The pseudotetrahedral complexes ZnL_2X_2 (X = Cl, Br or I; L = 2,6-dimethylthiopyrone) have been prepared; the ligand is coordinated *via* sulfur.[915] Thiazolidine-2-thione (HL) reacts with MCl_2 (M = Zn, Cd or Hg) as its deprotonated thiol to yield polymeric ML_2 complexes in which the ligand is N,S-bound.[916]

Stability constants for complexation of Hg^{2+} by a variety of potentially octadentate N_4S_4 chelating agents have been determined; the order of stability Hg > Zn > Cd was also noted.[917a]

56.1.7.3 Phosphine Sulfides and Selenides, Sulfur and Selenium Heterocycles

Complexes of dithiophosphate ligands[917b] have attracted attention recently; in $CdL_2(L')_2$ (HL = $(EtO)_2PS_2H$; L′ = hexamethylenetetramine) (**131**) the metal is in a distorted octahedral S_4N_2 environment,[918] whereas in $[NMe_4][CdL_3]$ (HL = $(Pr^iO)_2PS_2H$) the metal is again in a geometry intermediate between octahedral and trigonal prismatic (**132**).[919]



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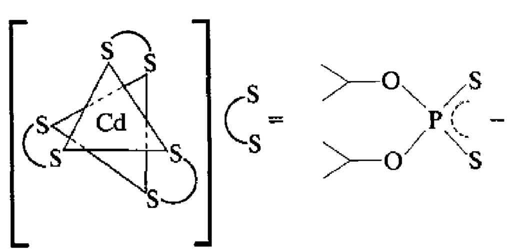


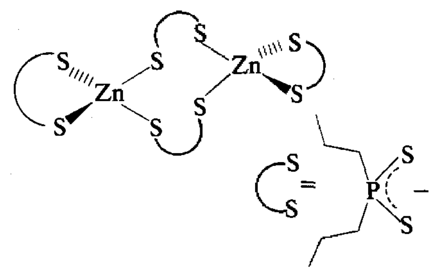
(**132**)

The crystal structure of bis(di-*n*-propyldithiophosphinate) zinc(II) has also been reported, and the compound shown to exist as discrete dimers is in the solid state (**133**).[920]

IR and Raman spectroscopic studies of the ligand tetraallyldiphosphine disulfide and its zinc complex $ZnLCl_2$ have been reported.[921]

Polymeric dithiophosphinate complexes of the type (**134**; M = Zn or Cd) have been obtained.[922] These complexes add py readily and reversibly to yield polymeric octahedral complexes.

The interaction of metal ions with vitamin B_1 (thiamine hydrochloride, **135**) continues to be of interest, and a combination of IR, ^1H and ^{13}C NMR techniques have been applied to the



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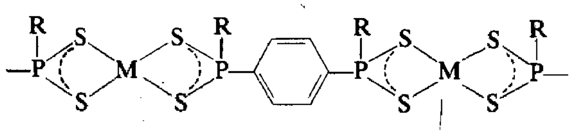


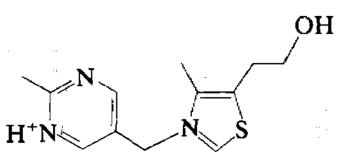
(134) R = pMeOC$_6$H$_4$

study of the zinc complex. It has been demonstrated that the metal is bonded to N-3′ of the pyrimidine ring, not to the sulfur atom.[923,924]

Cadmium complexes of the same ligand have been described, and, in general, resemble those reported for zinc.[923,924]

The complex [ZnL$_2$] (HL = **136**) has been shown to exist with the ligand in the illustrated tautomer, rather than as its double bond isomer, with the imine bond towards the benzene rings.[925]

A crystal structural analysis of CdL$_2$Br$_2$ (L = **137**) has been described.[926] The ligand is in the tautomeric form depicted, and is coordinated to the metal through N-1 to give an octahedral, polymeric complex.



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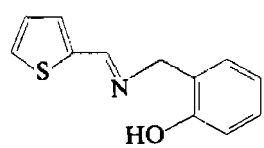

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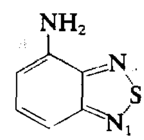


(137)

A number of complexes of zinc with benzothiazole and other sulfur-containing ligands have been described and the crystal structure of [NBu$_4$][Zn(S$_2$CNMe$_2$)$_2$]$_2$ (O$_2$CMe), which contains a square pyramidal {ZnS$_4$O} unit, has been reported.[917]

Zinc ethanoate behaves similarly to mercury(II) ethanoate on reaction with 2-(2-pyridyl)benzothiazole and gives complexes of a ring-opened ligand.[928]

Surveys of this area are available.[1468c–h]

56.1.8 Halides and pseudohalides

The history of zinc and cadmium halides is long and well documented.

The relatively recent application of physical techniques to the study of, for example, solution species in the molten salts or the nature of halometal anions in the solid state has revealed many interesting and remarkable findings which we now briefly explore.

56.1.8.1 Coordination of the Halides in the Molten State

Molten zinc chloride has a remarkably high viscosity at its melting point (318 °C) and an X-ray diffraction study at 323 °C has revealed that the liquid consists of $[ZnCl_4]^{2-}$ and Zn^{2+} ions, rather than molecular $ZnCl_2$.[929] The conductivity of $ZnCl_2$–LiCl melts has been investigated.[930]

On the other hand, the temperature-dependent viscosity and electrical conductivity of molten $ZnBr_2$ and $ZnCl_2$ has been interpreted in terms of large molecules having the composition $\{ZnCl_2\}_x$ and $\{ZnBr_2\}_y$, free Zn^{2+}, and Cl^- and Br^- anions arising from salt dissociation.[931] This is in contrast to a previous postulate of dissociation to give Zn^{2+} and $ZnCl_6^{4-}$ ions. Thermal conductivity studies of the molten MX_2–PbX_2 (M = Zn or Cd; X = Cl or Br) systems also indicate that the layer structure of the Zn and Cd halides is partially retained.[932]

A number of apparently conflicting reports have appeared, describing the liquid state for which molten zinc chloride has been taken as a model in non-compatible schemes. A neutron diffraction study of isotopically enriched molten zinc chloride suggests that metal–halide ion interactions are minor, and that the structure should be regarded as a mixture of zinc and chloride ions.[933] In contrast, an X-ray diffraction study at 330, 430 and 530 °C has suggested that the ligand phase closely resembles a loosely distorted α-, β- or γ-$ZnCl_2$ structure, with corner sharing $ZnCl_4$ units; there are four close Zn—Cl contacts at 2.30 Å at each temperature.[934] Further Raman studies of $ZnCl_2$–KCl melts are in accord with the presence of $[ZnCl_2]_n\cdot[ZnCl_4]^{2-}$ and other unidentified species.[935] The molten $CdCl_2$–KCl system has also been studied over the range 0–100 mol% $CdCl_2$ at 857 K.[936] Related reports have described studies on the molten MnF_2–ZnF_2 system,[937,938] $ZnCl_2$–$CuCl_2$,[939] $CdCl_2$–AgCl[940] and $CdCl_2$–$PbCl_2$[941] systems. The AgCl–$CdCl_2$ system is of some interest, in that vapour pressure measurements show it to exhibit a negative deviation from Raoult's law.[940] The ternary system $CdCl_2$–LiCl–NaCl has been investigated, and a range of chlorocadmate species characterized.[942]

The reactivity of a variety of non-aqueous zinc, cadmium and mercury systems has been described. A series of papers[943–947] reports several aspects of the inorganic chemistry of fused zinc chloride. The stoichiometry of the reactions of 15 oxyanions with fused zinc chloride has been established.[943] With hydroxide, carbonate, nitrate, peroxide and sulfite, oxide ion was the non-volatile product; bicarbonate was also decomposed to oxide, possibly *via* an intermediate basic carbonate chloride. Nitrite gave oxide as the final product, with partial intermediate formation of nitrate. Sulfate did not react, but its solution, and those of metaphosphate and pyrophosphate, could be quenched to glasses. Thiosulfate gave sulfide and sulfate as non-volatile products, while pyrosulfate, persulfate and bisulfate gave sulfate. Metabisulfite produced sulfate, sulfide and oxide, with the proportions varying with concentration. The stoichiometries of the reactions of eight halogen and pseudohalide anions with fused zinc chloride have been established.[944] Perchlorate and chlorate decompose to oxide, oxygen and chlorine, the latter with partial intermediate formation of perchlorate. Both bromate and iodate gave oxide, oxygen and free halogen, accompanied by extensive oxidation of the melt, while periodate gave oxygen and iodate, and at higher temperatures, oxide, accompanied by melt oxidation. Of the pseudohalides, cyanide did not react; cyanate gave cyanide as the main product while thiocyanate formed sulfide, cyanide and sulfur.

The reactions of four transition metal ions and oxyanions with fused zinc chloride have been further elucidated.[945] Potassium chromate dissolves without reaction at 350 °C (ν_{max} = 26 000 cm^{-1}) but at higher temperatures reacts to give zinc chromite, with slight melt oxidation. Potassium dichromate also gave zinc chromite through a chromate intermediate, but with more extensive melt oxidation. Silver oxide reacted to give silver chloride with no decomposition to silver metal, while sodium metavanadate reacted probably to give a zinc metavanadate species. The solubilities of cobalt(II) chloride, nickel(II) chloride, chromium(III) chloride, and zinc oxide and sulfide in fused zinc chloride have also been measured.[946] The spectra of nickel(II) and cobalt(II) dissolved in a zinc chloride–zinc sulfate melt showed a tetrahedral–octahedral coordination equilibrium, the octahedral species being favoured by an increase in temperature and zinc sulfate concentration.[947]

EMF measurements on the $ZnCl_2$–ACl (A = K, Rb or Cs) systems have yielded partial molar free energies, enthalpies and entropies, and the results have been interpreted in terms of an acid–base reaction.[948] The enthalpy of mixing consists of a contribution from the reaction to form the tetrahedral complex A_2ZnCl_4, and a contribution from the mixing of the products with remaining reactants to form a solution. The results indicate that as the polarizing power of the alkali metal cation decreases, the 'reaction' part of the enthalpy becomes more pronounced, reflecting the increased basicity of the alkali metal salt.

A dissolution mechanism for zinc, cadmium and mercury in their molten halides has been proposed on the basis of experimental and literature data.[949] Dissolution occurs at the metal–salt phase boundary. Adsorbed M^{2+} cations are reduced to M^+ ions which then migrate into the salt phase where M_2^{2+} dimers form. The stability of the M_2^{2+} ions was found to increase in the order Zn < Cd ≪ Hg (the latter is so stable that Hg^+ is undetectable in solution).

The stability constants in melts of $NH_4NO_3\cdot nH_2O$ of ZnX^+, ZnX_2 (n = 1–3; X = Cl or Br), CdX^+, CdX_2 (n = 1.5–3; X = Cl or Br) and HgX^+, HgX_2 (n = 2.5; X = Cl or Br) have been determined.[950,951] The behaviour of zinc is peculiar if the K_1 and K_2 values are compared with those of cadmium and mercury. The stability constants increase with temperature and the bromide is more stable than the chloride, trends which are opposite to those normally observed for the halide complexes of most metals in anhydrous or aqueous melts. The data also show that hydration of M^{2+} cations competes more significantly with ion association in the case of zinc, which is consistent with the much smaller Pauling radius of Zn^{2+} as compared with Cd^{2+} and Hg^{2+}.

Raman studies of bivalent Zn in fused $ZnCl_2$–KCl show conclusively the formation of the $[ZnCl_4]^{2-}$ anion,[952,953] although thermo-EMF[954] and thermal conductivity[955] studies of the systems $ZnCl_2$–CsCl and $CdCl_2$–KCl show maxima at a 1:1 molar composition. Thermal analysis, however, shows the presence of Cs_2ZnCl_4 and $CsZn_2Cl_5$.

Dissolution of $ZnCl_2$ in fused LiCl–KCl or CsCl–KCl yields the tetrahedral $[ZnCl_4]^{2-}$ ion ($\nu_1 = 267$, 275 cm^{-1}, respectively),[956] and dissolution of ZnI_2 in molten InI yields the $[ZnI_4]^{2-}$ ion.[957]

$ZnCl_2$ vapour pressures, activities and partial molar energies have been determined for the fused salt system shown in equation (7). Deviations from ideality at high $ZnCl_2$ concentrations are attributed to partial covalent bonding in $ZnCl_2$, while deviations at low $ZnCl_2$ concentrations are attributed to formation of complex ions.[958,959]

$$ZnCl_2 + Na_2SO_4 \rightleftharpoons ZnSO_4 + 2NaCl \qquad (7)$$

A study of the far IR spectra of the liquid, glass and crystalline states of $ZnCl_2$ has been reported[960] with particular reference to the effects of order and temperature on band shape.

A review discussing ZnF_2, its hydrates and some fluorozincates is available.[961] Enthalpy measurements on fused mixtures of ZnF_2 with KF indicate that the principal anionic complex in this system is $[ZnF_3]^-$ or a polymer of this composition.[962]

An X-ray characterization of the various compounds formed in the NaCl–$CdCl_2$ system has been reported.[963]

56.1.8.2 Solution Chemistry

The solution chemistry of zinc and cadmium halides is a topic of active interest, and numerous studies of the related equilibria shown in Scheme 3, in various solvents S, have been reported.

$$[M(S)_n]^{2+} + 2Cl^- \rightleftharpoons [MCl(S)_m]^+ \rightleftharpoons [MCl_2(S)_p]$$

$$[MCl_2(S)_p] + 2Cl^- \rightleftharpoons [MCl_3]^- + pS + Cl^- \rightleftharpoons [MCl_4]^{2-} + pS$$

Scheme 3

Extensive X-ray diffraction studies on cadmium–iodo complexes in aqueous and DMSO solution have confirmed the nature of the solute species. In water, complexes present include $[Cd(H_2O)_6]^{2+}$ (Cd—O, 2.292 Å; *cf.* Cd—O in crystalline $[Cd(H_2O)_6][ClO_4]_2$, 2.292 Å), $[Cd(H_2O)I]^+$ (Cd—I, 2.80 Å; Cd—O, 2.30 Å), $[CdI_4]^{2-}$ (Cd—I, 2.79 Å) and traces of $[CdI_3]^-$ and $[CdI_2(S)_p]$. In DMSO, the characterized species included $[Cd(DMSO)_6]^{2+}$ (Cd—O, 2.292 Å; *cf.* Cd—O in crystalline $[Cd(DMSO)_6][ClO_4]_2$, 2.291 Å), $[CdI_2\,(DMSO)_x]$ (Cd—I, 2.75 Å), $[CdI_3]^-$ (Cd—I, 2.773 Å, I—Cd—I, 112°) and $[CdI_4]^{2-}$ (Cd—I, 2.790 Å). The $[CdI_3]^-$ and $[CdI_4]^{2-}$ ions possessed the same structures in each solvent (trigonal and tetrahedral respectively), and showed no evidence for the additional coordination of solvent molecules within the first coordination shell.[966] These results are confirmed in studies on the $ZnBr_2$–MeOH and LiBr–$ZnBr_2$–MeOH systems, which show a coordination number of four about the metal in each case (presumably $[ZnBr_2(MeOH)_2]$ and $[ZnBr_4]^{2-}$) with only trace amounts of $[ZnBr_3]^-$.[965] The formation of chloro complexes in DMSO solutions of zinc perchlorate has also been studied.[966]

An EMF method has been used to study the interaction of $ZnCl_2$ with chloride ion in methanol. It is found that K_1 (7.76×10^3 M) is less than K_2 (1.74×10^4 M), a finding which is interpreted in terms of passing from an octahedral $[ZnCl(MeOH)_5]^+$ species to a tetrahedral $[ZnCl_2(MeOH)_2]$ complex.[967] Related studies have shown that the solubility of cadmium halides in water decreases with increasing pressure.[968,969] Anionic $[ZnCl_3]^-$ and $[ZnCl_4]^{2-}$ species are present in zinc chloride battery electrolyte, and are responsible for the observed negative transference numbers for zinc in aqueous acidic chloride medium.[970] In neutral chloride medium, the two simultaneous processes in Scheme 4 occur in the polarographic reduction of cadmium(II).[971]

$$[CdCl_n]^{(2-n)+} \rightleftharpoons [Cd(S)_n]^{2+} + nCl^-$$
$$[Cd(S)_n]^{2+} + 2e^- + Hg \rightleftharpoons Cd(Hg)$$

Scheme 4

The dissociation constants of MX_2 (M = Zn, Cd or Hg; X = Cl, Br, I or ClO_4) in DMF, acetone and ROH solvents have been measured.[972] The order of anion donor strength is found to be $ClO_4 < I > Br > Cl$; a small-angle neutron scattering study of D_2O solutions of zinc chloride has been reported.[973]

A conductometric study[974] of $CdCl_2$ solutions in HOAc–H_2O indicates association into ion pairs such as $[Cd_2Cl_2]^{2+}$. Measurements on MeOH–H_2O solutions of $CdCl_2$–KI indicate formation of the CdI_3^- ion.[975] Studies[976] of MX_2 dissociation in DMSO (M = Cd or Hg; X = Cl, Br, I or SCN) show, in the case of Hg, the same order of stability as found in aqueous solution (I > Br > Cl > SCN), while a different order of stability is found for the Cd complexes.

The careful study of Zn–Cl stretching frequencies by Raman spectroscopy in aqueous solutions of zinc chloride in hydrochloric acid solutions has allowed the quantitative study of $[ZnCl_4]^{2-}$ formation.[977]

Raman measurements on concentrated aqueous solutions of cadmium halides show the presence of chloro complexes of tetrahedral and octahedral symmetry, but the formation of only tetrahedral bromo complexes.[978] A combination of solution and solid state ^{113}Cd NMR spectroscopic results have allowed the compilation of ^{113}Cd chemical shifts for the complexes $[CdX]^+$, $[CdX_2]$, $[CdX_3]^-$ and $[CdX_4]^{2-}$, for X = Cl, Br or I.[979]

Stability constants for the complexes $[MX_n]^{(n-2)-}$ (M = Zn or Cd, n = 1–4, X = Cl; M = Zn, Cd or Hg, X = I, n = 4; M = Cd, X = SCN, n = 1 or 2; M = Zn or Cd, X = F, n = 1) have been measured in aqueous solution.[980–985]

Complexation of MI_2 (M = Zn, Cd or Hg) by I^- (as KI) in MeOH has been investigated.[986] No complex formation was found in the case of Zn, but for M = Cd the species $[CdI_3]^-$ was identified in contrast to the case of mercury for which the following reaction was shown to occur:

$$CdI_2 + KI + HgI_2 = KHgI_3 + CdHg_2I_6$$

The disscciation constants of H_2ZnCl_4 and H_2CdCl_4 in tributyl phosphate have been measured over a range of temperatures.[987] Values of the overall formation constants for the complexes $[ZnCl_n]^{(n-2)-}$ (n = 1–6) in mixed water–dimethylformamide systems (0–30 mol dm^{-3} in H_2O) decrease with increase in H_2O concentration.[985] Interaction with halide ions has also been studied[989] in DMF for Zn^{2+} and Cd^{2+}. For Zn^{2+}, values have been determined for n = 1–6 (Cl^- and Br^-), n = 1–5 (NCS^-) and n = 1–4 (I^-), whilst for Cd^{2+} overall formation constants have been determined for n = 1–5 with all these anions. In all cases higher coordination numbers and formation constants were obtained in DMF than in water, reflecting the weaker solvation by the former solvent.[988] Anionic zinc complexes can show differences, as between chloride and thiocyanate; the formation of halide and pseudohalide complexes has been investigated by a number of groups.[990–994] Although Zn^{2+}–SCN^- mixtures appear to give the tetrahedral ion $[Zn(NCS)_4]^{2-}$,[992] there is little evidence for the formation of the tetrachlorozincate(II) ion under similar conditions, the major species present in the Zn^{2+}–Cl^- system in DMSO being the 1:1, 1:2 and 1:3 complexes.[991]

The Zn^{2+}–Cl^- system has also been investigated in THF and 1,2-DME, and, once again, there is little evidence for the formation of the $[ZnCl_4]^{2-}$ ion, the major solution species being $[ZnCl_3]^-$.[995]

The extraction of the Group IIB metals from aqueous solution is of obvious commercial importance and continues to be investigated.[996–1000] The precise species which is extracted depends on the pH, but both Aliquat 336 and tri-n-butyl phosphate extract $[ZnCl_3]^-$ from LiCl solution and $[ZnCl_4]^{2-}$ from acidic media.

Raman spectral studies of the species $[MX_n]^{(n-2)-}$ (n = 2–4; M = Zn, Cd or Hg; X = Cl, Br or I) in anhydrous tributyl phosphate have been reported.[1001] For the MX_2 molecules, sufficient metal dihalide–solvent interaction exists to suggest bent X—M—X species with C_{2v} rather than $D_{\infty h}$ symmetry. The effect appears most marked for zinc(II) and least marked for mercury(II) which is in accord with the Lewis acidity sequence $ZnX_2 > CdX_2 > HgX_2$. A similar analysis of the anionic MX_3^- complexes formed from a 1:1 mixture of LiX and MX_2 again demonstrates solvent interaction, and a tetrahedral C_{3v} species is indicated, rather than the planar structure found in the solid state.

Much work has been devoted to the halide complexation of these elements in non-aqueous media. Equilibrium and calorimetric measurements for the formation of the $[MX_n]^{(n-2)-}$ (M = Zn or Cd; X = Cl, Br, I or SCN; n = 1–4) anions in dimethyl sulfoxide (DMSO) have shown that stability constants follow the same order, but are much larger than those found for aqueous solution; zinc exhibits an enhanced hardness as an acceptor in DMSO as compared to cadmium. Calorimetric measurements indicate a change from octahedral to tetrahedral coordination with increasing halide concentrations.[1002–1006]

Large-angle X-ray scattering measurements[1007] on solutions of CdI_2 and NaI in DMSO show the $[CdI_4]^{2-}$ species to be regularly tetrahedral [r(Cd—I) = 2.790 Å] and the $[CdI_3]^-$ group to be pyramidal [r(Cd—I) = 2.773 Å], while in $[CdI]^+$, r(Cd—I) was found to be 2.75 Å. These results suggest that CdI_2 does not occur as a dominant species; (formation constant data are to be found in ref. 1005).

Heats of formation of MI_3^- and MI_4^{2-} in a variety of non-aqueous solvents have been obtained by calorimetric titration of MI_2 with NaI (M = Zn, Cd or Hg).[1008] Interaction of MBr_2 (M = Zn, Cd or Hg) with $AlBr_3$ in DMF gives $(AlBr_2)_2MBr_4$.[1009]

Complex halide formation in DMF and DMSO involving the systems LiX–MX_2 (X = Br or I; M = Zn, Cd or Hg)[1010] and ZnX_2–CdX_2, CdX_2–HgX_2, and ZnX–HgX_2 (X = Br or I)[1011] has been studied using viscosity, density, electrical conductivity and cryoscopic measurements. In DMF only the $[MBr_3]^-$ species are observed, whereas in DMSO formation of the $[MX_4]^{2-}$ ion occurs. Titration of the MX_2 salts (M = Zn, Cd or Hg; X = Cl, Br, I or SCN) with LiX and NaCNS in either DMF or DMSO[1012] shows that the heats of formation of $[ZnCl_3]^-$, $[HgX_3]^-$ and $[HgX_4]^{2-}$ are exothermic in both solvents. Exothermic heats of formation are also observed for $[Zn(NCS)_4]^{2-}$, $[CdCl_4]^{2-}$ and $[CdBr_4]^-$ in DMF; all other complex species have endothermic heats of formation.

A study has been reported of the complexation of $ZnBr_2$ by Br^- (as LiBr) in solvents of low basicity but different dielectric permittivities (propylene carbonate, $(MeO)_2CO$ and EtOAc) using Raman spectroscopy and calorimetry.[1013] Both the $[ZnBr_3]^-$ and $[ZnBr_4]^{2-}$ anions are observed, except in the case of EtOAc, where only the 1:1 complex is formed. The dielectric permittivity has no effect on the $\Delta H_f^\ominus$ of the complexes.

The interaction of $CdCl_2$ with NH_4Cl or LiCl in THF or 1,2-DME has been studied; there is no evidence for the formation of $[CdCl_4]^{2-}$ in these solvents, the only products being $Li[CdCl_3]$ or $[NH_4][CdCl_3]$.[1014]

56.1.8.3 Pseudohalides and Related Species and Solid State Studies

A Raman study of zinc(II) coordination in aqueous thiocyanate solution has been reported.[1015] No bridging thiocyanate is observed, and bonding to the zinc is totally in the Zn—NCS mode. The results are consistent with the existence of all four species $[Zn(NCS)_{1-4}]$. There is strong evidence that the two lower species are octahedrally coordinated, while the higher species are tetrahedral.

Aqueous solutions containing cadmium and thiocyanate have also been shown to contain the species $[Cd(SCN)_n(H_2O)_x]$ (n = 1–4); there is no evidence for the formation of polynuclear complexes, although both S- and N-bonded thiocyanate are present.[1016]

The complex species $[Cd(SCN)_2]$ and $[Cd(SCN)_3]^-$ have been investigated, and it is thought that the thiocyanate is coordinated to the metal *via* sulfur in DMSO solution, but that in aqueous solution it is coordinated through the nitrogen atom.[1017]

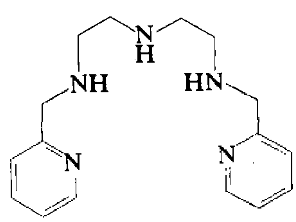
The Raman spectrum[1018] of coordinated zinc(II) in KSCN at 200 °C shows the presence of the tetrahedral $[Zn(NCS)_4]^{2-}$ species, somewhat distorted by polymerization, and bands due to Zn—NCS—Zn bridges are also observed. Linkage isomerism is also present, as evidenced by bands due to both Zn—NCS and Zn—SCN bonding modes.

Much recent interest in the Group IIB tetrahalometallate salts has centred on the dynamic behaviour and the phase transitions which they exhibit, and studies of $[R_4N]_2[ZnCl_4]$ (R = tetradecyl,[1019] H,[1020–1022] Me[1023]), $[MeNH_3]_2[ZnCl_4]$,[1024] $Rb_2[ZnCl_4]$,[1025–1028] $K_2[ZnCl_4]$,[1027] $Rb_2[ZnBr_4]$[1027] and $[RNH_3]_2[CdCl_4]$ (R = Me[1029] or Pr^n [1030]) using a variety of techniques have been described.

Structure determination of the $ZnCl_4^{2-}$ ion as its $MeNH_3^+$ and $Ni(MeCN)_6^{2+}$ salts show only slight distortions from perfect tetrahedral symmetry ($Zn–Cl = 2.27$ Å).[1031,1032]

The crystal structure of Cs_2ZnCl_4 has been determined.[1033] The anion shows only slight distortion from tetrahedral symmetry ($Zn—Cl = 2.28–2.31$ Å), in contrast to the same anion in the complex $[Co(NH_3)_6][ZnCl_4][Cl]$ where gross distortions are observed.[1034] Calculations indicate that in the latter complex, the major cause of bond length distortion is anisotropy in the applied electrostatic crystal forces. For the former complex charge distribution values were obtained from crystal force, NQR and MO calculations. The results were in overall agreement.

A number of other X-ray structural studies of tetrahalometallate complexes have been described. In $[Co(L)Cl][ZnCl_4]$ (L = **138**) the anion is in a distorted tetrahedral configuration, with Zn—Cl (average, 2.263 Å,[1035] whereas a more regular tetrahedral geometry is observed in $[ZnL_2(H_2O)][ZnCl_4]$ (L = 8-aminoquinoline) (Zn—Cl (average), 2.2 Å).[1036] The anion in $W_3O_2(OAc)_6(H_2O)_3$ $[ZnBr_4]$ is tetrahedral, with Zn—Br (average) 2.41 Å.[1037] Other complexes reported include $[CdL_4][ZnX_4]$ (L = $PhNH_2$, 2-, 3- or 4-$MeC_6H_4NH_2$; X = Cl, Br or I).[1038]



(138)

The far IR spectra of the $[ZnCl_4]^{2-}$ anion in salts with the 1,10-phenanthrolinium and 2,2-bipyridinium cations have been reported.[1039] The anion in the former salt appears to be tetrahedral, while that in the latter is believed to be halogen-bridged.

The crystallographic determination of the structures of the $CdCl_4^{2-}$ anion as its thiaminium salt shows it to have an almost regular tetrahedral arrangement, with $Cd–Cl = 2.45$ Å.[1040]

A crystallographic determination of the $[ZnI_4]^{2-}$ anion structure has been reported in its salt with the 2,4-dimethyl-1*H*-1,5-benzo diazepinium cation.[1041] It possesses rigorous C_2 symmetry ($Zn—I = 2.60$ Å) with deviations from the highest tetrahedral symmetry being due to packing forces.

The Raman and IR spectra of the $[Zn(CNO)_4]^{2-}$ anion have also been reported.[1042] The results are consistent with high tetrahedral symmetry, *i.e.* linear metal–CNO groups.

Single crystal structural analyses of $K_2[ZnF_4]$ and $K_3[Zn_2F_7]$ have been reported.[1043] Although the $[ZnF_4]^{2-}$ ion is perfectly tetrahedral, the $[Zn_2F_7]^{3-}$ ion shows a shortening of the terminal Zn—F bonds.

A number of complex halides have been structurally characterized, including $KCdF_3$,[1044] $RbZnCoF_6$,[1045] $CsZnAlF_6$,[1045] $Cd_2MgCl_6·12H_2O$,[1046] $Cd_2NiCl_6·12H_2O$[1047] and $KCd_3Cl_7·4H_2O$.[1048]

The novel derivatives $HZnI_3·L_3$ (L = Et_2O, py, $PhNH_2$) and $H_2ZnI_4·L_4$ (L = Et_2O or $PhNH_2$) have been described, and their structures discussed in detail.[1049]

The structure of the dimethylammonium pentachlorodicadmate(II), $Me_2NH_2Cd_2Cl_5·2H_2O$, involves polymeric chains of $\{CdCl_6\}$ and $\{CdCl_5(H_2O)\}$ octahedra, the dimethylammonium cations being located in the space between the chains.[1050] The compounds $[NH_4][CdCl_3]$ and $[Me_3NH][CdCl_3]$ also contain infinite chains of $\{CdCl_6\}$ octahedra.[1051,1052]

A determination of the crystal structure of $Cs[CdBr_3]$ has been reported and the metal shown to exist in trigonally distorted $\{CdBr_6\}$ octahedra.[1053] The Raman spectra of $Rb[CdX_3]$ (X = Cl or Br)[1054] and $[Pr_4N]_2[CdX_3Y]$ (X = Br or I; Y = Cl, Br or I) have been reported and the latter anions, like $[CdCl_3X]^{2-}$, shown to have a pseudotetrahedral geometry.[1055]

The interaction of $[R_4P]^+$ with aqueous Cd^{2+} and CN^- results in the formation of the complexes $[R_4P][Cd(CN)_3]$, examples of solid complexes containing the rare $[M(CN)_3]^-$ anion.[1056]

A structural determination[1057] of $CsCdCl_3$ reveals a polymer containing two distinct types of cadmium ion. One is surrounded by six chloride ions in a near perfect octahedron ($Cd—Cl = 2.60$ Å), while the other is surrounded by two distinct groups of chloride ions ($Cd—Cl = 2.64$, 2.59 Å) in a distorted octahedran. Alternatively, Raman spectral studies on $[Pr_4^nN][CdX_3]$ (X = Cl, Br or I) indicate discrete $[CdX_3]^-$ anions possessing C_{2v} symmetry.[1058]

Force constant calculations on the MX_3^- series, (M = Zn, Cd, (or Hg); X = Cl, Br, or I) indicate an order of metal–halogen bond strengths Cl > Br > I.[1059]

The $[Cd_2Cl_5]^-$ ion has been reported as its morpholinium salt.[1060]

The structure of $CdCl_2 \cdot 2.5H_2O$ contains two crystallographically distinct Cd atoms bridged by Cl atoms (Cd—Cl = 2.68, 2.71 Å). Both are octahedrally coordinated, one by five Cl and one H_2O, the other by four Cl and two H_2O (terminal Cd—Cl = 2.56 Å).[1061]

A crystallographic study[1062] of the mixed salt $CdCl_2 \cdot 2NaCl \cdot 3H_2O$ shows it to consist of sheets of chlorine octahedra. Of the four octahedral sites of one sheet, one is occupied by Cd and the other three by $\frac{1}{3}$Cd : $\frac{2}{3}$Na. Water molecules and Na atoms are located between these sheets, with only interstitial hydrogen bonds.

A crystallographic determination[1063] of the structure of the $[Zn_2Cl_6]^{2-}$ ion in its salt with the $(\pi\text{-}C_6H_4)Ni(PPh_3)_2^+$ cation shows the zinc to possess approximately tetrahedral coordination with two of the six chlorines acting as bridging ligands.

A series of adducts of organocadmium halides with neutral bidentate ligands RCdX·L (L = dioxane, bipy or phen) have been prepared by electrochemical oxidation of the metal in the presence of L and the alkyl halide. In the additional presence of $[N(n\text{-propyl})_4]X$, salts of the $[RCdX_2]^-$ anion may be isolated.[1064]

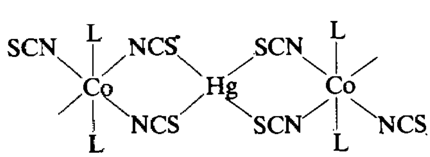
A crystal structure determination of $Cd(NCS)_2$ has been reported and the metal shown to be in an N_2S_4 environment.[1065]

Complexes with pyridine *N*-oxide of zinc thiocyanate and selenocyanate of the stoichiometry ZnL_3X_2 (X = SCN, SeCN) have been reported.[1066] IR evidence shows that they are best formulated as $[ZnL_6]^{2+}[ZnX_4]^{2-}$.

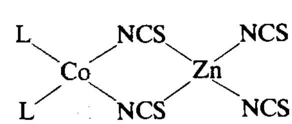
The structure of $Cd(SCN)_2$ contains Cd octahedrally surrounded by four sulfur and two *trans* nitrogen atoms with slightly distorted geometry (Cd—N = 2.24, Cd—S = 2.76 Å).[1067]

The structure of $Cd_2(pn)_2(NCS)_4$ is polymeric, containing bridging NCS groups. Two crystallographically distinct Cd atoms are again present; one is octahedrally coordinated by five N atoms (two from propylenediamine and three from SCN) and one S atom, the other by three N and three S atoms.[1068]

Several other complexes with N-donor ligands have been prepared.[1065] The complexes $CoM(NCS)_4(L)_6$ (M = Zn or Cd; L = 2-, 3- or 4-cyanopyridine, nicotinamide, ethyl nicotinate or isonicotinic acid hydrazide) are best formulated as $CoL_6M(SCN)_4$. The complexes $CoHg(SCN)_4L_2$ (L = 2-, 3- or 4-aminopyridine, 3-cyanopyridine or ethyl nicotinate) possess only bridging SCN ligands, and have the polymeric structure (**139**). On the other hand, the complexes $CoZn(NCS)_4L_2$ (L = 2-, 3- and 4-aminopyridine) contain both bridging and terminal SCN groups, and are postulated to have the dimeric structure (**140**).



(**139**)



(**140**)

The crystal structure of $[Cd(en)NCS]_2C_2O_4$ shows it to consist of infinite chains of $\{Cd(en)^{2+}\}$ ions bound by oxalate groups. Each Cd atom possesses a distorted octahedral configuration, with unidentate, N-bonded NCS.[1070] Molecular structure determinations of $[Cd(en)_2(NCS)_2]$ and $[Cd(en)_2(NCS)Cl]$ show the former to be *trans* octahedral and the latter to be *cis* octahedral. The NCS is unidentate and N-bonded, although the M—NCS is non-linear.[1071]

The free energy and enthalpy of formation of the $[Cd(SeCN)]^+$ cation indicate exclusively N-bonded selenocyanate.[1072]

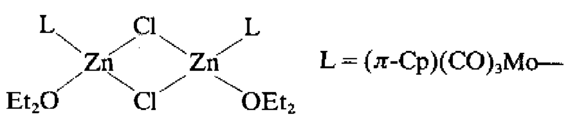
The complexes $K_2[CdN(CN)_2]_4$ and $K_2[Cd(C(CN)_3)_2(XCN)_2]$ (X = S or Se) have also been prepared. The former is octahedral, containing both bridging and terminal $N(CN)_2$ groups, while the two latter contain bridging XCN and unidentate$[C(CN)_3]$ groups. The complexes $K_2[Cd(C(CN)_3)_2(SCN)_2]$ and $K_4[Cd(N(CN)_2)_6]$ both contain only unidentate ligands. The XCN groups are N-bonded in all cases. The crystal structure of $KCd(NCO)_3$ shows the Cd atoms to be octahedrally coordinated by six N atoms; as in the $KCdCl_3$ N-bridged double chains along the *c*-axis are formed which are linked together by K atoms.[1073] Surveys of this area are available.[1468c–h]

56.1.9 MULTINUCLEAR COMPLEXES OF ZINC AND CADMIUM

Although reviews have appeared on the polyatomic cations of zinc, cadmium and mercury,[1074a,1468b] we shall be concerned here with complexes of ligands in which there are donor sites enabling it to coordinate more than one metal ion or where a ligand may have a bridging function giving rise to multi nuclear species.

Among the least structurally complicated compounds are the complex anions $(BH)_2[CoMCl_6]$ (M = Zn or Cd) and $(BH)_2[Co_2MCl_8]$ (M = Zn, Cd or Hg; B = NH_3 or en).[1074b] The former contain an M—Co bond with tetrahedral coordinations about both metal atoms; the latter contain a central M tetrahedrally connected by four bridging chlorines to two Co atoms whose tetrahedral coordination is completed by two terminal chlorines per cobalt. The complexes $(BH)_2[CoMCl_6]\cdot 2H_2O$ and $(BH)_2[Co_2MCl_8]\cdot 4H_2O$ have also been prepared; the water molecules complete an octahedral coordination for the cobalt atoms. The analogous complexes of Ni have also been prepared.[1075] IR, electronic and magnetic moment measurements have been reported on complexes of the type $[CoM(NCS)_4(L)_x]$ and $[NiM(NCS)_4(THF)_x]$ (M = Zn or Cd).[1076] In the cases where L = py or bipy, the complexes are best formulated as $[CoL_x][M(SCN)_4]$ ($x = 6$ and 3, respectively); when L = phen, six-coordination of the M atom is indicated in the formulation $[Co(phen)_3][M(NCS)_4phen]$. The complexes $NiCd(SCN)_4(THF)_2$ and $NiZn(NCS)_4(THF)_4$ contain bridging thiocyanate groups, with octahedral coordination about both metal atoms in the latter, but only about the Ni in the former. The complexes $Co[Zn(NCS)_4](en)_4$, $Co[Cd(NCS)_4](en)_3$ and $[M(NCS)_4]$ (triethylenetriamine)$_2$ (M = Zn or Cd) are postulated to contain Co in a square planar environment.

The preparations and molecular structure determinations of the complexes $[(\pi\text{-Cp})Mo(CO)_3ZnCl(OEt_2)]_2$ and $[(\pi\text{-Cp})Mo(CO)_3]_2Zn$ have been reported.[1077] The former is prepared from $(\pi\text{-Cp})Mo(CO)_3H$ and EtZnCl in Et_2O and has structure (**141**) (Mo—Zn = 2.63 Å, Zn—Cl = 2.40 Å, Zn—O = 2.09 Å). The Et_2O can be removed to give a polymeric species, $[(\pi\text{-Cp})Mo(CO)_3ZnCl]_x$, in which the pseudotetrahedral stereochemistry about the zinc is completed by oxygen coordination from one of the carbonyl groups. The latter complex is prepared by the reaction of $(\pi\text{-Cp})Mo(CO)_3H$ with Et_2Zn, and contains a linear Mo—Zn—Mo linkage (Zn—Mo = 2.54 Å). Analogous tungsten complexes can also be prepared.



(**141**)

The crystal structures of several Lewis base adducts of $Cd[Mn(CO)_5]_2$ have been determined. In the cases where the ligand is the terdentate pyridyl[1078] or diglyme (di-(2-methoxyethyl) ether),[1079] the coordination is best described as very distorted trigonal bipyramidal, with the $Mn(CO)_5$ groups occupying equatorial positions. In both complexes, deviations of the equatorial angles from 120° are attributed to the large size of the $Mn(CO)_5$ groups. In the former complex, considerable displacement of the nitrogen atoms from ideal axial geometry is due to restrictions imposed by the terpyridyl ligand, while the latter complex, the OCdO angle of 126° is due mainly to puckering of the chelate rings. The cadmium–manganese bond lengths (2.78 and 2.71 Å) are consistent with the view that weakening of the metal–metal bond occurs on adduct formation.

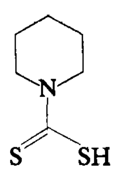
The structures of the bidentate bipyridyl and 1,10-phenanthroline adducts have also been reported.[1080] The cadmium is tetrahedrally coordinated, distorted by considerable reduction of the NCdN angle due to the geometrical limitations of the bidentate ligand, and expansion of the MnCdMn angle due to the bulky nature of the $Mn(CO)_5$ groups. The manganese–cadmium bond length (2.68 Å) is in keeping with the observation that the covalent radius increases with coordination number.

Reactions of $M^1M^2(SCN)_4$ (M^1 = Ni, Fe, Zn, Cu or Co; M^2 = Zn, Cd or Hg) with a wide variety of N-donor ligands (L) have been reported.[1081–1083] In general, the products are of three types: (a) $M^1M^2(SCN)_4\cdot 6L$ which are best formulated as $[M^1L_6][M^2SCN)_4]$; (b) $M^1M^2(SCN)_4\cdot 2L$ or $M^1M^2(SCN)_4\cdot 4L$, which are polymeric bridged complexes in which the octahedral coordination of M^1 or both M^2 and M^1 is completed by two or four L ligands, respectively; and (c) M^1M^2 $(SCN)_4\cdot 2L$ or $M^1M^2(SCN)_4\cdot 4L$, which are monomeric bridged complexes in which M^1

attains either tetrahedral or octahedral coordination, respectively. Complexes of the analogous selenocyanates $M^1M^2(SeCN)_4$ (M^1 = Co, M^2 = Zn, Cd or Hg with pyridine and bipyridine also show the same three types of structure.[1084]

A number of heteronuclear dithiocarbamate complexes $MCdL_4$ (M = VO, Mn, Fe, Co, Ni, Cu or Zn; HL = Et_2NCS_2H or **142**) in which the cadmium is in a tetrahedral S_4 environment have been described.[1085]

The reaction of (**143**) with metal salts results in dealkylation and the formation of the trimetallic species (**144**). Thus the reaction of (**143**) with $Cd(O_2CMe)_2$ results in the formation of (**144**; $M^1 = M^2$ = Cd; X = 2Br). A heteropolynuclear species, (**144**; M^2 = Ni; M^1 = Cd; X = $CdBr_4$) results from the reaction of (**144**; $M^1 = M^2$ = Ni; X = 2Br) with $Cd(O_2CMe)_2$.[1086]



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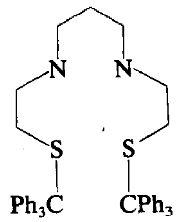

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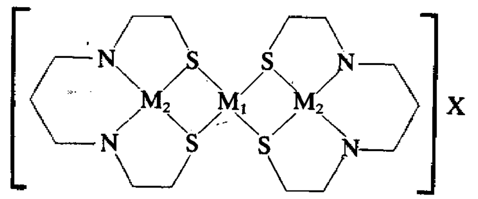
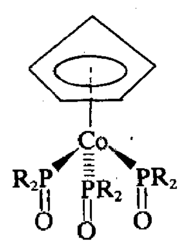


(144)

Zinc and cadmium complexes of the novel tripod ligand (**145**) have also been described.[1087]

The reaction of $Hg(HL)_2$ (HL = 2-mercaptobenzoic acid, **146**) with cadmium nitrate leads to the novel $CdHgL_2$ species, in which the cadmium is bonded to the carboxylate oxygen atom, and the mercury to the thiolate sulfur.[1088]



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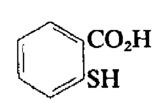


(146)

For derivatives of the type $M^1M^2(NCX)_4$ (X = S, Se), structure determination of $CdHg(SCN)_4$ reveals tetrahedral HgS_4 and CdN_4 coordination connected *via* bridging SCN, with deviations from strict tetrahedral symmetry being due to close approach of the two tetrahedra.[1089]

The crystal structure of cadmium hexacyanopalladate consists of an uninterrupted cubic Pd—C—N—Cd framework, with each metal at the centre of a perfect octahedron (Cd—N = 2.27 Å).[1090] The platinum(II) complex *trans*-$Pt(Cl)(PEt_3)_2(CH{=}NC_6H_4Me\text{-}4)$ acts as a monodentate ligand to $CdCl_2$.[1091]

The structure of Cd_2As_3I involves As atoms in a helical structure, while the Cd atoms are five-coordinate to three As and two I atoms, with *r*(Cd—As) at 2.62–2.74 Å and *r*(Cd—I) at 2.98–3.43 Å.[1092] A binuclear complex of Zn^{II} and Cu^{II} with histidine has also been reported.[1093]

Multinuclear complexes often have low solubility; Drago and co-workers have described an anion-bridged soluble dinuclear chelating system based on 4-*t*-butyl-2,6-bis[*N*-{[(heptylthio)-thiocarbonyl]amino}formimdoyl]phenol.[1461]

56.1.10 ZINC(I) AND CADMIUM(I)

The species Cd^+ and $[Cd_2]^{2+}$ are known, for example, in solutions of cadmium metal in molten cadmium halides, but are not well characterized. However, crystallographic data are now available[1094] on these species in zeolite A, which have been prepared by exposing fully Cd^{2+}-exchanged zeolite A to cadmium vapour. The crystal structure of the partially dehydrated, fully Cd^{2+}-exchanged zeolite A, $[Cd(H_2O)^{2+}]_3[Cd^{2+}]_3$-A, shows that all six Cd^{2+} ions are associated with six-oxygen rings of the aluminosilicate framework. Three of these Cd^{2+} extend into the large cavity and are three-coordinated by three framework oxides. The other three Cd^{2+} ions are recessed into the sodalite unit, where each is coordinated to three framework oxides and to a fourth group (OH^-) to give a near-tetrahedral structure. Upon exposure to cadmium vapour, the three-coordinate Cd^{2+} ions react to give Cd^+ and Cd_2^{2+} species. Two different coordination environments are present for the $[Cd_2]^{2+}$ ion, but the Cd—Cd distance is the same in both cases, at 2.35 Å. Each unit cell contains three Cd^{2+}, three Cd^+ and 1.5 Cd_2^{2+} ions.

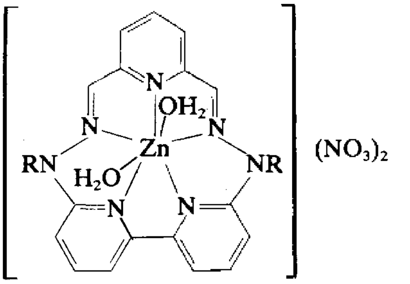
In general, cadmium(I) is a very unstable species but more examples of it are known than of zinc(I). The species Cd^+ has been produced by pulse radiolysis of solutions of cadmium(II) complexes,[1095,1096,1096a] and the complexes $[ZnL]^+$ and $[CdL]^+$ (L = [14] ane-1,4,8,11-N_4) have been prepared by this means.[1096] It is thought that the initial step in the pulse radiolysis is the decomposition of water to hydrated electrons and $[OH]^\bullet$, and that it is the former species which reduces the Cd^{II} to Cd^I.

^{113}Cd NMR relaxation data indicate that the addition of cadmium metal to CdI_2 results in the formation of Cd_2^{2+} and Cd^+, with the monomeric species having a half-life of about 10 ps.[1097]

56.1.11 MACROCYCLIC COMPLEXES

56.1.11.1 Cyclic Amine, Ether and Related Species

There is a considerable volume of recent work[1468i] on the preparation and properties of zinc and cadmium complexes of macrocyclic ligands having N, O or both in the ring as donor atoms. A frequently used route to such ligands is the condensation of a difunctional primary amine with a difunctional carbonyl compound, usually under conditions favouring template or promnastic reaction. Such condensations of primary amines with carbonyl groups to give macrocyclic imines (*e.g.* **147**) in which the template ion is coordinated to the imine groups are thought to proceed *via* carbinolamine intermediates, which then undergo elimination of water. Of considerable interest, therefore, is the isolation of a zinc complex (**148**) of a dicarbinolamine, which appears to be such an intermediate in the formation of the N_5 macrocycle. The carbinolamine complex has the carbinolamine C—O and N—H bonds disposed on the same side of the macrocycle.[1098]



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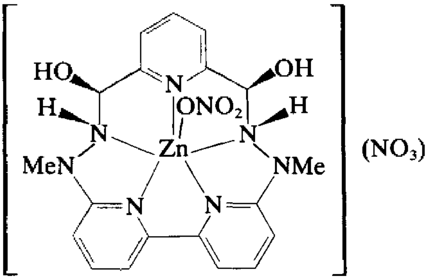


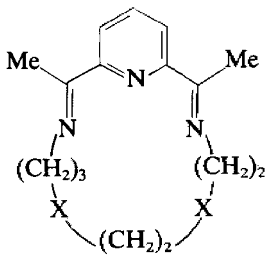
(148)

The Zn^{II} complex of a 14-membered hexaaza macrocycle can be prepared by the template condensation of 2,6-diacetylpyridine with hydrazine.[1099] Reaction of this diacetylpyridine with 4,7-diazadecane-1,10-diamine[1100] in the presence of Cd^{II} gives the complexed 17-membered pentaaza ligand (**149**; X = NH). This $[CdLBr]Br\cdot0.5H_2O$ species has a pentagonal pyramidal structure with an axial bromide ligand.

The tetraza macrocycle (**150**; LH_4), with four ethanoate groups, is readily prepared by treatment of the cyclic tetramine with bromoethanoic acid.[1101] Its complex $[ZnLH_2]$ utilizes two amino N atoms and two carboxylates as ligands. The fully deprotonated complex may be prepared in solution by treatment with NaOH.

The complex $[ZnL(H_2O)_2]^{2+}$ (L = 2,2,4-trimethyl-1,5,9-triazacyclododecane) loses a proton from an aqua group with a pK_a of 9.56.[1102] Macrocycles such as (**151**), with a pyridine group incorporated into the structure, react slowly with Zn^{2+} compared to other 14-membered cyclic aliphatic tetraaza systems,[1103] probably as a result of the rigidity introduced into their structure by the pyridine ring.

Reaction of $Zn(SO_3CF_3)_2$ with the macrocycle (**152**; H_2L), in the presence of a tertiary amine such as triethyl- or tri-*n*-propyl-amine, yields the complexes [ZnL(amine)]; NMR studies



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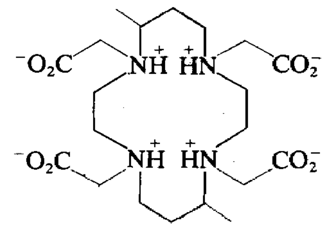

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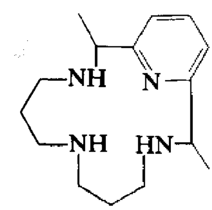
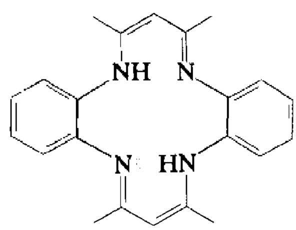


(151)

indicate the coordination geometry to be square pyramidal with apical amine.[1104] The complex $[CuL][ZnCl_4]$ (L = 3,10-Me-2,9-Ph_2-[14]-1,3,8,10-tetraene-1,4,8,11-N_4; **153**) undergoes a transmetallation reaction on treatment with zinc metal to give the five-coordinate complex $[ZnLCl]^+$, which may be isolated as its PF_6^- salt.[1105] It is interesting to note that the complex could not be prepared using zinc as the template metal.



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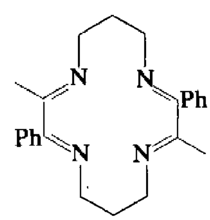
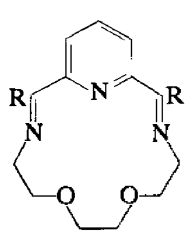


(153)

There are interesting preparative features to be found in this area of coordination chemistry; for example, the template condensation of 2,6-diacetylpyridine with 3,6-dioxaoctane-1,8-diamine in the presence of Cd^{2+} results in the formation of complexes of the 1 + 1 macrocycle (**154**).[1106] The macrocyclic complexes $[CdL(NCS)_2]$ (L = **155**; R = H or Me) have been prepared by template condensations or by metal exchange reactions,[1107] and the compound [CdLI]I (L = **156**) has also been described.[1108]



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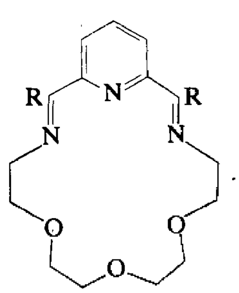

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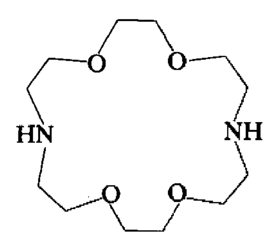
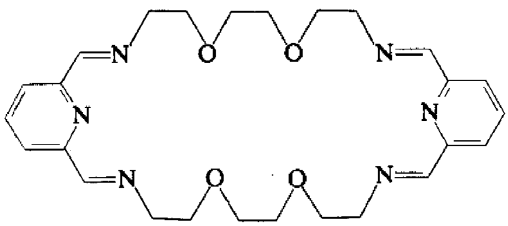


(156)

Zinc complexes of a number of saturated tetraaza macrocycles and their open-chain analogues have been investigated,[1109–1111] and it has been confirmed that the macrocyclic complexes are more stable than the non-cyclic complexes, whatever reference for stability is taken. It has been concluded that the stability is due to a favourable enthalpy term, although it has been noted that comparative studies mean little unless the coordination geometry is well characterized, and strictly comparable.[1109] The complexes $[ZnLX_2]$, $[ZnBr(py)L_2][ZnBr_4]$ (L = [14]ane-1,4,8,11-N_4; X = Cl or Br); $[ZnBr_2L]$ (L = [15]ane-1,4,8,12-N_4, [16]ane-1,5,9,13-N_4, 1,4,8,11-Me_4-[14]-ane-1,4,8,11-N_4) and $[ZnBr(EtOH)L_2][ZnBr_4]$ (L = 1,4,8,11-Me_4-[14]-ane-1,4,8,11-N_4) have been prepared, and their solution properties studied.[1110]

The transamination of open-chain ligands may be used in the preparation of macrocyclic complexes, and the template condensation of the zinc complex of 2,6-diacetylpyridine bispropylimine with 3,6-dioxaoctane-1,8-diamine results in the formation of the complex $[ZnL]^{2+}$ (L = **157**).[1112]

Reaction *in situ* of the macrocycles (L = **158**) with $ZnCl_2$ yields $[ZnLCl_2]$ complexes which are postulated to be octahedral; in contrast, $Cd(ClO_4)_4$ yields 2:1 complexes whose structures remain unclear.[1113]



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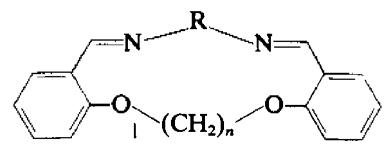
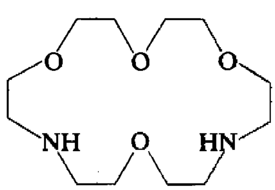


(158) R = $(CH_2)_{2,3}$ or CH_2CHMe $n = 2$ or 3

Cadmium complexes of the cryptands (**156**) and (**159**)–(**162**) have been investigated, and both $[CdL]^{2+}$ and the binuclear complexes $[Cd_2L]^{4+}$ are formed.[1114,1115]

Complexing of Cd^{II} by cryptands has been considered with the object of finding ligands that will bind Cd^{II} selectively with respect to Zn^{II} and Ca^{II}, and so ultimately provide a suitable ligand for chelation therapy (*cf.* however, Section 56.1.13.2.2). The cryptand (**163**) shows a remarkable selectivity, for Cd over Zn, of 10^6 and for Cd over Ca of 5×10^7. Lehn has reviewed these aspects of the cryptands.[1116] Interaction of diazapolyoxa macrocycles (**164**) with Zn^{II} have been reported.[1117]



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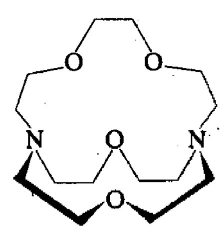

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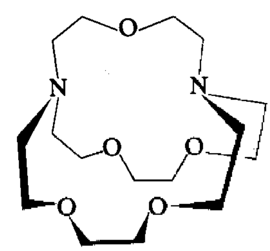

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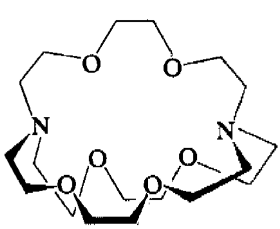

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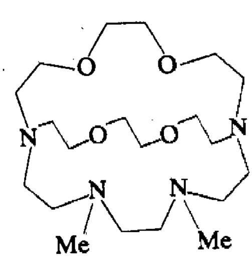

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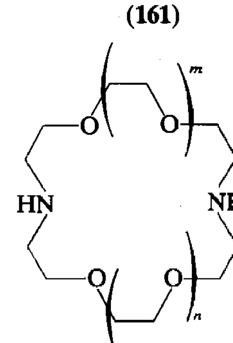


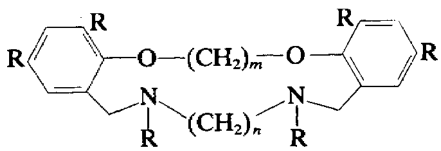
(164)

Cadmium complexes of the macrocycles (**165**; $n = 3$, $m = 2$, 3 or 4),[1118] [18]ane-1,4,7,10,13,16-N_6[1120] and [14]ane-1,4,8,11-N_4[1119] have been reported. The ^{15}N NMR spectrum of $[Cd([18]ane\text{-}1,4,7,10,13,16\text{-}N_6)][NO_3]_2$ has been described and shows satellite peaks due to coupling to ^{111}Cd and ^{113}Cd nuclei; interestingly the spectrum shows sets of resonances due to two conformations of the cation, one corresponding to a planar and one to a trigonal bipyramidal structure.[1119]

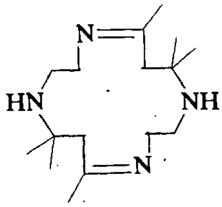
A zinc complex of [18]ane-1,4,7,10,13,16-N_6 has been reported,[1120] and the metal exchange of Cu^{II} for Zn^{II} in a range of cyclic polyamine complexes, $[ZnL]^{2+}$ (L = [12]ane-1,4,7,10-N_4, [13]ane-1,4,7,10-N_4, [14]ane-1,4,8,11-N_4 or [15]ane-1,4,8,11-N_4) in aqueous solutions buffered by ethanoate has been investigated.[1121] The metal exchange reaction was thought to involve a ligand dissociation (equation 8) as already proposed for the metal exchange reactions of porphyrin in DMF.

$$[ZnL]^{2+} + MeCO_2H \longrightarrow [Zn(O_2CMe)]^+ + HL^+ \quad (8)$$

The formation of the complex ions $[ZnL(H_2O)]^{2+}$ and $[ZnL(OH)]^+$ (L = 5,7,7,12,14,14-Me_6-[14]-4,11-diene-1,4,8,11-N_4; **166**) has been described.[1122] A number of mixed donor macrocycles of the type (**165**) have been prepared ($n = 2$, $m = 2$; $n = 3$, $m = 2$, 3 or 4) and their zinc complexes characterized. A determination of the crystal structure of the complex $[ZnLI_2]$ (L = 8,12-Me_2-5,6:14,15-Bzo_2-[14]-5,14-diene-8,12-N_2-1,4-O_2) has indicated that only the nitrogen atoms are coordinated to the metal.[1123] Lewis *et al.* have described a number of zinc complexes of macrocycles incorporating 2,2′-bipyridine or 1,10-phenanthroline subunits.[1124–1126]



(**165**)



(**166**)

The formation of zinc complexes with a further series of [14]ane-N_4 macrocycles has been investigated.[1127] The macrocycle [9]ane-1-O-4,7-N_2 forms a zinc complex,[1128] and the crown ether complex $[ZnL][SbCl_6]_2$ (L = 18-crown-6) has also been characterized.[1129] Zinc complexes of a range of encrypting ligands have been studied.[1130,1131]

The treatment of aqueous solutions containing Zn^{II} or Pb^{II} with crown ethers results in the preferential complexation of Pb^{II}, to give a complex which is readily transported across the $CHCl_3$–H_2O interface, and the method appears to have potential for the separation of these two metals.[1132] Polyethers have also been used for the extraction of zinc from aqueous media containing thiocyanate, and the distribution of the metal between the two phases has been shown to depend upon the solvent and any other cations which may be present.[1133]

This is a large and active area and a number of recent surveys are available.[9–15,1468o–i]

56.1.11.2 Porphyrin and Phthalocyanine Derivatives

This area of macrocyclic coordination chemistry is also the subject of much recent activity, partly because the zinc and cadmium complexes have interesting spectroscopic and photochemical properties.

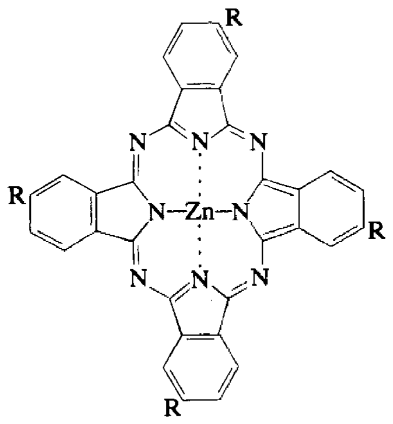
On the preparative side, template reactions are again useful; for example, the template condensation of phthalimide (or its potassium salt) with malonic acid or arylacetic acids in the presence of zinc or cadmium acetate has been shown to result in the formation of [ML] (H_2L = tetrabenzoporphyrin or *meso*-tetraaryltetrabenzoporphyrin).[1134,1135]

The template synthesis of phthalocyanine complexes [ZnL] by the condensation of dicyano compounds with urea in the presence of zinc chloride and ammonium molybdate has been described.[1136,1137]

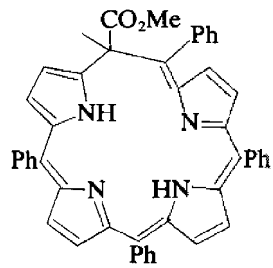
Zinc naphthalocyanine has been prepared in low yield (18%) by the template reaction of $Zn(O_2CMe)_2$, urea and 2,3-naphthalenedicarboxylic acid.[1138] The synthesis of zinc tetra-2,3-naphthoporphine by a template reaction has been described.[1139]

Several reactions of zinc porphyrins are of interest as ligand modification methods. Thus, the reduction of ZnL (H_2L = **167**) with $MeCHN_2CO_2Me$, followed by demetallation, gives the homoporphyrin (**168**) and the *N*-alkylated species (**169**).[1140] Vilsmeier–Haack formylation of zinc octaethylporphyrin gives (**170**).[1141] The formation of a zinc 'nitrotetrabenzoporphyrin' has also been reported.[1142] The reaction of *meso*-(dimethylaminomethyl)aetioporphyrin with alcohols ROH in the presence of $Zn(OAc)_2$ gives good yields of the complexes (**171**).[1143]

Cadmium complexes of macrocyclic ligands have not been as widely studied as the corresponding zinc complexes, but the fact that cadmium macrocycles undergo easy metal exchange should make them attractive subjects for future study. The crystal structure of [Cd(TPP)(dioxane)] and its ^{113}Cd NMR characteristics have been reported.[1144] The formation



(167) (**a**; R = SO_3H)(**b**; R = CMe_3)



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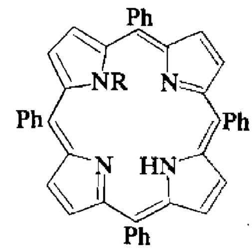

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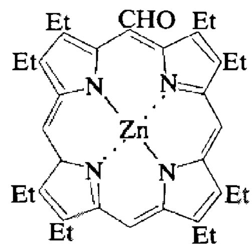

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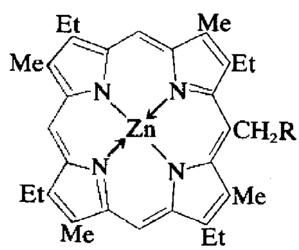


(171)

of cobalt(II) porphyrins by metal exchange of [ZnL], and [CdL] (L = TPP), with $CoCl_2$ in field desorption mass spectrometry has been reported.[1145] Metal exchange reactions of manganese(II) porphyrins with zinc have been studied.[1146]

The formation of porphyrin complexes by the reaction of H_2L (**167a**) or (**173d**) with Zn^{2+} has been investigated. In the case of (**167a**), an activated complex $[H_2L^{*}\cdots Zn(H_2O)_6]^{2+}$ was implicated as an intermediate,[1147] while the reaction of (**173d**) with Zn^{2+} was first order in each reactant, and faster than the corresponding reaction of (**173a**).[1148]

The metallation of $TPPH_2$ in D_2O or H_2O has been studied, and the rate difference ($k_H/k_D = 2.3$) shown to be due to differences in the concentration of OH and OD complexes, and not due to intrinsic differences in the reactivity of TPPH and TPPD.[1149] The synthesis and properties of porphyrins bearing cationic or anionic substituents are areas of active interest, and zinc complexes of the ligands (**172**), tetrabenzoporphyrin and octamethylporphyrin have been studied.[1150–1154]

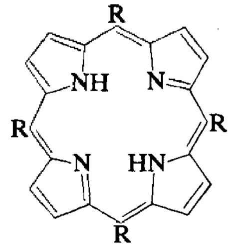
The formation of axially substituted complexes MLL′ (M = Zn or Cd; H_2L = porphyrin; L′ = another ligand) has been investigated by a number of groups.[1155–1158] An EXAFS study has shown that there is no short axial Zn—S interaction in peptide-substituted zinc porphyrins, in which the side chain bears a cysteine residue.[1159a]

Most of the work investigating the ability of porphyrins to act as photosensitizers uses the readily available *meso*-tetraphenylporphyrin (**173a**), although various anionic and cationic derivatives are being investigated. A review on this and related areas has recently been made by Porter and co-workers.[1159b] Many workers have used the 1,1′-dimethyl-4,4′-bipyridinium dication as an electron acceptor and the photoreduction of this species in the presence of [ZnL] (H_2L = **173a** or **173b**) has been investigated.[1160] Various chemical mixtures have been used for the photoreduction of water, including $[ZnL]^{4-}$ (H_6L = (**173b**)/Pt/H_2O),[1161] $[ZnL]^{4+}$ {$[H_2L]^{4+}$ = (**173c**)}/Pt/H_2O,[1161] and [ZnL] (H_2L = (**173a**)/edta/MV^{2+}/H_2O).[1162]. It is interesting that the reversible photooxidation of [ZnL] (H_2L = **167a**) provides a photocatalytic method for the reduction of quinones.[1163,1164]

A photoexcited Fe^{III}/Zn^{II} hybrid hemoglobin has been shown to have interesting electron transfer properties.[1164b]

The effect of substitution of the phenyl groups of the TPP ligand has been investigated.[1165]

SnO_2 semiconducting electrodes are photosensitized by zinc porphyrin complexes but the zinc species is consumed in a competing dimerization reaction.[1166]



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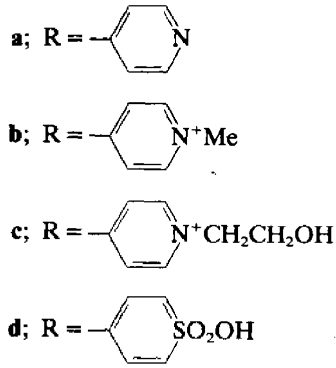
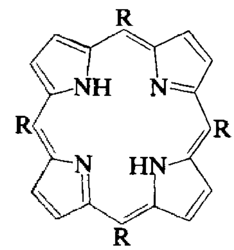




(173)

a; $R = Ph$
b; $R = 4\text{-}HO_3SC_6H_4$
c; $R =$ 4-(1-methylpyridinium)
d; $R = 4\text{-}Me_3NC_3H_4$

In cationic micelles, the anionic phthalocyanine, $Na_4[ZnL]$ (H_4L = **167a**), in the presence of cysteine, has been shown to sensitize the photoreduction of the 1,1′-dimethyl-4,4′-bipyridinium dication (methyl viologen, Paraquat) although, in the presence of a surfactant, [Zn(Pc)] was more effective.[1167]

A number of studies related to the spectroscopic properties of zinc and cadmium phthalocyanines in the context of the photocatalytic decomposition of water have been published.[1168–1171]

Zinc porphyrin complexes are also of interest in such photochemical systems, and photochemical studies of a series of porphyrin, porphine and related complexes have been reported.[1172–1177]

Related investigations have involved studies of the electronic, fluorescence and phosphorescence spectra[1178] and the polarized absorption and linear dichroism spectra[1179] of zinc porphyrins.

A number of workers have studied zinc tetraphenylporphyrin complexes, and an intensive study of the luminescence properties of [ZnTPP] has been reported.[1180a] [ZnTPP] is also used in the well-known 'synthetic leaf' experiments.[1180b]

Zinc tetrasulfophthalocyanine is an attractive choice for the chromophore in multicomponent systems for the photoreduction of water, but recent studies have shown that only low yields of photoproducts are obtained, and that porphyrin-based chromophores are more efficient.[1181,1182]

The results of CNDO/2 calculations for [Zn(Pc)] have been reported, and compared with the PPP and EHMO calculations for the same species.[1183]

The formation of the five-coordinate axial complexes ZnTPP(L) has been studied electrochemically, and thin-layer spectroelectrochemical techniques have been used to demonstrate the electrochemical and spectrochemical reversibility of the process:[1184,1185]

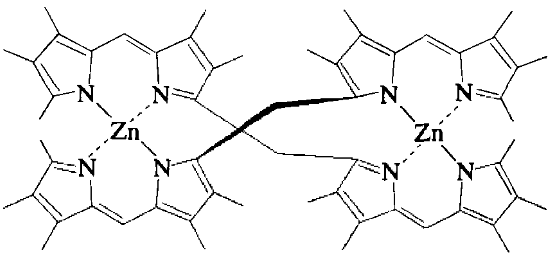
$$[ZnTPP(L)] \rightleftharpoons [ZnTPP(L)]^+$$

The electrochemical oxidation of zinc tetra-4-*t*-butylphthalocyanine (**167b**) in nitrobenzene or 1,2-dichlorobenzene has been reported.[1186]

The radical cations of zinc(II) porphyrins may be prepared from the parent complex ZnL, by reaction with Fe^{III},[1187] or by oxidation of a triplet state with Eu^{III};[1188] it photodisproportionates to [ZnL] and $[ZnL]^{2+}$.[1187]

A crystal structure of the complex [ZnL(py)] (L = isobacteriochlorin) has been reported; the metal is in a distorted planar environment.[1189]

A crystal structure of a dinuclear zinc complex of the porphin precursor, 1,2,3,7,8,12,13,17,18,19-decamethylbiladiene-a,c (**174**) has been described[1190,1191] and the octaethylisobacteriochlorin complex (**175**) has been studied as a model for siroheme enzymes.[1192]



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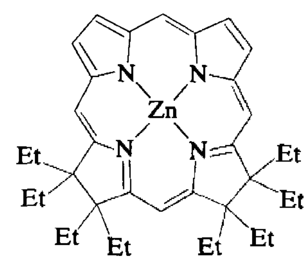


(175)

A number of studies concerning zinc complexes of porphyrins or related ligands have also been reported:[1193–1196] cadmium complexes of a number of porphyrins have also been investigated,[1197–1199] a number of NMR studies of zinc porphyrin complexes have been made[1200,1201] and a number of donor–acceptor complexes of zinc tetrapyrrole species with 1,3,5-trinitrobenzene have been described.[1202a] Recent developments in metallophthalocyamine chemistry, including aspects of zinc complexes, have been reviewed.[9–15,1202b,1468c–h]

56.1.12 KINETICS AND REACTIVITY

The kinetic and reactivity aspects of the coordination chemistry of, *inter alia,* zinc[1469f,g] and cadmium, have featured in the past in many full and comprehensive reviews[9–11,16–22b] which also include an account of these aspects of their bioinorganic chemistry; here we shall survey some recent studies in this area.[1468c–h]

The formation and dissociation kinetics for the complexation of Cu, Zn, Co and Ni with the quadridentate 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane to give five-coordinate species have been reported.[1203] The rate order (Cu > Zn > Co > Ni) is the same as that for H_2O exchange, but the rates are much slower, probably owing to conformational changes occurring in the ligand. The dissociation is acid-catalyzed; the five-coordinate species are found to be much less kinetically inert than four- or six-coordinate complexes. No macrocyclic effect was observed.

The kinetics of incorporation of zinc ions into the substituted tetraaza macrocycles 1,4,8,11-$(CH_2CO_2H)_4$-[14]ane-1,4,8,11-N_4 and 1,4,7,10-$(CH_2CO_2H)_4$-[12]ane-1,4,7,11-N_4 have been studied.[1204]

The kinetics of metal insertion into a range of H_2L species have been studied by a range of techniques.[1205–1207] A kinetic study of the ligand substitution reaction in equation (9) ($L = (H_2NCH_2CH_2NHCH_2CH_2)_2NH$) has been made[1208] and the kinetics of the ligand exchange reaction between $[Cu(edta)]^{2-}$ and $[Cd(trien)]^{2+}$ have been investigated.[1209]

$$[ZnL]^{2+} + [Cu(edta)]^{2-} \rightleftharpoons [Zn(edta)]^{2-} + [CuL]^{2+} \tag{9}$$

The kinetics of the reaction of [PbL] ($H_4L = (HO_2CCH_2)_2NCH_2CH_2OCH_2CH_2OCH_2CH_2N(CH_2CO_2H)_2$) with Cd^{2+} have been investigated and the product shown to be $[CdHL]^-$.[1210]

Ligand exchange processes in a number of phosphine oxide complexes have been investigated by ^{31}P NMR, and it is proposed that the ligand exchange of $[Zn(Ph_3PO)_4]^{2+}$ in CD_2Cl_2 proceeds *via* a dissociative mechanism, since the rate of exchange is independent of Ph_3PO concentration.[1211] Complexes of $(Me_2N)_3PO$, $(MeO)_3PO$ and $(MeO)_2MePO$ have been similarly investigated.[1212]

Studies on the complexing of Cd^{2+} by *N*-carboxymethyliminobis(ethylenenitrilo-*N*′,*N*′-diacetic acid) (H_5L) in the pH range 7–2 are consistent with stepwise protonation of the species $[CdL]^{3-}$ to give finally $[CdH_2L]^-$. The proton-assisted dissociation is interpreted as a stepwise unwrapping from one end of the molecule, with Cd—N fissions corresponding to the rate-determining steps.[1213]

^1H NMR studies of the Zn^{2+}-$HN(CH_2CO_2H)_2$ system have shown that 2:1 complexes are formed in aqueous solution, and that a variety of intra- and inter-molecular exchange processes occur.[1214]

An ultrasonic study of the zinc and cadmium complexes of H_4edta has demonstrated a dynamic equilibrium in solution interconverting the pentadentate and hexadentate forms in solution.[1215]

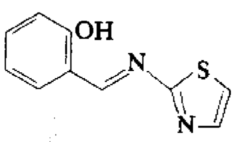
Measurement of stability constants for complex formation between Zn^{2+} and the Schiff bases derived from salicylaldehyde (sal) and either en or 1,3-diaminopropane indicate terdentate coordination by two nitrogen atoms and one oxygen atom. Zn^{2+} also promotes formation of these Schiff bases, and the rate constants are consistent with a mechanism which involves the preequilibrium formation of a mixed $[(sal)Zn(diamine)]^+$ complex.[1216]

NMR studies of several thioureas and their zinc complexes have been used to determine both activation energies for C—N bond rotation and activation energies and entropies for ligand exchange processes.[1217]

Complexes of zinc chloride and perchlorate with the carcinogenic *N,N'*-β-chloroethyl-ethylenediamine have been reported.[1218] The solvolysis rates of the free ligand and of the zinc complex have been studied by NMR spectroscopy.

The ligand exchange of $[Zn(tmtu)_4]^{2+}$ with tmtu in CD_2Cl_2 has been studied by ^1H NMR spectroscopy and the reaction shown to be first order in the complex.[1219]

The hydrolysis of the Schiff base (**176**) is catalyzed by the complex $Zn(im)_2L^+$ (LH = **176**).[1220]



(176)

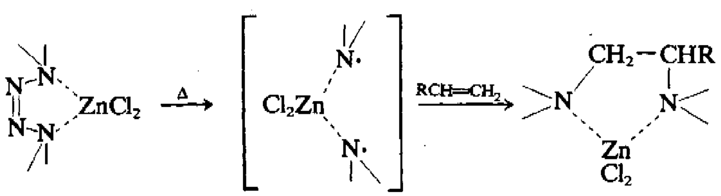
The zinc complex of $(HOCH_2)_3CNH_2$(tris) is a most effective catalyst for the hydrolysis and aminolysis of benzylpenicillin,[1221] and it is suggested that this observation may be of some relevance to the mode of action of zinc-dependent β-lactamases.

The formation constant for 1:1 complex formation between bipy and Zn^{2+} in DMSO has been determined; the interesting feature from the viewpoint of this section is that the dissociation of $[Zn(bipy)(DMSO)_4]^{2+}$ is catalyzed by Hg^{II}.[1222]

The zinc-ion-catalyzed aquation of *cis*-$[Cr(H_2O)_2L_2]^+$ (HL = $CH_2(CO_2H)_2$) has been shown to obey a rate law of the type in equation (10), although other transition metal ions are more effective catalysts.[1223]

$$k_{obs} = k[H^+] + k_{cat}[Z_n^{2+}] \tag{10}$$

A unique zinc complex containing a coordinated biradical has been postulated as an intermediate in the decomposition of the tetramethyl-2-tetrazene complex of zinc chloride (Scheme 5).[1224]



Scheme 5

Libipy reacts with RZnX at −100 °C to yield RZnbipy radicals, the half-lives of which depend on the R group.[1225]

56.1.13 APPLICATIONS

56.1.13.1 Industrial Uses

The metals themselves are widely used in alloys, anticorrosion finishes of various kinds, and a range of batteries but we are concerned here with compounds rather than the elements.

56.1.13.1.1 Zinc

A large scale use occurs on the vulcanization of rubber with sulfur, a process which can be carried out at a lower temperature in the presence of accelerators which include zinc dimethyldithiocarbamate, zinc oxide itself and zinc oxide/thiolobenzothiazole.

Zinc acetate is used in wood preservation, as a mordant in dyeing and in the manufacture of glazes for painting on porcelain. It also has use in veterinary medicine. The bromide is used in making silver bromide collodion emulsions for photography and in the shielding of viewing windows for nuclear reactors. A number of zinc carboxylates, *e.g.* the caprylate, are useful as fungicides. The carbonate is used as a pigment and in the manufacture of porcelain and pottery, and has been used topically as a mild antiseptic.

Zinc chloride has long enjoyed a wide range of uses as a deodorant, disinfecting and embalming material; alone or with phenols in preserving railway sleepers; fireproofing wood; with ammonium chloride as a flux for soldering; etching metals; in the manufacture of parchment paper, artificial silk, dyes, activated carbon, cold water glues; browning steel, galvanizing iron, copper plating iron; with magnesia in special cements; petroleum oil refining; cement for metals and for facing stone; a mordant in dyeing; carbonizing woollen goods, producing crepe and crimping fabrics; as a solvent for cellulose; preserving anatomical specimens; in textile microscopy for separating silk, wool and plant fibres; and as a dehydrating agent in organic synthesis.

Zinc chromate is a useful yellow pigment widely used in metal priming paints; zinc cyanide is used in electropating; the fluoride, ZnF_2, is used in the fluorination of organics, in the manufacture of phosphors for fluorescent electric lights, in glazes and enamels for porcelain and in wool preservation.

Zinc oxide has a wide range of uses apart from its use as an artist's pigment where it provides a more translucent white than flake white or titanium white. It is used in cosmetics, driers, quick-setting cements; with syrupy phosphoric acid or zinc chloride in dental cement; in the manufacture of opaque glass, enamels, car tyres, 'white' glue, matches, white printing inks and porcelain. The photophysics of zinc oxide has been reviewed.[1468a]

Zinc phenolsulfonate has been used in insecticide formulations and in veterinary practice for the treatment of ulcers. Zinc phosphate has been used in dental cement formulations and the phosphide in rat and field mice poisons. The propionate has been used as a fungicide on adhesive tape to reduce plaster irritation caused by moulds, fungi and bacteria; the silicate has been used in television screens.

Zinc stearate has uses in tablet manufacture, in cosmetic and pharmaceutical powders and ointments; as a flatting and sanding agent in lacquers; as a drying lubricant and as a dusting agent for rubber; as a plastic-mould releasing agent; as a waterproofing agent for concrete, rock wool, paper and textiles.

Zinc sulfate has been used as a mordant in calico printing; for preserving wood and skins; for the manufacture of other zinc salts; for clarifying glue and in electrodeposition processes. The sulfide is used as a pigment and as a source of other pigments; ZnS is used in X-ray and television screens and, with a trace of a radium or mesothorium salt, in luminous dials of watches. The telluride has been used as a photoconducting semiconductor.

56.1.13.1.2 Cadmium

Cadmium acetate is used in the pottery and porcelain industry for producing iridescent effects; the borotungstate forms an aqueous solution of high density when concentrated ($d = 3.28$), useful in the mechanical separation of minerals and in density gradient techniques; the bromide, like the zinc salt, is used in photography, process engraving and lithography.

Cadmium chloride is used in photography; in dyeing and calico printing; in radio valve manufacture; in the manufacture of cadmium yellows and reds; in galvanoplasty; in mirror manufacture.

Cadmium fluoride has similar uses to the zinc halide. Cadmium oxide is used in ceramic glazes; the sulfate, as a source of other cadmium compounds and in the radio valve industry; the sulfide is important as a yellow pigment for artists, and is used in the paint, soap, glass, textile, paper, rubber and pyrotechnics industries. Cadmium sulfide in admixture with other compounds such as the selenide gives rise to other pigments of value. It is also used in phosphors and fluorescent screens and in scintillation counters. Semiconductors such as CdS and CdSe can continuously convert low energy light into electricity but they are still self-destructive because of the oxidation at the photoanode: $CdS \rightleftharpoons Cd^{2+} + S + 2e^-$. Addition of sulfide or polysulfide anions to the electrolyte can protect the CdS from this type of oxidation and it has been suggested that a direct conversion of solar energy to split water into hydrogen and oxygen may become practical. The tungstate is also used in X-ray screens.

56.1.13.2 Medical Aspects

Zinc compounds have long been used in medical and veterinary applications and zinc preparations of a number of drugs[1226] are widely used. In this section we focus on insulin[1227] and on the toxicology of cadmium. An interesting short review on the general medical and biological aspects of zinc chemistry is available.[1228] Nutritional aspects have also been surveyed.[1244,1245]

56.1.13.2.1 Chemistry and biosynthesis of insulin: the occurrence of zinc

Insulin, RMM about 6000, is made up of two chains of amino acids joined by disulfide linkages. The sequence of amino acids in the two chains (termed A for acidic and B for basic) and the arrangement of the three disulfide bridges were worked out by Sanger and associates in the period 1945–1955.[1229] The complete synthesis of both ovine and human insulin was achieved in 1963.[1230,1231]

While it had been assumed that the A and B chains were synthesized separately and then joined together in the β cells of the pancreatic islets, Steiner and colleagues and Chance and associates demonstrated that the cells form insulin from a single-chain precursor termed proinsulin.[1232] On conversion of human proinsulin to insulin, four basic amino acids (arginine 31, arginine 32, lysine 64 and arginine 65) and the remaining connector or C-peptide (residues 33 to 63) are removed. The resultant insulin molecule has two chains, the A chain with glycine at the amino-terminal residue and the B chain with phenylalanine at the amino terminus.

An even larger molecule termed preproinsulin has been identified as a precursor of proinsulin. Preproinsulin is extended at the N terminus of the B chain by at least 23 amino acids, many of which are hydrophobic. It is cleaved to proinsulin in the endoplasmic reticulum, where it is synthesized, and is not therefore a product that accumulates in the β cell.

Hodgkin and co-workers[1233] determined the structure of insulin by single crystal X-ray analysis. Insulin can exist as a monomer, a dimer or a hexamer composed of three such dimers. Two Zn^{2+} ions are coordinated in the hexamer, which is presumably the form stored in the granules of the β cell. The hexamer has approximately D_3 symmetry and the two zinc ions lie one above the other, coordinated *via* histidine imidazoles, along the three-fold axis. The biologically active form of the hormone is thought to be the monomer. X-ray analysis has also shown that the two chains are compactly arranged, with the A chain positioned above the central helical portion of the B chain. From each end of this helical region the terminal portions of the B chain extend as arms, and the A chain is enclosed between them.

Many species variations are known, and some are of clinical significance. Further information on the pharmacological aspects of insulin is available.[1227,1466l]. The function of the zinc ions is not clear.

56.1.13.2.2 Toxicology of cadmium: medical and environmental aspects[1234]

Cadmium is close to lead and mercury as a metal of current toxicological concern.[1234b] Extraction of lead and zinc ores, which contain cadmium, pollutes the environment with cadmium. The use of cadmium before 1900 was infrequent; however, its valuable metallurgical properties, such as resistance to corrosion, increased its use markedly, for example in the manufacture of alloys and as a coating on steel. It is also now widely used in nickel cadmium ('nicad') batteries. Coal and other fossil fuels contain cadmium which is released into the environment on combustion.

Workers in smelters and other metal-processing plants may be exposed to high concentrations of airborne cadmium, but for most of the population, exposure from food contamination is most important. Uncontaminated foodstuffs contain less than 0.05 μg of cadmium per gram wet weight, and the average daily intake is about 50 μg. Drinking water normally does not significantly contribute to cadmium intake; cigarette smoking does. Shellfish and animal liver and kidney are among the foods that may have concentrations higher than 0.05 μg/g, even under normal circumstances. When foods such as rice and wheat are contaminated by cadmium in soil and water, the concentration of the metal may increase considerably (1 μg/g).

In Fuchu, Japan, shortly after World War II, numerous patients, mainly multiparous women, complained of rheumatic and myalgic pains; the disease was named *itai-itai* ('ouch-ouch'). Cadmium in the local rice was found to play an etiological role. The source of the metal was the effluent from a Pb–Zn–Cd mine located upstream from the rice fields.

Cadmium is poorly absorbed from the gastrointestinal tract whereas absorption from the respiratory tract appears to be more complete; cigarette smokers may absorb 10 to 40% of inhaled cadmium.[1235]

After absorption, cadmium has a strong preferential affinity for liver and kidney. About 50% of the total body burden is found in these two organs. Liver and kidney also contain a low-molecular-weight protein called metallothionein (see Section 56.1.14.2) because it has a high affinity for metals such as cadmium and zinc; one third of its amino acid residues are cysteine.[1236] This metal-binding protein may act as a scavenging agent and lower the concentration of cadmium at more critical sites within the cell. Interestingly, cadmium also appears to induce the synthesis of this protein.

The half-life of cadmium in the body is 10 to 30 years, and concentrations of the metal in tissues thus increase throughout life. Cadmium is probably the environmental poison most prone to accumulation.

(*i*) *Acute cadmium poisoning*

Acute poisoning may result from inhalation of cadmium dusts and fumes (usually cadmium oxide) and from the ingestion of cadmium salts. The major toxic effects are due to local irritation. In the case of oral intake, these include nausea, vomiting, salivation, diarrhoea and abdominal cramp. Cadmium is more toxic when inhaled. Signs and symptoms, which appear after a few hours, include irritation of the upper respiratory tract, chest pains, nausea, dizziness and diarrhoea. Permanent lung damage may occur in the form of emphysema and peribronchial and perivascular fibrosis. Death is usually due to massive pulmonary oedema.

(*ii*) *Chronic cadmium poisoning*

The toxic effects of chronic exposure to cadmium differ somewhat with the route of exposure. The kidney is affected following either pulmonary or gastrointestinal exposure; marked effects are observed in the lungs only after exposure by inhalation.

(a) *Kidney.* When the concentration of cadmium in the kidney reaches a level of 200 μg/g, there is renal injury. It seems probable that binding of the metal by metallothionein protects the organ when concentrations are lower.

(b) *Lung* Excessive inhalation of cadmium fumes and dusts causes loss of ventilatory capacity, with a corresponding increase in residual lung volume. The disease thus shows the main features of emphysema. The mechanism is not entirely understood but a discussion is to be found in ref. 1234a.

(c) *Cardiovascular system.* A most interesting and controversial issue concerning the effects of cadmium on man is the suggestion that the metal takes part in the etiology of hypertension. An initial epidemiological study[1237] showed that people dying from hypertension had significantly higher concentrations of cadmium and higher cadmium-to-zinc ratios in their kidneys than people dying of other causes. Similar correlations were later found. Cadmium-induced hypertension has been reported in female rats after prolonged exposure to the metal in their drinking water but this has not been uniformly confirmed and hypertension is not prominent in either industrial cadmium poisoning or *itai-itai.*

(d) *Bone.* There appears to be an interaction between cadmium, nutrition and bone disease. The effect of cadmium may be due to interference with renal regulation of calcium and phosphate balance.[1234a]

(iii) Therapy of cadmium poisoning

The management of cadmium poisoning presents difficulties, but several chelating agents have been studied with regard to mobilization of the metal. Dimercaprol (2,3-dithiolo-1-propanol) chelates and markedly increases urinary excretion of cadmium in rabbits; however, it also increases mortality from renal injury produced by cadmium.[1238] It is believed that some cadmium–dimercaprol chelate dissociates in the kidney and thereby increases the cadmium concentration and subsequent renal injury. $CaNa_2Edta$ has been shown to be an effective chelator in some studies[1239] but others have observed increased renal injury.[1240] Chelating agents are thus generally not indicated for the treatment of cadmium poisoning; the organism, provided that it is not overwhelmed by too large a dose rate, appears to develop its own defence through metallothionein biosynthesis.

56.1.14 ASPECTS OF THE BIOLOGICAL CHEMISTRY OF ZINC AND CADMIUM

Zinc has a role in biological systems second in importance only to iron; cadmium has a more restricted biological chemistry but its toxicology and physiological effects (Section 56.1.13.2) have several interesting features.[1470]

56.1.14.1 The Biological Role of Zinc Coordination Chemistry: Zinc Metalloenzymes

It is mainly in the area of zinc metalloenzymes that most work has been done, with useful recent surveys available,[1241,1262,1462] and this is the area we shall consider here.[1242,1243] Work on the transport of zinc within the organism is reviewed elsewhere, as is work on nutritional aspects.[1244,1245]

The first indication[1246] that zinc was required by a living organism appeared in 1869 when Raulin showed that lack of zinc retarded the growth of *Aspergillus niger*. Eight years later came the observation that zinc was a constituent of plants,[1247] vertebrates[1247] and animals;[1248] more than 50 years later still, conclusive evidence that zinc is essential for the normal growth of rodents was published.[1249] We now know that zinc is essential for all life forms.[1250–1252]

The second phase of zinc biological chemistry dates from the identification,[1253] in 1940, of the element in carbonic anhydrase. Not until 1955 was a second zinc metalloenzyme (carboxypeptidase) identified.[1254] Over one hundred zinc-containing metalloenzymes have now been identified, representing each of the six categories of enzymes designated by the International Union on Biochemistry Commission on enzymes (Table 1). Carbohydrates, lipids, proteins and nucleic acids are synthesized or degraded by processes which require[1255] zinc metalloenzymes as catalysts. Several valuable accounts and surveys[1465c–f] of the field have appeared including two stimulating key surveys by Vallee,[1255,1256] a discussion[1257] in depth of the best-characterized zinc metalloenzymes, a brief summary[1258] of recent developments, a more extensive discussion[1259] of the biochemistry of zinc metalloenzymes in relation to biological problems, an article[1260] on zinc and microorganisms, and detailed discussions[1261] of zinc chemistry and biochemistry. A valuable collection of short authoritative surveys of the main zinc metalloenzymes has also appeared.[1262] Recent work is surveyed in ref. 1462.

Zinc in metalloenzymes may (i) participate directly in the catalytic process, (ii) serve to stabilize protein structure or (iii) have a regulatory role. In each case, removal of the metal from the holoenzyme generally results in an apoprotein having no catalytic activity. The enzymes considered briefly below provide examples of each of these functions of Zn^{II}. The study of zinc metalloproteins has often in the past been beset by analytical problems and by contamination with traces of metal ions; a review covering these important topics has appeared.[1263] Another recent review deals with the physiological, nutritional and medical role of zinc.[1264]

Metal-substitution studies, especially those in which Co^{II} replaces Zn^{II}, have proved to be an important tool in the study of zinc metalloenzymes; the Co^{II}-substituted species often have activities approaching those of the Zn^{II} enzyme in its *in vivo* reaction. These modification procedures have been the subject of a recent review,[1265] which, however, focusses in particular on the use of substitution-inert metal ions. A recent innovation in metal-substitution techniques is the replacement of Zn^{II} in zinc metalloenzymes by $^{113}Cd^{II}$, which can then be examined by Cd NMR. The results of a recent such investigation[1266] indicate that the $^{113}Cd^{II}$ can serve as an

Table 1 Zinc metalloenzymes

Enzyme	*E.C. number*	*Source*
Class 1: Oxidoreductases		
Alcohol dehydrogenase	1.1.1.1	Plants, yeast, vertebrates
D-Lactate dehydrogenase	1.1.1.28	Bacteria
D-Lactate cytochrome reductase	1.1.2.4	Yeast
Superoxide dismutase	1.15.1.1	Plants, yeast, vertebrates
Class 2: Transferases		
Transcarboxylase	2.1.3.1	*P. shermanii*
Aspartate carbamoyl-transferase	2.1.3.2	*E. coli*
Phosphoglucomutase	2.7.5.1	Yeast
RNA polymerase I and II	2.7.7.6	*E. gracilis*, yeast, plants
DNA polymerase I and II	2.7.7.7	*E. coli*, invertebrates
Deoxynucleotidyl transferase	2.7.7	Vertebrates
Reverse transcriptase	2.7.7	Oncogenic viruses
3-Mercaptopyruvate sulfur transferase	2.8.1.2	*E. coli*
Class 3: Hydrolases		
Alkaline phosphatase	3.1.3.1	*E. coli*, vertebrates
Fructose 1,6-bisphosphatase	3.1.3.11	Vertebrates, chloroplasts
Phospholipase C	3.1.4.3	*B. cereus*
α-D-Mannosidase	3.2.1.24	Plants, vertebrates
Leucine aminopeptidase	3.4.11.1	Yeast, vertebrates
Carboxypeptidase A	3.4.12.2	Vertebrates
Carboxypeptidase B	3.4.12.3	Vertebrates
Carboxypeptidase Gl	3.4.12	*P. stutzeri*
Dipeptidase	3.4.13.11	Vertebrates
Neutral protease	3.4.24.4	Microorganisms
Collagenase	3.4.24.3	*Clostridum histolyticum*, vertebrates
Dihydropyrimidine amido hydrolase	3.5.2.2	Liver, plants
β-Lactamase II	3.5.2.8	*B. cereus*
Creatine amidino hydrolase	3.5.3.3	Bacteria
Pyrophosphatases	3.6.1.1	Widely distributed
Class 4: Lyases		
Aldolase	4.1.2.13	Bacteria, fungi, yeast (Class II)
L-Rhamnulose-1-phosphate aldolase	4.1.2.9	*E. coli*
Carbonic anhydrase	4.2.1.1	Vertebrates, plants
δ-Aminolaevulinic acid dehydrase	4.2.1.24	Vertebrates
Glyoxalase I	4.4.1.5	Vertebrates, yeast
Class 5: Isomerases		
Mannosephosphate isomerase	5.3.1.8	Yeast
Class 6: Ligases		
tRNA synthetase	6.1.1	*E. coli*
Pyruvate carboxylase	6.4.1.1	Yeast

extremely sensitive probe of the active site of zinc metalloenzymes; although care is needed in any mechanistic extrapolation to zinc since, typically, Cd^{II}-substituted metalloenzymes are often catalytically inactive.

Another technique which has greatly aided the study of zinc metalloenzymes is X-ray crystallography. A recent comparative study,[1267] involving the zinc proteins for which the tertiary structure has been determined, suggests that there exist significant similarities in the active-site regions of these enzymes. These similarities presumably arise in part from the coordination requirements of Zn^{II}. Even with this technique caution is necessary; slightly different procedures for growing the protein 'crystal' can lead to the isolation of different crystal forms which are both structurally different and have different reactivity. Examples of this are to be seen with carboxypeptidase A[1268] and doubtless other examples will emerge. Furthermore, the X-ray method applied to proteins, unlike its application to simpler crystals, depends on accurate knowledge of the amino acid sequence; cases exist, *e.g.* in earlier studies on carbonic anhydrase, where the sequence was in error at a residue and this obviously necessitated structural revision.

As Galdes and Hill point out in a valuable survey of work on zinc metalloenzymes for the year 1979,[1241c] it is remarkable that, in spite of intensive research, the precise function of zinc in metalloenzymes is still not fully understood. A survey of the enzymes reviewed then reveals that in almost every case zinc enzymes act on C—O groups; (i) as hydratases (*e.g.* carbonic anhydrase), or (ii) as hydrolyases (*e.g.* peptidases, β-lactamase II), or (iii) by aiding the oxidoreduction (*e.g.* alcohol dehydrogenase) and rearrangement (*e.g.* aldolases) of such groups. Two types of mechanism whereby the Zn^{II} can effect these reactions have been proposed. One, the zinc carbonyl mechanism, proposes that the substrates bind directly to the Zn^{II} through the oxygen of the C—O group, the Zn^{II} polarizes the group, facilitating nucleophilic attack at carbon (*e.g.* carbonic anhydrase, peptidases) or attack by the bound oxygen atom (*e.g.* nucleotidyl polymerases). The second, the zinc hydroxide mechanism, proposes that the Zn^{II} acts through a water molecule, bound to the metal ion, the function of the Zn^{II} being to lower the pK_a of the bound water molecule from ~14 to ~7. The resultant metal-bound hydroxide ion can then attack the carbon atom of the susceptible C—O group (*e.g.* carbonic anhydrase, peptidases), or acts as a proton acceptor and ionizes the oxygen atom to O^- (*e.g.* alcohol dehydrogenase). It is of course possible that Zn^{II} can act in either manner, depending on the enzyme in question. The zinc carbonyl mechanism has generally found more support than the zinc hydroxide mechanism, and at one time or another has been proposed to be operating for all the major zinc metalloenzymes, including carbonic anhydrase, carboxypeptidase, alcohol dehydrogenase and aldolase. The most definitive example of this type of mechanism was thought to be supplied by carboxypeptidase A, where X-ray diffraction studies have shown the pseudosubstrate Gly-Try is bound to the active site Zn^{II} through the peptide carbonyl group. However, the validity of this X-ray study to the mechanism of the enzyme has been questioned, and in 1979 it was claimed in one publication, for the first time since the diffraction results appeared over 10 years before, that the enzyme uses a zinc hydroxide mechanism in its catalysis. Perhaps the best case for a zinc hydroxide mechanism can be made for carbonic anhydrase; for this enzyme a large amount of experimental evidence obtained during the past decade and a half, including work reviewed below, supports such a mechanism. However, even for carbonic anhydrase, this mechanism has not yet found universal support, and there is some evidence that the C—O group of the substrate is bound to the metal during catalysis. Clearly the coordination flexibility of zinc, which we have seen demonstrated throughout Sections 56.1.3–12, makes it well suited to this function.

The latest proposed mechanisms[1462] for several zinc-containing metalloenzymes combine elements from both types of mechanism by suggesting that the substrate binds to the enzyme through the C—O group, but that in the process the metal-bound water molecule is not displaced, so that the reaction proceeds *via* a five-coordinate intermediate. This hybrid mechanism is discussed below in greater detail for alcohol dehydrogenase.

Concerning the role of observable intermediates, it should be pointed out that there is an important mechanistic principle[1269] which applies to all reactions (not only enzymic ones) which is commonly overlooked: it is simply that the isolation of an intermediate does not necessarily mean that the intermediate lies on the reaction pathway. Furthermore, the observation of an intermediate in a reaction which has reached a stationary state does not necessarily mean that that intermediate lies on the reaction pathway.[1269,1270] The problem can sometimes be solved by examining the non-stationary state, where more complex kinetics are then observed, *e.g.* consecutive, concurrent or mixed regimes may be used to reach the stationary state; or by examining the absolute magnitudes of rate constants bearing in mind such restrictions as diffusion limits; or, in some cases, by using isotope effects. Studies of these latter kinds have been done on some zinc metalloenzymes but not many.

We shall now briefly outline some of the features of the zinc metalloenzymes which have attracted most research effort; several reviews are available, these are indicated under the particular enzyme, and for more detailed information the reader is referred to these. Attention is focussed here, albeit briefly, on carbonic anhydrases,[1241,1262,1268] carboxypeptidases, leucine amino peptidase,[1241,1262] alkaline phosphatases and the RNA and DNA polymerases.[1241,1262,1462] Finally, we examine alcohol dehydrogenases in rather more detail to illustrate the use of the many elegant techniques now available. These enzymes have also attracted much effort from modellers of the enzymic reaction and such studies, which reveal much interesting coordination chemistry and often new catalytic properties in their own right—and often little about the enzyme system itself (except to indicate possibilities), will be mentioned in the next section of this chapter.

56.1.14.1.1 Carbonic anhydrases

Carbonic anhydrases are zinc metalloenzymes present in animals, plants and certain microorganisms; they catalyze the reversible hydration of carbon dioxide ($CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$). In addition to this physiological reaction, carbonic anhydrases also catalyze the hydrolysis of many esters and the hydration of several aldehydes. Those best characterized, the bovine and human enzymes, are monomeric, containing one mole of tightly bound zinc per 30 000 RMM.[1262,1271] X-ray crystallographic studies[1268,1272] of the human enzyme reveal that the zinc ion lies near the bottom of a deep cleft, coordinated to the imidazole groups of three histidyl residues in a distorted tetrahedral geometry. Two of the histidyl imidazoles are close together (residues 94 and 96) and are coordinated through the 3′ N; the remaining one is at a more remote site in the chain (residue 119) and is coordinated through the 1′ N. The fourth coordination site is presumably occupied by a water molecule. Such studies have undergone a number of revisions in detail.[1262,1268,1462]

Despite the fact that carbonic anhydrase was the first zinc metalloenzyme identified[1253] and a good deal is known of its structure, there is still controversy about the nature of the various active-site species and the detailed mechanisms of their action. In particular, the identity of the group with a pK_a of ~7 that is involved in the mechanism, and the stereochemistry around the zinc ion during catalysis, are still in dispute. The various mechanisms proposed assume either ionization of a histidine imidazole group (bound or not to the zinc) and nucleophilic attack on CO_2 by the coordinated imidazolate anion,[1273,1274] or ionization of the Zn^{II}-coordinated water and nucleophilic attack on CO_2 by OH^-.[1271] Many papers on this problem have appeared recently and the extensive literature is the subject of the several review articles referred to above.

56.1.14.1.2 Peptidases—carboxypeptidases

The zinc-containing carboxypeptidases are secreted as an inactive precursor or zymogen (procarboxypeptidase) in the pancreatic juice of animals.[1275] As their name implies, these enzymes catalyze the cleavage of the C-terminal amino acid from proteins and peptides; they also catalyze the hydrolysis of certain esters.[1276] Bovine carboxypeptidase A, one of the most intensively studied zinc metalloenzymes, contains one mole of zinc per mole of protein (RMM 34 500)[1277] and removal of the metal results in a totally inactive apoenzyme.[1278] The activity can be restored by zinc or one of a number of other metal(II) ions.[1279] These metal substitution studies provide an elegant demonstration of the role of the metal ion during catalysis. Table 2 compares the kinetic parameters for the Zn^{II}-, Co^{II}-, Mn^{II}- and Cd^{II}-enzyme-catalyzed hydrolysis of a peptide substrate and its structurally analogous ester substrate. These data indicate that the primary role of the metal in peptide hydrolysis is its catalytic function, and that it has little to do with peptide binding, while the reverse is true for ester hydrolysis.[1280] X-ray structural examination[1281,1282] shows the molecule to be ellipsoidal, with a cleft (containing the Zn) associated with the active site. The zinc is bound to two histidyl imidazole side chains (residues 69 and 196) and the carboxyl group of a glutamate residue (residue 72). The fourth position is presumed to be occupied by a water molecule which may be replaced by substrate when the substrate is bound. Distorted tetrahedral geometry is observed. Other catalytic residues in the active site include Glu-270, Tyr-248 and Arg-145 so here we have a beautiful illustration of the zinc ion working with other groups in the active site to achieve catalysis. This kind of organic–inorganic cooperativity is often a striking feature of metalloenzymes, aspects of which have been recently reviewed.[1462,1466a].

Based on the crystallographic data, detailed mechanisms for the carboxypeptidase A enzymic reaction have been proposed.[1283] These mechanisms and recent work relating to them have been reviewed.[1284,1285,1462,1466a] Although probably correct in general, these mechanistic conclusions are based on the assumption that the kinetic and chemical properties are conserved on crystallization. In general coordination chemistry examples abound where the structures of species in the crystal and in solution are markedly different and indeed it has been shown[1286,1287] that the detailed kinetics of carboxypeptidase A solutions differ from those of the enzyme crystals. It has been suggested that different conformations of the active site exist in the two physical states.[1288] Detailed kinetic studies on crystals over a range of enzyme concentrations, substrate concentrations and crystal sizes have been carried out[1289] and the results interpreted in terms of a recent theory for insolubilized enzymes.[1290] The marked differences

Table 2 Metallocarboxypeptidase-catalyzed hydrolysis of Bz-(Gly)$_2$-L-Phe and Bz-(Gly)$_2$-L-OPhe[a]

Metal	k_{cat} (min^{-1})	$10^{-3}K_M^{-1}$ ($1\ mol^{-1}$)	$10^{-4}K_{cat}$ (min^{-1})	K_M^{-1} ($1\ mol^{-1}$)
Cobalt	6000	1.5	3.9	3300
Zinc	1200	1.0	3.0	3000
Manganese	230	2.8	3.6	660
Cadmium	41	1.3	3.4	120

[a] Assays performed at 25 °C, pH 7.5, 1.0 M NaCl and a buffer concentration of 0.05 M Tris for peptide hydrolysis and 10^{-4} M Tris for ester hydrolysis.[1280]

between the kinetic behaviour of crystals and solutions were confirmed and shown to be genuine, and not due to artifacts arising from diffusion limitations or surface phenomena. It was found that, for all substrates examined, crystallization of the enzymes markedly reduces catalytic efficiency (k_{cat} is reduced 20- to 1000-fold). Also, substrate inhibition, apparent in solution for some di- and depsi-peptides, was not observed in reactions using the crystals. Larger substrates with normal kinetics in solution could exhibit activation with the crystals. The physical state of the enzyme also affected the mode of action of known modifiers of the peptidase activity of the enzyme. Similar differences between the solution and crystal kinetics were observed for carboxypeptidase B.[1291] It has been concluded[1289] that these differences raise serious questions about the capability of crystallography to delineate binding modes, as well as to visualize possible mechanisms of the enzymic reaction. Dynamic studies have shown the existence of rapidly interconvertible structures of carboxypeptidase A in solution. For example, resonance Raman spectra[1292] of arsanilazotyrosine-248 carboxypeptidase A solution contain multiple, discrete bands which change with pH, demonstrating the existence of interconvertible species, and similar conclusions have been reached on the basis of CD measurements;[1293] ^{15}N NMR has also been useful with this derivative.[1466c] Crystallization, however, might single out a particular conformation which does not permit the most efficient catalysis. This is suggested to be a possible reason for the observed kinetic differences between the crystals and the solutions of carboxypeptidase.[1289,1291] Different crystal habits may also be generated by changing the conditions of crystal growth and this has led to controversy concerning the disposition of the hydroxyphenyl side chain of tyrosine-248 in the resting enzyme; again the arsanilazo derivative of this side chain provided a useful means of resolving this controversy. Comprehensive reviews are available.[1241,1268,1262,1462,1466a] Other carboxy peptidases have also been studied recently; see for example ref. 1466b.

(*i*) *Leucine aminopeptidase*

The essential Zn^{II} atoms (two per subunit) in this hexameric enzyme from bovine lens have been substituted with Mn^{II}, Co^{II}, Cd^{II} and Mg^{II} by dialysis of the native enzyme against solutions of these cations.[1294] The amount of metal bound was reported to be in the range 6–12 moles per mole of protein. This substitution gives active Mn^{II}- and Co^{II}-substituted enzymes; the Mg^{II}- and Cd^{II}-substituted enzymes are inactive. The native bovine enzyme is activated by Mg^{II} and Mn^{II}.[1295] The stability of the hexameric structure of the bovine enzyme in solutions of guanidine hydrochloride has been investigated.[1296] The hexameric structure is retained in 0.5 M-guanidine hydrochloride (from 0.75 M to 2.5 M guanidine–HCl). Dissociation into trimers occurs, while above 2.75 M guanidine–HCl momomers dominate and partial unfolding of the subunits accompanies dissociation.[1296]

Reports relating to the quaternary structure of leucine aminopeptidases have appeared,[1297,1298] including a preliminary X-ray study.[1299] In the latter work at 2.2 Å resolution a $P6_322$ space group is revealed, the dimensions of the unit cell being $a = 132$ and $c = 122$ Å. The asymmetric unit is a protomer of RMM 54 000.

Leucine aminopeptidase may be isolated from *Aspergillus oryzae*.[1300] The RMM (37 500) of this enzyme is significantly smaller than that from mammalian sources, but, like the latter, it is a metalloenzyme.

(ii) Other proteases

The active site of thermolysin, a zinc endopeptidase isolated from *Bacillus thermoproteolyticus,* is reported[1301] to be similar to that of carboxypeptidase, and these two enzymes seem to be the product of convergent evolution. An NMR investigation[1302] of the ionizable residues at the active site of the Mn^{II}-substituted enzyme shows two perturbing groups with pK_a values of approximately 8.5 and 9.5. These were tentatively assigned to Tyr-157 and the metal-bound water molecule. The binding behaviour of the inhibitor *N*-trifluoroacetylphenylalanine to this Mn^{II}-substituted enzyme strongly suggests that there are two binding sites on the enzyme, the tighter of which leads to non-productive binding.

Some years ago, collagenase from the microorganisms *Clostridium histolyticum* was shown to be a zinc metalloenzyme;[1303] mammalian collagenases are also zinc metalloenzymes.[1304] The collagenase-like peptidase of rat testis[1305] has also been shown independently to be a zinc metalloenzyme.

Holmquist[1306] has shown that, in contradiction to earlier reports,[1307] *Bacillus cereus* 'microprotease' is a monomeric enzyme containing one mole of Zn^{II} per RMM of 34 000, and is thus a typical zinc-containing neutral protease. Earlier reports[1307] that this enzyme was oligomeric, with a subunit to RMM 2700, seem to have been due to autocatalytic digestion of the enzyme. Several reports[1308,1309] on the isolation and characterization of new metallo-neutral proteases have appeared recently and reviews are available.[1241,1462]

56.1.14.1.3 Alkaline phosphatases

Alkaline phosphatases from various species and locations catalyze[1257,1310] the hydrolysis of alkyl and aryl phosphates and show maximum activity in the pH range 7.5–10.0. Zinc is an integral component of those enzymes which have been adequately characterized, that from *Micrococcus sodonensis* being an exception.[1311] The enzyme from *E. coli,* RMM 80 000 has been most intensively investigated. It is dimeric with two identical subunits; when isolated with precaution against the zinc loss, *E. coli* alkaline phosphatase contains four moles of Zn^{II} per mole of the dimer. The addition of the first two zinc ions to the apoenzyme is sufficient to restore activity, the second two further stabilizing the protein structure. An early report[1312,1313] of the magnesium content was largely overlooked until relatively recently, when it was found[1314,1315] that the binding of magnesium increases the activity of the enzyme containing two moles Zn per mole and that containing four moles Zn per mole. It has been shown that,[1316] although the zinc ion content is clearly four moles per mole, the magnesium content is closely related to the conditions chosen for optimal growth of the organism and purification of the enzyme. These are not the conditions which optimize the binding of magnesium ion. As isolated, the enzyme often contains two moles Zn per mole, but the evidence seems conclusive that there are a maximum of six metal sites available, four of which normally bind Zn^{II} and two Mg^{II}. The relationship between the binding of the metal ions (Zn^{II} and Mg^{II}) required for full activity and the protein structure has been explored[1317] using differential scanning calorimetry. It is an interesting application of the latter technique which gives, *inter alia,* the thermodynamic parameters accompanying protein unfolding. It is found that binding of the first two Zn^{II} ions markedly increases the stability of the enzyme by 290 kJ mol^{-1}, and there is also some indication of cooperativity in binding. The next pair of Zn^{II} ions to be added further stabilize the protein by ~125 kJ mol^{-1}, and the suspected role of the Mg^{II} ion in further stabilizing the protein is confirmed by this study. As anticipated, Mg^{II} does not affect the stability of the protein when Zn^{II} is absent. The entropy contribution to the relative free energy suggests that the internal order in the metalloproteins is greater than that in the apoenzyme.

The enzyme can be reconstituted with six moles Co^{II} per mole; the Co^{II} can therefore presumably occupy both the sites accommodating the four Zn^{II} ions and those which are normally occupied by two Mg^{II} ions. In an investigation[1318] of the oxidation of the Co^{II} ions to Co^{III} (the latter having the useful property of being relatively inert with respect to the rate of replacement of its ligands, provided that structural distortion is not too severe), it was observed that alkaline phosphatase containing six moles of Co^{II} is more rapidly inactivated in H_2O_2 than that containing four moles, which in turn is more rapidly inactivated than that containing two moles. Only two moles of Co^{II} per mole of enzyme are oxidizable. It was suggested from a study of the peroxide oxidation in the presence of zinc and magnesium that Co^{II} ions bound to the site which normally binds Mg^{II} are not oxidizable and that only two moles of the Co^{II} at the remaining sites can be oxidized to Co^{III}. Interestingly, oxidation of only one mole of Co^{II} per dimer was sufficient to prevent reactivation on subsequent zinc addition, implying non-equivalence of the dimeric phosphatase metal-binding sites.

The relationship between the sites that bind metal ions has also been studied,[1319] using ^{31}P and ^{113}Cd NMR spectroscopy; these techniques have provided valuable information on the influence of metal-ion binding, cooperativity and phosphate binding.

Alkaline phosphatases from other sources have been investigated, for example, alkaline phosphatase from human liver has been purified[1320] and found to be a tetrameric glycoprotein of RMM about 136 000. The purification requires the presence of zinc and magnesium, otherwise activity is lost. Whereas the Mg^{II} could be replaced[1321] (with retention of activity) by Ca^{II} or Mn^{II}, no other metal ion, remarkably, not even Co^{II}, could replace the requirement for Zn^{II}. In these experiments the concentrations of the various metal ions were controlled by the addition of complexing agents. As pointed out by Galdes and Hill, this is not without risk since, not only do such agents inhibit the enzyme (by removing the metal ions), but they can bind quite tenaciously to the protein, perhaps, thereby, complicating studies of the binding of metal ions and its relation to activity.

Further information, especially concerning recent developments, on these intriguing species is to be found in recent reviews.[1241,1262,1462,1466d,e]

56.1.14.1.4 RNA and DNA polymerases

The RNA and DNA polymerases offer the first insight into the possible origin of the dramatic consequences of zinc deprivation or deficiency; their importance cannot be overemphasized. They may possibly have roles in processes from ageing to cancer. In studies[1322] on *Euglena gracilis,* for example, grown in a medium seriously deficient in zinc, defects were observed[1323] in nucleic acid and protein synthesis, and even in cellular division. The interesting feature is that all stages of cellular development in this organism were affected, *i.e.* those analogous to the first growth period, G_1, the period which follows (characterized by DNA synthesis), S, and the second growth period, G_2, to mitosis require zinc. There has been much activity in the investigation of these nucleotidyl transferases, in particular, DNA polymerases[1324–1326] and RNA polymerases.[1327–1329] It has previously been shown that some RNA-dependent DNA polymerases[1330–1332] (reverse transcriptases) from tumour viruses contain zinc. In addition, elongation factor 1 from rat liver, which catalyzes the binding of aminoacyl-tRNA to an RNA-ribosome site through the formation of an aminoacyl-tRNA–EF1–GTP ternary complex, requires zinc.[1333] An important recent report shows that the s-Met-tRNA synthetase from *E. coli* contains zinc.[1334] These and similar results emphasize the importance of zinc in the growth and development of all organisms.

There has been much research on the location of the zinc ions, the interaction of template or substrate with the enzymes, and the relationship of zinc and an 'activator' metal ion (usually magnesium) to the fidelity of transcription. The DNA-dependent RNA polymerase from *E. coli* which contains two moles of zinc ions per mole of enzyme has[1335] the subunit structure $\alpha_2\beta\beta'\sigma$. The separated subunits obtained in the presence of 7 M urea do not contain zinc. However, both the β and β' subunits take up zinc ions to give 0.6 ± 0.3 and 1.4 ± 0.5 moles of tightly bound zinc ions per mole of subunit respectively. It was suggested that at least one of the two tightly bound zinc ions in the RNA polymerase is located in the β' subunit, whilst the other Zn^{II} ion may be in β', or β, or at the contact domain of these two subunits.

Since methods for the replacement of zinc by other metal ions are relatively unexploited in this area, the reported isolation[1336] of the DNA-dependent RNA polymerase from *E coli* grown in a medium that is deficient in Zn^{II} and supplemented with Co^{II} is of great value in assessing the role of the metal ion. After a slight lag, upon the introduction of the Co^{II} ions, the growth of the organism recovered. This provides a dramatic illustration of the close similarity between the properties, both structural and functional, of the zinc proteins and of their Co^{II} analogues. The purified enzyme contains 1.8–2.2 moles of cobalt per mole of enzyme, it is enzymically as active as the Zn—RNA polymerase, and the physical properties are practically identical. The absorption spectrum in the 500–800 nm range of Co—RNA polymerase shows two major peaks which are thought to be associated with two different Co^{II} ions since they are differently affected by the addition of substrates or templates. Oxidation of the Co^{II} to Co^{III} results[1335] in at least one Co^{III} ion remaining tightly bound to the isolated β' subunit, even in the presence of 6.5 M urea. This is consistent with other work on the same enzyme, which suggested[1336] that one of the two intrinsic metal ions is located in the β' subunit that is responsible for DNA binding and the other metal ion may be in β' or β subunit, or at the contact domain of these two subunits. Unfortunately, in view of the recent[1337] interpretation of the inhibition mechanism, the effects of 1,10-phenanthroline upon the spectrum were not reported. Kinetic studies showed that the two enzymes had the same V_{max}; K_m values for UTP and ATP were also similar, though the apparent K_m for T7 DNA was less for the cobalt enzyme. Transcription accuracy was the same for both enzymes, but the Co—RNA polymerase is less efficient in initiating RNA chains, as revealed by rates of GTP/ATP incorporation into the 5′-terminal of RNA products. The important finding is that the metal ion of RNA polymerase is involved in recognition of the promotor and specific initiation in RNA synthesis.

These studies relate directly to the role(s) of the zinc. The zinc ion may coordinate the 3′-OH of the terminal nucleotide in the growing RNA chain, be involved in recognition of specific promotor sites on the DNA template, or be required for the maintenance of the proper subunit arrangement. Recent EXAFS studies on the zinc binding sites in the protein transcription factor IIIA used by RNA polymerase III show that each of the (probably nine) zinc ions present is coordinated by 2 His and 2 Cys, the protein being arranged in a series of chain-grasping fingers held in place by the zinc$(His)_2(Cys)_2$ units.[1463]

(*i*) *The role of the activator*

The interaction of Mn^{II}, substrates and initiators with the RNA polymerase from *E. coli* has been investigated.[1338] It was shown that Mn^{II} binds tightly to the enzyme and weakly at 6 ± 1 additional sites. It has been concluded that the tightly bound Mn^{II} is at the site responsible for chain elongation and that the Mn^{II} interacts with the leaving pyrophosphate group. In studies on human DNA polymerase activity *in vitro* it was found[1339] that the substitution of Mn^{II} for Mg^{II} has profound effects on the kinetic parameters of the polymerase reaction. Depending on the reaction conditions Mn^{II} may be as effective as Mg^{II}, strongly preferred or absolutely required. The metal 'activator', in contrast to the tightly bound zinc, appears to have a role concerned with the binding, alignment and conformational change in the incoming deoxynucleoside triphosphate within the active site of the polymerase.

An interesting study[1340] has been made of the effect of different metal activators on the fidelity of DNA synthesis, using the DNA polymerase from avian myeloblastosis virus. With poly[d(A–T)] as a template, the error frequencies for dCMP incorporation were 1:1400, 1:1100 and 1:600 for Mg^{II}, Co^{II} and Mn^{II} respectively. Increasing the concentration of Mg^{II} above that required for maximum activity had no effect on the error frequency, while increasing Co^{II} and Mn^{II} concentration resulted in greater error frequency, due to differential rates of complementary and non-complementary nucleotide incorporation. The effect of Ni^{II} on DNA synthesis was much the same as that of Mg^{II}, but addition of Ni^{II} (or Co^{II} or Mn^{II}) to the Mg^{II}-activated polymerase led to a decreased fidelity of DNA synthesis. It is possible that metal ions such as Mn^{II}, Co^{II} and Ni^{II}, in addition to binding at the Mg^{II} site, also bind to additional sites in the enzyme, with consequent structural changes. The relationship to the carcinogenicity of the metals is briefly considered in this report. Further information on recent developments in this fascinating area is to be found in reviews.[1241,1262,1462]

56.1.14.1.5 Alcohol dehydrogenases

We consider this enzyme, or group of enzymes, in rather more detail as a case history to illustrate the approach used in the study of a typical zinc metalloenzyme.

The enzyme alcohol dehydrogenase, E.C. 1.1.1.1, functions to catalyze the reversible reaction of alcohol oxidation and aldehyde or ketone reduction.

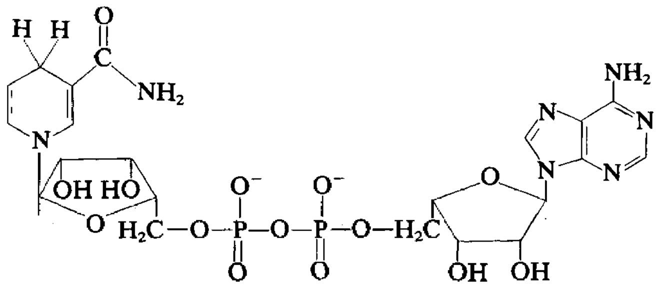
$$RCHO + NADH + H^+ \xrightleftharpoons{\text{dehydrogenase}} RCH_2OH + NAD^+$$

The major substrate is ethanol, but it deals successfully with many other alcohols and carbonyl compounds. The mammalian enzyme was first crystallized by Bonnichsen and Wassén from horse liver in 1947,[1341] but only in the past 15 years has complete structural information been obtained by determination of the complete amino acid sequence and X-ray structure.

Horse liver alcohol dehydrogenase has a molecular weight of 80 000 and is made up of two subunits, each containing two zinc atoms. The subunits are not active in the monomeric form.

The enzyme consists of three main isozymes formed by the dimeric combination of two different protein chains. The two types of protein chains have been labelled E (for ethanol active) and S (for steroid active). About 90% of liver alcohol dehydrogenase (LADH)) is EE and the remaining 10% consists of ES and SS. SS is also ethanol active, although lower than ES and EE, and *vice versa*. Polymeric forms of the isozymes are also known.

Functioning of the enzyme requires the presence of a coenzyme, nicotinamide adenine dinucleotide which exists in its oxidized (NAD^+) or reduced (NADH) forms. The structure of NADH is shown in (**177**). Reduction or oxidation occurs by transfer of the pro-*R* C-4 hydrogen atom of the nicotinamide stereospecifically to or from the substrate. The reaction is therefore a ternary one, with the substrate and coenzyme necessarily within the active site for the reaction to occur.[1465a]



(**177**) NADH

Alcohol dehydrogenase is also obtained from yeast. Yeast alcohol dehydrogenase (YADH) was the first pyridine nucleotide-dependent dehydrogenase to be crystallized by Negelein and Wulff in 1937.[1342] YADH is a tetramer of molecular weight 140 000–150 000. The amount of zinc determined varies,[1343] but there are strong indications that the subunits of YADH and LADH have similar structures, including the presence of two zinc atoms.

Three major isozymes of the yeast enzyme are known.[1344] Isozyme 1 is the classic yeast enzyme which functions in fermentation. The second isozyme has a broader substrate specificity and is selectively produced by yeast grown on lactate or ethanol as the sole carbon source. Both these isozymes are found in the cytoplasm and are repressed by high glucose levels. A third has been shown to be present in the mitochondrion but has been little investigated. The primary structures of the two cytoplasmic alcohol dehydrogenases have recently been determined.[1344] There are fifteen amino acid differences between the two isozymes. These differences are reflected in the different patterns of subunit cooperativity found between the enzymes, since the most significant amino acid differences are found at the interface between the main subunits of the isozyme, and near the cleft separating the coenzyme binding domain from the rest of the subunit. All the residues directly involved in the catalytic mechanism are the same in the two isozymes.

Yeast and mammalian alcohol dehydrogenases differ in substrate specificity and catalytic activity. The yeast enzyme is more specific for acetaldehyde and ethanol, but mammalian enzymes have a broad substrate specificity, and even with primary alcohols maximum activity is not observed with ethanol. Because of the large amount of alcohol dehydrogenase present in human liver and its role in alcohol metabolism in man, human liver alcohol dehydrogenase is of particular interest. It was first purified by Wartburg *et al.*[1345] and crystallized by Mourad and Woronick.[1346] Human liver alcohol dehydrogenase is a dimer with subunit structures analogous to those of horse liver, and each subunit probably contains two zinc atoms. Several different types of human ADH have been isolated.[1347,1348] with minor variations in amino acid composition and reactivity towards ethanol. Alcohol dehydrogenase has now been isolated from a wide variety of other sources including rat,[1349,1465i] monkey,[1350] drosophila,[1351,1352] wheat,[1353] bacteria[1354] and fungi;[1465h] the activities of such ADHs often differ from one source to another.

(*i*) *Structure of enzyme*

The enzyme has been well characterized, the complete amino acid sequence is known, and there have been many crystal structure determinations. The complete amino acid sequence for the liver enzyme was determined by Jörnvall in 1970;[1355] it contained 374 residues, consistent in nature with the tertiary structure, the distribution of hydrophobic residues correlating with the large hydrophobic cores in the protein.

Although the enzyme was first crystallized from horse liver in 1947, it was not until 1963 that preliminary X-ray work was undertaken by Yonetani and Theorell.[1356] The crystal form in which the enzyme is obtained depends on what other species are present. The free enzyme crystallizes in an orthorhombic space group. If other species are present, including the coenzyme, the enzyme crystallizes in two different crystal forms, triclinic and monoclinic, depending on the crystallizing conditions. It was thought that loss of crystallographic symmetry upon coenzyme binding was due to a conformational change induced by coenzyme binding.

The first electron density map obtained at 6 Å resolution gave the overall dimensions of the enzyme and the position of one zinc atom.[1357] A resolution of 5 Å for LADH in the presence of inhibitor revealed the coenzyme binding site.[1358] From a map at 2.9 Å resolution the general folding of the main chain and the position of the second zinc atom was established.[1359] This electron density map showed the organization of the subunit. It is divided into two parts, unequal in size and separated by a wide and deep cleft. The coenzyme-binding domain consists of a sequence of 120 amino acids in the smaller part of the subunit. The structure also revealed the two different types of zinc atom in the enzyme. One, known as the structural zinc atom, is near the surface of the enzyme but completely surrounded by protein chains and not accessible to chelating agents. It plays a role in maintaining the three-dimensional structure of the enzyme. The other zinc, which plays a role in the catalytic mechanism and therefore termed the catalytic zinc atom, is bound at the bottom of the cleft in the subunit by three protein chains.

The extension of this study to 2.4 Å resolution enabled the position of all the side chains to be established, and a plausible mechanism of action for the enzyme to be derived.[1360] The two domains of the LADH subunit are separated by a pocket lined almost entirely by hydrophobic residues. The catalytic zinc is at the bottom of this pocket. The coordination of the catalytic zinc was established as being distorted tetrahedral. It has three protein ligands; two sulfur atoms from Cys-46 and Cys-174 and one nitrogen from His-67. A water molecule or hydroxyl ion, depending on pH, completes a distorted tetrahedral coordination. This pocket is about 25 Å from the surface to the zinc atom. The zinc-bound water molecule is involved in a system of hydrogen bonds which include Ser-48 and His-51. These hydrogen bonds probably play an important part in proton release in the catalytic mechanism. The structural zinc atom is also ligated in a distorted tetrahedral arrangement by four sulfur atoms from cysteine residues 97, 100, 103 and 111. Binding of 1,10-phenanthroline and imidazole has been shown crystallographically to occur at the catalytic zinc and to displace the zinc-bound water molecule of the enzyme, but causes no other structural changes to the enzyme.[1361]

(*ii*) *Binding of coenzyme*[1465a,j]

Although it was initially thought that the coenzyme bound *via* the catalytic zinc atom, Weiner established that the coenzyme is able to bind to zinc-free LADH, and thus established that the zinc is not necessary for coenzyme binding, even though it is not possible for the zinc-free enzyme to react with a substrate.[1362] Further studies showed that the native enzyme possesses additional sites capable of binding the coenzyme.[1363] The coenzyme is bound less strongly at these sites than to the binding sites that also exist in the apoenzyme, but binding of coenzyme to these allosteric sites inhibits catalysis. The location of these additional sites, however, is not established.

Several crystal structures of the enzyme in the presence of the coenzyme and substrate or substrate analogues have served as important indicators of the role of the coenzyme in the enzymic reaction. A crystal structure of the enzyme in the presence of NAD^+ and *p*-bromobenzyl alcohol as substrate revealed that the oxygen of the alcohol is directly bound to the catalytic zinc, thus putting the carbon 1 of the alcohol 3.5 Å from carbon 4 of the nicotinamide ring; the substrate is thus positioned ideally for direct transfer of hydrogen. The position of the alcohol is close to where the water molecule is bound in the free enzyme, but it was not possible to establish whether this had been displaced on binding of the substrate.[1364]

A crystal structure of a ternary complex of horse liver alcohol dehydrogenase with NADH and the inhibitor, dimethyl sulfoxide, first at 4.5 Å resolution[1365] and a further refinement to 2.9 Å resolution,[1366] has been published by Eklund *et al.* The gross structure of the ternary complex is similar to that of the free enzyme structure. Each subunit is divided into a coenzyme-binding domain and a catalytic domain. The subunits are joined together near the coenzyme-binding areas towards the centre of the molecule and the catalytic domains are at the ends of the elongated molecule.

Since previous spectroscopic work indicated that binding of coenzyme triggers a conformational change, it is not surprising that the crystal form of the ternary complex is different from that of the free enzyme. Comparison of the structures show that the main differences of conformation in the presence of NADH are best described as a rotation of the catalytic domains with respect to the central part of the molecule by 7.5°. The two coenzyme-binding domains maintain their relative orientations. The outer edges of the catalytic domains move towards the centre, while the insides move away from the core. The functionally important result of this is that the clefts between the domains become narrower by 1–2 Å, causing the catalytic domain to move closer to the bound coenzyme, and, importantly, this conformational change has the effect of shielding the active zinc site and its surrounds from the solution; hydrogen transfer is thus an essentially nonaqueous process and this effect could play an important role in lowering the activation energy of the reaction.

The area of coenzyme binding within the enzyme is well established;[1343] about 140 amino acid residues build up a pattern of pleated sheets surrounded by α-helices which leads to the creation of a specific crevice for binding of the coenzyme *via* the adenine.

The 2.9 Å resolution structure reveals that the NADH is bound in the enzyme binding domains by an extensive series of hydrogen bonds through the oxygen atoms of the pyrophosphate and the amide group of the nicotinamide. However, no atom in the coenzyme molecule is within bonding distance of the active site zinc atom, the closest being 4.5 Å from the metal ion.

(*iii*) *Subunit equivalence and half-site reactivity*

Some early kinetic studies on the enzymic reaction indicated that LADH exhibits pre-steady state 'half-of-the-sites' reactivity. Bernard *et al.* reported that two distinct kinetic processes, well separated in rate, were observed for the conversion of reactants into products under conditions of excess enzyme.[1367] They also reported that each of the two phases corresponded to conversion of exactly one half of the limiting concentration of substrate being converted to products. On the basis of this they proposed two possible models, the favoured one based on catalytically non-equivalent but interconvertible states of the two binding sites, with the possibility that the asymmetry of the sites may be induced by coenzyme binding. Further evidence for this non-equivalence of the subunits was obtained in similar subsequent studies using a chromophoric nitroso substrate, *p*-nitroso-*N*,*N*-dimethylaniline with limiting NADH concentrations.[1368]

However, in their study of intermediates in the enzymic reduction of acetaldehyde, Shore and Gutfreund could find no inequivalence in the binding sites of the subunits at all NADH concentrations studied.[1369] This conclusion that the two active sites are kinetically equivalent is supported by kinetic studies by Hadorn *et al.*[1370] and by Kvassman and Pettersson.[1371] Work by Kordal and Parsons also supports this conclusion.[1372] They devised a method of persuading ^{3}H-labelled NADH to bind to one site per enzyme molecule and then, using a stopped-flow technique, to react this with excess unlabelled product. Full site reactivity was observed in either direction. They concluded that no half site reactivity was observed, and that there was no indication of subunit asymmetry induced by either the coenzyme binding or by chemical reaction.

In contrast to this Dunn *et al.* have proposed, on the basis of LADH-catalyzed kinetics of 4-deuterio-NADH with a series of substituted benzaldehydes, that the generally accepted mechanism of reaction cannot alone sufficiently account for the results obtained and again proposed that the subunits in the enzyme become kinetically non-equivalent during catalysis.[1373] The arguments put forward by Dunn in this paper have also been discussed by Anderson and Dahlquist who concluded that the biphasic rate behaviour of LADH reflects either a 'half-sites' reactivity mechanism or a complex and as yet not fully understood reaction mechanism.[1374]

In response to these papers, Andersson and Pettersson have published new results reaffirming their conclusions that the enzymic sites are equivalent.[1375] By refining their previous procedures to give increased sensitivity in their kinetic and spectroscopic measurements, they claim to have shown that there is no evidence for subunit inequivalence or interaction, and have shown that adequately interpreted, the results of Dunn[1373] can lead to the same conclusion, *i.e.* that there is no subunit interaction resulting in half-site reactivity and that kinetically the catalytic sites in the enzyme are equivalent.

(iv) *Role of zinc*

Initial attempts to determine the functional role of the zinc were based on the inhibitory effects of various chelating agents such as 1,10-phenanthroline and 2,2′-bipyridyl. These chelating agents inhibit the action of the enzyme by competing with the oxidized or reduced coenzyme, being partially competitive against ethanol, and showing complex behaviour with acetaldehyde. Since the chelating agents are large enough to exclude sterically other molecules, it was not possible to ascertain the role of zinc in binding coenzyme or substrate.[1376]

It was originally assumed that in LADH the zinc existed in an octahedral form with six bonds available for coordination, until in 1967 Vallee and co-workers showed that the enzyme contained two different types of zinc atom.[1377a] Loss of two zinc atoms from the enzyme resulted in loss of catalytic activity but maintained the tertiary structure. It was postulated from this that one metal ion per subunit played a role maintaining the tertiary structure, while the other zinc functioned in a catalytic role. Only two of the zinc ions in the liver enzyme interact with the inhibitors 1,10-phenanthroline and 2,2′-bipyridyl, thus demonstrating the different chemical reactivities of the zinc ions.[1378] It was also shown that one zinc per subunit could be selectively exchanged or removed by dialysis. This modified enzyme containing one zinc per subunit did not bind 1,10-phenanthroline, hence the catalytic zinc is removed first during dialysis.[1379] The second zinc atom can be selectively removed in preference to the catalytic zinc, by carboxymethylation followed by dialysis.[1377a]

(v) *The cobalt-substituted enzyme*[1377b,1464h]

Young and Wang,[1380] by observing the rates of cobalt substitution for zinc, provided further evidence that there are two distinct classes of metal ion present. They showed that cobalt specifically and rapidly replaced two 'easily exchangable' zinc atoms, and replaced the other two zinc atoms much more slowly. Enzymic activity also changed significantly upon replacement of the two easily exchangable metal ions. Kinetic studies by Shore and Santiago, comparing the native zinc and totally cobalt-substituted enzyme showed that the turnover rate at pH 7 was the same for both, but at pH 10 the turnover rate was significantly slower for the cobalt substituted enzyme. These differences would seem to indicate that the metal is involved in the catalytic hydrogen-transferring step of the liver alcohol dehydrogenase mechanism.[1381] The results show that the rate-determining step at pH 7 is NADH dissociation. The lower turnover rate at pH 10 shows a specific effect of pH on the rate-determining step of the cobalt enzyme, which was not shown for the native enzyme. Since a significant isotope effect was found at saturating concentrations of NAD^+ and ethanol, they concluded that the metal is probably involved in the catalytic hydrogen-transferring step of the LADH mechanism. However their findings were inconclusive as to whether there is direct NADH/metal and/or direct substrate/metal interaction at the active site.

Sytkowski and Vallee devised a method of specifically replacing either the non-catalytic or catalytic zinc atoms with ^{65}Zn and thus have been able to prepare $[(LADH)Zn_2{}^{65}Zn_2]$ and $[(LADH)^{65}Zn_2Zn_2]$.[1382] (The first pair are designated as the structural or non-catalytic pair; the second pair the catalytic pair.) They were also able to replace either just the non-catalytic zinc or both sets of metal ions by cobalt, thus preparing $[(LADH)Co_2Zn_2]$ and $[(LADH)Co_2Co_2]$. Preparation of these has enabled the catalytic and non-catalytic sites to be distinguished by their different reactivities.[1382,1383] 1,10-phenanthroline instantaneously and reversibly inhibits $[(LADH)Co_2Zn_2]$ in the same way as it does $[(LADH)Zn_2Zn_2]$, establishing that 1,10-phenanthroline interacts with the zinc in both cases, but in contrast the inhibition of $[(LADH)Co_2Co_2]$ is time dependent and irreversible, indicating that 1,10-phenanthroline competes successfully with the enzyme, presumably because cobalt is bound much more weakly than zinc. The difference in the mode of inhibition allows differentiation of the pair of metal atoms at the catalytic site.

The non-catalytic site can be identified by the much higher reactivity of these metal atoms in metal exchange reactions, and hence they exchange more rapidly. They suggest that the location of the non-catalytic site, near the surface of the molecule, and its more regular coordination (by four cysteine sulfurs) may contribute to the faster exchange rate, than the more distorted catalytic site 25 Å from the surface of the enzyme.

The UV spectra of these complexes are very similar to those found in tetrahedral complexes of Co^{II} known to have a somewhat distorted geometry, suggesting a similar geometry in the cobalt enzyme.[1383] Tetrahedral mercaptide complexes of the type $[Co(SPh)_4]^{2-}$ were also shown to have similar absorption characteristics to those of $[(LADH)Co_2Co_2]$. This work is in complete agreement with the X-ray crystallographic studies of the native LADH, already mentioned, which shows distorted tetrahedral coordination of both the catalytic and non-catalytic zinc atoms of the enzyme.

The structural and catalytic zinc atoms have also been replaced by cadmium-109 by equilibrium dialysis methods similar to that for cobalt, again either replacing just the structural zinc atoms giving $[(LADH)Cd_2Zn_2]$, or both types of zinc giving $[(LADH)Cd_2Cd_2]$. The enzymic activity of both species was similar to the native enzyme.[1384] The cadmium-substituted enzyme is similar in all other respects to the cobalt substituted enzyme, *i.e.* mode of inhibition, UV spectra. The ^{113}Cd NMR spectrum has been observed for the $^{113}Cd^{II}$ fully substituted enzyme and, as expected, shows two resonances corresponding to the two types of cadmium atoms in the enzyme.[1385]

A method has also been developed for specifically substituting the catalytic zinc ions for other transition metal ions in the liver enzyme. This was first reported for substitution by Co^{II}.[1386] In order to achieve this specific substitution, the zinc at the catalytic site is removed by dialysis and this species crystallized. Dialysis of this species against Co^{II} acetate in sufficiently low concentration yielded $[(LADH)Zn_2Co_2]$ with over 90% catalytic activity. The UV spectra show LMCT transitions between Co^{II} and the sulfur ligands at 283 and 370 nm, and a *d–d* transition originating from the metal binding site at 520 nm. These and other spectroscopic data are consistent with substitution at the active site only. Binding of NADH to this species to form the binary complex shows a large increase in the intensity of the cobalt *d–d* transition. Since these transitions are highly dependent on ligand geometry, this probably reflects a distortion of the coordination sphere of the catalytic cobalt ion caused by the conformational change involved.

Insertion of Cu^{II} ions into the enzyme depleted of catalytic Zn^{II} occurs slowly and the deep-blue resultant species, characteristic of type 1 copper proteins, shows little, if any, catalytic activity.[1387] On standing, a solution of this species changes from dark blue to colourless, which is thought to be due to an intramolecular redox reaction yielding the copper(I) species. Possibly, a disulfide bridge is formed between cysteines 46 and 174. This would enable the copper(I) ion to remain bound in the catalytic site, and would be analogous to known Cu^{I} systems.[1388] The blue solution resembles the behaviour of the catalytic-site-substituted cobalt species and the binding of coenzyme to this copper enzyme gives rise to changes in both the optical and ESR spectra which must be interpreted as distortions of the coordination sphere.

Magnetic relaxation studies of this active-site-substituted Cu^{II} enzyme indicate that although it is able to bind coenzyme, thereby distorting its metal binding site, it is unable to discriminate significantly between alcohol substrates and water. The resulting relatively weak binding of alcohol would explain the lack of catalytic activity for the Cu^{II} substituted enzyme.[1389]

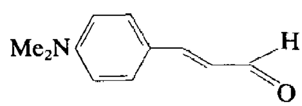
Nickel has also been substituted into the active site of the enzyme.[1390] Although the activity achieved was only about 12%, the spectroscopic properties are consistent with the nickel ions having entered the active site only, with the near tetrahedral geometry maintained. Attempted insertion of Ni^{II} into the non-catalytic sites was not successful.

Attempts to introduce manganese(II) ions into the liver enzyme depleted of zinc at the catalytic sites were unsuccessful.[1391] However, Mn^{II} does bind to the enzyme at two other sites, but the binding is relatively weak compared to what would have been expected at the catalytic sites. Binding of Mn^{II} to these sites is unaffected by the presence or absence of Zn^{II} at the catalytic site. It is also thought that Zn^{II} binds to these sites on reconstituting the enzyme depleted of zinc.

Cobalt-containing yeast alcohol dehydrogenase has been made by growing yeast in media containing cobalt with some zinc present.[1392] The ratio of cobalt to zinc was found to be very close to 1:2. The absorption spectrum of this cobalt-containing enzyme showed large differences from the native enzyme.[1393] By analogy with non-enzymic systems, the spectrum indicated that cobalt(II) was present in a roughly tetrahedral environment, coordinated to at least one cysteine. It was further shown that a water molecule can be displaced by a chelating ligand. In fact, the proposed coordination is remarkably similar to the coordination of the catalytic zinc in LADH, and is probably similar in YADH.

A manganese-containing YADH has been obtained from yeast grown in a zinc-free, manganese-rich medium.[1394] The enzyme was found to have four atoms of metal per enzyme molecule, all of which were manganese. This manganese enzyme is much less stable than the native zinc enzyme and the kinetic parameters are different.

Obviously much of the work following up the preparation of these species has focussed on interpretation of spectroscopic data and distinguishing the catalytic and non-catalytic sites, as well as comparison with the native enzyme. Further investigation of the properties of these transition-metal-substituted enzymes, and looking at the intermediates formed, is a useful means of probing the structural and electronic properties of the catalytic metal ion, and how the catalytic metal ion binds substrate. A particularly useful substrate for investigating the catalytic role of the active site metal ion in the enzyme mechanism has been the chromophoric aldehyde, *trans* 4-(*N*,*N*-dimethylamino)cinnamaldehyde, DACA. In the reduction of DACA, a transient chemical intermediate is formed with LADH and NADH at high pH.[1395] The UV spectra of the complex with the native zinc enzyme shows an absorption maximum of the chromophore red-shifted by 66 nm to 464 nm relative to the free DACA at 398 nm. This was cited as evidence for direct coordination of the carbonyl group of the substrate with the catalytic zinc ion, which acts as a Lewis acid. It was shown that not only is the presence of metal ions in the catalytic site a requirement for binding of the substrate, but also the binding of coenzyme must occur prior to substrate binding, triggering a conformational change before the substrate is coordinated.



(**178**) *trans*-4-(*N*,*N*-Dimethylamino)cinnamaldehyde (DACA)

When cobalt is substituted for zinc at the active site, a similar complex is formed.[1396] The absorption spectra also show a large red shift for the substrate maximum upon binding to form the ternary complex. Binding also causes a small shift in the d–d band.

The resonance Raman spectrum of a similar complex has been reported, that of a ternary complex of LADH, NADH and 4-(*N*,*N*-dimethylamino)benzaldehyde (DABA) with the disappearance of the carbonyl stretching frequency of the DABA at 1664 cm^{-1} also indicating strongly that inner sphere complexation of the substrate occurs, the zinc withdrawing electron density from the aldehyde oxygen forming a zinc–oxygen coordinate bond.[1397]

The Cd^{II}- and Ni^{II}-substituted enzymes also form ternary complexes at high pH with DACA, with similar red shifts of the absorption maxima.[1390] The magnitudes of the red shifts of the DACA absorptions in the ternary complexes with different metalloalcohol dehydrogenases are dependent on the metal present in the active site, as are the dissociation constants for the complexes. If the interaction between the neutral DACA ligand and the metal ion is described as a dipole–metal ion interaction, then the largest red shift will occur with the metal ion with the smallest ionic radius in tetrahedral symmetry. This seems to be the case, with Co^{II} having the smallest ionic radius producing the largest red shift, followed by Ni^{II}, Zn^{II} and the smallest shift for Cd^{II}, which possesses the largest ionic radius. This model is also supported by the dissociation constants showing that DACA is bound most strongly to the smallest ion, Co^{II}. These trends support the idea of a direct inner sphere coordination of the substrate to the metal ion, which is acting as a Lewis acid in these systems. The larger red shifts for Co^{II} and Ni^{II} over Zn^{II} mean that Co^{II} and Ni^{II} are stronger Lewis acids than Zn^{II}.

This conclusion has been further supported by kinetic investigations of the dissociation of DACA from the intermediate with all the metal-ion-substituted enzymes, and of the rate of hydride transfer. Formation of the DACA intermediate occurs as a reversible, rapid, pH-independent step between pH 4 and pH 10.[1398] The decay of the complex however is pH-dependent and undergoes a change in rate-determining step, from hydride transfer at low pH, to release of alcohol product at higher pH. The rate of decay varies with the active site metal present. The rate constant for the hydride transfer process is 1.4 times greater for the Co^{II} species over Zn^{II}, with Ni^{II} having a similar rate constant to the zinc.[1399] The value for Cd^{II} is 40 times smaller. This correlates with the expected order of Lewis acidities (for a tetrahedral ligand field) in the same way as the spectral data, *i.e.* $Co^{II} > Ni^{II} \geq Zn^{II} \gg Cd^{II}$. The large difference in rate constant for the Cd^{II} species is proposed to be a consequence of the longer bonds to Cd^{II}, which could result in a misalignment of reacting atoms and perhaps a different coordination geometry as well as the expected Lewis acid strength.

Not all the spectroscopic data lead to the conclusion that inner sphere coordination of the substrate occurs as a prerequiste for hydrogen transfer. Various NMR studies indicate that substrates are not bound directly to the metal. NMR studies by Sloan *et al.* on the cobalt-substituted enzyme, NADH and the aldehyde analogue isobutyramide measured the effect of Co^{II} on the relaxation rates of protons of the metal-bound water and isobutyramide.[1400] Coenzyme binding causes a small change in the H_2O relaxation, probably due to the conformational change, but binding of the substrate analogue decreases the number of fast exchanging protons by over 50%. From the relaxation measurements, assuming a predominant paramagnetic contribution, the distances between the methyl and methine protons of the isobutyramide and the metal ion were calculated as 7.6 and 7.2 Å respectively. These distances are too great to allow the isobutyramide to be directly coordinated to the active site cobalt ion. To account for this they suggested a model in which the water molecule coordinated to the active site metal ion forms a bridge between the functional group of the substrate and the metal ion, *i.e.* second sphere coordination. This model is substantially different from those proposed on the basis of X-ray diffraction studies.[1364–1366]

In order to show that the origin of this difference is not a function of the particular substrate analogue used, similar NMR relaxation studies have been performed with dimethyl sulfoxide (DMSO)[1401] since the crystal structure of the enzyme–NADH–DMSO ternary complex is well resolved.[1366] From the relaxation data, the distance between the methyl protons of DMSO and Co^{II} was calculated to be 8.9 ± 0.9 Å, again too great for direct coordination of the sulfoxide group to the metal ion. Since the cobalt enzyme appears to be functionally similar to the native enzyme, the difference is unlikely to be a direct result of substitution. One possibility is that there may actually be a difference between the solution and crystalline structure of the enzyme ternary complex, particularly since it is well established that the crystalline enzyme is 1000 times less active than in solution.[1402]

Second sphere coordination has also been proposed on the basis of ^{113}Cd NMR of binary and ternary complexes of cadmium-substituted LADH.[1403] The binding of coenzyme to the cadmium-substituted enzyme, either NAD^+ or NADH, causes the resonance due to the catalytic metal atom to move to higher field. This is not accounted for, but is thought to be due to the conformational change. Addition of butyramide to form a ternary complex shows no change in chemical shift or line width. ^{113}Cd NMR is thought to be very sensitive to nitrogen *vs.* oxygen ligation at cadmium,[1404] but the spectra of ternary complexes with either pyrazole or trifluoroethanol are identical. The authors suggest that these results agree with coordination of the substrate analogue in the second coordination sphere of the metal ion.

More recent NMR studies have questioned the concept of outer sphere coordination of substrate. Andersson *et al.* have suggested that the magnetic relaxation rate of solvent protons in solutions of LADH with Co^{II} ions substituted specifically for zinc at the catalytic site arises mainly from diamagnetic contributions, and the paramagnetic contributions are relatively small.[1389] This puts into doubt the conclusions of Sloan *et al.*[1400] and Drysdale and Hollis,[1401a] who assumed paramagnetic contributions were predominant; their results suggesting second sphere coordination of substrate may require some reinterpretation. ^{15}N NMR has also been informative in this system.[1401b]

(*vi*) *Other chemical modifications*

Carboxymethylation. It was found by Vallee and Li that one cysteine residue per subunit may be selectively carboxymethylated with iodoacetate.[1405] Since this reaction causes deactivation of the enzyme, this cysteine residue, later identified as Cys-46,[1406] was suggested to be at the active site. The deactivated carboxymethylated enzyme still binds NAD^+. The carboxymethylation of this residue is preceded by a reversible binding of iodoacetate to the enzyme.[1407] This observation has helped to identify an anion-binding site in the coenzyme-binding domain, where the pyrophosphate group of the coenzyme binds.

Subsequently this mechanism, known as the affinity labelling mechanism, has also been shown to operate with 2-bromopropionate, 3-bromopropionate and 2-bromobutyrate in a similar way. Iodoacetamide also deactivates the enzyme, but by direct alkylation.[1408]

The reactivity of Cys-46 is dependent on the metal present at the active site as revealed by studies on the fully substituted cobalt and cadmium enzymes.[1409] The rate of alkylation is in the order Co > Zn > Cd. This order correlates with Cys-46 being alkylated as a metal mercaptide, with a strong metal thiol complex making the sulfur a poor nucleophile. This is supported by model studies of alkylation of metal–mercaptoethanol complexes.[1408]

Denaturation. The stability of LADH and its denaturation has been studied under a variety of conditions including acid pH, and different concentrations of urea and guanidine hydrochloride. At pH 5, LADH loses its activity while still in the dimeric state, and at lower pH dissociation occurs, as can be seen in the drastic change in the fluorescence polarization spectrum.[1410] The spectral data obtained are consistent with unfolding of the tertiary structure, some of which occurs before subunit dissociation.

In 7 to 8 M urea, LADH dissociates into two subunits with considerable changes in the tertiary structure.[1411] Similar dissociation occurs in 6 M guanidine hydrochloride. Removal of hydrochloride leads to partial reactivation.[1412] The rates and percentage of reactivation are dependent on the concentrations of NAD^+ and Zn^{II} present. High concentrations of either promote the formation of inactive aggregates of the subunits.[1413] The kinetics of renaturation have been shown to be complex, with no dependence on NAD^+ concentration, but a marked dependence on the rate and yield of reactivation occurs on altering the Zn^{II} concentration. The exact nature of the mode of denaturation and reactivation is not understood, but it is probable that much peptide chain breaking occurs.

The yeast enzyme is reversibly denatured in urea at concentrations of less than 2 M, probably because of dissociation into subunits.[1410] At higher concentrations irreversible denaturation occurs as a result of unfolding of the polypeptide chains.

Inhibitor binding. There is much evidence, wherever binding to LADH has been studied in detail, that all molecules binding to LADH either bind at the coenzyme binding site or at the substrate binding site. Studies on inhibitors at the coenzyme binding site have shown that there are three main binding areas, the adenosine binding cleft, the anion binding site where the pyrophosphate group of the coenzyme binds, and the nicotinamide binding region.

The coenzyme binding region of alcohol dehydrogenase has been shown to be structurally similar to the coenzyme binding region in other pyridine-nucleotide-dependent dehydrogenases, thus it is not surprising to find that inhibitor molecules which are found to be coenzyme-competitive to one particular dehydrogenase would be expected to bind in a similar fashion to other dehydrogenases.[1359,1414]

Dawkins *et al.* have shown that salicylate is a coenzyme-competitive inhibitor to alcohol dehydrogenase as well as malate, lactate and isocitrate dehydrogenase.[1415] Salicylate binding has been studied because of the possible relation between inhibition of dehydrogenases and the pharmacological effects of this molecule. An X-ray study of the binding of iodo-substituted salicyclic acid to LADH shows that the salicylate binds in the same hydrophobic pocket in which the adenosine part of the coenzyme binds, in spite of their very different structures.[1416] The position of the phenyl ring partly overlaps the position of the adenine; the hydroxyl group of the salicylate forms a hydrogen bond to one of the carbonyl groups of Asp-223. This residue has been shown to be the same in several dehydrogenases, indicating its possible importance in coenzyme binding.

X-Ray structures have shown that the anion $[Pt(CN)_4]^{2-}$ binds at the same site on the enzyme as the pyrophosphate group of the coenzyme,[1360] and binds in strict competition with the coenzyme.[1417] UV difference and phosphorescence spectroscopy indicated that coenzyme binding is a result of a combination of ionic and non-polar environments at the adenine binding site of the enzyme and supports the crystallographic studies.[1418] The presence of this anion binding site in the coenzyme binding domain also rationalizes the mechanism of carboxymethylation of Cys-46, already mentioned. The reaction is preceded by a reversible binding of iodoacetate to the enzyme.[1407] The sulfur atom of Cys-46 is coordinated to zinc in a position so that one of its lone pairs is directed towards the anion binding site. The distance from the site to the sulfur atom of Cys-46 is about 8 Å. Therefore iodoacetic acid can be positioned by reversible binding to this anion binding site for subsequent attachment to Cys-46; a typical example of an active-site-directed irreversible inhibitor.

On the basis of the crystal structures available, it has been possible to design active-site-directed inhibitors for LADH. Plapp and Chen have successfully designed and evaluated a series of ω-(bromoacetamido) fatty acids, $[BrCH_2CONH(CH_2)_nCOOH]$, as inhibitors.[1419] As predicted, the carboxylate or carboxamide groups can bind to the catalytic zinc ion in the enzyme–coenzyme complex while the bromoacetamido groups could bind 14 Å away in the substrate-binding pocket. In the absence of coenzyme, the carboxylate groups did, as expected, bind to the anion binding site formed by Arg-47 and Lys-228, and alkylate Cys-46. The rate of deactivation was much retarded in the presence of coenzyme, the mode of deactivation being different.

Substrate-competitive inhibitors. The binding of chelating agents like 2,2′-bipyridine and 1,10-phenanthroline was used in initial attempts to determine the role of zinc in the catalytic mechanism. These inhibitors are competitive with NAD^+ and NADH, partially competitive with ethanol and show complex behaviour with acetaldehyde. It was not possible to ascertain whether the chelating agents were competitive with substrate.[1376] X-Ray studies of the 1,10-phenanthroline complex with the enzyme have shown that the chelating groups bind to the catalytic zinc and displace the zinc-bound water at the substrate binding site.[1361] The large size of the inhibitor molecule probably retards coenzyme binding.

Imidazole also acts as a substrate-competitive inhibitor, forming both binary complexes with LADH, and ternary complexes in the presence of coenzyme. X-Ray studies show that imidazole also binds to the catalytic zinc by displacing the water molecule.[1361] The presence of imidazole at the active site also enhances the rate of carboxymethylation[1465g] of Cys-46 with both iodoacetate and iodoacetamide.[1420] This enhancement of alkylation has become known as the 'promotion effect'.[1421] Imidazole promotion also improves the specificity of the alkylation.[1422] Since Cys-46 is thought to be alkylated as a metal–thiol complex, imidazole, on binding the active site metal, could enhance the reactivity by donating σ electrons to the metal atom, which distributes the increased electron density further to the other ligands in the coordination sphere. The increased nucleophilicity of the sulfur results in promoted alkylation.[1409]

Pyrazole, an isomer of imidazole, was also found to be a potent substrate-competitive inhibitor of LADH in the same way as imidazole. Theorell *et al.* demonstrated that the inhibition is due to the formation of an exceptionally strong enzyme–NAD^+–pyrazole complex.[1423] It has been shown that introducing a substituent on the pyrazole at positions 1 or 3 abolishes the inhibitory power, but substitution with iodine, bromine or alkyl groups in the 4-position greatly enhances its inhibitory action.[1424] However introduction of an unsaturated hydrocarbon residue at the 4-position rendered the pyrazole less active than the corresponding saturated analogues.[1425] The 4-substituted pyrazoles are very sensitive to the nature of the alkyl group; this sensitivity is thought to be due to a combination of lipophilic and electronic factors.[1424,1425]

The pyrazole is thought to coordinate to the catalytic zinc *via* the N-2 nitrogen, the N-1 being coordinated to the pyridine ring of NAD^+ with loss of the imino-H as a proton to neutralize charges. The loss of inhibitory action on substitution at N-1 is in agreement with the proposal on steric grounds, but there is no satisfactory explanation of inhibitor loss on 3-substitution. Andersson *et al.* have shown that the rate of pyrazole dissociation decreases with increasing pH, and that ionization of the enzyme-bound inhibitor has a pK_a value below 4.[1426] This would account for the exceptional stability of the ternary complex at neutral and alkaline pH, but they do not consider it necessary to assume that pyrazole and NAD^+ are covalently linked in the ternary complex formed.

Since a large number of enzymes are known to undergo irreversible deactivation with acetylenic substrates, Alston *et al.* tested for this with both horse liver and yeast alcohol dehydrogenase, using 3-butyn-1-ol.[1427] The substrate is oxidized to a product that is capable of then combining covalently with nucleophilic groups on the enzyme. By analogy with other enzymic systems, this is thought to be *via* an allene intermediate. Many molecules of butynol are oxidized for each enzyme molecule inactivated, and multiple sites of alkylation are suggested.

The first true latent inhibitor for ADH (*i.e.* an inhibitor produced by the catalytic act of the enzyme that is time dependent) was reported as being the substituted allyl alcohol, 3-ethylthioprop-2-en-1-ol.[1428] This is a substrate for LADH, but after a short period the enzyme loses its activity, the rate of deactivation being proportional to the concentration of the alcohol. Latent inhibition was confirmed by showing directly that the aldehyde is an inhibitor. A mechanism is proposed in which the aldehyde formed reacts with an unspecified nucleophilic site on the enzyme with subsequent protonation.[1429]

(*vii*) *Mechanisms for catalysis*[1462]

The catalytic activity of liver alcohol dehydrogenase is strongly pH dependent over a wide range. It has been well established that this pH dependence derives from the combined effects of pH on several steps in the catalytic mechanism. They are all proton equilibria involving ionizable groups, accounting for the net production or consumption of protons during catalysis. An understanding of the pH dependence therefore contributes a major part of the elucidation of the mechanism.

The dissociation of the enzyme–NAD^+ and enzyme–NADH complexes show a pronounced pH dependence which is not present for dissociation of the zinc-free enzyme–coenzyme complex.[1430,1431] Taniguchi *et al.* have calculated that the pH dependences of coenzyme binding to the enzyme can be interpreted as resulting from perturbation of a single residue of $pK_a \sim 8.6$.[1432] More recent investigations confirm this, showing that association of NAD^+ and NADH show the same pH dependence on rate, dependent on a group of $pK_a \sim 9.2$. NAD^+ dissociation is controlled by a group with a pK_a of ~7.6, but there is no pronounced dependence on pH for the rate of NADH dissociation.[1433,1434] Binding of alcohol to the binary complex is dependent on pH above a certain value which varies with substrate,[1433,1435] but a pK_a of ~7.6 controls the uptake. In contrast, there is no effect of pH on the rate of aldehyde binding to the binary complex.[1435]

Although early work by Dalziel indicated that the pK_a regulation of coenzyme binding involved several ionizable residues,[1436] it is now more widely believed that a single residue causes the pK_a perturbations,[1433] but for such a large perturbation, the perturbed group would have to be in the close proximity of the nicotinamide ring of the enzyme-bound NAD^+. The crystallographic results support this proposal,[1360] and the $pK_a \sim 7.6$ dependence of NAD^+ dissociation probably reflects the pK_a of the zinc-bound water molecule linked to a proton relay system in the enzyme.

The presence of coenzyme greatly increases the affinity of the enzyme for substrates.[1437] There is a wide body of evidence to support this.[1465b,c] Fluorescence quenching,[1438] CD spectra,[1439] thermodynamic studies[1440,1441] support evidence from UV studies[1395,1396] and X-ray data[1365] that coenzyme binding triggers a conformational change in the enzyme upon coenzyme binding.

The classical steady-state studies of Theorell and Chance showed that the increased affinity for substrate by the NADH-bound enzyme leads to a distinct sequence of the binding of coenzyme and substrate and subsequent reaction.[1442]. The binding of coenzyme is a compulsory step prior to substrate binding. Release of products from the enzyme site occurs *via* reversal of the sequence. This mechanism, known as an 'ordered bi-bi' mechanism because of the required order of association and dissociation of the coenzyme and substrate with ternary complex formation is summarized in Scheme 6, where E, S and P represent enzyme, substrate and product respectively.

$$\mathrm{E + NADH \rightleftharpoons E(NADH)}$$

$$\mathrm{E(NADH) + S \rightleftharpoons E(NADH, S)}$$

$$\mathrm{H^+ + E(NADH, S) \rightleftharpoons \ldots\ldots \rightleftharpoons E(NAD^+, P)}$$

$$\mathrm{E(NAD^+, P) \rightleftharpoons E(NAD^+) + P}$$

$$\mathrm{E(NAD^+) \rightleftharpoons E + NAD^+}$$

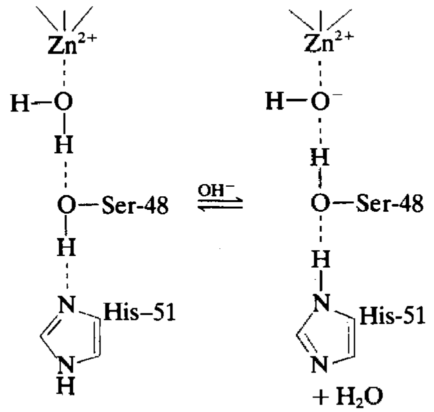
Scheme 6

This scheme accounts for the steady-state and transient-state kinetics of the enzyme under normal conditions.[1343,1371,1442]

Aldehyde formation during the catalytic action of the enzyme requires a net removal of two hydrogen atoms from the alcohol substrate. This dehydrogenation process is known to proceed by a mechanism of combined proton and hydride ion transfer, and it has been well established that transfer of hydride ion occurs directly between substrate and coenzyme in the productive ternary complex.

Various studies suggested that the rate-limiting step in the enzymic reaction involved carbon–hydrogen bond formation and/or breaking.[1369,1444] In the light of this, Jacobs *et al.* compared the electronic substituent effect on the rate of the LADH-catalyzed reduction of aromatic aldehydes with reduction by borohydride.[1445] In contrast to the large substituent effect with borohydride, the electronic substituent effect on LADH reduction is very small. This result was surprising if carbon–hydrogen bond formation or breaking were solely rate limiting. Lack of a substituent effect shows that the reaction cannot be considered as a simple hydride transfer, and so proton transfer must play an important part in modifying enzymic activity.

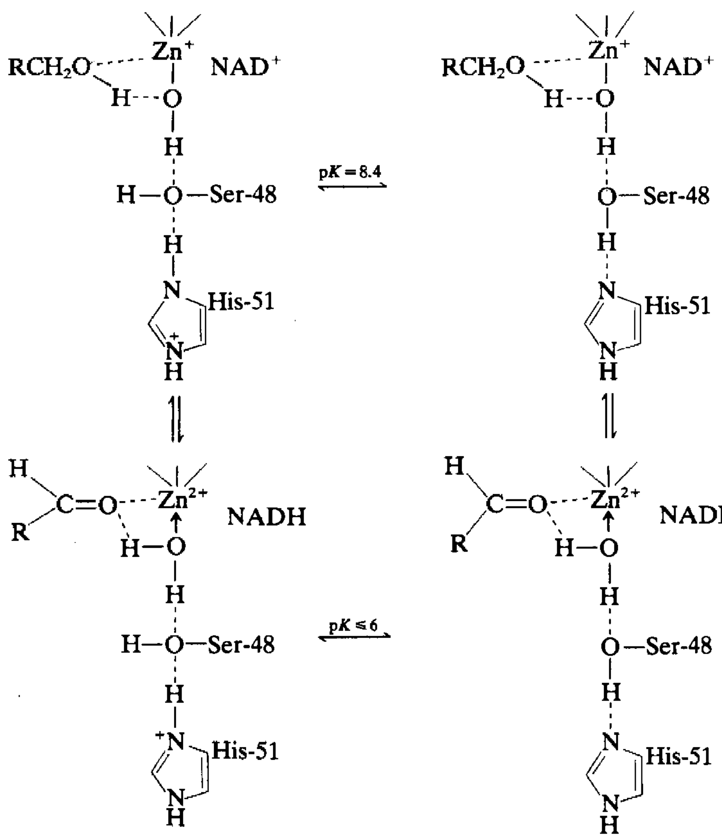
As previously described, there is a water molecule coordinated at the active-site zinc ion, and it has already been suggested that this plays an important role in the mechanism of the enzymic reaction. This water molecule is within hydrogen bonding distance of the hydroxyl group of Ser-48. In turn, this is located within hydrogen bonding distance of His-51. Brändén *et al.* suggested that this system may function as a 'proton charge relay' as illustrated[1360] in Scheme 7. It is suggested that this zinc-bound water molecule and the associated charge relay system plays an acid-base catalytic role in the reaction, and may together or individually account for the dependence of the reaction on several proton equilibria, and the pH dependence at various steps in the reaction.



Scheme 7 Proton charge relay system

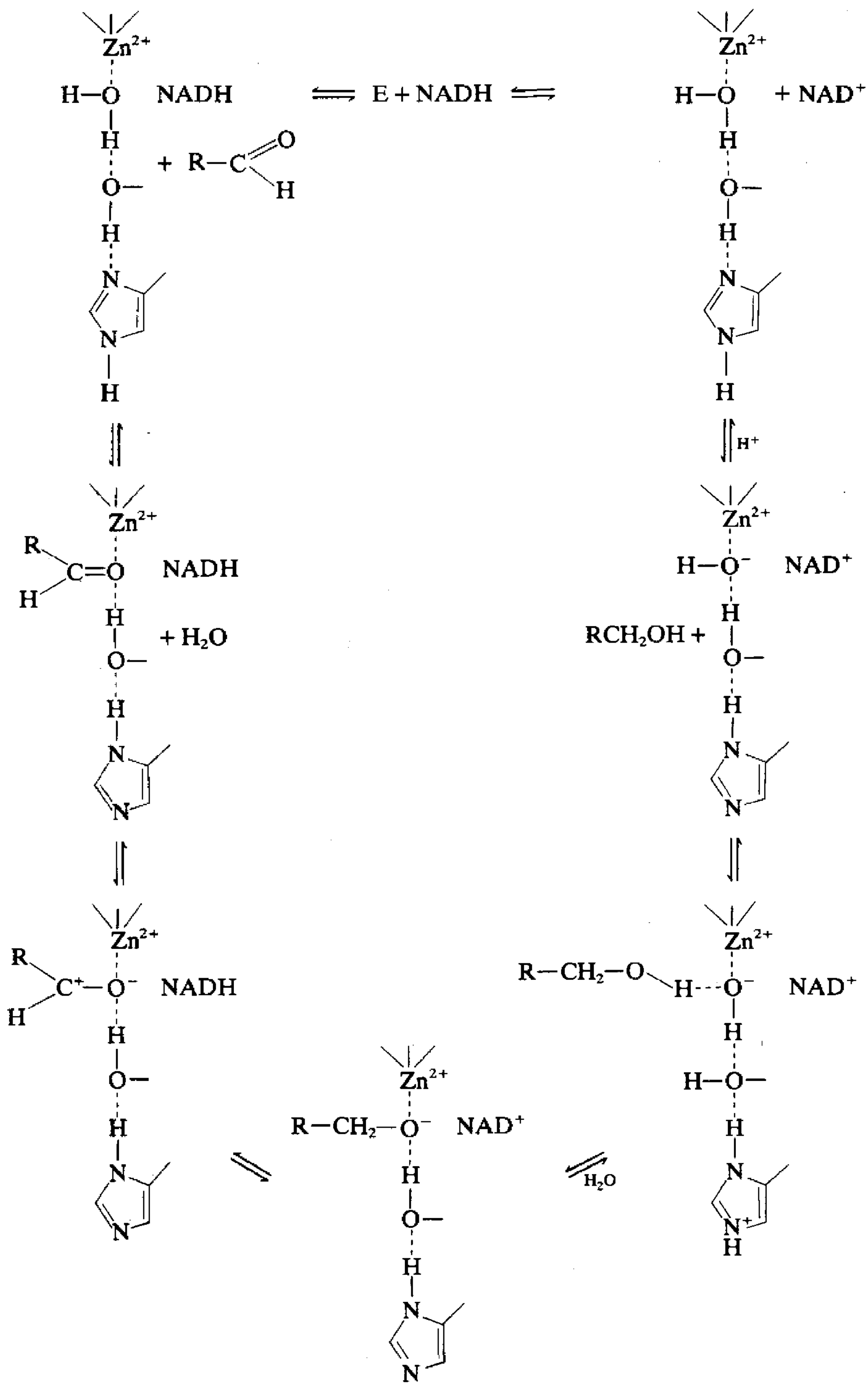
It has also been suggested that the ionization of the zinc-bound water affects the anion binding site of the coenzyme binding domain, the conformational change being triggered through electrostatic interactions in the polar anion binding region in the coenzyme binding domain.[1446]

Dworschack and Plapp presented a mechanism based on this proton relay system and this is shown in Scheme 8.[1447] The alcohol or carbonyl groups are bonded to the zinc, as is the water molecule, giving a five-coordinate zinc.



Scheme 8 Mechanism according to Dworschack and Plapp

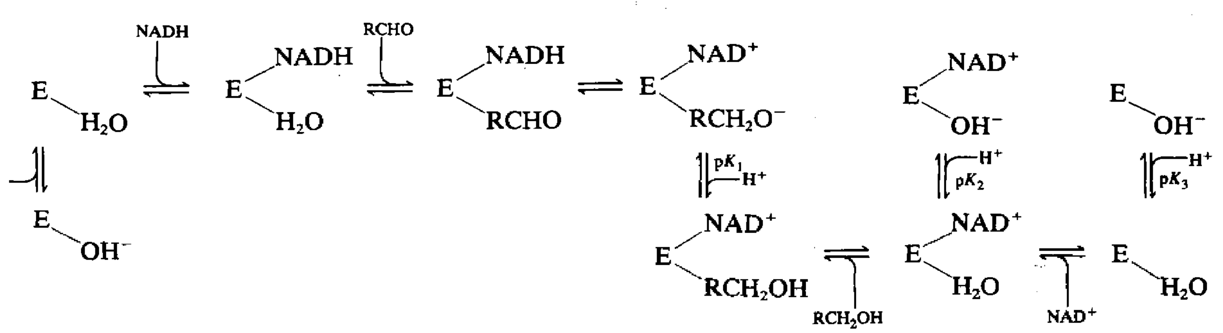
Dunn has also proposed a mechanism involving this charge relay system in ternary complex formation, but with the substrate displacing the zinc-bound water, as shown in Scheme 9.[1443] Hydride transfer from NADH, to form an alcoholate anion, has been shown to occur before protonation.[1398] As well as not requiring penta-coordinate zinc, this mechanism differs from Dworschack and Plapp's in postulating the formation of an alcoholate anion.



Scheme 9 Mechanism after Dunn *et al.*

Both these mechanisms propose that the alcohol substrate combines with the unprotonated form of the enzyme–NAD$^+$ complex. Kvassman and Pettersson have proposed an alternative mechanism in which alcohol binding to the binary complex requires the presence of a neutral water at the catalytic zinc atom.[1435] They also suggest that the kinetic data of Dworschack and Plapp can be understood without the assumption that the water remains in the coordination sphere of the zinc in the ternary complex. They suggest that the pH dependence of the reaction can be accounted for by displacement of water through a dissociative mechanism of ligand substitution of water for substrate.[1448a]

In their mechanism, presented as a series of proton equilibria in Scheme 10, the reaction is controlled by three steps; (a) ionization of the zinc-bound water, which destabilizes the binary complex to an extent that substrate binding cannot occur (pK_3, Scheme 10); (b) a stabilizing effect of alcoholate ion formation in the ternary complex. The pH dependence of this step is the result of ionization of the alcohol.[1449] (c) The dissociation of the alcohol from the ternary complex. This is similar in rate to the dissociation of aldehydes, which might be expected for a substitution mechanism, both neutral species forming structurally similar ternary complexes.



Scheme 10 Proton equilibria suggested to affect the catalytic activity of liver alcohol dehydrogenase by Kvassman and Pettersson

This mechanism, accounting for the observed pH perturbations, does not directly consider the proton charge relay system involving Ser-48 and His-51. However it is probable that this system is important in facilitating, by charge distribution, formation of the alcoholate anion and hydride transfer to NAD^+, and in the reverse reaction, neutralization of the alcoholate anion and alcohol dissociation.

(*viii*) *Other zinc metalloenzymes*

Many systems with intriguing properties and interesting chemical and biochemical properties have been observed recently and are reviewed in refs. 1241a–f, 1262, 1462, 1466f–k, 1468c.

Biomimetic modelling of many zinc metalloenzymes has been the subject of much research which is well served with useful reviews (refs. 9, 10, 11, 16–22, 1241a [pp. 35 *et seq.*]).

Other environmental aspects, which are wide-ranging, are considered in refs. 1448b and 1470.

56.1.14.2 Cadmium and Metallothioneins[1243,1449b,1467a–k]

We have seen (Section 56.1.13.2.2) that cadmium can induce the synthesis of a Cd-binding protein; in fact, the administration of copper, zinc, cadmium or mercury to animals induces the synthesis of these proteins called metallothioneins, which play an important role in the metabolism of these elements.

Historically, the term 'metallothionein' designates the cadmium-, zinc- and copper-containing sulfur-rich protein from horse renal cortex,[1450] and must satisfy several criteria.[1451] (a) The metal content, usually of Cd, Zn or Cu, is very high. (b) The cysteine content is about 30–35% of the total amino acid composition. (c) Aromatic amino acids, histidine and disulfide are usually absent; the mammalian proteins contain only a single methionine residue. (d) The ratio of metal ions bound to SH groups is one-third. Generally, there are seven moles of M^{2+} per 20 to 21 SH groups of metallothionein. (e) The metallothionein has no protein absorption band near 280 nm. (f) RMM's range from 6000 to 7000.

56.1.14.2.1 Occurrence

The metallothioneins have been found in several vertebrate species and in marine invertebrates.[1452] Prinz and Weser purified a copper-containing metallothionein from *Saccharomyces cerevisiae.*[1453] Another copper-binding protein was isolated from *Neurospora crassa.*[1452] The first unequivocal demonstration of a metallothionein in a vascular plant was recently reported.[1455] The amount of metallothionein in different species and tissues is variable. The concentration has been reported to increase up to 40-fold by the induction of its biosynthesis by certain metals such as cadmium or zinc. In new-born rat liver (one to four days old) the concentration of Zn– and Cu–metallothionein is 20 times that in 70-day-old adult rats.[1456] There are several recent reports and reviews in this active area.[1243,1467a–k]

56.1.14.2.2 Primary structure and evolution of metallothioneins

Comparative studies on amino acid sequences of 12 mammalian metallothioneins have been reported.[1457] They are all similar and contain 61 residues; *N*-acetylmethionine and alanine are at the N and C termini, respectively. The cysteinyl residues are distributed fairly uniformly along the polypeptide chain with a predominance of —Cys—X—Cys— sequences.

Metallothioneins from *Neurospora crassa* contain only 25 amino acid residues, but the primary structure is quite similar to the N-terminal part of the mammalian proteins.[1454] These data indicate that the gene that codes for the *Neurospora crassa* metallothionein is evolutionarily related to the gene of the vertebrate metallothioneins. Equine metallothionein exists in two major variants (metallothionein 1A and metallothionein 2A), which show remarkable similarities. Some allelic polymorphic variants also occur in man, horse and rabbit. Recent developments have been comprehensively reviewed.[1467a]

56.1.14.2.3 The metal-binding site

The —Cys—X—Cys— sequences are the primary metal-binding sites and most metal ions can bind at a third cysteinyl residue located elsewhere in the molecule. The resulting trithiolate complexes, $[(\text{metal})^{2+}(\text{Cys}^-)_3]^-$, endow the metallothionein with an overall negative charge at neutral pH. The metal ions are released, on lowering the pH, yielding the apometallothionein, which is stable at low pH but which polymerizes by forming disulfide bridges at neutral pH (reviewed in refs. 1457 and 1467a,b).

56.1.14.2.4 Optical properties and structure of metallothioneins

Since aromatic amino acids and cysteine are absent, there is no protein absorption above 270 nm. Metallothioneins exhibit a broad absorption peak, with the maximum at 190 nm. Absorptions due to the metal–thiolate complexes show as shoulders at 250 nm (Cd), 220 nm (Zn) and 270 nm (Cu).[1458,1459] Theoretical predictions based on the amino acid sequence of the peptide chain indicate that the α-helical conformation is forbidden, and β-structure is almost impossible to attain. CD and NMR studies on both the metal-containing and metal-free protein confirmed the predictions.[1459,1460] However, metallothioneins are stable to tryptic digestion and the slow exchange of many peptide hydrogens of metallothionein with those of the solvent suggest that the protein has a compact and well-defined tertiary structure.

The metabolism of metallothioneins and their role in metal toxicity (*cf.* Section 56.1.13.2) are the subject of a number of recent reviews and papers.[1243,1467a,c–i,k]

56.1.15 REFERENCES

1. B. J. Aylett, 'The Chemistry of Zinc, Cadmium and Mercury', Pergamon, New York, 1975.
2. F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry', 4th edn., Wiley-Interscience, New York, 1980.
3. N. V. Sidgwick, 'The Chemical Elements and their Compounds', Oxford University Press, London, 1950, vols. I and II.
4. M. C. Sneed and R. C. Brasted, 'Comprehensive Inorganic Chemistry', Van Nostrand, 1955, vol. 4.
5. L. Gmelin, 'Handbuch der Anorganischen Chemie', Verlag Chemie, Weinheim, 1924–1971, System Nos. 32 and 33 with supplementary volumes.

6. B. J. Aylett, in 'Comprehensive Inorganic Chemistry', ed. A. F. Trotman-Dickenson, Pergamon, Oxford, 1973, vol. 3, chap. 30.
7. Annual Reports of the Chemical Society, 'Transition Metals' and 'Crystallography' entries, vol. 45 *et seq.*
8. A. F. Wells, 'Structural Inorganic Chemistry', 5th edn., Clarendon, Oxford, 1984.
9. J. A. S. Howell and M. Hughes, 'The Inorganic Chemistry of the Transition Elements' (Specialist Periodical Reports), The Chemical Society, London, 1976, vol. 4, chap. 4, pp. 435 *et seq.*
10. J. A. S. Howell and P. Wyeth, 'The Inorganic Chemistry of the Transition Elements' (Specialist Periodical Reports), The Chemical Society, London, 1977, chap. 4, pp. 402 *et seq.*
11. J. A. S. Howell and P. Wyeth, 'The Inorganic Chemistry of the Transition Elements' (Specialist Periodical Reports), The Chemical Society, London, 1978, Chap. 4, pp. 395 *et seq.*
12. M. N. Hughes, *Coord. Chem. Rev.*, 1981, **37,** 297.
13. E. C. Constable, *Coord. Chem. Rev.*, 1982, **45,** 329.
14. E. C. Constable, *Coord. Chem. Rev.*, 1983, **52,** 1.
15. E. C. Constable, *Coord. Chem. Rev.*, 1984, **58,** 1.
16. J. Burgess (ed.), 'Inorganic Reaction Mechanisms' (Specialist Periodical Reports), The Chemical Society, London, 1971, vol. 1, pp. 179, 192, 237, 247, 260.
17. J. Burgess (ed.), see ref. 16, 1972, vol. 2, pp. 186, 188, 213, 234–236.
18. J. Burgess (ed.), see ref. 16, 1974, vol. 3, pp. 244–249, 280–281, 334, 338–341.
19. A. McAuley (ed.), see ref. 16, 1976, vol. 4, pp. 198, 201, 218, 251, 253–255, 267.
20. A. McAuley (ed.), see ref. 16, 1977, vol. 5, pp. 234, 277, 282–289.
21. A. McAuley (ed.), see ref. 16, 1979, vol. 6, pp. 168, 227, 259, 263, 268, 273, 287, 288, 305, 308–315, 337, 340, 456.
22. (a) A. G. Sykes (ed.), see ref. 16, 1981, vol. 7, pp. 111, 124, 157, 212, 237, 334, 339, 356–362. (b) K. Kustin and J. Swinehart, *Prog. Inorg. Chem.*, 1970, **13,** 107.
23. L. G. Sillén and A. E. Martell, 'Stability Constants', The Chemical Society, London, Chemical Society Special Publication No. 17, 1964 and Supplement No. 1, 1971.
24. (a) A. E. Martell and R. M. Smith, 'Critical Stability Constants', Plenum, New York, vol. 1, Amino Acids; 1975 vol. 2, Amines; vol. 3, Other Organic Ligands; 1976 vol. 4, Inorganic Complexes; vol. 5, First Supplement; (b) W. R. Harris, *J. Coord. Chem.*, 1983, **13,** 17.
25. J. J. Christensen and R. M. Izatt, 'Handbook of Metal—Ligand Heats', Dekker, New York, 1970.
26. (a) F. J. C. Rosotti and H. Rosotti, 'The Determination of Stability Constants and Other Equilibrium Constants in Solution', McGraw-Hill, New York, 1961; (b) F. R. Hartley, C. Burgess and R. Alcock, 'Solution Equilibria', Ellis Horwood, Chichester, 1980.
27. G. E. Maciel and M. Borzo, *J. Chem. Soc., Chem. Commun.*, 1973, 394.
28. R. J. Kostelnik and A. A. Bothner-By, *J. Magn. Reson.*, 1974, **14,** 141.
29. H. Krüger, O. Lutz, A. Schwenk and G. Stricker, *Z. Phys.*, 1974, **266,** 233.
30. R. Colton and D. Dakternieks, *Aust. J. Chem.*, 1980, **33,** 2405.
31. R. Colton and D. Dakternieks, *Aust. J. Chem.*, 1980, **33,** 1677.
32. C. F. Jensen, S. Deshmukh, H. J. Jakobson, R. R. Inners and P. D. Ellis, *J. Am. Chem. Soc.*, 1981, **103,** 3659.
33. B. R. Bobsein and R. J. Myers, *J. Biol. Chem.*, 1981, **256,** 5313.
34. J. L. Evelhoch and D. F. Bocian, *Biochemistry,* 1981, **20,** 4951.
35. P. G. Mennitt and M. P. Shatlock, *J. Phys. Chem.*, 1981, **85,** 2087.
36. P. D. Murphy and B. C. Gerstein, *J. Am. Chem. Soc.*, 1981, **103,** 3282.
37. V. M. Buznik, A. A. Sukhovskii and V. N. Voronov, *Zh. Strukt. Khim.*, 1980, **21,** 154.
38. A. D. Cardin, P. D. Ellis, J. D. Odom and J. W. Howard, *J. Am. Chem. Soc.*, 1975, **97,** 1672.
39. B. W. Epperlein, H. Krüger, O. Lutz and A. Schwenk, *Z. Naturforsch., Teil A,* 1974, **29,** 1533.
40. B. W. Epperlein, H. Krüger, O. Lutz and A. Schwenk, *Z. Naturforsch., Teil A,* 1974, **29,** 660.
41. B. W. Epperlein, H. Krüger, O. Lutz and A. Schwenk, *Phys. Lett. A,* 1973, **45,** 255.
42. T. Shimizu and M. Hatano, *Biochem. Biophys. Res. Commun.*, 1982, **104,** 1356.
43. P. A. W. Dean, *Can. J. Chem.*, 1981, **59,** 3221.
44. G. K. Carson and P. A. W. Dean, *Inorg. Chim. Acta,* 1982, **66,** 157.
45. G. K. Carson and P. A. W. Dean, *Inorg. Chim. Acta,* 1981, **56,** 59.
46. G. K. Carson and P. A. W. Dean, *Inorg. Chim. Acta,* 1982, **66,** 37.
47. A. M. Bond, R. Colton, D. Dakterniaks, M. L. Dillon, J. Hauenstein and J. E. Moir, *Aust. J. Chem.*, 1981, **34,** 1393.
48. H. J. Jakobsen and P. D. Ellis, *J. Phys. Chem.*, 1981, **85,** 3367.
49. C. C. Bryder and C. N. Reilley, *J. Am. Chem. Soc.*, 1982, **104,** 697.
50. R. W. Turner, P. F. Rodesiler and E. L. Amma, *Inorg. Chim. Acta,* 1982, **66,** L13.
51. D. Dakternieks, *Aust. J. Chem.*, 1982, **35,** 469.
52. J. L. Sudmeier, J. L. Evelhoch, S. J. Bell, M. C. Storm and M. F. Dunn, *Calcium-binding Proteins: Struct. Funct.*, 1980, 235.
53. P. D. Ellis, R. R. Inners and H. J. Jakobsen, *J. Phys. Chem.*, 1982, **86,** 1506.
54. T. Mantani and K. T. Suzuki, *Inorg. Nucl. Chem. Lett.*, 1979, **15,** 213.
55. A. A. Sukhovskii, V. M. Buznik and A. G. Lundin, *Fiz. Tverd. Tela,* 1979, **21,** 2852.
56. P. D. Murphy, W. C. Stevens, T. T. P. Cheung, S. Lacelle, B. C. Gerstein and D. M. Kurtz, Jr., *J. Am. Chem. Soc.*, 1981, **103,** 4400.
57. J. A. Happe, *J. Am. Chem. Soc.*, 1973, **95,** 6232.
58. D. K. Lavallee and J. D. Doi, *Inorg. Chem.*, 1981, **20,** 3345.
59. M. Sano, Y. Yoshikawa and H. Yamamoto, *Inorg. Chem.*, 1982, **21,** 2521.
60. B. Borzecka, S. P. Sagnowski and S. Hodorowicz, *Phys. Status Solidi A,* 1981, **64,** 557.
61. R. N. Pletnev, E. A. Nikonenko and V. A. Sharov, *Zh. Neorg. Khim.*, 1981, **26,** 1543.
62. H. B. Brom and J. Bartolome, *Physica B + C (Amsterdam)*, 1981, **111,** 183.
63. M. Hiura, *J. Sci. Hiroshima Univ., Ser. AII, Phys., Chem.*, 1982, **45,** 383.
64. B. Borzecka, S. Hodorowicz and S. Sagnowski, *Proc. 10th Conf. Appl. Crystallogr.*, 1980, 287.

65. M. B. Patel and H. D. Bist, *J. Phys. Colloq.* (*Orsay, Fr.*), 1981, 917.
66. A. B. Yaroslavtsev and Z. N. Prozorovskaya, *Zh. Neorg. Khim.*, 1981, **26**, 2031.
67. L. E. Nivorozhkin, V. I. Minkin, N. I. Borisenko, L. E. Konstantinovskii, M. S. Korobov and R. Ya. Olekhnovich, *Dokl. Akad. Nauk SSSR*, 1981, 5.
68. L. M. Avkhutskii, V. S. Kinchakov and A. N. Petrenko, *Zh. Strukt. Khim.*, 1981, **22**, 174.
69. G. Wulfsberg and A. Weiss, *Ber. Bunsenges. Phys. Chem.*, 1980, **84**, 474.
70. C. I. H. Ashby, W. F. Paton and T. L. Brown, *J. Am. Chem. Soc.*, 1980, **102**, 2990.
71. I. G. R. Gutz and E. F. A. Neves, *Simp. Bras. Electroquim. Electroanal.* (*An.*), *1st*, 1978, 98.
72. M. Kluczkiowski and L. Chmurzynski, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, 1979, **27**, 519.
73. G. V. Rubenacker and T. L. Brown, *Inorg. Chem.*, 1980, **19**, 392.
74. E. O. Azizov, V. S. Grechishkin, T. G. Balicheva and I. V. Pologikh, *Russ. J. Phys. Chem.* (*Engl. Transl.*), 1979, **53**, 90.
75. G. V. Rubenacker and T. L. Brown, *Inorg. Chem.*, 1980, **19**, 392.
76. M. Wada, A. Sawada and Y. Ishibashi, *J. Phys. Soc. Jpn.*, 1979, **47**, 1185.
77. R. Blinc, S. Juznic, V. Rutar and J. Seliger, *Phys. Rev. Lett.*, 1980, **44**, 609.
78. E. Francke, M. Le Postollec and J. P. Mathieu, *Solid State Commun.*, 1980, **35**, 183.
79. M. Takashige and T. Nakamura, *J. Phys. Soc. Jpn.*, 1980, **48**, 150.
80. R. Blinc, V. Rutar, J. Seliger and S. Zumer, *Solid State Commun.*, 1980, **34**, 895.
81. R. Blinc, M. Burgar, J. Slak, V. Rutar and F. Milia, *Phys. Status Solidi A*, 1979, **56**, K65.
82. F. Milia and M. Voudouris, *Phys. Lett. A*, 1980, **76**, 350.
83. X. Han, D. Ji, G. Cheng and Z. Fang, *Kexue Tongbao* (*Engl. Transl.*), 1981, **26**, 1297 (*Chem. Abstr.*, 1982, **96**, 134 613).
84. (a) T. Fujita, T. Yamaguchi and H. Ohtaki, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 3539; (b) C. Furlani, *Coord. Chem. Res.*, 1982, **43**, 355.
85. (a) A. F. Orchard and N. V. Richardson, *J. Electron Spectrosc. Relat. Phenom.*, 1975, **6**, 61; (b) see also A. Almenningen, T. V. Helgaker, A. Harland and S. Samdal, *Acta Chem. Scand., Ser. A*, 1982, **36**, 159.
86. P. Burroughs, S. Evans, A. Hamnett, A. F. Orchard and N. V. Richardson, *J. Chem. Soc., Chem. Commun.*, 1974, 595.
87. J. Berkowitz, *J. Chem. Phys.*, 1974, **61**, 407.
88. G. W. Boggess, J. D. Allen and G. K. Schweitzer, *J. Electron Spectrosc. Relat. Phenom.*, 1973, **2**, 467.
89. L. C. Cussacks, F. A. Grimm and G. K. Schweitzer, *J. Electron Spectrosc. Relat. Phenom.*, 1974, **3**, 229.
90. B. G. Cocksey, J. H. D. Eland and C. J. Danby, *J. Chem. Soc., Faraday Trans. 2*, 1973, **69**, 1558.
91. (a) E. P. F. Lee, D. Law and A. W. Potts, *J. Chem. Soc., Faraday Trans. 2*, 1980, **76**, 1314; (b) R. A. Walton, *Coord. Chem. Rev.*, 1980, **31**, 183.
92. V. I. Nefedov, *J. Electron Spectrosc. Relat. Phenom.*, 1975, **6**, 231.
93. Y. V. Solyn, V. I. Nefedov, M. A. Sarukhanov and Y. Y. Kharitonov, *Koord. Khim.*, 1975, **1**, 945.
94. M. A. Sarukhanov, *Zh. Neorg. Khim.*, 1975, **20**, 2901.
95. T. Yoshida and S. Sawada, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 333.
96. J. Escard, G. Mavel, J. E. Guerchais and R. Kergoat, *Inorg. Chem.*, 1974, **13**, 695.
97. W. von Niessen and L. S. Cederbaum, *Mol. Phys.*, 1981, **43**, 897.
98. L. H. Jones, *Inorg. Chem.*, 1974, **13**, 2289.
99. D. M. Adams and R. E. Christopher, *Inorg. Chem.*, 1973, **12**, 1609.
100. S. J. Cyvin, B. N. Cyvin and R. Andreassen, *J. Mol. Struct.*, 1975, **25**, 141.
101. A. Muller, K. H. Schmidt and G. Vandrish, *Spectrochim. Acta, Part A*, 1974, **30**, 651.
102. G. Dehnicke, K. Dehnicke, H. Ahsbahs and E. Hellner, *Chem. Abstr.*, 1975, **82**, 91 826.
103. J. R. Kessler, E. Monberg and M. Nicol, *J. Chem. Phys.*, 1974, **60**, 5057.
104. A. Givan and A. Loewenschuss, *J. Chem. Phys.*, 1980, **72**, 3809.
105. V. A. Kulikov, V. V. Ugarov and N. G. Rambidi, *Zh. Strukt. Khim.*, 1980, **21**, 201.
106. A. Anderson, Y. W. Lo and J. P. Todoeschuck, *Spectrosc. Lett.*, 1981, **14**, 105.
107. Y. Y. Kharitonov, I. K. Kireeva and A. N. Goryachev, *Koord. Khim.*, 1981, **7**, 701.
108. (a) N. Yellin and Y. Marcus, *J. Inorg. Nucl. Chem.*, 1974, **36**, 1331; (b) P. M. Burkinshaw and C. T. Mortimer, *Coord. Chem. Rev.*, 1983, **48**, 101.
109. A. Sadoc, A. Fontaine, P. Lagarde and D. Raoux, *J. Am. Chem. Soc.*, 1981, **103**, 6287.
110. V. Kothekar, A. Pullman and D. Demoulin, *Inst. J. Quantum Chem.*, 1978, **14**, 779.
111. M. Sano and H. Tamatera, *Chem. Lett.*, 1980, 1495.
112. J. H. Lehn, G. Wipff and J. Demuynck, *Chem. Phys. Lett.*, 1980, **76**, 344.
113. D. L. Kepert, *J. Chem. Soc., Dalton Trans.*, 1974, 612.
114. J. J. Watkins and E. C. Ashby, *Inorg. Chem.*, 1974, **13**, 2350.
115. E. C. Ashby and H. S. Prasad, *Inorg. Chem.*, 1975, **14**, 1608.
116. N. N. Maltseva, N. S. Kedrova, V. V. Klinkova and N. A. Chumaevski, *Zh. Neorg. Khim.*, 1975, **20**, 608.
117. E. C. Ashby and J. J. Watkins, *Inorg. Chem.*, 1973, **12**, 2493.
118. M. A. Porai-Koshits, A. S. Antsyshkina, A. A. Pasynskii, G. G. Sadikov, Yu. V. Skripkin and V. N. Ostrikova, *Inorg. Chim. Acta*, 1979, **34**, L285.
119. A. B. Goel, S. Goel and E. C. Ashby, *Inorg. Chem.*, 1979, **18**, 1433.
120. K. H. Schmidt and A. Müller, *Inorg. Chem.*, 1975, **14**, 2183; K. H Schmidt and A. Müller, *Coord. Chem. Rev.*, 1976, **19**, 41.
121. K. Schmidt, W. Hauswirth and A. Müller, *J. Chem. Soc., Dalton Trans.*, 1975, 2199.
122. T. Yamagughi and H. Ohtaki, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 3227.
123. T. Yamagughi and H. Ohtaki, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 1223.
124. T. Fujita, T. Yamagughi and H. Ohtaki, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 3539.
125. E. C. Constable, *Coord. Chem. Rev.*, 1983, **52**, 1.
126. T. Yamaguchi and O. Lindqvist, *Acta Chem. Scand., Ser. A*, 1981, **35**, 811.
127. K. F. Tebbe, *Z. Kristallogr.*, 1980, **153**, 297.

128. M. C. Chakravorti and M. B. Sarkar, *Transition Met. Chem.* (*Weinheim, Ger.*), 1982, **7**, 19.
129. C. Tellez, *Semina* (*Londrina, Braz.*), 1980, **2**, 73 (*Chem. Abstr.*, 1982, **95**, 228 494).
130. T. Yamagughi and O. Linqvist, *Acta Chem. Scand., Ser. A.*, 1981, **35**, 727.
131. A. Sopkova and J. Bubanec, *J. Mol. Struct.*, 1981, **75**, 73.
132. S. Akyuz, A. B. Dempster and R. L. Morehouse, *Spectrochim. Acta, Part A*, 1974, **30**, 1989.
133. A. B. Dempster, R. L. Morehouse, and H. Uslu, *Spectrochim. Acta, Part A*, 1975, **31**, 1775.
134. T. Iwamoto and M. Kiyoki, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 2414.
135. D. Ulku, *Z. Kristallogr.*, 1976, **143**, 271.
136. P. Gans and J. B. Gill, *J. Chem. Soc., Dalton Trans.*, 1976, 779.
137. P. L. A. Everstein, A. P. Zur and W. L. Driessen, *Inorg. Nucl. Chem. Lett.*, 1976, **12**, 277.
138. A. R. Bates, L. T. H. Ferris and T. E. Jenkins, *J. Phys. Chem.*, 1979, **12**, 2945.
139. M. Drew, L. Guernas, P. Chevalier, P. Palvadeau and J. Rouxel, *Rev. Chim. Miner.*, 1975, **12**, 419.
140. M. N. Hughes and K. Shrimanker, *Inorg. Chim. Acta.*, 1976, **128**, 69.
141. M. A. Sarukhanov, S. S. Val'dan abd N. A. Parpiev, *Chem. Abstr.*, 1975, **84**, 115 299.
142. S. Ahrland and E. Avsar, *Acta Chem. Scand., Ser. A*, 1975, **29**, 890.
143. S. Ahrland and E. Avsar, *Acta Chem. Scand., Ser. A*, 1976, **30**, 15.
144. D. W. Franco, E. A. Neves, and P. Senise, *Chem. Abstr.*, 1975, **83**, 66 340.
145. A. C. Brunner and H. Krischner, *Z. Kristallogr.*, 1975, **142**, 24.
146. G. F. Platzer and H. Krischner, *Z. Kristallogr.*, 1975, **141**, 363.
147. H. T. Spath, H. G. Winkler and K. D. Hendel, *Monatsh. Chem.*, 1976, **107**, 209.
148. H. Winkler and H. Krischner, *Indian J. Chem.*, 1975, **13**, 611.
149. S. S. Val'dman, Z. M. Musaev and Kh. T. Sharipov, *Zh. Neorg. Khim.*, 1981, **26**, 3132.
150. K. C. Patil, C. Nesmani and V. R. P. Verneker, *Synth. React. Inorg. Metal-Org. Chem.*, 1982, **12**, 383.
151. L. Yu Lamanskii and K. I. Tikhonov, *Zh. Obshch. Khim.*, 1979, **49**, 1143; *Zh. Neorg. Khim.*, 1979, **24**, 921; D. W. Franco, E. A. Neeves and M. A. C. Dellatore, *Cienc. Cult.* (*Sao Paulo*), 1978, **30**, 1450.
152. P. Glavic, J. Slivnik and A. Bole, *J. Inorg. Nucl. Chem.*, 1975, **37**, 345.
153. E. A. Nikonenko, E. I. Krylov and V. A. Sharov, *Zh. Neorg. Khim.*, 1975, **20**, 864.
154. Y. Y. Kharitonov, R. I. Machkhoshvili and P. P. Metreveli, *Koord. Khim.*, 1976, **2**, 131.
155. S. S. Nagebashvili, R. I. Machkhosvili, A. E. Shvelashvili, P. V. Gogorishvili and Y. Y. Kharitonov, *Koord. Khim.*, 1975, **1**, 1458.
156. Y. Y. Kharitonov, R. I. Machkhoshvili, P. V. Gogorishvili, and S. S. Nagebashvili, *Zh. Neorg. Khim.*, 1975, **20**, 2630.
157. Y. Y. Kharitonov, R. I. Machkhoshvili, G. V. Tsintsadze, P. V. Gogorishvili and L. K. Nagornaya, *Zh. Neorg. Khim.*, 1975, **20**, 1281.
158. Y. Y. Kharitonov, R. I. Machkhoshvili, L. V. Goeva and R. N. Shchelokov, *Koord. Khim.*, 1975, **1**, 333.
159. Y. Y. Kharitonov, R. I. Machkhoshvili and L. V. Goeva, *Koord. Khim.*, 1975, **1**, 1449.
160. Y. Y. Kharitonov, R. J. Machkhoshvili and L. V. Goeva, *Koord. Khim.*, 1979, **5**, 985.
161. R. M. Issa, Y. M. Temerk, M. R. Mahmound and M. A. Khattab, *Monatsh. Chem.*, 1976, **107**, 485.
162. A. E. Shvelashvili, E. B. Miminoshvili, P. V. Gogorishvili, R. T. Machkhoshvili, N. N. Vekula, A. I. Kvitashvili and B. M. Shchedrin, *Zh. Neorg. Khim.*, 1976, **21**, 292.
163. K. J. Fisher, *Inorg. Nucl. Chem. Lett.*, 1973, **9**, 921.
164. A. Chiesi-Villia, L. Coghi, A. Gaetani-Manfredotti and C. Guastini, *Cryst. Struct. Commun.*, 1974, **3**, 739.
165. A. Chiesi-Villa, L. Coghi, A. Mangia, M. Nardelli and G. Pellizi, *J. Cryst. Mol. Struct.*, 1971, **1**, 291.
166. M. Goldstein and R. J. Hughes, *Inorg. Chim. Acta*, 1980, **40**, 229.
167. A. V. Ablov, G. F. Volodina and L. I. Kabachenko, *Dokl. Akad. Nauk SSSR*, 1980, **4**.
168. J. A. Lee-Thorp, J. E. Rueede and D. A. Thornton, *J. Mol. Struct.*, 1978, **50**, 65.
169. E. W. Abel and S. A. Mucklejohn, *Inorg. Chim. Acta.*, 1979, **37**, 107.
170. E. W. Abel, S. A. Mucklejohn, T. S. Cameron and R. Cordes, *Z. Naturforsch., Teil B*, 1978, **33**, 339.
171. A. Samantray, S. B. Mishra and B. K. Mohapatra, *J. Indian Chem. Soc.*, 1980, **57**, 14.
172. I. Sovago and A. Gergely, *Magy. Kem. Foly.*, 1979, **85**, 428.
173. I. Sovago and A. Gergely, *Inorg. Chim. Acta*, 1979, **37**, 233.
174. N. A. Bell and P. T. Moseley, *Acta Crystallogr., Sect. B*, 1980, **36**, 2950.
175. T. Fujita and H. Ohtaki, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 930.
176. J. Skorsepa, E. Matejcikova and J. Chomic, *Zb. Celostatnej Konf. Term. Anal., 8th*, 1979, 231.
177. W. Bachmann, J. R. Guenter and H. R. Oswald, *Experientia, Suppl.* (*Angew. Chem. Thermodyn. Thermoanal.*), 1979, **37**, 36.
178. S. Nishikiori and T. Iwamoto, *Chem. Lett.*, 1979, 1509.
179. A. E. Shvelashvili and M. A. Porai-Koshits, *Koord. Khim.*, 1975, **1**, 463.
180. A. E. Shvelashvili and M. A. Porai-Koshits, *Koord. Khim.*, 1975, **1**, 467.
181. A. Diaz, M. Massacesi, G. Ponticelli and G. Paschina, *J. Inorg. Nucl. Chem.*, 1975, **37**, 2469.
182. A. E. Shvelashvili, L. M. Chanturiya, N. I. Pirtskhalava, M. Tavberidze, A. I. Kvitashvili and B. M. Shchedrin, *Chem. Abstr.*, 1975, **82**, 10 186.
183. A. E. Shvelashvili, M. A. Porai-Koshits, A. I. Kvitashvili and B. M. Shchedrin, *Zh. Strukt. Khim.*, 1974, **15**, 310.
184. I. S. Ahuja and R. Singh, *Inorg. Nucl. Chem. Lett.*, 1973, **9**, 289.
185. I. S. Ahuja, and R. Singh, *Inorg. Nucl. Chem. Lett.*, 1974, **10**, 421.
186. S. Gothlicher and P. Ochsenreiter, *Chem. Ber.*, 1974, **107**, 391.
187. A. E. Shvelashvili, *Zh. Neorg. Khim.*, 1974, **19**, 568.
188. A. E. Shvelashvili and L. P. Sarishvili, *Zh. Neorg. Khim.*, 1973, **18**, 3133.
189. A. E. Shvelashvili and L. P. Sarishvili, *Zh. Neorg. Khim.*, 1974, **19**, 1015.
190. A. E. Shvelashvili and L. P. Sarishvili, *Chem. Abstr.*, 1974, **80**, 55 448.
191. G. Brun and G. Jourdan, *C.R. Hebd. Seances Acad. Sci., Ser. C*, 1974, **279**, 129.
192. P. K. Migal and E. P. Koptenko, *Zh. Neorg. Khim.*, 1974, **19**, 2313.

193. K. K. Mui and W. A. E. McBryde, *Can. J. Chem.*, 1974, **52**, 1821.
194. S. Htoon and M. F. C. Ladd, *J. Cryst. Mol. Struct.*, 1973, **3**, 95.
195. S. Htoon and M. F. C. Ladd, *J. Cryst. Mol. Struct.*, 1974, **4**, 97.
196. T. Yano, H. Kobayashi and K. Ueno, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 3033.
197. K. D. Gupta, K. K. Goudhary and J. N. Gaur, *J. Indian Chem. Soc.*, 1980, **57**, 382.
198. A. K. S. Ahmed, M. A. Salam and J. A. Khan, *Nucl. Sci. Appl., Ser. B*, 1978, **11**, 24.
199. M. S. Ma and R. J. Angelici, *Inorg. Chem.*, 1980, **19**, 924.
200. S. Nishikiori and T. Iwamoto, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 2236.
201. J. Chomic, J. Skorsepa and J. Cernak, *Monatsh. Chem.*, 1982, **113**, 713.
202. S.-I. Nishikiori and T. Iwamoto, *Chem. Lett.*, 1981, 1775.
203. L. Fabrizzi, M. Micheloni and P. Paoletti, *Inorg. Chem.*, 1976, **15**, 1451.
204. E. Dazzi and M. T. Falqui, *Gazzetta*, 1974, **104**, 589.
205. R. Yang and L. J. Zompa, *Inorg. Chem.*, 1976, **15**, 1499.
206. R. W. Hay and G. A. Lawrence, *J. Chem. Soc., Dalton Trans.*, 1975, 1466.
207. R. W. Hay and B. P. Piplani, *J. Inorg. Nucl. Chem.*, 1976, **38**, 1403.
208. N. F. Curtis, I. R. N. McCormick and T. N. Waters, *J. Chem. Soc., Dalton Trans.*, 1973, 1537.
209. A. Sabatini and A. Vacca, *J. Chem. Soc., Dalton Trans.*, 1980, 519.
210. L. Fabrizzi, M. Micheloni and P. Paoletti, *J. Chem. Soc., Dalton Trans.*, 1980, 1055.
211. L. Banci and A. Dei, *Inorg. Chim. Acta*, 1980, **39**, 35.
212. R. Barbucci, P. Paoletti and A. Vacca, *Inorg. Chem.*, 1975, **14**, 302.
213. C. Y. Ng, R. J. Motekaito and A. E. Martell, *Inorg. Chem.*, 1979, **18**, 2982.
214. B. R. Penfold and P. G. Hodgson, *J. Chem. Soc., Dalton Trans.*, 1974, 1870.
215. A. Vacca and A. Sabatini, *Coord. Chem. Rev.*, 1975, **16**, 161.
216. M. De Ronde, D. Driscoll, R. Yang and L. J. Zompa, *Inorg. Nucl. Chem. Lett.*, 1975, **11**, 521.
217. M. Cannas, G. Carta, A. Cristini and G. Marongiu, *J. Chem. Soc., Dalton Trans.*, 1976, 210.
218. M. Orama and P. Tilus, *Finn. Chem. Lett.*, 1980, 50.
219. M. Cannas, G. Marongiu and G. Saba, *J. Chem. Soc., Perkin Trans. 1*, 1980, 2090.
220. P. K. S. Gupta, L. W. Houk, D. Van der Helm and M. B. Hossain, *Acta Crystallogr., Sect. B*, 1982, **38**, 1818.
221. I. S. Ahuja, R. Singh and C. L. Yadava, *Curr. Sci.*, 1981, **50**, 1017.
222. I. S. Ahuja, C. L. Yadava and R. Singh, *J. Mol. Sci.*, 1982, **81**, 229.
223. I. S. Ahuja, R. Singh and C. L. Yadava, *Spectrochim. Acta, Part A*, 1981, **37**, 407.
224. J. Pickardt, *Z. Naturforsch., Teil B*, 1981, **36**, 1225.
225. L. Sacconi, P. Paoletti and M. Ciampolini, *J. Chem. Soc.*, 1961, 5115.
226. R. Barbucci, L. Fabrizzi, P. Paoletti and A. Vacca, *J. Chem. Soc., Dalton Trans.*, 1973, 1763.
227. E. K. Barefield and F. Wagner, *Inorg. Chem.*, 1973, **12**, 2435.
228. E. J. Billo, *Inorg. Nucl. Chem. Lett.*, 1975, **11**, 491.
229. J. H. Coates, G. J. Gentle and S. F. Lincoln, *Nature (London)*, 1974, **249**, 773.
230. M. Ciampolini, A. Cristini, A. Diaz and G. Ponticelli, *Inorg. Chim. Acta*, 1973, **7**, 549.
231. P. T. Beurskens, W. P. J. H. Bosman and J. A. Cras, *J. Cryst. Mol. Struct.*, 1972, **2**, 183.
232. K. Brodersen, G. Thiel and G. Groz, *Z. Anorg. Allg. Chem.*, 1973, **401**, 217.
233. A. Dei, *Inorg. Chim. Acta*, 1975, **12**, 79.
234. M. J. Potasek, P. G. Debrunner, W. H. Morrison and D. N. Henrickson, *J. Chem. Soc., Chem. Commun.*, 1974, 170.
235. S. Richter, C. Daul and A. V. Zelewsky, *Inorg. Chem.*, 1976, **15**, 943.
236. *Met. Ions Biol. Syst.*, 1979, **9**.
237. see also ref. 1241(a)–(f).
238. A. Gergely and I. Sovago, *Met. Ions Biol. Syst.*, 1979, **9**, 77.
239. D. L. Rabenstein and R. Guevremont, *Met. Ions Biol. Syst.*, 1979, **9**, 103.
240. H. Stunzi, D. D. Perrin, T. Teitei and R. L. N. Harris, *Aust. J. Chem.*, 1979, **32**, 21.
241. R. S. Bottei, H. Chang and D. A. Lusardi, *J. Inorg. Nucl. Chem.*, 1979, **41**, 909.
242. G. Marcotrigiano, P. Morini, L. Menabue and G. C. Pellacani, *Transition Met. Chem.*, 1979, 119.
243. Kh. Kh. Khakimov, N. T. Alimkhodzhaeva, U. F. Khodzhaer and Kh. Kh. Khodzhaeva, *Koord. Khim.*, 1979, **5**, 21.
244. G. Marcotrigiano, L. Antolini, L. Menabue and G. Pellacani, *Inorg. Chim. Acta*, 1979, **35**, 177.
245. A. Demaret, L. Abello, M. Fourati and G. Lapluge, *J. Chem. Res. (S)*, 1978, 354.
246. G. Marcotrigiano, L. Menabue, G. C. Pellacani and M. Saladini, *Inorg. Chim. Acta*, 1979, **32**, 149.
247. S. K. Bhasin and O. Parkashj, *J. Electrochem. Soc. India*, 1980, **29**, 215.
248. I. R. Amiraslanov, G. N. Nadzhafov and B. T. Usubaliev, *Zh. Strukt. Khim.*, 1980, **21**, 140.
249. R. W. Turner, N. G. Charles and E. L. Amma, *Cryst. Struct. Commun.*, 1982, **11**, 241.
250. R. Thulasidhass and J. K. Mohanarao, *Curr. Sci.*, 1980, **49**, 349.
251. S. Bunel, G. Larrazabal and A. Decinti, *J. Inorg. Nucl. Chem.*, 1981, **43**, 2781.
252. H. Soyly, D. Ulku and J. C. Morrow, *Chem. Abstr.*, 1975, **82**, 79077.
253. J. B. Hodgson, G. C. Percy and D. A. Thornton, *Spectrosc. Lett.*, 1979, **12**, 297.
254. L. P. Balkunova and M. K. Kydynov, *Zh. Neorg. Khim.*, 1982, **27**, 1040.
255. A. Gergely, *Inorg. Chim. Acta*, 1981, **56**, L75.
256. M. S. Nair, K. Venkatachalapathi and M. Santappa, *J. Chem. Soc., Dalton Trans.*, 1981, 555.
257. L. D. Pettit and J. L. M. Swash, *J. Chem. Soc., Dalton Trans.*, 1982, 485.
258. H. Kondo, H. Yoshinaga and K. Morita, *Chem. Lett.*, 1982, 31.
259. Z. B. Bakasova, T. T. Tokorbaev, T. S. Kozhanova, V. S. Isaeva, K. A. Dzhusupova and I. G. Druzhinin, *Izv. Akad. Nauk Kirg. SSSR*, 1981, 50 (*Chem. Abstr.*, 1982, **96**, 209 832).
260. R. S. Saxena and S. K. Dhawan, *J. Electrochem. Soc. India*, 1981, **30**, 221.
261. V. V. Ramanujam and V. M. Selverajan, *J. Indian Chem. Soc.*, 1981, **58**, 1131.
262. J. C. Khatri, A. Varshney and Krishna, *Indian J. Chem., Sect. A*, 1981, **20**, 1144.

263. M. M. Islam and B. G. Bhat, *Trans. SAEST,* 1981, **16,** 215.
264. M. Y. Muzumdar and B. I. Nemade, *J. Electrochem. Soc. India,* 1981, **30,** 316.
265. A. R. Aggarwal, K. B. Pendeya and R. P. Singh, *Ann. Chim.* (*Rome*), 1981, **71,** 387.
266. M. Y. Mazumdar and B. I. Nemade, *Trans. SAEST,* 1982, **17,** 5.
267. H. Matsui and H. Ohtaki, *Bull. Chem. Soc. Jpn.*, 1982, **55,** 461.
268. H. Matsui, *J. Inorg. Nucl. Chem.*, 1981, **43,** 2187.
269. M. J. A. Rainer and B. M. Rode, *Inorg. Chim. Acta,* 1982, **58,** 59.
270. M. Y. Nifad'eva and M. K. Kydynov, *Izv. Akad. Nauk Kirg. SSSR.*, 1980, 48 (*Chem. Abstr.*, 1981, **94,** 24 276).
271. G. S. Malik, S. P. Singh and J. P. Tandon, *Indian J. Chem., Sect. A,* 1980, **19,** 922.
272. D. Reddy, B. Sethuram and T. N. Rao, *Indian J. Chem., Sect. A,* 1981, **20,** 150.
273. R. Andreoli, G. B. Gavioli and L. Benedetti, *Inorg. Chim. Acta,* 1980, **46,** 215.
274. V. V. Ramanujam and V. M. Sewlverajan, *J. Indian Chem. Soc.*, 1981, **58,** 125.
275. S. Z. Haider, A. H. M. Ahmed and A. Habib, *J. Bangladesh Acad. Sci.*, 1979, **3,** 81.
276. S. Zhong and W.-D. Yang, *Kao Teng Hsueh Hsiao Hua Hsueh Hsueh Pao,* 1980, **1,** 29 (*Chem. Abstr.*, 1981, **94,** 37 382).
277. A. Gergely, T. Kiss and G. Deak, *Inorg. Chim. Acta,* 1981, **56,** 35.
278. C. Preti and G. Tosi, *J. Coord. Chem.*, 1980, **10,** 209.
279. M. Claude, M. Paris and J. P. Scharff, *J. Chem. Res.* (*S*), 1981, 222.
280. F. Bigoli, E. Leoprati and M. A. Pellinghelli, *J. Chem. Soc., Dalton Trans.*, 1981, 1961.
281. E. Farkas, A. Gergely and E. Kas, *J. Inorg. Nucl. Chem.*, 1981, **43,** 1591.
282. A. R. Aggarwal and H. K. Arora, *J. Inorg. Nucl. Chem.*, 1981, **43,** 601.
283. L. P. Balkunova, M. Y. Nifad'eva and M. K. Kydynov, *Izv. Akad. Nauk Kirg. SSSR,* 1980, 40.
284. D. G. Dhuley and V. G. Dongre, *Indian J. Chem., Sect. A,* 1981, **20,** 208.
285. S. N. Prabhu, S. S. Kelkar and B. I. Nemade, *J. Electrochem. Soc. India,* 1980, **29,** 178.
286. M. M. Palrechae and J. N. Gaur, *J. Electrochem. Soc. India,* 1979, **28,** 233.
287. A. R. Aggarwal and K. B. Pendeya, *Ann. Chim.* (*Rome*), 1981, **71,** 387.
288. R. S. Saxena and S. P. Bansal, *Trans. SAEST,* 1980, **15,** 189.
289. A. K. Jain, K. D. Jain and U. Sharma, *J. Indian Chem. Soc.*, 1980, **57,** 965.
290. V. V. Pal'chevskii and I. V. Mikhailova, *Zh. Prikl. Khim.* (*Leningrad*), 1981, **54,** 739 (*Chem. Abstr.*, 1981, **95,** 31 283).
291. S. K. Shah, K. M. Suyan and C. M. Gupta, *Trans. SAEST,* 1980, **29,** 215.
291. R. S. Sandhu and R. Kumar, *J. Indian Chem. Soc.*, 1981, **58,** 659.
293. R. S. Sandhu and R. Kumar, *Ann. Chim.* (*Rome*), 1980, **70,** 387.
294. A. Goswami, K. K. Chaudhary and J. N. Gaur, *Indian J. Chem., Sect. A,* 1979, **17,** 202; I. Haq, *Monatsh. Chem.*, 1979, **110,** 1205.
295. Kh. Kh. Khakimov and N. T. Alimkhodzhaeva, *Chem. Abstr.*, 1979, **90,** 96 782.
296. V. Zelano, E. Roletto and A. Vanni, *Ann. Chim.* (*Rome*), 1979, **69,** 73.
297. P. G. Daniele and G. Ostacoli, *J. Inorg. Nucl. Chem.*, 1978, **40,** 1273.
298. P. G. Daniele and G. Ostacoli, *Ann. Chim.* (*Rome*), 1978, **68,** 129.
299. P. G. Daniele and P. Amico, *Ann. Chim.* (*Rome*), 1978, **68,** 933.
300. M. S. Mohan, D. Bancroft and E. H. Abbott, *Inorg. Chem.*, 1979, **18,** 2468.
301. I. Haq, *J. Inorg. Nucl. Chem.*, 1978, **40,** 1182.
302. N. P. Sachan and C. M. Gupta, *Indian J. Chem., Sect. A,* 1979, **18,** 82.
303. V. N. Nikitenko, K. I. Litovchenko and V. S. Kublanovskii, *Zh. Neorg. Khim.*, 1979, **24,** 662.
304. H. Matsui, *Chem. Abstr.*, 1979, **91,** 217 721.
305. K. M. Suyan, N. P. Sachan, S. K. Shah and C. M. Gupta, *Indian J. Chem., Sect. A,* 1979, **18,** 81.
306. L. D. Pettit and J. L. M. Swash, *J. Chem. Soc., Dalton Trans.*, 1976, 588.
307. L. D. Pettit and G. Brookes, *J. Chem. Soc., Dalton Trans.*, 1976, 1224.
308. J. H. Ritsma, *J. Inorg. Nucl. Chem.*, 1976, **38,** 907.
309. T. Imanura, C. Hatanaka and N. Kato, *Chem. Abstr.*, 1975, **83,** 209 975.
310. A. Gergely and E. Farkas, *Chem. Abstr.*, 1976, **84,** 35 947.
311. G. D. Zegzhda, V. N. Kabanova and F. M. Tulyupa, *Zh. Neorg. Khim.*, 1975, **20,** 2325.
312. M. Ikram and D. B. Powell, *Chem. Abstr.*, 1975, **83,** 187 583.
313. G. J. M. Heijne and W. E. VanderLinden, *Talanta,* 1975, **22,** 923.
314. A. Braibanti, G. Mori and F. Dallavalle, *J. Chem. Soc., Dalton Trans.*, 1976, 826.
315. J. H. Ritsma, *Recl. Trav. Chim. Pays-Bas,* 1975, **94,** 174.
316. G. K. R. Makar, M. L. D. Touche and D. R. Williams, *J. Chem. Soc., Dalton Trans.*, 1976, 1016.
317. A. M. Corrie, M. D. Walker and D. R. Williams, *J. Chem. Soc., Dalton Trans.*, 1976, 1012.
318. Y. Kojima, *Chem. Lett.*, 1981, 61.
319. G. D. Segzhda, S. I. Neikovskii, F. M. Tulyupa and A. P. Gulya, *Koord. Khim.*, 1979, **5,** 632.
320. R. A. D. Wentworth, P. S. Dahl, C. J. Huffman, W. O. Gillun, W. E. Streib and J. C. Huffman, *Inorg. Chem.*, 1982, **21,** 3060.
321. G. A. Nicholson, J. C. Petersen and B. J. McCormick, *Inorg. Chem.*, 1982, **21,** 3274.
322. V. V. Ramanujam and B. Sivasankar, *J. Indian, Chem. Soc.*, 1981, **58,** 1152.
323. K. Lal, *Chim. Acta Turc.*, 1981, **9,** 361.
324. S. B. Belgarevich, S. I. Adamova, D. Ya. Movshovich, A. A. Polunin, V. A. Kogan, O. A. Osipov and M. V. Khashchina, *Zh. Obshch. Khim.*, 1981, **51,** 2314.
325. W. Kanda, M. Nakamura and H. Okawa, *Bull. Chem. Soc. Jpn.*, 1982, **55,** 471.
326. A. Syamal and B. K. Gupta, *J. Indian Chem. Soc.*, 1981, **58,** 413.
327. A. A. Medzhidov, V. T. Kasumov and K. S. Mamedov, *Koord. Khim.*, 1981, **7,** 66.
328. V. T. Kasumov, M. K. Gusejnova and A. A. Medzhidov, *Zh. Strukt. Khim.*, 1981, **22,** 90.
329. N. B. Pahor, L. Randaccio and E. Libertini, *Inorg. Chim. Acta,* 1980, **45,** L11.
330. V. A. Bhagwat, V. A. Mukhedkar and A. J. Mukhedkar, *J. Chem. Soc., Dalton Trans.*, 1980, 2319.

331. M. Consiglio, *Inorg. Nucl. Chem. Lett.*, 1980, **16**, 227.
332. D. P. Freyburg, G. M. Mockler and E. Sinn, *J. Chem. Soc., Dalton Trans.*, 1976, 447.
333. H. Kanatomi, T. Demura and I. Murase, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 2039.
334. A. C. Braithwaite, P. E. Wright and T. N. Waters, *J. Inorg. Nucl. Chem.*, 1975, **37**, 1669.
335. A. C. Braithwaite and T. N. Waters, *J. Inorg. Nucl. Chem.*, 1973, **35**, 3223.
336. G. C. Percy and D. A. Thornton, *J. Inorg. Nucl. Chem.*, 1973, **35**, 2319.
337. A. Recca and F. A. Bottino, *J. Inorg. Nucl. Chem.*, 1980, **42**, 479.
338. V. P. Litvinov, I. L. Sokol'skaya and Y. P. Popov, *Izv. Akad. Nauk SSSR, Ser. Khim*, 1980, 1774.
339. M. Takahashi and T. Iwamoto, *J. Inorg. Nucl. Chem.*, 1981, **43**, 253.
340. A. R. Hendrickson, J. M. Hope and R. L. Martin, *J. Chem. Soc., Dalton Trans.*, 1979, 1497.
341. D. C. Liles, M. McPartlin, P. A. Tasker, H. C. Lip and L. F. Lindoy, *J. Chem. Soc., Chem. Commun.*, 1976, 549.
342. S. M. Nelson, F. S. Esho and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, 1982, 407.
343. L. Casella and M. Gullotti, *J. Am. Chem. Soc.*, 1981, **103**, 6338.
344. D. Wester and G. J. Palenik, *J. Chem. Soc., Chem. Commun.*, 1975, 74.
345. L. F. Lindoy and D. H. Busch, *Inorg. Chem.*, 1974, **13**, 2494.
346. D. Webster and G. J. Palenik, *J. Am. Chem. Soc.*, 1973, **95**, 6505.
347. P. R. Blum, R. M. C. Wei and S. C. Cummings, *Inorg. Chem.*, 1974, **13**, 450.
348. R. C. Mehrotra, A. K. Rai, A. Singh and R. Bohra, *Inorg. Chim. Acta*, 1975, **13**, 91.
349. H. K. J. Powell and J. M. Russell, *Aust. J. Chem.*, 1978, **31**, 2409.
350. R. R. Gagne, W. A. Marriott, D. N. Marks and W. O. Siegl, *Inorg. Chem.*, 1981, **20**, 3260.
351. P. H. Merrell, E. C. Alyea and L. Ecott, *Inorg. Chim. Acta*, 1982, **59**, 25.
352. B. B. Mahapatra, S. S. Dash and S. K. Pujari, *J. Indian Chem. Soc.*, 1980, **57**, 96.
353. A. Y. Tsivadze, Y. Y. Kharitonov, G. V. Tsintsadze, A. N. Smirnov and M. N. Tevzadze, *Zh. Neorg. Khim.*, 1974, **19**, 2621.
354. H. Herceg and J. Fischer, *Acta Crystallogr., Sect B*, 1974, **30**, 1289.
355. A. Berdiev, B. I. Imanakunov and P. T. Yun, *Zh. Neorg. Khim.*, 1981, **26**, 1110.
356. A. N. Smirnov, A. Y. Tsivadze and G. V. Tsintsadze, *Zh. Neorg. Khim.*, 1980, **25**, 3232.
357. M. A. Porai-Koshits, V. P. Nikolaev and L. A. Butman, *Koord. Khim.*, 1980, **6**, 793.
358. R. C. Aggarwal, B. Singh and T. B. Singh, *Indian J. Chem., Sect. A*, 1980, **19**, 137.
359. A. E. Shvelashrili and R. I. Machkhoshvili, *Zh. Neorg. Khim.*, 1980, **25**, 1779.
360. C. Airoldi, A. P. Chagas and F. P. Assuncao, *J. Chem. Soc., Dalton Trans.*, 1980, 1823.
361. H. O. Desseyn, V. van Riel, L. van Haverbeke and A. Geominne, *Transition Met. Chem. (Weinheim, Ger.)*, 1980, **5**, 230.
362. R. L. Chapman and R. S. Vagg, *Inorg. Chim. Acta*, 1979, **33**, 227.
363. S. K. Sahni, *Transition Met. Chem. (Weinheim, Ger.)*, 1979, **4**, 73.
364. C. Airoldi and A. S. Goncalves, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1817.
365. A. S. Goncalves, A. P. Chagas and C. Airoldi, *J. Chem. Soc., Dalton Trans.*, 1979, 159; C. Airoldi and A. P. Chagas, *Thermochim. Acta*, 1979, **33**, 371.
366. G. V. Tsintadze, A. Yu. Tsivadze and T. V. Kuchuloriya, *Chem. Abstr.*, 1979, **90**, 214 472.
367. B. Dusek and F. Kutek, *Zh. Neorg. Khim.*, 1980, **25**, 2926.
368. S. Z. Haider, K. M. A. Malik and K. J. Ahmed, *J. Bangladesh Acad. Sci.*, 1981, **5**, 81.
369. B. Kamenar and G. Jovanovski, *Cryst. Struct. Commun.*, 1982, **11**, 257.
370. R. I. Machkhoshvili, T. V. Shalamberidze and R. N. Shchelokov, *Zh. Neorg. Khim.*, 1982, **27**, 1725.
371. M. M. Mostafa and D. Nicholls, *Inorg. Chim. Acta*, 1981, **51**, 35.
372. R. I. Machkhoshvili and G. Sh. Mitaishvili, *Zh. Neorg. Khim.*, 1982, **27**, 972.
373. I. A. Krol, M. S. Kvernadze, V. M. Agre and N. I. Pirtskhalova, *Soobshch. Akad. Nauk Gruz. SSSR*, 1981, **103**, 601 (*Chem. Abstr.*, 1982, **96**, 173 287).
374. G. V. Tsintsadze, T. I. Tsivtsivadze, A. I. Kvitashvili and T. N. Turiashvili, *Dokl. Akad. Nauk SSSR (Crystallogr.)*, 1981, **260**, 1136.
375. Y. D. Fridman, O. P. Svanidze, N. V. Dologashova and P. V. Gogorishvili, *Zh. Neorg. Khim.*, 1974, **19**, 3304.
376. J. Macicek, V. K. Trunov and R. I. Machkhoshvili, *Zh. Neorg. Khim.*, 1981, **26**, 1690.
377. F. G. Kramarenko, T. N. Polynova, M. A. Porai-Koshits, Y. P. Chalyi and N. D. Mitrofan'ova, *Koord. Khim.*, 1975, **1**, 1423.
378. U. C. Sinkha, F. G. Kramarenko, T. N. Polynova, M. A. Porai-Koshits and M. D. Mitrofan'ova, *Chem. Abstr.*, 1975, **82**, 163 633.
379. I. Benedikovic, P. Balgavy, J. Majer and E. Fuleova, *Chem. Zvesti*, 1980, **34**, 93.
380. E. V. Lazarevski, L. V. Kubasova and N. N. Chudinova, *Izv. Akad. Nauk SSSR Neorg. Mater.*, 1980, **16**, 120.
381. Yu. M. Kozlov and V. A. Babich, *Zh. Obshch. Khim.*, 1980, **50**, 1116.
382. M. Jawaid, *Talanta*, 1980, **27**, 95.
383. R. W. Hay, K. B. Nolan and M. Shuaib, *Transition Met. Chem. (Weinheim, Ger.)*, 1980, **5**, 230.
384. A. K. Saxena, *Indian J. Chem., Sect. A*, 1979, **17**, 626.
385. J. E. Poldoski and T. J. Bydalek, *J. Inorg. Nucl. Chem.*, 1979, **41**, 205.
386. L. I. Tikhonova, O. I. Samoilova and V. G. Yashunskii, *Zh. Neorg. Khim.*, 1979, **24**, 1237.
387. R. W. Hay, K. B. Nolan and M. M. Shuaib, *Transition Met. Chem.*, 1979, **4**, 142.
388. T. J. Janjic, L. B. Pfenat and V. Popov, *J. Inorg. Nucl. Chem.*, 1979, **41**, 63.
389. R. J. Gualtin, W. A. E. McBryde and H. K. J. Powell, *Can. J. Chem.*, 1979, **57**, 113.
390. E. A. Lance and R. Nakon, *Inorg. Chim. Acta*, 1981, **55**, L1.
391. R. W. Hay, K. B. Nolan and M. Shuaib, *Transition Met. Chem. (Weinheim, Ger.)*, 1980, **5**, 230.
392. J. G. Kloosterboer, *Inorg. Chem.*, 1975, **14**, 536.
393. N. A. Kostromina, D. A. Korovaikov, N. V. Beloshitskii and I. N. Marov, *Zh. Neorg. Khim.*, 1974, **19**, 1192.
394. Y. Yano and M. Houda, *Chem. Abstr.*, 1975, **82**, 38 052.
395. K. H. Shroeder and B. G. Johnsen, *Talanta*, 1974, **21**, 671.

396. L. I. Myachina, V. A. Logvinenko and Z. A. Grankina, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1981, **91** (*Chem. Abstr.*, 1981, **95**, 90 346).
397. Z. Skokanova and J. Krocan, *Zb. Ved. Pr. Vys. Sk. Tech. Kosiciach*, 1980, **71** (*Chem. Abstr.*, 1982, **96**, 96 359).
398. P. Mirti and M. C. Gennaro, *J. Inorg. Nucl. Chem.*, 1981, **43**, 3221.
399. E. H. Curzon, N. Herron and P. Moore, *J. Chem. Soc., Dalton Trans.*, 1980, 721.
400. S. Gonzalez Garcia and F. J. Sanchez Santos, *An. Quim., Ser. B*, 1981, **77**, 178.
401. S. Gonzalez Garcia, F. J. Sanchez Santos and M. R. Morales Ayala, *An. Quim., Ser. B*, 1982, **78**, 22.
402. F. Salinas, A. Guiraum and J. C. Avila Roson, *Afinidad*, 1981, **38**, 531.
403. N. N. Kananaeva, M. Ya. Gorokhovatskaya and N. A. Kostromina, *Ukr. Khim. Zh. (Russ. Ed.)*, 1981, **47**, 1191.
404. V. K. Chitale, S. C. Lavale and K. S. Pitre, *Natl. Acad. Sci. Lett. (India)*, 1981, **4**, 323.
405. U. I. Tikhonova, *Zh. Neorg. Khim.*, 1982, **27**, 1713.
406. R. K. P. Singh, J. R. Yadava and K. L. Yadava, *J. Electrochem. Soc. India*, 1981, **30**, 250.
407. J. Podlahova and J. Podlaha, *Collect. Czech. Chem. Commun.*, 1982, **47**, 1078.
408. R. L. Dutta and R. Sharma, *J. Inorg. Nucl. Chem.*, 1981, **43**, 1062.
409. P. T. Joseph, O. F. Thomas, M. T. Rawther and P. N. Mohandas, *Indian J. Chem.*, 1975, **13**, 970.
410. E. W. Abel and S. A. Mucklejohn, *Inorg. Chim. Acta*, 1979, **37**, 107.
411. V. W. Day, D. H. Campbell and C. J. Michejda, *J. Chem. Soc., Chem. Commun.*, 1975, 118.
412. C. A. Bear, K. A. Duggan and H. C. Freeman, *Acta Crystallogr., Sect. B*, 1975, **31**, 2713.
413. L. R. Nassimbeni and A. C. Rodgers, *Acta Crystallogr., Sect. B*, 1976, **32**, 257.
414. M. R. Cairns, L. R. Nassimbeni and G. Orpen, *Acta Crystallogr., Sect. B*, 1976, **32**, 140.
415. J. C. Jansen and J. Reedijk, *Recl. Trav. Chim. Pays-Bas*, 1976, **95**, 52.
416. K. F. Slyusarenko, M. V. Artemenko, O. M. Kononenko and M. M. Polyachenko, *Chem. Abstr.*, 1976, **84**, 83 515.
417. B. C. Cornilsen and K. Nakamoto, *J. Inorg. Nucl. Chem.*, 1974, **36**, 2467.
418. P. Lumme and P. Virtanen, *Acta Chem. Scand., Ser. A*, 1974, **28**, 1055.
419. J. B. Jensen, *Acta Chem. Scand., Ser. A*, 1975, **29**, 250.
420. I. Granberg and S. Sjoeberg, *Acta Chem. Scand., Ser. A*, 1981, **35**, 193.
421. W. D. Horrocks, Jr., J. N. Ishley and R. R. Whittle, *Inorg. Chem.*, 1982, **21**, 3265.
422. W. D. Horrocks, Jr., J. N. Ishley and R. R. Whittle, *Inorg. Chem.*, 1982, **21**, 3270.
423. P. G. Daniele and P. Amico, *Inorg. Chim. Acta*, 1982, **66**, 65.
424. M. K. Shivhare, N. Jain and M. Singh, *J. Inorg. Nucl. Chem.*, 1981, **43**, 2885.
425. M. Shivhare and M. Singh, *J. Electrochem. Soc. India*, 1981, **30**, 277.
426. P. K. S. Gupta, L. W. Houk, D. Van der Helm and M. B. Hossain, *Acta Crystallogr., Sect. B*, 1982, **38**, 1818.
427. R. J. Broekema, P. F. M. Durville and J. Reedijk, *Transition Met. Chem. (Weinheim, Ger.)*, 1982, **7**, 25.
428. L. Li and G. Xu, *Huaxue Xuebao*, 1982, **40**, 1.
429. J. B. Hodgson, G. C. Percy and D. A. Thornton, *J. Mol. Struct.*, 1980, **66**, 81.
430. L. G. Marzilli, B. de Castro, J. P. Caradonna, R. C. Stewart and C. P. van Vuuren, *J. Am. Chem. Soc.*, 1980, **102**, 916.
431. R. Lehnert and F. Seel, *Z. Anorg. Allg. Chem.*, 1980, **464**, 187.
432. K. F. Slyusarenko, M. V. Artemenko and G. A. Pokhodnya, *Ukr. Khim. Zh.*, 1981, **47**, 350 (*Chem. Abstr.*, 1981, **95**, 17 318).
433. P. J. M. W. L. Birker, A. J. Schierbeek, G. C. Verschoor and J. Reedijk, *J. Chem. Soc., Chem. Commun.*, 1981, 1124.
434. R. J. Read and M. N. G. James, *Acta Crystallogr., Sect. B*, 1980, **36**, 3100.
435. S. V. Laroinov, G. N. Mironova and V. I. Ovcharenko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 977.
436. N. V. Kozhemyak, N. V. Podberezskaya and V. V. Bakakin, *Zh. Strukt. Khim.*, 1980, **21**, 124.
437. J. N. Helbert, P. W. Kopf, E. H. Poindexter and B. E. Wagner, *J. Chem. Soc., Dalton Trans.*, 1975, 998.
438. M. Alei, L. O. Morgan and W. E. Wagermann, *Inorg. Chem.*, 1981, **20**, 940.
439. K. F. Slyusarenko, M. V. Artemenko and G. A. Pokhodnya, *Ukr. Khim. Zh. (Russ. Ed.)*, 1982, **48**, 121.
440. R. Parkash, B. Singh and R. Bala, *Trans. SAEST*, 1981, **16**, 141.
441. I. Soetofte and K. Nielsen, *Acta Chem. Scand., Ser. A*, 1981, **35**, 739.
442. D. I. Semenishin, A. V. Yurchak and Z. V. Slobodyan, *Visn. L'viv. Politekh. Inst.*, 1981, **149**, 7 (*Chem. Abstr.*, 1982, **96**, 114 882).
443. A. Anagnostopoulos, *J. Inorg. Nucl. Chem.*, 1976, **38**, 435.
444. K. Fukushima, T. Miyamoto, and Y. Sasaki, *Inorg. Chim. Acta*, 1975, **15**, 105.
445. J. R. Jezorek and W. H. McCurdy, *Inorg. Chem.*, 1975, **14**, 1939.
446. M. Guichelaar, J. A. M. van Hest and J. Reedijk, *Inorg. Nucl. Chem. Lett.*, 1974, **10**, 999.
447. R. W. M. Ten Hoedt and L. Reedijk, *Inorg. Chim. Acta*, 1981, **51**, 23.
448. R. Faure, H. Loiseleur, R. Bartnik and S. Lesniak, *Cryst. Struct. Commun.*, 1981, **10**, 515.
449. A. Kayali and G. Berthon, *Bioelectrochem. Bioenerg.*, 1979, **6**, 337.
450. R. Lenarcik and B. Barszcz, *J. Chem. Soc., Dalton Trans.*, 1980, **24**.
451. M. S. Subhani, *Pak. J. Sci. Ind. Res.*, 1979, **22**, 35.
452. B. Lenarcik, K. Kirdziel and M. Gabryszewski, *J. Inorg. Nucl. Chem.*, 1980, **42**, 587.
453. P. L. Franke and W. L. Groeneveld, *Transition Met. Chem. (Weinheim, Ger.)*, 1980, **5**, 240.
454. G. V. Kharitonov, V. M. Bolotov and R. I. Kharitonova, *Zh. Neorg. Khim.*, 1979, **24**, 3337.
455. L. G. Lavrenova, S. V. Larionov and W. A. Grankina, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1979, 306.
456. N. B. Singh and J. Singh, *Indian J. Chem., Sect. A*, 1979, **17**, 424.
457. D. W. Engelfriet, W. den Brinker and G. C. Verschoor, *Acta Crystallogr., Sect. B*, 1979, **35**, 2922.
458. B. Pradhan and D. V. R. Rao, *Indian J. Chem., Sect. A*, 1980, **19**, 72.
459. H. Sakaguchi, H. Anzai and K. Furuhata, *Fuksokan Kagaku Toronokai Koen Yoshishu, 12th*, 1979, 306.

460. V. N. Savitskii, V. V. Skopenko, P. V. Gilyanovski, M. I. Knyazhanski, O. A. Osipov, A. D. Garnovski and Z. K. Barkovskaya, *Chem. Abstr.*, 1976, **84**, 68 886.
461. C. Preti and G. Tosi, *J. Inorg. Nucl. Chem.*, 1976, **38**, 1125.
462. A. Cristini, G. Ponticelli and C. Preti, *J. Inorg. Nucl. Chem.*, 1974, **36**, 2473.
463. M. Massacesi, G. Ponticelli and C. Preti, *J. Inorg. Nucl. Chem.*, 1976, **38**, 1556.
464. G. Devoto, G. Ponticelli, C. Preti and G. Tosi, *J. Inorg. Nucl. Chem.*, 1976, **38**, 1744.
465. R. C. Van Lanschoot, J. A. M. Van Hest and J. Reedijk, *J. Inorg. Nucl. Chem.*, 1976, **38**, 185.
466. T. J. Kemp, P. A. Lampe, P. Moore and G. R. Quick, *J. Chem. Soc., Dalton Trans.*, 1981, 2137.
467. W. L. Dreissen and P. L. A. Everstijn, *Inorg. Chim. Acta*, 1980, **41**, 179.
468. J. Terheijden and W. L. Dreissen, *Transition Met. Chem.* (*Weinheim, Ger.*), 1980, **5**, 346.
469. W. Freyer and R. Radeglia, *Monatsh. Chem.*, 1981, **112**, 105.
470. E. Uhlig, *Z. Chem.*, 1978, **18**, 440.
471. D. Attanasio, G. Dessy and V. Fares, *J. Chem. Soc., Dalton Trans.*, 1979, **28**.
472. M. Goldstein and R. J. Hughes, *Inorg. Chim. Acta*, 1979, **37**, 71.
473. A. Furuhashi and H. Yokota, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 3753; B. P. Mishra and D. V. R. Rao, *J. Indian Chem. Soc.*, 1979, **56**, 439; B. K. Mohanty, D. Satyanarayana and B. K. Mohapatra, *J. Indian Chem. Soc.*, 1979, **56**, 526; N. B. Singh and J. Singh, *J. Inorg. Nucl. Chem.*, 1979, **41**, 1384; F. Capitan, E. J. Alonso and M. Jimenez Ruedas, *Chem. Abstr.*, 1979, **90**, 161 393; A. G. Galinos, J. K. Kouinis and P. V. Ioannou, *Z. Naturforsch., Teil B*, 1979, **34**, 1101.
474. J. Esmel and G. Berthon, *Bull. Soc. Chim. Fr.*, 1979, **68**; B. Lenarcik and M. Rzepka, *Pol. J. Chem.*, 1978, **52**, 1629; S. K. Bhasin, O. M. Prakash and J. N. Gaur, *J. Electrochem. Soc. India*, 1978, **27**, 159.
475. O. F. Khodzhaev, T. A. Azizov and N. A. Parpiev, *Zh. Neorg. Khim.*, 1978, **23**, 2942; I. S. Ahuja, R. Singh and R. Sriramulu, *J. Mol. Struct.*, 1979, **53**, 301; A. Yu. Tsivadze, Yu. Ya. Kharitonov, A. N. Smirnov, G. V. Tsintsadze and L. V. Sverdtsiteli, *Zh. Neorg. Khim.*, 1979, **24**, 1269.
476. T. S. Khodashova and M. A. Porai-Koshits, *Koord. Khim.*, 1978, **4**, 1753; V. S. Sergienko and M. A. Porai-Koshits, *Koord. Khim.*, 1978, **4**, 1760.
477. P. T. T. Wong, *Can. J. Chem.*, 1974, **52**, 2005.
478. W. L. Steffen and G. J. Palenik, *Acta Crystallogr., Sect. B*, 1976, **32**, 298.
479. P. T. T. Wong, *Inorg. Chem.*, 1975, **14**, 2271.
480. P. T. T. Wong, *J. Chem. Phys.*, 1975, **63**, 5108.
481. V. I. Berezin and W. Ganin, *Koord. Khim.*, 1976, **2**, 550.
482. T. A. Babushkina, O. K. Poleschuk, Y. K. Maksyutin, A. M. Aylmov, S. D. Solokov and E. I. Mikhailovskaya, *Koord. Khim.*, 1975, **1**, 1266.
483. T. Ibusuki and Y. Saito, *Inorg. Chim. Acta*, 1976, **19**, 87.
484. B. B. Mohapatra, B. K. Mohapatra and S. Curu, *J. Indian Chem. Soc.*, 1979, **56**, 836.
485. A. Furuhashi and H. Yokota, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 3753.
486. J. K. Howie, P. Bosserman and D. T. Sawyer, *Inorg. Chem.*, 1980, **19**, 2293.
487. R. Singh and I. S. Ahuja, *Transition Met. Chem.* (*Weinheim, Ger.*), 1980, **5**, 206.
488. C. D. Rao, B. K. Mohapatra and S. Guru, *J. Indian Chem. Soc.*, 1979, **56**, 631.
489. M. C. Kerr, H. S. Preston, H. L. Ammon, J. E. Huheey and J. M. Stewart, *J. Coord. Chem.*, 1981, **11**, 111.
490. R. J. Collin, *J. Inorg. Nucl. Chem.*, 1975, **37**, 334.
491. J. Bould and B. J. Brisbon, *Inorg. Chim. Acta*, 1976, **19**, 159.
492. H. W. Smith, *Acta Crystallogr., Sect. B*, 1975, **31**, 2701.
493. H. G. Biederman and W. Graf, *Z. Naturforsch., Teil B*, 1974, **29**, 65.
494. H. G. Biederman and E. Griessl, *Z. Naturforsch., Teil B*, 1974, **29**, 132.
495. I. S. Ahuja and R. Singh, *J. Inorg. Nucl. Chem.*, 1974, **36**, 1505.
496. H. Matsui and H. Ohtaki, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 2131.
497. Q.-H. Shi, J.-X. Zhanh and H.-Y. Hu, *Hua Hsueh Hsueh Pao*, 1981, **39**, 272 (*Chem. Abstr.*, 1982, **95**, 210 594).
498. G. V. Tsintsadze, R. A. Kiguradze, A. N. Shnulin and I. R. Amiraslanov, *Nauchn. Tr.-Gruz. Politekh. Inst. Im. V. I. Lenina*, 1980, 5 (*Chem. Abstr.*, 1982, **96**, 95 350).
499. I. S. Ahuja, R. Sriramulu and R. Singh, *Indian J. Chem., Sect. A*, 1980, **19**, 909.
500. D. S. Jain and L. K. Agarwal, *J. Electrochem. Soc. India*, 1979, **28**, 227.
501. A. S. Antsyshkina and M. A. Porai-Koshits, *Koord. Khim.*, 1981, **7**, 461.
502. V. S. Sergienko, V. N. Schurkina and T. S. Khodashova, *Koord. Khim.*, 1980, **6**, 1606.
503. F. Bigoli, A. Braibanti, M. A. Pellinghelli and A. Tiripicchio, *Acta Crystallogr.*, 1973, **29**, 2708.
504. T. P. E. Auf Der Heyde and C. S. Green, *Spectrosc. Lett.*, 1980, **13**, 31.
505. L. S. Gelfand, F. J. Iaconianni, L. L. Pytlewski, A. N. Speca, C. M. Mikulski and N. M. Karayannis, *J. Inorg. Nucl. Chem.*, 1980, **42**, 377.
506. G. V. Tsintsadze and Sh. A. Samsoniya, *Soobshch. Akad. Nauk Gruz. SSSR*, 1979, **96**, 85.
507. L. Kh. Minacheva and T. S. Khodashova, *Koord. Khim.*, 1979, **5**, 1889.
508. V. Scheller-Krattiger, K. H. Scheller, E. Sinn and R. B. Martin, *Inorg. Chim. Acta*, 1982, **60**, 45.
509. J. D. Ortega, S. Upalawanna and S. Amanollaki, *J. Inorg. Nucl. Chem.*, 1979, **41**, 593.
510. Ya. Ya. Kharitonov and G. V. Tsintsadze, *Zh. Neorg. Khim.*, 1980, **25**, 857.
511. S. Barbu and G. Macarovici, *Rev. Roum. Chim.*, 1980, **25**, 207.
512. S. O. Wandiga, *Kenya, J. Sci. Technol., Ser. A*, 1980, **1**, 23.
513. S. E. Livingstone and J. E. Oluka, *Transition Met. Chem.* (*Weinheim, Ger.*), 1980, **5**, 77.
514. R. H. Prince and P. Wyeth, *J. Inorg. Nucl. Chem.*, 1981, **43**, 839.
515. Y. Y. Kharitonov and G. V. Tsintsadze, *Koord. Khim.*, 1980, **6**, 1874.
516. R. Singh and R. S. S. Rao, *J. Mol. Struct.*, 1981, **71**, 23.
517. I. S. Maslennikova, *Zh. Fiz. Khim.*, 1981, **55**, 1038.
518. R. S. Sandhu and R. K. Kalia, *Ann. Chim.* (*Rome*), 1980, **70**, 625.
519. N. Ray and B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1980, 1105.
520. B. Walsh and B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1980, 681.
521. A. J. de Koning, J. Boersma and G. J. M. van der Kerk, *J. Organomet. Chem.*, 1980, **186**, 159.

522. A. J. de Koning, J. Boersma and G. J. M. van der Kerk, *J. Organomet. Chem.*, 1980, **186**, 173.
523. M. Mikami-Kido and Y. Saito, *Acta Crystallogr., Sect B*, 1982, **38**, 452.
524. S. R. Ebner and R. J. Angelici, *Inorg. Chem.*, 1981, **20**, 2971.
525. S. G. Mamuliya, I. V. Pyatnitskii and L. L. Kolomiets, *Zh. Anal. Khim.*, 1980, **35**, 1306.
526. J. Suh, E. Lee and E. S. Jang, *Inorg. Chem.*, 1981, **20**, 1932.
527. E. Uhlig and M. Doering, *Z. Chem.*, 1981, **21**, 73.
528. V. L. Doedken and G. C. Christoph, *Inorg. Chem.*, 1973, **12**, 2136.
529. B. E. Fischer and H. Sigel, *J. Inorg. Nucl. Chem.*, 1975, **37**, 2127.
530. R. C. Agarwal, N. K. Singh and R. P. Singh, *Inorg. Chem.*, 1981, **20**, 2794.
531. J. D. Korp, I. V. Bernal, C. L. Merrill and L. J. Wilson, *J. Chem. Soc., Dalton Trans.*, 1981, 1951.
532. M. G. B. Drew, J. Nelson and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1981, 1685.
533. Y. Yamamoto, K. Shibahara and S. Takei, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 809.
534. H. Boeland and R. Mueller, *Z. Chem.*, 1976, **16**, 66.
535. H. Stuenzi, R. L. N. Harris and D. D. Perrin, *Aust. J. Chem.*, 1980, **33**, 2207.
536. M. S. El-Ezaby and T. E. El-Khalafawy, *J. Inorg. Nucl. Chem.*, 1981, **43**, 831.
537. D. M. Thompson and W. Balenovich, *Inorg. Chim. Acta*, 1980, **46**, 199.
538. J. Hajdu and E. C. Armstrong, *J. Am. Chem. Soc.*, 1981, **103**, 232.
539. H. P. Calhoun, N. L. Paddock and J. N. Wingfield, *Can. J. Chem.*, 1975, **53**, 1765.
540. P. Orioli, R. Cini, D. Donati and S. Mangani, *Nature (London)*, 1980, **283**, 691.
541. A. N. Speca, C. Mikulsi and F. J. Iaconiani, *Inorg. Chim. Acta*, 1979, **37**, L551.
542. S. Shirotake, *Chem. Pharm. Bull.*, 1980, **28**, 1673.
543. L. G. Marzilli, B. de Castro, J. P. Caradonna, R. C. Stewart and C. P. van Vuuren, *J. Am. Chem. Soc.*, 1980, **102**, 916.
544. J. A. Happe and R. L. Ward, *J. Phys. Chem.*, 1979, **83**, 3457.
545. S. Ahrland, E. Avsar and T. Berg, *J. Organomet. Chem.*, 1979, **181**, 17.
546. N. B. Behrens and D. M. L. Goodgame, *Inorg. Chim. Acta*, 1980, **46**, 15.
547. C. H. Wei and K. B. Jacobson, *Inorg. Chem.*, 1981, **20**, 356.
548. W. S. Sheldrick, *Z. Naturforsch., Teil B*, 1982, **37**, 653.
549. M. Goodgame and K. W. Johns, *Inorg. Chim. Acta*, 1980, **46**, 23.
550. K. H. Scheller, F. Hofstetter, P. R. Mitchell, B. Prijs and H. Sigel, *J. Am. Chem. Soc.*, 1981, **103**, 247.
551. P. Orioli, R. Cini, D. Donati and S. Mangani, *J. Am. Chem. Soc.*, 1981, **103**, 4446.
552. R. Cini and P. Orioli, *J. Inorg. Biochem.*, 1981, **14**, 95.
553. R. Ghose and A. K. Dey, *Rev. Chim. Miner.*, 1980, **17**, 492 (*Chem. Abstr.*, 1981, **94**, 146 097).
554. T. Beringhelli, M. Freni, F. Morazzoni, P. Romiti and R. Dervida, *Spectrochim. Acta, Part A*, 1981, **37**, 763.
555. A. N. Speca, L. L. Pytlewski, C. M. Mikulski and N. M. Karayannis, *Inorg. Chim. Acta*, 1982, **66**, L53.
556. C. M. Mikulski, R. T. B. T. De Prince, F. J. Iaconianni, L. L. Pytlewski, A. N. Speca and N. M. Karayannis, *Inorg. Chim. Acta*, 1981, **56**, 163.
557. C. M. Mikulski, L. Mattucci, Y. Smith and T. Ba Tran, *Inorg. Chim. Acta*, 1982, **66**, L71.
558. E. V. Komarov, M. I. Lifshits and M. M. Mogil'nitskii, *Koord. Khim.*, 1981, **7**, 1425.
559. B. T. Khan and R. M. Raju, *Indian J. Chem., Sect. A*, 1981, **20**, 860.
560. L. G. Marzilli, B. de Castro and C. Solorzano, *J. Am. Chem. Soc.*, 1982, **104**, 461.
561. M. J. McCall and M. R. Taylor, *Acta Crystallogr., Sect. B*, 1976, **32**, 1687.
562. E. A. H. Griffith, N. G. Charles and E. L. Amma, *Acta Crystallogr., Sect. B*, 1982, **38**, 942.
563. R. G. Bhattacharyya and I. Bhaduri, *J. Inorg. Nucl. Chem.*, 1978, **40**, 733.
564. M. S. Mohan and M. M. T. Khan, *J. Coord. Chem.*, 1979, **8**, 207.
565. P. R. Mitchell, B. Prijs and H. Sigel, *Helv. Chim. Acta*, 1979, **62**, 1723.
566. N. K. Dzyuba and G. D. Zegzhda, *Zh. Neorg. Khim.*, 1979, **29**, 978.
567. C. Gagnon, A. L. Beauchamp and D. Tranqui, *Can. J. Chem.* 1979, **57**, 1372.
568. K. Aoki, *Acta Crystallogr., Sect. B*, 1976, **32**, 1454.
569. L. G. Purnell, E. D. Estes and D. J. Hodgson, *J. Am. Chem. Soc.*, 1976, **98**, 740.
570. S. D. Rothenberger, M. S. Zitzman and W. J. Birdsall, *J. Inorg. Nucl. Chem.*, 1981, **43**, 1673.
571. Y. Vandewalle and J. Nicole, *Bull. Soc. Chim. Fr.*, 1978, 363.
572. M. M. T. Khan and M. S. Jyoti, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1731.
573. S. K. Bhasin, O. J. Parkash, D. S. Jain and J. N. Caur, *J. Indian Chem. Soc.*, 1979, **56**, 334.
574. N. Barba-Behrens, D. M. L. Goodgame and Z. Warnke, *Inorg. Chim. Acta*, 1978, **31**, 257.
575. M. A. Guichelaar and J. Reedijk, *Recl. Trav. Chim. Pays-Bas*, 1978, **97**, 295.
576. A. N. Speca, C. M. Mikulski, F. J. Iaconianni, L. L. Pytlewski and N. M. Karayannis, *Inorg. Chim. Acta*, 1979, **37**, L551.
577. L. Nassimbeni and A. Rodgers, *Acta Crystallogr.*, 1974, **30**, 1953.
578. J. Lauterwein, P. Hemmerich and J. M. Lhoste, *Inorg. Chem.*, 1975, **14**, 2152.
579. M. Goodgame and K. W. Johns, *Inorg. Chim. Acta*, 1979, **37**, L559.
580. P. R. Mitchell, *J. Chem. Soc., Dalton Trans.*, 1980, 1079.
581. J. J. Habeeb, A. Osman and D. G. Tuck, *J. Organomet. Chem.*, 1980, **185**, 117.
582. T. Ohno and S. Kato, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 2953.
583. M. K. de Armond, C. M. Calin and W. L. Huang, *Inorg. Chem.*, 1980, **19**, 62.
584. J. Kotlicka and Z. R. Grabowski, *J. Photochem.*, 1979, **11**, 413.
585. M. S. Henry and M. Z. Hoffman, *J. Am. Chem. Soc.*, 1977, **99**, 5201.
586. P. R. Mitchell, *J. Chem. Soc., Dalton Trans.*, 1979, 771.
587. B. E. Fischer and H. Sigel, *Inorg. Chem.*, 1979, **18**, 425.
588. I. S. Ahuja, R. Singh and C. P. Rai, *J. Inorg. Nucl. Chem.*, 1978, **40**, 924.
589. C. C.-Y. Lee and P. Hemmes, *Inorg. Chem.*, 1980, **19**, 485.
590. S. K. Kozlov, A. K. Pyartman and V. M. Potekhin, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1981, **24**, 407.

591. R. G. Goel, W. P. Henry and N. K. Jha, *Inorg. Chem.*, 1982, **21**, 2551.
592. R. G. Goel and N. K. Jha, *Can. J. Chem.*, 1981, **59**, 3267.
593. N. Palta, S. N. Dubey and D. M. Puri, *J. Indian Chem. Soc.*, 1982, **59**, 261.
594. R. Cini, P. Orioli, M. Sabat and H. D. Gillman, *Inorg. Chim. Acta*, 1982, **59**, 225.
595. A. A. Baseggio and R. L. Grassi, *J. Inorg. Nucl. Chem.*, 1981, **43**, 3275.
596. L. W. Houk, P. K. S. Gupta, M. B. Hossain and D. Van der Kelm, *Acta Crystallogr., Sect. B*, 1982, **38**, 91.
597. L. Hiltunen, M. Leskela and S. P. Sinha, *Cryst. Struct. Commun.*, 1982, **11**, 119.
598. R. M. Goel, W. P. Henry and R. C. Srivastava, *Inorg. Chem.*, 1981, **20**, 1727.
599. R. M. Goel, W. P. Henry, M. J. Olivier and A. L. Beauchamp, *Inorg. Chem.*, 1981, **20**, 3924.
600. N. A. Bell, T. D. Dee and M. Goldstein, *Inorg. Chim. Acta*, 1980, **38**, 191.
601. S. Ahrland, E. Avsar and T. Berg, *J. Organomet. Chem.*, 1979, **181**, 17.
602. J. E. Fergusson and P. F. Heveldt, *Inorg. Chim. Acta*, 1978, **31**, 145.
603. R. J. Read and M. N. G. James, *J. Am. Chem. Soc.*, 1981, **103**, 6947.
604. M. R. Churchill and A. H. Reis, *Inorg. Chem.*, 1973, **12**, 2280.
605. R. S. Brown, N. J. Curtis and J. Huguet, *J. Am. Chem. Soc.*, 1981, **103**, 6953.
606. W. Van Doorne and T. P. Dirkse, *J. Electrochem. Soc.*, 1975, **122**, 1.
607. A. G. Briggs, N. A. Hampston and A. Marshall, *J. Chem. Soc., Faraday Trans. 2*, 1974, **70**, 1978.
608. M. S. Okunev, *Chem. Abstr.*, 1974, **81**, 42 223.
609. G. S. Semenova, *Ukr. Khim. Zh.* (*Russ. Ed.*), 1979, **45**, 1148.
610. K. R. Wambach and R. Hoppe, *Z. Anorg. Allg. Chem.*, 1978, **445**, 91.
611. S. Ghose and C. Wan, *Acta Crystallogr., Sect. B*, 1979, **35**, 819.
612. R. J. Hill, *Am. Mineral*, 1976, **61**, 979; F. C. Hawthorne, *Can. Mineral*, 1976, **14**, 143.
613. V. V. Kuznetsov, V. N. Trostin and G. A. Krestov, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Teknol.*, 1981, **24**, 709 (*Chem. Abstr.*, 1981, **95**, 157 663).
614. (a) R. Audinos and R. Zana, *J. Chim. Phys. Phys.-Chim. Biol.*, 1981, **78**, 183; (b) S. P. Dagnall, D. N. Hague and D. C. A. Towl, *J. Chem. Soc., Faraday Trans. 2*, 1982, **78**, 2161; (c) G. Licheri, G. Paschina, G. Piccaluga and G. Pinna, *Z. Naturforsch., Teil A*, 1982, **37**, 1205; (d) T. Radnai, G. Palinkas and R. Caminiti, *ibid.*, 1982, **37**, 1247.
615. T. E. Jenkins and J. Lewis, *Spectrochim. Acta, Part A*, 1981, **37**, 47.
616. J. T. Bulmer, D. E. Irish and L. Odberg, *Can. J. Chem.*, 1975, **53**, 3806.
617. R. D. Brown and M. C. R. Symons, *J. Chem. Soc., Dalton Trans.*, 1976, 426.
618. P. Andreev, L. A. Myund and L. S. Lilich, *Chem. Abstr.*, 1975, **83**, 66 398.
619. H. Ohtaki, M. Maeda and S. Ito, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 247.
620. J. C. Sprowles and R. A. Plane, *J. Phys. Chem.*, 1975, **79**, 1711.
621. R. L. Berg and C. E. Vanderzee, *J. Chem. Thermodyn.*, 1975, **7**, 219.
622. N. I. Zinevich and L. A. Garmash, *Zh. Neorg. Khim.*, 1975, **20**, 2838.
623. R. A. Reichle, K. G. McCurdy and L. G. Hepler, *Can. J. Chem.*, 1975, **53**, 3841.
624. H. Kanno and J. Hiraishi, *J. Raman Spectrosc.*, 1980, **9**, 85.
625. H. Sugano and J. Hiraishi, *Koen Yoshishu-Bunshi Kozo Sogo Toronkai*, 1979, 128.
626. D. Petrovic and B. Ribar, *Acta Crystallogr., Sect. B*, 1975, **31**, 1795.
627. M. Mannoorettonnil and J. Gilbert, *Bull. Soc. Chim. Belg.*, 1974, **83**, 9.
628. A. Clearfield, M. J. Sims and R. Gopal, *Inorg. Chem.*, 1976, **15**, 335.
629. C. Giquel-Mayer and G. Perez, *Rev. Chim. Miner.*, 1975, **12**, 537.
630. A. Whitaker, *Acta Crystallogr., Sect. B*, 1975, **31**, 2026.
631. I. Tordjman, A. Durif, M. T. Averburch-Pouchot and J. C. Guitel, *Acta Crystallogr., Sect. B*, 1975, **31**, 1143.
632. S. Zloczyski, H. Hartl and R. Frydrych, *Acta Crystallogr., Sect. B*, 1976, **32**, 753.
633. F. Charbonnier, R. Faure and H. Loiseleur, *J. Appl. Crystallogr.*, 1975, **8**, 400.
634. F. Charbonnier, R. Faure and H. Loiseleur, *J. Appl. Crystallogr.*, 1975, **8**, 493.
635. L. F. Power, J. A. King and F. H. Moore, *J. Chem. Soc., Dalton Trans.*, 1975, 2073.
636. J. Whitnall, C. H. L. Kennard and J. Nimmo, *Cryst. Struct. Commun.*, 1975, **4**, 717.
637. M. Louer, D. Louer and D. Grandjean, *Acta Crystallogr., Sect. B*, 1982, **38**, 909.
638. V. V. S. Murty, M. Seshasayee and B. V. R. Murty, *Indian J. Phys., Part A*, 1981, **55**, 310.
639. R. C. Paul, V. P. Kapila and R. K. Mahajan, *J. Inorg. Nucl. Chem.*, 1980, **42**, 281.
640. F. Charbonnier, R. Faure and H. Loiseleur, *Rev. Chim. Miner.*, 1979, **16**, 555.
641. J. Labarre, D. Louer, M. Louer and D. Grandjean, *Cryst. Struct. Commun.*, 1975, **4**, 1657.
642. A. Finney and M. A. Hitchman, *Aust. J. Chem.*, 1981, **34**, 2061.
643. C. Brassy, M. C. Michaud, J. Delettre and J. P. Mornon, *Acta Crystallogr., Sect B*, 1974, **30**, 2848.
644. D. E. Irish and R. V. Thorpe, *Can. J. Chem.*, 1975, **53**, 1414.
645. N. Milinski and B. Ribar, *Cryst. Struct. Commun.*, 1974, **3**, 757.
646. B. Matkovic, B. Ribar, B. Zelenko and S. W. Peterson, *Acta Crystallogr.*, 1966, **21**, 719.
647. A. L. Lott, *Inorg. Chem.*, 1974, **13**, 667.
648. C. Bellito, L. Gastaldi and A. A. G. Tomlinson, *J. Chem. Soc., Dalton Trans.*, 1976, 989.
649. M. Begieu-Bencher, J. C. Guitel, I. Tordjman and A. Durif, *Chem. Abstr.*, 1975, **83**, 69 548.
650. Y. A. Ivanov, M. A. Simonov and N. V. Belov, *Chem. Abstr.*, 1976, **84**, 158 265.
651. M. T. Averbuch-Pouchot, A. Durif and J. C. Guitel, *Acta Crystallogr., Sect B*, 1975, **31**, 2453.
652. M. T. Averbuch-Pouchot, *J. Appl. Crystallogr.*, 1975, **8**, 388.
653. M. T. Averbuch-Pouchot, A. Durif and J. C. Guitel, *Acta Crystallogr., Sect. B*, 1976, **32**, 1533.
654. A. Durif, M. T. Averbuch-Pouchot and J. C. Guitel, *Acta Crystallogr., Sect. B*, 1975, **31**, 2680.
655. M. T. Averbuch-Pouchot, A. Durif and J. C. Guitel, *Acta Crystallogr., Sect. B*, 1975, **31**, 2483.
656. M. T. Averbuch-Pouchot and A. Durif, *J. Appl. Crystallogr.*, 1975, **8**, 564.
657. M. T. Averbuch-Pouchot and J. C. Guitel, *Acta Crystallogr., Sect. B*, 1976, **32**, 1670.
658. H. D. Gillman and J. L. Eichelberger, *Inorg. Chem.* 1976, **15**, 840.
659. M. H. Youinou and J. E. Guerchais, *J. Chem. Soc., Dalton Trans.*, 1976, 293.
660. A. G. Menke and F. Walmsley, *Inorg. Chim. Acta*, 1976, **17**, 193.
661. G. Brun and G. Jourdan, *Rev. Chim. Miner.*, 1975, **12**, 39.

662. K. L. Idler and C. Calvo, *Can. J. Chem.*, 1975, **53,** 3665.
663. C. M. Mikulski, L. L. Pytlewski and N. M. Karayannis, *Inorg. Chem.*, 1975, **14,** 1559.
664. J. R. Rea and E. Kostiner, *Acta Crystallogr., Sect. B,* 1974, **30,** 2901.
665. T. Palanisamy, J. Gopalakrishnan and M. V. C. Sastri, *J. Inorg. Nucl. Chem.*, 1976, **38,** 1372.
666. P. I. Fedorov, V. K. Andreev and N. P. Slotvinskii-Sidak, *Zh. Neorg. Khim.*, 1976, **21,** 1127.
667. P. I. Fedorov, V. K. Andreev, N. P. Slotvinskii-Sidak and G. S. Beklenisheva, *Chem. Abstr.*, 1975, **83,** 52 491.
668. M. Yu. Matuzenko, V. I. Zarembo, L. V. Pucjkov and V. N. Gilyarov, *Zh. Prikl. Khim.* (*Leningrad*), 1982, **55,** 770 (*Chem. Abstr.*, 1982, **96,** 224 201).
669. R. Caminiti, *Z. Naturforsch., Teil A,* 1981, **36,** 1062.
670. R. Caminiti and G. Johansson, *Acta Chem. Scand., Ser. A,* 1981, **35,** 373.
671. M. Yu. Matuzenko, V. I. Zarembo, L. V. Puchkov and V. N. Gilyarov, *Zh. Prikl. Khim.* (*Leningrad*), 1982, **55,** 816 (*Chem. Abstr.*, 1982, **96,** 206 273).
672. K. Aurivillius and C. Staalhandski, *Z. Kristallogr.*, 1980, **153,** 121.
673. H. K. Ng and C. Calvo, *Can. J. Chem.*, 1975, **53,** 1449.
674. L. Walter-Levy, D. Groult and J. W. Visser, *Bull. Soc. Chim. Fr.*, 1974, **67,** 383.
675. Z. Gabelica, *C.R. Hebd. Seances Acad. Sci., Ser. C,* 1974, **279,** C. 509.
676. B. Bosson, *Acta Crystrallogr., Sect. B,* 1976, **32,** 2044.
677. C. S. Alleyne and R. C. Thompson, *Can. J. Chem.*, 1974, **52,** 3218.
678. E. Lindner, D. W. R. Frembs and D. Krug, *Chem. Ber.*, 1975, **108,** 291.
679. E. Lindner, D. W. R. Frembs and D. Langner, *Z. Naturforsch., Teil B,* 1974, **29,** 569.
680. Z. Gabelica, E. G. Derouane and R. Hubin, *J. Therm. Anal.*, 1980, **18,** 315.
681. Z. Gabelica, E. G. Derouane and R. Hubin, *J. Therm. Anal.*, 1980, **18,** 329.
682. E. Koenigner-Ahlborn and A. Mueller, *Angew. Chem.*, 1974, **86,** 709.
683. K. F. Hesse and F. Liebau, *Chem. Abstr.*, 1976, **84,** 114 669.
684. H. M. M. Shearer and C. B. Spencer, *Acta Crystallogr., Sect. B,* 1980, **36,** 2046.
685. M. Ishimori, T. Hagiwara, T. Tsuruta and Y. Kai, *Bull. Chem. Soc. Jpn.*, 1976, **49,** 1165.
686. W. Haase, R. Mergehenn and R. Allmann, *Acta Crystallogr., Sect. B,* 1975, **31,** 1184.
687. V. J. Shiner and M. A. Beg, *Inorg. Chem.*, 1975, **14,** 157.
688. B. Adler, A. Lechowicz and K. H. Thiele, *Z. Anorg. Allg. Chem.*, 1976, **423,** 27.
689. B. M. Antti, *Acta Chem. Scand., Ser. A,* 1976, **30,** 103.
690. R. Iwamoto and H. Wakano, *J. Am. Chem. Soc.*, 1976, **98,** 3764.
691. L. J. Krause and J. A. Morrison, *J. Chem. Soc., Chem. Commun.*, 1980, 671.
692. K. Sawada, M. Nakamo, H. Mori and M. Tanaka, *Bull. Chem. Soc. Jpn.*, 1975, **48,** 2282.
693. B. K. Choudhary and B. Prasad, *J. Indian Chem. Soc.*, 1975, **52,** 679.
694. E. John, *Chem. Abstr.*, 1976, **85,** 10 851.
695. V. A. Fedorov, A. I. Khokhlova and G. E. Chernikova, *Zh. Neorg. Khim.*, 1976, **21,** 344.
696. I. Kruhak, B. Grabaric, J. Filipovic and I. Piljac, *Croat. Chem. Acta,* 1976, **48,** 119.
697. E. Bottari, R. Jasionowska and P. Ronaccia, *Ann. Chim.* (*Rome*), 1975, **65,** 69.
698. C. Y. Liu, H. J. Chang, S. S. Uang and P. J. Sun, *Chem. Abstr.*, 1976, **84,** 53 322.
699. S. S. Sandhu, R. S. Sandhu and J. N. Kumaria, *Thermochim. Acta,* 1976, **15,** 244.
700. A. Gergely and T. Kiss, *Met. Ions. Biol. Syst.*, 1979, **9,** 143.
701. A. Gergely, T. Kiss and G. Deak, *Inorg. Chim. Acta,* 1979, **36,** 113; *Magy. Kem. Foly.*, 1978, **84,** 307.
702. T. Kiss and A. Gergely, *Inorg. Chim. Acta,* 1979, **36,** 31; *Magy. Kem. Foly.*, 1978, **84,** 307.
703. K. S. Rajan, S. Mainer and J. M. Davis, *J. Inorg. Nucl. Chem.*, 1978, **40,** 2089.
704. A. Mossett, F. Nepveu-Juras, R. Huran and J. J. Bonnet, *J. Inorg. Nucl. Chem.*, 1978, **40,** 1259.
705. G. Sawitzki and H. G. von Schnering. *Chem. Ber.*, 1974, **107,** 3266.
706. J. Padmos and A. Van Veen, *Spectrochim. Acta, Part A,* 1982, **38,** 97.
707. J. S. Wood, R. O. Day, C. P. Keijers, E. de Boer, A. E. Yildirim and A. A. Klaassen, *Inorg. Chem.*, 1981, **20,** 1982.
708. L. S. Gelfand, L. L. Pytlewski, D. L. Cosgrave, C. M. Mikulski, A. N. Speca and N. M. Karayannis, *Inorg. Chim. Acta,* 1979, **32,** 59.
709. R. Palepu and M. M. Morrison, *Inorg. Chim. Acta,* 1979, **36,** L437.
710. F. J. Iaconianni and L. L. Pytlewski, *Inorg. Chim. Acta,* 1981, **53,** L21.
711. S. A. Boyd, R. E. Kohrman and D. X. West, *J. Inorg. Nucl. Chem.*, 1976, **38,** 607.
712. A. N. Speca, L. S. Gelfand, L. L. Pytlewski, C. Owens and N. M. Karayannis, *Inorg. Chem.*, 1976, **15,** 1493.
713. S. A. Boyd, R. E. Kohrman and D. X. West, *J. Inorg. Nucl. Chem.*, 1976, **38,** 1605.
714. J. B. Hodgson and G. C. Percy, *Spectrochim. Acta, Part A,* 1979, **34,** 777.
715. J. Reedijk, H. Schrijver and J. A. Welleman, *Recl. Trav. Chim.*, 1975, **94,** 40.
716. C. Preti and G. Tosi, *J. Chem. Soc., Dalton Trans.*, 1976, 685.
717. C. A. Kosky, J.-P. Gayda, J. F. Gibson, S. F. Jones and D. J. Williams, *Inorg. Chem.*, 1982, **21,** 3173.
718. J. P. Rose, R. A. LaLancette and J. A. Potenza, *Acta Crystallogr., Sect. B,* 1980, **36,** 2409.
719. Z. Zak, J. Kozisek and T. Glowiak, *Z. Anorg. Allg. Chem.*, 1981, **477,** 221.
720. Y. Hase and O. L. Alves, *J. Mol. Struct.*, 1978, **50,** 293.
721. M. W. G. De Bolstor, C. Boutkhan and T. A. Van der Knaap, *Z. Anorg. Allg. Chem.*, 1978, **443,** 269.
722. P. O. Dunstan and C. Maieru, *An. Acad. Bras. Cienc.*, 1978, **50,** 479; P. O. Dunstan and F. A. P. Matos, *An. Acad. Bras. Cienc.*, 1979, **51,** 211.
723. N. Kumagai and H. Mase, *Nippon Kagaku Kaishi,* 1975, 814.
724. P. O. Dunstan, G. Vicentini and Y. Kawano, *Chem. Abstr.*, 1975, **83,** 157 134.
725. S. H. Hunter, G. A. Rodley and K. Emerson, *Inorg. Nucl. Chem. Lett.*, 1976, **12,** 113.
726. C. M. Mikulski, L. L. Pytlewski and N. M. Karayannis, *Inorg. Chim. Acta,* 1979, **32,** 263.
727. B. D. Mul'kina, S. I. Zhdanov and E. A. Mambetkaziev, *Zh. Obsch. Khim.*, 1979, **49,** 391.
728. A. Apelblat and R. Levin, *J. Inorg. Nucl. Chem.*, 1979, **41,** 115.
729. C. M. Mikulski, W. Henry and L. L. Pytlewski, *J. Inorg. Nucl. Chem.*, 1978, **40,** 769.
730. C. M. Mikulski, J. Unruh, L. L. Pytlewski and N. M. Karayannis, *Transition Met. Chem.*, 1979, **4,** 98.

731. A. Y. Tsivadze, G. V. Tsintsadze, N. P. Gongadze and Y. Y. Kharitonov, *Koord. Khim.*, 1975, **1**, 1221.
732. A. Y. Tsivadze, G. V. Tsintsadze, N. P. Gongadze and Y. Y. Kharitonov, *Koord. Khim.*, 1975, **1**, 1212.
733. A. Y. Tsivadze, G. V. Tsintsadze, N. P. Gongadze and Y. Y. Kharitonov, *Koord. Khim.*, 1975, **1**, 1385.
734. I. Persson, *Acta Chem. Scand., Ser A*, 1982, **36**, 7.
735. S. Ahrland and I. Persson, *Acta Chem. Scand., Ser. A*, 1980, **34**, 645.
736. E. Lindner, D. W. R. Frembs and D. Langner, *Chem. Ber.*, 1974, **107**, 3254.
737. M. J. Mays and P. A. Vergnano, *Inorg. Nucl. Chem. Lett.*, 1975, **11**, 387.
738. G. V. Tsintsadze, T. I. Tsivtsivadze and F. V. Orbeladze, *Zh. Strukt. Khim.*, 1975, **16**, 319.
739. Z. Durski, H. Boniuk and S. Majorowski, *Rocz. Chem.*, 1975, **49**, 2101.
740. O. F. Khodzaek, T. A. Azizov, D. Ergeshbaev and I. A. Parpiev, *Koord. Khim.*, 1976, **2**, 304.
741. Y. Y. Molchanov and O. F. Golubev, *Zh. Neorg. Khim.*, 1976, **21**, 869.
742. A. Kircheiss and I. Gleichemann, *Z. Chem.*, 1976, **16**, 26.
743. C. Dragulescu, E. Petrovici and I. Lupu, *Monatsh. Chem.*, 1974, **105**, 1176.
744. S. Shibata and M. Ohta, *J. Mol. Struct.*, 1981, **77**, 265.
745. M. L. Niven and D. A. Thornton, *Spectrosc. Lett.*, 1980, **13**, 419.
746. G. A. Prik, B. E. Kozer and T. A. Tselyapina, *Russ. J. Phys. Chem.*, 1979, **53**, 493.
747. R. B. Birdy and M. Goodgame, *Inorg. Chim. Acta*, 1979, **36**, 281.
748. T. Ohno and S. Kato, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 1901.
749. T. M. Greaney, C. L. Raston and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1975, 876.
750. E. N. Maslen, T. M. Greaney, C. L. Raston and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1974, 400.
751. W. O. McSharry, M. Cefola and J. G. White, *Inorg. Chim. Acta*, 1980, **38**, 161.
752. F. Izumi, R. Kurosawa, J. Kawamoto and H. Akaiwa, *Bull. Chem. Soc. Jpn.*, 1979, **48**, 3188.
753. J. L. Garnett, I. K. Gregor and D. Nelson, *Inorg. Chim. Acta*, 1976, **18**, L11.
754. A. Samantaray, P. K. Panda and B. K. Mohaptra, *J. Inorg. Nucl. Chem.*, 1980, **42**, 621.
755. W. L. Driessen and P. L. A. Everstijn, *Recl. Trav. Chim. Pays-Bas*, 1980, **99**, 238.
756. M. Das and S. E. Livingstone, *Aust. J. Chem.*, 1974, **27**, 2109.
757. M. Das and S. E. Livingstone, *Aust. J. Chem.*, 1975, **28**, 513.
758. M. Das and S. E. Livingstone, *Aust. J. Chem.*, 1974, **27**, 53, 749, 1177, 2115.
759. D. R. Dakternieks and D. P. Graddon, *Aust. J. Chem.*, 1974, **27**, 1351.
760. B. F. Hoskins and C. D. Pannan, *Inorg. Nucl. Chem. Lett.*, 1975, **11**, 405.
761. R. Beckett and B. F. Hoskins, *J. Chem. Soc., Dalton Trans.*, 1975, 908.
762. J. A. Faniran, K. S. Patel and L. O. Nelson, *J. Inorg. Nucl. Chem.*, 1976, **38**, 77.
763. K. S. Patel, J. A. Faniran and L. O. Nelson, *J. Inorg. Nucl. Chem.*, 1976, **38**, 81.
764. R. Tomlonovic, R. L. Hough, M. D. Glick and R. L. Lintvedt, *J. Am. Chem. Soc.*, 1975, **97**, 2925.
765. M. D. Glick, R. L. Lindvedt, D. P. Gavel and B. Tomlonovic, *Inorg. Chem.*, 1976, **15**, 1654.
766. R. L. Linvedt, M. D. Glick, B. K. Tomlonovic and D. P. Gavel, *Inorg. Chem.*, 1976, **15**, 1646.
767. (a) U. Doraswamy and P. K. Bhattacharya, *J. Inorg. Nucl. Chem.*, 1975, **37**, 1665; (b) see for example G. B. Deacon and R. J. Phillips, *Coord. Chem. Rev.*, 1980, **33**, 227.
768. M. L. Post and J. Trotter, *Acta Crystallogr., Sect. B*, 1974, **30**, 1880.
769. G. Webber, *Acta Crystallogr., Sect. B*, 1980, **36**, 1947.
770. L. S. Itkina and K. A. Nadzharyan, *Zh. Neorg. Khim.*, 1981, **26**, 515.
771. K. A. Nadzharyan, L. S. Itkina and I. N. Lepeshkov, *Zh. Neorg. Khim.*, 1981, **26**, 519.
772. L. S. Itkina, K. A. Nadzharyan and I. N. Lepeshkov, *Zh. Neorg. Khim.*, 1981, **26**, 1086.
773. K. A. Nadzharyan and L. S. Itkina, *Zh. Neorg. Khim.*, 1981, **26**, 1097.
774. P. H. Tedesco and J. Martinez, *An. Asoc. Quim. Argent.*, 1981, **69**, 219.
775. M. K. Johnson, D. B. Powell and R. D. Cannon, *Spectrochim. Acta, Part A*, 1981, **37**, 899.
776. A. V. Capilla and R. A. Aranda, *Cryst. Struct. Commun.*, 1979, **8**, 795.
777. J. Charalambous, R. G. Copperthwaite, S. W. Jeffs and D. E. Shaw, *Inorg. Chim. Acta*, 1974, **14**, 53.
778. V. V. Panevchik and V. M. Goryaev, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1980, **23**, 115.
779. M. E. Ekwunife, M. W. Nwachukwu, F. P. Rinehart and S. J. Sime, *J. Chim. Soc., Faraday Trans. 2*, 1975, **71**, 1432.
780. P. Beraldi and G. Fabbri, *Spectrochim. Acta, Part A*, 1981, **37**, 89.
781. M. I. Lebedeva, B. I. Isaeva and A. N. Dubovitskaya, *Zh. Fiz. Khim.*, 1981, **55**, 1274.
782. J. A. Adejumobi, J. A. Faniran and K. S. Patel, *Spectrochim. Acta Part A*, 1978, **34**, 625.
783. M. L. Post and J. Trotter, *J. Chem. Soc., Dalton Trans.*, 1974, 285.
784. G. Smith, E. J. O'Reilly, C. H. L. Kennard, K. Stadnicka and B. Oleksyn, *Inorg. Chim. Acta*, 1981, **47**, 111.
785. C. H. L. Kennard, G. Smith, E. J. O'Reilly, K. M. Stadnicka and B. J. Oleksyn, *Inorg. Chim. Acta*, 1982, **59**, 241.
786. H. N. Nadzhafev, A. N. Shnulin and K. S. Mamedov, *Dokl. Akad. Nauk Az. SSSR*, 1980, **36**, 55 (*Chem. Abstr.*, 1981, **94**, 148 660).
787. A. N. Shnulin, G. N. Nadzhafov and K. S. Mamedov, *Zh. Strukt. Khim.*, 1981, **22**, 106.
788. G. N. Nadzhafov, B. T. Usubaliev and I. R. Amiraslanov, *Koord. Khim.*, 1981, **7**, 770.
789. S. Natarajan, D. S. Sake Gowda and L. Cartz, *Acta Crystallogr., Sect. B*, 1974, **30**, 401.
790. Y. Nakacho, T. Misawa, T. Fujiwara, A. Wakahara and K. Tomita, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 58.
791. Y. Nakacho, T. Misawa, T. Fujiwara, A. Wakahara and K. Tomita, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 595.
792. A. T. Reed and A. Karipides, *Acta Crystallogr., Sect. B*, 1976, **23**, 2085.
793. (a) K. D. Singh, S. C. Jain, T. D. Sakore and A. B. Biswas, *Z. Kristallogr.*, 1975, **141**, 473; (b) M. G. B. Dewar, *Coord. Chem. Rev.*, 1977, **24**, 179.
794. I. R. Amiraslanov, Kh. S. Mamedov, E. M. Movsumov, F. N. Musaev, A. I. Magerramov and G. N. Madzhafov, *Zh. Strukt. Khim.*, 1979, **20**, 498.
795. J. C. Jansen, H. Van Koningsveld and J. A. V. Van Ooijen, *Cryst. Struct. Commun.*, 1979, **8**, 499.
796. M. Cartwright, D. A. Edwards and J. M. Potts, *Inorg. Chim. Acta*, 1979, **34**, 211.

797. S. V. Larionov, V. I. Ovcharenko, V. N. Kirichenko, R. Z. Sagdeev and L. B. Volodarskii, *Koord. Khim.*, 1978, **4**, 1878.
798. J. P. Deloume and H. Loiseleur, *Acta Crystallogr., Sect. B*, 1974, **30**, 607.
799. P. Richard, D. Tran Qui and E. F. Bertaut, *Acta Crystallogr., Sect. B*, 1974, **30**, 628.
800. R. Aruga, *J. Inorg. Nucl. Chem.*, 1979, **41**, 845.
801. E. A. Nikonenko, V. A. Sharov and I. I. Olikov, *Zh. Neorg. Khim.*, 1982, **27**, 975.
802. A. I. Falicheva and Z. A. Miroshnik, *Izv. Vyssh. Uchebn., Zaved., Khim. Khim. Tekhnol.*, 1981, **24**, 1530 (*Chem. Abstr.*, 1982, **96**, 75 360).
803. S. S. Kelkar and B. I. Nemade, *J. Electrochem. Soc. India*, 1981, **30**, 228.
804. N. J. Ray and B. J. Hathaway, *Acta Crystallogr., Sect. B*, 1982, **38**, 770.
805. E. A. H. Griffith, N. G. Charles and E. L. Amma, *Acta Crystallogr., Sect. B*, 1982, **38**, 262.
806. M. I. Bruce, J. K. Walton, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1983, 2221.
807. S. K. Srivastava, S. Sarkar, B. Sharma, R. K. Shukla and R. C. Maurya, *Acta Cienc. Indica*, 1979, **5**, 72.
808. K. Nagase, K. Saton and N. Tanaka, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 868.
809. E. Canals, C. Verro and R. Deyrieux, *Rev. Chem. Miner.*, 1974, **11**, 498.
810. M. Israeli and L. D. Pettit, *J. Chem. Soc., Dalton Trans.*, 1975, 414.
811. M. Israeli and L. D. Pettit, *J. Inorg. Nucl. Chem.*, 1975, **37**, 999.
812. L. Walter-Levy, J. Perrotey and J. W. Visser, *Bull. Soc. Chim. Fr.*, 1973, 2596.
813. M. L. Post and J. Trotter, *J. Chem. Soc., Dalton Trans.*, 1974, 1922.
814. M. L. Post and J. Trotter, *J. Chem. Soc., Dalton Trans.*, 1973, 674.
815. Y. Yonishi and H. Saijo, *Chem. Abstr.*, 1975, **82**, 25 370.
816. (a) K. D. Singh, S. C. Jain, T. D. Sakore and A. B. Biswas, *Acta Crystallogr., Sect. B*, 1975, **31**, 990; (b) C. G. Kuehn and S. S. Isied, *Prog. Inorg. Chem.*, 1980, **27**, 153.
817. I. G. Dance, *Inorg. Chem.*, 1981, **20**, 2155.
818. F. F. Said and D. G. Tuck, *Inorg. Chim. Acta*, 1982, **59**, 1.
819. J. L. Hencher, M. Khan, F. F. Said and D. G. Tuck, *Inorg. Nucl. Chem. Lett.*, 1981, **17**, 187.
820. K. S. Hagen, D. W. Stephan and R. H. Holm, *Inorg. Chem.*, 1982, **21**, 3928.
821. G. W. Adamson, N. A. Bell and H. M. M. Shearer, *Acta Crystallogr., Sect. B*, 1982, **38**, 462.
822. I. G. Dance, *J. Am. Chem. Soc.*, 1980, **102**, 3445.
823. I. G. Dance, *J. Chem. Soc., Chem. Commun.*, 1980, 818.
824. M. Masaki, S. Matsunami, T. Kimura and T. Oshima, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 502.
825. S. Matsunami, S. Fujimura, K. Okimoto and M. Masaki, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 536.
826. O. G. Matyukhina, J. Ozols, B. T. Ibragimov, J. Lejejs, L. E. Terent'eva and N. V. Belov, *Zh. Strukt. Khim.*, 1981, **22**, 144.
827. J. C. Bayon, M. C. Brianso, J. L. Brianso and P. Gonzalez-Duarte, *Inorg. Chem.*, 1979, **18**, 3478.
828. R. V. Gadag and M. R. Gajendragad, *J. Indian Chem. Soc.*, 1980, **57**, 270.
829. I. W. Nowell, A. G. Cox and E. S. Raper, *Acta Crystallogr., Sect. B*, 1979, **35**, 3047.
830. A. K. Singh and R. P. Singh, *J. Inorg. Nucl. Chem.*, 1980, **42**, 286.
831. D. M. L. Goodgame and G. A. Leach, *Inorg. Chim. Acta*, 1979, **37**, L505.
832. D. M. L. Goodgame, I. Jeeves and G. A. Leach, *Inorg. Chim. Acta*, 1980, **38**, 247.
833. R. Battistuzzi and G. Peyronel, *Spectrochim. Acta, Part A*, 1980, **36**, 113.
834. F. A. Derillanova and G. Verani, *Aust. J. Chem.*, 1980, **33**, 279.
835. L. C. Egorova and V. L. Nirenburg, *Zh. Obshch. Khim.*, 1980, **50**, 426.
836. R. Aruga, *J. Inorg. Nucl. Chem.*, 1979, **41**, 849.
837. H. Sigel, K. H. Scheller, V. M. Rheinberger and B. E. Fischer, *J. Chem. Soc., Dalton Trans.*, 1980, 1022.
838. Z. A. Ardic, E. Gellert and O. Bekaroglu, *Transition Met. Chem. (Weinheim, Ger.)*, 1979, **4**, 378.
839. S. K. Tiwari and D. P. S. Rathore, *Natl. Acad. Sci. Lett. (India)*, 1979, **2**, 293.
840. J. A. McCleverty, S. Gill, R. S. Z. Kowalski, N. A. Bailey, H. Adams, K. W. Lumbard and M. A. Murphy, *J. Chem. Soc., Dalton Trans.*, 1982, 493.
841. M. C. Brianso, J. L. Brianso, W. Gaete, J. Ros and C. Suner, *J. Chem. Soc., Dalton Trans.*, 1981, 852.
842. G. Cauquis and A. Deronzier, *J. Inorg. Nucl. Chem.*, 1979, **41**, 1163.
843. D. M. L. Goodgame and G. A. Leach, *Inorg. Chim. Acta*, 1979, **32**, 69.
844. A. C. Skapski and K. A. Woode, *Acta Crystallogr., Sect. B*, 1979, **35**, 59.
845. H. Sigel, V. M. Rheinberger and B. E. Fischer, *Inorg. Chem.*, 1979, **18**, 3334.
846. H. Sigel, B. Prijs and D. B. McCormick, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1678.
847. R. Aruga, *Aust. J. Chem.*, 1979, **32**, 709.
848. W. G. Mitchell and M. M. Jones, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1957.
849. R. Aruga, *J. Inorg. Nucl. Chem.*, 1979, **41**, 849.
850. R. Aruga, *Atti. Accad. Sci. Torino, Cl. Sci. Fis. Mat. Nat.*, 1978, **112**, 345.
851. V. P. Litvinov, I. L. Sokol'Skaya and V. Y. Mortikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 1777.
852. B.-H. Mu, *Hua Hsueh Tung Pao*, 1980, 403 (*Chem. Abstr.*, 1981, **94**, 83 699).
853. P. C. Savino and R. D. Bereman, *Inorg. Chem.*, 1973, **12**, 173.
854. B. J. Kalbacher and R. D. Bereman, *Inorg. Chem.*, 1973, **12**, 2997.
855. D. N. Sen and U. N. Kantak, *Indian J. Chem.*, 1975, **13**, 72.
856. F. Y. Petillon, J. Y. Calves, J. E. Guerchais and Y. M. Pourier, *J. Inorg. Nucl. Chem.*, 1973, **35**, 3751.
857. M. Das, S. E. Livingstone, J. H. Mayfield, D. S. Moore and N. Saha, *Aust. J. Chem.*, 1976, **29**, 767.
858. S. E. Livingstone and N. Saha, *Aust. J. Chem.*, 1975, **28**, 1249.
859. S. E. Livingstone and D. S. Moore, *Aust. J. Chem.*, 1976, **29**, 283.
860. Y. Kidani, S. Naga and H. Koike, *Chem. Pharm. Bull.*, 1975, **23**, 1652.
861. L. Pecs, J. Ozols, A. Ievans and A. Sturis, *Chem. Abstr.*, 1976, **84**, 114 497.
862. F. Bigoli, E. Leporati and M. A. Pellinghelli, *Cryst. Struct. Commun.*, 1976, **5**, 593.
863. F. Bigoli, E. Leporati and M. A. Pellinghelli, *Cryst. Struct. Commun.*, 1976, **5**, 597.
864. S. H. Whitlow, *Acta Crystallogr., Sect. B*, 1975, **31**, 2531.

865. M. Bonamico, G. Dessy, V. Fares and L. Scaramuzze, *J. Chem. Soc., Dalton Trans.*, 1976, 67.
866. E. M. Movsumov, R. A. Alekperov, S. T. Amirov and K. S. Mamedov, *Chem. Abstr.*, 1976, **85**, 13 147.
867. S. N. Choi and J. R. Wasson, *Inorg. Chem.*, 1975, **14**, 1964.
868. B. L. Kallbacher and R. D. Bereman, *J. Inorg. Nucl. Chem.*, 1976, **38**, 471.
869. G. Rudzitis, I. Baltgalve and A. Viksna, *Latv. PSR Zinat. Vestis, Kim. Ser.*, 1979, 440.
870. M. J. Hewlins, *J. Chem. Soc., Dalton Trans.*, 1975, 429.
871. M. G. B. Drew, D. A. Rice and C. W. Timewell, *J. Chem. Soc., Dalton*, 1975, 144.
872. A. Cormier, K. Nakamoto, P. Christophliemk and A. Mueller, *Spectrochim. Acta, Part A*, 1974, **30**, 1059.
873. C. L. Raston, A. H. White and G. Winter, *Aust. J. Chem.*, 1976, **29**, 731.
874. C. L. Raston and A. H. White, *Aust. J. Chem.*, 1976, **29**, 739.
875. M. Das and S. E. Livingstone, *Inorg. Chim. Acta*, 1976, **19**, 5.
876. Z. Gabelica, *Ann. Soc. Sci. Bruxelles*, 1975, **89**, 149.
877. Z. Gabelica, *Chem. Abstr.*, 1975, **83**, 66 328.
878. R. D. Harcourt and G. Winter, *J. Inorg. Nucl. Chem.*, 1975, **37**, 1039.
879. A. C. Fabretti and G. C. Peyronel, *J. Inorg. Nucl. Chem.*, 1975, **37**, 603.
880. M. R. Udupa and M. Padmanabhan, *Inorg. Chim. Acta*, 1975, **13**, 239.
881. A. Müller, P. Christophliemk, I. Tossidis and C. K. Jorgensen, *Z. Anorg. Allg. Chem.*, 1973, **401**, 274.
882. D. K. Laing and L. D. Pettit, *J. Chem. Soc., Dalton Trans.*, 1975, 2297.
883. C. Preti and G. Tosi, *Spectrochim. Acta, Part A*, 1975, **31**, 1139.
884. V. V. Movchan, F. M. Tulyupa and E. Ya. Baiubarova, *Chem. Abstr.*, 1979, **90**, 96 808; F. M. Tulyupa, E. Ya. Baibarova, V. V. Movchan and O. G. Dozyuba, *Zh. Neorg. Khim.*, 1979, **24**, 389.
885. V. V. Movchan, F. M. Yulyupa and E. Ya. Baibarova, *Zh. Neorg. Khim.*, 1979, **24**, 1603; P. K. Migal, V. A. Tsiplyakovas and Vu Ngoc Ban, *Chem. Abstr.*, 1979, **90**, 44 635.
886. P. B. Trinderup, *Acta Chem. Scand., Ser. A.*, 1979, **33**, 7.
887. B. Merzubraimov, *Zh. Neorg. Khim.*, 1978, **23**, 3149.
888. N. C. Mishra, B. K. Mohapatra and S. Guru, *Indian J. Chem., Sect. A*, 1978, **16**, 904.
889. N. C. Mishra, B. K. Mohapatra and S. Guru, *J. Inorg. Nucl. Chem.*, 1979, **41**, 408.
890. V. I. Bondar, V. G. Rau and Tu. T. Struchkov, *Dokl. Akad. Nauk SSSR*, 1980, 4.
891. T. Ya. Ashikhmira, A. S. Karenaukhov and N. N. Runov, *Resp. Sb. Nauchn. Tr.-Yarosl. Gos. Pedagog. Inst. Ushinskogo*, 1978, **169**, 34.
892. C. S. G. Prasad and S. K. Banerji, *J. Inorg. Nucl. Chem.*, 1975, **37**, 1989.
893. S. Baggio, R. F. Baggio and P. K. de Perazzo, *Acta Crystallogr., Sect. B*, 1974, **30**, 2166.
894. G. Marcotrigiano, *Z. Anorg. Allg. Chem.*, 1976, **422**, 80.
895. G. Marcotrigiano, *Z. Anorg. Allg. Chem.*, 1976, **417**, 75.
896. (a) Z. Gabelica, *Chem. Abstr.*, 1976, **84**, 82 089; (b) V. I. Ovcharenko and S. V. Larinov, *Zh. Neorg. Khim.*, 1981, **26**, 2758.
897. G. C. Pellacani, G. Peyronnel, G. Pollacci and R. Coronati, *J. Inorg. Nucl. Chem.*, 1976, **38**, 1619.
898. L. Menabue, G. C. Pellacani and G. Peyronel, *Inorg. Nucl. Chem. Lett.*, 1974, **10**, 187.
899. A. C. Fabretti, G. C. Pellacani and G. Peyronel, *Gazetta*, 1973, **103**, 1259.
900. G. C. Pellacani, A. C. Fabretti and G. Peyronel, *Inorg. Nucl. Chem. Lett.*, 1973, **9**, 897.
901. A. C. Fabretti, G. C. Pellacani and G. Peyronel, *J. Inorg. Nucl. Chem.*, 1974, **36**, 1751.
902. J. A. McCleverty, S. Gill, R. S. Z. Kowalski, N. A. Bailey, H. Adams, K. W. Lumbard and M. A. Murphy, *J. Chem. Soc., Dalton Trans.*, 1982, 493.
903. H. Sauter and M. Dobler, *Helv. Chim. Acta*, 1982, **65**, 1297.
904. S. Burman and D. N. Sathyanarayana, *J. Inorg. Nucl. Chem.*, 1981, **43**, 1940.
905. D. L. Greeve, B. J. McCormick and C. G. Pierpont, *Inorg. Chem.*, 1973, **12**, 2148.
906. A. Nieuwport, A. H. Dix, P. A. T. W. Porskamp and J. G. M. van der Linden, *Inorg. Chim. Acta*, 1979, **35**, 221.
907. C. C. Ashworth, W. A. Bailey, M. Johnson, J. A. McCleverty, N. Morrison and B. Tabbiner, *J. Chem. Soc., Chem. Commun.*, 1976, 743.
908. J. A. McCleverty and N. J. Morrison, *J. Chem. Soc., Chem. Commun.*, 1974, 1048.
909. D. Gattegnio and A. M. Guillani, *J. Inorg. Nucl. Chem.*, 1974, **36**, 1553.
910. M. F. Iskander, M. Mishrikey and L. El-Sayed, *J. Inorg. Nucl. Chem.*, 1979, **41**, 231.
911. B. B. Mahapatra, A. Panda and N. C. Misra, *J. Inst. Chem., Calcutta*, 1980, **52**, 121.
912. E. Larsen and P. B. Trinderup, *Acta Chem. Scand., Ser. A*, 1975, **29**, 481.
913. E. M. Movsumov, R. A. Alekperov, S. T. Amirov and K. S. Mamedov, *Chem. Abstr.*, 1976, **85**, 13 147.
914. G. Colombini and C. Preti, *J. Inorg. Nucl. Chem.*, 1975, **37**, 1159.
915. K. Kato, Y. Sugitani and K. Nagashima, *J. Inorg. Nucl. Chem.*, 1975, **37**, 2057.
916. C. Preti and G. Tosi, *Can. J. Chem.*, 1976, **54**, 1558.
917. (a) R. L. Coates and M. M. Jones, *J. Inorg. Nucl. Chem.*, 1976, **38**, 1549; (b) J. A. McLeverty *et al.*, *Transition Met. Chem.*, 1981, **6**, 64.
918. M. Shimoi, A. Ouchi, M. Aikawa, S. Saot and Y. Saito, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 2089.
920. H. Wunderlich, *Acta Crystallogr., Sect. B*, 1982, **38**, 614.
921. A. J. Blake, G. P. McQuillan and I. A. Oxton, *Spectrochim. Acta, Part A*, 1980, **36**, 501.
922. W. Kuchen, J. Delventhal and H. Kech, *Chim. Ber.*, 1974, **107**, 2938.
923. J. Gary and A. Adeyemo, *Inorg. Chim. Acta*, 1981, **55**, 93.
924. A. D. Adeyemo, *Inorg. Chim. Acta*, 1981, **55**, 177.
925. V. A. Mukhedar, U. A. Bhagwat and A. J. Mukhedar, *J. Chem. Soc., Dalton Trans.*, 1982, 1899.
926. B. E. Zaitsev, T. M. Ivanova and V. V. Davyolov, *Zh. Neorg. Khim.*, 1980, **25**, 3031.
927. J. A. McCleverty, N. Spencer, N. A. Bailey and S. L. Shackleton, *J. Chem. Soc., Dalton Trans.*, 1980, 1823.
928. F. Capitan, F. Salinas and L. F. Capitan-Vallvey, *Bull. Soc. Chim. Fr.*, 1979, 185.
929. R. Triolo and A. H. Narten, *J. Chem. Phys.*, 1981, **74**, 703.
930. S. Benhenda and J. B. Lesourd, *Can. J. Chem.*, 1980, **58**, 1562.

931. M. V. Susic and S. V. Mentus, *J. Chem. Phys.*, 1975, **62**, 744.
932. B. M. Voronin, S. P. Baranov and V. O. Prisyazhnyi, *Chem. Abstr.*, 1975, **82**, 48 261.
933. S. Biggin and J. E. Enderby, *J. Phys. C*, 1981, **14**, 3129.
934. Y. Takagi and T. Nakamura, *Nippon Kagaku Kaishi*, 1982, 928.
935. M. Itoh, K. Sakai and T. Nakamura, *Inorg. Chem.*, 1982, **21**, 3552.
936. B. Cristol, J. Houriez and D. Balesdent, *J. Chem. Thermodyn.*, 1981, **13**, 937.
937. S. V. Petrov and Yu. F. Orekhov, *Zh. Neorg. Khim.*, 1982, **27**, 750.
938. H. Salamati-Mashhad, G. S. Dixon and J. J. Martin, *J. Appl. Phys.*, 1982, **53**, 1929.
939. S. P. Singh, J. P. Gupta, N. Singh and N. B. Singh, *Thermochim. Acta*, 1982, **54**, 369.
940. B. P. Burylev, *Komplksn. Ispol'z. Miner. Syr'ya*, 1982, 26.
941. S. Nakazawa, *Tohoku Daigaku Senko Seiren Kenkyusho Iho* (*Chem. Abstr.*, 1981, **37**, 161).
942. I. I. Il'yasov, T. I. Denaeva and V. V. Kantaurov, *Zh. Neorg. Khim.*, 1982, **27**, 499.
943. D. H. Kerridge and I. A. Sturton, *Inorg. Chim. Acta*, 1973, **7**, 701.
944. D. H. Kerridge and I. A. Sturton, *Inorg. Chim. Acta*, 1973, **8**, 31.
945. D. H. Kerridge and I. A. Sturton, *Inorg. Chim. Acta*, 1973, **8**, 37.
946. D. H. Kerridge and I. A. Sturton, *Inorg. Chim. Acta*, 1973, **8**, 27.
947. D. H. Kerridge and I. A. Sturton, *Inorg. Chim. Acta*, 1974, **10**, 13.
948. N. J. Robertson and A. S. Kicharski, *Can. J. Chem.*, 1973, **51**, 3114.
949. Z. Gregorczyk, *Chem. Abstr.*, 1974, **80**, 74 848.
950. R. M. Nicolic and I. J. Gal, *J. Chem. Soc., Dalton Trans.*, 1972, 162.
951. R. M. Nicolic and I. J. Gal, *J. Chem. Soc., Dalton Trans.*, 1974, 985.
952. K. B. Yatsimirskii, S. V. Volkov, N. P. Evtushenko and N. I. Buryak, *Chem. Abstr.*, 1975, **83**, 18 034.
953. W. Bues and W. Brockner, *Z. Phys. Chem.*, 1974, **88**, 290.
954. B. F. Markov and V. Y. Loichenko, *Chem. Abstr.*, 1974, **81**, 143 029.
955. E. M. Gildebrandt and P. V. Polyanov, *Chem. Abstr.*, 1975, **83**, 16 685.
956. S. V. Volkov, N. P. Evtushenko and K. B. Yatsimirskii, *Chem. Abstr.*, 1976, **84**, 157 526.
957. Y. N. Denisov, N. S. Malova and P. I. Fedorov, *Zh. Neorg. Khim.*, 1975, **20**, 3145.
958. R. G. Anthony and H. Bloom, *Aust. J. Chem.*, 1975, **28**, 2587.
959. R. G. Anthony and H. Bloom, *Aust. J. Chem.*, 1976, **29**, 65.
960. C. A. Angell, C. H. Wegdam and J. van der Elsken, *Spectrochim. Acta, Part A*, 1974, **30**, 665.
961. C. B. Lindahl, *Kirk-Othmer Encyl. Chem. Technol., 3rd Ed.*, 1980, **10**, 526.
962. G. J. Kleppa and M. Wakihara, *J. Inorg. Nucl. Chem.*, 1976, **38**, 715.
963. C. J. J. van Loon and D. J. W. Ijdo, *Acta Crystallogr., Sect. B*, 1975, **31**, 770.
964. H. Ohtaki and G. Johansson, *Pure Appl. Chem.*, 1981, **53**, 1357.
965. M. Christahl and J. Thoennissen, *Z. Naturforsch., Teil A*, 1982, **37**, 224.
966. W. Libus, R. Pastewski and T. Sadowska, *J. Chem. Soc., Faraday Trans.*, 1982, **78**, 377.
967. H. Doe and T. Kitagawa, *Inorg. Chem.*, 1982, **21**, 2273.
968. L. A. Monyakina and B. P. Churgalov, *Zh. Fiz. Khim.*, 1982, **56**, 951.
969. B. R. Churagulov and L. A. Monyakina, *Zh. Fiz. Khim.*, 1982, **56**, 337.
970. J. Jorne and W. T. Ho, *J. Electrochem. Soc.*, 1982, **129**, 907.
971. N. A. Ramos, V. A. Vicente and A. S. Lorica, *Natl. Appl. Sci. Bull.*, 1980, **32**, 159.
972. A. P. Kreshkov, S. M. Milaev and M. M. Baldshov, *Chem. Abstr.*, 1974, **81**, 111 930.
973. G. Maisano, P. Migliardo and F. Wanderlingh, *J. Phys., Colloq.* (*Orsay, Fr.*), 1981, 51.
974. R. L. Blokhra and M. L. Parmar, *Chem. Abstr.*, 1975, **82**, 116 959.
975. J. A. Swamy, B. Sethuran and T. N. Rao, *Chem. Abstr.*, 1975, **82**, 175 977,
976. V. M. Samoilenko, V. I. Lyashenko and N. V. Polishchuk, *Zh. Neorg. Khim.*, 1974, **19**, 2984.
977. H. F. Shurvell and A. Dunham, *Can. J. Spectrosc.*, 1978, **23**, 160.
978. C. K. Moller, *Acta Chem. Scand., Ser. A*, 1979, **33**, 11.
979. J. J. H. Ackerman, T. V. Orr, V. J. Bartuska and G. E. Maciel, *J. Am. Chem. Soc.*, 1979, **101**, 341.
980. E. A. Belousov and A. A. Alovyainikov, *Zh. Neorg. Khim.*, 1975, **20**, 1428.
981. Z. Libus and H. Tialowska, *J. Solution Chem.*, 1975, **4**, 1011.
982. E. Y. Gorenbein, A. K. Trofimchuk and M. N. Vainshtein, *Chem. Abstr.*, 1975, **83**, 137 737.
983. S. C. Lal and B. Prasad, *J. Indian Chem. Soc.*, 1975, **53**, 136.
984. P. Beutler, K. Christen and H. Gamsjaeger, *Chimia*, 1976, **30**, 104.
985. R. Aruga, *Ann. Chim.* (*Rome*), 1974, **64**, 439.
986. A. K. Trofimchuck and Y. N. Nizel'skii, *Zh. Neorg. Khim.*, 1974, **19**, 2308.
987. V. A. Prokuev and E. A. Belousov, *Russ. J. Phys. Chem.* (*Engl. Transl.*), 1979, **53**, 756.
988. L. Yu. Lamanskii and K. I. Tikhonov, *Zh. Neorg. Khim.*, 1979, **24**, 1204.
989. D. W. France, E. A. Neaves and M. A. C. Dellatone, *Cienc. Cult.* (*Sao Paulo*) 1978, **30**, 1450; L. Y. Lamanskii and K. I. Tikhonov, *Zh. Obshch. Khim.*, 1979, **49**, 1143.
990. S. Ahrland, N. O. Bjoerk and I. Persson, *Acta Chem. Scand., Ser. A*, 1981, **35**, 67.
991. F. Gaizer and H. B. Silber, *J. Inorg. Nucl. Chem.*, 1980, **42**, 1317.
992. I. Persson, A. Iverfeldt and S. Ahrland, *Acta Chem. Scand., Ser. A*, 1981, **35**, 295.
993. V. V. Skopenko, V. M. Samoilenko and O. G. Movchan, *Biol. Nauki*, 1981, **55** (*Chem. Abstr.*, 1981, **95**, 125 306).
994. V. V. Skopenko, O. G. Movchan and V. M. Samoilenko, *Biol. Nauki*, 1981, **51** (*Chem. Abstr.*, 1981, **95**, 50 389).
995. J. C. Folest and M. Troupel, *Bull. Soc. Chim. Fr.*, 1980, 181.
996. H. Daud and R. W. Cattrall, *J. Inorg. Nucl. Chem.*, 1981, **43**, 599.
997. H. Daud and R. W. Cattrall, *J. Inorg. Nucl. Chem.*, 1981, **43**, 779.
998. V. A. Prokuev and E. A. Belousov, *Zh. Fiz. Khim.*, 1980, **54**, 3143.
999. V. A. Prokuev and E. A. Belousov, *Zh. Neorg. Khim.*, 1980, **25**, 3343.
1000. V. A. Prokuev and E. A. Belousov, *Zh. Neorg. Khim.*, 1981, **26**, 444.
1001. D. N. Waters, E. L. Short, M. Tharwat and D. F. C. Morrison, *J. Cryst. Mol. Struct.*, 1973, **17**, 389.

1002. S. Ahrland, N. O. Bjork and R. Portanova, *Acta Chem. Scand., Ser. A*, 1976, **30**, 270.
1003. S. Ahrland and N. P. Bjork, *Acta Chem. Scand., Ser. A*, 1976, **30**, 265.
1004. S. Ahrland and N. P. Bjork, *Acta Chem. Scand., Ser. A*, 1976, **30**, 257.
1005. S. Ahrland and N. P. Bjork, *Acta Chem. Scand., Ser. A*, 1976, **30**, 249.
1006. E. Y. Gorenbein and V. M. Shevchenko, *Chem. Abstr.*, 1976, **84**, 156 342.
1007. S. Pocev, R. Triolo and G. Johansson, *Acta Chem. Scand., Ser. A*, 1979, **33**, 179.
1008. E. Y. Gorenbein, M. N. Vainshtein, E. P. Skorobogatko and A. K. Trofinchuk, *Zhur. Obshch. Khim.*, 1974, **44**, 1558.
1009. E. Y. Gorenbein and E. Y. Shapiro, *Zh. Obshch. Khim.*, 1976, **46**, 212.
1010. E. Y. Gorenbein, *Zh. Obshch. Khim.*, 1974, **44**, 2391.
1011. E. Y. Gorenbein, *Zh. Obshch. Khim.*, 1974, **44**, 2388.
1012. E. Y. Gorenbein, M. N. Vainshtein and E. P. Skorobogat'ko, *Chem. Abstr.*, 1975, **82**, 8287.
1013. D. Paoli and M. Chabanal, *C.R. Hebd. Seances Acad. Sci.*, 1975, **280**, C. 243.
1014. J. C. Folest and M. Troupel, *Bull. Soc. Chim. Fr.*, 1980, 182.
1015. D. P. Strommen and R. A. Plane, *J. Chem. Phys.*, 1974, **60**, 2643.
1016. A. Antic-Jovanovic, M. Jeremic and D. A. Long, *J. Raman. Spectrosc.*, 1982, **12**, 91.
1017. I. Persson, A. Iverfeldt and S. Ahrland, *Acta Chem. Scand. Ser. A*, 1981, **35**, 295.
1018. N. P. Evtushenko, V. A. Susko and J. V. Volkov, *Chem. Abstr.*, 1974, **80**, 32 090.
1019. J. Fernandez, C. Socias, M. A. Arriandiaga, M. J. Tello and A. Lopez Echarri, *J. Phys. C*, 1982, **15**, 1151.
1020. G. A. Smolenskii, I. G. Sinii and S. D. Prokhorova, *Ferroelectrics*, 1981, **36**, 351.
1021. C. S. Sundaram and J. Ramakrishna, *Curr. Sci.*, 1981, **50**, 1064.
1022. J. Warczewski, J. Broda and D. Kucharczyk, *Phase Transitions*, 1981, **2**, 131.
1023. G. Marion, R. Almairac, J. Lefebvre and M. Ribet, *J. Phys. C*, 1981, **14**, 3177.
1024. J. M. Perez-Mato, J. L. Manes and J. Fernandez, *Phys. Status Solidi A*, 1981, **68**, 29.
1025. V. Dvorak and R. Kind, *Phys. Status Solidi A*, 1981, **107**, K109.
1026. N. E. Massa, *J. Phys., Colloq. (Orsay, Fr.)*, 1981, 593.
1027. M. Quilichini, J. P. Mathieu and M. Le Postollec, *J. Phys. (Les Ulis, Fr.)*, 1982, **43**, 787.
1028. R. Blinc, I. P. Aleksandrova and A. S. Chaves, *J. Phys. C*, 1982, **15**, 547.
1029. A. Rahman, P. R. Clayton and L. A. K. Staveley, *J. Chem. Thermodyn.*, 1981, **13**, 735.
1030. M. A. White, N. W. Granville, N. J. Davies and L. A. K. Staveley, *J. Phys. Chem. Solids*, 1981, **42**, 953.
1031. B. Morosin and K. Emerson, *Acta Crystallogr., Sect B*, 1976, **32**, 294.
1032. I. Sotofte, R. G. Hazell and S. E. Rasmussen, *Acta Crystallogr., Ser. B*, 1976, **32**, 1692.
1033. J. A. McGinnety, *Inorg. Chem.*, 1974, **13**, 1057.
1034. D. W. Meek and J. A. Ibers, *Inorg. Chem.*, 1960, **9**, 465.
1035. G. Bombieri, E. Forsellini, A. Del Pra and M. L. Tobe, *Inorg. Chim. Acta*, 1981, **51**, 177.
1036. M. C. Kerr, H. S. Preston, H. L. Ammon, J. E. Huheey and J. M. Stewart, *J. Coord. Chem.*, 1981, **11**, 111.
1037. M. Ardon, F. A. Cotton, Z. Dori, A. Fang, M. Kapon, G. M. Reisner and M. Shaia, *J. Am. Chem. Soc.*, 1982, **104**, 5394.
1038. K. Davarski, M. Genchev, N. Khalachev and L. Konovalov, *Koord. Khim.*, 1981, **7**, 1474.
1039. S. N. Ghosh, *J. Inorg. Nucl. Chem.*, 1973, **35**, 2329.
1040. M. F. Richardson, K. Franklin and D. M. Thompson, *J. Am. Chem. Soc.*, 1975, **97**, 3204.
1041. P. L. Orioli and H. C. Lip, *Cryst. Struct. Commun.*, 1974, **3**, 477.
1042. W. Beck, C. J. Oetker and P. Swoboda, *Z. Naturforsch., Teil B*, 1973, **28**, 229.
1043. E. Herdtweck and D. Babel, *Z. Kristallogr.*, 1980, **153**, 189.
1044. M. Kidaka and S. Hosogi, *J. Phys. (Les Ulis, Fr.)*, 1982, **43**, 1227.
1045. T. Fleischer and R. Hoppe, *J. Fluorine Chem.*, 1982, **19**, 529.
1046. M. Ledesert and J. C. Monier, *Acta Crystallogr., Sect. B*, 1982, **38**, 237.
1047. A. Leclaire and M. M. Borel, *Acta Crystallogr., Sect. B*, 1982, **38**, 234.
1048. M. Ledesert, *Acta Crystallogr., Sect. B*, 1982, **38**, 1569.
1049. A. G. Galinos and S. P. Perlepes, *Monatsh. Chem.*, 1980, **11**, 829.
1050. J. W. Bats, H. Friess and A. Daoud, *Acta Crystallogr., Sect. B*, 1979, **35**, 1706.
1051. M. M. Rolies and C. J. De Ranter, *Acta Crystallogr., Sect. B*, 1978, **34**, 3057.
1052. U. Walther, D. Brinkmann, G. Chapuis and H. Arend, *Solid State Commun.*, 1978, **27**, 901.
1053. G. L. McPherson and A. M. McPherson, *J. Phys. Chem. Solids*, 1980, **41**, 495.
1054. M. Natarjan, H. E. Howard-Lock and I. D. Brown, *Proc. Int. Conf. Raman Spectrosc., 6th*, 1978, **2**, 354.
1055. J. G. Contreras and T. M. Meyer, *Spectrochim. Acta, Part A*, 1980, **36**, 273.
1056. S. Papp and E. Keszei, *Z. Anorg. Allg. Chem.*, 1979, **458**, 241.
1057. J. R. Chang, G. L. McPherson and J. L. Attwood, *Inorg. Chem.*, 1975, **14**, 3079.
1058. J. G. Contreras and D. G. Tuck, *Can. J. Chem.*, 1975, **53**, 3487.
1059. N. K. Sanyal, P. K. Goel and A. N. Pandey, *Indian J. Phys.*, 1975, **49**, 546.
1060. M. A. Saraukhamov, S. S. Val'kman and N. A. Parpiev, *Chem. Abstr.*, 1974, **81**, 98 790.
1061. H. Leligny and J. C. Monier, *Acta Crystallogr., Sect. B*, 1975, **31**, 728.
1062. R. Roistelle, G. Pepe, B. Simon and A. Leclaire, *Acta Crystallogr. Sect. B*, 1974, **30**, 2200.
1063. M. Socchie and A. Albinati, *J. Organomet. Chem.*, 1974, **77**, C40.
1064. J. J. Habeeb, A. Osman and D. G. Tuck, *J. Chem. Soc., Chem. Commun.*, 1976, 379.
1065. G. Srdanov, R. Herak and B. Prelsnik, *Glas. Hem. Drus., Beograd.*, 1979, **44**, 561.
1066. G. B. Aitken and G. P. McQuillan, *J. Chem. Soc., Dalton Trans.*, 1973, 2637.
1067. M. Cannas, G. Carta, A. Cristini and G. Marongiu, *J. Chem. Soc., Dalton Trans.*, 1976, 300.
1068. A. E. Shvelashvili, A. I. Kvitashvilli, B. M. Shchedrin, A. R. Khvoles and L. M. Chanturiya, *Chem. Abstr.*, 1975, **82**, 79 112.
1069. P. P. Singh and S. A. Khan, *Inorg. Chim. Acta*, 1975, **14**, 143.
1070. A. E. Shvelashvili, *Chem. Abstr.*, 1975, **82**, 66 716.

1071. A. E. Shvelashvili, M. A. Porai-Koshits, A. I. Kvitashvili, B. M. Shchedrin and L. P. Sarishvili, *Zh. Strukt. Khim.*, 1974, **15**, 315.
1072. D. Satyanarayana and G. Sahu, *J. Chem. Soc., Dalton Trans.*, 1975, 2236.
1073. G. Thiele and P. Hilfrich, *Z. Naturforsch., Teil B*, 1975, **30**, 19.
1074. (a) B. D. Cutforth, R. J. Gillespie and P. K. Ummat, *Rev. Chim. Minérale*, 1976, **13**, 119; (b) M. Brezeanu and L. Patron, *Chem. Abstr.*, 1974, **81**, 98 798.
1075. M. Brezeanu and L. Patron, *Chem. Abstr.*, 1974, **81**, 98 797.
1076. P. P. Singh, U. P. Shukla, R. Makhija and R. Rivest, *J. Inorg. Nucl. Chem.*, 1975, **37**, 679.
1077. J. St. Denis, W. Butler, M. D. Glick and J. P. Oliver, *J. Am. Chem. Soc.*, 1974, **96**, 5429.
1078. W. Clegg and P. J. Wheatley, *J. Chem. Soc., Dalton Trans.*, 1973, 90.
1079. W. Clegg and P. J. Wheatley, *J. Chem. Soc., Dalton Trans.*, 1973, 424.
1080. W. Clegg and P. J. Wheatley, *J. Chem. Soc., Dalton Trans.*, 1973, 511.
1081. P. P. Singh and S. A. Khan, *Z. Anorg. Allg. Chem.*, 1976, **423**, 173.
1082. P. P. Singh and J. N. Seth, *Inorg. Chim. Acta*, 1975, **15**, 227.
1083. P. P. Singh, S. A. Khan and R. B. Pal, *Inorg. Nucl. Chem. Lett.*, 1975, **11**, 807.
1084. P. P. Singh, A. K. Srivastava and R. Rivest, *J. Inorg. Nucl. Chem.*, 1976, **38**, 439.
1085. R. C. Aggarwal, B. Singh and M. K. Singh, *J. Indian Chem. Soc.*, 1982, **59**, 269.
1086. M. G. B. Drew, D. A. Rice and K. M. Richards, *J. Chem. Soc., Dalton Trans.*, 1980, 2075.
1087. G. Anderegg and W. Klau, *Z. Naturforsch., Teil B*, 1981, **36**, 949.
1088. E. A. H. Griffith, N. G. Charles and E. L. Amma, *Acta Crystallogr., Sect. B*, 1982, **38**, 262.
1089. P. M. Fedorov, L. S. Andreyanova and V. Pakhomov, *Khoord. Khim.*, 1975, **1**, 252.
1090. H. J. Buser, G. Ron, A. Ludi and P. Engel, *J. Chem. Soc., Chem. Commun.*, 1974, 2473.
1091. F. Bonati and H. C. Clark, *Can. J. Chem.*, 1979, **57**, 483.
1092. P. A. Rebbah, A. Leclaire, J. Yazbeck and A. Deschariures, *Acta Crystallogr., Sect. B*, 1979, **35**, 2197.
1093. P. Amico, P. G. Daniele, G. Arena, G. Ostacoli, E. Rizzarelli and S. Sammartano, *Inorg. Chim. Acta*, 1979, **35**, L383.
1094. L. B. McCusker and K. Seff, *J. Am. Chem. Soc.*, 1979, **101**, 5235.
1095. P. Natarajan and N. V. Raghavan, *J. Chem. Soc., Chem. Commun.*, 1980, 268.
1096. (a) J. K. Weddell, A. L. Allred and D. Meyerstein, *J. Inorg. Nucl. Chem.*, 1980, **42**, 219; (b) G. V. Buxton and R. M. Sellers, *Coord. Chem. Rev.*, 1977, **22**, 195.
1097. V. G. I. Deshmukh, G. A. Styles and E. F. W. Seymour, *Phys. Lett. A*, 1980, **78**, 119.
1098. Z. P. Haque, M. McPartlin and P. A. Tasker, *Inorg. Chem.*, 1979, **18**, 2920.
1099. W. Radecka-Paryzek, *Inorg. Chim. Acta*, 1979, **34**, 5.
1100. M. G. B. Drew, S. G. McFall and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1979, 575.
1101. H. Hafliger and T. A. Kaden, *Helv. Chim. Acta*, 1979, **62**, 683.
1102. R. W. Renfrew, R. S. Jamison and D. C. Weatherburn, *Inorg. Chem.*, 1979, **18**, 1584.
1103. P. Schultz-Grunow and T. A. Kaden, *Helv. Chim. Acta*, 1978, **61**, 2291; 2296.
1104. D. R. Neves and J. C. Dabrowiak, *Inorg. Chem.*, 1976, **15**, 129.
1105. B. K. Coltrain and S. C. Jackels, *Inorg. Chem.*, 1981, **20**, 2032.
1106. S. M. Nelson, C. V. Knox, M. McCann and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, 1981, 1670.
1107. D. E. Fenton and R. Leonaldi, *Inorg. Chim. Acta*, 1981, **55**, L51.
1108. S. Kulstad and L. A. Malmsten, *J. Inorg. Nucl. Chem.*, 1980, **42**, 1193.
1109. M. Micheloni and P. Paoletti, *Inorg. Chim. Acta*, 1980, **43**, 109.
1110. D. P. Graddon, M. Micheloni and P. Paoletti, *J. Chem. Soc., Dalton Trans.*, 1981, 336.
1111. K. B. Yatsimirskii and V. V. Pavlishchuk, *Zh. Neorg. Khim.*, 1981, **26**, 1812.
1112. S. M. Nelson, C. V. Knox, M. McCann and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, 1981, 1669.
1113. L. F. Lindoy, H. C. Lip, L. F. Power and J. H. Rea, *Inorg. Chem.*, 1976, **15**, 1724.
1114. B. Spiess and F. Arnaud-Neu, *Helv. Chim. Acta*, 1980, **63**, 2287.
1115. N. Morel-Desrosiers and J. P. Morel, *J. Am. Chem. Soc.*, 1981, **103**, 4743.
1116. J. M. Lehn, *Pure Appl. Chem.*, 1978, **50**, 871.
1117. B. Spiess, F. Arnaud-Neu and M.-J. Schwing-Weill, *Helv. Chim. Acta*, 1979, **62**, 1531.
1118. L. F. Lindoy, H. C. Lip, J. H. Rea, R. J. Smith, K. Henrick, M. McPartlin and P. A. Tasker, *Inorg. Chem.*, 1980, **19**, 3360.
1119. E. H. Curzon, N. Herron and P. Moore, *J. Chem. Soc., Dalton Trans.*, 1980, 721.
1120. M. Kodama, E. Kimura and S. Yamaguchi, *J. Chem. Soc., Dalton Trans.*, 1980, 2536.
1121. M. Kodama and E. Kimura, *J. Chem. Soc., Dalton Trans.*, 1980, 2447.
1122. K. B. Yatsimirskii and V. V. Pavlishchuk, *Zh. Neorg. Khim.*, 1980, **25**, 1784.
1123. L. F. Lindoy, H. C. Lip, J. H. Rea, R. J. Smith, K. Henrick, M. McPartlin and P. A. Tasker, *Inorg. Chem.*, 1980, **19**, 3360.
1124. J. Lewis and T. D. O'Donoghue, *J. Chem. Soc., Dalton Trans.*, 1980, 741.
1125. J. Lewis and T. D. O'Donoghue, *J. Chem. Soc., Dalton Trans.*, 1980, 736.
1126. J. Lewis, T. D. O'Donoghue, Z. P. Haque and P. A. Tasker, *J. Chem. Soc., Dalton Trans.*, 1980, 1664.
1127. K. B. Yatsimirskii, V. P. Vasil'ev, T. D. Orlova and V. V. Pavlishchuk, *Zh. Neorg. Khim.*, 1981, **26**, 2937.
1128. R. D. Hancock and V. J. Thom, *J. Am. Chem. Soc.*, 1982, **104**, 291.
1129. W. L. Dreissen and M. den Heijer, *Transition Met. Chem. (Weinheim, Ger.)*, 1981, **6**, 338.
1130. R. J. Motekaitis, A. E. Martell, J.-M. Lehn and E.-I. Watanabe, *Inorg. Chem.*, 1982, **21**, 4253.
1131. F. Arnoud-Neu, B. Speiss and M. J. Schwing-Weill, *J. Am. Chem. Soc.*, 1982, **104**, 5641.
1132. J. D. Lamb, R. M. Izatt, P. A. Robertson and J. J. Christensen, *J. Am. Chem. Soc.*, 1980, **102**, 2452.
1133. T. Suzuki and N. Murakami, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 1453.
1134. V. N. Kopranenkov, E. A. Makarova and E. A. Luk'yanets, *Zh. Obshch. Khim.*, 1981, **51**, 2727.
1135. V. N. Kopranenkov, S. N. Dashkevich and E. A. Luk'Yanets, *Zh. Obshch. Khim.*, 1981, **51**, 2513.
1136. G. I. Goncharova, M. G. Gal'pern and E. A. Luk'yanets, *Zh. Obshch. Khim.*, 1983, **52**, 666.
1137. S. A. Mikhalenko and V. M. Derkacheva, *Zh. Obshch. Khim.*, 1981, **51**, 1650.

1138. A. Vegler and H. Kinkely, *Inorg. Chim. Acta,* 1980, **44,** L209.
1139. V. N. Kopranenkov and A. M. Vorotnikov, *Zh. Obshch. Khim.,* 1979, **49,** 2783.
1140. H. J. Callot and E. Schaeffer, *Nouv. J. Chim.,* 1980, **4,** 307.
1141. G. V. Ponomarev, G. V. Kirillova and G. B. Maravin, *Khim. Geterotsikl. Soedin.,* 1979, 776.
1142. B. D. Berezin, I. K. Barvinskaya and L. I. Sharova, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.,* 1980, **23,** 285.
1143. G. V. Ponomarev, *Khim. Geterotsikl. Soedin.,* 1980, 943.
1144. P. Natarajan and N. V. Raghavan, *J. Chem. Soc., Chem. Commun.,* 1980, 268.
1145. N. B. H. Henis, T. L. Youngless and M. M. Bursey, *J. Chem. Soc., Dalton Trans.,* 1980, 1416.
1146. R. R. Das and K. N. Rao, *Inorg. Chim. Acta,* 1980, **42,** 227.
1147. J. Turay and P. Hambright, *Inorg. Chem.,* 1980, **19,** 562.
1148. A. N. Thompson and M. Krishnamurthy, *J. Inorg. Nucl. Chem.,* 1979, **41,** 1251.
1149. D. K. Lavallee and G. M. Onady, *Inorg. Chem.,* 1981, **20,** 907.
1150. A. Harriman and G. Porter, *J. Chem. Soc., Faraday Trans. 2,* 1981, **77,** 833.
1151. T. I. Potapova, R. A. Petrova and L. I. Kalenkova, *Zh. Fiz. Khim.,* 1981, **55,** 116.
1152. N. Kobayashi, M. Fujihgira and T. Osa, *Bull. Chem. Soc. Jpn.,* 1980, **53,** 2195.
1153. A. Shamim and P. Hambright, *J. Inorg. Nucl. Chem.,* 1980, **42,** 1645.
1154. N. V. Ivashin, S. N. Terekhov and I. F. Gurinovich, *Zh. Prikl. Spectrosk.,* 1981, **34,** 124.
1155. R. J. Abraham, G. R. Bedford and B. Wright, *Org. Magn. Reson.,* 1982, **18,** 45.
1156. T. A. Koroleva, O. I. Koifman and B. D. Berezin, *Koord. Khim.,* 1981, **7,** 1642.
1157. K. M. Kadish and L. R. Shiue, *Inorg. Chem.,* 1982, **21,** 3623.
1158. (a) K. J. Reimer and M. M. Reimer, *Inorg. Chim. Acta,* 1981, **56,** L5; (b) R. S. Drago, *Coord. Chem. Rev.,* 1980, **33,** 251; (c) B. D. Berezin and O. I. Koifman, *Russ. Chem. Rev.* (*Engl. Transl.*), 1980, **49,** 1188; (d) P. D. Smith, *Coord. Chem. Rev.,* 1981, **39,** 31.
1159. (a) J. Goulon, C. Goulon, F. Nierdercorn, C. Selve and B. Castro, *Tetrahedron,* 1981, **37,** 3707; (b) J. R. Darwent, P. Douglas, A. Harrison, G. Porter and M. C. Richoux, *Coord. Chem. Rev.,* 1982, **44,** 83.
1160. I. Okura, M. Takeuchi and N. Kim-Thuan, *Chem. Lett.,* 1980, 765.
1161. K. K. Sundaran and M. Graetzel, *Helv. Chim. Acta,* 1980, **63,** 478.
1162. G. McLendon and D. S. Miller, *J. Chem. Soc., Chem. Commun.,* 1980, 533.
1163. M. P. Pileni, *Chem. Phys. Lett.,* 1980, **71,** 317.
1164. (a) A. Harriman, G. Porter and N. Searle, *J. Chem. Soc., Faraday Trans. 2,* 1979, **75,** 1515; (b) K. L. McGourty *et al., J. Am. Chem. Soc.,* 1983, **105,** 4470.
1165. B. D. Berezin, G. A. Tsetkov and L. P. Shormanova, *Zh. Neorg. Khim.,* 1980, **25,** 2645.
1166. M. Nimani and K. Nakajima, *Kokagaku Toronokai Koen Yoehishu,* 1979, 72.
1167. J. R. Darwent, *J. Chem. Soc., Chem. Commun.,* 1980, 805.
1168. A. G. Vinogradskii and A. N. Sidorov, *Teor. Eksp. Khim.,* 1982, **18,** 118.
1169. V. I. Gavrilov, E. A. Luk'yanets and I. V. Shelepin, *Elektrokhimiya,* 1981, **17,** 1183.
1170. I. V. Renge, V. A. Kuz'min, A. F. Mironov and Y. E. Borisevich, *Dokl. Akad. Nauk SSSR* (*Phys. Chem.*), 1982, 1.
1171. L. M. Gurdzhiyan, V. M. Derkacheva, A. V. Butenin, O. L. Kaliya and E. A. Luk'yanets, *Zh. Obshch. Khim.,* 1982, **52,** 1439.
1172. I. Tabushi and A. Yazaki, *Tetrahedron,* 1981, **37,** 4185.
1173. K. Dzilinski and G. N. Sinyakov, *Teor. Eksp. Khim.,* 1982, **18,** 227.
1174. H. M. van Noort *et al., Mol. Phys.,* 1982, **45,** 1259.
1175. S. Inoue *et al., Chem. Lett.,* 1982, 317.
1176. P. Neta, *J. Phys. Chem.,* 1981, **85,** 3678.
1177. K. M. Kadish and L. R. Shiue, *Inorg. Chem.,* 1982, **21,** 3623.
1178. P. J. Spellane, M. Gouterman, A. Antipas, S. Kim and Y. C. Liu, *Inorg. Chem.,* 1980, **19,** 386.
1179. N. Fischer, E. V. Goldammer and J. Pelzl, *J. Mol. Struct.,* 1979, **56,** 95.
1180. (a) A. Harriman, *J. Chem. Soc., Faraday Trans. 1,* 1980, **76,** 1978; (b) see, for example, F. J. Kampas, K. Yamashita and J. Fajer, *Nature,* 1980, **284,** 40 and refs. therein.
1181. A. Harriman and M. C. Richoux, *J. Photochem.,* 1980, **14,** 253.
1182. A. Harriman and M. C. Richoux, *J. Chem. Soc., Faraday Trans. 2,* 1980, **76,** 1618.
1183. V. G. Maslov, *Teor. Eksp. Khim.,* 1980, **16,** 93.
1184. K. M. Kadish, L. R. Shiue, R. K. Rhodes and L. A. Bottomley, *Inorg. Chem.,* 1981, **20,** 1274.
1185. K. M. Kadish and R. K. Rhodes, *Inorg. Chem.,* 1981, **20,** 2961.
1186. V. I. Gavrilov, L. G. Thomilova and I. V. Shelepin, *Tezisy Dokl.-Vses. Soveshch. Polyarogr., 7th,* 1978, 58.
1187. W. Potter, R. N. Young and G. Levin, *J. Am. Chem. Soc.,* 1980, **102,** 2471.
1188. W. Potter and G. Levin, *Photochem. Photobiol.,* 1979, **30,** 225.
1189. K. M. Barkigia, J. Fajer, L. D. Spaulding and G. J. B. Williams, *J. Am. Chem. Soc.,* 1981, **103,** 176.
1190. W. S. Sheldrick and J. Engel, *Acta Crystallogr., Sect. B,* 1981, **37,** 250.
1191. W. S. Sheldrick and J. Engel, *J. Chem. Soc., Chem. Commun.,* 1980, 5.
1192. A. M. Stolzenberg, L. O. Spreer and R. H. Holm, *J. Am. Chem. Soc.,* 1980, **102,** 364.
1193. F. A. Walker, V. L. Balke and G. A. McDermott, *Inorg. Chem.,* 1982, **21,** 3342.
1194. I. F. Gurinovich and S. N. Terekhov, *Teor. Eksp. Khim.,* 1981, **17,** 705.
1195. D. Luo and Z. Zhao, *Wuhan Daxue Xuebao, Ziran Kexueban,* 1982, **98** (*Chem. Abstr.,* 1983, **97,** 103 494).
1196. V. Rasetti, K. Hilpert, A. Faessler, A. Pfasltz and A. Eschenmoser, *Angew. Chem.,* 1981, **93,** 1108; M. D. Maines and J. C. Veltman, *Biochem. J.,* 1984, **217,** 409.
1197. R. Thulasidhass and J. K. Mohanarao, *Curr. Sci.,* 1980, **49,** 349.
1198. V. H. Rao and V. Krishnan, *Inorg. Chem.,* 1985, **24,** 3538; P. F. Rodesiler, E. A. H. Griffith, N. G. Charles, L. Lebioda and E. L. Amma, *Inorg. Chem.,* 1985, **24,** 4595.
1199. R. B. Koehorst and J. F. Kleibeuker, *J. Chem. Soc., Perkin Trans. 2,* 1981, 1005.
1200. A. M. Shul'ga, G. P. Gurinovich and L. I. Krasovskaya, *Dokl. Akad. Nauk SSSR,* 1980, **24,** 176.

1201. R. J. Abraham and S. C. M. Fell, *Tetrahedron*, 1979, **35**, 1759.
1202. (a) T. K. Chandreshekar and V. Krishnan, *Inorg. Chem.*, 1981, **20**, 2782; (b) K. Kasuga and M. Tsutsui, *Coord. Chem. Rev.*, 1980, **32**, 67.
1203. L. Hertli and T. A. Kaden, *Helv. Chim. Acta*, 1974, **57**, 1328.
1204. S. P. Kasprzyk and R. G. Wilkins, *Inorg. Chem.*, 1982, **21**, 3349.
1205. O. A. Golubchikov, E. M. Kuvshinova, O. I. Koifman, B. D. Berezin, L. V. Oparin and V. V. Zvezdina, *Probl. Sol'vatsii I Kompleksoobraz., Ivanovo*, 1980, 9.
1206. B. D. Berezin, O. A. Golubchikov, L. V. Klopova and A. V. Sviridov, *Zh. Fiz. Khim.*, 1982, **56**, 1639.
1207. A. Valiotti, A. Adeyemo, R. F. X. Williams, L. Ricks, J. North and P. Hambright, *J. Inorg. Nucl. Chem.*, 1981, **43**, 2653.
1208. T. Katsuyama and T. Kumai, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 1050.
1209. E. Mentasti, *J. Chem. Soc., Dalton Trans.*, 1980, 958.
1210. T. Nozaki, K. Noda and M. Sakamoto, *Nippon Kagaku Kaishi*, 1979, 1430.
1211. S. F. Lincoln, D. L. Pisaniello, T. M. Spotswood and M. N. Tkaczuk, *Aust. J. Chem.*, 1981, **34**, 283.
1212. M. N. Tzaczuk and S. F. Lincoln, *Aust. J. Chem.*, 1980, **33**, 2621.
1213. P. Letkeman and J. B. Westmore, *J. Chem. Soc., Dalton Trans.*, 1975, 480.
1214. M. C. Gennaro and P. Mirti, *J. Inorg. Nucl. Chem.*, 1981, **43**, 1711.
1215. Y. Funaki, S. Harada, K. Okumiya and T. Yasunaga, *J. Am. Chem. Soc.*, 1982, **104**, 5325.
1216. R. S. McQuate and D. L. Leussing, *J. Am. Chem. Soc.*, 1975, **97**, 5117.
1217. D. R. Eaton and K. Zaw, *J. Inorg. Nucl. Chem.*, 1976, **38**, 1007.
1218. H. P. Fritz and F. Tiedt, *Z. Naturforsch., Teil B*, 1973, **28**, 176.
1219. M. N. Tkachzuk and S. F. Lincoln, *Aust. J. Chem.*, 1979, **32**, 1915.
1220. A. C. Dash, B. Dash and S. Praharaj, *J. Chem. Soc., Dalton Trans.*, 1981, 2063.
1221. M. A. Schwartz, *Bioorg. Chem.*, 1982, **11**, 4.
1222. D. M. W. Buck and P. Moore, *J. Chem. Soc., Dalton Trans.*, 1976, 638.
1223. A. K. Basak, D. Banerjea, R. W. Hay and C. Chatterjee, *J. Coord. Chem.*, 1981, **11**, 195.
1224. C. J. Michejda and D. H. Campbell, *J. Am. Chem. Soc.*, 1974, **96**, 929.
1225. J. Boersma, A. Mackor and J. G. Noltes, *J. Organomet. Chem.*, 1975, **99**, 337.
1226. 'Merck Index of Chemical Drugs', 10th edn., Merck, New York, 1983.
1227. J. Larner, in 'The Pharmacological Basis of Therapeutics', ed. A. G. Gilman, L. S. Goodman and A. Gilman, 6th edn., Macmillan, New York, 1980, pp. 1497 *et seq.*
1228. N. J. Birch and P. J. Sadler, in 'Inorganic Biochemistry' (Specialist Periodical Reports), ed. H. A. O. Hill, The Chemical Society, London, 1979, vol. 1, p. 389; see also 1982, vol. 3, p. 385.
1229. F. Sanger, *Br. Med. Bull.*, 1960, **16**, 183.
1230. P. G. Katsoyannis *et al.*, *J. Am. Chem. Soc.*, 1963, **85**, 2863.
1231. J. Meienhofer, *et al.*, *Z. Naturforsch., Teil C*, 1963, **18**, 1120.
1232. D. F. Steiner, *Diabetes*, 1977, **26**, 322–340; D. F. Steiner, in 'Endocrinology Handbook of Physiology', ed. D. F. Steiner and N. Freinkel, American Physiological Society, Washington D.C., 1972, vol. 1, sect. 7, pp. 175–198.
1233. D. C. Hodgkin and D. Mercola, in 'Endocrinology Handbook of Physiology', ed. D. F. Steiner and N. Freinkel, American Physiological Society, Washington D.C., 1972, vol. 1, sect. 7, pp. 139–157.
1234. (a) C. D. Klaassen, see Ref. 1227, pp. 1632 *et seq.*; (b) A. K. Prokof'ev, *Russ. Chem. Rev.* (*Engl. Transl.*), 1981, **50**, 32; see also ref. 1470.
1235. L. Friberg *et al.*, 'Cadmium in the Environment', 2nd edn., C.R.C. Press, Cleveland, 1974.
1236. J. Kägi and B. L. Vallee, *J. Biol. Chem.*, 1960, **235**, 3460; J. Kägi and B. L. Vallee, *J. Biol. Chem.*, 1961, **236**, 2435.
1237. H. A. Schroeder, *J. Chronic Dis.*, 1965, **18**, 217–228.
1238. A. Gilman *et al.*, *J. Pharmacol. Exp. Ther.*, 1946b, **87**, Suppl., 85–101.
1239. K. J. Sivjakov, *Toxicol. Appl. Pharmacol.*, 1959, **1**, 602–607; V. Eybl and J. Sykora, *Acta Biol. Med. Ger.*, 1966, **16**, 61–64.
1240. L. Friberg, *Arch. Ind. Health*, 1956, **13**, 13–23.
1241. (a) A. Galdes and H. A. O. Hill, in 'Inorganic Biochemistry' (Specialist Periodical Reports), ed. H. A. O. Hill, The Chemical Society, London 1979, vol. 1, p. 317; (b) A. Galdes, ref. 1241(a), vol. 2, p. 16; (c) A. Galdes, ref. 1241(a), vol. 3, p. 268; (d) J. Howell and M. Hughes, in 'Inorganic Chemistry of the Transition Elements' (Specialist Periodical Reports), The Chemical Society, London, 1976, vol. 4, 462; (e) J. Howell and P. Wyeth, see ref. 1241(d), vol. 5, p. 435; (f) J. Howell and P. Wyeth, ref. 1241(d), vol. 6, p. 422; (g) T. Hofmann, in 'Metalloproteins', ed. P. M. Harrison, Macmillan, London, 1985, part 2, p. 1; for recent surveys see particularly ref. 1462.
1242. P. M. Harrison and A. Treffry, in 'Inorganic Biochemistry', (Specialist Periodical Reports), ed. H. A. O. Hill, The Chemical Society, London, 1979, Vol. 1, p. 151.
1243. R. R. Crichton and J.-C. Mareschal, see ref. 1242, 1982, vol. 3, p. 118; P. E. Hunziker and J. H. R. Kägi, in 'Metalloproteins', ed. P. M. Harrison, Macmillan, London, 1985, part 2, p. 149.
1244. J. R. Arthur *et al.*, ref. 1242, 1981, vol. 2, p. 304.
1245. J. R. Arthur *et al.*, ref. 1242, 1982, vol. 3, p. 363; J. K. Chesters, *Chem. Soc. Rev.*, 1981, **10**, 270.
1246. J. Raulin, *Ann. Sci. Nat. Bot. Biol. Veg.*, 1869, **11**, 93.
1247. G. Lechartier and G. Bellamy, *C.R. Hebd. Seances Acad. Sci.*, 1877, **84**, 687.
1248. F. Raoult and H. Breton, *C.R. Hebd. Seances Acad. Sci.*, 1877, **85**, 40.
1249. G. Bertaud and R. C. Bhattacherjee, *C.R. Hebd. Seances Acad. Sci.*, 1934, **198**, 1823.
1250. A. S. Prasad (ed.), 'Trace Elements in Human Health and Disease', Academic, New York, 1976.
1251. F. J. Hewitt and T. A. Smith, 'Plant Mineral Nutrition', English Universites Press, London, 1975.
1252. E. J. Underwood, 'Trace Elements in Human and Animal Nutrition', 4th edn., Academic, New York, 1977.
1253. D. Keilen and T. Mann, *Biochem. J.*, 1940, **34**, 1163.
1254. B. L. Vallee and H. Neurath, *J. Biol. Chem.*, 1955, **217**, 253.
1255. B. L. Vallee, *Trends Biochem. Sci.*, 1976, **1**, 88.

1256. B. L. Vallee, in 'Biological Aspects of Inorganic Chemistry', ed. A. W. Addison, W. R. Cullen, D. Dolphin and B. R. James, Wiley-Interscience, New York, 1977.
1257. J. F. Chlebowski and J. E. Coleman, in 'Metal Ions in Biological Systems', ed. H. Sigel, Dekker, New York, 1976, vol. 6, p. 77.
1258. J. F. Riordan, *Ann. Clin. Lab. Sci.*, 1977, **7**, 119.
1259. J. F. Riordan and B. L. Vallee, in 'Trace Elements in Human Health and Disease', ed. A. S. Prasad, Academic, New York, 1976.
1260. M. L. Failla, in 'Microorganisms and Minerals', ed. E. D. Weinberg, Dekker, New York, 1977, p. 151.
1261. M. R. Dunn, *Struct. Bonding (Berlin)*, 1975, **23**, 61.
1262. T. G. Spiro, in 'Metal Ions in Biology', Wiley-Interscience, New York, 1983, vol. 5.
1263. C. Veillon and B. L. Vallee, *Methods Enzymol.*, 1978, **54**, 446.
1264. B. L. Vallee, in 'New Trends in Bio-Inorganic Chemistry', ed. R. J. P. Williams and J. R. R. F. de Silva, Academic, London, 1978, p. 11; see also ref. 1470.
1265. J. I. Legg, *Coord. Chem. Rev.*, 1978, **25**, 103.
1266. I. M. Armitage, A. J. M. Schoot Uiterkamp, J. R. Chlebowski and J. E. Coleman, *J. Magn. Reson.*, 1978, **29**, 375; see also H. Beinert, *Coord. Chem. Rev.*, 1980, **33**, 55.
1267. P. Argos, R. M. Garavito, W. Eventoff, M. G. Rossmann and C. I. Brändén, *J. Mol. Biol.*, 1978, **126**, 141.
1268. See, for example, work cited in R. H. Prince, *Adv. Inorg. Chem. Radiochem.*, 1979, **22**, 349.
1269. J. Halpern, *J. Chem. Educ.*, 1958, **456**, 372, especially 374 *et seq.*
1270. R. G. Wilkins, 'The Study of the Kinetics and Mechanism of Reactions of Transition Metal Complexes', Allyn and Bacon, Boston, 1974.
1271. S. Lindskog *et al.*, in 'The Enzymes', ed. P. D. Boyer, Academic, New York, 1971, vol. 5, p. 587.
1272. K. K. Kannan *et al.*, *Proc. Natl. Acad. Sci. USA*, 1975, **72**, 51.
1273. J. M. Pesando, *Biochemistry*, 1975, **14**, 675.
1274. R. K. Gupta and J. M. Pesando, *J. Biol. Chem.*, 1975, **250**, 2630.
1275. E. Walschmidt-Leitz and A. Purr, *Chem. Ber.*, 1929, **62B**, 2217.
1276. J. F. Riordan and B. L. Vallee, *Biochemistry*, 1963, **2**, 1460.
1277. B. L. Vallee and H. Neurath, *J. Am. Chem. Soc.*, 1954, **76**, 5006.
1278. J. P. Felber, T. L. Coombs and B. L. Vallee, *Biochemistry*, 1962, **1**, 231.
1279. J. E. Coleman and B. L. Vallee, *J. Biol. Chem.*, 1960, **235**, 390.
1280. D. S. Auld and B. Holmquist, *Biochemistry*, 1974, **13**, 4355.
1281. G. N. Reeke, J. A. Hartsuck, M. L. Ludwig, F. A. Quiocho, T. A. Steiz and W. N. Lipscomb, *Proc. Natl. Acad. Sci. USA*, 1967, **58**, 2220.
1282. W. N. Lipscomb, J. A. Hartsuck, G. N. Reeke, F. A. Quiocho, P. H. Bethge, M. L. Ludwig, T. A. Steitz, J. Muirhead and J. C. Coppola, *Brookhaven Symp. Biol.*, 1968, **21**, 24.
1283. W. N. Lipscomb, *Chem. Soc. Rev.*, 1972, **1**, 319.
1284. S. Scheiner and W. N. Lipscomb, *J. Am. Chem. Soc.*, 1977, **99**, 3466.
1285. R. Breslow and D. L. Wernick, *Proc. Natl. Acad. Sci. USA*, 1977, **74**, 1303.
1286. C. A. Spilburg, *Fed. Proc. Fed. Am. Soc. Exp. Biol.*, 1974, **33**, 1529.
1287. C. A. Spilburg, J. L. Bethune and B. L. Vallee, *Proc. Natl. Acad. Sci. USA*, 1974, **71**, 3922.
1288. J. F. Riordan and G. Muszynska, *Biochem. Biophys. Res. Commun.*, 1974, **57**, 447.
1289. C. A. Spilburg, J. L. Bethune and B. L. Vallee, *Biochemistry*, 1977, **16**, 1142; see also ref. 1462.
1290. E. Katchalski, I. Silman and R. Goldman, *Adv. Enzymol. Relat. Area & Mol. Biol.*, 1971, **34**, 445.
1291. G. M. Alter, D. L. Leussing, H. Neurath and B. L. Vallee, *Biochemistry*, 1977, **16**, 3663.
1292. R. K. Scheule, H. E. Van Wart, B. L. Vallee and H. A. Scheraga, *Proc. Natl. Acad. Sci. USA*, 1977, **24**, 3272.
1293. A. A. Klesov and B. L. Vallee, *Bioorg. Khim.*, 1977, **3**, 964.
1294. U. Kettmann, *Ergeb. Exp. Med.*, 1977, **24**, 103.
1295. M. Ludwig, *Ergeb. Exp. Med.*, 1977, **24**, 83.
1296. G. Lassmann, W. Damerau, D. Schwartz, R. Kleine and M. Frohne, *Studi. Biophys.*, 1977, **63**, 149.
1297. M. Ludwig, H. Hanson, N. A. Kiselev, V. Ta. Stel'mashcuh and V. L. Tsuprun, *Acta Biol. Med. Ger.*, 1977, **36**, 157.
1298. G. Wangermann, I. M. Edintsov, G. R. Ivanitskii, A. S. Kuniskii, R. Reichelt and M. A. Tsyganoy, *Biofizika*, 1977, **22**, 599.
1299. F. Jurnak, A. Rich, L. Van Loon-Klassen, H. Bloemendal, A. Taylor and F. H. Carpenter, *J. Mol. Biol.*, 1977, **112**, 149.
1300. N. M. Ivanova, T. L. Vaganova, A. Ya. Strongin and V. M. Stepanov, *Biokhimiya*, 1977, **42**, 843.
1301. W. R. Kester and B. W. Matthews, *J. Biol. Chem.*, 1977, **252**, 7704.
1302. W. L. Bigbee and F. W. Dahlquist, *Biochemistry*, 1977, **16**, 3798.
1303. E. Marper and S. Seifter, *Isr. J. Chem.*, 1974, **12**, 515.
1304. J. L. Seltzer, J. J. Jeffrey and A. Z. Eisen, *Biochem. Biophys. Acta*, 1977, **485**, 179.
1305. J. Lukac and E. Koren, *J. Reprod. Fertil.*, 1977, **49**, 95.
1306. D. Holmquist, *Biochemistry*, 1977, **16**, 4591.
1307. R. U. Schenk and J. Bjorksten, *Fin. Kemistsamf. Medd*, 1974, **82**, 26.
1308. P. T. Varandani and L. A. Shroyer, *Arch. Biochem. Biophys.*, 1977, **181**, 82.
1309. A. T. H. Abdelal, E. H. Kennedy and D. G. Ahearn, *J. Bacteriol.*, 1977, **130**, 1125.
1310. H. N. Fernley, *Enzymes*, 1971, **4**, 417.
1311. R. H. Glew and E. C. Heath, *J. Biol. Chem.*, 1971, **246**, 1556.
1312. D. J. Plocke and B. L. Vallee, *Biochemistry*, 1962, **1**, 1039.
1313. R. T. Simpson and B. L. Vallee, *Biochemistry*, 1968, **7**, 4343.
1314. W. F. Bosron, F. S. Kennedy and B. L. Vallee, *Biochemistry*, 1974, **14**, 2275.
1315. R. A. Anderson, W. F. Bosron, F. S. Kennedy and B. L. Vallee, *Proc. Natl. Acad. Sci. USA*, 1975, **72**, 2989.
1316. W. F. Bosron, R. A. Anderson, M. C. Falk, F. S. Kennedy and B. L. Vallee, *Biochemistry*, 1977, **16**, 610.
1317. J. F. Chlebowski and S. Mabrey, *J. Biol. Chem.*, 1977, **252**, 7042.

1318. R. A. Anderson and B. L. Vallee, *Biochemistry,* 1977, **16,** 4388.
1319. J. F. Chlebowski, I. M. Armitage and J. E. Coleman, *J. Biol. Chem.*, 1977, **252,** 7053.
1320. K.-D. Gerbeitz, H. I. Kolb and O. H, Wieland, *Z. Physiol. Chem.*, 1977, **358,** 435.
1321. K.-D. Gerbitz, *Z. Physiol. Chem.*, 1977, **358,** 1491.
1322. K. H. Falchuk, D. W. Fawcett and B. L. Vallee, *J. Cell. Sci.*, 1975, **17,** 57.
1323. K. H. Falchuk, A. Krishan and B. L. Vallee, *Biochemistry,* 1975, **14,** 3439.
1324. J. P. Slater, A. S. Mildvan and L. A. Loeb, *Biochem. Biophys. Res. Commun.*, 1971, **44,** 37.
1325. C. F. Springgate, A. S. Mildvan, R. Abramson, J. L. Engle and L. A. Loeb, *J. Biol. Chem.*, 1973, **248,** 5987.
1326. J. P. Slater, A. S. Mildvan and L. A. Loeb, *Biochem. Biophys. Res. Commun.*, 1971, **44,** 37.
1327. M. C. Scrutton, W. C. Wu and D. A. Goldthwait, *Proc. Natl. Acad. Sci. USA,* 1971, **58,** 2497.
1328. D. S. Auld, I. Atsuya, C. Campino and P. Valenzuela, *Biochem. Biophys. Res. Commun.*, 1976, **69,** 548.
1329. H. Lattke and U. Weser, *FEBS Lett.*, 1976, **65,** 288.
1330. D. S. Auld, H. Kawaguchi, D. M. Livingstone and B. L. Vallee, *Proc. Natl. Acad. Sci. USA,* 1974, **71,** 2091.
1331. D. S. Auld, H. Kawaguchi, D. M. Livingstone and B. L. Vallee, *Biochem. Biophys. Res. Commun.*, 1975, **62,** 296.
1332. B. J. Poiesz, G. Seal and L. A. Loeb, *Proc. Natl. Acad. Sci. USA,* 1974, **71,** 4892.
1333. S. Kotsiopoulos and S. C. Mohr, *Biochem. Biophys. Res. Commun.*, 1975, **67,** 979.
1334. L. M. Psorski, D. S. Auld and M. Cohn, *Fed. Proc., Fed. Am. Soc. Exp. Biol.*, 1977, **36,** 706.
1335. C.-W. Wu, F. Y.-H. Wu and D. C. Speckhard, *Biochemistry,* 1977, **16,** 5449.
1336. D. C. Speckhard, F. Y.-H. Wu and C.-W. Wu, *Biochemistry,* 1977, **16,** 5228.
1337. V. d'Aurora, A. M. Stern and D. S. Sigman, *Biochem. Biophys. Res. Commun.*, 1977, **78,** 170.
1338. R. Koren and A. S. Mildvan, *Biochemistry,* 1977, **16,** 241.
1339. T. S.-F. Wang, D. C. Eichler and D. Korn, *Biochemistry,* 1977, **22,** 4927.
1340. M. A. Sirover and L. A. Loeb, *J. Biol. Chem.*, 1977, **252,** 3605.
1341. R. K. Bonnichsen and A. M. Wassén, *Arch. Biochem. Biophys.*, 1948, **18,** 361.
1342. E. Negelein and H. J. Wulff, *Biochem. Z.*, 1937, **289,** 436.
1343. C. I. Brändén, H. Jörnvall, H. Eklund and B. Furugren, in 'The Enzymes', ed. P. D. Boyer, 3rd edn., Academic, 1975, vol. 11A, chap. 3, pp. 103–190.
1344. C. Wills and H. Jörnvall, *Eur. J. Biochem.*, 1979, **99,** 323.
1345. J. P. von Wartburg, J. L. Bethune and B. L. Vallee, *Biochemistry,* 1964, **3,** 1775.
1346. N. Mourad and C. L. Woronick, *Arch. Biochem. Biophys.*, 1967, **121,** 431.
1347. W. F. Bosron, T. K. Li, W. P. Dafeldecker and B. L. Vallee, *Biochemistry,* 1979, **18,** 1101.
1348. W. F. Bosron, T. K. Li and B. L. Vallee, *Proc. Natl. Acad. Sci. USA,* 1980, **77,** 5784.
1349. G. M. Hanozet, M. Simonetta, D. Barisio and A. Gurritore, *Arch. Biochem. Biophys.*, 1979, **196,** 46.
1350. W. P. Dafeldecker, X. Parés, B. L. Vallee, W. F. Bosron and T. K. Li, *Biochemistry,* 1981, **20,** 856.
1351. M. Schwartz, J. O'Donnell and W. Sofer, *Arch. Biochem. Biophys.*, 1979, **194,** 365.
1352. E. Juan and R. González-Duarte, *Biochem. J.*, 1980, **189,** 105.
1353. P. J. Langston, G. E. Hart and C. N. Pace, *Arch. Biochem. Biophys.*, 1979, **196,** 611.
1354. C. Willis, P. Kratofil, D. Londo and T. Martin, *Arch. Biochem. Biophys.*, 1981, **210,** 775.
1355. H. Jörnvall, *Eur. J. Biochem.*, 1970, **16,** 25.
1356. T. Yonetani and H. Theorell, *Arch. Biochem. Biophys.*, 1963, **100,** 554.
1357. C. I. Brändén, E. Zeppezauer, T. Boiwe, C. Söderlund, B. O. Soderbeg and B. Nordström, in 'Pyridine Nucleotide Dependent Dehydrogenases', ed. H. Sund, Springer-Verlag, Berlin, 1970, p. 133.
1358. C. I. Brändén, E. Zeppezauer, B. O. Soderbeg, T. Boiwe, B. Nordström, G. Söderlund, M. Zeppezauer, P. E. Werner and Å. Åkeson, 'Structure and Function of Oxidation–Reduction Enzymes', eds. Å. Åkeson and A. Ehrenberg, Pergamon, Oxford, 1972, p. 93.
1359. C. I. Brändén, H. Eklund, B. Nordström, T. Boiwe, G. Söderlund, E. Zeppezauer, I. Ohlsson and Å. Åkeson, *Proc. Natl. Acad. Sci. USA,* 1973, **70,** 2439.
1360. H. Eklund, B. Nordström, E. Zeppezauer, G. Söderlund, I. Ohlsson, T. Boiwe and C. I. Brändén, *Biochem. Soc. Lett.*, 1974, **44,** 200.
1361. T. Boiwe and C. I. Brändén, *Eur. J. Biochem.*, 1977, **77,** 173.
1362. H. Weiner, *Biochemistry,* 1969, **8,** 526.
1363. I. Iweibo and H. Weiner, *J. Biol. Chem.*, 1979, **250,** 1959.
1364. B. V. Plapp, H. Eklund and C. I. Brändén, *J. Mol. Biol.*, 1978, **122,** 23.
1365. H. Eklund and C. I. Brändén, *J. Biol. Chem.*, 1979, **254,** 3458.
1366. H. Eklund, J. P. Samama, L. Wallén, C. I. Brändén, Å. Åkeson and T. A. Jones, *J. Mol. Biol.*, 1981, **146,** 561.
1367. S. A. Bernhard, M. F. Dunn, P. L. Luisi and P. Schack, *Biochemistry,* 1970, **9,** 185.
1368. M. F. Dunn and S. A. Bernhard, *Biochemistry,* 1971, **10,** 4569.
1369. J. D. Shore and H. Gutfreund, *Biochemistry,* 1970, **9,** 4655.
1370. M. Hadorn, V. A. John, F. K. Meier and H. Dulter, *Eur. J. Biochem.*, 1975, **54,** 65.
1371. J. Kvassman and G. Pettersson, *Eur. J. Biochem.*, 1976, **69,** 279.
1372. R. J. Kordal and S. M. Parsons, *Arch. Biochem. Biophys.*, 1979, **194,** 439.
1373. M. F. Dunn, S. A. Bernhard, D. Anderson, A. Copeland and R. G. Morris, *Biochemisty,* 1979, **18,** 2346.
1374. D. C. Anderson and F. W. Dahlquist, *Biochemistry,* 1980, **19,** 5486.
1375. P. Andersson and G. Pettersson, *Eur. J. Biochem.*, 1982, **122,** 599.
1376. B. L. Vallee and F. L. Hoch, *J. Biol. Chem.*, 1957, **225,** 185.
1377. (a) D. E. Drum, J. H. Harrison, T. K. Li, J. L. Bethune and B. L. Vallee, *Proc. Natl. Acad. Sci. USA,* 1967, **57,** 1434; (b) S. S. Eaton and G. R. Eaton, *Coord. Chem. Rev.*, 1978, **26,** 207; I. Bertini and C. Luchinat, *Acc. Chem. Res.*, 1983, **16,** 272.
1378. D. E. Drum and B. L. Vallee, *Biochemistry,* 1970, **9,** 4078.
1379. D. E. Drum, T. K. Li and B. L. Vallee, *Biochemistry,* 1969, **8,** 3783.
1380. J. M. Young and J. H. Wang, *J. Biol. Chem.*, 1971, **246,** 2815.
1381. J. D. Shore and D. Santiago, *J. Biol. Chem.*, 1975, **250,** 2008.

1382. A. J. Sytkowski and B. L. Vallee, *Proc. Natl. Acad. Sci. USA,* 1976, **73,** 344.
1383. A. J. Sytkowski and B. L. Vallee, *Biochemistry,* 1978, **17,** 2850.
1384. A. J. Sytkowski and B. L. Vallee, *Biochemistry,* 1979, **18,** 4095.
1385. B. R. Bobsein and R. J. Myers, *J. Am. Chem. Soc.,* 1980, **102,** 2454.
1386. W. Maret, I. Andersson, H. Dietrich, H. Schneider-Bernlöhr, R. Einarsson and M. Zeppezauer, *Eur. J. Biochem.,* 1979, **98,** 501.
1387. W. Maret, H. Dietrich, H. H. Ruf and M. Zeppezauer *J. Inorg. Biochem.,* 1980, **12,** 241.
1388. R. Österberg, *Coord. Chem. Rev.,* 1974, **12,** 309.
1389. I. Andersson, W. Maret, M. Zeppezauer, R. D. Brown, III and S. H. Koenig, *Biochemistry,* 1981, **20,** 3424.
1390. H. Dietrich, W. Maret, H. Kozlowski and M. Zeppezauer, *J. Inorg. Biochem.,* 1981, **14,** 297.
1391. I. Andersson, W. Maret, M. Zeppezauer, R. D. Brown, III and S. H. Koenig, *Biochemistry,* 1981, **20,** 3433.
1392. A. Curdel and M. Iwatsubo, *Fed. Eur. Biochem. Soc., Lett.,* 1968, **1,** 133.
1393. M. A. Foster, H. A. O. Hill and R. J. P. Williams, *Biochem. Soc. Symp.,* 1970, **31,** 187.
1394. P. L. Coleman and H. Weiner, *Biochemistry,* 1973, **12,** 3466.
1395. M. F. Dunn and J. S. Hutchinson, *Biochemistry,* 1973, **12,** 4882.
1396. H. Dietrich, W. Maret, L. Wallén and M. Zeppezauer, *Eur. J. Biochem.,* 1979, **100,** 267.
1397. P. W. Jagodzinski and W. L. Peticolas, *J. Am. Chem. Soc.,* 1981, **103,** 234.
1398. R. G. Morris, G. Saliman and M. F. Dunn, *Biochemistry,* 1980, **19,** 725.
1399. M. F. Dunn, H. Dietrich, A. K. H. MacGibbon, S. C. Koerber and M. Zeppezauer, *Biochemistry,* 1982, **21,** 354.
1400. D. S. Sloan, J. M. Young and A. S. Mildvan, *Biochemistry,* 1975, **14,** 1998.
1401. (a) B. A. Drysdale and D. P. Hollis, *Arch. Biochem. Biophys.,* 1980, **205,** 267; (b) K. Kanamori and J. D. Roberts, *Acc. Chem. Res.,* 1983, **16,** 35.
1402. H. Theorell, B. Chance and T. Yonetani, *J. Mol. Biol.,* 1966, **17,** 513.
1403. B. R. Bobsein and R. J. Myers, *J. Biol. Chem.,* 1981, **256,** 5313.
1404. R. A. Haberkorn, L. Que, W. O. Gillum, R. H. Holm, C. S. Liu and R. C. Lord, *Inorg. Chem.,* 1976, **15,** 2408.
1405. T. K. Li and B. L. Vallee, *Biochemistry,* 1964, **3,** 869.
1406. H. Jörnvall, *Eur. J. Biochem.,* 1970, **14,** 521.
1407. C. H. Reynolds, D. L. Morris and J. S. McKinley-McKee, *Eur. J. Biochem.,* 1970, **14,** 14.
1408. K. H. Dahl and J. S. McKinley-McKee, *Eur. J. Biochem.,* 1981, **118,** 507; see also ref. 1465g.
1409. K. H. Dahl and J. S. McKinley-McKee, *Eur. J. Biochem.,* 1981, **120,** 451.
1410. L. Brand, J. Everse and N. O. Kaplan, *Biochemistry,* 1962, **1,** 423.
1411. J. A. Koepke, Å. Åkeson and R. Pietruszko, *Enzyme,* 1972, **13,** 177.
1412. J. Gerschitz, R. Rudolph and R. Jaenicke, *Eur. J. Biochem.,* 1978, **87,** 591.
1413. R. Rudolph, J. Gerschitz and R. Jaenicke, *Eur. J. Biochem.,* 1978, **87,** 601.
1414. M. Buehner, G. C. Ford, D. Moras, K. W. Olsen and M. G. Rossman, *Proc. Natl. Acad. Sci. USA,* 1973, **70,** 3052.
1415. P. D. Dawkins, B. J. Gould, J. A. Struman and M. J. H. Smith, *J. Pharm. Pharmacol.,* 1967, **19,** 355.
1416. R. Einarsson, H. Eklund, E. Zeppezauer, T. Boiwe and C. I. Brändén, *Eur. J. Biochem.,* 1974, **49,** 41.
1417. P. O. Gunnarsson, G. Pettersson, and M. Zeppezauer, *Eur. J. Biochem.,* 1974, **43,** 479.
1418. S. Subramanian, J. B. A. Ross, P. D. Ross and L. Brand, *Biochemistry,* 1981, **20,** 4086.
1419. W. S. Chen and B. V. Plapp, *Biochemistry,* 1978, **17,** 4916.
1420. N. Evans and B. R. Rabin, *Eur. J. Biochem.,* 1968, **4,** 548.
1421. R. G. Khalifah and W. McIver Sutherland, *Biochemistry,* 1979, **18,** 391.
1422. E. Zeppezauer, H. Jörnvall and I. Ohlsson, *Eur. J. Biochem.,* 1975, **58,** 95.
1423. H. Theorell, T. Yonetani and B. Sjoberg, *Acta Chem. Scand.,* 1969, **23,** 255.
1424. B. R. Tolf, J. Piechaczek, R. Dahlbom, H. Theorell, Å. Åkeson and G. Lundquist, *Acta Chem. Scand., Ser. B,* 1979, **33,** 483.
1425. B. Tolf, R. Dahlbom, H. Theorell and Å. Åkeson, *Acta Chem. Scand., Ser. B,* 1982, **36,** 101.
1426. P. Andersson, J. Kvassman, A. Lindstrom, B. Oldén and G. Pettersson, *Eur. J. Biochem.,* 1981, **114,** 549.
1427. T. A. Alston, L. Mela and H. J. Bright, *Arch. Biochem. Biophys.,* 1979, **197,** 516.
1428. D. Schorstein, C. J. Suckling and R. Wrigglesworth, *J. Chem. Soc., Chem. Commun.,* 1978, 795.
1429. I. MacInnes, D. E. Schorstein, C. J. Suckling and R. Wrigglesworth, *J. Chem. Soc., Perkin Trans. 1,* 1981, 1103.
1430. I. Iweibo and H. Weiner, *Biochemistry,* 1972, **11,** 1003.
1431. P. L. Coleman, I. Iweibo and H. Weiner, *Biochemistry,* 1972, **11,** 1010.
1432. S. Taniguchi, H. Theorell and Å. Åkeson, *Acta Chem. Scand.,* 1967, **21,** 1903.
1433. J. Kvassman and G. Pettersson, *Eur. J. Biochem.,* 1979, **100,** 115.
1434. P. Andersson, J. Kvassman, A. Lindstrom, B. Olden and G. Pettersson, *Eur. J. Biochem.,* 1981, **113,** 425.
1435. J. Kvassman and G. Pettersson, *Eur. J. Biochem.,* 1980, **103,** 557.
1436. K. Dalziel, *J. Biol. Chem.,* 1963, **238,** 2850.
1437. H. Sund and H. Theorell, in 'The Enzymes', ed. P. D. Boyer, H. Lardy and K. Myrback, 2nd edn., Academic, London, 1963, vol. 7, chap. 2, pp. 25–83.
1438. M. A. Abdallah, J. Biellmann, P. Wiget, R. Joppich-Kuhn and P. L. Luisi, *Eur. J. Biochem.,* 1978, **89,** 397.
1439. R. Joppich-Kuhn and P. L. Luisi, *Eur. J. Biochem.,* 1978, **83,** 593.
1440. S. Subramanian and P. D. Ross, *Biochemistry,* 1978, **17,** 2193.
1441. M. A. Greeves and A. L. Fink, *J. Biol. Chem.,* 1980, **255,** 3248.
1442. H. Theorell and B. Chance, *Acta Chem. Scand.,* 1951, **5,** 1127.
1443. M. F. Dunn, *Struct. Bonding* (*Berlin*), 1975, **23,** 61.
1444. J. T. McFarland and S. A. Bernhard, *Biochemistry,* 1972, **11,** 1486.
1445. J. W. Jacobs, J. T. McFarland, I. Wainer, D. Jeanmaier, C. Ham, K. Hamm, M. Wnuk and M. Lam, *Biochemistry,* 1974, **13,** 60.
1446. P. Andersson, J. Kvassman, A. Lindström, B. Oldén and G. Pettersson, *Eur. J. Biochem.,* 1980, **108,** 303.

1447. R. T. Dworschak and B. V. Plapp, *Biochemistry*, 1977, **16**, 2716.
1448. (a) J. Kvassman and G. Pettersson, *Eur. J. Biochem.*, 1980, **103**, 565; (b) See, for example, M. E. Farago, *Coord. Chem. Rev.*, 1981, **36**, 155; E. Frieden, *J. Chem. Educ.*, 1985, **62**, 917.
1449. (a) J. Kvassman, A. Larsson and G. Pettersson, *Eur. J. Biochem.*, 1981, **114**, 555; (b) B. J. Aylett, *Top Environ. Health*, 1979, **2**, 1.
1450. J. H. R. Kagi and B. L. Vallee, *J. Biol. Chem.*, 1960, **235**, 3460.
1451. B. L. Vallee, *Experientia, Suppl.*, 1979, **34**, 19.
1452. R. W. Olafson, R. G. Suin and A. Kearns, *Experientia, Suppl.*, 1979, **34**, 197.
1453. R. Prinz and U. Weser, *Hoppe-Seyler's Z. Physiol. Chem.*, 1975, **356**, 767.
1454. K. Lerch, *Experientia, Suppl.*, 1979, **34**, 173.
1455. W. E. Rauser and N. R. Curvetto, *Nature (London)*, 1980, **287**, 563.
1456. K. L. Wong and C. D. Klaassen, *J. Biol. Chem.*, 1979, **254**, 12 399.
1457. M. Nordberg and Y. Kojima, *Experientia, Suppl.*, 1979, **34**, 57.
1458. U. Weser and H. Rupp, *Experientia, Suppl.*, 1979, **34**, 221.
1459. R. H. O. Bühler and J. H. R. Kagi, *Experientia, Suppl.*, 1979, **34**, 211.
1460. A. Galdes, H. A. O. Hill, J. H. R. Kagi, M. Vasak, I. Bremner and B. W. Young, *Experientia, Suppl.*, 1979, **34**, 241.
1461. R. S. Drago, M. J. Desmond, B. B. Corden and K. A. Miller, *J. Am. Chem. Soc.*, 1983, **105**, 2287.
1462. I. Bertini, C. Luchinat and M. Zeppezauer (eds.), *Prog. Bioinorg. Chem. Biophys.*, 1986, **10**, 'Zinc Enzymes' (cf. also ref. 1470, vol 10, *et seq.*).
1463. G. P. Diakun, L. Fairall and A. Klug, *Nature*, 1986, **324**, 698; L. Fairall, D. Rhodes and A. Klug, *J. Mol. Biol.*, 1986, **192**, 577.
1464. (a) W. N. Lipscomb, *Annu. Rev. Biochem.*, 1983, **52**, 17; (b) M. R. Pincus and H. A. Scheraga, *Acc. Chem. Res.*, 1981, **14**, 299; (c) W. N. Lipscomb, *Acc. Chem. Res.*, 1982, **15**, 232; (d) T. Keleti and G. R. Welch, *Biochem. J.*, 1984, **223**, 299; (e) N. Niccolai, E. Tiezzi and G. Valensin, *Chem. Rev.*, 1982, **82**, 359; (f) T. H. Maren and G. Sanyal, *Annu. Rev. Pharmacol. Toxicol.*, 1983, **23**, 439; (g) R. Bauer, P. Limkilde and J. T. Johansen, *Biochemistry*, 1976, **15**, 334; (h) I. Bertini and C. Luchinat, *Acc. Chem. Res.*, 1983, **16**, 272; (i) A. Shiels, S. Jeffery, C. Wilson and N. Carter, *Biochem. J.*, 1984, **218**, 281; (j) S. Jeffery, N. D. Carter and C. Wilson, *Biochem. J.*, 1984, **221**, 927.
1465. (a) J.-F. Biellmann, *Acc. Chem. Res.*, 1986, **19**, 321; (b) C. A. Ross, *Annu. Rep. Prog. Chem., Sect. B*, 1981, **78**, 390; (c) F. A. Armstrong and H. A. O. Hill, *Annu. Rep. Prog. Chem., Sect. C*, 1981, **78**, 201, esp. p. 213 *et seq.*; (d) I. Bertini, C. Luchinat and R. Monnanni, *J. Chem. Educ.*, 1985, **62**, 924; (e) R. J. P. Williams, *Polyhedron*, 1987, **6**, 61; (f) R. J. P. Williams, *Endeavour, New Ser.*, 1984, **8**, 65; (g) K. H. Dahl, H. Ecklund and J. S. McKinley–McKee, *Biochem. J.*, 1983, **211**, 391; (h) E. H. Creaser, R. L. Porter, K. A. Britt, J. A. Pateman and C. H. Doy, *Biochem. J.*, 1985, **225**, 449; (i) P. Julià, J. Farrés and X. Parés, *Biochem. J.*, 1983, **213**, 547; (j) C. S. Tsai and J. H. White, *Biochem. J.*, 1983, **209**, 309.
1466. (a) D. Gani, *Annu. Rep. Prog. Chem., Sect. B*, 1985, **82**, 309; (b) P. Charlier, O. Dideberg, J.-C. Jamoulle, J.-M. Frère, J.-M. Ghuysen, G. Dive and J. Lamotte-Brasseur, *Biochem. J.*, 1984, **219**, 763; (c) K. Kanamori and J. D. Roberts, *Acc. Chem. Res.*, 1983, **16**, 35; (d) M. Cohn and G. H. Reed, *Annu. Rev. Biochem.*, 1982, **51**, 365; (e) C. Y. Huang, S. G. Rhee and P. B. Chock, *Annu. Rev. Biochem.*, 1982, **51**, 935; (f) K. G. Strothkamp and S. J. Lippard, *Acc. Chem. Res.*, 1982, **15**, 318; (g) N. J. Blackburn, S. S. Hasnain, N. Binsted, G. P. Diakun, C. D. Garner and P. F. Knowles, *Biochem. J.*, 1984, **219**, 985; (h) *idem, ibid.*, 1983, **213**, 765; (i) S. L. Marklund, *Biochem. J.*, 1984, **220**, 269 and 1984, **222**, 649; (j) I. Fridovich, *Annu. Rev. Pharmacol. Toxicol.*, 1983, **23**, 239; (k) P. N. Gibbs, M. G. Gore and P. M. Jordan, *Biochem. J.*, 1985, **225**, 573; (l) J. K. Chesters, *Chem. Soc. Rev.*, 1981, **10**, 270; (m) C. R. Kahn, *Annu. Rev. Med.*, 1985, **36**, 429.
1467. (a) D. H. Hamer, *Annu. Rev. Biochem.*, 1986, **55**, 913; (b) J. K. Nicholson, P. J. Sadler, K. Cain, D. E. Holt, M. Webb and G. E. Hawkes, *Biochem. J.*, 1983, **211**, 251; (c) M. Sato and I. Bremner, *Biochem. J.*, 1984, **223**, 475; (d) S. R. Quinones and R. J. Cousins, *Biochem. J.*, 1984, **219**, 959; (e) S. Koizumi, T. Sone, N. Otaki and M. Kimura, *Biochem. J.*, 1985, **227**, 879; (f) K. Cain and D. N. Skilleter, *Biochem. J.*, 1983, **210**, 769; (g) R. K. Mehra and I. Bremner, *Biochem. J.*, 1985, **227**, 903; (h) *idem, ibid.*, 1984, **219**, 539; (i) S. Klauser, J. H. R. Kägi and K. J. Wilson, *Biochem. J.*, 1983, **209**, 71; (j) D. M. Templeton and M. G. Cherain, *Biochem. J.*, 1984, **221**, 569; (k) K. Cain and B. L. Griffiths, *Biochem. J.*, 1984, **217**, 85.
1468. (a) W. H. Hirschwald, *Acc. Chem. Res.*, 1985, **18**, 228; (b) M. D. Morse, *Chem. Rev.*, 1986, **86**, 1049; (c) D. Dakternieks, *Coord. Chem. Rev.*, 1985, **62**, 1; (d) J. Silver, *Annu. Rep. Prog. Chem., Sect. A*, 1984, **81**, 318; (e) *idem, ibid.*, 1985, **82**, 338; (f) *idem, ibid.*, 1983, **80**, 295; (g) P. O'Brien, *ibid.*, 1982, **79**, 353; (h) *idem, ibid.*, 1981, **78**, 293; (i) R. M. Izatt, J. S. Bradshaw, S. A. Nielsen, J. D. Lamb, J. J. Christensen and D. Sen, *Chem. Rev.*, 1985, **85**, 271; (j) H. Sigel and R. B. Martin, *Chem. Rev.*, 1982, **82**, 385; M. D. Maines and J. C. Veltman, *Biochem. J.*, 1984, **217**, 409.
1469. (a) S. P. Dagnall, D. N. Hague and A. D. Moreton, *J. Chem. Soc., Dalton Trans.*, 1986, 1505; (b) *idem, ibid.*, 1986, 1499; (c) S. P. Dagnall, D. N. Hague, M. E. McAdam and A. D. Moreton, *J. Chem. Soc., Dalton Trans.*, 1985, 2381; (d) *idem., J. Chem. Soc., Faraday Trans. 1*, 1985, **81**, 1483; (e) S. P. Dagnall, D. N. Hague and M. E. McAdam, *J. Chem. Soc., Perkin Trans. 2*, 1984, 435; (f) D. W. Margerum, G. R. Cayley, D. C. Weatherburn and G. K. Pagenkopf in 'Coordination Chemistry', ed. A. E. Martell, A.C.S. Monograph 174, American Chemical Society, Washington, 1978, vol. 2; (g) G. R. Cayley and D. N. Hague, *Trans. Faraday Soc.*, 1971, **67**, 786; (h) D. N. Hague and K. G. Moodley, *S. Afr. J. Chem.*, 1983, **36**, 10; (i) S. P. Dagnall, D. N. Hague and A. D. C. Towl, *J. Chem. Soc., Faraday Trans. 2*, 1982, **78**, 2161; (j) *idem, ibid.*, 1983, **79**, 1817.
1470. H. Sigel (ed.), 'Metal Ions in Biological Systems', Dekker, New York, 1974, vol. 4; 1976, vol. 5; 1976, vol. 6; 1979, vol. 8; 1979, vol. 9; 1980, vol. 10; 1980, vol. 11; 1982, vol. 14; 1983, vol. 15; 1983, vol. 16; 1984, vol. 18; 1986, vol. 20.

56.2
Mercury

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56.2.1 INTRODUCTION

The coordination chemistry of mercury differs from the coordination behaviour of other late transition elements since the Hg^{2+} ion, which has configuration d^{10}, exhibits neither paramagnetism nor '*d*–*d*' transition spectra. However, the current interest in the interference of mercury with biological systems makes it necessary to understand more completely the ability of mercury to bind donors. The resulting stereochemistry of the mercury atom is characterized by coordination number two, which is often expanded to an effective coordination number 'two plus four' on the basis of a van der Waals radius for mercury of 150 pm.[1] Recently a van der Waals radius of 171–176 pm has been discussed; this larger radius would result in an expansion of the coordination sphere of the mercury atom.[2] Relationships between the valence-orbital-binding energies and crystal structures of mercury compounds have been shown.[3]

A comprehensive review of mercury coordination chemistry in Gmelin covers the literature up to 1960 (and up to 1965 in later parts).[4] In this chapter the literature has been covered up to the middle of 1985.

56.2.1.1 Bibliography

There are a number of books and articles on general aspects of the coordination compounds of mercury; annual surveys are published in *Coordination Chemistry Reviews*[5] and the *Annual Reports on the Progress of Chemistry, Section A* (*Inorganic Chemistry—Mercury*).[6] McAuliffe's book 'The Chemistry of Mercury' covers the literature up to May 1975.[7] The coordination chemistry of mercury(II) halides has been summarized by Dean, covering papers up to 1977.[8] A review of dimercury(I) coordination compounds was published by Brodersen in 1981,[9] and in the same year Grdenić reviewed bonding in the crystal structures of mercury compounds.[10]

56.2.1.2 General

Mercury has the electronic configuration $(Xe)4f^{14}5d^{10}6s^2$. The first three ionization potentials are 10.43, 18.65 and 34.4 eV, therefore under chemically significant conditions no more than two electrons are removed from the mercury atom. Only one complex of mercury(III), with d^9 configuration and a half-life of 5 s at −78 °C, has been synthesized. The synthesis involved electrochemical oxidation of Hg(1,4,8,11-tetraazacyclotetradecane)$(BF_4)_2$ in propiononitrile solution.[11] In contrast to most other metals mercury forms polycations, *e.g.* Hg_2^{2+}, Hg_3^{2+} or Hg_4^{2+}.

Consideration of the standard potentials yields equations (1) and (2).[12] This shows that the dimercury(I) ion, Hg_2^{2+}, is stable to disproportionation as long as no ligand appreciably reduces the activity of the Hg^{2+} ion either by complexation or by precipitation. Since many ligands bind the Hg^{2+} ion very strongly, the number of coordination compounds of Hg_2^{2+} is limited.

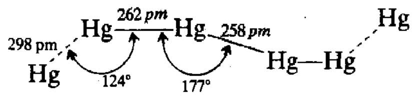
$$Hg_2^{2+} \longrightarrow Hg + Hg^{2+} \quad (E^\circ = -0.115\ V) \tag{1}$$

$$K = [Hg^{2+}]/[Hg_2^{2+}] = 1.15 \times 10^{-2} \text{ (in aqueous solution)} \tag{2}$$

56.2.2 MERCURY COORDINATION COMPOUNDS WITH MERCURY OXIDATION NUMBERS LOWER THAN +1

There are mercury compounds with mercury oxidation numbers lower than +1, *e.g.* +0.5,[16,21] +0.67[13,15,27] or +0.35.[18,20] Yellow crystals of $Hg_3(AsF_6)_2$ have been formed by the reaction of metallic mercury with AsF_5 in liquid SO_2.[13] X-Ray structure determination showed a linear polycation Hg^+—Hg—Hg^+ with Hg—Hg distances of 255 pm.[15] Metallic mercury and SbF_5 react in liquid SO_2 to form $Hg_3(Sb_2F_{11})_2$.[15,23] The Hg—Hg distances in the complex $Hg_3(AlCl_4)_2$ are 256 pm;[14] the Hg—Cl distances are 251 and 256 pm; the Hg—Hg—Hg angle is 174°. Dark red crystals of $Hg_4(AsF_6)_2$ were obtained in liquid SO_2.[16] This coordination compound contains centrosymmetric Hg_4^{2+} ions, which are connected to chains (see **1**).[21]

An excess of metallic mercury reacts with AsF_5 in liquid SO_2 to form 'alchemist's gold' ($Hg_{2.86}AsF_6$ or $Hg_{2.82}(AsF_6)_{0.94}$), which contains infinite chains of mercury atoms in two



(1)

perpendicular directions between the close packed AsF_6^- octahedra.[17,20,23,26] The Hg—Hg distances in the chains are 264 pm; the formal charge of each mercury atom in the chains is +0.35. 'Alchemist's gold' is an anisotropic metallic conductor in the direction of the mercury chains and is therefore a 'one-dimensional metal.[18,20,22,24,28] The isostructural $Hg_{2.9}SbF_6$ contains mercury chains with Hg—Hg distances of 266 pm.[19,23] Structural data for compounds of these polycations are summarized in Table 1.

Table 1 (a) Polycations with Oxidation Numbers Lower Than +1 and (b) Cluster Compounds of Mercury

Compound	*d(Hg—Hg)* (pm)	*Shortest Hg ··· X* (pm)	*Hg—Hg—Hg angle* (°)	*Ref.*
(a)				
$Hg_3(AsF_6)_2$	255.2(5)	238(5)	180.0	15
$Hg_3(AlCl_4)_2$	255.1(1)	251.7(3)	174.42(4)	14, 27
	256.2(1)	256.2(4)		
$Hg_4(AsF_6)_2$	258.8(2)	271(3)	177.27(9)	16, 21
	262.0(2)	287(4)		
	298.5(3)			
$Hg_{2.86}AsF_6$ (Hg chain)	264(1)	287	180.0	17, 18, 25
$Hg_{2.91}SbF_6$ (Hg chain)	266(2)	286(1)	180.0	19
(b)				
$Hg_3Os_9(CO)_{33}$ (Hg_3 ring)	308.2(3)	271.7(4) (Hg ··· Os)	60.0	415
	309.7(3)			
	312.2(3)			
$Hg_4Mn_4(CO)_8(\eta^5\text{-}MeC_5H_4)_4$ (Hg_4 ring)	288.8(2)	264.0(7) (Hg ··· Mn)	90.0	416
$Hg_6Rh_4(PMe_3)_{12}$ (Hg_6 octahedron)	313.1(3)	271.2(4)	60.0	29
	314.4(3)			
	314.6(3)			
	314.9(3)			

Hg—Hg spin coupling was recently studied by ^{199}Hg NMR.[26a] It can be seen that the Hg—Hg bond length increases with decreasing formal charge on the mercury atoms.

Recently cluster compounds of mercury with an Hg_3 ring, an Hg_4 ring and an Hg_6 octahedron with four capped tetrahedrally correlated faces have been described.[29,415,416] Structural data are listed in Table 1.

56.2.3 MERCURY(I) (Hg_2^{2+}) COORDINATION COMPOUNDS

The reaction between dimercury(I) salts and molecules with an electron-pair-donating atom normally destroys the metal–metal bond of the dimercury(I) ion Hg^+—Hg^+ by disproportionation, forming metallic mercury and a mercury(II) compound, but the use of nonpolar solvents, weak Lewis bases and dialytic crystallization methods has contributed to the successful preparation of single crystals of several dimercury(I) coordination compounds in the past 25 years.[9,30,31] The myth that the dimercury(I) species Hg_2^{2+} forms few coordination compounds has been exploded.

56.2.3.1 Halide and Pseudohalide Ligands

There is little evidence for the formation of soluble complexes in aqueous solutions of Hg^I halide and pseudohalide systems,[12,32] but the mercury(I) halides themselves are well-known substances. X-ray studies on the dimercury(I) dihalides show that all these compounds possess similar structures with linear X—HgHg—X molecules and four more-distant X neighbours for each of the two mercury atoms of the Hg_2^{2+} ion. Data are presented in Table 2. At low temperatures Hg_2X_2 (X = Cl, Br) transforms to a phase of lower symmetry; Raman spectra measured up to a pressure of 16 kbar revealed increasing disorder with increasing pressure.[36] The solid dimercury(I) dihalides are soluble in molten mercury(II) dibromide.[37] The halides Hg_2X_2 are solvobases in $HgBr_2$ melts, *i.e.* in these solutions only a few dissociated complexes $\{Hg_2X(Hg_2X_2)_n\}^+$ $(HgBr_2X)^-$ exist; they react with a solvoacid HgBrA ($A = ClO_4^-$) to give mixed mercury(I) salts $Hg_2X(ClO_4)$.[37] High pressure and high temperature studies on mercury(I) chloride show a structural transition at 5–20 kbar (orthorhombic phase).[38] The ferroelastic transitions of Hg_2Cl_2 and Hg_2Br_2 at 100–300 K were studied by X-ray diffractometry.[39] The longwave optical vibrations in mixed dimercury(I) halides $Hg_2(Cl_xBr_{1-x})_2$ on single crystals were studied.[40] A space experiment for studying the effects of weightlessness on the creep of annealed and sublimation grown Hg_2X_2 polycrystals (X = Cl, Br, I) has been described.[41] The structure of the mineral terlinguaite ($2HgO{\cdot}Hg_2Cl_2$) has been redetermined (Table 2).[340,341]

Table 2 Structural Data on Dimercury(I) Halide Coordination Compounds and the Mineral Terlinguaite ($2HgO{\cdot}Hg_2Cl_2$)[a]

Compound	*d(Hg—Hg)* (pm)	*Shortest Hg ··· X* (pm)	*Ref.*
BrHgHgBr	249.0(10)	270.7(12)	33, 34, 35
FHgHgF	250.8(1)	215.7(18)	33, 34, 35
ClHgHgCl	252.6(6)	242.6(35)	33, 34, 35
IHgHgI	267		34

[a] The mineral terlinguaite $Hg_4O_2Cl_2$ contains three mercury atoms forming an equilateral triangle (Hg—Hg = 270.8(2) pm). The structure can be described as being built up of endless chains $(Hg_4O_2Cl_2)_n$ fused to a network by contacts Hg—Cl = 284(1) pm. Within the chains the interatomic distances are Hg—Cl = 260(1) pm and Hg—O = 223(3) pm for each mercury atom belonging to the triangle; for mercury outside the triangle the distances are Hg—O = 202(3) pm and Hg—Cl = 317 pm. One quarter of the mercury atoms are outside the triangle; they are bonded to two oxygen atoms (202 pm) forming (—Hg—O—) chains. The oxidation number +4/3 (*i.e.* $Hg_2^{2+}:Hg^{2+} = 1:1$) may be formally attributed to the other mercury atoms forming the triangle.[340,341]

56.2.3.2 Oxygen Ligands

There are stable complexes of the Hg_2^{2+} ion with the following oxygen donors: pyrophosphate, tripolyphosphate, oxalate, α-dimethylmalonate and succinate.[309] The dihydrates of ionic dimercury(I) salts contain the nearly linear ion $(H_2O—Hg—Hg—OH_2)^{2+}$, *e.g.* in $Hg_2(NO_3)_2{\cdot}2H_2O$[42,56] or $Hg_2SiF_6{\cdot}2H_2O$.[43] Saturated organic ethers such as 1,4-dioxane or ethyleneglycol dimethyl ether form crystalline adducts of composition 1:1 or 1:2 with $Hg_2(NO_3)_2$.[44,55] The 1:1 coordination compound with 1,4-dioxane (**2**) contains infinite chains with coordinated NO_3 at each Hg atom $\{—(ONO_2)—Hg—Hg—(O_2NO)—O(CH_2)_4O—\}_n$. In $Hg_2(pyoxide)_4(ClO_4)_2$[45] three of the four ligands form bridges with the neighbouring dimeric Hg_2 units; each mercury atom of the $Hg^+—Hg^+$ ion is irregularly four- or five-coordinated. The coordination compounds between Ph_3PO and $Hg_2(ClO_4)_2$ contain six[46] or four ligand molecules,[47] and the one between Hg_2SiF_6 and $OPPh_3$ contains five ligand molecules.[47] In the structure of dimercury(I) *o*-phthalate, $Hg_2\{C_6H_4(CO_2)_2\}_2$,[48] the Hg_2^{2+} ion is linearly bonded to O atoms of different phthalate groups. Other dimercury(I) salts, *e.g.* $Hg_2(BrO_3)_2$,[49] Hg_2SO_4,[50] Hg_2SeO_4,[50] $Hg_2(ClO_4)_2{\cdot}nH_2O$ (n = 2 or 4),[51] $Hg_2(MeCO_2)_2$,[52,59,61] $Hg_2(H_2PO_4)_2$,[57] $Hg_4PO_4NO_3$[58] and $Hg_6(AsO_4)_2$,[53] contain Hg—Hg—O bonds with Hg—O distances between 208 and 277 pm. Vibrational spectra of crystalline hydrolysis products of dimercury(I) dinitrate have been reported.[60] Recently a crystal structure of one of these phases exhibited infinite chains $^1_\infty(—Hg—Hg(OH)—)_n$ (with Hg—Hg = 250.4(4) and 250.6(4) pm) as well as Hg_2^{2+} ions coordinated to the OH groups in the chains (Hg—Hg = 249.8(3) pm) and NO_3^- ions coordinated with one oxygen atom to the Hg_2^{2+} ions (Hg—O = 221 pm).[417] Coordination compounds of $Hg_2(ClO_4)_2$ with Ph_3PO and Ph_3AsO have been reported.[62] In the structure of $Hg_5Re_2O_{10}$ there are $(Hg_2O)_4$ rings bridged by Hg^{2+} ions forming a layer $^2_\infty\{(Hg^I_2O)_4Hg^{II}_{4/2}\}^{4+}_n$, which is connected by ReO_4^- anions.[344] Structural data of dimercury(I) coordination compounds with O donors are summarized in Table 3.

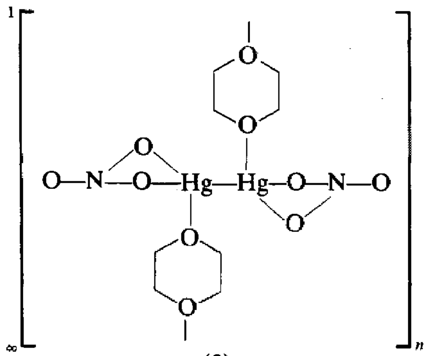


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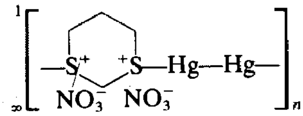
Table 3 Structural Data of Dimercury(I) Coordination Compounds with O Donors

Compound	*d(Hg—Hg)* (pm)	*d(Hg—O)* (pm)	*Hg—Hg—O angle* (°)	*Ref.*
$Hg_2(ClO_4)_2{\cdot}2H_2O$	248	—	—	51
$Hg_2SiF_6{\cdot}2H_2O$	249.5(3)	220(3)	170.9(9)	35, 43
$Hg_2(H_2PO_4)_2$	249.9(1)	214.2	167.2(4)	57
		251.4(13)		
Hg_2SO_4	250.0(3)	224.2	164.9(6)	35, 50
			193.2(6)	
$Hg_2(ClO_4)_2{\cdot}4H_2O$	250	214	180	51
$Hg_2(F_3CCO_2)_2$	250.5(3)	214(3)	166.6	54
$Hg_2(MeCO_2)_2$	250			52, 59
$Hg_2(NO_3)_2{\cdot}$(1,4-dioxane)	250.6	211, 273 (O_2NO)	171, 102	44, 55
		262 (O dioxane)	111	
$Hg_2(BrO_3)_2$	250.7(6)	216(4)	174(1)	35, 49
$Hg_2(NO_3)_2{\cdot}2H_2O$	250.8(2)	213(2)	167.5(7)	42, 56
$(Hg_2)_2PO_4NO_3{\cdot}H_2O$	250.8(2)	213(2)	164.9(6)	58
	253.2(2)	211(2)	168.1(6)	
Hg_2SeO_4	251(1)	221(5)	160(1)	35, 50
Hg_2(*o*-phthalate)	251.9(4)	208(5)	171	48, 61
		216(5)	175	
$Hg_2(OPPh_3)_6(ClO_4)_2$	252.2(2)	229(2)	116.0(5)	46, 47
		243(2)	140.0(5)	
$Hg_2(ONC_5H_5)_4(ClO_4)_2$	252.3(2)	219(2)	105.9(6)	45
		277(2)	159.9(7)	
$(Hg_2)_3(AsO_4)_2$	253.5(4)	216(4)	146(1)	53
		223(5)	157(1)	
$\{(Hg_2O)_4Hg_{4/2}\}_n^{4+}{\cdot}4n(ReO_4)^-$	254.6(2)	205(2)	110(1)	344
			114(2)	
			119(2)	
Hg_2AgPO_4	260.8(2)	222.4(11)	101.2(3)	553
		231.3(11)	140.1(3)	
		234.8(12)	142.9(3)	

56.2.3.3 Sulfur Ligands

$Hg_2(SCN)_2$ probably contains building blocks S—Hg—Hg—S.[61] For a long time, however, only one compound was known which contained dimercury(I) as well as mercury(II) bonded to sulfur atoms, namely $Hg^{I}_2Hg^{II}_2S_2(ClO_4)_2$.[63] Recently the reaction of 1,3-dithiane with $Hg_2(NO_3)_2$ or $Hg_2(ClO_4)_2$ in methanol as solvent has led to stable coordination compounds Hg_2(1,3-dithiane)$(A)_2$ (**3** and **4**).[64,65] Further compounds of this species are formed with 1,4-dithiane (**5** and **6**) or 1,3,5-trithiane (**7**). The X-ray structure determination of the 1,3-dithianedimercury(I) dinitrate shows chains $(\text{—}SC_4H_8S\text{—}Hg\text{—}Hg\text{—})_n$ (Figure 1 and Table 4). Normally the coordination compounds of sulfur donors with $Hg_2(NO_3)_2$ are 1:1 adducts with chain structures, but only two of the three sulfur atoms of the 1,3,5-trithiane are donor atoms to the Hg^+—Hg^+ ion, forming a chain and not the expected layer structure. The coordination compounds with $Hg_2(ClO_4)_2$ are only 1:2 adducts since the ClO_4^- anion is well known as a very weak O donor in contrast to the NO_3^- anion. Further dimercury(I)–sulfur complexes have been



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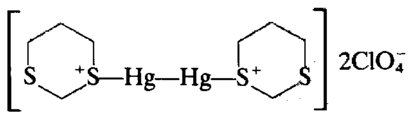

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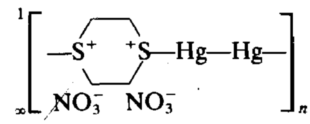

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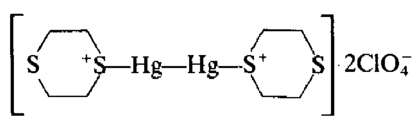

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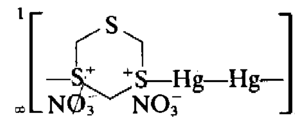


(7)

prepared by the reactions of $Hg_2(NO_3)_2$, $Hg_2(ClO_4)_2$ or Hg_2SiF_6 in methanolic solutions (or the two phase systems water/benzene or water/dichloromethane) with the following S donors: 1,3-dithiolane, 2-phenyl-1,3-dithiolane, 2,2′-trimethylenebis(1,3-dithiolane), bis(benzylthiomethane) and dibenzyl sulfide.[66] Polydentate sulfur ligands with a neopentane framework form stable complexes with $Hg_2(NO_3)_2$ and $Hg_2(ClO_4)_2$.[67] Stable coordination compounds have also been prepared between $Hg_2(NO_3)_2$ and the sulfur donor ligands 2,2,4,4-tetrachloro-1,3-dithietane, *exo*-3,4,5-trithiatricyclo[5.2.1.0]decane and 1,4-dimethyl-2,5,7-trithiabicyclo-1,3,5-trithiane.[68] In liquid SO_2 1:1 adducts between $Hg_2(AsF_6)_2$ and Ph_3PS or $(p\text{-}FC_6H_4)_3PS$, which contain Hg—Hg—S bonds, are stable.[69,70]

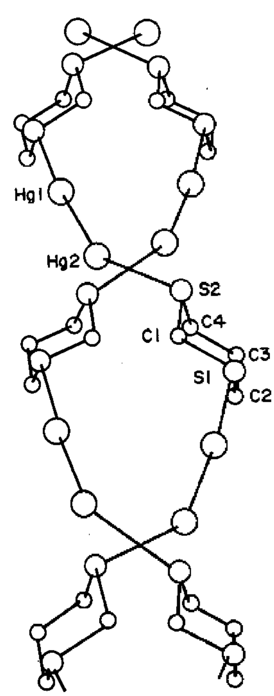


Figure 1 The packing of the $\{(C_4H_8S_2)\text{—Hg—Hg—}\}_n$ chains in the structure of the dimercury(I) sulfur complex $Hg_2(1,3\text{-dithiane})(NO_3)_2$

Table 4 Structural Data of Dimercury(I) Coordination Compounds with S Donors

Compound	*d(Hg—Hg)* (pm)	*d(Hg—S)* (pm)	*Hg—Hg—S angle* (°)	*Ref.*
$Hg_2(1,3\text{-dithiane})(NO_3)_2$	252.69(14)	249.15(60)	174.05(19)	65

56.2.3.4 Selenium Ligands

Normally the coordination compounds of mercury in the oxidation state +2 are more stable than the complexes with the dimercury(I) ion; this is true for almost all Lewis bases. However, if a nonbonding electron pair of a selenium atom is used in forming adducts between mercury salts and a selenium compound of this kind, then mercury(II) (Hg^{2+}) forms no adducts[71,72] and mercury(I) (Hg_2^{2+}) is able to form stable coordination compounds.[73] The X-ray structure of tetrakis(diphenylseleno)dimercury(I) diperchlorate is shown in Figure 2 (yellow modification).[73] There also exists a red modification of this compound,[74] which is shown in Figure 3. In both modifications of the polymorphic $Hg_2(Ph_2Se)_4(ClO_4)_2$ different Hg—Se distances and Hg—Hg—Se angles are found (Scheme 1 and Table 5). The diphenyl selenide ligand forms stable 1:1 complexes with both $Hg_2(NO_3)_2$ and $Hg_2(ClO_4)_2$.[73] 1:1 adducts between $Hg_2(AsF_6)_2$ and selenium donors such as Ph_3PSe in liquid SO_2 have been described.[69,70] This behaviour of mercury in both oxidation states +1 and +2 is important with regard to the role of selenium as a mercury antagonist in biological systems.[75]

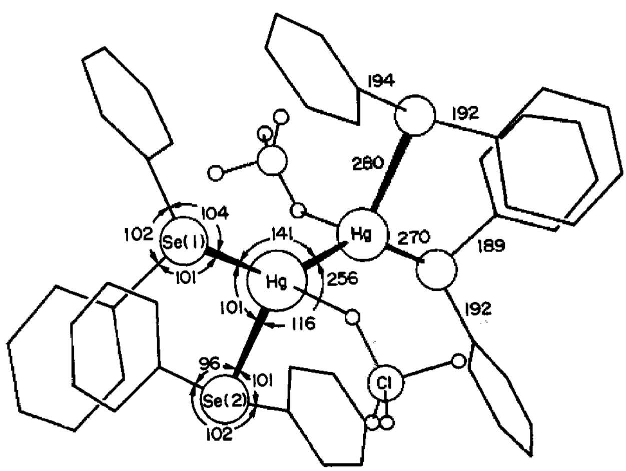


Figure 2 The yellow modification of the dimercury(I) selenium complex $Hg_2(Ph_2Se)_4(ClO_4)_2$

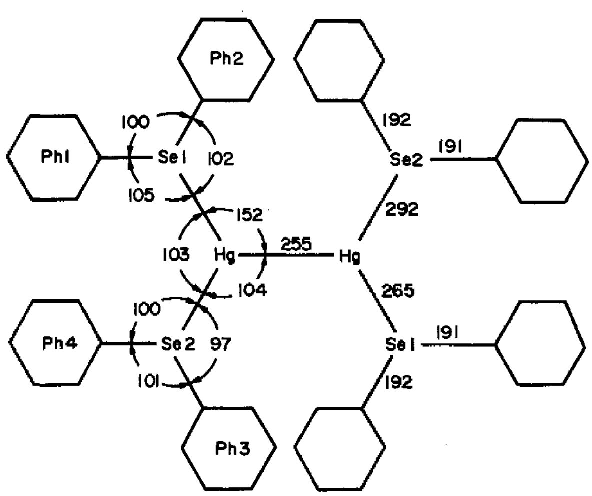
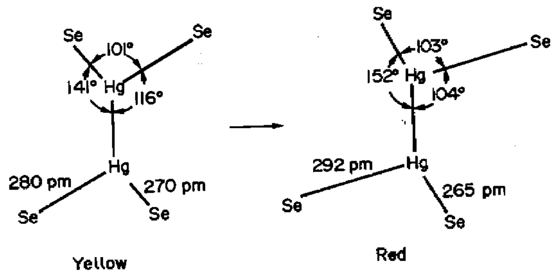


Figure 3 The red modification of the dimercury(I) selenium complex $Hg_2(Ph_2Se)_4(ClO_4)_2$

56.2.3.5 Nitrogen Ligands

Dimercury(I) salts react with basic nitrogen compounds such as ammonia to form insoluble black products, which were originally considered to be dimercury(I) coordination compounds,[76] but by X-ray examination it was shown that, in addition to finely dispersed black metallic



Scheme 1

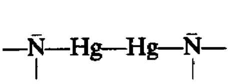
Table 5 Structural Data for $Hg_2(SePh_2)_4(ClO_4)_2$

	d(*Hg—Hg*) (pm)	*d*(*Hg—Se*) (pm)	*Hg—Hg—Se angle* (°)	*Ref.*
Yellow modification	255.79(8)	270.12(16) 280.17(18)	141.05(5) 116.39(5)	73
Red modification	255.3(1)	265.3(2) 291.9(2)	152.0(3) 104.4(3)	74

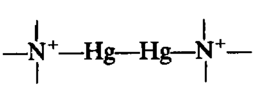
mercury, only mercury(II) nitrogen compounds with four-coordinated nitrogen atoms were present (equation 3).[77–89] This disproportionation reaction is caused by the formation of stable complexes of Hg^{2+} with electron pair donors. If the activity of the mercury(II) is not much decreased by the Lewis bases, then the dimercury(I) ion $Hg^+—Hg^+$ will be stable to disproportionation.[9] Dimercury(I) nitrogen coordination compounds are formed, therefore, if the stability constants of the complexes with the two oxidation states of mercury are not too different. Thus dimercury(I) coordination compounds can be expected with nitrogen compounds of low basicities.[90]

$$Hg_2X_2 + 2NH_3 \longrightarrow Hg + HgNH_2X + NH_4X \qquad (3)$$
$$X = Cl, Br$$

The building blocks (a) and (b) exist for the dimercury(I) nitrogen coordination compounds.



(a) amides (tricoordinated N atoms)

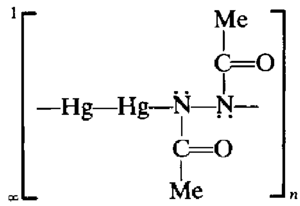


(b) amines (tetracoordinated N atoms)

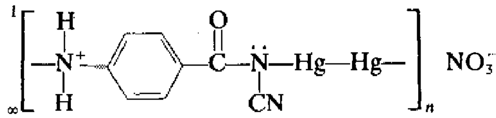
The first true dimercury(I) nitrogen compound was obtained by the reaction of diacetylhydrazide (NH acidic) with dimercury(I) dinitrate in aqueous solution.[31] This compound is an amide and contains tricoordinated nitrogen atoms.[91] Dimercurated amines with tetracoordinated nitrogen atoms have been obtained by reactions of amines of lower basicities with dimercury(I) salts.[92,93]

56.2.3.5.1 Nitrogen ligands with tricoordinated nitrogen atoms: amides

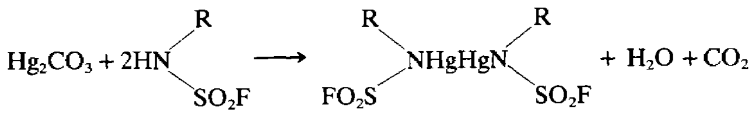
The reaction of acetamide with HgO at 240 °C is accompanied by the bonding of mercury not only to nitrogen but also to carbon atoms; under these circumstances a small amount of metallic mercury is observed together with the formation of diacetylhydrazide.[94] This has led to the preparation of the first true compound of this class, $Hg_2\{N_2(COMe)_2\}$ (**8**).[31] Similar compounds of the type $Hg_2\{N_2(COCX_3)_2\}$, with X = F, Cl, probably also have a chain structure.[91] NH acidic acylamides and hydrazides react with freshly prepared Hg_2CO_3 as shown in equation (4). Saccharin, bis(fluorosulfuryl)ureide and other NH acidic compounds react in a similar manner.[91] Aromatic sulfonyl- and acyl-cyanamides react with the $Hg^+—Hg^+$ ion to form compounds Hg_2L_2 with $L = H_2NC_6H_4SO_2NCN^-$, $C_5H_4NSO_2NCN^-$ or $C_5H_4NCONCN^-$ with group structures, and $Hg_2L(NO_3)$ with $L = H_2NC_6H_4CONCN^-$.[95] The IR spectra do not allow a decision as to whether the Hg_2^{2+} ion is bonded to the nitrogen atom of the amide group or the N of the pyridine ring; this means that these coordination compounds can have either tri- or tetra-coordinated nitrogen atoms. Only the *p*-aminobenzoylcyanamidedimercury(I) nitrate (**9**) possesses both types of coordinated nitrogen atoms in a chain structure.[95] Structural data for N donor complexes are given in Table 6.



(**8**)



(**9**)



(4)

$R = SO_2F, CO_2Et, CO_2Me, CONEt_2$

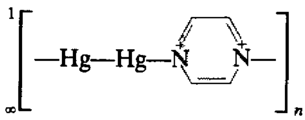
Table 6 Structural Data for Dimercury(I) Coordination Compounds with N Donors

Compound	*d(Hg—Hg)* (pm)	*d(Hg—N)* (pm)	*Hg—Hg—N angle* (°)	*Ref.*
Hg_2(diacethydrazide)	246	—	—	31, 91
$Hg_2(NCOCF_3NCOCF_3)$	247	—	—	91
$Hg_2(3\text{-Clpy})_2(ClO_4)_2$	248.7(2)	221	167.4	106
$Hg_2(3\text{-}SO_3py)_2\cdot 2H_2O$	249.9(1)	220.3(13)	165.6(2)	104
$Hg_2(4\text{-CNpy})_2(ClO_4)_2$	249.8(2)	216	176	105
$Hg_2(1,4\text{-diazine})(NO_3)_2$	249.99(11)	225.5(1.6)	167.57(2.71)	97, 99
$Hg_2(4\text{-benzyl-py})_4(ClO_4)_2$	250.84(7)	222.7(7)	118.4	111
		247.6(7)	153.9	
$Hg_2(m\text{-}H_2NC_6H_4SO_3)_2$	251.0(2)	219(2)	168.3(4)	123
$Hg_2(m\text{-}H_2NC_6H_4SO_3)_2\cdot 2H_2O$	252.2(1)	220(1)	172.8(1)	123
$Hg_2(p\text{-}H_2NC_6H_4SO_3)_2$	250.1(1)	219(1)	170.6(3)	123
$Hg_2(\text{naphthyridine})_2(ClO_4)_2$	251.1(1)	203(3)	174.4(5)	107
		278(1)	128.2(3)	
$Hg_2(3\text{-}NH_2py)_2(ClO_4)_2$	251.1(1)	219(3)	162(1)	103
		225(3)	172(1)	
$Hg_2(\text{phen})(NO_3)_2$	251.6(7)	248(4)	136.7(9)	98
		230(4)	78(1)	
$Hg_2(\text{acridine})_2(ClO_4)_2$	251.77(5)	215.0(5)	180.0	109
$Hg_2(\text{quinoline})_2(NO_3)_2$	255.1(2)	217.8(42)	164.5(24)	100
$Hg_2(N_3)_2$	C_{2h} symmetrical structure			112

56.2.3.5.2 Nitrogen ligands with tetracoordinated nitrogen atoms: amines

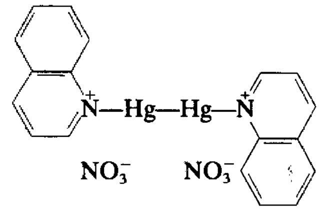
The first coordination compound of this type was the aniline complex $Hg(PhNH_2)_2(NO_3)_2$,[96] but later research revealed that up to six ligands are coordinated to $Hg_2(NO_3)_2$.[97] The first X-ray crystal structure determination of this type of coordination compound was published in 1967 for $Hg_2(phen)(NO_3)_2$.[98] In this complex one Hg atom of the Hg^+—Hg^+ ion is bonded to both N atoms of 1,10-phenanthroline; the other Hg atom is coordinated to oxygen atoms of the nitrate ions.[98] More recently X-ray structure determinations have been made with complexes of $Hg_2(NO_3)_2$ with either 1,4-diazine (**10**)[99] or quinoline (**11**).[100]

Other addition compounds of $Hg_2(NO_3)_2$ with aromatic amines[97] contain two molecules of the N ligand and one molecule of $Hg_2(NO_3)_2$; with 4-fluoroaniline four molecules of the ligand are coordinated.[97] Similar results have been obtained with $Hg_2(NO_3)_2$ or $Hg_2(ClO_4)_2$ and mono-, di- and tri-substituted anilines, pyridines and 1,4-diazabicyclo[2.2.2]octane.[101,102] Coordination compounds are also formed with aminopyridine, trichloroacetaminopyridine and aminochloropyridine.[103] The X-ray structure determination of the coordination compound between $Hg_2(ClO_4)_2$ and 3-aminopyridinium perchlorate revealed the structure (**12**).[103]



NO_3^- NO_3^-

(10)



NO_3^- NO_3^-

(11)

$2(ClO_4)^-(H\overset{+}{N}C_5H_4\overset{+}{N}H_2—Hg—Hg—\overset{+}{N}H_2C_5H_4\overset{+}{N}H)2(ClO_4)^-$

(**12**) (group structure)

Chain structures are formed by the complexes with *p*-aminobenzoic acid (**13**) and nicotinic acid (**14**).[104]

$^1_\infty[—Hg—Hg—\overset{+}{N}H_2C_6H_4CO_2—]_n$
$(NO_3)^-$ or $(ClO_4)^-$
(**13**)

$^1_\infty[—Hg—Hg—\overset{+}{N}C_5H_4CO_2—]_n$
$(NO_3)^-$ or $(ClO_4)^-$
(**14**)

The compound $Hg_2(3\text{-}SO_2py)_2{\cdot}2H_2O$, dimercury(I)pyridine-3-sulfonate dihydrate, is an inner salt with N—Hg—Hg—N bonds and only weakly coordinated water molecules (Figure 4).[104]

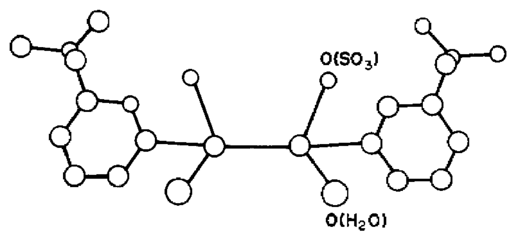


Figure 4 The structure of dimercury(I) pyridine-3-sulfonate dihydrate $Hg_2(py\text{-}3\text{-}SO_3)_2{\cdot}2H_2O$

The dimercury(I) salts of metanilic acid, $Hg_2(m\text{-}H_2NC_6H_4SO_3)_2{\cdot}2H_2O$ (Figure 6), $Hg_2(m\text{-}H_2NC_6H_4SO_3)_2$ (layer resp. band structure) (Figure 5), and that of sulfanilic acid, $Hg_2(p\text{-}H_2NC_6H_4SO_3)_2$ (layer structure) (Figure 7), contain nearly linear N—Hg—Hg—N bonds (Hg—N = 218–220 pm) with weakly coordinated oxygen atoms (Hg—O = 270 pm) from the SO_3 groups.[123]

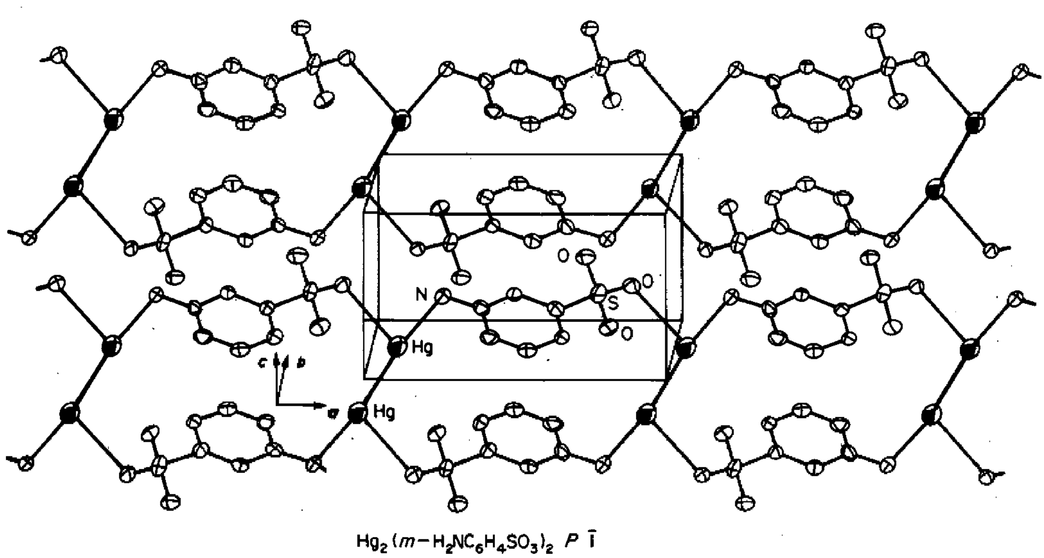


Figure 5 The structure of the $P\bar{1}$ modification of dimercury(I) methanilate $Hg_2(m\text{-}H_2NC_6H_4SO_3)_2$

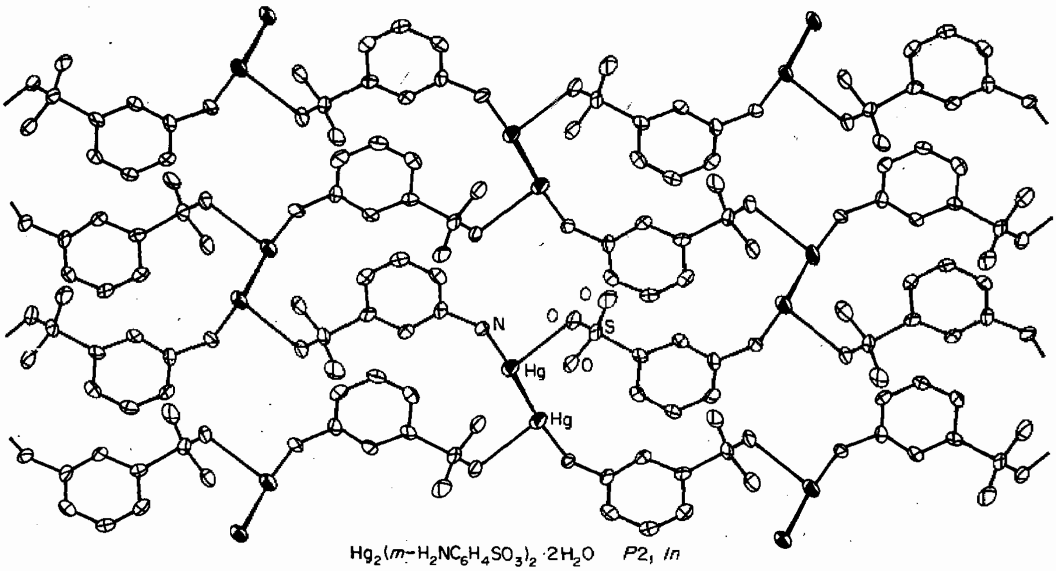


Figure 6 The structure of the $P\,2_1/n$ modification of dimercury(I) methanilate, $Hg_2(m\text{-}H_2NC_6H_4SO_3)_2 \cdot 2H_2O$

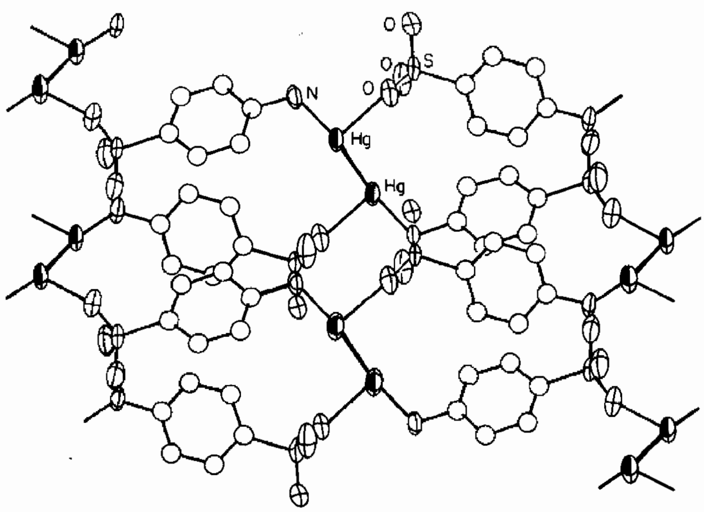


Figure 7 The structure of dimercury(I) sulfanilate, $Hg_2(p\text{-}H_2NC_6H_4SO_3)_2$

According to X-ray examinations the compounds of $Hg_2(ClO_4)_2$ with 4-CNpy,[105] 3-Clpy[106] and 1,8-naphthyridine[107] contain tetracoordinated nitrogen atoms with different Hg—N bond lengths; in all three cases two molecules of the ligand are coordinated to one molecule of $Hg_2(ClO_4)_2$. A similar situation exists for the ligands 2-Clpy, 5-NO_2quinoline, picoline, 2-methylpicoline, 2,6-lutidine and 2,4,6-trimethylpyridine.[102,108] The structure of $Hg_2(acridine)_2(ClO_4)_2$ is known by X-ray examination.[109] Cyano carbanions such as the tricyanomethanide anion, $C(CN)_3^-$, the *p*-tricyanovinylphenyldicyanomethanide and some propionides, *e.g.* the 1,1,3,3-tetracyanopropionide, form complexes with the Hg_2^{2+} ion with N—Hg—Hg—N— bonds.[110] Dianions such as 2-dicyanomethylene-1,1,3,3-tetracyanopropanediide also form stable coordination compounds with the dimercury(I) cation.[110] For structural data of N donor complexes see Table 6.

56.2.3.6 Phosphorus ligands

Trifluorophosphine complexes of the dimercury(I) ion Hg_2^{2+} in liquid SO_2 have been detected by ^{19}F NMR.[69,70] Cations such as $(Hg_2PF_3)^{2+}$ or $\{Hg_2P(CF_3)Ph_2\}^{2+}$ in these solutions are also confirmed by Raman data. The ^{13}C NMR data show little metal to phosphorus back-bonding in these phosphine complexes.[113] Although many attempts have been made,[114,115] it has so far not been possible to prepare single crystals of dimercury(I) phosphorus coordination compounds because of the disproportionation reaction.

56.2.3.7 Arsenic Ligands

$AsPh_3$ seems to form a 1:1 adduct with $Hg_2(AsF_6)_2$ in liquid SO_2.[69,70] $Hg_2(NO_3)_2$ reacts with $As(CF_3)_3$, forming the coordination compound $\{O_2NOHgHgAs(CF_3)_3\}^+(NO_3)^-$.[116]

56.2.3.8 Antimony Ligands

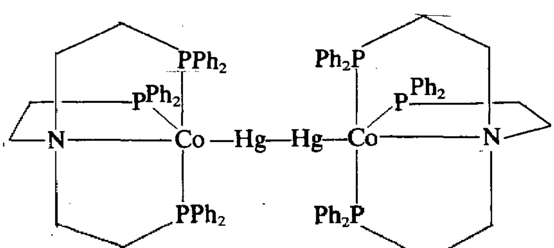
Only triphenylstibine reacts with $Hg_2(AsF_6)_2$ in liquid SO_2 to form a 1:1 adduct.[69,70]

56.2.3.9 Metal Ligands

Complex formation between the lone pair of tin(II) and the dimercury(I) ion takes place during the reaction between $SnBr_2$ and $Hg(ClO_4)_2$ in molten $HgBr_2$ at 250 °C (equation 5),[37,117] but it is not possible to isolate the orange precipitate of $Hg_2Sn_2Br_5(ClO_4)$ in molten $HgBr_2$ without decomposition. The ions $Hg_2Sn_2Br^+$ and $Hg_2Sn_2^+$ have been identified by mass spectrometry.[118]

$$NEt_4ClO_4 + Hg_2Br_2 + 2SnBr_2 \longrightarrow NEt_4Br + Br{-}Sn(Br)_2HgHg\overset{+}{Sn}(Br)_2\ (ClO_4)^- \qquad (5)$$

The reaction of $\{N(CH_2CH_2PPh_2)_3\}CoCl^+(BPh_4)^-$ with sodium amalgam leads to a coordination compound (**15**) with linear —Co—Hg—Hg—Co— groups which contains a relatively long Hg—Hg bond distance of 265.1 pm.[119]



(**15**)

56.2.3.10 π Donor Ligands

Dimercury(I) π complexes are formed between aromatic compounds and $Hg_2(AsF_6)_2$ in liquid SO_2 as solvent.[113,121] Insoluble complexes with the ratio arene:Hg_2^{2+} = 1:1 (arene = benzene, naphthalene, 2-methylnaphthalene, 2,6-dimethylnaphthalene, acenaphthene, fluoranthrene, phenanthrene, anthracene, 9,10-dimethylanthracene or 1,3-dinitrobenzene) or 1:2 (arene = 9,10-benzophenanthrene) have been characterized by elemental analysis and, in some cases, by Raman spectrometry.[113,120] The ^{13}C NMR data allow the estimation of formation constants for the hexamethylbenzene, *p*-xylene and 1,4-dichlorobenzene complexes together with the chemical shifts for the bound substrates in these cases.[121] Probably the coordination compounds of dimercury(I) salts with carbazole, dibenzofuran and dibenzothiophene are also π complexes.[122]

56.2.4 MERCURY(II) (Hg^{2+}) COORDINATION COMPOUNDS

56.2.4.1 Halide Ligands

Mercury(II) fluoride, HgF_2, is obtained by fluorination of metallic mercury or $HgCl_2$;[124] it is a white crystalline solid, which darkens in colour on exposure to air due to hydrolysis. Cubic eight coordination of mercury atoms is found in HgF_2, which possesses the fluorite structure; it is one of the few mercury(II) compounds in which the bonding is believed to be mainly ionic.[125] By dissolving yellow HgO in aqueous HF a dihydrate, $HgF_2{\cdot}2H_2O$, is formed, which can be thermally decomposed into Hg(OH)F.[126] The structure of mercury(II) fluoride hydroxide involves $\{Hg(OH)\}_n^{n+}$ chains with three Hg–F interactions at 249–250 pm, so that the structure approximates to zigzag columns of (HgO_3F_3) octahedra and is better described as a polymeric mercuronium fluoride $\{Hg(OH)\}_n^{n+}nF^-$.[127–129] There is another hydroxyfluoride, $Hg_3F_4(OH)_2{\cdot}3H_2O$, which is formed by the hydrolysis of mercury(II) fluorosulfonate.[130]

The other three mercury(II) halides, HgX_2 (X = Cl, Br, I), are simply obtained from the reactions of the elements. In the lattices of $HgCl_2$, $HgBr_2$ and the high temperature (yellow) form of HgI_2 (stable above 127 °C) 'molecules' of the halides are present.[131] In each of these structures four halogen atoms from neighbouring 'molecules' approach the mercury atom at relatively long distances. The behaviour is in agreement with Grdenić's classification of effective and characteristic coordination of mercury in crystal structures.[1,10] $HgBr_2$ and yellow HgI_2 are isostructural, having a distorted brucite structure.[131] The red form of HgI_2, which is stable at room temperature, consists of corner-linked HgI_4 tetrahedra, while the unstable orange form, which contains Hg_4I_{10} units, is formed by four corner-linked HgI_4 tetrahedra.[133,134] Structural data are listed in Table 7.

Table 7 Mercury(II) Halides

Compound	Structure (pm; °)		Ref.
HgF_2	CaF_2 type,	8 × Hg—F = 246	124
$HgCl_2$	Distorted octahedral, *Pnma*, Z = 4	2 × Hg—Cl = 225 2 × Hg—Cl = 334 2 × Hg—Cl = 363 Cl—Hg—Cl = 177.8	135, 136
$HgBr_2$	Brucite type, *Cmc*2$_1$, Z = 4	2 × Hg—Br = 248 4 × Hg—Br = 323 Br—Hg—Br = 180	132
HgI_2 (yellow)	Brucite type, *Cmc*2$_1$, Z = 4	Hg—I = 261.5(6) Hg—I = 262.0(6) I—Hg—I = 178.3(3)	133
HgI_2 (red)	Distorted tetrahedral, *P*4$_2$/*nmc*, Z = 2	4 × Hg—I = 278.3(3) 2 × Hg—I = 350.7(6) 2 × Hg—I = 351.0(6) I—Hg—I = 112.72; 103.14	133

Besides the high temperature form of HgI_2 there is a high pressure form, HgI_2 (h.p.). Compression of the red form above 10 kbar induces a change to a phase which appears yellow under the microscope.[137] The far-IR and Raman spectra of HgI_2 (h.t.) and HgI_2 (h.p.) are significantly different from each other and suggest that the two yellow materials have different structures. Above 75 kbar there is a further transition to a form with a structure believed to be that of the 8 H poly-type of CdI_2.[138,139]

Mercury(II) bromide exists in four polymorphic modifications, which have been studied by IR and Raman spectroscopy.[139–141] $HgBr_2$ has been used as a nonaqueous solvent in its molten state at 250 °C; it contains in the melt $HgBr^+$ cations and $HgBr_3^-$ anions; the ion product $[HgBr^+] \times [HgBr_3^-] = 2 \times 10^{-8}$.[81] From compression measurements Bridgman found that $HgCl_2$ shows only one phase transition up to 45 kbar at ambient temperature.[140] A recent NQR study has revealed a second-order transition below this and all three phases have been investigated by IR and Raman spectroscopy under conditions of or near hydrostatic compression up to 40 kbar.[142,143]

The electronic spectra of HgX_2 (X = Cl, Br, I) have been measured in several solvents in an endeavour to characterize the solution structures of these compounds.[144] The peak maxima correlate linearly with dielectric constants and Kosower's *Z* value for solvent polarity in accordance with the solvation of linear mercury(II) halides in the equatorial position. Solvent effects upon $\delta(^{199}Hg)$ in HgX_2 (X = Cl, Br, I) have been studied.[145] The ^{199}Hg chemical shifts in a number of nonaqueous solvents cover a range of 2400 p.p.m. Solvent and temperature dependence and the difference of $\delta(Hg)$ are related to the donor abilities of the solvent. The solvent effects upon $\delta(Hg)$ are smallest for $HgCl_2$ and largest for HgI_2 (over 1800 p.p.m.).[145]

Numerous mixed halides HgXY (Scheme 2; X≠Y) have been characterized by X-ray powder patterns. Rastogi *et al.*[146–148] studied HgClI, HgBrI, HgFBr, HgFI and HgClBr by X-ray powder patterns in order to rule out the possibility that these products are mixtures of the corresponding symmetrical mercury(II) halides. The structures of the mixed fluorohalides HgXF (X = Cl, Br, I) have been established by vibrational spectrometry.[149] The reactions (6) and (7) yield two forms of the mixed halide HgClBr.[150] The powder pattern and all parameters of the α-HgClBr (see Table 8) are similar to those of $HgCl_2$, therefore it is possible that the chlorine atoms in the linear HgX_2 molecules of $HgCl_2$ have been replaced by Br atoms. Since the radius of the Br atom is larger than that of the Cl atom, the lattice is dilated in this case.

$$\tfrac{1}{2}HgX_2 + \tfrac{1}{2}HgY_2 \rightleftharpoons HgXY \rightleftharpoons \tfrac{1}{2}Hg_2X_2 + \tfrac{1}{2}Y_2$$

Scheme 2

$$Hg_2Cl_2 + Br_2 \longrightarrow \underset{\alpha\text{-form}}{2HgClBr} \tag{6}$$

$$HgCl_2 + HgBr_2 \longrightarrow \underset{\beta\text{-form}}{2HgClBr} \tag{7}$$

Table 8 Cell Parameters of the Two Forms of HgClBr (pm; g cm^{-3})

Compound	*Parameters*		*Ref.*
α-HgClBr	$a = 619.6$	*Pnmb*	150
	$b = 1312$	$Z = 4$	
	$c = 427$	$\rho = 5.91$	
β-HgClBr	$a = 678$	*Pnmb*	150
	$b = 1317.5$	$Z = 4$	
	$c = 417$	$\rho = 5.40$	

The parameters of β-HgClBr (see Table 8) are the same as those reported for β-Hg(Cl, Br)$_2$ and its X-ray powder patterns is similar to $HgCl_2$.[151] This phase, therefore also possesses linear halogen—Hg—halogen molecules but the distribution of all Cl and Br atoms may be random. There are numerous halomercurates(II) with various cations. Some compounds with alkali and alkaline earth metal ions are listed in Gmelin,[4] and some with sulfonium, phosphonium, arsonium *etc.* cations have been listed by Gmelin[4] and Deacon.[152] The major species present in solutions of $HgX_2 + X^-$ are HgX^+, HgX_2, HgX_3^- and HgX_4^{2-} and the thermodynamics of the formation of $(HgX_n)^{(2-n)}$ (X = Cl, Br; n = 1, 2) has been discussed.[153] Mixed halomercurates(II), *e.g.* $(HgBrI_2)^-$, $(HgBr_2I)^-$ and $(HgX_2X'X'')^{2-}$ (X≠X'≠X") have been characterized by Raman spectrometry.[154–158] Changes in electronic spectra of aqueous solutions of HgX_2 (X = Cl, Br, I) on adding F^- ions have been interpreted in terms of the formation of $(HgX_2F)^-$ and possibly $(HgX_2F_2)^{2-}$.[159] The stability of halomercurate(II) ions in aqueous solution is F ≪ Cl < Br < I,[160,161] therefore only some fluoromercurates(II) are known. The compounds $MHgF_3$ (M = K, Rb, Cs, Tl^I) are formed by the fluorination of $HgCl_2{\cdot}2NH_3$ + MCl while the reaction of $HgF_2{\cdot}2H_2O$ with py and HF yields $(pyH)_2HgF_4{\cdot}2H_2O$.[126,161,163] Halomercurates have been intensively studied by IR and Raman spectroscopic methods in order to establish the nature of the anions.[164–167] Nowadays there are a lot of X ray structural data available on halomercurate(II) complexes (see Table 9).

Isolated $HgCl_4$ groups appear in the complex with perloline and in $(MeNH_3)_2HgCl_4$.[171,175] Alkylammonium tetrachloromercurates(II) are of interest for the phase transitions in the solid state.[175,187] The phase transitions are due to the organic part of the crystal 'melting' while the inorganic portion remains virtually unchanged.[188] Raman studies of $PCl_5{\cdot}HgCl_2$ melts indicate

Table 9 Structural Data for Some Halomercurates(II)

Compound	*Structure* (pm; °)	*Ref.*
$KHgF_3$	Orthorhombic, $a = 620$; $b = 628$; $c = 881$	162, 163
$RbHgF_3$	Cubic, $a = 447$	
$CsHgF_3$	Perovskite, $a = 457$	
$TlHgF_3$	$a = 447.5$	
$K_2HgCl_4 \cdot H_2O$	*Pbam*, orthorhombic $a = 825.8(2)$; $b = 1166.3(2)$; $c = 892.6(2)$ six-coordinated Hg; chains $^1_\infty(HgCl_2Cl_{4/2})$ $2 \times Hg—Cl = 238.3(1)$; $Cl—Hg—Cl = 169.96(4)$ $2 \times Hg—Cl = 289.7(1)$ $2 \times Hg—Cl = 325.1(1)$	167, 168
α-NH_4HgCl_3	Tetragonal, distorted $HgCl_6$ groups connected to layers $^2_\infty(HgCl_2HgCl_{4/4})$ $2 \times Hg—Cl = 234$; $4 \times Hg—Cl = 296$	169
β-NH_4HgCl_3	Isomorphous with NH_4CdCl_3	170
$(Perloline)_2HgCl_4 \cdot H_2O$	Tetrahedral $HgCl_4$ units $Hg—Cl = 250$	171
$NaHgCl_3 \cdot 2H_2O$	Orthorhombic; twofold ribbons of $(Hg_2Cl_6)^{2-}$ $^1_\infty(HgClCl_{3/3}Cl_{2/2})$; $Hg—Cl = 235, 240$; $2 \times Hg—Cl = 281$; $2 \times Hg—Cl = 327$	171
$(Et_4N)HgCl_3$	$P\bar{1}$; $a = 764.4(1)$; $Z = 2$ $b = 974.9(2)$ $c = 1032.5(2)$ five-coordinated Hg; trigonal, bipyramidal; $3 \times Hg—Cl = 243$; $Hg—Cl = 305.4, 301.7$	173
$(C_6H_{13}N_4)HgCl_3$	*Cmcm*; $a = 944.3(4)$; $Z = 4$ $b = 1826.4(5)$ $c = 739.4(3)$ five-coordinated Hg; trigonal, bipyramidal; $2 \times Hg—Cl = 242.3$; $1 \times Hg—Cl = 243.4$ $2 \times Hg—Cl = 303.0$	174
$(MeNH_3)HgCl_3$	Four-coordinated Hg; $^1_\infty(HgCl_2Cl_{2/2})$ chains $Hg—Cl = 232.0(9)$; $237.1(11)$; $271.2(10)$; $281.7(10)$	175
$(MeNH_3)_2HgCl_4$	Tetrahedrally coordinated Hg with $Hg—Cl = 247.0$	175
$(MeNH_3)Hg_2Cl_5$	Similar to $(MeNH_3)HgCl_3$	175
$\{(CH_2)_6N_2H_2\}HgCl_4 \cdot H_2O$	Orthorhombic, $P2_12_12_1$ distorted $HgCl_4$ tetrahedra $Hg—Cl = 243, 246, 248, 254$	266
$MgHg_3Cl_8 \cdot 6H_2O$	$P\bar{1}$; $a = 911.2(6)$; $Z = 1$ $b = 723.8(7)$ $c = 749.5(5)$ linear pseudo molecules $HgCl_2$ [$Hg—Cl = 232.1(3)$] and binuclear Hg_2Cl_6 anions [$Hg—Cl = 271.0(3)–349.2(3)$]	176
$Tl_{10}Hg_3Cl_{16}$	$I4/m$; $a = 849.0(2)$; $c = 2372.9(6)$ $HgCl_4$ tetrahedra; $4 \times Hg—Cl = 245.1(5)$ six-coordinated Hg: $2 \times Hg—Cl = 236.0(3)$ $4 \times Hg—Cl = 309.8(17)$	177
$TlHg_5Cl_{11}$	$C2/m$; $a = 1171.6(1.1)$; $\beta = 118.55(90)$ $b = 1415.0(1.4)$ $c = 646.0(6)$ double salt $TlCl \cdot 5HgCl_2$; $2 \times Hg—Cl = 227.3(11)$	178
$(Et_4N)_2Hg_2PtCl_8$	Trinuclear anions, $(Hg_2MCl_8)^{2-}$, linked by Cl bridges involving the terminal Hg—Cl bonds	350
$(Et_4N)_2Hg_3MCl_{10}$ (M = Pt or Pd)	Trinuclear anions as above, linked by the HgClM bridging Cl atoms *via* linear $HgCl_2$ units	350
Cs_2HgBr_4	Isolated $HgBr_4$ tetrahedra $2 \times Hg—Br = 255.2$; $2 \times Hg—Br = 250.7$	180
$KHgBr_3 \cdot H_2O$	$HgBr_4$ tetrahedra sharing corners	179
$\{Mg(OH_2)_6\}Hg_2Br_6$	Binuclear Hg_2Br_6 anions $Hg—Br = 247.1–281.4$	182
Tl_4HgBr_6	Six-coordinated Hg $2 \times Hg—Br = 254.0$, $4 \times Hg—Br = 310.9$	181
Cs_2HgI_4	HgI_4 tetrahedra; $Hg—I = 271–291$	183
$(Me_3S)HgI_3$	Trigonal planar coordinated Hg $2 \times Hg—I = 271$; $Hg—I = 265$	184
$\{Mg(OH_2)_6\}Hg_2I_6$	Similar to $\{Mg(OH_2)_6\}Hg_2Br_6$	182
$MHgI_4 \cdot 8H_2O$ (M = Ca, Sr)	HgI_4 tetrahedra; $Hg—I = 274–285$	185
Tl_4HgI_6	Compressed HgI_6 octahedra six-coordinated Hg: $2 \times Hg—I = 266.6(2)$ $Hg—I = 311.2(4)–366.5(9)$	186

the presence of the salts $(PCl_4)HgCl_3$ and $(PCl_4)_2HgCl_4$.[189] Mass spectrometry has been used to identify a species $HgAlCl_5$ formed by the reaction of $HgCl_2$ with $AlCl_3$.[190] $\{Cr(NH_3)_6\}HgCl_5$, which exists in two modifications, contains mercury atoms in distorted trigonal bipyramidal coordination with short equatorial Hg—Cl bonds (241.7–243.1 pm) and very long axial Hg—Cl bonds (287.1–303.8 pm).[191] In $HgINO_3$ and $Hg_2I_2TiF_6$, $(HgI^+)_n$ chains pass through the structure, while in $Ag_2HgI_2(NO_3)_2{\cdot}H_2O$ I—Hg—I segments with an angle of 176.9° and two Hg—I distances of 263 pm are found.[301,302]

The literature contains numerous reports of complexes formed between mercury(II) halides, HgX_2 (X = Cl, Br, I), and neutral donor ligands containing the donor atoms N, P, As, Sb, S, Se or Te. Some of these species are described in subsequent sections. For a recent survey consult ref. 555 and papers cited therein.

56.2.4.2 Pseudohalide Ligands

Mercury(II) cyanide consists of almost linear NC—Hg—CN molecules, with Hg—C = 201.5 pm and C—Hg—C = 175°.[191] Moreover, each mercury atom is surrounded by two sets of equidistant nitrogen atoms from neighbouring molecules, completing a distorted octahedron around the Hg. The effect of high pressure upon $Hg(CN)_2$ has been studied using Raman spectroscopy and interpreted in terms of structural distortion within the crystal.[193] $Hg(CN)_2$ forms stable adducts with many solvents.[194] In the solvate with THF, $5Hg(CN)_2{\cdot}4C_4H_8O$, the Hg atoms have octahedral surroundings.[195] Two corners are occupied by C atoms of the same $Hg(CN)_2$ molecule, while four others are engaged by four O atoms of the THF rings, or by four N atoms of the neighbouring $Hg(CN)_2$ molecules, or by two O and two N atoms. When HgO is dissolved in aqueous $Hg(CN)_2$ solution, a compound $\{Hg(CN)\}_2O$ is formed which has a molecular oxo-bridged structure in the solid state but exists as Hg(CN)(OH) in solution.[196] In solutions of Hg^{2+} and CN^- the species $Hg(CN)_2$, $Hg(CN)_3^-$ and $Hg(CN)_4^{2-}$ have been characterized by spectroscopic, potentiometric and polarographic methods.[197–200] There is no evidence for the existence of mononuclear complexes $Hg(CN)_x^{(x-2)-}$ with $x > 4$.[200] The trigonal-planar-coordinated $Hg(CN)_3^-$ group is found in the compound $CsHg(CN)_3$.[201] Tetracyanomercurates(II) with alkaline ions $M_2Hg(CN)_4$ (M = Li, Na, K, Rb, Cs, Tl^I) have been prepared and characterized by X-ray methods.[202–205] The potassium salt possesses a spinel structure, while the other compounds have a deformed spinel lattice. Recently the structure of $BaHg(CN)_4{\cdot}4py$ has been solved;[206] the compound consists of tetrahedral $Hg(CN)_4$ and bisdisphenoid $Ba(CN)_4(py)_4$ groups, which are linked together by Hg—CN—Ba bridges. The analogous Sr compound is isostructural.[206]

Numerous complexes of the type $MHg(CN)_2X{\cdot}nH_2O$ (M = Na, K, Rb, Cs; X = Cl, Br, I, NCO, NCS, N_3) have been prepared by the reactions of MX with $Hg(CN)_2$.[207,208] The compounds are double salts closely related to $KHg(CN)_2I$, which consists of $Hg(CN)_2$ molecules with each mercury weakly bonded to four iodines (Hg—I = 338 pm).[209] Some species with bivalent cations have been established. The compounds $M\{Hg(CN)_2SCN\}_2{\cdot}4H_2O$ (M = Mg, Ca, Sr, Ba), formed by the reactions between $Hg(CN)_2$ and the corresponding $M(SCN)_2$, have been characterized by X-ray structural analysis.[210] The Mg salt has a difficult structure with six- and seven-coordinated mercury (Figure 8); the other three complexes have layer structures similar to $KHg(CN)_2I$.

The compounds $KHgX_2(CN){\cdot}H_2O$ (X = Cl, Br) are obtained by reacting equimolecular amounts of HgX_2 and KCN in aqueous solutions. Their structures can be described as double salts $Hg(CN)_2{\cdot}HgX_2{\cdot}2KX{\cdot}2H_2O$.[211] In the structure of $Hg(CN)_2{\cdot}AgNO_3{\cdot}2H_2O$ there are approximately linear chains —Ag—NC—Hg—CN—Ag—, while the homogenous chain —Hg—CN—Hg—CN is found in $Hg(CN)(NO_3)$.[282,283] The compound $(MeHgCNHgMe)^+NO_3^-$ contains the unit —Hg—CN—Hg—.[298] Mercury(II) azide, $Hg(N_3)_2$, is formed from HgO and aqueous HN_3 or by metathesis in aqueous solution between $Hg(NO_3)_2$ and NaN_3. It exists in two modifications, the very explosive β form and the more stable α form.[212,213] The IR spectrum suggests the presence of N_3—Hg—N_3— units.[112] This has been proved by X-ray structural analysis of the α form.[214] This structure consists of N_3—Hg—N_3 molecules with almost linear N—Hg—N bonds. Every Hg atom is coordinated by five additional N atoms belonging to neighbouring molecules. The coordination polyhedron around the Hg can be described as a distorted capped trigonal prism. The complexes $Hg(N_3)_4^{2-}$, $Hg(N_3)_3^-$, $(Ph_3P)_2Hg(N_3)_2$ and $\{Hg(CNO)_2N_3\}^-$ have also been described.[215]

Mercury(II) cyanate is formed from AgNCO and $HgCl_2$ in methanol.[51] The potassium salt

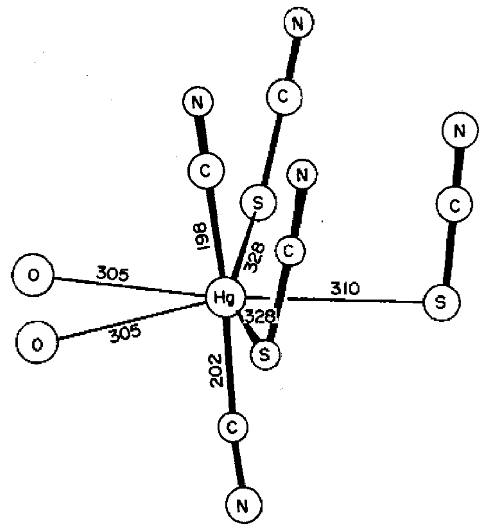


Figure 8 The coordination of Hg^{II} in the compound $Mg\{Hg(CN)_2SCN\}_2 \cdot 4H_2O$

$K_2Hg(OCN)_4$ contains O-bonded Hg atoms on the basis of IR measurements, but ^{14}N NMR on the tetraalkylammonium analogues suggests N bonding.[216,217] By mixing aqueous solutions of $Hg(MeCO_2)_2$ and $MOCN$ (M = K, Rb, Cs) the triclinic compounds $M_2Hg_3(NCO)_8$ are formed;[242] they are double salts $2MHg(NCO)_3 \cdot Hg(NCO)_2$. Mercury(II) fulminate is obtained by reaction of mercury with nitric acid and methanol.[194] The compound was introduced by Nobel as a detonator but it has been replaced by $Pb(N_3)_2$, which is more stable.[194]

$Hg(CNO)_2$ is decomposed by heat (equation 8).[4] It crystallizes in the orthorhombic form and contains linearly coordinated mercury.[218] It reacts with alkali metal fulminate solutions to form the highly explosive compounds $M_2Hg(CNO)_4$ (M = K, Rb, Cs); with larger cations such as Ph_4As^+ more stable complexes are formed.[219,220] Besides the homogeneous anionic mercury(II) fulminato complexes there are a few mixed species with unknown structures, *e.g.* $Na\{Hg(CNO)_2X\}$ (X = Cl, Br) or $Na_2S_2O_3 \cdot 2Hg(CNO)$.[221]

$$Hg(CNO)_2 \longrightarrow Hg + 2CO + N_2 \tag{8}$$

$Hg(SCN)_2$ is formed by reaction (9). $Hg(SCN)_2$ belongs to the monoclinic space group *C*2/*m* with Hg forming collinear S—Hg—S bonds to two coplanar SCN groups. An octahedral environment is achieved by weak interaction of Hg with the N atoms of four neighbouring molecules.[222] The compound burns in air to yield a voluminous spongy ash of unknown composition ('Pharaoh's serpents'). The complex $Hg(SCN)_3^-$ is formed by the reaction of $Hg(SCN)_2$ with MSCN (M = K, Cs, NH_4, Me_4N, *etc.*) and numerous X-ray data are available on the solid compounds (see Table 10).[223] The cesium salt contains the trigonal planar $Hg(SCN)_3$ group, while the other complexes are isomorphous and can be described as double salts.[201,241] In the tetrathiocyanatomercurates(II) tetrahedral $Hg(SCN)_4$ groups are present which are ligands to a number of ions (see Table 10).

$$Hg(NO_3)_2 + 2NaNCS \xrightarrow{H_2O} Hg(SCN)_2 + 2NaNO_3 \tag{9}$$

The solvent influences on the complex formation and stability have been reviewed by Golub *et al.*[194] Several monomeric complexes of $Hg(SCN)_2$ with N, O, P, As and S donor ligands are known with terminal Hg—SCN bonds.[224–232] Some thiocyanate-bridged dimeric complexes of mercury(II) are also known.[225,226] Recently the isolation of a mercury(II) thiocyanate complex with hexamethylenetetramine with exclusively N-bonded SCN groups has been published (Figure 9).[233] The compounds $(CH_2)_6N_4 \cdot Hg(SCN)_2$ and $(CH_2)_6N_4 \cdot 2Hg(SCN)_2$ exhibit covalently bonded Hg—S.[594,595]

Mixed halide–thiocyanate compounds Hg(SCN)X (X = Cl, Br, I) are formed from equimolar amounts of the pure components. They contain six-coordinated mercury(II) achieved by bridging X and SCN groups.[234] The formation constants of the mixed thiocyanato complexes have been detected spectroscopically.[235] Raman spectra of mixed halothiocyanatomercurate(II) complexes have been reported by Cooney and Hall.[236] The structure of ammonium

Table 10 Structural Data of Some Thiocyanatomercurates(II)

Compound	*Structure* (pm; °)	*Ref.*
$KHg(SCN)_3$	Four-coordinated Hg 2S and 2N atoms	194
$RbHg(SCN)_3$	SCN^- ions and $Hg(SCN)_2$ groups Hg—S = 240, 245	241
$CsHg(SCN)_3$	Trigonal planar $Hg(SCN)_3$ groups Hg—S = 244, 245, 256	201
$(PPh_4)Hg(SCN)_3$	Four-coordinated tetrahedral Hg SCN bridges: Hg—S = 259; Hg—N = 240; 2 × Hg—S = 246	238
$CoHg(SCN)_4$	HgS_4 tetrahedra, 4 × Hg—S = 255.8	239
$CuHg(SCN)_4$	HgS_4 tetrahedra, 2 × Hg—S = 252 2 × Hg—S = 258	240
$CoHg_2(SCN)_6{\cdot}C_6H_6$	Double tetrahedra Hg_2S_6 Hg—S = 242.4–285.5	243
$MgHg(SCN)_4{\cdot}2H_2O$	HgS_4 tetrahedra, 2 × Hg—S = 257.9(7) 2 × Hg—S = 252.3(8)	244
$CaHg(SCN)_4{\cdot}3H_2O$	HgS_4 tetrahedra Hg—S = 249.1(5)–260.2(4)	245
$SrHg(SCN)_4{\cdot}3H_2O$	HgS_4 tetrahedra 2 × Hg—S = 261.0(2) 2 × Hg—S = 249.5(3)	246
$(PPh_4)_2Hg(SCN)_4$	HgS_4 tetrahedra Hg—S = 249.1(3)–255.2(3)	247
$Co(DMF)_2Hg(SCN)_4$	HgS_4 tetrahedra Hg—S = 252.5	248
$Pb\{CoHg(SCN)_6\}$	Anionic double tetrahedra $\{Co(NCS)_2(NCS)_{2/2}Hg(SCN)_2(SCN)_{2/2}\}^{2-}$	249
$\{Zn(phen)_2\}Hg(SCN)_4$	HgS_4 tetrahedra connected by two SCN bridges with ZnN_6 octahedra	418
$Zn(phen)Hg(SCN)_4$	Double tetrahedra ZnN_4 and HgS_4 with two NCS bridges	418

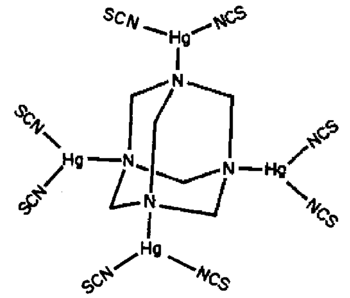
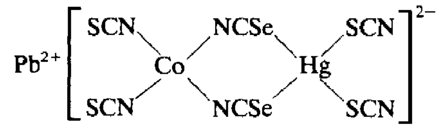


Figure 9 An example of Hg—NCS bonding[233]

dichlorothiocyanato-*S*-mercurate(II) contains Hg in a distorted octahedral coordination sphere.[237] There are two covalent bonds (Hg—S = 238.9(9), Hg—Cl = 233.9(7) pm); Hg is also linked to four Cl atoms (2 × Hg—Cl = 278(2) and 2 × Hg—Cl = 348 pm). $Hg(SeCN)_2$ is formed by the reaction between $Hg(MeCO_2)_2$ and KNCSe.[250] On the basis of IR measurements it was suggested that selenocyanate bridges are present in $Hg(SeCN)_2$.[251] The anionic complexes $Hg(SeCN)_3^-$ and $Hg(SeCN)_4^{2-}$ are more stable than the corresponding thiocyanatomercurates(II).[252,253] Nevertheless, the complexes $M^IHg(SeCN)_3$ or $M^I_2Hg(SeCN)_4$ have been studied less than the sulfur analogues. Some compounds $MHg(SeCN)_4$ (M = Cu, Pb, Zn, Co, Cd) have been prepared and should contain SeCN bridges with Hg—Se bonds.[254–256] Some other mixed metal complexes involving $Hg(SeCN)_4^{2-}$ have been characterized.[257–258] Compounds formulated as $Pb\{MHg(SeCN)_6\}$ (M = Co, Ni) have been reported and their reactions with Lewis bases have been described.[259] The X-ray structure of $SrHg(SeCN)_4{\cdot}4py$ reveals a tetrahedral mercury with four Hg—Se = 264.1(2) pm.[260] The nature of selenocyanate bonding in the complexes $MHg(SeCN)_4$ (M = Co, Ni) with certain pyridine derivatives has been determined by IR and electronic spectral studies.[261] An interesting species is the compound lead(II)di(isothiocyanato)bis(μ-selenocyanato)di(thiocyanato)cobaltate(II)mercurate(II) (**16**).[262]



(16)

Mercury(II) tricyanomethanide, $Hg\{C(CN)_3\}_2$ is an ionic compound which is cleaved by hydrolysis.[263] The compound is decomposed by heat to yield a voluminous brown ash. Mercury(II) dicyanamide has been described and a polymeric structure is suggested (Figure 10).[194,264]

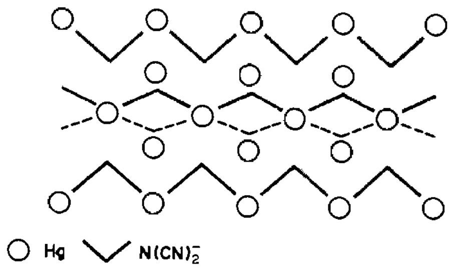


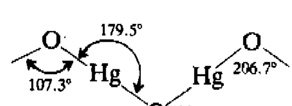
Figure 10 The structure of $Hg\{N(CN)_2\}_2$[194]

The interaction of mercury(II) with nonlinear pseudohalide ions $N(CN)_2^-$, $ONC(CN)_2^-$ and $C(CN)_3^-$ in MeOH, MeCN, DMSO and Me_2NAc has been investigated potentiometrically.[265]

56.2.4.3 Oxygen Ligands

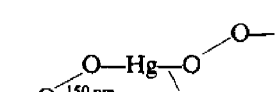
56.2.4.3.1 Oxides

The two well known forms of HgO are the stable orthorhombic and the metastable hexagonal form.[267,268] The former is made by heating the nitrate in air, or by precipitation of aqueous mercury(II) salts with alkali metal hydroxide. The dry methods produce the red form and the wet method yields yellow HgO. The different colours are caused by particle sizes; the yellow form is more finely divided and chemically more active. The structure is built up of infinite planar zigzag chains (**17**). There are four O atoms of different chains at 281–285 pm from the Hg atoms in addition to the two O atoms in the chain. The hexagonal modification is produced by slow precipitation from dilute solutions of K_2HgI_4 and KOH. The compound is isostructural with cinnabar (HgS) and contains chains in which the bond angles and bond lengths are the same as in the planar chains of the orthorhombic form. Two further O atoms at 279 and two at 290 pm complete a very distorted octahedral coordination around Hg.[268] HgO decomposes on heating, and is converted to HgX_2 by halogens.



(17)

By reaction of $HgCl_2$ with KOH and H_2O_2 in alcohol HgO_2 is formed. It is a polymorphic compound. The α form has monoclinic crystals (space group *C*2/*m*),[272] while the β form is orthorhombic with Hg and O_2 groups forming infinite zigzag chains (**18**), similar to PdS_2.[273]



(18)

Alkali metal compounds of the type $M_2Hg_2O_3$ (M = Na, K) should be mentioned, though the structures are not established.[274] The compounds M_2HgO_2 (M = Li, Na, K, Rb, Cs) are formed by heating HgO with MO_x in oxygen; they contain linear $(O—Hg—O)^{2-}$ ions (Hg—O = 195 pm).[274,276] The formation of mononuclear hydroxo complexes of Hg^{2+} has been studied by measuring the H^+ concentration of solutions with various Hg^{2+} concentrations.[286] The experimental data may be explained by assuming the equilibria (10) and (11).

$$Hg^{2+} + H_2O \longrightarrow HgOH^+ + H^+ \quad \log K_1 = -3.48 \pm 0.03 \qquad (10)$$

$$Hg^{2+} + 2H_2O \longrightarrow Hg(OH)_2 + 2H^+ \quad \log (K_1K_2) = -6.18 \pm 0.02 \qquad (11)$$

56.2.4.3.2 Complexes with carboxylates and related ligands

The weak base HgO can be dissolved in weak acids to form mercury(II) salts. Usually an excess of the acid is necessary to prevent hydrolysis and the formation of basic salts. The complex formation between mercury(II) and carbonate has been studied.[277] Three complexes were found, the simplest formulations being as shown in equations (12)–(14).

$$Hg^{2+} + H^+ + CO_3^{2-} \longrightarrow HgHCO_3^+ \quad \log K_1 = 15.05 \pm 0.10 \qquad (12)$$

$$Hg^{2+} + CO_3^{2-} \longrightarrow HgCO_3 \quad \log K_2 = 10.45 \pm 0.20 \qquad (13)$$

$$Hg^{2+} + CO_3^{2-} + H_2O \longrightarrow HgOHCO_3^- + H^+ \quad \log K_3 = 4.40 \pm 0.10 \qquad (14)$$

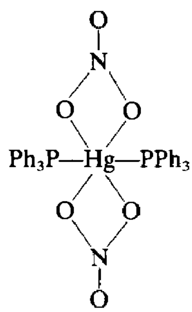
Anhydrous mercury(II) acetate crystallizes on cooling from a hot solution of HgO in 50% acetic acid.[278] The structure consists of isolated $(MeCO_2)_2Hg$ molecules with an Hg—O distance of 207 pm and O—Hg—O angle of 176°. Chains are formed by two weak Hg—O interactions of 273 pm. By the packing of these chains the Hg gets a fifth O neighbour at a distance of 275 pm, yielding a nearly tetragonal pyramid as the coordination polyhedron of Hg.[279] Other mercury(II) carboxylates, such as the oxalate, HgC_2O_4, or the tartrate, $HgC_4H_4O_6$, have been prepared.[4,280] Different complexes in the systems HgC_2O_4—X—H_2O (X = NO_2^-, Br^-, SCN^-, $MeCO_2^-$) have been studied by paper ionophoresis.[281] The resulting complexes are more stable than the simple HgC_2O_4. The synthesis and properties of mercury(II) trifluoracetate and its use in the mercuration of aromatic compounds have been reviewed.[284] In the complex formed between $(CF_3CO_2)_2Hg$ and 1,4-dioxane (1:1) the Hg is coordinated to the $CF_3CO_2^-$, with Hg—O = 208 pm. The 1,4-dioxane molecules bridge the Hg atoms with Hg—O = 264 pm.[285] There are a lot of complexes with carboxylic acids and related ligands of the general composition HgL_2. Some examples are given in Table 11. Mercury(II) trifluoromethylsulfonate salts are of considerable interest; they are inconvenient to handle, but the solid salt $\{Hg(DMSO)_6\}(F_3CSO_3)_2$ has been shown to possess attractive properties as it is a stable compound.[314] The ligands are fixed *via* oxygen; a ^{199}Hg NMR study of a series of derivatives has been reported.[314]

Table 11 Some Compounds HgL_2 with L = Oxygen Donor Ligand

Compound	*Characteristics*	*Ref.*
Mercury(II) trichloroethanoate	Preparation of the pyridine adducts	287
Hg(nitrilotriacetate)(phen)	Determination of formation constants	288
$Hg(O_2CR)_2$ ($R = C_nH_{2n+1}$, n = 2–9)	Study of the vibrational spectra	289
$Hg(O_2CCH_2OPh)_2$	Octahedrally coordinated Hg with bridging carboxylate groups	290
Hg^{II} tropolonate	X-ray structure analysis; six-coordinated mercury atoms	291
$\{Hg(DMSO)_6\}(O_3SCF_3)_2$	Preparation and properties	314

56.2.4.3.3 Complexes with inorganic oxo anions

Mercury(II) nitrite seems to have a nitro, $O_2N—Hg—NO_2$, rather than a nitrito structure.[292] The complex $K_3\{Hg(NO_2)_4\}(NO_3)$, obtained from KNO_2 and $Hg(NO_3)_2$, contains the $Hg(NO_2)_4^{2-}$ ion.[293] In this complex eight-coordinated mercury(II) is found with a very distorted square antiprism arrangement of O atoms around the metal (HgO_8; Hg—O = 234–258 pm).[293] Moreover the complexes $K_2\{Hg(NO_2)_4\}$ and $Rb_2Hg\{Hg(NO_2)_6\}$ have been reported.[294,295] The IR spectrum of the former suggests that the NO_2^- ligands are chelating.[294] The species $MHg(NO_2)_3$ (M = Rb, Cs, Tl^I) are cubic, crystallizing in a form having space group $Pm3m$.[296] Mercury(II) nitrate is obtained by the reaction of HgO with N_2O_4 to produce $Hg(NO_3)_2{\cdot}N_2O_4$, which loses N_2O_4 to yield $Hg(NO_3)_2$.[297] By dissolution of metallic mercury in excess nitric acid the species $Hg(NO_3)_2{\cdot}nH_2O$ are obtained ($n = 1, 2, 8$).[4] $Hg(py)_2(NO_3)_2$ has been crystallized from a mixture of yellow HgO, pyridine and HNO_3 in ethanol.[299] The compound explodes when heated. The IR spectrum confirms coordinated NO_3 groups.[299] The compound $Hg(PPh_3)_2(NO_3)_2$ (**19**) contains mercury(II) in a (2 + 2 + 2) coordination sphere because NO_3^- acts as a chelate ligand (Hg—P = 245.1 pm, Hg—O = 250.7, 279.0 pm).[481,300]



(**19**)

In the corresponding $Hg(PPh_3)(NO_3)_2$, the mercury(II) has a distorted tetrahedral coordination with Hg—O bond lengths of 219.0, 242.8 and 256.0 pm and an Hg—P distance of 235.9 pm. There are two distinct types of NO_3 groups bonded to Hg. One is an unshared unidentate ligand and the other acts as a bridging group joining two Hg atoms.[303] The complex $(Me_4N)_2Hg(NO_3)_4$ is obtained from $(Me_4N)NO_3$ and $Hg(NO_3)_2$ in ethanol.[296] The IR spectrum indicates that the overall symmetry of the anion $\{Hg(NO_3)_4\}^{2-}$ is lower than T_d and confirms coordinated nitrate.[299] The compounds $Hg(CN)_2{\cdot}AgNO_3{\cdot}2H_2O$ and $Hg(CN)(NO_3)$ have been mentioned earlier (see Section 56.2.4.2) because the main features of their structures are infinite chains —CN—Hg—CN—Ag—CN— and —Hg—CN—Hg—CN— respectively.[282,283] In each structure the characteristic coordination number (two) of mercury(II) is extended by oxygen atoms. In $Hg(CN)_2{\cdot}AgNO_3{\cdot}2H_2O$ the Hg atoms have five contacts with O atoms (Hg—O = 255–306 pm), while in $Hg(CN)(NO_3)$ mercury(II) interacts with six O atoms of three NO_3 groups (Hg—O = 273 pm).[282,283] A similar coordination of mercury is found in $HgI(NO_3)$(Hg—I = 266.1, 264.4 pm; 6 × Hg—O = 264.8–325.7 pm) and $Ag_2HgI_2(NO_3)_2{\cdot}H_2O$, where six O atoms of NO_3^- groups form a hexagon in the equatorial plane perpendicular to the I—Hg—I segment.[301]

Several mercury(II) phosphates are known: $Hg_3(PO_4)_2$,[304,305] $HgHPO_4$,[304] $Hg_2P_2O_7$[306] and some polyphosphates.[307] In the mercury(II) phosphate the Hg atoms are two-coordinated in a nearly linear way; the Hg—O distances vary between 206 and 213 pm and the O—Hg—O angles between 163.4 and 169.9°.[312] All O atoms belong to phosphate tetrahedra. Each Hg atom is bonded to one O atom of each of two phosphate tetrahedra and each phosphate group is bonded to three Hg atoms.[312] The structure of $HgHPO_4$ has been determined.[308] The two independent Hg atoms in the cell have six- and seven-coordination polyhedra. The pairs of short Hg—O bonds are approximately *trans* and the average Hg—O distance is 207 pm.[305] A mercury(II) pyrophosphate complex has been studied by potentiometric methods.[309] The principal species seems to be $Hg(OH)(P_2O_7)^{3-}$. Mercury(II) arsenates have been reported, but are generally ill defined.[310]

A redetermination of mercury(II) sulfate has been done.[311] There are very distorted HgO_4 tetrahedra in the structure (O—Hg—O = 84.4–143.4°). $HgSO_4{\cdot}H_2O$ crystallizes from solutions of the anhydrous compound in moderately dilute acid. Mercury is coordinated with one sulfate O atom and one water molecule, forming discrete $HgSO_4{\cdot}H_2O$ groups connected by H bonds to form a three-dimensional structure. Four more-distant O atoms of different SO_4 tetrahedra complete an irregular octahedron around mercury.[313] Mercury(II) selenite, $HgSeO_3$, is obtained from mercury(II) nitrate solutions on addition of Na_2SeO_3.[315] The selenate, $HgSeO_4$, is isomorphous with $HgSO_4$.[313] However, the mercury(II) selenate monohydrate and

$HgSO_4 \cdot H_2O$ have different structures. Mercury(II) is coordinated to six oxygen atoms forming a distorted octahedron with Hg—O distances of 226.0–249.9 pm. The shortest distances of 226 and 228 pm are the ones to the selenate groups. Four of the oxygen atoms in the coordination octahedron belong to four different selenate groups and two to H_2O. The $HgO_4(OH_2)_2$ octahedra and the SeO_4 tetrahedra build up the three-dimensional structure by sharing corners.[317] Several mercury(II) tellurates have been prepared: $HgTeO_3$, Hg_3TeO_6, $Hg_2H_2TeO_6$.[315,318,319] The structure of Hg_3TeO_6 contains octahedral TeO_6 and tetrahedral HgO_4 units with each oxygen bonded to one Te and three Hg atoms (Hg—O = 233, Te—O = 198 pm).

The mercury(II) salts of halogen oxy acids, $Hg(ClO_3)_2 \cdot 2H_2O$, $Hg(BrO_3)_2 \cdot 2H_2O$ and $Hg(ClO_4)_2 \cdot 6H_2O$ are obtained by dissolving the oxide in the appropriate acid. The perchlorate is the most important and crystallizes trigonally with the space group $P\bar{3}m1$. The structure is built up from discrete octahedral $Hg(OH_2)_6^{2+}$ units and ClO_4^- ions. The six Hg—O bonds are equivalent to bond lengths of 234.1 pm.[320] In $Hg(ClO_4)_2 \cdot 6L$ (L = pyridine 1-oxide) the water of crystallization is formally substituted by L; nevertheless the structure is similar to $Hg(ClO_4)_2 \cdot 6H_2O$. It consists of cubic close-packed layers of $(HgL_6)^{2+}$ cations with ClO_4^- anions in trigonal holes of the array.[318] Mercury(II) has regular octahedral coordination with Hg—O = 235 pm.[321] The iodate, $Hg(IO_3)_2$, is obtained by precipitation from aqueous solutions. Some complexes with oxo anions of the *d* metals have been prepared and characterized by means of X-ray crystal structure analysis. Details are listed in Table 12.

Table 12 Complexes with Oxo Anions Involving *d* Metals

Compound	*Structure* (pm; °)	*Ref.*
$HgCrO_4$	Linear O—Hg—O groups (Hg—O = 210, 212); different CrO_4 tetrahedra forming endless zigzag chains	321
$HgCrO_4 \cdot 1/2H_2O$	Similar chains to those in $HgCrO_4$ (Hg—O = 205.5, 206.4; O—Hg—O = 179.98)	323
$HgMoO_4$	Linear O—Hg—O groups (2 × Hg—O = 203); four more distant O (2 × Hg—O = 267, 2 × Hg—O = 277)	324, 325
α-$Hg_2V_2O_7$	Hg links two $(VO_3)_n$ chains by ionic bonds forming $\{Hg(VO_3)_2\}_n$ units between neutral $(Hg—O)_n$ chains	325

56.2.4.3.4 Basic salts of mercury(II)

Because HgO is only weakly basic, most mercury(II) salts hydrolyze to basic salts in aqueous solutions unless acidified. Therefore numerous basic salts are known and have been reviewed elsewhere.[4,7] X-Ray scattering measurements on acidified mercury(II) perchlorate solutions indicate the presence of $Hg(OH_2)_6^{2+}$.[336] Hydrolysis produces polynuclear species which are thought to be of the types $Hg_2(OH)(OH_2)_2^{3+}$, $Hg_3O(OH_2)_3^{4+}$ or $Hg_4O(OH)(OH_2)_3^{5+}$.[336] The dominant features in the structures of basic salts of mercury(II) are infinite zigzag chains (see Figures 11 and 12) or complicated oxo-bridged groups as in $Hg_3O_2(NO_3)_2$[329] or $Hg_3O_2Cl_2$.[340,341] Isolated molecules are rare; one example is given in Figure 13.[300] Structural data of some basic mercury(II) compounds are given in Table 13.

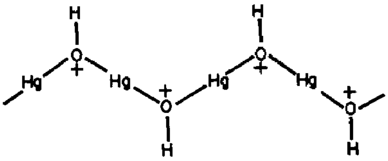


Figure 11 Chains $\{Hg(OH)^+\}_n$ in basic mercury(II) salts

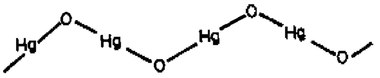


Figure 12 Zigzag chains in basic mercury(II) salts

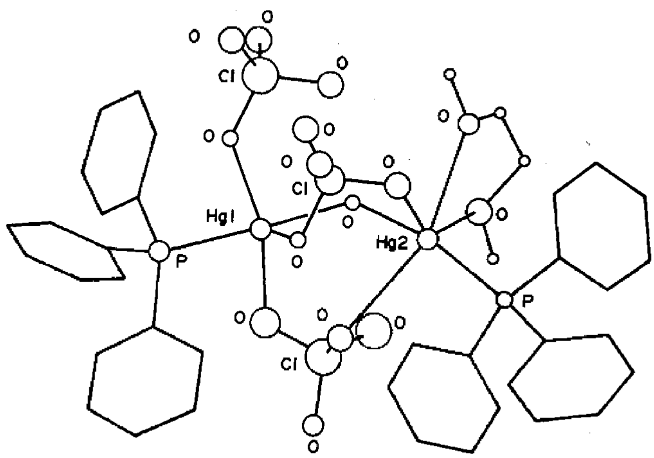


Figure 13 Structure of the mercury(II) complex compound $Hg_2(PPh_3)_2(OH)(ClO_4)_3 \cdot egdm$

Table 13 Some Basic Compounds of Mercury(II)

Compound	*Structure* (pm; °)	*Ref.*
$Hg(OH)NO_3$	Infinite chains $\{Hg(OH)\}_n^{n+}$; Hg—O = 203.1, 205.4	327, 328
$Hg_3O_2(NO_3)_2$	Hg_3O_2 honeycomb, Hg—O = 264–281	329
$Hg_3(OH)_2(SO_4)_2 \cdot H_2O$	Zigzag chains O—Hg—(OH)—Hg—(OH)—Hg—O with terminal O atoms provided by sulfate	330, 331
$HgSO_4 \cdot 2HgO$	$(Hg_3O_2)_n^{2n+}$ layers	332, 333
$HgSeO_4 \cdot 2HgO$	$(Hg_3O_2)_n^{2n+}$ layers	332
$Hg(OH)ClO_3$ and $Hg(OH)BrO_3$	Infinite chains $\{Hg(OH)\}_n^{n+}$, mercury being further coordinated by 6O from XO_3^-	335
$Hg_5O_2(OH)_2(ClO_4)_4(H_2O)_x$	Infinite Hg—O polymers	336, 337
$Hg_7O_4(OH)_2(ClO_4)_4$		
$Hg_2O(OH)(ClO_4)$		
$Hg_2(PPh_3)_2(OH)(ClO_4)_3 \cdot egdm$ (egdm = ethyleneglycol dimethylether)	Isolated molecules (see Figure 13) Hg—P = 235; Hg(2)—O = 203; Hg(1)—O = 210	300
$Hg(OH)F$	Infinite $\{Hg(OH)\}_n^{n+}$ chains	338
$Hg_3O_2Cl_2$	Two-coordinated Hg (2 × Hg—O = 207); three-coordinated Hg (Hg—O = 217, 232, 233)	
Hg_3OCl_4	$\{O(HgCl)_3\}Cl^-$ (Hg—O = 206)	339
$Hg_4O_2Cl_2$	$(Hg_4O_2Cl_2)_n$ chains (2 × Hg—O = 202; 2 × Hg—O = 223)	340, 344
$Hg_5O_4Br_2$	Infinite (Hg—O—Hg—O) chains (Hg—O = 205); HgO_4 groups	342
$2HgO \cdot NaI$	Infinite (Hg—O—Hg—O) chains (Hg—O = 201·4)	343
$Hg_5Re_2O_{10}$	${}^2_\infty[(Hg_2O)_4Hg_{4/2}]_n^{4+}$ macro cations, Hg^I—O rings connected by Hg^{II} (Hg^I—O = 219, 214; Hg^{II}—O = 205)	344

56.2.4.3.5 Oxygen donor ligands

Almost every mercury(II) salt forms stable complexes with oxygen donor molecules. Some details have been reviewed by McAuliffe[7] and by Dean.[8] Table 14 lists some examples which have been studied by structural analysis.

56.2.4.4 Sulfur Ligands

56.2.4.4.1 Inorganic compounds

Mercury(II) sulfide, HgS, is dimorphic. Metacinnabarite, a rare mineral, is obtained by precipitation from aqueous acidified mercury(II) chloride by H_2S.[351] It crystallizes in the zinc blende structure in which Hg^{II} forms tetrahedral bonds (Hg—S = 253 pm); it is stable above 400 °C.[352] The more common form, cinnabar, is obtained from the elements or by passing H_2S into mercury(II) acetate in hot glacial acetic acid containing NH_4SCN.[351] It crystallizes in the space group $P\,3_221$ and consists of infinite —Hg—S—Hg—S— chains spirally wound on axes

Table 14 Mercury(II) Complexes with Oxygen Donor Ligands

Compound	*Structure* (pm; °)	*Ref.*
$Hg(ClO_4)_2·4DMSO$	$Hg_2(DMSO)_8^{4+}$	345
$HgCl_2·Ph_2SO$	$Hg—OSPh_2$ coordination (Hg—O = 258; Hg—Cl = 229.1, 228.9, 323.0, 328.4)	346
$HgCl_2·(DMSO)_{2/3}$	$HgCl_2$ molecules (Hg—Cl = 220.6) (DMSO)·$HgCl_2$ units (Hg—O = 252, 256; Hg—Cl = 230.9, 232)	347
$HgCl_2·2MeOH$	2 × Hg—Cl = 231; 2 × Hg—O = 282	348
$HgBr_2·(dioxane)_2$	Distorted octahedral $HgBr_2O_4$ units (Hg—Br = 243; Hg—O = 283)	349

parallel to the three-fold axis (Hg—S = 236.8 pm, S—Hg—S = 172.8°, Hg—S—Hg = 104.7°).[353] In these chains mercury has two more neighbours at 310 pm. Cinnabar is notable for its extraordinarily large optical rotatory power in the solid state. The structural properties of the type $A^{II}B^{VI}$ semiconductor alloys in the system HgTe—HgS have been studied.[354] Replacement of S atoms in the lattice of cinnabar by Te atoms did not cause noticeable structural distortion.

Mercury(II) sulfide reacts with K_2S or Rb_2S to give the complex mercurates(II) K_6HgS_4 and Rb_6HgS_4.[355,356] The crystal structure of K_6HgS_4 is similar to that of Na_6ZnO_4 and consists of isolated HgS_4 tetrahedra (Hg—S = 254.2, 3 × Hg—S = 259.1 pm). Several complex sulfides M_2HgS_2 (M = Na, K) have been mentioned, although no recent studies appear to have been reported.[4] Recently the sulfur-rich anionic complex $\{Hg(S_6)_2\}^{2-}$ with tetrahedrally coordinated mercury(II) (Hg—S = 250.5–260.6 pm) has been synthesized.[499] $Hg_2P_2S_6$[357] and $Hg_2P_2S_7$[358] contain P_2S_6 or P_2S_7 groups respectively. The Hg atoms are surrounded by four sulfur atoms in a deformed tetrahedral arrangement ($Hg_2P_2S_7$: mean distance Hg—S = 259.1 pm; $Hg_2P_2S_6$: mean distance Hg—S = 261.5 pm). The compounds Hg_3PS_3, Hg_3PS_4, $Hg_4P_2S_7$, $HgPS_3$ and $HgPS_2$ have been prepared and characterized by X-ray diffraction studies.[359] The complex $Hg_2^IHg_2^{II}S_2(ClO_4)_2$ should be mentioned although nothing is known of its structure.[63] There are several mixed halogeno-sulfur-mercury(II) compounds listed in Table 15. Numerous mercury(II) thiocyanato complexes with exclusively S-bonded SCN^- have been mentioned in Section 56.2.4.2.

Table 15 Structural Data of Mercury(II) Sulfur Complexes

Compound	*Structural data* (pm; °)	*Ref.*
$Hg_3S_2F_2$	Orthorhombic; *Fmmm*; a = 1260, b = 2870, c = 723 Cubic; $I\,2_13$; a = 814 (isostructural with $Hg_3S_2Cl_2$)	360, 361, 366
$Hg_3S_2Cl_2$	Infinite planar chains S—Hg—S—Hg—; 2 × Hg—S = 242; S—Hg—S = 165.1; Hg—S—Hg = 94.1	362, 363
γ-$Hg_3S_2Cl_2$	OD structure, Hg_3S pyramids with shared Hg forming $(Hg_3S_2)_n^{2+}$ layers	364
$HgX_2·2HgS$ (X = Cl, Br, I)	X = I; $HgI_2·2HgS$; orthorhombic; a = 936, b = 969, c = 1850	365

The complex $Na_2Hg(SO_3)_2·H_2O$ has been prepared. It contains discrete $Hg(SO_3)_2^{2-}$ anions with S-bonded SO_3 units (Hg—S = 240.2, 241.1 pm).[393,394] Mercury(II) thiosulfate complexes obtained in solution also appear to be S bonded.[395] Mercury(II) forms numerous compounds with different sulfur donor ligands. Many of them have been reviewed by McAuliffe[7] and by Constable.[5]

56.2.4.4.2 Thiols

The compounds RSHgX (R = Me, Et, Pr, Bu; X = Cl, Br, I) have been studied by vibrational spectrometry.[367,368] The species MeSHgX (X = Cl, Br) are isostructural[369] with a polymeric structure in which the mercury is in a pseudo-octahedral environment.[368] IR and Raman measurements on a series of RSHgX have demonstrated the formation of a range of monomeric, dimeric and polymeric structures in the solid state, but they also have established the compounds to be monomeric in pyridine solution.[367] In pyridine solution the equilibrium

(15) is established. Mercury(II) sulfides $Hg(SR)_2$ are also formed from HgO and RSH. Some compounds $Hg(SR)_2$ are summarized in Table 16.

$$2RSHgX \longrightarrow Hg(SR)_2 + HgX_2 \quad (15)$$

Table 16 Mercury(II) Sulfides, $Hg(SR)_2$

Compound	*Method*	*Structure* (pm; °)	*Ref.*
R = Me, Et, Pr^n, Pr^i	IR	Linear S—Hg—S units	370
R = Me	X-ray	Five-coordinated Hg; 2 × Hg—S = 236; 3 × Hg—S = 326	371
R = Et	X-ray	Discrete molecules; four-coordinated Hg; 2 × Hg—S = 245; Hg—S = 353, 356	372, 373
R = Bu^t	X-ray	Polymeric, tetrahedrally coordinated Hg; 2 × Hg—S = 259; 2 × Hg—S = 266	370, 372

56.2.4.4.3 Sulfides

^{35}Cl NQR measurements on the compounds $2HgCl_2 \cdot Et_2S$ and $3HgCl_2 \cdot 2Me_2S$ have been reported.[374] Crystal structures are known by X-ray analysis for the complexes $(EtSMe)HgCl_2$, $HgLBr_2$ and $HgL(SCN)_2$ ($L = HO_2CCH_2SCH_2CH_2SCH_2CO_2H$).[375,376] In the compound $2HgCl_2 \cdot$(tetrathiafulvene) the ligand acts as a tetradentate donor so that Hg^{II} is in an octahedral environment (Figure 14).[377] In $HgCl_2 \cdot 2$(1,4-thioxane) the mercury(II) is tetrahedrally coordinated by two S and two Cl functions (2 × Hg—S = 257, 2 × Hg—Cl = 248 pm).[378,379] 1,3,5-Trithiane forms $HgX_2 \cdot L$ (X = Cl, Br, I) complexes.[380–383] The chloro complex is built up of one-dimensional chains with tetrahedrally coordinated mercury (2 × Hg—Cl = 244, 2 × Hg—S = 261 pm) (Figure 15).

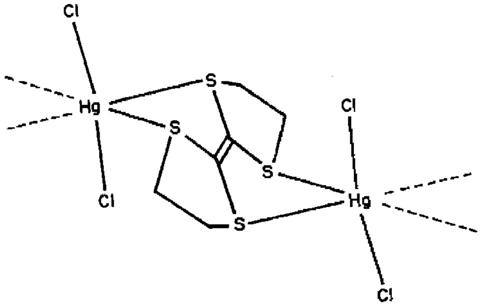


Figure 14 The structure of the complex compound $2HgCl_2 \cdot$(tetrathiafulvene)

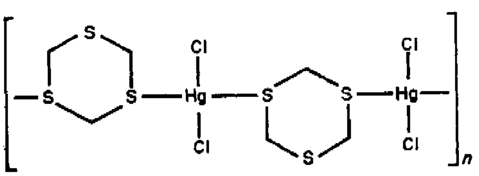
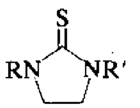


Figure 15 The chain structure of $HgCl_2 \cdot$(1,3,5-trithiane)

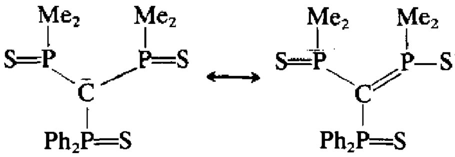
The stability constants for 1:1 complexes between 2,2′-thiodiethanol, tetrahydrothiophene, diethyl sulfide and Hg^{II} were detected in H_2O and mixed aqueous solvent systems.[384]

56.2.4.4.4 Thione and related ligands

HgX_2 (X = Cl, Br, I) reacts with imidazolinethiones **(20)** to give HgL_2X_2 and $HgL'X_2$ respectively.[385] In HgL_2X_2 the mercury atom adopts a distorted tetrahedral coordination (Hg—Cl = 251, 252 pm; Hg—S = 249, 250 pm), but in $HgL'Cl_2$ it has a trigonal pyramidal geometry (Hg—Cl = 236, 258, 270 pm; Hg—S = 242 pm).[385] Complexes with 1,4,6-trimethylpyrimidine-2-thione (L) and the 1-methylpyrimidine-2-thione (L′), HgL_2X_2 (X = Cl, Br, I), $Hg_2L'_3X_4$ (X = Cl, Br) and $HgL'X_2$ involve N—S chelating thione ligands for HgL_2X_2 and $HgL'I_2$.[386] The far-IR spectrum of $HgL'I_2$ includes a band at 154 cm^{-1} assigned to $\nu(Hg—I)_{terminal}$, implying it to be tetrahedral in structure. The other compounds involve halogen-bridged octahedral structures. The compounds $Hg_2L'_3X_4$ probably involve compositions of the type $HgL_3{\cdot}HgX_4$.[386] In $\{(Me_2PS)_2(Ph_2PS)C\}HgCl$ (see **21**) the mercury is in a distorted tetrahedral coordination geometry with mean S—Hg—S and S—Hg—Cl bond angles of 102.1° and 115.8° respectively (Hg—S = 252.2, 255.0, 271.6 pm; Hg—Cl = 240.8 pm).[387]



(**20**) R = H, R′ = Me, Et(L)
R = R′ = Me, Et(L′)



(**21**)

Diethyldithiophosphate forms a disordered structure with mercury of composition $Hg\{S_2P(OEt)_2\}_2$.[388] Mercury is surrounded tetrahedrally by four S atoms at 256 pm. The complex $Hg(NO_3)_2{\cdot}2Ph_3PS$ has been prepared and the structure discussed.[400] A series of species $Hg(Bu^n_3PS)_2X_2$ (X = Cl, Br, I) have been described and their ^{31}P NMR spectra have been reported.[401]

56.2.4.4.5 Thiourea and related ligands

The complexing of Hg^{II} by several sulfur ligands, including thiourea, in mixed solvents has been studied.[389] In $Hg(H_2NCSNH_2)_3Cl_2$ the mercury atom is inside a distorted trigonal bipyramid surrounded by two Cl and three S atoms with axial covalent Hg—Cl bond lengths of 224 and 236 pm and equatorial Hg—S bond lengths of 237, 261 and 310 pm.[390] However, in diiodobis(thiourea)mercury(II) each Hg atom is tetrahedrally coordinated to two S atoms at short Hg—S distances of 246 pm and to two I atoms at distances of 284 pm. Two further I atoms at Hg—I distances of 386 pm complete the Hg coordination polyhedron to form a flattened octahedron.[390]

56.2.4.4.6 Xanthates and dithiocarbamates

Mercury(II) forms stable complexes with anionic sulfur ligands.[391,392] Mercury(II) ethylxanthate, $Hg(S_2COEt)_2$, contains Hg^{II} in a distorted tetrahedral environment (Hg—S = 234, 249, 276, 294 pm).[396] In the structure of mercury(II) isopropylxanthate,[397] four Hg atoms and four bridging xanthate groups link together alternately to form a centrosymmetric 16-membered ring. A xanthate group chelates the first Hg in the ring and another xanthate group bridges the second together with the corresponding one in the adjacent ring. The latter bridging groups are arranged around a two-fold axis generating an infinite —Hg—S—C—S—Hg— helical chain (Figure 16).[397]

A crystallographic and spectrometric study of mercury(II) dithiocarbamate showed tetrahedrally coordinated mercury with Hg—S distances of 249.9–262.9 pm.[398] The compounds $(Bu_4N)Hg(R_2dtc)_3$ (R = Me, Et) have been prepared. The tris anion is not completely dissociated in acetone solution.[398a]

56.2.4.5 Selenium and Tellurium Ligands

Mercury(II) coordination compounds containing Se or Te donor atoms constitute a rather neglected area of coordination chemistry. Often the species show similarities to the corresponding sulfur compounds (see Table 17). Mercury(II) selenide, HgSe, and mercury(II) telluride, HgTe, are simply formed by direct combination of the elements.[4] Single crystals are available by chemical transport methods using a pure H_2 or Ar stream.[402] X-Ray diffraction

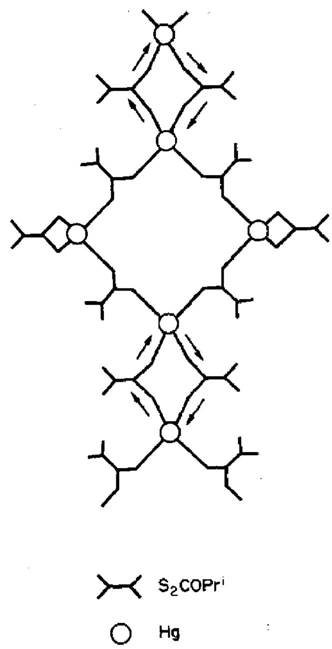


Figure 16 The two-dimensional network of the tetramer linked with the helical chains represented by arrows in the complex compound $Hg(S_2COPr^i)_2$. The two-dimensional sheet is perpendicular to the plane of paper

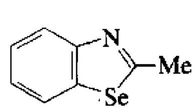
showed that the crystals belong to the cubic system with $a = 608$ pm for HgSe and $a = 643$ pm for HgTe. At 600 °C the structure of both compounds is of the sphalerite type, while the common structure is the zinc blende type.[402,403] Both compounds are semiconductors; HgTe in particular also shows thermoelectric and IR photoconductivity effects. The thermal expansion of HgSe has been studied with a high temperature powder X-ray camera and the expression for the thermal expansion coefficient has been given.[404] A crystallographic and magnetic investigation of the mercury chromium sulfide selenide system, $HgCr_2(S_xSe_{1-x})_4$ has been made.[405] The distribution of cations in tetrahedral and octahedral sites, as well as the lattice constants, have been studied. The magnetization and susceptibility were detected as functions of the magnetic field.

Table 17 Mercury(II) Coordination Compounds with Se or Te Donors[a]

Compound	*Isostructural S compound*	*Structural data* (pm)	*Ref.*
$Hg_3Se_2F_2$	$Hg_3S_2F_2$	—	360, 366
$Hg_3Se_2Cl_2$			
$Hg_3Te_2Cl_2$	$Hg_3S_2Cl_2$	—	362
$Hg_2P_2Se_6$	$Hg_2P_2S_6$	Hg—Se = 258–383.3	357
K_6HgSe_4	K_6HgS_4	—	355
Rb_6HgSe_4	K_6HgS_4	—	355

[a] These compounds are isostructural with the corresponding S compounds in Section 56.2.4.4.1.

Pseudo halogenomercurates(II) containing Se atoms have been mentioned in Section 56.2.4.2. Preparative details for the complexes $HgLX_2$ (L = tolylphosphineselenide; X = Cl, Br, I) and $3Hg(NO_3)_2 \cdot 4Ph_3PSe$ have been reported and the structures of the products have been discussed.[400] The species $Hg(Bu^n_3PSe)_2X_2$ (X = Cl, Br) and $Hg_2I_4(Bu^n_3PSe)_2$ have been characterized by their ^{31}P NMR spectra.[401] Several complexes containing the ligand 2-methylbenzoselenazole (**22**; L), namely $HgLX_2$ (X = Cl, Br) and $HgL_{1.5}X_2$ ($X = ClO_4$, NO_3) have been described. Some more species of addition complexes with Se or Te donors are listed in Table 18.



(**22**)

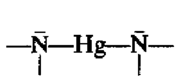
Table 18 Some Addition Compounds Containing Se or Te Donors

Compound	*Ref.*	*Compound*	*Ref.*
$(HgCl_2{\cdot}TeBu_2)_2$	407	$HgCl_2{\cdot}$1,4-diselenane	410
$HgCl_2{\cdot}TeEt_2$	408	$HgX_2{\cdot}SePPh_3$ (X = Cl, Br, I)	411–413
$HgI_2{\cdot}TePh_2$	555	$HgCl_2{\cdot}$selenourea	414
$HgCl_2{\cdot}MeSe(CH_2)_nSeMe$ (n = 2, 3)	409	$HgX_2{\cdot}$(selenourea)$_2$ (X = Cl, Br, I)	414

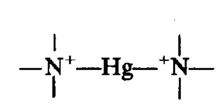
The structure of tetraphenylphosphoniumtris(tellurophenolato)mercurate(II) contains isolated cations and anions. In the trigonal planar anion $\{Hg(TePh)_3\}^-$ the ligand has a propeller-like arrangement around the central Hg atom. The mean Hg—Te distance is 269.7 pm.[472] Recently the structure and vibrational spectra of the coordination compound $HgI_2{\cdot}TePh_2$ have been described.[555] The molecule was found to exhibit a tetrameric structure involving two types of I bridges.

56.2.4.6 Nitrogen Ligands

The chemistry of mercury(II) nitrogen coordination compounds has been unclear for a long time. In addition to coordination complexes of nitrogen ligands there are compounds of the types $Hg(NR_2)_2$ with tricoordinated nitrogen atoms. Furthermore for compounds first described more than 100 years ago, *e.g.* Millon's base, $Hg_2N(OH){\cdot}2H_2O$, the 'fusible' $Hg(NH_3)_2X_2$ (X = Cl, Br), and the 'infusible white precipitates', $HgNH_2X$, their compositions have been doubtful for a long time. Only modern instrumental methods like X-ray structure determinations or modern spectroscopic techniques have revealed the real structures of these compounds.[90] They contain building blocks (a) and (b).



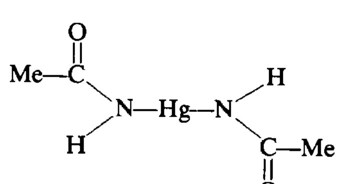
(a) amides (tricoordinated N atoms)



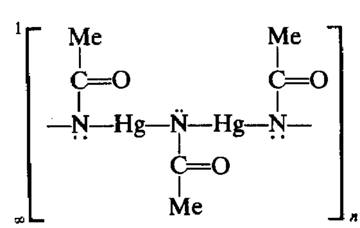
(b) amines (tetracoordinated N atoms)

56.2.4.6.1 Nitrogen ligands with tricoordinated nitrogen atoms: amides

Since its first preparation in 1852 by the dissolution of HgO in molten acetamide, the mercury(II) acetamide $Hg(NHCOMe)_2$ (**23**) has been used frequently as the starting material for the preparation of other mercury(II) compounds.[419] X-ray structure determination together with NMR data clearly show that the acetamide ligand is monodentate and Hg—N bonded: (Hg—N = 206 pm).[420,421] It has also been shown that the supposed difference between the N—C and C—O bond lengths leading to the tautomeric iminol structure is statistically without significance. Mercury(II) acetamide on heating to above 240 °C (m.p. 203 °C), or upon addition of acetone to its methanolic solution, disproportionates into acetamide and a polymer of composition $(HgNCOMe)_n$ (**24**).[94] Structural data for some mercury(II) amides are listed in Table 19.



(**23**)



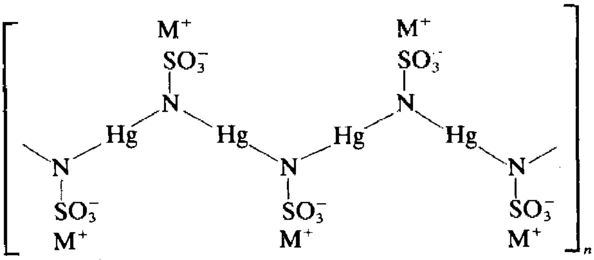
(**24**)

$Hg\{N(CF_3)_2\}_2$ has been prepared from $F_3CN{=}CF_2$ or cyanogen chloride and HgF_2.[422] $Hg\{(F_3C)_2NNCF_3\}_2$ is formed from HgF_2 and $(F_3C)_2NN{=}CCl_2$.[423] Since the Hg—N— bonds are readily cleaved by halogens, these compounds are valuable precursors to *N*-halogenoamines and $(F_3C)_2N$ compounds.[424] $Hg\{N(SiMe_3)_2\}_2$ contains a linear N—Hg—N

Table 19 Structural Data of Mercury(II) Nitrogen Compounds: Amides

Compound	*Structure* (pm, °)	*Ref.*
$Hg(NHCOMe)_2$	Plane centrosymmetric molecules; Hg—N = 206(6); 2O atoms of neighbouring molecules with Hg—O = 288(6)	421
$Hg(NSF_2)_2$	Molecule with C_2 symmetry; Hg—N = 205.0(1.3); nearly linear N—Hg—N	434
$Hg\{N(CO)(SO_2)(C_6H_4)\}_2$ Mercury(II) saccharinate	Two crystallographically independent molecules with different geometries (1) Hg—N = 204 and 205; N—Hg—N = 167 (2) Hg—N = 203 and 206; N—Hg—N = 175	437
Dioxadiazadiphosphadimercuracyclododecane	$P2_1/c$, contains a twelve-membered ring with N—Hg—C bonds	438
$Hg\{N(CSCF_3)_4\}_2$	$C2/c$ discrete molecules with $\bar{1}$ symmetry, Hg—N = 201.7(5)	439
$Hg(NHCOPh)_2$	$C2/c$, Hg almost linearly bonded to two N [Hg—N = 206(3), 204(2), N—Hg—N 172(1)] and also equatorially to two O of adjacent molecules [Hg—O = 267(2), 283(3)]	440

system with trigonal planar nitrogen.[425] Mercury(II) amidosulfates, $\{M(O_3SN)\}Hg$ (M = Na, K, *etc.*), have been synthesized in alkaline solutions by dissolving $HgCl_2$ or HgO in the alkali metal amidosulfate;[426,427] they probably possess chain structures (**25**).



(**25**)

On heating under vacuum these compounds decompose into bis(amidobisulfato)mercurates, $M_4[\{(O_3S)_2N\}_2Hg]$[429] (M = Na, K, *etc.*), also obtained from $Hg(NO_3)_2$ and the metal imidosulfate, $HN(SO_3M)_2$.[428] Sulfamide, $SO_2(NH_2)_2$, sulfimide or hydroxylamidosulfuric acid reacts with mercury(II) acetamide or acetate in aqueous solutions to yield mixtures which should contain $(\text{—HN—SO}_2\text{HN—Hg—})_n$ units.[430] S_7NH and $S_4N_4H_4$ react with mercury(II) acetate to form $Hg(NS_7)_2$ and $Hg(NS)_2$ or $Hg_5(NS)_8$;[431,432] no structural data are available on these compounds. HgF_2 reacts with $OCFNSF_2$ to give $Hg(NSF_2)_2$,[433] which decomposes *in vacuo* to NSF and HgF_2. The structure of $Hg(NSF_2)_2$ contains nearly linear N—Hg—N bonds (Hg—N = 205 pm) and the very short N—S distance of 144 pm.[434] Mercury(II) bis(sulfinylamide) and mercury(II) fluorosulfurylisocyanate have been synthesized.[435,436] Mercury(II) saccharinate contains mercury bonded to two nitrogen atoms with Hg—N bond lengths 203–206 pm and N—Hg—N angles of 167° or 175°.[437] Mercury(II) bis (diphenylphosphinic-*N*-methylamide) contains N—Hg—N bonds.[438] The structure of bis[2,3,4,5-tetrakis(trifluoromethylthio)pyrrolyl]mercury(II), $Hg\{N(CSCF_3)_4\}_2$, contains Hg—N bonds of length 201.7(5) pm.[439] Bis(benzamido)mercury(II) also contains N—Hg—N bonds (Hg—N = 206 or 204 pm; N—Hg—N = 172°; Hg—O = 267 or 283 pm).[440] Imidazole and histidine form mercury(II) complexes with tri- and tetra-coordinated N atoms.[470,471]

56.2.4.6.2 Nitrogen ligands with tetracoordinated nitrogen atoms: amines

(*i*) *Ammonia addition and substitution compounds*

Millon's base, $(Hg_2N)(OH)\cdot 2H_2O$, originally obtained by Millon in 1845 by dissolving yellow HgO in an aqueous solution of ammonia, forms salts with different anions; the structure is anion dependent.[77,84] The basic building block of the salts of Millon's base and the base itself is a three-dimensional network of connected NHg_4 tetrahedra similar to the network in SiO_2. The anions or water molecules are situated in the holes of this $^3_\infty(NHg_{4/2})^+$ network.[90] Each mercury atom is coordinated to two nitrogen atoms and each nitrogen atom is bound to four mercury atoms. The Hg—N distances vary from 204 to 209 pm.[77,81,84,87,90] The substance formulated as $HgNH_2F$ is the fluoride of Millon's base with NH_4F in the holes of the framework, $(Hg_2N)F{\cdot}NH_4F$.[87] The iodide of Millon's base, Hg_2NI, is the basis for the detection of ammonia in drinking water by Nessler's method.[90] With weakly coördinating anions such as ClO_4^- the $(NHg_{4/2})$ network has a cubic structure; with halides the hexagonal form is more stable (see Figures 17 and 18).[90]

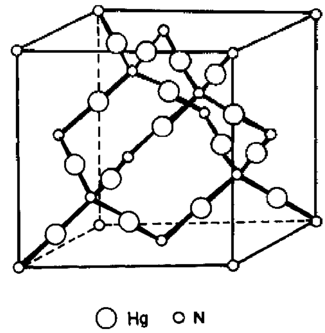


Figure 17 The cubic $(Hg_2N)^+$ network of Millon's base in $(Hg_2N)(OH){\cdot}2H_2O$

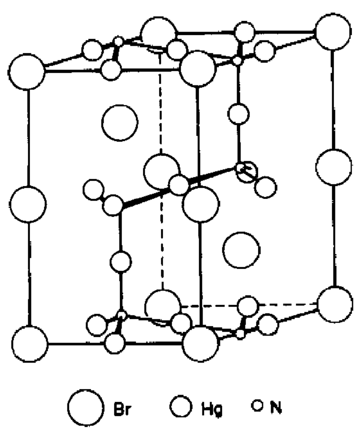


Figure 18 The hexagonal $(Hg_2N)^+$ network in the bromide of Millon's base $(Hg_2N)Br$

Millon's base and its salts are members of the $^{n-1}_{\infty}(NH_{4-n}Hg_{n/2})^+$ series. This allows the 'fusible white precipitates' $Hg(NH_3)_2X_2$ (X = Cl, Br) to be regarded as the first members of this series of mercury-substituted ammonium ions and not only as normal coordination complexes of two NH_3 to one Hg^{2+} ion.[90] The structure of the compounds $Hg(NH_3)_2X_2$ (X = Cl, Br) consists of linear $H_3\overset{+}{N}$—Hg—$\overset{+}{N}H_3$ groups inserted in a simple cubic lattice (see Figure 19). The compound $Hg(NH_3)_2Br_2$ forms mixed crystals with either NH_4Br or $HgNH_2Br$ in a cubic phase up to 55 mol % NH_4Br or up to 60 mol % $HgNH_2Br$.[83] These solid solutions demonstrate that the pure $HgNH_2Br$ contains infinite chains $(—\overset{+}{N}H_2—Hg—\overset{+}{N}H_2—Hg—)_n$ with no particular orientation (see Figure 20).[83,85] A rhombic form of $HgNH_2Br$ is stabilized by forming solid solutions with up to 5 mol % $HgBr_2$; this modification contains the infinite chains $(—Hg—\overset{+}{N}H_2—)_n$ in parallel orientation (see Figure 21).[79]

The cubic modification of $HgNH_2Br$ is disordered with regard to the positions of the mercury atoms; this means that the $(—Hg—\overset{+}{N}H_2—)_n$ chains are randomly orientated in the lattice. This cubic modification becomes ordered on being cooled to absolute zero, yet it shows no transition of any kind and does not change into the rhombic form with parallel orientation of the $(—Hg—\overset{+}{N}H_2—)_n$ chains. The entropies of the cubic and the rhombic forms are the same at 100 K; below this temperature the entropy of the cubic form is greater than that of the rhombic form.[441] There are $(H_3\overset{+}{N}—Hg—\overset{+}{N}H_3)$ groups, $(—Hg—\overset{+}{N}H_2—)_n$ chains and a three-dimensional network $(NHg_{4/2})_n$; the two-dimensional layer structure has been found in the compound Hg_2NHBr_2,[85] which contains three-mercurated ammonium ions and is better formulated as $^{2}_{\infty}\{Hg_3(\overset{+}{N}H)_2\}Br^-(HgBr_3^-)$.[86] The slightly puckered $^{2}_{\infty}\{(\overset{+}{N}H)Hg_{3/2}\}_n$ layers with Br^- ions in the

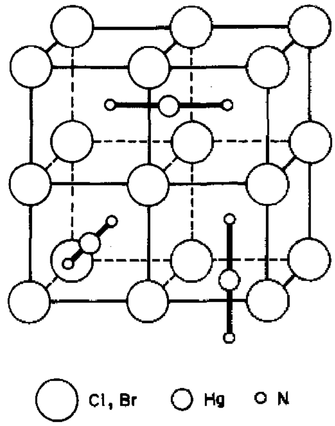


Figure 19 The elementary cell of the 'fusible white precipitate' $Hg(NH_3)_2Br_2$

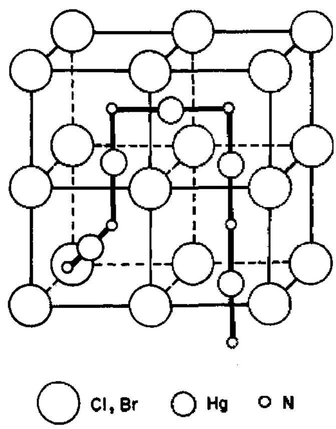


Figure 20 The elementary cell of the 'infusible white precipitate' $HgNH_2Br$, cubic modification

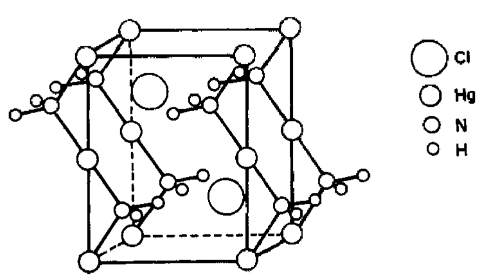


Figure 21 The elementary cell of the rhombic modification of $HgNH_2Br$

holes of the six-cornered layers and $HgBr_3^-$ ions between the layers have Hg—N distances of 213 pm; the Hg—Br distance in the $HgBr_3^-$ ions is 260 pm (see Figure 22). Structural data for some mercury(II) amines are summarized in Table 20.

(*ii*) *Hydrazine addition and substitution compounds*

Hydrazine forms 1:1 and 1:2 coordination compounds with HgX_2. The 1:1 adduct contains infinite chains $(\text{—Hg—}\overset{+}{N}H_2\text{—}\overset{+}{N}H_2\text{—})_n$, while the 1:2 adduct contains $(H_2N\overset{+}{N}H_2\text{—Hg—}\overset{+}{N}H_2NH_2)$ groups.[442] All Hg—N compounds have been examined by IR or Raman spectroscopy and due to the great difference in scattering power for X-rays between mercury and nitrogen atoms, much additional information on the constitution of these compounds has been obtained.[88] With hydrazine a coordination compound $Hg_2(N_2H_2)Cl_2$, which has a sheet structure, is obtained by substitution of H atoms by two bonding Hg atoms. This layer structure

Table 20 Structural Data of Mercury(II) Nitrogen Compounds: Amines

Compound	*Structure* (pm, °)	*Ref.*
$Hg(NH_3)_2Br_2$	Linear $H_3\overset{+}{N}$—Hg—$\overset{+}{N}H_3$ groups; Hg—N = 211	82, 83
$HgNH_2Br$(cubic modification)	(—Hg—NH_2—) chains; Hg—N = 217, Hg—N—Hg = 90	85, 83
$HgNH_2Br$(rhombic modification)	(—Hg—NH_2—) chains; Hg—N = 206, Hg—N—Hg = 109	78, 79
Hg_2NHBr_2	$\{Hg_3(\overset{+}{N}H)_2\}$ layers with Br^- in holes and trigonal $(HgBr_3)^-$ between the layers, Hg—N = 213	86
Hg_2NBr	Tridymite-type three-dimensional framework $(\overset{+}{N}Hg_{4/2})$ with Br^- in the holes, Hg—N = 206	84
$Hg_2N(OH)\cdot 2H_2O$	Cristobalite-type three-dimensional framework $(\overset{+}{N}Hg_{4/2})$ with $(OH)^-$ and H_2O in the holes, Hg—N = 204	77, 84
$Hg_2N_2H_2Cl_2$	$(Hg_2\overset{+}{N}_2H_2)$ layers with Cl^- between them, the mercurated $\overset{+}{N}H$—$\overset{+}{N}H$ group is in the *cis* configuration (no N—N frequency in IR)	443
$\{(PhCH_2NMe_2)_2Hg\}$	Hg—N = 289(1) Hg—C = 210(2) N—Hg—N = 180 C—Hg—C = 180	460
$\{Hg(bipy)(NO_3)\}^+(NO_3)^-$	Hg—N = 222.2(8) Hg—N = 231.3(10) Hg—O = 216.2(8) almost planar	461
$Hg(bipy)_2(NO_3)_2\cdot 2H_2O$	Hg—N = 229(4×) Hg—O = 272(3×) The N atoms of bipy form a flattened tetrahedron around the Hg; three nitrate O complete the coordination of mercury	462
$Hg(bipy)(CF_3CO_2)_2$	Hg—N = 230(2); 228(2) Hg—N = 224(2); 236(2) Hg—O = 223(1); 235(2) 278(3); 282(2) Hg—O = 221(1); 253(2) 258(2); 281(2); 282(2) The structure contains two independent Hg atoms each coordinated to one bipy ligand	463
Dichloronicotinemercury(II)	Hg—N = 239.7 (pyrrolidine) Hg—N = 245.4 (pyridine) Each nicotine molecule is bonded to two adjacent Hg atoms, one through the pyrrolidine and the other through the pyridine. The coordination around the Hg is completed by two Cl (Hg—Cl = 236.4; 238.4) to a highly distorted tetrahedron	464
Phenylmercury(II) dithizonate (yellow form)	Hg—C = 210; Hg—N = 266 Hg—S = 237; S—Hg—N = 73.6(4) S—Hg—C = 168.0(7) N—Hg—C = 118.4(8) The complex is virtually planar except for the Hg—phenyl ring which is twisted out of the plane by *ca.* 60°	468
Dichloro(9-methylhypoxanthine)mercury(II)	Hg—N = 229.9(7) Hg—Cl = 240.1(2); 235.3(3) N—Hg—Cl = 101.4(2); 118.0(2) Cl—Hg—Cl = 140.5(1) Distorted trigonal planar coordination around the Hg atom; two further Hg···Cl interactions which link the complex molecules together at distances 292.5(3) and 297.9(3); with an angle Cl—Hg—Cl = 165.8(1)	469
Tris(1,8-naphthyridine)(perchlorato)mercury(II) perchlorate; $\{Hg(N_2C_8H_6)_3(ClO_4)\}(ClO_4)$	Hg is irregularly seven-coordinated with the three asymmetrically bidentate ligands and one ClO_4 ion. Hg—N = 264(2); 230(2); 284(2); 214(2); 287(2); 220(2) Hg—O = 293.4(4) The thermal motion of the perchlorate is high, but there appears to be no disorder	488
Mercury(II) 8-mercaptoquinolinate; $Hg(C_9H_6NS)_2$	Hg is surrounded by 2N and 2S atoms; the distances are: Hg—S = 232 and 233; Hg—N = 250 and 236. N—Hg—N = 90; S—Hg—N = 80 and 81; S—Hg—S = 163	489

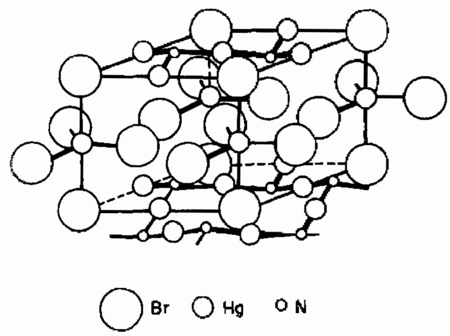


Figure 22 The structure of $NH(HgBr)_2$ consisting of $\{Hg_3(NH)_2\}_n$ layers, Br^- ions in the holes of the layers and $(HgBr_3)^-$ ions between the layers[86]

is derived from the chain structure of $HgNH_2Cl$ by connecting nitrogen atoms of the parallel chains (formal oxidation of mercurated NH_3 to mercurated N_2H_4) (Figures 23, 24 and 25).[443]

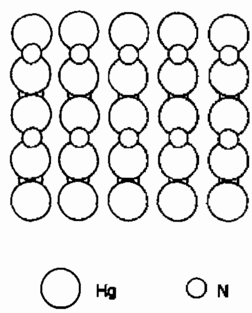


Figure 23 The $(\text{—}Hg\text{—}NH_2\text{—})_n$ chains in mercury(II) amidochloride, $HgNH_2Cl$

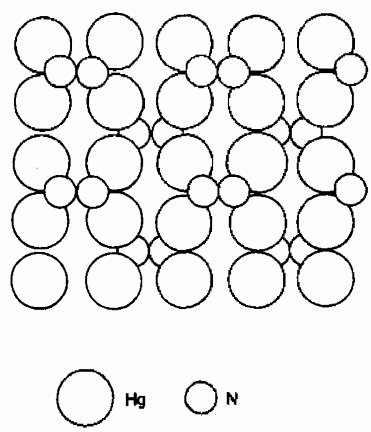


Figure 24 The $(\text{—}Hg_2N_2H_2\text{—})_n$ layers in mercury(II) hydrazinochloride, $Hg_2N_2H_2Cl_2$

(*iii*) *Other nitrogen donor ligands*

Nearly all nitrogen donor compounds form complexes of variable composition with mercury(II) compounds of all kinds. Since the literature of these coordination compounds of mercury(II) is listed up to May 1975 in McAuliffe's book,[7] only some new complexes will be mentioned here.

Amido mercury(II) sulfonic acid is an inner salt, $H_3\overset{+}{N}\text{—}Hg\text{—}SO_3^-$, but it is not clear if it is a mixture of $H_3\overset{+}{N}\text{—}Hg\text{—}\overset{+}{N}H_3$ with $^-O_3S\text{—}Hg\text{—}SO_3^-$ groups or only $H_3\overset{+}{N}\text{—}Hg\text{—}SO_3^-$.[444] The compound $(Me\text{—}Hg\text{—}\overset{+}{N}H_3)F^-$ has been obtained by the reaction of MeHgF and NH_3.[444] Organomercurioammonium complexes $^{n-1}_{\infty}\{NH_{4-n}(HgMe)_n\}^+$ and

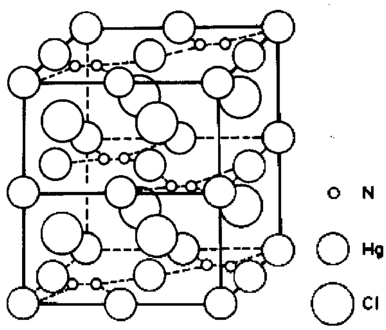


Figure 25 The elementary cell of mercury(II) hydrazinochloride, $Hg_2N_2H_2Cl_2$

$\{NH_{4-(m+n)}Me_m(HgMe)_n\}^+$ have also been obtained.[445,446,447] The compound $N(HgMe)_3$ has also been synthesized.[448,449]

In addition to the $Hg(NH_3)_2X_2$ compounds described in Section 56.2.4.6.2.i other coordination complexes with ammonia have been reported, namely $HgF_2{\cdot}nNH_3$ ($n = 2, 4, 5$), $HgCl_2{\cdot}nNH_3$ ($n = 3/2, 2, 4, 8, 9, 5, 12$), $HgBr_2{\cdot}nNH_3$ ($n = 2, 8$), $HgI_2{\cdot}nNH_3$ ($n = 4/3, 2, 6, 12$).[4] More information about the coordination compounds of mercury(II) oxo salts with ammonia or primary, secondary or tertiary amines or aromatic amines is obtainable in McAuliffe's book,[7] but a clear reinvestigation is desirable.

The complexes between mercury(II) salts and ethylenediamine (en) are well known. Results of IR and X-ray measurements show that the structure of $Hg(en)Cl_2$ contains infinite chains in the *trans* form $\{$—Hg—NH_2—$(CH_2)_2$—NH_2—$\}_n$.[450] Bis(en) complexes are known with HgX_2 (X = NO_3, ClO_4, I, SO_4).[451–453] The compound $(en)_2{\cdot}3HgI_2$ is built up of trigonal planar $HgI(en)^+$, HgI_3^- and tetrahedral $HgI_2(en)$.[554] $Hg(CN)_2{\cdot}$en and $Hg(SCN)_2{\cdot}$en contain mononuclear species with chelating en in the *cis* form.[454] Diethylenetriamine, $H_2NCH_2CH_2NHCH_2CH_2NH_2$, forms five-coordinated $HgLX_2$ (X = Cl, Br, I, CN) and six-coordinated octahedral HgL_2Y_2 (Y = ClO_4, SCN).[455] $Me_2NCH_2CH_2CH_2NH_2$ forms complexes of the composition $Hg_3L_2Cl_6$.[456] 1,2-Dimethylhydrazine forms a tetrahedral complex with $HgCl_2$.[457] Tetramethyl-2-tetrazine yields complexes $HgX_2{\cdot}L$ (X = Cl, Br).[458]

One of the many organomercurial compounds with 'secondary' chelating N—Hg—N bonds[459] is the bis[(dimethylamino)methyl]phenylmercury(II);[460] this compound contains linear C—Hg—C bonds (Hg—C = 210 pm) and also linear N—Hg—N bonds (Hg—N = 289 pm). Some recent crystal structure determinations have been made on 2,2′-bipyridylmercury(II) nitrate,[461] bis(2,2′-bipyridyl)mercury(II) nitrate dihydrate[462] and the 1:1 complex of $Hg(CF_3CO_2)_2$ with 2,2′-bipyridyl;[463] the Hg—N distances are between 222 and 236 pm. The X-ray structure of dichloronicotinemercury(II) has been solved; each ligand is bonded to two adjacent mercury atoms, one through the pyrrolidine nitrogen (Hg—N = 239.7 pm) and the other through the pyridine nitrogen (Hg—N = 245.4 pm), forming endless polymeric chains. The coordination around the Hg is completed by two Cl ligands (Hg—Cl = 236.4 and 238.4 pm), resulting in a highly distorted tetrahedral arrangement.[464] The crystal structure of the $HgCl_2$ complex with *racemo*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (tetb) has been reported.[465] The macrocyclic ligand (tetb) is fixed by two $HgCl_2$ molecules; the structural unit is a Cl-bridged species, (tetb)$Hg(\mu\text{-}Cl)_2HgCl_2$, which contains both six- and four-coordinated mercury atoms; the (tetb) ligand is folded so that the four nitrogen atoms occupy adjacent sites on a distorted octahedron; the configuration at each chiral center is 1*S*(*R*), 4*S*(*R*), 7*S*(*R*), 8*S*(*R*), 11*S*(*R*), 14*S*(*R*). The six-coordinated mercury atoms are bonded to two nitrogen atoms (Hg—N = 227.4 pm), two further nitrogen atoms (Hg—N = 244.0 pm) and two Cl atoms (Hg—Cl = 284.2 pm). The four-coordinated mercury atoms are bonded to two bridging Cl (Hg—Cl = 252.9 pm) and two terminal Cl (Hg—Cl = 242.1 pm).[465] The X-ray structure of dichloro(1,5-diphenylcarbazonato-*N*,*N*′)dimercury(II)[466] has been solved. π-Electron delocalization in the Ph—N—N—C—N—N—Ph chain, which was found in the structurally related dithizone molecule, does not occur, but a localized single bond for C(Ph)—N and a localized double bond for N—N were found. Each mercury atom, sandwiched between the planes of two benzene rings, forms an almost linear bond with one N and one Cl in a diagonal coordination.[466]

There are many studies of the analytical detection and quantitative determination of mercury based on reactions with N donors, *e.g.* the spectrophotometric determination of mercury(II) with 5,6-diphenyl-2,3-dihydro-1,2,4-triazine-3-thione.[467] This highly selective method for the determination of 0.05–0.55 mg Hg using the yellow 1:2 complex extracted into $CHCl_3$ at pH 10 is based on the measurement of absorbance at 430 nm, $\varepsilon = 8.1 \times 10^3\ M^{-1}$. The only interfering ions are CN^-, Tl^+ and Pd^{2+}. There might be some chelating Hg—S and Hg—N bonding in this case.[467] The yellow form of phenylmercury(II) dithizonate is a three-coordinated mercury(II) complex; solutions in organic solvents of the 1:1 complexes of organomercury(II) cations and dithizone undergo reversible photoisomerization (yellow ⇌ blue) at convenient rates. X-Ray structure determination also indicates a chelating effect in the yellow form (Hg—S = 237 pm; Hg—N = 266 pm; angles S—Hg—C = 168°, S—Hg—N = 73.6°, N—Hg—C = 118.4°).[468] A further three-coordinated mercury(II) complex is dichloro(9-methylhypoxanthine)mercury(II).[469] This structure is of interest concerning the well known binding of mercury(II) ions to nucleic acids. The Hg—N distance is 229.9(7) pm; the two Hg—Cl distances are 240.1(2) pm. The three angles centred on mercury are: N—Hg—Cl = 101.4(2)°, 118.0(2)° and Cl—Hg—Cl = 140.5(1)°. The coordination plane is twisted relative to that of the purine ring system; the angle between the two planes is 60°.[469] Adducts such as $L_2Hg(CN)_2$ (L = imidazole, substituted imidazoles, or 3,5-dimethylpyrazole), and (1-vinylimidazole)$_4Hg_3(CN)_6$ are obtained and characterized using IR and NMR data; the adducts are dissociated in acetone solutions.[471] It is evident that the reactivity of mercury(II) depends very much on the anion involved. As a consequence, any generalization should be looked at with caution, especially if it concerns the behaviour of mercury(II) in solution towards natural products containing nitrogen donors, *e.g.* nucleic acids or purines.

56.2.4.7 Phosphorus Ligands

$P(HgCl)_3$ is formed by reaction of PH_3 and $HgCl_2$.[473] The very unstable product $Hg\{P(CF_3)_2\}_2$ is obtained by reaction between $(CF_3)_2PH$ and divinylmercury(II).[474] Compared to $Hg\{P(CF_3)_2\}_2$, $Hg(PBu^t_2)_2$ is remarkably stable towards oxidation and thermal decomposition.[475] The system HgX_2–PMe_3 has been studied intensively. The mercury adducts with X = Cl, Br, I and CN react with $AgNO_3{\cdot}PMe_3$ to form $\{Hg(PMe_3)X\}NO_3$ or $\{Hg(PMe_3)_2\}^{2+}$ depending on the amount of $AgNO_3{\cdot}PMe_3$.[476] By reaction of HgX_2 and nPMe$_3$ various products have been isolated (equation 16) and characterized by their Raman, IR and ^{31}P NMR spectra.[477] The 1:1 complexes should be halide-bridged dimers, while $Hg(CN)_2{\cdot}PMe_3$ has an oligomeric structure.[477] Generally mercury(II) salts are known to form complexes with tertiary phosphines in the HgX_2:PR_3 ratios of 1:1, 1:2, 2:3, 2:4 and 3:2; numerous X-ray structures on such species are available (Table 21).

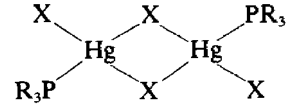
$$HgX_2 + nPMe_3 \longrightarrow HgX_2{\cdot}nPMe_3 \qquad (16)$$

$$X = Cl, Br, I; \quad n = 1, 2$$

$$X = CN; \quad n = 1, 2, 4$$

$$X = SCN; \quad n = 4$$

Tri(t-butyl)phosphine and tri(o-tolyl)phosphine form 1:1 complexes with mercury(II) halides and with $Hg(SCN)_2$. Physicochemical measurements, *i.e.* conductance, molecular weight determinations, IR and Raman spectra, indicate a dimeric structure (**26**) of C_{2h} skeletal symmetry.[493]



(**26**)

Besides structural determinations there have been a considerable number of ^{31}P NMR spectroscopic investigations. The dimeric complexes $Hg_2X_4(PBu_3)_2$ (X = Cl, Br, I) have been investigated by ^{199}Hg and ^{31}P NMR techniques.[500] The ^{199}Hg–^{31}P spin–spin coupling constants and the chemical shifts $\delta\ ^{31}$P were measured for 1:1 and 1:2 complexes of HgX_2 (X = Cl, Br, I, SCN and CN) with R_3P (R = Bu, n-octyl and EtO).[494] The ligand electronegativity has a stronger effect on the coupling constants and the chemical shifts than in the corresponding Pt^{II}

Table 21 Mercury(II) Compounds with P Donor Ligands

Compound	*Structure* (pm; °)	*Ref.*
$HgCl_2 \cdot PR_3$; R = Me, Et, Ph	R = Ph; discrete Cl-bridged dimers R = Et; chain-like arrangements of monomeric $Et_3P \cdot HgCl_2$ R = Me; ions $(Me_3P \cdot HgCl)^+Cl^-$	478, 483, 484
$HgCl_2$(tricyclohexylphosphine)	Two independent centrosymmetric dimers Hg_1: Hg—P = 241.6; Hg—Cl = 239.1; Hg—Cl = 264.1; 266.5; Hg_2: Hg—P = 241.2; Hg—Cl = 241.3; Hg—Cl = 260.2	479
$HgCl_2 \cdot (PEt_3)_2$	Monomeric complex	482
$(Me_2EtP)_3(HgCl_2)_2$	$\{Hg(Me_2EtP)_2Cl\}^+$ cation with linear P—Hg—P $\{Hg(Me_2EtP)Cl_3\}^-$ anion with tetrahedrally coordinated Hg^{II}	485, 490
$(Bu^n_3P)HgCl_2$	Alternating four- and five-coordinated Hg^{II}; tetrameric structure	490
$\{Hg(NO_3)_2L\}_2$ (L = trimesitylphosphine)	Six-coordinated Hg^{II} Hg_1: Hg—P = 239.5; Hg—O = 218.0, 241.9 Hg_2: Hg—P = 241.8; Hg—O = 225.7, 234.2 three additional weaker Hg—O bonds (258–290)	492
$HgCl_2 \cdot L$ (L = (*N,N*-diethylaminoethyl)-diphenylphosphine)	Tetrahedrally coordinated Hg^{II} Hg—Cl = 244.3, 244.5; Hg—P = 241.7; Hg—N = 264.1	504
$HgCl_2 \cdot L$ (L = Me_2PPMe_2)	Polymeric structure $(—Hg—P—P—Hg—P—P—Hg—)_n$	505
$HgClClO_4 \cdot P(o\text{-tolyl})_3$	Dimeric centrosymmetric molecules; four-coordinated Hg^{II} Hg—P = 239.5; Hg—Cl = 233.2; Hg—O = 273	510
$HgBr_2 \cdot$(*cis*-$Ph_2PCH{=}CHPPh_2$)	Distorted tetrahedrally coordinated Hg^{II} 2 × Hg—P = 257.5	481
$Hg(CN)_2 \cdot (Ph_2PCH_2CH_2PPh_2)$	Infinite chains $\{Hg(CN)_2(Ph_2PCH_2)_2\}_n$ Hg—P = 260.6, 253.4	480
$Hg(CN)_2 \cdot PPh_3$	Distorted tetrahedrally coordinated Hg^{II} Hg—P = 243.4; 258.9	481, 300
α-$Hg(SCN)_2 \cdot PPh_3$	Five-coordinated Hg^{II}; equatorial Hg—P = 246.1; Hg—S = 253.9, 246.9; axial Hg—N = 268.0, 280.0	486
β-$Hg(SCN)_2 \cdot PPh_3$	Hg_1: five-coordinated; equatorial: Hg—P = 242.9; Hg—S = 249.1, 251.9; axial: Hg—N = 271, 289 Hg_2: four-coordinated; Hg—S = 264.8, 245.4; Hg—N = 240; Hg—P = 243.2	487
$Hg(NO_3)_2(PPh_3)_2$	Distorted tetrahedrally coordinated Hg^{II} 2 × Hg—P = 245.1	481
$Hg(NO_3)_2 \cdot PPh_3$	Distorted tetrahedrally coordinated Hg^{II} Hg—O = 219.0, 242.8, 256.0; Hg—P = 235.9	491
$Hg(MeCO_2)_2 \cdot P(Me_3C)_3$	Distorted trigonal bipyramidal coordination of Hg^{II}, five-coordinated Hg—P = 237.1; Hg—O = 225, 227, 266, 258	508
$Hg(MeCO_2)_2 \cdot L$ (L = tricyclohexylphosphine)	Dimeric molecules, three nearly coplanar bonds Hg—P = 237.8; Hg—O = 219.4, 229.2	509
$Hg(MeCO_2)_2 \cdot L$ (L = tri-*o*-tolylphosphine)	Hg—P = 241; Hg—O = 236, 220 six-fold coordination by weak bonds Hg—O = 252–292	

complexes.[494] A range of mercury(II) ethanoates, $\{Hg(PPh_3)_n(O_2CR)_2\}$ (n = 1, 2, 3; R = Me, CH_2F, CHF_2, CF_3), has been studied.[495] The 1:1 and 2:1 complexes are monomeric species in which the carboxylate groups are bidentate. The ^{199}Hg–^{31}P coupling constants and the ^{31}P chemical shifts for these complexes increase in the order $O_2CMe < O_2CCH_2F < O_2CCHF_2 < O_2CCF_3$. Possible correlations with the pK_a values of the carboxylic acids are discussed.[495] An increase in the ^{31}P–^{199}Hg coupling constants for the complexes $\{HgL_2(ClO_4)_2\}$ (L = tertiary phosphine) is observed with decreasing basicity of the phosphine.[496] Variable temperature ^{31}P NMR spectral data have been used to investigate ligand exchange rates in a wide range of arylphosphine complexes. The previously described compound $\{Hg(NO_3)_2(PR_3)\}$ (R = 2,4,6-trimethylphenyl) is of interest as it exhibits the largest ^{199}Hg–^{31}P coupling constant yet observed ($\delta(^{31}P)$ = 1.81 p.p.m.; $J(^{199}Hg$–$^{31}P)$ = 10 278 Hz).[499]

The ^{199}Hg NMR technique has been used for the interpretation of solution equilibria.[501–503] Mercury(II) perchlorate reacts with a variety of tertiary phosphines in EtOH to form four-coordinated complexes $HgL_3(OClO_3)(ClO_4)$ (L = Ph_3P, $(p\text{-}MeC_6H_4)_3P$).[506] Conductance measurements and IR spectra suggest that one of the perchlorate groups is coordinated to the metal in these complexes.[506] Thermodynamics of the complex formation in DMSO between Hg^{II} and ligands coordinating *via* nitrogen, phosphorus, arsenic, antimony or bismuth have been studied by Ahrland *et al.*[507] The measurements are feasible only if X = N, P or As, as the ligands Ph_3Sb and Ph_3Bi are rapidly oxidized. For the systems measured the stabilities follow the sequence $N \ll P > As$.[507] Several structural studies of steric effects in phosphine complexes have been performed.[508–510] Ligand profiles for $(Me_3C)_3P$ and (*o*-tolyl)$_3$P have been given and the maximum cone angles are 187° and 198° respectively.[508,510] Anionic phosphito-*P*-mercury(II) complexes $[Hg\{P(O)(OEt)_2\}_n]^{(n-2)-}$ ($n = 3, 4$) have been formed from HgL_2 and NaL ($HL = HP(O)(OEt)_2$; equation 17) and characterized by ^{31}P and ^{199}Hg NMR spectroscopy.[511]

$$HgL_2 + n\,NaL \rightleftharpoons Na_n[HgL_{(n+2)}] \qquad (17)$$
$$n = 1, 2$$

The Hg atom in bis(dimethylphosphonate)mercury(II) forms strong bonds with two P atoms (Hg—P = 241 pm; P—Hg—P = 165.9°).[512] Two phosphoryl O atoms from neighbouring molecules interact weakly with the mercury atoms ($Hg \cdots O = 254$ pm) to give a very distorted tetrahedral coordination around Hg.[512] The reaction of *O*-butylphenylphosphonite, $Ph(Bu^nO)P(H)O$, with either HgO or mercury(II) acetate results in the formation of $\{Ph(Bu^nO)P(O)\}_2Hg$; multinuclear NMR studies on this and related complexes have been reported.[513] The mercury(II) halophosphides Hg_2P_3Cl and Hg_2P_3Br have been prepared.[514] Hg_2P_3Cl has the monoclinic Cd_2P_3Cl structure while Hg_2P_3Br has a related orthorhombic structure. Both are black semiconductors and stable in HCl and HNO_3.

56.2.4.8 Arsenic and Antimony Ligands

Although monodentate tertiary phosphines form mercury(II) complexes in several ratios, much less work has been reported with tertiary arsines; only a few stibine complexes are known. Mercury(II) halides HgX_2 (X = Cl, Br, I) react with trimethylarsine to yield $\{Hg(AsMe_3)X\}^+$ and $\{Hg(AsMe_3)_2\}^{2+}$.[473] The analogous reaction with $SbMe_3$ produces only metallic mercury, but methyldiphenylstibine reacts with the mercury(II) halides in methanol or acetone solution to form the 1:1 complexes $\{Hg(SbMePh_2)X_2\}_2$ (X = Cl, Br, I); these complexes are dimers with halogen-bridged structures.[532] Alkylarsine complexes are generally 1:1 or 2:1; they are expected to have structures analogous to the corresponding phosphine compounds. The ligands that have been studied are listed in Table 22. Only a few X-ray structures are available; some results are listed in Table 23.

Table 22 Arsines Suitable for Complex Formation with HgA_2[a]

Ligand	*Ref.*
$AsMe_3$	473
$AsEt_3$	515, 516, 517
$AsPr_3$	515
$AsBu_3$	515, 518
$AsPh_3$	478, 506
$AsPh_2Pr$	506, 519
$AsPh_2Me$	506
$AsPh_2Et$	506
$AsMe_2(p\text{-}Me_2NC_6H_4)$	520
$AsPhMe_2$	519, 521
$As(p\text{-}MeOC_6H_4)_3$	551
$MeC(CH_2AsPh_2)_3$	551
$Ph_2As(CH_2)_nAsPh_2$ (n = 1, 2, 3)	551
As(mesityl)$_3$	552

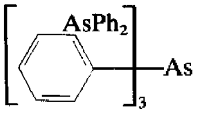
[a] A = halide, pseudohalide, NO_3, ClO_4.

A number of 1:1 complexes of $HgCl_2$ with 1-naphthylarsines have been described.[524] Complexes of mercury(II) bromide with some diarylalkylarsines have been prepared by treating $R_2R'As$ with $HgBr_2$ in Et_2O (R = $MeOC_6H_4$, *p*-EtC_6H_4, α-naphthyl; R' = alkyl, $PhCH_2$); their IR spectra have been discussed.[525] Mercury(II) perchlorate reacts with a variety of tertiary arsines in EtOH to form four- and three-coordinated complexes of the types $HgL_3(OClO_3)(ClO_4)$ (L = Ph_2MeAs, Ph_2EtAs, Ph_2PrAs) and $HgL_2(OClO_3)(ClO_4)$ (L =

Table 23 Some Compounds Containing As or Sb Donor Ligands

Compound	*Structure* (pm; °)	*Ref.*
$Ph_3As·HgCl_2$	Discrete Cl-bridged dimers, isostructural with $Ph_3P·HgCl_2$	478
$HgBr_2·L·CH_2Cl_2$ (L = tris(*o*-diphenylarsinophenyl)arsine)	Tetrahedrally coordinated Hg^{II} Hg—As = 260, 282 Hg—Br = 255, 262	528
$Ph_3As·Hg(SCN)_2$	Planar trigonally coordinated Hg^{II} Hg—As = 260 Hg—S = 253, 255	522
$Ph_3Sb·Hg(SCN)_2$	*Trans* dimeric structure	523
$MePh_2Sb·HgX_2$ (X = Cl, Br, I)	Halogen-bridged dimers	532
$\{HgAs(mesityl)_3(NO_3)_2\}_2$	Discrete centrosymmetric dimers of dinitrato(trimesitylarsine) mercury(II) Hg—As = 247.6(3); 248.2(3) Hg—O = 241(2), 220(2); 228(2), 239(2)	552

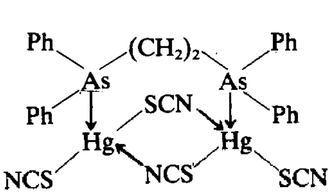
(dinaphthyl)MeAs, (dinaphthyl)EtAs, (cyclohexyl)$_3$As) with one perchlorate ion, which is directed to the metal.[506] The IR spectra of the *o*-phenylenebis(dimethylarsine) complexes $HgL_2(ClO_4)_2$ and $HgLX_2$ (X = Cl, Br) have been recorded by Deacon *et al.*[526] Assignments of the observed frequencies, including those for the metal–halogen stretching frequencies, are proposed and discussed in relation to the structures of the complexes. An X-ray structural analysis of $\{(C_6F_5)_2Hg\}_2Ph_2AsCH_2AsPh_2$ revealed approximately planar coordinated mercury.[527] The Hg—As distance of 340 pm is only slightly less than the sum of the van der Waals radii of 350 pm. Tris(*o*-diphenylarsinophenyl)arsine (**27**) forms complexes of the types HgX_2(chelate) and Hg(chelate)$(ClO_4)_2$.[528] In the former compounds (X = halide) only two of the donor atoms of the quadridentate ligand are bonded to the central mercury atom, which is tetrahedrally coordinated.



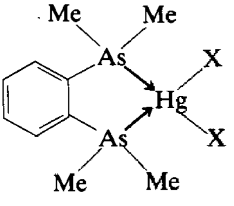
(**27**)

In $HgBr_2$(chelate)$·CH_2Cl_2$ mercury is coordinated to two terminal arsenic atoms at 260 and 282 pm and to two bromine atoms which are at distances of 255 and 262 pm, respectively. *o*-Phenylenebis(dimethylarsine) forms HgL_2X_2 (X = halide) with tetrahedrally coordinated mercury(II) in the solid state, but shows some evidence of isomerism in solution (equation 18).[526,530,531] The resulting cation $(HgL_2)^{2+}$ is present in the corresponding diperchlorate complex.[530,531] Jain has studied complexes containing mercury(II) pseudohalides HgX_2 (X = SCN, CN) and polydentate ligands bis(1,2-diphenylarsino)ethane (bdpae) (**28**) and *o*-phenylenebis(dimethylarsine) (diars; see **29** and **30**) by recording their IR spectra in the region 4000–200 cm^{-1}.[523]

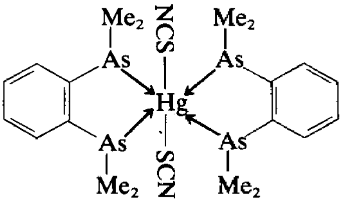
$$2HgLX_2 \rightleftharpoons (HgL_2)^{2+} + (HgX_4)^{2-} \qquad (18)$$



(**28**)



(**29**) X = CN, Cl



(**30**)

Tri(*o*-tolyl)stibine reacts with mercury(II) halides in cold benzene solution to form 1:1 complexes.[529] Under reflux the stibine is chlorinated to R_3SbCl_2 by $HgCl_2$, which is reduced to Hg_2Cl_2. In refluxing THF the products are RHgCl and R_2SbCl.[529] Triarylbismuthines

R_3Bi (R = Ph, *o*-tolyl, *p*-tolyl) are chlorinated to R_2BiCl by $HgCl_2$.[529] The complex ($HgI_2 \cdot Ph_2SbCH_2SbPh_2$) is an insoluble yellow solid, which probably has a polymeric structure.[533]

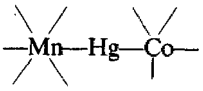
56.2.4.9 Metal Ligands

56.2.4.9.1 Group IIIb and IVb compounds

Mercury(II) forms a lot of compounds containing Hg—Si, Hg—Ge or Hg—Sn bonds. Suitable synthetic routes include the reactions of the appropriate R_3EH with R'_2Hg and of R_3EX with sodium amalgam (R, R′ = alkyl or aryl; X = Cl, Br; E = Si, Ge).[534–536] By reaction of Bu^t_2Hg and R_3SnH the compound $(R_3Sn)_2Hg$ (R = Me, Et, Pr^n) is formed below −10 °C. Decaborane(14), $B_{10}H_{14}$, reacts with $HgCl_2$ in diethyl ether to form $(B_{10}H_{14-n})(HgCl)_n$ (n = 7, 8), but in THF or with $HgBr_2$ reduction to dimercury(I) occurs.[538] The complex $(Me_4N)_2Hg(B_{10}H_{12})_2$ has been prepared from $HgCl_2$ and $(Me_4N)(B_{10}H_{13})$ in THF with an ^{11}B NMR spectrum similar to the zinc analogue.[539]

56.2.4.9.2 Transition metals

Mercury(II) forms a series of compounds in which it is bonded to a transition metal to form heteronuclear Hg—M bonds.[540,541] The most widely used synthetic routes have been reviewed elsewhere.[542–549] Besides heteronuclear bonds M—Hg there are structural elements M—Hg—M′,[550] *e.g.* (**31**), or cyclic arrangements as in $\{Os_3(CO)_{11}Hg\}_3$[415] or $\{(\eta^5\text{-}MeC_5H_4)Mn(CO)_2Hg\}_4$.[416] A trigonal prismatic coordination of mercury has been reported in the green zerovalent mixed metal cluster $[Hg\{Pt(2,6\text{-}Me_2C_6H_3NC)_6\}]$.[416a]



(**31**)

56.2.5 APPENDIX

56.2.5.1 Mercury(I) Compounds and Compounds with Mercury Oxidation Numbers Lower than +1

Recently a review on extended linear chain compounds, including the species $Hg_{3-\delta}AsF_6$ and $Hg_{3-\delta}SbF_6$, has appeared.[556] Two more members of this series, $Hg_{3-\delta}NbF_6$ and $Hg_{3-\delta}TaF_6$ have been prepared and their structures are reported.[557] Both compounds are isostructural with $Hg_{3-\delta}AsF_6$ and consist of chains of metallically bonded Hg atoms in an incommensurate MF_6^- host lattice.[557] The new compounds Hg_3MF_6 (M = Nb, Ta) are trigonal and can be obtained from $Hg_{3-\delta}MF_6$. They consist of hexagonal sheets of Hg atoms, which are separated by sheets of MF_6^- ions.[558] Mercury atoms in similar sheets can be found in the graphite intercalate $KHgC_4$.[559] Although the Hg—Hg distances are similar in both the intercalate and Hg_3NbF_6 (285 and 290 pm respectively), the sheets differ in that in the Nb compound each Hg has six nearest Hg neighbours and a formal charge of $1/3^+$, while in the intercalate each Hg has only three Hg neighbours and a formal charge of 0.

The mercury cations Hg^{2+}, Hg_2^{2+}, Hg_3^{2+} and Hg_4^{2+} have been studied by ^{199}Hg NMR spectroscopy.[560] For Hg_3^{2+} the largest nuclear spin–spin coupling constant reported to date was observed.

56.2.5.1.1 Oxygen ligands

The structure of $Hg_2(NO_2)_2$ has been determined. There are discrete centrosymmetric planar $Hg_2(NO_2)_2$ units with Hg—Hg = 251.6(2) pm. The NO_2 ligand is monodentate through an oxygen atom with Hg—O = 224(2) pm.[561]

The crystal structure of $Hg_{10}(OH)_4(NO_3)_6$ contains finite cationic chains $[(Hg_2)_5(OH)_4(NO_3)_6]^{4+}$.[562] These chains are joined together by weak van der Waals interactions between neighbouring Hg and O atoms forming ribbons running along the crystallographic *a* axis. The basic dimercury(I) nitrate contains linear infinite chains $^1_\infty[Hg_2OH(Hg_2)_{2/2}]^{3+}$. These are interconnected to a three-dimensional framework by nitrate ions coordinated to mercury (Hg—Hg = 249.9(3), 250.5(3) 2×).[563]

In the crystal structure of the mixed valent compound $Hg_4O_2(NO_3)_2$ there is a two-dimensional framework $^2_\infty[(Hg^{II})_{2/2}O(Hg_2^I)_{1/2}]^+$.[564] A three dimensional structure is obtained by additional weak Hg—O contacts *via* NO_3^- anions. A novel mercury(I, II) compound has been reported.[565]

The structure of Hg_2OI is built up of layers with bond distances Hg^I—Hg^I = 253.4, Hg—O = 213–216 and Hg—I = 305–314 pm. The layers are connected by Hg—O bonds (247 pm) to form a three-dimensional structure.[565]

The compound $K_5Cs_5[(Hg_2)_2WO(H_2O)(AsW_9O_{33})_2]$ has been synthesized and its crystal structure determined. There are dinuclear Hg_2^{2+} cations, each coordinated to four oxygen atoms and inserted between two AsW_9 groups (Hg—Hg = 244.6(6), 245.0(5), 252.1(6), 254.5(6) pm).[566]

56.2.5.2 Mercury(II) Coordination Compounds

56.2.5.2.1 General

Recently Constable's annual review of mercury coordination chemistry appeared, covering 187 references.[567]

56.2.5.2.2 Halide ligands

The compounds $(EtNH_3)_2HgCl_4$ and $(PrNH_3)_2HgCl_4$ form ferroelastic perovskite layers.[568] With thermal and dielectric measurements several phase transitions were detected in the ferroelastic region at about 200 K. The compounds $(MeNH_3)HgX_3$ (X = Br, I) can be obtained from stoichiometric mixtures of the methylammonium halogenides and the mercury(II) halogenides in methanol.[569] For X = Br the environment of Hg^{2+} is trigonal bipyramidal with Hg—Br = 252.7(2)–256.5(2) (equatorial) and 319.2(2) pm (axial). The bipyramids from double chains with $MeNH_3^+$ cations between them. The structure of $MeNH_3HgI_3$ consists of chains of corner-sharing distorted tetrahedra (Hg—I = 270.8(3) and 277.7(3) pm).[569] Crystals of $MeNH_3HgCl_3$ belong to the trigonal system (space group $P\,3_2$) exhibiting two phase transitions at 215 and 330 K. A three-dimensional ferroelectric character has been supposed on the basis of a low value of spontaneous polarization.[570]

For the coordination compounds $(LH)_2HgCl_4$ and $(LH_2)HgCl_4$ (LH = *N*-ethylmorpholinium cation, LH_2 = *N*-ammoniumethylmorpholinium dication) the crystal structures were determined. Both compounds are composed of discrete monomeric $[HgCl_4]^{2-}$ units with Hg—Cl distances ranging from 239.5(3) to 256.2(3) pm.[571]

The crystal structure of $HgCl_2\{P(2\text{-thienyl})_3\}_2$ has been determined. The complex is found to be a distorted tetrahedral monomer with Hg—Cl = 253.9(2) and 251.9(2), Hg—P = 247.2(2) and 251.3(2) pm.[572] The geometry about mercury has been compared with that found in $HgCl_2(PR_3)_2$ (R = Et or Ph).

In the crystal structure of the complex salt $Na[Hg_4(\mu\text{-}Cl)_4\{P(O)(OEt)_2\}_8]\cdot 6H_2O$ there are also contacts Hg—Cl and Hg—P. The molecular structure consists of discrete eight-membered $(Hg—Cl)_4$ rings with Hg positioned at the corners (Hg—Cl (mean) = 285.3 pm). Two $P(O)(OEt)_2$ ligands are coordinated to each mercury atom (Hg—P (mean) = 240.2 pm).[573]

The complex $[HgBr_2\{P(CH_2CH_2CN)_3\}_2]\cdot Me_2CO$ is found to be monomeric, while in $[HgCl_2\{P(CH_2CH_2CN)_3\}]_n$ there is a polymeric structure in which almost linear Cl—Hg—$P(CH_2CH_2CN)_3$ units are linked by chlorine atoms to give single chains.[574] The geometry about mercury in the two complexes indicates tris(2-cyanoethyl)phosphine to be a strong σ donor and comparable with triethylphosphine in its interactions with mercury(II) halides. In the crystal structure of tris(chloromercurio)acetic acid dimethyl sulfoxide solvate, $(ClHg)_3CCO_2H\cdot DMSO$, the mean value for Hg—Cl is observed at 233 pm.[575]

Chloro-bridged dimeric $Hg_2Cl_6^{2-}$ anions are found in $(TePh_3)_2[Hg_2Cl_6]$.[576] They consist of two distorted $HgCl_4$ tetrahedra sharing an edge, with Hg—Cl = 268.4(2), 271.7(2) (bridging) and 235.0(2) (terminal).

$HgCl_2$ forms a 1:1 complex with 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) with hexagonal bipyramidal coordinated mercury.[577] The chlorine atoms are strongly coordinated in the axial positions and the 18-crown-6 in the equatorial position (Hg—Cl = 231.4(1), Hg—O = 282.5(4) pm).[577]

The coordination compounds $HgCl_2{\cdot}K_2Cr_2O_7$ and $HgCl_2{\cdot}(NH_4)_2Cr_2O_7$ comprise Cr_2O_7 groups which show no unusual features. In the ammonium salt, finite centrosymmetrical $Hg_2Cl_4O_8$ groups are present while infinite $HgCl_2O_2$ chains exist in the potassium salt.[578] The centrosymmetric anion $[Hg_2I_6]^{2-}$ is present in $(PPh_4)[HgI_3]$. In the anion two iodines bridge two HgI_2 units, and the coordination about mercury is approximately tetrahedral (Hg—I (terminal) = 270.7(1), 269.0(1); Hg—I (bridge) = 286.4(1) and 296.2(1) pm).[579]

Cs_2HgBr_4 is representative of the β-K_2SO_4-type structure exhibiting several phase sequences upon cooling.[580] The phase transformations are explained by a rotation wave through the $HgBr_4$ tetrahedron.

56.2.5.2.3 Sulfur ligands

The compound $(NBu^n_4)[Hg(SPh)_3]$ consists of a rare example of trigonal-planar-coordinated Hg; there are no weaker, intermolecular Hg···S axial interactions (Hg—S = 240.7(3), 243.1(3) and 250.7(3) pm).[581]

56.2.5.2.4 Nitrogen and phosphorus ligands

The crystal and molecular structures of $HgN_2S{\cdot}NH_3$ and $2Hg(NH_3)_2I_2{\cdot}S_4N_4$ have been reported.[582] In the former compound two Hg atoms are bridged to form eight-membered rings $[Hg(N{=}S{=}N)]_2$. In addition, each Hg is coordinated by an NH_3 molecule and by an N atom of an adjacent ring (Hg—N = 209.8(24) (2×) and 247.2(22) pm). $2Hg(NH_3)_2I_2{\cdot}S_4N_4$ is an inclusion compound with S_4N_4 molecules in the holes of the lattice of the large $Hg(NH_3)_2I_2$ tetrahedra (Hg—N = 230 pm).

The cationic eight-membered metallacyclic compound $[Hg_2(\mu\text{-dppm})_2(DMSO)_4]^{4+}$ $(CF_3SO_3^-)_4$ has been prepared in high yield and characterized using ^{31}P and ^{199}Hg NMR spectroscopy. For the first time a metal–metal spin–spin coupling in $[M_2(\mu\text{-dppm})_2]$ rings without a formal metal–metal bond is reported ($J(^{199}Hg–^{199}Hg)$ = 699–1061 Hz depending on the solvent).[583]

The bidentate ligands $L = Ph_2P(CH_2)_nPPh_2$, $n = 1, 2$ (dppm and dppe) form stable and isolable complexes of stoichiometry $[HgL_2](O_3SCF_3)_2$ using mercury(II) trifluoromethanesulfonate.[584] The ^{199}Hg NMR spectra of the $[HgL_2]^{2+}$ complexes consist of 1:4:6:4:1 quintets, indicating four equivalent phosphorus atoms to be coordinated to mercury. The first structurally characterized homoleptic phosphine complex of Hg^{II} is present in $[Hg(PMe_2Ph)_4][Ta_2Cl_{10}O]$.[585] There are $[Hg(PMe_2Ph)_4]^{2+}$ units with Hg—P (average) = 253.7 and P—Hg—P = 102.4–111.9°. ^{31}P and ^{199}Hg NMR measurements have been widely used to study phosphine complexes of Hg^{II} in solution. Data are reported for a series of mercury(II) complexes $HgX_2\{P(cyclohexyl)_3\}(PBu_3)$ (X = ClO_4, O_3SCF_3, NO_3, CF_3CO_2, $MeCO_2$, Cl, Br, I, SCN, CN) in dichloromethane solution.[586] The two-bond coupling $^2J(P'–P)$ of these asymmetric complexes decreases with increasing coordination ability of the anion and range between 198 and 85 Hz. Data are also presented for $Hg(O_3SCF_3)_2\{P(cyclohexyl)_3\}_2$ and $Hg(O_3SCF_3)_2(PBu_3)_n$ (n = 2, 3, 4) which imply that the perchlorate anion may be more strongly involved in coordination to mercury, in solution, than the $CF_3SO_3^-$ anion.[586]

56.2.5.2.5 Metal ligands

The compound $Hg_9As_4Bi_2Br_{12}$ is obtained by solid state reaction. The structure consists of a polymeric cationic framework $^3_\infty[Hg_7(HgBr)_2As_4^{4+}]$ (Figure 26) formed by chains of Hg_4As tetrahedra, which are connected by mercury atoms.[587] At several positions this connection is truncated by terminal HgBr groups (Hg—As = 242.8–253.0 pm).

Recently the cluster anion $[Hg_4Te_{12}]^{4-}$ and the polymer $[Hg_2Te_5]^{2-}$ have been prepared and

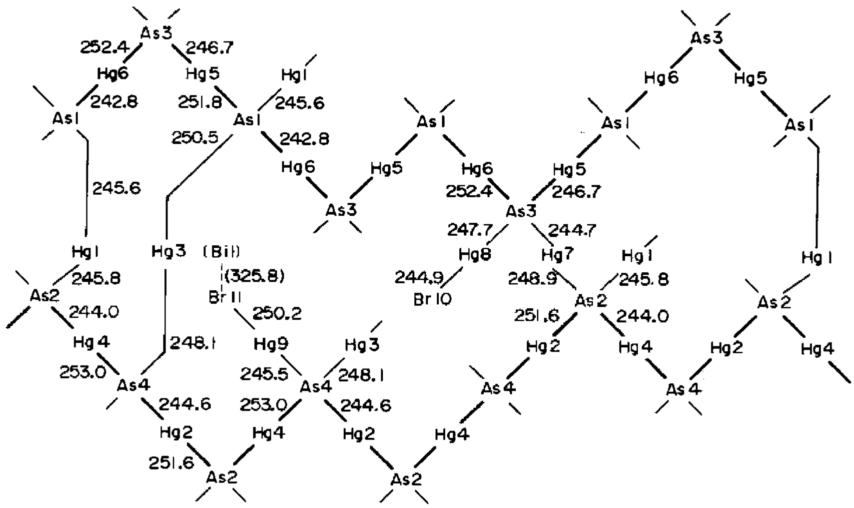


Figure 26 Structure of $Hg_9As_4Bi_2Br_{12}$

characterized by X-ray structural analysis.[588] The cluster anion contains tetrahedrally coordinated Hg^{II} with Hg—Te = 270.6–298.3 pm. The anion in $(Ph_4P)_2[Hg_2Te_5]$ consists of $^1_\infty[Hg_2Te_5]^{2-}$ chains. In the crystal structure of $[Rh_2HgCl(\mu\text{-}H)(CO)_2\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]$ the rhodium and mercury atoms adopt a triangular structure with the rhodium–rhodium and rhodium–mercury distances corresponding to those normally found with formal Rh—Rh and Rh—Hg bonds (Rh—Rh = 276.2(1), Rh—Hg = 271.1(1) and 277.8(1) pm).[589]

In $[Ru_3(NO)(CO)_{10}]_2Hg$ the mercury atom links two Ru_3 triangular units by bridging an Ru—Ru edge of each unit (Hg—Ru = 286.8(1) and 285.5(1) pm).[590] An unusual asymmetric Rh—Hg—Rh bridge contains the crystal structure of $[Rh_2Cl_3(\mu\text{-}HgCl)(CO)_2(\mu\text{-dppm})_2]$, in which only one Rh is oxidized by insertion into an Hg—Cl bond.[591] The corresponding Pt—Hg—Pt chain in $[(PPh_3)_2(2,4,6\text{-}C_6H_2Cl_3)Pt]_2Hg$ is a more symmetric one with Pt—Hg—Pt = 169.57(4)° and Pt—Hg bonds (263.7 pm) which are the longest so far described.[592]

The compound $[(CF_3)_3GePt(PPh_3)_2]_2Hg$ contains a Ge—Pt—Hg—Pt—Ge chain of C_2 symmetry with bond lengths Pt—Hg = 263.0(2) and 266.5(2) pm.[593]

56.2.6 REFERENCES

1. D. Grdenić, *Q. Rev.*, 1965, **19**, 303.
2. A. J. Canty and G. B. Deacon, *Inorg. Chim. Acta*, 1980, **45**, L225.
3. J. A. Tossell and D. J. Vaughan, *Inorg. Chem.*, 1981, **20**, 3333.
4. 'Gmelin's Handbuch der Anorganischen Chemie', 8th edn., part B, Mercury, Nos. 1–4, Verlag Chemie, Weinheim, 1965–1969.
5. E. C. Constable, *Coord. Chem. Rev.*, 1982, **45**, 367; 1983, **52**, 53; 1984, **58**, 53.
6. P. O'Brien, *Annu. Rep. Prog. Chem., Sect. A, Phys. Inorg. Chem.*, 1982, **79**, 357; 1983; **80**, 300; 1984, **81**, 321; 1985, **82**, 343.
7. W. Levason and C. A. McAuliffe, in 'The Chemistry of Mercury', ed. C. A. McAuliffe, Macmillan, London, 1977.
8. P. A. W. Dean, *Prog. Inorg. Chem.*, 1978, **24**, 109.
9. K. Brodersen, *Comments Inorg. Chem.*, 1981, **1**, 207.
10. D. Grdenić, in 'Structural Studies of Molecular Biological Interest', ed. G. Dodson, J. P. Glusker and D. Sayre, Clarendon Press, Oxford, 1981, p. 207.
11. R. L. Deming, A. L. Allred, A. R. Dahl, A. W. Herlinger and M. O. Kestner, *J. Am. Chem. Soc.*, 1976, **98**, 4132.
12. 'Stability Constants of Metal Ion Complexes', Chemical Society Publication No. 17, The Chemical Society, London, 1964.
13. G. C. Davies, P. A. W. Dean, R. J. Gillespie and P. K. Ummat, *Chem. Commun.*, 1971, 782.
14. R. D. Ellison, H. A. Levy and K. W. Fung, *Inorg. Chem.*, 1972, **11**, 833.
15. B. D. Cutforth, C. G. Davies, P. A. W. Dean, R. J. Gillespie, P. R. Ireland and P. K. Ummat, *Inorg. Chem.*, 1973, **12**, 1343.
16. B. D. Cutforth, R. J. Gillespie and P. R. Ireland, *J. Chem. Soc., Chem. Commun.*, 1973, 723.
17. R. J. Gillespie and P. K. Ummat, *Chem. Commun.*, 1971, 1168.
18. I. D. Brown, B. D. Cutforth, C. G. Davies, R. J. Gillespie, P. R. Ireland and J. E. Vekris, *Can. J. Chem.*, 1974, **52**, 791.

19. Z. Tun and I. D. Brown, *Acta Crystallogr., Sect. B,* 1982, **38,** 2321.
20. N. D. Miro, A. G. MacDiarmid, A. J. Heeger, A. F. Garito, C. K. Chiang, A. J. Schultz and J. M. Williams, *J. Inorg. Nucl. Chem.*, 1978, **40,** 1351.
21. B. D. Cutforth, R. J. Gillespie, P. Ireland, J. F. Sawyer and P. K. Ummat, *Inorg. Chem.*, 1983, **22,** 1344.
22. A. J. Heeger and A. G. MacDiarmid, NATO Conf. Ser., (Ser.) 6, 1978 (pub. 1979), 1 (MolMet.), 419.
23. B. D. Cutforth and R. J. Gillespie, *Inorg. Synth.*, 1979, **19,** 22.
24. A. J. Heeger and A. G. MacDiarmid, *Ann. N.Y. Acad. Sci.*, 1978, **313,** 800.
25. A. J. Schultz, J. M. Williams, N. D. Miro, A. G. MacDiarmid and A. J. Heeger, *Inorg. Chem.*, 1978, **17,** 646.
26. B. D. Cutforth, R. J. Gillespie and P. K. Ummat, *Rev. Chim. Miner.*, 1976, **13,** 119.
26. (a) R. J. Gillespie, P. Granger, K. R. Morgan and G. J. Schrobilgen, *Inorg. Chem.*, 1984, **23,** 887.
27. G. Torsi, K. W. Fung, G. M. Begun and G. Mamantow, *Inorg. Chem.*, 1971, **10,** 2285.
28. M. Kaveh and E. Ehrenfreund, *Solid State Commun.*, 1979, **31,** 709.
29. R. A. Jones, F. M. Real, G. Wilkinson, A. M. R. Galas and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1981, 126.
30. K. Brodersen, J. Hoffmann and R. Erdmann, *Z. Anorg. Allg. Chem.*, 1981, **482,** 217.
31. K. Brodersen and L. Kunkel, *Chem. Ber.*, 1958, **91,** 2698.
32. Y. Marcus, *J. Phys. Chem. Ref. Data,* 1981, **9,** 1307.
33. E. Dorm, *Chem. Commun.*, 1971, 466.
34. H. Stammreich and T. Teixeira Sans, *J. Mol. Struct.*, 1967, **1,** 55.
35. E. Dorm, *Chem. Commun., Univ. Stockholm,* 1970, **3,** 24.
36. P. W. Richter, P. T. T. Wong and E. Whalley, *J. Chem. Phys.*, 1977, **67,** 2348.
37. K. Brodersen and J. Hoffmann, *Z. Anorg. Allg. Chem.*, 1980, **469,** 32.
38. Y. C. Venudhar, T. R. Prasad, L. Iyengar, K. S. Murthy and K. V. K. Rao, *Therm. Expans.* (*Proc. Int. Symp.*) *7th, 1979* (Pub. 1982).
39. M. E. Boiko, B. S. Zadokhin and Yu. F. Markov, *Kristallografiya,* 1981, **26,** 400.
40. M. F. Limonov and Yu. F. Markov, *Fiz. Tverd. Tela* (*Leningrad*), 1983, **25,** 1081.
41. A. Triska, C. Barta and F. Vodak, *Adv. Space Res.*, 1983, **83,** 187.
42. D. Grdenić, *J. Chem. Soc.*, 1956, 1312.
43. E. Dorm, *Acta Chem. Scand.*, 1971, **25,** 1655.
44. K. Brodersen and R. Eder, *Chem. Ber.*, 1977, **110,** 2392.
45. D. L. Kepert, D. Taylor and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1973, 392.
46. D. L. Kepert, D. Taylor and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1973, 1658.
47. R. A. Potts and A. L. Allred, *Inorg. Chem.*, 1966, **5,** 1066.
48. B. Lindh, *Acta Chem. Scand.*, 1967, **21,** 2743.
49. E. Dorm, *Acta Chem. Scand.*, 1967, **21,** 2834.
50. E. Dorm, *Acta Chem. Scand.*, 1969, **23,** 1607.
51. G. Johansson, *Acta Chem. Scand.*, 1966, **20,** 553.
52. H. Puff, G. Lorbacher and R. Skrabs, *Z. Kristallogr.*, 1965, **122,** 156.
53. B. Kamenar and A. Kaitner, *Acta Crystallogr., Sect. B,* 1973, **29,** 1666.
54. M. Sikirica and D. Grdenić, *Acta Crystallogr., Sect. B,* 1974, **30,** 144.
55. R. Eder, Dissertation, University of Erlangen-Nürnberg, 1978.
56. D. Grdenić, M. Sikirica and I. Vickovic, *Acta Crystallogr., Sect. B,* 1975, **31,** 2174.
57. Bo. A. Nilsson, *Z. Kristallogr.*, 1975, **141,** 321.
58. A. Durif, I. Tordjman, R. Masse and J. C. Guitel, *J. Solid State Chem.*, 1978, **24,** 101.
59. R. P. J. Cooney and J. R. Hall, *J. Inorg. Nucl. Chem.*, 1972, **34,** 1519.
60. K. H. Tan and M. J. Taylor, *Aust. J. Chem.*, 1978, **31,** 2601.
61. E. Dorm and B. Lindh, *Acta Chem. Scand.*, 1967, **21,** 1661.
62. K. H. Tan and M. J. Taylor, *Inorg. Nucl. Chem. Lett.*, 1980, **16,** 337.
63. J. W. Bouknight, R. Layton and J. E. Lewis, *Inorg. Nucl. Chem. Lett.*, 1967, **3,** 103.
64. K. Brodersen, G. Liehr and W. Rölz, *Chem. Ber.*, 1975, **108,** 3243.
65. K. Brodersen, G. Liehr and W. Rölz, *Z. Anorg. Allg. Chem.*, 1977, **428,** 166.
66. K. Brodersen and W. Rölz, *Chem. Ber.*, 1977, **110,** 1042.
67. K. Brodersen, W. Rölz, G. Jordan, R. Gerbeth and J. Ellermann, *Chem. Ber.*, 1978, **111,** 132.
68. K. Brodersen and G. Jordan, *Chem. Ber.*, 1978, **111,** 1221.
69. P. A. W. Dean and D. G. Ibbott, *Inorg. Nucl. Chem. Lett.*, 1975, **11,** 119.
70. P. A. W. Dean and D. G. Ibbott, *Can. J. Chem.*, 1976, **54,** 177.
71. E. S. Gould and A. Amendola, *J. Am. Chem. Soc.*, 1955, **77,** 2103.
72. K. Lederer, *Ber. Dtsch. Chem. Ges.*, 1914, **47,** 277.
73. K. Brodersen, G. Liehr and M. Rosenthal, *Chem. Ber.*, 1977, **110,** 3291.
74. K. Brodersen, G. Liehr and M. Rosenthal, *Z. Naturforsch., Teil B,* 1978, **33,** 1227.
75. G. N. Schrauzer, 'Selenium', Fischer, Heidelberg, 1983.
76. E. Gleditsch and T. F. Egidius, *Z. Anorg. Allg. Chem.*, 1936, **226,** 265; **228,** 249.
77. S. D. Arora, W. N. Lipscomb and M. C. Sneed, *J. Am. Chem. Soc.*, 1951, **73,** 1015.
78. L. Nijssen and W. N. Lipscomb, *Acta Crystallogr.*, 1952, **5,** 604.
79. W. N. Lipscomb, *Anal. Chem.*, 1953, **25,** 737.
80. W. N. Lipscomb, *Ann. N.Y. Acad. Sci.*, 1956/57, **65,** 427.
81. G. Jander and K. Brodersen, *Z. Anorg. Allg. Chem.*, 1951, **265,** 117.
82. W. Rüdorff and K. Brodersen, *Z. Naturforsch., Teil B,* 1952, **7,** 56.
83. W. Rüdorff and K. Brodersen, *Z. Anorg. Allg. Chem.*, 1952, **270,** 145.
84. W. Rüdorff and K. Brodersen, *Z. Anorg. Allg. Chem.*, 1953, **274,** 323.
85. K. Brodersen and W. Rüdorff, *Z. Anorg. Allg. Chem.*, 1954, **275,** 141.
86. K. Brodersen, *Acta Crystallogr.*, 1955, **8,** 723.

87. K. Brodersen and W. Rüdorff, *Z. Anorg. Allg. Chem.*, 1956, **287**, 24.
88. K. Brodersen and H. J. Becher, *Chem. Ber.*, 1956, **89**, 1487.
89. K. Brodersen and M. Neuberger, *Isr. J. Chem.*, 1966, **4**, 10.
90. D. Breitinger and K. Brodersen, *Angew. Chem.*, 1970, **82**, 379; *Angew. Chem., Int. Ed. Engl.*, 1970, **9**, 357.
91. D. Breitinger, K. Brodersen and J. Limmer, *Chem. Ber.*, 1970, **103**, 2388.
92. J. Limmer, N. Hacke and K. Brodersen, *Chem. Ber.*, 1973, **106**, 2185.
93. T. Wirth and N. Davidson, *J. Am. Chem. Soc.*, 1964, **86**, 4314.
94. K. Brodersen and L. Kunkel, *Z. Anorg. Allg. Chem.*, 1959, **298**, 34.
95. K. Brodersen and R. Dölling, *Z. Anorg. Allg. Chem.*, 1981, **475**, 67.
96. M. S. Barnikow, I. S. Bukhareva and Yu. S. Varshavskii, *Zh. Neorg. Khim.*, 1965, **10**, 2293; C. A. 1966, **64**, 1490.
97. K. Brodersen and N. Hacke, *Chem. Ber.*, 1974, **107**, 3260.
98. R. C. Elder, J. Halpern and J. S. Pond, *J. Am. Chem. Soc.*, 1967, **89**, 6877.
99. K. Brodersen, N. Hacke and G. Liehr, *Z. Anorg. Allg. Chem.*, 1974, **409**, 1.
100. K. Brodersen, N. Hacke and G. Liehr, *Z. Anorg. Allg. Chem.*, 1975, **414**, 1.
101. F. Brodersen, R. Eder and H. Menne, *Chem. Ber.*, 1976, **109**, 2762.
102. K. H. Tan and M. J. Taylor, *Aust. J. Chem.*, 1980, **33**, 1753.
103. K. Brodersen, R. Dölling and G. Liehr, *Chem. Ber.*, 1978, **111**, 3354.
104. K. Brodersen, R. Dölling and G. Liehr, *Z. Anorg. Allg. Chem.*, 1980, **464**, 17.
105. D. L. Kepert, D. Taylor and A. H. White, *Inorg. Chem.*, 1972, **11**, 1639.
106. D. L. Kepert, D. Taylor and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1973, 893.
107. J. C. Dewan, D. L. Kepert and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1975, 490.
108. D. L. Kepert and D. Taylor, *Aust. J. Chem.*, 1974, **27**, 1199.
109. D. Taylor, *Aust. J. Chem.*, 1976, **29**, 723.
110. R. Schneeweiß, Dissertation, University of Erlangen-Nürnberg, 1980.
111. D. Taylor, *Aust. J. Chem.*, 1977, **30**, 2647.
112. D. Seybold and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1968, **361**, 277.
113. D. G. Ibbott, *Diss. Abstr. Int. B*, 1977, **37**, 5067.
114. M. Rosenthal, Diploma research, University of Erlangen-Nürnberg, 1975.
115. G. Schottner, Diploma research, University of Erlangen-Nürnberg, 1983.
116. G. Taubmann, Diploma research, University of Erlangen-Nürnberg, 1976.
117. K. Brodersen and J. Hoffmann, *Z. Anorg. Allg. Chem.*, 1981, **482**, 226.
118. J. Hoffmann, Dissertation, University of Erlangen-Nürnberg, 1979.
119. C. A. Ghilardi, S. Midollini and S. Moneti, *J. Chem. Soc., Chem. Commun.*, 1981, 865.
120. P. A. W. Dean, D. G. Ibbott and J. B. Stothers, *J. Chem. Soc., Chem. Commun.*, 1973, 626.
121. P. A. W. Dean, D. G. Ibbott and J. B. Stothers, *Can. J. Chem.*, 1976, **54**, 166.
122. G. Beck, Dissertation, University of Erlangen-Nürnberg, 1977.
123. R. Beck, Dissertation, University of Erlangen-Nürnberg, 1984.
124. O. Ruff and G. Bahlan, *Ber. Dtsch. Chem. Ges.*, 1918, **51**, 1752.
125. F. Ebert and H. Woitinek, *Z. Anorg. Allg. Chem.*, 1933, **210**, 269.
126. R. Dötzer and A. Meuwsen, *Z. Anorg. Allg. Chem.*, 1961, **308**, 79.
127. C. Stalhandske, *Acta Crystallogr., Sect. B*, 1979, **35**, 949.
128. Yu. Z. Nozik, L. E. Fykin, V. I. Bukin and N. M. Laptash, *Koord. Khim.*, 1979, **5**, 276.
129. D. Grdenić and M. Sikirica, *Inorg. Chem.*, 1973, **12**, 544.
130. J. E. Roberts and G. H. Cady, *J. Am. Chem. Soc.*, 1960, **82**, 353.
131. R. F. Rolsten, 'Iodide Metals and Metal Iodides', Wiley, New York, 1961, p. 215.
132. H. J. Verweel and J. M. Bijvoet, *Z. Kristallogr.*, 1931, **77**, 122.
133. G. A. Jeffrey and M. Vlasse, *Inorg. Chem.*, 1976, **6**, 396.
134. D. Schwarzenbach, *Z. Kristallogr.*, 1969, **128**, 97.
135. V. H. Subramanian and P. T. Narasimhan, *J. Mol. Struct.*, 1980, **58**, 193.
136. S. Segupta and D. Giezendanner, *J. Magn. Reson.*, 1980, **38**, 553.
137. D. M. Adams and R. Appleby, *Inorg. Chim. Acta*, 1978, **26**, L43.
138. H. Mikler, *Monatsh. Chem.*, 1972, **103**, 110.
139. C. W. F. T. Pistorius, *Prog. Solid State Chem.*, 1976, **11**, 1.
140. P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, 1937, **72**, 45.
141. D. M. Adams and R. Appleby, *J. Chem. Soc., Dalton Trans.*, 1977, 1535.
142. D. B. Balashov and D. A. Ikhenov, *Fiz. Tverd. Tela (Leningrad)*, 1975, **17**, 2993.
143. D. M. Adams and R. Appleby, *J. Chem. Soc., Dalton Trans.*, 1977, 1530.
144. T. R. Griffiths and R. A. Anderson, *J. Chem. Soc., Faraday Trans. 2*, 1979, **75**, 957.
145. P. Peringer, *Inorg. Chim. Acta*, 1980, **39**, 67.
146. R. P. Rastogi and B. L. Dubey, *J. Am. Chem. Soc.*, 1967, **89**, 200.
147. R. P. Rastogi and B. L. Dubey, *J. Inorg. Nucl. Chem.*, 1969, **31**, 1530.
148. R. P. Rastogi, B. L. Dubey and N. D. Agrawal, *J. Inorg. Nucl. Chem.*, 1975, **37**, 1167.
149. A. Givan and A. Loewenschuss, *J. Chem. Phys.*, 1980, **72**, 3809.
150. S. Mehdi and S. M. Ansari, *J. Solid State Chem.*, 1981, **40**, 122.
151. W. Scholten and J. M. Bijvoet, *Z. Kristallogr.*, 1941, **103**, 415.
152. G. B. Deacon, *Rev. Pure Appl. Chem.*, 1963, **13**, 189.
153. V. P. Vasil'ev, E. V. Kozlovskii and A. A. Mokeev, *Zh. Neorg. Khim.*, 1980, **25**, 1765.
154. I. Eliezer, *J. Phys. Chem.*, 1964, **68**, 2722.
155. M. Stan and F. Zalaru, *Chem. Abstr.*, 1973, **79**, 38 082x.
156. M. Stan, F. Zalaru and G. S. Ionescu, *Chem. Abstr.*, 1973, **78**, 66 392w.
157. M. L. Deliwaule, *Bull. Soc. Chim. Fr.*, 1955, 1294.
158. J. A. Rolfe, D. E. Sheppard and L. A. Woodward, *Trans. Faraday Soc.*, 1954, **50**, 1275.

159. A. A. Kaplyanskii, S. N. Popov and C. Barta., *Magn. Reson. Relat. Phenom., Proc. Congr. Ampère, 20th, 1978,* 1979, 383.
160. Chemical Society Special Publication, No. 17, II, The Chemical Society, London, 1958.
161. L. G. Sillén, *Acta Chem. Scand.*, 1949, **3,** 505.
162. R. Hoppe and R. Homann, *Z. Anorg. Allg. Chem.*, 1969, **369,** 212.
163. C. Hebecker, *Naturwissenschaften*, 1973, **60,** 154.
164. J. T. R. Dunsmuir and A. P. Lane, *J. Inorg. Nucl. Chem.*, 1971, **33,** 4361.
165. Z. Kantarci, N. N. Rahman and D. N. Waters, *Proc. Int. Conf. Raman Spectrosc., 6th,* 1978, **2,** 280.
166. H. Poulet and J. P. Mathieu, *J. Phys. (Orsay, Fr.)*, 1979, **40,** 1079.
167. K. Aurivillius and C. Stalhandske, *Acta Chem. Scand., Ser. A,* 1976, **30,** 735.
168. M. Falk and O. Knop, *Can. J. Chem.*, 1977, **55,** 1736.
169. E. J. Harmsen, *Z. Kristallogr.*, 1938, **100,** 208.
170. R. M. Barr and M. Goldstein, *Inorg. Nucl. Chem. Lett.*, 1974, **10,** 33.
171. J. A. D. Jeffries, G. A. Sim, R. H. Burnell, W. I. Taylor, R. E. Corbett, J. Murray, Jr. and B. J. Sweetman, *Proc. Chem. Soc. (London)*, 1963, 171.
172. D. V. Ninković, *Chem. Abstr.*, 1958, **52,** 2493f.
173. M. Sandström and D. Hay Liem, *Acta Chem. Scand., Ser. A,* 1978, **32,** 509.
174. J. Pickhardt and T. Schendler, *Z. Naturforsch., Teil B,* 1982, **37,** 930.
175. A. Ben Salah, J. W. Bats, R. Kalus, H. Fuess and A. Daoud, *Z. Anorg. Allg. Chem.*, 1982, **493,** 178.
176. K. Brodersen, G. Pezzei and G. Thiele, *Z. Anorg. Allg. Chem.*, 1983, **499,** 169.
177. K. Brodersen, K.-P. Jensen and G. Thiele, *Z. Naturforsch., Teil B,* 1980, **35,** 259.
178. K. Brodersen, K.-P. Jensen and G. Thiele, *Z. Naturforsch., Teil B,* 1980, **35,** 253.
179. V. M. Padmanabhan and V. S. Yadava, *Acta Crystallogr., Sect. B,* 1969, **25,** 647.
180. V. I. Pakhomov, P. M. Fedorov and I. N. Ivanova-Korfini, *Koord. Khim.*, 1978, **4,** 1765.
181. K. Brodersen, G. Thiele and G. Görz, *Z. Anorg. Allg. Chem.*, 1973, **401,** 217.
182. K. Brodersen, G. Pezzei and G. Thiele, *Z. Anorg. Allg. Chem.*, 1983, **502,** 209.
183. V. I. Pakhomov and P. M. Fedorov, *Kristallografiya,* 1972, **17,** 942.
184. R. H. Fenn, J. W. H. Oldham and D. C. Phillips, *Nature (London)*, 1963, **198,** 381.
185. G. Thiele, K. Brodersen and G. Pezzei, *Z. Anorg. Allg. Chem.*, 1982, **491,** 308.
186. H. J. Berthold, D. Haas, R. Tamme, K. Brodersen, K.-P. Jensen, D. Messer and G. Thiele, *Z. Anorg. Allg. Chem.*, 1979, **456,** 29.
187. A. Ben Salah, J. W. Bats, H. Fuess and A. Daoud, *Inorg. Chim. Acta,* 1982, **63,** 169.
188. V. Busico and V. Salerno, *Gazz. Chim. Ital.*, 1979, **109,** 581.
189. A. F. Demiray and W. Brockner, *Z. Naturforsch., Teil A,* 1980, **35,** 103.
190. H. Schaefer and U. Floerke, *Z. Anorg. Allg. Chem.*, 1981, **479,** 84.
191. W. Clegg, *J. Chem. Soc., Dalton Trans.*, 1982, 593.
192. R. C. Seccombe and C. H. L. Kennard, *J. Organomet. Chem.*, 1969, **18,** 243.
193. P. T. T. Wong, *J. Chem. Phys.*, 1980, **72,** 6721.
194. A. M. Golub and H. Köhler, 'Chemistry of the Pseudohalides', Hüthig-Verlag, Heidelberg, 1979.
195. M. Frey and M. Ledésert, *Acta Crystallogr., Sect. B,* 1971, **27,** 2119.
196. A. Weiss and G. Hofmann, *Z. Naturforsch., Teil B,* 1960, **15,** 679.
197. W. P. Griffith, *J. Chem. Soc.*, 1964, 4070.
198. R. A. Penneman and L. H. Jones, *J. Inorg. Nucl. Chem.*, 1961, **20,** 19.
199. N. Tanaka and T. Murayama, *Z. Phys. Chem.*, 1957, **11,** 366.
200. K. G. Ashurst, N. P. Finkelstein and L. A. Gould, *J. Chem. Soc. (A)*, 1971, 1899.
201. G. Thiele, R. Bauer and D. Messer, *Naturwissenschaften,* 1974, **61,** 215.
202. R. Bauer, Dissertation, University of Erlangen-Nürnberg, 1973.
203. L. D. C. Bok and J. G. Leipoldt, *Z. Anorg. Allg. Chem.*, 1966, **344,** 86.
204. L. D. C. Bok, J. G. Leipoldt and J. L. Myburgh, *J. S. Afr. Chem. Inst.*, 1967, **20,** 197.
205. R. G. Dickinson, *J. Am. Chem. Soc.*, 1922, **44,** 774.
206. K. Brodersen, I. Beck, R. Beck, H. U. Hummel and G. Liehr, *Z. Anorg. Allg. Chem.*, 1984, **516,** 30.
207. G. Thiele, K. Brodersen and H. Frohring, *Z. Naturforsch., Teil B,* 1981, **36,** 180.
208. G. Thiele and P. Hilfrich, *Z. Anorg. Allg. Chem.*, 1980, **461,** 109.
209. F. H. Kruse, *Acta Crystallogr.*, 1963, **16,** 105.
210. K. Brodersen and H. U. Hummel, *Z. Anorg. Allg. Chem.*, 1983, **500,** 171.
211. K. Brodersen, H. M. Frohring and G. Thiele, *Z. Anorg. Allg. Chem.*, 1981, **483,** 86.
212. F. D. Miles, *J. Chem. Soc.*, 1931, 2532.
213. F. P. Bowden, *Proc. R. Soc. London, Ser. A,* 1958, **246,** 146.
214. U. Müller, *Z. Anorg. Allg. Chem.*, 1973, **399,** 183.
215. W. Beck, W. P. Fehlhammer, P. Pöllmann, E. Schuierer and K. Feldt, *Chem. Ber.*, 1967, **100,** 2335.
216. A. Y. Tsivadze, Y. Y. Kharitonov and G. V. Tsintsadze, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1972, **17,** 1417.
217. K. F. Chew, W. Derbyshire, N. Logan, A. H. Norbury and A. I. P. Sinha, *Chem. Commun.*, 1970, 1708.
218. A. Suzuki, *J. Ind. Explos. Soc. Jpn.*, 1953, **14,** 142.
219. W. Beck and E. Schuierer, *Z. Anorg. Allg. Chem.*, 1966, **347,** 304.
220. L. Hackspill and W. Schumacher, *Chem. Abstr.*, 1938, **32,** 4338.
221. L. Wöhler and A. Berthann, *Ber. Dtsch. Chem. Ges.*, 1929, **62,** 2748.
222. A. L. Beauchamp and D. Goutier, *Can. J. Chem.*, 1972, **50,** 977.
223. A. Larbot and A. L. Beauchamp, *Rev. Chim. Miner.*, 1973, **10,** 465.
224. S. C. Jain and R. Rivest, *Inorg. Chim. Acta,* 1970, **4,** 291.
225. A. R. Davis, C. J. Murphy and R. A. Plane, *Inorg. Chem.*, 1970, **9,** 423.
226. I. S. Ahuja and A. Garg, *J. Inorg. Nucl. Chem.*, 1972, **34,** 1929, 2074.
227. I. S. Ahuja and R. Singh, *Inorg. Nucl. Chem. Lett.*, 1973, **9,** 289.
228. I. S. Ahuja and R. Singh, *Inorg. Chim. Acta,* 1973, **7,** 565.

229. I. S. Ahuja and R. Singh, *Spectrochim. Acta, Part A*, 1974, **30**, 2955.
230. I. S. Ahuja and R. Singh, *J. Coord. Chem.*, 1975, **4**, 181.
231. D. Grdenić, B. Kamenar, M. Sikirica and J. Vernic, *Cryst. Struct. Commun.*, 1976, **5**, 833.
232. A. L. Beauchamp, B. Saperas and R. Rivest, *Can. J. Chem.*, 1974, **52**, 2923.
233. I. S. Ahuja and C. L. Yadava, *Inorg. Chim. Acta*, 1983, **78**, L1.
234. Z. V. Zvonkova and G. S. Zhdanov, *Zh. Fiz. Khim.*, 1952, **26**, 586.
235. V. I. Belevantsev and A. V. Shuvaev, *Zh. Neorg. Khim.*, 1978, **23**, 924.
236. R. P. Cooney and J. R. Hall, *Chem. Abstr.*, 1971, **74**, 10 495k.
237. L. Dupont, O. Dideberg, A. Rulmont and P. Nyssen, *Acta Crystallogr., Sect. C*, 1983, **39**, 323.
238. A. Sakhri and A. L. Beauchamp, *Inorg. Chem.*, 1975, **14**, 740.
239. J. W. Jeffrey and K. M. Rose, *Acta Crystallogr., Sect. B*, 1968, **24**, 653.
240. A. Korczynski, *Rocz. Chem.*, 1962, **26**, 1539.
241. G. Thiele and D. Messer, *Z. Anorg. Allg. Chem.*, 1976, **421**, 24.
242. G. Thiele and P. Hilfrich, *Z. Naturforsch., Teil B*, 1978, **33**, 597.
243. R. Grönbaek and J. D. Dunitz, *Helv. Chim. Acta*, 1964, **47**, 1889.
244. K. Brodersen and H. U. Hummel, *Z. Anorg. Allg. Chem.*, 1982, **491**, 34.
245. K. Brodersen and H. U. Hummel, *Z. Naturforsch., Teil B*, 1983, **38**, 911.
246. K. Brodersen and H. U. Hummel, *Z. Anorg. Allg. Chem.*, 1983, **499**, 15.
247. A. Sakhri and A. L. Beauchamp, *Acta Crystallogr., Sect. B*, 1975, **31**, 409.
248. M. R. Udupa and B. Krebs, *Inorg. Chim. Acta*, 1980, **42**, 37.
249. P. P. Singh and N. Singh, *J. Coord. Chem.*, 1979, **9**, 197.
250. C. A. Cameron and E. W. Davy, *Chem. News*, 1881, **44**, 63.
251. J. J. Charitonov and V. V. Skopenko, *Zh. Neorg. Khim.* 1965, **10**, 1803.
252. V. F. Torpova, *Zh. Neorg. Khim.*, 1956, **1**, 243.
253. T. Murayama and A. Takayanagi, *Bull. Soc. Chim. Jpn.*, 1972, 45.
254. J. J. Charitonov and V. V. Skopenko, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1965, **10**, 984.
255. A. Swinarski and A. Lodzinska, *Rocz. Chem.*, 1958, **32**, 1053.
256. A. Turco, C. Pecile and M. Nicolini, *J. Chem. Soc.*, 1962, 3008.
257. P. P. Singh, A. K. Srivastava and L. P. Pathak, *J. Coord. Chem.*, 1979, **9**, 65.
258. M. Nagao, H. Inoue and S. Yanagisawa, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1686.
259. P. P. Singh, N. Singh and R. C. Verma, *J. Less-Common Met.*, 1980, **70**, 143.
260. K. Brodersen, M. Cygan and H. U. Hummel, *Z. Naturforsch., Teil B*, 1984, **39**, 582.
261. P. P. Singh and S. B. Sharma, *J. Coord. Chem.*, 1976, **6**, 65.
262. P. P. Singh and N. Singh, *J. Mol. Struct.*, 1979, **54**, 1207.
263. H. Köhler, *Z. Anorg. Allg. Chem.*, 1964, **331**, 237.
264. W. Madelung and E. Kern, *Justus Liebigs, Ann. Chem.*, 1922, **427**, 1.
265. V. M. Samoilenko, O. G. Movchan and V. V. Skopenko, *Ukr. Khim. Zh.* (*Russ. Ed.*), 1980, **46**, 1286 (*Chem. Abstr.*, 1981, **94**, 53 782d).
266. L. Book, T. C. W. Mak, *Inorg. Chim. Acta*, 1983, **77**, L57.
267. K. Aurivillius, *Acta Chem. Scand.*, 1954, **8**, 523.
268. K. Aurivillius and I. B. Carlsson, *Acta Chem. Scand.*, 1958, **12**, 1297.
269. G. R. Levi, *Gazz. Chim. Ital.*, 1924, **54**, 709.
270. P. Laruelle, *C.R. Hebd. Seances Acad. Sci.*, 1955, **241**, 802.
271. W. L. Roth, *Acta Crystallogr.*, 1956, **9**, 277.
272. M. Puselj, Z. Ban and E. Lukacevic, *J. Appl. Crystallogr.*, 1983, **16**, 357.
273. N. G. Vannerberg, *Prog. Inorg. Chem.*, 1962, **4**, 125.
274. A. Weiss, 'Zehn Jahre Fonds der Chemischen Industrie', Verlag Chemie, Weinheim, 1960, p. 157.
275. R. Hoppe and H. J. Röhrborn, *Naturwissenschaften*, 1962, **49**, 419.
276. R. Hoppe and H. J. Röhrborn, *Z. Anorg. Allg. Chem.*, 1964, **329**, 110.
277. S. Hietanen and E. Hogfeldt, *Chem. Scr.*, 1976, **10** (1), 37.
278. E. R. Allen, J. Cartlidge, M. M. Taylor and C. F. H. Tipper, *J. Phys. Chem.*, 1959, **63**, 1442.
279. R. Allmann, *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.*, 1973, **138**, 366.
280. A. S. Tichonov, *Zh. Neorg. Khim.*, 1958, **3**, 296.
281. A. M. Zajdler and D. M. Gzakis-Sulikowska, *Rocz. Chem.*, 1975, **49**, 487.
282. C. Mahon and D. Britton, *Inorg. Chem.*, 1971, **10**, 586.
283. C. Mahon and D. Britton, *Inorg. Chem.*, 1971, **10**, 2331.
284. C. D. Garner and B. Hughes, *Adv. Inorg. Chem. Radiochem.*, 1975, **17**, 1.
285. R. W. H. Small, *Acta Crystallogr., Sect. B*, 1982, **38**, 2886.
286. L. Ciavatta, D. Ferri, M. Grimaldi and F. Salvatore, *Ann. Chim.* (*Rome*), 1979, **69**, 463.
287. Y. A. Ol'deKop, N. A. Maier, A. A. Erdman and Z. P. Zubreichuk, *Zh. Obshch. Khim.*, 1979, **49**, 411.
288. K. Kapoor, V. Kumari and R. C. Sharma, *Chem. Era*, 1978, **14**, 33.
289. V. V. Panevchik and I. A. Shingel, *Tezisy Dokl.—Resp. Konf. Molodykh Uch. Khim., 2nd*, 1977, **2**, 40.
290. C. Natarajan and R. Rengasamy, *Indian J. Chem., Sect. A*, 1979, **18**, 356.
291. R. Allmann, K. Dietrich and H. Musso, *Justus Liebigs Ann. Chem.*, 1976, **7**, 1185.
292. N. V. Sidgwick, 'The Chemical Elements and their Compounds', Oxford University Press, London, 1950, Vol. 1, p. 326.
293. L. F. Power, K. E. Turner and F. H. Moore, *Inorg. Nucl. Chem. Lett.*, 1972, **8**, 809.
294. D. M. L. Goodgame and M. A. Hitchman, *J. Chem. Soc.* (*A*), 1967, 612.
295. A. Ferrari and C. Colla, *Gazz. Chim. Ital.*, 1935, **65**, 789.
296. A. Ferrari and C. Colla, *Gazz. Chim. Ital.*, 1935, **65**, 795.
297. C. C. Addison and N. Logan, *Adv. Inorg. Chem. Radiochem.*, 1964, **6**, 71.
298. W. Morell and D. Breitinger, *J. Organomet. Chem.*, 1974, **71**, C43.
299. J. I. Bullock and D. G. Tuck, *J. Chem. Soc.*, 1965, 1877.
300. R. Erdmann, Dissertation, University of Erlangen-Nürnberg, 1983.

301. K. Persson and B. Holmberg, *Acta Crystallogr., Sect. B,* 1982, **38,** 900, 904.
302. K. Köhler, D. Breitinger and G. Thiele, *Angew. Chem.*, 1974, **86,** 863.
303. S. H. Whitlow, *Can. J. Chem.*, 1974, **52,** 198.
304. R. Klement and H. Haselbeck, *Z. Anorg. Allg. Chem.*, 1964, **334,** 27.
305. J. C. Huttner, *Ann. Chim. (Paris)*, 1953, **8,** 450.
306. M. T. Fournier and M. Capestan, *Bull. Soc. Chem. Fr.*, 1972, 573.
307. E. Thilo and I. Grunze, *Z. Anorg. Allg. Chem.*, 1957, **290,** 209.
308. E. Dubler, L. Beck, L. Linowsky and G. B. Jameson, *Acta Crystallogr., Sect. B,* 1981, **37,** 2214.
309. T. Yamane and N. Davidson, *J. Am. Chem. Soc.*, 1960, **82,** 2123.
310. H. Guérin and B. Boulitrop, *C.R. Hebd. Seances Acad. Sci.*, 1950, **230,** 447; 1951, **232,** 65.
311. K. Aurivillius and C. Stalhandske, *Z. Kristallogr.*, 1980, **153,** 121.
312. K. Aurivillius and Bo. A. Nilsson, *Z. Kristallogr.*, 1975, **141,** 1.
313. C. Stalhandske, *Acta Crystallogr., Sect. B,* 1980, **36,** 23.
314. P. Peringer, *J. Inorg. Nucl. Chem.*, 1980, **42,** 1501.
315. M. J. Redman and W. W. Harvey, *J. Less-Common Met.*, 1967, **12,** 395.
316. K. Aurivillius and B. Malmros, *Acta Chem. Scand.*, 1961, **15,** 1932.
317. C. Stalhandske, *Acta Crystallogr., Sect. B,* 1978, **34,** 1408.
318. M. T. Falqui, *Chem. Abstr.*, 1965, **62,** 1143c.
319. O. H. J. Christie, *Acta Crystallogr.*, 1962, **15,** 94.
320. G. Johansson and M. Sandström, *Acta Chem. Scand., Ser. A,* 1978, **32,** 109.
321. D. L. Kepert, D. Taylor and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1973, 670.
322. C. Stalhandske, *Acta Crystallogr., Sect. B,* 1978, **34,** 1968.
323. K. Aurivillius and C. Stalhandske, *Z. Kristallogr.*, 1975, **142,** 129.
324. W. Jeitschko and A. W. Sleight, *Acta Crystallogr., Sect. B,* 1973, **29,** 869.
325. G. Blasse, *J. Inorg. Nucl. Chem.*, 1975, **37,** 97.
326. M. Quarton, J. Angenault and A. Rimsky, *Acta Crystallogr., Sect. B,* 1973, **29,** 567.
327. B. Ribar, B. Matkiovic, M. Sljukic and F. Gabela, *Z. Kristallogr.*, 1971, **134,** 311.
328. B. Matkovic, B. Ribar, B. Prelesnik and R. Herak, *Inorg. Chem.*, 1974, **13,** 3006.
329. H. Behm, *Acta Crystallogr., Sect C,* 1983, **39,** 1319.
330. K. Aurivillius and C. Stalhandske, *Z. Kristallogr.*, 1976, **144,** 1.
331. G. Björnlund, *Acta Chem. Scand., Ser. A,* 1974, **28,** 169.
332. G. Nagorsen, S. Lyng, A. Weiss and A. Weiss, *Angew. Chem.*, 1962, **74,** 119.
333. A. Bonifacic, *Acta Crystallogr., Sect. A,* 1963, **16,** 30.
334. A. Weiss, L. Lyng and A. Weiss, *Z. Naturforsch., Teil B,* 1960, **15,** 678.
335. G. Björnlund, *Acta Chem. Scand.*, 1971, **25,** 1645.
336. G. Johansson, *Acta Chem. Scand.*, 1971, **25,** 2787, 2799.
337. G. Johansson, *Acta Chem. Scand.*, 1971, **25,** 1905.
338. K. Aurivillius and C. Stalhandske, *Acta Crystallogr., Sect. B,* 1974, **30,** 1907.
339. K. Aurivillius, *Ark. Kemi,* 1964, **22,** 537.
340. K. Aurivillius and L. Folkmarson, *Acta Chem. Scand.*, 1968, **22,** 2529.
341. S. Scavnicar, *Acta Crystallogr.*, 1956, **9,** 956.
342. K. Aurivillius, *Ark. Kemi,* 1964, **23,** 469; 1967, **28,** 279.
343. K. Aurivillius, *Acta Chem. Scand.*, 1960, **14,** 2196; 1964, **18,** 1305.
344. J. P. Picard, G. Baud, J. P. Besse, R. Chevalier and M. Gasperin, *Acta Crystallogr., Sect. B,* 1982, **38,** 2242.
345. M. Sandström, *Acta Chem. Scand., Ser. A,* 1978, **32,** 627.
346. P. Biscarini, L. Fusina, G. D. Nivellini, A. Mangia and G. Pelizzi, *J. Chem. Soc., Dalton Trans.*, 1973, 159.
347. P. Biscarini, L. Fusina, G. D. Nivellini, A. Mangia and G. Pelizzi, *J. Chem. Soc., Dalton Trans.*, 1974, 1846.
348. H. Brusset and F. Madaule-Aubry, *Bull. Soc. Chim. Fr.*, 1966, 3121.
349. M. Frey and J. C. Monier, *Acta Crystallogr., Sect. B,* 1971, **27,** 2487.
350. R. M. Barr, M. Goldstein, T. N. D. Hairs, M. McPartlin and A. J. Markwell, *J. Chem. Soc., Chem. Commun.*, 1974, 221.
351. G. Brauer, 'Handbuch der Präparativen Anorganischen Chemie', 3rd edn., Enke-Verlag, Stuttgart, 1978, p. 1054.
352. K. Aurivillius, *Acta Chem. Scand.*, 1950, **4,** 1413.
353. P. Auvray and F. Genet, *Bull. Soc. Fr. Mineral. Crystallogr.*, 1973, **96,** 218.
354. E. I. Nikol'skaya, *Chem. Abstr.*, 1965, **62,** 11 238g.
355. H. Sommer, R. Hoppe and M. Jansen, *Naturwissenschaften,* 1976, **63,** 194.
356. H. Sommer and R. Hoppe, *Z. Anorg. Allg. Chem.*, 1978, **443,** 201.
357. M. Z. Jandali, G. Eulenberger and H. Hahn, *Z. Anorg. Allg. Chem.*, 1978, **447,** 105.
358. M. Z. Jandali, G. Eulenberger and H. Hahn, *Z. Anorg. Allg. Chem.*, 1978, **445,** 184.
359. Yu. V. Voroshilov, I. D. Olekseyuk, M. I. Golovei and A. V. Bogdanova, *Chem. Abstr.*, 1977, **86,** 36 595n.
360. K. Köhler and D. Breitinger, *Naturwissenschaften,* 1974, **61,** 684.
361. G. Will, W. Scharenberg, W. Schaefer and M. O. Bargouth, *Chem. Abstr.*, 1972, **77,** 170 435c.
362. H. Puff and J. Küster, *Naturwissenschaften,* 1962, **49,** 464.
363. K. Aurivillius, *Ark. Kemi,* 1967, **26,** 497.
364. S. Durovic, *Acta Crystallogr., Sect. B,* 1968, **24,** 1661.
365. K. Takei and H. Hagiwara, *Bull. Chem. Soc. Jpn.*, 1976, **49,** 1425.
366. H. Puff, D. Heine and G. Lieck, *Naturwissenschaften,* 1968, **55,** 298.
367. P. Biscarini and L. Fusna, *Spectrochim. Acta, Part A,* 1980, **36,** 593.
368. A. J. Canty, *Spectrochim. Acta, Part A,* 1981, **37,** 283.
369. A. J. Canty, C. L. Raston and A. H. White, *Aust. J. Chem.*, 1979, **32,** 311, 1165.
370. P. Biscarini, L. Fusina and G. Nivellini, *J. Chem. Soc., Dalton Trans.*, 1974, 2140.
371. D. C. Bradley and N. R. Kunchur, *J. Chem. Phys.*, 1964, **40,** 2258.

372. N. R. Kunchur, *Nature (London)*, 1964, **204**, 468.
373. D. C. Bradley and N. R. Kunchur, *Can. J. Chem.*, 1965, **43**, 2786.
374. K. R. Buck, *Inorg. Nucl. Chem. Lett.*, 1979, **15**, 117.
375. M. Sakakibara, Y. Yonemura and Z. Tanaka, *J. Mol. Struct.*, 1980, **69**, 53.
376. L. M. Shkol'nikova and M. A. Porai-Koshits, *Koord. Khim.*, 1980, **6**, 1281.
377. M. D. Glick, W. H. Isley and A. R. Siedle, *Inorg. Chem.*, 1981, **20**, 3819.
378. R. A. Walton, *Inorg. Chem.*, 1966, **5**, 643.
379. R. S. McEwen and G. A. Sim, *J. Chem. Soc.*, 1967, 271.
380. J. A. W. Dalziel and T. G. Hewitt, *J. Chem. Soc.*, 1966, 233.
381. J. A. W. Dalziel, T. G. Hewitt and S. D. Rose, *Spectrochim. Acta*, 1966, **22**, 1267.
382. J. A. W. Dalziel, M. J. Hitch and S. D. Ross, *Spectrochim. Acta, Part A*, 1969, **25**, 1055.
383. W. R. Costello, A. T. Mcphail and G. A. Sim, *Nature (London)*, 1965, **205**, 383.
384. H. Sigel, V. M. Rheinberger and B. E. Fischer, *Inorg. Chem.*, 1979, **18**, 3334.
385. M. Cannas, F. A. Devillanova, G. Marongiu and G. Verani, *J. Inorg. Nucl. Chem.*, 1981, **43**, 2383.
386. D. M. L. Goodgame and G. A. Leach, *Inorg. Chim. Acta*, 1979, **32**, 69.
387. S. O. Grim, S. Nittolo, H. L. Ammon, P. H. Smith, I. J. Colquhoun, W. McFarlane and J. R. Holden, *Inorg. Chim. Acta*, 1983, **77**, L241.
388. Y. Watanabe, *Sci. Pap. Inst. Phys. Chem. Res. (Jpn.)*, 1980, **74**, 150.
389. V. V. Morchan, F. M. Tulypa and E. Ya. Baibarova, *Zh. Neorg. Khim.*, 1979, **24**, 2557.
390. A. Korczynski, *Rocz. Chem.*, 1968, **42**, 1207, 393.
391. D. Coucouvanis, in 'Progress in Inorganic Chemistry', Wiley-Interscience, New York, 1972, p. 233.
392. G. Gattow and W. Behrendt, 'Carbon Sulfides and their Inorganic Complex Chemistry', Thieme, Stuggart, 1977.
393. B. Nyberg and I. Cynkier, *Acta Chem. Scand.*, 1972, **26**, 4175.
394. L. K. Templeton, D. H. Templeton and A. Zalkin, *Acta Crystallogr.*, 1964, **17**, 933.
395. C. J. Nyman and J. Salazar, *Anal. Chem.*, 1961, **33**, 1467.
396. Y. Watanabe and H. Hayihara, *Acta Crystallogr., Sect. A*, 1972, **28**, 589.
397. Y. Watanabe, *Acta Crystallogr., Sect. B*, 1981, **37**, 553.
398. C. Chieh and S. K. Cheung, *Can. J. Chem.*, 1981, **59**, 2746.
398. (a) A. Nieuwpoort, A. H. Dix, P. A. T. Porskamp and J. G. M. van der Linden, *Inorg. Chim. Acta*, 1979, **35**, 221.
399. M. Ito and H. Iwasaki, *Acta Crystallogr., Sect. B*, 1979, **35**, 2720.
400. T. S. Lobana, S. S. Sandhu and T. R. Gupta, *J. Indian Chem. Soc.*, 1981, **58**, 80.
401. S. O. Grim, E. D. Walton and L. C. Satek, *Can. J. Chem.*, 1980, **58**, 1476.
402. E. Cruceanu, D. Niculesku and A. Vanku, *Kristallografiya*, 1964, **9**, 537.
403. M. F. Climent, C. Ruiz-Dana and J. L. L. Rodriguez, *An. Quim., Ser. B*, 1982, **78**, 387.
404. H. P. Singh and B. Dayal, *Acta Crystallogr., Sect. A*, 1970, **26**, 363.
405. D. Konopka, I. Kozłowska, S. Kubiak, W. Zarek, Z. Drzazga, J. Krok and A. Chlkowski, *Tr. Mezhdunar. Konf. Magn., 1973*, 1974, **1**, 194 (*Chem. Abstr.*, 1974, **85**, 55 598).
406. A. Giusti and G. Peyronel, *Z. Anorg. Allg. Chem.*, 1981, **478**, 233.
407. G. E. Coates and D. Ridley, *J. Chem. Soc.*, 1964, 166.
408. J. E. Fergusson and K. S. Loh, *Aust. J. Chem.*, 1973, **26**, 2615.
409. E. E. Aynsley, N. N. Greenwood and J. B. Leech, *Chem. Ind. (London)*, 1966, 379.
410. P. J. Hendra and N. Sadasivan, *J. Chem. Soc.*, 1965, 2063.
411. P. Nicpon and D. W. Meek, *Chem. Commun.*, 1966, 398.
412. M. G. King and G. P. McQuillan, *J. Chem. Soc. (A)*, 1967, 898.
413. L. S. D. Glasser, L. Ingram, M. G. King and G. P. McQuillan, *J. Chem. Soc. (A)*, 1969, 2501.
414. G. B. Aitken, J. L. Duncan and G. P. McQuillan, *J. Chem. Soc., Dalton Trans.*, 1972, 2103.
415. M. Fajardo, H. D. Holden, B. F. G. Johnson, J. Lewis and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1984, 24.
416. W. Gäde and E. Weiss, *Angew. Chem.*, 1981, **93**, 796; *Angew. Chem., Int. Ed. Engl.*, **20**, 803.
416. (a) A. Yamamoto, H. Yamazaki and T. Sakurai, *J. Am. Chem. Soc.*, 1982, **104**, 2329.
417. K. Brodersen, G. Liehr, G. Schottner and D. Prochaska, *Z. Anorg. Allg. Chem.*, 1985, **521**, 215.
418. A. Santos and P. Tigeras, *Inorg. Chim. Acta*, 1984, **81**, 175.
419. W. Schoeller and W. Schrauth, *Ber. Dtsch. Chem. Ges.*, 1909, **42**, 784.
420. D. B. Brown and M. B. Robin, *Inorg. Chim. Acta*, 1969, **3**, 644.
421. B. Kamenar and D. Grdenić, *Inorg. Chim. Acta*, 1969, **3**, 25.
422. H. J. Emeléus and G. L. Hurst, *J. Chem. Soc. (A)*, 1964, 396.
423. R. C. Dobbie and H. J. Emeléus, *J. Chem. Soc. (A)*, 1966, 933.
424. H. G. Ang and Y. C. Syn, *Adv. Inorg. Chem. Radiochem.*, 1974, **16**, 1.
425. H. Bürger, W. Sawodny and U. Wannagat, *J. Organomet. Chem.*, 1965, **3**, 113.
426. K. A. Hofmann, E. Biesalski and E. Söderlund, *Ber. Dtsch. Chem. Ges.*, 1912, **45**, 1731.
427. B. Picaud and M. Capestan, *Bull. Soc. Chim. Fr.*, 1966, 3984.
428. E. Divers and T. Haga, *J. Chem. Soc.*, 1892, **61**, 943; 1896, **69**, 1620.
429. P. Picaud and M. Capestan, *C.R. Hebd. Seances Acad. Sci., Ser. C*, 1967, **264**, 1118.
430. K. Brodersen, L. Stumpp and G. Krauss, *Chem. Ber.* 1960, **93**, 375.
431. A. Meuwsen and F. Schlossnagel, *Z. Anorg. Allg. Chem.*, 1953, **271**, 226.
432. A. Meuwsen and M. Lösel, *Z. Anorg. Allg. Chem.*, 1953, **271**, 217, 221.
433. O. Glemser, R. Mews and H. W. Roesky, *Chem. Ber.*, 1969, **102**, 1523.
434. B. Krebs, E. Meyer-Hussein, O. Glemser and R. Mews, *Chem. Commun.*, 1968, 1578.
435. R. E. Noftle and J. Crews, *Inorg. Chem.*, 1974, **13**, 3031.
436. W. Verbeek and W. Sundermeyer, *Angew. Chem.*, 1969, **81**, 330.
437. B. Kamenar, G. Jovanovski and D. Grdenić, *Cryst. Struct. Commun.*, 1982, **11**, 263.
438. E. Fluck, H. Richter and W. Schwarz, *Z. Anorg. Allg. Chem.*, 1983, **498**, 161.
439. D. J. Brauer, *Acta Crystallogr., Sect. B*, 1979, **35**, 1770.

440. J. Halfpenny and R. W. H. Small, *Acta Crystallogr., Sect. B,* 1980, **36,** 1194.
441. R. D. Worswick, D. F. Mayers and L. A. K. Staveley, *J. Chem. Soc., Faraday Trans. 2,* 1972, **68,** 539.
442. K. Brodersen, *Z. Anorg. Allg. Chem.*, 1957, **290,** 24.
443. K. Brodersen, *Z. Anorg. Allg. Chem.*, 1956, **285,** 5.
444. K. Brodersen, *Chem. Ber.*, 1957, **90,** 2703.
445. N. Q. Dao and D. K. Breitinger, *Spectrochim. Acta, Part A,* 1971, **27,** 905.
446. W. Beitelschmidt, Dissertation, University of Erlangen-Nürnberg, 1972.
447. W. Kreß, Dissertation, University of Erlangen-Nürnberg, 1983.
448. J. Lorberth and F. Weller, *J. Organomet. Chem.*, 1971, **32,** 145.
449. W. Thiel, F. Weller, J. Lorberth and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1971, **381,** 57.
450. K. Brodersen, *Z. Anorg. Allg. Chem.*, 1959, **298,** 142.
451. P. Pfeiffer, E. Schmitz and A. Böhm, *Z. Anorg. Allg. Chem.*, 1952, **270,** 287.
452. J. Peacock, F. C. Schmidt, R. E. Davis and W. B. Schaap, *J. Am. Chem. Soc.*, 1955, **77,** 5829.
453. T. D. O'Brien, *J. Am. Chem. Soc.*, 1948, **70,** 2771.
454. I. S. Ahuja and R. Singh, *Inorg. Nucl. Chem. Lett.*, 1973, **9,** 289.
455. G. Cova, D. Galizzioli, D. Giusto and F. Morazzoni, *Inorg. Chim. Acta,* 1972, **6,** 343.
456. J. Dwyer, W. Levason and C. A. McAuliffe, *J. Inorg. Nucl. Chem.*, 1976, **38,** 1919.
457. P. Barz and H. P. Fritz, *Z. Naturforsch., Teil B,* 1972, **27,** 1131.
458. W. E. Bull, J. A. Seaton and L. F. Audrieth, *J. Am. Chem. Soc.*, 1958, **80,** 2516.
459. A. J. Canty, N. Chaichit, B. M. Gatehouse and E. E. George, *Inorg. Chem.*, 1981, **20,** 4293.
460. J. L. Atwood, D. E. Berry, S. R. Stobart and M. J. Zaworotko, *Inorg. Chem.*, 1983, **22,** 3480.
461. D. Grdenić, B. Kamenar and A. Hergold-Brundic, *Cryst. Struct. Commun.*, 1978, **7,** 165.
462. D. Grdenić, B. Kamenar and A. Hergold-Brundic, *Croat. Chem. Acta,* 1979, **52,** 339.
463. J. Halfpenny, *Acta Crystallogr., Sect. B,* 1982, **38,** 2049.
464. M. R. Udupa and B. Krebs, *Inorg. Chim. Acta,* 1980, **40,** 161.
465. M. R. Burke and M. F. Richardson, *Inorg. Chim. Acta,* 1983, **69,** 29.
466. N. M. Blaton, O. M. Peeters and C. J. De Ranter, *Bull. Soc. Chim. Belg.*, 1983, **92,** 445.
467. M. Endrissi, *Microchem. J.*, 1982, **27,** 323.
468. A. T. Hutton and H. M. N. H. Irving, *J. Chem. Soc., Chem. Commun.*, 1979, 1113.
469. N. B. Behrens, B. A. Cartwright, D. M. L. Goodgame and A. C. Skapski, *Inorg. Chim. Acta,* 1978, **31,** L471.
470. P. Brooks and N. Davidson, *J. Am. Chem. Soc.*, 1960, **82,** 2118.
471. A. Cingolani, A. Lorenzotti, D. Leonesi and F. Bonati, *Inorg. Chim. Acta,* 1984, **81,** 127.
472. U. Behrens, K. Hoffmann and G. Klar, *Chem. Ber.*, 1977, **110,** 3672.
473. D. V. Sokols'ki, Y. A. Dorfman, I. A. Kazantsera and G. S. Uteyenova, *Zh. Fiz. Khim.*, 1970, **44,** 2263.
474. J. Grobe and R. Demuth, *Angew. Chem., Int. Ed. Engl.*, 1972, **11,** 1097.
475. M. Baudler and A. Zarkadas, *Chem. Ber.*, 1972, **105,** 3844.
476. P. L. Goggin, R. J. Goodfellow, S. R. Haddock and J. G. Eary, *J. Chem. Soc., Dalton Trans.*, 1972, 647.
477. H. Schmidbaur and K. H. Raethlein, *Chem. Ber.*, 1973, **106,** 2491.
478. N. A. Bell, M. Goldstein, T. Jones and I. W. Nowell, *J. Chem. Soc., Chem. Commun.*, 1976, 1039.
479. N. A. Bell, T. D. Dee, M. Goldstein and I. W. Nowell, *Inorg. Chim. Acta,* 1983, **70,** 215.
480. M. Camalli, F. Caruso and L. Zambonelli, *Acta Crystallogr., Sect. B,* 1982, **38,** 2468.
481. H. B. Buergi, E. Fischer, R. W. Kunz, M. Parvez and P. S. Pregosin, *Inorg. Chem.*, 1982, **21,** 1246.
482. N. A. Bell, T. D. Dee, P. L. Goggin, M. Goldstein, R. J. Goodfellow, T. Jones, K. Kessler, D. M. McEwan and I. W. Nowell, *J. Chem. Res. (S),* 1981, 2.
483. N. A. Bell, M. Goldstein, T. Jones and I. W. Nowell, *Inorg. Chim. Acta,* 1981, **48,** 185.
484. N. A. Bell, M. Goldstein, T. Jones and I. W. Nowell, *Inorg. Chim. Acta,* 1980, **43,** 87.
485. N. A. Bell, M. Goldstein, T. Jones and I. W. Nowell, *Acta Crystallogr., Sect. B,* 1980, **36,** 708.
486. C. Gagnon and A. L. Beauchamp, *Acta Crystallogr., Sect. B,* 1979, **35,** 166.
487. R. C. Makhija, R. Rivest and A. L. Beauchamp, *Can. J. Chem.*, 1979, **57,** 2555.
488. J. M. Epstein, J. C. Dewan, D. L. Kepert and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1974, 1949.
489. A. Ozola, J. Ozols and A. Ievins, *Latv. PSR Zinat. Akad. Vestis, Kim. Ser.*, 1972, 361 (*Chem. Abstr.*, 1972, **77,** 80 694g).
490. N. A. Bell, M. Goldstein, T. Jones and I. W. Nowell, *Inorg. Chim. Acta,* 1978, **28,** L169.
491. Z. M. El Saffer, *Acta Crystallogr., Sect. B,* 1973, **29,** 1732.
492. E. C. Alyea, S. A. Dias, G. Ferguson and M. Parvez, *Inorg. Chim. Acta,* 1979, **37,** 45.
493. E. C. Alyea, S. A. Dias, R. G. Goel and W. O. Ogini, *Can. J. Chem.*, 1977, **55,** 4227.
494. A. Yamasaki and E. Fluck, *Z. Anorg. Allg. Chem.*, 1973, **396,** 297.
495. T. Allman, R. G. Goel and P. Pilon, *Can. J. Chem.*, 1979, **57,** 91.
496. T. Allman and R. G. Goel, *Inorg. Nucl. Chem. Lett.*, 1979, **15,** 199.
497. E. C. Alyea and S. A. Dias, *Can. J. Chem.*, 1979, **57,** 83.
498. S. O. Grim, D. P. Shah, C. K. Haas, J. M. Ressner and P. H. Smith, *Inorg. Chim. Acta,* 1979, **36,** 139.
499. A. Müller, Z. Schimanski and U. Schimanski, *Angew. Chem.*, 1984, **96,** 158.
500. P. L. Goggin, R. J. Goodfellow, D. M. McEwan and K. Kessler, *Inorg. Chim. Acta,* 1980, **44,** L111.
501. R. Colton and D. Dakternieks, *Aust. J. Chem.*, 1980, **33,** 1463.
502. R. Colton and D. Dakternieks, *Aust. J. Chem.*, 1980, **33,** 1677.
503. R. Colton and D. Dakternieks, *Aust. J. Chem.*, 1981, **34,** 323.
504. P. K. S. Gupta, L. W. Houk, D. V. D. Helm and M. B. Hossain, *Inorg. Chim. Acta,* 1980, **44,** L235.
505. F. Seel and H. W. Heyer, *Z. Anorg. Allg. Chem.*, 1979, **456,** 217.
506. S. B. Naikar, N. Gowda, M. Nanje and G. K. N. Reddy, *Indian J. Chem., Sect. A,* 1981, **20,** 436.
507. S. Ahrland, T. Berg and P. Blaeuenstein, *Acta Chem. Scand., Ser. A,* 1978, **32,** 933.
508. P. J. Roberts, G. Ferguson, R. G. Goel, W. O. Ogini and R. J. Restivo, *J. Chem. Soc., Dalton Trans.*, 1978, 253.
509. E. C. Alyea, S. A. Dias, G. Ferguson, M. A. Khan and P. J. Roberts, *Inorg. Chem.*, 1979, **18,** 2433.

510. E. C. Alyea, S. A. Dias, G. Ferguson and M. A. Khan, *Can. J. Chem.*, 1979, **57**, 2217.
511. P. P. Winkler and P. Peringer, *Inorg. Chim. Acta*, 1983, **76**, L59.
512. G. G. Mather and A. Pidcock, *J. Chem. Soc., Dalton Trans.*, 1973, 560.
513. J. Eichbichler and P. Peringer, *Inorg. Chim. Acta*, 1980, **43**, 121.
514. P. C. Donohue, *J. Solid State Chem.*, 1973, **6**, 587.
515. R. C. Evans, F. G. Mann, H. S. Peiser and D. Purdue, *J. Chem. Soc.*, 1940, 1207.
516. G. B. Deacon and B. O. West, *J. Inorg. Nucl. Chem.*, 1962, **24**, 169.
517. M. M. Baig, W. R. Cullen and D. S. Dawson, *Can. J. Chem.*, 1962, **40**, 46.
518. W. J. C. Dyke, G. Davies and W. J. Jones, *J. Chem. Soc.*, 1931, 185.
519. W. J. Jones, W. J. C. Dyke, G. Davies, D. C. Griffiths and J. H. E. Webb, *J. Chem. Soc.*, 1932, 2284.
520. R. C. Cass, G. E. Coates and R. G. Hayter, *J. Chem. Soc.*, 1955, 4007.
521. F. Challenger and L. Ellis, *J. Chem. Soc.*, 1935, 396.
522. R. C. Makhija, A. L. Beauchamp and R. Rivest, *J. Chem. Soc., Chem. Commun.*, 1972, 1043.
523. S. C. Jain, *J. Inorg. Nucl. Chem.*, 1973, **35**, 413.
524. R. D. Gigauri and B. D. Chernok'alskii, *Soobshch. Akad. Nauk Gruz. SSSR*, 1979, **95**, 329.
525. R. D. Gigauri, E. S. Vachnadze, N. G. Natenadze and M. G. Talakvadze, *Soobshch. Akad. Nauk Gruz. SSSR*, 1983, **109**, 549.
526. G. B. Deacon and J. H. S. Green, *Spectrochim. Acta, Part A*, 1968, **24**, 959.
527. B. M. Gatehouse and A. J. Canty, *J. Chem. Soc. (D)*, 1971, 443.
528. G. Dyer, D. C. Goodall, R. H. B. Mais, H. M. Powell and L. M. Venanzi, *J. Chem. Soc. (A)*, 1966, 1110.
529. G. Deganello, G. Dolcetti, M. Guistiniani and U. Belluco, *J. Chem. Soc. (A)*, 1969, 2138.
530. G. J. Sutton, *Aust. J. Chem.*, 1959, **12**, 637.
531. J. Lewis, R. S. Nyholm and D. J. Phillips, *J. Chem. Soc.*, 1962, 2177.
532. K. Brodersen, R. Palmer and D. Breitinger, *Chem. Ber.*, 1971, **104**, 360.
533. W. Levason and C. A. McAuliffe, *J. Coord. Chem.*, 1974, **4**, 47.
534. K. A. Hooton, *Prep. Inorg. React.*, 1968, **4**, 85.
535. F. Glockling, 'The Chemistry of Germanium', Academic, New York, 1968, p. 171.
536. A. F. Clemmit and F. Glockling, *J. Chem. Soc.*, 1971, 1164.
537. U. Blaukat and W. P. Neumann, *J. Organomet. Chem.*, 1973, **63**, 27.
538. N. N. Greenwood and N. F. Travers, *Chem. Commun.*, 1967, 216.
539. N. N. Greenwood and D. N. Sharrocks, *J. Chem. Soc.*, 1969, 2334.
540. M. C. Baird, *Prog. Inorg. Chem.*, 1968, **9**, 1.
541. A. T. T. Hsieh and M. J. Mays, *MTO Int. Rev. Sci.: Inorg. Chem., Ser. One*, 1972, **6**, 43.
542. W. Hieber and W. Schropp, *Chem. Ber.*, 1960, **93**, 455.
543. R. S. Nyholm and K. Vrieze, *J. Chem. Soc.*, 1965, 5337.
544. A. J. Layton, R. S. Nyholm, G. A. Pneumaticakis and M. L. Tobe, *Chem. Ind. (London)*, 1967, 465.
545. D. J. Cook and R. D. W. Kemmit, *Chem. Ind. (London)*, 1966, 946.
546. D. J. Cook, J. L. Dawes and R. D. W. Kemmitt, *J. Chem. Soc.*, 1967, 1547.
547. I. W. Nowell and D. R. Russell, *J. Chem. Soc., Dalton Trans.*, 1972, 2393.
548. I. W. Nowell and D. R. Russell, *J. Chem. Soc., Dalton Trans.*, 1972, 2396.
549. M. Casey and A. R. Manning, *J. Chem. Soc.*, 1970, 2258.
550. M. Zöller and M. L. Ziegler, *Angew. Chem.*, 1976, **88**, 188.
551. D. Prochaska, Dissertation, University of Erlangen-Nürnberg, 1987.
552. E. C. Alyea, S. A. Dias, G. Ferguson and P. Y. Siew, *Can. J. Chem.*, 1983, **61**, 257.
553. R. Masse, J. C. Guitel and A. Durif, *J. Solid State Chem.*, 1978, **23**, 369.
554. D. Grdenić, M. Sikirica and I. Vickovic, *Acta Crystallogr., Sect. B*, 1977, **33**, 1630.
555. F. W. B. Einstein, C. H. W. Jones, I. Jones and R. D. Sharma, *Inorg. Chem.*, 1983, **22**, 3924.
556. Joel S. Miller (ed.), 'Extended Linear Chain Compounds', Plenum, New York, 1983, vol. 3.
557. Z. Tun, I. D. Brown and P. K. Ummat, *Acta Crystallogr., Sect. C*, 1984, **40**, 1301.
558. I. D. Brown, R. J. Gillespie, K. R. Morgan, Z. Tun and P. K. Ummat, *Inorg. Chem.*, 1984, **23**, 4506.
559. P. Lagrange, M. El Makrini and A. Herold, *Rev. Chim. Miner.*, 1983, **20**, 229.
560. R. J. Gillespie, P. Granger, K. R. Morgan and G. J. Schrobilgen, *Inorg. Chem.*, 1984, **23**, 887.
561. R. B. English, D. Röhm and C. J. H. Schutte, *Acta Crystallogr., Sect. C*, 1985, **41**, 997.
562. K. Brodersen, G. Liehr and G. Schottner, *Z. Anorg. Allg. Chem.*, 1985, **529**, 15.
563. K. Brodersen, G. Liehr, D. Prochaska and G. Schottner, *Z. Anorg. Allg. Chem.*, 1985, **521**, 215.
564. K. Brodersen, G. Liehr and G. Schottner, *Z. Anorg. Allg. Chem.*, 1985, **531**, 158.
565. C. Stalhandske, K. Aurivillius and G. I. Bertinsson, *Acta Crystallogr., Sect. C*, 1985, **41**, 167.
566. J. Martin-Frére and Y. Jeannin, *Inorg. Chem.*, 1984, **23**, 3394.
567. E. C. Constable, *Coord. Chem. Rev.*, 1985, **62**, 37.
568. A. Ben Salah, A. Daoud, J. L. Miane, J. Ravez and P. Hagenmuller, *Rev. Chim. Miner.*, 1984, **21**, 795.
569. M. Körfer, H. Fuess, J. W. Bats and G. Klebe, *Z. Anorg. Allg. Chem.*, 1985, **525**, 23.
570. A. Ben Salah, A. Daoud, J. L. Miane and J. Ravez, *Rev. Chim. Miner.*, 1984, **21**, 34.
571. I. M. Vezzosi, A. Benedetti, A. Albinati, F. Ganazzoli, F. Cariati and L. Pellicciari, *Inorg. Chim. Acta*, 1984, **90**, 1.
572. D. W. Allen, N. A. Bell, S. T. Fong, L. A. March and I. W. Nowell, *Inorg. Chim. Acta*, 1985, **99**, 157.
573. P. Peringer, P. P. Winkler, G. Huttner and L. Zsolnai, *J. Chem. Soc., Dalton Trans.*, 1985, 1061.
574. N. A. Bell, M. Goldstein, L. A. March and I. W. Nowell, *J. Chem. Soc., Dalton Trans.*, 1984, 1621.
575. D. Grdenić, B. Korpar-Colig and M. Sikirica, *J. Organomet. Chem.*, 1984, **276**, 1.
576. M. N. Ponnuswamy and J. Trotter, *Acta Crystallogr., Sect. C*, 1984, **40**, 1671.
577. C. R. Paige and M. F. Richardson, *Can. J. Chem.*, 1984, **62**, 332.
578. M. T. Averbuch-Pouchot, N. El-Horr and J. C. Guitel, *Acta Crystallogr., Sect. C*, 1984, **40**, 725.
579. B. Zacharie, J. D. Wuest, M. J. Olivier and A. L. Beauchamp, *Acta Crystallogr., Sect. C*, 1985, **41**, 369.
580. D. Altermatt, H. Arend, V. Gramlich, A. Niggli and W. Petter, *Acta Crystallogr., Sect. B*, 1984, **40**, 347.

581. G. Christou, K. Folting and J. C. Huffman, *Polyhedron*, 1984, **3**, 1247.
582. H. Martan and J. Weiss, *Z. Anorg. Allg. Chem.*, 1984, **515**, 225.
583. M. Lusser and P. Peringer, *Chem. Ber.*, 1985, **118**, 2140.
584. P. Peringer and M. Lusser, *Inorg. Chem.*, 1985, **24**, 109.
585. F. A. Cotton, S. A. Duraj and W. J. Roth, *Acta Crystallogr., Sect. C*, 1985, **41**, 881.
586. D. Dakternieks, *Inorg. Chim. Acta*, 1984, **89**, 209.
587. H. Puff, M. Grönke, B. Kilger and P. Möltgen, *Z. Anorg. Allg. Chem.*, 1984, **518**, 120.
588. R. C. Haushalter, *Angew. Chem.*, 1985, **97**, 414.
589. J. S. Field, R. J. Haines, E. Meintjies, B. Sigwarth and P. H. van Rooyen, *J. Organomet. Chem.*, 1984, **268**, C43.
590. M. P. Gómez-Sal, B. F. G. Johnson, J. Lewis, P. R. Raithby and S. N. A. B. Syed-Mustaffa, *J. Organomet. Chem.*, 1984, **272**, C21.
591. A. R. Sanger, *Inorg. Chim. Acta*, 1985, **99**, 95.
592. O. Rossell, M. Seco, I. Torra, X. Solans and M. Font-Altaba, *J. Organomet. Chem.*, 1984, **270**, C63.
593. M. N. Bochkarev, N. L. Ermolaev, L. N. Zakharov, Yu. N. Safyanov, G. A. Razevaey and Yu. T. Struchkov, *J. Organomet. Chem.*, 1984, **270**, 289.
594. T. C. W. Mak and Yuk-Kuen Wu, *Inorg. Chim. Acta*, 1985, **104**, 149.
595. T. C. W. Mak and Yuk-Kuen Wu, *Inorg. Chim. Acta*, 1986, **121**, L37.

51
Palladium

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51.1 INTRODUCTION

Palladium occurs in combination with platinum and is the second most abundant platinum group metal (pgm), accounting for 38% of pgm reserves. The USSR produces over 50% of the world's palladium, which is more than double that produced in South Africa. Two major sources of the metal are braggite, a mixed sulfide of platinum, palladium and nickel, which contains 16–20% palladium, and michenerite ($PdBi_3$).

Wollaston discovered palladium in 1802 in the course of refining platinum and since then it has found industrial usage. In 1984 demand for palladium was 3.1 million ounces compared with a supply of 2.9 million ounces. The major applications of the metal are in the electronics industry, where it is used as an alloy with silver as an electrical contact material or in palladium-bearing thick film pastes in miniature solid state devices and in integrated circuits. These applications account for 41% of the demand for the metal. Palladium also finds widespread use in dentistry as it is as inert as gold but considerably less expensive: this accounts for a further 31% of demand. Other applications of palladium are in automobile exhaust catalysts (11%) and jewellery (6%).

The metal exists as six naturally occurring isotopes: ^{102}Pd (0.8% relative abundance), ^{104}Pd (9.3%), ^{105}Pd (22.6%), ^{106}Pd (27.2%) ^{108}Pd (26.8%) and ^{110}Pd (13.5%). A list of the physical properties of the element are given in Table 1.

Table 1 Physical Properties of Palladium

Atomic number	46
Atomic weight	106.4
Crystal lattice	fcc
Cell constant *A* (nm)	0.389
Atomic radius (nm)	0.1375
Specific gravity ($g\,cm^{-3}$)	12.02
Melting point (°C)	1554
Specific heat at 0 °C ($J\,g^{-1}$)	0.244
Thermal conductivity ($W\,m^{-1}\,K^{-1}$)	75.3
Linear coefficient of thermal expansion ($°C^{-1}$)	11.1×10^{-6}
Electrical resistivity μ (ohm cm)	
at 0 °C	9.93
at 20 °C	9.96
Emf *vs.* Pr at 1000 °C (mv)	−11.491
Binding energy (eV)	3.91
Ionization potential (eV)	8.33
Work function (eV)	5.32
Tensile strength (annealed) (MPa)	165.5
Young's modulus of elasticity (GPa)	117.2
Pauling electronegativity	2.2
Hardness (annealed condition)	
Vicker's hardness number	41

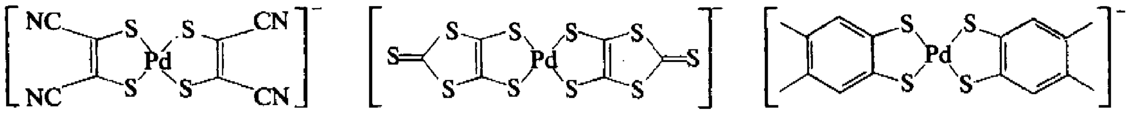
Palladium is one of the 4*d* transition elements and has the electronic configuration $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $3d^{10}$, $4s^2$, $4p^6$, $4d^{10}$ with a completely filled 4*d* shell which is quite easy to break. The most characteristic feature of its chemistry is its similarity with platinum, its 5*d* congener. It differs from platinum in that it is more reactive and this is reflected in the chemistry of the metal in various oxidation states. Palladium has a well-established chemistry in the 0, I, II and IV oxidation states. Palladium(IV) complexes are less stable than the corresponding platinum compounds and are readily reduced to palladium(II). Palladium(II) is the dominant oxidation state and usually the compounds are diamagnetic with low spin d^8. Pd^{II} is generally regarded as a class b (soft) metal and this is reflected in the rich chemistry with sulfur and phosphorus donor ligands (see Sections 51.8 and 51.9). However, palladium(II) will also complex with hard ligands such as oxygen and nitrogen (Sections 51.4 and 51.5). There is also an extensive organometallic chemistry of palladium(II), which has been dealt with in a companion volume.[2]

Palladium(I) complexes are in general dimeric or oligomeric and consequently, although they have a d^9 configuration, they are usually diamagnetic. The chemistry of this oxidation state is discussed in Section 51.3. Unlike most transition metals, the chemistry of low valent palladium is not dominated by carbonyls: $[Pd(CO)_4]$ is only stable at 80 K in a matrix. As with platinum, the most common complexes are those containing phosphines, where complexes of the type $[PdL_n]$ ($n = 2, 4$) have been isolated. The chemistry of palladium(0) is dealt with in Section 51.2 and elsewhere.[2]

Palladium(V) and palladium(III) complexes have also been reported. Two complexes of palladium(V) have been isolated: $(O_2)[PdF_6]$ and $Na[PdF_6]$. These were formed by the oxidation of PdF_4 in HF with KrF_2 in the presence of O_2 and NaF respectively.[3] The dioxygenyl salt may also be prepared by the reaction of palladium powder with an F_2/O_2 mixture at 320 °C and 60 000 psi. The Raman spectrum of $[PdF_6]^-$ is comparable with other MF_6 ions, showing bands for ν_1, ν_2 and ν_3 at 643, 570 and 268 cm^{-1}.

Compounds of palladium(III) are also extremely rare. PdF_3 and $[PdX_3(amine)]$ do not have a

d^7 configuration but have been shown to consist of two metals, one divalent and one tetravalent. However, palladium(III) dithiolene complexes have been prepared by the oxidation of the corresponding divalent dithiolene compound and the EPR spectrum has been reported in liquid or frozen solution.[5,6] For complexes (**1**)–(**3**) the single crystal EPR spectra have been studied.[5,6] These show an intense line due to those palladium isotopes without a nuclear spin and a hyperfine sextet resulting from the interaction of the unpaired electron with ^{105}Pd ($I = \frac{5}{2}$). It is perhaps worth emphasizing that dithiolene ligands are known to form complexes where the oxidation state of the transition metal is unusual.[7,8]



(**1**) (**2**) (**3**)

Further details of common palladium precursors and general palladium chemistry may be found in refs. 2 and 9–12.

51.2 COORDINATION COMPLEXES OF PALLADIUM(0)

51.2.1 Introduction

Palladium(0) compounds have a d^{10} configuration and unlike most transition metals this oxidation state is dominated by phosphine complexes rather than carbonyls. In fact binary carbonyl complexes with palladium are unstable at room temperature. The highest coordination number known for Pd^0 is four and $[PdL_4]$ complexes adopt a square planar structure. Dissociation of ligands from $[PdL_4]$ occurs readily to generate the 16- and 14-electron species $[PdL_3]$ and $[PdL_2]$: these are trigonal planar and linear respectively. Another notable feature of Pd^0 is that facile oxidation to d^8 Pd^{II} occurs.

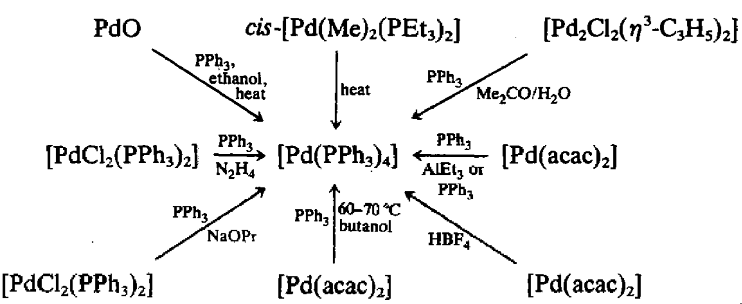
A review on the organometallic complexes of palladium(0) has been published recently in a companion volume[13] and here we restrict ourselves to considering areas of particular interest to coordination chemists.

51.2.2 Phosphine and Phosphite Complexes of Palladium(0)

These are readily prepared by the reduction of palladium(II) compounds in the presence of excess phosphines (equation 1). Typical reducing agents include copper,[14] hydrazine,[15] borohydride,[16] propoxide[17] ions and alkylaluminum compounds.[18,19] The palladium precursors may be simple salts such as $PdCl_2$ or PdO,[14] complexes such as $[PdCl_2L_2]$[15] (*e.g.* $L = PPh_3$) or β-diketonate compounds.[20] The latter complexes undergo facile reduction and a range of organic reducing agents which contain an activated hydrogen have been employed.[21]

$$Pd^{II} \xrightarrow[\text{ii, phosphine}]{\text{i, reductant}} [PdP_4] \qquad (1)$$

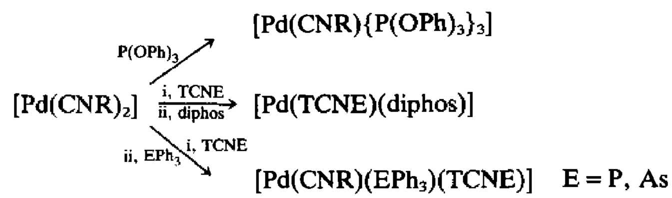
A range of methods for the preparation of $[Pd(PPh_3)_4]$ are exemplified in Scheme 1. Triphenylphosphine has been the most widely employed phosphine;[14] however, complexes incorporating PF_3,[14] phosphites[22] and arsines and stibines[23] have been prepared in similar fashion.



Scheme 1

The lability of the ligands in $[PdL_n]$ is a convenient tool which has been used in the synthesis of mixed ligand complexes (see Scheme 2).[21,24,25]

$$[Pd(PPh_3)_4] + 2SbPh_3 \longrightarrow [Pd(PPh_3)_2(SbPh_3)_2]$$



Scheme 2

A novel method of preparing palladium(0) mixed phosphine complexes was reported by Fahey (equation 2).[26]

$$trans\text{-}[PdBr(Ph)(PEt_3)_2] + LiPPh_2 \longrightarrow [Pd(PPh_3)(PEt_3)_2] \quad (2)$$

$[PdL_3]$ complexes have been prepared by reaction (3).[27–29]

$$[Pd_2Cl_2(\eta^3\text{-}C_3H_5)_2] + 6L \xrightarrow{PhCH_2NH_2} [PdL_3] \quad (3)$$

$$L = PPh_3, P(OPh)_3, P(4\text{-}ClC_6H_4)_3, P(4\text{-}MeC_6H_4)_3$$

The monomeric 14-electron complexes $[PdL_2]$ have only been isolated where L is extremely bulky, *e.g.* PBu^t_3, $P(C_6H_{11})_3$, PBu^t_2Ph.[30]

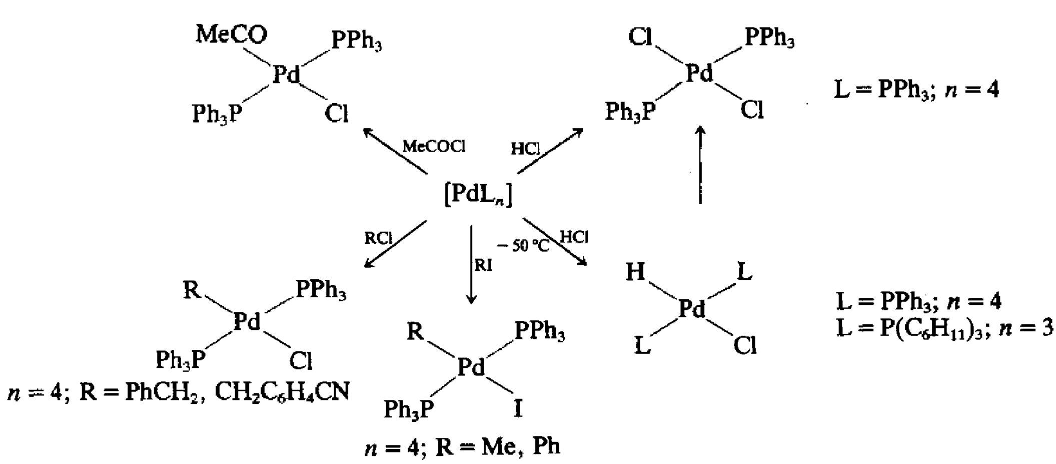
Confirmation that the equilibria (4) and (5) are dependent on the steric bulk and basicity of the phosphine has come from ^{31}P NMR studies.[31,32]

$$[PdL_4] \rightleftharpoons [PdL_3] + L \quad (4)$$

$$[PdL_3] \rightleftharpoons [PdL_2] + L \quad (5)$$

The structures of the complexes $[PdL_2]$ ($L = P(C_6H_{11})_3$, PBu^t_2Ph) have been confirmed by X-ray studies on single crystals.[33,34] Although these compounds both exhibit C_2 symmetry, the tricyclohexylphosphine complex is bent (P—Pd—P = 158°), whereas the di-*t*-butylphenylphosphine complex is linear (P—Pd—P = 170°). An adequate explanation of these differences has not been made; however, they are not due to packing effects.

Palladium(0) complexes undergo oxidative addition to form Pd^{II} d^8 complexes readily. They form hydrido, chloro or dichloro species with HCl[14,24,35] and also react with alkyl and aryl halides.[36–52] These reactions are exemplified in Scheme 3.



Scheme 3

The oxidative reactions of palladium(0) compounds with a range of organic compounds are described in ref. 13.

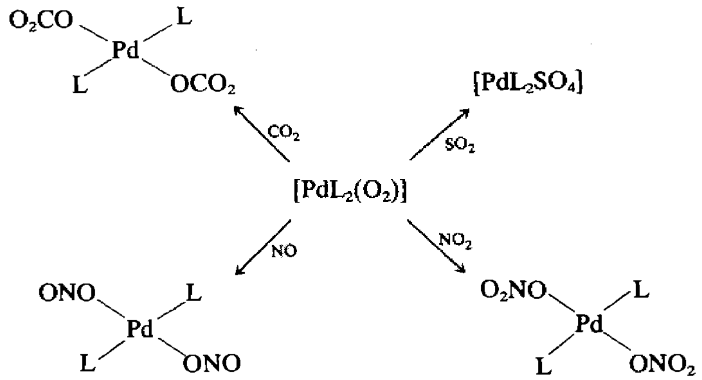
A range of main group organometallic compounds such as $Cd(GePh_3)_2$, $Ph_3PbPbPh_3$ and $Hg\{Ge(C_6F_5)_3\}_2$ have been shown to react with $[Pd(PPh_3)_4]$ to form Pd^{II} compounds which contain Pd—M bonds.[53,54]

The azide complex $[Pd(N_3)_2(PPh_3)_2]$ has been prepared from the reaction of $[Pd(PPh_3)_4]$ with RN_3 (R = Me, Et)[55] and an isonitrile dichloro compound has been isolated from reaction (6).

$$RNCCl_2 + [Pd(PPh_3)_4] \longrightarrow [PdCl_2(CNR)(PPh_3)]^{56} \quad (6)$$

The dimeric complex $[Pd_2(dppm)_3]$ has been shown to react with iodine or pentafluorophenyl disulfide to form palladium(I) adducts $[Pd_2(dppm)_2X_2]$ (X = I, SC_6F_5). Further reaction with oxidant gave the d^8 species $[Pd(dppm)X_2]$.[57] $[PdL_4]$ species are known to react with small molecules such as NO, SO_2, CS_2[58] and O_2[59,60] to form $[PdL_2L']$.

The complexes $[PdL_2(O_2)]$ are active oxidizing agents and oxidize CO_2,[59–61] SO_2, NO_2[62,63] and NO[58] (see Scheme 4). The rate of oxidation increases in the order $L = PPh_3 < C_6H_{11}NC < PBu_3$.[64]



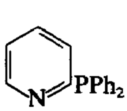
Scheme 4

51.3 PALLADIUM(I) COMPLEXES AND CLUSTERS

51.3.1 Introduction

In 1971 only two complexes of palladium(I) had been identified.[65] Although the area has grown significantly, the relative paucity of palladium cluster compounds can be attributed, in part, to the surprising weakness of palladium–carbon monoxide bonds and in particular those where CO is bound terminally. In this chapter the chemistry of palladium(I) and clusters of palladium in other oxidation states will be considered. However, complexes containing organic ligands such as allyl and cyclopentadienyl will not be dealt with as this area has been reviewed recently in a companion volume.[66]

Palladium(I) complexes should be paramagnetic, having a d^9 configuration; generally, however, those characterized complexes are diamagnetic and multinuclear. Over the past eight years an extensive chemistry of palladium dimers containing bidentate ligands with a small bite angle, such as $Ph_2P(CH_2)PPh_2$ and, more recently, diphenylphosphinopyridine (4), has been developed.



(4)

51.3.2 Dinuclear Complexes

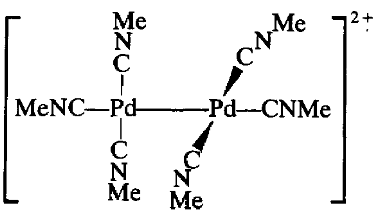
51.3.2.1 Isonitrile complexes

The first reported palladium(I) isonitrile complex was $[Pd_2Cl_2(Bu^tNC)_4]$.[67] More recently this compound has been prepared in high yield by reaction (7).[68]

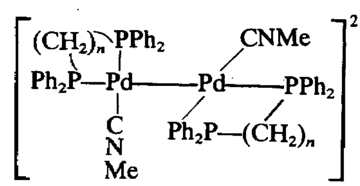
$$[Pd_2(dba)_4] + 2[PdCl_2(PhCN)_2] + 8Bu^tNC \longrightarrow 2[Pd_2Cl_2(Bu^tNC)_4] + 4dba + 4PhCN \quad (7)$$

dba = dibenzylideneacetone (1,5-diphenyl-1,4-pentadien-3-one)

The related compound $[Pd_2(CNMe)_6]^{2+}(PF_6^-)_2$ has been prepared from the reaction of $Na_2[PdCl_4]$ with MeNC followed by treatment with NH_4PF_6. Equivalent conductance measurements have shown the species to be dimeric and the IR spectrum indicated the presence of terminal and not bridging isocyanide ligands.[69] A single crystal X-ray determination has shown this complex to have the structure (**5**) with a palladium–palladium bond of 2.5310(9) Å and in which the isocyanide ligands adopt a staggered configuration.[69,70] While the ^1H NMR spectrum of this compound in acetone-d^6 was consistent with the solid state structure at −30 °C, at higher temperatures the two methyl signals coalesced and this fluxionality was later rationalized in terms of an exchange mechanism similar to that for $[Pd_2\{Ph_2P(CH_2)PPh_2\}_2(CNR)_2](PF_6)_2$.

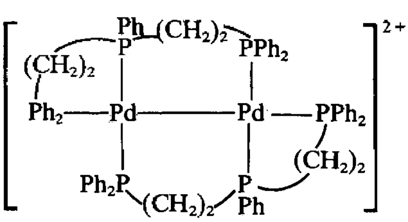


(**5**)

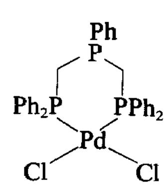


(**6**)

$[Pd_2\{Ph_2P(CH_2)_nPPh_2\}_2(CNMe)_2](PF_6)_2$ has been prepared from the reaction of $[Pd_2(CNMe)_6](PF_6)_2$ with $Ph_2P(CH_2)_nPPh_2$ (n = 2, 3 or 4). The structure (**6**) is consistent with the ^1H and ^{31}P NMR and IR characterization studies. This compound is fluxional and its behaviour has been rationalized in terms of a transient polarization of the Pd—Pd bond to give Pd^0—Pd^{II} intermediates. The pseudotetrahedral geometry created at Pd^0 permits the two ends of the phosphine to become equivalent and reversion to planar geometry permits the interchange of axial and equatorial sites. A complex $[Pd_2\{Ph_2P(CH_2)_2PPh(CH_2)_2PPh_2\}_2](PF_6)_2$ (**7**) has been prepared from the reaction of $[Pd_2(CNMe)_6](PF_6)_2$ with triphos.[71] However, attempts to prepare palladium(I) complexes from the reaction of $[PdCl_2(PhCN)_2]$ with bis(diphenylphosphinomethyl)phenylphosphine resulted in the formation of (**8**).[72]



(**7**)



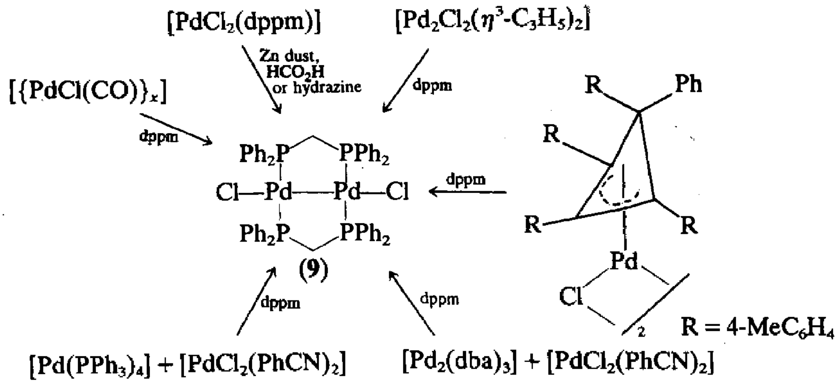
(**8**)

The Pd—Pd bond can be cleaved using UV light. UV irradiation of a frozen solution of (**5**) in an EPR cavity indicated the presence of a metal-based radical with g = 2.12. Irradiation of a solution of (**5**) in CX_4 (X = Cl, Br) gave $[Pd^{II}X(CNMe)_3]PF_6$ and with $[Pt_2(CNMe_6)](PF_6)_2$ present the heterobimetallic complex $[PdPt(CNMe)_6](PF_6)_2$ was observed.[73]

51.3.2.2 Phosphine complexes

$[Pd_2Cl_2(\mu\text{-dppm}_2)]$ (**9**) has been synthesized by the reduction of $[PdCl_2(dppm)]$, from $[Pd_2Cl_2(\eta^3\text{-}C_3H_5)_2]$,[74] from a cyclobutenyl derivative,[75] from $[Pd_2(dba)_3]$ or $[Pd(PPh_3)_4]$ and $[PdCl_2(PhCN)_2]$,[74,76,77] and from $[\{PdCl(CO)\}_x]$ (see Scheme 5).[78]

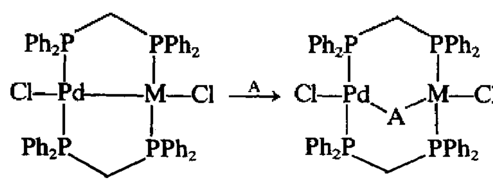
The heterobinuclear complex $[PdPtCl_2(\mu\text{-dppm})_2]$ can also be prepared by treating the product from the reaction of dppm and $[Pd(PPh_3)_4]$ with $[PtCl_2(NCBu^t)_2]$.[76] The corresponding bromide, iodide and thiocyanate dipalladium and palladium–platinum complexes have been prepared by metathesis of the dichloride (**9**) with NaX.[76]



dba = PhCH=CHCOCHPh

Scheme 5

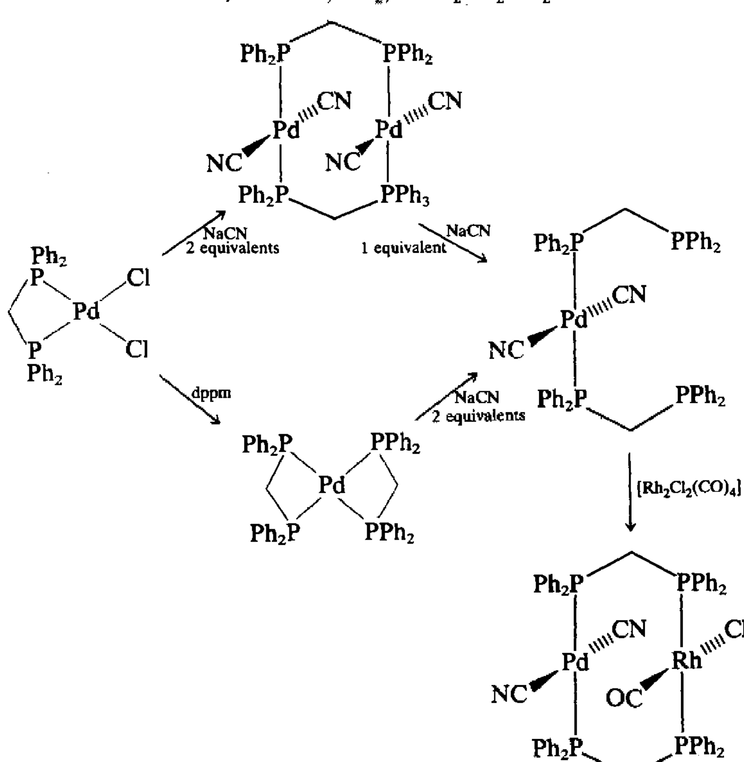
For both the dipalladium and palladium–platinum complexes the metal–metal bond is unusually reactive and a number of small molecules undergo an insertion reaction with (**9**) to give (**10**; equation 8). The corresponding sulfide-bridged dipalladium dimer can be prepared from the reaction of S_8 or $MeCHCH_2S$ with (**9**).[83] A mixed rhodium–palladium dimer can also be prepared from (**9**) (see Scheme 6).[84]



(**9**) (**10**) (8)

M = Pt; A = CO, CS_2, SO_2, $MeO_2CC_2CO_2Me$[74,76]

M = Pd; A = CO, SO_2, $MeO_2CC_2CO_2Me$[79–82]



Scheme 6

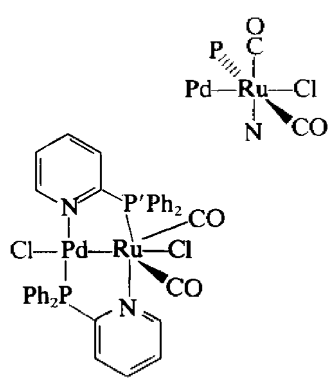
Table 2 Pd—Pd Bond Lengths in Palladium(I) dppm Complexes

Complex	*Pd—Pd bond length* (Å)	*Refs.*
$[Pd_2Br_2(dppm)_2]$	2.699	78
$[Pd_2Cl_2(dppm)_2]$	2.652	85
$[Pd_2Cl_2(dppm)_2S]$	3.258(2)	79
$[Pd_2Cl(dppm)_2(SO_2)]$	3.383(4)	79
$[Pd_2\{\mu\text{-}C_2(CO_2Me)_2\}Cl_2(dppm)_2]$	3.492(1)	83
$[Pd(\mu\text{-}CO)Br_2(dam)_2]$	3.274	86
$[Pd_2Co_2Cl_2(CO)_7(dppm)_2]$	2.586	87

The structural determinations on a number of these palladium dppm dimers have been carried out and the palladium–palladium bond lengths are summarized in Table 2.

Diphenylphosphinopyridine has been used in the synthesis of a range of hetero- and homo-metallic dimers of palladium(I) (see Scheme 7).[88–91] These compounds have been extensively characterized by NMR and IR spectroscopy.

A structural determination on (**11**; Scheme 7) showed an Rh—Pd bond length of 2.594 Å, which is indicative of a metal–metal bond.[88,91] One of the ruthenium–palladium complexes has been isolated and shown to have the structure (**12a**), where the palladium–ruthenium bond length is 2.66 Å and the P′RuPd angle is 74.7°.[90]

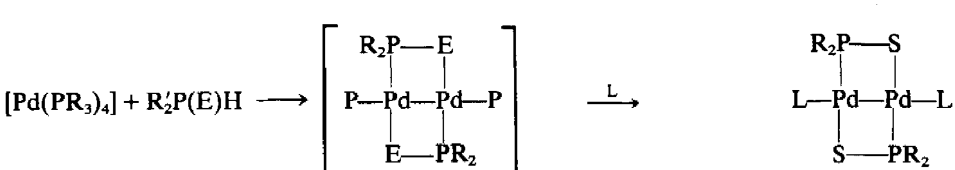


(**12a**)

The Pd—Pd bond in (**13**; Scheme 7) is not as reactive as in the dppm complexes. This compound is carbonylated to give terminally bound CO groups as shown by IR spectroscopy. As would be predicted, the CO is bound weakly and attempts to isolate the product resulted in recovery of starting materials.[89] The metal–metal bond is also preserved on reacting (**13**) with MeNC. The product $[Pd_2(CNMe)_4(PPh_2py)_2](PF_6)_2$ is believed to have uncoordinated pyridine from the similarity of its spectra with those of the corresponding PPh_3 compounds. The lack of reactivity of Pd—Pd in (**13**) has been ascribed to the inflexibility of the ligand and the ease of replacement of the pyridine nitrogen.[89] ^{31}P NMR data on selected diphenylphosphinopyridine complexes are given in Table 3.

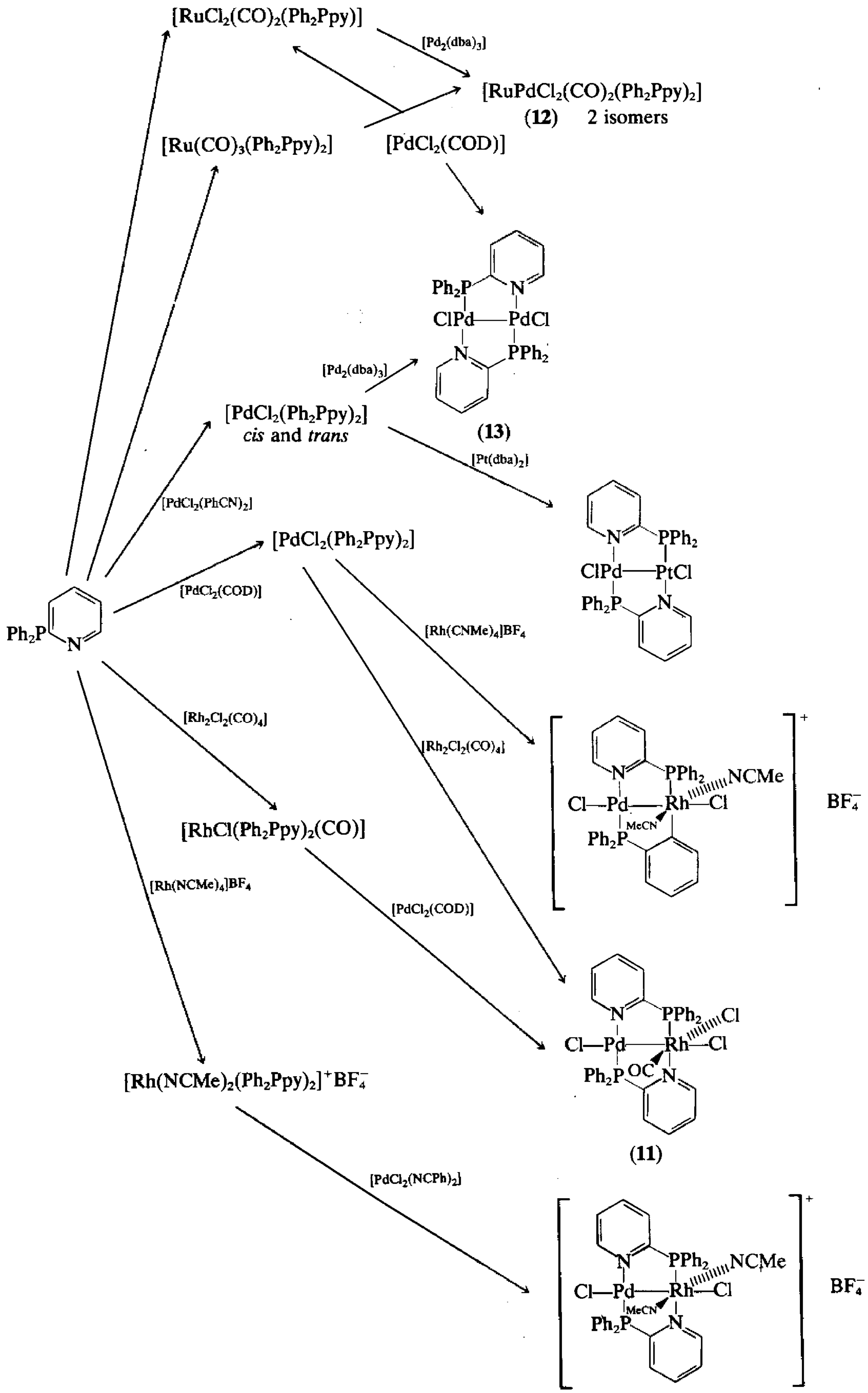
Mixed metal dimers have also been prepared from *trans*-$[MCl_2L_2]$ species (see Scheme 8).[87,92–94]

Pd—Pd bonds have also been observed in thiophosphide complexes as illustrated below. A crystallographic study of (**14**; equation 9; L = MeNC) confirmed the structure with Pd—Pd 2.608 Å.[95,96]



(9)

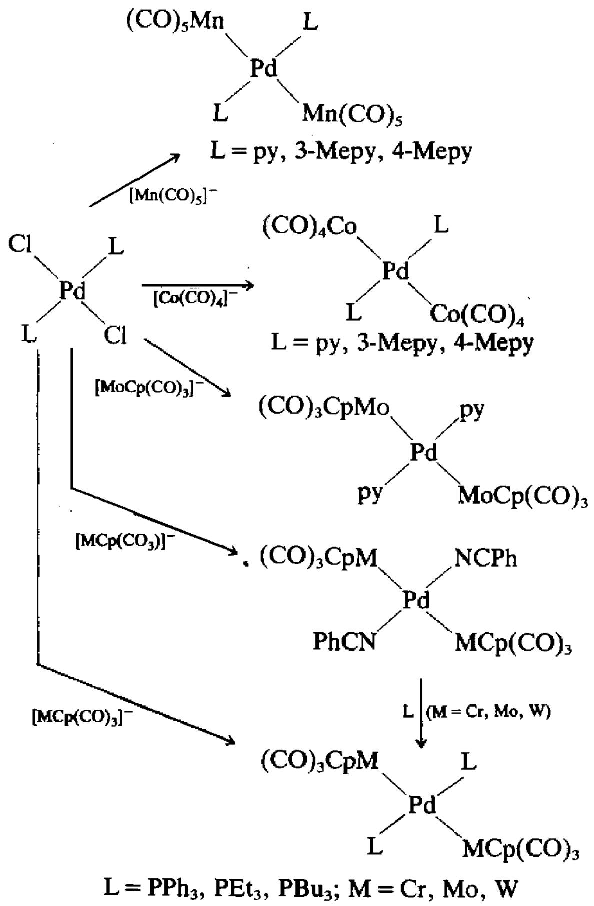
R, R′ = alkyl, phenyl; E = S, Se (**14**) R = Et, Ph; L = $P(OPh_3)_3$, $PPh(OPh)_2$, MeNC, Bu^tNC, dppm


[RuCl2(CO)2(Ph2Ppy)]
[Pd2(dba)3]
[RuPdCl2(CO)2(Ph2Ppy)2]
(12) 2 isomers
[Ru(CO)3(Ph2Ppy)2]
[PdCl2(COD)]
Ph2P
N
ClPd
PdCl
PPh2
(13)
[Pd2(dba)3]
[PdCl2(Ph2Ppy)2]
cis and trans
[Pt(dba)2]
PtCl
[PdCl2(PhCN)2]
[PdCl2(Ph2Ppy)2]
[PdCl2(COD)]
[Rh(CNMe)4]BF4
NCMe
Cl—Pd
Rh—Cl
MeCN
BF4−
[Rh2Cl2(CO)4]
[Rh2Cl2(CO)4]
[RhCl(Ph2Ppy)2(CO)]
[Rh(NCMe)4]BF4
[PdCl2(COD)]
OC
(11)
[Rh(NCMe)2(Ph2Ppy)2]+BF4−
[PdCl2(NCPh)2]

Scheme 7

Table 3 ^{31}P NMR Data on Selected Diphenylphosphinopyridine Complexes

	δ (p.p.m.)	$J'(Rh-P)$ (Hz)	$J(P-P)$ (Hz)
HT [$RhPdCl_3(CO)(\mu\text{-}PPh_2py)$]	21.9, 16.2	112.7 (2.3)	17.4
HT [$RhPdBr_3(CO)(\mu\text{-}PPh_2py)$]	19.6, 14.3	112.0 (2.9)	17.3
HT [$RhPdCl_2(CNMe)_2(\mu\text{-}PPh_2py)$]$PF_6$	26.9, 17.5	108.9 (1.6)	
HH [$RhPdCl_2(CNMe)_2(\mu\text{-}PPh_2py)$]$BPh_4$	7.9	94.2	
HT [$RhPdCl_2(CNMe)_2(\mu\text{-}PPh_2py)$]$BPh_4$	27.6	109.3	17.1
[$Pd_2Cl_2(\mu\text{-}PPh_2py)_2$]	23.8, 29.3		
[$Pd(CNMe)_4(PPh_2py)_2$]$(PF_6)_2$	11.8		

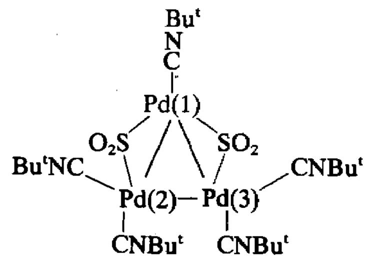


Scheme 8

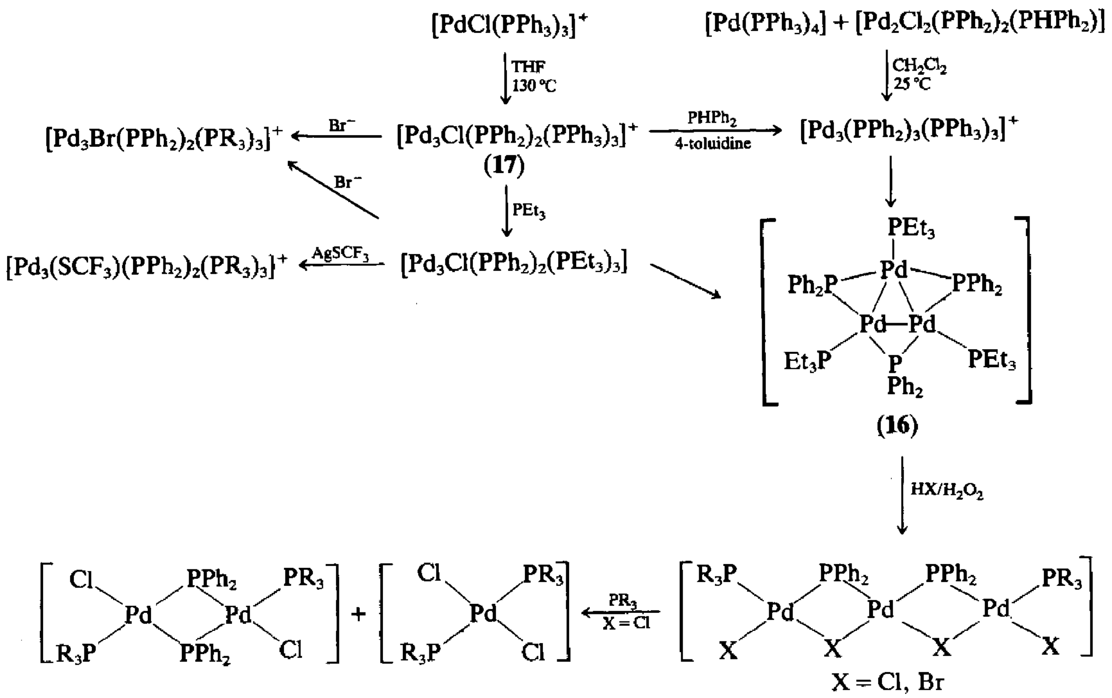
51.3.3 Trinuclear and Tetranuclear Clusters

There are few characterized Pd_3 or Pd_4 clusters; however, the structures of the compounds isolated embody a variety of geometries. The most common structure encountered for Pd_3 species is a *triangulo* arrangement. Otsuka *et al.* have described the synthesis of the sulfur dioxide-bridged complex [$Pd_3(SO_2)_2(Bu^tNC)_5$]·$2C_6H_6$ from the reaction of [$Pd(Bu^tNC)_2$] with SO_2. The compound was originally formulated as a dimer;[97] however, a crystallographic study has shown it to be a *triangulo* species **(15)** with Pd(1)—Pd(2) and Pd(1)—Pd(3) bond distances of 2.734 Å and Pd(2)—Pd(3) 2.760 Å.[98]

Triangulo diphenylphosphido species have been generated and these are illustrated in Scheme 9.[99] The structure of **(16)** has been confirmed crystallographically; the metal–metal bond lengths are 2.90 Å.[100] The complex [$Pd_3Cl_2(PPh_2)_2(PPh_3)_3$], originally prepared by Coulson,[101] has been reformulated as **(17)**, where the metal–metal distances are virtually identical with **(16)**.[102]



(15)

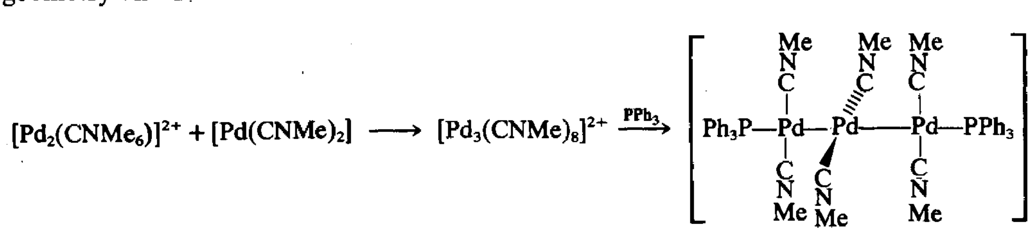


cations as BF_4 salts

Scheme 9

Although binary palladium carbonyls have yet to be isolated, phosphine-stabilized systems do exist. Thus $[Pd_3(CO)_x(PPh_3)_y]$ ($x = 1$, $y = 3$; $x = 3$, $y = 3$, 4) has been prepared by the reaction of $[Pd(acac)_2]$ with CO in the presence of triphenylphosphine and triethylaluminum[103,104] or by the carbonylation of $[PdCl_2(PPh_3)_3]$ in methanol containing amines.[105] $[Pd_3(CO)_3(PPh_3)_3]$ loses triphenylphosphine at 500 atm of CO to form $[Pd_3(CO)_3(PPh_3)]$.[106]

Balch *et al.* have described the preparation of (**18**; equation 10).[107] This unusual cluster contains a linear array of palladium atoms, each palladium atom having a square planar geometry and Pd—Pd 2.592 Å.



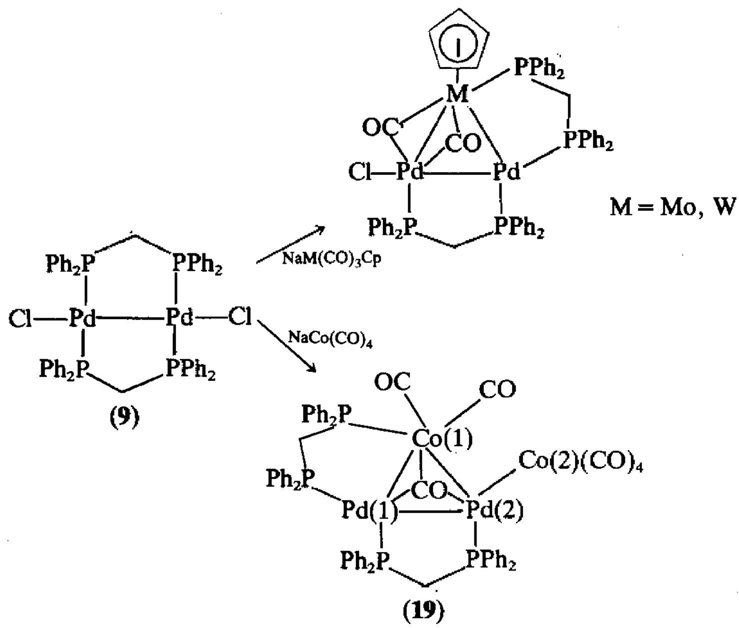
(10)

(18)

While palladium acetate exists as a trimer with acetate bridges in both solution and the solid state, the metal–metal distance is too long to invoke a Pd—Pd bond.[108,109]

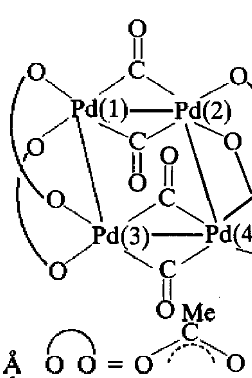
The reaction of $[Pd_2Cl_2(dppm)_2]$ (**9**) with metalloanions yields trimers and tetramers (see

Scheme 10).[87] The structural determination of (**19**) revealed the following bond lengths: Pd—Pd 2.586(1) Å, Pd(2)—Co(2) 2.729 Å, Pd(1)—Co(1) 2.511(1) Å.



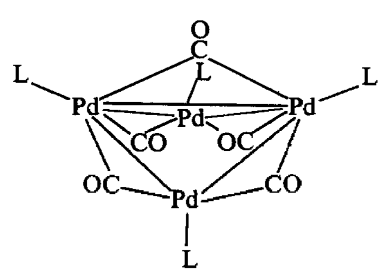
Scheme 10

While palladium carboxylates generally decompose in a CO atmoshere to give metal, the compounds $[Pd(O_2CR)(CO)] \cdot nRCO_2H$ ($n = 0$, 0.5; R = Me, CD_3, Et or Ph) have been prepared from the corresponding Pd^{II} acetate in carboxylic acid–benzene solution. A crystallographic study on the acetate complex showed it to have the tetrameric structure (**20**).[110] The compound consists of two dimeric palladium(I) units linked by acetate bridges.



Pd(1)—Pd(2) 2.663 Å
Pd(1)—Pd(3) 2.909 Å

(**20**)



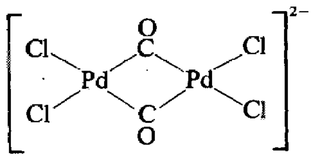
(**21**)

A Pd_4 species has been isolated from the reaction of CO with $[Pd(NO_2)_2L_2]$ (L = PPh_3, PPh_2Me, $PPhMe_2$). The complex has been shown to have the *nido* structure (**21**) with Pd—Pd (bonded) 2.750 Å and Pd—Pd (non-bonded) 3.365 Å.[111]

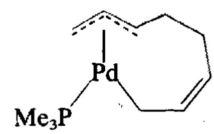
51.3.4 High Nuclearity Clusters

A number of reports of high nuclearity palladium clusters have been made in recent years.

Palladium halocarbonyl clusters of unspecified nuclearity $[PdX(CO)]_n$ (X = Cl, Br) have been prepared by several groups of workers through the carbonylation of $[PdCl_2(MeCN)_2]$ or PdX_2 (X = Cl, Br).[112–114] These decompose in solution to give Pd^{II} and Pd^0. When $Na_2[PdCl_4]$ was used as a precursor, then an anionic palladium(II) dimer (**22**) resulted.[113]



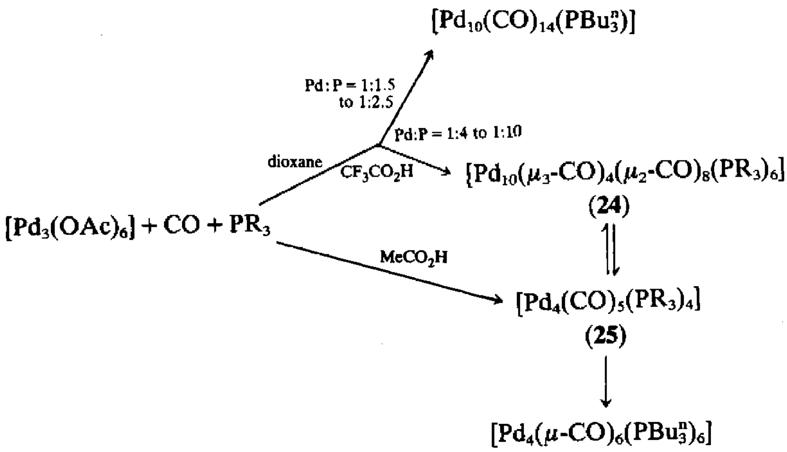
(22)



(23)

$[Pd_7(CO)_7(PMe_3)_7]$ has been isolated from the reaction of **(23)** with CO.[115] This cluster has a monocapped octahedral structure with one phosphine attached to each Pd atom. Four of the carbonyl ligands bridge the octahedral faces, while the other carbonyls edge bridge (Pd—Pd 2.79(2) Å).

A number of clusters have been prepared from $[Pd_3(OAc)_6]$ as indicated in Scheme 11.[116,117] The structural determination of **(24)** ($R = Bu^n$) has been carried out. The molecule consists of a Pd_6 octahedron with four Pd atoms unsymmetrically centred on non-adjacent faces (Pd_{oct}—Pd_{capped} 2.709 Å; Pd_{oct}—Pd_{oct} 2.825 Å; Pd_{apical}—Pd_{capped} 3.300–3.422 Å). The Pd_4 cluster **(25)** is tetrahedral with symmetrically bridging CO ligands (Pd—Pd 2.778–2.817 Å).



Scheme 11

High nuclearity Fe—Cd clusters have been prepared from the reaction of iron cluster anions with palladium salts (see Scheme 12).[118] Complex **(26)** has an unusual structure: the metal framework consists of a trigonal antiprismatic array of six Pd atoms where the six Fe atoms cap the lateral faces: 12 of the carbonyls are terminally bound to Fe (two per atom), six bridge the Fe—Pd bonds and six triply bridge the $FePd_2$ triangles. It is interesting to note that each Pd is bound to three different CO groups and the Pd—C bonds are shorter than in the Fe_4Pd cluster **(27)**. There are two Fe—Pd bond lengths (2.698 and 2.609 Å) and two Pd—Pd bond lengths (2.810 and 2.948 Å). The formation of these Pd_6Fe_6 species has been rationalized in terms of loss of CO terminally bound to Pd from the hypothetical Pd_3Fe_3 species **(28)** to give $[Fe_3Pd_3(CO)_{12}]^{2-}$. Subsequent condensation of two clusters in a staggered conformation along the C_3 axis would result in formation of the Fe_6Pd_6 cluster.[118]

$$[TMBA]_2[Fe_3(CO)_{11}] \xrightarrow[[PdCl_2(PhCN)_2],\ [PdCl_2(SEt_2)_2]]{PdCl_2,\ K_2[PdCl_4],} [Fe_4Pd(CO)_{16}]^{2-}$$

(27)

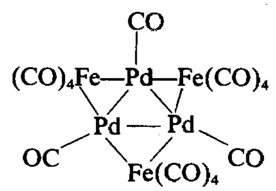
$$[TMBA]_2[Fe_4(CO)_{13}] \xrightarrow[THF]{K_2[PdCl_4]} [TMBA]_4[Fe_6Pd_6(CO)_{24}] + [TMBA]_3[Fe_6Pd_6(CO)_{24}H]$$

(26)

$$[Fe_6Pd_6(CO)_{24}H]^{3-} \underset{MeCN}{\overset{Me_2SO}{\rightleftharpoons}} [Fe_6Pd_6(CO)_{24}]^{4-} + H^+$$

$$TMBA = PhCH_2NMe_3^+$$

Scheme 12



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51.4 PALLADIUM(II): OXYGEN DONOR COMPLEXES

51.4.1 Introduction

Palladium(II), as a soft metal ion, does not form strong bonds with oxygen donors and therefore complexes with unidentate ligands readily undergo substitution reactions. The chelate effect leads to a greater number of stable complexes for bidentate ligands. Oxygen donors can also be stabilized by incorporation in a bidentate ligand with other more strongly binding atoms such as nitrogen or sulfur.

51.4.2 Palladium(II) Complexes of Oxygen-containing Solvents

Oxygen-containing solvents such as water, alcohols or ethers are such poor donors that few complexes with palladium(II) have been isolated. The most important class of complexes of this type consists of those containing water, which are formed as intermediates in the substitution reactions of palladium(II) when carried out in aqueous solution. In these reactions their formation is in competition with the second order reaction of the complex with the incoming ligand. The aqua complexes can also be formed by reaction of halo complexes with silver salts (*e.g.* NO_3, ClO_4, BF_4) in water. These complexes are acidic, being in equilibrium with hydroxo complexes in neutral or basic media.

Reaction of halo complexes with silver perchlorate or tetrafluoroborate (equation 11) has been used in the preparation of a number of complexes $[Pd(dppe)S_2]Y_2$.[119,120] Products have been isolated with acetone, water and O-bonded DMSO. With methanol or THF attempts to isolate the complexes yield only $[PdY_2(dppe)]$, while with ethanol attempted isolation results in the formation of Pd metal. Dimethyl sulfoxide normally shows the expected preference of palladium(II) for metal–sulfur bonding; however, steric effects can alter this preference leading to metal–oxygen bonding, for example $[Pd(DMSO)_4]$ exists as *cis*-$[Pd(DMSO)_2(DM\mathit{S}O)_2]^{2+}$. As the alkyl groups become bulkier, the *trans* isomer is preferred (*e.g.* *trans*-$[Pd(Bu^n_2S\mathit{O})_2(Bu^n\mathit{S}O)_2]^{2+}$) and finally all ligands become oxygen-bound, *e.g.* $[Pd\{(i\text{-}C_5H_{11})_2S\mathit{O}\}_4]$.[121–123] While the complexes $[Pd(dppe)(DMS\mathit{O})_2]Y_2$ are stable in solution and in the solid state, the mono-DMSO complexes are not. The palladium–oxygen bond is very labile and in CH_2Cl_2/DMSO solution the DMSO ligand readily reduces to dimethyl sulfide (Scheme 13).[124]

$$[PdCl_2(dppe)] + 2AgY \xrightarrow{S} [Pd(dppe)S_2]Y_2 \qquad (11)$$

$$S = \text{solvent};\ Y = ClO_4 \text{ or } BF_4$$

$$[\{PdCl(dppe)\}_2]Y_2 + 2DMSO \rightleftharpoons 2[PdCl(dppe)(DMSO)]Y \longrightarrow$$
$$[PdCl(dppe)(SMe_2)]Y \longrightarrow [\{PdCl(dppe)\}_2]Y_2 + 2SMe_2$$

Scheme 13

51.4.3 Palladium(II) Complexes Containing Simple Oxyanions

Hydroxo complexes are in equilibrium with aqua complexes in water, as indicated above, but they have rarely been isolated. In a non-aqueous medium hydroxo complexes can prove quite stable; for example, reaction of $[PdCl_2(PPh_3)_2]$ with $AgBF_4$ in moist acetone yields the hydroxo-bridged dimer $[Pd_2(OH)_2(PPh_3)_4](BF_4)_2$. This complex does not react with excess PPh_3 in contrast to the chloro-bridged analogue, which reacts by bridge cleavage.[125]

Anions such as sulfate and nitrate bond weakly to palladium, forming complexes which dissociate to a significant extent in water or any donor solvent. They may be isolated from concentrated aqueous solutions following reaction of $[PdCl_2L_2]$ (L = neutral donor) with AgX ($X = \frac{1}{2}SO_4$ or NO_3).[126–128] A variety of complexes containing triphenylphosphine may be prepared by reactions of $[Pd(O_2)(PPh_3)_2]$ with the appropriate oxide (equations 12–14).

$$[Pd(O_2)(PPh_3)_2] + CO_2 \xrightarrow[-PPh_3O]{PPh_3} [Pd(CO_3)(PPh_3)_2]^{129} \tag{12}$$

$$[Pd(O_2)(PPh_3)_2] + SO_2 \longrightarrow [Pd(SO_4)(PPh_3)_2]^{130,131} \tag{13}$$

$$[Pd(O_2)(PPh_3)_2] + N_2O_4 \longrightarrow [Pd(NO_3)_2(PPh_3)_2]^{131} \tag{14}$$

The sulfato and nitrato triphenylphosphine complexes were also obtained by the reaction of sulfuric or nitric acid with $[Pd(PPh_3)_4]$ in ethanol.[132] Nitrato complexes can also be prepared by isolation of $[Pd(NO_3)_2(H_2O)_2]$, obtained by dissolution of Pd metal in concentrated nitric acid,[133,134] and subsequent reaction with ligands L (*e.g.* L_2 = 2,2′-bipyridyl).[135] A crystal structure determination has been carried out for the complex *cis*-$[Pd(NO_3)_2(DMSO)_2]$.[136]

51.4.4 Palladium(II) Complexes Containing Alkoxide Ligands

Palladium alkoxide complexes are thought to be formed in the reactions of alcohols catalyzed by palladium(II) chloride. These reactions include the oxidation of alcohols, yielding acetals or ketones,[137,138] and their carbonylation, yielding esters.[139] Alkoxide intermediates are also thought to be involved in the reaction of sulfur dioxide with $[PdCl_2]$ suspended in alcohol (equation 15).[140,141]

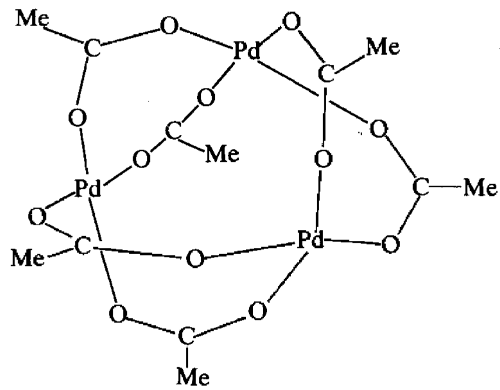
$$2SO_2 + 2ROH + 2PdCl_2 \longrightarrow trans\text{-}[Pd_2Cl_4(SO_2OR)_2]^{2-} \quad R = Me, Et, Pr \tag{15}$$

As with many other examples of palladium compounds containing oxygen donors, alkoxide complexes have very rarely been isolated. Two compounds which have been obtained are *trans*-$[Pd(OMe)(CN)(PEt_3)_2]$[142] and the methoxide-bridged dimer $[Pd_2(\mu\text{-}OMe)_2$(2,2,6,6-tetramethylheptanedionato)$_2]$.[143]

51.4.5 Palladium(II) Complexes Containing Carboxylate Ligands

Palladium forms binary complexes $[Pd(O_2CR)_2]_n$ with monocarboxylic acids.[144,145] The value of n varies under different circumstances. A crystal structure determination for $[Pd(O_2CMe)_2]_3$ confirms a trimeric form for this compound in the solid state. This structure (**29**) allows each palladium atom to retain essentially square planar coordination with each acetate ligand bridging two metal atoms. Depending on the solvent, monomeric, dimeric or trimeric forms may exist in solution.[147] Different carboxylate ligands also give different positions of equilibrium with, for example, the fluorocarboxylates giving preference to the monomer.[144] In substitution reactions with unidentate ligands such as PR_3 or AsR_3 these complexes react to give products containing monodentate carboxylates $[Pd(O_2CR^1)L_2]$ (L = PR_3 or AsR_3). Reaction of $[PdL_4]$ (L = PPh_3 or $\frac{1}{2}Ph_2PCH_2CH_2PPh_2$) with dibenzoyl peroxide at room temperature also yields complexes $[Pd(O_2CPh)L_2]$.[148] Reaction of $[Pd(O_2CR)_2]_n$ with bidentate ligands leads to complete displacement of the carboxylate ligand.[144]

Reaction of $[PdCl_2(diene)]$ with silver carboxylates yields complexes $[Pd_2(\mu\text{-}carboxylate)_2(carboxycyclo\text{-}ene)_2]$.[149,150] NMR studies have shown that both the bridging carboxylate and the 'ester' carboxylate exchange with free carboxylate in solution in independent equilibria, the exchange of the bridging ligand being rapid on the NMR timescale at ambient temperature.[149] NMR studies have also been carried out on other complexes $[Pd_2(\mu\text{-}O_2CMe)_2(\eta^3\text{-}C_3H_5)_2]$[151] and $[Pd_2(\mu\text{-}O_2CR)_2X_2L_2]$ (selection of R = Me, CF_3, CMe_3, CPh_3, CCl_3, CH_2Cl, CH_2Br; X = Cl, Br, I; L = PMe_2Ph, $AsMe_2Ph$)[152] containing bridging carboxylate ligands. The complexes undergo rapid conformational exchange involving solvolysis of one metal carboxylate bond to give a mono-μ-carboxylate intermediate. Involvement



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of the solvent was shown by the study of complexes $[Pd_2\{O_2C(CH_2)_8CO_2\}Cl_2(PMe_2Ph)_2]$ in which the two bridging carboxylate groups are linked, and the marked effect of the addition of small amounts of different solvents to $CHCl_3$ solutions of the complexes on the coalescence temperature for the two methyl resonances of the PMe_2Ph ligands.[152]

Dicarboxylic acids form monomeric complexes with palladium(II), $K_2[Pd(X_2)_2]$ (X_2 = oxalate, malonate, *etc.*).[153,154] They may be prepared by warming a suspension of palladium(II) chloride with a concentrated solution of the alkali metal dicarboxylate or by using other palladium complexes containing readily substituted ligands such as $[Pd(OH)_2]$, $[Pd(NO_3)_2(H_2O)_2]$ or $[Pd(O_2CMe)_2]_3$.[155] These complexes are claimed to have useful antitumour properties.[155] Complexes $[Pd(X_2)L_2]$ (X_2 = dicarboxylate; L = amine or L_2 = diamine) may be prepared by reaction of the dichloro complex with a carboxylate salt.[156,128]

51.4.6 Palladium(II) Complexes Containing β-Diketonate Ligands

Palladium(II) β-diketonates may be prepared by reacting $[PdCl_2]$ with the β-diketone and potassium hydroxide,[157,158] or by treating a methanolic solution of $Na_2[Pd_2Cl_6]$ with excess β-diketone.[143]

Crystallographic studies of [Pd{PhC(O)CHC(O)Me}$_2$], *cis*[159,160] and *trans*[161] isomers, show that the complexes have almost perfect square planar geometry indicating the suitability of β-diketones as chelating ligands for palladium(II). The palladium–oxygen bonds are 1.98 Å in length. Considerable effort has been given to the analysis of the infrared spectra of these compounds.[162] The spectra are complex, requiring isotopic labelling (*e.g.* with ^{104}Pd and ^{110}Pd[163]) to confirm assignment of bands.

Substitution and exchange kinetics for $[Pd(acac)_2]$ have been studied where the kinetic equations derived are those typical of square planar substitution reactions.[164,165] The substitution chemistry of palladium β-diketonates is complex due to the many coordination modes adopted by these ligands: O,O-chelates, η^3 bonding,[166] Pt—C bonding through the γ carbon,[166,168] singly O-bonded.[169] The complex $[Pd(hfac)_2]$ reacts with PPh_3, $P(o\text{-tolyl})_3$[169] or $Ph_2PC_2H_4P(Ph)C_2H_4PPh_2$ (triphos)[170] to form five-coordinate compounds. Two of these compounds $[Pd(hfac)_2\{P(o\text{-tolyl})_3\}]$ and [Pd(hfac)(triphos)] have been studied by X-ray crystallography and both have essentially square pyramidal geometry. The apex of the pyramid is occupied by an oxygen atom of hfac with the bond being significantly longer than normal (2.80 Å and 2.65 Å respectively). Variable temperature NMR studies indicated rapid intramolecular exchange involving the apical O site. There was no evidence of similar five-coordinate compounds being formed for other β-diketonates, *e.g.* acac, tfac.[169]

The extent of substitution for these complexes is governed by a combination of the steric requirements of the incoming nucleophile and electronic factors. The mode of bonding of any remaining β-diketonate ligands is generally governed by electronic effects. Thus with a series of nitrogen donors complexes $[Pd(O,O\text{-hfac})\{CH(OCF_3)_2\}L]$ (L = $NHMe_2$, 2,6-dimethylpyridine, 2,4,6-trimethylpyridine) may be obtained.[167] Displacement of one β-diketonate ligand yields complexes $[Pd(hfac)L_2](hfac)$ (L = Ph_3As, $\frac{1}{2}(Ph_2As)_2CH_2$, NMe_3, $NHMe_2$, Bu^{t}NC, phenothiazine, phenoselenazine, $\frac{1}{2}$bipy and $\frac{1}{2}$tetrathianaphthacene[171] or aniline[172]) or complexes $[Pd(acac)L_2]BF_4$ after treatment of $[Pd(acac)_2]$ with HBF_4 and L (L = PEt_2Ph, PPh_3,

$P(4\text{-}C_6H_4Me)_3$ or $AsPh_3$).[173] In contrast to the reaction of $[Pd(hfac)_2]$ with aniline, $[Pd(acac)_2]$ yields an anilide-bridged dimeric complex $[Pd(acac)(\mu\text{-NHPh})]_2$.[172] Reaction of $[Pd(tfac)_2]$ with tertiary phosphines followed by a heterocyclic nitrogen base generates complexes of tfac dianion $[Pd(C,O\text{-tfac})LL^1]$ (*e.g.* $L = PPh_3$, L^1 = 2,6-dimethylpyridine).[174] Where steric factors permit, reaction with excess ligand leads to displacement of both β-diketonate ligands.[175]

Reactions of the coordinated β-diketonate ligand are those typical of aromatic ring systems[176] with electrophilic substitution at the γ carbon being favoured, *e.g.* reaction with nitric oxide.[177]

51.4.7 Palladium(II) Complexes with Other Chelating Ligands Containing an Oxygen Donor

1,2-Dihydroxybenzene derivatives readily form complexes of the type $[Pd(O_2C_6H_3R)(PPh_3)_2]$.[178,179] The increased acidity of aromatic alcohols compared with aliphatic alcohols combined with the chelate effect makes these compounds much more stable than alkoxide complexes. Their stability is such that they can be subjected to further reactions involving the side chain group R to generate compounds suitable for use as indicators for immunoassay.[178]

Aromatic hydroxy groups also act as donors in a variety of N,O chelating ligands, *e.g.* salicylaldimine, salicylaldoxime, 8-hydroxyquinoline, *etc.* (see Section 51.5.4).

Another example where the strength of the Pd—N bond and the chelate effect combine to yield a series of stable complexes is the α-amino acids. The complexes with glycine have been the most studied.[180,181] The thermodynamically preferred isomer of $[Pd(glycine)_2]$ is the *cis* form, in contrast to the majority of palladium amine complexes.[181] On treatment of *cis*-$[Pd(glycine)_2]$ with acid, one carboxylate group is displaced followed by cleavage of the palladium–amine bond, yielding $[PdX_2(glycine)]$ ($X = H_2O$ or acid anion, *e.g.* Cl). Continued reaction results in the displacement of the second glycine ligand.[180–182]

51.5 PALLADIUM(II): NITROGEN DONOR COMPLEXES

51.5.1 Introduction

A wide variety of organic compounds contain nitrogen atoms which are capable of acting as donors in coordination complexes. The strength of the palladium–nitrogen bond has led to a large number of stable compounds being prepared. The absence of low-lying *d* orbitals for nitrogen leads to the bonds being exclusively σ in character in the majority of the complexes. In consequence these ligands lie low in the *trans* influence and *trans* effect series, which is reflected in the stability of these compounds.

51.5.2 Amines

The largest class of complexes of this type is $[PdX_2L_2]$ (X = halide or pseudohalide; L = amine), the complexes being readily prepared by addition of the amine to $[PdCl_4]^{2-}$ in aqueous solution or by reaction of the amine with $[PdCl_2]$ or $[PdCl_2(PhCN)_2]$ in organic solution. Complexes of the majority of simple amines have been prepared,[183] including recently those of hydroxylamine,[184] aziridine[185] and the tertiary amine NMe_3.[186] Normally the *trans* isomer (or a mixture of isomers) is isolated, though by control of the conditions the pure *cis* isomer may be obtained. Thus, for example, treatment of tetraamminepalladium(II) perchlorate with excess perchloric acid generates *cis*-$[Pd(NH_3)_2(H_2O)_2]^{2+}$ in solution. Addition of a concentrated solution of sodium halide to this results in the precipitation of the *cis* isomer.[187] The chloro and bromo complexes are stable in the solid state, while the iodo complex isomerizes over a period of about one year. The success of this method relies on the low *trans* effect of the aqua and halide ligands and the corresponding complexes with ligands of higher *trans* effect (*e.g.* SCN, NO_2) cannot be prepared in the *cis* form.[187]

Tetramine complexes $[PdL_4]X_2$ are also common.[183] The salts $[Pd(NH_3)_4][PdCl_4]$ and $[Pd(NH_3)_4][PtCl_4]$ have a solid state structure similar to $[Pt(NH_3)_4][PtCl_4]$, where the square planar molecular units are stacked vertically with short axial metal–metal distances (3.25 Å), leading to anomalous visible spectra, semiconductivity and photoconductivity.[188] These properties are not due to metal–metal bonding but are thought to arise from the overlap of the p_z and d_{z^2} metal orbitals creating a filled and empty band structure.[189]

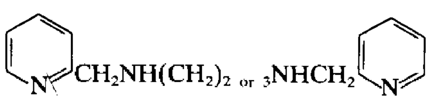
Complexes containing only one or three amine ligands are less common. The monoammine complex $[PdCl_3(NH_3)]^-$ has been isolated as its tetraaminepalladium(II) salt $[Pd(NH_3)_4][PdCl_3(NH_3)]_2$[190] and the trimethylamine complex $(NPr_4)[PdCl_3(NMe_3)]$ has been prepared.[186] A range of complexes *trans*-$[PdX_2L(amine)]$ (X = Cl or Br) may be obtained when L = phosphorus or arsenic donor by reaction of the dimer $[Pd_2X_4L_2]$ with an amine.[191–193] Attempts to perform similar reactions for L = Group VI donor result in disproportionation, so that only complexes $[PdCl_2L_2]$ and $[PdCl_2(amine)_2]$ are isolated. Triammine complexes $[Pd(SO_3)(NH_3)_3]^+$ and $[Pd(NO_2)(NH_3)_3]^+$ have been isolated and their crystal structures determined.[194,195]

Multidentate amine ligands react readily with palladium(II) halides to yield chelated products. Crystal structure determinations have been carried out for 1,2-diaminoethane complexes $[PdCl_2(en)]$,[196] $[Pd(en)_2]Cl_2$[197] and $[Pd(en)_2][Pd(S_2O_3)_2(en)]$.[198] A variety of 1,2-diaminoethane, 1,2-diaminocyclohexane[199] and 1,3-diaminocyclohexane[200] complexes have been prepared because their necessarily *cis* geometry makes them analogous to the antitumour platinum complexes. In contrast to compounds *trans*-$[PdX_2L_2]$ these former complexes are claimed to have activity comparable with or greater than that of cisplatin.[199]

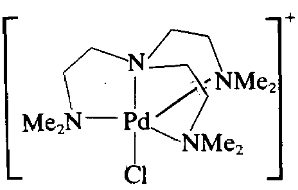
Diaminopropane complexes $[PdCl_2(NH_2CH_2CHXCH_2NH_2)]$ (*e.g.* X = OH) exist in different crystal forms where the polymorphism is thought to be due to different conformations of the chelate ring.[201,202] The solution state equilibria have been studied by NMR spectroscopy.[203]

N-(2-Aminoethyl)-1,2-diaminoethane (dien) yields complexes [PdX(dien)]X (X = Cl or I).[204,205] A range of solvated complexes may be obtained by reaction of [PdI(dien)] with $AgClO_4$ in the appropriate solvent. As for the platinum analogue, the aqua complex $[Pd(dien)(H_2O)](ClO_4)_2$ reacts with tetraphenylborate to yield $[PdPh(dien)](BPh_4)$. Reaction of the hydroxo complex with carbon monoxide yields CO_2 and palladium metal is deposited.[206]

N,N'-Di(2-aminoethyl)-1,2-diaminoethane (trien) acts as a tetradentate ligand in complexes $[Pd(trien)]X_2$ ($X = PF_6$, ClO_4). A crystal structure determination for $[Pd(trien)](PF_6)_2{\cdot}KPF_6$ confirmed that the palladium atom retains planar coordination with the four nitrogen atoms in a trapezoidal arrangement (Pd—N varying from 1.95 to 2.08 Å).[207] The related ligands (**30**) also act as tetradentate donors when only perchlorate or hexafluorophosphate anions are present, but one of the pyridine rings is displaced in the presence of halide.[208] The tris[2-(dimethylamino)ethyl]amine ligand acts as a tridentate donor in neutral or acid solution but in strongly alkaline media (pH > 12) the ligand is tetradentate, the complex having a trigonal bipyramidal coordination geometry (**31**).[209–211]



(**30**)



(**31**)

Palladium–nitrogen bond lengths for a variety of amine complexes are given in Table 4.

Table 4 Palladium–Nitrogen Bond Lengths in Palladium Amine Complexes

Complex	*Pd—N (mean)* (Å)	*Ref.*
$[Pd(NH_3)_4]^{2+}$	2.004(3)	193
trans-$[Pd(SO_3)_2(NH_3)_2]$	2.060(9)	300
$[Pd(SO_3)(NH_3)_3]^+$	2.105(20)	192
$[PdCl_2(en)]$	1.978(12)	194
$[Pd(en)_2]^{2+}$	2.036	195
$[PdCl_2(dimethylpiperazine)]$	2.00	301
$[Pd(2,2'\text{-bipyridyl})_2]^{2+}$	2.034	215
$[Pd(NO_2)_2(2,9\text{-dimethylphen})]$	2.09	302

51.5.3 Aromatic Heterocyclic Amines

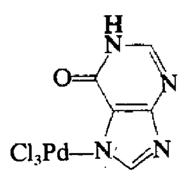
The inclusion of the nitrogen donor atom in an aromatic heterocycle allows the possibility of π-bonding with the metal centre, giving these ligands some similarities to tertiary phosphines. Thus pyridyl and bipyridyl ligands stabilize organometallic complexes of palladium (see companion volume).[212]

While ligands (L) such as 1,10-phenanthroline and 1,8-naphthyridine normally act as bidentate donors, they are essentially monodentate in complexes *cis*-$[PdCl(PEt_3)_2L]X$ ($X = BF_4$ or ClO_4). The heterocyclic ligands are fluxional with a dissociative mechanism being dominant above $-10\,°C$ and an intramolecular exchange occurring at lower temperatures.[213] The preference for bidentate coordination can lead to a departure from the normal rule of square planar coordination for palladium(II). Thus the halobis(2,9-dimethyl-1,10-phenanthroline)palladium(II) ion has a trigonal bipyramidal structure and dicyanobis(2,9-dimethyl-1,10-phenanthroline)palladium(II) has an octahedral geometry.[214] Distortion of the square planar structure towards a tetrahedral arrangement due to steric interactions has been noted for $[Pd(2,2'\text{-bipyridyl})_2](NO_3)_2{\cdot}H_2O$.[215]

Imidazoles act as monodentate donors for palladium, forming complexes $[PdCl_2L_2]$ and $[PdL_4]Cl_2$.[216–221] Both *cis* and *trans* isomers of the former complexes have been isolated and their antitumour properties investigated.[216] A polymeric compound $[Pd(\text{imidazolato})_2]_n$ has also been isolated which contains bidentate bridging imidazolato ligands.

A variety of pyrimidine derivatives, L, have been used to synthesize complexes $[PdX_2L_2]$ ($X = Cl$ or Br).[222,223] A study of the coordination site in complexes $[PdCl_3L]$ and $[PdCl_2L_2]$ showed the metal to be bound to N(1).[224,225]

Reaction of $[PdCl_4]^{2-}$ with purine nucleosides (1:1) in dimethylformamide yields complexes $K[PdCl_3(LH)]$ (LH = guanosine, inosine or xanthosine; **32**) bonded through the N(7) atom of the purine. In aqueous solution these complexes decompose, the nucleoside chelating through N(7) and O(6) with deprotonation of the imine nitrogen atom N(1). If the solution is kept at pH ≈ 9, chloro-bridged dimeric products are isolated.[226] Reactions of $K_2[PdCl_4]$ with two molar equivalents of nucleoside in aqueous media can yield either the bis chelate *trans*-$[PdL_2]$ or *cis*-$[PdCl_2L_2]$ as indicated in Scheme 14.[227] Further substitution reactions with additional equivalents of nucleoside yield complexes $[PdL_2L'_2]Cl_2$ similar to the compounds $[PdL_4]Cl_2$ synthesized previously.[228]



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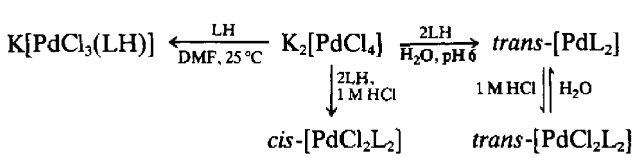


LH = guanosine or inosine

Scheme 14

The interaction of $[PdCl(\text{dien})]Cl$ with nucleosides and nucleotides has been studied by NMR spectroscopy. While guanosine, xanthosine and inosine bind through N(7), cytidine is coordinated through N(3) and adenosine monophosphate acts as a bidentate bridging ligand coordinating through N(1) and N(7). A crystal structure for $[Pd(\text{dien})(\text{guanosine})](ClO_4)_2$ has been reported.[229]

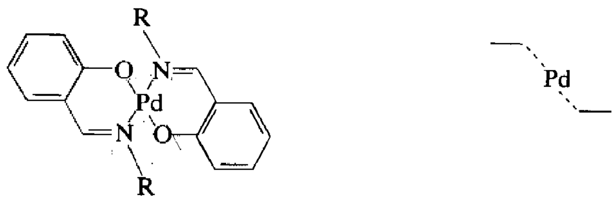
These reactions, and in particular the ease of formation of the N(7)–O(6) chelate, may be relevant to the mechanism of action of the anticancer transition metal compounds such as *cis*-$[PtCl_2(NH_3)_2]$.[230]

51.5.4 Carbonyl Condensation Products

A wide range of potential ligands can be formed by condensation reactions of carbonyl compounds with RNH_2 derivatives.

51.5.4.1 Imines

A variety of salicylaldimine complexes have been synthesized where the ligand chelates through the N and O atoms in a *trans* isomeric form **(33)**. While the Pd atom retains square planar coordination in these complexes, the ligands bend away from the planar form, which gives the maximum delocalized π bonding. The extent of this folding increases with the increasing bulk of the R substituent.[231–236] The same effect was subsequently noted for salicylaldoximato,[237] dipyrromethene[238] and tetraaza-14-annulene[239] complexes. The *cis* configuration for complexes of this type has only been obtained where the nitrogen atoms are fixed by a linking group, *e.g.* ligands obtained through condensation reactions of 1,2-diaminoethane derivatives.[240,242]



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Reaction of the bis(salicylidenimine)palladium(II) complexes with mineral acids yields N-bonded complexes *trans*-$[PdX_2(LH)_2]$ (X = Cl, Br, I, SCN; LH = HOC_6H_4CHNPh).[243]

α-Diimines (RN=CHCH=NR, R = Pr^i, Bu^t, $EtMe_2C$; R-dim) react with equimolar amounts of $[PdX_2(PhCN)_2]$ (X = halide) in dichloromethane to yield chelates *cis*-$[PdX_2$(R-dim)] similar to the bipyridyl complexes which contain an analogous N=C—C=N skeleton. However, in contrast to the bipyridyl ligand, which is almost invariably bidentate, if the above reaction is carried out using excess α-diimine, then complexes containing the monodentate ligand *trans*-$[PdX_2(\text{R-dim})_2]$ are formed. Reacting the α-diimine with $[PdCl_2(PPh_3)_2]$ again yields complexes containing the monodentate ligand, $[PdCl_2(PPh_3)(\text{R-dim})]$, where NMR studies have shown the metal–ligand bond to be fluxional between N and N′ donor atoms. A mechanism involving a pentacoordinate intermediate or transition state is proposed.[244]

Similarly, 1,3-diaryltriazenes ArNNNHAr, formed by condensation of $ArNH_2$ with diazonium salts, behave as monodentate ligands in complexes *cis*- and *trans*-$[Pd(ArNNNAr)_2(PPh_3)_2]$[245,246] and $[PdCl_2(ArNNNAr)L]$ (L = PPh_3, PEt_3, $AsPh_3$, $PMePh_2$).[247] These complexes undergo an intramolecular N(1)–N(3) exchange, which has also been studied by ^1H NMR spectroscopy, and $\Delta H^\ddagger$ values of 32–44 kJ mol^{-1} with negative $\Delta S^\ddagger$ have been measured.[247]

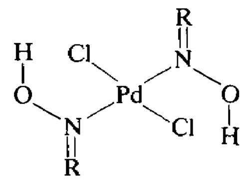
Carbodiimides also act as monodentate ligands forming complexes *trans*-$[PdX_2(RN{=}C{=}NBu^t)_2]$ (X = Cl or Br; R = Me or Bu^t).[248]

51.5.4.2 Oximes

Reaction of palladium chloride with monooximes yields stable bis complexes of *trans* stereochemistry **(34)**.[249] Tetrakis(monooxime) complexes may be obtained by reaction with $[Pd(acac)_2]$.[250]

Dioximes form bis complexes **(35)** where the ligand normally chelates through the nitrogen atoms.[251–253] Detailed studies have been made of the partially oxidized compounds obtained from reaction of bis(diphenylglyoximato)- and bis(benzoquinone dioximato)-palladium with iodine[254,255] and bromine.[256] These complexes contain polyhalide anions and possess the high anisotropic electrical conductivity associated with many complexes which crystallize as stacked molecular units.[257]

Ligand geometry may alter the coordination properties of dioximes as illustrated by a study of the complexes of camphorquinone dioxime (H_2CQD). This ligand exists in four isomeric



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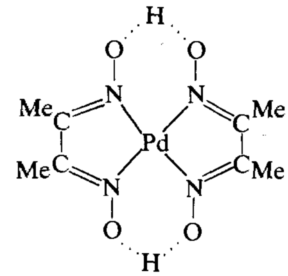
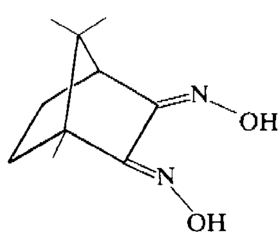
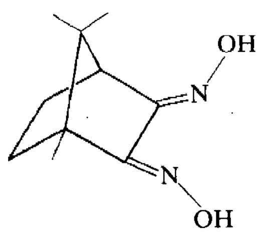


(35)

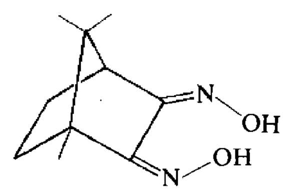
forms (**36**)–(**39**), which differ in the orientation of the OH groups. In complexes $[Pd(HCQD)_2]$ the β isomer is chelated through both nitrogen atoms but the δ isomer forms an N,O chelate. The neutral ligand also forms complexes $[PdCl_2(H_2CQD)_n]$, where the β isomer again chelates through the nitrogen atoms ($n = 1$) but the α, γ and δ isomers are monodentate, bound through only one nitrogen atom ($n = 2$).[258]



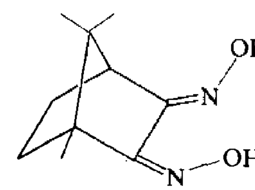
(**36**) α



(**37**) β



(**38**) γ



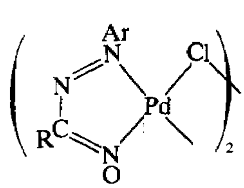
(**39**) δ

Arylazooximes (LH) react with tetrachloropalladate(II) to yield chloro-bridged dimers (**40**) or the bis chelates $[PdL_2]$,[259,260] though the dimeric complexes are better prepared by reaction of LH with $[PdCl_2]$ or $[PdCl_2(PhCN)_2]$.[261] Reaction of these complexes with PPh_3 results in splitting of the chloro bridge, while addition of excess PPh_3 generates an equilibrium between the chelated azooxime and its monodentate N(oxime) bound form (equation 16).

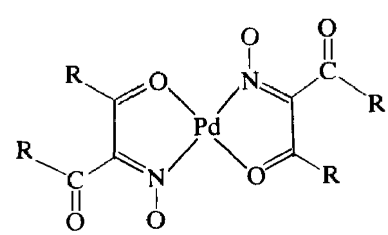
$$[PdClL(PPh_3)] \xrightleftharpoons{PPh_3} \textit{trans}\text{-}[PdClL(PPh_3)_2] \quad (16)$$

Reaction of the chelate with HCl gas in chloroform yields the dimeric product $[Pd_2Cl_4L_2]$ in which the oxime is protonated and the azooxime is bonded through N(azo) only.[261]

Reactions of β-diketones with nitrous acid yield oximes, derivatives which are more commonly referred to as isonitroso compounds.[262] These bond to palladium through the nitrogen atom and one ketone group (**41**).[263–265]

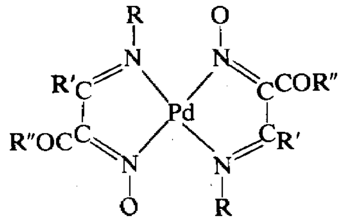


(**40**)



(41)

The free carbonyl function of this ligand may undergo further condensation reactions. With amines RNH_2, products [PdLL′] are obtained where both L and L′ may be N,N′-bonded chelates (**42**; R = Me, Et, Pr, Bu)[264,265] or L′ may be bonded through N(imine) and O(oxime) (**43**; R = H).[266] Similar linkage isomerism is seen for other oximato ligands of this type.[267]



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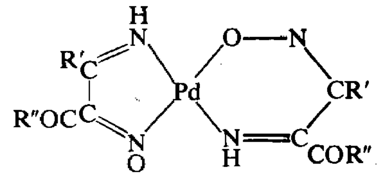

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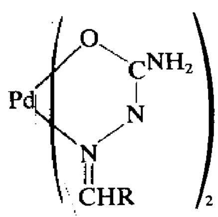
51.5.4.3 *Other carbonyl condensation products*

Semicarbazones form complexes *trans*-[PdL_2], chelating through the iminic nitrogen atom and the enolic oxygen atom (**44**).[268] Hydrazones also bond through the iminic nitrogen to yield complexes of structure (**45**). Hindered rotation about the Pd—N bond results in two isomeric forms which exist in equilibrium in solution and may be distinguished by ^{1}H NMR spectroscopy.[269] Glutaraldehyde bis(dimethylhydrazone) is a ligand suited to the formation of large ring chelates and has been used to synthesize [Pd_2Cl_4{Me_2NN=CH(CH_2)$_3$-CH=$NNMe_2$}$_2$], which contains a 16-membered ring.[270]



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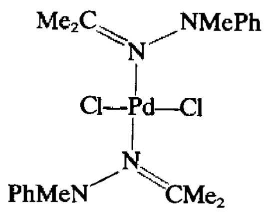


(45)

Multiple condensation reactions involving diketones or condensations with bifunctional carbonyl-containing compounds (*e.g.* salicylaldehyde) yield a variety of multidentate ligands but their coordination behaviour is generally as expected from studies of the simpler ligands, allowing for the restrictions that ligand geometry places on which atoms may form bonds (for examples, see refs. 271–280).

51.5.5 Macrocylic Ligands

A logical extension of the condensation reactions which yield multidentate nitrogen donors is the formation of macrocyclic ligands. The preference of palladium for square planar coordination makes it an ideal metal for the formation of complexes of these ligands. Thus palladium porphyrins are very stable and resistant to demetallation.[281] Both 14- and 16-atom macrocycles have been used to form complexes. The ligand 1,8-dihydro-5,7,12,14-tetramethyl-dibenzo[*b,i*][1,4,8,11]tetraaza[14]annulene reacts with [$PdCl_2(PhCN)_2$] to yield the complex (**46**).

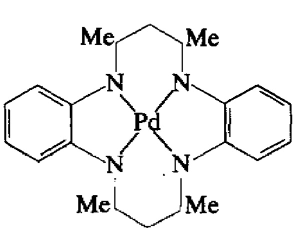
A crystal structure determination for this compound showed that while the square planar coordination of palladium is retained, strain within the molecule is relieved by a folding of the ligand[239] similar to that described above for salicylaldimine complexes. The β position of these ligands may be substituted by electrophilic reagents before or after complexation.[282]

Tetrabenzo-1,5,9,13-tetraazacyclohexadeca-1,5,9,13-tetraenepalladium dichloride (**47**) may be formed by template condensation of *o*-aminobenzaldehyde.[283]

Reaction with nucleophiles yields 2,10-disubstituted products.[284] Partial oxidation of these macrocyclic complexes with iodine yields mixed valence non-stoichiometric compounds of high electrical conductivity.[285,286]

51.5.6 Azide

An extensive series of papers has been published describing azide complexes of palladium. By precipitation with large cations, non-explosive binary azide complexes may be isolated.



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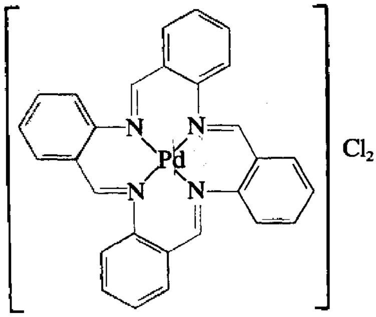
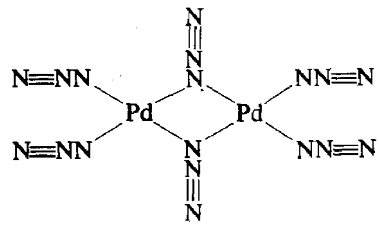


(47)

Mononuclear $[CTA]_2[Pd(N_3)_4]$[287] and binuclear $[AsPh_4][Pd_2(N_3)_6]$ **(48)**[288] forms have been characterized.



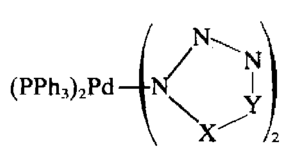
(48)

Examination of the former complex in conjunction with other azide complexes has allowed classification of azide in the spectrochemical series between S-bonded SCN^- and diethyldithiophosphate.[289] The bridged species reacts with neutral donors to give compounds $[Pd(N_3)_2L_2]$ (*e.g.* $L = PPh_3$), which are convenient materials for studies of the reactions of coordinated azide.[290] Characterization of $[Pd(N_3)_2(PPh_3)_2]$ by IR spectroscopy and X-ray diffraction suggests that while the two azide ligands are equivalent in the solid state this is not so in solution.[290] This complex tends to dimerize in solution and even in the solid state to yield $[Pd_2(N_3)_4(PPh_3)_2]$ with a structure analogous to **(48)**.[291] Dimeric azide-bridged cationic compounds $[Pd_2(N_3)_2(PPh_3)_4]X_2$ ($X = ClO_4$, BF_4, PF_6) may be prepared by reaction of $[Pd(N_3)_2(PPh_3)_2]$ with the corresponding nitrosyl salt.[292]

The coordinated azide undergoes addition reactions with a variety of unsaturated compounds. Thus with carbon monoxide under very mild conditions the azide is converted to isocyanate with the loss of nitrogen (equation 17).[293–295]

$$[Pd(N_3)_2(PPh_3)_2] + 2CO \xrightarrow[CHCl_3]{20\,^{\circ}C} [Pd(NCO)_2(PPh_3)_2] + 2N_2 \tag{17}$$

Cycloaddition reactions occur with a wide variety of compounds, yielding products of structure **(49)**.[296–298] These reactions may be used as a convenient route for the synthesis of the organic heterocycles.



(49)

X—Y
RC≡N
N≡C
RSC≡N
RN=C=O
RN=C=S
S=C=S
RC≡CR

51.5.7 Other Organic Ligands

Palladium will form complexes with the great majority of other organic compounds containing potential nitrogen donor atoms. Of all of these, the most useful are probably those of alkyl and aryl nitriles. These complexes $[PdX_2(NCR)_2]$ (*e.g.* $X = Cl$; $R = Me$) are stable compounds of great value as synthetic intermediates.[299] They are readily prepared by heating the palladium(II) halide in the nitrile and precipitating with light petroleum. The complexes are soluble in a range of solvents and readily undergo substitution reactions in which the nitrile ligand is displaced.

51.6 PALLADIUM(IV) COMPLEXES

51.6.1 Introduction

Palladium(IV) is a relatively rare oxidation state. The paucity of isolated complexes in comparison with Pt^{IV} has been ascribed to the much higher ionization potential required to produce Pd^{4+} (109.5 *vs.* 97.16 eV for Pt^{IV}).[303] Binary complexes with oxide and the chalcogenides have been well characterized as have PdF_4 and $[PdX_6]^{2-}$ (X = F, Cl, Br). The chemistry of platinum group metals in higher oxidation states has been the subject of a recent review.[304]

51.6.2 Halide Complexes of Palladium(IV)

PdF_4 has been prepared by the fluorination of PdF_3 under pressure.[305,306] A purer product may be obtained when $PdSnF_6$ or $PdGeF_6$ is used as the starting material.[305,307] Neutron diffraction studies have shown that PdF_4 is isostructural with PtF_4. It is composed of PdF_6 octahedra where the terminal Pd—F bonds are 1.94 Å and the bridging Pd—F bonds are 1.91 and 2.05 Å.[305,308]

The fluorination of alkali metal salts of tetrachloropalladate(II) and hexachloropalladate(IV) or mixtures of $(NH_4)_2[PdCl_4]$ and group II carboxylates using F_2, ClF_3 or BrF_3 gives hexafluoropalladate(IV) salts.[309–316]

The mixed valence complex $Pd^{II}[Pd^{IV}F_6]$ has been prepared from the reaction of $PdBr_2$ with BrF_3. The relevant bond lengths in this compound are Pd^{II}—F 2.17 Å and Pd^{IV}—F 1.90 Å.[306,309,310,317,318] The structures of other hexafluoropalladate(IV) salts are dependent on the counterion (see Table 5).

Table 5 Structures of Hexachloropalladate(IV) Salts[312–314,317,321,322]

Compound	*Lattice type*
$Li_2[PdF_6]$	$Na_2[SnF_6]$
$Na_2[PdF_6]$	$Na_2[SiF_6]$
$K_2[PdF_6]$	$K_2[GeF_6]$ or $K_2[MnF_6]$
$Cs_2[PdF_6]$	$K_2[PtCl_6]$
$M'[PdF_6]^a$	$Li[SbF_6]$

a M' = Ca, Zn, Cd, Hg.

The compounds $(NO)_2[PdF_6]$[319] and $[XeF_5]_2[PdF_6]$[320] have been reported. A structural determination on the latter compound showed bond lengths of 1.89 Å (Pd—F).[320] It has been suggested that the xenon complex $XePd_2F_{10}$ is in fact an XeF^+ salt of $[Pd_2F_9]_n^{n-}$.[307]

While the free acids $H_2[PdX_6]$ (X = Cl, Br) have been prepared in solution, attempts to isolate them have been unsuccessful.[323] Hexachloro- or hexabromo-palladate(IV) can be isolated by reacting the free acid with halogen or alkali metal halide.[324–327]

Synthesis of the corresponding iodide salt was elusive until recently when $Cs_2[PdI_6]$ was prepared by the treatment of an acid solution of $[PdCl_6]^{2-}$ with a large excess of cesium iodide.

Table 6 Vibrational Stretching Frequencies for $[PdX_6]^{2-}$

X	ν_1 *(Ag)*	ν_2 *(Eg)*	ν_3 *(F₁u)*	ν_4 *(F₁u)*	ν_5 *(F₂g)*	*Refs.*
F	573	554	602	280	246	319, 331
Cl	317	293	358	175	154	332–340
Br	198	176	253	130	100	

This compound is stable to air and humidity but decomposes on heating to give $Cs_2[PdI_4]$, which in turn reduces further to the metal.[328] The chloride salts $M_2[PdCl_6]$ (M = NH_4, alkali metal) may also be reduced readily to the corresponding palladium(II) species with halogen loss at 200 °C.[326,329] Both $Cs_2[PdI_6]$ and $(NH_4)_2[PdCl_6]$ have $K_2[PtCl_6]$ type structures[328,330] (Pd—Cl in the latter complex is 2.3 Å). Vibrational spectra of $[PdX_6]^{2-}$ have been reported and these are summarized in Table 6.

51.6.3 Complexes of Palladium(IV) with N, P and As Donor Atoms

51.6.3.1 Palladium(IV) complexes containing N donor atoms

$[PdCl_4(NH_3)_2]$ has been synthesized by the chlorination of $[PdCl_2(NH_3)_2]$ in water[341] or $CHCl_3$ or CCl_4. On heating it decomposes to the palladium(II) starting material,[342] while on standing a partial reduction to $[PdCl_2(NH_3)_2][PdCl_4(NH_3)_2]$ occurs.[342–345]

A number of related amine complexes $[PdCl_4L_2]$ have been prepared by similar methods (L = $MeNH_2$, piperidine,[341,343] NMe_3,[346] 1-phenylethylamine,[347] pyridine,[341,342,346,348] α-picoline;[341] L_2 = bipy,[349] phen,[350] 2,9-dimethyl-1,10-phenanthroline,[351] biguanidine).[353–356] The pyridine complex has also been formed by NOCl oxidation of $[PdCl_2py_2]$.[348] These workers also reported the synthesis of $[PdI_2Cl_2py_2]$ *via* iodine oxidation of the chloropalladium(II) analogue.

While the chlorine oxidation of $[PdCl_2en]$ in chloroform gave $[PdCl_4en]$, when the reaction was carried out in water, hexachloropalladate salts resulted.[343]

In general these neutral amine complexes are reduced on heating. The 2,9-dimethyl-1,10-phenanthroline and bipyridyl complexes are more stable. For example $[PdCl_4bipy]$ does not decompose in boiling water. Thermal gravimetric analysis has shown, however, that this complex is reduced to the palladium(II) analogue at higher temperatures.[341]

The yellow cationic compound $[PdCl_2(NH_3)_4]Cl_2$ has been formed in the chlorine oxidation of $[Pd(NH_3)_4]Cl_2$.[356,357] This is also thermally unstable and reverts to palladium(II) in aqueous solution or on heating.

The oxidation of $[PdCl_2(en)_2]$ with nitric acid was reported to give $[PdCl_2(en)_2](NO_3)_2$.[358–360] However, this assignment has been disputed by other workers who have characterized this dark green material as $[Pd(en)_2Cl_2Pd(en)_2](NO_3)_4$, a mixed valence complex of palladium(II) and palladium(IV).[361] For $[PdCl_2(en)_2]$ more severe oxidizing conditions were required to achieve a complete oxidation, for example bromine oxidation in aqueous HBr resulted in the formation of $[PdBr_2(en)_2]Br_2$, an orange solid.[363] However, yellow *trans*-$[PdCl_2$(L-propylenediamine)]$(NO_3)_2$ was synthesized readily by nitric acid oxidation of the palladium(II) analogue.[362]

There is a recent report of the preparation of the anionic complex of $(NR_4)[PdX_5L]$ (X = Cl, L = NMe_3, py; X = Br, L = NMe_3).[346]

51.6.3.2 Palladium(IV) complexes containing P or As donor atoms

The preparation of palladium(IV) complexes containing monodentate phosphine and arsine ligands has proved elusive until recently. A particular problem in these systems is that an excess of oxidant, *e.g.* Cl_2, results in the formation of $[PdCl_6]^{2-}$ together with the oxidized ligand, *e.g.* PPh_3O, $AsPh_3O$, $AsPh_3Cl_2$.[346] The controlled chlorination of *trans*-$[PdCl_2L_2]$ (L = PPr^n_3, $AsMe_2Ph$) has been shown to give the *trans* palladium(IV) analogues and the anionic species $(NR_4)[PdX_5L]$ (X = Cl, L = $AsEt_3$, PPh_3S; X = Br, L = $AsEt_3$, PEt_2Ph).[346] The stability of these complexes is strongly dependent on the nature of L. The complexes *trans*-$[PdCl_4L_2]$ (L = PMe_2Ph, PPh_3, PPr^i_3, $AsEt_3$, $AsMe_2Ph$, $SbMe_3$) have borderline stability and are difficult to purify. The other complexes indicated above decompose slowly at room temperature but are stable for months at −20 °C.

$[PdX_2(diars)_2](ClO_4)_2$ (X = Cl, Br) has been prepared *via* the nitric acid oxidation of $[PdX_2(diars)_2]$ followed by acidification with perchloric acid.[363] Similar methods have been used to prepare a range of other arsines and phosphines and the stabilities decrease in the order diars > $AsMePh_2$ ⋙ $AsMe[(CH_2)_3AsMe_2]_2$.[364]

Direct halogenation of the corresponding palladium(II) species has been used to prepare $[PdCl_2(QAs)]Cl_2$ (QAs = $As(2\text{-}C_6H_4AsPh_2)_3$)[367] and very recently a range of complexes

$[PdX_4(LL)]$ (X = Cl, LL = $Ph_2P(CH_2)_2PPh_2$, $Me_2P(CH_2)_2PMe_2$, $Ph_2As(CH_2)_2AsPh_2$, 2-$C_6H_4(AsMe_2)_2$, $Me_2As(CH_2)_3AsMe_2$; X = Br, LL = $Me_2P(CH_2)_2PMe_2$, 2-$C_6H_4(AsMe_2)_2$, $Me_2As(CH_2)_3AsMe_2$) and $[PdCl_2(LL)_2]Cl_2$ (LL = $Me_2P(CH_2)_2PMe_2$, 2-$C_6H_4(PMe_2)_2$).[368]

51.6.4 Palladium(IV) Cyano Complexes

Hexacyanopalladate(IV) salts may be produced *via* metathesis of $[PdCl_6]^{2-}$. For example $K_2[Pd(CN)_6]$ has been obtained in low yield from the reaction of $K_2[PdCl_6]$ with KCN in the presence of $K_2S_2O_8$, where the latter prevents reduction to palladium(II).[369] Salts with other anions have also been prepared.[370–376]

A crystal structure determination on $Cd[Pd(CN)_6]$ has shown that both metals have a perfectly octahedral environment (Pd—C = 2.07(2) Å).[377]

51.6.5 Complexes of Palladium(IV) Containing Group VI Donor Atoms

A dark red solid, formulated as $PdO_2{\cdot}nH_2O$ ($n = 1, 2$), was produced by the treatment of $K_2[PdCl_6]$ with alkali.[378] This is slowly reduced to PdO at room temperature with the loss of O_2. This compound is readily reduced by H_2, H_2O_2 and organic compounds. It reacts with mineral acids to give palladium(II) species and it is slightly soluble in concentrated alkali, giving $[Pd(OH)_6]^{2-}$.[379,380]

The corresponding anhydrous compound PdO_2 has been formed by heating PdO with $KClO_3$ at 950 °C and 65 kbar. This is insoluble in acids and alkalis and loses O_2 very readily.[381] Other established palladate(IV) species include $M_2[Pd_2O_7]$ (M = lanthanide)[382] and $Na_2[PdO_3]$.[383] Attempts at preparing K and Rb analogues of the latter compound resulted in the formation of a paramagnetic material with approximately the correct composition; the paramagnetism was ascribed to the presence of Pd^{II} impurities.[383,384]

A number of other Pd^{IV} species with group VI donors have been prepared as shown in equations (18)–(23).

$$[Pd(NO_3)_2] + N_2O_5 \longrightarrow [Pd(NO_3)_4]^{385} \tag{18}$$

$$Pd(metal) + HNO_3 \longrightarrow [Pd(NO_3)_2(OH)_2]^{385} \tag{19}$$

$$Pd(metal) + HSO_3F/S_2O_6F_2 \longrightarrow Pd[Pd(SO_3F)_6]^{386,387} \tag{20}$$

$$Pd(metal) + HSO_3F/S_2O_6 + MI \longrightarrow M[Pd(SO_3)_6]^{387} \tag{21}$$

$$(M = Cs, Ba, NO, ClO_2)$$

$$[Pd(OH)_6]^{2-} + [H_2IO_6]^{3-} + KOH \longrightarrow K_6[Pd(IO_6)_2]KOH^{388} \tag{22}$$

$$PdCl_2 + [Te(OH)_6] + NaOH + NaOCl \longrightarrow Na_5H_3[Pd(TeO_6)_2]{\cdot}4H_2O^{389} \tag{23}$$

Palladium(IV) compounds containing $SeMe_2O$,[390] dithiocarbamates,[391,392] *N*-aminorhodamine,[393] thiosemicarbazones,[394] quinazoline-2,4-dithione,[396] and 1,3,4-thiadiazole-2,5-dithiol[397] have also been reported.

The anionic palladium(IV) species $(NPr_4)[PdCl_5(SMe_2)]$ has been prepared by chlorine oxidation of the corresponding palladium(II) species. It undergoes facile decomposition at room temperature like the phosphine analogue.[346] The neutral compound *trans*-$[PdCl_4(SMe_2)_2]$ could not be characterized, however, because of thermal decomposition.

51.7 REFERENCES

1. G. G. Robson (ed.), 'Platinum 1985', Johnson Matthey.
2. P. M. Maitlis, P. Espinet and M. J. H. Russell, in 'Comprehensive Organometallic Chemistry', ed. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, 1982, vol. 6, chap. 38, p. 233.
3. V. B. Sokolov, Yu. V. Drobyshevskii, V. N. Prusakov, A. V. Ryshkov and S. S. Koroshev, *Dokl. Akad. Nauk SSSR*, 1976, **229**, 641.
4. W. E. Falconer, F. J. DiSavlo, A. J. Edwards, J. E. Griffiths, W. A. Sunder and M. J. Vasile, *Inorg. Nucl. Chem. Lett.*, 1976, **12**, 59.
5. R. Kirmse and W. Dietzch, *J. Inorg. Nucl. Chem.*, 1976, **38**, 225.
6. R. Kirmse, J. Stach, W. Dietzch, G. Steimecke and E. Hoyer, *Inorg. Chem.*, 1980, **19**, 2679.

7. J. A. McCleverty, *Prog. Inorg. Chem.*, 1968, **10**, 49.
8. G. N. Schrauzer, *Acc. Chem. Res.*, 1969, **2**, 72.
9. F. R. Hartley, 'The Chemistry of Platinum and Palladium', Applied Science, London, 1973.
10. R. N. Goldberg and L. G. Hepler, *Chem. Rev.*, 1968, **68**, 229.
11. 'Platinum Group Metals and Compounds', *Adv. Chem. Ser.*, 1971, No. 98.
12. S. A. Cotton and F. A. Hart, 'The Heavy Transition Elements', Wiley-Halstead, New York, 1975.
13. P. M. Maitlis, P. Espinet and M. J. H. Russell, in 'Comprehensive Organometallic Chemistry', ed. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, 1982, vol. 6, chap. 38.2, p. 243.
14. T. Kruck and K. Baur, *Angew. Chem., Int. Ed. Engl.*, 1965, **4**, 521.
15. L. Malatesta and M. Angoletta, *J. Chem. Soc.*, 1957, 1186.
16. J. Chatt, F. A. Hart and H. R. Watson, *J. Chem. Soc.*, 1962, 2537.
17. R. Roffia, F. Conti and G. Gregorio, *Chim. Ind.* (*Milan*), 1972, **54**, 317.
18. G. Wilke, E. W. Muller, M. Kroner, P. Heimbach and H. Breit, *Fr. Pat.* 1 320 729 (1963) (*Chem. Abstr.*, 1963, **59**, 14 026).
19. E. O. Greaves, C. J. L. Lock and P. M. Maitlis, *Can. J. Chem.*, 1968, **46**, 3879.
20. D. A. White and G. W. Parshall, *Inorg. Chem.*, 1970, **9**, 2358.
21. S. Miyamoto, *Jpn. Pat.* 72 18 836 (*Chem. Abstr.*, 1972, **77**, 152 359).
22. M. Meier, F. Basolo and R. G. Pearson, *Inorg. Chem.*, 1969, **8**, 795.
23. B. F. G. Johnson, T. Keating, J. Lewis, M. S. Subramanian and D. A. White, *J. Chem. Soc.* (*A*), 1969, 1793.
24. T. Kashiwagi, N. Yasuoka, T. Ueki, N. Kasai, M. Kakudo, S. Takahashi and N. Hagihara, *Bull. Chem. Soc. Jpn.*, 1968, **41**, 296.
25. T. Boschi, P. Uguagliati and B. Crociani, *J. Organomet. Chem.*, 1971, **30**, 283.
26. D. R. Fahey, *US Pat.* 4 055 582 (*Chem. Abstr.*, 1978, **88**, 23 150).
27. W. Kuran and A. Musco, *J. Organomet. Chem.*, 1972, **40**, C47.
28. L. Malatesta and M. Angoletta, *J. Chem. Soc.*, 1957, 1186.
29. E. Smutny, H. Chung, K. C. Dewhurst, W. Keim, T. M. Shryne and H. E. Thyret, *Prepr., Div. Pet. Chem., Am. Chem. Soc.*, 1969, **14**, B100, B112.
30. S. Otsuka, T. Yoshida, M. Matsumoto and K. Nakatsu, *J. Am. Chem. Soc.*, 1976, **98**, 5850.
31. B. E. Mann and A. Musco, *J. Chem. Soc., Dalton Trans.*, 1975, 1693.
32. C. A. Tolman, W. C. Seidel and D. H. Gerlach, *J. Am. Chem. Soc.*, 1972, **94**, 2669.
33. A. Immirzi and A. Musco, *J. Chem. Soc., Chem. Commun.*, 1974, 400.
34. S. Otsuka, T. Yoshida and M. Matsumoto, *J. Am. Chem. Soc.*, 1976, **98**, 5850.
35. J. F. Nixon and M. D. Sexton, *Inorg. Nucl. Chem. Lett.*, 1968, **4**, 275.
36. P. Fitton, M. P. Johnson and J. E. McKeon, *Chem. Commun.*, 1968, 6.
37. D. T. Rosevear and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 164.
38. C. D. Cook and J. S. Jauhal, *Can. J. Chem.*, 1967, **45**, 401.
39. M. C. Baird and G. Wilkinson, *J. Chem. Soc.* (*A*), 1967, 865.
40. W. J. Bland and R. D. W. Kemmitt, *J. Chem. Soc.* (*A*), 1968, 1278.
41. R. Ros, M. Lenarda, T. Boschi and R. Roulet, *Inorg. Chim. Acta*, 1977, **25**, 61.
42. P. Fitton, J. E. McKeon and B. C. Ream, *Chem. Commun.*, 1969, 370.
43. O. N. Temkin, G. Shestakov, S. M. Stallovski, R. N. Flid and A. P. Aseeva, *Kinet. Katal.*, 1970, **11**, 1592.
44. H. D. Empsall, M. Green, S. K. Shakshooki and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1971, 3472.
45. H. Werner and W. Bertleff, *J. Chem. Res.*, 1978, 201.
46. S. Otsuka, A. Nakamura, T. Yoshida, M. Naruto and K. Ataka, *J. Am. Chem. Soc.*, 1973, **95**, 3180.
47. G. W. Parshall, *J. Am. Chem. Soc.*, 1974, **96**, 2360.
48. P. Fitton and E. A. Rick, *J. Organomet. Chem.*, 1971, **28**, 287.
49. A. V. Kramer, J. A. Labinger and J. A. Osborn, *J. Am. Chem. Soc.*, 1974, **96**, 7145.
50. A. V. Kramer and J. A. Osborn, *J. Am. Chem. Soc.*, 1974, **96**, 7832.
51. K. Suzuki and H. Yamamoto, *J. Organomet. Chem.*, 1973, **54**, 385.
52. G. Yoshida, Y. Matsumura, H. Kurosawa and R. Okawara, *J. Organomet. Chem.*, 1975, **92**, C53.
53. V. I. Sokolov, V. V. Bashilov, L. M. Anishchenko and O. A. Reutov, *J. Organomet. Chem.*, 1974, **71**, C41.
54. V. I. Sokolov, V. V. Bashilov, O. A. Reutov, M. N. Bochkarev, L. P. Mayorova and G. A. Razuvaev, *J. Organomet. Chem.*, 1976, **112**, C47.
55. R. Hessett, J. H. Morris and P. G. Perkins, *Inorg. Nucl. Chem. Lett.*, 1971, **7**, 1149.
56. M. Tanaka and H. Alper, *J. Organomet. Chem.*, 1979, **168**, 97.
57. C. T. Hunt and A. L. Balch, *Inorg. Chem.*, 1981, **20**, 2267.
58. J. J. Levison and S. D. Robinson, *Chem. Commun.*, 1967, 198.
59. C. J. Nyman, C. E. Wymore and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 561.
60. P. J. Hayward, D. M. Blake, C. J. Nyman and G. Wilkinson, *J. Am. Chem. Soc.*, 1970, **92**, 5873.
61. P. J. Hayward, D. M. Blake, C. J. Nyman and G. Wilkinson, *Chem. Commun.*, 1969, 987.
62. C. D. Cook and J. S. Jauhal, *J. Am. Chem. Soc.*, 1967, **89**, 3066.
63. S. Takahashi, K. Sonogashira and N. Hagihara, *Nippon Kagaku Zasshi*, 1966, **87**, 610.
64. S. Takahashi, K. Sonogashira and N. Hagihara, *Mem. Inst. Sci. Ind. Res., Osaka Univ.*, 1966, **23**, 69.
65. F. R. Hartley, 'The Chemistry of Palladium and Platinum', Applied Science, London, 1973.
66. P. M. Maitlis, P. Espinet and M. J. H. Russell, in 'Comprehensive Organometallic Chemistry', ed. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, 1982, vol. 6, chap. 38.3, p. 265.
67. S. Otsuka, Y. Tatsuno and K. Ataka, *J. Am. Chem. Soc.*, 1971, **93**, 6705.
68. M. F. Rettig and P. M. Maitlis, *Inorg. Synth.*, 1977, **17**, 134.
69. D. J. Doonan, A. L. Balch, S. Z. Goldberg, R. Eisenberg and J. S. Miller, *J. Am. Chem. Soc*, 1975, **97**, 1961.
70. S. Z. Goldberg and R. Eisenberg, *Inorg. Chem.*, 1976, **15**, 535.
71. C. H. Lindsay, L. S. Benner and A. L. Balch, *Inorg. Chem.*, 1980, **19**, 3503.
72. R. R. Guimerans, M. M. Olmstead and A. L. Balch, *J. Am. Chem. Soc.*, 1983, **105**, 1677.
73. T. D. Miller, M. A. St. Clair, M. K. Reinking and C. P. Kublak, *Organometallics*, 1983, **2**, 767.

74. P. G. Pringle and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1983, 889.
75. S. H. Taylor and P. M. Maitlis, *J. Am. Chem. Soc.*, 1978, **100**, 4700.
76. P. G. Pringle and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1982, 81.
77. A. L. Balch and L. S. Benner, *Inorg. Synth.*, 1982, **21**, 47.
78. R. G. Holloway, B. R. Penfold, R. Colton and M. J. McCormick, *J. Chem. Soc., Chem. Commun.*, 1976, 485.
79. A. L. Balch, L. S. Benner and M. M. Olmstead, *Inorg. Chem.*, 1979, **18**, 2996.
80. J. R. Boehm and A. L. Balch, *Inorg. Chem.*, 1977, **16**, 778.
81. M. M. Olmstead, H. Hope, L. S. Benner and A. L. Balch, *J. Am. Chem. Soc.*, 1977, **99**, 5502.
82. L. S. Benner, M. M. Olmstead, H. Hope and A. L. Balch, *J. Organomet. Chem.*, 1978, **153**, C31.
83. A. L. Balch, C. L. Lee, C. H. Lindsay and M. M. Olmstead, *J. Organomet. Chem.*, 1979, **177**, C22.
84. P. G. Pringle and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1982, 956.
85. M. P. Brown, R. J. Puddephatt, M. Rashidi, L. Manojlovic-Muir, K. W. Muir, T. Solomuin and K. R. Seddon, *Inorg. Chim. Acta*, 1977, **23**, L33.
86. R. Colton, M. J. McCormick and C. D. Pannan, *J. Chem. Soc., Chem. Commun.*, 1977, 823.
87. P. Braunstein, J.-M. Jud, Y. Dusausey and J. Fischer, *Organometallics*, 1983, **2**, 180.
88. J. P. Farr, M. M. Olmstead and A. L. Balch, *J. Am. Chem. Soc.*, 1980, **102**, 6654.
89. A. Maisonnat, J. P. Farr and A. L. Balch, *Inorg. Chim. Acta*, 1981, **53**, L217.
90. A. Maisonnat, J. P. Farr and A. L. Balch, *Inorg. Chem.*, 1982, **21**, 3961.
91. J. P. Farr, M. M. Olmstead and A. L. Balch, *Inorg. Chem.*, 1983, **22**, 1229.
92. R. G. Pearson and J. Dehand, *J. Organomet. Chem.*, 1969, **16**, 485.
93. P. Braunstein and J. Dehand, *J. Organomet. Chem.*, 1970, **24**, 497.
94. P. Braunstein and J. Dehand, *J. Chem. Soc., Chem. Commun.*, 1972, 164.
95. B. Messbauer, H. Meyer, B. Walther, M. J. Heeg, A. F. M. Maqsudor Rahman and J. P. Oliver, *Inorg. Chem.*, 1983, **22**, 272.
96. B. Walther, B. Messbauer and H. Meyer, *Inorg. Chim. Acta*, 1979, **37**, L525.
97. S. Otsuka, A. Nakamura, Y. Tatsuno and M. Miki, *J. Am. Chem. Soc*, 1972, **94**, 3761.
98. S. Otsuka, Y. Tatsuno, M. Miki, T. Aoki, M. Matsumoto, H. Yasioka and K. Nakatsu, *J. Chem. Soc., Chem. Commun.*, 1973, 445.
99. S. J. Cartwright, K. R. Dixon and A. D. Rattray, *Inorg. Chem.*, 1980, **19**, 1120.
100. K. R. Dixon and A. D. Rattray, *Inorg. Chem.*, 1978, **17**, 1099.
101. D. R. Coulson, *J. Am. Chem. Soc.*, 1969, **91**, 200.
102. G. W. Bushnell, K. R. Dixon, P. M. Moroney, A. D. Rattray and C. Wan, *J. Chem. Soc., Chem. Commun.*, 1977, 709.
103. A. Misono, Y. Uchida, M. Hidai and K. Kudo, *J. Organomet. Chem.*, 1969, **20**, P7.
104. K. Kudo, M. Hidai and Y. Uchida, *J. Organomet. Chem.*, 1971, **33**, 393.
105. M. Hidai, K. Kokura and Y. Uchida, *J. Organomet. Chem.*, 1973, **52**, 431.
106. R. Whyman, *J. Organomet. Chem.*, 1973, **52**, 541.
107. A. L. Balch, J. R. Boehm, H. Hope and M. M. Olmstead, *J. Am. Chem. Soc.*, 1976, **98**, 7431.
108. T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer and G. Wilkinson, *J. Chem. Soc.*, 1965, 3632.
109. A. C. Skapski and M. L. Smart, *Chem. Commun.*, 1970, 658.
110. I. I. Moiseev, T. A. Stromnova, M. N. Vargaftig, G. J. Mazo, L. G. Kuzmina and Y. T. Struchkov, *J. Chem. Soc., Chem. Commun.*, 1978, 27.
111. J. Dubrawski, J. C. Kriege-Simondsen and R. D. Feltham, *J. Am. Chem. Soc.*, 1980, **102**, 2089.
112. Y. A. Kushnikov, A. Z. Belina and V. F. Vodvizhenskii, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1971, **16**, 218.
113. P. L. Goggin and J. Mink, *J. Chem. Soc., Dalton Trans.*, 1974, 534.
114. R. L. Colton, R. H. Farthing and M. J. McCormick, *Aust. J. Chem.*, 1973, **26**, 2607.
115. R. Goddard, P. W. Jolly, C. Kruger, K. P. Schick and G. Wilke, *Organometallics*, 1982, **1**, 1709.
116. E. G. Mednikov, N. K. Eremenko, S. P. Gubin, Y. L. Slovokhotov and Y. T. Struchkov, *J. Organomet. Chem.*, 1982, **239**, 401.
117. E. G. Mednikov, N. K. Eremenko, V. Mikhailov, S. P. Gubin, Y. L. Slovokhotov and Y. T. Struchkov, *J. Chem. Soc., Chem. Commun.*, 1981, 989.
118. G. Longoni, M. Manassero and M. Sansoni, *J. Am. Chem. Soc.*, 1980, **102**, 3242.
119. J. A. Davies, F. R. Hartley and S. G. Murray, *J. Chem. Soc., Dalton Trans.*, 1980, 2246.
120. J. A. Davies, F. R. Hartley and S. G. Murray, *Inorg. Chem.*, 1980, **19**, 2299.
121. B. B. Wayland and R. F. Schramm, *Chem. Commun.*, 1968, 1465.
122. B. B. Wayland and R. F. Schramm, *Inorg. Chem.*, 1969, **8**, 971.
123. J. H. Price, R. F. Schramm and B. B. Wayland, *Chem. Commun.*, 1970, 1377.
124. J. A. Davies, F. R. Hartley and S. G. Murray, *J. Chem. Soc., Dalton Trans.*, 1979, 1705.
125. G. W. Bushnell, K. R. Dixon, R. G. Hunter and J. J. McFarland, *Can. J. Chem.*, 1972, **50**, 3694.
126. H. J. S. King, *J. Chem. Soc.*, 1938, 1338.
127. L. V. Popov, N. N. Zheligovskaya, A. M. Grevtsev, E. A. Kharina and V. I. Spitsyn, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1977, 1677 (*Chem. Abstr.*, 1977, **87**, 110 728).
128. D. S. Gill, in 'Platinum Coordination Complexes in Cancer Chemotherapy', ed. M. P. Hacker, E. B. Douple and I. H. Krakoff, Martinus Nijhoff, Boston, 1984, p. 267.
129. C. J. Nyman, C. E. Wymore and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 561.
130. J. J. Levison and S. D. Robinson, *Inorg. Nucl. Chem. Lett.*, 1968, **4**, 407.
131. J. J. Levison and S. D. Robinson, *J. Chem. Soc.* (*A*), 1971, 762.
132. F. Cariati, R. Ugo and F. Bonati, *Inorg. Chem.*, 1966, **5**, 1128.
133. B. M. Gatehouse, S. E. Livingstone and R. S. Nyholm, *J. Chem. Soc.*, 1957, 4222.
134. V. S. Shmidt, N. A. Shorokhov, A. A. Vashman and V. E. Samsonov, *Zh. Neorg. Khim.*, 1982, **27**, 1254.
135. S. E. Livingstone, *J. Proc. R. Soc. NSW*, 1952, **86**, 32.
136. D. A. Langs, C. R. Hare and R. G. Little, *Chem. Commun.*, 1967, 1080.

137. A. V. Nikiforova, I. I. Moiseev and Ya. K. Syrkin, *Zh. Obshch. Khim.*, 1963, **33**, 3239 (*Chem. Abstr.*, 1963, **60**, 3995c).
138. W. G. Lloyd, *J. Org. Chem.*, 1967, **32**, 2816.
139. M. Graziani, P. Uguagliati and G. Carturan, *J. Organomet. Chem.*, 1971, **27**, 275.
140. M. Graziani, R. Ros and G. Carturan, *J. Organomet. Chem.*, 1971, **27**, C19.
141. R. Ros, G. Carturan and M. Graziani, *Transition Met. Chem.* (*Weinheim, Ger.*), 1975, **1**, 13.
142. F. Glockling and E. H. Brooks, *Prepr., Div. Pet. Chem., Am. Chem. Soc.*, 1969, **14**, B135.
143. D. A. White, *J. Chem. Soc.* (*A*), 1971, 143.
144. T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer and G. Wilkinson, *J. Chem. Soc.*, 1965, 3632.
145. T. Yeh and H. Frye, *J. Inorg. Nucl. Chem.*, 1977, **39**, 705.
146. A. C. Skapski and M. L. Smart, *Chem. Commun.*, 1970, 658.
147. M. Tamura and T. Yasui, *J. Chem. Soc. Jpn., Ind. Chem. Sect.*, 1968, **71**, 1855 (*Chem. Abstr.*, 1969, **70**, 61 532).
148. C. Bird, B. L. Booth, R. N. Haszeldine, G. R. H. Neuss, M. A. Smith and A. Flood, *J. Chem. Soc., Dalton Trans.*, 1982, 1109.
149. M. N. S. Hill, B. F. G. Johnson and J. Lewis, *J. Chem. Soc.* (*A*), 1971, 2341.
150. C. B. Anderson and B. J. Burreson, *J. Organomet. Chem.*, 1967, **7**, 181.
151. J. Powell, *J. Am. Chem. Soc.*, 1969, **91**, 4311.
152. J. Powell and T. Jack, *Inorg. Chem.*, 1972, **11**, 1039.
153. M. J. Schmelz, T. Miyazama, S. Mizushima, T. J. Lane and J. V. Quagliano, *Spectrochim. Acta*, 1957, **9**, 51.
154. M. J. Schmelz, I. Nakagawa, S. Mizushima and J. V. Quagliano, *J. Am. Chem. Soc.*, 1959, **81**, 287.
155. European Patent Application, EP98134.
156. F. G. Mann, D. Crowfoot, D. C. Gattiker and N. Wooster, *J. Chem. Soc.*, 1935, 1642.
157. G. A. Barbieri, *Atti. Accad. Lincei, Rend.*, 1914, **23**, 334 (*Chem. Abstr.*, 1914, **8**, 2988).
158. A. A. Grinberg and L. K. Simonova, *Zh. Prikl. Khim.*, 1953, **26**, 880 (*Chem. Abstr.*, 1953, **47**, 11 060).
159. S. Okeya, H. Asai, S. Ooi, K. Matsumoto, S. Kawaguchi and H. Kuroya, *Inorg. Nucl. Chem. Lett.*, 1976, **12**, 677.
160. S. Okeya, S. Ooi, K. Matsumoto, Y. Nakamura and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 1085.
161. P.-K. Hon, C. E. Pfluger and R. L. Bedford, *Inorg. Chem.*, 1967, **6**, 730.
162. M. Mikami, I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta, Part A*, 1967, **23**, 1037.
163. K. Nakamoto, C. Udovich and J. Takemoto, *J. Am. Chem. Soc.*, 1970, **92**, 3973.
164. R. G. Pearson and D. A. Johnson, *J. Am. Chem. Soc.*, 1964, **86**, 3983.
165. K. Saito and M. Takahashi, *Bull. Chem. Soc. Jpn.*, 1969, **42**, 3462.
166. N. Yanase, Y. Nakamura and S. Kawaguchi, *Inorg. Chem.*, 1980, **19**, 1575.
167. A. R. Siedle and L. H. Pignolet, *Inorg. Chem.*, 1981, **20**, 1849.
168. S. Okeya, H. Sazaki, M. Ogita, T. Takemoto, Y. Onuki, Y. Nakamura, B. K. Mohapatra and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 1978.
169. S. Okeya, T. Miyamoto, S. Ooi, Y. Nakamura and S. Kawaguchi, *Inorg. Chim. Acta*, 1980, **45**, L135.
170. A. R. Siedle, R. A. Newmark and L. H. Pignolet, *J. Am. Chem. Soc.*, 1981, **103**, 4947.
171. A. R. Siedle, R. A. Newmark, A. A. Kruger and L. H. Pignolet, *Inorg. Chem.*, 1981, **20**, 3399.
172. S. Okeya, H. Yoshimatsu, Y. Nakamura and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 483.
173. B. F. G. Johnson, J. Lewis and D. A. White, *Synth. Inorg. Met.-Org. Chem.*, 1971, **1**, 243.
174. S. Okeya, Y. Kawakita, S. Matsumoto, Y. Nakamura, S. Kawaguchi, N. Kanehisa, K. Miki and N. Kasai, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 2134.
175. A. R. Siedle and L. H. Pignolet, *Inorg. Chem.*, 1982, **21**, 135.
176. J. P. Collman, *Angew. Chem., Int. Ed. Engl.*, 1965, **4**, 132.
177. D. A. White, *J. Chem. Soc.* (*A*), 1971, 233.
178. O. Gandolfi, G. Dolcetti, M. Ghedini and M. Lais, *Inorg. Chem.*, 1980, **19**, 1785.
179. M. Ghedini, G. De Munno, G. Denti and G. Dolcetti, *Transition Met. Chem.* (*Weinheim, Ger.*), 1981, **6**, 298.
180. F. W. Pinkard, E. Sharratt, W. Wardlaw and E. G. Cox, *J. Chem. Soc.*, 1934, 1012.
181. J. S. Coe and J. R. Lyons, *J. Chem. Soc.* (*A*), 1971, 829.
182. L. E. Maley and D. P. Mellor, *Aust. J. Sci. Res., Ser. A*, 1949, **2**, 579 (*Chem. Abstr.*, 1951, **45**, 3279c).
183. J. W. Mellor, 'A Comprehensive Treatise on Inorganic and Theoretical Chemistry', Longmans, Green and Co. Ltd., London, 1936, vol. XV.
184. I. S. Shaplygin and V. B. Lazarev, *Zh. Neorg. Khim.*, 1978, **23**, 603.
185. I. S. Mirskova, G. A. Sytov, I. M. Skanazarova, V. G. Avakyan, V. N. Perchenko and N. S. Nametkin, *Dokl. Akad. Nauk SSSR.* 1977, **237**, 346.
186. P. L. Goggin, R. J. Goodfellow and F. J. S. Reed, *J. Chem. Soc., Dalton Trans.*, 1972, 1298.
187. J. S. Coe and J. R. Lyons, *Inorg. Chem.*, 1970, **9**, 1775.
188. J. R. Miller, *Proc. Chem. Soc.*, 1960, 318.
189. J. R. Miller, *J. Chem. Soc.*, 1965, 713.
190. 'Gmelin's Handbuch der Anorganischen Chemie', Verlag Chemie, Berlin, 1942, vol. 65.
191. J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 1955, 3858.
192. J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 1957, 2445.
193. J. Chatt and F. G. Mann, *J. Chem. Soc.*, 1939, 1622.
194. M. A. Spinnler and L. N. Becka, *J. Chem. Soc.* (*A*), 1967, 1194.
195. F. P. Boer, V. B. Carter and J. W. Turley, *Inorg. Chem.*, 1971, **10**, 651.
196. J. Iball, M. Macdougall and S. Scrimgeour, *Acta Crystallogr., Sect. B*, 1975, **31**, 1672.
197. J. R. Wiesner and E. C. Lingafelter, *Inorg. Chem.*, 1966, **5**, 1770.
198. S. Baggio, L. M. Amzel and L. N. Becka, *Acta Crystallogr., Sect. B*, 1970, **26**, 1698.
199. D. S. Gill, in 'Platinum Coordination Complexes in Cancer Chemotherapy', ed. M. P. Hacker, E. B. Douple and I. H. Krakoff, Martinus Nijhoff, Boston, 1984, p. 267.

200. R. Saito and Y. Kidani, *Chem. Lett.*, 1977, 1141.
201. T. G. Appleton and J. R. Hall, *Inorg. Chem.*, 1970, **9**, 1800.
202. T. G. Appleton and J. R. Hall, *Inorg. Chem.*, 1972, **11**, 112.
203. T. H. Appleton and J. R. Hall, *Inorg. Chem.*, 1970, **9**, 1807.
204. C. Burgess, F. R. Hartley and G. W. Searle, *J. Organomet. Chem.*, 1974, **76**, 247.
205. W. H. Baddley and F. Basolo, *J. Am. Chem. Soc.*, 1966, **88**, 2944.
206. P. F. Chin and F. R. Hartley, *Inorg. Chem.*, 1976, **15**, 982.
207. F. Hori, K. Matsumato, S. Ooi and H. Kuroya, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 138.
208. J. C. Gibson and G. D. McKenzie, *J. Chem. Soc. (A)*, 1971, 1666.
209. C. V. Senoff, *Inorg. Chem.*, 1978, **17**, 2320.
210. F. S. Walker, S. N. Bhattacharya and C. V. Senoff, *Inorg. Synth.*, 1982, **21**, 129.
211. S. N. Bhattacharya and C. V. Senoff, *Inorg. Chim. Acta*, 1980, **41**, 67.
212. P. M. Maitlis, P. Espinet and M. J. H. Russell, in 'Comprehensive Organometallic Chemistry', ed. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, 1982, vol. 6, chap. 38, p. 233.
213. J. B. Brandon, M. Collins and K. R. Dixon, *Can. J. Chem.*, 1978, **56**, 950.
214. R. D. Gillard, L. A. P. Kane-Maguire and P. A. Williams, *Transition Met. Chem. (Weinheim, Ger.)*, 1977, **2**, 55.
215. P. C. Chieh, *J. Chem. Soc., Dalton Trans.*, 1972, 1643.
216. J. Reedijk and J. K. de Ridder, *Inorg. Nucl. Chem. Lett.*, 1976, **12**, 585.
217. T. N. Hazarika and T. Bora, *Transition Met. Chem. (Weinheim, Ger.)*, 1982, **7**, 210.
218. L. K. Mishra, *J. Indian Chem. Soc.*, 1982, **59**, 408.
219. M. C. Navarro Ranninger and M. Gayoso, *An. Quim.*, 1978, **74**, 717.
220. M. C. Navarro Ranninger and M. Gayoso, *An. Quim.*, 1978, **74**, 722.
221. C. G. Van Kralingen, J. K. de Ridder and J. Reedijk, *Inorg. Chim. Acta*, 1979, **36**, 69.
222. P. C. Kong and F. D. Rochon, *Can. J. Chem.*, 1981, **59**, 3293.
223. A. Adeyemo and A. Shodeinde, *Inorg. Chim. Acta*, 1981, **54**, L105.
224. A. Adeyemo, Y. Teklu and T. Williams, *Inorg. Chim. Acta*, 1981, **51**, 19.
225. A. Adeyemo and R. P. Raval, *Inorg. Chim. Acta*, 1982, **66**, L1.
226. N. Hadjiliadis and G. Pneumatikakis, *J. Chem. Soc., Dalton Trans.*, 1978, 1691.
227. G. Pneumatikakis, N. Hadjiliadis and T. Theophanides, *Inorg. Chem.*, 1978, **17**, 915.
228. J. Dehand and J. Jordanov, *J. Chem. Soc., Dalton Trans.*, 1977, 1588.
229. F. D. Rochon, P. C. Kong, B. Coulombe and R. Melanson, *Can. J. Chem.*, 1980, **58**, 381.
230. G. Pneumatikakis, N. Hadjiliades and T. Theophanides, *Inorg. Chim. Acta*, 1977, **22**, L1.
231. S. Yamada and K. Yamanouchi, *Bull. Chem. Soc. Jpn.*, 1969, **42**, 2543.
232. E. Frasson, C. Panattoni and L. Sacconi, *Acta Crystallogr.*, 1964, **17**, 85.
233. E. Frasson, C. Panattoni and L. Sacconi, *Acta Crystallogr.*, 1964, **17**, 477.
234. R. L. Braun and E. C. Lingafelter, *Acta Crystallogr.*, 1967, **22**, 787.
235. P. C. Jain and E. C. Lingafelter, *Acta Crystallogr.*, 1967, **23**, 127.
236. V. W. Day, M. D. Glick and J. L. Hoard, *J. Am. Chem. Soc.*, 1968, **90**, 4803.
237. C. E. Pfluger, R. L. Harlow and S. H. Simonsen, *Acta Crystallogr., Sect. B*, 1970, **26**, 1631.
238. F. C. March, D. A. Couch, K. Emerson, J. E. Fergusson and W. T. Robinson, *J. Chem. Soc. (A)*, 1971, 440.
239. M. Tsutsin, R. L. Bobsein, G. Cash and R. Pettersen, *Inorg. Chem.*, 1979, **18**, 758.
240. K. S. Patel and J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, 1971, **33**, 1399.
241. J. D. Goddard, *Inorg. Nucl. Chem. Lett.*, 1977, **13**, 555.
242. B. R. Singhvi, M. R. Mali and R. K. Mehta, *Curr. Sci.*, 1977, **46**, 636.
243. E. A. Andronov, Y. N. Kukushkin and Y. V. Murashkin, *Izv. Vyssh. Uchebn. Zaved., Khim. Tekhnol*, 1976, **19**, 1479 (*Chem. Abstr.*, 1977, **86**, 50075).
244. H. van der Prel, G. van Koten and K. Vrieze, *Inorg. Chem.*, 1980, **19**, 1145.
245. K. R. Laing, S. D. Robinson and M. F. Uttley, *J. Chem. Soc., Dalton Trans.*, 1974, 1205.
246. L. D. Brown and J. A. Ibers, *Inorg. Chem.*, 1976, **15**, 2794.
247. C. J. Cresswell, M. A. M. Queiuros and S. D. Robinson, *Inorg. Chim. Acta*, 1982, **60**, 157.
248. B. M. Bycroft and J. D. Cotton, *J. Chem. Soc., Dalton Trans.*, 1973, 1867.
249. A. V. Babeva and M. A. Mosyagina, *Dokl. Akad. Nauk SSSR*, 1953, **89**, 293.
250. S. Imamura, T. Kajimoto, Y. Kitano and J. Tsuji, *Bull. Chem. Soc. Jpn.*, 1969, **42**, 805.
251. M. Calleri, G. Ferraris and D. Viterbo, *Inorg. Chim. Acta*, 1967, **1**, 297.
252. C. Panattoni, E. Frasson and R. Zanetti, *Gazz. Chim. Ital.*, 1959, **89**, 2132.
253. D. E. Williams, G. Wohlauer and R. E. Rundle, *J. Am. Chem. Soc.*, 1959, **81**, 755.
254. M. Cowie, A. Gleizes, G. W. Grynkewich, D. W. Kalina, M. S. McClure, R. P. Scaringe, R. C. Teitelbaum, S. L. Ruby, J. A. Ibers, C. R. Kannewurf and T. J. Marks, *J. Am. Chem. Soc.*, 1979, **101**, 2921.
255. L. D. Brown, D. W. Kalina, M. S. McClure, S. Schultz, S. L. Ruby, J. A. Ibers, C. R. Kannewurf and T. J. Marks, *J. Am. Chem. Soc.*, 1979, **101**, 2937.
256. D. W. Kalina, J. W. Lyding, M. T. Ratujack, C. R. Kannewurf and T. J. Marks, *J. Am. Chem. Soc.*, 1980, **102**, 7854.
257. J. T. Devreese, R. P. Evrard and V. E. van Doren, 'Highly Conducting One-Dimensional Solids', Plenum, New York, 1979.
258. M. S. Ma and R. J. Angelici, *Inorg. Chem.*, 1980, **19**, 363.
259. K. C. Kalia and A. Chakravorty, *Inorg. Chem.*, 1969, **8**, 2586.
260. P. K. Mascharak, S. K. Adhikari and A. Chakravorty, *Inorg. Nucl. Chem. Lett.*, 1972, **13**, 27.
261. P. K. Mascharak and A. Chakravorty, *J. Chem. Soc., Dalton Trans.*, 1980, 1698.
262. E. Wolff, *Justus Liebigs Ann. Chem.*, 1902, **325**, 139.
263. U. B. Talwar and B. C. Haldar, Proc. Int. Conf. Coord. Chem., 10th, Tokyo, 1967, p. 395.
264. D. A. White, *J. Chem. Soc. (A)*, 1971, 233.
265. B. P. Sudha, N. S. Dixit and C. C. Patel, *Z. Anorg. Allg. Chem.*, 1978, **444**, 237.
266. K. S. Bose, B. C. Sharma and C. C. Patel, *Inorg. Chem.*, 1973, **12**, 120.

267. B. P. Sudha, N. S. Dixit and C. C. Patel, *Bull. Chem. Soc. Jpn.*, 1978, **51,** 2160.
268. C. B. Mahto, *J. Indian Chem. Soc.*, 1980, **57,** 553.
269. G. Natile, F. Gasparrini, D. Misiti and G. Perego, *J. Chem. Soc., Dalton Trans.*, 1977, 1747.
270. A. G. Constable, W. S. McDonald and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1979, 1109.
271. M. M. Patel, M. R. Patel and B. N. Mankad, *J. Indian Chem. Soc.*, 1976, **53,** 454.
272. M. M. Patel, M. R. Patel and B. N. Mankad, *J. Indian Chem. Soc.*, 1977, **54,** 1188.
273. M. M. Patel and M. R. Patel, *J. Indian Chem. Soc.*, 1980, **57,** 748.
274. M. M. Patel and M. R. Patel, *J. Indian Chem. Soc.*, 1980, **57,** 676.
275. R. C. Agarwal, V. Singh and G. K. Agarwal, *J. Inorg. Nucl. Chem.*, 1980, **42,** 1073.
276. M. F. Iskander, M. M. Mishrikey, L. El-Sayed and A. El-Toukhy, *J. Inorg. Nucl. Chem.*, 1979, **41,** 815.
277. Y. Thakur and B. N. Jha, *J. Inorg. Nucl. Chem.*, 1980, **42,** 449.
278. S. E. Livingstone and J. E. Oluka, *Transition Met. Chem. (Weinheim, Ger.)*, 1977, **2,** 163.
279. S. E. Livingstone and J. E. Oluka, *Transition Met. Chem. (Weinheim, Ger.)*, 1977, **2,** 190.
280. H. Elias, E. Hilms and H. Paulus, *Z. Naturforsch., Teil B*, 1982, **37,** 1266.
281. V. Eisner and M. J. C. Harding, *J. Chem. Soc.*, 1964, 4089.
282. T. Tokumitsu and T. Hayashi, *Bull. Chem. Soc. Jpn.*, 1981, **54,** 2348.
283. S. Brawner and K. B. Mertes, *J. Inorg. Nucl. Chem.*, 1979, **41,** 764.
284. K. B. Yatsimirskii, A. N. Boiko, V. A. Bidzilya and L. P. Kazanskii, *Zh. Neorg. Khim.*, 1982, **27,** 2586.
285. K. B. Merkes and J. R. Ferraro, *J. Chem. Phys.*, 1979, **70,** 646.
286. W. E. Hatfield, *Gov. Rep. Announce. Index (U.S.)*, 1981, **81,** 362 (*Chem. Abstr.*, 1981, **95,** 17 252).
287. H. H. Schmidtke and D. Garthoff, *J. Am. Chem. Soc.*, 1967, **89,** 1317.
288. W. Beck, K. Feldl and E. Schuierer, *Angew. Chem., Int. Ed. Engl.*, 1965, **4,** 439.
289. W. Beck, W. P. Fehlhammer, P. Pollmann, E. Schuierer and K. Feldl, *Chem. Ber.*, 1967, **100,** 2335.
290. K. Bowman and Z. Dori, *Inorg. Chem.*, 1970, **9,** 395.
291. W. Beck, W. P. Fehlhammer, P. Pullmann and R. S. Tobias, *Inorg. Chim. Acta*, 1968, **2,** 467.
292. W. Beck, P. Kreutzer and K. Van Werner, *Chem. Ber.*, 1971, **104,** 528.
293. W. Beck and W. P. Fehlhammer, *Angew. Chem., Int. Ed. Engl.*, 1967, **6,** 169.
294. W. Beck, W. P. Fehlhammer, P. Pollmann and H. Schahl, *Chem. Ber.*, 1969, **102,** 1976.
295. J. P. Collman, M. Kubota and J. W. Hosking, *J. Am. Chem. Soc.*, 1967, **89,** 4809.
296. P. Kreutzer, Ch. Weiss, H. Boehme, T. Kemmerich, W. Beck, C. Spencer and R. Mason, *Z. Naturforsch., Teil B*, 1972, **27,** 745.
297. W. Beck, K. Burger and W. P. Fehlhammer, *Chem. Ber.*, 1971, **104,** 1816.
298. W. Beck, W. P. Fehlhammer, H. Bock and M. Bauder, *Chem. Ber.*, 1969, **102,** 3637.
299. J. R. Doyle, P. E. Slade and H. B. Jonassen, *Inorg. Synth.*, 1960, **6,** 218.
300. M. V. Capparelli and L. N. Becka, *J. Chem. Soc. (A)*, 1969, 260.
301. O. Hassel and B. F. Pedersen, *Proc. Chem. Soc.*, 1959, 394.
302. L. F. Power, *Inorg. Nucl. Chem. Lett.*, 1970, **6,** 791.
303. F. R. Hartley, 'The Chemistry of Palladium and Platinum', Applied Science, London, 1973.
304. D. J. Gulliver and W. Levason, *Coord. Chem. Rev.*, 1982, **46,** 1.
305. P. R. Row, A. Tressaud and N. Bartlett, *Inorg. Nucl. Chem. Lett.*, 1976, **12,** 23.
306. N. Bartlett and P. R. Rao, *Proc. Chem. Soc.*, 1964, 393.
307. N. Bartlett, B. Zemva and L. Graham, *J. Fluorine Chem.*, 1976, **7,** 301.
308. A. F. Wright, B. E. F. Fender, N. Bartlett and K. Leary, *Inorg. Chem.*, 1978, **17,** 748.
309. A. G. Sharpe, *J. Chem. Soc.*, 1950, 3444.
310. B. Cox, D. W. A. Sharp and A. G. Sharpe, *J. Chem. Soc.*, 1956, 1242.
311. D. D. Partukhova, I. M. Cheremisina and S. V. Zeruskov, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1972, 67 (*Chem. Abstr.*, 1973, **78,** 66 411).
312. A. G. Sharpe, *J. Chem. Soc.*, 1953, 197.
313. R. Hoppe and W. Klemm, *Z. Anorg. Allg. Chem.*, 1952, **268,** 364.
314. H. Henkel and R. Hoppe, *Z. Anorg. Allg. Chem.*, 1968, **359,** 160.
315. S. V. Zemskov, Yu. I. Nikonorov, E. D. Pastukhova and V. N. Mit'kin, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1976, 83 (*Chem. Abstr.*, 1976, **85,** 86 494).
316. S. V. Zemskov, A. A. Opalovskii, K. A. Grigorova, I. M. Cheremisina and E. V. Sobolev, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1970, 97 (*Chem. Abstr.*, 1971, **73,** 41 323).
317. N. Bartlett and J. W. Quail, *J. Chem. Soc.*, 1961, 3228.
318. A. Tressaud, M. Wintenberger, N. Bartlett and P. Hagenmuller, *C. R. Hebd. Seances Acad. Sci., Ser. C*, 1976, **282,** 1069.
319. W. A. Sunder, A. L. Wayda, D. Distefano, W. E. Falconer and J. E. Griffiths, *J. Fluorine Chem.*, 1979, **14,** 299.
320. K. Leary, D. H. Templeton, A. Zalkin and N. Bartlett, *Inorg. Chem.*, 1973, **12,** 1726.
321. D. Babel, *Struct. Bonding (Berlin)*, 1967, **3,** 1.
322. D. H. Brown, K. R. Dixon, R. D. W. Kemmitt and D. W. A. Sharp, *J. Chem. Soc.*, 1965, 1559.
323. L. Wohler and F. Muller, *Z. Anorg. Allg. Chem.*, 1925, **149,** 377.
324. A. Gutbier and A. Krell, *Chem. Ber.*, 1905, **38,** 2385.
325. A. Gutbier and C. Fellner, *Z. Anorg. Allg. Chem.*, 1916, **95,** 129.
326. F. Puche, *Ann. Chim. (Paris)*, 1938, **9,** 233 (*Chem. Abstr.*, 1938, **32,** 5322).
327. A. Gutbier and F. Bauriedel, *Chem. Ber.*, 1909, **42,** 4243.
328. D. Sinram, C. Brendel and B. Krebs, *Inorg. Chim. Acta*, 1982, **64,** L131.
329. L. B. Shubochkin, L. D. Sorokina and E. F. Shubochkin, *Zh. Neorg. Khim.*, 1976, **21,** 2567.
330. J. D. Bell, D. Hall and T. N. Waters, *Acta Crystallogr.*, 1966, **21,** 440.
331. R. D. Peacock and D. W. A. Sharp, *J. Chem. Soc.*, 1959, 2762.
332. P. J. Hendra and P. J. D. Park, *Spectrochim. Acta, Part A*, 1967, **23,** 1635.
333. M. Debau and H. Poulet, *Spectrochim. Acta, Part A*, 1969, **25,** 1553.
334. Y. M. Bosworth and R. J. H. Clark, *J. Chem. Soc., Dalton Trans.*, 1974, 1749.

335. D. A. Kelly and M. L. Good, *Spectrochim. Acta, Part A*, 1972, **28**, 1529.
336. D. H. Brown, K. R. Dixon, C. M. Livingston, R. H. Nuttall and D. W. Sharp, *J. Chem. Soc. (A)*, 1967, 100.
337. H. Hirashi, I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, 1964, **20**, 819.
338. H. Hamaguchi, I. Harada and T. Shimanouchi, *J. Raman Spectrosc.*, 1974, **2**, 517.
339. R. W. Berg, *J. Chem. Phys.*, 1979, **71**, 2531.
340. D. M. Adams and D. M. Morris, *J. Chem. Soc. (A)*, 1967, 1666.
341. Yu. N. Kukushkin, G. N. Sedova and R. A. Vlasova, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1978, **23**, 1032.
342. H. D. K. Drew, F. W. Pinkard, G. H. Preston and W. Wardlaw, *J. Chem. Soc.*, 1932, 1895.
343. Yu. N. Kukushkin, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1963, **8**, 417.
344. R. J. H. Clark and W. R. Trumble, *Inorg. Chem.*, 1976, **15**, 1030.
345. A. J. Cohen and N. Davidson, *J. Am. Chem. Soc.*, 1951, **73**, 1955.
346. D. J. Gulliver and W. Levason, *J. Chem. Soc., Dalton Trans.*, 1982, 1895.
347. B. Bosnich, *J. Chem. Soc. (A)*, 1966, 1394.
348. A. Rosenheim and T. A. Maass, *Z. Anorg. Allg. Chem.*, 1898, **18**, 331.
349. S. E. Livingstone, *J. Proc. R. Soc. NSW*, 1952, 31.
350. S. E. Livingstone, *J. Proc. R. Soc. NSW*, 1951, 151.
351. L. F. Power, *Synth. React. Inorg. Met.-Org. Chem.*, 1975, **5**, 181.
352. D. Sen, *Sci. Cult.*, 1962, **28**, 292.
353. D. Spacu and G. Georghui, *Z. Anorg. Allg. Chem.*, 1967, **351**, 201.
354. D. Spacu, G. G. Georghui and N. Vladescu, *Rev. Roum. Chim.*, 1967, **12**, 269.
355. D. Sen, *J. Indian Chem. Soc.*, 1974, **51**, 183.
356. A. V. Babaeva and E. Y. Khananova, *Dokl. Akad. Nauk SSSR*, 1964, **159**, 586.
357. A. V. Babaeva and E. Y. Khananova, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1965, **10**, 1402.
358. A. V. Babaeva and E. Y. Khananova, *Dokl. Akad. Nauk SSSR*, 1965, **164**, 807.
359. A. V. Babaeva and E. Y. Khananova, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1965, **10**, 1441.
360. A. V. Babaeva and E. Y. Khananova, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1967, **12**, 202.
361. W. R. Mason, *Inorg. Chem.*, 1973, **12**, 20.
362. H. Ito, J. Fujita and K. Saito, *Bull. Chem. Soc. Jpn.*, 1969, **42**, 1286.
363. C. M. Harris, R. S. Nyholm and D. J. Phillips, *J. Chem. Soc.*, 1960, 4379.
364. G. A. Barclay, R. S. Nyholm and R. V. Parish, *J. Chem. Soc.*, 1961, 4433.
365. L. F. Warren and M. A. Bennett, *Inorg. Chem.*, 1976, **15**, 3126.
366. G. A. Barclay, M. A. Collard, C. M. Harris and J. V. Kingston, *J. Chem. Soc. (A)*, 1969, 830.
367. J. G. Hartley, L. M. Venanzi and D. C. Goodall, *J. Chem. Soc.*, 1963, 3930.
368. L. R. Gray, D. J. Gulliver and W. Levason, *J. Chem. Soc., Dalton Trans.*, 1983, 133.
369. H. Siebert and A. Siebert, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 600.
370. H. Siebert and A. Siebert, *Z. Anorg. Allg. Chem.*, 1970, **378**, 160.
371. D. L. Swihart and W. R. Mason, *Inorg. Chem.*, 1970, **9**, 1749.
372. H. Siebert and M. Wiese, *Z. Naturforsch., Teil B*, 1975, **30**, 33.
373. H. Siebert and A. Siebert, *Z. Naturforsch., Teil B*, 1969, **22**, 674.
374. H. Siebert and M. Weise, *Z. Naturforsch., Teil B*, 1972, **27**, 865.
375. A. Ludi and G. Ron, *Chimia*, 1971, **25**, 333.
376. H. Siebert and W. Jentsch, *Z. Anorg. Allg. Chem.*, 1980, **469**, 87.
377. H. J. Buser, G. Ron, A. Ludi and P. Engel, *J. Chem. Soc., Dalton Trans.*, 1974, 2473.
378. L. Wohler and J. Konig, *Z. Anorg. Allg. Chem.*, 1905, **46**, 323.
379. B. N. Ivanov-Emin, N. V. Venskoskii, I. N. Linko, B. Zaitsev and L. D. Borzova, *Koord. Khim.*, 1980, **6**, 928 (*Chem. Abstr.*, 1980, **93**, 106 193).
380. B. N. Ivanov-Emin, L. D. Borzova, A. M. Egorov and D. Subzhben, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1974, **19**, 855.
381. I. S. Shaplygin, G. L. Aparnikov and V. L. Blazarev, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1978, **23**, 488.
382. A. W. Sleight, *Mater. Res. Bull.*, 1968, **3**, 699.
383. M. Wilhelm and R. Hoppe, *Z. Anorg. Allg. Chem.*, 1976, **424**, 5.
384. H. Sabrowsky and R. Hoppe, *Naturwissenschaften*, 1966, **53**, 501.
385. C. C. Addison and B. G. Ward, *Chem. Commun.*, 1966, 155.
386. K. C. Lee and F. A. Aubke, *Can. J. Chem.*, 1977, **55**, 2473.
387. K. C. Lee and F. A. Aubke, *Can. J. Chem.*, 1979, **57**, 2058.
388. H. Siebert and W. Mader, *Z. Anorg. Allg. Chem.*, 1967, **351**, 146.
389. M. W. Lister and P. M. McLeod, *Can. J. Chem.*, 1965, **43**, 1720.
390. K. A. Jensen and V. Krishnan, *Acta Chem. Scand.*, 1967, **21**, 1988.
391. J. Willense and J. A. Cras, *Recl. Trav. Chim. Pays-Bas*, 1972, **91**, 1309.
392. J. Willemse, J. A. Cras, J. G. Wynhoven and P. T. Bewskens, *Recl. Trav. Chim. Pays-Bas*, 1973, **92**, 1199.
393. A. C. Frabetti, G. C. Franchini and G. Peyronel, *Transition Metal Chem. (Weinheim, Ger.)*, 1980, **5**, 350.
394. S. K. Shani, P. C. Jain and V. B. Rann, *Indian J. Chem.*, 1974, **12**, 631.
395. D. Singh, M. M. P. Rukhaiyar, R. K. Mehra and R. J. Sinha, *Indian J. Chem., Sect. A*, 1979, **17**, 520.
396. V. Agarwala and L. Agarwala, *J. Inorg. Nucl. Chem.*, 1972, **34**, 251.
397. M. R. Gagendragad and V. Agarwala, *Aust. J. Chem.*, 1975, **28**, 763.

51.8

Palladium(II): Sulfur Donor Complexes

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51.8.1 INTRODUCTION

Palladium(II) is a class b or 'soft' metal ion and therefore generally forms stronger complexes with sulfur donors than with oxygen donor ligands. A comparison of the complexes of the simple oxygen and sulfur ligands shows that H_2O and ROH form more stable complexes than H_2S and RSH, that OH^- forms complexes of comparable stability to SH^-, and that R_2O and RO^- form very much less stable complexes than R_2S and RS^-.[1] An electrostatic model of the bonding predicts the relative positions of the neutral ligands since the permanent dipole moments and coordinating abilities of the oxygen ligands decrease in the order $H_2O > ROH > R_2O$, whereas for the sulfur ligands they both increase in the order $H_2S < RSH < R_2S$. The greater polarizability of sulfur means that this permanent dipole moment will be augmented by an induced dipole moment, which will be greater for the sulfur than for the oxygen ligands. Another contribution to the strength of the palladium(II)–sulfur bond could be made by π back-donation of electron density from the metal atom to the empty, relatively low energy *d* orbitals on sulfur. On the other hand, both electrostatic and covalent descriptions of the σ bonding in the complexes of the anionic ligands suggest that the stability should decrease in the order $RO^- > RS^-$, whereas in fact the reverse is found experimentally.[1] This suggests that π back-donation of electron density from metal to ligand may be important in the thiolato complexes, explaining the observed stability order $RS^- > RO^-$, since π back-donation will be absent in the alkoxide complexes due to the lack of suitable empty low energy orbitals on oxygen. Complexes of palladium(II) with sulfur, selenium or tellurium donor ligands generally exhibit similar stabilities, though the actual stability sequence within this group of donor atoms depends on the nature of the other ligands bound to the metal.

Ligands such as sulfite ions, thiosulfate ions, thiourea and dialkyl thioethers that bind to palladium(II) through a sulfur atom generally exhibit a high *trans* effect as deduced from preparative studies.[2] However, the *trans* influence of these ligands is negligible; this has been deduced, for example, from the IR stretching frequencies of Pd—Cl bonds *trans* to dialkyl thioethers and from X-ray crystallographic determinations of palladium–ligand bond lengths in *trans* positions.[1] The *trans* effect of these ligands is therefore probably a π *trans* effect resulting from π back-donation of electron density from the palladium atom to sulfur, leaving the ligand with little or no *trans* influence. However, it should be remembered that it is possible for a ligand that has no apparent *trans* influence to exert a polarization or σ *trans* effect. Reference 1 discusses these topics in depth.

This section of the coverage of palladium(II) coordination chemistry will concentrate on complexes of the more common, usually unidentate ligands containing sulfur, selenium or tellurium donor atoms; coverage of the vast number of chelate complexes of bi- or multi-dentate ligands will be limited but the reader will find references to most classes of palladium(II) chelate complexes and these will provide an entry into the literature.

51.8.2 UNIDENTATE LIGANDS

51.8.2.1 Sulfides, Hydro-sulfides and -selenides and Other Small Ligands

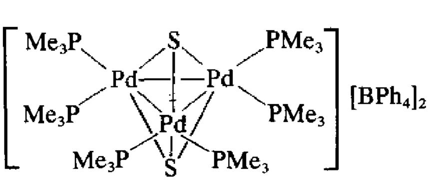
The simplest sulfur ligand is the sulfide anion S^{2-} but the simple, water insoluble, binary compound PdS is not usually regarded as a coordination complex and is discussed elsewhere along with PdSe and PdTe.[1,3,4,5] A simple sulfide complex can be prepared by reacting sodium sulfide with $[PdCl_2(dppe)]$ as in equation (1).[6] The yellow palladium(II) complex apparently requires a bidentate phosphine for stabilization, whereas for the corresponding platinum(II) complex monodentate phosphines are adequate. The rôle of the bidentate phosphine for palladium(II) is probably to stabilize the *cis* geometry, since the platinum(II) product with monodentate phosphines is *cis*. This is seen again in the requirement of a bidentate phosphine for the preparation of the rare HE^- (E = S or Se) complexes shown in equations (2)[6,7] and (3),[6,7,8] although reaction of the azido complex $[Pd(N_3)_2(PPh_3)_2]$ in dichloromethane at −30 °C with H_2S does give the yellow di(hydrosulfido) complex $[Pd(SH)_2(PPh_3)_2]$.[9]

$$[PdCl_2(dppe)] + 2Na_2S{\cdot}9H_2O \xrightarrow[\text{reflux 72 h}]{\text{EtOH}} Na_2[Pd(S)_2(dppe)] + 2NaCl + 9H_2O \quad (1)$$

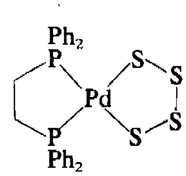
$$[PdCl_2(dppe)] + 2H_2S + 2NEt_3 \xrightarrow{C_6H_6} [Pd(SH)_2(dppe)] + 2[NEt_3H]Cl \quad (2)$$

$$[PdCl_2(dppe)] + 2NaHE \xrightarrow[\text{(E=S or Se)}]{\text{EtOH/}C_6H_6} [Pd(EH)_2(dppe)] + 2NaCl \quad (3)$$

Reactions of H_2S with $[Pd(NCMe)_4][ClO_4]_2$ and tertiary phosphines PR_3 give the trinuclear thiocluster $[Pd_3(\mu_3\text{-}S)_2(PEt_3)_6][ClO_4]_2$ when R = Et, and the di(hydrosulfido) complex $[Pd(SH)_2\{P(CH_2CHMe_2)_3\}_2]$ when R is the more bulky Bu^i fragment. An X-ray analysis of the latter complex shows a *trans* square planar geometry around the Pd atom with Pd—S distances of 2.305(1) Å.[10] Triply bridging sulfide ligands are also found in $[Pd_3(\mu_3\text{-}S)_2(PMe_3)_6][BPh_4]_2$, the X-ray structure of which (**1**) shows an approximately trigonal bipyramidal structure with one triply bridging sulfide ligand lying above and one below a distorted Pd_3 triangle; one Pd—Pd distance is significantly shorter than the other two.[11] This trinuclear cluster, and the $PMePh_2$ analogue, is formed from $[Pd(NCMe)_4][BF_4]_2$, hydrogen sulfide and the corresponding phosphine in the presence of $NaBPh_4$. The PMe_3 derivative is also obtained in low yield as a secondary product in the reaction of $[PdH(PMe_3)_3][BPh_4]$ with COS.[11]



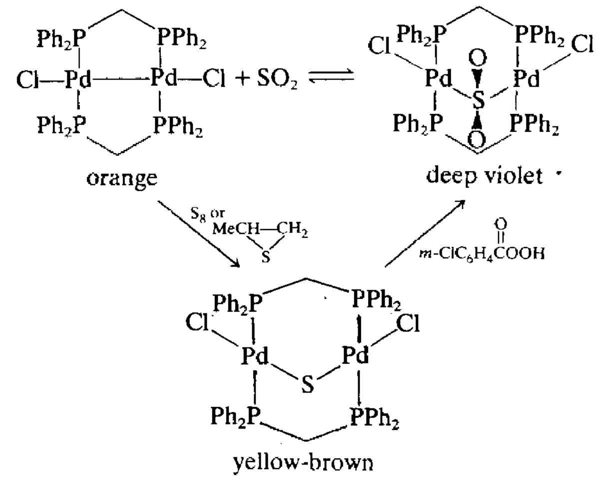
(**1**)



(**2**)

A red crystalline tetrasulfide complex $[PdS_4(dppe)]$, again containing a chelating diphosphine, is obtained when $[PdCl_2(dppe)]$ in ethanol is treated with either Na_2S_4 or 'Na_2S_5'.[12] This tetrasulfide complex was first synthesized by reaction of elemental sulfur with $[Pd(dppe)_2]$ in benzene at room temperature[13] and most likely contains a five-membered PdS_4 ring, as structure (**2**). Recently the platinum analogue was shown by X-ray crystallography to have this structure, with the tetrasulfido ligand behaving as a dianionic chelating ligand.[14]

Sulfur and selenium dichlorides coordinate through the chalcogen atom to form complexes of the type $[PdCl_2(ECl_2)_2]$ (E = S, Se) and these have a *trans* square planar structure.[15] Sulfur dioxide easily inserts into the metal–metal bond of $[Pd_2Cl_2(\mu\text{-dppm})_2]$, which also abstracts sulfur from S_8 or propylene sulfide to give sulfur insertion into the Pd–Pd bond. The coordinated (bridging) S^{2-} can be oxidized using *m*-chloroperbenzoic acid to SO_2, which remains coordinated. These reactions are depicted in Scheme 1; the structures have been confirmed by X-ray crystallography.[16]

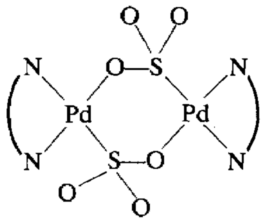


Scheme 1

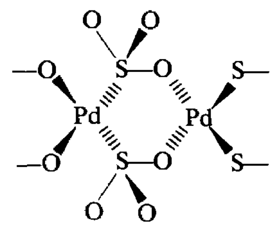
51.8.2.2 Sulfites

The potentially ambidentate sulfite ion SO_3^{2-} generally binds to palladium as a unidentate ligand through sulfur, as in the complexes $[Pd(SO_3)(H_2O)_n(NH_3)_{3-n}]$ ($n = 0$–3).[17] These are obtained as yellow-orange (or white when $n = 0$) crystalline precipitates by addition of an appropriate amount of concentrated NH_4OH to an aqueous solution of the triaqua complex $[Pd(SO_3)(H_2O)_3]$, itself best prepared from $PdCl_2$, $AgSO_3$ and water, although some workers have formulated the solid thus obtained as $[Pd(SO_3)(H_2O)_2]$.[18,19] It seems probable that the diaqua and triaqua species are two distinct compounds, each obtainable depending on the extent to which water is removed at reduced pressure. It also seems likely that in water solution both compounds exist as the triaqua complex. The complexes containing aqua groups cannot be dehydrated to form the corresponding bidentate sulfite compounds, as has been done with sulfate complexes: instead, decomposition occurs. These aqua complexes, absorbed on silica gel, have been used to detect the presence of carbon monoxide in gas streams: the high *trans* effect of the sulfite group labilizes a water ligand, which is readily replaced by CO to give a transient sulfito–carbonyl–palladium(II) complex. This rapidly decomposes to Pd metal, which is detected visually.[17] Evidence for unidentate Pd—S bonding comes mainly from detailed IR[20,21] and Raman[22] spectroscopic studies and this mode of bonding has been confirmed in the X-ray crystal structures of $[Pd(SO_3)(NH_3)_3]$ (Pd—S 2.25 Å),[23] *trans*-$Na_2[Pd(SO_3)_2(NH_3)_2]\cdot6H_2O$ (Pd—S 2.29 Å)[24] (preparation of a *cis* isomer has been reported[17,20]) and $Na_6[Pd(SO_3)_4]\cdot2H_2O$.[25] Although the crystal structure of this last complex has only recently been determined, it was first made by Wöhler as long ago as 1874 when he added sodium hydroxide to an aqueous solution of $PdCl_2$ previously saturated with SO_2.[26] The structure shows that the $[Pd(SO_3)_4]^{6-}$ anion contains remarkably long Pd—S bonds (mean 2.33 Å).[25] Another early report describes a bright red complex $[NH_4]_3[PdCl_3(SO_3)]$, obtained by saturating a concentrated solution of ammonium sulfite with $(NH_4)_2PdCl_4$.[27]

The reaction at room temperature of $[Pd(SO_3)(H_2O)_2]$ in water with triamines such as L_3 = dien or $HN(C_2H_4NEt_2)_2$ is exothermic and gives rise to the stable complexes $[Pd(SO_3)L_3]$.[19] 1,10-Phenanthroline derivatives such as $[Pd(SO_3)(NH_3)(phen)]$ or $Na_2[Pd(SO_3)_2(phen)]$ may also be obtained, the nature of the products formed usually depending on the extent of hydrolysis of the starting sulfito complexes.[18] These complexes all contain unidentate S-bonded sulfite groups, but the insoluble complex $[Pd(SO_3)(phen)]$, which is resistant to hydrolysis even in boiling water, probably has the dimeric structure (**3**), in which the sulfite ligand functions as a bidentate bridging group bonding through both S and O atoms.[18] A polymeric structure containing bridging sulfite groups was originally suggested for the $[Pd(SO_3)_2]^{2-}$ complex anion,[17] and indeed a crystal structure determination of $K_2[Pd(SO_3)_2]\cdot H_2O$ (prepared from K_2SO_3, $K_2S_2O_5$ and $PdCl_2$) has shown that the nearly planar, distorted square environment of Pd is formed by two *cis*-coordinated S and two O atoms belonging to four different sulfite groups, *i.e.* two adjacent Pd atoms are linked by two bidentate sulfite ligands to form infinite undulating chains of six-membered rings, as structure (**4**). The S—O bond distances confirm that S coordination of the sulfite group strengthens all the S—O bonds by enhancement of π bonding, while the Pd—S bond length is 2.24 Å.[28] It is considered likely that aqueous solutions of Na_2 (or K_2) $[Pd(SO_3)_2]$ and $Na_6[Pd(SO_3)_4]$ contain hydrated species such as $[Pd(SO_3)(H_2O)_n]$ ($n = 2$ or 3) and $[Pd(SO_3)_2(H_2O)]^{2-}$, some species probably having dimeric structures involving bridging as well as unidentate sulfite groups.[18]



(**3**) N N = phen



(**4**)

51.8.2.3 Arenesulfinates

Complexes with the arenesulfinate anion $ArSO_2^-$ can be prepared by treating a palladium(II) tetrahalide complex with sodium arenesulfinate, as equation (4).[29,30] Further reactions, as equations (5) and (6), suggest that the arenesulfinate ligand, in common with other S-bonded ligands, exerts a strong *trans* effect.[29,30] This was originally ascribed to a pronounced π acceptor ability for the $PhSO_2^-$ ligand, but later work with platinum(II) complexes suggests that the high *trans* effect of arenesulfinate ligands is in fact due to the $ArSO_2^-$ group being a very strong σ donor.[31] It can therefore be presumed that the coordinated water in (**5**) is *trans* to a sulfinate ligand and *cis* configurations can be assigned to all the products of equations (4)–(6). The halo aqua complexes (**5**) are bright orange air stable materials, whereas the diaqua complexes (**6**) decompose rapidly to Pd^0, the biaryl compounds and SO_2. The diaqua complex (**6**) can more easily be prepared directly from palladium(II) chloride or nitrate, as equation (7). The water bound in this complex is easily exchanged for neutral uni- or bi-dentate ligands, as equation (8).[29,30] The products of the reaction are yellow or colourless air stable solids, though the PPh_3 complex is stable only under nitrogen and the PPh_3 dissociates in organic solvents. Detailed IR and electronic spectral studies[30] confirm that these complexes all have *cis* configurations (except for the py complexes, which appear to be *trans*) and in all complexes the $ArSO_2^-$ ligand is coordinated to Pd through S. Other complexes that have been prepared are $[PdX_2(PhSO_2)_2]^{2-}$ (X = Cl or Br, probably *cis*), $[PdCl(PhSO_2)L_2]$ (L = py, piperidine or PPh_3, probably *trans*; L_2 = phen) and $[Pd(OH)(PhSO_2)(PPh_3)_2]$ (probably *trans*).[29,32]

$$Na_2[PdX_4] + 2ArSO_2Na + H_2O \xrightarrow[H_2O]{20\,^\circ C} Na[PdX(ArSO_2)_2(H_2O)] + 3NaX \quad (4)$$

X = Cl, Br; Ar = Ph, 4-MeC_6H_4 (**5**)

$$(\mathbf{5}) + H_2O \xrightarrow[H_2O]{20\,^\circ C} [Pd(ArSO_2)_2(H_2O)_2] + NaCl \quad (5)$$

X = Cl, Ar = Ph, 4-MeC_6H_4 (**6**)

$$(\mathbf{5}) + NaSCN \longrightarrow Na[Pd(CNS)(PhSO_2)_2(H_2O)] + NaCl \quad (6)$$

X = Cl, Ar = Ph

$$PdX_2 + 2ArSO_2Na + 2H_2O \xrightarrow[H_2O]{20\,^\circ C} (\mathbf{6}) + 2NaX \quad (7)$$

X = Cl, Ar = 4-MeC_6H_4; X = NO_3, Ar = Ph

$$[Pd(ArSO_2)_2(H_2O)_2] + nL \longrightarrow [Pd(ArSO_2)_2L_n] + 2H_2O \qquad (8)$$

$n = 1$; L = bipy, phen, en, o-$(Ph_2P)_2C_6H_4$
$n = 2$; L = py, PPh_3
Ar = Ph, 4-MeC_6H_4

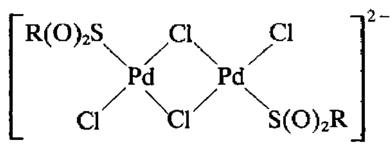
The selenium analogue of (**6**) can be obtained in similar fashion to the sulfinate compound: addition of $ArSeO_2Na$ to Na_2PdCl_4 or '$Pd(NO_3)_2$' in water gives the orange-brown areneseleninate complexes $[Pd(ArSeO_2)_2(H_2O)_2]$, in which coordination is through Se.[33]

Anionic tetra(organosulfinato)palladium(II) complexes, also bonded through S, are obtained by the reaction of silver organosulfinates with $[AsPh_4]_2[PdCl_4]$ (itself made from $PdCl_2$ and $2[AsPh_4]Cl$ in acetonitrile at 80 °C). The yellow products, as equation (9), decompose after a few minutes in polar organic solvents or even as solids under nitrogen.[30]

$$[AsPh_4]_2[PdCl_4] + 4RSO_2Ag \xrightarrow[MeCN]{0\,°C} [AsPh_4]_2[Pd(RSO_2)_4] + 4AgCl \qquad (9)$$

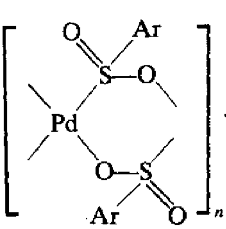
R = Me, Ph, 4-MeC_6H_4

Binuclear palladium(II) arenesulfinate complexes are air stable and have the chloride ligands bridging and sulfinate groups S-bonded and terminal. Treatment of the filtrate from the reaction shown in equation (4) (X = Cl, Ar = Ph) with $[AsPh_4]Cl$ gives $[AsPh_4]_2[Pd_2Cl_4(PhSO_2)_2]$, which on the basis of its IR spectrum has a cation with a centre of symmetry, as structure (**7**) (R = Ph). Similar treatment of the filtrate from reactions (**5**) (X = Cl, Ar = Ph) or (**7**) (X = Cl, Ar = 4-MeC_6H_4) gives $[AsPh_4]_2[Pd_2Cl_2(ArSO_2)_4]$.[30,32]



(**7**)

Although coordination of arenesulfinate ligands to a 'soft' metal centre such as Pd^{II} is invariably through sulfur, simultaneous coordination through oxygen may occur in order to reach a favoured coordination number (in this case four) in the absence of a competing ligand. Thus the removal of water from the diaqua complexes $[Pd(ArSO_2)_2(H_2O)_2]$ by means of 2,2-dimethoxypropane gives golden yellow diamagnetic complexes which are polymeric, as equation (10). The additional Pd—O bond is very weak and is readily cleaved, *e.g.* reversibly by L = MeOH or MeCN to give $[Pd(ArSO_2)_2L_2]$ in solution, or irreversibly by uni- or bi-dentate ligands such as L = PPh_3, py or L_2 = bipy to form the known compounds $[Pd(ArSO_2)_2L_2]$.[34]

$n[Pd(ArSO_2)_2(H_2O)_2 \rightleftharpoons$  $+ 2nH_2O$ (10)

Ar = Ph, 4-MeC_6H_4

It has long been proposed that the oxidation of alcohols catalyzed by $PdCl_2$ involves labile Pd—OR intermediates. Such an intermediate can be trapped by SO_2 insertion into a Pd—OR bond to form the stable binuclear anions (**7**) (R = OMe, OEt, OPr^n). These may be precipitated as their $[Ph_4As]^+$ or $[Ph_4P]^+$ salts, or will react with neutral ligands with displacement of the RSO_2^- groups to give $[PdCl_2L_2]$ (L = PPh_3, py; L_2 = bipy, dppe, nbd, cod) or $[Pd_2Cl_4(PPh_3)_2]$. Similarly, $PdBr_2$ suspended in MeOH reacts with SO_2 to give $[Pd_2Br_4(SO_2OMe)_2][PPh_4]_2$.[35]

Complexes such as (**6**) have been postulated as intermediates in the $PdCl_2$-catalyzed dimerization of arenesulfinic acids or their sodium salts to give the corresponding organic biaryls.[36]

51.8.2.4 Thiosulfates

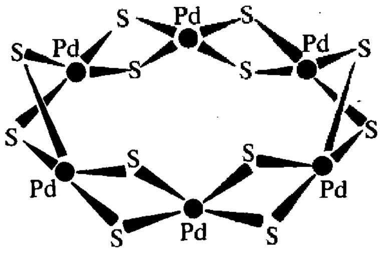
Thiosulfate complexes of Pd^{II} are similar to those of Pt^{II}, though in contrast to the reactions of the tetrachloroplatinate(II) anion, the reaction of equimolar quantities of K_2PdCl_4 and $Na_2S_2O_3$ precipitates all the palladium as a mixture of PdS and PdS_2O_3.[37] However, when 2 mol equiv. of $Na_2S_2O_3$ are treated with 1 mol equiv. of K_2PdCl_4, the thiosulfate complex $K_2[Pd(S_2O_3)_2]$ is obtained in both soluble and insoluble modifications. The brownish-yellow insoluble form is believed to involve polymeric complex anions of the type $[\{Pd(\mu\text{-}S{-}SO_3)_2\}_n]^{2n-}$ with S-bridging thiosulfate groups, whereas the brown soluble modification probably contains two S,O-chelating thiosulfate groups coordinated to a single Pd^{II} ion.[38]

Reaction of $[Pd(en)_2]Cl_2$ (1 mol equiv.) with $Na_2S_2O_3$ (2 mol equiv.) in water forms a yellowish-green precipitate of $[Pd(S_2O_3)(en)]$ in which the thiosulfate ligand is again said to be S,O-chelated,[37] though a more recent study obtained only the product with empirical formula $Pd_2(S_2O_3)_2(en)_3$ and this was correctly formulated as the salt $[Pd(en)_2][Pd(S_2O_3)_2(en)]$ (*vide infra*).[38] Addition of alcohol to the solution remaining after separation of either of these complexes gives a yellow precipitate of $Na_2[Pd(S_2O_3)_2(en)]$, in which the thiosulfate groups are unidentate and coordinated to the metal by palladium–sulfur bonds only.[37,38] This is the more usual form of thiosulfate coordination and examples of such complexes, generally prepared by displacement of halide ligands by $S_2O_3^{2-}$ anions, include $[Pd(S_2O_3)(NH_3)_2(H_2O)]$ from *trans*-$[PdCl_2(NH_3)_2]$,[37] $[Pd(NH_3)_4]S_2O_3$, $[Pd(S_2O_3)(NH_3)_3]$ and $[Pd(S_2O_3)_2(NH_3)_2]^{2-}$ from $[Pd(NH_3)_4]Cl_2$,[37,38] and *trans*-$[Pd(S_2O_3)(H_2O)(tu)_2]$ and *trans*-$Na_2[Pd(S_2O_3)_2(tu)_2]$ from $[Pd(tu)_4]Cl_2$ (tu = thiourea).[37] The complexes $[Pd(S_2O_3)(triamine)]$ [triamine = $HN(C_2H_4NEt_2)_2$, $MeN(C_2H_4NEt_2)_2$ or $MeN(C_2H_4NMe_2)_2$], in which the amine is tridentate and the thiosulfate unidentate, are orange powders and are synthesized by addition of the triamine to $[Pd(S_2O_3)(NH_3)_3]$ suspended in water, with gentle heating. They have been used in the course of a study of the rates and mechanism of substitution reactions of sterically hindered Pd^{II} complexes.[19]

As a consequence of its coordination through sulfur the thiosulfate ligand has a high *trans* effect, as deduced from preparative studies,[2] but negligible *trans* influence. This follows from the X-ray crystal structure of $[Pd(en)_2][Pd(S_2O_3)_2(en)]$,[39] which comprises discrete $[Pd(en)_2]^{2+}$ cations and *cis*-$[Pd(S_2O_3)_2(en)]^{2-}$ anions, and where the mean Pd—N bond lengths are 2.07(1) Å *trans* to ethylenediamine in the cation and 2.08(1) Å *trans* to thiosulfate in the anion. The $S_2O_3^{2-}$ groups are bonded to palladium through sulfur with nearly tetrahedral Pd—S—SO_3 angles. The coordinated $S_2O_3^{2-}$ groups maintain the pyramidal shape of the free ion but there is a significant lengthening of the S—S bonds, from 2.013(3) Å in MgS_2O_3 to a mean of 2.066(6) Å in this complex. Thus it is clear that the S—S bonds are weaker and in consequence the S—O bonds should be stronger, which is in agreement with the interpretation of the IR spectra of these Pd thiosulfate complexes.[38,40] In view of this structural determination it would seem that the correct structural formula for the compounds previously formulated as $[M(NH_3)_4]_3[Pd(S_2O_3)_4]$ ($M = Pd^{37}$ or Pt^{40}) is probably $[M(NH_3)_4][Pd(S_2O_3)_2(NH_3)_2]$.[39]

51.8.2.5 Thiolates

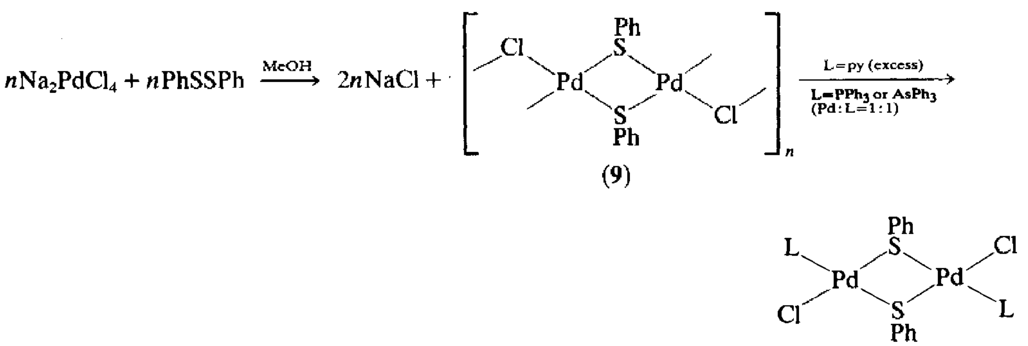
The thiolate ion RS^-, being highly polarizable, forms strong bonds with 'soft' metal ions such as Pd^{II}. The simple thiolato compounds such as $Pd(SR)_2$ (R = alkyl or aryl) are highly associated in solutions of organic solvents, with the phenyl and ethyl derivatives being virtually insoluble and probably having a linear polymeric structure.[41–43] The *n*-propyl and higher members are more soluble in organic solvents, however, and can be crystallized, and the X-ray crystal structure of the *n*-propyl derivative shows that the molecule exists as the hexamer $[Pd(SPr^n)_2]_6$ in the solid state. The Pd atoms form a six-membered puckered ring and each adjacent pair of metal atoms is joined by a double thiolate bridge, which is folded along the sulfur–sulfur axis, as structure (**8**). The molecule thus has a cage structure and has a large hole of 7 Å diameter within it.[44] The $Pd(SR)_2$ complexes are made by treating a finely powdered $[PdCl_4]^{2-}$ salt in chloroform with the appropriate thiol in chloroform: hydrogen chloride is evolved. Alternatively an aqueous solution of $[PdCl_4]^{2-}$ salt may be shaken with the thiol. With benzenethiol the latter method precipitates quantitatively $Pd(SPh)_2$ as a bright vermilion, amorphous powder. As no similar colour is developed when benzenethiol is added to aqueous solutions of complexes or simple salts of Pt, Ir, Rh, Au or Ag, the reagent can be used for the detection and determination of Pd in the presence of these metals.[41,45]



(8)

Treatment of Na_2PdCl_4 with diphenyl disulfide in methanol yields a wine red polymeric complex $[PdCl(SPh)]_n$ containing alternate chloride and thiolato bridges, as (**9**).[46] If $[PdCl_2(NCMe)_2]$ is used as the starting material, a dithioether-bridged complex $[Cl_2Pd(\mu\text{-}PhSSPh)_2PdCl_2]$ is formed in benzene. This gives the original monothiolato-chloro-bridged polymer (**9**) on refluxing in methanol.[46] The chloro bridges in this complex are cleaved by neutral ligands such as pyridine or triphenylphosphine (equation 11).

Reaction of (**9**) with an excess of ethylenediamine gives $[(en)Pd(\mu\text{-}SPh)_2Pd(en)]^{2+}$, or treatment with a stoichiometric amount of Cl^- gives $[Cl_2Pd(\mu\text{-}SPh)_2PdCl_2]^{2-}$, while reaction of (**9**) with dppe (1:1) or PPh_3 (excess) leads to simultaneous cleavage of both halogen and sulfur bridges to give monomeric species.[46]



(9)

(11)

Clearly one common feature of complexes containing the coordinated group SR^- is their tendency to form polymeric units. However, it has been demonstrated that if the group R has strong electron-withdrawing properties the tendency to polymerize is reduced. In this respect the pentafluorobenzenethiolato group $C_6F_5S^-$ behaves like a halide ion and monomeric complexes have been prepared (equations 12 and 13).[47] Reaction (13) also yields some of the thiolato-bridged dimer *trans*-$[(PPh_3)(C_6F_5S)Pd(\mu\text{-}SC_6F_5)_2Pd(SC_6F_5)(PPh_3)]$, the X-ray structure of which shows square planar stereochemistry about Pd and the two $PdPS_3$ planes perpendicular to each other.[48] Other golden yellow or orange monomeric thiolato complexes have also been prepared, *e.g.* by equations (14)[42] and (15).[49]

$$K_2PdCl_4 + 2[Bu_4N]Cl + 4C_6F_5SH \xrightarrow{EtOH/H_2O} [Bu_4N]_2[Pd(SC_6F_5)_4] + 2KCl + 4HCl \quad (12)$$

$$[Pd(SC_6F_5)_2]_n + 2nPPh_3 \xrightarrow{EtOH;\ boil} n[Pd(SC_6F_5)_2(PPh_3)_2] \quad (13)$$

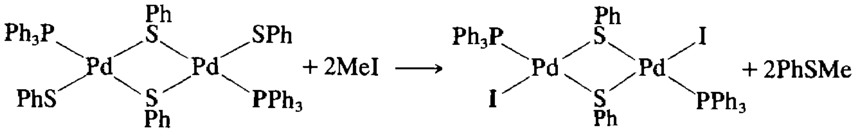
$$[PdCl_2(PR_3)_2] + 2NaSR' \xrightarrow{EtOH} [Pd(SR')_2(PR_3)_2] + 2NaCl \quad (14)$$

$PR_3 = PEt_3$; $R' = Ph$
$PR_3 = \frac{1}{2}dppe$; $R' = Ph, Et$

$$[Pd(N_3)_2(PPh_3)_2] + RSSR \xrightarrow[R=Me,\ Bu^n,\ Ph]{CHCl_3,\ reflux\ 2\text{-}3\ h} [Pd(SR)_2(PPh_3)_2] + 3N_2 \quad (15)$$

It is well established that whereas halogen-bridged dimeric complexes of Pd^{II} are readily cleaved by unidentate ligands such as pyridine or PPh_3, the corresponding thiolato-bridged complexes are not.[46,50,51] Furthermore, only the *cis* isomers of the Pd^{II} thiolato-bridged complexes $[(PR_3)ClPd(\mu\text{-}SR')_2PdCl(PR_3)]$ are formed, whereas with Pt^{II} both *cis* and *trans* isomers can be prepared.[51,52] The complexes $[(PR_3)ClPd(\mu\text{-}Cl)(\mu\text{-}SR')PdCl(PR_3)]$, which contain both chloro and thiolato bridging ligands, are also always *cis* and this is consistent with the high *trans* effect of the thiolate ligand.[51]

Cleavage of the aryl disulfides Ar_2S_2 by $[Pd(PPh_3)_4]$ gives the red dimeric compound (**10**) when Ar = Ph, which produces the diiodo complex (**11**) when treated with MeI, as equation (16).[53] The formation of PhSMe probably occurs *via* an electrophilic attack of the positive end of $H_3C^+\cdots I^-$ on the sulfur atom of the terminal —SPh group; nucleophilic substitution of PhS^- by I^- can be ruled out since no reaction occurs between (**10**) and iodide ion. The platinum analogue of (**10**) reacts with $[PdCl_2(NCMe)_2]$ to give the interesting heterobimetallic complex $[(PPh_3)_2Pt(\mu\text{-}SPh)_2PdCl_2]$ with bridging thiolate groups.[53] Furthermore, the monomeric species $[Pd(SAr)_2(PPh_3)_2]$ can be made when electron-withdrawing substituents are incorporated in the aryl disulfides, *e.g.* when *o*- or *m*-nitrophenyl disulfide is used.[53]


(16)

(**10**) (**11**)

Mention may be made here of the red-brown insoluble arenetellurolate-bridged polymers $[Pd(TeAr)_2]_n$ formed from the reaction of ArTeCOAr' or Ph_3MTeAr (M = Ge or Sn) with $[PdCl_2(NCPh)_2]$.[54] The exact mechanism is unknown, but it is thought likely that an unstable intermediate, $[PdCl_2(ArTeCOAr')_2]$ or $[PdCl_2(Ph_3MTeAr)_2]$, decomposes with formation of $Pd(TeAr)_2$ and the chloride-containing by-products Ar'COCl or Ph_3MCl. Related dimeric complexes with both terminal and bridging $ArTe^-$ ligands have been prepared by oxidative addition reactions of $[Pd(PPh_3)_4]$ and diaryl ditellurides to give $[Pd(TeAr)_2(PPh_3)]_2$ (Ar = 2-thienyl or p-$EtOC_6H_4$).[55]

51.8.2.6 Thio- and Seleno-cyanates

51.8.2.6.1 Thiocyanates

The thiocyanate ligand is probably the most widely studied of ambidentate ligands and it forms innumerable complexes with Pd^{II}, usually bonding through sulfur, but the nature of the other ligands in the complex and also steric factors may determine the way in which the thiocyanato group is bound. The factors affecting the mode of coordination and the physical methods available for determining this are discussed at length in a comprehensive review of the coordination chemistry of the cyanate, thiocyanate and selenocyanate ions.[56] Throughout this account palladium–thiocyanate bonding is represented as Pd(SCN), palladium–isothiocyanate bonding is represented as Pd(NCS), and when no specific bonding mode is implied Pd(CNS) is used.

A red precipitate of $Pd(SCN)_2$ forms when KSCN is added to a solution of K_2PdCl_4. With excess KSCN a red solution containing the $[Pd(SCN)_4]^{2-}$ anion is produced and this is normally isolated as the $[Et_4N]^+$ salt.[57,58] The crystal structure of $K_2[Pd(SCN)_4]$ shows square planar coordination of the palladium atom with S-bonded thiocyanate groups. The two crystallographically independent Pd—S bond lengths [2.31(1) and 2.39(1) Å] are significantly different and the complex ions form infinite chains with one of the independent sulfur atoms on one complex ion lying in the axial position with respect to the palladium atom in the adjacent complex ion (3.66 Å). The independent Pd—S—CN angles are 101(2) and 109(2)°.[59]

X-Ray diffraction is certainly the most reliable method for determining the structure of thiocyanate complexes but S- and N-bonded complexes can often be distinguished using IR spectroscopy.[56,60–62] The typical $\nu(CN)$ range for S-bonded thiocyanate is 2130–2085 cm^{-1} (usually a sharp peak), while that for N-bonded thiocyanate is 2100–2050 cm^{-1} (often broad); the $\nu(CS)$ and $\delta(NCS)$ frequencies are also sometimes useful (see ref. 56). Table 1 gives a selection of typical homoleptic and mixed ligand thio- and seleno-cyanate complexes of Pd^{II} along with their $\nu(CN)$ stretching frequencies. The IR frequency criteria are not entirely satisfactory since the ranges overlap to some extent, but the two possibilities can generally be distinguished by measuring the integrated intensity of the ν(CN) absorption, since for S-bonded thiocyanate ligands this is less than the free ion value, whereas for N-bonded thiocyanate ligands it is greater.[63] The far-IR region can also help in distinguishing between S- and N-bonded thiocyanate ligands, since Pd—SCN complexes exhibit a band in the region 320–290 cm^{-1} that has been ascribed to the ν(Pd—S) stretching mode, whereas Pd—NCS complexes have a band around 270–260 cm^{-1} due to ν(Pd—N).[61]

In general, looking at Table 1, it would appear that the presence of ligands that can accept electron density from the metal encourages the formation of Pd—NCS bonds, whereas ligands

Table 1 Typical Palladium(II)–Thiocyanate and –Selenocyanate Complexes and IR Data[a]

Compound	*Coordination mode*	*ν(CN)* (cm^{-1})	*Refs.*
$K_2[Pd(SCN)_4]$	*S,S,S,S*	2093, 2122	1
$[Et_4N]_2[Pd(SCN)_4]$	*S,S,S,S*	2109(s, sp), 2112(sh)	1
$[Pd(SCN)_2(NH_3)_2]$	*S,S*	2100, 2116	2
$[Pd(SCN)_2py_2]$	*S,S*	2112	3, 4
$[Pd(SCN)_2(4\text{-}NO_2py)_2]$	*S,S*	2115	3
$[Pd(SCN)_2\{SC(NH_2)_2\}_2]$	*S,S*	2107	5
$[Pd(SCN)_2(SbPh_3)_2]$	*S,S*	2115, 2119(sh)	4, 5
$[Pd(SCN)_2\{Ph_2P(o\text{-}C_6H_4SMe)\}]$	*S,S*	2111, 2122	6
$[Pd(SCN)_2\{Ph_2P(o\text{-}C_6H_4SeMe)\}]$	*S,S*	2110, 2120	6
$[Pd(SCN)_2phen]$	*S,S*	2116	3, 4, 5
$[Pd(SCN)_2(5\text{-}Me\text{-}6\text{-}NO_2phen)]$	*S,S*	2114	3
$[Pd(SCN)_2(5\text{-}NO_2phen)]$	*S,S*	2122	7
$[Pd(NCS)_2(5\text{-}NO_2phen)]$	*N,N*	2093	3, 4, 7
$[Pd(NCS)_2(PEt_3)_2]$	*N,N*	2089	2
$[Pd(NCS)_2(PPh_3)_2]$	*N,N*	2095	4, 5, 8
$[Pd(C_6F_5)(NCS)(PPh_2Me)_2]$	*N*	2092[b]	9
$[Pd(SCN)_2(AsPh_3)_2]$	*S,S*	2119(s, sp)	5
$[Pd(NCS)_2(AsPh_3)_2]$	*N,N*	2089(s, br)	5
$[Pd(SCN)_2bipy]$	*S,S*	2108(s, sp), 2117(m, sp)	5
$[Pd(NCS)_2bipy]$	*N,N*	2100(s, br)	5
$[Pd(SCN)_2(4,7\text{-}Ph_2phen)]$	*S,S*	2113(s, sp), 2120(sh)	3
$[Pd(NCS)_2(4,7\text{-}Ph_2phen)]$	*N,N*	2110(s, br)	3
$[Pd(SCN)(Et_4dien)][PF_6]$	*S*	2125	10
$[Pd(NCS)(Et_4dien)][PF_6]$	*N*	2060	10
$[Pd(SCN)(NCS)(4,4'\text{-}Me_2bipy)]$	*S,N*	2120(s, sp); 2090(s, br)	3
$[Pd(SCN)(NCS)\{Ph_2As(o\text{-}C_6H_4PPh_2)\}]$	*S,N*	2117; 2085	6
$[Pd(SCN)(NCS)(Ph_2PCH_2CH_2NMe_2)]$	*S,N*	2126; 2108	6
$[Pd(SCN)(NCS)(Ph_2PCH_2CH_2PPh_2)]$	*S,N*	2118; 2095	6
$[Pd(SCN)(NCS)(\overline{RPCH{=}CMe{-}CMe{=}CH})_2]$	*S,N*	2116; 2090	11
$[Et_4N]_2[Pd(SeCN)_4]$	*Se,Se,Se,Se*	2068(w), 2116(s, sp)	12
$[Pd(SeCN)(dien)][BPh_4]$	*Se*	2118	13
$[Pd(SeCN)(Et_4dien)][BPh_4]$	*Se*	2121	13
$[Pd(NCSe)(Et_4dien)][BPh_4]$	*N*	2085	13
$[Pd(SeCN)_2bipy]$	*Se,Se*	2112, 2116	14
$[Pd(SeCN)_2\{Ph_2As(o\text{-}C_6H_4PPh_2)\}]$	*Se,Se*	2120, 2126	6, 15
$[Pd(SeCN)_2(Ph_2AsCH_2CH_2AsPh_2)]$	*Se,Se*	2120, 2126	6

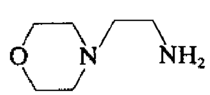
[a] Recorded as Nujol mull spectra unless otherwise indicated; br = broad, m = medium, s = strong, sh = shoulder, sp = sharp, w = weak.
[b] In acetone solution.

1. A. Sabatani and I. Bertini, *Inorg. Chem.*, 1965, **4**, 959.
2. A. Turco and C. Pecile, *Nature (London)*, 1961, **191**, 66.
3. I. Bertini and A. Sabatini, *Inorg. Chem.*, 1966, **5**, 1025.
4. A. Sabatini and I. Bertini, *Inorg. Chem.*, 1965, **4**, 1665.
5. J. L. Burmeister and F. Basolo, *Inorg. Chem.*, 1964, **3**, 1587.
6. D. W. Meek, P. E. Nicpon and V. I. Meek, *J. Am. Chem. Soc.*, 1970, **92**, 5351; see also W. Levason and C. A. McAuliffe, *J. Chem. Soc., Dalton Trans.*, 1974, 2238.
7. W. C. Fultz and J. L. Burmeister, *Inorg. Chim. Acta*, 1980, **45**, L271.
8. C. Pecile, *Inorg. Chem.*, 1966, **5**, 210.
9. J. L. Burmeister and N. J. DeStefano, *Inorg. Chem.*, 1971, **10**, 998.
10. F. Basolo, W. H. Baddley and K. J. Weidenbaum, *J. Am. Chem. Soc.*, 1966, **88**, 1576.
11. J. J. MacDougall, E. M. Holt, P. de Meester, N. W. Alcock, F. Mathey and J. H. Nelson, *Inorg. Chem.*, 1980, **19**, 1439; J. H. Nelson, J. J. MacDougall, N. W. Alcock and F. Mathey, *Inorg. Chem.*, 1982, **21**, 1200.
12. D. Forster and D. M. L. Goodgame, *Inorg. Chem.*, 1965, **4**, 1712; J. L. Burmeister and L. E. Williams, *Inorg. Chem.*, 1966, **5**, 1113; H.-H. Schmidtke and D. Garthoff, *Helv. Chim. Acta*, 1967, **50**, 1631.
13. J. L. Burmeister, H. J. Gysling and J. C. Lim, *J. Am. Chem. Soc.*, 1969, **91**, 44.
14. J. L. Burmeister and M. Y. Al-Janabi, *Inorg. Chem.*, 1965, **4**, 962; J. L. Burmeister and H. J. Gysling, *Inorg. Chim. Acta*, 1967, **1**, 100.
15. P. Nicpon and D. W. Meek, *Inorg. Chem.*, 1967, **6**, 145.

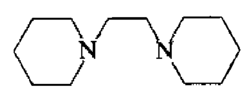
with no π-bonding ability tend to encourage Pd—SCN bonding. There are numerous exceptions to this, however, and in addition many complexes contain both N- and S-bonded thiocyanate in the same molecule. Since the order of decreasing softness is $SCN^- > NCS^-$ it is readily seen that anti-symbiosis[64] can explain the observation that the hard N-bonded thiocyanate in $[Pd(NCS)(SCN)(Ph_2PCH_2CH_2CH_2NMe_2)]$ is *trans* to the softer phosphorus, while the soft S-bonded thiocyanate is *trans* to the harder nitrogen of the bidentate ligand.[65] When discussing the S- or N-bonded nature of thiocyanate ligands it is important to remember that the factors that tip the balance in favour of one mode of bonding over another must be very small. For example, both the S- and N-bonded linkage isomers of $[Pd(CNS)_2(AsPh_3)_2]$ and $[Pd(CNS)_2(bipy)]$ can be isolated by first forming the kinetically favoured S-bonded isomer and then rearranging this to the thermodynamically more stable N-bonded isomer, *e.g.* equation (17).[66]

$$[Pd(SCN)_4]^{2-} + 2AsPh_3 \xrightarrow[\text{EtOH}]{0\,°C} [Pd(SCN)_2(AsPh_3)_2] \xrightarrow[\text{solid state}]{156\,°C\,(30\,\text{min})} [Pd(NCS)_2(AsPh_3)_2] \quad (17)$$

The small energy difference between the S- and N-bonded thiocyanates enables steric factors to modify the mode of bonding. N-bonded thiocyanate complexes might be expected when there is steric crowding around the metal since the M—N—CS grouping is usually linear, whereas the M—S—CN grouping is bent with an M—S—C bond angle around 105°. Thus in $[Pd(SCN)(dien)][NO_3]$ the diethylenetriamine ligand allows sufficient room for a non-linear Pd—S—CN grouping,[67] whereas in $[Pd(NCS)(Et_4dien)][SCN]$ the four bulky ethyl groups prevent the non-linear Pd—S—CN geometry from forming but allow the formation of the linear Pd—N—CS grouping.[68] IR and UV–visible spectral studies on the complexes $[Pd(CNS)L][BPh_4]$ ($L = Et_4dien$ or $MeEt_4dien$) reveal that they undergo S- to N-bonded linkage isomerism in solution, with N- to S-bonded reisomerizations in the solid state.[69] A systematic study[70] of steric control of the mode of thiocyanate bonding in $[Pd(CNS)_2(diamine)]$ and $[Pd(diamine)_2][SCN]_2$ shows that diamines presenting the least steric hindrance ($H_2NCH_2CMe_2NH_2$, $MeHNCH_2CH_2NHMe$, *etc.*) form the ionic complexes; diamines with intermediate steric demands, *e.g.* (**12**), yield S-bonded neutral complexes; and the most sterically demanding diamines, *e.g.* (**13**), yield the N-bonded neutral complexes.

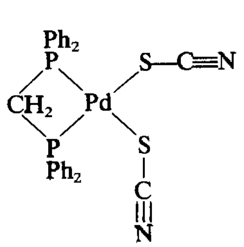


(**12**)

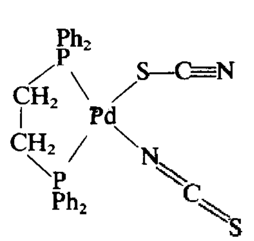


(**13**)

The diphosphine complexes $[Pd(CNS)_2\{Ph_2P(CH_2)_nPPh_2\}]$ show a nice change in the mode of coordination of the thiocyanate ligands from both S for $n = 1$ (see **14**), through one S and one N for $n = 2$ (see **15**), to both N for $n = 3$ (see **16**). This implies that the coordination here is controlled by steric factors alone, since π-bonding capabilities remain constant in this series. X-Ray data show that an increase in n is accompanied by an increase in the P—Pd—P angle and a large increase in steric interaction between the phenyl groups and the coordinated thiocyanate.[71] The distribution of linkage isomers in $[Pd(CNS)_2(diphosphine)]$ and the diphosphine-bridged bimetallic complexes $[Pd_2(CNS)_2(diphosphine)_2]$ has been studied by ^{31}P NMR spectroscopy.[72] Near 25 °C only a single broadened resonance due to time averaging over several environments is observed but at −40 to −60 °C well-defined resonances assignable to the various possible linkage isomers can be observed.



(**14**)



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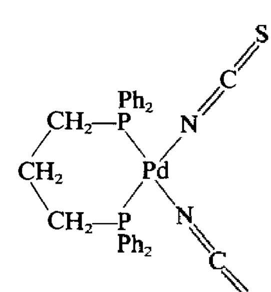


(**16**)

The crystal structures of *trans*-$[Pd(SCN)_2\{P(OPh)_3\}_2]$ and *trans*-$[Pd(NCS)_2(PPh_3)_2]$ show that the presence of N-bonded thiocyanate ligands in the latter complex is probably a result of intramolecular steric crowding rather than Pd—P π bonding.[73] An interesting study of the structure and solution behaviour of Pd^{II} thiocyanate complexes of 1-substituted-3,4-dimethylphospholes shows that in the complexes $[Pd(CNS)_2\{\overline{RPCH{=}CMe{-}CMe{=}CH}\}_2]$ the thiocyanates are both S-bonded (R = Me), both N-bonded (R = Bu^t) or one S- and one N-bonded (R = Ph or Bz).[74] The complexes are *cis* in the solid state with the exception of R = Bu^t, which is *trans*. Upon dissolution of the complexes in $CDCl_3$, linkage isomerism occurs in all cases and geometrical isomerism in some cases, giving mixtures of isomers in solution.

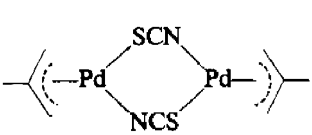
The nature of the anion can play a part in determining the mode of bonding in the solid state. Thus the complex cation $[Pd(CNS)(Et_4dien)]^+$ has an N-bonded thiocyanate ligand in its most stable form when SCN^- is the counterion,[75] but when PF_6^- or BPh_4^- are the counterions the stable isomer in the solid state has S-bonded thiocyanate ligands.[75,76]

The physical state of the complex can also affect the mode of bonding of the thiocyanate ligand. Thus it is S-bonded in $[Pd(SCN)_2(AsBu^n_3)_2]$ in the solid state, whereas on melting this complex partially isomerizes to a mixture of the N- and S-bonded linkage isomers. On resolidification the melt yields only the S-bonded isomer.[62] In view of the possibility of S- or N-bonding, molten thiocyanate is of some interest as a non-aqueous solvent: electronic spectra of Pd^{II} in both aqueous and molten thiocyanate indicate that highly tetragonally distorted octahedral species are present.[77]

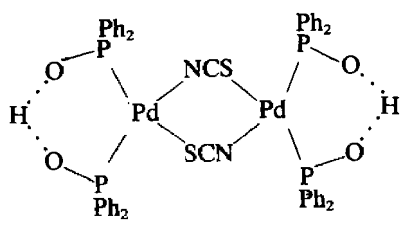
The nature of the solvent may modify the mode of thiocyanate coordination of certain complexes in solution. For example, a study of the behaviour of $[Pd(NCS)_2(AsPh_3)_2]$ and its linkage isomer in a number of different solvents concludes that Pd—SCN bonding is promoted by solvents with high dielectric constants, whereas solvents with low dielectric constants result in a mixture of Pd—NCS, Pd—SCN and Pd—SCN—Pd bonding modes.[78]

Some five-coordinate Pd^{II} thiocyanate complexes have been reported. Both $[Pd(SCN)(2,9\text{-}Me_2phen)_2][ClO_4]$[79] and $[Pd(NCS)\{As(o\text{-}C_6H_4AsMe_2)_3\}][SCN]$[80] have been characterized, but the mode of coordination is unspecified in $[Pd(CNS)L_2][SCN]$ [L = 1,8-bis(dimethylarsino)naphthalene];[81] in the latter system it would appear that six-coordination occurs in solution.

Dimeric compounds of the type $[Pd_2(CNS)_2X_2L_2]$ (X = Cl, CNS; L = $AsPr^i_3$, $AsBu_3$, PBu_3) have been isolated and shown to contain NCS bridges,[82] and such bridging is also believed to occur in the low-temperature form of 2-methylallylpalladium(II) thiocyanate (**17**) (whereas the coalescence of the ^1H NMR spectrum at higher temperatures is believed to be due to the formation of a tetramer).[83] The dinuclear complex $[Pd(SCN)\{(PPh_2O)_2H\}]_2$ has been prepared by metathetical reaction from the chloro-bridged dimer and the X-ray structure (**18**) shows square planar coordination around the Pd with an unusual symmetrically hydrogen-bonded $\{(PPh_2O)_2H\}^-$ anionic ligand.[84]



(**17**)



(**18**)

51.8.2.6.2 Selenocyanates

Similar complexes to the thiocyanate complexes are formed by selenocyanate ions and once again the Se- and N-bonded linkage isomers can be distinguished by IR spectroscopy.[56] Some typical complexes are listed in Table 1. The mode of bonding of the selenocyanate ligand to Pd^{II} is much less sensitive to electronic effects than that of the thiocyanate ligand and in $[Pd(SeCN)_2L_2]$, when L is varied from a σ-bonding to a π-bonding ligand, the selenocyanate ligand is always Se-bonded, with possible exceptions such as $[Pd(NCSe)_2(PBu^n_3)_2]$ in which steric crowding favours the linear Pd—N—CSe grouping.[85] The $[Pd(CNSe)(Et_4dien)]^+$ complexes are very similar to the corresponding thiocyanate systems: the compound $[Pd(SeCN)(Et_4dien)][BPh_4]$ is the kinetic product of the reaction of Et_4dien with

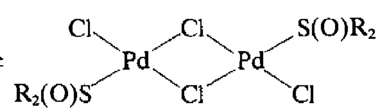
$K_2[Pd(SeCN)_4]$, but when dissolved in a variety of solvents it isomerizes and solid $[Pd(NCSe)(Et_4dien)][BPh_4]$ can be isolated. This latter compound reisomerizes in the solid state to give again the Se-bonded compound. With dien, only the Se-bonded compound $[Pd(SeCN)(dien)][BPh_4]$ is observed.[76,86]

51.8.2.7 Sulfoxides

The coordination chemistry of sulfoxides with transition metals is a much-studied topic.[87] Academic interest has often centred on their ambidentate donor ability, while dimethyl sulfoxide (DMSO) is of intrinsic importance as one of the most effective aprotic solvents known. Higher sulfoxides have found application in the extraction of metals during refining processes and some potential in the separation of platinum group metals has been noted.[88]

While sulfoxides such as the ubiquitous Me_2SO (DMSO) form complexes with many metals by coordinating through oxygen, the pronounced class b behaviour of ions such as Pd^{II}, Pt^{II} or Ir^{III} leads to complexes in which the sulfoxide ligands are usually bound to the metal through sulfur. Many diorganosulfoxide complexes of the type $[PdX_2(R_2SO)_2]$ [X = halide, nitrate, *etc.*; R = alkyl or aryl, $R_2 = (CH_2)_4$] have been prepared by dissolution of PdX_2 in the appropriate hot sulfoxide or by treating $[PdCl_2(NCPh)_2]$ with an excess of sulfoxide in benzene.[89–92] These complexes have been shown by IR spectroscopy to contain S-bonded sulfoxide ligands: there is no exception to the generalization that an increase in $\nu(S{=}O)$ from the free ligand values of around 1020–1055 cm^{-1} to values in the range 1100–1180 cm^{-1} indicates coordination through sulfur, whereas a decrease in $\nu(S{=}O)$ to the range 910–960 cm^{-1} indicates O coordination. An X-ray crystal structure determination of $[PdCl_2(Me_2SO)_2]$ confirms the S coordination and *trans* configuration,[93] but the nitrato complex $[Pd(NO_3)_2(Me_2SO)_2]$ turns out to be an example of a Pd^{II} complex with a *cis* configuration.[94] In it the Pd—S bonds (2.23 and 2.25 Å) are significantly shorter than in the *trans*-$[PdCl_2(Me_2SO)_2]$ complex (2.30 Å) and this, along with an increase in $\nu(S{=}O)$ from 1116 cm^{-1} in the *trans* complex to 1136 and 1157 cm^{-1} in the *cis* complex, suggests enhanced d_π–d_π bonding in *cis*-$[Pd(NO_3)_2(Me_2SO)_2]$. The complex $[Pd(SO_4)(Me_2SO)_2]$ contains *cis*, S-bonded sulfoxide ligands and a chelating sulfato group.[95]

IR and NMR studies show that the solid *trans*-$[PdCl_2(R_2SO_2)]$ complexes on dissolution in chloroform yield the chloro-bridged binuclear species $[PdCl_2(R_2SO)]_2$ with essentially little or no persistance of the mononuclear form (equation 18).[91] These binuclear complexes can also be isolated in the solid state, and their IR spectra have been studied;[96] they revert to the $[PdCl_2(R_2SO)_2]$ types on treatment with R_2SO.[91] On the other hand, *trans*-$[PdCl_2(Me_2SO)_2]$ is said to convert to the *cis* configuration upon dissolution in acetonitrile.[97] No thermal *trans*$\rightarrow$*cis* isomerization is observed and thermogravimetry indicates decomposition at the melting point.[98] It should be noted that the bis complexes $[PdX_2(Me_2SO)_2]$ (X = Cl, Br) cannot be prepared from aqueous solution: treatment of K_2PdX_4 in aqueous solution with an excess of Me_2SO yields only $K[PdX_3(Me_2SO)]$.[90] The complexes $K[PdX_3(Me_2SO)]$, $[PdCl_2(Me_2SO)_2]$ and $[PdCl_2(Me_2SO)]_2$ have been studied as active catalyst precursors for the decomposition of hydrogen peroxide.[99]

$2[PdCl_2(R_2SO)_2] \rightleftharpoons$  $+ 2R_2SO$ (18)

The Pd^{II} halide-bridged dimeric complexes of the type $[PdCl_2L]_2$ ($L = R_2SO$, R_2S, but not thiourea) are cleaved in methanol by carbon monoxide to yield monomeric *trans*-$[PdCl_2(CO)L]$ species.[96,100] The high *trans* effect of S-bonded Me_2SO causes rapid cleavage of the *trans* halide bridge in the dimers and the variation in rate constant for this reaction with the nature of the sulfur donor has been measured and a *trans* effect series constructed: $(CH_2)_4S > S\text{-}Et_2SO > S\text{-}Me_2SO > Et_2S$.[101] The values of $\nu(CO)$ and $\nu(Pd{-}C)$ in the complexes *trans*-$[PdCl_2(CO)(S\text{-}R_2SO)]$ (R = Me, Et, benzyl) and *trans*-$[PdCl_2(CO)(SR_2)]$ [R = Me, Et, Pr; $R_2 = (CH_2)_4$] have been correlated with the variations in π acceptor abilities of the sulfur ligands.[102] It is also observed that $\nu(S{=}O)$ is at a lower frequency in the *trans*-$[PdCl_2(CO)(S\text{-}R_2SO)]$ complexes than in the $[PdCl_2(S\text{-}R_2SO)]_2$ dimers, and this is explained in terms of reduced π back-donation from the metal centre to the p_π–d_π orbital of the O=S bond in the former complex because of competition for metal π electron density from the *trans* carbonyl group.

The dicationic tetrakis(dialkylsulfoxide)palladium(II) complexes $[Pd(R_2SO)_4]^{2+}$ can be prepared by treating a solution of $PdCl_2$ dissolved in dialkyl sulfoxide at an elevated temperature with an acetone solution of $AgClO_4$ or $AgBF_4$, or by a metathesis reaction between $[Pd(NCMe)_4][BF_4]_2$ and an excess of the appropriate sulfoxide ligand.[97,103,104] IR spectroscopy has shown that both S- and O-bonded dialkyl sulfoxide ligands are present in these tetrakis complexes[97,103] and interesting structural changes are revealed as the steric requirements of the alkyl groups are increased. Thus DMSO and tetramethylene sulfoxide form *cis*-$[Pd(O\text{-}R_2SO)_2(S\text{-}R_2SO)_2]^{2+}$ [R = Me or $R_2 = (CH_2)_4$] complexes, di-*n*-propyl and di-*n*-butyl sulfoxides both form *trans*-$[Pd(O\text{-}R_2SO)_2(S\text{-}R_2SO)_2]^{2+}$ (R = Pr^n or Bu^n) and diisopentyl sulfoxide forms an entirely oxygen-bonded homoleptic dication $[Pd(O\text{-}Pe^i_2SO)_4]^{2+}$.[104,105] The structure of *cis*-$[Pd(O\text{-}Me_2SO)_2(S\text{-}Me_2SO)_2][BF_4]$ has been confirmed by X-ray crystallography.[106] This series suggests that when severe steric influences are not predominant, for example in $[PdCl_2(Me_2SO)_2]$, the dialkyl sulfoxides exhibit their true preference for Pd—S bonding. However, increasing the steric effects, for example in $[Pd(R_2SO)_4]^{2+}$ [R = Me or $R_2 = (CH_2)_4$], can prevent Pd—S bonding but still allow Pd—O bonding so that a mixed S- and O-bonded complex cation is obtained, with electronic effects (anti-symbiosis)[64] dictating a *cis* configuration. In the Pr^n and Bu^n derivatives the steric influence apparently increases to such an extent that a *trans* structure is obtained, and finally $[Pd(O\text{-}Pe^i_2SO)_4]^{2+}$ represents the limiting case in which the steric influence becomes completely dominant, permitting only oxygen bonding.

The dicationic S-bonded complex $[Pd(dien)(S\text{-}Me_2SO)][ClO_4]_2$ can be made from $[PdI(dien)][I]$ (dissolved in Me_2SO) by halide abstraction with $AgClO_4$,[107] while the complexes $[Pd(dppe)(O\text{-}Me_2SO)_2][Y]_2$ and $[PdCl(dppe)(O\text{-}Me_2SO)][Y]$ (Y = ClO_4 or PF_6), in which the large diphosphine ligands make coordination *via* sulfur extremely sterically hindered, are *O*-bonded.[108] The latter complex readily forms the corresponding thioether (SMe_2) complex by loss of oxygen from the Me_2SO.[108] Sulfoxide deoxygenation has also been reported in the reaction of $PdCl_2$ with tetramethylene sulfoxide: at ambient temperature the bis(*S*-sulfoxide) complex $[PdCl_2\{S\text{-}(CH_2)_4SO\}_2]$ is formed but in the presence of acetone and hydrochloric acid at higher temperature deoxygenation results to give the tetrahydrothiophene complex $[PdCl_2\{S(CH_2)_4\}_2]$.[92]

51.8.2.8 Thio- and Seleno-ureas

Thiourea and selenourea, and their nitrogen-substituted derivatives, act as unidentate ligands towards Pd^{II}, coordinating through their sulfur or selenium atoms.[109–113] X-Ray diffraction analyses of $[Pd\{SC(NH_2)_2\}_4]Cl_2$ show that the PdS_4 atoms are distorted slightly from a square plane towards a tetrahedral arrangement with a mean Pd—S bond length of 2.33(1) Å and two essentially ionic axial chloride ions at 3.594(3) and 3.791(3) Å from Pd.[114] Conductometric and electronic spectral measurements provide evidence for five-coordinate complexes of the type $[PdXL_4][Y]$ (X = halide; Y = halide, ClO_4 or BPh_4; L = *N,N'*-disubstituted thio- and selenourea) and the equilibrium shown by equation (19) is reported to occur in solutions of PdX_2L_4 in weakly coordinating and not highly polar solvents.[111,112] In the presence of an excess of X^- the square pyramidal species $[PdXL_4]^+$ form the expected four-coordinate complexes $[PdX_2L_2]$, which are reported to be generally unstable in the solid state.[112] However, several have been readily synthesized[113,115] and used in the course of vibrational spectroscopic studies on Pd^{II}-thiourea complexes.[110,113,115] Polymeric complexes of the type $[PdX_2L]_n$ have also been reported.[96]

$$[PdXL_4]^+ + X^- \rightleftharpoons [PdX_2L_2] + 2L \qquad (19)$$

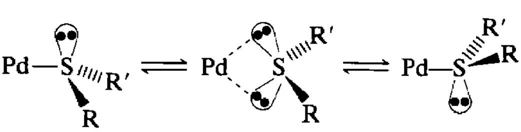
Spectrophotometric studies have been carried out on solutions of Pd^{II} containing thiourea in perchlorate, chloride, bromide and thiocyanate media,[116] such solutions being of practical importance in the analytical chemistry of palladium.[117]

51.8.2.9 Tertiary Phosphine or Arsine Sulfides and Selenides

Although the donor properties of $Ph_3P{=}S$ and $Ph_3P{=}Se$ appear to be weaker than that of $Ph_3P{=}O$, complexes of the type $[PdX_2L_2]$ (X = Cl, Br; L = Ph_3PS, Ph_3PSe or Ph_3AsS) are known.[118–121] These rather insoluble compounds are prepared by treating $PdCl_2$ in dilute hydrochloric acid solution with the ligand in alcohol or acetone solution. Complexes of stoichiometry $[Pd_2Br_4L_3]$ have been obtained on reaction of $PdBr_2$ with Ph_3PS or Ph_3PSe.[119] The ν(P—S) or ν(P—Se) IR stretching frequency of the ligand is lowered on coordination, indicating Pd—S or —Se coordination;[120] this is consistent with the charge distribution in the single bond formulation of these ligands ($Ph_3P^+—S^-$).[121] The complex *trans*-$[PdCl_2L_2]$ $[L = SeP(NMe_2)_3]$ has been prepared from $PdCl_2$ and L. In solution this complex loses one phosphine selenide ligand to form the dimer $[PdCl_2L]_2$, which was also prepared by an independent route from $[PdCl_2(NCPh)_2]$ and L. The dimer $[PdCl_2L]_2$ in turn, in the presence of free ligand L, affords *cis*-$[PdCl_2L_2]$.[122] In general complexes of unidentate phosphine sulfides and selenides are somewhat less stable than those of their bidentate analogues.

51.8.2.10 Thio-, Seleno- and Telluro-ethers

Many monomeric palladium(II) complexes of the type $[PdX_2(ER_2)_2]$ (X = wide variety of anionic ligand, E = S or Se, R = alkyl or aryl) have been prepared, generally by the reaction of the organic sulfide with an aqueous solution of $[PdX_4]^{2-}$.[3,41,123–127] Displacement of benzonitrile from *trans*-$[PdX_2(NCPh)_2]$ in benzene is an alternative method which has been used to make diaryl telluroether complexes.[55] They exist only in the *trans* configuration (the α form of early work) and do not thermally isomerize. The crystal structures of, for example, *trans*-$[PdCl_2(SeEt_2)_2]$[128] and $[Pd(SCN)_2(Te\{(CH_2)_3SiMe_3\}_2)_2]$[129] confirm this *trans* geometry and show that the chalcogen atoms are pyramidal. The generally yellow or brown complexes are soluble in benzene, chloroform and light petroleum. The selenoether complexes are similar to the thioether complexes but the stabilities generally decrease in the series $SR_2 > SeR_2 > TeR_2$. Many examples of the $[PdX_2(ER_2)_2]$ complexes have been studied by variable temperature ^1H NMR to study inversion at coordinated chalcogen:[127,130–134] at low temperature the chalcogen atoms are pyramidal, but on warming to above the coalescence temperature a rapid inversion occurs, which is not a dissociative–associative process. A simplistic view of the mechanism generally proposed[135] is the displacement at the palladium(II) centre of the lone pair of the chalcogen used in the Pd—E bond by the lone pair not involved in the bonding *via* a planar intermediate in which the chalcogen atom remains pyramidal, as in equation (20). For thioether and selenoether complexes a second coalescence at higher temperature is observed involving free and coordinated ligands.[132,134] The ease of exchange between free and coordinated ligands is in the order $TeEt_2 \gg SeEt_2 > SEt_2$, as are the relative inversion barrier energies.[131,133] The whole area of stereodynamics of metal complexes of sulfur-, selenium- or tellurium-containing ligands has recently been reviewed.[136]



(20)

The IR and Raman spectra of these *trans*-$[PdX_2(ER_2)_2]$ complexes have been studied.[125–127,137,138] They show ν(Pd—S) stretching vibrations around $310 \pm 30\ cm^{-1}$, ν(Pd—Se) at *ca.* $220\ cm^{-1}$ and ν(Pd—Te) at *ca.* $200\ cm^{-1}$. The electronic spectra exhibit three main bands: one due to a $d_{xy} \rightarrow d_{x^2-y^2}$ transition at 22 000–24 000 cm^{-1}, one due to charge transfer from the S or Se bonding orbitals to the Pd $d_{x^2-y^2}$ orbital at about 32 000 cm^{-1} and a third at 40 700–42 300 cm^{-1} in $[PdCl_2(SeEt_2)_2]$ due to a charge transfer from the chloride ligands to the Pd $d_{x^2-y^2}$ orbital.[126,127]

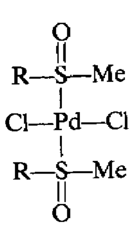
Thio-, seleno- and telluro-ethers may be used as reagents for the determination of palladium by solvent extraction and spectrophotometric measurement of $[PdX_2(ER_2)_2]$.[139] Alkyl phenyl sulfides form similar yellow monomeric $[PdCl_2(SPhR)_2]$ complexes when the alkyl group has a straight carbon chain, but when R = Bu^t or Me_2EtC the red polymeric complexes $[Pd_2Cl_4(SPhR)]_n$ are formed and these probably have a tetrameric structure ($n = 2$) with bridging chlorides.[140] Cyclic thioethers such as thiophane ($SCH_2CH_2CH_2CH_2$, L) also form *trans*-$[PdX_2L_2]$ complexes as well as chloro-bridged $[Pd_2Cl_4L_2]$ dimers,[141] though thiophene (SCH=CHCH=CH) does not form complexes, which, in view of the aromatic nature of thiophene, is doubtless due to the involvement of the unshared electron pairs on the sulfur atom in the formation of a stable π electron sextet. The structure of the 1,4-thioxane complex *trans*-$[PdCl_2(SCH_2CH_2OCH_2CH_2)_2]$ has been confirmed by X-ray crystallography.[142]

Complexes of the type $[PdX_3(SR_2)]^-$ (X = Cl, Br; R = Me, Et) can be prepared by reacting the halo-bridged dimeric compounds $[Pd_2X_4(SR_2)_2]$ (*vide infra*) with $[Pr^n_4N]Cl$ in 1:2 molar proportions.[138,143] The dimeric $[Pd_2X_4(SR_2)_2]$ complexes can also be cleaved by amines to prepare the mixed-ligand complexes *trans*-$[PdCl_2(am)(SR_2)]$.[144,145] Much of the early work on the transmission of electronic effects through a heavy metal atom (*trans* influence) used mixed ligand complexes of the type $[MX_2(am)L]$ where M = Pt or Pd and L included thioethers:[145,146] the change in ν(N—H) was studied with changing *trans* ligands. Once formed they are unstable to disproportionation, giving a mixture of *trans*-$[PdCl_2(SR_2)_2]$ and *trans*-$[PdCl_2(am)_2]$.[144,145] These mixed ligand complexes have also been prepared with seleno- or telluro-ethers,[145] and they too tend to disproportionate to the symmetrical species. A study has been made of the kinetics of displacement of amine ligands to give mixed thioether–amine complexes, as in equation (21).[147] Plots of $\log k_2$ (k_2 = second order rate constant) against the sum of the Taft σ^* values for the entering thioether in these reactions were all straight lines with alkyl and aryl thioethers lying on the same line. This suggests that d_π–d_π bonding is either non-existent or minimal in these Pd—S bonds since the reactivity of the thioether is dominated by its σ donor ability.

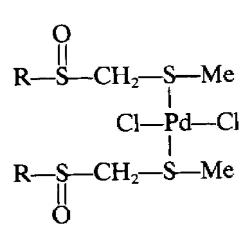
$$trans\text{-}[PdCl_2(amine)_2] + RSR' \xrightarrow[\text{R, R}'=\text{alkyl or aryl}]{\text{1,2-dimethoxyethane, 25 °C}} trans\text{-}[PdCl_2(amine)(SRR')] + amine \quad (21)$$

The mixed thioether σ-carbon ligand complexes *trans*-$[PdX(EEt_2)_2Ar]$ (X = Cl, Br, I; E = Se or Te; Ar = variety of aryl groups) have been prepared by reaction of the dihalo complexes *trans*-$[PdX_2(EEt_2)_2]$ with the appropriate arylmagnesium halides.[148] The analogous sulfur-containing σ-aryl derivatives, however, could not be obtained from *trans*-$[PdX_2(SR_2)_2]$ (R = Et or Ph) complexes and only reduction to metallic palladium occurred. Attempts to obtain σ-methyl Pd^{II} derivatives resulted in complete recovery of the starting complexes, while the use of an excess of Grignard reagent did not give the diaryl species *trans*-$[PdAr_2(ER_2)_2]$, although the corresponding diaryl Pt^{II} derivatives are known.[148]

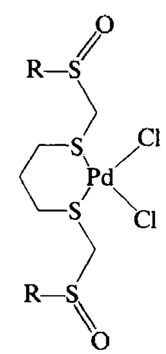
That sulfides coordinate to palladium(II) more strongly than the corresponding sulfoxides has received an interesting confirmation in a study of the complexes (**19**)–(**21**) (R = 4-MeC_6H_4).[149] The complex (**19**) is the best catalyst both for cyclotrimerization of diphenylethyne and for isomerization of allyl ethanoates. In both processes a vacant metal coordination site is essential and the thioether sulfur is too strongly bound (in **20** and **21**) for facile dissociation.



(**19**)



(**20**)



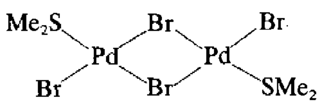
(**21**)

The dimeric complexes $[Pd_2X_4(ER_2)_2]$ may be prepared according to either equation (22) or (23).[150] As pointed out above, they are readily cleaved by unidentate ligands such as amines to give monomeric *trans*-$[PdX_2(am)(ER_2)]$ complexes.[144,145] Initial studies with these dimeric species were concerned with the relative stabilities of complexes such as $[M_2Cl_4(ER_2)_2]$: for M = Pd the stability order is $SR_2 > SeR_2 > TeR_2$, whereas for M = Pt the sequence $SR_2 \gg SeR_2 < TeR_2$ is found.[150] The Pd^{II} complexes are generally more soluble and less stable than their Pt^{II} analogues except for the SeR_2 complexes where the Pd^{II} species are the more stable. This difference in the sequence of stabilities may be due to the relative sizes of the orbitals used for M—E σ bonds, those of Se being comparable with those of Pd and those of Te with Pt.

$$[PdX_2(ER_2)_2] + Na_2PdCl_4 \xrightarrow{\text{EtOH}} [Pd_2X_4(ER_2)_2] + 2NaCl \quad (22)$$

$$2ER_2 + 2Na_2PdCl_4 \xrightarrow{\text{EtOH}} [Pd_2X_4(ER_2)_2] + 4NaCl \quad (23)$$

These dimeric complexes were initially assumed to be halide bridged; however, subsequent X-ray diffraction studies[151] of the complexes $[Pd_2Br_4(SMe_2)_2]$ and $[Pt_2Br_4(SEt_2)_2]$ have confirmed the suggestion made on the basis of their relative solubilities and IR spectra[152] that in the Pd^{II} complex the SMe_2 ligands are terminal [as (**22**)], whereas in the Pt^{II} complex the SEt_2 ligands are bridging [as (**23**)]. A notable feature of these two structures is that when the thioether is in a bridging situation, the M—S bond is significantly shorter [2.22(1) Å] than when it is terminal [2.30(2) Å]. The stronger M—S bond when the thioether ligand is bridging than when it is terminal may be due to the fact that the S atom in the terminal position in the Pd^{II} complex carries a lone pair of electrons which can act repulsively with non-bonded *d* electrons on the metal, whereas when the S atom is in the bridging position in the Pt^{II} complex all the sulfur outer electrons are accommodated in bonding orbitals, eliminating the repulsive interactions and allowing a stronger bond. However, the total number of repulsions between the ligand non-bonding lone pairs and the metal non-bonding *d* electrons is not altered on transferring a bromide from terminal to bridging since a terminal bromide has three non-bonding lone pairs, whereas a bridging bromide has only two. It is therefore not obvious why these Pd^{II} and Pt^{II} complexes adopt such different structures, though the explanation may lie in the spatial dissimilarity of the 4*d* and 5*d* orbitals.



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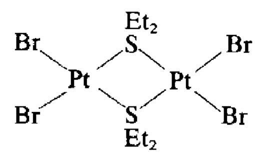


(23)

51.8.3 BIDENTATE AND MULTIDENTATE LIGANDS

The number and variety of coordination complexes of palladium(II) with sulfur-containing bidentate or multidentate ligands is legion, and it is possible here only to summarize the different kinds of complexes formed and to guide the reader into the literature. Table 2 contains a selection of typical palladium(II) complexes of bi- or multi-dentate sulfur or selenium donor ligands, and comments on pertinent aspects of particular complexes. Chelate

Table 2 Some Typical Palladium(II) Complexes of Bi- or Multi-dentate Sulfur or Selenium Donor Ligands

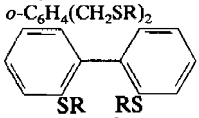
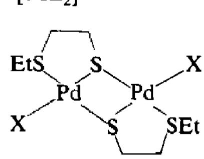
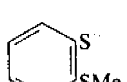
Ligand (L)	*Complexes formed*	*Remarks*	*Refs.*
Bis(thioether) complexes			
$RS(CH_2)_nSR$ (R = alkyl or aryl)			
$n = 2, 3$	$[PdX_2L]$	Early studies	1, 2
$n = 2, 3$	$[PdX_2L]$	Studies on inversion at sulfur	3, 4, 5
$n = 6, 8$ (R = Ph)	$[PdX_2L]_x$	Polymers formed	4
$n = 12$ (R = Ph)	*trans*-$[PdCl_2L]$	First S donor *trans*-chelating ligand	4, 6
$n = 2, 3$	$[PdL_2][ClO_4]_2$	Obtained from $[Pd(NCMe)_4][ClO_4]_2$ precursor	4
o-$C_6H_4(SR)_2$	$[PdX_2L]$		4, 7
o-$C_6H_4(CH_2SR)_2$	$[PdX_2L]$		8
	$[PdX_2L]$		8
cis-RSCH=CHSR	$[PdX_2L]$		4, 5, 7
Thioether–thiolate complexes			
cis-$RSCH{=}CHS^-$ (R = Me, Et, Bu)	$[PdL_2]$	*Cis* and *trans* isomers observed	9
$EtS(CH_2)_3S^-$		Thiolate-bridged	10, 11
	$[PdL_2]$	Only *trans* isomer	12
	$[XPdL_2PdX]$	Thiolate-bridged	10
$MeSCH_2CH_2S^-$	$[PdL_2]_x$	Polymer. From $Pd(PPh_3)_4$ and $(MeSCH_2CH_2S)_2$	13

Table 2 (*continued*)

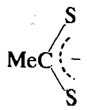
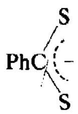
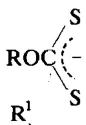
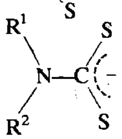
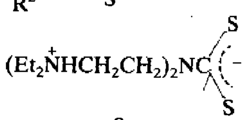
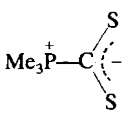
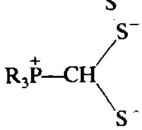
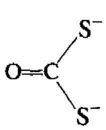
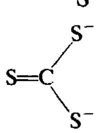
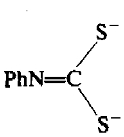
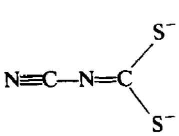
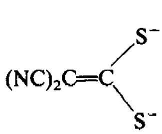
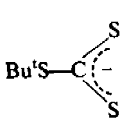
Ligand (L)	*Complexes formed*	*Remarks*	*Refs.*
1,1-*Dithiolate complexes*			
	$[PdL_2]$, $[PdL_2]_2$	Dithioacetate complex. Three distinct modifications known, all 2:1 L:Pd ratio. One contains alternate mononuclear and binuclear (bridging L) units stacked in columns (X-ray structure), one contains dimers only (X-ray structure), while the structure of the third form is not established	14
	trans-$[PdIL(PMe_3)_2]$	From insertion of CS_2 into *trans*-$[PdMeI(PMe_3)_2]$	15
	$[PdL_2]$	Dithiobenzoate complex. X-Ray structure shows virtual planarity of all atoms; intermolecular Pd···S distances suggest interaction	16
	$[PdL_2]$	Alkylxanthate complexes	17
	$[PdL_2]$ ($R^1 = R^2 = H$)	Dithiocarbamate complex	18
	$[PdL_2]$ (R^1, R^2 alkyl)	Dialkylthiocarbamate complexes. These are generally more stable than the xanthate complexes	18–21
	$[PdL(PMe_3)_2][BPh_4]$ ($R^1 = H$, $R^2 = Me$)		22
	$[PdL_2]Cl_4$	Cationic dithiocarbamate complex	21
	$[PdRL(PMe_3)_2][BPh_4]$, $[PdIRL(PMe_3)]$	Zwitterionic chelating ligand by insertion of CS_2 into Pd—PMe_3 bonds	15
	$[PdL(PR_3)_2][BPh_4]$		15
	$[PdL(PMePh_2)_2]$	Dithiocarbonate complex. From debenzylation of $[Pd(S_2COBz)_2]$ with excess $PMePh_2$, or from $Pd(PR_3)_n$ and COS. X-Ray structure shows coplanar P_2PdS_2CO atoms	23
	$[Ph_4As]_2[PdL_2]$	Trithiocarbonate complex	24
	$[PdL(PMe_2Ph)]$	Dithiocarbimate complex. From $[Pd(PMe_2Ph)(\eta^2\text{-}SCNPh)]$ and SCNPh	22
	$[Pr_4N]_2[PdL_2]$	*N*-Cyanodithiocarbimate complex	24
	$[Pr_4N]_2[PdL_2]$	1,1-Dicyanoethylene-2,2-dithiolate complex	24
	$[PdL(SBu^t)]_2$	*t*-Butylthioxanthate or *t*-butyltrithiocarbonate complex. X-Ray analysis shows a bis-*t*-butylthiolate-bridged dimeric structure	25

Table 2 *(continued)*

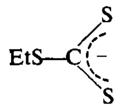
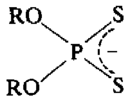
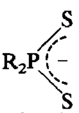
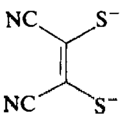
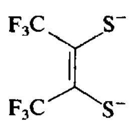
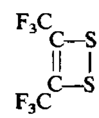
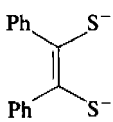
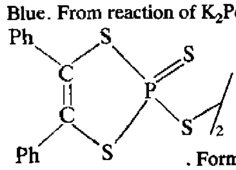
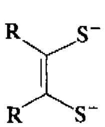
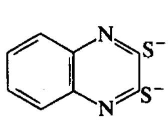
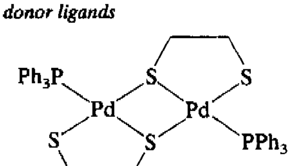
Ligand (L)	*Complexes formed*	*Remarks*	*Refs.*
	$[PdL(SEt)]_3$	X-Ray analysis shows a tris-ethylthiolate-bridged trimeric structure with an isosceles triangle of Pd atoms, each Pd surrounded by a square of S atoms	25
	$[PdL_2]$	Dialkyldithiophosphate complexes	20, 26
 (R = alkyl, aryl, F)	$[PdL_2]$	Dithiophosphinate complexes. These form 1:1 and 1:2 tertiary phosphine adducts $[Pd(\eta^1\text{-}S_2PR_2)(\eta^2\text{-}S_2PR_2)(PR'_3)]$ and $[Pd(\eta^2\text{-}S_2PR_2)(PR'_3)_2][R_2PS_2]$	27
1,2-Dithiolene complexes[a]			
	$[R_4N]_2[PdL_2]$	Maleonitriledithiolate or *cis*-1,2-dicyanoethylene-1,2-dithiolate complex. Green. From $[Pd(NH_3)_4]Cl_2$ or $PdCl_2$ and $Na_2S_2C_2(CN)_2$	28, 29
	$[R_4N][PdL_2]$	Dark red. From $[R_4N]_2[PdL_2]$ by oxidation with I_2 or $[Ni\{S_2C_2(CF_3)_2\}_2]$	29, 30
	$[PdL(PPh_3)_2]$	Deep pink. From $[PdCl_2(PPh_3)_2]$	31
	$[PdL(PPh_3)_2]$	Pale pink. From $Pd(PPh_3)_4$ and bis(perfluoromethyl)-1,2-dithietene: 	31
	$[C_9H_{10}N][PdL_2]$	Red-brown. From $[PdL(PPh_3)_2]$ and $(CF_3)_2C_2S_2$	31
	$[Ph_4As]_2[PdL_2]$	Pale green. From $[PdL(PPh_3)_2]$ and $(CF_3)_2C_2S_2$, then hydrazine	31
	$[PdL_2]$	Blue. From reaction of K_2PdCl_4 and  . Forms labile yellow-brown 1:1 adducts with dialkenes. X-Ray structure of 1:1 adduct with cyclohexa-1,3-diene shows that a 1,8-cycloaddition reaction occurs with formation of two new C—S bonds	32, 33
	$[N_2H_5]_2[PdL_2]$	Orange. From reaction of $[PdL_2]$ with hydrazine	32
	$[PdL(PR_3)_2]$, [PdL(dppe)]	Red	32, 34
	$[PdL(PPh_3)]_2$	Green	34
	$[Et_4N][PdL_2]$ (R = H)	Brown-violet. From $PdCl_2$ and $Na_2S_2C_2H_2$	35, 36
	$[PdL_2]$ (R = H)	Black. From I_2 oxidation of $[Et_4N][PdL_2]$. X-Ray structure shows two square planar $[PdL_2]$ units in eclipsed relationship joined by a Pd—Pd bond of 2.790(2) Å to form a dimeric structure	37
	$[PdL_2]$ (R = Me, *p*-$MeOC_6H_4$)		36
	$[Bu^n_4N]_2[PdL_2]$	Orange. From the analytical reagent quinoxaline-2,3-dithiol	38
o-$C_6H_4(S^-)_2$	$[PdL(PBu_3)]_2$	Bridging dithiolate	39
Other complexes of bidentate sulfur donor ligands			
$^-SCH_2CH_2S^-$		Thiolate bridged. From oxidative addition to $Pd(PPh_3)_4$, or from $PdCl_2(PPh_3)_2$ or $Pd(CN)_2(PPh_3)_2$ in presence of base. Also from $Pd(PPh_3)_4$ and $MeSCH_2CH_2SH$ with *S* demethylation	13

Table 2 (*continued*)

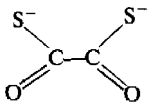
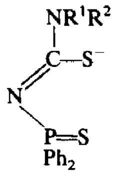
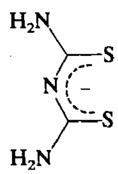
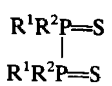
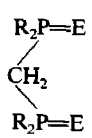
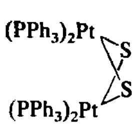
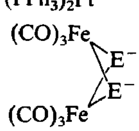
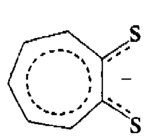
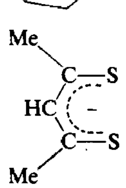
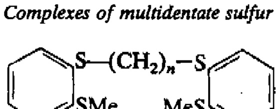
Ligand (L)	*Complexes formed*	*Remarks*	*Refs.*
	$[PdL(PMe_2Ph)_2]$	Cleavage of above dimer with PMe_2Ph	13
	$[PdL(diars)]$	From $PdCl_2(diars)$. Less strongly coordinating chelate ligands than diars give a polymeric product $[PdL]_x$	13
	$K_2[PdL_2]$	Dithiooxalate complex. Very stable; strong Pd—S bonds. X-Ray diffraction shows square planar, S-bonded	40
	$[PdL_2]$ ($R^1 = R^2 = Et$; $R^1 = Ph$, $R^2 = H$)	Complex of diphenylphosphinothioyl derivative of thiourea. Bound through S only, not N or P	41
	$[PdL_2]$	Dithiobiuret complex. X-Ray structure shows PdS_4 planar, ligands non-planar	42
	*cis*-$[PdL_2]$	Blue. X-Ray structure shows PdS_4 planar with *cis* ligands	43, 44
	$[PdL(S_2N_2H)]$	Black solid, green solutions	44
	$[PdX_2L]$	Di(tertiary phosphine) sulfides, *e.g.* $R^1 = R^2 = Me$. X-Ray structures of $R^1 = R^2 = NEt_2$ and $R^1 = NEt_2$, $R^2 = C_6H_{11}$ show L in *gauche* conformation	45, 46
 (E = S, Se)	$[PdX_2L]$		45
	$[PdL_2][BF_4]_2$, $[LPd(\mu\text{-}Cl)_2PdL][PF_6]_2$, $[PdL(dppe)][PF_6]_2$, $[PdClL(PPh_3)][PF_6]$	Sulfur-bridged diplatinum species functioning as bidentate ligand	47
 (E = S, Se, Te)	$[PdL(PPh_3)_2]$	Chalcogen-bridged di-iron species functioning as bidentate ligand	48
	$[PdL_2]$	Dithiotropolonate complex. Violet	49
	$[PdL_2]$	Dithioacetylacetonate complex. Bright red	50
Complexes of multidentate sulfur donor ligands			
 (n = 2, 3, 4)	$[Pd_2X_4L]$	Tetrathioether complex with bridging L. Complicated *S*-dealkylation reactions on prolonged reflux in DMF	51
	$[PdL][ClO_4]_2$		51

Table 2 (*continued*)

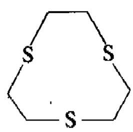
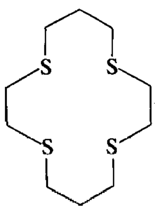
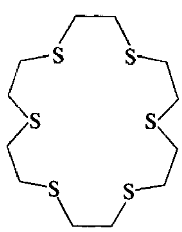
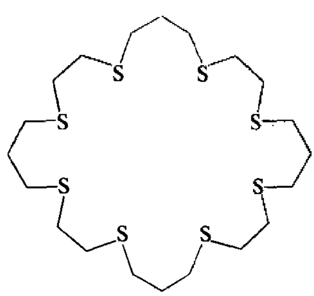
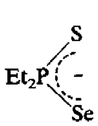
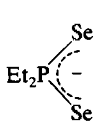
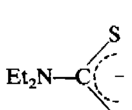
Ligand (L)	*Complexes formed*	*Remarks*	*Refs.*
$^{-}SCH_2CH_2SCH_2CH_2S^{-}$	$[PdL]_3$	X-Ray structure shows trimeric structure with an isosceles triangle of Pd atoms, each Pd surrounded by a square of S atoms	52
	$[PdL_2][PF_6]_2$, $[PdBr_2L]$	X-Ray structures show two normal Pd—S bonds and one Pd···S interaction for each L. Electrochemical oxidation of $[PdL_2]^{2+}$ affords the relatively stable trivalent palladium(III) species, $[PdL_2]^{3+}$	53
	$[PdL]^{2+}$		54
	$[PdL][BPh_4]_2$	X-Ray structure shows that Pd is coordinated to four S atoms in a square planar fashion; only long range weak axial interactions are observed with the two remaining S atoms, i.e. the conformation of the macrocycle is an S-shaped double boat, with the Pd^{II} ion at the molecular inversion centre	55
	$[Pd_4Cl_8L]$	Very stable complex, soluble in DMF. L acts in a bidentate fashion toward each of the four Pd^{II} ions resulting in four square planar metal ions per molecule	56
Complexes of bidentate and multidentate selenium donor ligands			
	$[PdL_2]$	Diethylselenothiophosphinate complex	27
	$[PdL_2]$	Diethyldiselenophosphinate complex. The Se complexes are not as stable as their S analogues and decompose in daylight and on heating	57
	$[PdL_2]$	Selenothiocarbamate complex	58
$RSe(CH_2)_nSeR$ ($R = Me, Ph$; $n = 2, 3$)	$[PdX_2L]$	Diselenoether complexes. There is a ring contribution to the ^{77}Se NMR chemical shifts dependent upon the chelate ring size.	59

Table 2 (*continued*)

Ligand (L)	*Complexes formed*	*Remarks*	*Refs.*
cis-MeSeCH=CHSeMe	$[PdX_2L]$	Studied by ^1H and ^{77}Se NMR	59
o-$C_6H_4(SeMe)_2$	$[PdX_2L]$	Studied by ^1H and ^{77}Se NMR	59
$MeSe(CH_2)_6SeMe$	$[PdCl_2L]_x$	Probably polymeric with bridging L	59
$MeC(CH_2SeMe)_3$	$[PdCl_2L]$	Triselenoether complexes. Studied by ^{77}Se NMR;	60
$(MeSeCH_2CH_2CH_2)_2Se$	$[PdCl_2L]$	bidentate with one SeMe group not coordinated	60
$C(CH_2SeMe)_4$	$[Cl_2PdLPdCl_2]$	Tetraselenoether complex; bridging L	60
$CH_2(CH_2SeCH_2CH_2SeMe)_2$	$[Cl_2PdLPdCl_2]$	Insoluble; bridging L	61

[a] The ligands L are drawn for convenience with localized valence bonds and ionic charges. Reversible oxidation–reduction sequences are a characteristic feature of many 1,2-dithiolene complexes, and there is difficulty in assigning meaningful oxidation states to metal atoms in a redox series when the electronic configuration of the ligands themselves may also be undergoing change.

1. 'Gmelins Handbuch der anorganischen Chemie', 8th edn., Verlag Chemie, Weinheim, 1942, system no. 65, part 2.
2. J. R. Durig, R. Layton, D. W. Sink and B. R. Mitchell, *Spectrochim. Acta*, 1965, **21**, 1367; V. G. Munroe, M. E. Peach and D. A. Stiles, *Inorg. Nucl. Chem. Lett.*, 1969, **5**, 977.
3. R. J. Cross, G. J. Smith and R. Wardle, *Inorg. Nucl. Chem. Lett.*, 1971, **7**, 191; R. J. Cross, I. G. Dalgleish, G. J. Smith and R. Wardle, *J. Chem. Soc., Dalton Trans.*, 1972, 992.
4. F. R. Hartley, S. G. Murray, W. Levason, H. E. Soutter and C. A. McAuliffe, *Inorg. Chim. Acta*, 1979, **35**, 265.
5. E. W. Abel, S. K. Bhargava, K. Kite, K. G. Orrell, V. Šik and B. L. Williams, *Polyhedron*, 1982, **1**, 289.
6. C. A. McAuliffe, H. E. Soutter, W. Levason, F. R. Hartley and S. G. Murray, *J. Organomet. Chem.*, 1978, **159**, C25.
7. R. Heber and E. Hoyer, *J. Prakt. Chem.*, 1976, **318**, 19.
8. D. W. Allen, P. N. Braunton, I. T. Millar and J. C. Tebby, *J. Chem. Soc. (C)*, 1971, 3454.
9. R. Heber and E. Hayer, *J. Prakt. Chem.*, 1973, **315**, 106.
10. S. E. Livingstone, *J. Chem. Soc.*, 1956, 1989.
11. S. E. Livingstone, *J. Chem. Soc.*, 1956, 1994.
12. S. E. Livingstone, *J. Chem. Soc.*, 1956, 437.
13. T. B. Rauchfuss and D. M. Roundhill, *J. Am. Chem. Soc.*, 1975, **97**, 3386.
14. O. Piovesana, C. Bellitto, A. Flamini and P. F. Zanazzi, *Inorg. Chem.*, 1979, **18**, 2258.
15. H. Werner and W. Bertleff, *Chem. Ber.*, 1980, **113**, 267.
16. C. Furlani and M. L. Luciani, *Inorg. Chem.*, 1968, **7**, 1586; M. Bonamico and G. Dessy, *Chem. Commun.*, 1968, 483.
17. G. W. Watt and B. J. McCormick, *J. Inorg. Nucl. Chem.*, 1965, **27**, 898.
18. K. Nakamoto, J. Fujita, R. A. Condrate and Y. Morimoto, *J. Chem. Phys.*, 1963, **39**, 423.
19. J. Chatt, L. A. Duncanson and L. M. Venanzi, *Suom. Kemistil. B*, 1956, **29**, 75 (*Chem. Abstr.*, 1957, **51**, 5559d); C. G. Sceney and R. J. Magee, *Inorg. Nucl. Chem. Lett.*, 1974, **10**, 323.
20. C. K. Jørgenson, *J. Inorg. Chem.*, 1962, **24**, 1571.
21. B. J. McCormick, B. P. Stormer and R. I. Kaplan, *Inorg. Chem.*, 1969, **8**, 2522.
22. W. Bertleff and H. Werner, *Chem. Ber.*, 1982, **115**, 1012.
23. J. P. Fackler and W. C. Seidel, *Inorg. Chem.*, 1969, **8**, 1631; H. Werner, W. Bertleff, B. Zimmer-Gasser and U. Schubert, *Chem. Ber.*, 1982, **115**, 1004.
24. J. P. Fackler and D. Coucouvanis, *J. Am. Chem. Soc.*, 1966, **88**, 3913.
25. J. P. Fackler, Jr. and W. J. Zegarski, *J. Am. Chem. Soc.*, 1973, **95**, 8566.
26. S. H. H. Chaston, S. E. Livingstone, T. N. Lockyer, V. A. Pickles and J. S. Shannon, *Aust. J. Chem.*, 1965, **18**, 673.
27. W. Kuchen and H. Hertel, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 89; T. A. Stephenson and B. D. Faithful, *J. Chem. Soc. (A)*, 1970, 1504: J. M. C. Alison and T. A. Stephenson, *Chem. Commun.*, 1970, 1092; F. N. Tebbe and E. L. Muetterties, *Inorg. Chem.*, 1970, **9**, 629.
28. E. Billig, R. Williams, I. Bernal, J. H. Waters and H. B. Gray, *Inorg. Chem.*, 1964, **3**, 663.
29. J. F. Weiher, L. R. Melby and R. E. Benson, *J. Am. Chem. Soc.*, 1964, **86**, 4329.
30. A. Davison, N. Edelstein, R. H. Holm and A. H. Maki, *Inorg. Chem.*, 1963, **2**, 1227.
31. A. Davison, N. Edelstein, R. H. Holm and A. H. Maki, *Inorg. Chem.*, 1964, **3**, 814.
32. G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, 1965, **87**, 1483.
33. G. R. Clark, J. M. Waters and K. R. Whittle, *J. Chem. Soc., Dalton Trans.*, 1973, 821.
34. V. P. Mayweg and G. N. Schrauzer, *Chem. Commun.*, 1966, 640.
35. E. Hoyer, W. Dietzsch, H. Hennig and W. Schroth, *Chem. Ber.*, 1969, **102**, 603.
36. D. C. Olson, V. P. Mayweg and G. N. Schrauzer, *J. Am. Chem. Soc.*, 1966, **88**, 4876.
37. K. W. Browall, T. Bursh, L. V. Interrante and J. S. Kasper, *Inorg. Chem.*, 1972, **11**, 1800.
38. L. J. Theriot, K. K. Ganguli, S. Kavarnos and I. Bernal, *J. Inorg. Nucl. Chem.*, 1969, **31**, 3133.
39. J. Chatt and F. G. Mann, *J. Chem. Soc.*, 1938, 1949.
40. C. S. Robinson and H. O. Jones, *J. Chem. Soc.*, 1912, **101**, 62: E. G. Cox, W. Wardlaw and K. C. Webster, *J. Chem. Soc.*, 1935, 1475.
41. I. Ojima, T. Iwamoto, T. Onishi, N. Inamoto and K. Tamaru, *Chem. Commun.*, 1969, 1501.
42. R. L. Girling and E. L. Amma, *Chem. Commun.*, 1968, 1487.
43. J. Weiss and H.-S. Neubert, *Z. Naturforsch., Teil B*, 1966, **21**, 286.
44. J. D. Woollins, R. Grinter, M. K. Johnson and A. J. Thomson, *J. Chem. Soc., Dalton Trans.*, 1980, 1910.
45. T. S. Lobana and K. Sharma, *Transition Met. Chem. (Weinheim, Ger.)*, 1982, **7**, 333, and refs. therein.
46. D. Troy and J. P. Legros, *Phosphorus Sulfur*, 1983, **14**, 377; J. P. Legros and D. Troy, *Acta Crystallogr., Sect. B*, 1983, **39**, 337.
47. C. E. Briant, T. S. A. Hor, N. D. Howells and D. M. P. Mingos, *J. Chem. Soc., Chem. Commun.*, 1983, 1118.
48. D. Seyferth, R. S. Henderson and M. K. Gallagher, *J. Organomet. Chem.*, 1980, **193**, C75; D. A. Lesch and T. B. Rauchfuss, *J. Organomet. Chem.*, 1980, **199**, C6.
49. C. E. Forbes and R. H. Holm, *J. Am. Chem. Soc.*, 1968, **90**, 6884; 1970, **92**, 2297.
50. R. L. Martin and I. M. Stewart, *Nature (London)*, 1966, **210**, 522.

51. W. Levason, C. A. McAuliffe and S. G. Murray, *J. Chem. Soc., Dalton Trans.*, 1975, 1566; *Inorg. Chim. Acta*, 1976, **17**, 247; C. A. McAuliffe and S. G. Murray, *Inorg. Nucl. Chem. Lett.*, 1976, **12**, 897. See also F. R. Hartley, S. G. Murray and C. A. McAuliffe, *Inorg. Chem.*, 1979, **18**, 1394.
52. E. M. McPartlin and N. C. Stephenson, *Acta Crystallogr., Sect. B*, 1969, **25**, 1659.
53. K. Wieghardt, H.-J. Küppers, E. Raabe and C. Krüger, *Angew, Chem., Int. Ed. Engl.*, 1986, **25**, 1101; A. J. Blake, R. O. Gould, A. J. Holder, T. I. Hyde, A. J. Lavery, M. O. Odulate and M. Schröder, *J. Chem. Soc., Chem. Commun.*, 1987, 118.
54. M. N. Bell, A. J. Blake, R. O. Gould, A. J. Holder, T. I. Hyde, A. J. Lavery and M. Schröder, in 'Proceedings of the XI International Symposium on Macrocyclic Chemistry', Department of Chemistry, University of Florence, Florence, 1986, p. 74.
55. A. J. Blake, R. O. Gould, A. J. Lavery and M. Schröder, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 274.
56. K. Travis and D. H. Busch, *Chem. Commun.*, 1970, 1041.
57. W. Kuchen and B. Knop, *Angew. Chem., Int. Ed. Engl.*, 1965, **4**, 244.
58. R. Heber, R. Kirmse and E. Hoyer, *Z. Anorg. Allg. Chem.*, 1972, **393**, 159.
59. D. J. Gulliver, E. G. Hope, W. Levason, S. G. Murray and G. L. Marshall, *J. Chem. Soc., Dalton Trans.*, 1985, 1265.
60. E. G. Hope, W. Levason, S. G. Murray and G. L. Marshall, *J. Chem. Soc., Dalton Trans.*, 1985, 2185.
61. W. Levason, C. A. McAuliffe and S. G. Murray, *J. Chem. Soc., Dalton Trans.*, 1976, 269.

complexes containing thioether or selenoether donor groups are covered in a comprehensive review,[123] and there are several detailed accounts available on the complexes of the important 1,1-dithiolate[153] and 1,2-dithiolene[154] ligands. Other more general reviews cover structural systematics of 1,1-dithiolate and 1,2-dithiolene chelates,[155] stereochemical aspects of bis chelate complexes including sulfur and selenium donors,[156] multinuclear complexes with sulfur-containing ligands,[157] and complexes with 1,2-dithiolium ions and dithio-β-diketonate ligands.[158] A recent theoretical study deals with dimerization and stacking in the metal complexes of dithiolenes and tetrathiolenes.[159]

51.8.4 REFERENCES

1. F. R. Hartley, 'The Chemistry of Platinum and Palladium', Applied Science Publishers, London, 1973.
2. J. V. Quagliano and L. Schubert, *Chem. Rev.*, 1952, **50**, 201.
3. 'Gmelins Handbuch der anorganischen Chemie', 8th edn., Verlag Chemie, Weinheim, 1942, system no. 65, part 2.
4. S. E. Livingstone, in 'Comprehensive Inorganic Chemistry', ed. J. C. Bailar, H. J. Emeléus, R. Nyholm and A. F. Trotman-Dickenson, Pergamon, Oxford, 1973, vol. 3, chap. 43, p. 1163.
5. A. F. Wells, 'Structural Inorganic Chemistry', 5th edn., Clarendon, Oxford, 1984.
6. M. Schmidt and G. G. Hoffmann, *Z. Naturforsch., Teil B*, 1978, **33**, 1334.
7. M. Schmidt and G. G. Hoffmann, *Z. Anorg. Allg. Chem.*, 1980, **464**, 209.
8. M. Schmidt, G. G. Hoffmann and R. Höller, *Inorg. Chim. Acta*, 1979, **32**, L19.
9. B. Kreutzer, P. Kreutzer and W. Beck, *Z. Naturforsch., Teil B*, 1972, **27**, 461.
10. C. A. Ghilardi, S. Midollini, F. Nuzzi and A. Orlandini, *Transition Met. Chem. (Weinheim, Ger.)*, 1983, **8**, 73.
11. H. Werner, W. Bertleff and U. Schubert, *Inorg. Chim. Acta*, 1980, **43**, 199.
12. M. Schmidt and G. G. Hoffmann, *Z. Naturforsch., Teil B*, 1979, **34**, 451.
13. J. Chatt and D. M. P. Mingos, *J. Chem. Soc. (A)*, 1970, 1243.
14. C. E. Briant, M. J. Calhorda, T. S. A. Hor, N. D. Howells and D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.*, 1983, 1325.
15. Z. A. Fokina, N. I. Timoshchenko and S. V. Volkov, *Koord. Khim.*, 1979, **5**, 443 (*Chem. Abstr.*, 1979, **90**, 179 385); Z. A. Fokina, S. V. Volkov, I. B. Baranovskii, N. I. Timoshchenko and V. I. Pekhn'o, *Zh. Neorg. Khim.*, 1981, **26**, 1835 (*Chem. Abstr.*, 1981, **95**, 143 305); S. V. Volkov, Z. A. Fokina and N. I. Timoshchenko, *Rev. Chim. Miner.*, 1983, **20**, 776 (*Chem. Abstr.*, 1984, **100**, 184 733).
16. A. L. Balch, L. S. Benner and M. M. Olmstead, *Inorg. Chem.*, 1979, **18**, 2996.
17. G. A. Earwicker, *J. Chem. Soc.*, 1960, 2620.
18. R. Eskenazi, J. Raskovan and R. Levitus, *J. Inorg. Nucl. Chem.*, 1965, **27**, 371.
19. J. B. Goddard and F. Basolo, *Inorg. Chem.*, 1968, **7**, 936.
20. G. Newman and D. B. Powell, *Spectrochim. Acta*, 1963, **19**, 213.
21. B. Nyberg and R. Larsson, *Acta Chem. Scand.*, 1973, **27**, 63.
22. J. P. Hall and W. P. Griffith, *Inorg. Chim. Acta*, 1981, **48**, 65.
23. M. A. Spinnler and L. N. Becka, *J. Chem. Soc. (A)*, 1967, 1194.
24. M. V. Capparelli and L. N. Becka, *J. Chem. Soc. (A)*, 1969, 260.
25. D. Messer, D. K. Breitinger and W. Haegler, *Acta Crystallogr., Sect. B*, 1981, **37**, 19.
26. F. Wöhler, *Justus Liebigs Ann. Chem.*, 1874, **174**, 199.
27. A. Rosenheim and H. Itzig, *Z. Anorg. Chem.*, 1900, **23**, 28.
28. D. Messer, D. Breitinger and W. Haegler, *Acta Crystallogr., Sect. B*, 1979, **35**, 815.
29. B. Chiswell and L. M. Venanzi, *J. Chem. Soc. (A)*, 1966, 1246.
30. I.-P. Lorenz, E. Lindner and W. Reuther, *Z. Anorg. Allg. Chem.*, 1975, **414**, 30.
31. J. Chatt and D. M. P. Mingos, *J. Chem. Soc. (A)*, 1969, 1770.
32. C. W. Dudley and C. Oldham, *Inorg. Chim. Acta*, 1969, **3**, 3.
33. C. Preti, G. Tosi, D. de Filippo and G. Verani, *Inorg. Nucl. Chem. Lett.*, 1974, **10**, 541.
34. I.-P. Lorenz, E. Lindner and W. Reuther, *Angew Chem., Int. Ed. Engl.*, 1975, **14**, 256.

35. M. Graziani, R. Ros and G. Carturan, *J. Organomet. Chem.*, 1971, **27**, C19; R. Ros, G. Carturan and M. Graziani, *Transition Met. Chem.* (*Weinheim, Ger.*), 1975, **1**, 13.
36. K. Garves, *J. Org. Chem.*, 1970, **35**, 3273; R. Selke and W. Thiele, *J. Prakt. Chem.*, 1971, **313**, 875 (*Chem. Abstr.*, 1972, **76**, 85 468).
37. D. I. Ryabchikov and A. P. Isakova, *Dokl. Akad. Nauk SSSR*, 1943, **41**, 169 (*Chem. Abstr.*, 1944, **38**, 4527).
38. R. Eskenazi and R. Levitus, *J. Inorg. Nucl. Chem.*, 1969, **31**, 2195.
39. S. Baggio, L. M. Amzel and L. N. Becka, *Acta Crystallogr., Sect. B*, 1970, **26**, 1698.
40. J. A. Costamagna and R. Levitus, *J. Inorg. Nucl. Chem.*, 1966, **28**, 1116.
41. F. G. Mann and D. Purdie, *J. Chem. Soc.*, 1935, 1549.
42. R. G. Hayter and F. S. Humiec, *J. Inorg. Nucl. Chem.*, 1964, **26**, 807.
43. G. E. Hunter and R. A. Krause, *Inorg. Chem.*, 1970, **9**, 537.
44. N. R. Kunchur, *Acta Crystallogr., Sect. B*, 1968, **24**, 1623; 1971, **27**, 2292.
45. Yu. N. Kukushkin, R. A. Vlasova and V. N. Shvedova, *Zh. Prikl. Khim.* (*Leningrad*), 1970, **43**, 2726 (*Chem. Abstr.*, 1971, **74**, 134 550r).
46. T. Boschi, B. Crociani, L. Toniolo and U. Belluco, *Inorg. Chem.*, 1970, **9**, 532.
47. W. Beck, K. H. Stetter, S. Tadros and K. E. Schwarzhans, *Chem. Ber.*, 1967, **100**, 3944; W. Beck, W. P. Fehlhammer, K. H. Stetter and S. Tadros, *Chem. Ber.*, 1967, **100**, 3955; R. S. Nyholm, J. F. Skinner and M. H. B. Stiddard, *J. Chem. Soc.* (*A*), 1967, 38.
48. R. H. Fenn and G. R. Segrott, *J. Chem. Soc.* (*A*), 1970, 3197.
49. B. Kreutzer, P. Kreutzer and W. Beck, *Z. Naturforsch., Teil B*, 1972, **27**, 461.
50. J. Chatt and F. G. Mann, *J. Chem. Soc.*, 1938, 1949.
51. J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1953, 2363.
52. J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1960, 2807.
53. R. Zanella, R. Ros and M. Graziani, *Inorg. Chem.*, 1973, **12**, 2736.
54. S. A. Gardner and H. J. Gysling, *J. Organomet. Chem.*, 1980, **197**, 111; S. A. Gardner, P. J. Trotter and H. J. Gysling, *J. Organomet. Chem.*, 1981, **212**, 35.
55. L.-Y. Chia and W. R. McWhinnie, *J. Organomet. Chem.*, 1978, **148**, 165.
56. A. H. Norbury, *Adv. Inorg. Chem. Radiochem.*, 1975, **17**, 231.
57. A. Sabatini and I. Bertini, *Inorg. Chem.*, 1965, **4**, 959.
58. H.-H. Schmidtke and D. Garthoff, *Helv. Chim. Acta*, 1967, **50**, 1631.
59. A. Mawby and G. E. Pringle, *Chem. Commun.*, 1970, 385; *J. Inorg. Nucl. Chem.*, 1972, **34**, 2213.
60. P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 1960, 1912; A. Turco and C. Pecile, *Nature* (*London*), 1961, **191**, 66; A. H. Norbury and A. I. P. Sinha, *Q. Rev., Chem. Soc.*, 1970, **24**, 69.
61. R. N. Keller, N. B. Johnson and L. L. Westmoreland, *J. Am. Chem. Soc.*, 1968, **90**, 2729.
62. A. Sabatini and I. Bertini, *Inorg. Chem.*, 1965, **4**, 1665.
63. S. Fronaeus and R. Larsson, *Acta Chem. Scand.*, 1962, **16**, 1447; C. Pecile, *Inorg. Chem.*, 1966, **5**, 210; R. Larsson and A. Miezis, *Acta Chem. Scand.*, 1969, **23**, 37.
64. R. G. Pearson, *Inorg. Chem.*, 1973, **12**, 712.
65. G. R. Clark, G. J. Palenik and D. W. Meek, *J. Am. Chem. Soc.*, 1970, **92**, 1077; G. R. Clark and G. J. Palenik, *Inorg. Chem.*, 1970, **9**, 2754.
66. J. L. Burmeister and F. Basolo, *Inorg. Chem.*, 1964, **3**, 1587.
67. F. Basolo, H. B. Grey and R. G. Pearson, *J. Am. Chem. Soc.*, 1960, **82**, 4200.
68. F. Basolo, W. H. Baddley and J. L. Burmeister, *Inorg. Chem.*, 1964, **3**, 1202.
69. J. L. Burmeister, R. L. Hassel, K. A. Johnson and J. C. Lim, *Inorg. Chim. Acta*, 1974, **9**, 23.
70. J. J. McDougall, J. H. Nelson, W. C. Fultz, J. L. Burmeister, E. M. Holt and N. W. Alcock, *Inorg. Chim. Acta*, 1982, **63**, 75.
71. G. J. Palenik, M. Mathew, W. L. Steffen and G. Beran, *J. Am. Chem. Soc.*, 1975, **97**, 1059.
72. C. T. Hunt and A. L. Balch, *Inorg. Chem.*, 1982, **21**, 1242.
73. A. J. Carty, P. C. Chieh, N. J. Taylor and Y. S. Wong, *J. Chem. Soc., Dalton Trans.*, 1976, 572.
74. J. J. MacDougall, E. M. Holt, P. de Meester, N. W. Alcock, F. Mathey and J. H. Nelson, *Inorg. Chem.*, 1980, **19**, 1439; J. H. Nelson, J. J. MacDougall, N. W. Alcock and F. Mathey, *Inorg. Chem.*, 1982, **21**, 1200.
75. F. Basolo, W. H. Baddley and K. Wiedenbaum, *J. Am. Chem. Soc.*, 1966, **88**, 1576.
76. J. L. Burmeister, H. J. Gysling and J. C. Lim, *J. Am. Chem. Soc.*, 1969, **91**, 44.
77. K. S. de Haas, *J. Inorg. Nucl. Chem.*, 1973, **35**, 3231.
78. J. L. Burmeister, R. L. Hassel and R. J. Phelan, *Chem. Commun.*, 1970, 679. See also J. L. Burmeister, R. L. Hassel and R. J. Phelan, *Inorg. Chem.*, 1971, **10**, 2032.
79. R. A. Plowman and L. F. Power, *Aust. J. Chem.*, 1971, **24**, 309.
80. O. St. C. Headley, R. S. Nyholm, C. A. McAuliffe, L. Sindellari, M. L. Tobe and L. M. Venanzi, *Inorg. Chim. Acta*, 1970, **4**, 93.
81. R. Ros and E. Tondello, *J. Inorg. Nucl. Chem.*, 1971, **33**, 245.
82. J. Chatt and L. A. Duncanson, *Nature* (*London*), 1956, **178**, 997.
83. D. L. Tibbetts and T. L. Brown, *J. Am. Chem. Soc.*, 1969, **91**, 1108.
84. D. V. Naik, G. J. Palenik, S. Jacobson and A. J. Carty, *J. Am. Chem. Soc.*, 1974, **96**, 2286.
85. J. L. Burmeister and H. J. Gysling, *Inorg. Chim. Acta*, 1967, **1**, 100.
86. J. L. Burmeister and H. J. Gysling, *Chem. Commun.*, 1967, 543; J. L. Burmeister and J. C. Lim, *Chem. Commun.*, 1968, 1346.
87. J. A. Davies, *Adv. Inorg. Chem. Radiochem.*, 1981, **24**, 115 and references therein.
88. See, for example, M. Ziegler and H. Schroeder, *Z. Naturforsch., Teil B*, 1967, **22**, 552; P. A. Lewis, D. F. C. Morris, E. L. Short and D. N. Waters, *J. Less-Common Met.*, 1976, **45**, 193.
89. F. A. Cotton and R. Francis, *J. Am. Chem. Soc.*, 1960, **82**, 2986; F. A. Cotton, R. Francis and W. D. Horrocks, *J. Phys. Chem.*, 1960, **64**, 1534; J. Selbin, W. E. Bull and L. H. Holmes, *J. Inorg. Nucl. Chem.*, 1961, **16**, 219; R. Francis and F. A. Cotton, *J. Chem. Soc.*, 1961, 2078.
90. Yu. N. Kukushkin, Yu. E. Vyaz'menskii, L. I. Zorina and Yu. L. Pazukhina, *Russ. J. Inorg. Chem.* (*Engl.*

Transl.), 1968, **13**, 835; Yu. N. Kukushkin, R. A. Vlasova and Yu. L. Pazukhina, *Zh. Prikl. Khim.* (*Leningrad*), 1968, **41**, 2381 (*Chem. Abstr.*, 1969, **71**, 56 171q).
91. W. Kitching, C. J. Moore and D. Doddrell, *Inorg. Chem.*, 1970, **9**, 541.
92. D. W. Meek, W. E. Hatfield, R. S. Drago and T. S. Piper, *Inorg. Chem.*, 1964, **3**, 1637.
93. M. J. Bennett, F. A. Cotton and D. L. Weaver, *Nature* (*London*), 1966, **212**, 286; M. J. Bennett, F. A. Cotton, D. L. Weaver, R. J. Williams and W. H. Watson, *Acta Crystallogr.*, 1967, **23**, 788.
94. D. A. Langs, C. R. Hare and R. G. Little, *Chem. Commun.*, 1967, 1080.
95. R. Eskenazi, J. Raskovan and R. Levitus, *J. Inorg. Nucl. Chem.*, 1966, **28**, 521.
96. Yu. N. Kukushkin, L. V. Konovalov, E. A. Andronov and R. A. Vlasova, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1972, **17**, 1207.
97. B. B. Wayland and R. F. Schramm, *Inorg. Chem.*, 1969, **8**, 971.
98. Yu. N. Kukushkin, Yu. E. Vyaz'menskii and E. S. Postnikova, *Zh. Prikl. Khim.* (*Leningrad*), 1969, **42**, 926 (*Chem. Abstr.*, 1969, **71**, 27 055z).
99. Yu. N. Kukushkin and R. A. Vlasova, *Zh. Prikl. Khim.* (*Leningrad*), 1968, **41**, 1407 (*Chem. Abstr.*, 1968, **69**, 80 733d).
100. E. A. Andronov, Yu. N. Kukushkin and V. G. Churakov, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1971, **16**, 1235.
101. E. A. Andronov, Yu. N. Kukushkin and V. G. Churakov, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1972, **17**, 1312.
102. E. A. Andronov, Yu. N. Kukushkin, V. G. Churakov and Yu. V. Murashkin, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1975, **20**, 634.
103. B. B. Wayland and R. F. Schramm, *Chem. Commun.*, 1968, 1465.
104. J. H. Price, A. N. Williamson, R. F. Schramm and B. B. Wayland, *Inorg. Chem.*, 1972, **11**, 1280.
105. J. H. Price, R. F. Schramm and B. B. Wayland, *Chem. Commun.*, 1970, 1377.
106. B. F. G. Johnson, J. Puga and P. R. Raithby, *Acta Crystallogr., Sect. B*, 1981, **37**, 953.
107. P.-K. F. Chin and F. R. Hartley, *Inorg. Chem.*, 1976, **15**, 982.
108. J. A. Davies, F. R. Hartley and S. G. Murray, *J. Chem. Soc., Dalton Trans.*, 1979, 1705.
109. N. Kurnakov, *Zh. Russ. Fiz.-Khim. Ova.*, 1894, **25**, 565; *J. Prakt. Chem.*, 1894, **50**, 485; F. W. Pinkard, E. Sharratt, W. Wardlaw and E. G. Cox, *J. Chem. Soc.*, 1934, 1012.
110. A. Yamaguchi, R. B. Penland, S. Mizushima, T. J. Lane, C. Curran and J. V. Quagliano, *J. Am. Chem. Soc.*, 1958, **80**, 527; T. J. Lane, A. Yamaguchi, J. V. Quagliano, J. A. Ryan and S. Mizushima, *J. Am. Chem. Soc.*, 1959, **81**, 3824.
111. C. Furlani and T. Tarantelli, *Inorg. Nucl. Chem. Lett.*, 1966, **2**, 391.
112. T. Tarantelli and C. Furlani, *J. Chem. Soc.* (*A*), 1968, 1717.
113. P. J. Hendra and Z. Jović, *Spectrochim. Acta, Part A*, 1968, **24**, 1713.
114. S. Oi, T. Kawase, K. Nakatsu and H. Kuroya, *Bull. Chem. Soc. Jpn.*, 1960, **33**, 861; D. A. Berta, W. A. Spofford, III, P. Boldrini and E. L. Amma, *Inorg. Chem.*, 1970, **9**, 136.
115. M. Schafer and C. Curran, *Inorg. Chem.*, 1966, **5**, 265; D. M. Adams and J. B. Cornell, *J. Chem. Soc.* (*A*), 1967, 884.
116. V. I. Shlenskaya, A. A. Biryukov and E. M. Moskovkina, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1966, **11**, 325.
117. See, for example, W. Nielsch, *Mikrochim. Acta*, 1954, **5**, 532; M. B. Bardin, N. S. Balandina and G. I. Todorova, *Zh. Anal. Khim.*, 1964, **19**, 1228 (*Chem. Abstr.*, 1965, **62**, 2236f).
118. E. Bannister and F. A. Cotton, *J. Chem. Soc.*, 1960, 1959.
119. T. S. Lobana and K. Sharma, *Transition Met. Chem.* (*Weinheim, Ger.*), 1982, **7**, 333, and refs. therein.
120. P. Nicpon and D. W. Meek, *Chem. Commun.*, 1966, 398.
121. M. G. King and G. P. McQuillan, *J. Chem. Soc.* (*A*), 1967, 898.
122. M. Aresta, M. De Fazio, A. Ingrosso and P. Bruno, *J. Inorg. Nucl. Chem.*, 1979, **41**, 1801.
123. S. G. Murray and F. R. Hartley, *Chem. Rev.*, 1981, **81**, 365. Review of thio-, seleno- and telluro-ether complexes of the transition metals with 748 references.
124. E. G. Cox, H. Saenger and W. Wardlaw, *J. Chem. Soc.*, 1934, 182; H. D. K. Drew and G. H. Wyatt, *J. Chem. Soc.*, 1934, 56; R. J. Cross, T. H. Green and R. Keat, *J. Chem. Soc., Dalton Trans.*, 1976, 382; O. A. Serra, L. R. M. Pitombo and Y. Iamamoto, *Inorg. Chim. Acta*, 1978, **31**, 49.
125. R. J. H. Clark, G. Natile, V. Belluco, L. Cattalini and C. Filippin, *J. Chem. Soc.* (*A*), 1970, 659.
126. B. E. Aires, J. E. Ferguson, D. T. Howarth and J. M. Miller, *J. Chem. Soc.* (*A*), 1971, 1144.
127. J. E. Fergusson and K. S. Loh, *Aust. J. Chem.*, 1973, **26**, 2615.
128. P. E. Skakke and S. E. Rasmussen, *Acta Chem. Scand.*, 1970, **24**, 2634.
129. H. J. Gysling, H. R. Luss and D. L. Smith, *Inorg. Chem.*, 1979, **18**, 2696.
130. R. J. Cross, I. G. Dalgleish, G. J. Smith and R. Wardle, *J. Chem. Soc., Dalton Trans.*, 1972, 992; J. C. Barnes, G. Hunter and M. W. Lown, *J. Chem. Soc., Dalton Trans.*, 1976, 1227.
131. R. J. Cross, T. H. Green and R. Keat, *J. Chem. Soc., Chem. Commun.*, 1974, 207.
132. R. J. Cross, T. H. Green, R. Keat and J. F. Paterson, *Inorg. Nucl. Chem. Lett.*, 1975, **11**, 145.
133. R. J. Cross, T. H. Green and R. Keat, *J. Chem. Soc., Dalton Trans.*, 1976, 1150.
134. R. J. Cross, T. H. Green, R. Keat and J. F. Paterson, *J. Chem. Soc., Dalton Trans.*, 1976, 1486.
135. P. C. Turley and P. Haake, *J. Am. Chem. Soc.*, 1967, **89**, 4617.
136. E. W. Abel, S. K. Bhargava and K. G. Orrell, *Prog. Inorg. Chem.*, 1984, **32**, 1.
137. J. R. Durig, R. Layton, D. W. Sink and B. R. Mitchell, *Spectrochim. Acta*, 1965, **21**, 1367; J. R. Allkins and P. J. Hendra, *J. Chem. Soc.* (*A*), 1967, 1325; J. R. Allkins and P. J. Hendra, *Spectrochim. Acta, Part A*, 1968, **24**, 1305; J. R. Allkins, R. J. Obrenski, C. W. Brown and E. R. Lippincott, *Inorg. Chem.*, 1969, **8**, 1450.
138. P. L. Goggin, R. J. Goodfellow, S. R. Haddock, F. J. S. Reed, J. G. Smith and K. M. Thomas, *J. Chem. Soc., Dalton Trans.*, 1972, 1904.
139. L. R. M. Pitombo and E. Q. Cartaxo, *Talanta*, 1974, **21**, 965 and refs. therein.
140. V. N. Ipatieff and B. S. Friedman, *J. Am. Chem. Soc.*, 1939, **61**, 684.
141. Yu. N. Kukushkin and Ts. Todorova, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1969, **14**, 1486.
142. J. M. Fowler and A. Griffiths, *Acta Crystallogr., Sect. B*, 1978, **34**, 1712.
143. R. J. Goodfellow, P. L. Goggin and D. A. Duddell, *J. Chem. Soc.* (*A*), 1968, 504.

144. J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 1957, 2445.
145. J. Chatt, L. A. Duncanson and L. M. Venanzi, *J. Chem. Soc.*, 1958, 3203.
146. J. Chatt, L. A. Duncanson, B. L. Shaw and L. M. Venanzi, *Discuss. Faraday Soc.*, 1958, **26,** 131.
147. L. Catallini, G. Marangoni and M. Martelli, *Inorg. Chem.*, 1968, **7,** 1495.
148. S. Sergi, F. Faraone, L. Silvestro and R. Pietropaolo, *J. Organomet. Chem.*, 1971, **33,** 403.
149. K. Ogura, T. Aizawa, K. Uchiyama and H. Iida, *Bull. Chem. Soc. Jpn.*, 1983, **56,** 953.
150. J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 1957, 2351.
151. D. L. Sales, J. Stokes and P. Woodward, *J. Chem. Soc. (A)*, 1968, 1852.
152. P. L. Goggin, R. J. Goodfellow, D. L. Sales, J. Stokes and P. Woodward, *Chem. Commun.*, 1968, 31.
153. D. Coucouvanis, *Prog. Inorg. Chem.*, 1970, **11,** 233; 1979, **26,** 301; R. P. Burns, F. P. McCullough and C. A. McAuliffe, *Adv. Inorg. Chem. Radiochem.*, 1980, **23,** 211.
154. E. Hoyer, W. Dietzsch and W. Schroth, *Z. Chem.*, 1971, **11,** 41; J. A. McCleverty, *Prog. Inorg. Chem.*, 1968, **10,** 49; R. P. Burns and C. A. McAuliffe, *Adv. Inorg. Chem. Radiochem.*, 1979, **22,** 303; C. Mahadevan, *J. Crystallogr. Spectrosc. Res.*, 1986, **16,** 347.
155. R. Eisenberg, *Prog. Inorg. Chem.*, 1970, **12,** 295.
156. R. H. Holm and M. J. O'Connor, *Prog. Inorg. Chem.*, 1971, **14,** 241.
157. J. P. Fackler, Jr., *Prog. Inorg. Chem.*, 1976, **21,** 55.
158. T. N. Lockyer and R. L. Martin, *Prog. Inorg. Chem.*, 1980, **27,** 223.
159. S. Alvarez, R. Vicente and R. Hoffmann, *J. Am. Chem. Soc.*, 1985, **107,** 6253.

51.9

Palladium(II): Phosphorus Donor Complexes

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51.9.1 INTRODUCTION

The excellent monograph by McAuliffe and Levason[1] reviews much of the work in this field up to the end of 1977. Hartley's book[2] also includes much of relevance to this area, as does the relevant section of 'Comprehensive Inorganic Chemistry'.[3] Care should be exercised, however, in using these older texts, as some generalizations current at that time have since been found to be erroneous. In addition, there are useful annual reviews of the literature covering the period 1979–1983.[4] The vast organometallic chemistry of palladium(II) with phosphorus, arsenic or antimony donor ligands falls outside the scope of this work, and is dealt with in the companion series 'Comprehensive Organometallic Chemistry'.[5] This includes the extremely important selective oxidation of alkenes by palladium(II) catalysts.[6]

51.9.2 PHOSPHINE, ARSINE AND STIBINE COMPLEXES

51.9.2.1 Unidentate Ligands

Complexes of the following stoichiometries are known (E = P, As or Sb; R = alkyl, aryl, *etc.*; X = singly charged anion, *e.g.* halide): $[PdX_2(ER_3)_2]$*, $[PdX_2(ER_3)_3]$, $[PdX(ER_3)_3]^+$, $[Pd(ER_3)_4]^{2+}$, $[PdX_3(ER_3)]^-$, $[Pd_2X_4(ER_3)_2]$* and $[Pd_2X_2(ER_3)_4]^{2+}$. Those complexes marked with an asterisk are by far the most numerous.

51.9.2.1.1 Complexes of the type $[PdX_2(ER_3)_2]$

Innumerable complexes of the type *cis*- and *trans*-$[PdX_2(ER_3)_2]$ have been prepared. Some typical examples are listed in Table 1.

Table 1 Typical Complexes of the Type $[PdX_2(ER_3)_2]$

ER_3	X	Ref.
PMe_3	*cis*-Cl, Br; *trans*-I	1
PBu^tMe_2	*trans*-Cl, Br, I	2
PBu^t_2Me	*trans*-Cl, Br, I	2
PPh_3	*trans*-Cl, NCO	3
$AsPh_3$	*trans*-Cl, NCO	3
$SbPh_3$	*cis*-Cl	4, 5
$PPh_2(CH_2OCOMe)$	*cis*-Cl; *trans*-Br, I	6
$PMe_2(CH_2OCOMe)$	*cis*-Cl; *trans*-Cl	6
$PBu^t_2(CH_2OCOMe)$	*trans*-Cl	6
$PPh_2(C{\equiv}CEt)$	*cis*-Cl, Br; *trans*-I	7
$PPh_2(C{\equiv}CPr^i)$	*cis*-Cl, Br; *trans*-I	7
$PPh_2(C{\equiv}CBu^t)$	*cis*-Cl, Br, I	7
Sb(*o*-tolyl)$_3$	*trans*-Br, I, SCN, NO_2	5
Sb(*m*-tolyl)$_3$	*cis*-Br, I, SCN, NO_2	5
Sb(*p*-tolyl)$_3$	*cis*-Br, I, SCN, NO_2	5

1. J. G. Evans, P. L. Goggin, R. J. Goodfellow and J. G. Smith, *J. Chem. Soc. (A)*, 1968, 464; R. J. Goodfellow, J. G. Evans, P. L. Goggin and D. A. Duddell, *ibid.*, 1968, 1604.
2. B. E. Mann, B. L. Shaw and R. M. Slade, *J. Chem. Soc. (A)*, 1971, 2976.
3. A. H. Norbury and A. I. P. Sinha, *J. Inorg. Nucl. Chem.*, 1973, **35**, 1211.
4. J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 1953, 70.
5. C. A. McAuliffe, I. E. Niven and R. V. Parish, *Inorg. Chim. Acta*, 1977, **22**, 239.
6. J. Chatt, G. J. Leigh and R. M. Slade, *J. Chem. Soc., Dalton Trans.*, 1973, 2021.
7. R. T. Simpson and A. J. Carty, *J. Coord. Chem.*, 1973, **2**, 207.

(*i*) *Compounds with X = halide*

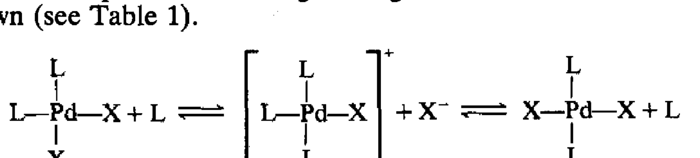
The dihalide complexes $[PdX_2(ER_3)_2]$ are formed when solutions of $[PdX_4]^{2-}$ (X = Cl, Br or I) are treated with two equivalents of a tertiary phosphine, arsine or stibine, as in equation (1).[7]

$$[PdX_4]^{2-} + 2ER_3 \longrightarrow [PdX_2(ER_3)_2] + 2X^- \qquad (1)$$

The products are generally yellow air stable crystalline solids. Their thermal stability decreases in the order $PR_3 > AsR_3 > SbR_3$.[8] Because of their ease of preparation, their diamagnetism and their ready solubility in a range of organic solvents, the $[PdX_2(ER_3)_2]$ complexes have been extensively studied spectroscopically. Notable references are given in Table 2.

It is particularly important to be able to distinguish between *cis* and *trans* isomers. In solution, NMR spectroscopy (^1H, ^{31}P, ^{13}C) is the most useful technique; in the solid state the far-IR spectra are usually diagnostic, since both the number of bands (two for *cis*, one for *trans*) and the frequency of absorption (ν_{Pd-X}) are characteristic of the isomer present.

In solution a *cis–trans* equilibrium mixture is rapidly established, though usually only one form is obtained on working up (in contrast to the chemistry of the analogous Pt^{II} compounds).[9] The mechanism of *cis–trans* isomerization is generally agreed to be one of consecutive displacement, the process being accelerated by addition of excess ER_3, as shown in equation (2) ($L = ER_3$).[10] In general the *cis* isomer is more stable than the *trans* isomer,[11] the amount of *trans* isomer in solution decreasing with basicity of the ligand and increasing dipole moment of the solvent. Bulky ligands, however, tend to favour the *trans* isomer, as evidenced by the fact that few *cis* complexes containing the ligands PBu^t_2R, PBu^tR_2, P(*o*-tolyl)$_2$R or P(*o*-tolyl)R_2 are known (see Table 1).


(2)

The halide complexes $[PdX_2(ER_3)_2]$ are precursors to a wide variety of derivatives, which

Table 2 Spectroscopic Studies on Complexes of the Type $[PdX_2(ER_3)_2]$

Technique	*Ref.*
ESCA	1
IR	2
NMR	
^{1}H	3
$^{1}H-\{^{31}P\}$	4
^{13}C	5
$^{13}C-\{^{1}H\}$	6
^{31}P	7
^{35}Cl NQR	8

1. G. Kumar, J. R. Blackburn, R. G. Albridge, W. E. Moddeman and M. M. Jones, *Inorg. Chem.*, 1972, **11**, 296; F. Holsboer and W. Beck, *Z. Naturforsch., Teil B*, 1972, **27**, 884; D. T. Clark and D. B. Adams, *Chem. Commun.*, 1971, 602.
2. K. Shobatake and K. Nakamoto, *J. Am. Chem. Soc.*, 1970, **92**, 3332; K. Konya and K. Nakamoto, *Spectrochim. Acta, Part A*, 1973, **29**, 1965.
3. J. H. Nelson and D. A. Redfield, *Inorg. Nucl. Chem. Lett.*, 1973, **9**, 807; B. E. Mann, *ibid.*, 1974, **10**, 273; A. W. Verstuyft, L. W. Cary and J. H. Nelson, *Inorg. Chem.*, 1975, **14**, 1495.
4. R. J. Goodfellow and B. F. Taylor, *J. Chem. Soc., Dalton Trans.*, 1974, 1676.
5. G. Balimann, H. Motschi and P. S. Pregosin, *Inorg. Chim. Acta*, 1977, **23**, 191.
6. D. A. Redfield, J. H. Nelson and L. W. Cary, *Inorg. Nucl. Chem. Lett.*, 1974, **10**, 727.
7. B. E. Mann, B. L. Shaw and R. M. Slade, *J. Chem. Soc. (A)*, 1971, 2976; A. W. Verstuyft, J. H. Nelson and L. W. Cary, *Inorg. Nucl. Chem. Lett.*, 1976, **12**, 53.
8. C. W. Fryer and J. A. S. Smith, *J. Chem. Soc. (A)*, 1970, 1029.

may in general be prepared by simple substitution reactions. In addition to their use in oxidation,[6] compounds of this class have found useful catalytic applications in a number of areas. A range of compounds $[PdX_2(ER_3)_2]$ with added $SnCl_2$ are recognized catalysts for the reduction of diene and triene esters to monoenes;[12] the rate of hydrogenation has been studied in some cases.[13] The complex $[PdCl_2(PPh_3)_2]$ has also been used in the catalysis of hydrosilylation reactions.[14]

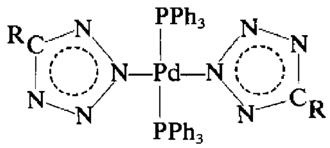
(*ii*) *Compounds with X = pseudohalide*

The pseudohalide complexes $[PdX_2(ER_3)_2]$ ($X = N_3$, NCO, CNS or CN) may be prepared by metathesis of the chloro complexes with NaX or LiX.

Particular interest attaches to the thiocyanate complexes since the mode of coordination of this ambidentate ligand is markedly influenced by the other ligands present:[15] isomerization can be brought about in a number of cases by heating the solid complex or by dissolution in an appropriate solvent. The type of coordination found in a particular complex may in general only be rationalized by a consideration of both electronic and steric factors. As an example of the latter, *trans*-$[Pd(NCS)_2(PPh_3)_2]$ contains N-bonded, linear NCS groups, but in the analogous complex containing the less sterically demanding triphenyl phosphite ligand, *trans*-[Pd(SCN)$_2${P(OPh)$_3$}$_2$], the thiocyanate ligand is S-bonded and non-linear.[16] Phosphine and arsine complexes of palladium(II) containing thio- or seleno-cyanate ligands are discussed further in Section 51.8.2.6.

The preparation of fulminate (CNO) and isocyanate (NCO) complexes, and their reactions, have been reported.[17] These include the conversion of [Pd(NCO)$_2$(PPh$_3$)$_2$] to [Pd(NCO)(CO$_2$R)(PPh$_3$)$_2$] on reaction with CO and ROH (R = Me, Et).

Coordinated azido ligands also undergo unusual reactions: for example, with RCN, [Pd(N$_3$)$_2$(PPh$_3$)$_2$] yields the cyclic compound shown in structure (**1**).[18]



(**1**)

(iii) Other compounds

Numerous compounds with other ligands are known, including complexes with SCF$_3^-$,[19] S$_2$CNR$_2^-$,[20] S$_2$COR$^-$, S$_2$PR$_2^-$ and S$_2$P(OR)$_2^-$.[21] These are discussed further in Sections 51.8.2.5 and 51.8.3.

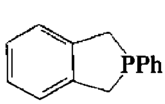
Complexes of type [PdX$_2$(ER$_3$)L] and [PdXY(ER$_3$)$_2$] are readily obtained, usually by bridge-splitting reactions with [Pd$_2$X$_4$(ER$_3$)$_2$] and L, or [Pd$_2$X$_2$(ER$_3$)$_4$]$^{2+}$ and Y$^-$.

The dihydrides [PdH$_2$(ER$_3$)$_2$] have not been isolated; this is in sharp contrast to the ready formation of [PtH$_2$(ER$_3$)$_2$]. The tris(triethylphosphine) complex [Pd(PEt$_3$)$_3$] forms a hydride in solution under hydrogen pressure at −63 °C, but it has not been isolated.[22] Hydridohalides are similarly much less stable than their platinum analogues. The X-ray structure of *trans*-[PdHCl(PEt$_3$)$_2$] has been reported:[23] a long Pd—Cl bond (2.43 Å) is consistent with the hydride being *trans* to chlorine.

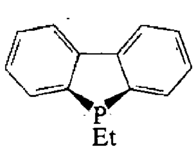
51.9.2.1.2 Complexes of the type [PdX$_2$(ER$_3$)$_3$]

Five-coordination is much less common for Pd^{II} than for Ni^{II}. Nonetheless, ligands with suitable steric requirements can, under favourable conditions, yield [PdX$_2$(ER$_3$)$_3$] complexes, *e.g.* [PdCl$_2$(PBzMe$_2$)$_3$].[24] Partial dissociation of X$^-$ in solution often occurs and [PdX(ER$_3$)$_3$][Y] can frequently be isolated by adding a large anion (Y = ClO$_4$, BPh$_4$, *etc.*). Stibines in particular seem to favour high coordination numbers.

The X-ray crystal structures of a number of compounds of general formula [PdBr$_2$L$_3$] have been determined, for example when L = 2-phenylisophosphinoline (**2**), the structures of both racemic and optically resolved forms were determined,[25] and when L = (**3**), the structure of [PdBr$_2$L$_3$]·PhCl was obtained.[26] The geometry of all these molecules is similar, being distorted tetragonal pyramidal with an apical bromine.



(**2**)



(**3**)

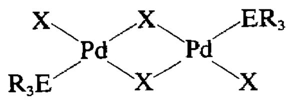
51.9.2.1.3 Mononuclear ionic complexes

[PdX(ER$_3$)$_3$][Y] may be prepared either from or *via* [PdX$_2$(ER$_3$)$_3$] (*vide supra*),[27] or by addition of ER$_3$ to solutions of [Pd$_2$X$_2$(ER$_3$)$_4$]$^{2+}$.[28] A comparison of the spectral properties of [PdX$_2$L$_2$], [PdX$_2$L$_3$] and [PdXL$_3$]$^+$ (L = PPhMe$_2$) has been reported.[29] The dications [Pd(PR$_3$)$_4$]$^{2+}$ (R = Ph, OPh) are prepared by oxidation of [Pd(PR$_3$)$_4$] using Ph$_3$C$^+$.[30] The [PdX$_3$(ER$_3$)]$^-$ anions are best obtained by treatment of [Pd$_2$X$_4$(ER$_3$)$_2$] with R$_4$NX in dichloromethane.[31] The X-ray structure of $[Ph_3PCH_2CH_2COMe]^+[PdCl_3(PPh_3)]^-$ has been determined.[32]

51.9.2.1.4 Complexes of the type $[Pd_2X_4(ER_3)_2]$

The binuclear complexes $[Pd_2X_4(ER_3)_2]$ are readily prepared, commonly by reaction of ER_3 with excess $[PdX_4]^{2-}$, or by reaction of $[PdX_2(ER_3)_2]$ with $[PdX_4]^{2-}$, either in solution in alcohols, in suspension in organohalogen solvents, or by melting together.[33] The usual geometry is the *sym–trans* structure (**4**). Typical examples are listed in Table 3. These binuclear compounds are generally less soluble than the analogous mononuclear derivatives.

Bulky phosphines favour the formation of $[Pd_2X_4(PR_3)_2]$ from $[PdX_2(PR_3)_2]$, presumably since this results in a release of steric strain. Thus, metathesis of *trans*-$[PdCl_2(PPhBu^t_2)_2]$ with LiI yields only $[Pd_2I_4(PPhBu^t_2)_2]$,[34] and reaction of $[PdCl_4]^{2-}$ with $PBu^t_2(o\text{-}C_6H_4Pr^i)$ yields $[PdCl_4(PR_3)_2]$ and not $[PdCl_2(PR_3)_2]$.[35]



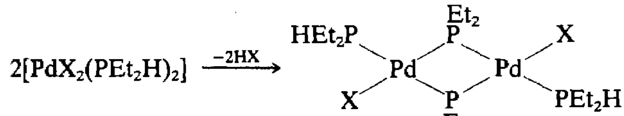
(**4**)

Table 3 Typical Binuclear Complexes of the Type $[Pd_2X_4(ER_3)_2]$

Complex	*Comments*
$[Pd_2(\mu\text{-}Cl)_2Cl_2(PEt_3)_2]$	Orange-red
$[Pd_2(\mu\text{-}Cl)_2Cl_2(AsEt_3)_2]$	Deep-red
$[Pd_2(\mu\text{-}Cl)_2Cl_2(SbEt_3)_2]$	Tan
$[Pd_2(\mu\text{-}Br)_2Br_2(AsMe_3)_2]$	Reddish-brown
$[Pd_2(\mu\text{-}I)_2I_2(PBu^n_3)_2]$	Deep reddish-purple
$[Pd_2(\mu\text{-}SCN)_2(SCN)_2(PBu^n_3)_2]$	Orange
$[Pd_2(\mu\text{-}NO_2)_2(NO_2)_2(PBu^n_3)_2]$	Yellow
$[Pd_2(\mu\text{-}C_2O_4)_2(NO_2)_2(PBu^n_3)_2]$	Yellow
$[Pd_2(\mu\text{-}SEt)_2Cl_2(PBu^n_3)_2]$	Deep-yellow
$[Pd_2(\mu\text{-}SC_6F_5)_2(SC_6F_5)_2(PPh_3)_2]$	X-Ray structure[1]
$[Pd_2(\mu\text{-}MeCO_2)_2Cl_2(PPhMe_2)_2]$	X-Ray structure[2]

1. R. H. Fenn and G. R. Segrott, *J. Chem. Soc. (A)*, 1970, 3197.
2. J. Powell and T. Jack, *Inorg. Chem.*, 1972, **11**, 1039.

Complexes with a variety of other bridging groups are known, including phosphido-, thio-[36] and carboxylato-bridged compounds.[37] Reaction of base with the secondary phosphine complexes $[PdX_2(PEt_2H)_2]$ eliminates HX to form a dialkylphosphido-bridged complex, as in equation (3); the ease of elimination of HX decreases in the order $X = I > Br > Cl$.[38] The elimination of HX also depends on the phosphine, decreasing in the order $PPh_2H > PEtPhH > PEt_2H$. The dichloro complex $[PdCl_2(PPh_2H)_2]$ is too unstable with respect to loss of hydrogen chloride to be isolated. Secondary diarylphosphine complexes yield both mononuclear and dinuclear products.[39]



(3)

A number of compounds related to the $[Pd_2X_4(ER_3)_2]$ complexes are known. Reaction of *trans*-$[Pd(C{\equiv}CH)_2(PMe_3)_2]$ with $[PdCl_2(PMe_3)_2]$ in Et_2NH and CuCl as catalyst yields the ethynediyl-bridged complex $[(PMe_3)_2ClPd{-}C{\equiv}C{-}PdCl(PMe_3)_2]$ in which the acetylide bonds in an $\eta^2(\sigma,\sigma)$ fashion.[40] The heterobimetallic complexes $[(ER_3)_2Pd(\mu\text{-}X)_2HgY_2]$ are formed on reacting either *cis*- or *trans*-$[PdX_2(ER_3)_2]$ with HgY_2 (Y = Cl, Br or I), though these cannot always be isolated, and in some cases the HgY_2 'extracts' ligands to form $[(HgY_2)_n(ER_3)_2]$ ($n \geq 1$) and $[Pd_2X_4(ER_3)_2]$.[41] Reaction of *trans*-$[PdCl_2(AsMe_3)_2]$ with $[IrCl_4(PMe_2Ph)_2]$ yields the palladium–iridium heterobimetallic complex $[(Me_3As)ClPd(\mu\text{-}Cl)_2IrCl_2(PMe_2Ph)_2]$, the structure of which has been determined by X-ray crystallography.[42]

51.9.2.1.5 Complexes of the type $[Pd_2X_2(ER_3)_4]^{2+}$

The halide-bridged dications $[Pd_2X_2(ER_3)_4]^{2+}$ are obtained by treatment of the dihalo complex $[PdX_2(ER_3)_2]$ with the alkylating agents $S(F)O_2(OMe)$, $[Me_3O][BF_4]$ or $[Et_3O][BF_4]$, or, less generally, with BX'_3 ($X' = F$, Cl, Br) or AgY ($Y = BF_4$, ClO_4, *etc.*).[43] Alkylating agents can also be used to extract other anions, including $X = N_3$, NCS, NO_2 or NO_3, from $[PdX_2(ER_3)_2]$ to yield either anion-bridged or (from NO_2 and NO_3 complexes) hydroxo-bridged cations.[44] The hydroxo-bridged dication $[Pd_2(\mu\text{-}OH)_2(PPh_3)_4]^{2+}$ has also been obtained by metathesis of $[PdCl_2(PPh_3)_2]$ with $AgBF_4$ in wet acetone,[45] as well as from treatment of $[Pd(O_2)(PPh_3)_2]$ with $[NO][BF_4]$ in CH_2Cl_2.[46] The hydroxo bridges are unexpectedly difficult to cleave, for example bridge-splitting does not occur with PR_3 under ordinary conditions. However, the bridge-splitting reactions of the halide-bridged cations with a range of anionic or neutral ligands (L) provide a valuable synthetic route to $[PdXL(ER_3)_2]^{n+}$ ($n = 0, 1$) complexes.[47]

51.9.2.2 Bidentate Ligands Containing Two P, As or Sb Donor Atoms

51.9.2.2.1 Complexes of the type *cis*-[PdX₂(L—L)]

Complexes of bidentate ligands L—L are predominantly of the type *cis*-$[PdX_2(L—L)]$ and some typical examples are given in Table 4. Direct reaction of $[PdX_4]^{2-}$ with L—L often (but not always) leads to formation of the insoluble Magnus-type salts $[Pd(L—L)_2][PdX_4]$. The stability of the latter with respect to rearrangement into $[PdX_2(L—L)]$ depends markedly on L—L; some rearrange to the 1:1 complexes on stirring under gentle reflux in ethanol, whilst for others reflux in *N,N*-dimethylformamide or ethanolic HX is necessary.[48–50] The $[PdX_2(L—L)]$ complexes are planar, diamagnetic and generally soluble in organic solvents, in which they are monomeric non-electrolytes. It is possible to avoid Magnus-type salt formation by using PdX_2 in place of $[PdX_4]^{2-}$, although the poor solubility of many of the palladium dihalides in suitable solvents makes reaction slow. A better procedure is displacement of a neutral ligand from a preformed complex, often $[PdX_2(NCPh)_2]$. Special preparative methods may be appropriate for particular complexes, for example cyanogen converts $[Pd(L—L)_2]$ (L—L = dppe, dppp) to $[Pd(CN)_2(L—L)]$.[51]

Table 4 Typical Complexes of the Type *cis*-$[PdX_2(L—L)]$

L—L	*X*	*Ref.*
$Ph_2P(CH_2)_2PPh_2$	Cl, Br, I, NCS/SCN	1
$Ph_2As(CH_2)_2AsPh_2$	Cl, Br, I, SCN	1
$Ph_2Sb(CH_2)_3SbPh_2$	Cl, Br, I, SCN	2
o-$C_6H_4(PPh_2)_2$	Cl, Br, I, NCS	3
o-$C_6H_4(AsPh_2)_2$	Cl, Br, I, NCS/SCN	4
o-$C_6H_4(SbPh_2)_2$	Cl, Br, I	5

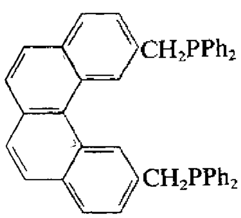
1. D. W. Meek, P. E. Nicpon and V. I. Meek, *J. Am. Chem. Soc.*, 1970, **92**, 5351.
2. W. Levason and C. A. McAuliffe, *Inorg. Chem.*, 1974, **13**, 2765.
3. W. Levason and C. A. McAuliffe, *Inorg. Chim. Acta*, 1976, **16**, 167.
4. W. Levason and C. A. McAuliffe, *J. Chem. Soc., Dalton Trans.*, 1974, 2238.
5. W. Levason, C. A. McAuliffe and S. G. Murray, *Inorg. Nucl. Chem. Lett.*, 1976, **12**, 849.

Much interest has centred upon the $[Pd(CNS)_2(L—L)]$ complexes, since the nature of the thiocyanate coordination is influenced by the particular ligand present. Thus, X-ray diffraction studies have shown that the mode of thiocyanate coordination in $[Pd(CNS)_2\{Ph_2P(CH_2)_nPPh_2\}]$ changes from both *S* for $n = 1$ (dppm), through one *S* and one *N* for $n = 2$ (dppe), to both *N* for $n = 3$ (dppp).[52] Linkage isomerism amongst these compounds has also been studied by

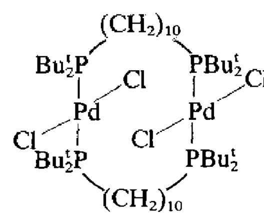
^{31}P NMR spectroscopy.[53] Steric factors account for the different coordination modes, while the influence of electronic factors is evidenced by the difference in structure between analogous palladium(II) and platinum(II) compounds, for example, the thiocyanates are N- and S-bonded in [Pd(NCS)(SCN)(diars)], but only S-bonded in $[Pt(SCN)_2(diars)]$.[54] These and other diphosphine or diarsine complexes of palladium(II) with thio- or seleno-cyanate ligands are further discussed in Section 51.8.2.6.

51.9.2.2.2 Complexes of the type **trans**-*$[PdX_2(L—L)]$*

The rigid ligand 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene (**5**) forms *trans* planar complexes $[PdX_2(L—L)]$ (X = Cl, Br, I);[55] the steric properties of the ligand effectively prevent it coordinating to produce *cis* planar or tetrahedral complexes. *Trans* chelation has also been achieved with flexible ligands of the correct backbone length under appropriate conditions; thus, for example, *trans*-$[PdCl_2\{Bu^t_2P(CH_2)_nPBu^t_2\}]$ ($n = 10, 12$)[56] and *trans*-$[PdCl_2\{Me_2As(CH_2)_{12}AsMe_2\}]$[57] have been prepared. In addition to these mononuclear complexes, the binuclear compounds $[PdCl_2\{Bu^t_2P(CH_2)_nPBu^t_2\}]_2$ ($n = 10, 12$) have been isolated and the structure of the compound with $n = 10$ has been determined by X-ray crystallography as (**6**).[56]



(**5**)



(**6**) Pd—P = 2.37 Å
Pd—Cl = 2·26, 2.29 Å

51.9.2.2.3 Complexes of the type $[Pd(L—L)_2]^{2+}$

Planar bis-ligand complexes of the type $[Pd(L—L)_2][ClO_4]_2$ are known for a wide range of ligands and are usually obtained by treatment of $[PdCl_2(L—L)_2]$ or $[PdCl_2(L—L)]$ and L—L with $NaClO_4$ or dilute $HClO_4$ in a suitable solvent, often an aqueous alcohol. There are similar complexes with BF_4^-, PF_6^-, BPh_4^-, *etc.*, as counterions. Typical examples are the complexes formed by the ligands *o*-$C_6H_4(EPh_2)_2$ (E_2 = P,P; As,P; As,As; Sb,P) with palladium(II).[49,54] These are 1:2 electrolytes, and the IR and electronic spectra confirm the ionic formulation.[58] The X-ray crystal structure of $[Pd(PhMePCH_2CH_2PMePh)_2][Cl]_2$ has been determined.[59]

51.9.2.2.4 Complexes of the type $[PdX_2(L—L)_2]$

The bis-ligand complexes $[PdX_2(L—L)_2]$ (X = Cl, Br, I) are formed by some ligands but not all; for instance, alkyl-substituted diphosphines fail to yield this type of complex even with a large excess of ligand.[60] The most extensive series of compounds is formed by the *o*-phenylene ligands *o*-$C_6H_4(EMe_2)E'Me_2$ (E, E′ = P, As, Sb).[50,58] The structure of $[PdI_2\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$ has been determined by X-ray crystallography.[61] The Pd atom is six-coordinate with long *trans* axial Pd—I bonds; electronic spectral differences between $[PdX(L—L)_2][ClO_4]$ (*vide infra*) and $[PdX_2(L—L)_2]$ suggest that the latter may generally be hexaccoordinate and tetragonal.[49,54]

In solution there is a tendency for $[PdX_2(L—L)_2]$ to form pentacoordinate $[PdX(L—L)_2]^+$ ions, which may be isolated as perchlorate salts. The relative stabilities of the complexes of types $[PdX_2(L—L)_2]$, $[PdX(L—L)_2]^+$ and $[PdX_2(L—L)]$ are influenced by two factors: (a) the increasing promotion of pentacoordination along the series P < As < Sb; and (b) the decreased stability of the bis-ligand complexes with respect to their $[PdX_2(L—L)]$ analogues for weaker donors such as aryl-arsines and -stibines, such that ionic halides can displace one of the bidentate ligands. Thus, $[PdX_2(diars)_2]$ is a 1:1 electrolyte in solution, whose conductivity is increased by addition of excess L—L. This behaviour may be explained in terms of the partial dissociation of L—L in solution, as in equation (4).[54] The $[PdX_2(L{-}L)_2]$ complexes decompose on heating in the solid state to $[PdX_2(L{-}L)]$ and L—L.

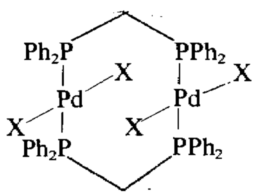
$$[PdX_2(diars)_2] \rightleftharpoons [PdX(diars)_2]^+ + X^- \rightleftharpoons [PdX_2(diars)] + diars \qquad (4)$$

The thiocyanate complexes $[Pd(CNS)_2(L{-}L)_2]$ are known for some bidentate ligands L—L; in general the tendency to five-coordination is markedly less than for the corresponding halide complexes, although the same order with respect to donor is followed.[49,50]

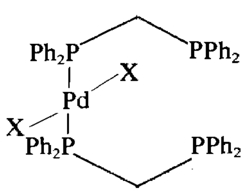
51.9.2.2.5 Complexes of bis(diphenylphosphino)methane

Much interest has recently been devoted to complexes of $Ph_2PCH_2PPh_2$ (dppm) which, because of its small bite, often prefers to bridge rather than chelate.[62]

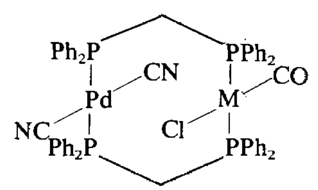
The complex $[PdCl_2(dppm\text{-}PP')]$, in which the dppm ligand is bidentate, reacts with NaCN to give the binuclear 'face to face' complex $[(NC)_2Pd(\mu\text{-dppm})_2Pd(CN)_2]$ (**7**; X = CN). When the salt $[Pd(dppm\text{-}PP')_2][Cl]_2$ is treated with NaCN the compound *trans*-$[Pd(CN)_2(dppm\text{-}P)_2]$ (**8**; X = CN) is formed, in which the dppm is monodentate. This complex is fluxional at 20 °C due to rapid 'end over end' exchange of the monohapto dppm ligands. When *trans*-$[Pd(CN)_2(dppm\text{-}P)_2]$ (**8**; X = CN) is treated with $[Rh_2Cl_2(CO)_4]$ or *trans*-$[IrCl(CO)(PPh_3)_2]$, the two free phosphorus atoms coordinate to the second metal and heterobimetallic complexes of the type $[(NC)_2Pd(\mu\text{-dppm})_2M(CO)Cl]$ (**9**; M = Rh or Ir) are formed, while treatment with $[Mo(CO)_3(C_7H_8)]$ (C_7H_8 = cyclohepta-1,3,5-triene) or $HgCl_2$ produces $[(NC)_2Pd(\mu\text{-dppm})_2Mo(CO)_3]$ or $[(NC)_2Pd(\mu\text{-dppm})_2HgCl_2]$, respectively.[63]



(**7**)



(**8**)

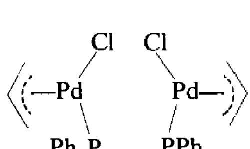


(**9**)

Analogous acetylide complexes containing monodentate dppm, *trans*-$[Pd(C{\equiv}CR)_2(dppm\text{-}P)_2]$ (**8**; X = C≡CR), can be made by treating the heterobimetallic complexes $[(RC{\equiv}C)_2Pd(\mu\text{-dppm})_2HgCl_2]$ with sodium sulfide, the palladium–mercury complexes themselves being obtained from treatment of $[Pd(dppm\text{-}PP')_2][Cl]_2$ with $Hg(C{\equiv}CR)_2$. A wide range of heterobimetallic complexes containing palladium(II) can then be made by treating (**8**; X = C≡CR) with suitable substrates (as for the dicyanides, *vide supra*), or by displacing the d^{10} metals from heterobimetallic complexes, especially of Hg^{II} or Ag^{I}, in transmetallation reactions.[64] Similar chemistry pertains to the isonitrile palladium(II) dppm complexes (RNC being isoelectronic with $RC{\equiv}C^-$),[65] and there is an X-ray crystal structure of $[Pd(CNBu^t)_2(dppm\text{-}P)_2][BPh_4]_2$.[66]

Binuclear palladium(II) complexes of dppm may also be prepared by oxidation, for example of $[ClPd(\mu\text{-dppm})_2PdCl]$ with S_8 to give the sulfur-bridged 'A-frame' molecule $[Pd_2Cl_2(\mu\text{-S})(\mu\text{-dppm})_2]$,[67] or of $[Pd_2(\mu\text{-dppm})_3]$ with $CHRX_2$ to give the 'A-frame' $[Pd_2X_2(\mu\text{-CHR})(\mu\text{-dppm})_2]$.[68]

Treatment of η^3-allylpalladium chloride with dppm results in several products, *e.g.* $[PdCl(\eta^3\text{-}C_3H_5)(dppm\text{-}P)]$, $[Pd(\eta^3\text{-}C_3H_5)(dppm\text{-}P)_2]^+$ and $[Pd(\eta^3\text{-}C_3H_5)(dppm\text{-}PP')]^+$, as well as the bimetallic $[ClPd(\mu\text{-dppm})_2PdCl]$.[69,70] The products depend on the molar proportions, the solvent and the counterion: treatment of η^3-allylpalladium chloride with 0.5 mole equivalents of dppm in acetonitrile gives $[(\eta^3\text{-}C_3H_5)ClPd(\mu\text{-dppm})PdCl(\eta^3\text{-}C_3H_5)]$, which probably has structure (**10**).[70]



(**10**)

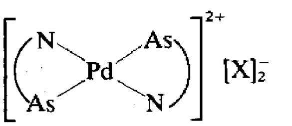
Bis(diphenylstibino)methane (dpsm) also prefers to bridge rather than chelate, forming $[X_2Pd(\mu\text{-dpsm})_2PdX_2]$ and $[PdX_2(\text{dpsm-}Sb)_2]$, but not $[PdX_2(\text{dpsm-}SbSb')]$.[71]

51.9.2.3 Bidentate Ligands Containing One P, As or Sb Donor Atom

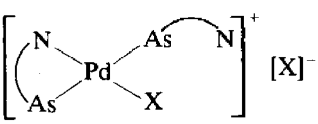
Complexes formed by hybrid bidentate ligands usually fall into the classes covered in the above sections and only the bis-ligand (2:1) complexes will be treated here, together with some related chemistry.

51.9.2.3.1 Complexes of ligands containing a nitrogen donor atom

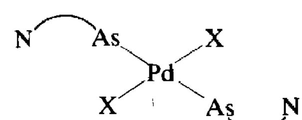
The substituted pyridine ligands $Ph_2ECH_2CH_2C_5H_4N$ (E = P, As) bond only through the E atom in $[PdCl_2(L—L)_2]$, the pyridine nitrogen remaining uncoordinated.[72] Similarly, the amine–stibine $o\text{-}C_6H_4(SbMe_2)NMe_2$ coordinates only through the antimony atom in $[PdX_2(L—L)_2]$ (X = Cl, Br, I).[73] Ligands containing N donors strongly favour four-coordination of palladium(II): a study of various amine—arsine complexes of the type $[PdX_2(L—L)_2]$ showed that $Ph_2AsCH_2CH_2NH_2$ was more likely to chelate than *o*-substituted anilines, and that, depending on L—L and X, some or all of the structures (**11**)–(**13**) may be adopted.[74] Deprotonation of the primary amine complexes $[PdX_2(L—L)_2]$ [L—L = $o\text{-}C_6H_4(AsR_2)NH_2$] occurs on treatment with aqueous base to form $[Pd(L—L—H)_2]$, where L—L—H = $o\text{-}C_6H_4(AsR_2)NH$.



(**11**)



(**12**)

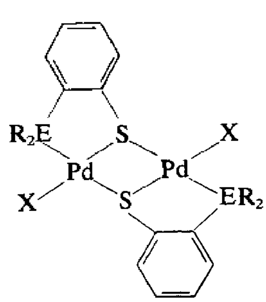


(**13**)

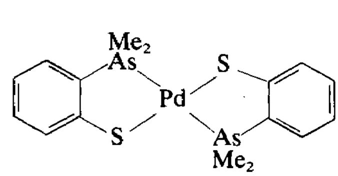
51.9.2.3.2 Complexes of ligands containing a sulfur donor atom

Sulfur-phosphorus bidentate ligands such as $o\text{-}C_6H_4(PPh_2)SMe$ fail to form 2:1 complexes with palladium(II) halides, but $o\text{-}C_6H_4(AsPh_2)SMe$ forms $[PdX_2(L—L)_2]$ (X = Cl, Br) from aqueous acetone.[75] The crystal structure of the diiodide complex has been determined and shows a pseudohexacoordinate palladium(II) centre with long *trans* axial Pd · · · S interactions (3.84 Å).[76]

S-Dealkylation of coordinated thioethers is well known. For example, the complexes $[PdX_2(L—L)]$ [L—L = $o\text{-}C_6H_4(ER_2)SMe$] dealkylate on heating in *N,N*-dimethylformamide to give either dimers (as **14**) or monomers.[75,77] The monomers are formed in the presence of excess ligand and the structure of the product for E = As, R = Me has been determined by X-ray crystallography as (**15**), with Pd—As = 2.34 Å and Pd—S = 2.30 Å.[78] The demethylated ligand can be readily realkylated.[75,77,79]



(**14**)



(**15**)

51.9.2.4 Multidentate Ligands

Planar [PdXL][Y] complexes have been prepared for a variety of X, Y and tridentate L. Typical examples are given in Table 5. The X-ray crystal structure of

$[PdBr\{MeAs(CH_2CH_2CH_2AsMe_2)_2\}][Br]$ has been determined.[80] The triarsine $MeAs(o\text{-}C_6H_4AsMe_2)_2$ forms [PdXL][X] complexes which, though 1:1 electrolytes in nitromethane, appear to be five-coordinate in acetone.[81] The same ligand also forms $[PdL_2][ClO_4]_2$, which is a 1:2 electrolyte in nitromethane.

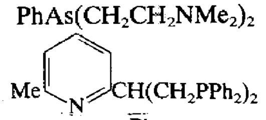
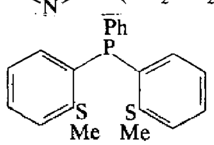
Table 5 Typical Complexes of the Type [PdXL][Y]

L	*X*	*Y*	*Ref.*
$PhP(CH_2CH_2PPh_2)_2$	I	I	1
$PhP(CH_2CH_2AsPh_2)_2$	Cl	PF_6	2
$MeP(CH_2CH_2PMe_2)_2$	Cl	Cl	3

1. R. B. King, P. N. Kapoor and R. N. Kapoor, *Inorg. Chem.*, 1971, **10**, 1841.
2. R. B. King and P. N. Kapoor, *Inorg. Chim. Acta*, 1972, **6**, 391.
3. R. B. King, P. Zinich and J. C. Cloyd, *Inorg. Chem.*, 1975, **14**, 1554.

Planar $[PdX_2L]$ complexes are formed by a number of hybrid tridentate ligands with one donor remaining uncoordinated. Typical examples are given in Table 6.

Table 6 Typical Complexes of the Type $[PdX_2L]$

L	*Donor set*	*Ref.*
$PhAs(CH_2CH_2NMe_2)_2$	As, N, X, X	1
	P, P, X, X	2
	P, S, X, X	3
$PhP(CH_2CH_2CH{=}CH_2)_2$	P, alkene, X, X	4

1. T. L. Morris and R. C. Taylor, *J. Chem. Soc., Dalton Trans.*, 1973, 175.
2. W. V. Dahlhoff, T. R. Dick, G. H. Ford, W. S. J. Kelly and S. M. Nelson, *J. Chem. Soc. (A)*, 1971, 3495.
3. T. N. Lockyer, *Aust. J. Chem.*, 1974, **27**, 259.
4. P. E. Garrou and G. E. Hartwell, *J. Organomet. Chem.*, 1974, **71**, 443.

The linear tetraphosphine 'tetraphos', $Ph_2PCH_2CH_2PPhCH_2CH_2PPhCH_2CH_2PPh_2$, forms the planar dicationic complex $[PdL][PF_6]_2$,[82] while the tripod ligand $P(CH_2CH_2PR_2)_3$ (R = neopentyl), which cannot adopt the arrangement required to yield a monomeric planar structure, yields the complex $[PdClL]^+$, in which one PR_2 group remains uncoordinated.[83] Five-coordinate complexes [PdXL][Y] are formed by the tetraarsine ligands $o\text{-}C_6H_4\{As(o\text{-}C_6H_4AsMe_2)Me\}_2$,[84] $Me_2AsCH_2CH_2AsPhCH_2CH_2AsPhCH_2CH_2AsMe_2$,[85] and $As(o\text{-}C_6H_4AsR_2)_3$ (R = Me, Ph).[86] The kinetics of the substitution reactions for L = $As(o\text{-}C_6H_4AsMe_2)_3$ have been examined and the mechanism probably involves a planar intermediate with one or two arsenic atoms temporarily uncoordinated.[87]

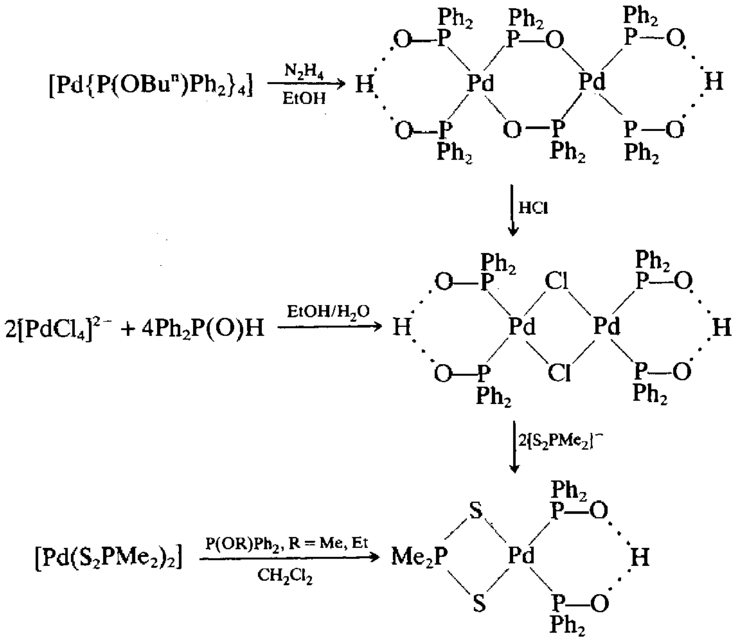
51.9.3 PHOSPHITE, PHOSPHONITE, PHOSPHINITE AND OTHER COMPLEXES

The chemistry of phosphite, phosphonite and phosphinite complexes of palladium(II) generally resembles that of their phosphine analogues. Its description here will therefore be brief, attention being paid to those areas where differences in behaviour are apparent.

The planar phosphite complexes $[PdX_2\{P(OR)_3\}_2]$ have been prepared by a variety of methods, such as the reaction of $P(OR)_3$ with $[PdX_4]^{2-}$ in ethanol in the presence of LiX.[88] The palladium(II) iodide and $P(O\text{-}o\text{-}tolyl)_3$ complexes have *trans* structures or are *cis*/*trans* mixtures, but the others are predominantly *cis* isomers. The phosphonites, $P(OR)_2Ph$, and phosphinites, $P(OR)Ph_2$, similarly yield *cis*-$[PdCl_2L_2]$. A large number of complexes $[PdCl_2L(PR_3)]$ [L = $P(OR)_3$, $P(OR)_2Ph$ or $P(OR)Ph_2$] have been obtained by evaporating 1:1 mixtures of $[PdCl_2(PR_3)_2]$ and $[PdCl_2L_2]$ in chloroform.[89] The X-ray crystal structure of *trans*-$[Pd(SCN)_2\{P(OPh)_3\}_2]$ has been determined (see Section 51.9.2.1.1.ii),[16] while the structure of the diphosphinylamino complex $[PdCl_2\{(Ph_2P)_2NEt\}]$ shows *cis* planar P_2Cl_2 coordination with Pd—P 2.22 Å, Pd—Cl 2.37 Å and P—Pd—P 71.5°.[90] The phosphine–phosphinites, $Ph_2P(CH_2)_nOPPh_2$ (n = 2,3), similarly yield planar [PdCl₂(L—L)] complexes.[91]

Cationic complexes $[PdClL_3][BPh_4]$ [L = $P(OR)_3$] are formed by treatment of $[PdCl_2L_2]$ with a small excess of L and $NaBPh_4$.[92] The five-coordinate species $[PdL_5]^{2+}$ [L = $P(OR)_3$] are obtained by treating $PdCl_2$ with $P(OR)_3$ in ROH, MeCN or THF, followed by addition of $NaBPh_4$.[93] Recrystallization of the pentakis complex in the absence of excess phosphite leads to isolation of $[Pd\{P(OR)_3\}_4]^{2+}$ complexes.[92,94] The reaction of the cycloocta-1,5-diene complexes $[PdCl_2(cod)]$ with $P(OMe)Ph_2$ yields $[Pd\{P(OMe)Ph_2\}_4]^{2+}$ complexes, but the phosphonite analogues are unstable.

The dimeric complex $[Pd_2(\mu\text{-}Cl)_2Cl_2L_2]$ [L = P(O-*o*-tolyl)₃] has been obtained by treatment of $[PdCl_2L_2]$ with $PdCl_2$;[95] dimeric complexes derived from phosphinites are also known (see Scheme 1).[96]



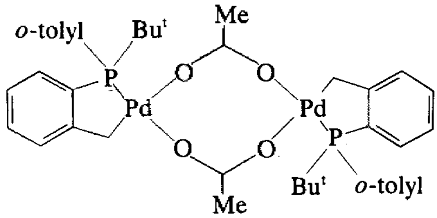
Scheme 1

51.9.4 SOME REACTIONS OF COORDINATED LIGANDS

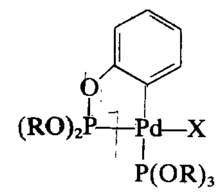
51.9.4.1 Cyclometallation

The tendency of palladium(II) complexes to undergo cyclometallation is significantly less than that of their platinum(II) analogues. There are, however, still many examples. The X-ray crystal structures of *trans*-$[PdI_2(PR_3)_2]$ ($R_3 = Me_2Ph$, Ph_3) demonstrate the existence of short intramolecular Pd—*o*-H contacts.[97] The sterically hindered phosphines PBu^t_2(*o*-tolyl) and PBu^t(*o*-tolyl)₂ readily yield metallated derivatives of palladium of the type $[Pd_2X_2(P\text{—}C)_2]$.[98] Metallation is easier with the PBu^t_2(*o*-tolyl) ligand than with PBu^t(*o*-tolyl)₂. The bridges in $[Pd_2Cl_2(P\text{—}C)_2]$ are cleaved by a variety of ligands (L) to yield mononuclear [PdCl(P—C)L] complexes. The X-ray crystal structure of $[Pd_2(OAc)_2\{o\text{-}CH_2C_6H_4PBu^t(o\text{-tolyl})\}_2]$ has been determined (see structure **16**).[99]

In contrast, the arsine analogues $AsBu^t_2$(*o*-tolyl) and $AsBu^t$(*o*-tolyl)₂ yield the complexes *trans*-$[PdCl_2L_2]$ and these produced only metallic palladium under conditions which induced cyclometallation in the case of their platinum analogues.[100] The ligand $PBu^t_2(o\text{-}C_6H_4Et)$ metallates at the α position, but $PBu^t_2(o\text{-}C_6H_4Pr^i)$ produced only metallic palladium.[35] Bidentate phosphines are generally reluctant to metallate internally. An exception is



(16)

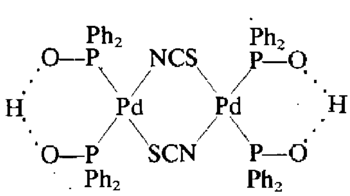


(17)

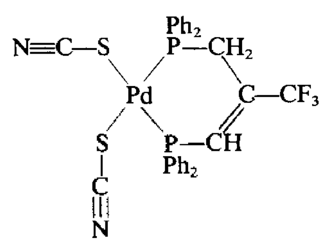
m-$C_6H_4(CH_2PBu^t{}_2)_2$, which reacts with $[PdCl_2(NCPh)_2]$ *via* metallation at the 2-position of the benzene ring.[101] Internal metallation of triarylphosphites on palladium(II) proceeds easily in boiling decalin to yield five-membered ring products, *e.g.* as (**17**).[95,102] These are rapidly reconverted to the phosphite complexes on treatment in solution with HX, in contrast to the irreversible cyclometallation of phosphines.

51.9.4.2 Phosphinoacetylene Ligands

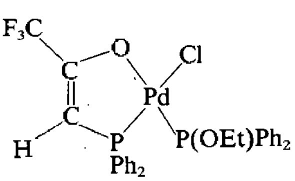
The electronic effect of the coordinated R_2P group upon the multiple bond in phosphinoacetylene complexes activates it towards certain reagents. *cis*-$[PdCl_2(Ph_2PC{\equiv}CCF_3)_2]$ may be prepared by reaction of $[PdCl_2(NCPh)_2]$ or $[PdCl_4]^{2-}$ and $Ph_2PC{\equiv}CCF_3$ in benzene. Under reflux in aqueous ethanol this is converted into $[Pd(\mu\text{-}Cl)(PPh_2O)\{PPh_2(OH)\}]_2$ (see also Scheme 1) and *cis*-$[PdCl_2\{Ph_2PCH_2C(CF_3){=}CHPPh_2\}_2]$. The X-ray crystal structures of the thiocyanate analogues of these complexes have been determined (see structures **18** and **19**). Under milder conditions this reaction yields several other products; the crystal structure of $[PdCl\{Ph_2PCH{=}C(CF_3)O\}\{P(OEt)Ph_2\}]$ has been determined as (**20**).[103]



(**18**) Pd—S = 2.45 Å
Pd—N = 2.08 Å
O···O = 2.42 Å



(**19**) Pd—S = 2.37 Å
Pd—P = 2.27, 2.28 Å



(**20**) Pd—P = 2.22, 2.25 Å
Pd—O = 2.09 Å
Pd—Cl = 2.36 Å

Treatment with HCl converts *cis*-$[PdCl_2(Ph_2PC{\equiv}CCF_3)_2]$ into *trans*-$[PdCl_2\{Ph_2PCH{=}C(Cl)CF_3\}_2]$. An X-ray examination of this complex shows that the HCl adds *trans* across the alkynic triple bond.[104]

51.9.5 REFERENCES

1. C. A. McAuliffe and W. Levason, 'Phosphine, Arsine and Stibine Complexes of the Transition Elements', Studies in Inorganic Chemistry 1, Elsevier, Amsterdam, 1979.
2. F. R. Hartley, 'The Chemistry of Platinum and Palladium', Applied Science Publishers, London, 1973.
3. S. E. Livingstone, in 'Comprehensive Inorganic Chemistry', ed. J. C. Bailar, H. J. Emeléus, R. Nyholm and A. F. Trotman-Dickenson, Pergamon, Oxford, 1973, vol. 3, chap. 43.

4. F. R. Hartley, *Coord. Chem. Rev.*, 1981, **35,** 143; 1982, **41,** 319; 1985, **67,** 1; P. A. Chaloner, *ibid.*, 1986, **71,** 235; 1986, **72,** 1.
5. P. M. Maitlis, P. Espinet and M. J. H. Russell, in 'Comprehensive Organometallic Chemistry', ed. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, 1982, vol. 6, chap. 38.
6. J.-E. Bäckvall, *Acc. Chem. Res.*, 1983, **16,** 335.
7. F. G. Mann and D. Purdie, *J. Chem. Soc.*, 1935, 1549.
8. G. Booth, *Adv. Inorg. Chem. Radiochem.*, 1964, **6,** 1.
9. D. A. Redfield and J. H. Nelson, *Inorg. Chem.*, 1973, **12,** 15; A. W. Verstuyft, L. W. Cary and J. H. Nelson, *ibid.*, 1975, **14,** 1495.
10. D. G. Cooper and J. Powell, *Can. J. Chem.*, 1973, **51,** 1634; D. A. Redfield, L. W. Cary and J. H. Nelson, *Inorg. Chem.*, 1975, **14,** 50.
11. A. W. Verstuyft and J. H. Nelson, *Inorg. Chem.*, 1975, **14,** 1501.
12. H. Itatini and J. C. Bailar, *J. Am. Chem. Soc.*, 1967, **89,** 1592.
13. E. W. Stern and R. K. Maples, *J. Catal.*, 1972, **27,** 120, 134.
14. M. Hara, K. Ohno and S. Tsuji, *Chem. Commun.*, 1971, 247.
15. A. H. Norbury, *Adv. Inorg. Chem. Radiochem.*, 1975, **17,** 231.
16. A. J. Carty, P. C. Chieh, N. J. Taylor and Y. S. Wong, *J. Chem. Soc., Dalton Trans.*, 1976, 572.
17. W. Beck and K. V. Werner, *Chem. Ber.*, 1971, **104,** 2901; W. Beck, K. Schorpp and C. Oetker, *ibid.*, 1974, **107,** 1380.
18. P. Kreutzer, C. Weis, H. Boehme, T. Kemmerich, W. Beck, C. Spencer and R. Mason, *Z. Naturforsch., Teil B,* 1972, **27,** 745.
19. K. R. Dixon, K. C. Moss and M. A. R. Smith, *J. Chem. Soc., Dalton Trans.*, 1973, 1528.
20. N. Sonoda, S. Araki, T. Onishi and T. Tanaka, *J. Inorg. Nucl. Chem.*, 1974, **36,** 1985.
21. J. M. C. Alison, T. A. Stephenson and R. O. Gould, *J. Chem. Soc. (A)*, 1971, 3690.
22. R. A. Schunn, *Inorg. Chem.*, 1976, **15,** 208.
23. M. L. Schneider and H. M. M. Shearer, *J. Chem. Soc., Dalton Trans.*, 1973, 354.
24. R. L. Bennett, M. T. Bruce and F. G. A. Stone, *J. Organomet. Chem.*, 1972, **38,** 325.
25. K. M. Chui and H. M. Powell, *J. Chem. Soc., Dalton Trans.*, 1974, 2117.
26. K. M. Chui and H. M. Powell, *J. Chem. Soc., Dalton Trans.*, 1974, 1879.
27. H. C. Clark and K. R. Dixon, *J. Am. Chem. Soc.*, 1969, **91,** 596.
28. K. R. Dixon and D. J. Hawke, *Can. J. Chem.*, 1971, **49,** 3252.
29. W. J. Louw, D. J. A. de Waal and G. J. Kruger, *J. Chem. Soc., Dalton Trans.*, 1976, 2364.
30. S. Yamazaki, *Inorg. Chem.*, 1982, **21,** 1638.
31. R. J. Goodfellow, P. L. Goggin and D. A. Duddell, *J. Chem. Soc. (A)*, 1968, 504.
32. R. Bardi, A. M. Piazzesi, A. Del Pra, G. Cavinato and L. Toniolo, *Inorg. Chim. Acta,* 1983, **75,** 15.
33. F. G. Mann and D. Purdie, *J. Chem. Soc.*, 1936, 873; J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 1957, 2351.
34. B. E. Mann, B. L. Shaw and R. M. Slade, *J. Chem. Soc. (A)*, 1971, 2976.
35. D. F. Gill, B. E. Mann and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1973, 270.
36. K. R. Moss, K. C. Moss and M. A. R. Smith, *J. Chem. Soc., Dalton Trans.*, 1974, 971.
37. J. Powell and T. Jack, *Inorg. Chem.*, 1972, **11,** 1039.
38. R. G. Hayter and F. S. Humiec, *Inorg. Chem.*, 1963, **2,** 306.
39. R. G. Hayter, *J. Am. Chem. Soc.*, 1962, **84,** 3046.
40. H. Ogawa, T. Joh, S. Takahashi and K. Sonogashira, *J. Chem. Soc., Chem. Commun.*, 1985, 1220.
41. P. R. Brookes and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1973, 783.
42. C. E. Briant, K. A. Rowland, C. T. Webber and D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.*, 1981, 1515.
43. C. Eaborn, N. Farrell, J. L. Murphy and A. Pidcock, *J. Chem. Soc., Dalton Trans.*, 1976, 58.
44. W. Beck, P. Kreutzer and K. V. Werner, *Chem. Ber.*, 1971, **104,** 528.
45. G. W. Bushnell, K. R. Dixon, R. G. Hunter and J. J. McFarland, *Can. J. Chem.*, 1972, **50,** 3694.
46. D. A. Phillips, M. Kubota and J. Thomas, *Inorg. Chem.*, 1976, **15,** 118.
47. K. R. Dixon and A. D. Rattray, *Can. J. Chem.*, 1973, **51,** 618.
48. W. Levason and C. A. McAuliffe, *Inorg. Chem.*, 1974, **13,** 2765.
49. W. Levason and C. A. McAuliffe, *Inorg. Chim. Acta,* 1976, **16,** 167.
50. P. Nicpon and D. W. Meek, *Inorg. Chem.*, 1967, **6,** 145.
51. M. Bressan, G. Favero, B. Corain and A. Turco, *Inorg. Nucl. Chem. Lett.*, 1972, **7,** 203.
52. G. J. Palenik, M. Mathew, W. L. Steffen and G. Beran, *J. Am. Chem. Soc.*, 1975, **97,** 1059; W. L. Steffen and G. J. Palenik, *Inorg. Chem.*, 1976, **15,** 2432.
53. G. L. Hunt and A. L. Balch, *Inorg. Chem.*, 1982, **21,** 1242.
54. W. Levason and C. A. McAuliffe, *J. Chem. Soc., Dalton Trans.*, 1974, 2238.
55. N. J. DeStefano, D. K. Johnson and L. M. Venanzi, *Helv. Chim. Acta,* 1976, **59,** 2683.
56. A. J. Pryde, B. L. Shaw and B. Weeks, *J. Chem. Soc., Dalton Trans.*, 1976, 322.
57. W. E. Hill, D. M. A. Minahan and C. A. McAuliffe, *Inorg. Chem.*, 1983, **22,** 3382.
58. K. K. Chow, W. Levason and C. A. McAuliffe, *Inorg. Chim. Acta,* 1974, **15,** 79.
59. P. Groth, *Acta Chem. Scand.*, 1970, **24,** 2785.
60. E. C. Alyea and D. W. Meek, *Inorg. Chem.*, 1972, **11,** 1029.
61. C. M. Harris, R. S. Nyholm and N. C. Stephenson, *Nature (London)*, 1956, **177,** 1127.
62. R. J. Puddephatt, *Chem. Soc. Rev.*, 1983, **12,** 99.
63. F. S. M. Hassan, D. P. Markham, P. G. Pringle and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1985, 279.
64. C. R. Langrick, P. G. Pringle and B. L. Shaw, *Inorg. Chim. Acta,* 1983, **76,** L263; G. R. Cooper, A. T. Hutton, D. M. McEwan, P. G. Pringle and B. L. Shaw, *ibid.*, L267.
65. C. R. Langrick, P. G. Pringle and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1984, 1233.
66. M. M. Olmstead, C.-L. Lee and A. L. Balch, *Inorg. Chem.*, 1982, **21,** 2712.
67. A. L. Balch, L. S. Benner and M. M. Olmstead, *Inorg. Chem.*, 1979, **18,** 2996.
68. A. L. Balch, C. T. Hunt, C.-L. Lee, M. M. Olmstead and J. P. Farr, *J. Am. Chem. Soc.*, 1981, **103,** 3764.

69. K. Issleib, H. P. Abicht and H. Winkelmann, *Z. Anorg. Allg. Chem.*, 1972, **388,** 89.
70. P. G. Pringle and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1983, 889.
71. W. Levason and C. A. McAuliffe, *J. Coord. Chem.*, 1974, **4,** 47.
72. E. Uhlig and S. Keiser, *Z. Anorg. Allg. Chem.*, 1974, **406,** 1.
73. L. Volponi, B. Zarli and G. De Paoli, *Gazz. Chim. Ital.*, 1974, **104,** 897.
74. B. Chiswell, R. A. Plowman and K. Verrall, *Inorg. Chim. Acta*, 1972, **6,** 275.
75. T. N. Lockyer, *Aust. J. Chem.*, 1974, **27,** 259.
76. J. P. Beale and N. C. Stephenson, *Acta Crystallogr., Sect. B*, 1970, **26,** 1655.
77. L. F. Lindoy, S. E. Livingstone and T. N. Lockyer, *Inorg. Chem.*, 1967, **6,** 652.
78. S. E. Livingstone, *J. Chem. Soc.*, 1958, 4222; J. P. Beale, L. F. Lindoy and S. E. Livingstone, *Inorg. Nucl. Chem. Lett.*, 1971, **7,** 851; J. P. Beale and N. C. Stephenson, *Acta Crystallogr., Sect. B*, 1971, **27,** 73; 1972, **28,** 557.
79. P. G. Eller, J. M. Rieker and D. W. Meek, *J. Am. Chem. Soc.*, 1973, **95,** 3540.
80. G. A. Mair, H. M. Powell and D. E. Henn, *Proc. Chem. Soc.*, 1960, 415.
81. R. G. Cunninghame, R. S. Nyholm and M. L. Tobe, *J. Chem. Soc., Dalton Trans.*, 1972, 229.
82. R. B. King, R. N. Kapoor, M. S. Saran and P. N. Kapoor, *Inorg. Chem.*, 1971, **10,** 1851.
83. R. B. King, J. C. Cloyd and R. H. Reimann, *Inorg. Chem.*, 1976, **15,** 449.
84. T. L. Blundell and H. M. Powell, *J. Chem. Soc. (A)*, 1967, 1650.
85. B. Bosnich, W. G. Jackson and S. T. D. Lo, *Inorg. Chem.*, 1975, **14,** 2999.
86. O. St. C. Headley, R. S. Nyholm, C. A. McAuliffe, L. Sindellari, M. L. Tobe and L. M. Venanzi, *Inorg. Chim. Acta*, 1970, **4,** 93.
87. T. D. B. Morgan and M. L. Tobe, *Inorg. Chim. Acta*, 1971, **5,** 563.
88. N. Ahmad, E. W. Ainscough, T. A. James and S. D. Robinson, *J. Chem. Soc., Dalton Trans.*, 1973, 1148.
89. A. W. Verstuyft, D. A. Redfield, L. W. Cary and J. H. Nelson, *Inorg. Chem.*, 1976, **15,** 1128.
90. J. A. A. Mokuolu, D. S. Payne and J. C. Speakman, *J. Chem. Soc., Dalton Trans.*, 1973, 1443.
91. S. O. Grim, W. L. Briggs, R. C. Barth, C. A. Tolman and J. P. Jesson, *Inorg. Chem.*, 1974, **13,** 1095.
92. D. A. Couch and S. D. Robinson, *Inorg. Chim. Acta*, 1974, **9,** 39.
93. J. P. Jesson and P. Meakin, *Inorg. Nucl. Chem. Lett.*, 1973, **9,** 1221.
94. D. A. Couch and S. D. Robinson, *Inorg. Nucl. Chem. Lett.*, 1973, **9,** 1079.
95. D. J. Tune and H. Werner, *Helv. Chim. Acta*, 1975, **58,** 2240.
96. K. R. Dixon and A. D. Rattray, *Can. J. Chem.*, 1971, **49,** 3997; Pi-Chang Kong and D. M. Roundhill, *J. Chem. Soc., Dalton Trans.*, 1974, 187; M. C. Cornock, R. O. Gould, C. L. Jones and T. A. Stephenson, *ibid.*, 1977, 1307.
97. T. Debaerdemaeker, A. Kutoglu, G. Schmid and L. Weber, *Acta Crystallogr., Sect. B*, 1973, **29,** 1283; N. A. Bailey and R. Mason, *J. Chem. Soc. (A)*, 1968, 2594.
98. A. J. Cheney and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1972, 860.
99. G. J. Gainsford and R. Mason, *J. Organomet. Chem.*, 1974, **80,** 395.
100. B. L. Shaw and R. E. Stainbank, *J. Chem. Soc., Dalton Trans.*, 1973, 2394.
101. C. J. Moulton and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1976, 1020.
102. N. Ahmad, E. W. Ainscough, T. A. James and S. D. Robinson, *J. Chem. Soc., Dalton Trans.*, 1973, 1151.
103. A. J. Carty, S. E. Jacobson, R. T. Simpson and N. J. Taylor, *J. Am. Chem. Soc.*, 1975, **97,** 7254.
104. N. J. Taylor, S. E. Jacobson and A. J. Carty, *Inorg. Chem.*, 1975, **14,** 2648.

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