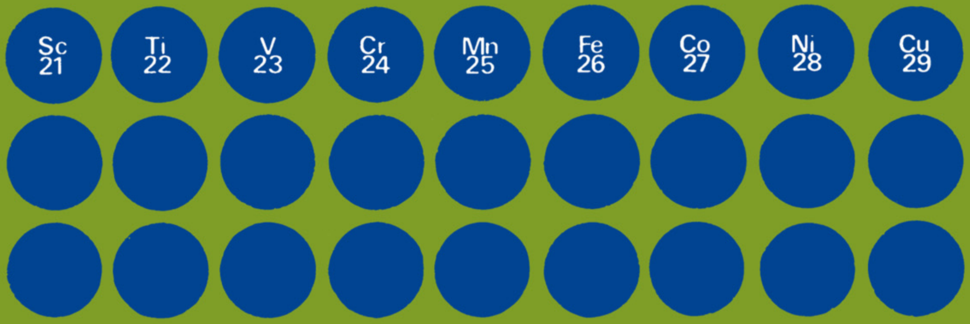
Complexes and First-Row Transition Elements



DAVID NICHOLLS

COMPLEXES AND FIRST-ROW TRANSITION ELEMENTS

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To Wendy

Preface

Transition-metal chemistry is very largely concerned with the chemistry of complexes and so it is fitting therefore that both subjects should be dealt with in the same textbook. We deal here with the general aspects of complexes first and then with the specific chemistry of the first-row transition elements. For several reasons this book deals only with the chemistry of the first-row transition elements at a level suitable for first- or second-year undergraduates in British universities. The chief of these is that the first member of each group of transition elements differs significantly in properties from the subsequent members, and thus vertical comparisons within the groups are less valuable than horizontal ones. Further, the explanations of the magnetic and spectral properties are more simply dealt with in the first-row transition elements and the aqueous chemistry can be systematised more easily. The second- and third-row transition elements are covered in a companion volume (S. A. Cotton and F. A. Hart: *The Heavy Transition Elements*), which also gives a more detailed treatment of organometallic compounds and the bonding therein (as well as other topics such as metal carbonyls and metal–metal bonding) at a level more appropriate to final-year honours students in British universities.

In the present text a little basic physical chemistry is assumed, in particular the concepts of atomic orbitals, elementary kinetics and thermodynamics and electrode potentials. Throughout the text emphasis is placed on the properties and reactions of metal aquo-ions and the donor–acceptor properties of transition-metal compounds. In the author's opinion a knowledge of these concepts can give the student a general understanding of the more elementary reactions of transition-metal compounds.

Liverpool David Nicholls
1974

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1 The Development of Co-ordination Chemistry

1.1 Introduction to Complexes

The chemistry of the transition elements is very largely concerned with the chemistry of co-ordination compounds. Co-ordination compounds or, as they are perhaps more usually called, *complexes* play a very important part in our lives today; the study of them has contributed greatly to our understanding of the chemical bond and of inorganic chemistry as a whole. The number of possible co-ordination compounds in chemistry is almost infinite. Present-day research workers prepare many new complexes every week; most of these will be of academic interest only, but just a few will be of considerable economic importance as well. For many years complexes were regarded as of interest to the theoretical and inorganic chemist only, but now they are playing vital roles in analytical chemistry, in the synthesis of organic chemicals, in polymerisation processes, and in our understanding of biological processes. Perhaps the most important are the naturally occurring complexes such as chlorophyll, the magnesium complex that is important in plant photosynthesis, and haemoglobin, the iron complex that is a carrier of oxygen in blood.

What do we understand by the term 'complexes'? It is difficult to define the term in a formal way. However, as a guide we can say that a complex is formed when a number of ions or molecules combine with a central atom to form an entity in which the number of atoms directly attached to the central atom exceeds the normal covalency (oxidation state) of this atom. Complexes may be neutral (no charge), cationic (positively charged), or anionic (negatively charged). Thus silver chloride (not a complex) dissolves in ammonia solution to form the ion $[Ag(NH_3)_2]^+$ which is a complex because the number of bonded groups exceeds the +1 oxidation state of silver. The reader will almost certainly have come across this and many other reactions in which complex ions are formed. The pretty blue solution of copper(II) sulphate, which we meet very early in our experience of chemistry, is a solution of complex ions formed by the reaction

$$\underset{\text{white}}{CuSO_4} + H_2O\,(\text{excess}) \rightarrow \underset{\text{blue}}{[Cu(H_2O)_6]^{2+}} + SO_4{}^{2-}\,(\text{aq.})$$

This complex ion is responsible for the blue colour of the solution; indeed most of the familiar blue copper(II) salts are complexes containing co-ordinated water molecules. So we begin to see that complex formation has a marked effect on the properties (for example solubility and colour) of simple salts. Some other well-known complex compounds are listed in Table 1.1.

The groups bonded to the central atom are called *ligands* or donor molecules; in the formation of a complex, the ligands are often said to donate a pair of electrons to the metal or other central atom. Complexes are thus the products of co-ordinate bond formation. It is because water is a ligand that it is impossible to place a transition-metal ion in aqueous solution without complex formation

TABLE 1.1 SOME COMPLEX COMPOUNDS

'Simple' compound or ion	Ligand	Complex
BF_3	NMe_3	$Me_3N.BF_3$
$AgCl$	Cl^-	$[AgCl_2]^-$
Cu^{2+}	NH_3	$[Cu(NH_3)_6]^{2+}$
Al^{3+}	F^-	$[AlF_6]^{3-}$
Ni^{2+}	H_2O	$[Ni(H_2O)_6]^{2+}$
Co^{3+}	NO_2^-	$[Co(NO_2)_6]^{3-}$

occurring; if no other co-ordinating groups are present, this complex will usually be the hexa-aquo-ion $[M(H_2O)_6]^{n+}$. In this connexion the reader should notice that the solvents have not been specified for the 'reactions' cited in Table 1.1. Reaction of the Cu^{2+} ion with ammonia only (that is in liquid ammonia) yields the hexammine-copper(II) cation, while in concentrated aqueous solutions of ammonia there is competition between the ammonia and water molecules for the Cu^{2+} ion; the composition $[Cu(NH_3)_4(H_2O)_2]^{2+}$ (sometimes abbreviated to $[Cu(NH_3)_4]^{2+}$) of the so-called cupritetrammine ion is largely reached.

We can further qualify our description of complex compounds to distinguish them from double salts. In a complex ion, the anion or cation concerned is actually present as a discrete entity either in solution or in the solid state or in both. In double salts, the individuality of the constituent salts is maintained. For example, potash alum $KAl(SO_4)_2.12H_2O$ reacts chemically as a mixture of potassium sulphate and aluminium sulphate and does not contain or show reactions of the $[Al(SO_4)_2]^-$ ion. However, there is a complex ion within this double salt. Potash alum contains the ion $[Al(H_2O)_6]^{3+}$ and like aluminium sulphate it gives this ion in aqueous solution. A more instructive way to write the formula for potash alum is thus $K^+[Al(H_2O)_6]^{3+}(SO_4{}^{2-})_2.6H_2O$.

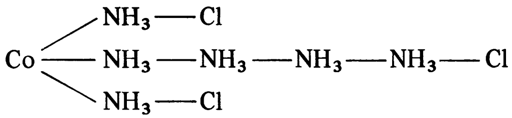
1.2 The Historical Development of Co-ordination Chemistry

The first complexes to be the subject of any great study were the cobaltammines. As early as 1798 Tassaert observed that a solution of a cobalt(II) salt in aqueous ammonia becomes brown on exposure to air, the colour changing to wine red on boiling. Some decades later, Frémy showed that the cobalt had been oxidised to cobalt(III) and that the new salt is associated with up to six ammonia molecules, for example $CoCl_3.6NH_3$. This compound stimulated interest because it was difficult to understand how the two compounds $CoCl_3$ and NH_3, each with its valency satisfied, could combine together to form a stable compound. Many more complexes of ammonia were prepared subsequently. The reactions of nickel chloride and copper sulphate solutions with an excess of ammonia were found to give deeply coloured solutions from which the purple $NiCl_2.6NH_3$ and the deep blue $CuSO_4.4NH_3.H_2O$ could be isolated. However, it was with cobalt(III) and platinum(II) that a wide variety of ammonia complexes (ammines) could be prepared, and it was the study of the properties of these series of ammines that was to shed much light on the structures of co-ordination compounds.

While their structures were unknown, these new compounds were often named according to their colour. Thus the orange-yellow $CoCl_3.6NH_3$ was called *luteocobaltic chloride,* the purple $CoCl_3.5NH_3$ *purpureocobaltic chloride,* and the green isomer of $CoCl_3.4NH_3$ *praseocobaltic chloride.* Other complexes were named after their discoverers, for example Magnus' green salt $PtCl_2.2NH_3$ (now formulated as $[Pt(NH_3)_4[PtCl_4]$) and Reinecke's salt $Cr(SCN)_3.NH_4SCN.2NH_3$ (now formulated as $NH_4[Cr(NH_3)_2(NCS)_4]$). Around 1830 Zeise found that ethylene could form compounds with platinum salts, and he was able to isolate complexes of formulae $PtCl_2.C_2H_4$ and $PtCl_2.KCl.C_2H_4$. These compounds were the first organometallic compounds of the transition elements to be prepared; their structures have been elucidated only fairly recently and the potassium compound (now formulated as $K[PtCl_3(C_2H_4)]$) is still often called Zeise's salt. Today complexes are named systematically; rules for naming them are given at the end of this chapter.

1.2.1 The Werner Theory

Our understanding of co-ordination compounds dates from the time of Alfred Werner. Werner presented his first paper on this subject in 1891 at the age of twenty-five; in 1913 he received the Nobel prize for chemistry. Prior to Werner, other theories had been put forward to explain the structures of complex compounds. One such theory was the *chain theory* in which, for example, $CoCl_3.6NH_3$ was formulated as



This theory followed naturally from the well-known catenation of carbon in aliphatic chains, but such structures were soon shown to be incorrect. It will be appropriate to discuss here some of the experimental evidence that was available at the time of Werner.

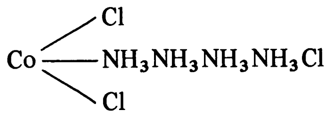
1.2.2 Ionisable Chloride

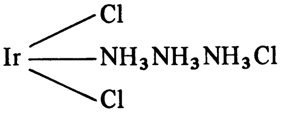
When the cobaltammine chlorides are treated with silver nitrate solution, they do not all behave similarly; all the chlorine present in the complexes is not always precipitated instantly and quantitatively at room temperature. This statement is elaborated in Table 1.2. In $CoCl_3.5NH_3$, for example, two-thirds of the total chlorine present is precipitated by silver nitrate solution at room temperature; this is known as the ionisable chloride. The other one-third can be liberated only by breaking down the complex, for example by boiling with sodium hydroxide solution; this chlorine is known as the nonionisable chloride. From these facts Werner concluded that the nonionisable chlorines are bonded covalently to the cobalt. The ionisable chlorides are just the number of free chloride ions required to balance the charge on the cobalt cation as a whole; hence the formulation of these complexes as in Table 1.2. The cobaltammine $CoCl_3.3NH_3$ would then be expected to have

TABLE 1.2 CHLORIDE ION PRECIPITATION FROM COBALTAMMINES

Complex	No. of Cl^- ions precipitated	Present formulation
$CoCl_3.6NH_3$	3	$[Co(NH_3)_6]Cl_3$
$CoCl_3.5NH_3$	2	$[Co(NH_3)_5Cl]Cl_2$
$CoCl_3.4NH_3$	1	$[Co(NH_3)_4Cl_2]$ Cl

the structure $[CoCl_3(NH_3)_3]$ with no ionisable chlorides. Unfortunately this compound cannot be prepared but the iridium analogue $IrCl_3.3NH_3$ is found to have no ionisable chlorides. This was an important result in showing the weakness of the chain theory, since it would predict the same number of ionisable chlorides (two) for $CoCl_3.4NH_3$ and $IrCl_3.3NH_3$, namely





1.2.3 *Molar Conductivity*

A further method of testing the degree of ionisation of a complex is the measurement of its electrical conductivity in solution. The more ions that a complex liberates in solution, the greater the conductivity; a complex that does not ionise will have negligible conductivity. For comparison purposes, the molar conductivities (Λ_M) are most useful. By measuring the molar conductivities of some simple salts, the relationship between the number of ions present per molecule and the conductivity can be established. Thus Λ_M values in water (at 10^{-3} M) are about 120 ohm^{-1} cm^2 for salts giving two ions (for example NaCl), about 260 ohm^{-1} cm^2 for three ions (for example $BaCl_2$), and about 400 ohm^{-1} cm^2 for four ions (for example $CeCl_3$). Table 1.3 shows the molar conductivities and the consequent formulations of some platinum ammines.

TABLE 1.3 CONDUCTIVITIES OF SOME PLATINUM AMMINES

Complex	Λ_M (ohm^{-1} cm^2)	No. of ions	Present formulation
$PtCl_4.6NH_3$	523	5	$[Pt(NH_3)_6]^{4+}$ $4Cl^-$
$PtCl_4.5NH_3$	404	4	$[Pt(NH_3)_5Cl]^{3+}$ $3Cl^-$
$PtCl_4.4NH_3$	229	3	$[Pt(NH_3)_4Cl_2]^{2+}$ $2Cl^-$
$PtCl_4.3NH_3$	97	2	$[Pt(NH_3)_3Cl_3]^+$ Cl^-
$PtCl_4.2NH_3$	0	0	$[Pt(NH_3)_2Cl_4]$

1.2.4 *Werner's Postulates*

Not only did Werner suggest the formulations that are considered correct today for the cobaltammines, as for example in Table 1.2, but he went on to develop a theory that is still applicable without essential alteration. We may summarise Werner's postulates as follows.

(1) Metals possess two types of valency, the primary (ionisable) valency and the secondary (nonionisable) valency. We now call these *oxidation state* and *co-ordination number* respectively.

(2) Primary valencies are satisfied by negative ions, and secondary valencies by negative ions or neutral molecules, both valencies being satisfied.

(3) The secondary valencies are directed to fixed positions in space about the central metal ion.

The first two postulates give a straightforward rationalisation of the structural formulae of complex compounds. Thus in the cobaltammines (Table 1.2) the primary valency of cobalt is in each case three and the secondary valency is six. The second postulate is exemplified by the formulations for the ammines in Tables 1.2 and 1.3. In every case the primary and secondary valencies are satisfied; for the platinum ammines the primary valency is four but the secondary valency is still six. We shall see that many metals have a preferred co-ordination number of six, that is they prefer to have six groups (ligands) directly attached to the metal atom; these six ligands are said to be in the co-ordination sphere of the metal. The ligands in the co-ordination sphere are bonded to the metal by co-ordinate bonds whereas the ions outside the co-ordination sphere are bonded ionically to the co-ordination sphere as a whole. Thus, when $[Co(NH_3)_5Cl]Cl_2$ is dissolved in water, the ions $[Co(NH_3)_5Cl]^{2+}$ and Cl^- are present in the solution. The addition of silver nitrate precipitates the free Cl^- ions but the chlorine bonded co-ordinately in the $[Co(NH_3)_5Cl]^{2+}$ cation is not readily available as chloride ion.

The third postulate was perhaps the most significant but it was the most difficult to prove. It predicted the occurrence of various types of isomers (compounds having the same empirical formula but different structures), and it took Werner nearly twenty years to prove this by the resolution of an inorganic complex into its predicted optical isomers. The significance of the third postulate lies in its contribution to the development of inorganic stereochemistry. The fact that so many of the then known complexes had a co-ordination number of six raised the important question of how the six ligands were distributed spatially around the metal ion. Before the advent of direct methods for structural determination, for example by use of X-rays, the choice of structure was made on the basis of the number of stereoisomers obtainable.

Let us consider the ways in which six groups might be arranged spatially around a metal. The most symmetrical structures are those illustrated in Figure 1.1. Now let us consider the number of isomers that each of these would give for a compound of formula MA_4B_2. The hexagonal planar structure (Figure 1.1*a*) would give three stereoisomers (equivalent to the benzene *ortho-*, *meta-*, and *para-*isomers) with the B groups in, for example, positions 1,2, 1,3, or 1,4. Similarly the trigonal prismatic structure (Figure 1.1*b*) would give rise to three isomers with B groups in, for example, 1,2, 1,4, and 1,5 positions. However, the octahedral structure (Figure 1.1*c*) can give rise to only two isomers, with B groups in, for example, 1,2 *(cis)* or 1,6 *(trans)* positions. For numerous complexes of the formula MA_4B_2, only two isomers were in fact found; in no case could three isomers be isolated, so the evidence indicated that the octahedral structure was correct. Prior to confirmation

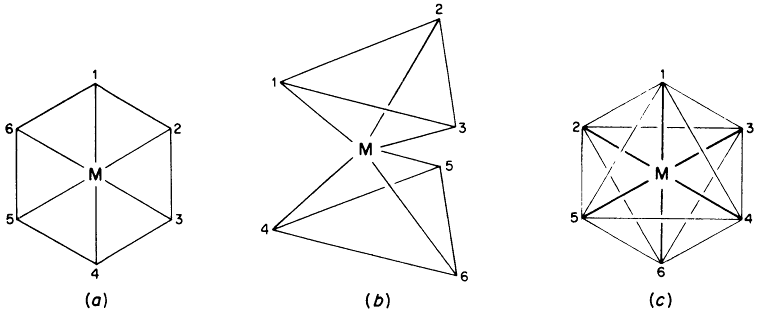


Figure 1.1 Arrangements of six groups around a metal: (*a*) hexagonal planar; (*b*) trigonal prismatic; (*c*) octahedral

of this by X-ray analysis, Werner set about proving the octahedral structure in a more positive way than that so far described. This involved the resolution into optical isomers of complexes of the type $M(AA)_3$ where AA is a chelating ligand (see chapter 4). Neither the hexagonal planar nor the trigonal prismatic structure would give optical isomers with these complexes, so the octahedral structure was proved to be correct.

1.3 Nomenclature of Co-ordination Compounds

Because of the enormous number and wide variety of co-ordination compounds it is important to have a systematic way of naming compounds unambiguously. Fortunately, definitive rules for the nomenclature of inorganic compounds were laid down in 1958 by a commission of the International Union of Pure and Applied Chemistry; these *IUPAC rules* (with very minor modifications) are now in widespread use and are the basis of the nomenclature presented here.

Perhaps the biggest advance in recent years has been the general acceptance of the Stock notation. In this, the oxidation state of a metal is designated by a Roman numeral in parentheses immediately after its name; the endings -ous, -ic, -yl, etc., are thus rendered obsolete. A few examples of the names of simple compounds will suffice to show the advantages of this method. The old problem to the student beginning chemistry of whether ferrous ion is di- or tri-valent now no longer arises; iron(II) chloride is clearly $FeCl_2$. Other simple examples are given in Table 1.4.

TABLE 1.4 STOCK NOTATION COMPARED WITH OLDER NOMENCLATURE

Formula	Stock notation	Older name
$CuSO_4$	copper(II) sulphate	cupric sulphate
Hg_2Cl_2	mercury(I) chloride	mercurous chloride
WO_3	tungsten(VI) oxide	tungstic oxide
$VOCl_2$	vanadium(IV) oxide dichloride	vanadyl chloride
$VOCl_3$	vanadium(V) oxide trichloride	vanadyl trichloride

There is no need to use the notation in unambiguous cases such as sodium chloride or calcium sulphate, and, particularly for other than transition elements, the prefixes mono-, di-, tri-, tetra-, etc. are frequently used to denote the stoichiometry instead of using oxidation states, for example carbon monoxide and sulphur trioxide.

For complex compounds, as with simple salts, the cation is named first followed by the anion. The ligands are arranged in front of the central metal atom, negative ones first then neutral ones; the oxidation state is written immediately after the metal as in naming the simple salts. The number of each type of ligand is specified by the Greek prefixes mono-, di-, tri-, tetra-, penta-, hexa-, hepta-, and octa-. It will be noticed that negative ligands end in -o, for example chloro (Cl^-) and cyano (CN^-), while neutral ligands keep their usual names except for water which is *aquo* and ammonia which is *ammine*.

Anionic complexes. If the complex is in an anionic form, the ending -ate is attached to the name of the metal and this is followed by the oxidation state according to the Stock notation, for example

K_2TiCl_6	potassium hexachlorotitanate(IV)
$Na_3Co(NO_2)_6$	sodium hexanitrocobaltate(III)
$K_4Fe(CN)_6$	potassium hexacyanoferrate(II)
$NaMn(CO)_5$	sodium pentacarbonylmanganate(−I)

The names of five metals change when they are in an anionic form; we have seen the example above of iron which becomes ferrate. The others are copper, which becomes cuprate, gold which becomes aurate, lead which becomes plumbate, and tin which becomes stannate. It is not necessary to specify the number of cations in the complexes named above; for example, we do not say 'dipotassium hexachlorotitanate(IV)' because, if the complex has $TiCl_6{}^{2-}$ anions, it must have two K^+ ions to balance the charges.

Cationic complexes. These have the cation, named according to the aforementioned rules, followed by a space and then the name of the anion, for example

$[Co(NH_3)_6]Cl_3$	hexa-amminecobalt(III) chloride
$[CoCl(NH_3)_5]Cl_2$	chloropenta-amminecobalt(III) chloride
$[CrCl_2(H_2O)_4]Cl$	dichlorotetra-aquochromium(III) chloride

Neutral complexes. These are named in one word, for example

$[PtCl_2(NH_3)_2]$	dichlorodiammineplatinum(II)
$[Co(NO_2)_3(NH_3)_3]$	trinitrotriamminecobalt(III)

Complicated ligands. When the ligand has the prefix di- or tri- in its name, for example diethyl ether or triphenylphosphine, the number of ligand molecules present in the complex is denoted by the prefixes bis-, tris-, tetrakis-, pentakis-, hexakis-, etc., and the name of the ligand is placed in parentheses, for example

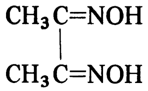
$TiCl_4(Et_2O)_2$	tetrachlorobis(diethyl ether)titanium(IV)
$Ni(CO)_2(Ph_3P)_2$	dicarbonylbis(triphenylphosphine)nickel
$[Fe(en)_3][Fe(CO)_4]$	tris(ethylenediamine)iron(II) tetracarbonylferrate(−I)

These prefixes are also used when any ambiguity might arise; for example, the compound $SiCl_4(NH_2Me)_2$ might be wrongly named tetrachlorodimethylaminesilicon(IV) whereas the name tetrachlorobis(methylamine)silicon(IV) is unambiguous.

Organic ligands that lose a proton when they react with a metal ion are treated as anionic and give the ending -ato, for example

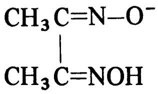
$Ni(C_4H_7O_2N_2)_2$	bis(dimethylglyoximato)nickel(II)
$CoCl_2(C_4H_8O_2N_2)_2$	dichlorobis(dimethylglyoxime)cobalt(II)

(dimethylglyoxime =



$$\begin{array}{c} CH_3C{=}NOH \\ | \\ CH_3C{=}NOH \end{array}$$

; dimethylglyoximato =



$$\begin{array}{c} CH_3C{=}N{-}O^- \\ | \\ CH_3C{=}NOH \end{array}$$

)

$Cr(acac)_3$	tris(acetylacetonato)chromium(III)

(acetylacetone = $CH_3COCH_2COCH_3$; acetylacetonato = $CH_3CO\overset{-}{C}HCOCH_3$)

Bridging groups. A bridging group is indicated by placing the Greek letter μ immediately before its name, for example

$[(NH_3)_5Cr{-}OH{-}Cr(NH_3)_5]Cl_5$	μ-hydroxo-bis[penta-amminechromium(III)] chloride.
$(CO)_3Fe(CO)_3Fe(CO)_3$	tri-μ-carbonyl-bis(tricarbonyliron).

2 Lewis Acids and Bases

2.1 The Simple Lewis Approach

We saw in chapter 1 that complex compounds are often formed by direct reaction between a 'simple' molecule or ion and a ligand. How do we know which 'simple' substances will react with ligands? One way of dealing with this problem is to use the theory of acids and bases put forward by G.N. Lewis in 1938. Lewis called those substances capable of acting as ligands *bases* and the substances with which these react *acids*. The formal definitions may be summarised as follows

Lewis acid – an acceptor of an electron pair
Lewis base – a donor of an electron pair

The reaction between a Lewis base and a Lewis acid is thus a donor–acceptor reaction involving the formation of a co-ordinate bond and, more often than not, a complex compound. The importance of the word 'pair' in the definitions must be stressed. Lewis acids are not necessarily oxidising agents; these become reduced by accepting any number of electrons but Lewis acids can accept only pairs of electrons, and these pairs are normally not transferred completely to the acid but are used in the formation of covalent bonds. The terms *electrophile* and *nucleophile*, as used in organic chemistry, are synonymous with Lewis acid and Lewis base respectively. The more important types of species that are capable of acting as Lewis acids and bases are listed in Tables 2.1 and 2.2.

TABLE 2.1 LEWIS ACIDS (ELECTROPHILES)

Type	Examples
1. Positive ions	H^+, Ag^+, Cu^{2+}, Al^{3+}
2. Molecules, especially halides, formed by elements in the first row of the periodic table, that have incomplete octets	$BeCl_2$, BF_3
3. Compounds, especially halides, in which the central atom may exceed its octet (for example by by use of d orbitals)	$SiCl_4$, $TiCl_4$, VCl_4, $TaCl_5$

2.1.1 *Types of Lewis Acid*

Let us now consider these various types of acid and base, and give examples of the reactions that can occur. The types of acids and bases in Tables 2.1 and 2.2 (with the exception of the type 3 bases, which react only with certain acids) will normally react together; we are thus provided immediately with a rough guide as to whether or not two substances will react together, given favourable circumstances.

TABLE 2.2 LEWIS BASES (LIGANDS)

Type	Examples
1. Negative ions	OH^-, F^-, CN^-
2. Molecules with one or two lone pairs of electrons	NH_3, NEt_3, $P(C_6H_5)_3$, H_2O, Me_2S
3. Molecules having carbon–carbon multiple bonds	$CH_2{=}CH_2$, $HC{\equiv}CH$, C_6H_6

Obviously positive ions will react with negative ions to form salts, but a complex compound may be produced if there is an excess of the ligand, for example

$$Ag^+ + 2Cl^- \rightarrow [AgCl_2]^-$$
$$Co^{2+} + 4Cl^- \rightarrow [CoCl_4]^{2-}$$
$$Fe^{3+} + 6CN^- \rightarrow [Fe(CN)_6]^{3-}$$

Positive ions may also react with type 2 (Table 2.2) bases; complex cations then result, for example

$$Ag^+ + 2NH_3 \rightarrow [Ag(NH_3)_2]^+$$
$$Cu^{2+} + 6H_2O \rightarrow [Cu(H_2O)_6]^{2+}$$
$$Ni^{2+} + 6NH_3 \rightarrow [Ni(NH_3)_6]^{2+}$$

Other things being equal, the acid strength of the cations increases with increasing charge and with decreasing radius. While all cations attract strong bases such as water molecules to some extent, the interactions of cations with unsaturated organic molecules are largely confined to the later transition elements, for example

$$[PtCl_4]^{2-} + C_2H_4 \rightarrow [PtCl_3(C_2H_4)]^- + Cl^-$$

Apart from cations, nearly all the other Lewis acids are elemental halides (types 2 and 3 in Table 2.1). Other neutral molecules, such as $AlMe_3$ and $B(OR)_3$, are Lewis acids but not usually such strong acids as the corresponding compounds containing the electron-withdrawing halogen atoms. In the first row of the periodic table, beryllium and boron halides react with two molecules and one molecule of a unidentate base respectively, thus completing the octet around the central atom in forming a tetrahedral complex, for example

$$BeCl_2 + 2Cl^- \rightarrow [BeCl_4]^{2-}$$
$$BF_3 + F^- \rightarrow [BF_4]^-$$
$$BeCl_2 + 2Et_2O \rightarrow BeCl_2(OEt_2)_2$$
$$BBr_3 + Et_3N \rightarrow BBr_3(NEt_3)$$

For these halides the central atoms use 2s and 2p atomic orbitals for bonding; the 3d orbitals are too high in energy to be used, so no more than eight electrons can be accommodated. In carbon tetrachloride the carbon atom already has a complete octet, so it does not show acceptor properties; unlike the halides of beryllium and boron, the carbon halides do not react under normal conditions with, for example, water, alcohols, ethers, and chloride ions.

With the halides of the second and subsequent rows of the periodic table, the octet rule no longer applies, and twelve or more electrons form stable electronic arrangements about the central atoms. Instead of the formation of tetrahedral complexes, six-co-ordination is more common, especially with the halides of the transition elements, for example

$$\begin{array}{llll} SiF_4 & + 2F^- & \rightarrow & SiF_6{}^{2-} \\ VCl_4 & + 2py & \rightarrow & VCl_4(py)_2 \\ TiBr_4 & + 2OEt_2 & \rightarrow & TiBr_4(OEt_2)_2 \end{array}$$

The ease of hydrolysis of the silicon tetrahalides compared with the relative inertness of the carbon compounds is attributed to the failure of the carbon halides to form the intermediate adduct. The hydrolysis reaction is not thermodynamically unfavourable but the activation-energy barrier in forming the intermediate is too high to be reached under ordinary conditions. For silicon (and other covalent halides of the type MX_4) we can write

$$SiCl_4 \quad + 2H_2O \quad \rightarrow \quad SiCl_4(H_2O)_2$$

This intermediate undergoes further reactions in the presence of an excess of water; for simplicity we may write these as gas-phase equilibria

$$\begin{array}{lllll} SiCl_4(H_2O)_2 & + H_2O & \rightleftharpoons & SiCl_3(OH)(H_2O)_2 & + HCl \\ SiCl_3(OH)(H_2O)_2 & + H_2O & \rightleftharpoons & SiCl_2(OH)_2(H_2O)_2 & + HCl \\ SiCl_2(OH)(H_2O)_2 & + H_2O & \rightleftharpoons & SiCl(OH)_3(H_2O)_2 & + HCl \\ SiCl(OH)_3(H_2O)_2 & + H_2O & \rightleftharpoons & Si(OH)_4(H_2O)_2 & + HCl \end{array}$$

In aqueous solution they are more appropriately treated as ionic equilibria of the type

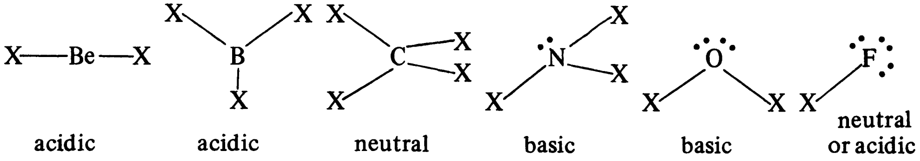
$$(H^+)_2[SiCl_4(OH)_2]^{2-} + H_2O \rightleftharpoons (H^+)_2[SiCl_3(OH)_3]^{2-} + HCl$$

in which the nature of the predominant hydroxochloro-species present depends on the concentration of the hydrochloric acid. Thus, with many halides of this type, addition to concentrated hydrochloric acid gives the net result of chloride ion acceptance rather than hydrolysis, for example

$$\begin{array}{llll} TiCl_4 & + \text{conc. HCl} & \rightarrow & (H^+)_2[TiCl_6]^{2-} \\ SnCl_4 & + \text{conc. HCl} & \rightarrow & (H^+)_2[SnCl_6]^{2-} \end{array}$$

2.2 Types of Lewis Base (Ligands)

We have already seen many examples of anions acting as ligands, and since all simple anions are capable of acting in this way we need not further classify them at this stage. However, with neutral molecules it is important to be able to distinguish between molecules that can act as ligands and those that cannot. The simple compounds formed by elements in the first row of the periodic table can be represented by the six structures shown, where X is any other atom or group and two dots denote a lone pair of electrons.

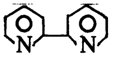
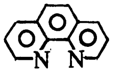
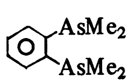
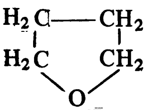
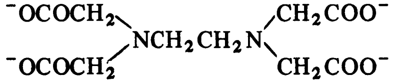


We can now see that the molecules possessing one or two pairs of electrons, over and above those used in bonding, are those containing trivalent nitrogen and divalent oxygen atoms. The base strength will depend on the nature of X. If X is an electron-withdrawing atom or group such as chlorine, the lone pair of electrons is not so readily available for co-ordinate bond formation as when X is an electron-repelling group such as CH_3. The generally expected trend for base strengths of nitrogen donors is thus

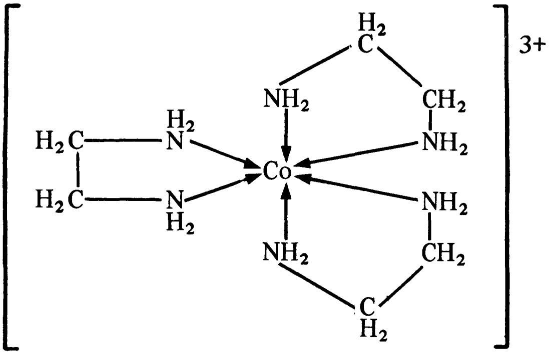
$$NF_3 < NH_3 < NMe_3$$

The other elements in group Vb, for example phosphorus and arsenic, will be similarly basic in their trivalent compounds, and in group VIb sulphur, like oxygen, has two lone pairs of electrons in compounds in which it is divalent. Some of the more important ligands formed by these elements are given in Table 2.3. Note that virtually any organic molecule containing trivalent nitrogen or phosphorus, or divalent oxygen or sulphur, is potentially capable of acting as a ligand. Thus all amines, phosphines, alcohols, ethers, thioalcohols, thioethers, aldehydes, and ketones act in this way, as well as many other types of compound. The number of co-ordination compounds that can be synthesised is thus enormous.

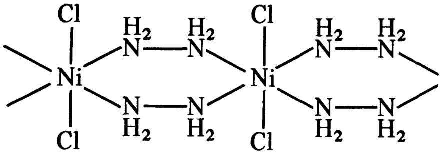
TABLE 2.3 SOME IMPORTANT LIGANDS

Formula	Name	Abbreviation
NH_3	ammonia	–
NH_2NH_2	hydrazine	–
C_5H_5N	pyridine	py
$NH_2CH_2CH_2NH_2$	ethylenediamine	en
	2,2′-bipyridyl	bipy
	1,10-phenanthroline	phen
$(C_6H_5)_3P$	triphenylphosphine	Ph_3P
	*o*-phenylenebisdimethylarsine	diars
	tetrahydrofuran	THF
$CH_3CO\bar{C}HCOCH_3$	acetylacetonato anion	acac.
 $(^{-}OCOCH_2)_2NCH_2CH_2N(CH_2COO^{-})_2$	ethylenediaminetetraacetate anion	EDTA
$(C_2H_5)_2S$	diethyl sulphide	Et_2S

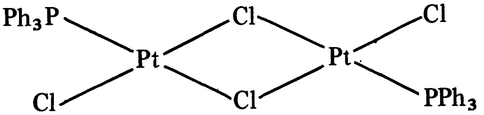
Ligands having only one atom possessing lone-pair electrons are called *unidentate ligands* since they can bond via one atom only; examples are NH_3, H_2O, and pyridine. When two atoms possessing lone-pair electrons are present in a molecule it may (but not necessarily) bond via both of these atoms; it is then called a *bidentate ligand,* examples being hydrazine, ethylenediamine, and 2,2-bipyridyl. Similarly, ligands with three, four, five, and six donor sites are known. These multidentate ligands may act in either of two different ways. They may bond with all their donor atoms, linked to the same metal atom as in the tris(ethylenediamine)cobalt(III) cation



In this example, the ethylenediamine is acting as a *chelate* ligand; chelating ligands form stable rings with metal ions and are the most important type of multidentate ligand. The alternative mode of bonding is that in which the multidentate ligand is bonded to two metal atoms with the formation of a bridge, for example in the polymeric $NiCl_2(N_2H_4)_2$



Anionic ligands are also capable of bridging and chelation. Unidentate anions can form bridges; for example, $PtCl_2(PPh_3)$, which is dimeric, has the structure



In this structure the chlorines in the bridges are still unidentate in the sense that only one atom is acting as the donor. Hydroxide ions commonly form bridges (*ol* bridges) in the deprotonation of hexa-aquo-cations. Chelating anions include oxalato and acetylacetonato, and the analytically important EDTA anion, the magnesium salt of which is illustrated in Figure 2.1.

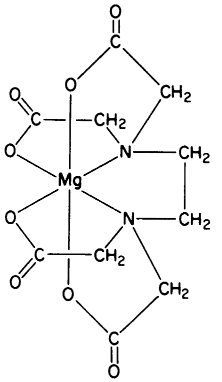


Figure 2.1 Magnesium complex of the anion from ethylenediaminetetraacetic acid (EDTA)

2.3 Hard and Soft Acids and Bases (Pearson)

While the simple Lewis theory enables qualitative predictions to be made about complex formation, it is the quantitative aspects of the theory that are lacking. Ideally, if it were possible to construct scales of Lewis acid and Lewis base strengths, the relative stabilities of all acid–base complexes could be predicted, and we would be in a position to predict the direction of chemical reactions of the type

$$\mathrm{ML} + \mathrm{L}' \rightleftharpoons \mathrm{ML}' + \mathrm{L}$$

where L and L′ represent competing ligands. However, while the strengths of bases can frequently be quantified with respect to a particular acid, the order of base strength so obtained is not independent of the acid. A useful series of base strengths can be constructed for aqueous solution by using the proton as reference acid, but a scale of Lewis acid strengths has not been constructed, partly because so many Lewis acids react with water. Broadly speaking it is found that acids as well as bases can be classified under two different headings. For the proton as reference acid, it is found that those bases containing nitrogen, oxygen, or fluorine as the donor atom are stronger than those containing phosphorus, sulphur, or iodine. The reverse is true for acids such as Hg^+, Cu^+, and Pt^{2+} which give more stable complexes with, for example, phosphorus ligands than with nitrogen ligands. The terms *hard* and *soft* have been used to describe these two classes of acids and bases. Donors having high electronegativity, low polarisability, and high resistance to oxidation are described as hard, while donors having low electronegativity, high polarisability, and which are readily oxidised are described as soft. The acids are then classified simply according to whether they prefer hard or soft bases. Some examples of hard and soft acids and bases are listed in Table 2.4. Some acids and bases can be considered as borderline cases; bases in this category include Br^-, py, and N_2, while Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, GaH_3, and BMe_3 can be considered as borderline acids.

Although we have still not quantified our acid–base approach, we have clarified some of the anomalies found in the simple Lewis approach. The fact that hard acids prefer to bind to hard bases, and soft acids to soft bases, is not only useful in prediction but also in the correlation of inorganic facts.

TABLE 2.4 HARD AND SOFT ACIDS AND BASES

Hard		Soft	
Acids	Bases	Acids	Bases
$BeMe_2$	H_2O	BH_3	R_2S
$AlCl_3$	R_2O	$GaCl_3$	R_3P
BF_3	ROH	Cu^+	R_3As
H^+	NH_3	Ag^+	CO
Be^{2+}	NR_3	Au^+	RNC
Mn^{2+}	N_2H_4	Hg^+	C_2H_4
Sc^{3+}	OH^-	Pd^{2+}	C_6H_6
Cr^{3+}	F^-	Pt^{2+}	CN^-
Fe^{3+}	Cl^-	Hg^{2+}	1^-
Th^{4+}	CH_3COO^-	Pt^{4+}	SCN^-

The factors affecting the hardness of acids and bases are size, charge or oxidation state, electronic structure, and the nature of attached groups already present. With metal ions, hardness as acids increases with oxidation state. In their zero oxidation states, metals behave as soft acids and are stabilised by carbon monoxide and phosphine ligands. For a given oxidation state, the transition metal ions become softer as we cross the series, all the really soft acceptor ions having at least a half-filled outer d shell. Indeed, the soft character of metals such as Cu(I), Ag(I), Pt(II), Pd(II), and Rh(I) appears to depend on the availability of metal d electrons for dative π-bonding with carbon ligands such as carbon monoxide and olefins. These ligands form stable complexes only with soft acids, and this fact can be used as a test for softness. In boron chemistry we see from Table 2.4 that when fluorine is bonded to boron(III) we have a hard acid, but when hydrogen is so bonded a soft acid results. This we might expect since the amount of positive charge on the boron atom is greater when it is bonded to the electronegative fluorines than when it is bonded to the soft hydride ions. Carbon monoxide thus forms borine carbonyl, BH_3CO, in its reaction with diborane but has no effect on boron trifluoride.

A slightly different method of classifying acids and bases was introduced somewhat earlier by Ahrland, Chatt, and Davies. From a survey of the relative affinities of ligand atoms for metal ions, they concluded that metals could be divided into two classes. In *class a* are metals that form more stable complexes with ligands whose donor atoms are first-row elements (N, O, F), while in *class b* are metals that prefer to bond to ligands having second-row elements as donor atoms (P, S, Cl). Examples of metals falling in these two classes are shown in Table 2.5; acceptors that do not show predominantly either character are listed as borderline. The degree of b-character of a metal is dependent on its oxidation state. In low oxidation states where the metals possess nonbonding electrons capable of being used in $d_\pi - p_\pi$ or $d_\pi - d_\pi$ bonding with the ligands, the degree of b-character is greatest. Ligands such as CO, C_2H_4, and RNC only co-ordinate strongly with class-b

TABLE 2.5 CLASS a AND b ACCEPTORS

Class a	Class b
H, Li, Na, K, Rb, Cs	Rh, Ir
Be, Mg, Ca, Sr, Ba	Pd, Pt
Sc, Y, Lanthanides	Ag, Au
Actinides, Ti, Zr, Hf	Hg
V, Nb, Ta, Cr, Zn	
Al, Ga, In	
Si, Ge, Sn	
Borderline behaviour	
Mo, W, Mn, Tc, Re, Fe, Ru, Os, Co, Ni, Cu, Cd, Tl, Pb, Bi, Te, Po	

metals and the borderline acceptors when their b-character is enhanced by a low oxidation state. The similarities between the 'a' and 'hard' acceptors and 'b' and 'soft' acceptors can be further seen by comparison of the data in Tables 2.4 and 2.5.

3 The Preparation and Stability of Complex Compounds

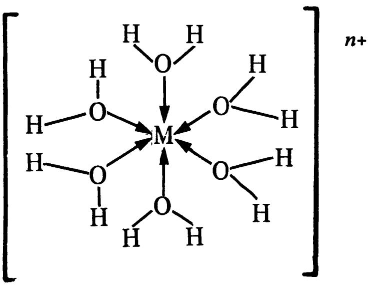
3.1 The Preparation of Complexes

A wide variety of methods are used in synthesising co-ordination compounds; we shall summarise here only the more general methods. In view of its ubiquitous nature, water has most frequently been used as a solvent for preparing complex compounds. However, since all cations form some kind of bond with water molecules, it is not often appropriate to consider the water as an inert solvent that plays no part in the chemical reaction. For this reason we shall now consider the species $M(H_2O)_6{}^{n+}$, known as the *hexaquo-ion,* and see how its reactions lead to other complex cations.

3.1.1 The Hexaquo-ion; Aqueous Substitution Reactions

For the alkali metal cations, and to some extent the alkaline earth metal cations, the bonding to water molecules is of a relatively weak ion–dipole type. That is to say, the cation is attracted electrostatically to the negative end of the water dipole. For many chemical reactions these cations can be regarded as reacting in the form of unsolvated species since, although a co-ordination sphere of water molecules surrounds each cation, these molecules do not take part in the overall reaction. However, with triply charged cations and transition metal cations, the water molecules are held by much stronger bonding forces, and these bonded molecules cannot be ignored if we are to understand the processes occurring in aqueous solution. In general, octahedral (or distorted octahedral) complexes are formed when water molecules co-ordinate to di- and tri-positive transition metal ions of the first transition series, so we may represent the hexaquo-ion formation as

$M^{n+} + 6H_2O \rightarrow$



There is much spectroscopic evidence for the presence of these ions in solution, and many have been shown by X-ray crystallography to occur as discrete species in the solid phase. We saw in chapter 1 that the alums contain the $[Al(H_2O)_6]^{3+}$ species, and many apparently simple salts such as $NiSO_4.7H_2O$ actually contain complex aquo-ions in the solid state, that is $[Ni(H_2O)_6]^{2+}$ (the extra water molecule is held by hydrogen bonds to the oxygen atoms of sulphate ions and the hydrogen atom of co-ordinated water molecules).

Two very important reactions of the hexaquo-ion, namely substitution and acid–base reactions, lead to new complex compounds. The most frequently used preparative method is that of substitution at the hexaquo-ion. The replacement of water molecules by other ligands occurs in a stepwise fashion and may or may not be complete in the presence of excess of the ligand. Thus, if we add an aqueous solution of nickel(II) bromide to an excess of concentrated aqueous ammonia, the hexamminenickel(II) ion is formed and this precipitates as a violet crystalline salt with the bromide ions

$$[Ni(H_2O)_6]^{2+} + 6NH_3 \rightarrow [Ni(NH_3)_6]^{2+} + 6H_2O$$

However, with copper(II) salts complete substitution of the water molecules with ammonia does not occur in aqueous solution. Instead the stepwise replacement occurs, and in concentrated ammonia solutions approximately four of the water molecules have been replaced

$$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$$

If a solution of copper(II) sulphate is added to an excess of concentrated aqueous ammonia, the colour changes from blue to violet indicating that replacement of water molecules has occurred. If we now induce precipitation from this solution by the addition of ethanol, the precipitate does not have quite the composition $[Cu(NH_3)_4(H_2O)_2]SO_4$ expected. Instead the precipitate has the formula $[Cu(NH_3)_4(H_2O)]SO_4$ in which the co-ordination geometry is that of a square-based pyramid with the copper atom slightly out of the plane of the four nitrogen atoms. This is an example of a rather general point, namely, complexes that can be isolated from solution are not necessarily the same as the species present in the solution. The stepwise replacement of ligands will be discussed, along with the stability constants of the various species, later in this chapter. For the present, the failure of $[Cu(H_2O)_6]^{2+}$ to form $[Cu(NH_3)_6]^{2+}$ in aqueous solution can be attributed to the high concentration of water in the solution which is competing with the ammonia for the co-ordination sites. Other species such as $[Cu(NH_3)(H_2O)_5]^{2+}$, $[Cu(NH_3)_2(H_2O)_4]^{2+}$, and $[Cu(NH_3)_3(H_2O)_3]^{2+}$ will also be present in such solutions, although in strong ammonia their concentrations will be low and species such as $[Cu(NH_3)_5(H_2O)]^{2+}$ will become more important. The hexamminecopper(II) complexes such as $[Cu(NH_3)_6]Br_2$ are readily prepared by using liquid ammonia. Many neutral ligands are organic molecules rather insoluble in water; preparations then involve the dissolution of the ligand in alcohol, as in the preparation of bipyridyl complexes

$$[Fe(H_2O)_6]^{2+} + 3\text{bipy} \rightarrow [Fe(\text{bipy})_3]^{2+} + 6H_2O$$

Substitution of the water molecules in aquo-ions by anions can lead to neutral and to anionic complexes. The acetylacetonates of the transition elements can frequently be prepared in aqueous solution by using a metal salt, acetylacetone, and a weak base (which deprotonates the diketone without precipitating the hydroxide of the metal), for example

$$[Cr(H_2O)_6]^{3+} + 3(\text{acac})^- \rightarrow Cr(\text{acac})_3 + 6H_2O$$

Compounds of this type frequently precipitate from water or can be crystallised from water. Anionic complexes tend to be more soluble but they will usually crystallise from solutions concentrated in the ligand anion, or they can be precipitated by ethanol. The preparation of potassium cyanoferrate(II) is thus achieved by reaction of an aqueous solution of iron(II) sulphate with an excess of hot potassium cyanide solution; cooling of the mixture causes the product to crystallise.

$$[\mathrm{Fe(H_2O)_6}]^{2+} + 6\mathrm{CN}^- \rightarrow [\mathrm{Fe(CN)_6}]^{4-} + 6\mathrm{H_2O}$$

As far as substitution reactions are concerned, complexes can be divided into two classes. *Labile* complexes are those that undergo rapid substitution reactions, while *inert* complexes undergo such reactions relatively slowly. In the examples we have seen so far, the displacement of water molecules from the copper(II) ion by ammonia occurs almost instantaneously on mixing since the copper(II) ion forms labile complexes. However, with the hexaquochromium(III) ions the substitution occurs slowly, and several hours may be required in a preparation from the 'inert' chromium(III) ion. It is important to realise that these terms refer to kinetic stability only, that is rate of reaching equilibrium conditions, and that they must not be confused with thermodynamic stability which is concerned with the concentrations of species when equilibrium has been reached. The kinetics and mechanisms of substitution reactions are discussed in chapter 8. Obviously preparative methods for complexes do depend upon the lability of the compounds as well as on the thermodynamics of the reaction (denoted by the stability constants of the complexes).

Substitution reactions are of course not confined to aquo-ions although many of them are most conveniently carried out in aqueous solution. Thus the pale yellow Zeise's salt is prepared (as a monohydrate) by shaking a solution of potassium tetrachloroplatinate(II) with ethylene

$$[\mathrm{PtCl_4}]^{2-} + \mathrm{C_2H_4} \rightarrow [\mathrm{PtCl_3(C_2H_4)}]^- + \mathrm{Cl}^-$$

Substitution of nitro groups in hexanitrocobaltate(III) ions by ethylenediamine can be achieved by using aqueous solutions of the reagents at 70°

$$[\mathrm{Co(NO_2)_6}]^{3-} + 2\mathrm{en} \rightarrow cis\text{-}[\mathrm{Co(NO_2)_2(en)_2}]^+ + 4\mathrm{NO_2}^-$$

the brown *cis*-isomer precipitates from the solution on cooling. Substitution *by* water molecules (rather than *of* water molecules) is an important type of reaction known as *aquation.* Two kinetically well-studied aquation reactions are those of the inert chloropentamminecobalt(III) and trisoxalatochromate(III) ions

$$[\mathrm{Co(NH_3)_5Cl}]^{2+} + \mathrm{H_2O} \rightarrow [\mathrm{Co(NH_3)_5(H_2O)}]^{3+} + \mathrm{Cl}^-$$
$$[\mathrm{Cr(C_2O_4)_3}]^{3-} + 2\mathrm{H_2O} \rightarrow [\mathrm{Cr(C_2O_4)_2(H_2O)_2}]^- + \mathrm{C_2O_4}^{2-}$$

Sometimes a particular complex ion that is known to be formed in solution cannot be precipitated or crystallised from the solution by ordinary techniques. This is often the situation in substitution reactions in which two or more complex species may be present in solution and the required complex is more soluble than, or present in smaller amounts than, other complex species. In these cases we must increase the lattice energy effects of the required complex. A general method of isolation of such species is to use a precipitating ion of approximately the same size as the complex ion (usually large) and of equal but opposite charge. In the reaction of potassium cyanide with nickel(II) salts the species $[\mathrm{Ni(CN)_4}]^{2-}$ and $[\mathrm{Ni(CN)_5}]^{3-}$

are formed in solutions of high cyanide concentration. The predominating $[Ni(CN)_4]^{2-}$ crystallises readily as the orange potassium salt $K_2Ni(CN)_4.H_2O$. The trivalent anion will crystallise if a large trivalent cation is used; for example, with $[Cr(en)_3]^{3+}$ the salt $[Cr(en)_3][Ni(CN)_5].1.5H_2O$ is obtained.

This method is frequently of use in the stabilisation of ions of unusual co-ordination number. The unusual hexachloro-complexes of Cr^{III}, Mn^{III}, and Fe^{III} can be stabilised with the tris(propylenediamine)cobalt(III) cation, giving stable solids $[Co(pn)_3][MCl_6]$. Elements that normally form hexachloro-species can similarly have the five-co-ordinate species stabilised, for example $CuCl_5{}^{3-}$ by $[Cr(NH_3)_6]^{3+}$, $VCl_5{}^-$ by $PCl_4{}^+$, and $GeF_5{}^-$ by $[AsPh_4]^+$.

3.1.2 The Hexaquo-ion; Lowry–Brönsted Acidity

The second important reaction of aquo-ions is their Lowry–Brönsted acidity. Their power to act as proton donors according to the equation

$$[M(H_2O)_6]^{n+} + H_2O \rightleftharpoons [M(H_2O)_5(OH)]^{(n-1)+} + H_3O^+$$

varies widely; however, the presence of this equilibrium must always be remembered even if the equilibrium constant for the forward reaction is small, since addition of a base will remove H_3O^+ and encourage the hydrolysis reaction. In general terms, the greater the charge on the aquo-ion the greater its acidity. While dipositive transition metal ions are only weakly acidic, the tripositive ions are strong acids; ions of the type $[M(H_2O)_6]^{4+}$ are not formed by elements in the first transition series because they are too strongly acidic and undergo hydrolysis. Whilst a knowledge of this hydrolytic reaction is not of great use in preparing complexes, its importance lies in informing us which complex salts may be difficult or impossible to prepare in aqueous solution. Let us exemplify these statements by considering the aqueous chemistry of iron. The pale violet $[Fe(H_2O)_6]^{3+}$ undergoes the following hydrolytic equilibria to give hydroxo-species which are yellow because of a charge-transfer absorption that tails into the visible

$$\begin{aligned}
&[Fe(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+} + H_3O^+ \\
&\qquad\qquad\qquad\qquad\qquad\qquad (K_1 = 10^{-3.05}) \\
&[Fe(H_2O)_5(OH)]^{2+} + H_2O \rightleftharpoons [Fe(H_2O)_4(OH)_2]^{+} + H_3O^+ \\
&\qquad\qquad\qquad\qquad\qquad\qquad (K_2 = 10^{-3.26})
\end{aligned}$$

These solutions are thus strongly acidic; we can write the pK values for these equilibria as 3.05 and 3.26 respectively (where $pK = -\log_{10}K$). Any attempt to raise the pH above 2 causes these reactions to proceed to the right, and eventually, in the final equilibrium, $Fe(H_2O)_3(OH)_3$ [probable composition $FeO(OH)aq$] precipitates. Thus the addition of sodium carbonate solution to an iron(III) chloride solution does not result in the formation of iron(III) carbonate but rather in the precipitation of the 'hydroxide' with evolution of much carbon dioxide. Similarly, if magnesium ribbon is used in place of sodium carbonate, the solvated protons are removed by the reaction.

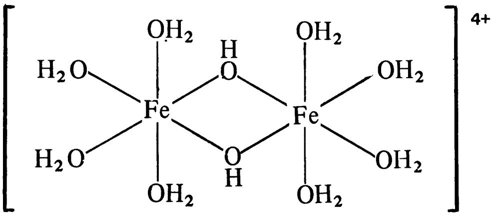
$$2H_3O^+ + Mg \rightarrow Mg^{2+} + H_2 + 2H_2O$$

effervescence occurs, hydrogen is evolved, and the 'hydroxide' eventually precipitates. On the other hand, the addition of noncomplexing acids, such as

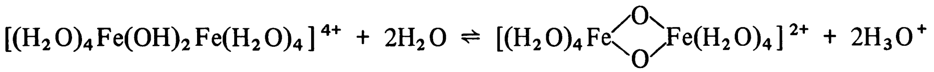
HNO_3 and $HClO_4$, to these partially hydrolysed solutions causes the re-formation of the violet $[Fe(H_2O)_6]^{3+}$ ion. In addition to the mononuclear hydroxo-species, the formation of binuclear cations occurs by the *olation* reaction

$$2[Fe(H_2O)_6]^{3+} + 2H_2O \rightleftharpoons [Fe_2(H_2O)_8(OH)_2]^{4+} + 2H_3O^+ \quad (K = 10^{-2.91})$$

This binuclear species, in which the iron atoms are bridged by OH groups (called *ol* bridges), has the structure



In the presence of base, further proton donation by this ion, followed by olation, leads to larger aggregates until eventually colloidal gels are formed and the iron(III) 'hydroxide' precipitates. The formation of oxo bridges, known as *oxolation,* is probably an important process in this aggregation



$$[(H_2O)_4Fe(OH)_2Fe(H_2O)_4]^{4+} + 2H_2O \rightleftharpoons [(H_2O)_4Fe(O)_2Fe(H_2O)_4]^{2+} + 2H_3O^+$$

The exact nature of these species in solution is not known with certainty; for example, the binuclear iron species may be oxo-bridged, that is $[(H_2O)_5FeOFe(H_2O)_5]^{4+}$. However, the general ideas of olation and oxolation are useful concepts in understanding the aggregation of aquo-ions.

Aqueous solutions of iron(II) salts are hardly acidic ($K_1 = 10^{-9.5}$); iron(II) carbonate can be precipitated from them by the addition of sodium carbonate. The slight acidity of other divalent cations frequently results in the formation of *basic salts.* Thus nickel(II), cobalt(II), and copper(II) salts give basic carbonates unless a high pressure of carbon dioxide is maintained above the solutions. Basic salts frequently precipitate also when strong alkalis such as sodium hydroxide are added to solutions of transition metal cations, especially when the latter are in excess. For example, treatment of copper(II) sulphate solution with a little dilute sodium hydroxide solution results in the precipitation of basic sulphates having a composition that varies depending on the conditions used, that is concentrations of solutions and relative concentrations of the two reagents. Once the initial stage in the stepwise hydrolysis of these cations has proceeded, olation can occur and aggregates are formed that are large enough to precipitate with the sulphate anions. A typical product thus might be $[Cu(OH)(H_2O)_5]_2SO_4$ which in basic salt nomenclature would be written $Cu(OH)_2.CuSO_4.10H_2O$.

3.1.3 Preparation of Complexes by Direct Reaction

In theory this is the simplest method for preparing complexes; it is the reaction of a Lewis acid with a Lewis base. The reactions we have already seen indicate that since water is a base it is in competition with any other base we add for the acidic site.

Most 'direct' acid–base reactions are therefore carried out in the complete absence of water, that is in the gas phase, or in an inert solvent such as a hydrocarbon, or even by direct mixing if one or both of the reagents are liquid. Such methods frequently necessitate the use of high-vacuum apparatus or dry-box techniques.

When both reagents are gaseous, a carefully controlled flow of each gas is passed into a large vessel. With boron trifluoride and trimethylamine the product is deposited as a white powder

$$BF_3 + NMe_3 \rightarrow BF_3.NMe_3$$

More usually, at least one reagent is in the liquid or solid state, and then an inert solvent is used as diluent. Thus the trimethylamine adduct of boron trichloride is prepared by mixing the reagents in benzene from which it precipitates. Inert organic solvents such as hydrocarbons and halogenated hydrocarbons are widely used because they frequently dissolve both the acceptor (for example, covalent halides such as $SnCl_4$, VCl_4, and $TiCl_4$) and the donor (wide variety of organic ligands) and yet cause precipitation of the complexes, which often have polymeric structures. Just a few examples will suffice here; many others occur throughout this book.

$$VCl_4 + 2py \xrightarrow[-20^\circ]{\text{toluene}} VCl_4.2py$$

$$SnCl_4 + 2Et_2O \xrightarrow{\text{benzene}} SnCl_4.2(OEt_2)$$

$$WOCl_4 + \text{THF} \xrightarrow{\text{dichloromethane}} WOCl_4.\text{THF}$$

Often the ligand itself conveniently serves as the solvent, and the complex is obtained by evaporation of the solvent. For example, ammines are prepared by condensing liquid ammonia on to a metal salt and then letting the ammonia (b.p. −33°) evaporate. Many ammonia complexes cannot be prepared in water because of the precipitation of metal hydroxides. Iron(II) chloride thus yields the hydroxide with aqueous ammonia whereas with liquid ammonia a series of ammoniates is formed of which the stable species at room temperature is the hexammine

$$FeCl_2 + 6NH_3 \rightarrow [Fe(NH_3)_6]Cl_2$$

Ammonia, like water, is a protonic solvent; in the same way that hydrolysis occurs in water, so ammonolysis occurs in ammonia. The more covalent halides thus do not form simple ammoniates but rather ammonolytic derivatives, for example

$$VBr_3 + 7NH_3 \rightarrow [V(NH_3)_5(NH_2)]Br_2 + NH_4Br$$
$$TiCl_4 + 6NH_3 \rightarrow TiCl(NH_2)_3 + 3NH_4Cl$$

Other ligands that react directly with Lewis acids include aliphatic amines, hydrazines, nitriles, alcohols, ethers, ketones, and organic sulphides. Again examples from the first transition series illustrate the types of complex formed

$$CoCl_2 + 6N_2H_4 \rightarrow [Co(N_2H_4)_6]Cl_2$$
$$VBr_3 + 3MeCN \rightarrow VBr_3(MeCN)_3$$
$$CoBr_2 + 2(acacH) \rightarrow CoBr_2(acacH)_2$$

3.1.4 Oxidation – Reduction Reactions

So far we have used examples in which the oxidation state of the metal remains unchanged throughout the preparations. However, many ligands can act as reducing agents, and for some metals stabilisation of high oxidation states is achieved by co-ordination. The most celebrated example is in cobalt chemistry. Here the 'simple' salts of cobalt(II) are stable while the 'simple' cobalt(III) salts are oxidising agents in aqueous solution; that is, with water as the ligand the cobalt(II) state is stabilised. However, with nitrogen ligands the cobalt(III) state is stabilised preferentially to the divalent state. In the preparation of cobaltammines therefore a cobalt(II) salt in aqueous ammonia is oxidised by, for example, bubbling air through the mixture. By use of cobalt(II) chloride, ammonium chloride, and a charcoal catalyst, the orange hexammine is obtained.

$$4[Co(H_2O)_6]Cl_2 + 4NH_4Cl + 20NH_3 + O_2 \rightarrow 4[Co(NH_3)_6]Cl_3 + 26H_2O$$

In the absence of charcoal, and with hydrogen peroxide instead of air, the aquopentamminecobalt(III) salt is formed; this is readily converted into the red chloropentamminecobalt(III) chloride by treatment with concentrated hydrochloric acid

$$2[Co(H_2O)_6]Cl_2 + 2NH_4Cl + 8NH_3 + H_2O \rightarrow 2[Co(NH_3)_5(H_2O)]Cl_3 + 12H_2O$$

$$[Co(NH_3)_5(H_2O)]Cl_3 \rightarrow [Co(NH_3)_5Cl]Cl_2 + H_2O$$

It is particularly useful to start with cobalt(II) salts because cobalt(II) complexes being labile undergo rapid substitution reactions whereas cobalt(III) complexes are inert. The cobalt(III) complexes are thus produced by substitution of ligand molecules for co-ordinated water molecules around cobalt(II) followed by oxidation of the cobalt(II) ammine to a cobalt(III) ammine.

Preparative reactions in which the transition element is reduced are somewhat more common. Frequently the ligand itself is the reducing agent. In the preparation of the *cis*- and *trans*-isomers of potassium dioxalatodiaquochromate(III), potassium dichromate is reduced with oxalic acid

$$K_2Cr_2O_7 + 7H_2C_2O_4 \rightarrow 2K[Cr(C_2O_4)_2(H_2O)_2] + 6CO_2 + 3H_2O$$

Anhydrous copper(II) chloride is reduced by anhydrous hydrazine with the formation of bis(hydrazine)copper(I) chloride

$$2CuCl_2 + 8N_2H_4 \rightarrow 2Cu(N_2H_4)_2Cl + 2N_2H_4.HCl + 2NH_3 + N_2$$

Even ligands such as aliphatic amines, 2,2′-bipyridyl, pyridine, and nitriles, which one might not consider to be strong reducing agents, often cause reduction of transition metal salts in their higher oxidation states. Therefore, in studying reactions of such ligands, one of the co-ordination chemist's first objectives is to establish the oxidation state of the metal in the product. Vanadium(IV) chloride is especially prone to reduction and gives several interesting five-co-ordinate vanadium(III) compounds when treated with an excess of these ligands, for example $VCl_3(NMe_3)_2$ and $VCl_3(SMe_2)_2$; however, the six-co-ordinate complexes $VCl_3(py)_3$ and $VCl_3(MeCN)_3$ are produced when pyridine or acetonitrile is used as the reductant. Whether or not reduction occurs may depend on the conditions, particularly the temperature at which the reaction is carried out. We saw earlier that at –20° in an inert solvent the vanadium(IV)–pyridine complex $VCl_4(py)_2$ can be isolated; in this preparation the vanadium(IV) chloride is deliberately kept in excess over the reducing ligand. It seems likely that in these reductions the initial step after co-ordination is that of electron transfer to the metal to give a radical anion $(VCl_4\bullet)^-$ and a radical cation $(C_5H_5N\bullet)^+$. In the reductions of tungsten(VI) chloride and tungsten(V) bromide with pyridine, the oxidation product of the pyridine has been identified as the 1-(4-pyridyl)pyridinium ion.

Complexes in which the central metal ion is in an unusually low oxidation state are conveniently prepared in nonaqueous solvents. By virtue of its ability to dissolve the alkali metals as well as many inorganic complexes, liquid ammonia has been extensively used for this purpose. The solvent must be used in a vacuum apparatus to prevent oxidation of the products by the atmosphere, but this proves to be no real hindrance to its use. When potassium tetracyanonickelate(II) is treated with potassium in ammonia, a bright red precipitate forms while the nickel is in excess; this is believed to contain the binuclear nickel(I) anion $[Ni_2(CN)_6]^{2-}$. With excess of potassium, a bulky yellow precipitate of the tetracyanonickelate(0) is obtained.

$$K_2Ni(CN)_4 + 2K \rightarrow K_4Ni(CN)_4$$

Similar low oxidation state cyanides which can be thus prepared include $(NH_4)_4Pd(CN)_4$, $K_4Co(CN)_4$, and $K_6Cr(CN)_6$. In all of these the oxidation state of the metal is formally zero and the compounds do behave as strong reducing agents, being rapidly oxidised in air and liberating hydrogen from water.

Similar low oxidation state complexes containing ligands such as carbon monoxide and phosphines can be prepared by using solutions of alkali metals in ammonia. Such ligands are capable of stabilising the low oxidation states by enabling charge to be transferred from the metal ion to the ligand. Ammonia has been considered incapable of this π-bonding, so it was somewhat surprising to find that reduction of certain metal halides in ammonia produces ammines of metals in their zero oxidation states. Tetrammineplatinum(0) is precipitated as a yellow-white solid when tetrammineplatinum(II) bromide is reduced with potassium in ammonia at the boiling point

$$[Pt(NH_3)_4]Br_2 + 2K \rightarrow Pt(NH_3)_4 + 2KBr$$

Pentammineiridium(0) $Ir(NH_3)_5$ is prepared similarly. These compounds are decomposed thermally to give ammonia and the metals only.

A rather special and recently systematised type of oxidation is the *oxidative addition* reaction of metal complexes having the d^8 configuration. In these reactions the metal increases its oxidation state by two units, that is it assumes a d^6 configuration and its co-ordination number is increased by co-ordination of the constituent parts of the oxidising molecule. The tendency to form stable adducts having the d^6 configuration increases as we descend the group (Figure 3.1) and

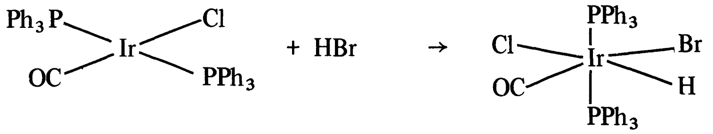
Fe^0	Co^I	Ni^{II}
Ru^0	Rh^I	Pd^{II}
Os^0	Ir^I	Pt^{II}

Figure 3.1 Metals involved in oxidative addition reactions

also as we cross from right to left within group VIII; thus the relative ease of oxidation is

Pt(II) > Pd(II) > Ni(II) ;
Os(0) > Ir(I) > Pt(II)

Vaska's compound *trans*-$[Ir(PPh_3)_2(CO)Cl]$ is particularly versatile. In this, iridium(I) becomes oxidised to iridium(III) as illustrated by the reaction with hydrogen bromide

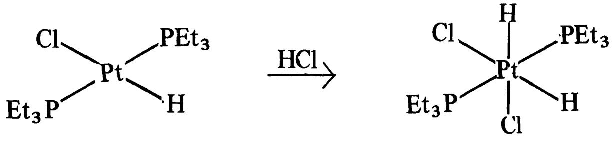


For many molecules, for example O_2, H_2, and SO_2, reversible uptake occurs

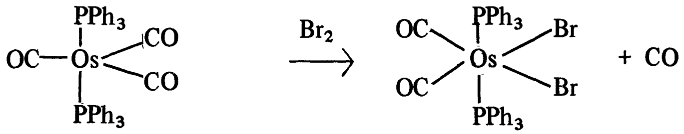
$$Ir(PPh_3)_2(CO)Cl \underset{\text{vacuum}}{\overset{O_2 \text{ in benzene}}{\rightleftharpoons}} O_2Ir(PPh_3)_2(CO)Cl$$

and it is this reversibility of the processes that makes this type of system so useful in organic synthesis. The reverse process is known for obvious reasons as *reductive elimination.*

Platinum(II) complexes resemble those of iridium(I) in going from square to octahedral



but the trigonal bipyramidal osmium(0) complexes dissociate a ligand in changing to octahedrally co-ordinated osmium(II)



3.1.5 *Thermal Decompositions*

When thermally decomposed, many complexes evolve any neutral and volatile ligand molecules in a stepwise fashion; by careful control of the temperature, new complexes can be obtained that may be difficult to prepare by other routes. In the reactions of nickel(II) salts with an excess of nitrogen ligands, complexes of the type $[NiL_6]X_2$ or NiL_4X_2 are commonly produced. By heating these the intermediate complexes NiL_2X_2 and $NiLX_2$ can frequently be isolated. Thus $NiCl_2(NH_3)_2$ is obtained from $[Ni(NH_3)_6]Cl_2$ at 100°, and the decomposition of the nickel(II) bromide–pyridine complex can be illustrated by the scheme.

$$NiBr_2(py)_4 \xrightarrow{140^\circ} NiBr_2(py)_2 \xrightarrow{200^\circ} NiBr_2(py) \xrightarrow{300^\circ} NiBr_2$$

As is usual in thermal dissociation reactions, the co-ordination number of the nickel has remained constant (at six) in these reactions.

The study of these thermal dissociations is greatly aided by the techniques of thermogravimetric analysis (t.g.a.) and differential thermal analysis (d.t.a.). In t.g.a. a crucible containing the complex is attached to one pan of a balance and, by enclosing the crucible in a furnace, the weight of the complex can be recorded as the temperature is increased. The temperatures at which dissociation occurs for the various complexes are thus easily recorded together with the weight of ligand evolved. In d.t.a. two crucibles, one containing the complex and the other a thermally stable reference compound, are heated together in an enclosed space. The temperatures within each crucible are measured continuously, and when dissociation of the complex occurs the temperatures will differ depending on whether the process is exothermic or endothermic. From d.t.a. studies, the temperature and enthalpy of the dissociation are measured.

3.1.6 *Metal Carbonyls and Organometallic Compounds*

Compounds containing metal–carbon bonds have become exceedingly numerous in the last two decades and are now a very important part of co-ordination chemistry. The first metal carbonyl was discovered by Mond in 1890; he obtained nickel carbonyl $Ni(CO)_4$ by the reaction of carbon monoxide with nickel powder at atmospheric pressure and below 100°. This carbonyl is prepared on an industrial scale today in the refining of nickel by using pressures of up to 15MPa and temperatures of up to 150°. The reaction between carbon monoxide and iron or cobalt similarly yields carbonyls directly. For carbonyls of other metals the general preparative route is the reduction of metal halides in a solvent such as ammonia (see section 3.1.4), tetrahydrofuran, or diglyme under a 20–30 MPa pressure of carbon monoxide and at up to 300°. The various reducing agents used include alkali metals, magnesium, aluminium, and aluminium alkyls. We may exemplify these reactions by the preparation of vanadium hexacarbonyl

$$VCl_3 + CO + Na \xrightarrow[100^\circ,\ 25\ MPa]{diglyme} [Na(diglyme)_2]^+[V(CO)_6]^- \xrightarrow{H_3PO_4} V(CO)_6$$

In this reaction, the solvated sodium salt of the hexacarbonylvanadate(–I) ion is first formed, and this is converted into the carbonyl via thermal decomposition of the as yet unisolated $HV(CO)_6$. Carbon monoxide acts both as reducing agent and as ligand when it reacts under conditions of heat and high pressure with rhenium or technetium heptoxides

$$Re_2O_7 + 17CO \longrightarrow Re_2(CO)_{10} + 7CO_2$$

The metal carbonyls thus prepared are the starting point for the preparation of an enormous number and variety of derivatives. Just a few of the reactions of iron pentacarbonyl in Figure 3.2 must suffice to indicate the scope of such reactions.

Organometallic complexes contain metal–carbon σ bonds or metal–carbon π bonds (or both). The simple σ bonded alkyls and aryls MR_x are relatively rare; however, such M–C σ bonds are greatly stabilised if π bonding ligands such as CO, PPh_3, or cyclopentadienyl ($C_5H_5^-$) are present. Many preparative routes are used; three common methods are those involving the use of Grignard reagents,

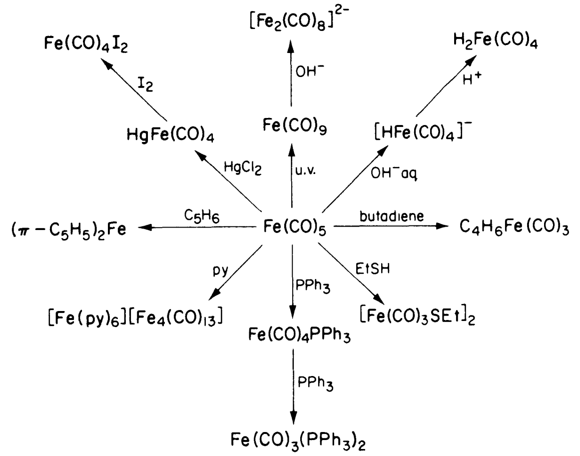
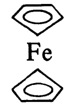


Figure 3.2 Reactions of iron pentacarbonyl

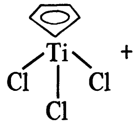
metathesis between an alkyl halide and a sodium carbonylmetallate, and the addition of unsaturated hydrocarbons to complex hydrides, for example

$$(Et_3P)_2PtCl_2 + 2MeMgBr \rightarrow (Et_3P)_2PtMe_2 + MgBr_2 + MgCl_2$$
$$Na[Co(CO)_4] + MeI \rightarrow MeCo(CO)_4 + NaI$$
$$(\pi\text{-}C_5H_5)Fe(CO)_2H + CF_2{=}CF_2 \rightarrow (\pi\text{-}C_5H_5)Fe(CO)_2CF_2CF_2H$$

Complexes with unsaturated hydrocarbons bonded to transition metals are very much more stable and exceedingly numerous. Such complexes may contain, for example, olefins, acetylenes, cyclic unsaturated systems, or allyl groups π-bonded to the metal. We mentioned earlier the first olefin complex prepared, Zeise's salt. Perhaps the most celebrated complex is bis(cyclopentadienyl)iron, called ferrocene. This is an orange crystalline solid with remarkable thermal stability (it boils without decomposition at 230°), and it is not attacked by alkali or concentrated hydrochloric acid. It was the discovery of this compound in 1951 that sparked off the development of the now enormous organic chemistry of the transition metals. Ferrocene contains two cyclopentadienide rings which form a 'sandwich' with the iron atom between them. It is prepared in the laboratory from iron(II) chloride by treatment with sodium cyclopentadienide in tetrahydrofuran or ethylene glycol dimethyl ether

$FeCl_2 + 2C_5H_5Na \rightarrow$  $+ 2NaCl$

This reaction is indeed a general route to π-cyclopentadienyl-metal compounds which may contain up to four cyclopentadienyl rings, for example

$TiCl_4 + \frac{1}{2}Mg(C_5H_5)_2 \rightarrow$  $+ \frac{1}{2}MgCl_2$

$$UCl_4 + 4KC_5H_5 \rightarrow U(C_5H_5)_4 + 4KCl$$

Olefin complexes are usually prepared by the reaction of the olefin with a metal halide or carbonyl. A solvent is usually used but is sometimes unnecessary. Copper(I) halides combine directly with butadiene at −10°, and palladium halides combine with liquid straight-chain olefins at room temperature to give complexes of the formula $[PdCl_2(olefin)]_2$. Substitution by olefins into metal carbonyls can be effected either thermally or photochemically by using ultraviolet irradiation.

$$C_2H_4 + C_5H_5Mn(CO)_3 \xrightarrow{\text{u.v.}} (C_5H_5)Mn(CO)_2(C_2H_4) + CO$$

Complexes of benzene π-bonded to a metal are known as *arene* metal complexes. The carbonyl route is used for their preparation as for olefin complexes, for example

$$C_6H_6 + Mo(CO)_6 \xrightarrow{\text{u.v.}} C_6H_6Mo(CO)_3 + 3CO$$

However, the more commonly applicable route is Fischer's reducing Friedel – Crafts method. In this, the metal halide is reduced with aluminium powder in the presence of the arene ligand and aluminium chloride

$$3CrCl_3 + 2Al + AlCl_3 + 6C_6H_6 \rightarrow 3[Cr(C_6H_6)_2]^+[AlCl_4]^-$$

In this example bis(benzene)chromium, the first arene complex to be prepared, is obtained by reduction of the cation with aqueous sodium dithionite

$$2[Cr(C_6H_6)_2]^+ + S_2O_4^{2-} + 4OH^- \rightarrow 2Cr(C_6H_6)_2 + 2SO_3^{2-} + 2H_2O$$

3.2 The Stability of Complex Ions in Solution

We have already mentioned the need to differentiate between thermodynamic and kinetic stabilities. Indeed the word stability may take on even further connotations; a compound may be thermally stable yet react violently with water at room temperature, that is be hydrolytically unstable. The word 'stable' must always be qualified when talking about a compound; on its own it raises the immediate question: stable to what? In this section we are concerned with the thermodynamic stability of complex ions in solution; that is, the extent to which the complex ion will tend to be formed from, or dissociate into, its component species when the system has reached equilibrium. The kinetic stability of complexes, that is the rate at which the equilibria are reached, will concern us in chapter 8.

3.2.1 Stability Constants

When a metal ion reacts with a ligand in aqueous solution, stepwise replacement of the co-ordinated water molecules by the ligand occurs. Consider a metal ion M (for convenience we shall neglect the charge) and a ligand L. The first step in the replacement of water molecules is represented by

$$[M(H_2O)_n] + L \rightarrow [M(H_2O)_{n-1}L] + H_2O$$

If the equilibrium lies to the right we say a complex has been formed (despite the fact that a complex was already present on the left-hand side of the equation). For convenience such equilibria are usually written as

$$M + L \rightarrow ML$$

If we assume activity coefficients of unity, for this equilibrium we can write

$$K_1 = \frac{[\mathrm{ML}]}{[\mathrm{M}]\,[\mathrm{L}]}$$

For the stepwise replacement of further water molecules, we can write the stepwise equilibrium constants as follows

$$\mathrm{ML} + \mathrm{L} \rightleftharpoons \mathrm{ML_2} \qquad K_2 = \frac{[\mathrm{ML_2}]}{[\mathrm{ML}]\,[\mathrm{L}]}$$

$$\mathrm{ML_2} + \mathrm{L} \rightleftharpoons \mathrm{ML_3} \qquad K_3 = \frac{[\mathrm{ML_3}]}{[\mathrm{ML_2}]\,[\mathrm{L}]}$$

$$\mathrm{ML_3} + \mathrm{L} \rightleftharpoons \mathrm{ML_4} \qquad K_4 = \frac{[\mathrm{ML_4}]}{[\mathrm{ML_3}]\,[\mathrm{L}]}$$

These equilibrium constants K_1 to K_4 representing the formation of complexes are called the *stepwise formation constants* or *stability constants.* The numerical values of these constants nearly always decrease in the order $K_1 > K_2 > K_3 > K_4 > K_n$. For any particular reaction we may be more interested in the overall stability constant (denoted by the symbol β), as given by

$$\beta_4 = \frac{[\mathrm{ML_4}]}{[\mathrm{M}]\,[\mathrm{L}]^4}$$

Thus an alternative way of expressing formation constants is to represent the equilibria as

$$\mathrm{M} + \mathrm{L} \rightleftharpoons \mathrm{ML} \qquad \beta_1 = \frac{[\mathrm{ML}]}{[\mathrm{M}]\,[\mathrm{L}]}$$

$$\mathrm{M} + 2\mathrm{L} \rightleftharpoons \mathrm{ML_2} \qquad \beta_2 = \frac{[\mathrm{ML_2}]}{[\mathrm{M}]\,[\mathrm{L}]^2}$$

$$\mathrm{M} + 3\mathrm{L} \rightleftharpoons \mathrm{ML_3} \qquad \beta_3 = \frac{[\mathrm{ML_3}]}{[\mathrm{M}]\,[\mathrm{L}]^3}$$

and so on. It is readily apparent that

$$\beta_4 = K_1 K_2 K_3 K_4$$

(substitute the values for K_1 to K_4 and multiply out if you do not see this immediately), or more generally that

$$\beta_n = \frac{[ML_n]}{[M]\,[L]^n}$$

These terms β_n are called the *overall formation constants* or *stability constants.* Some numerical values of stability constants are listed in Table 3.1. Since these values occur over a very wide range, they are normally reported on a logarithmic scale. A large value of the stability constant for a particular complex indicates that the concentration of the complex is much greater than the concentrations of the species of which it is composed. An overall stability constant of around 10^8 or greater normally indicates the formation of what we would regard as a thermodynamically stable complex (the β values given in Table 3.1 are the products of the K values listed, that is β_4 for Cu^{2+}, β_6 for Ni^{2+}, etc.). The blank spaces in Table 3.1 are those for which the stability constants would be very low or negative; for example, in the formation of $[Cu(NH_3)_5(OH_2)]^{2+}$ $\log K_5$ is approximately –0.5.

TABLE 3.1 STEPWISE AND OVERALL STABILITY CONSTANTS

M	L	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$	$\log K_5$	$\log K_6$	$\log \beta$
Cu^{2+}	NH_3	4.17	3.53	2.88	2.05			12.6
Ni^{2+}	NH_3	2.80	2.24	1.73	1.19	0.75	0.03	8.7
Ag^+	NH_3	3.14	3.82					7.0
Hg^{2+}	CN^-	18.00	16.70	3.83	2.98			41.5
Hg^{2+}	I^-	12.87	10.95	3.67	2.37			29.9
Cu^{2+}	en	10.55	9.05					19.6
Ni^{2+}	en	7.45	6.23	4.34				18.0

For the simple substitution reactions in which no change of stereochemistry occurs, a steady decrease in the stepwise stability constants in any particular system, for example Ni^{2+}–NH_3, is generally observed. This decrease is to be expected solely on statistical grounds; the probability of exchanging a water molecule is greater in $[Ni(H_2O)_6]^{2+}$ than in $[Ni(H_2O)_5(NH_3)]^{2+}$, and so on. Other factors such as steric effects (the ligand being larger than a water molecule) are also important. When a stereochemical change occurs on substitution, a sudden change in the values of the stability constants may occur, and the magnitude may even increase in going from K_n to K_{n+1}. Thus the sudden drop from K_2 to K_3 for Hg^{2+} complexes with halide and cyanide ions can be attributed to a change from linear HgX_2 to tetrahedral $[HgX_3(H_2O)]^-$with consequent change in hybridisation of the mercury from sp to sp^3. The increase in stability constant from K_1 to K_2 in the Ag^+–NH_3 system may indicate that a nonlinear species $[Ag(NH_3)(H_2O_n]^+$ becomes linear in $[Ag(NH_3)_2]^+$. As long as n is greater than unity this reaction, that is

$$[Ag(NH_3)(H_2O)_n]^+ + NH_3 \rightleftharpoons [Ag(NH_3)_2]^+ + nH_2O$$

proceeds from left to right with an increase in entropy and consequently an increase in the equilibrium constant K_2.

So far we have used concentrations in our expressions for equilibrium constants, but this would be quantitatively acceptable only in very dilute solution. If a stability constant is measured by determining the concentrations of the various species in the expression for the equilibrium constant, it is called a *concentration constant.* Concentration constants are quantitatively valid only under the conditions at which they were measured, but they are very useful in a semiquantitative way. Stability constants expressed in terms of activities are called *thermodynamic constants.* In very dilute solutions concentrations are equal to activities, so thermodynamic constants could in theory be measured in such solutions. However, this is not convenient in practice so these are usually measured by determining the stability constants in a series of solutions containing different concentrations of a noncomplexing electrolyte such as sodium perchlorate. The thermodynamic constants are then obtained by extrapolation to zero ionic strength.

3.2.2 Stability Trends

A large amount of stability constant information is to be found in *Stability Constants* and *Stability Constants Supplement No. 1* (Special Publications Nos. 17 and 25 of The Chemical Society, London, 1964 and 1971). We shall now examine some of the trends to be found in stability constants, and the reasons for them.

If we use a simple electrostatic model for a complex compound we can fairly readily understand some of the trends in stabilities. Since the formation of a complex may be regarded as an interaction between a cation and either an anion or the negative end of a dipole, we should expect the magnitudes of the charges to be important as well as the sizes of the interacting species. Obviously, the smaller the interacting species or the larger the charge on them, the greater the electrostatic attraction and the more stable the resultant complex. It should be noted that this model is more appropriate to hard acids and bases; for soft acids and bases, other factors such as covalent bonding are important. Thus, for cations and hard bases the stability constants of complexes of a base with a metal increase as the oxidation state of the metal increases (for example, the stabilities of EDTA complexes in Table 3.2). In a series of ions of approximately the same ionic radius, the stability constants with a given ligand decrease as the charge decreases, for example $Th^{4+} > Y^{3+} > Ca^{2+} > Na^+$. Instead of just the charge or size, it is usual to talk about the ratio of charge to radius or the ionic potential of ions. For a given ligand and divalent ions of the first transition series, the stability constants roughly follow the order of the ionic potentials (and sizes) of the metal ions, that is

$$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$$

This 'natural' order is often known as the Irving–Williams order. Copper(II) does not fit well into the series since it is reluctant to co-ordinate a fifth or sixth ligand very strongly. This order of size of the metal ions and the stability of the various complexes is more readily understood in terms of ligand field theory (chapter 5).

Entropy effects appear to make a major contribution to the stabilities of complexes. In order to understand this we must remember that the equilibrium constant is related to the standard free energy of a reaction by the equation

$$\Delta G^\circ = -RT \ln K$$

and that the free-energy change is related to the enthalpy and entropy changes by

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Thus we can see that the stability constant for the formation of a complex depends on the enthalpy and entropy changes in the complexing process. Enthalpy changes in reactions of the type

$$[M(H_2O)_6]^{n+} + xL \rightleftharpoons [M(H_2O)_{6-x}L_x]^{n+} + xH_2O$$

are usually small, and entropy contributions may become significant. We saw earlier some examples of this affecting the stepwise stability constants when a stereochemical change occurs during the reaction. If, during a substitution reaction, we produce more free molecules than we started with, the increased randomness of the system results in an increase of entropy. This occurs in substitution reactions in which a unidentate ligand is replaced by a chelating ligand; the extra stability of chelate complexes over complexes of unidentate ligands having the same donor atoms is known as the *chelate effect.* In Table 3.1 we can see the stability constants for ethylenediamine complexes. The reactions

$$[Cu(H_2O)_6]^{2+} + 3en \rightleftharpoons [Cu(en)_3]^{2+} + 6H_2O$$
$$[Ni(H_2O)_6]^{2+} + 3en \rightleftharpoons [Ni(en)_3]^{2+} + 6H_2O$$

proceed from left to right with a net production of three extra free molecules; thus they have a positive entropy change. This multiplied by the absolute temperature T gives a substantial value of $T\Delta S^\circ$ and, because of the minus sign in front of this term, a negative contribution to ΔG° and hence a positive contribution to the equilibrium constant K. Therefore, not only do we expect the stability constants of these complexes to exceed those of the corresponding ammonia complexes, but also that reactions of the type

$$[Ni(NH_3)_6]^{2+} + 3en \rightleftharpoons [Ni(en)_3]^{2+} + 6NH_3$$

will be thermodynamically favourable. In this particular system it has been shown experimentally that the substitution reaction occurs with a large entropy change accompanied by a substantial change in enthalpy.

The stability of complexes containing chelate rings increases as the number of rings increases, but decreases as the ring size increases from five to seven-membered. Complexes containing eight-membered ring systems are unknown. Because of the stability of chelates they find many uses in industrial and analytical chemistry. The most widely used chelating agent is ethylenediaminetetraacetic acid (EDTA). The disodium salt of this acid reacts with metal ions to form very stable complexes containing up to five five-membered rings (Figure 2.1). The ligand is normally hexadentate, so 1 : 1 complexes are formed, that is, six water molecules are replaced by only one EDTA anion, resulting in a large entropy increase

$$[M(H_2O)_6]^{2+} + \text{EDTA}^{4-} \rightleftharpoons [M(\text{EDTA})]^{2-} + 6H_2O$$

Table 3.2 shows the magnitude of the stability constants of some metal ions with EDTA. Commercially EDTA is known as Complexone or Sequestrene because of its ability to reduce the concentration of simple (that is hydrated) metal ions in solution by forming stable complexes. It can be used in water-softening, for example,

TABLE 3.2 STABILITY CONSTANTS OF EDTA COMPLEXES

Metal ion	$\log K_1$ for EDTA
Ag^+	7.3
Ca^{2+}	10.8
Cu^{2+}	18.7
Ni^{2+}	18.6
Fe^{2+}	14.3
Fe^{3+}	25.1
Co^{2+}	16.1
Co^{3+}	36.0
V^{2+}	12.7
V^{3+}	25.9

leaving no free calcium or magnesium ions to precipitate with soaps. In volumetric analysis a large number of metal ions can be titrated directly with EDTA using indicators that form weaker complexes with metals than does EDTA, and that possess a colour in the free state different from that in the complexed state.

Further reading

For the preparation of any specific complex the reader should consult *Inorganic Syntheses,* McGraw-Hill, New York, vol. I (1939) – vol. XIV (1973). More general reviews appear in *Preparative Inorganic Reactions,* Interscience, New York, vol. I (1964) – vol. 5 (1968). Brauer's *Handbuch der Praparativen Anorganischen Chemie,* Enke, Stuttgart (1962), will also be found useful.

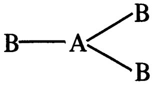
4 Co-ordination Numbers and Stereochemistry

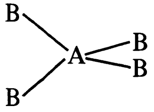
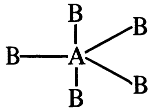
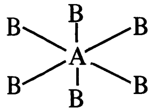
So far we have considered what types of species combine together to form complexes, and how stable the resultant complex may be. We must now consider the various known co-ordination numbers and how (that is in what shape) the ligands are arranged spatially around the central ion. Werner's prediction that certain metals have preferred co-ordination numbers, for example cobalt six and platinum four, and that the ligands surround the metal in a preferred definite shape enabled great advances to be made in the understanding of co-ordination compounds. Today a wide range of physical methods are available for determining the structure of complexes. Of these methods, the most direct is X-ray crystallography by which the positions of the various atoms are located and bond lengths and angles estimated. Other useful but less direct methods include electronic and vibrational spectroscopy, dipole-moment measurements, and magnetic-susceptibility studies. As a result of such measurements on a large number of compounds, the most commonly occurring stereochemistries for the various co-ordination numbers have been established. We shall deal with these in turn but first it will prove useful to consider, with the help of some very simple theory, the possible geometries that may occur.

4.1 Valence-Shell Electron-Pair Repulsion (VSEPR) Theory

The simple idea that localised electron pairs on atoms repel one another was first developed by Sidgwick and Powell around 1940 but has more recently been refined in detail by Gillespie and Nyholm. The theory has had particular success in explaining the shapes of molecules containing typical elements; the transition elements present some complications but the simple ideas are considered worthwhile at this stage.

In VSEPR theory we assume that the outermost or valency electrons surrounding the central atom in a molecule exist in localised pairs, that is occupying localised molecular orbitals. Each pair of electrons thus occupies a well-defined area of space, and these electron pairs behave as though they repel one another and get as far apart from each other as possible, that is they maximise the least distance apart. Thus if we have two pairs of valency electrons in a molecule they will be at 180° from each other, so the molecule will be linear. With three pairs, the angle between them will be 120° in a planar structure; four pairs will arrange themselves tetrahedrally at an angle of 109°28′ apart. These deductions, together with those for five and six electron pairs, can be summarised diagrammatically if we assume that an element B contributes one electron to each bond and various elements A contribute one electron to each bond with B.

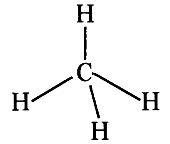
AB_2	linear	B——A——B
AB_3	trigonal planar	

AB$_4$	tetrahedral	
AB$_5$	trigonal bipyramidal	
AB$_6$	octahedral	

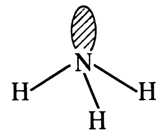
As well as bonding pairs of electrons, we must consider nonbonding or lone pairs of electrons, and again we assume that they are localised in a doubly filled orbital. The ligands water and ammonia are therefore not linear and trigonal planar respectively because of the presence of the lone pairs of electrons. In each case the total number of electron pairs is four, so the structures are based on the tetrahedral shape. However, they are not regular tetrahedra since the lone pairs of electrons are more localised on the oxygen and nitrogen atoms than are the bonding electrons which rather occupy sausage-shaped orbitals between the bonded atoms. This results in greater repulsion forces between lone-pair electrons and bonding pairs of electrons than between two bonding pairs. In general we can say that repulsions between electron pairs decrease in the order

lone pair – lone pair > lone pair – bond pair > bond pair – bond pair

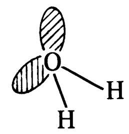
The bond angles in the water and ammonia molecules are thus reduced from the tetrahedral angle because of the effect of the lone pairs. This effect is best seen by comparing the bond angles in methane, ammonia, and water.



HCH = 109°28′



HNH = 107°18′



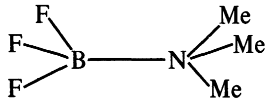
HOH = 104°30′

For complexes formed by main-group elements and by transition elements having d^0, d^5 (spin free), or d^{10} configurations, this approach is remarkably successful in predicting molecular shape. Transition-metal complexes having other configurations have not a symmetrical distribution of the d electrons and we must use ligand-field theory (chapter 5) to comprehend the resulting stereochemistries. Let us take some examples to illustrate the application of VSEPR theory to complex compounds.

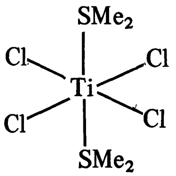
In the $[Ag(NH_3)_2]^+$ ion silver is in oxidation state +1, so its ground-state electronic configuration is [Kr]4d^{10}. Each ammonia molecule is donating a pair of electrons to form the co-ordinate bonds, so we have only two bond pairs to consider (the d electrons being spherically symmetrical about the silver ion); the bond angle will be 180°; that is the ion is linear.

$$[H_3N-Ag-NH_3]^+$$

In $BF_3(NMe_3)$ boron provides three electrons, the three fluorines each provide one electron, and the nitrogen atom of the trimethylamine provides two electrons. We thus have eight electrons or four pairs of electrons, so the resulting structure is tetrahedral (around both boron and nitrogen)



In $TiCl_4(SMe_2)_2$ we have titanium in oxidation state +4, so its electronic configuration is [Ar] $3d^0$. Each chloride ion and each sulphur atom is regarded as donating a pair of electrons to form the bonds, so we have six bonding pairs and consequently an octahedral structure



An alternative way of treating this example is to say that titanium ($3d^2$ $4s^2$) provides four electrons, each chlorine atom provides one electron, and each sulphur atom provides two electrons, to constitute the six bonding pairs. Although this is perhaps better chemically ($TiCl_4$ does not actually contain Ti^{4+} ions but is covalent like CCl_4), it does not readily indicate that we are dealing with what may be regarded as a d^0 system and consequently that VSEPR theory applies.

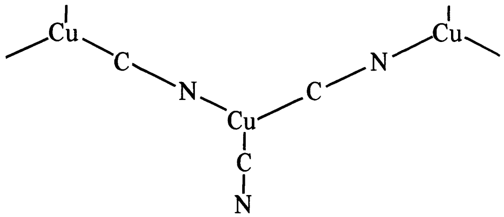
4.2 Co-ordination Numbers and Stereochemistries

4.2.1 Co-ordination Numbers Two and Three

Complexes of co-ordination number two are relatively uncommon and are confined principally to Cu^I, Ag^I, and Au^I ; however, for these species it is the characteristic feature of their chemistry. The linear complexes may be cationic, neutral, or anionic, examples being $[H_3N-Cu-NH_3]^+$, $Et_3P-Au-C{\equiv}CPh$, and $[Cl-Ag-Cl]^-$. Even bidentate ligands form linear complexes by bridging, for example $ClAgNH_2CH_2CH_2NH_2AgCl$. Mercury(II) also shows a considerable tendency toward two-co-ordination. Solutions of mercury(II) chloride contain largely $HgCl_2$ rather than $HgCl_3^-$ and $HgCl_4^{2-}$. The preferential stability of the linear two-co-ordinate species is indicated by the sudden fall in stability constants from K_2 to K_3 in mercury(II) complexes with, for example, NH_3, CN^-, and I^-(see Table 3.1).

Co-ordination number three occurs only extremely rarely in transition metal complexes. Trigonal planar three-co-ordination occurs in the NO_3^- and CO_3^{2-} ions but not in complexes such as $CsCuCl_3$ or $K_2Ni(CN)_3$. In the former complex the

X-ray crystal structure shows each copper atom to be surrounded by four coplanar chlorines in a bridged structure ($Cl-MCl_2-Cl-MCl_2$); the diamagnetism of the nickel complex suggests that it exists as dimeric anions $[Ni_2(CN)_6]^{4-}$. While simple halides of the trivalent typical elements, for example BCl_3, often have the discrete trigonal planar structure, trivalent transition metals give halides, such as VF_3, having giant lattices in which the metal atoms are usually surrounded octahedrally by halide ions. Authentic examples of planar three-co-ordination in transition metal chemistry are the HgI_3^- ion in $[Me_3S]^+[HgI_3]^-$ and in $KCu(CN)_2$ where the anion exists in spiral polymeric chains with the copper atoms three-co-ordinate by virtue of cyanide bridges

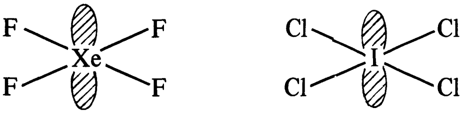


The carbon and nitrogen atoms bound to copper are almost coplanar with the metal atom but the CCuC angle is about 134° (rather than 120°). This structure is not found in the silver and gold cyano-ions; these contain the two-co-ordinate metals in discrete $[NC-M-CN]^-$ ions.

The compounds $M[N(SiMe_3)_2]_3$, in which M = Ti, V, Cr, or Fe, have recently been shown to contain three-co-ordinated metals but their structures are not yet known in detail.

4.2.2 Co-ordination Number Four

On VSEPR theory we expect only tetrahedral complexes for this co-ordination number unless lone-pair electrons are present as in, for example, XeF_4 and ICl_4^- which may be represented as square complexes



with the lone-pair electrons occupying the fifth and sixth octahedral positions. A large number of tetrahedral complexes are thus formed by the elements in the second row (Li to Ne) of the periodic table when they achieve their octet; beryllium and boron form especially numerous species of the types BeX_4^{2-}, BeX_2L_2, BX_4^-, and BX_3L (where L represents a unidentate ligand and X a univalent anion). Tetrahedral complexes are also predominant in four-co-ordinate complexes of the transition elements but the alternative square planar configuration is also common and is a characteristic feature of the chemistry of some metals, notably those with a d^8 electronic configuration such as Pt^{II}.

Tetrahedral complexes of transition elements are mostly anionic or neutral. Cationic complexes such as $[Cd(NH_3)_4]^{2+}$ are uncommon. The simple covalent molecules such as $TiCl_4$, VCl_4, and $Ni(CO)_4$ are tetrahedral. With some metals tetrahedral complexes are formed in solution even in the presence of an excess of ligand, the rather general aqueous substitution reaction of halide ions being

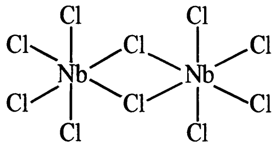
$$[M(H_2O)_6]^{n+} + 4X^- \rightleftharpoons [MX_4]^{(4-n)-} + 6H_2O$$

The addition of concentrated hydrochloric acid to solutions of iron(III) and cobalt(II), for example, results in the formation of $FeCl_4^-$ and $CoCl_4^{2-}$ complexes (rather than $FeCl_6^{3-}$ and $CoCl_6^{4-}$). With other metals, tetrahedral halide complexes can be prepared in the presence of an excess of halide ions but not in strongly co-ordinating solvents such as water. Salts containing species such as VX_4^-, MnX_4^{2-}, and NiX_4^{2-} can be crystallised from solvents such as acetonitrile and alcohol in the presence of an excess of halide ions. Other well-characterised tetrahedral anions include $[Co(NCS)_4]^{2-}$ and $[CoX_3(H_2O)]^-$. While tetrahedral species are common for cobalt(II) they are unknown in cobalt(III) chemistry; they are similarly unknown for chromium(III). Neutral tetrahedral complexes are formed particularly by cobalt(II) and sometimes by nickel(II); they are of the type MX_2L_2, examples being $CoCl_2(py)_2$ and $NiBr_2(Ph_2AsO)_2$. The factors involved in determining whether tetrahedral or octahedral complexes will be the more stable under any given set of conditions are not completely understood; some of these factors will be discussed in chapter 5. It is important to remember that the empirical formula of a compound does not give any information about stereochemistry; for example $NiCl_2(py)_2$ is not tetrahedral but six-co-ordinate with chloride bridges.

Square planar four-co-ordination occurs commonly for Rh^I, Ir^I, Pd^{II}, Pt^{II}, and Au^{III}; for these species it is the most frequently occurring stereochemical form. The occurrence of so many complexes of platinum(II) with this stereochemistry is of considerable historical importance since the occurrence of isomers of formula PtX_2L_2 led Werner to suggest the square structure for these complexes. In the solid state and in solution, cationic, neutral, and anionic complexes of platinum(II) are square, for example $[Pt(NH_3)_4]^{2+}$, $Pt(NH_3)_2Cl_2$, and $PtCl_4^{2-}$. Square planar complexes formed by the other d^8 elements are exemplified by $[Rh(CO)_2Cl]_2$ which contains chlorine bridges, $Ir(CO)Cl(PPh_3)_2$, $PdCl_4^{2-}$, and $AuCl_4^-$. As well as these elements, nickel(II) forms many square complexes but it is more commonly six-co-ordinate. Square nickel(II) complexes include the $[Ni(CN)_4]^{2-}$ ion in, for example, $Na_2Ni(CN)_4.3H_2O$, and the vivid red precipitate of bis(dimethylglyoximato)nickel(II) obtained when dimethylglyoxime is added to neutral nickel(II) solutions. For other metals the square planar configuration occurs only rarely.

4.2.3 Co-ordination Number Five

Complex compounds in this co-ordination number are considerably less numerous than those in co-ordination numbers four and six. Some apparently five-co-ordinate complexes are in fact polymers, and some are mixtures. The pentachlorides of niobium, tantalum, and molybdenum are five-co-ordinate (trigonal bipyramidal) in the gas phase but exist as dimeric molecules in the solid state with slightly distorted octahedral co-ordination



The caesium salt Cs_2CoCl_5 contains the slightly distorted tetrahedral $CoCl_4{}^{2-}$ ions as well as Cl^- ions in the lattice. Of the several possible polyhedra for five-co-ordination, only two are commonly found, the trigonal bipyramid and the square-based pyramid.

While the trigonal bipyramidal structure is predicted on VSEPR theory (and is indeed found for the s and p block elements), the energy difference between this structure and the alternative square pyramidal structure is very small for complexes of the transition elements. Indeed the two structures can be readily interconverted; the displacements of the atoms necessary for this interconversion are illustrated in Figure 4.1. The consequence of this small energy difference and structural similarity is that both of the idealised structures are found as well as a large number of compounds with stereochemistries in between the two extremes indicated in Figure 4.1.

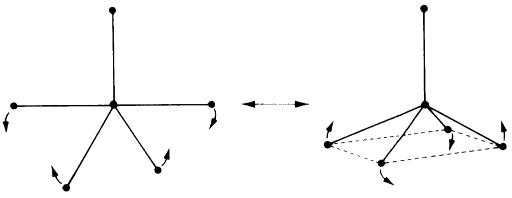
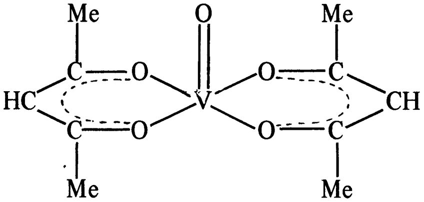
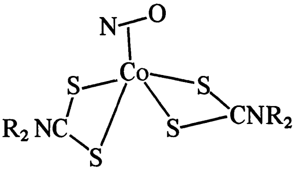


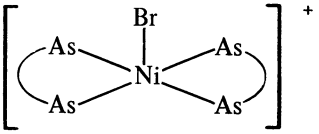
Figure 4.1 Interconversion of trigonal bipyramidal and square pyramidal structures

The trigonal bipyramidal structure is generally found for compounds having five identical ligands. The pentahalides PF_5, PCl_5, $TaCl_5$, $NbBr_5$, and $MoCl_5$ have this structure in the vapour phase, and $SbCl_5$ retains its five-co-ordination in the solid state. Iron pentacarbonyl $Fe(CO)_5$ and ionic species such as $[Mn(CO)_5]^-$, $[Pt(SnCl_3)_5]^{3-}$, $[Ni(CN)_5]^{3-}$, $CuCl_5{}^{3-}$, and $[Co(NCMe)_5]^+$ also have the trigonal bipyramidal structure. Substituted derivatives of iron carbonyl of the types $Fe(CO)_4L$ and $Fe(CO)_3L_2$ and several complexes of vanadium(III) halides of the general formula VX_3L_2 have structures based upon the trigonal bipyramid. The complexes $MCl_3(NMe_3)_2$ (M = Ti, V, Cr) are isostructural, being *trans*-trigonal bipyramidal (the three chlorines occupy the terminal positions in the equatorial plane).

Square pyramidal arrangements in which the metal atom sits in the basal plane probably do not occur; distortion of such structures is expected even on simple VSEPR theory. The metal atom is thus normally out of the basal plane and inside the pyramid. In square pyramidal complexes the chemical nature of the apical ligand is frequently different from that of the four ligands in the plane. Examples include VO(acac)$_2$, Co(NO) (S$_2$CNR$_2$)$_2$, and [NiBr(diars)$_2$]$^+$







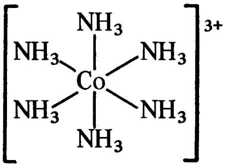
Such species as these do not always retain their five-co-ordinate structures in solution; for example, there is considerable spectroscopic evidence to suggest that, in solutions of VO(acac)$_2$ in co-ordinating solvents, a solvent molecule occupies the sixth or 'octahedral' position. The π-bonding such as is shown for VO(acac)$_2$ appears to be an important feature in stabilising the square pyramidal structure relative to that of the trigonal bipyramid.

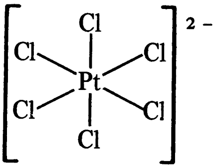
Square (four-co-ordinate) doubly charged complexes of d^8 configurations may, by the addition of a fifth ligand (which may be only loosely bonded), produce square pyramidal complexes that can often be regarded as having only slightly perturbed square structures. Such is the case with the diarsine complexes of platinum(II) and palladium(II), for example

$$[\mathrm{Pt(diars)_2}]^{2+} + \mathrm{X}^- \rightleftharpoons [\mathrm{Pt(diars)_2X}]^+$$

4.2.4 *Co-ordination Number Six*

This is by far the most commonly occurring co-ordination number, and the most important for transition metal complexes. The great majority of six-co-ordinate complexes have structures based upon the octahedron. The octahedron has eight faces and six corners, and an atom at the centre is symmetrically surrounded by atoms placed at each of the corners; all the bond lengths are equal and all the bond angles are 90°. It is usual to draw octahedral structures as in the following examples





It is important to realise that each ammonia molecule in [Co(NH$_3$)$_6$]$^{3+}$ is in an environment identical to that of all the other ammonia molecules; that is, there is nothing special about the ammonia molecules we have drawn in the vertical bond positions. Let us consider the symmetry of the octahedron in more detail. It will be convenient here to introduce the concept of a symmetry axis. If rotation through an angle 360°/n about an axis produces a configuration indistinguishable from the original one, this axis is called a C_n axis. Some of the symmetry axes of an octahedron are shown in Figure 4.2. The axes of highest symmetry are the fourfold rotation axes (labelled C_4); there are three of these, passing through the centre of symmetry and through opposite corners of the octahedron. Four threefold axes C_3 pass through the centre and through the midpoints of opposite triangular faces. Twofold axes C_2 join the midpoints of opposite edges of the octahedron via the centre of symmetry; as well as these six C_2 axes, there is a set of C_2 axes coincident with the C_4 axes.

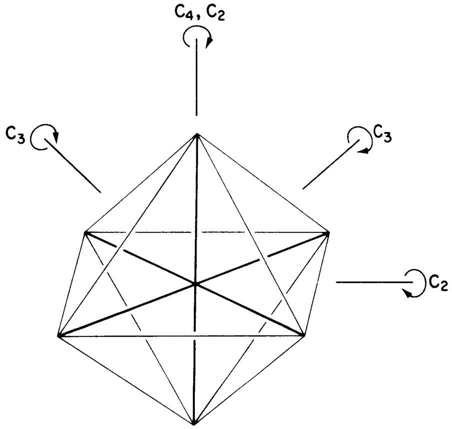


Figure 4.2 Symmetry axes of an octahedron

Although there are many fairly regular octahedral complexes, many complexes that are loosely described as octahedral have structures in which the octahedron has been distorted in some way. Two forms of such distortion are common. In *tetragonal distortion* the octahedron is either stretched or compressed along a C_4 (fourfold) axis. This results in the production of a structure with four coplanar bonds of the same length and two bonds at right-angles to these but longer or shorter than those in the set of four. The effects of these tetragonal distortions on bond lengths are illustrated in Figure 4.3. The new structures are less symmetrical than that of the

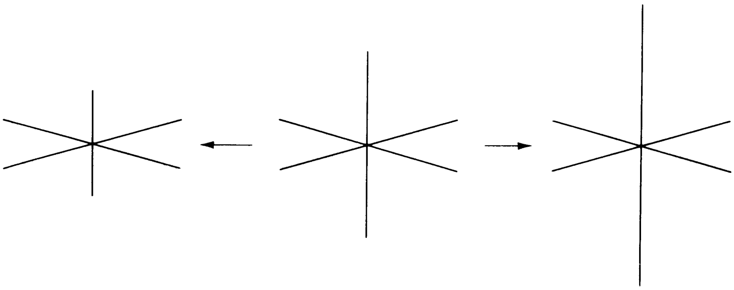


Figure 4.3 Tetragonal distortions of the octahedral structure

octahedron, they belong to the symmetry class D_{4h}. The effect of increasing tetragonal elongation of the octahedron is eventually to remove the axial ligands from the co-ordination 'sphere' of the central atom, leaving a square planar structure. There is therefore no sharp dividing line between tetragonal and square structures. Many copper(II) complexes, including $[Cu(H_2O)_6]^{2+}$, are tetragonal with two long bonds, and these have frequently been treated in elementary texts as being square, for example $[Cu(H_2O)_4]^{2+}$ and $[Cu(NH_3)_4]^{2+}$. In the nickel(II) dimethylglyoxime complex, which we considered (section 4.2.2) to contain nickel in a square planar environment, the X-ray crystal structure of the solid shows that the $\mathrm{Ni(DMG)_2}$ units stack on top of each other, so the structure can be considered as tetragonal with long Ni–Ni bonds.

In *trigonal distortion* the octahedron is stretched or compressed along one of the C_3 (threefold) axes. In this deformation the octahedron becomes a trigonal antiprism of symmetry class D_{3d}. The effect of this is shown in Figure 4.4; the octahedron is placed on a triangular base and then stretched (in this case) along the vertical C_3 axis. Examples of trigonal distortions are to be found in the hexaquo-complexes of some trivalent transition metal ions in the alums, for example $(NH_4^+)\ [V(H_2O)_6]^{3+}(SO_4^{2-})_2 . 6H_2O$. There is considerable X-ray spectroscopic and magnetic evidence to indicate that both tetragonal and trigonal distortions occur in the solid state as well as in solution. We shall consider the reasons for these distortions in chapter 5.

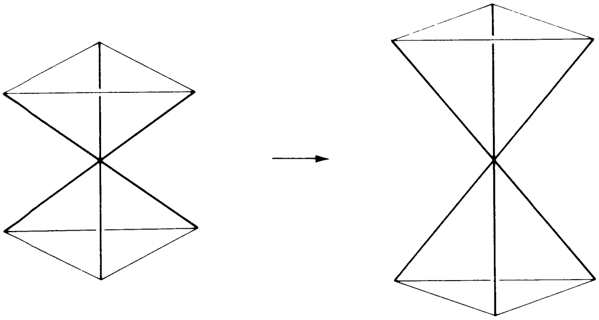
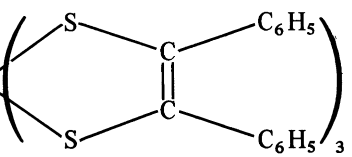


Figure 4.4 Trigonal distortion of the octahedral structure

Other possible structures for six-co-ordination include the hexagonal planar structure (Figure 1.1*a*), which has not yet been found, and the trigonal prismatic structure (Figure 1.1*b*). This latter structure occurs only rarely, but particularly with some bidentate sulphur ligands such as *cis*-1,2-diphenylethane-1,2-dithiolate, for example in the vanadium complex



4.2.5 Co-ordination Numbers Greater than Six

Co-ordination numbers seven, eight, nine, ten, eleven, and twelve are known in complex compounds. These high co-ordination numbers are found only rarely with first-row transition elements but are more common with the second and third-row transition elements. The major factors responsible for this are the sizes of the heavier elements and the availability of closely energetic orbitals. The ligands that stabilise high co-ordination numbers are small electronegative unidentate ligands such as H^-, F^-, CN^-, and chelates of the electronegative oxygen and nitrogen atoms. The idealised shapes of species with high co-ordination number can be rationalised in terms of the VSEPR theory. However, as with five-co-ordination, the difference between these idealised shapes for any particular co-ordination number is very small; these differences appear to be comparable to the distortion imposed by vibrationally excited states. We shall consider only one or two examples here.

At least four types of structure are found in seven-co-ordination. The pentagonal bipyramid (Figure 4.5*a*) is found in the potassium salt of the $[UO_2F_5]^{3-}$ ion. The addition of a seventh ligand above one of the rectangular faces of a trigonal prism gives the capped trigonal prism structure as found in NbF_7^{2-} and TaF_7^{2-} (Figure 4.5*b*). Similarly the capped octahedral structure has a seventh ligand added above the centre of one face of an octahedron; the $NbOF_6^{3-}$ ion has this structure. The tetragonal base–trigonal base structure is illustrated in Figure 4.5*c* for the iron carbonyl cyclobutadiene complex $Fe(CO)_3C_4(C_6H_5)_4$.

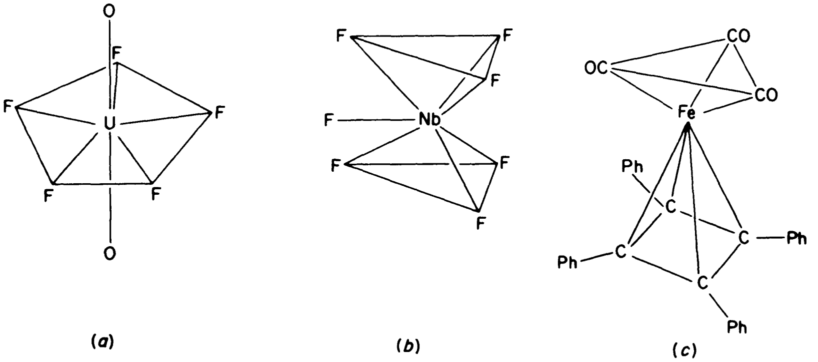


Figure 4.5 Some seven-co-ordinate structures

Eight-co-ordination is considerably more common. The cubic structure as found in ionic lattices such as caesium chloride is not commonly found for molecular species. Instead, two figures that can be constructed by distortion of the cube are observed; these are the square antiprism and the dodecahedron. The square antiprism is formed when one square face of a cube is rotated by 45° relative to the face opposite to it. A structure like this is found in ions such as TaF_8^{3-} (Figure 4.6) and ReF_8^{2-}, as well as in the tetrakis(acetylacetonates) of zirconium(IV), cerium(IV), and thorium(IV). The dodecahedral structure is typified

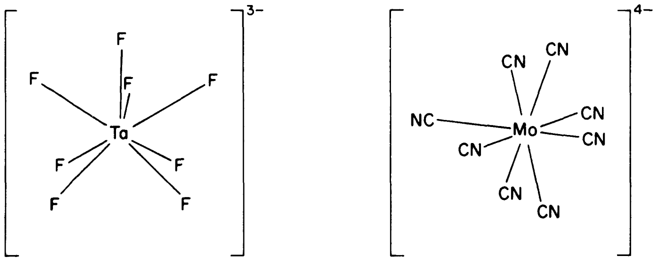


Figure 4.6 Some eight-co-ordinate structures

by the $[Mo(CN)_8]^{4-}$ion (Figure 4.6); it occurs also in $Na_4Zr(C_2O_4)_4.3H_2O$ and $TiCl_4(diars)_2$. It is also found in polymeric eight-co-ordinate units; for example, K_2ZrF_6 contains zirconium surrounded by eight fluorines, four of which are shared. A further structural type of eight-co-ordination is that of the planar hexagonal bipyramid; this is found mainly in the actinide series of elements, and particularly for dioxouranium(VI) compounds. In $Rb[UO_2(NO_3)_3]$, for example, the collinear OUO group is bisected by a plane of three nitrate groups, each nitrate group being bidentate with respect to the uranium atom.

Perhaps the most remarkable nine-co-ordinate species are the complex hydrides $TcH_9^{2-}$and ReH_9^{2-}. These have the tricapped trigonal prismatic structure in which the basic trigonal prismatic structure has an extra hydride ion centred over each of its three rectangular faces. Nonahydrates of the trivalent rare earth ions, for example $[Nd(H_2O)_9]^{3+}$, also have this structure, as do a large number of ionic lattices containing these ions. In hexagonal $NaNdF_4$, for example, there are two Nd^{3+} sites, and in each the neodymium ions are nine-co-ordinated by fluoride ions.

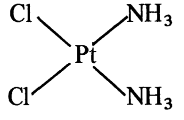
Co-ordination numbers ten, eleven, and twelve are not commonly found for molecular species; again they occur principally in the lanthanide and actinide series. Ten-co-ordination is established in $La[(O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2H)CH_2CO_2].4H_2O$ in which a three-dimensional X-ray analysis has revealed two nitrogen atoms, four oxygen atoms from carboxylate groups, and four oxygen atoms from water molecules to be within bonding distance of the lanthanum. In the sulphate $La_2(SO_4)_3.9H_2O$, twelve sulphate oxygen atoms are bonded to lanthanum in the twelve-co-ordinate eicosahedral structure.

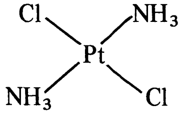
4.3 Isomerism in Co-ordination Compounds

In chapter 1 we mentioned briefly how Werner, using the phenomenon of isomerism, was able to conclude that the six-co-ordinate compounds he had been studying possessed the octahedral structure. The two most important types of isomerism found in co-ordination chemistry are geometrical and optical isomerism; there are many other kinds but we shall mention these only briefly.

4.3.1 Geometrical Isomerism

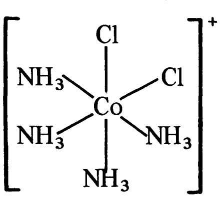
This kind of isomerism occurs in planar (but not tetrahedral) four-co-ordinate and in six-co-ordinate complexes. Planar compounds of the type MA_2B_2 may show *cis-trans* isomerism; the classic examples of this occur in platinum(II) chemistry, for example

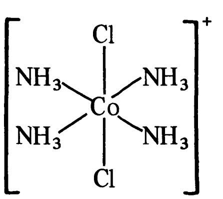

cis


trans

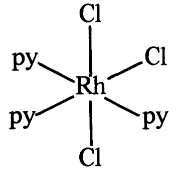
For complexes of formula MABCD, three isomers are possible (with B, C, or D *trans* to A), and all three have been isolated in several cases, for example $PtCl(Br)(py)(NH_3)$.

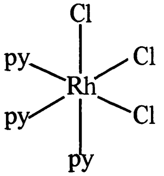
Octahedral complexes of this type MA_4B_2 similarly exhibit *cis-trans* isomerism


cis


trans

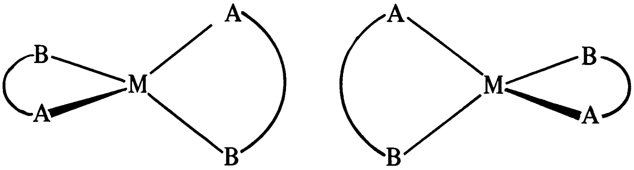
Even when compounds occur or can be isolated in only one form, the *cis* and *trans* nomenclature is useful as a method of describing a structure. Two (and only two) isomeric forms are possible for octahedral MA_3B_3 complexes; these isomers are distinguished by the prefixes *mer* and *fac* (meridional and facial). Both isomers can be isolated in the case of $RhCl_3(py)_3$


mer

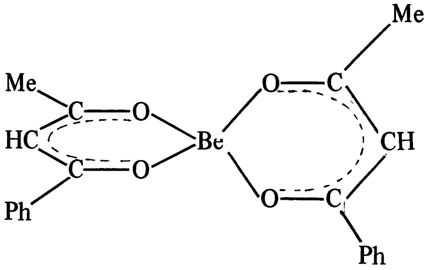

fac

4.3.2 Optical Isomerism

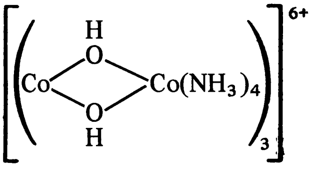
Optically active substances are capable of rotating the plane of polarised light. If a complex is to show optical activity it must be asymmetric. The complex must have no plane of symmetry, and the structure and its mirror image must be different, that is nonsuperimposable. A useful analogy is left and right hands; the left hand has no plane of symmetry, and its mirror image (the right hand) cannot be superimposed on to the left hand because of the different orientations of the thumb and fingers. In organic chemistry many optically active compounds exist in which a central carbon atom is tetrahedrally surrounded by four different groups. Because of the much greater kinetic reactivity of tetrahedral inorganic complexes, it is difficult enough to prepare compounds of the type MABCD (tetrahedral) let alone resolve them into optical isomers. Tetrahedral complexes containing unsymmetrical chelate ligands can be more easily prepared, and some have been resolved. Their mirror images can best be visualised with the aid of models but can be represented for the general formula M(A–B)$_2$ by



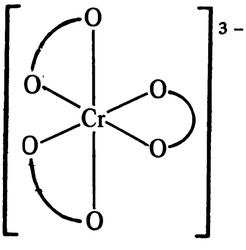
Beryllium(II), zinc(II), and boron(III) form resolvable chelates of this type. The letters A and B in the structures above do not represent necessarily different donor elements but rather the ends of unsymmetrical chelates. Thus a typical example is bis(benzoylacetonato)beryllium(II)

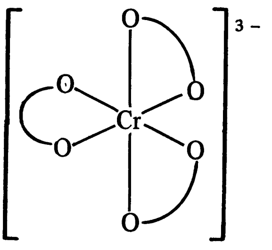


A much larger class of optically active complexes is that of octahedral complexes having chelate ligands (no complex of unidentate ligands MABCDEF has been resolved). The two classes that have been most extensively studied are the tris-bidentate M(L–L)$_3$ and bis-bidentate M(L–L)$_2$X$_2$ complexes. These bidentate ligands frequently contain carbon; Werner, setting out to prove that their activity was not necessarily due to the presence of carbon, succeeded in resolving the hydroxo-bridged complex



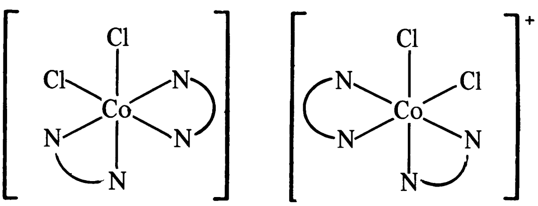
Complexes of the type M(L–L)$_3$ can be exemplified by the tris(oxalato)chromate(III) anion



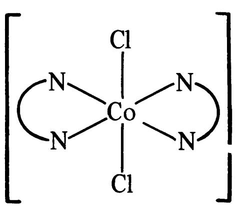


The fact that these compounds can be resolved into optical isomers is good evidence that they have the octahedral structure; neither the hexagonal planar nor the trigonal prismatic structure would show optical activity. Resolution of such compounds is not always possible owing to the speed at which racemisation takes place.

Optical activity in complexes of the type $M(L-L)_2X_2$ proves the *cis* structure since the *trans* form has a plane of symmetry. Thus for $[Co(en)_2Cl_2]Cl$ three forms exist, two optically active *cis* forms and an inactive *trans* form



cis forms; active



trans form; inactive

4.3.3 *Other Types of Isomerism in Complexes*

When two compounds having the same molecular formula dissolve to give different ionic species in solution, these compounds are called *ionisation isomers.* Typical examples are $[Pt(NH_3)_4Cl_2]Br_2$ and $[Pt(NH_3)_4Br_2]Cl_2$; the former gives bromide ions in aqueous solution while the latter gives chloride ions. A similar type is *hydration isomerism;* there are, for example, three isomers of $CrCl_3.6H_2O$ which can be formulated as $[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl]Cl_2.H_2O$, and $[Cr(H_2O)_4Cl_2]Cl.2H_2O$ according to the number of ions they produce in solution and the number of chloride ions that can be precipitated immediately with silver nitrate solution. When ligands possess more than one donor atom, *linkage isomerism* may occur, for example thiocyanato (S-bonded) and isothiocyanato (N-bonded) complexes, $(Ph_3P)_2Pd(SCN)_2$ and $(Ph_3P)_2Pd(NCS)_2$. Nitro (N-bonded) and nitrito (O-bonded) complexes also show this kind of isomerism, for example $[Co(NH_3)_5ONO]^{2+}$ and $[Co(NH_3)_5NO_2]^{2+}$. In *co-ordination isomerism* the isomers consist of complex cations and anions in which the ligands are bound to different metals in each isomer, for example $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$. Substances with the same empirical composition but differing in the size of the smallest unit are called *polymerisation isomers,* for example $Pt(NH_3)_2Cl_2$ and $[Pt(NH_3)_4][PtCl_4]$.

5 Theories of Bonding in Complex Compounds

5.1 Magnetic Properties of Complexes

Studies of the magnetic properties of complex compounds have played a very important part in discussions of bonding theories. We must first consider elementary magnetism before the bonding theories are introduced. A more detailed account of the magnetic properties of transition metal ions will be met in chapter 7.

The magnetic properties of substances arise principally from the charge and from the spin and orbital angular momenta of the electrons. We need to distinguish initially between *diamagnetism* and *paramagnetism.* Diamagnetic materials are repelled by a magnetic field whereas paramagnetic materials are attracted by a magnetic field. All substances possess the property of diamagnetism. This effect derives from the presence of closed shells of electrons within substances, and results from an induced magnetic moment being set up in opposition to the applied magnetic field. Paramagnetism derives from the spin and orbital angular momenta of electrons. If all the electrons exist in pairs, their spin and orbital angular momenta cancel each other out, so paramagnetism occurs in substances having unpaired electrons. Because the paramagnetic effect is very much greater (about 10^3 times) than the diamagnetic effect, substances with unpaired electrons are usually paramagnetic. In calculating the extent of the paramagnetism we must correct for the diamagnetism due to the closed shells of electrons since these have the effect of reducing the paramagnetism due to the unpaired electrons. Paramagnetism is very easily measured in the laboratory (chapter 7); it is usual to express it in terms of the magnetic moment μ.

For ions in the first transition series the magnetic moment is given by

$$\mu = \sqrt{[4S(S+1) + L(L+1)]}$$

where S is the total spin quantum number, and L is the total orbital angular momentum quantum number. In practice it is found that the orbital contribution is often considerably less than the spin contribution, so a further approximation can be written

$$\mu = \sqrt{[4S(S+1)]}$$

Now, since $s = \pm\frac{1}{2}$ only and $S = \Sigma s$, the number of unpaired electrons in a system is given by $n = 2S$. Hence, by substitution for S in the above equation we get

$$\mu = \sqrt{[n(n+2)]}$$

This important result is known as the *spin-only formula.* It follows that we should expect:

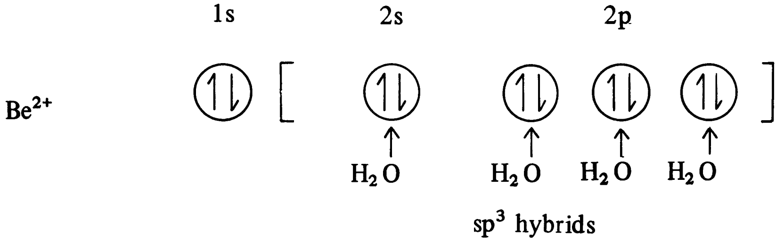
for 1 unpaired electron, $\mu = \sqrt{3} = 1.73$ B.M.
for 2 unpaired electrons, $\mu = \sqrt{8} = 2.83$ B.M.
for 3 unpaired electrons, $\mu = \sqrt{15} = 3.87$ B.M.

and so on. The unit of magnetic moment in use here is the Bohr Magneton (B.M.)

(=9.273 × 10^{-24} A m^2 $molecule^{-1}$). The experimental moments found for ions in the first transition series are often quite close to those given by the spin-only formula but in some cases they are considerably in excess of this theoretical value. It is these deviations (most commonly due to orbital contribution) from the spin-only value that enable magnetic measurements to be of value in determining the stereochemistry of metal complexes (chapter 7).

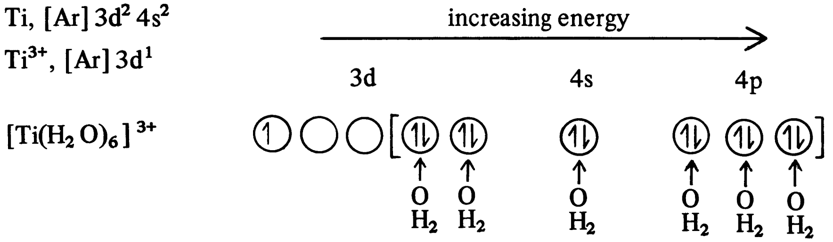
5.2 The Valence-Bond Theory

The ideas involved in the formation of complexes by donor–acceptor reactions were extended by Linus Pauling into the valence bond (VB) theory of the bonding in complex compounds. The basic idea is that pairs of electrons from the donor atoms are donated into empty orbitals on the metal ions. In order to receive these electron pairs, the atomic orbitals on the metal hybridise to give a set of equivalent orbitals having the required symmetry properties. The beryllium ion, for example, thus forms tetrahedral sp^3 hybrid orbitals, which can receive electron pairs from ligands. We can represent the electronic structure of $[Be(H_2O)_4]^{2+}$ thus



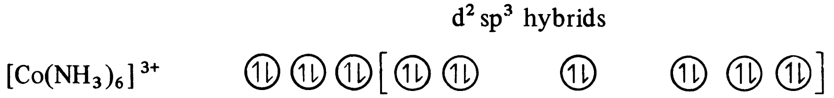
For square complexes the metal orbitals are dsp^2 hybridised, and for octahedral complexes d^2sp^3 hybridisation is assumed.

In an octahedral complex the set of six equivalent σ orbitals have their lobes pointing to the corners of a regular octahedron. These hybrids are thus constructed using the metal s, p_x, p_y, p_z, d_{z^2}, and $d_{x^2-y^2}$ orbitals (the d_{xy}, d_{xz}, and d_{yz} orbitals do not point towards the corners of the octahedron). Since two of the metal d orbitals are used in the formation of the hybrid orbitals, only three are left in which to accommodate any electrons possessed by the metal ion. No problems arise for metal ions of configuration d^1, d^2, or d^3; we can illustrate the bonding in the hexaquotitanium(III) ion thus

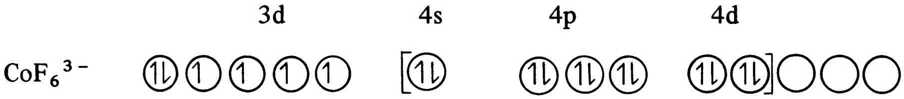


The $[Ti(H_2O)_6]^{3+}$ ion is indeed paramagnetic, with a magnetic moment corresponding to the presence of one unpaired electron per titanium ion.

If we now consider an ion with more than three d electrons, we see that we cannot always accommodate these electrons in the 3d orbitals if we wish to feed the electrons in with the maximum number of unpaired spins (that is applying Hund's rules). Cobalt(III) complexes can be used to illustrate the d^6 case. If the six electrons enter the three vacant 3d orbitals, the resulting complex would contain no unpaired electrons and thus be diamagnetic. Such is experimentally found to be the case for the cobaltammines, for example $[Co(NH_3)_6]^{3+}$ (bracketed orbitals contain electrons from the ligands)



We might therefore predict that all cobalt(III) complexes will be diamagnetic, but it was found that in the ion $CoF_6{}^{3-}$ four unpaired electrons are present, so the above description cannot apply. Initially this latter complex was regarded as being an ionic complex having Co^{3+} ions (six electrons to feed into five d orbitals, hence four remain unpaired) and F^- ions. The diamagnetic complexes were then described as 'covalent'. This theory was later replaced by the concept of inner and outer-orbital complexes. In $CoF_6{}^{3-}$ it is assumed that the 'outer' 4d orbitals are used in the hybridisation as opposed to the use of the 'inner' 3d orbitals in $[Co(NH_3)_6]^{3+}$. We can illustrate this as follows



While the valence-bond theory is still widely used in organic chemistry and to some extent in the chemistry of the typical (main group) elements, it has now been superseded in transition metal chemistry by the molecular orbital and ligand-field theories. The greater usefulness of these theories will become apparent as the reader becomes familiar with them. We can criticise the VB approach to complexes on the following grounds. Firstly, it assumes that all the 3d orbitals have the same energy in the complex; we shall see that this directly contradicts the other theories mentioned. Secondly, the rather arbitrary use of 3d and 4d orbitals for bonding when they are known to possess widely differing energies is, to say the least, unsatisfactory. Thirdly, the theory gives us no understanding of electronic spectra (chapter 6), and finally, it does not adequately explain the magnetic data (see chapter 7).

5.3 The Molecular-Orbital Theory

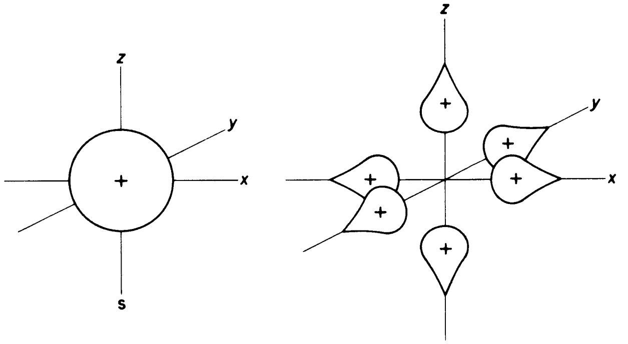
In molecular orbital (MO) theory we construct a series of molecular orbitals from atomic orbitals on the metal ion and on the ligand. Then, when we have a molecular orbital energy-level diagram, we feed in the electrons from the ligands and from the metal ion, filling the lowest energy levels first. The method by which we combine the atomic orbitals is the LCAO (linear combination of atomic orbitals) method. The overlap of atomic orbitals will occur only when these orbitals have the same symmetry;

we therefore need to consider the symmetry properties of the various metal and ligand orbitals.

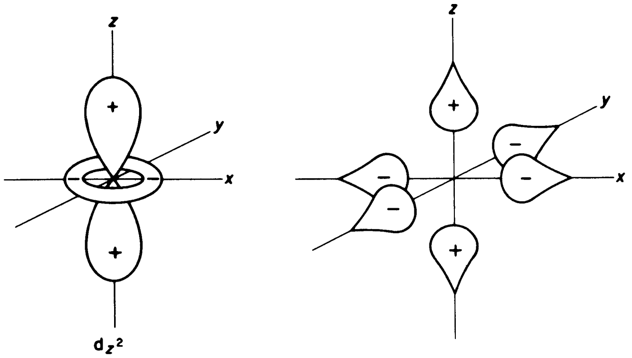
Let us first consider the octahedral complex ML_6, in which we shall assume that only σ-bonding is important. We first pick out the valence shell atomic orbitals for the metal and the ligands. For a first-row transition metal ion these are the 3d, 4s, and 4p orbitals. Of these nine orbitals only six have lobes pointing towards the corners of an octahedron; these are the $3d_{x^2-y^2}$, $3d_{z^2}$, 4s, $4p_x$, $4p_y$, and $4p_z$ orbitals. The $3d_{xy}$, $3d_{xz}$, and $3d_{yz}$ orbitals have lobes lying between the cartesian co-ordinates and are therefore not suitably shaped for σ-bonding (but they are for π-bonding) in an octahedral complex. In group theoretical terminology we classify the σ-bonding orbitals on the metal as follows

$3d_{x^2-y^2}$, $3d_{z^2}$	e_g
4s	a_{1g}
$4p_x$, $4p_y$, $4p_z$	t_{1u}

These new labels refer to symmetry classes of the orbitals. The label a_{1g} represents a single orbital that is totally symmetrical, e_g represents a pair of orbitals that are equivalent except for their spatial orientations, while t_{1u} represents a set of three orbitals that are equivalent except for their spatial orientations. The symmetry of these orbitals is shown in Figure 5.1.



a_{1g} set



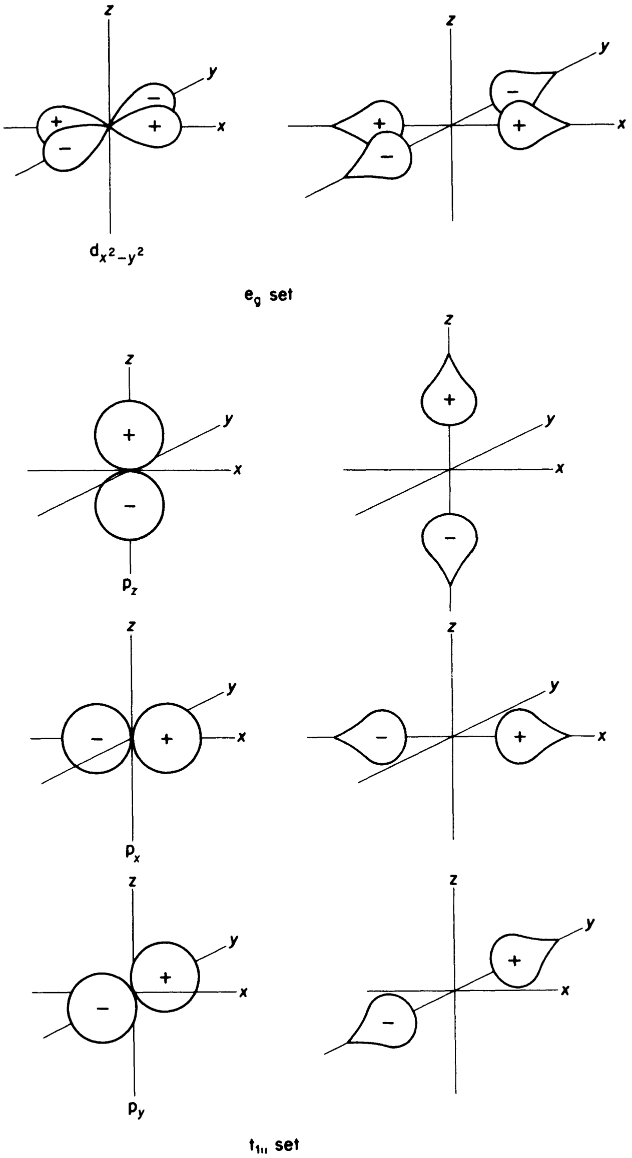


Figure 5.1 The metal orbitals (left-hand side) and their matching ligand group orbitals for an octahedral σ-bonded complex

We must now consider the valence shell orbitals on the ligands. The σ valence orbitals will of course vary from ligand to ligand but they will frequently be composed of s and p atomic orbitals; they can be represented as lobes (see Figure 5.1). We now have to find the linear combinations of ligand σ orbitals that may bond with the metal a_{1g}, e_g, and t_{1u} orbitals. This is readily done by writing down the linear combination of σ orbitals that has the same symmetry properties as each of the metal orbitals. Thus the linear combination of ligand σ orbitals that has the same symmetry as the $d_{x^2-y^2}$ orbital has a plus sign in the $+x$ and $-x$ directions and a minus sign in the $+y$ and $-y$ directions. This is the combination $(\sigma_x + \sigma_{-x} - \sigma_y - \sigma_{-y})$. The combinations for the other matching ligand orbitals are found similarly; these with their appropriate normalisation constants are listed in Table 5.1 under the heading 'ligand group orbitals'. The only one that presents any difficulty is the d_{z2} matching combination. The d_{z2} orbital is a shorthand notation for $d_{2z^2-x^2-y^2}$, and hence the ligand group orbital. Note that the d_{z^2} orbital (Figure 5.1) has a negative collar surrounding the positive lobes along the z axis.

In order to construct an energy-level diagram for our complex ML_6 we must make some assumptions about the energies of the atomic orbitals (3d, 4s, 4p, and σ_L) from which we are forming molecular orbitals. For transition metal complexes the most usual order of energies of metal orbitals is nd $<$ (n+1)s $<$ (n+1)p, so for first-row complexes we shall write 3d $<$ 4s $<$ 4p. For most ligands, for example H_2O, NH_3, and F^-, the σ_L orbitals used for bonding to the metal are lower in energy, that is more stable, than the metal valence orbitals. The energy-level diagram thus resulting from an octahedral σ-bonded complex is shown in Figure 5.2. For each combination of metal and ligand orbitals we get a lower-energy bonding molecular orbital and a higher-energy antibonding (denoted by an asterisk) molecular orbital. The t_{2g} orbitals on the metal, that is the d_{xy}, d_{xz}, and d_{yz} orbitals, are nonbonding in a σ-bonded octahedral complex, so their energy remains unchanged.

TABLE 5.1 METAL AND LIGAND ORBITAL COMBINATIONS FOR A σ-BONDED OCTAHEDRAL COMPLEX

Symmetry	Metal orbitals	Ligand-group orbitals
a_{1g}	s	$(1/\sqrt{6})(\sigma_x + \sigma_{-x} + \sigma_y + \sigma_{-y} + \sigma_z + \sigma_{-z})$
e_g	d_{z2}	$(1/\sqrt{12})(2\sigma_z + 2\sigma_{-z} - \sigma_x - \sigma_{-x} - \sigma_y - \sigma_{-y})$
	d_{x2-y2}	$(1/2)(\sigma_x + \sigma_{-x} - \sigma_y - \sigma_{-y})$
t_{1u}	p_z	$(1/\sqrt{2})(\sigma_z - \sigma_{-z})$
	p_y	$(1/\sqrt{2})(\sigma_y - \sigma_{-y})$
	p_x	$(1/\sqrt{2})(\sigma_x - \sigma_{-x})$

In order to apply this diagram to any particular complex, we feed the six pairs of electrons from the ligands into the lowest energy levels, that is the a_{1g}, t_{1u}, and e_g levels, which thus all become filled (each horizontal line in Figure 5.2 represents an orbital that can contain up to two electrons). Notice the similarity here to the VB approach. The molecular orbitals here that 'receive' the donated electron pairs correspond to the sp^3d^2 orbitals on VB theory. Any valence shell electrons in the

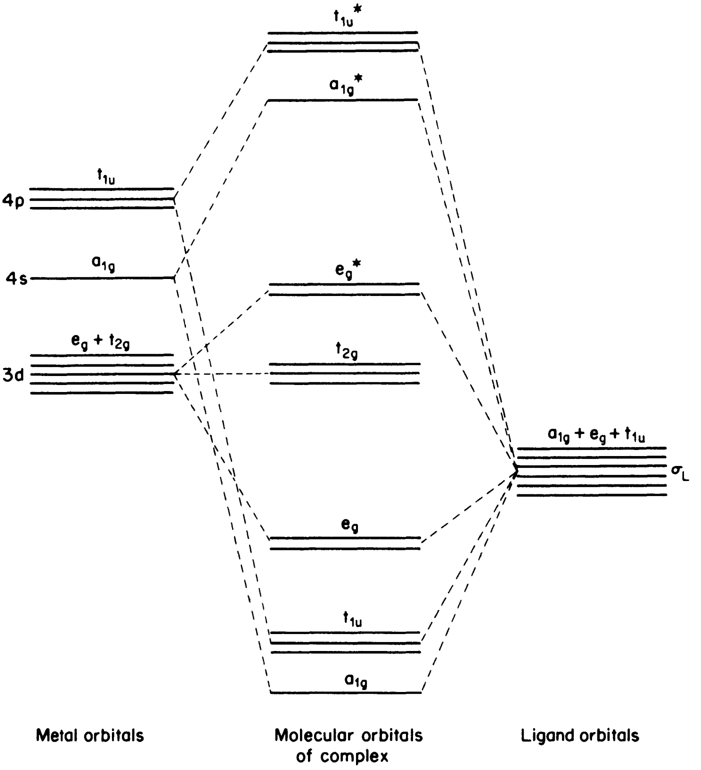


Figure 5.2 Molecular-orbital energy-level diagram for a σ-bonded octahedral complex ML_6

metal ion are placed in the t_{2g} and e_g* orbitals. These orbitals, because they lie closer in energy to the metal orbitals from which they were derived, have largely the character of the pure metal orbitals. Similarly, the a_{1g}, t_{1u}, and e_g molecular orbitals are largely ligand orbitals and, as we have seen, accommodate the ligand electrons. The result of forming molecular orbitals from the metal d orbitals has thus been to separate the initially degenerate d levels into a set of two (e_g*) and a set of three (t_{2g}).

Let us now see how simple magnetic and spectroscopic properties of transition metal complexes can be explained by using this MO method. The simplest case of a d^1 complex ion available in aqueous solution is the hexaquotitanium(III) ion $[Ti(H_2O)_6]^{3+}$. We can construct the energy-level occupation as follows for this ion

$$
\begin{array}{ll}
\text{Ti} & [\text{Ar}]\,3d^2\,4s^2 \\
\text{Ti}^{3+} & [\text{Ar}]\,3d^1 \\
[\text{Ti}(\text{H}_2\text{O})_6]^{3+} & \underbrace{(a_{1g})^2\ (t_{1u})^6\ (e_g)^4}_{\text{paired electrons from water molecules}}\ (t_{2g})^1
\end{array}
$$

We are thus left with one unpaired electron in the t_{2g} orbital, and this satisfactorily accounts for the paramagnetism of this ion ($\mu \approx 1.7$ B.M. at room temperature). The ions of d^2 and d^3 configuration follow naturally with the outermost electronic configurations of $(t_{2g})^2$ and $(t_{2g})^3$. With the d^4 configuration we have a choice; either we can begin to pair up electrons in the t_{2g} level to give the configuration $(t_{2g})^4$, or we can put the fourth electron in the e_g* level to give the configuration $(t_{2g})^3\,(e_g{}^*)^1$. Which of these two configurations is actually obtained will depend on the energy separation between the t_{2g} and the e_g* orbitals. This energy gap is usually referred to as Δ or $10\,Dq$. If Δ is small, the electrons will be expected to fill the levels so as to leave the maximum number of electrons with unpaired spins (Hund's rules). If Δ is large, the energy required to put an electron in the higher-energy e_g* orbitals may be greater than that required to pair electrons in the t_{2g} levels. We thus predict two possible types of complexes with metal ions of configurations d^4, d^5, d^6, and d^7. We can now use the example that we used on VB theory, that is the d^6 Co^{3+} ion, to illustrate this point. The diamagnetic complexes of cobalt(III) are those having all the d electrons paired in the t_{2g} levels. The paramagnetic complexes have the six electrons distributed between the two levels so as to give the maximum number of unpaired electrons. We can write this as follows

Co	$[Ar]\,3d^7\,4s^2$
Co^{3+}	$[Ar]\,3d^6$
$[Co(NH_3)_6]^{3+}$	$(a_{1g})^2(t_{1u})^6(e_g)^4(t_{2g})^6$
$[CoF_6]^{3-}$	$(a_{1g})^2(t_{1u})^6(e_g)^4(t_{2g})^4(e_g{}^*)^2$

The $CoF_6{}^{3-}$ ion thus has four unpaired electrons (two in the e_g* level and two in the t_{2g} levels). These complexes possessing the maximum number of unpaired electrons are called *high-spin* or *spin-free* complexes, while those in which the d electrons are paired as far as possible are referred to as *low-spin* or *spin-paired* complexes. In the cobalt example, $[CoF_6]^{3-}$ is a high-spin complex and $[Co(NH_3)_6]^{3+}$ is a low-spin complex. We shall be considering the factors favouring the formation of high and low-spin complexes in more detail shortly. For the moment we may just observe that the energy separation Δ is less for $CoF_6{}^{3-}$ (and hence the electrons remain unpaired) than for $[Co(NH_3)_6]^{3+}$ where a lower-energy state is obtained by pairing the electrons in the t_{2g} orbitals.

As well as giving a satisfactory explanation of the magnetic data, the molecular orbital diagram accounts satisfactorily for the electronic spectra of complexes. For many electron systems we must use spectroscopic states in place of orbitals when discussing spectra (see chapter 6) but d^1 systems can be simply described by using the molecular orbital energy-level diagram. The best-characterised octahedral d^1 complexes are the ions $[Ti(H_2O)_6]^{3+}$ and $[VCl_6]^{2-}$. The violet hexaquotitanium(III) ion has the visible absorption spectrum shown in Figure 5.3. The ground state of this ion has the outermost electron configuration $(t_{2g})^1$. The first excited state corresponds to $(t_{2g})^0(e_g{}^*)^1$. The absorption of visible light of a frequency $\nu = \Delta/h$ results in the excitation of the electron from the $(t_{2g})^1$ ground state to the $(e_g{}^*)^1$ excited state. We say that the violet colour of the $[Ti(H_2O)_6]^{3+}$ ion is due

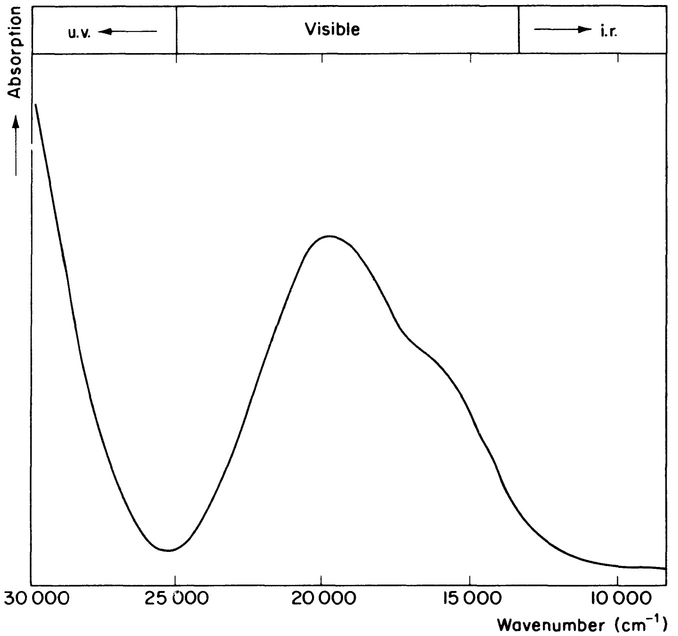


Figure 5.3 The visible absorption spectrum of the $[Ti(H_2O)_6]^{3+}$ ion

to the $t_{2g} \rightarrow e_g{}^*$ transition. Because we have measured the frequency at which absorption occurs and Planck's constant *h* is known, the energy separation between the t_{2g} and e_g levels has been determined by experiment. For convenience the spectra are usually measured in units of reciprocal centimetres or wavenumbers, cm^{-1}, and by convention this unit is also used as the unit of energy. The spectrum of $[Ti(H_2O)_6]^{3+}$ thus shows an absorption maximum at 20 000 cm^{-1} and the $t_{2g} - e_g{}^*$ separation Δ thus equals 20 000 cm^{-1} (note that 20000 cm^{-1} ≡ 5000 Å ≡ 239 kJ mol^{-1} ≡ 2.479 eV). The rising absorption towards the ultraviolet shown in Figure 5.3 is due to charge-transfer transitions (chapter 6). The spectrum of the $[VCl_6]^{2-}$ion is very similar in general shape to that of the $[Ti(H_2O)_6]^{3+}$ ion; the absorption maximum occurs at 15 400 cm^{-1}, so for $VCl_6{}^{2-}$ Δ = 15400 cm^{-1}. We shall consider more detailed aspects of these spectra in chapter 6.

Molecular orbital energy-level diagrams can be constructed in a similar way for other stereochemistries. However, when the effects of π-bonding are included some of these diagrams become very complicated and hence their general utility is diminished.

5.4 The Crystal-Field Theory

In the MO method we considered the overlap of orbitals, that is covalent bonding, as being of paramount importance. Crystal field (CF) theory starts at the opposite extreme, that is it is an electrostatic theory. We assume that the bonding in a complex is a result of electrostatic interaction between the positive nucleus of the metal cation and the negatively charged electrons of the ligands. Electrons contained in the cation exert a repulsion force on the ligand electrons.

5.4.1 Octahedral Complexes

Let us consider an octahedral complex which we represent on CF theory as shown in Figure 5.4; that is we choose the cartesian axes to be the fourfold axes of the octahedron. The ligand electrons are assumed to constitute an electrostatic field around the metal ion (just as in ionic crystals). We now consider the effect of this field on the energies of the metal orbitals. In view of the spherical symmetry of s orbitals it is apparent that an electron in, for example, the metal 4s orbital is affected equally by the electrostatic field in all six directions. The energy of the 4s orbital is merely raised by the presence of the electrostatic field. Similarly the p orbitals, which lie along the cartesian co-ordinates are equally affected by the field, so they remain degenerate (that is they all have the same energy) in the complex although again their energy is raised compared with that in the free ion. It is with the d orbitals that the presence of the crystal field becomes most important.

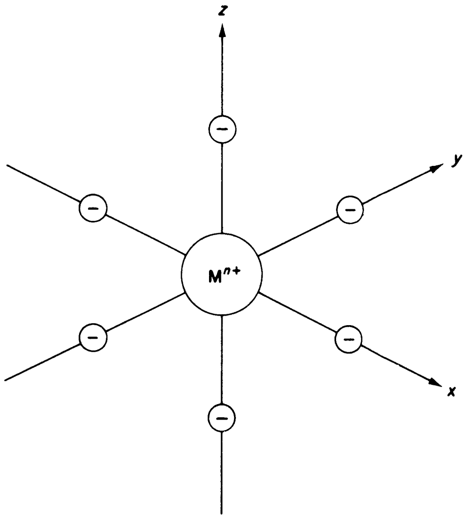


Figure 5.4 Crystal-field model of an octahedral complex

The five d orbitals have the approximate electron-density distribution indicated in Figure 5.5. The e_g set, that is the d_{z^2} and the $d_{x^2-y^2}$ orbitals, point directly along the cartesian co-ordinates and consequently directly at a ligand atom. The t_{2g} set, that is the d_{xy}, d_{xz}, and d_{yz} orbitals, have their lobes pointing between the axes and therefore do not point directly at the ligand atoms in an octahedral complex. It follows that an electron in an e_g orbital is repelled more strongly by the ligand electrons than is an electron in a t_{2g} orbital. An electron in a t_{2g}

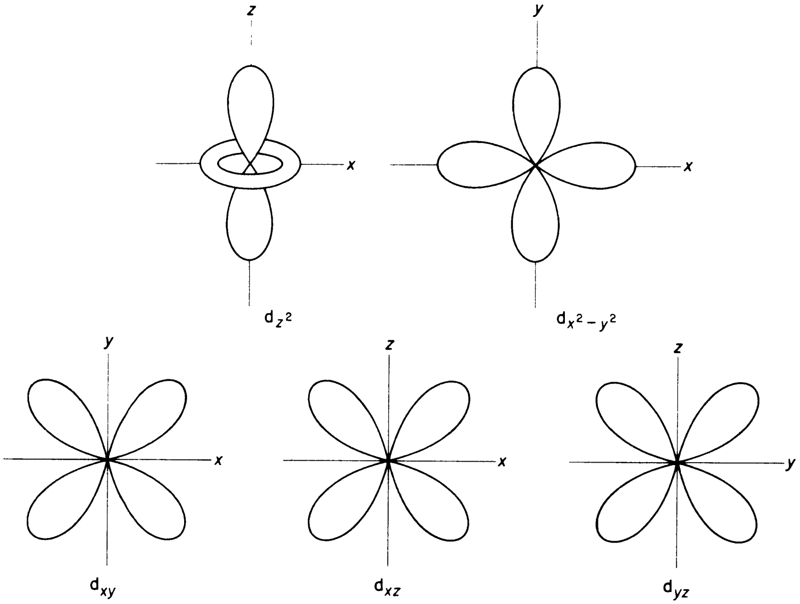


Figure 5.5 The electron-density distribution in the d orbitals

orbital is thus in a lower-energy state than one in an e_g orbital. We therefore deduce from simple electrostatics that in an octahedral field the five d orbitals are split into a group of two orbitals (e_g, higher energy) and a group of three orbitals (t_{2g}, lower energy). This is represented diagrammatically in Figure 5.6. In this figure we have chosen to ignore the increase in energy of all the d orbitals that results upon application of the crystal field; we have focused our attention on the splitting of the orbitals since this is the informative part of the diagram. We therefore draw the free-ion d orbital energies as though they are at the centre of gravity of the energies of the orbitals in the complex.

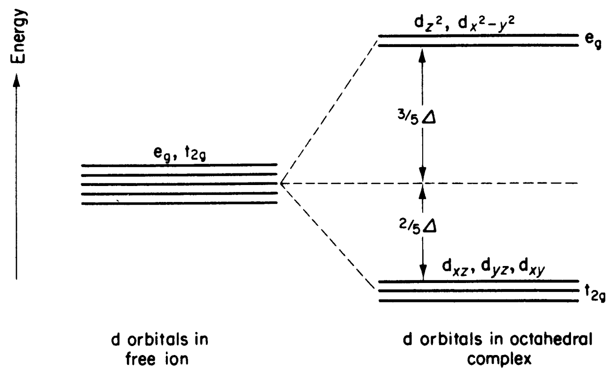


Figure 5.6 Crystal-field splitting diagram for an octahedral complex

We have thus arrived at the same conclusion as when using MO theory, that is, the degeneracy of the d orbitals is removed in an octahedral complex, the e_g set (denoted e_g* on MO theory) being at a higher energy than the t_{2g} set. Further, the separation between these levels, that is Δ, is justified experimentally. The CF theory enables the splitting of the d orbitals to be obtained very simply, regardless of the stereochemistry. However, it does start with the extreme assumption that only electrostatic bonding is important; there is now ample spectroscopic and magnetic evidence that in most complexes at least some covalent bonding occurs. In order to solve this difficulty, most authors use (as we shall here) the term *ligand field theory* to encompass the two extremes of CF and MO. Ligand-field theory can thus be regarded as derived from CF theory by the admission of covalent bonding, or from just the d orbital part of the complete MO diagram. Because the d orbital energy-level diagrams are most easily obtained by using CF theory, we shall now consider the splitting of the d orbitals in crystal fields other than octahedral.

5.4.2 Tetrahedral Complexes

In order to derive the d orbital energy-level diagram for a tetrahedral complex, we must first visualise the tetrahedral structure as being related to a cube. This is shown in Figure 5.7 which illustrates that the tetrahedral structure is formed by joining opposite corners of the top and bottom sides of a cube to the centre. With the cartesian co-ordinates drawn as before, we can now envisage the crystal-field interactions with electrons in the d orbitals in a tetrahedral environment. The d_{z^2}

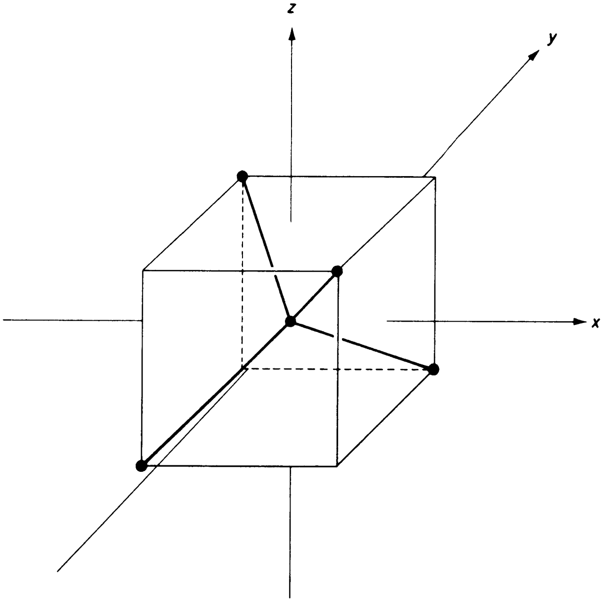


Figure 5.7 The relationship between the tetrahedral structure and a cube.

and $d_{x^2-y^2}$ orbitals now do not point in the direction of the ligand charges and hence are at a lower energy than the d_{xy}, d_{xz}, d_{yz} set which point more closely to the ligand positions. Unlike the situation in the octahedral case, notice that in the tetrahedral field none of the d orbitals points exactly at the ligands. The d_{xy}, d_{xz}, and d_{yz} orbitals have lobes that can be imagined to intersect the edges of the cubes at a distance equal to half a cube edge away from a ligand position, while the lobes of the d_{z^2} and $d_{x^2-y^2}$ orbitals intersect the cube faces at a distance equal to half a diagonal away from a ligand position. The energy separation between the two sets of orbitals is thus less than it was in the octahedral case. This is illustrated in Figure 5.8 which compares the splitting in octahedral and tetrahedral fields. The splitting in the tetrahedral case is thus inverted compared with that in the octahedral case. and detailed calculations show that, other things being equal, it is only four-ninths of that in the octahedral case, that is

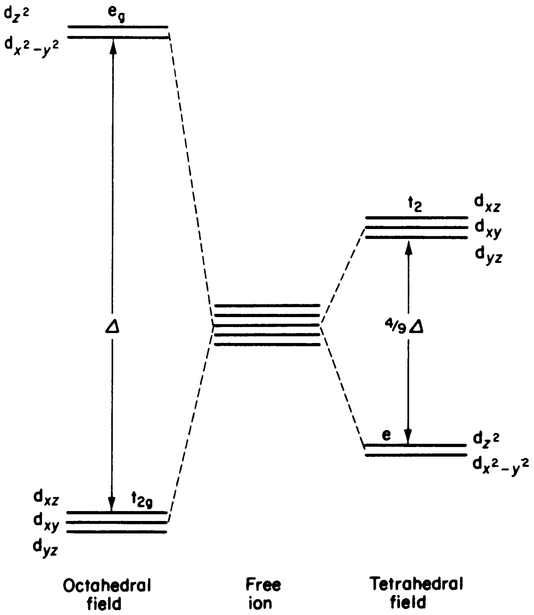


Figure 5.8 Comparison of crystal-field splitting diagrams for octahedral and tetrahedral fields.

$$\Delta_{tet} = (4/9)\Delta_{oct}$$

In general terms, with complexes of a metal in a given oxidation state, the value of Δ for a tetrahedral complex with a ligand is expected to be about half that for an octahedral complex with the same ligand. This is found experimentally to be the case.

In the tetrahedral case we feed metal electrons into the lower-energy doublet first. Notice that this orbital doublet carries the label e and the upper orbital triplet carries the label t_2. The subscripts g and u do not apply in the tetrahedral case since this does not possess a centre of symmetry (the g and u subscripts refer to symmetry properties with respect to inversion about a centre of symmetry). For the simplest case of a d^1 ion we can illustrate the crystal field approach by using the VCl_4 molecule (despite the obvious covalency in this compound). The configuration of this molecule is represented by $(e)^1(t_2)^0$. The absorption of light by this molecule results in the electronic transition $e \rightarrow t_2$; this absorption is a fairly broad band centred around 8000 cm^{-1}, that is Δ_{tet} for $VCl_4 \approx 8000$ cm^{-1}. This is in reasonable agreement with Δ_{oct} for the VCl_6^{2-} ion which we saw earlier is 15 400 cm^{-1}, that is about twice the value for Δ_{tet} in VCl_4.

5.4.3 Crystal-field Splittings in Stereochemistries Other than Octahedral or Tetrahedral

The energy-level splittings for the d orbitals in other stereochemical environments can be deduced by using the same ideas of electrostatics and symmetry that were used in the octahedral and tetrahedral cases.

The square planar crystal-field diagram can be obtained in one of two ways. Either we can imagine the square plane as being derived from the octahedral shape by removal of two *trans*-axial ligands to infinity, or we can start with the square planar structure. The former method is appropriate to tetragonal complexes, and we shall see the energy-level diagrams obtained by this method later in this chapter. In the square planar structure, the ligands are attached to the metal ion along the x and y axes (using the same model as in the octahedral case). The orbital of highest energy is thus the $d_{x^2-y^2}$ orbital since this points directly at the ligands. The d_{xy} orbital is expectedly the next highest in energy because it lies in the same plane as the ligands. The d_{xz} and d_{yz} orbitals will be degenerate and may be higher in energy than the d_{z^2} orbital which has its major component pointing along the z axis away from the ligands. Thus we arrive at the qualitative square planar energy-level diagram as shown in Figure 5.9. While this diagram is believed to be correct in the case of, for example, the $[PtCl_4]^{2-}$ ion, for other combinations of metal

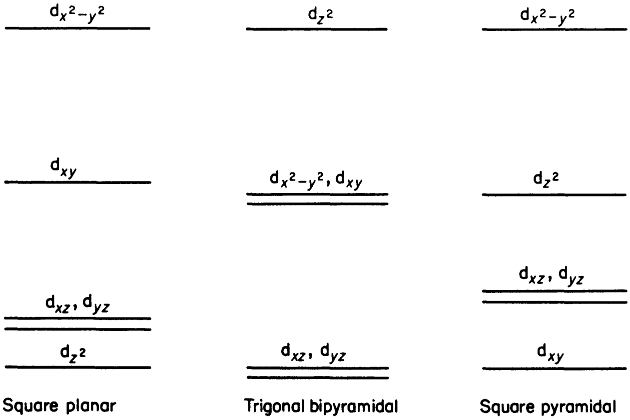


Figure 5.9 Qualitative crystal-field splitting diagrams for different stereochemistries.

ion and ligand the d_{z^2} level may rise above that of the d_{xz} and d_{yz} orbitals. This is also the case when there are ligands in the z axes that are too far away to be normally considered as being bonded, and of course in tetragonal complexes.

The two crystal-field splitting diagrams for the pure five-co-ordinate geometries are also included in Figure 5.9; their main features follow from the arguments that we have made for other stereochemistries.

5.5 Ligand-Field Theory in Application

5.5.1 High- and Low-spin Complexes

We have already seen that on MO and CF theories the magnetic and spectral properties of transition metal complexes are concerned principally with nonbonding electrons. We shall now examine the number of these electrons in each of the configurations from d^1 to d^{10} for octahedral complexes.

For the configurations d^1, d^2, d^3, d^8, d^9, and d^{10} there is only one possible way to distribute the electrons among the t_{2g} and e_g orbitals so as to obtain the lowest-energy configurations. We obtain the lowest-energy configurations for d^1, d^2, and d^3 species by feeding electrons first into the lower-energy t_{2g} levels with the electron spins unpaired. With d^8, d^9, and d^{10} configurations the t_{2g} level is necessarily filled with electrons and the e_g level fills by maintaining the maximum number of unpaired electron spins. These configurations are illustrated in Figure 5.10 together with the magnetic moment expected for each configuration if the spin-only formula is assumed to apply.

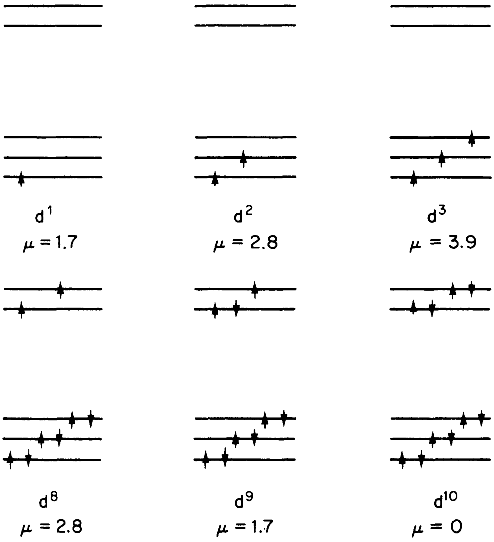


Figure 5.10 Ligand-field diagrams showing the ground state electron occupancy and spin-only magnetic moments (in B.M. units) for six of the configurations from d^1 to d^{10} for octahedral complexes.

For the configurations d^4, d^5, d^6 and d^7 there are two possibilities as was pointed out in section 5.3. The most important single factor in determining whether high-spin or low-spin complexes arise is the ligand-field splitting parameter Δ. When Δ is larger than the pairing energy P for the electrons, the electrons pair in the t_{2g} orbitals as far as is possible. If the energy required to pair up the spins of the electrons and place them in the same orbital (electrostatic repulsion) is greater than Δ, the electrons will distribute themselves between the t_{2g} and e_g levels so as to have the maximum number of unpaired spins. In the former case we have the *strong-field* ($\Delta > P$) arrangement with low-spin complexes, while in the latter we have the *weak-field* ($\Delta < P$) arrangement with high-spin complexes. These configurations are illustrated in table 5.2 together with the number of unpaired electrons and hence the *spin-only* magnetic moment for each type of complex.

Complexes of configurations d^1, d^2, d^3, d^8, and d^9 have the same number of unpaired electrons as in the free ion, while those of configurations d^4, d^5, d^6, and d^7 may or may not have the maximum number of unpaired electrons. Two examples will suffice here to illustrate that this is found experimentally. We saw the electronic structures of the d^6 complexes $[Co(NH_3)_6]^{3+}$ and $[CoF_6]^{3-}$ described on VB and MO theories, and for comparison we describe them here using ligand field notation

TABLE 5.2. HIGH AND LOW-SPIN COMPLEXES OF OCTAHEDRAL d^4, d^5, d^6, AND d^7 CONFIGURATIONS

	High-spin				Low-spin			
No. of d electrons	Weak-field arrangement		No. of unpaired electrons	μ (B.M.)	Strong-field arrangement		No. of unpaired electrons	μ (B.M.)
	t_{2g}	e_g			t_{2g}	e_g		
4	↑↑↑	↑	4	4.9	↑↓↑↓		2	2.8
5	↑↑↑	↑↑	5	5.9	↑↓↑↓↑		1	1.7
6	↑↓↑↑	↑↑	4	4.9	↑↓↑↓↑↓		0	0
7	↑↓↑↓↑	↑↑	3	3.9	↑↓↑↓↑↓	↑	1	1.7

$[CoF_6]^{3-}$ μ(experimental) = 4.3 B.M. high-spin $t_{2g}^4 e_g^2$
$[Co(NH_3)_6]^{3+}$ μ(experimental) = 0 low-spin t_{2g}^6

Iron(III) complexes provide an example from the d^5 configuration

$[FeF_6]^{3-}$ μ(experimental) = 5.9 B.M. high-spin $t_{2g}^3 e_g^3$
$[Fe(CN)_6]^{3-}$ μ(experimental) = 2.4 B.M. low-spin t_{2g}^5

In these two examples the deviations of the experimentally determined magnetic moments at room temperature from the spin-only moments are considerable, but the moments leave no doubt about the existence of the two separate classes of complex.

In tetrahedral fields complexes of the first-row transition elements are always high-spin. This is to be expected in view of the lesser splitting in the tetrahedral case.

5.5.2 The Magnitude of Δ; the Spectrochemical Series

Studies of the electronic spectra of transition-metal complexes enable the ligand-field splitting parameter Δ ($10Dq$) to be determined experimentally. From the values so obtained (table 5.3 shows typical values) certain generalisations can be made.

TABLE 5.3 SOME TYPICAL VALUES OF Δ (cm^{-1}) FOR OCTAHEDRAL COMPLEXES

Metal ion	Ligands			
	$6F^-$	$6H_2O$	$6NH_3$	$6CN^-$
Ti^{3+}	17 500	20 100		
V^{3+}	16 100	18 500		23 400
Cr^{3+}	15 100	17 400	21 600	26 600
Fe^{3+}	14 000			35 000
Co^{3+}	13 000	19 100	22 900	34 800
Fe^{2+}		10 400		33 800
Co^{2+}		9 300	11 000	
Ni^{2+}		8 500	10 800	

(1) For a given ligand, Δ does not vary much among ions of the first transition series in the same oxidation state. For example, values of Δ for hydrates of M^{2+} lie within the region 7 500 – 12 000 cm^{-1}.
(2) For a given ligand Δ increases rapidly with increase in oxidation state of the metal; for example values of Δ for hydrates of M^{3+} are in the 14 000 – 25 000 cm^{-1} region.
(3) For a given ligand and stereochemistry the metal ions can be arranged in order of increasing Δ, and this order is more or less independent of the nature of the ligand.
(4) For a given metal ion the ligands can be arranged in order of increasing Δ; this order is more or less independent of the nature of the metal ion.

These last two series are known as the *spectrochemical series.* The spectrochemical series for common metal ions in the first transition series is

$$Mn^{2+} < Ni^{2+} < Co^{2+} < Fe^{2+} < V^{2+} < Fe^{3+} < Cr^{3+} < V^{3+} < Co^{3+}$$

For the more common ligands the spectrochemical series is

$$I^- < Br^- < Cl^- < S^{2-} < F^- < OH^- < CH_3COO^- < C_2O_4{}^{2-} \approx O^{2-}$$
$$< H_2O < py \approx NH_3 < en < bipy < phen < PR_3 < CO \approx CN^-$$

This spectrochemical series for ligands is found to be useful in a semiquantitative way. The ligands are arranged in order of increasing ligand field strength. For example, the CN^- ion is known as a strong-field ligand while the I^- ion is known as a weak-field ligand. Ligands such as water and ammonia are said to have medium field strengths. If we know the position of the absorption maxima in the spectrum of a metal ion with one ligand, we can make approximate predictions about the positions of the bands for complexes of this ion with other ligands. Similarly, if a metal forms low-spin complexes with, for example, ethylenediamine, it will form low-spin complexes with, for example, bipyridyl or cyanide ions. However, the series must be used with some caution since minor variations sometimes occur. The order in the series is very difficult to understand on crystal-field theory; for example, it is hard to envisage why the negatively charged F^- ion exerts a weaker field than a neutral water molecule. Ligand-field theory, which takes covalent bonding into account, does account for these apparent anomalies.

A certain amount of rationalisation of the spectrochemical series of ligands can be achieved through the consideration of π-bonding. In the molecular orbital diagram for an octahedral complex (Figure 5.2) we deliberately, for the sake of simplicity, included only σ-bonding. However, the value of Δ is affected by π-bonding. The t_{2g} orbitals on the metal ion are nonbonding with σ-ligands but become bonding orbitals with ligands having π symmetry. The ligand π orbitals may be p or d orbitals or π^* molecular orbitals. Some suitable combinations of metal and ligand π-bonding orbitals are shown in Figure 5.11. (For simplicity only one ligand orbital is drawn in each example.) The effects that π-bonding of these types have upon the value of Δ can now be considered. For simplicity we shall consider two extreme but important cases.

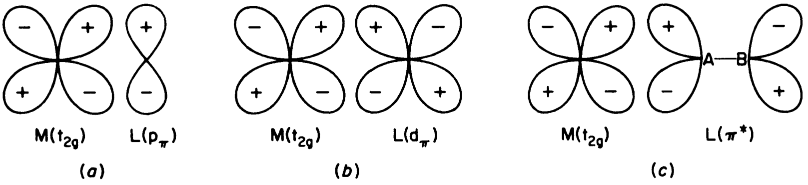
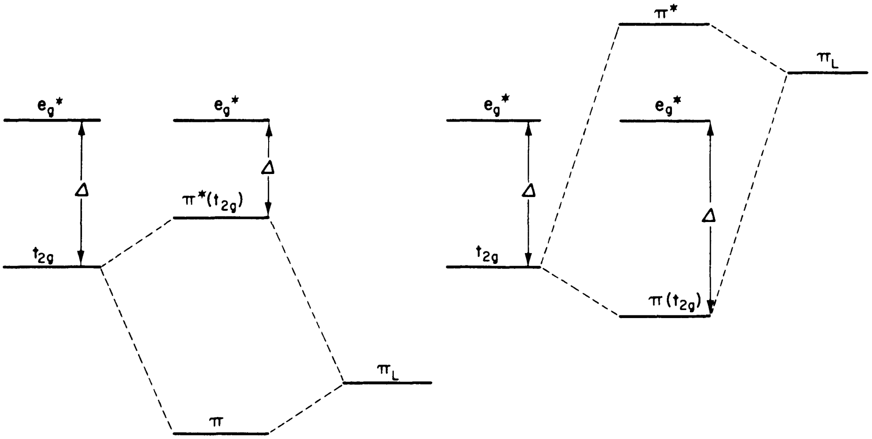


Figure 5.11 Some suitable combinations of metal and ligand π-bonding orbitals.

In the first case we have ligand orbitals of π symmetry filled with electrons and low in energy. Such a case is represented by filled p orbitals on F^- or Cl^- ions, and the overlap by Figure 5.11*a*. The π-bonding molecular orbital that is formed has a lower energy than the p_π atomic orbitals from which it was formed (Figure 5.12*a*), and contains the electrons from the filled ligand π orbitals. This could thus be represented as L→M π interaction in which the ligand is regarded as a π electron donor. The π-antibonding molecular orbital has a higher energy than the original t_{2g} metal orbital, and since the bonding π orbital is filled, the π^* t_{2g} orbital must contain the metal electrons. The net effect is to decrease Δ, the separation between the orbitals that have largely the character of the original d orbitals on the metal. We thus expect to find ligands such as halide ions at the weak-field end of the spectrochemical series.

The second case to consider is that of ligands possessing vacant high-energy π orbitals. These are the so-called π-acceptor ligands which give rise to M→L π interaction. The effect of the π interaction here is to stabilise the t_{2g} level, thus



(a) (b)

Figure 5.12 The effect of π-bonding on the magnitude of Δ: (*a*) with low-energy filled π orbitals on the ligand; (*b*) with high-energy empty π orbitals on the ligand

increasing the value of Δ (Figure 5.12*b*). Note that because π_L is empty the π (t_{2g}) level still contains only the electrons originally present on the metal. Ligands capable of behaving in this way include phosphorus, arsenic, and sulphur donors which possess vacant d orbitals that can overlap as shown in Figure 5.11*b*, and polyatomic ligands possessing multiple bonds. In this latter class are ligands such as CO, CN^-, and ethylene which possess empty π* molecular orbitals; these are represented as A–B in Figure 5.11*c*. These ligands cause a large splitting of the d levels and are thus the strong-field ligands found at the strong-field end of the spectrochemical series. The ligands of intermediate field strength have little or no π-bonding effects.

5.5.3 Crystal-field Stabilisation Energies

In an octahedral complex of a d^1 ion the d electron resides in a t_{2g} orbital. This orbital lies (see Figure 5.6) at an energy $(2/5)\Delta$ below the arbitrary zero of energy that we assign to the unsplit d orbitals in the presence of a ligand field. This extra stability arising out of the splitting of the d orbitals is known as the *crystal-field stabilisation energy* (CFSE). Some authors refer to this as ligand-field stabilisation energy, but since it had its origin in crystal-field theory we retain here the more commonly used term CFSE.

Every electron that resides in a t_{2g} orbital of an octahedral complex contributes 0.4Δ to the CFSE. However, an electron in an e_g orbital is at a higher energy than that of the unsplit d orbitals, and thus it destabilises the system by $(3/5)\Delta$. Every electron in an e_g orbital therefore contributes -0.6Δ to the total CFSE. It is thus easy to work out the total CFSE for all octahedral configurations; the results are shown in table 5.4. Since values of Δ are in the region 10–30 000 cm^{-1} it follows that CFSEs will typically lie in the range 5 000–40 000 cm^{-1}, that is 60–480

TABLE 5.4. CRYSTAL-FIELD STABILISATION ENERGIES FOR OCTAHEDRAL COMPLEXES

Number of d electrons	High-spin Configuration		High-spin CFSE (Δ)	Low-spin Configuration		Low-spin CFSE (Δ)
d^1	t_{2g}^{1}	e_g^{0}	0.4			
d^2	t_{2g}^{2}	e_g^{0}	0.8			
d^3	t_{2g}^{3}	e_g^{0}	1.2			
d^4	t_{2g}^{3}	e_g^{1}	0.6	t_{2g}^{4}	e_g^{0}	1.6
d^5	t_{2g}^{3}	e_g^{2}	0.0	t_{2g}^{5}	e_g^{0}	2.0
d^6	t_{2g}^{4}	e_g^{2}	0.4	t_{2g}^{6}	e_g^{0}	2.4
d^7	t_{2g}^{5}	e_g^{2}	0.8	t_{2g}^{6}	e_g^{1}	1.8
d^8	t_{2g}^{6}	e_g^{2}	1.2			
d^9	t_{2g}^{6}	e_g^{3}	0.6			
d^{10}	t_{2g}^{6}	e_g^{4}	0.0			

kJ mol^{-1}. These amounts of energy are not insignificant, and we shall now try to illustrate how their existence adds to the power of ligand-field theory in interpreting the properties of transition-metal complexes.

5.5.4 Stabilities of Hexaquo-ions

Let us consider the heats of hydration of divalent metal ions in the first transition series, that is the heats of the reactions

$$M^{2+}(g) + H_2O\,(\text{excess}) \rightarrow [M(H_2O)_6]^{2+}aq$$

If the ratio of charge to radius were the only factor affecting the bond strength, we should expect the heats of hydration of the metal ions to increase steadily from Ca^{2+} to Zn^{2+} as the ions become progressively smaller. The actual values are those illustrated by circles in Figure 5.13. However, if the value of the CFSE for each hydrated ion (all high-spin) is deducted from the observed value of the hydration energy, we get the expected smooth curve passing through the crosses in Figure 5.13. Notice that for the Ca^{2+} (d^0), Mn^{2+} (d^5), and Zn^{2+} (d^{10}) ions which have no CFSE the experimental values already lie on this smooth curve. The idea that CFSE is playing an important part in the energy cycle is thus justified.

5.5.5 Octahedral or Tetrahedral Co-ordination?

The three most commonly found stereochemistries for first-row transition metal complexes are octahedral, tetrahedral, and square planar. Of these the octahedral structure, which uses the largest number (six) of the available σ-bonding orbitals on

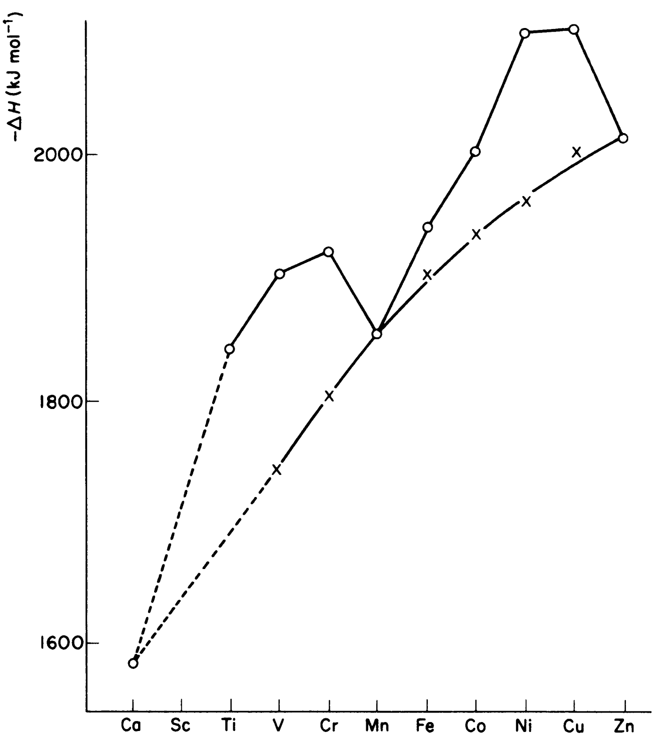


Figure 5.13 Hydration energies of divalent metal ions: O, experimental values; X, values corrected for CFSE.

the metal, is the most stable unless significant steric or electronic effects are present.

The steric effects that may be important in determining the shapes of complex ions concern ligand–ligand repulsion forces. Repulsion between bonded ligands in complexes occurs through coulombic and van der Waals type forces. Large negatively charged one-atom ions such as $I^-$and Br^-will experience greatest repulsion, while small neutral molecules such as H_2O and NH_3 will exhibit the smallest interligand repulsion forces. Large molecules and small ions will be in the intermediate repulsion range. Since the splitting of the d orbitals and hence the CFSE is least with the weak-field ligands, it follows that the tetrahedral structure is most likely to be preferred with weak-field ligands that have large mutual repulsion effects. In general terms we observe that, while water and ammonia form predominantly octahedral complexes, it is the iodide and bromide ions that form a large number of tetrahedral complexes. These ions combine weak ligand fields with maximum interligand repulsions. Cyanide ion, which exerts less interligand repulsion, has also one of the strongest ligand fields, so the difference between the octahedral and tetrahedral CFSE for any particular metal is at a maximum for this ion. This results in a considerable preference for the octahedral shape in most cases.

In the first-row transition series, certain metal ions have a greater tendency than others to form tetrahedral complexes. The number of electrons in the d orbitals in each case is responsible for the electronic effects that contribute to this tendency. The CFSE for tetrahedral complexes can be calculated in the same way as for octahedral complexes. In tetrahedral complexes the metal d electrons enter the e levels first (Figure 5.8) and each e electron contributes $(3/5)\Delta_{tet}$ to the CFSE. Electrons in t_2 levels contribute $-(2/5)\Delta_{tet}$ to the total CFSE. Since $\Delta_{tet} = (4/9)\Delta_{oct}$ we can compare the CFSEs for tetrahedral and octahedral fields by using Δ_{oct} as a common unit. Thus for d^1 in a tetrahedral field the CFSE is

$$\begin{aligned}(3/5)\Delta_{tet} &= (3/5) \times (4/9)\Delta_{oct} \\ &= 0.266\Delta_{oct}\end{aligned}$$

The values of CFSE thus obtained for all the d^0 to d^{10} configurations are plotted in Figure 5.14 (lower graphs) along with the values for octahedral high-spin

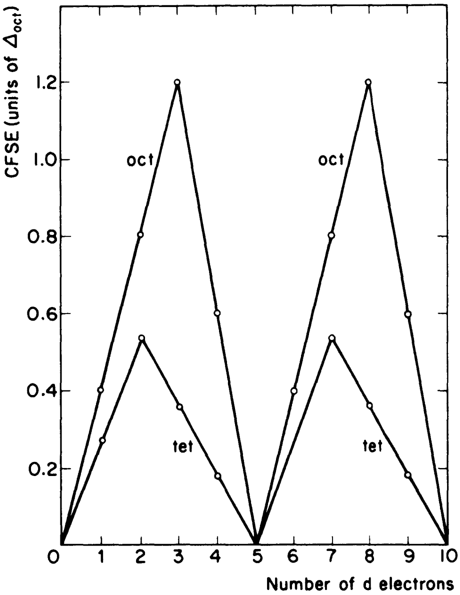


Figure 5.14 Crystal-field stabilisation energies for d^0 to d^{10} high-spin ions in octahedral and tetrahedral fields.

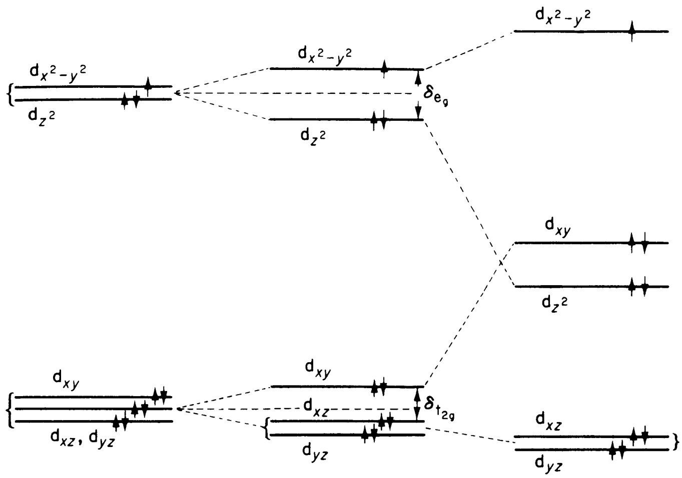
configurations (upper graphs). The figure shows that in terms of CFSE the octahedral field is preferred most by the d^3 and d^8 configurations. Chromium(III) (d^3) and nickel(II) (d^8) do indeed show an exceptional preference for octahedral as opposed to tetrahedral co-ordination; tetrahedral chromium(III) complexes are virtually unknown. The d^4 and d^9 configurations also show a strong preference for octahedral stereochemistry, for example Mn(III) and Cu(II), but, as we shall see shortly, distortion is common in these cases. For the d^1, d^2, d^6, and d^7 ions the preference for octahedral stereochemistry is not so great, and tetrahedral complexes are expected to be more common. Thus, unlike Cr(III), vanadium(II) (d^2) forms tetrahedral VX_4^- species (X = Cl, Br, I), and unlike nickel(II), cobalt(II) (d^7) forms a very large number of tetrahedral complexes with neutral ligands as well as with anions. For the configurations d^0, d^5 (high-spin), and d^{10}, the d electrons have no influence on stereochemistry since there is no CFSE in either case.

5.5.6 Distortions from Perfect Symmetry; the Jahn–Teller Effect

So far we have considered the electronic effects that contribute towards the stability of octahedral as opposed to tetrahedral stereochemistry. A very important electronic effect tells us that in many cases these pure stereochemistries will not be obtained but that distortion will occur. This effect was first formulated by Jahn and Teller in 1937 and is named after them. We shall begin by considering the copper(II) ion which perhaps provides the best illustration of this effect.

In an octahedral field the copper(II) ion (d^9) has the electronic structure $t_{2g}{}^6\ e_g{}^3$ as shown in Figure 5.15*a*. Since the e_g levels are degenerate, we do not know whether the $d_{x^2-y^2}$ or the d_{z^2} orbital is doubly filled. Let us assume that the d_{z^2} orbital is doubly filled and the $d_{x^2-y^2}$ singly filled. The result of this orbital occupancy is that the ligands along the *x* and *y* axes are drawn closer to the metal. This is because they experience the electrostatic attraction of the Cu^{2+} ion more than do the ligands along the *z* axis which are shielded from the Cu^{2+} ion by an extra electron. We thus have a tetragonal distortion in which the octahedron has been contracted along the *x* and *y* axes. If we had chosen the $d_{x^2-y^2}$ as the doubly filled orbital, again a tetragonal distortion would occur but this time with a contraction along the z axis. For copper(II) compounds the distortion frequently observed experimentally is in fact the contraction along the *x* and *y* axes resulting in a structure having four short bonds and two longer bonds. We thus have the $d_{x^2-y^2}$ orbital singly filled as shown in the tetragonal energy-level diagrams in Figure 5.15*b* and *c*. The pair of electrons thus prefer to be in the d_{z^2} orbital where they feel less repulsion from the ligands. The energy of the d_{z^2} orbital is thus no longer degenerate with that of the $d_{x^2-y^2}$ orbital but is instead below it in energy. As the tetragonal distortion increases with elongation along the *z* axis, so the level of the d_{z^2} orbital drops while the levels of the $d_{x^2-y^2}$ and d_{xy} orbitals rise (Figure 5.15*c*). Eventually, if the ligands along the *z* axis are removed completely, we have the square planar structure (Figure 5.9) in which the d_{z^2} level may even drop below that of the d_{xz} and d_{yz} doublet level.

A close examination of Figure 5.15 will enable the reader to see that, in this d^9 case, distortion has resulted in a lower energy for the system, that is distortion has caused stabilisation. Since the *centre of gravity* rule applies to the tetragonal splittings, the energy of the system in Figure 5.15*b* is less than that in Figure 5.15*a* by an amount equal to $0.5\delta_{e_g}$ (there is no net energy change in the t_{2g} orbitals since the increase in energy of the two electrons in the d_{xy} orbital is equal to twice the amount by which the four electrons in the d_{xz} and d_{yz} orbitals are decreased in energy). Therefore, with copper(II) complexes, tetragonal rather than octahedral complexes are found even when six identical ligands are present as in $[Cu(H_2O)_6]^{2+}$. In many copper(II) compounds the distortion is so great (represented by Figure 5.15*c*) that the co-ordination is almost square.



(*a*) Octahedral (*b*) Small tetragonal distortion (*c*) Large tetragonal distortion

Figure 5.15 Tetragonal distortion of an octahedral d^9 complex; bracketed levels are degenerate.

In general terms this Jahn–Teller effect, or theorem as it is sometimes known, can be stated: *If, as first represented, a molecular system gives a degenerate electronic state, it will be found to have distorted itself so as to split the degenerate state.* The theorem tells us only that a distortion will occur; it does not indicate the direction or magnitude of the distortion. As well as the $t_{2g}^6\ e_g^3$ configuration we should expect the $t_{2g}^6\ e_g^1$ configuration to undergo distortion with similar stabilising effect. Low-spin cobalt(II) and nickel(III) have this configuration and their 'octahedral' complexes are indeed found to have undergone distortion. Such distortions would also be correctly predicted for ions of the $t_{2g}^3\ e_g^1$ configuration, that is high-spin chromium(II) and manganese(III). For ions of configurations

$$t_{2g}^3;\ t_{2g}^3\ e_g^2;\ t_{2g}^6;\ t_{2g}^6\ e_g^2;\ t_{2g}^6\ e_g^4$$

no distortions are expected; these are the configurations most likely to give rise to perfectly octahedral ML_6 complexes.

Interesting cases arise with complexes containing partly filled t_{2g} levels. The extent of the splitting of the t_{2g} levels (δt_{2g}; Figure 5.15*b*) is considerably less than that of the e_g levels because the t_{2g} orbitals do not point directly at the ligand positions. Thus, while we should expect distortion for the configurations t_{2g}^1, t_{2g}^2, t_{2g}^4, and t_{2g}^5, it is more difficult to detect experimentally; however, these small distortions can be detected by magnetic measurements (chapter 7). In the first excited states of these configurations, electrons are present in e_g orbitals; these excited states undergo the larger Jahn–Teller distortion, and it is these distortions that are readily observed in the electronic spectra. For the d^1

case $t_{2g}^1\ e_g^0$ becomes $t_{2g}^0\ e_g^1$ in the excited state. This state splits in the same way as the d^9 configuration (bearing in mind that we do not know which of the levels d_{z^2} or $d_{x^2-y^2}$ lies highest). If we ignore the relatively small splitting of the t_{2g} levels for the moment, we see that for the d^1 case two electronic transitions are possible which we may write (using the nomenclature in Figure 5.15) as

$$d_{xz,yz} \longrightarrow d_{z^2}$$
$$d_{xz,yz} \longrightarrow d_{x^2-y^2}$$

If we now consult the visible spectrum of the $[Ti(H_2O)_6]^{3+}$ ion (Figure 5.3), we observe that it does in fact consist of two overlapping bands, one at around 17 000 cm^{-1} and the other at 20 000 cm^{-1}. The $d_{xz,yz} \rightarrow d_{xy}$ transition will not be observed in the visible spectrum; the energy separation is of the order of a few hundred wavenumbers, so this transition will occur in the infrared region of the spectrum. Similar broadenings of visible absorption bands are observed in the case of d^6 spin-free ions whose ground state $t_{2g}^4\ e_g^2$ becomes $t_{2g}^3\ e_g^3$ in the first excited state.

6 Electronic Spectra of Transition-metal Complexes

6.1 Introduction

We have, to a very limited extent, already discussed the magnetic and spectral properties of complexes in chapter 5. We now look at these topics in greater detail. The theory behind this material is difficult; in order that some progress can be made towards understanding the spectra and magnetism of complexes, it will be assumed that the student has some elementary knowledge of spectroscopic term symbols. Some of the more theoretical aspects of electronic spectra and a discussion of term symbols are to be found in the references cited in the bibliography. The study of the spectral and magnetic properties of complexes provides us with much information that we have seen can shed considerable light on bonding theories. Spectral properties are concerned with differences between the ground state and the excited states of molecules, whereas the magnetic properties are concerned with the nature of states very close in energy to the ground state. Since electronic spectra can be measured directly in a few minutes, information is often quickly forthcoming from this technique. Because these electronic spectral bands are usually very broad, the spectra are not often used as 'fingerprints' or in looking for functional groups as is done in infrared spectroscopy. However, a combination of spectral and magnetic studies often enables the stereochemistry of a complex to be determined, and may also indicate something about the extent of distortion therein.

The visible and ultraviolet regions of the spectrum, that is 10 000–50 000 cm^{-1}, are those in which electronic excitations usually occur. Light of these wavelengths may be absorbed by a complex for a variety of reasons. These possible interactions can be classified as follows.

(1) *Ligand spectra.* Ligands such as water or organic molecules possess characteristic absorption bands that are normally in the ultraviolet. These bands remain in the spectra of the complexes but may be shifted somewhat from their original position.

(2) *Counter-ion spectra.* A complex ion must be associated with a counter-ion; a knowledge of the spectrum of this counter-ion must be known in order to interpret the spectrum due to the complex ion.

(3) *Charge-transfer spectra.* These spectra arise from transitions between orbitals that are principally those of the metal and orbitals that are largely ligand orbitals.

(4) *Ligand-field spectra.* These arise from transitions between the d orbitals of the metal that have been split in a ligand field; they are otherwise known as d–d spectra.

It is principally this last category with which we shall be most concerned, but a brief indication of the importance of each of the other spectral types will now be given.

6.1.1 *Ligand Spectra*

Some organic ligands possess visible absorption, and virtually all absorb in the ultraviolet region of the spectrum. There are three principal types of ligand absorption which we now consider in turn.

(1) $n \rightarrow \sigma^*$ *transitions.* When atoms in molecules possess lone-pair electrons that are not involved in the internal bonding, the transition of lowest energy is $n \rightarrow \sigma^*$. The σ-bonding orbitals are filled and lower in energy than the level containing the nonbonding electrons. These transitions are found in molecules such as water, alcohols, amines, and alkyl halides. This ultraviolet absorption limits the use of these substances as solvents in which to measure spectra. For example, it becomes difficult to balance spectroscopic cells with water above 50 000 cm^{-1} or with chloroform above 40 000 cm^{-1} because of the intense absorption above these frequencies.

(2) $n \rightarrow \pi^*$ *transitions.* These transitions can occur in molecules containing atoms that are involved in π-bonding and that also contain nonbonding electron pairs. Such molecules are aldehydes and ketones which contain the $>C{=}O$ group. Again the nonbonding electrons are in a level higher than the σ and π-bonding levels but now the lowest unoccupied level is the π^* level. Hence the transition of lowest energy is $n \rightarrow \pi^*$; this occurs in the ultraviolet region. The next transition is $\pi \rightarrow \pi^*$; this normally occurs above 50000 cm^{-1}, in what is described as the vacuum ultraviolet.

(3) $\pi \rightarrow \pi^*$ *transitions.* Molecules possessing double or triple bonds but no atoms with nonbonding electrons have the π-bonding orbital as the highest occupied level and the π^* orbital as the lowest unoccupied level. The transition of lowest energy is thus $\pi \rightarrow \pi^*$. Such transitions occur in olefins, dienes, and aromatic systems.

Some ligands possess more than one of these types of band. Pyridine, for example, has $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. In complexes containing these ligands, the ligand absorption does not change significantly and is frequently recognisable by its characteristic band shape.

6.1.2 *Counter-ion Spectra*

There are many simple anions that do not absorb radiation in the visible or ultraviolet regions, for example Cl^-, $SO_4{}^{2-}$, and $ClO_4{}^-$. However, of these only perchlorate does not form stable complexes with metal ions. Therefore, if we wish to measure the spectrum of a hexaquo-ion, the solution must be acidic to prevent hydrolysis, so perchloric acid would be a suitable acid to add. The spectrum of $[Ti(H_2O)_6]^{3+}$ (figure 5.3) is thus obtained in perchloric acid, but if hydrochloric acid is used the positions of the band maxima move to lower wavenumbers as species such as $[TiCl(H_2O)_5]^{2+}$ begin to become important. Many oxo-anions such as $NO_3{}^-$ and $NO_2{}^-$ have intense absorptions in the ultraviolet, and others have absorption bands that either tail into the visible, for example $CrO_4{}^{2-}$, or actually absorb in the visible, for example $MnO_4{}^-$.

6.1.3 *Charge-transfer Spectra*

The chromate and permanganate ions mentioned above owe their absorptions to charge-transfer transitions. These transitions take place between molecular orbitals of which one is largely a metal orbital and the other is largely a ligand orbital. They thus correspond either to a transfer of an electron from the metal to the ligand (*metal oxidation*) or to a transfer of an electron from the ligand to the metal (*metal reduction*). They are intense absorptions usually located in the ultraviolet but frequently tailing into the visible. They account for the colours of d^0 complexes such as $TiCl_6{}^{2-}$ and $CrO_4{}^{2-}$, and of d^{10} compounds such as the red HgI_2. The transitions are not of course limited to these configurations; they occur widely in the spectra of transition metal complexes. Because they are so much more intense than the ligand-field bands, they may obscure the ligand-field spectra if the two types of transition are close to each other in energy. We shall now consider the various types of charge-transfer spectra.

(1) *Ligand-to-metal charge transfer.* Since this corresponds to metal reduction, the more easily the metal is reduced and the ligand oxidised, the lower the energy of the transition. Thus iodide, being a readily oxidisable ligand, frequently forms compounds that have charge-transfer absorption in the visible region; cations that are reducible are thus expected to form coloured iodides, for example TiI_4 violet-black, HgI_2 red, AgI yellow, etc.

The spectra of the hexahalo-complexes $MX_6{}^{n-}$ have been studied in some detail. Figure 6.1 shows a simplified molecular orbital energy-level diagram for this type

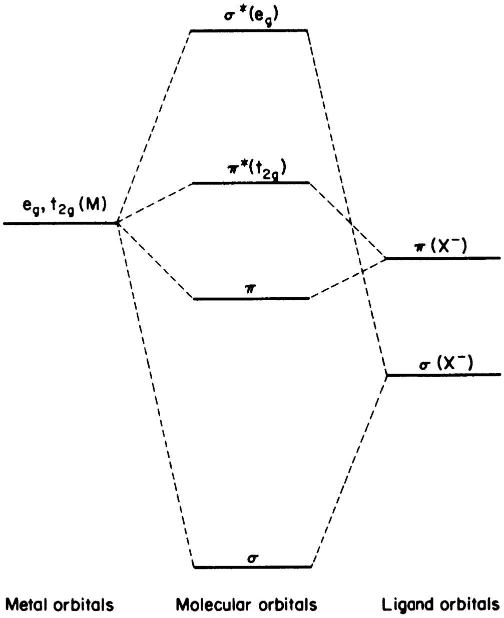


Figure 6.1 Simplified molecular orbital energy-level diagram for an octahedral $MX_6{}^{n-}$ complex (X^- = a halide ion)

of complex. The σ and π levels are filled with bonding electrons while the π^* and σ^* levels are vacant. Four transitions are thus expected; in order of increasing energy these are

$$\begin{array}{ll} \pi\rightarrow\pi^* & (t_{2g}) \\ \pi\rightarrow\sigma^* & (e_g) \\ \sigma\rightarrow\pi^* & (t_{2g}) \\ \sigma\rightarrow\sigma^* & (e_g) \end{array}$$

Notice that each of these represents transfer of charge from an orbital that has largely the character of the ligand to an orbital that has largely the character of the metal. The spectra of some d^0 and ^{1} complexes MX_6^{2-} are listed in table 6.1. The spectra are not quite as simple as the table implies, and they are not yet fully understood. However, some general features become apparent from the limited assignments in the table. The energy of the $\pi\rightarrow\pi^*$ (t_{2g}) transition decreases in the order $ZrCl_6^{2-} > TiCl_6^{2-} > VCl_6^{2-}$. This is in accord with the established order of ease of reduction of these metal ions, which increases in the series $Zr^{4+} < Ti^{4+} < V^{4+}$. A similar logical sequence is found with the bromides. Only the first transition is located (up to 50 000 cm^{-1}) for $ZrBr_6^{2-}$. Titanium(IV) is a better oxidising agent than zirconium(IV), so for $TiBr_6^{2-}$ the resulting shift of the absorption bands to lower energies means that two bands are now observed for the titanium(IV) complex. Vanadium(IV) is such a strong oxidising agent to bromide ions that no VBr_6^{2-} complex has yet been prepared. It should be mentioned that other bands have been observed in the spectrum of the VCl_6^{2-} ion but these have not been assigned with any certainty and so are not included in table 6.1.

TABLE 6.1 SPECTRA OF HEXAHALO-SALTS (in cm^{-1})

Complex	$\pi\rightarrow\pi^*$ (t_{2g})	$\pi\rightarrow\sigma^*$ (e_g)
$TiCl_6^{2-}$	31 850	42 500
$TiBr_6^{2-}$	25 200	36 500
$ZrCl_6^{2-}$	42 400	
$ZrBr_6^{2-}$	38 900	
VCl_6^{2-}	21 400	

Strongly oxidising cations often have ligand-to-metal charge-transfer bands that are low enough in energy to encroach into the visible region. Thus the iron(III) ion forms many coloured complexes with ligands that act as good electron donors (reducing agents), for example phenols, halide ions, and thiocyanate ions. In the first-row tetrahedral complexes of formula MO_4^{n-}, the trend observed in their colours follows that expected from the oxidising power (oxidation state) of the metal ion. Thus the transition of lowest energy (oxygen to metal) decreases in energy in the series

$$VO_4^{3-} > CrO_4^{2-} > MnO_4^-$$

white yellow purple

(2) *Metal-to-ligand charge transfer.* In this case it is necessary for the metal to be readily oxidisable and the ligand to be readily reducible. Ligands that have low-lying vacant orbitals suitable for receiving an electron from the metal include pyridine, 2,2′-bipyridyl, and 1,10-phenanthroline. These have vacant π^* orbitals and consequently give strongly coloured complexes with readily oxidised cations such as Ti^{3+}, V^{2+}, Fe^{2+}, and Cu^+. Spectra of this M→L type have not been very thoroughly studied. In order to be observed the charge-transfer bands must lie lower in energy than the $\pi \rightarrow \pi^*$ transitions in the ligand. We can represent the charge-transfer transitions diagrammatically as in figure 6.2. Two transitions are possible and are represented as ν_1 and ν_2; however, assignments of this class of spectra have so far been only tentative.

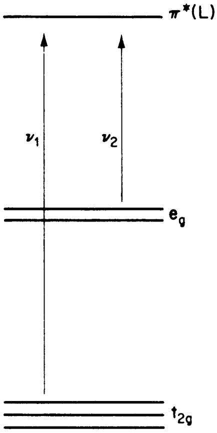


Figure 6.2 A simple representation of metal-to-ligand charge-transfer transitions.

(3) *Metal-to-metal charge transfer.* Whenever an inorganic compound contains a metal in two different oxidation states, 'intravalence' charge transfer can occur, one metal ion acting as the ligand, so to speak. Compounds in which this occurs are typically intensely coloured. Well-known examples include Prussian blue $KFe^{III}[Fe^{II}(CN)_6]$, molybdenum blue which contains Mo^{IV} or Mo^V in MoO_3, and the black gold compound $Cs_2Au^IAu^{III}Cl_6$. In this latter compound intravalence electron transfer occurs between $[Au^{III}Cl_4]^-$ and $[Au^ICl_2]^-$ groups.

6.2 Ligand-Field Spectra

6.2.1 Terms and Russell–Saunders States

So far we have discussed electronic spectra as though one electron is being excited into a higher energy level, and we have ignored the effect of other electrons that might interact with this electron. For the d^1 case as in $[Ti(H_2O)_6]^{3+}$ we have only one electron in the valence shell, so complications from other electrons do not arise. However, when more than one valence electron is present we must take into account the interactions or *couplings* between the quantum numbers for the individual electrons. An electron in an ion can initially be assigned to a set of four one-electron quantum numbers, which are designated as n (the principal quantum number), l (the azimuthal or orbital angular momentum quantum number), m_l (the magnetic orbital quantum number), and s (the spin quantum number). If we now consider a two-electron system, for example a d^2 ion, the interactions that can occur are of three types. These are spin–spin coupling in which the spin angular momenta of the two electrons couple, orbit–orbit coupling in which the orbital angular momenta couple, and spin–orbit coupling. In spin–orbit coupling we are concerned with coupling of spin and orbital angular momenta on the same electrons; the coupling of the spin of one electron with the orbital angular momentum of a different electron is so small that it is ignored. In the Russell–Saunders scheme it is assumed that

spin–spin coupling > orbit–orbit coupling > spin–orbit coupling

This is found to be the case for the elements in the first transition series, and in general for elements up to an atomic number of 30. Thereafter spin–orbit coupling becomes more important, so with heavy elements a different scheme known as *jj* coupling applies; we shall not be concerned with this here. It will now be appropriate to consider these various types of coupling in turn.

Spin–spin coupling. The resultant spin quantum number for a system of electrons is denoted by the capital letter S. It is obtained by coupling the spin quantum numbers for the separate electrons according to

$$S = (s_1 + s_2), (s_1 + s_2 - 1), \ldots\ldots, (s_1 - s_2)$$

Thus for two electrons $S = 1$ or 0. For $S = 1$ we can represent the spins as being coupled in parallel, that is ↑↑, while for $S = 0$ they are coupled with their spins opposed, that is ↑↓. For three electrons we can have $S = 3/2$ (↑↑↑) and $S = ½$ (↑↑↓) only, while for four electrons $S = 2$ (↑↑↑↑), 1 (↑↑↑↓), or 0 (↑↑↓↓).

Orbit–orbit coupling. For two electrons whose orbital angular momenta we can represent as l_1 and l_2, the total orbital angular momentum quantum number L is obtained by adding l_1 and l_2 vectorially. Thus

$$L = (l_1 + l_2), (l_1 + l_2 - 1), \ldots, (l_1 - l_2)$$

For two p electrons, $l_1 = 1$ and $l_2 = 1$, so L can have values 2, 1, and 0. For two d electrons, $l_1 = l_2 = 2$, so L can have values 4, 3, 2, 1, and 0. Now, just as for single electrons the value of l defines an orbital (that is $l = 0$ means we have an *s* orbital, $l = 1$ a p orbital, and so on), so the value of L defines a quantum number or energy state for a system of electrons. We use capital letters for these states or *term letters* as follows

L	0	1	2	3	4	5	6
Term letter	S	P	D	F	G	H	I

Spin–orbit coupling. The total angular momentum quantum number J, for a system of electrons, is obtained by coupling the resultant spin and orbital momenta according to

$$J = (L + S), (L + S - 1), \ldots, (L - S)$$

Terms of different L values have appreciably different energies; for given values of L and S we get several *levels* close together. The number of these levels is called the *multiplicity*. The multiplicity is given by the formula $(2S + 1)$. This is readily seen by considering examples

$S = 0$	$J = L$	multiplicity 1 (singlet)
$S = \frac{1}{2}$	$J = (L + \frac{1}{2}), \ (L - \frac{1}{2})$	multiplicity 2 (doublet)
$S = 1$	$J = (L + 1), L, (L - 1)$	multiplicity 3 (triplet)

Note that if $L = 0$ the multiplicity can only be 1, that is S terms can only have one value of J.

All this information that we have been considering can be conveyed in one symbol, known as a *term symbol.*

$$\text{Term symbol} = {}^{(2S+1)}L_J$$

For example, if $L = 2$ and $S = 1$ the term symbol is ^{3}D and the three states of the triplet are ${}^3D_3$, ${}^3D_2$, ${}^3D_1$.

Terms for d *electron systems.* In the d^1 case we have only one electron, so $L = l = 2$ and $S = \frac{1}{2}$. The only term arising is thus ^{2}D.

The d^2 case gives rise to L values of 4, 3, 2, 1, and 0, and so gives G, F, D, P, and S terms and multiplicities of 1 and 3. Not all of these terms are allowed since some of them correspond to a contravention of the Pauli exclusion principle. The terms that are allowed are ^{3}P, ^{3}F, ^{1}S, ^{1}D, and ^{1}G. We can decide the lowest-energy or *ground* term with the help of Hund's rules.

(1) The most stable state is the one with maximum multiplicity.
(2) For a group of terms with the same multiplicity, the one with the largest value of L lies lowest in energy.

We thus have ^{3}F as the ground term for d^2; the order of the higher terms may also be indicated, but less reliably, by these rules.

We are now in a position to summarise the Russell–Saunders coupling scheme for a d^2 ion in one diagram, that is figure 6.3. The energy separations in this figure are not drawn to scale. The separations between the levels obtained by spin–orbit coupling are measured in terms of a spin–orbit coupling constant λ; the separation between the levels of J values J and $(J + 1)$ is $(J + 1)\lambda$. Thus for the ^{3}F term, $L = 3$ and $S = 1$, so $J = (3 + 1)$, 3, and $(3 - 1)$, that is the three states are ${}^3F_4$, ${}^3F_3$, and ${}^3F_2$. These have separations of 4λ between ${}^3F_4$ and ${}^3F_3$, and 3λ between ${}^3F_3$ and ${}^3F_2$.

In addition to these couplings, a further splitting of the energy levels can occur under the influence of an external magnetic field (the Zeeman effect). The J levels are split into $(2J + 1)$ equally spaced levels corresponding to the number of values that can be assumed by the magnetic quantum number m. These values are

$-J, \ldots, 0, \ldots, +J$; the separation between them is $g\beta H$ where g is known as the Landé splitting factor, β is the Bohr magneton, and H is the applied magnetic-field strength. The Lande formula relates g to L, S, and J.

$$g = \frac{3}{2} + \frac{S(S + 1) - L(L + 1)}{2J(J + 1)}$$

It can be seen from this equation that g varies between 1 and 2 as J varies between L ($S = 0$) and S ($L = 0$).

The terms arising from the other d^n configurations can similarly be deduced and Russell–Saunders coupling applied. Since many terms arise from the d^3, d^4, d^5, d^6, and d^7 configurations, these are normally consulted in reference books rather than committed to memory. The terms arising from all the d^n configurations are listed in table 6.2 (numbers in parentheses refer to the number of times the term occurs).

TABLE 6.2 TERMS ARISING FROM THE d^n CONFIGURATIONS

Configuration	Terms
d^1, d^9	^2D
d^2, d^8	^3F, ^3P, ^1G, ^1D, ^1S
d^3, d^7	^4F, ^4P, ^2H, ^2G, ^2F, $^2D(2)$, ^2P
d^4, d^6	^5D, ^3H, ^3G, $^3F(2)$, ^3D, $^3P(2)$, ^1I, $^1G(2)$, ^1F, $^1D(2)$, $^1S(2)$
d^5	^6S, ^4G, ^4F, ^4D, ^4P, ^2I, ^2H, $^2G(2)$, $^2F(2)$, $^2D(3)$, ^2P, ^2S

It is useful to know the ground term arising from each d^n configuration. Fortunately this can readily be deduced as follows. Since the ground term is the one with the largest value of S, we can write down the multiplicity, bearing in mind that there are five degenerate d orbitals in the free ion, so pairing of spins necessarily begins after d^5. The multiplicities of the ground terms in going from d^1 to d^9 are thus 2, 3, 4, 5, 6, 5, 4, 3 and 2. We now need to find the maximum value of M_L ($M_L = L, L-1, \ldots, -L$) corresponding to the maximum number of unpaired spins and obeying the Pauli exclusion principle. This operation is readily performed as shown in table 6.3. Apart from the d^5 case all the configurations give rise to D or F ground terms. This fact, together with the fact that the terms arising from the configuration d^n are the same as those from d^{10-n}, considerably simplifies our treatment of spectral and magnetic data.

Energies of terms above ground terms. The energy separation between the various terms can be described in terms of two *electron-repulsion* parameters known as *Racah parameters B* and *C*. If we are concerned only with d electrons, the energy differences between states of different spin multiplicities are given by sums of multiples of B and C. Energy differences between states of the same spin multiplicity are often multiples of B only. For example, in the d^3 V^{2+} ion

$$^4F - {}^4P \text{ separation} = 15B$$
$$^4F - {}^2G \text{ separation} = 4B + 3C$$

TABLE 6.3 GROUND TERMS FOR d^n CONFIGURATIONS

Configuration	Example	m_l					M_L	S	Ground term
		2	1	0	−1	−2			
d^1	Ti^{3+}	↑					2	1/2	^2D
d^2	V^{3+}	↑	↑				3	1	^3F
d^3	Cr^{3+}	↑	↑	↑			3	3/2	^4F
d^4	Cr^{2+}	↑	↑	↑	↑		2	2	^5D
d^5	Mn^{2+}	↑	↑	↑	↑	↑	0	5/2	^6S
d^6	Fe^{2+}	↑↓	↑	↑	↑	↑	2	2	^5D
d^7	Co^{2+}	↑↓	↑↓	↑	↑	↑	3	3/2	^4F
d^8	Ni^{2+}	↑↓	↑↓	↑↓	↑	↑	3	1	^3F
d^9	Cu^{2+}	↑↓	↑↓	↑↓	↑↓	↑	2	1/2	^2D

Ions of the first transition series have a C/B ratio of about 4, with $B \approx 1000$ cm^{-1}. These parameters are determined experimentally from the spectra.

6.2.2 *Selection Rules*

We saw in figure 5.3 that the intensity of the absorption by the $[Ti(H_2O)_6]^{3+}$ ion due to the d–d transition was much less than that due to charge transfer, that is the rising absorption in the ultraviolet. This is because the d–d transition is *forbidden* under the quantum-mechanical selection rules for light absorption. These rules may be stated as follows.

(1) *Spin forbidden.* Transitions in which there is a change in the number of unpaired electron spins are forbidden; that is, for a transition to give optical absorption, $\Delta S = 0$. Transitions for which $\Delta S \neq 0$ are said to be spin-forbidden.

(2) *Orbitally forbidden (Laporte rule).* Transitions involving the redistribution of electrons in a single quantum shell are forbidden. Thus d→d and p→p transitions are forbidden but s→p and p→d transitions are allowed. Transitions should only involve one electron, so that for a transition to be allowed $\Delta L = \pm 1$. Transitions of the type g→g and u→u are described as being *parity forbidden.*

If these selection rules held strictly, we should neither observe ligand field spectra nor see the colours of transition metal ions. Indeed, when both rules apply, for example in the d^5 case Mn^{2+}, the intensity of the absorption and hence the colour is very weak. The spin selection rule is relaxed somewhat by spin–orbit coupling. The intensities of spin-forbidden bands relative to those of spin-allowed bands increase with increase in the spin–orbit coupling constants. However, spin-forbidden bands are extremely weak.

The Laporte selection rule may be relaxed as follows. If a complex contains a centre of symmetry it must use a vibronic mechanism to show optical absorption. For an octahedral complex, for example, there are a number of normal modes of vibration, some of which are antisymmetric with respect to the inversion centre, that is they are u-type vibrations. On mixing the vibrational and electronic parts of the wave function (so-called *vibronic coupling*), the ground term may become mixed with a g-type vibration and the excited term with a u-type vibration. The transition thus instead of being g→g becomes partly g→u and is allowed. If the complex already lacks a centre of symmetry, mixing of p and d orbitals can occur to some extent. Thus transitions can occur between d orbitals containing different amounts of p character. Using the molecular orbital picture, covalent bonding utilising p orbitals of the ligand and d orbitals of the metal causes mixing. In a tetrahedral complex the g character of the bonding d orbitals, that is the t_2 set, is partly lost. The nonbonding e levels (π-bonding ignored) retain all the g character of the pure d orbitals. Transitions of the type $e \rightarrow t_2$ thus occur between states having different amounts of u character and become partially allowed. It is thus commonly found that tetrahedral complexes have absorption bands of the order of 10^2 times as intense as those of similar octahedral complexes.

Finally, there is the phenomenon known as *intensity stealing.* When a ligand-field transition occurs close to a charge-transfer band, its intensity often increases markedly. This is believed to be due to mixing of the electronic wave functions of the forbidden excited term with the allowed level, resulting in electronic transitions to the excited term becoming more allowed. This gaining of intensity decreases rapidly as the separation between the allowed and forbidden bands increases.

Experimentally the intensities of absorption bands are measured in terms of the *molar absorption coefficient* (ϵ) Spectrophotometers measure optical density (d) as a function of wavelength; d is given by

$$d = \log_{10} \frac{I_0}{I}$$

where I_0 is the intensity of the light incident on the sample and I the intensity of the emergent light. The molar absorption coefficient is then given by

$$\epsilon = \frac{d}{cl}$$

where c is the concentration of the solution in gram-moles per litre and l is the path length in centimetres (1-cm cells are frequently used). Typical values of the molar extinction coefficient for the types of absorption that we have discussed are indicated in table 6.4.

Band breadths. If the transitions occurred between one discrete energy level and other discrete levels, we would expect to find sharp absorption peaks corresponding to the energy differences between the levels. In practice electronic spectral bands are usually very broad with band widths commonly of the order 1 000–3 000 cm^{-1}. The principal reasons for this broadening are the accompanying vibrational excitations, the occurrence of the Jahn–Teller effect, and spin–orbit coupling effects.

TABLE 6.4 MOLAR ABSORPTION COEFFICIENTS FOR VARIOUS TYPES OF TRANSITION METAL COMPLEX

Type of transition	Example	Typical value of ϵ
Spin forbidden, Laporte forbidden	$[Mn(H_2O)_6]^{2+}$	0.1
Spin allowed, Laporte forbidden	$[Ti(H_2O)_6]^{3+}$	10
Spin allowed, Laporte 'partially allowed' by d–p mixing	$[CoCl_4]^{2-}$	5×10^2
Spin allowed, Laporte allowed (charge transfer)	$[TiCl_6]^{2-}$	10^4

The effect of vibrations in complex molecules is to modulate the ligand-field strength. On the crystal-field model we should expect the magnitude of Δ ($10Dq$) to vary rapidly as the metal–ligand bond distance changes. Thus the energy separations between the terms is spread over a range of energies corresponding to the values of Δ obtained during the bond vibrations. This broadening can be overcome to some extent by measuring spectra at low temperatures where fewer vibrational levels are occupied and the probability of transition is reduced.

Broadening due to the Jahn–Teller effect has already been discussed in chapter 5. Similar broadening and splitting of absorption bands occurs when the ligands surrounding the metal ion are not all the same. The ligand-field strength then varies in different directions and the symmetry is lower than when all the ligands are identical.

When terms are split by spin–orbit coupling, the separation between the resulting states (figure 6.3) is a multiple of the spin–orbit coupling constant and is normally of the order of several hundreds of wavenumbers. We might therefore expect to see fine structure in bands due to this coupling. However, this is normally observed only when the spin–orbit coupling constants are very large, notably with some second and third-row transition metal ions. Usually this fine structure is obscured by the vibrational broadening.

6.2.3 *Terms arising in Ligand Fields*

We have so far considered the terms arising from free ions. Before we can interpret the spectra of complex ions we must consider the effect of ligand fields on the terms in the Russell–Saunders scheme. Two cases need to be considered. In the *weak-field case* we assume that the crystal-field perturbation is small compared with the interelectronic repulsion forces but larger than the spin–orbit coupling forces. We thus derive the terms arising for the free ion and then consider the effect of the crystal field on these terms. In the *strong-field case* electron pairing may occur, so here the crystal field is more important than the interelectronic repulsions. In this case therefore it is more appropriate to consider the ligand-field splitting first and then to superimpose effects due to the

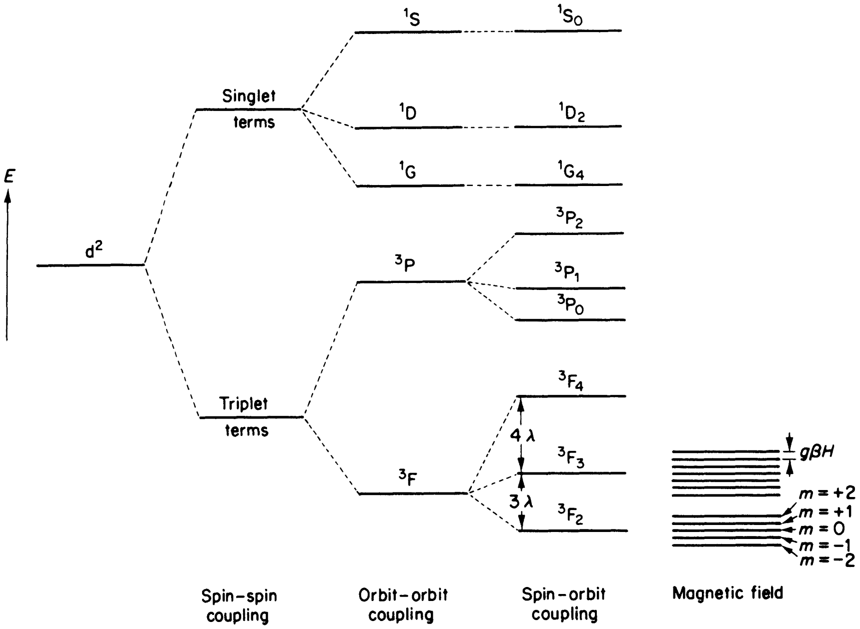


Figure 6.3 The effect of Russell–Saunders coupling on the d^2 configuration.

interelectronic repulsions. We shall confine ourselves to the weak-field case here and deal with the spectra of high-spin ions.

The terms arising from free-ion d^n configurations in octahedral and tetrahedral fields are listed in table 6.5. In the octahedral case the subscript g must be added to the crystal-field terms. These terms are known as Mulliken symbols; they are of group theoretical origin and their derivation is described in Urch's book (see bibliography, page 207). While they can be regarded merely as labels, some cursory examination of their meaning may be helpful.

TABLE 6.5 TERMS ARISING FROM d^n CONFIGURATIONS IN OCTAHEDRAL AND TETRAHEDRAL FIELDS

Free-ion term	Terms arising in cubic fields
S	A_1
P	T_1
D	$E + T_2$
F	$A_2 + T_1 + T_2$
G	$A_1 + E + T_1 + T_2$

The symbols for the crystal-field spectroscopic states have meanings similar to those of the small letters that we used in molecular orbital theory. Thus A and B represent an orbital singlet state, E a doublet, and T a triplet. The S state of the free ion can be likened to an s orbital. In a crystal field an s orbital is not split and is totally symmetric, so the state arising from the S term is A_1. Similarly, p orbitals are not split in a cubic crystal field, so they remain degenerate and the state from a P term is thus T_1. As we have already seen, the d orbital splits into a doublet and a triplet and thus the D term gives rise to E and T_2 states. Of the seven f orbitals, one is unique in that it has eight lobes directed to the corners of a cube. The other six f orbitals are of two kinds. Of one set of three, each orbital has lobes pointing along one of the x, y, or z axes (that is like the three p orbitals) with two rings one above and one below the nodal plane, that is the xy plane in the case of the orbital lying along the z axis. The other set of three orbitals each have eight lobes. They can be imagined to be constructed by splitting the lobes of, for example, a $d_{x^2-y^2}$ orbital so that each original lobe gives a lobe above the xy plane and one below it. In a crystal field therefore the degeneracy of the f orbitals is removed to an orbital singlet and two orbital triplets, that is an F term gives rise to $A_2 + T_1 + T_2$ states. Similarly, there are nine g orbitals, which give rise to an orbital singlet, a doublet, and two triplets in a cubic field.

6.2.4 *Spectra of* d^1 *and* d^9 *Ions*

d^1 *ions in octahedral and tetragonal fields.* The d^1 electronic configuration gives rise to only one term, that of ^2D. In octahedral complexes this term gives rise to an upper doublet ^2E_g and a lower triplet $^2T_{2g}$. The separation between these states is dependent on the ligand-field strength. This dependence is usually illustrated in an energy-level diagram (figure 6.4). Thus, as we saw in figure 5.3, the spectrum of

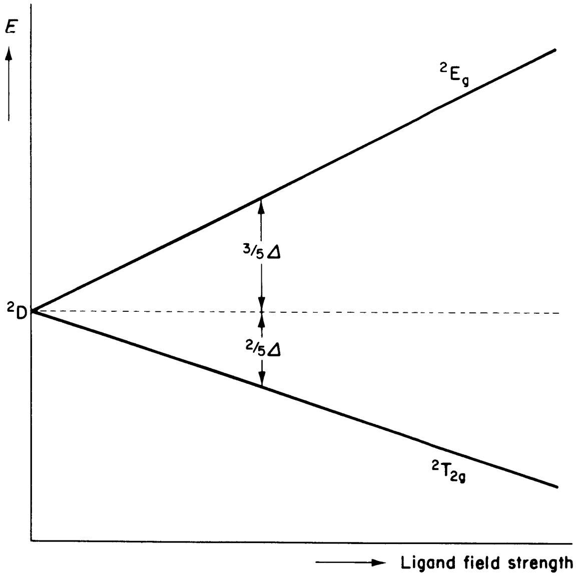


Figure 6.4 Energy-level diagram for a d^1 ion in an octahedral field.

$[Ti(H_2O)_6]^{3+}$ shows a peak at 20 100 cm^{-1} that we can now assign to the $^2T_{2g} \rightarrow {}^2E_g$ transition. The transition is spin-allowed but Laporte-forbidden, so $\epsilon \approx 6$ 1 mol^{-1} cm^{-1}. If we prepare a series of complexes $[TiL_6]^{3+}$ and measure their visible spectra, we can determine the spectrochemical series with Ti^{3+} as the reference ion. When this is done we obtain the following series (numbers in brackets after the ligand are the values of Δ)

$$H_2O\,(20\,100) \;>\; \text{urea}\,(17\,550) \;>\; Cl\,(12\,750) \;>\; Br\,(11\,750)$$

We can increase the number of ligands in the series if we use Jørgensen's rule of average environment. This states that the position of the peak in a complex TiX_3L_3 will be midway between that for $TiL_6{}^{3+}$ and $TiX_6{}^{3-}$ provided that all three complexes have the same stereochemistry. Thus, for example, since $TiCl_3.3CH_3COCH_3$ absorbs at 15 400 cm^{-1} and $TiCl_6{}^{3-}$ at 12 750 cm^{-1}, we can calculate Δ for $[Ti(CH_3COCH_3)_6]^{3+}$ (which has not been prepared) as follows

$$\begin{aligned} \Delta[TiCl_3.3CH_3COCH_3] &= \tfrac{1}{2}\Delta\,[TiCl_6{}^{3-}] + \tfrac{1}{2}\Delta\,[Ti(CH_3COCH_3)_6{}^{3+}] \\ 15\,400 &= 6\,375 + \tfrac{1}{2}\Delta\,[Ti(CH_3COCH_3)_6{}^{3+}] \\ \Delta[Ti(CH_3COCH_3)_6{}^{3+}] &= 18\,050\,\text{cm}^{-1} \end{aligned}$$

The rule can also be used, with some caution, to indicate the nature of species present in solution. However, complexes containing a mixture of ligands frequently have low-symmetry components to the ligand field, so considerable band splitting occurs and the rule becomes inapplicable.

Tetragonal distortion of the octahedral structure occurs commonly for d^1 complexes, particularly those of vanadium(IV) of the type VCl_4L_2. In these compounds, for example *trans*-VCl_4L_2, the tetragonal distortion is already 'built in' to the complex by the different M–Cl and M–L bond lengths and ligand-field strengths. The spectra frequently then show two bands rather than one band with Jahn–Teller distortion.

The effect of tetragonal distortion on the octahedral term is shown in figure 6.5

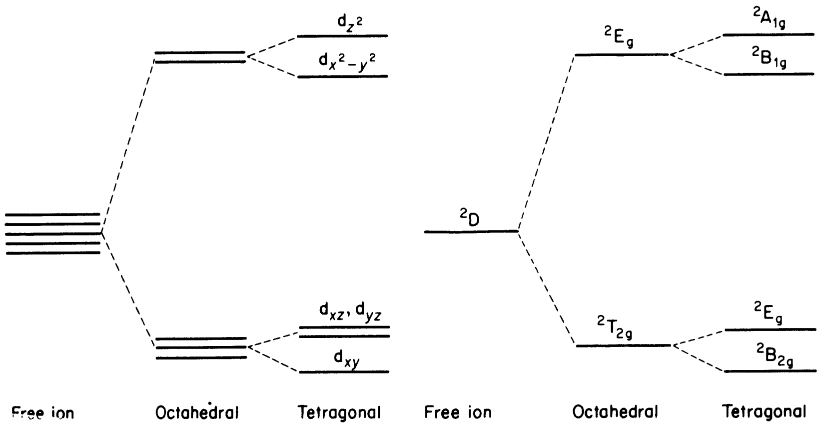


Figure 6.5 Splitting of the free-ion term for d^1 in octahedral and tetragonal fields, with the orbital splitting for comparison.

with the corresponding orbital diagram for comparison. This diagram is also appropriate to many titanium(III) complexes. The E_g (in octahedral field) level is always split in these complexes either by the Jahn–Teller effect or by other low-symmetry fields as well as tetragonal, so the spectra alone cannot be used to diagnose stereochemistry.

The tetragonal distortion in figure 6.5 represents that in which the M–L bonds in the z axis are shorter than the bonds in the x and y axes, that is an octahedron compressed along the z axis. Notice that this results in a different orbital splitting diagram from that represented in figure 5.15 which is for the octahedron elongated along the z axis. Which of these types of tetragonal distortion is actually present in any complex cannot be deduced from the electronic spectra, so assignments of tetragonal spectra are tentative until the actual stereochemistry is known from, for example X-ray crystallographic studies. We shall assume that figure 6.5 is applicable to d^1 systems (figure 5.15 is certainly more appropriate for d^9 Cu^{2+} complexes).

Because only one d electron is present, the symbols used for the tetragonal field states can be understood by comparison with the orbital splitting diagram in figure 6.5. Since *trans*-VCl_4L_2 has a centre of symmetry, the subscripts g and u apply. All the states are even *(gerade)* with respect to inversion through the centre, since the sign of the wave function in the d orbital does not change on inversion (this can be seen for the t_{2g} orbitals in figure 5.11, and it is also true for the e_g set). They thus all carry the subscript g. The only level corresponding to an orbital doublet has the symbol E. The other levels corresponding to orbital singlets carry the labels A or B depending on whether or not the orbitals with which they can be equated are symmetrical with respect to rotation about the principal axis of the molecule. The d_{z^2} orbital is symmetrical with respect to rotation by an angle 360°/4 about the C_4 axis (the z axis), and thus the state carries the label A. The $d_{x^2-y^2}$ and d_{xy} orbitals are antisymmetric with respect to this rotation; for example, rotation of the d_{xy} orbital (figure 5.11) by 90° about the z axis causes + and – signs to change; the states corresponding to an electron in those orbitals thus carry the label B. The subscripts 1 and 2 relate to whether or not the orbitals are symmetrical with respect to rotation about a C_2 axis perpendicular to the principal axis, in this case the C_4 (z) axis. Both the d_{z^2} and $d_{x^2-y^2}$ orbitals do not change when they are rotated by 180° about a C_2 axis, for example the x axis. Hence the states corresponding to these carry the subscript 1. However, the d_{xy} orbital on 180° rotation about the x or y axes is not symmetrical; the signs on the lobes are interchanged. It thus gives rise to a B_2 state. Note that the spin multiplicities of the states are unchanged as a result of the ligand field splittings, and all the states carry the superscript 2, being derived from ^2D.

The splitting of the ^2E_g and $^2B_{2g}$ terms is relatively small (about 1 000 cm^{-1}), with a somewhat larger splitting of the upper $^2A_{1g}$ and $^2B_{1g}$ terms. Two excitations are thus expected to be observed in the visible and ultraviolet region, corresponding to $^2B_{2g} \rightarrow {}^2B_{1g}$ and $^2B_{2g} \rightarrow {}^2A_{1g}$ transitions. Table 6.6 lists some typical spectra of d^1 compounds that we have interpreted according to this scheme.

TABLE 6.6 ELECTRONIC SPECTRA (cm^{-1}) OF SOME TETRAGONAL d^1 COMPLEXES

Complex	$^2B_{2g}\rightarrow{}^2B_{1g}$	$^2B_{2g}\rightarrow{}^2A_{1g}$
$TiCl_3$.3THF	13 500	14 700
$TiCl_3$.bipy	13 500	15 750
$TiCl_3$.3MeCN	14 700	17 100
VCl_4.2THF	13 600	18 100
VCl_4.2PhCOPh	14 300	20 400
VCl_4.bipy	17 400	21 300

d^9 *ions in octahedral and tetragonal fields.* The d^9 configuration also gives rise to the ^2D ground term. However, in an octahedral field the odd electron resides in an e_g orbital, so the ground term now becomes ^2E_g rather than $^2T_{2g}$. In other words, the spectroscopic levels are inverted relative to d^1. This is an example of a more general phenomenon, that is that a d^{10-n} configuration has the same behaviour in the crystal field as the d^n configuration except that inversion occurs. This is sometimes known as the *hole formalism* in which the shortage of one electron, that is one hole, is regarded as the presence of one positron. On application of crystal-field theory we see that the positron is most stable in those orbitals in which the electrons are least stable. Thus the positron will occupy the ϵ_g set of orbitals and on absorption of radiation will be excited into the t_{2g} set.

In octahedral copper(II) complexes we might expect a single absorption band in the visible spectrum corresponding to the $^2E_g\rightarrow{}^2T_{2g}$ transition. The energy-level diagram for this configuration is shown in figure 6.6. In fact, as we have already

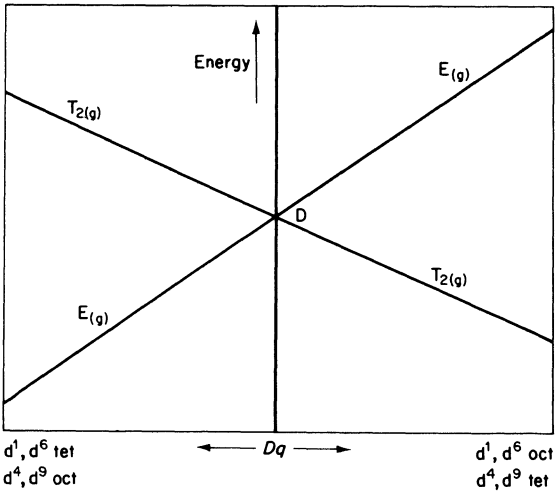


Figure 6.6 The splitting of free-ion D terms in octahedral and tetrahedral fields.

discussed (chapter 5), the Jahn–Teller distortion in the d^9 case is considerably greater than that in the d^1 case. Thus, instead of one band in the spectrum, six-co-ordinate copper(II) complexes show spectra having broad bands resulting from several overlapping bands. For $[Cu(H_2O)_6]^{2+}$ the broad band has a long tail into the near infrared; Δ is above 12 000 cm^{-1}.

Tetrahedral fields. The orbital splitting diagram for d^1 in tetrahedral fields is inverted relative to that in octahedral fields. That is, the ^2E state corresponding to the $e^1\ t_2{}^0$ configuration is the ground state, and the first excited state corresponding to $e^0\ t_2{}^1$ is the $^2T_2$ state. The spectra of tetrahedral d^1 complexes are thus expected to show a band due to the transition $^2E \rightarrow {}^2T_2$. This band will be at a lower energy $[\Delta_{tet} = (4/9)\,\Delta_{oct}]$ than in corresponding octahedral complexes. It is thus apparent that the D term in d^1 tetrahedral splits in the same way as in d^9 octahedral (both inverted with respect to d^1 octahedral). In more general terms we have the following relationships.

(1) Octahedral d^n splits in the same way as tetrahedral d^{10-n}.
(2) Octahedral d^n splits inversely to octahedral d^{10-n}.

These relationships are exemplified in figure 6.6 which shows the splitting of D terms for the d^1, d^4, d^6, and d^9 configurations in octahedral and tetrahedral fields. The spin multiplicities are omitted since they are 2 for d^1, d^9 and 5 for d^4, d^6. The d^4 and d^6 configurations give rise to the ^5D ground term. The general rule relating the splitting patterns from these configurations is

(3) d^{n+5} splits in the same way as d^n.

Thus d^6 splits as for d^1, the spherically symmetrical half-filled d shell accounting for this relationship. Similarly, d^4 and d^9 configurations are related as shown in figure 6.6.

Because of these relationships we are able to discuss the spectra arising from the configurations d^2, d^3, d^5, d^7, and d^8 in the pairs d^2, d^8 and d^3, d^7, but d^5 is unique. For this configuration, applying the rules above, we have

(4) d^5 octahedral splits in the same way as d^5 tetrahedral.

6.2.5 *Spectra of* d^2 *and* d^8 *Ions*

d^2 *ions in octahedral fields.* The d^2 configuration gives rise to the ^3F ground term with higher-energy terms ^3P, ^1G, ^1D, and ^1S. In an octahedral field these terms split to give the states listed in table 6.5. The energy-level diagram for a d^2 ion is thus considerably more complicated than those we have seen for d^1 and d^9 ions. The variation in energies of the various levels with increasing ligand field strength has been calculated by Orgel for the weak-field case and by Tanabe and Sugano for the strong-field case. The resulting energy-level diagrams are named after them. The Orgel diagram for the d^2 ion is shown in figure 6.7. This diagram is only of qualitative application; for semiquantitative work the Tanabe–Sugano diagrams must be consulted (these can be found in the books by Lever, Sutton, or Figgis). The continuous lines in the diagrams are those representing spin triplet states while the broken lines represent the spin singlet states. Since the ground state at all ligand field strengths is $^3T_{1g}(F)$, the only spin-allowed transitions will be those to

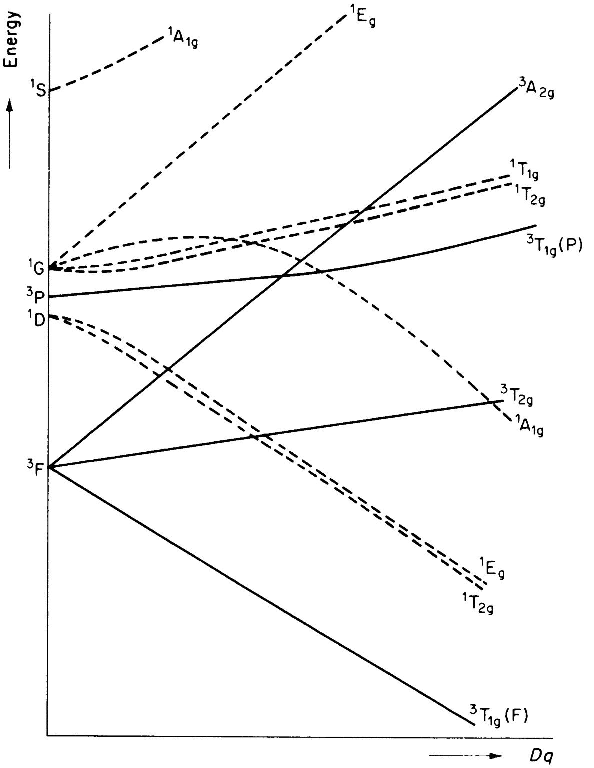


Figure 6.7 Orgel diagram for a d^2 ion (V^{3+}) in an octahedral field

the other spin triplet states. Transitions from $^3T_{1g}(F)$ to the singlet states will be spin-forbidden and observed at the most as very weak bands in the spectra.

The electronic spectrum of the d^2 ion $[V(H_2O)_6]^{3+}$ (as the perchlorate salt) is illustrated in figure 6.8. It shows two low-intensity bands in the visible and near-ultraviolet regions; further into the ultraviolet only high-intensity (charge-transfer) bands are observed. Since no other bands are observed at lower energies (until the infrared spectrum is recorded) we can tentatively assign these two observed bands to the two spin-allowed transitions of lowest energy indicated on the energy-level diagram, thus

$$^3T_{1g}(F) \rightarrow {}^3T_{2g} \qquad \nu_1 = 17\,250\ \text{cm}^{-1}$$

$$^3T_{1g}(F) \rightarrow {}^3T_{1g}(P) \qquad \nu_2 = 25\,000\ \text{cm}^{-1}$$

Now, if the diagram (figure 6.7) has been constructed specifically for V^{3+} (with a ^3P—^3F separation of $15B$, using the free-ion value for B), we should be able to deduce the expected position of the $^3T_{1g}(F) \rightarrow {}^3A_{2g}$ (ν_3) transition. To do this we need to calculate the observed ratio of ν_1 to ν_2 and then find the vertical line that fits this ratio in the diagram. The point at which this vertical line cuts the

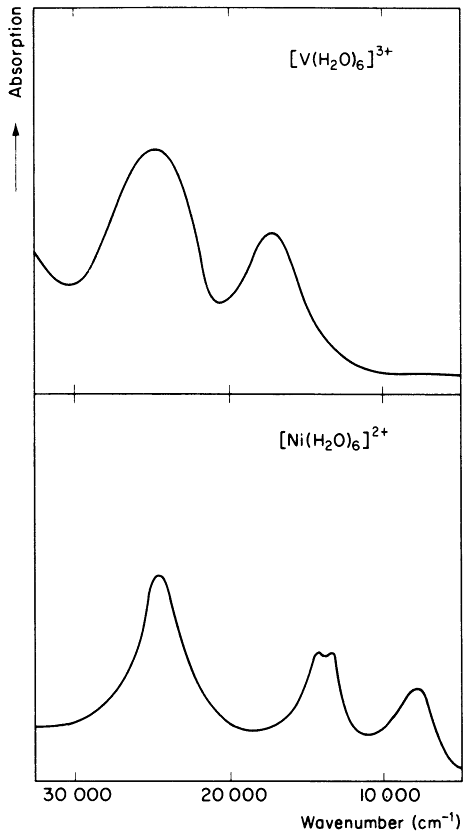


Figure 6.8 Electronic spectra of the ions $[V(H_2O)_6]^{3+}$ (d^2) and $[Ni(H_2O)_6]^{2+}$ (d^8)

$^3A_{2g}$ level enables the ratio of ν_1 to ν_3 or of ν_2 to ν_3 to be found, and hence ν_3 can be calculated. This method corresponds to a pure crystal-field approach and assumes that the value of the free-ion Racah parameter B is maintained in the complex. In practice it is found that this does not usually give very satisfactory results. A better fit between theory and experiment is obtained if B is treated as a variable parameter. In the more quantitative Tanabe–Sugano diagrams, the energy (ordinate) is plotted as a ratio E/B while the abscissa is plotted in units of Dq/B. The ratio method then enables Dq, B, and ν_3 to be determined from the two experimentally observed bands. The original assignments of ν_1 and ν_2 then become justified if physically realistic values result for $10Dq$ and B. Notice that it will be slightly more convenient to use $10Dq$ in place of Δ in discussing spectra, but these symbols are interchangeable throughout the text; $Dq = 0.1\Delta$.

Alternatively, we can calculate these parameters directly from the mathematical equations. In an octahedral field the ^3F term of a d^2 complex splits into the three terms $^3T_{1g}$ (−6 Dq), $^3T_{2g}$ (2 Dq), and $^3A_{2g}$ (12 Dq), with the energies given in parentheses relative to the unsplit ^3F term. The ^3P term also gives rise to a $^3T_{1g}$ term, and these two $^3T_{1g}$ terms interact with one another; it is this interaction that results in the curvature of lines possessing identical designations. When this interaction is taken into account the energies of the various transitions can be described in terms of Dq and B as follows

Transition		Energy
ν_1, $^3T_{1g}(F) \rightarrow {}^3T_{2g}$	=	$5Dq - 7.5B + 0.5(100Dq^2 + 180Dq.B + 225B^2)^{1/2}$
ν_2, $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$	=	$(100Dq^2 + 180Dq.B + 225B^2)^{1/2}$
ν_3, $^3T_{1g}(F) \rightarrow {}^3A_{2g}$	=	$15Dq - 7.5B + 0.5(100Dq^2 + 180Dq.B + 225B^2)^{1/2}$

From the values experimentally obtained for ν_1 and ν_2, Dq is calculated to be 1850 cm^{-1} and B 602 cm^{-1}. Using these values in the equation for ν_3, we find that ν_3 should be observed at 35 700 cm^{-1}. This transition is not observable for the hexaquovanadium(III) ion because of the strong charge-transfer absorption in this region. However, this ν_3 band has been observed in a similar system, that of vanadium corundum (V^{3+} in Al_2O_3) at 34 500 cm^{-1}.

Spin-forbidden transitions are too weak to be observed in the spectrum of $[V(H_2O)_6]^{3+}$, but they have been observed for fluoro-complexes, for example $VF_6{}^{3-}$, for which the assignments have been made as follows

$^3T_{1g}(F) \rightarrow {}^1E_g, {}^1T_{2g}$	10 200 cm^{-1}
$^3T_{1g}(F) \rightarrow {}^3T_{2g}$	14 800 cm^{-1}
$^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$	23 000 cm^{-1}

The nephelauxetic effect. The free-ion value of the electron repulsion parameter B is 860 cm^{-1} for V^{3+}, so we see a considerable reduction in the value of B in the complex. This is a very generally observed phenomenon, that the value of B in a complex is approximately 70 per cent of the free-ion value. Similarly, the Racah parameter C becomes reduced by about 70 per cent on complex formation (we have not been concerned here with this parameter because we have been dealing with transitions between states of the same spin multiplicity). These results show that the interelectronic repulsions of the d electrons in a complex are less than in the free ion since it is these repulsions that are responsible for the separations between the Russell–Saunders states. If the interelectronic repulsions have decreased it would suggest that the electrons are further apart in the complex, that is that the d orbital electron clouds have expanded to some extent. The effect is thus known as the *nephelauxetic effect* (Greek nephelauxetic = cloud expanding). The major part of the reduction in the value of B is believed to be a direct result of covalency within the complex. We saw on MO theory (chapter 5) that in an octahedral complex the e_g electrons become σ-antibonding and the t_{2g} electrons may be involved in π-bonding. The electrons are thus no longer pure metal electrons but are to some extent delocalised on to the ligands. This delocalisation increases the average separation between the various d electrons and thus reduces B. It can then be argued that the greater the reduction in the value of B the greater the covalency in the metal–ligand bond. The ratio

$$\frac{B \text{ in complex}}{B \text{ in free ion}} = \beta$$

It is found that ligands can be arranged in order of decreasing β, that is increasing covalency. This order is more or less independent of the metal ion and is known as the *nephelauxetic series.* The series for the more common ligands is

$$F^- > H_2O > NH_3 > \text{en} \approx C_2O_4{}^{2-} > NCS^- > Cl^- \approx CN^- > Br^- > S^{2-} \approx I^-$$

Ionic ligands such as F^- ions give β values close to unity, indicating ionic complexes, while the more covalently bonding ligands such as sulphur donors and I^- ions give values of β as low as 0.3. We can similarly draw up a nephelauxetic series for metal ions with a constant ligand. The more polarising the metal ion, the more covalent the metal–ligand bond and hence the lower the value of β. The order for some metals is

$$Mn^{2+} \approx V^{2+} > Ni^{2+} \approx Co^{2+} > Mo^{3+} > Cr^{3+} > Fe^{3+} > Co^{3+} > Pt^{4+} \approx Mn^{4+}$$

d^8 *ions in octahedral fields.* The relative energies of the free-ion terms for d^8 are the same as for d^2, so spin-allowed transitions will result from transitions between levels derived from ^3F and ^3P. As with d^1 and d^9, however, we get inversion of the crystal-field states derived from the free-ion terms. The simplified energy-level diagram for d^8 ions (showing only states giving rise to spin-allowed transitions) is given in figure 6.9. This diagram is useful in that it summarises all the spin-allowed

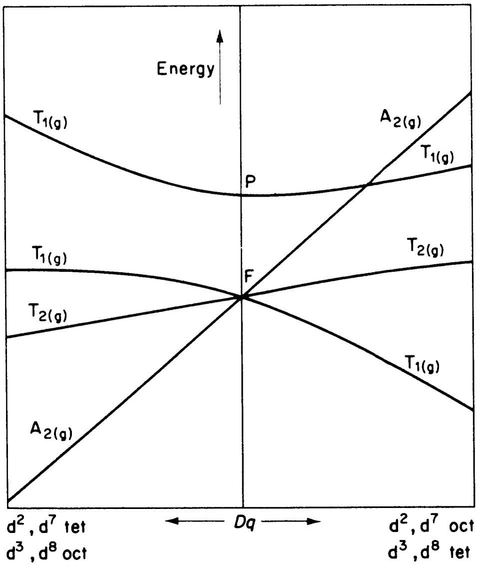


Figure 6.9 Simplified energy-level diagram for spin triplet terms of d^2, d^8 and spin quartet terms of d^3, d^7 ions in octahedral and tetrahedral fields.

transitions for d^2, d^3, d^7, and d^8 ions in octahedral and tetrahedral fields. In conjugation with figure 6.6 which covers the d^1, d^4, d^6, and d^9 ions, these diagrams represent all the octahedral and tetrahedral d^n configurations except d^5 which presents a special case.

The octahedral d^8 transitions are given on the left-hand side of figure 6.9 (note that the d^2 octahedral diagram on the right-hand side of this figure is a simplified picture of figure 6.7). Again three transitions are expected from the ground term (which is now ${}^3A_{2g}$), and these are frequently observed in octahedral complexes of nickel(II). The spectrum of the hexaquonickel(II) ion is illustrated in figure 6.8. The three bands are assigned for some representative $[NiL_6]^{2+}$ complexes in table 6.7. The trends of the spectrochemical series are readily

TABLE 6.7 ELECTRONIC SPECTRA (cm^{-1}) OF SOME OCTAHEDRAL NICKEL(II) COMPLEXES

Complex	${}^3A_{2g} \to {}^3T_{2g}$	${}^3A_{2g} \to {}^3T_{1g}(F)$	${}^3A_{2g} \to {}^3T_{1g}(P)$
$NiCl_2$	6 800	11 800	20 600
$[Ni(H_2O)_6]^{2+}$	8 500	13 800	25 300
$[Ni(NH_3)_6]^{2+}$	10 750	17 500	28 200
$[Ni(en)_3]^{2+}$	11 200	18 350	29 000
$[Ni(bipy)_3]^{2+}$	12 650	19 200	obscured

discernible from nickel(II) complexes such as those in the table. The three bands move toward the ultraviolet as *Dq* increases, or toward the infrared on lowering *Dq*. Nickel(II) chloride is included in the table since in the solid state it contains a nickel(II) ion octahedrally surrounded by chloride ions. Transitions to spin singlet levels are sometimes observable.

d^2 *and* d^8 *ions in tetrahedral fields.* Again using figure 6.9, we see that three transitions are possible for these species. However, two general points must be noted. Firstly, because these complexes have no centre of symmetry, their absorptions will be much more intense than those of the corresponding octahedral species. Secondly, because of the smaller splitting in the tetrahedral field, we are dealing with smaller values of *Dq* here and are thus closer to the centre of figure 6.9 on the *Dq* scale than we were with the octahedral complexes. It is therefore often the case that the transition of lowest energy gives rise to absorption in the infrared and has often not been located.

Vanadium(III) in tetrahedral fields is typified by the VCl_4^- ion. This has two absorption bands (figure 6.10) which are assigned as follows

${}^3A_2 \to {}^3T_2$	not found
${}^3A_2 \to {}^3T_1(F)$	8 900 cm^{-1}
${}^3A_2 \to {}^3T_1(P)$	15 000 cm^{-1}

The band of lowest energy is calculated to occur around 5 500 cm^{-1} but has not been found experimentally.

Tetrahedral nickel(II) complexes absorb light from the red part of the spectrum

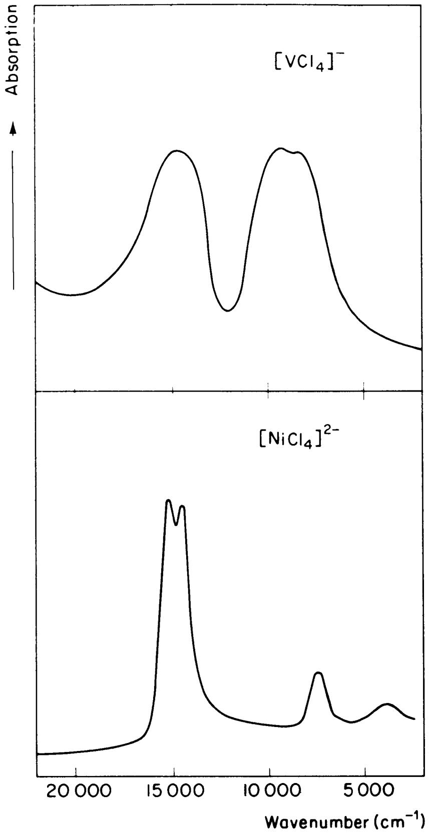


Figure 6.10 Electronic spectra of the tetrahedral anions $[VCl_4]^-$ (d^2) and $[NiCl_4]^{2-}$(d^8)

and hence appear intensely blue. A typical spectrum, that of $NiCl_4{}^{2-}$, is shown in figure 6.10, and assignments are made using figure 6.9

$^3T_1 \rightarrow {}^3T_2$	4 000 cm^{-1}
$^3T_1 \rightarrow {}^3A_2$	7 500 cm^{-1}
$^3T_1 \rightarrow {}^3T_1(P)$	15 000 cm^{-1}

In general, tetrahedral nickel(II) complexes show a strong multiple absorption band ($\epsilon \approx 10^2$ l mol^{-1} cm^{-1}) near 15 000 cm^{-1}, with a weaker band near 8 000 cm^{-1}; the lowest-energy transition is not very often observed. Weak bands sometimes observed on the high and low-energy sides of the 15 000 cm^{-1} band have been assigned to spin-forbidden bands to levels derived from ^1D and ^1G free-ion terms.

6.2.6 *Spectra of* d^3 *and* d^7 *Ions*

The high-spin d^3 and d^7 ions give rise to two spin quartet free-ion terms ^4F and ^4P

(table 6.2) and numerous doublet states. The splitting of the quartet terms is shown in figure 6.9. We shall exemplify these configurations from cobalt(II) complexes (there is a lack of tetrahedral d^3 complexes).

The colour of cobalt(II) complexes has interested chemists for many years. The pale pink octahedral complexes have a weak ($\epsilon \approx 10$ l mol^{-1} cm^{-1}) multiple absorption band in the visible near 20 000 cm^{-1} and another weak band around 8 000 cm^{-1}. The spectrum of the $[Co(H_2O)_6]^{2+}$ ion is illustrated in figure 6.11.

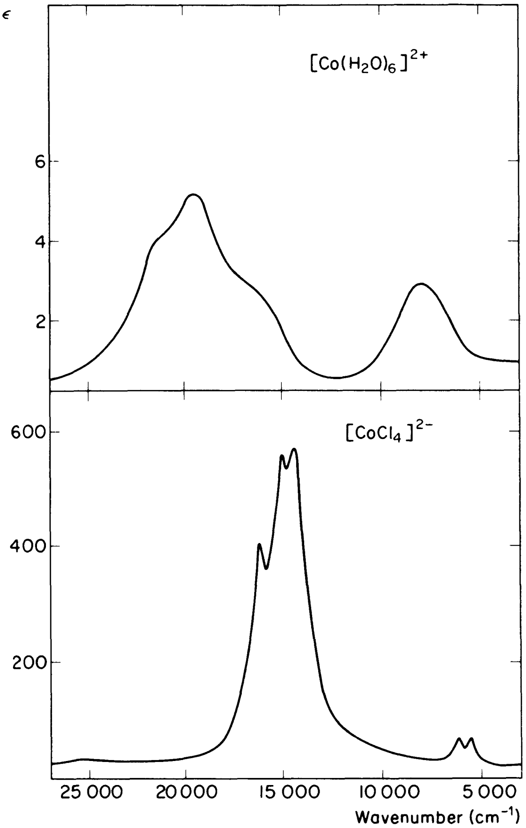


Figure 6.11 Electronic spectra of $[Co(H_2O)_6]^{2+}$ and $[CoCl_4]^{2-}$

Its assignment is not straightforward partly because of the poor resolution of the bands around 20 000 cm^{-1}. The lowest-energy band at 8 000 cm^{-1} is unambiguously assigned to the $^4T_{1g} \rightarrow ^4T_{2g}$ transition. This leaves three bands, at around 16 000, 19 400, and 21 600 cm^{-1}. It is apparent that we are on that part of the energy-level diagram where the $^4A_{2g}$ and $^4T_{1g}(P)$ states are close together, that is near the intersection, and this, coupled with the poorly resolved spectrum, means that assignments are still somewhat tentative. Most authors favour the following

$$^4T_{1g} \rightarrow {}^4A_{2g} \qquad 16\,000\ \text{cm}^{-1}$$

$$^4T_{1g} \rightarrow {}^4T_{1g}(P) \qquad 19\,400\ \text{cm}^{-1}$$

with the extra band (shoulder on the high-frequency side) being attributed to spin–orbit coupling effects or to transitions to doublet states.

Tetrahedral cobalt(II) complexes are frequently an intensely blue colour, and as such are readily distinguishable from octahedral complexes. The intensity of the visible band of $[CoCl_4]^{2-}$ can be compared with that of the octahedral $[Co(H_2O)_6]^{2+}$ in figure 6.11. There is no ambiguity about the principal assignments in tetrahedral complexes because only two bands are to be expected, the lowest-energy band being in the infrared. The $[CoCl_4]^{2-}$ assignments are thus

$$^4A_2 \rightarrow {}^4T_1(F) \qquad 5\,800\ \text{cm}^{-1}$$

$$^4A_2 \rightarrow {}^4T_1(P) \qquad 15\,000\ \text{cm}^{-1}$$

With these assignments the $^4A_2 \rightarrow {}^4T_2$ transition is expected to lie at 3 300 cm^{-1}. The reasons for the fine structure of the bands have been variously debated. Spin–orbit coupling effects almost certainly contribute to the fine structure as well as transitions to doublet states.

6.2.7 *Spectra of* d^5 *Ions*

The d^5 configuration gives rise to only one sextet term in the free ion, that is ^6S (table 6.2), as well as many quartet and doublet terms. The result of this is that any transitions between crystal field states will be spin-forbidden (the ^6S term gives rise to only one term, that is $^6A_{1g}$, in octahedral fields). Consequently the spectra of d^5 ions are very weak, as are the colours of d^5 complexes (which are free from charge-transfer absorption); for example the pale violet iron(III) alum and the pale pink manganese(II) salts. Since we are dealing with d^5 cases, we need consider only one stereochemistry (octahedral splitting ≡ tetrahedral splitting for d^5).

The spectrum of the hexaquomanganese(II) ion in perchlorate media is illustrated in figure 6.12. Several features of this spectrum are unusual where it is

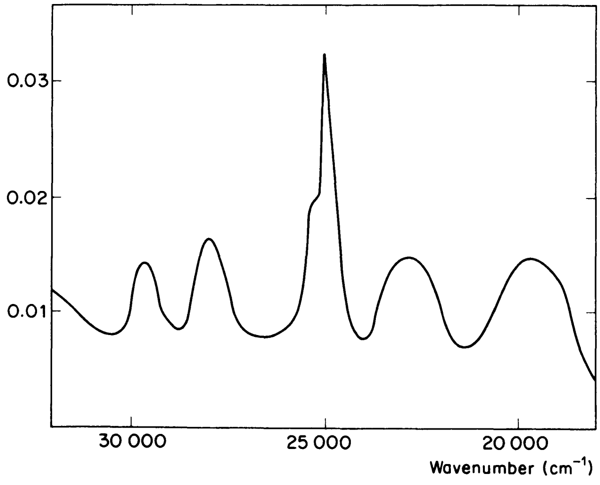


Figure 6.12 Electronic spectrum of the ion $[Mn(H_2O)_6]^{2+}$

compared with the spectra that we have seen previously. Firstly, there is the weakness of the bands; compare these with the bands for cobalt(II) complexes in figure 6.11. Secondly, there is the relative sharpness of some of the bands. Spin-allowed bands are invariably broad whereas we see here that spin-forbidden bands may be broad or sharp.

The Orgel diagram for octahedral Mn^{2+} is shown in figure 6.13. In this diagram the ground state $^6A_{1g}$ is drawn coincident with the abscissa. The diagram is also applicable to tetrahedral complexes if the g subscripts are omitted. Only the quartet terms have been included because transitions from the $^6A_{1g}$ state to spin doublet states are doubly spin-forbidden and not likely to be observed. Using the diagram, the bands shown in figure 6.12 are assigned as follows

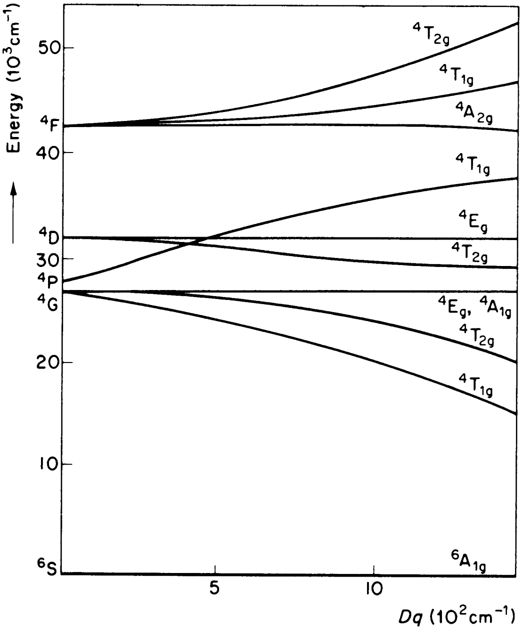


Figure 6.13 Orgel diagram for octahedral Mn^{2+} (d^5)

$^6A_{1g} \rightarrow {}^4T_{1g}$	18 900 cm^{-1}
$^6A_{1g} \rightarrow {}^4T_{2g}(G)$	23 100 cm^{-1}
$^6A_{1g} \rightarrow {}^4E_g, {}^4A_{1g}$	24 970, 25 300 cm^{-1}
$^6A_{1g} \rightarrow {}^4T_{2g}(D)$	28 000 cm^{-1}
$^6A_{1g} \rightarrow {}^4E_g(D)$	29 700 cm^{-1}

An interesting feature of the Orgel diagram for Mn^{2+} is that the $^4A_{1g}$, $^4E_g(G)$, $^4E_g(D)$, and $^4A_{2g}(F)$ terms have energies that are independent of the crystal field. It is thus very easy to measure the separation between the free-ion states at zero

Dq. By comparison of the assignments above and the energies of the free-ion states in figure 6.13, the usual reduction of the interelectron repulsion parameters can be seen to have occurred.

The sharpness of the bands is connected with the ratio of the slope of the curve for the upper state to that of the ground state. During vibrations of the complex ion, the ligand field strength 10*Dq* varies about some mean value. If the energy separation between two levels is not dependent on ligand-field strength, a sharp absorption band is expected. However, if the slope of the line for the upper state is considerable (bearing in mind the zero slope of the $^6A_{1g}$ line as we have drawn it), the transition energy will vary as the ligand field varies during the vibrations. The sharp bands are thus due to the transitions to the ^4E_g, $^4A_{1g}$(G), $^4T_{2g}$(D), and ^4E_g(D) states, while transitions to the heavily sloping $^4T_{1g}$(G) and $^4T_{2g}$(G) states give rise to broader bands.

7 Magnetic Properties of Transition-metal Complexes

7.1 Introduction

In this chapter we continue from the very brief introduction given to magnetism in chapter 5. We begin by defining the terms and quantities that are used in magnetochemistry.

Magnetic susceptibility and paramagnetism. When a compound is placed inside a magnetic field of strength H, the magnetic field inside the compound, that is the magnetic induction of flux B, is given by

$$B = H + 4\pi I$$

where I is the intensity of magnetisation. Chemists use a quantity known as susceptibility, the *volume susceptibility* K being given by

$$K = \frac{I}{H}$$

The *gram susceptibility* is then given by

$$\chi = \frac{K}{\rho}$$

where ρ is the density. The *molar susceptibility* χ_M is defined as $(\chi \times M)$ where M is the molecular weight of the compound appropriate to one metal atom. If B is smaller than H the substance is *diamagnetic;* it is repelled by the field and its susceptibility is negative. When B is larger than H the substance is *paramagnetic;* it is attracted into the field and has a positive susceptibility.

Compounds in which the paramagnetic centres are separated from one another by numbers of diamagnetic atoms (from ligands, etc.) are said to be *magnetically dilute.* If the ligands or other diamagnetic species are removed from such a system, the neighbouring paramagnetic centres interact with one another. These interactions give rise to *ferromagnetism* (neighbouring magnetic dipoles aligned in the same direction) and *antiferromagnetism* (neighbouring magnetic dipoles aligned in alternate directions). Ferromagnetic materials have a greatly enhanced paramagnetism; the phenomenon is rare and confined largely to iron and other metals and alloy systems. Antiferromagnetism is much more common; its effect is to reduce the susceptibility and hence the magnetic moment of the compound. It is commonly found to occur in transition-metal halides and oxides where a reduction in effective spin is observed. Thus at room temperature the following magnetic moments are obtained for $TiCl_3$ and VCl_2

$$\alpha\text{-}TiCl_3 \quad \mu = 1.31 \text{ B.M.} \quad (\mu_{\text{spin only}} = 1.73 \text{ B.M.})$$

$$VCl_2 \quad \mu = 2.42 \text{ B.M.} \quad (\mu_{\text{spin only}} = 2.83 \text{ B.M.})$$

These various forms of paramagnetism exhibit characteristic relationships between susceptibility and temperature. These are shown qualitatively in figure 7.1.

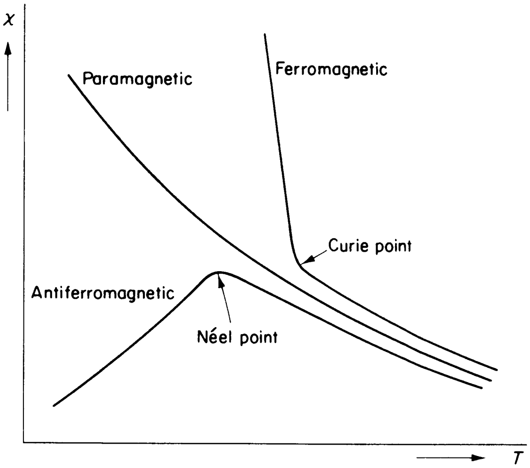


Figure 7.1 Temperature dependence of susceptibility for paramagnetic, ferromagnetic, and antiferromagnetic materials

Normal paramagnetic substances obey *Curie's Law* which states that paramagnetic susceptibilities depend inversely on temperature, that is

$$\chi \propto \frac{1}{T} = \frac{C}{T}$$

where C is the Curie constant. Thus a plot of $1/\chi$ against T gives a straight line of slope C passing through the origin (0 K). The constant C is given by the Langevin expression which relates the susceptibility χ_M to the magnetic moment μ in Bohr magnetons

$$\chi_M = \frac{N\mu^2}{3kT}$$

where N is the Avogadro number, k is the Boltzmann constant, and T is the absolute temperature. Thus

$$C = \frac{N\mu^2}{3k}$$

Many substances give straight lines that intersect the temperature axis a little above or below 0 K. These compounds are said to obey the *Curie–Weiss Law,* that is

$$\chi = \frac{C}{T + \theta}$$

in which θ is known as the Weiss constant.

Ferromagnetic materials behave as normal paramagnetics at high temperatures, but at some temperature known as the Curie point (figure 7.1) there is a marked increase in χ accompanied by a marked dependence of the susceptibility on the field strength. For pure iron the Curie point is at 768 °C. Antiferromagnetic materials also behave as normal paramagnetics until (figure 7.1) the Néel point is reached when the susceptibility decreases with temperature. The Néel point is often below 100K although, as we have already mentioned, there are many substances that are antiferromagnetic at room temperature.

7.1.1 Determination of Susceptibility; The Gouy Method

Many methods are available for the experimental determination of magnetic susceptibilities. We shall confine ourselves here to the simplest and most widely used method, the Gouy method.

The apparatus consists of an accurate balance (capable of weighing to five decimal places) and a powerful magnet. The sample is hung by a fine thread from one pan of the balance so that one end lies in the field of the magnet and the other end in the earth's magnetic field only. This is shown in figure 7.2. The sample is contained in a cylindrical tube (usually about the size of a long 'ignition tube') and is weighed in the magnetic field and out of the magnetic field. The out-of-field weight is obtained either by switching off the current if an electromagnet is used, or by moving the magnet away if a permanent magnet is used. The force on the sample in the magnetic field is given by

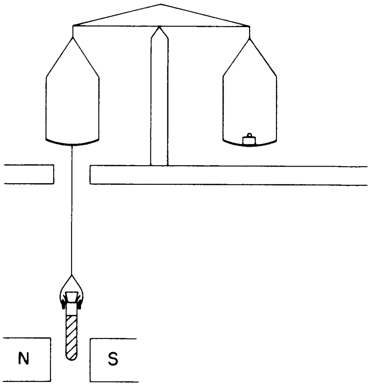


Figure 7.2 Diagrammatic representation of the Gouy method.

$$F = \tfrac{1}{2}(K_1 - K_2)(H_2^2 - H_1^2)A$$

where K_1 is the volume susceptibility of the sample, K_2 is the volume susceptibility of air, H_2 is the magnetic field strength, H_1 is the earth's magnetic field strength, and A is the cross-sectional area of the sample.

Of these terms, F and A are measured and K_2 is known. The magnetic field strength is usually calibrated by using a substance of known K_1. The above expression then reduces to

$$F = \tfrac{1}{2}(K_1 - K_{\text{air}}) \times \text{constant}$$

Thus, by measuring F for the unknown in a calibrated apparatus (that is of known constant), K_1 is calculated. The density of the sample is required in order to convert K into χ

$$\chi = \frac{K}{\rho}$$

We convert χ into χ_M by multiplying by the molecular weight. The magnetic moment of the sample is then given (from the Langevin expression) by

$$\mu = \sqrt{\left(\frac{3RT\chi_M}{N}\right)} = 2.83\sqrt{(\chi_M T)}$$

In order to obtain the magnetic moment of the metal ion alone, we must correct for the diamagnetic effects of the ligands (and strictly also for the inner-core diamagnetism of the metal ion). These diamagnetic parts of the sample were in fact exerting a force away from the magnetic field, thus making the sample appear lighter in the magnetic field than out of it, whereas the paramagnetic ions were exerting a force into the magnetic field, hence giving an apparently increased weight of sample in the magnetic field. Tables for such diamagnetic corrections are available in the literature (see the bibliography). These are normally added on to χ_M thus

$$\chi'_M = \chi_M \text{ corrected for diamagnetism of ligands.}$$

The effective magnetic moment of the metal ion is then given by

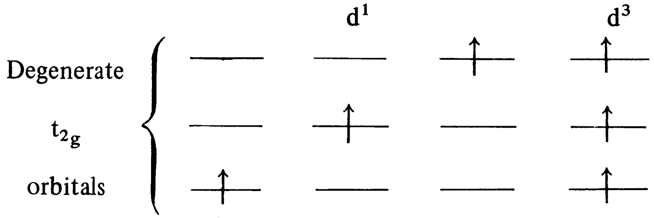
$$\mu_{\text{eff}} = 2.83\sqrt{(\chi'_M T)}$$

7.2 Orbital Contribution to Magnetic Moments

We saw in chapter 5 that the spin-only formula often gives a reasonable experimental fit between the magnetic moment and the number of unpaired electrons present. Whether or not a good agreement results in this way depends largely on whether or not the orbital contribution to the moment is significant. We shall now see how deviations (or lack of them) from the spin-only formula are useful in diagnosing the stereochemistry of complexes.

In order that an electron can have orbital angular momentum, it must be possible to transform the orbital that it occupies into an exactly equivalent and degenerate orbital by rotation. The electron is then effectively rotating about the axis used for the orbital rotation. In an octahedral complex, the degenerate t_{2g} orbitals (d_{xz}, d_{yz}, d_{xy}) can be interconverted by 90° rotations. For example, the d_{xz} orbital is transformed into the d_{yz} orbital by a rotation of 90° about the z axis. During this rotation the electron is in part orbiting the nucleus. Thus an electron in a t_{2g} orbital does contribute orbital angular momentum. However, the e_g orbitals (d_{z^2} and $d_{x^2-y^2}$) cannot be interconverted by rotation about any axis because of their different shapes; an electron in the e_g set therefore cannot contribute to orbital angular momentum. Electrons in t_{2g} orbitals will not always contribute orbital angular momentum. Consider the d^3, $t_{2g}{}^3$ case for example.

An electron in the d_{xz} orbital cannot by rotation be placed in the d_{yz} orbital because this orbital already contains an electron with the same spin as the incoming electron. In other words, in the d^1 case we have three possible arrangements while in the d^3 case there is only one, that is



Three possible arrangements; orbital angular momentum

One arrangement only; no orbital angular momentum.

Tetrahedral complexes can be treated in the same way except that we now fill the e orbitals first and electrons in these do not contribute orbital angular momentum. It becomes apparent that, for many configurations, octahedral and tetrahedral complexes differ in whether or not they contribute to orbital angular momentum. This fact is useful in enabling magnetic measurements to distinguish between these two stereochemistries. In table 7.1 are listed all the d^1 to d^9 configurations, including high and low-spin complexes, with the ground term for the complex and a statement of whether or not orbital contribution to the magnetic moment is expected.

Examination of table 7.1 shows that the configurations corresponding to A_1 (from free-ion S term), E (from D term), or A_2 (from F term) are those for which there is no orbital angular momentum. Configurations that give rise to either a T_2 term (from D term) or a T_1 term (from F term) as the lowest terms are those for which orbital contribution to the magnetic moment is expected. We shall now examine these two groups of magnetic behaviour.

7.2.1 *Magnetic Properties of Complexes with A and E Ground Terms*

These complexes possess no orbital contribution in the ground state, so the magnetic moment is expected to follow the spin-only formula

$$\mu = \sqrt{[4S(S+1)]} = \sqrt{[n(n+2)]}$$

We now see why this formula was apparently so successful in interpreting magnetic data. It so happens that no orbital contribution is expected for many very common configurations, for example d^3 (Cr^{3+}), d^5 (Mn^{2+}, Fe^{3+}), d^8 (Ni^{2+}), and d^9 (Cu^{2+}). Since the spin-only formula contains no temperature term, the magnetic moment μ is expected to be independent of temperature. In table 7.2 are listed some salts containing octahedral $[M(H_2O)_6]^{n+}$ cations or tetrahedral $[MCl_4]^{n-}$ anions, all of which possess A or E ground terms (compare table 7.1). Their magnetic moments at two widely different temperatures show in every case that the moment does not vary with temperature. However, the fit with the spin-only moment is not always good; this is because spin–orbit coupling, although it cannot

TABLE 7.1 ORBITAL CONTRIBUTION FOR d^1 TO d^9 IONS IN OCTAHEDRAL AND TETRAHEDRAL STEREOCHEMISTRIES

Number of d electrons	Octahedral complexes			Tetrahedral complexes		
	Configuration	Ground term	Orbital contribution	Configuration	Ground term	Orbital contribution
1	$t_{2g}{}^1$	${}^2T_{2g}$	yes	e^1	${}^2E$	no
2	$t_{2g}{}^2$	${}^3T_{1g}$	yes	e^2	${}^3A_2$	no
3	$t_{2g}{}^3$	${}^4A_{2g}$	no	$e^2\ t_2{}^1$	${}^4T_1$	yes
4	$t_{2g}{}^3\ e_g{}^1$	${}^5E_g$	no	$e^2\ t_2{}^2$	${}^5T_2$	yes
	$t_{2g}{}^4$	${}^3T_{1g}$	yes			
5	$t_{2g}{}^3\ e_g{}^2$	${}^6A_{1g}$	no	$e^2\ t_2{}^3$	${}^6A_1$	no
	$t_{2g}{}^5$	${}^2T_{2g}$	yes			
6	$t_{2g}{}^4\ e_g{}^2$	${}^5T_{2g}$	yes	$e^3\ t_2{}^3$	${}^5E$	no
	$t_{2g}{}^6$	${}^1A_{1g}$	no			
7	$t_{2g}{}^5\ e_g{}^2$	${}^4T_{1g}$	yes	$e^4\ t_2{}^3$	${}^4A_2$	no
	$t_{2g}{}^6\ e_g{}^1$	${}^2E_g$	no			
8	$t_{2g}{}^6\ e_g{}^2$	${}^3A_{2g}$	no	$e^4\ t_2{}^4$	${}^3T_1$	yes
9	$t_{2g}{}^6\ e_g{}^3$	${}^2E_g$	no	$e^4\ t_2{}^5$	${}^2T_2$	yes

occur as a first-order effect, is able to mix in some orbital contribution from higher T terms of the same multiplicity as the ground term. This occurs because the spin and orbital angular momenta of the free ion are coupled by spin–orbit coupling and the ligand field is unable to effect a perfect separation of the terms of the same multiplicity according to their different orbital angular momenta. The ground term thus contains some orbital angular momentum.

The A_1 ground terms present no problems. The d^5 (Mn^{2+}) configuration gives rise to no higher T terms of the sextuplet spin multiplicity, so no mixing occurs and manganese(II) complexes therefore give the spin-only moment (table 7.2). The low-spin d^6 configurations give rise to diamagnetism only.

For the A_2 (from F) and E (from D) terms there is necessarily a higher T term of the same multiplicity as the ground state. For these terms the magnetic moment is given by

$$\mu_{\text{eff}} = \mu_{\text{spin only}}\left(1 - \frac{a\lambda}{10Dq}\right)$$

where $a = 2$ for an E term or 4 for an A_2 term. The spin–orbit coupling constant λ has a positive sign for d shells less than half filled and is negative (J values inverted

TABLE 7.2 MAGNETIC MOMENTS OF SOME COMPLEXES WITH A OR E GROUND TERMS

Number of d electrons	Compound	Stereochemistry	μ_{eff} 80K	μ_{eff} 300K	μ_{eff} spin-only
1	VCl_4	tetrahedral	1.6	1.6	1.73
3	$KCr(SO_4)_2.12H_2O$	octahedral	3.8	3.8	3.87
4	$CrSO_4.6H_2O$	octahedral	4.8	4.8	4.90
5	$K_2Mn(SO_4)_2.6H_2O$	octahedral	5.9	5.9	5.92
7	Cs_2CoCl_4	tetrahedral	4.5	4.6	3.87
8	$(NH_4)_2Ni(SO_4)_2.6H_2O$	octahedral	3.3	3.3	2.83
9	$(NH_4)_2Cu(SO_4)_2.6H_2O$	octahedral	1.9	1.9	1.73

for d^6 to d^9) for d shells more than half filled. We can thus get magnetic moments that are slightly less than, or slightly more than, the spin-only moment depending on the sign of λ. The effect is normally of the order of a few tenths of a Bohr magneton. We can exemplify the effect with the help of table 7.2. The d^1 (V^{4+}), d^3 (Cr^{3+}), and d^4 (Cr^{2+}) ions have λ positive and hence $\mu_{\text{eff}} < \mu_{\text{spin only}}$. The d^7 (Co^{2+}), d^8 (Ni^{2+}), and d^9 (Cu^{2+}) ions have λ negative, and hence, by substitution in the above equation, $\mu_{\text{eff}} > \mu_{\text{spin only}}$. By using values of λ and $10Dq$ obtained from the electronic spectra, a good fit is obtained between the experimental and calculated moments. Because the difference in energy between the ground term and the term being mixed in is very large (approximately 10^4 cm^{-1}) compared with kT (approximately 200 cm^{-1} at room temperature) this spin–orbit contribution to the moment is independent of temperature.

7.2.2 Magnetic Properties of Complexes with T Ground Terms

The situation for these ground terms is very much more complex and we can indicate only the results here. The T terms are split by spin–orbit coupling to produce levels whose energy differences are frequently of the order of kT. Temperature will thus have a direct effect on the population of the levels arising in a magnetic field, so for these terms we expect magnetic moments to vary with temperature. A study of magnetic properties over a temperature range thus enables a distinction to be made between these two types of ground terms, and hence permits the deduction of stereochemistry of complexes. Notice (table 7.1) that only for the d^5 case do the octahedral and tetrahedral stereochemistries give rise to the same type of ground term.

Some representative magnetic moments for complexes with T ground terms are listed in table 7.3. The room-temperature moment is in excess of the spin-only moment for all except the V^{3+} case which we shall discuss shortly. This increase in magnetic moment is as expected on the simple picture of orbital contribution. Notice that this contribution is significantly greater than that usually observed for complexes of the same element having an A or E ground term, that is in a different stereochemistry.

The extent of orbital contribution in these complexes can be deduced only when the extent of the splittings of the various levels is known. Calculations have thus been performed to determine the effect of the spin–orbit coupling on the orbitally degenerate ground term. The results are best expressed in terms of a graph of μ_{eff} against the parameter kT/λ which is a convenient scale of temperature. These plots are sometimes known as *Kotani plots* after the originator of the equation on which they are based. Two graphs can be drawn for each term, one for which λ is positive and one for which λ is negative. The graphs for all the T terms are to be found in the works by Figgis, or Figgis and Lewis (see bibliography).

TABLE 7.3 MAGNETIC MOMENTS OF SOME COMPLEXES WITH T GROUND TERMS

Number of d electrons	Compound	Stereochemistry	μ_{eff} 80K	300K	spin-only
1	Cs_2VCl_6	octahedral	1.4	1.8	1.73
2	$(NH_4)V(SO_4)_2.12H_2O$	octahedral	2.7	2.7	2.83
4	$K_3[Mn(CN)_6]$	octahedral	3.1	3.2	2.83
5	$K_3[Fe(CN)_6]$	octahedral	2.2	2.4	1.73
6	$(NH_4)_2Fe(SO_4)_2.6H_2O$	octahedral	5.4	5.5	4.90
7	$(NH_4)_2Co(SO_4)_2.6H_2O$	octahedral	4.6	5.1	3.87
8	$(Et_4N)_2NiCl_4$	tetrahedral	3.2	3.8	2.83

We shall show here the general variations by using the curves for the T terms derived from D configurations; these are drawn in figure 7.3. The moments of appropriate individual ions are marked on the curves using the free-ion values of λ and $T = 300$ K. The bottom curve in the figure represents the variation of magnetic moment with temperature for the octahedral d^1 case. At absolute zero the magnetic moment is zero because the orbital and spin moments ($l = 1, s = ½$) cancel each other out, that is the lowest level corresponds to the orbital and spin contributions being in opposite directions. As the temperature is increased, higher levels become occupied corresponding to an alignment of the spin and orbital moments. The spin-only value (1.73 B.M.) is reached around $kT/\lambda = 1$. In the limit when $kT/\lambda \rightarrow \infty$, the formula $\mu = \sqrt{[4S(S+1) + L(L+1)]}$ applies and a moment of $\sqrt{5}$, that is 2.24 B.M., is expected. We can see that the success of the spin-only formula for T terms, such as in Ti^{3+} and V^{3+}, is rather fortuitous; it so happens that at room temperature the values of λ and T sometimes give moments close to the spin-only value.

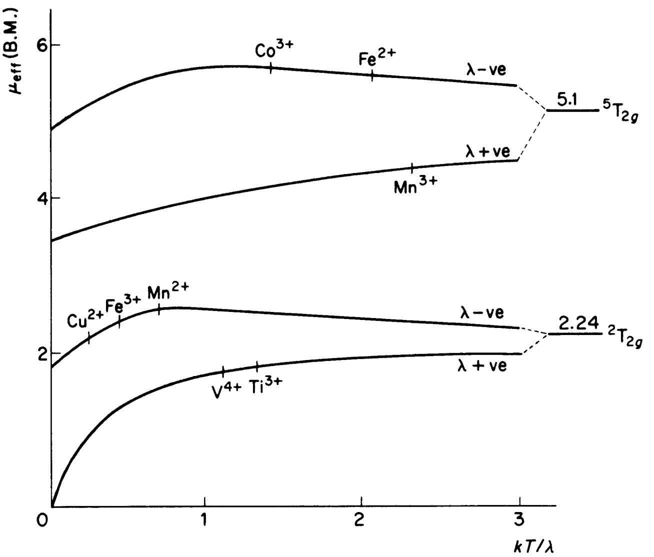


Figure 7.3 The variation of magnetic moment with temperature for d electron T terms

In practice, measurements of magnetic moments over a temperature range do not fit these curves very well. In many cases, for example V^{3+} (see table 7.3), the variation of the moment with temperature is much less than that predicted. Several factors are responsible for this. Firstly, we have used the free-ion value for λ in the plots, and this differs from the actual values found in the complexes; no allowance has been made for electron delocalisation. If covalent bonding is present it is unlikely that the unpaired electron(s) remain permanently on the metal. In the presence of σ or π-bonding, an electron can be removed from the metal to the ligand, in which position it can no longer contribute to orbital angular momentum around the metal. The reduction in the value of the spin–orbit coupling constant in the complex compared with that in the free ion is best interpreted in terms of this covalency. Even when this delocalisation is taken into account a poor fit is still found with, for example, vanadium and titanium(III) alums. We have assumed cubic (that is pure octahedral or tetrahedral) symmetry for the complexes throughout, and this is evidently an unjustified assumption. The $[Ti(H_2O)_6]^{3+}$ and $[V(H_2O)_6]^{3+}$ ions which are present in the alums contain orbitally degenerate ground levels as first written, and as such are subject to Jahn–Teller distortion. In this distortion the ground T level is split into orbital singlet and doublet levels (figure 5.15). The ground term is now not T but A or E, and the moment is thus expected to be invariant with temperature. The separation between the singlet and doublet levels produced varies from zero, that is pure T level, to around 2000 cm^{-1}, but is commonly of the order of a few hundred cm^{-1}. Compared with the primary ligand-field splitting ($10Dq$), this splitting is thus very small and difficult to detect spectroscopically. However, magnetic properties of complexes are very sensitive to these small ground-state variations and are thus useful in detecting these small distortions. The magnitude of this distortion can be discovered by attempting to fit the experimental plot of μ against T with various ratios of δ/λ where δ is the separation between the singlet and doublet levels (figure 5.15). The best fit gives the value of δ, a value of $\delta = 0$ corresponding to octahedral symmetry.

7.3 High-spin–low-spin Equilibria

We have so far assumed that each complex occurs in a given structural form with a given high or low-spin configuration. Complications arise when a complex is in a given stereochemical form but in high-spin–low-spin equilibrium or when a complex readily changes stereochemistry (and hence the number of unpaired electrons) in different chemical environments. Each of these types of equilibrium is now discussed briefly.

7.3.1 Thermal Equilibria between Spin States

Ions of the d^4 to d^7 configurations in octahedral fields may give high or low-spin complexes depending on the strength of the ligand field. For any metal ion the change from high-spin to low-spin configuration might be expected to occur abruptly at a certain value of the ligand-field splitting parameter Δ. If we can choose a ligand field close to this *cross-over point,* a chemical equilibrium of the two forms might occur. Further, if the energy separation between the two spin states is of the order of kT, temperature will have a great effect on the position of the high-spin–low-spin equilibrium.

Such equilibria are well known, occurring particularly in iron complexes. The d^6 iron(II) systems are especially suitable for experimental studies because the low-spin state is diamagnetic and the change in the number of unpaired electrons in going to the high-spin state is four. In figure 7.4 is shown the variation of magnetic moment

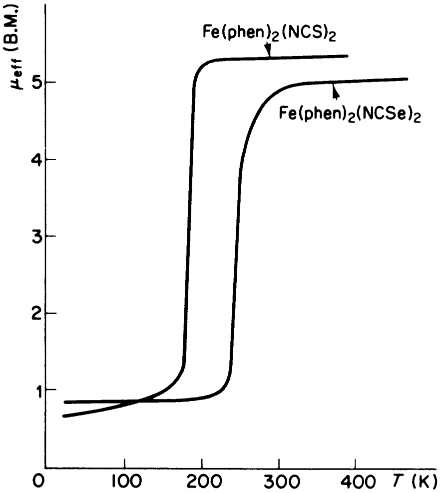


Figure 7.4 Variation of magnetic moment with temperature for some iron(II) complexes near the $^5T_2-^1A_1$ cross-over

with temperature for two octahedral iron(II) phenanthroline complexes. At room temperature $Fe(phen)_2(NCS)_2$ and $Fe(phen)_2(NCSe)_2$ exist in the high-spin $^5T_2$ ground state (table 7.1) with magnetic moments in excess of the spin-only value for four unpaired electrons. At 174 K the moment of $Fe(phen)_2(NCS)_2$ suddenly drops to below 1 B.M., and a similar drop occurs for $Fe(phen)_2(NCSe)_2$ at 232 K. Below these temperatures the complexes have the $^1A_{1g}$ ground state, and changes in the electronic spectra support this.

Similar magnetic behaviour is shown by iron(III) surrounded by six sulphur ligands as in the dialkyldithiocarbamates $[Fe(S_2CNR_2)_3]$. Such complexes have magnetic moments at room temperature that lie between those expected for high and low-spin octahedral complexes; this behaviour persists in benzene in which the complexes are monomeric. The thermal equilibrium between spin states $S = ½$ and $S = {}^5/_2$ is thus occurring.

7.3.2 Structural Equilibria between Spin States

When the energy difference between two stereochemistries for a particular combination of metal ion plus ligand is small, a slight change of conditions may bring about a structural change and consequently a magnetic change. In this class are a large number of nickel(II) complexes that were for many years regarded as 'anomalous'. These are conveniently classified under three headings.

Octahedral–square-planar equilibria in solution. The solutions of a large number of nickel(II) complexes in organic solvents have magnetic moments the magnitude of which depends on factors such as the concentration, the temperature, and the nature of the solvent. In donor solvents, square (diamagnetic) and octahedral (paramagnetic) complexes are often interconvertible by way of the equilibrium

$$NiL_4 + 2L' \rightleftharpoons trans\text{-}[NiL_4L'_2]$$

The Lifschitz salts, that is nickel(II) complexes of substituted ethylenediamines, can be represented by the formula NiL_2X_2 where X is an anion. These often occur in hydrated form and are of two types: yellow and diamagnetic (usually square planar); blue and paramagnetic (usually tetragonal). The form that is obtained in any reaction depends on a large number of factors such as the nature of the solvent, the nature of the anion, and the temperature.

Monomer–polymer equilibria. The diamagnetic bis-(*N*-alkylsalicylaldimine)nickel(II) complexes become paramagnetic when dissolved in a nonco-ordinating solvent. This is attributed to a polymerisation process whereby the nickel becomes at least five-co-ordinate. Similarly, an equilibrium exists between a red monomer and a green polymer when many nickel(II) *β*-ketoenolates are dissolved in organic solvents. The colours and magnetic properties of these solutions depend on the concentration, the temperature, and the nature of the solvent.

Tetrahedral–square-planar equilibria. With some ligands, especially phosphines, nickel(II) salts form square or tetrahedral complexes when only minor changes occur in the conditions or the nature of the ligand. Solution equilibria often occur between square and tetrahedral complexes, and unlike that in the octahedral–square equilibrium, this does not involve co-ordination by solvent molecules. The solid square planar complex $NiBr_2[Pr^iP(Ph)_2]_2$ is stable at 0 °C but isomerises to the tetrahedral form in about one day at 25 °C. Perhaps even more remarkable is the occurrence of $(PhCH_2PPh_2)_2NiBr_2$ in two forms. The red form is diamagnetic and square planar; the green form has a magnetic moment of 2.7 B.M. at room temperature. This green form has been shown by an X-ray structural analysis to contain nickel in two different environments, both the square and the tetrahedral. Its structure can be represented by the formula (writing L for the phosphine) NiL_2Br_2(square).$2NiL_2Br_2$(tetrahedral). If allowance is made for one-third of the molecules being diamagnetic, a reasonable recalculated moment of 3.3 B.M. is obtained for the tetrahedral form.

8 Mechanisms of Complex-ion Reactions

8.1 Introduction

In chapter 3 we mentioned that substitution reactions of metal aquo-ions, for example

$$[M(H_2O)_6]^{n+} + L \rightleftharpoons [M(H_2O)_5L]^{n+} + H_2O$$

do not all occur instantaneously even though the stability constant may show that the equilibrium lies well over to the right-hand side. Those complexes for which equilibrium is attained rapidly, for example in less than one minute, are called *labile* while those for which ligand substitution is a slow process are called *inert.* These terms labile and inert are concerned with kinetics and must not be confused with stability which, when unqualified, refers to thermodynamic stability. It is thus possible to have complexes which are unstable but inert, or conversely stable but labile. For example, the cobaltammines are thermodynamically unstable in acid solution with respect to the formation of $[Co(H_2O)_6]^{2+}$ and oxygen. Such solutions can however be kept for days at room temperature without noticeable decomposition; that is, the rate of decomposition is very low because the complexes are inert.

Measurements of the rates of reaction of complex compounds can provide information concerning the mechanisms of the reactions. Many kinetic studies on such systems have been performed but here we shall concern ourselves with only the general conclusions to be gained from these studies; more detailed discussions are to be found in the books recommended in the bibliography. Inert complexes are easily studied kinetically by so-called 'static' methods. The reactants are mixed and the rate of reaction is measured with time, using, for example, a spectrophotometric method of observing the increase or decrease in concentration of particular species. Labile complexes are more difficult to study. By using a flow system reactants can be mixed in shorter time than by conventional 'static' mixing, and observations can be made on moderately fast reactions. However, very fast reactions require very specialised techniques such as relaxation methods. In these methods the position of the equilibrium is suddenly changed by, for example, a temperature or pressure jump, and the speed with which the new equilibrium is reached is measured.

The results of such rate studies give information from which some broad generalisations emerge. Taube was the first to point out the existence of a relationship between the rate of reaction of complexes and their electronic structure.

8.1.1 Inert and Labile Complexes

Taube suggested that for inner-orbital complexes (valence bond nomenclature) at least one vacant d orbital needed to be present to confer lability. The substitution process is envisaged as the addition of the new ligand to form a seven-co-ordinate activated complex which then evolves one of the original ligands. Thus, if no vacant orbital is available the activation energy for the formation of the activated complex will be high, and reaction rates correspondingly slow.

Basolo and Pearson have used the crystal-field approach to correlate lability with d electron configurations. In this method the crystal field stabilisation energy of the complex is compared with that of its activated complex (that is the configuration of reactant molecules from which reaction can proceed without further addition of energy). If the CFSE of the initial complex is much greater than that of the activated complex, the complex will be inert, but if the difference between the CFSEs is small the complex will be labile. Assuming, for example, that an octahedral complex reacts via a square pyramidal five-co-ordinate activated complex, the difference in CFSEs for the various d electron configurations can be calculated. This simple approach is only a crude approximation but nevertheless has led to useful correlations.

For d^0, d^5, and d^{10} ions the CFSE is zero in both the initial complex and activated complex, so complexes of these configurations are labile. Similarly, in the d^1, d^2, and high-spin d^6, d^7, d^9 cases the change in CFSE is negligible and labile complexes result. Inert complexes are expected on CFSE argument for d^3 $(t_{2g}{}^3)$ and d^8 $(t_{2g}{}^6e_g{}^2)$ and low-spin d^4 $(t_{2g}{}^4)$, d^5 $(t_{2g}{}^5)$, and d^6 $(t_{2g}{}^6)$ configurations. The predicted order of decreasing reaction rates for inert complexes is $d^5 > d^4 > d^8 \approx d^3 > d^6$. In general the experimental rates found support this order except for the d^8 configuration. Nickel(II) complexes of the $t_{2g}{}^6e_g{}^2$ configuration are generally labile although their reaction rates are usually slower than those of Mn(II) $(t_{2g}{}^3e_g{}^2)$, Co(II) $(t_{2g}{}^5e_g{}^2)$, Cu(II) $(t_{2g}{}^6e_g{}^3)$, and Zn(II) $(t_{2g}{}^6e_g{}^4)$.

As a general rule, four-co-ordinate complexes react more rapidly than similar six-co-ordinate systems. They are consequently often difficult to study kinetically. Their greater lability is attributed to the ease of formation of five-co-ordinate intermediates which then break down with liberation of one of the originally bound ligands. We shall now consider substitution reactions of six and four-co-ordinate complexes.

8.2 Substitution Reactions of Metal Complexes

The reactions with which we are concerned here are of the general type

$$MX_5Y + L \rightarrow MX_5L + Y$$

For these reactions two limiting mechanisms can be defined.

If the intermediate formed in the rate-determining step is of lower co-ordination number than the original complex, this is called a *dissociative* mechanism (symbol D). In other words the mechanism can be written in the form

$$MX_5Y \xrightarrow{\text{slow}} MX_5 + Y$$

followed by

$$MX_5 + L \xrightarrow{\text{fast}} MX_5L$$

In this mechanism the rate-determining step involves the first process; the rate of disappearance of MX_5Y is proportional to the concentration of this species and, as only one reactant is involved in the rate-determining step, the process is unimolecular. An alternative label for this overall process is S_N1, that is *s*ubstitution, *n*ucleophilic, *uni*molecular.

The alternative mechanism is that in which the rate-determining step involves the formation of an intermediate of higher co-ordination number than the starting compound. This is the *associative* mechanism (symbol A). The process can be written

$$MX_5Y + L \xrightarrow{\text{slow}} MX_5YL$$

followed by

$$MX_5YL \xrightarrow{\text{fast}} MX_5L + Y$$

The rate of disappearance of MX_5Y is now proportional to the concentrations of both MX_5Y and L, the process is bimolecular, and the mechanism is labelled S_N2, that is *s*ubstitution, *n*ucleophilic, *bi*molecular.

These two mechanistic routes represent extreme cases, and any particular reaction may proceed with say S_N1 character. This would imply that M—Y bond breaking is of primary importance but the ligand L may be present in the co-ordination sphere of M before the five-co-ordinate intermediate is actually formed.

In the first transition series, substitution reactions of the inert d^3 Cr(III) ions and d^6 Co(III) ions occur slowly enough to permit easy measurement of rates. The consequence is that an enormous amount of information is available on the substitution reactions of these elements. However, with the advent of fast-reaction techniques, rate studies on complexes of the more labile ions have become possible. It is impossible to give an adequate treatment to all this work in this book; we shall look only at a few important generalisations.

8.2.1 Substitution Reactions of Octahedral Complexes

Substitution in aquo-ions. The most fundamental substitution reaction of aquo-ions is that of water exchange between hydrated cations and the solvent water. Studies on a number of aquo-cations have been performed using relaxation methods. Except for a few cations, notably Cr(III) and Rh(III), these reactions are very fast. The general trends are as follows. Within a periodic group of ions of the same charge, for example Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, the rates of exchange increase with the size of the cation (Be^{2+}, $k \approx 10^2\ s^{-1}$; Ba^{2+}, $k \approx 10^9\ s^{-1}$). The more highly charged M^{3+} ions undergo water exchange more slowly than M^{2+} and M^+. Now, the $M—OH_2$ bond strength is expected to increase with charge on M and decrease with size of M for ions of the same charge. It follows therefore that the breaking of the $M—OH_2$ bond is of greater importance than the making of a new bond in the transition state. The exchange reactions thus appear to occur largely by dissociative or S_N1 processes.

The rates of replacement of water molecules by other ligands in general depend on the concentration of metal ion but not on the concentration of the added ligand, that is, they follow a first-order rate law. Surprisingly, the rates of substitution for a given metal aquo-ion do not vary much with the nature of the added ligand.

Aquation reactions. Substitution reactions carried out in aqueous solution appear to proceed always via the intermediate formation of the aquo-complex. This aquation reaction, that is

$$[MX_5Y]^{n+} + H_2O \rightleftharpoons [MX_5(H_2O)]^{n+} + Y$$

is thus of prime importance in the study of substitution reactions, and many studies have been performed on cobalt(III) complexes. The reaction is often given the inappropriate name of *acid hydrolysis;* this term is meant to imply that the hydration occurs under acid conditions. The reaction

$$[MX_5Y]^{n+} + OH^- \rightleftharpoons [MX_5(OH)]^{n+} + Y^-$$

is called *base hydrolysis.*

In the aquation reactions ($pH < 4$) the entering ligand H_2O is present in such a high and effectively constant concentration ($\approx 55.5M$) that the rate law cannot help in deciding whether an associative or a dissociative mechanism is in operation. The observed rates are of course dependent on the concentrations of $[MX_5Y]^{n+}$ only. In order to decide which mechanism is the more important, evidence from the hydration of closely related ions must be sought.

The dissociative process would be expected to be favoured if bulky groups are attached to the cobalt, causing some steric strain and discouraging the possibility of association to a seven-co-ordinate intermediate. To this end, studies have been made on the rates of 'hydrolysis' of $[Co(LL)_2Cl_2]^+$ in which LL represents a chelating ligand derived from ethylenediamine. The rate of substitution for the process

$$[Co(LL)_2Cl_2]^+ + H_2O \rightarrow [Co(LL)_2Cl(H_2O)]^{2+} + Cl^-$$

is indeed found to increase with the size of the ligand LL, and a dissociative process is indicated. Steric effects may not be the only important ones here however; dissociation might be assisted by inductive effects from the more highly substituted ligands, increasing the electron density on the cobalt ion and facilitating the dissociation of the chloride ion.

Further evidence that a dissociative process predominates comes from a comparison of the rates of aquation of complexes having similar ligands but different charges. The aquation of $[Co(NH_3)_4Cl_2]^+$, for example, is of the order of 10^3 times faster than that of $[Co(NH_3)_5Cl]^{2+}$. The increase of charge on a complex is expected to increase the metal-ligand bond strengths and hinder metal–ligand bond cleavage. It should however facilitate the bonding of a seventh ligand and thereby enhance the associative process. The fact that substitution occurs more slowly with the more highly charged ions is indicative of a D process.

8.2.2 *Substitution Reactions of Square Complexes*

The complexes of platinum(II) are square planar and fairly inert, so these have received most detailed study. The rates of substitution reactions in platinum(II) chemistry are insensitive to the charge on the complex ion, indicating that both bond breaking and bond formation are important. Further, the overall kinetics is second-order with a two-term rate law. For example, for the reaction

$$[Pt(NH_3)_3Cl]^+ + Y^- \rightarrow [Pt(NH_3)_3Y]^+ + Cl^-$$

the rate is given by

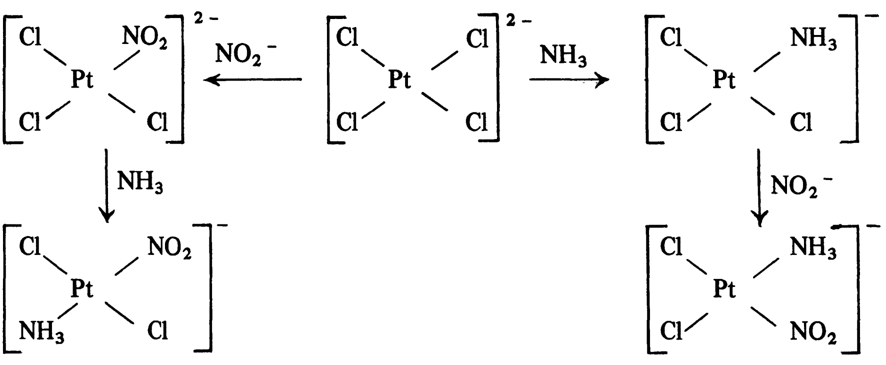
$$\text{Rate} = k[Pt(NH_3)_3Cl^+] + k'[Pt(NH_3)_3Cl^+][Y^-]$$

Such a rate law implies that the reaction proceeds by two parallel paths, one of which involves Y^- in the rate-determining step, and one involving the solvent. These mechanisms are illustrated below.

$$\begin{aligned}
&[Pt(NH_3)_3Cl]^+ + Y^- \xrightleftharpoons{\text{slow}, k'} [Pt(NH_3)_3ClY] \\
&\qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\
&\qquad\qquad\qquad\qquad\qquad [Pt(NH_3)_3Y]^+ + Cl^- \\
&[Pt(NH_3)_3Cl]^+ + H_2O \xrightleftharpoons{\text{slow}, k} [Pt(NH_3)_3H_2O]^{2+} + Cl^- \\
&\qquad\qquad\qquad\qquad\qquad\qquad \Big\downarrow Y^-, \text{fast} \\
&\qquad\qquad\qquad\qquad\qquad [Pt(NH_3)_3Y]^+ + H_2O
\end{aligned}$$

Both paths are believed to proceed via the associative process A, involving a trigonal bipyramidal intermediate.

The trans *effect.* One of the most remarkable features of substitution reactions of platinum(II) complexes is the so-called *trans* effect. This concerns the effect of *trans* substituents on the lability of the leaving group in substitution reactions. As an example let us consider the following reaction schemes:

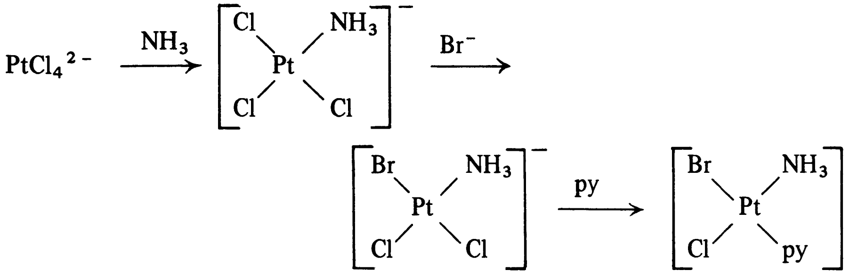


trans *cis*

In these schemes the order in which the $PtCl_4{}^{2-}$ ion is treated with ammonia and nitrite ion determines which of the two isomers of $[PtCl_2(NO_2)(NH_3)]^-$ is predominantly produced. It is apparent that the $NO_2{}^-$ ion has labilised the chloride ion *trans* to itself in the reaction of $[PtCl_3(NO_2)]^{2-}$ with ammonia, whereas in the reaction of $[PtCl_3(NH_3)]^-$ with $NO_2{}^-$ it is the chloride ion which has labilised a chloride ion *trans* to itself. The order of *trans* effect for these ligands is thus $NO_2{}^- > Cl^- > NH_3$. By studying a vast number of these substitution reactions it is possible to draw up a series of ligands of decreasing *trans* effect

$$CO \approx CN^- \approx C_2H_4 \approx PR_3 \approx H^- > NO_2{}^- \approx I^- \approx SCN^- > Br^-$$
$$> Cl^- > NH_3 \approx py > OH^- > H_2O$$

This order can then be used to predict preparative methods for particular isomers. Consider the preparation of $[PtClBr(NH_3)py]$ from $PtCl_4{}^{2-}$. One isomer can be prepared as follows.



In this sequence, the reaction with Br^-occurs in the manner shown since Cl^-has a greater labilising effect than ammonia; the reaction with pyridine proceeds as shown because Br^- has a greater labilising effect than either Cl^- or NH_3. Obviously by altering the starting material and order of reactants the other two possible isomers of the product (that is, with NH_3 and Cl *trans* to Br) can be synthesised.

Theories which attempt to explain the observed order of *trans* effect have been generally debated and no conclusive explanation has been reached. However, those ligands of high *trans* effect are those having either high π-acceptor properties, for example CO, CN^-, and C_2H_4, or strong σ-donor properties (to metal p orbitals), for example H^- and PR_3. The $NO_2{}^-$ ion probably has a large π-acceptor contribution but a poor σ-donor effect in comparison with CO and CN^-.

8.3 Oxidation–Reduction Reactions

Reactions in which an electron is transferred from one complex to another are mechanistically of two main types. These are called the *outer-sphere* and *inner-sphere* processes. In the outer-sphere process each complex maintains its own co-ordination shell during the electron transfer. This process is the one occurring between inert complexes; in these, substitution reactions are slower than electron transfer reactions. Inner-sphere processes are those in which electron transfer takes place through a bridging atom or group which is common to the co-ordination spheres of both complexes. They occur between reactants which are labile to substitution processes.

8.3.1 Outer-sphere Reactions

These reactions have a rate law that is first order in both reactants. Usually both reactants are inert. Many examples of these reactions are to be found in electron exchange reactions which do not represent overall chemical reactions. Consider, for example, the electron-exchange reaction between $[Fe(CN)_6]^{4-}$and $[Fe(CN)_6]^{3-}$. The rate of this exchange can be studied by labelling one of the complexes with a radioactive isotope of iron

$$[\overset{*}{Fe}(CN)_6]^{4-} + [Fe(CN)_6]^{3-} \rightarrow [\overset{*}{Fe}(CN)_6]^{3-} + [Fe(CN)_6]^{4-}$$

The hexacyanoferrate(III) is a low-spin d^5 system and hexacyanoferrate(II) is a low-spin d^6 system, both of which are inert to substitution, and hence the loss or exchange of cyanide ions is very small. The electron-exchange rate is very fast and thus the possibility of a bridged activated complex being important is ruled out since the mere formation of such a complex amounts to a substitution process. Other 'reactions' proceeding similarly are included in table 8.1; the rate constants indicate the wide range of rates exhibited, but accurate values are not quoted since the reactions were often measured under different conditions.

The direct electron transfer process between complexes presents some interesting theoretical problems. The Franck–Condon principle states that electronic transitions occur virtually instantaneously as compared to the time of atomic rearrangements. In other words we can expect the electron to move very much faster than the atoms in the complexes. In the hexacyanoferrate complexes, the Fe–C bond length is shorter in $[Fe(CN)_6]^{3-}$ than it is in $[Fe(CN)_6]^{4-}$. If no movement of the atoms occurs during electron transfer, then in the newly formed $[Fe(CN)_6]^{3-}$ the Fe–C bond will be longer than the equilibrium value for this ion, and the newly formed $[Fe(CN)_6]^{4-}$ will have an Fe–C bond shorter than the equilibrium value. Both of these new ions are thus in excited states, that is with higher energy, so it appears that energy has been created. Since this cannot be the case (conservation of energy principle) the activation energy that needs to be supplied to the reaction is that necessary to produce a transition state in which each species has the same dimensions. Since the bond lengths are not very different in $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$, only a small activation energy is required, so the electron transfer is fairly rapid. The exchange between $[Co(NH_3)_6]^{3+}$ and $[Co(NH_3)_6]^{2+}$ (table 8.1) is extremely slow. These complexes however do not have very dissimilar bond lengths, so an alternative explanation must be sought for the remarkable rate differences. In the cobalt ammine case the complexes differ widely in electronic structure; $[Co(NH_3)_6]^{3+}$ has the t_{2g}^6 ground state while $[Co(NH_3)_6]^{2+}$ has the ground state $t_{2g}^5 e_g^2$. It is therefore apparent that changes in electronic arrangement as well as bond lengths must occur before electron transfer in such systems.

TABLE 8.1 SOME OUTER-SPHERE REACTIONS

Reactants	Rate constant ($dm^3\ mol^{-1} s^{-1}$)
$[W(CN)_8]^{3-}$, $[W(CN)_8]^{4-}$	10^5
$[IrCl_6]^{2-}$, $[IrCl_6]^{3-}$	10^5
$[Mo(CN)_8]^{3-}$, $[Mo(CN)_8]^{4-}$	10^4
MnO_4^-, MnO_4^{2-}	10^3
$[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$	10^2
$[Co(phen)_3]^{3+}$, $[Co(phen)_3]^{2+}$	1
$[Co(en)_3]^{3+}$, $[Co(en)_3]^{2+}$	10^{-4}
$[Co(NH_3)_6]^{3+}$, $[Co(NH_3)_6]^{2+}$	10^{-12}

8.3.2 Inner-sphere Reactions

In these reactions the mechanism involves a bridged complex formed by substitution into one of the reactants of a ligand from the other reactant. Provided that the substituting ligand remains bonded to the original metal ion as well as to the new ion, a bridge is formed. This bridging group is usually transferred along with the electron, and thus its presence in the product of the new ion (that is, not that to which it was originally bonded) is evidence for the bridge mechanism.

There are not very many systems that are suitable for studying this mechanistic process. An ideal reducing agent is Cr^{2+} because it is labile to substitution and forms chromium(III) complexes, which are inert. Any transfer of ligand must occur therefore in the activated complex. Suitable inert oxidising agents include Cr(III), Co(III), and Pt(IV). Taube has demonstrated the generality of the reaction

$$[Co(NH_3)_5X]^{2+} + [Cr(H_2O)_6]^{2+} + 5H_3O^+ \rightarrow [Cr(H_2O)_5X]^{2+} + [Co(H_2O)_6]^{2+} + 5NH_4^+$$

for a wide range of inorganic and organic anions. Thus the reaction between $[Co(NH_3)_5Cl]^{2+}$ and $[Cr(H_2O)_6]^{2+}$ results in quantitative transfer of the chloride ion from cobalt to chromium. Further, if labelled $^{36}Cl^-$ is used in the $[Co(NH_3)_5Cl]^{2+}$ ion and unlabelled chloride ion is also present in the solution which reacts with Cr^{2+}, the product contains only labelled Cl^-, proving that the Cl^- had come only from the cobalt cation. The bridged intermediate in these reactions can thus be written as $[(NH_3)_5Co^{III}{-}X{-}Cr^{II}(H_2O)_5]^{4+}$. Sometimes such bridged intermediates can be isolated in the solid state. For example, in the oxidation of $[Co(CN)_5]^{3-}$(this ion may be hydrated) with $[Fe(CN)_6]^{3-}$, the barium salt of the ion $[(NC)_5Fe^{II}CNCo^{III}(CN)_5]^{6-}$ has been separated from the reaction mixture by fractional crystallisation.

9 Introduction to the First-row Transition Elements

9.1 Introduction

The elements of the first transition series are those for which the 3d electron shell contains between one and nine electrons. Copper is included because, although its outer electronic configuration is $3d^{10}\ 4s^1$, it has the $3d^9$ configuration in its commonly occurring +2 oxidation state. Zinc is not normally considered a transition element since in both the element and its compounds the 3d electron shell remains filled. It therefore does not show the characteristic properties of coloured compounds and paramagnetism shown by the other elements in at least one of their oxidation states. Scandium is included by the definition, but so far only the +3 oxidation state has been established with certainty. Its compounds are thus diamagnetic with no colour from d–d transitions, and its chemistry thus resembles that of aluminium rather than that of the other transition elements. We shall not deal specifically with its chemistry here; interested readers should consult Remy.

The elements with their outermost electronic configurations are listed in table 9.1.

TABLE 9.1 ELECTRONIC CONFIGURATIONS AND IONISATION ENERGIES OF THE FIRST-ROW TRANSITION ELEMENTS

Element	Configuration	Ionisation energies (kJ mol^{-1})			
		1st	2nd	3rd	4th
Sc	$3d^1\ 4s^2$	631	1235	2389	7130
Ti	$3d^2\ 4s^2$	656	1309	2650	4173
V	$3d^3\ 4s^2$	650	1414	2828	4600
Cr	$3d^5\ 4s^1$	653	1592	3056	4900
Mn	$3d^5\ 4s^2$	717	1509	3251	5020
Fe	$3d^6\ 4s^2$	762	1561	2956	5510
Co	$3d^7\ 4s^2$	758	1644	3231	5114
Ni	$3d^8\ 4s^2$	737	1752	3489	5404
Cu	$3d^{10}\ 4s^1$	745	1958	3545	5683

In the atoms of these elements the 3d and 4s orbitals have similar energies. The 4s orbitals are conventionally denoted as the outermost orbitals in table 9.1. This is because the radial probability plots of the 4s and 3d orbitals indicate that there is a greater probability of the 4s electron being furthermost from the nucleus. Further, on ionisation, the neutral atoms usually lose a 4s electron first. In other words, for charged atoms the 3d orbitals are the most stable. Calcium has the outer electron configuration $4s^2$, so the first transition element is scandium with the configuration $3d^1\ 4s^2$. Along the transition series the 3d shell is then filled up regularly with the exceptions of Cr $3d^5\ 4s^1$ and Cu $3d^{10}\ 4s^1$ whose configurations are attributable to the stabilities of half-filled and filled d shells respectively. However, no great practical importance is attached to the configurations of the atoms; it is the ions with which we shall more often be concerned. Thus the divalent state corresponding to the ionisation of the two s electrons is well-established for all the elements except scandium. Oxidation states less than two are usually found (except in the case of Cu^I) only with π-acceptor ligands. Copper(I) has the extra stability associated with the $3d^{10}$ closed-shell configuration.

The trends in the ionisation energies of the elements (table 9.1) illustrate some features of transition metal chemistry. In general the ionisation energies double as the oxidation state increases by one unit, at least up to the fourth ionisation energy. The fourth ionisation energy of scandium indicates that Sc(IV) is unlikely to occur normally, whereas Ti(IV) and V(IV) for example do occur commonly. Unfortunately many factors are important in determining the stability of oxidation states, so we cannot decide which states will occur on the basis of ionisation energies alone. Unipositive ions of these elements are not normally stable in aqueous solution because of the significant sublimation energy term in the process

$$\mathrm{M(s)} \xrightarrow{\Delta H_{\mathrm{subl}}} \mathrm{M(g)} \xrightarrow{I} \mathrm{M^+(g)} \xrightarrow{\Delta H_{\mathrm{hydration}}} \mathrm{M^+(aq.)}$$

As we go to dipositive ions the sublimation energy term remains the same, while the ionisation and hydration energies increase markedly. The sublimation energy thus becomes less significant and the formation of hydrated dipositive ions is favourable. The increased third ionisation energies of nickel and copper, compared with those of the other elements, are significant in the instability of Ni(III) and Cu(III) in aqueous solution.

9.2 Oxidation States

The factors that influence the stability of oxidation states are many. As with compounds the word 'stable' must be modified when applied to the term oxidation state. Thus copper(I) is a thermally stable oxidation state of copper but it is an unstable state with respect to disproportionation in aqueous solution. If we ignore for the moment the complexes of the elements with π-acceptor ligands such as carbon monoxide, which give the very low oxidation states (that is 0, −1, −2), we can tabulate the known oxidation states as in table 9.2.

In the first half of the series, that is up to manganese, the highest oxidation state corresponds to the periodic group number. Thereafter the high oxidation states are difficult to obtain and the maximum oxidation state reached no longer corresponds to the removal of all the 3d and 4s electrons. The oxidation state of +2 is strongly reducing for Ti, V, and Cr, but much more redox stable for Mn and the elements that follow. Indeed, the existence of any particular oxidation state for a metal with a given ligand or anion depends largely on the redox properties of the metal–ligand combination. For example, vanadium in its reactions with the halogens gives a

TABLE 9.2 KNOWN OXIDATION STATES OF THE FIRST-ROW TRANSITION ELEMENTS

Element	Oxidation states						
Sc			3				
Ti		2	3	4			
V		2	3	4	5		
Cr		2	3	4	5	6	
Mn		2	3	4	5	6	7
Fe		2	3	4	5	6	
Co		2	3	4	5		
Ni		2	3	4			
Cu	1	2	3				

fluoride VF_5, a chloride VCl_4, and a bromide VBr_3. In other words vanadium(V) is too strong an oxidising agent to exist in sole combination with chloride or bromide ions; they become oxidised to the free halogens. We shall now consider the effects of the nature of the ligand and of pH on the stability of high and low oxidation states.

9.2.1 *High Oxidation States*

These are exhibited when the metals are in combination with fluoride ions or oxide ions. These are the small, highly electronegative, and hence most difficultly oxidised, anions. Fluorine is often said to bring out the maximum covalency of any element, and we have already seen one example of this in vanadium chemistry. With oxide ions we get the stabilisation of the highest oxidation states of V, Cr, and Mn in the vanadate $VO_4{}^{3-}$, chromate $CrO_4{}^{2-}$, and permanganate $MnO_4{}^{-}$ions. The high oxidation states of iron and cobalt (that is greater than +3) and of nickel and copper (that is greater than +2) almost invariably occur in compounds containing oxygen or fluorine. Examples of these compounds will be found under the individual elements concerned in the chapters that follow.

In aqueous solution high oxidation states are favoured in alkaline solution; indeed, oxidation of transition metal hydroxides by atmospheric oxygen is a characteristic feature of these elements. The addition of sodium hydroxide solution to an iron(II) salt, for example, gives a pale green precipitate of $Fe(OH)_2$ which turns brown on standing in the air owing to oxidation to iron(III). We can understand such oxidations simply in terms of the equilibria

$$[M(H_2O)_6]^{n+} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} [M(OH)_6]^{(6-n)-}$$

It is easier to remove an electron from (that is oxidise) the negatively charged hydroxo-species than from the positively charged aquo-ion. It follows that, in order to stabilise lower oxidation states in aqueous solution, nonoxidising acids must be used.

9.2.2 *Low Oxidation States*

The ligands that favour low oxidation states are those that are capable of bonding by both σ-donor and π-acceptor bonds. In order to do this the ligands must possess both lone-pair electrons and vacant orbitals of π symmetry. The electrons from the ligand are donated along the σ bond; the build-up of negative charge on the metal is then delocalised back on to the ligand via π-bonding. Since the ligands are accepting electron density in the π-bond they are sometimes called *π-acid ligands.* Typical π-acid ligands are CO, N_2, NO, PR_3, RNC, bipy, and phen.

Since carbon monoxide is uncharged, the binary metal carbonyls, for example $Cr(CO)_6$ and $Fe(CO)_5$, contain the metals in zero oxidation states. The bonding in these carbonyls consists of an M—C σ bond formed by donation of the lone pair of electrons on carbon and an M—C π bond formed by donation of electron density from metal d orbitals into the vacant antibonding molecular orbitals (π^*p) on carbon monoxide. These two types of bond are illustrated in figure 9.1. In many complexes the metal has a formally negative oxidation state. In the sodium salts $Na[Co(CO)_4]$ and $Na[Mn(CO)_5]$, for example, the metals are present in uninegative anions, and since there is no charge on the CO ligands, the metals are in the -1 oxidation state. The $+1$ oxidation state occurs in the carbonyl halides such as $Mo(CO)_5Cl$.

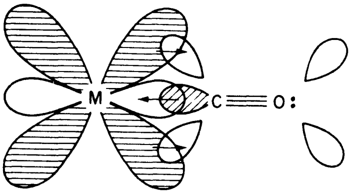


Figure 9.1 The σ and π-bonding in metal carbonyls; only the M—C bonding orbitals are included; shaded orbitals are filled and unshaded orbitals vacant.

Complexes containing molecular nitrogen (usually called dinitrogen complexes) resemble the carbonyls in that the M—N_2 bond involves σ donation and π acceptance by the nitrogen. Typical dinitrogen complexes are $Co(N_2)H(PPh_3)_3$ and $Fe(N_2)H_2(Ph_2EtP)_3$ which contain linear M—N—N groupings. Some complexes containing bridging rather than terminal dinitrogen groups are known, for example $[(NH_3)_5RuN{=}NRu(NH_3)_5]^{4+}$. However, the range of dinitrogen complexes is much less extensive than that of the carbonyl complexes (the first N_2 complex was obtained in 1965), and N_2 complexes are less stable than those of CO.

Complexes of nitrogen monoxide usually contain the ligand bonded as NO^+. In the carbonyl nitrosyl complexes we have the isoelectronic series $MnCO(NO)_3$, $Fe(CO)_2(NO)_2$, $Co(CO)_3NO$ [and $Ni(CO)_4$]. Since the physical evidence indicates that these compounds contain NO^+, the oxidation states of the metals in this series are Mn(-III), Fe(-II), Co(-I) [and Ni(0)].

While phosphorus and arsenic ligands can stabilise low oxidation states because of their vacant d orbitals (which can form π bonds with the metal d orbitals), simple nitrogen donors cannot act effectively in this way. The d orbitals on nitrogen are too high in energy, and the antibonding molecular orbitals on ammonia are of σ symmetry. One or two compounds having only ammonia bonded to a metal have been prepared, for example tetrammineplatinum(0), $Pt(NH_3)_4$. However, compounds of this type have low thermal stability and have not been obtained for the first-row transition elements. If the donor nitrogen atom is connected to a delocalised π system as in bipy and phen, the π^* orbitals of the ring can be used in π-bonding to the metal. Typical of such compounds are $Ti(bipy)_3$ and $Li[Ti(bipy)_3] . 3.5THF$ which formally contain Ti(0) and Ti(–I) respectively. However, these oxidation state assignments assume uncharged bipy ligands; an alternative assignment involves the bipy being reduced to radical anions $bipy^{-\cdot}$ with the extra electrons occupying π^* orbitals in the ring.

9.2.3 *Ionic and Basic Character*

The lower oxidation states in table 9.2 are those in which the elements show their most pronounced ionic character. As the oxidation state increases the charge density on the metal increases and hence the tendency to polarisation of the anion charge cloud and covalency increases. Compounds of these elements in the divalent state are thus largely ionic, and a general trend to covalency as the oxidation number increases is observed. This is shown for example in the halides

$TiCl_2$	$TiCl_3$	$TiCl_4$	
VCl_2	VCl_3	VCl_4	$VOCl_3$
Solids, insoluble in benzene; weak acids		Liquids, soluble in benzene; strong acids	

$$\xrightarrow[\text{increasing covalent character}]{\qquad\qquad\qquad\qquad\qquad\qquad}$$

Accompanying this increase in charge on the metal, as the oxidation state increases, is a corresponding increase in acidity. The more covalent halides are strong Lewis acids and hydrolyse violently in water. The more ionic halides have weaker Lewis acidity; they form aquo-ions in water, $[M(H_2O)_6]^{2+}$ being almost neutral while $[M(H_2O)_6]^{3+}$ is acidic. Similar trends are to be observed in the more common oxides

TiO	Ti_2O_3	TiO_2		
VO	V_2O_3		V_2O_5	
CrO	Cr_2O_3			CrO_3
basic	amphoteric		acidic	

The oxides of the metals (Ti to Co) in their maximum oxidation states are decidedly acidic and give oxo-anion salts with alkalis. Thus titanium(IV) oxide forms titanates(IV), for example TiO_4^{4-}, vanadium(V) oxide forms vanadates(V), for example VO_4^{3-}, and chromium(VI) oxide forms chromates(VI), for example

CrO_4^{2-}. At the other extreme the oxides of metals in the +2 oxidation state show only basic properties, dissolving in acids to form aquo-ions but having little reaction with alkalis.

9.3 Physical and Chemical Properties of the Elements

9.3.1 Physical Properties

All the first-row transition elements are typical metals, many of which find great use as engineering materials. They are characterised by high melting and boiling points, high densities, and low atomic volumes. Some of these properties are listed in table 9.3.

TABLE 9.3 SOME PHYSICAL PROPERTIES OF FIRST-ROW TRANSITION ELEMENTS

Element	M.p. (K)	B.p. (K)	Density (g/cm^3)	Sublimation energy ($kJ\ mol^{-1}$) (298 K)
Sc	1810	3000	3.0	326
Ti	1950	3530	4.5	473
V	2160	3270	6.0	515
Cr	2160	2750	7.2	397
Mn	1520	2370	7.2	281
Fe	1810	3270	7.9	416
Co	1760	3170	8.9	425
Ni	1730	3010	8.9	430
Cu	1356	2868	8.9	339

The horizontal relationships between transition metal ions in the same oxidation state are related to the very similar sizes, and hence charge-to-size ratios, found along the series. Although one cannot strictly define the size of an atom, it is useful to have a relative scale of sizes of the various atoms for comparative purposes. In table 9.4 are listed some atomic and ionic radii obtained by the method of Pauling. A general decrease in size is observed as the transition series is traversed. This is due to contraction of the electron cloud, all the electrons being in the same shell and hence not adequately screening each other from the effects of the increased nuclear charge. The overall decrease in size along the series is not large, and there are some striking size similarities. The chemistry of Ti^{3+} resembles that of V^{3+} in many respects, as is to be expected from their similar ionic radii. In the so-called *transition triads* of group VIII a very close similarity is observed between the metals iron, cobalt, and nickel (see table 9.3). There are considerable similarities also in the properties of their M^{2+} ions, particularly in those properties dependent primarily on charge-to-size ratio rather than electronic configuration, for example solubilities of salts and acidity of the $[M(H_2O)_6]^{2+}$ ions.

TABLE 9.4 ATOMIC AND IONIC RADII (nm)

Element	Atomic radius	Ionic radii M^{2+}	Ionic radii M^{3+}
Ti	0.132	0.090	0.076
V	0.122	0.088	0.074
Cr	0.117	0.084	0.069
Mn	0.117	0.080	0.066
Fe	0.116	0.076	0.064
Co	0.116	0.074	0.063
Ni	0.115	0.072	0.062
Cu	0.117	0.072	

9.3.2 *Chemical Properties*

The first-row transition elements are reactive metals which undergo reaction with a very large number of the chemical elements. A characteristic feature of their chemistry is alloy formation between themselves as well as with nontransition metals. With the light nonmetallic elements, H, B, C, N, and O, interstitial solid solutions are formed. In these 'compounds' the light atoms occupy positions in the interstices of the metal lattices. The structures of the metals are often preserved but may be distorted somewhat; the formulae of the compounds are determined by solubilities, so these compounds are nonstoichiometric. The ratio of the atomic radii of the nonmetal to the metal needs to be less than 0.59 for interstitial compound formation to occur. Stoichiometric compounds do arise when the available interstitial holes are all filled by the light element. Thus, if all the 'octahedral holes' in a face-centred cubic close-packed structure are filled, a 1:1 stoichiometry results as in TiB, TiC, TiN, and TiO. Such compounds have the rock salt structure. These interstitial compounds are usually hard, of high melting point, and chemically inert. Some of them are of great commercial importance, for example steel. When carbon dissolves in iron it can occur as cementite Fe_3C or austenite. In cementite the carbon atoms are at the centres of nearly regular trigonal prisms of iron atoms, while in austenite there are insufficient carbon atoms to form a regular structure and they probably occupy octahedral holes in the γ-Fe lattice. Other interstitial compounds, for example TiB_2, have extreme hardness coupled with inertness to chemical attack.

The elements are extremely reactive in an excess of oxygen; they are often pyrophoric in air especially when in powdered form. The free energies of formation of the oxides in the maximum oxidation states of the metals are among the highest known. The reaction of iron with oxygen in the presence of water, that is rusting, is of great economic importance. With the halogens reaction again occurs very exothermically to produce the highest oxidation state halides, that is the ones which are stable at the temperature of preparation. The hydrogen halides are less reactive toward the transition metals but at elevated temperatures usually react to give halides of lower oxidation states. Thus, for example, the reaction of fluorine with titanium gives TiF_4 while that of hydrogen fluoride leads to TiF_3.

Towards aqueous acids the metals behave in varying ways. Hydrochloric acid dissolves them, Ti and V giving aquo (or chloroaquo) ions of M^{3+}, while Cr, Mn, Fe, Co, and Ni give M^{2+} aquo (or chloroaquo) ions. Oxidising acids such as concentrated nitric acid often have a passivating effect, for example on Fe and Cr. The metals can then be dissolved only with difficulty in other acids, presumably because of a protective oxide film on the surface of the metal. Metals that react with concentrated nitric acid give hydrous oxides (or oxo-ions) if the maximum oxidation state of the metal is +4 or over; thus Ti gives TiO_2.aq. The formation of oxides from nitric acid reactions on metals is due to the great acidity of, for example, $[M(H_2O)_6]^{4+}$ ions which, in the presence of water as a base, become $[M(OH)_4(H_2O)_2]$, that is MO_2.aq. Copper is rather unique in the series in requiring nitric acid to dissolve it rapidly.

10 General Preparative Methods

10.1 Introduction

The preparation of compounds will always be an important part of chemistry whether it be industrial production or the synthesis of new compounds on the research scale. Occasionally the synthesis of a new compound has an enormous impact on our progress and understanding in chemistry. Such was the case with ferrocene $Fe(\pi\text{-}C_5H_5)_2$, discovered in 1951, and xenon tetrafluoride XeF_4, first prepared in 1962.

In this chapter we consider the preparation of the metals and of their simple compounds. The general methods will be illustrated so that in studying the chemistry of each element in the subsequent chapters there will be no need to repeat preparative details of simple compounds. With a knowledge of general methods the reader should then be able to devise syntheses for a large number of simple compounds without a detailed knowledge of the particular element involved.

10.2 Occurrence and Extraction of the Transition Metals

10.2.1 Occurrence of Elements in the Earth's Crust

The approximate abundances of the elements of the first transition series in the earth's crust are indicated in table 10.1. The table includes some other elements for comparison purposes. One can see by inspection of the table that iron and titanium are the most plentiful transition elements and that all the other first-row transition elements are more plentiful than such 'common' elements as zinc. Since

TABLE 10.1 ABUNDANCE OF THE FIRST-ROW TRANSITION ELEMENTS IN THE EARTH'S CRUST

Element	Abundance (wt %)	Element	Abundance (wt %)
O	46	Cl	0.1
Si	28	Cr	0.04
Al	8.1	C	0.03
Fe	5.1	V	0.02
Ca	3.6	Ni	0.008
Na	2.9	Cu	0.007
K	2.6	Co	0.002
Mg	2.1	Pb	0.001
Ti	0.6	Sc	0.0005
Mn	0.1	Zn	0.0001

oxygen is the most plentiful of all the elements and is also electronegative, the elements are most likely to occur as oxides often in combination with silica, silicon being the next most plentiful element. Some typical ores with their approximate compositions are listed in table 10.2.

The extraction of a metal from its ore involves in the first place a concentration of the ore. Various processes are used to separate the ore from sundry unwanted rock etc. These processes include gravity separation and flotation methods as well as aqueous leaching processes (hydrometallurgy). We shall not elucidate them here but shall confine ourselves to the extraction of the metals from their purified ores. In general the ore must be reduced to the metal. The choice of reducing agent is governed by economic as well as chemical factors and is also dependent on the purity of metal required and the use to which it is to be put. The most important methods involve the reduction of oxides with carbon, hydrogen, or aluminium, the reduction of chlorides with active metals, and electrolysis of salts either molten or in aqueous solution. We consider these methods below.

TABLE 10.2 SOME COMMON ORES OF THE TRANSITION ELEMENTS

Element	Ore	Typical composition
Sc	thortveitite	$ScSi_2O_7$
Ti	ilmenite	$FeTiO_3$
	rutile	TiO_2
V	patronite	$V_2S_5.nS$
	vanadinite	$3Pb_3(VO_4)_2.PbCl_2$
Cr	chromite	$FeCr_2O_4$
Mn	pyrolusite	MnO_2
	rhodocrosite	$MnCO_3$
Fe	haematite	Fe_2O_3
	magnetite	Fe_3O_4
	siderite	$FeCO_3$
	pyrites	FeS_2
Co	smaltite	$CoAs_2$
	cobaltite	$CoAsS$
Ni	pentlandite	$(Ni,Fe)_9S_8$
	garnierite	$(Ni,Mg)_6Si_4O_{10}(OH)_8$
Cu	chalcocite	Cu_2S
	chalcopyrite	$CuFeS_2$

10.2.2 *Extraction from Oxides by Thermal Methods*

The thermal reduction of a metal oxide with carbon is frequently the preferred route to a metal on economic grounds. Because the general reaction, that is

$$MO + C \rightarrow M + CO$$

proceeds from left to right with the net production of carbon monoxide, a gas of large entropy, the reaction will become thermodynamically feasible for all metals at some temperature or other. This is because in the equation

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

the ΔS term is positive; thus, provided that T is large enough, ΔG° becomes negative and hence favourable for reaction. In practice temperatures of over 2000°C are uneconomical and other methods are used to extract metals that form very stable oxides. Metals that are normally extracted by carbon reduction of oxides include lead and zinc.

However, with the transition elements there is a complication, interstitial compound formation. If titanium(IV) oxide is heated with an excess of carbon, for example, the reaction

$$TiO_2 + 3C \rightarrow TiC + 2CO$$

proceeds and titanium carbide is the product. For titanium, vanadium, and chromium this method cannot be used. However, the later transition elements can be obtained in impure form by this method, for example

$$Mn_3O_4 + 4C \rightarrow 3Mn + 4CO$$

$$Co_2O_3 + 3C \rightarrow 2Co + 3CO$$

Iron is the most important example economically. The reduction of iron oxides by coke in the blast furnace gives 'pig iron' which contains about 4.6 per cent carbon (the solubility limit of carbon in iron). This excess of carbon is removed by oxidation using air or oxygen with the molten metal in a Bessemer converter or an open hearth. Steels rather than pure iron are obtained in this way; pure iron has no industrial importance. Despite the fact that we have written carbon as the reducing agent in the equations, the effective reducing agent is probably carbon monoxide, the carbon serving to reduce the carbon dioxide produced back to the monoxide, for example

$$CO + FeO \rightarrow Fe + CO_2$$

$$CO_2 + C \rightarrow 2CO$$

Hydrogen reduction of metal oxides is not so cheap or effective as carbon reduction, but when contamination from carbon is undesirable it may be a useful process. Thus pure iron can be obtained by heating high purity Fe_2O_3 in hydrogen; cobalt, molybdenum, and tungsten are similarly obtained free from carbides by, for example, the reaction

$$Co_2O_3 + 3H_2 \rightarrow 2Co + 3H_2O$$

Alternatively, if the temperature for carbon reduction is too high and/or carbon contamination is a problem, reduction by an active metal such as calcium, magnesium, or aluminium can be used. The 'thermit' process is used in the extraction of chromium and of carbon-free ferrovanadium and ferrotitanium

$$Cr_2O_3 + 2Al \rightarrow 2Cr + Al_2O_3$$

Vanadium is obtained from the oxide by reduction with silicon or calcium

$$2V_2O_5 + 5Si \rightarrow 4V + 5SiO_2$$

In the pyrometallurgical process for extracting copper from sulphide ores, the sulphur in the ores is used as reducing agent after about half of the copper has been oxidised, that is

$$2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$$

A rather special process is used for refining nickel; this is known as the Mond or carbonyl process. The impure nickel obtained by carbon reduction of NiO is treated with carbon monoxide at 50°, and the volatile carbonyl so produced is decomposed to the pure metal at 180°

$$Ni + 4CO \underset{180^\circ}{\overset{50^\circ}{\rightleftharpoons}} Ni(CO)_4$$

Pure iron can similarly be obtained by thermal decomposition of $Fe(CO)_5$.

10.2.3 Extraction from Halides

Transition-metal halides have been reduced by alkali metals and alkaline earth metals, by hydrogen, and by thermal decomposition. The most important production from halides is by the Kroll process which accounts for virtually all the titanium manufactured commercially. In this process, titanium(IV) chloride is reduced by magnesium or sodium at around 800° in an atmosphere of argon

$$TiCl_4 + 2Mg \rightarrow Ti + 2MgCl_2$$

This rather expensive process ($TiCl_4$ must be manufactured from $TiO_2 + C + Cl_2$) is used for many reasons. Firstly, titanium is required (unlike iron) in a pure form for use as an engineering metal, and impurities lower the ductility of the metal. Secondly, titanium has a large affinity for oxygen and carbon, so carbon reduction of the oxide cannot be used. Thirdly, titanium forms interstitial compounds with nitrogen and hydrogen, and hence the more expensive argon has to be used as the protective atmosphere. The magnesium chloride is removed from the titanium by sublimation in a vacuum or by leaching with water.

Scandium is obtained in a similar process, using the reduction of the fluoride by calcium under an inert atmosphere at a temperature in excess of 1000°

$$2ScF_3 + 3Ca \rightarrow 2Sc + 3CaF_2$$

Laboratory methods for preparing titanium include passing the chloride $TiCl_4$ in hydrogen through a red-hot tube or over a heated filament

$$TiCl_4 + 2H_2 \rightarrow Ti + 4HCl$$

A purification process used for refining some of the transition metals (notably Ti and Zr) on a laboratory scale is that due to van Arkel and de Boer. The impure metal is allowed to react with iodine at a moderate temperature (about 200°), and the volatile iodide produced is then decomposed on a hot filament (about 1300°), for example

$$\text{Ti(crude)} + 2\text{I}_2 \xrightarrow{200^\circ} \text{TiI}_4 \xrightarrow{1300^\circ} \text{Ti(pure)} + 2\text{I}_2$$

10.2.4 Electrolytic Methods

Electrolysis of molten salts has not been used widely for the preparation of first-row transition elements, since the later elements in the series can be deposited by electrolysis of aqueous solutions. Methods similar to that used commercially for aluminium have been developed for titanium. The oxide can be electrolysed in a bath of molten calcium, magnesium, or alkali metal fluorides; alternatively, the lower chlorides can be electrolysed in molten alkali metal chloride baths. Scandium was initially produced by electrolysis of its chloride in a molten salt bath, but the product is not as pure as that obtained by calcium reduction.

Aqueous electrolysis is widely used as a method of refining impure samples of metals such as chromium, nickel, and copper. The crude metal is cast into anodes and used in electrolytic cells containing a solution of the metal sulphate or chloride. On electrolysis, the metal dissolves from the anode and is deposited on the pure metal cathode; the impurities remain as the 'anode sludge'.

10.3 Preparation of Simple Transition-metal Compounds

The distinction between simple and complex compounds is a very arbitrary one, and we shall concern ourselves here largely with compounds formed between the metals and simple anions (there being no ligand present other than the anion). In chapter 3, the hexaquo-ion was discussed, and at this point the reader should be reminded that reactions in aqueous solution are not likely to lead to simple salts. The products of the dissolution of a transition-metal oxide in an acid, for example, are not simple salts. Rather, they contain complex ions with water and/or anions from the acid in the co-ordination sphere of the metal. The consequence of this is that, in transition metal chemistry, preparative procedures for simple compounds must usually be carried out in the absence of water. Thus, reactions frequently involve vacuum-line techniques, inert atmospheres, or nonaqueous solvent systems. Because of the variable oxidation states shown by these elements, the absence of oxygen from preparations is also frequently desirable.

10.3.1 Preparation of Halides

Direct reaction with halogens. The reaction between the metals and the halogens is the most straightforward way of preparing the more covalent metal halides. If the pure metal and halogen are available, and the product can be separated easily from excess halogen, a product free from impurities is readily obtained. The reactions are exothermic and once started will usually continue without further heat, but a temperature of a few hundred degrees is often necessary to start the reaction. When the halide is relatively involatile, continuous heating of the reaction zone may be necessary to effect a sublimation of the halide away from the metal.

For fluorides and chlorides, the undiluted halogen is passed over the heated metal in a combustion tube, and any products are collected in a cooled vessel as they emerge from the tube. Simple fractionation or evacuation is then necessary to separate the halide from adsorbed or dissolved halogen. Some halides typically prepared in this way are indicated in the equations

$$Ti + 2F_2 \rightarrow TiF_4$$

$$V + 2Cl_2 \rightarrow VCl_4$$

$$2Fe + 3Cl_2 \rightarrow 2FeCl_3$$

With bromine and iodine, a carrier gas such as nitrogen must be used if the halogen vapour is to be transported over the heated metal. Alternatively, the reaction can be carried out using a solvent or with the halogen itself as solvent. Titanium(IV) bromide is most easily prepared, for example, by adding granules of titanium, in small amounts, to an excess of liquid bromine. The metal burns with incandescence; the bromine may eventually boil and the vapour is returned to the reaction vessel by a reflux condenser. The excess of bromine is finally distilled off and the bromide remaining is distilled in a vacuum. Titanium(IV) iodide is most easily prepared by heating titanium and iodine under reflux in a solvent such as benzene.

Direct reaction with hydrogen halides. Metals react with hydrogen halides at high temperatures to produce a low oxidation state halide. Typical reactions and conditions are given in the equations

$$V + 2HCl \xrightarrow{950^\circ} VCl_2 + H_2$$

$$Cr + 2HBr \xrightarrow{750^\circ} CrBr_2 + H_2$$

$$Cu + HCl \xrightarrow{900^\circ} CuCl + \tfrac{1}{2}H_2$$

From metal oxides. When the metal is not readily available, or is expensive compared with the price of its oxide, the halogen can be caused to react in a flow system with a mixture of the metal oxide and carbon. Examples are

$$TiO_2 + 2C + 2Cl_2 \xrightarrow{500^\circ} TiCl_4 + 2CO$$

$$Cr_2O_3 + 3C + 3Cl_2 \xrightarrow{800^\circ} 2CrCl_3 + 3CO$$

Alternatively, carbon tetrachloride can be passed over the hot oxide; CCl_4 decomposes into carbon and chlorine above 400°.

Some metals form oxohalides as well as the binary halides; for these metals, problems of contamination may arise if oxides are used as starting materials. Thus chlorination of a mixture of vanadium(V) oxide and carbon can produce both

VCl_4 and $VOCl_3$

$$V_2O_5 + 5C + 4Cl_2 \xrightarrow{800^\circ} 2VCl_4 + 5CO$$

$$V_2O_5 + 3C + 3Cl_2 \xrightarrow{350^\circ} 2VOCl_3 + 3CO$$

Since both VCl_4 and $VOCl_3$ are dark red liquids with similar boiling points, contamination of one chloride by the other is likely. In the corresponding bromine reaction, however, the reaction products are VBr_3 and $VOBr_3$

$$V_2O_5 + 5C + 3Br_2 \rightarrow 2VBr_3 + 5CO$$

$$V_2O_5 + 3C + 3Br_2 \rightarrow 2VOBr_3 + 3CO$$

Since VBr_3 is a black relatively involatile solid and $VOBr_3$ is a brown liquid, no contamination problems arise; the $VOBr_3$ distils out of the hot zone and the VBr_3 remains as a condensate on the cooler parts of the combustion tube.

Reduction of higher oxidation state halides. The lower oxidation state halides of titanium, vanadium, and chromium are conveniently prepared by reduction of the higher halides. Reducing agents include hydrogen, aluminium, and the element itself

$$2VBr_3 + H_2 \xrightarrow{450^\circ} 2VBr_2 + 2HBr$$

$$3TiBr_4 + Al \xrightarrow{200^\circ} 3TiBr_3 + AlBr_3$$

$$2CrCl_3 + Cr \xrightarrow{900^\circ} 3CrCl_2$$

Apart from the reductions with hydrogen, these reactions are carried out in sealed tubes; glass 'Carius tubes' are satisfactory for the lower-temperature reactions (for example $TiBr_3$ preparation) while metal bombs must be used for reactions that involve high vapour pressures of the metal halide.

Sometimes internal oxidation–reduction occurs when a transition metal halide is heated. The preferred method of preparing VCl_3, for example, is to heat VCl_4 under reflux (b.p. 150°) in an inert atmosphere. The brown liquid decomposes smoothly leaving the violet trichloride

$$2VCl_4 \rightarrow 2VCl_3 + Cl_2$$

In this reaction the chloride ion has been oxidised to chlorine and the vanadium(IV) reduced to vanadium(III). Many similar reactions occur with halides in high oxidation states; this redox process is of course the reason for the instability of compounds such as VCl_5, VBr_4, and $CrCl_6$. Some other examples of thermal decompositions are

$$2VOBr_3 \xrightarrow{100^\circ} 2VOBr_2 + Br_2$$

$$2FeBr_3 \xrightarrow{120^\circ} 2FeBr_2 + Br_2$$

$$2CuBr_2 \xrightarrow{150^\circ} 2CuBr + Br_2$$

When the metallic element undergoes both oxidation and reduction, we have disproportionation occurring. If the products are readily separated, the reaction can be of preparative use. The involatile halides of titanium(II) and vanadium(II) are conveniently prepared in this way because of the volatility of the higher halides, for example

$$2TiBr_3 \xrightarrow{400^\circ} TiBr_2 + TiBr_4$$

$$2VCl_3 \xrightarrow{450^\circ} VCl_2 + VCl_4$$

Exchange reactions. Because the reaction of fluorine with the later transition elements tends to produce ionic fluorides that coat the surface of the metals and hence prevent further reaction, exchange reactions are often found preferable for preparing fluorides. In these reactions, another halide is caused to react with fluorine, a halogen fluoride, or hydrogen fluoride. The ionic starting materials are used in a flow system; the more covalent and volatile halides can be treated in solution. Examples illustrating the preparation of fluorides are

$$2CoCl_2 + 3F_2 \xrightarrow{250^\circ} 2CoF_3 + 2Cl_2$$

$$FeCl_3 + ClF_3 \xrightarrow{500^\circ} FeF_3 + 2Cl_2$$

$$NiCl_2 + 2HF \xrightarrow{600^\circ} NiF_2 + 2HCl$$

Similar exchange reactions can be used for the other halides. The most useful are those in which a halide is obtained directly from the metal oxide. Typical of the reagents that can effect this exchange are thionyl chloride, boron tribromide, and aluminium iodide, for example

$$V_2O_3 + 3SOCl_2 \xrightarrow{200^\circ} 2VCl_3 + 3SO_2$$

$$Fe_2O_3 + 2BBr_3 \xrightarrow{100^\circ} 2FeBr_3 + B_2O_3$$

$$V_2O_3 + 2AlI_3 \xrightarrow{330^\circ} 2VI_3 + Al_2O_3$$

From hydrated halides. The reader may have noticed that in the examples given so far the elements titanium, vanadium, and chromium have featured frequently. The halides of these elements are best prepared under nonaqueous conditions; their M^{3+} and M^{2+} halide hydrates are not easily dehydrated thermally without hydrolysis occurring, for example

$$VBr_3(H_2O)_6 \xrightarrow[\text{vacuum}]{200^\circ} VOBr + 2HBr + 5H_2O$$

The elements toward the other end of the first transition series, that is iron, cobalt, nickel, and copper, readily form hydrated halides in aqueous solution, from which the anhydrous halides can frequently be obtained by dehydration.

Some hydrated salts evolve the water of co-ordination when heated to above 100° in a vacuum. Manganese(II), iron(II), cobalt(II), and nickel(II) halides can be dehydrated in this way, for example

$$MnCl_2(H_2O)_4 \xrightarrow{210^\circ} MnCl_2 + 4H_2O$$

In order to be certain that no hydrolysis has occurred, it is usually preferable to dehydrate the halides in a stream of the dry hydrogen halide gas or sublime the crude anhydrous halide in an atmosphere of the hydrogen halide

$$CuCl_2(H_2O)_2 \xrightarrow[HCl]{150^\circ} CuCl_2 + 2H_2O$$

Chemical methods of dehydration are also used. Thionyl chloride has particular advantage in that, in its reaction with water, only volatile products result

$$SOCl_2 + H_2O \rightarrow SO_2 + 2HCl$$

A standard method for chlorides is thus to treat the hydrated chloride with an excess of thionyl chloride and heat under reflux if necessary. Effervescence is observed as the water reacts. No protection from water vapour in the atmosphere is necessary during the dehydration since thionyl chloride reacts more readily with water than does the anhydrous metal chloride. This method has been used successfully for the dehydration of $MCl_3 . 6H_2O$ (M = Cr, Fe) and $MCl_2 . xH_2O$ (M = Mn, Fe, Co, Ni, Cu). The disadvantage of the method is that the final traces of thionyl chloride (and possibly other sulphur compounds) are difficult to remove from the metal chloride even by continued evacuation on a vacuum line. Other chemical dehydrating agents include acetyl halides and 2,2-dimethoxypropane

10.3.2 Preparation of Nitrates

Anhydrous nitrates of the first-row transition elements were unknown some fifteen years ago. Thermal dehydration of the hydrated salts cannot be used because decomposition of the nitrate sets in before all the water has been removed.

As with so many transition metal salts, isolation of the anhydrous nitrates has proved possible by using nonaqueous solvents. The ideal solvent for preparing metal nitrates is dinitrogen tetroxide. This solvent undergoes the autoionisation

$$N_2O_4 \rightarrow NO^+ + NO_3^-$$

This ionisation is greatly increased if a donor solvent such as acetonitrile or ethyl acetate is used. Copper metal will dissolve with effervescence in such solvent mixtures

$$Cu + 2N_2O_4 \rightarrow Cu(NO_3)_2 + 2NO$$

The nitrate is isolated as a blue-green solid of composition $Cu(NO_3)_2 .N_2O_4$; when this is heated in a vacuum to 120° the blue nitrate remains. This nitrate, unlike the hydrated salt, can be sublimed in a vacuum at 200°. Manganese(II) and cobalt(II) nitrates can be prepared similarly starting from the metals. Vanadium, however, gives $VO_2(NO_3)$ under this treatment.

The other first-row transition elements are insoluble in N_2O_4 or its mixtures with donor solvents. Other methods must therefore be used to prepare their nitrates. One method is to solvolyse a metal halide or carbonyl. Nickel(II) nitrate is conveniently prepared, for example, by adding acetonitrile to a suspension of nickel(II) chloride in N_2O_4

$$NiCl_2 + 2N_2O_4 \xrightarrow{MeCN} Ni(NO_3)_2 + 2NOCl$$

The nitrate is isolated as the adduct $Ni(NO_3)_2.3MeCN$ which is desolvated at 170° to give lime green $Ni(NO_3)_2$.

The early transition elements in their high oxidation states show a tendency to form oxide nitrates in the reactions of their halides with N_2O_4; titanium(IV) chloride forms $TiO(NO_3)_2$ for example. The more highly nitrated product can usually be obtained using dinitrogen pentoxide N_2O_5 instead of N_2O_4. Thus the reaction of vanadium(V) oxide or oxide trichloride with N_2O_5 yields the oxide trinitrate

$$V_2O_5 + 3N_2O_5 \rightarrow 2VO(NO_3)_3$$

[compare $VO_2(NO_3)$ from V + N_2O_4]. When chromium carbonyl is added to N_2O_5 in carbon tetrachloride solution, the green nitrate is formed as a precipitate.

$$Cr(CO)_6 + 3N_2O_5 \rightarrow Cr(NO_3)_3 + 6CO + 3NO_2$$

This nitrate cannot be readily obtained using N_2O_4 since the product $Cr(NO_3)_3.2N_2O_4$ is difficult to desolvate without decomposition of the $Cr(NO_3)_3$. Dinitrogen pentoxide is the anhydride of nitric acid and is capable of removing water from hydrated metal nitrates. Hydrated titanium(IV) nitrate is thus converted into $Ti(NO_3)_4$ by reaction with N_2O_5; sublimation at 100° in a vacuum gives the pure nitrate.

10.3.3 Preparation of Other Oxo-salts

Salts such as sulphates, phosphates, acetates, etc. are more thermally stable than nitrates, so they can frequently be obtained by thermal dehydration of the salts crystallising from aqueous solution, for example

$$CuSO_4.5H_2O \xrightarrow{200^\circ} CuSO_4 + 5H_2O$$

This is most commonly true for salts of the later transition elements, that is manganese to copper. The early transition elements in their more covalent oxidation states yield oxo-anion salts, for example $TiOSO_4$ and $VO(OCOCH_3)_2$, if aqueous solutions are used in preparation, owing to the great acidity of $[M(H_2O)_6]^{4+}$ ions. Nonaqueous solvents or reactions must therefore be used. For sulphates, sulphuric acid or sulphur trioxide is used, for example

$$TiCl_4 + 6SO_3 \rightarrow Ti(SO_4)_2 + 2S_2O_5Cl_2$$

Acetates are best prepared in acetic acid to which a little acetic anhydride has been added to remove any water from the system. Thus vanadium(III) acetate is prepared by dissolving vanadium diboride (vanadium does not react) in acetic acid

$$2VB_2 + 6CH_3COOH \rightarrow V_2(O_2CCH_3)_6 + 3H_2 + 4B$$

10.3.4 Preparation of Amides, Imides, and Nitrides

Just as the solvent used to prepare hydroxides is water, so for amides the solvent used is liquid ammonia (transition metal amides are hydrolysed by water). The general route to transition-metal amides involves the addition of the stoichiometric quantity of potassium amide to an ammonia-soluble salt of the metal. The amides, like hydroxides, are polymeric and are precipitated, for example

$$[Mn(NH_3)_6](SCN)_2 + 2KNH_2 \xrightarrow{\text{liq.}NH_3} Mn(NH_2)_2 + 2KSCN + 6NH_3$$

$$[Co(NH_3)_6](NO_3)_3 + 3KNH_2 \xrightarrow{\text{liq.}NH_3} Co(NH_2)_3 + 3KNO_3 + 6NH_3$$

Amides are sometimes produced in the ammonolysis (using ammonia only) of covalent compounds of the early transition elements, but frequently only partial ammonolysis occurs, for example

$$VCl_4 + 6NH_3 \rightarrow VCl(NH_2)_3 + 3NH_4Cl$$

Thermal decomposition of amides produces imides and nitrides (compare hydroxides → oxides), for example

$$Co(NH_2)_3 \rightarrow CoN + 2NH_3$$

Nitrides can also be produced directly by passing a mixture of ammonia and a volatile metal halide (such as $TiCl_4$) over an incandescent filament.

Transition-metal amides are usually amphoteric in liquid ammonia, dissolving in an excess of the added base to form amido- or imido-complexes

$$Cr(NH_2)_3 + KNH_2 \rightarrow KCr(NH_2)_4$$

$$Ti(NH_2)_3 + KNH_2 \rightarrow KTi(NH)_2 + 2NH_3$$

11 Titanium

11.1 The Element

Titanium is the most naturally abundant transition metal after iron, and is widely distributed throughout the earth's surface. Despite this fact, the metal has been of commercial importance only during the last two or three decades. Although it has some very desirable physical properties as an engineering metal, the high cost of production of the pure metal (Kroll process, chapter 10) still hinders its utilisation. It is used in supersonic aircraft, in which its high strength-to-weight ratio is important, and in the construction of chemical plant where its corrosion resistance (particularly to moist chlorine) is its important feature.

Titanium (atomic number 22) is a silver-grey metal with a density of 4.5 and a melting point around 1670°. It is about as strong as steel yet only half as dense; however, its strength and resistance to corrosion drop rapidly above 800°. When finely divided, the metal is pyrophoric in air at room temperature; at higher temperatures the massive metal reacts with oxygen, nitrogen, carbon, and boron to give TiO_2, TiN, TiC, and TiB_2 as limiting products (in excess of the nonmetal). Hydrogen is absorbed reversibly. Dilute mineral acids have little effect in the cold, but the metal is dissolved in hot dilute hydrochloric acid or cold dilute hydrofluoric acid. Hot concentrated nitric acid slowly attacks the metal with the formation of insoluble $TiO_2.nH_2O$. Titanium is not attacked by hot aqueous alkali.

The ground state outer electronic configuration of titanium is $3d^2\ 4s^2$. The maximum oxidation state is +4 and this is the commonest state found; compounds in lower oxidation states are readily oxidised. Certain similarities are shown to other group IV metals, notably tin; for example, the chlorides MCl_4 are covalent colourless liquids readily hydrolysed in moist air and forming complexes such as $MCl_6{}^{2-}$. We shall discuss now the compounds of titanium in the various oxidation states, but for convenience will consider the organometallic compounds separately at the end.

11.2 Compounds of Titanium(IV) (d^0)

11.2.1 Aqueous Chemistry

The +4 oxidation state for titanium gives rise to largely covalent compounds. The ion $[Ti(H_2O)_6]^{4+}$ is unknown; its high charge-to-size ratio leads to great acidity and hence only hydrolysed derivatives are obtained in aqueous solution. In dilute noncomplexing acids such as $HClO_4$, the hydrolytic equilibrium probably lies in the region indicated by

$$[Ti(H_2O)_4(OH)_2]^{2+} + H_2O \rightleftharpoons [Ti(H_2O)_3(OH)_3]^{+} + H_3O^{+}$$

The addition of a base causes the precipitation of the hydrous oxide, that is the equilibrium

$$[Ti(H_2O)_3(OH)_3]^{+} + H_2O \rightleftharpoons [Ti(H_2O)_2(OH)_4] + H_3O^{+}$$

lies to the right. The hydrous oxide is normally regarded as $TiO_2.nH_2O$ [$n = 4$ in the formula $Ti(H_2O)_2(OH)_4$], there being no evidence for $Ti(OH)_4$. The hydrolytic equilibrium is of course (see chapter 3) complicated by olation and oxolation. However, the simple monomeric species $[TiO(H_2O)_5]^{2+}$ does not appear to be important; contrast this with the aqueous chemistry of vanadium(IV) in which $[VO(H_2O)_5]^{2+}$ is a predominant species. In subsequent chemical equations we shall for simplicity write TiO^{2+} as the species present, it being obviously preferable to Ti^{4+} as a realistic species. Oxo-species of titanium(IV) are usually polymeric with –Ti–O–Ti–O– chains. Such a structure has been found, for example, in the solid $TiOSO_4.H_2O$ in which each titanium atom is approximately octahedrally co-ordinated by oxygen atoms. The TiO group is believed to occur in salts of the $TiOCl_4{}^{2-}$ion which have a tetragonal pyramidal structure for the anion.

In acids containing anions capable of co-ordinating to the titanium, complexes containing the anions are formed. The exact nature of these depends on the concentration of the acid (that is the ligand). Thus the hydrolysis of titanium(IV) chloride in water does not lead to the precipitation of much TiO_2.aq; rather, the titanium is kept in solution as anionic complexes of the type $[Ti(OH)Cl_5]^-$ and $[TiCl_6]^{2-}$. Salts of this hexachlorotitanate(IV) anion can be precipitated from solutions of $TiCl_4$ in saturated hydrochloric acid.

In excess of aqueous alkali the initially precipitated TiO_2.aq dissolves to form titanates; such titanates are more readily formed in the fused state between TiO_2 and metal oxides. These titanates are basically of two types, the metatitanates $M^I{}_2TiO_3$ and $M^{II}TiO_3$, and the orthotitanates $M^I{}_4TiO_4$ and $M^{II}{}_2TiO_4$. In most cases they do not contain discrete titanate anions but have mixed oxide type structures, that is the perovskite $CaTiO_3$, ilmenite $FeTiO_3$, and spinel $M^{II}{}_2TiO_4$ structures.

A very useful and characteristic reaction of aqueous titanium(IV) solutions is that with hydrogen peroxide; the orange coloration produced in mildly acidic solutions can be used to estimate titanium colorimetrically. The nature of the species responsible for the colour is not known but various peroxo-complexes have been isolated in the solid state from these solutions. These include $Ti(O_2)SO_4.3H_2O$ obtained by the addition of hydrogen peroxide to a solution of $TiOSO_4$ in concentrated sulphuric acid, $M^I{}_3[Ti(O_2)F_5]$, and $M^I{}_2[Ti(O_2)(SO_4)_2].nH_2O$. A yellow solid, probably $TiO_3.2H_2O$, is obtained when a solution of $TiOSO_4$ containing hydrogen peroxide is precipitated at pH 8.6 by the addition of ethanol.

11.2.2 Titanium(IV) *Oxide*, TiO_2

This oxide exists in three crystalline forms, rutile, anatase, and brookite. In all three forms the titanium atoms are co-ordinated to six oxygen atoms. Rutile is the more commonly occurring natural form but all three forms have been prepared synthetically. Titanium dioxide is commercially very important as a white pigment. It is nontoxic, chemically inert, and gives an opaque white finish when coating other colours. It is prepared industrially by two processes. In one process, ilmenite is dissolved in sulphuric acid and the sulphate $TiOSO_4$ allowed to hydrolyse in hot water. The TiO_2.aq that precipitates is ignited at 900° to give the anhydrous oxide. In the other process, rutile is converted into $TiCl_4$ by heating with carbon and chlorine. The tetrachloride is then combusted with dry oxygen at around 700°

$$TiCl_4 + O_2 \rightarrow TiO_2 + 2Cl_2$$

Titanium(IV) oxide is dissolved with difficulty in hot concentrated sulphuric acid but more readily in fused alkali metal bisulphates. With fused alkali metal carbonates, titanates are formed. Because of its constant composition and high thermal stability it is used in the gravimetric estimation of titanium. All the metal is precipitated from solution with aqueous ammonia, and the precipitate is ignited to constant weight at 900° and weighed as TiO_2.

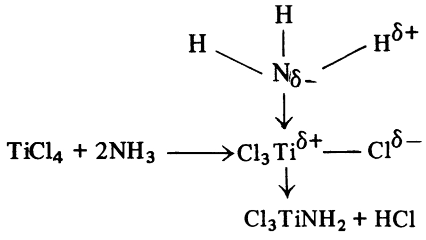
11.2.3 *Titanium*(IV) *Halides*

The physical properties of the titanium(IV) halides are listed in table 11.1. The fluoride differs from the other halides in having a relatively high boiling point and in being insoluble in nonpolar solvents. It is probably a fluorine-bridged polymer with six-co-ordinate titanium atoms. The solid is hygroscopic but can be readily purified by vacuum sublimation. It dissolves in aqueous hydrogen fluoride to form the $TiF_6{}^{2-}$ ion; salts of this ion are stable to hydrolysis in water.

TABLE 11.1 PHYSICAL PROPERTIES OF TITANIUM(IV) HALIDES

Halide	Colour	M.p. (°C)	B.p. (°C)
TiF_4	white	–	284
$TiCl_4$	colourless	−23	136
$TiBr_4$	yellow	39	230
TiI_4	violet-black	150	377

The chloride, bromide, and iodide behave as covalent monomers in nonpolar solvents. They are strong Lewis acids, and fume copiously in moist air owing to hydrolysis. Their reactions with Lewis bases can be considered in two categories, those in which only adduct formation occurs and those in which adduct formation is followed by the elimination of hydrogen halide, that is solvolysis. Solvolytic reactions, for example hydrolysis, ammonolysis, etc., occur when the ligand has protonic hydrogen atoms adjacent to the donor atom or close to it. Some of these reactions are illustrated in figure 11.1. Even in an excess of the base, solvolysis is usually incomplete. The mechanism of these reactions is believed to occur via the intermediate formation of adducts, for example



$$TiCl_4 + 2NH_3 \longrightarrow Cl_3\overset{\overset{H_2N^{\delta-}H^{\delta+}}{\downarrow}}{Ti^{\delta+}}\text{—}Cl^{\delta-} \;\downarrow\; Cl_3TiNH_2 + HCl$$

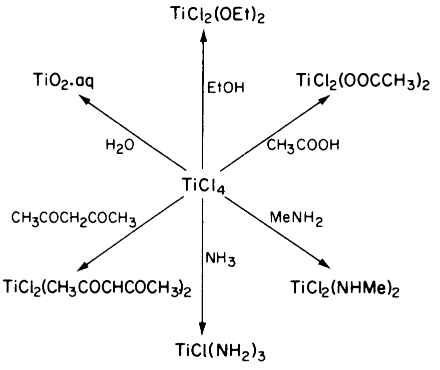


Figure 11.1 Some solvolytic reactions of titanium(IV) chloride.

In this representation we draw in one molecule of the base for simplicity (most known adducts are six-co-ordinate). The donation of electron density from the ligand donor atom does two things. Firstly, it partially neutralises the charge on the titanium atom, and secondly, it increases the charge on the protons adjacent to the donor atom (by the electron drift towards the titanium). The protonic hydrogen can then form a hydrogen bond with the adjacent chloride 'ions'. When this interaction is strong, the N–H bond breaks and HCl is eliminated. This HCl will normally be found in combination with the base, that is as NH_4Cl in the example quoted. The titanium compound so produced may then co-ordinate another molecule of base which again may eliminate HCl, and so on to complete solvolysis. Each time a chlorine is replaced by a less electronegative group (such as NH_2), the electron drift away from the titanium atom, and hence its fractional positive charge, is decreased. The Lewis acidity of the substitution products is thus progressively reduced until such a time as co-ordination of further ligand occurs only weakly, and only weak hydrogen-bonding occurs, so no elimination of the HCl results. In liquid ammonia, for example, $TiCl_4$ forms $TiCl(NH_2)_3(NH_3)_2 + 3NH_4Cl$. On warming to room temperature, the weakly bonded ammonia molecules are evolved leaving the amido-chloride $TiCl(NH_2)_3$.

The extent of solvolysis can be increased by base catalysis. Alkoxides, for example, are prepared by the reaction with alcohols in the presence of ammonia

$$TiCl_4 + 4ROH + 4NH_3 \rightarrow Ti(OR)_4 + 4NH_4Cl$$

These solvolytic products are usually polymeric, containing six-co-ordinate titanium, and have low solubilities in solvents that do not destroy them. In the solid state $Ti(OEt)_4$, for example, is tetrameric with approximately octahedral co-ordination around each titanium; in benzene, however, this and many other alkoxides are trimeric.

The adducts formed between titanium(IV) halides and an excess of nitrogen, phosphorous, arsenic, oxygen, and sulphur donor molecules are in general six-co-ordinate. Although Ti(IV) is a $3d^0$ system, the adducts are usually coloured yellow, red, or black through charge-transfer absorption bands reaching into the visible region. They are generally insoluble in nonpolar solvents and their structures are mostly not known with certainty. The range of adducts is illustrated for the chloride in figure 11.2. X-ray studies on the phosphorus oxochloride adducts $TiCl_4(OPCl_3)_2$ and $TiCl_4(OPCl_3)$ have established the octahedral structure for titanium in both cases. The bis-complex is *cis*-octahedral while $TiCl_4(OPCl_3)$ is dimeric with halogen bridges (figure 11.3). However, the 1 : 1 adduct with trimethylamine is monomeric in benzene and hence five-co-ordinate; its infrared spectrum has been interpreted on the basis of a trigonal bipyramidal structure.

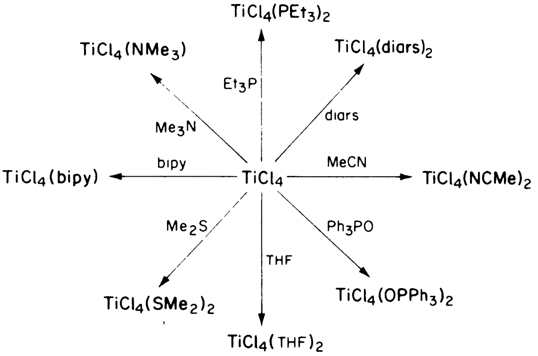


Figure 11.2 Some adducts of titanium(IV) chloride.

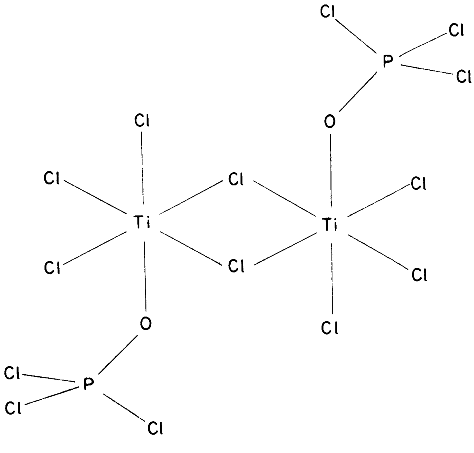


Figure 11.3 The structure of $[TiCl_4(OPCl_3)]_2$

Bidentate ligands usually form 1 : 1 adducts containing six-co-ordinate titanium. However, with certain bidentate ligands eight-co-ordinate complexes are formed. Typical of these are $TiCl_4[o\text{-}C_6H_4(PMe_2)_2]_2$ and the arsine analogue $TiCl_4(diars)_2$. The dodecahedral structure of the latter (figure 11.4) has been established by X-ray crystallography. A similar eight-co-ordinate structure occurs in $Ti(NO_3)_4$

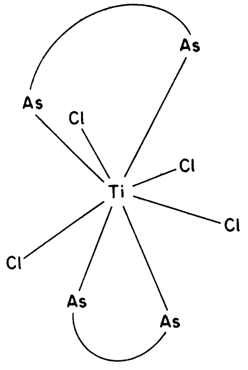


Figure 11.4 The structure of $TiCl_4(diars)_2$

in which each nitrate group acts as a bidentate ligand.

Anionic complexes are formed in the reactions of the halides with halide ions. The octahedral hexahalotitanates(IV) containing the $TiCl_6^{2-}$ and $TiBr_6^{2-}$ ions can be precipitated from hydrohalic acid solutions of the appropriate halide in the presence of a halide of a univalent cation. Salts such as yellow $(NH_4)_2TiCl_6$ and black $(NH_4)_2TiBr_6$ (unlike the salts of TiF_6^{2-}) undergo extensive hydrolysis in aqueous solution. The charge-transfer spectra of these complexes have been considered in chapter 6. The reaction between PCl_5 and $TiCl_4$ gives a compound of formula $(PCl_4TiCl_5)_n$. This does not contain $TiCl_5^-$ ions but instead has octahedrally co-ordinated titanium in halogen-bridged $[Ti_2Cl_{10}]^{2-}$ anions. The anion $[Ti_2Cl_9]^-$ similarly contains bridging chlorines, the two $TiCl_6$ octahedra being joined at one face; it is isolated as the tetraethylammonium salt from dichloromethane solution.

11.3 Compounds of Titanium(III) (d^1)

11.3.1 Aqueous Chemistry

In its +3 oxidation state, titanium has the ground state outer electronic configuration $3d^1$. Unlike Ti(IV) compounds therefore Ti(III) compounds are paramagnetic ($\mu_{eff} \approx 1.7$ B.M.) and coloured through d—d absorption even when charge-transfer absorptions are absent. This oxidation state is less acidic than the +4 state, and its compounds show a considerably greater degree of ionic character. The hexaquo-ion $[Ti(H_2O)_6]^{3+}$ is readily prepared by reduction of solutions containing Ti(IV) with zinc and hydrochloric acid or electrolytically. There is, however, some substitution of water molecules by chloride ions in high acid concentrations, species such as $[Ti(H_2O)_5Cl]^{2+}$ and $[Ti(H_2O)_4Cl_2]^+$ being predominant in these solutions. Solutions containing Ti(III) are also readily obtained by dissolving the metal in hydrochloric acid.

The violet aquo-ion is strongly acidic

$$[Ti(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Ti(OH)(H_2O)_5]^{2+} + H_3O^+ \quad (pK_1 = 1.4)$$

The addition of salts of weak acids to titanium(III) solutions thus results in the precipitation of the hydrous oxide. The reaction with sodium carbonate solution, for example, results in evolution of carbon dioxide

$$[Ti(H_2O)_6]^{3+} + 3H_2O \rightleftharpoons Ti(OH)_3(H_2O)_3 + 3H_3O^+$$

$$2H_3O^+ + CO_3{}^{2-} \rightarrow CO_2 + 3H_2O$$

Water-stable titanium(III) salts are thus limited to salts of strong nonoxidising acids, that is halides and sulphate. The dark purple hydrous oxide is often written as $Ti(OH)_3$ but since there is considerable evidence for 'polymerisation', that is olation and oxolation, in the formation of this product, it is probably best considered as Ti_2O_3.aq.

In acidic solution Ti^{3+} is a strong reducing agent (slightly stronger than Sn^{2+})

$$TiO^{2+} + 2H^+ + e \rightarrow Ti^{3+} + H_2O \quad (E^\circ = 0.1\ V)$$

The solution is oxidised by air and must be kept under nitrogen. It is used in volumetric analysis as a one-electron reductant; in organic chemistry it is used to estimate nitro-compounds since these are reduced to amines

$$RNO_2 + 4Ti^{3+} + 12H_2O \rightarrow RNH_2 + 4TiO^{2+} + 10H_2O + 4H^+$$

In alkaline media titanium(III) is an even stronger reducing agent, Ti_2O_3.aq being rapidly oxidised in air.

Complexes of titanium(III) with neutral donor molecules are normally hydrolysed in water and therefore must be prepared under anhydrous conditions. The $[Ti(NH_3)_6]^{3+}$ ion, for example, can be prepared in liquid ammonia but when added to water substitution and hydrolysis occur

$$[Ti(NH_3)_6]^{3+} + 6H_2O \rightleftharpoons \underbrace{[Ti(H_2O)_6]^{3+} + 6NH_3}_{\downarrow \atop Ti_2O_3.aq}$$

A remarkably stable complex (both oxidatively and hydrolytically) is that with urea, $Ti[OC(NH_2)_2]_6I_3$. This can be prepared in aqueous solution; its crystal structure contains titanium atoms octahedrally co-ordinated by oxygen atoms from the ligand.

Anionic complexes containing halide ions can be obtained from strongly acidic solutions. When titanium is dissolved in hot hydrobromic acid and the resulting solution is cooled, violet crystals of $TiBr_3(H_2O)_6$ form. Spectroscopic evidence indicates that these, as well as $TiCl_3(H_2O)_6$, contain the *trans*-octahedral $[TiX_2(H_2O)_4]^+$ ion rather than the hexaquo-ion. In the presence of added cations, salts such as $Cs_2[TiCl_5(H_2O)]$ and $Cs_2[TiBr_5(H_2O)].2H_2O$ can be crystallised. Some cyanide and thiocyanate complexes have also been prepared, for example $K_4Ti(CN)_7.KCN$ (in liquid ammonia) and $NH_4[Ti(SCN)_4(H_2O)_2]$.

The green sulphate $Ti_2(SO_4)_3$ is obtained by electrolytic reduction of titanium(IV) solutions in sulphuric acid and is precipitated from the hot concentrated acid. It is insoluble in water but gives violet solutions in dilute sulphuric and hydrochloric acids. The alums such as $CsTi(SO_4)_2.12H_2O$ have been shown by X-ray studies to contain the octahedral $[Ti(H_2O)_6]^{3+}$ ion in the solid state; they give this ion also in aqueous solution.

11.3.2 Titanium(III) *Halides*

The blue crystalline fluoride TiF_3 is prepared by passing a mixture of hydrogen and hydrogen fluoride over titanium at 700°. It is magnetically dilute (μ_{eff} = 1.75 B.M.) at room temperature. In the crystal each titanium is surrounded by a slightly distorted octahedral array of fluoride ions. Very little of its chemistry has been studied. It is insoluble in water and stable in air at room temperature. Above 950° disproportionation occurs

$$4TiF_3 \rightarrow Ti + 3TiF_4$$

The violet-black iodide has also been little studied. Unlike the fluoride it is antiferromagnetic; it is prepared by the reaction of stoichiometric quantities of titanium and iodine in a sealed tube at 700°.

The chloride and bromide are more readily prepared, for example by reduction of the tetrahalides with hydrogen. The chloride exists in at least two different modifications. The commonly found violet α-form results from the high-temperature reductions of the tetrachloride. It has a layer lattice with octahedrally co-ordinated titanium. The brown β-form arises in the relatively low-temperature reductions of the tetrachloride with, for example, organoaluminium compounds. It has a fibrous structure with single chains of $TiCl_6$ octahedra each sharing two faces. The halides disproportionate above 400° in a vacuum into the di- and tetra-halides, and at higher temperatures the involatile dihalides disproportionate further

$$\begin{tikzcd} 2TiCl_3(s) \arrow[r, "450°"] & TiCl_4(g) + TiCl_2(s) \arrow[d, "700°"] \\ & \tfrac{1}{2}Ti(s) + \tfrac{1}{2}TiCl_4(g) \end{tikzcd}$$

The halides $TiCl_3$, $TiBr_3$, and TiI_3 are readily oxidised in moist air (to TiO_2.aq). They are insoluble in nonpolar solvents, but dissolve readily in the aqueous hydrogen halides, forming halo-aquo-complexes such as $[TiCl_2(H_2O)_4]^+$. They are less Lewis acidic than their TiX_4 analogues but react with a variety of donor molecules. Unidentate ligand molecules form mainly pseudo-octahedral complexes $TiX_3.3L$ (L = CH_3CN, CH_3COCH_3, THF, py) and five-co-ordinate complexes $TiX_3.2L$ (L = Me_3N, α-picoline). The five-co-ordinate complexes have the *trans*-trigonal bipyramidal structure. The dimethyl sulphide adducts $TiX_3.2SMe_2$, however, are dimeric with octahedral co-ordination around titanium. Neutral bidentate ligands form complexes of the types $Ti(LL)_3X_3$ (LL = en, propylenediamine) and $TiX_3.1.5LL$ (LL = bipy, phen). While compounds of the former type are cationic, for example $[Ti(en)_3]Cl_3$, the structures of the latter type are as yet unknown. Anionic complexes $TiCl_6{}^{3-}$ and $TiBr_6{}^{3-}$ occur in chloride ion melts; the pyridinium salts can be isolated by reaction between the pyridinium halide and $TiX_3.3MeCN$ in chloroform. At high temperatures in molten LiCl–KCl the tetrahedral tetrachlorotitanate(III) ion probably exists in equilibrium with the octahedral ion.

$$TiCl_6{}^{3-} \rightleftharpoons TiCl_4{}^- + 2Cl^-$$

11.4 Compounds of Titanium in Lower Oxidation States

Oxidation state +2 is a strongly reducing state for titanium. Compounds of Ti^{II} reduce water to hydrogen, so scarcely any aqueous chemistry of Ti^{2+} is known. The halides $TiCl_2$, $TiBr_2$, and TiI_2 evolve hydrogen from water, as do their blue-black complexes with donor molecules, for example $TiCl_2.2$DMF and $TiCl_2.2MeCN$. The complex chlorides $RbTiCl_3$ and Rb_2TiCl_4 have been prepared by fusing together the stoichiometric quantities of the constituent chlorides under an inert atmosphere. TiO is obtained from TiO_2 and Ti at 1600°; it has the rock-salt structure but tends not to be stoichiometric, with vacant sites in the lattice.

Oxidation states of 0 and −1 occur only in complexes with bipyridyl. The reduction of $TiCl_4$ by lithium in tetrahydrofuran in the presence of an excess of bipyridyl results in the formation of the green-blue $Ti(bipy)_3$ ($\mu_{eff} = 0$) and the blue-violet $LiTi(bipy)_3.3.5$THF ($\mu_{eff} = 1.72$ B.M). These compounds are extremely sensitive to air and moisture, and oxidation-state titrations with iodine confirm that they at least formally contain titanium in oxidation states 0 and −1 respectively.

Titanium does not form any stable binary carbonyls or nitrosyls but a few complexes are known containing other π-bonded ligands in addition to these ligands, for example $(\pi\text{-}C_5H_5)_2Ti(CO)_2$ and $[(\pi\text{-}C_6H_6)Ti(CO)_4]Br$.

11.5 Organometallic Compounds of Titanium

Compounds in which titanium is bonded directly to carbon via a σ or π bond were scarcely known prior to 1960. The discovery by Ziegler that a mixture of an organoaluminium compound and a titanium halide was a successful catalyst for the polymerisation of α-olefins led to intense activity in the field of organotitanium chemistry. A typical heterogeneous catalyst is a mixture of $AlEt_3$ and $TiCl_4$ in heptane; when ethylene is bubbled through this mixture at room temperature and atmospheric pressure 'linear' polyethylene is produced. While the mechanism of such polymerisation processes is incompletely understood, many intermediate complexes have been isolated from such systems. The reaction between $(\pi\text{-}C_5H_5)_2TiCl_2$ and $AlEt_3$ gives as one of the products the blue crystalline compound $(\pi\text{-}C_5H_5)_2TiCl_2AlEt_2$ (figure 11.5). Solutions of this compound polymerise ethylene.

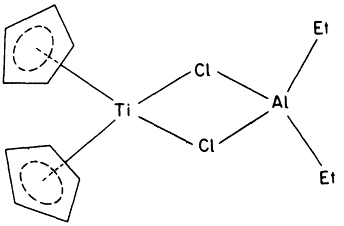


Figure 11.5 The structure of $(\pi\text{-}C_5H_5)_2TiCl_2AlEt_2$

The σ-bonded alkyls of titanium are very unstable to oxidation, and most are thermally unstable at room temperature. The tetramethyl $TiMe_4$, for example, can be prepared by the slow addition of lithium methyl in ether solution to a suspension of $TiCl_4(OEt_2)_2$ in ether at –80°. The yellow crystalline $TiMe_4$ begins to decompose above –78°. The alkyl titanium halides such as $MeTiCl_3$ and Me_2TiCl_2 behave as Lewis acids and form adducts with donor molecules. The π-cyclopentadienyl compounds of titanium are very much more stable to oxidation and heat. Titanocene $Ti(\pi\text{-}C_5H_5)_2$ forms dark green pyrophoric crystals, which decompose at 200° in a vacuum. More stable are the roughly tetrahedral compounds $(\pi\text{-}C_5H_5)_2TiCl_2$ and $(\pi\text{-}C_5H_5)TiCl_3$. These are orange diamagnetic solids, stable to dry air, which can be sublimed in a vacuum without decomposition. They have consequently been used as the starting points for the synthesis of a large number of other organotitanium compounds. One unusual property of $(\pi\text{-}C_5H_5)_2TiCl_2$ is that, when mixed with a Grignard reagent, it is capable of 'fixing' molecular nitrogen. The mixture absorbs nitrogen at room temperature, and subsequent hydrolysis produces ammonia. The mechanism of this process is not yet understood.

12 Vanadium

12.1 The Element

Unlike titanium, vanadium shows a wide range of oxidation states (+5 to +2) in aqueous solution, as well as the low oxidation states of +1, 0, and −1. As a result of this, vanadium is perhaps the most colourful of the transition elements, showing compounds of every colour and even with considerable colour variation within each oxidation state. It was because of the beauty of these colours that Sefstrom in 1830 named the element vanadium in honour of the Scandinavian goddess Vanadis.

Vanadium (atomic number 23) is a silver-grey metal having a body-centred cubic crystal structure. The metal itself does not find any great engineering applications and most of the metal produced is in the form of the iron–vanadium alloy ferrovanadium; this is used in the production of vanadium steels. Vanadium dissolves in oxidising acids such as HNO_3 and H_2SO_4, and also in HF. It combines with most nonmetals on heating; interstitial and nonstoichiometric products often result. Oxygen gives the lower oxides (which sometimes coat the metal at room temperature) and ultimately V_2O_5.

The outer electronic configuration in the ground state is $3d^3\ 4s^2$. The maximum oxidation state is thus +5, corresponding to a d^0 configuration. Compounds in this oxidation state are consequently diamagnetic and frequently colourless. In the +4, +3, and +2 oxidation states compounds are normally coloured and paramagnetic with magnetic moments corresponding to one, two, and three unpaired electrons per vanadium respectively. The chemistry of vanadium shows little resemblance to that of the elements in group VB, As, Sb, and Bi.

12.2 Compounds of Vanadium(V) (d^0)

12.2.1 Vanadium(V) Oxide and its Aqueous Chemistry

Vanadium(V) is a strongly oxidising state, so its thermally stable compounds are largely limited to those containing the electronegative ligands oxide and fluoride. The oxide V_2O_5 is the most important oxide and most vanadium chemicals are derived from it. It is a brown poisonous solid obtained on complete oxidation of the metal or its sulphides, nitrides, or lower oxides. It is also formed when vanadium(V) oxohalides are hydrolysed and when ammonium vanadate is heated

$$2NH_4VO_3 \rightarrow V_2O_5 + 2NH_3 + H_2O$$

It is used industrially as a catalyst particularly in the oxidation of SO_2 to SO_3 in the contact process for the manufacture of sulphuric acid. Some reactions of the pentoxide are summarised in figure 12.1.

V_2O_5 is an acidic oxide; it is sparingly soluble in water to give a feebly acidic solution, and in alkalis to give vanadates. In reducing acids, the vanadium is reduced. Thus boiling of V_2O_5 in hydrochloric acid results in the evolution of chlorine and the formation of blue vanadium(IV) species ($[VO(H_2O)_5]^{2+}$ in dilute solutions). V_2O_5 is also easily dissolved in dilute sulphuric acid in the presence

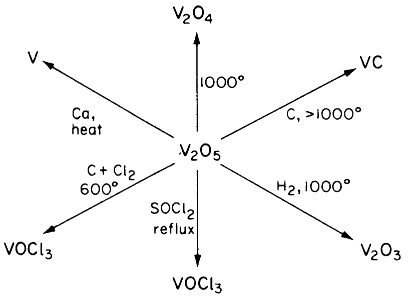


Figure 12.1 Some reactions of V_2O_5

of sulphite ions, $[VO(H_2O)_5]^{2+}$ again being formed. The nature of the solutions in alkali, that is the vanadates, depends on the pH. These solutions have been extensively studied but we can present only the most general findings here. The orthovanadate ion VO_4^{3-} is a colourless mononuclear tetrahedral ion existing in the most basic solutions (pH > 12.6). As the acidity of the solution is increased, condensed oxo-anions begin to form and the initially colourless solution becomes yellow and then red. Typical equilibria present in these solutions are indicated in the equations

$$\begin{aligned}
VO_4^{3-} + H^+ &\rightleftharpoons [VO_3(OH)]^{2-}\\
2[VO_3(OH)]^{2-} + H^+ &\rightleftharpoons [V_2O_6(OH)]^{3-} + H_2O\\
3[VO_3(OH)]^{2-} + 3H^+ &\rightleftharpoons V_3O_9^{3-} + 3H_2O\\
10V_3O_9^{3-} + 12H^+ &\rightleftharpoons 3V_{10}O_{28}^{6-} + 6H_2O\\
V_{10}O_{28}^{6-} + H^+ &\rightleftharpoons HV_{10}O_{28}^{5-}\\
HV_{10}O_{28}^{5-} + H^+ &\rightleftharpoons H_2V_{10}O_{28}^{4-}\\
H_2V_{10}O_{28}^{4-} + 14H^+ &\rightleftharpoons 10VO_2^+ + 8H_2O
\end{aligned}$$

Salts of the $(VO_3^-)_n$ ion are known as metavanadates. The decavanadate ions occur naturally in minerals such as pascoite $Ca_3V_{10}O_{28}.16H_2O$. In strongly acidic solutions (pH < 1) the dioxovanadium ion VO_2^+ is the stable species (the degree of hydration in this and the other species is unknown).

12.2.2 Vanadium(V) *Halides*

Because the V^{5+} state is so strongly oxidising, the only stable binary halide is the fluoride VF_5. This is a white solid (m.p. 19.5°) which is extremely readily hydrolysed by moist air. In the vapour phase it is monomeric with the trigonal bipyramidal structure. It is a violent oxidising and fluorinating agent, and with ligands often gives adducts of vanadium(IV) fluoride, such as $VF_4.NH_3$, $VF_4.py$, and $V(en)_3F_4$. Salts of the VF_6^- ion have been prepared by the reaction of BrF_3 on a mixture of VCl_3 and an alkali metal halide; KVF_6 is obtained by direct reaction between KF and VF_5 at room temperature.

The thermal stabilities of the oxide halides VOF_3, $VOCl_3$, and $VOBr_3$ decrease rapidly from the fluoride to the bromide; $VOBr_3$ begins to liberate bromine at room temperature, and VOI_3 is yet to be prepared. This is in accord with the relative reducing power of the halide anions. $VOCl_3$ and $VOBr_3$ behave as covalent monomers; they are soluble in nonpolar solvents, and $VOCl_3$ is known, from electron-diffraction studies, to have the tetrahedral structure in the vapour phase. These halides are very readily hydrolysed in moist air, giving copious brown fumes of V_2O_5. The acceptor properties of VOF_3 have not been studied; three types of reaction may occur in the reactions of $VOCl_3$ and $VOBr_3$ with ligands. These are addition reactions, substitution (solvolytic) reactions, and reduction. The chemistry of $VOBr_3$ is, as may be expected, dominated by reduction reactions; it is reduced to V^{IV} derivatives by most ligands. With bromide ions, for example, in acetonitrile solution, salts of the $VOBr_3^-$ and $VOBr_4^{2-}$ ions are formed depending on the nature of the cation. $VOCl_3$ is reduced by amines and thioethers; reduction by chloride ions to $VOCl_4^{2-}$ occurs in aqueous but not ethanolic media. Some reactions of $VOCl_3$ are summarised in figure 12.2.

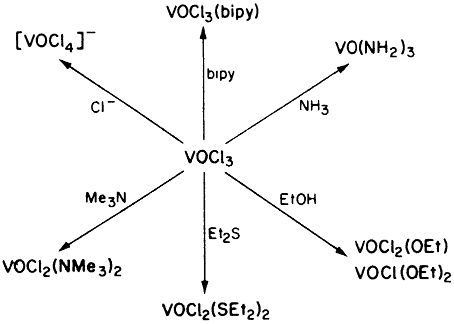


Figure 12.2 Some reactions of $VOCl_3$

12.3 Compounds of Vanadium(IV) (d^1)

12.3.1 Aqueous chemistry and VO^{2+} *compounds*

The +4 oxidation state is the most important one for vanadium in aqueous solutions; it is neither strongly oxidising nor reducing, and acidified solutions are stable to atmospheric oxidation

$$[V(OH)_4]^+ + 2H^+ + e \rightarrow VO^{2+} + 3H_2O \quad (E^\circ = 1.0\ V)$$

V(IV) is quantitatively oxidised to V(V) by acid permanganate at 70°, and this is used in the volumetric estimation of vanadium. The vanadium compound is first boiled with an excess of acidified $KMnO_4$ to convert all the vanadium into the +5 state which is then readily reduced by sodium sulphite to V(IV). Excess sulphur dioxide is removed by boiling, and the V(IV) solution is then titrated with permanganate. The hexaquo-ion is far too acidic to exist in water, and the blue solutions of vanadium(IV) in noncomplexing acids contain the oxovanadium(IV) or vanadyl ion $[VO(H_2O)_5]^{2+}$. The aqueous chemistry of vanadium(IV) is in fact dominated by that of the VO^{2+} group; literally hundreds of compounds containing this group have been studied. The VO^{2+} ion is one of the most stable diatomic cations known, and since it has the $3d^1$ configuration its compounds have attracted widespread spectroscopic interest. While cationic species of V^{4+} are virtually unknown ($[V(en)_3]F_4$ may be an exception), oxovanadium(IV) derivatives may be cationic, anionic, or neutral.

The $[VO(H_2O)_5]^{2+}$ ion is weakly acidic

$$[VO(H_2O)_5]^{2+} + H_2O \rightleftharpoons [VO(OH)(H_2O)_4]^+ + H_3O^+ \quad (pK_1 = 6.0)$$

The yellow-brown $VO(OH)_2$aq is precipitated by the addition of sodium carbonate solution; in strong alkalis, soluble vanadates(IV) are formed, and from these solutions crystalline compounds of the type $M^I_2[V_4O_9].7H_2O$ have been isolated. Aerial oxidation to vanadium(V) occurs much more readily in these alkaline solutions.

The structures of several oxovanadium(IV) salts have been determined by X-ray methods. In general the compounds have either five or six-co-ordination around the vanadium. The structures are usually based on that of the tetragonal pyramid with the oxygen atom of the V=O bond at the apex of the pyramid and with the site *trans* to this atom either vacant as in the five-co-ordinate structures or filled when a six-co-ordinate structure results. An example of the five-co-ordinate structure is shown by $VO(acac)_2$, the structure of which is illustrated in section 4.2.3. In the sulphate $VOSO_4.5H_2O$ the six-co-ordination involves one oxygen atom, four water molecules, and one oxygen from sulphate. These six-co-ordinate structures are distorted from octahedral by the short V=O bond; in $VOSO_4.5H_2O$, V=O is 159 pm, V–OH_2 is 198–205 pm, and V–OSO_3 is 222 pm. The multiple VO bond involves π-bonding from filled $2p_\pi$ orbitals on oxygen and vacant 3d orbitals on vanadium. Evidence for this multiple VO bonding is also gained from infrared spectroscopy. All oxovanadium(IV) compounds show a strong sharp band in the region 985 ± 50 cm^{-1} corresponding to the metal–oxygen stretching frequency. The highest frequencies are shown by those compounds that are known from X-ray studies to possess the shortest V–O bond lengths.

The five-co-ordinate compounds can become six-co-ordinate by accepting a ligand molecule in the 'vacant' site *trans* to the oxygen atom of the V=O bond. Thus $VO(acac)_2$ dissolves in nonpolar solvents (such as C_6H_6 and CS_2) to give solutions that show ν(V–O) around 1006 cm^{-1}, that is very close to the 996 cm^{-1} observed for the solid state. When bases such as pyridine, ethylenediamine, or thiocyanate ion are added to these solutions, ν(V–O) is decreased by about 50 cm^{-1}, indicating that co-ordination has occurred, accompanying shifts, etc. also observed in the electronic spectra. Six-co-ordination is also achieved in polymeric complexes in which the vanadium atoms are joined through V–O–V bonding. Thus the grey-green acetate $VO(OCOCH_3)_2$ is a remarkably air and water-stable compound (it is insoluble in water) showing ν(V–O) at 898 cm^{-1} in accord with a polymeric structure involving not only oxygen but also acetate bridging.

Oxovanadium(IV) complexes are often most conveniently prepared from V_2O_5 since this is reduced by many anions in acid solution. Thus salts of the $[VOCl_4]^{2-}$ and $[VO(C_2O_4)_2]^{2-}$ ions are isolated from solutions of V_2O_5 in hot hydrochloric and oxalic acids respectively. Examples of cationic complexes are $[VO(DMSO)_5](ClO_4)_2$ (DMSO = dimethyl sulphoxide) and $[VO(bipy)_2](ClO_4)_2$, while neutral complexes include $VO(C_2O_4)_2.2H_2O$ and $VOCl_2(NMe_3)_2$. The last-named complex differs from most vanadyl compounds in that its structure approximates more closely to that of a trigonal bipyramid with the Me_3N groups occupying the *trans*axial positions.

The high V═O bond strength thus results in all complexes of vanadium(IV) being obtained from aqueous solution containing VO^{2+} as well as being obtained from other systems such as reduction reactions of $VOCl_3$. The V═O bond can, however, be broken by reaction with thionyl chloride, for example in the preparation of hexachlorovanadates(IV)

$$(pyH)_2VOCl_4 + SOCl_2 \rightarrow (pyH)_2VCl_6 + SO_2$$

The electronic spectra of oxovanadium(IV) complexes have been studied very extensively. Unfortunately, although it is the easiest of the d^1 systems to use experimentally, the interpretation of the spectra has been complicated by the deviation of the complexes from regular octahedral stereochemistry. Three bands are normally observed in the spectra, in the regions 11 000–15 000 cm^{-1}, 14 500–20 000 cm^{-1}, and 21 000–31 000 cm^{-1}. On a simple crystal-field model these would be interpreted (figure 6.5) as the transitions from the $^2B_2$ ground term to the ^2E, $^2B_1$, and $^2A_1$ terms. However, such a treatment does not give a good quantitative fit to the spectra, and in the more complex molecular orbital treatment of the $[VO(H_2O)_5]^{2+}$ ion the axial π-bonding is taken into account. It is still not possible to assign the spectra of these complexes with confidence.

12.3.2 Vanadium(IV) *Halides*

Vanadium(IV) fluoride is a lime-green solid that hydrolyses in moist air and forms 1 : 1 adducts with SeF_4, NH_3, and py. It undergoes disproportionation slowly even at room temperature and rapidly at 100°

$$2VF_4 \rightarrow VF_3 + VF_5$$

The tetrabromide VBr_4 has only recently been isolated by careful condensation of the vapours from the thermal decomposition of VBr_3 at 325°. The purple VBr_4 is condensed at –78°; it is unstable above –23°, decomposing into VBr_3 and bromine. It is therefore not surprising that the chloride VCl_4 is the only vanadium(IV) halide to be studied in detail. The iodide has not been prepared.

VCl_4 is a dark red-brown liquid that fumes in moist air and readily forms the blue $[VO(H_2O)_5]^{2+}$ ion in water. It decomposes slowly at room temperature, and rapidly under reflux, into VCl_3 and chlorine. Electron-diffraction studies on the vapour phase show the molecule to be tetrahedral. It resembles $TiCl_4$ in its Lewis acidity, forming a large number of adducts and substitution products all of which are neutral or anionic. It is considerably more susceptible to reduction than $TiCl_4$; these properties are illustrated in figure 12.3. The products from these reactions are commonly six-co-ordinate but five-co-ordination is common when reduction to vanadium(III) occurs. Eight-co-ordination occurs with *o*-phenylenebisdimethylarsine, the compound $VCl_4(diars)_2$ being isomorphous with the titanium analogue. The 1 : 1 compound formed between PCl_5 and VCl_4 has the ionic structure $[PCl_4^+][VCl_5^-]$ with a five-co-ordinate VCl_5^- anion.

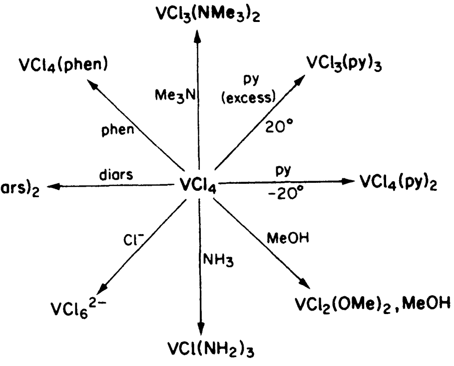


Figure 12.3 Some reactions of VCl_4

12.4 Compounds of Vanadium(III) (d^2)

In this oxidation state vanadium has the outer electron configuration $3d^2$ in the ground state; the spectroscopic properties arising from this configuration have been considered in section 6.2.1. Magnetically dilute vanadium(III) compounds have magnetic moments close to the spin-only value, that is around 2.8 B.M. at room temperature. The only important simple compounds of V^{III} are the halides, all of which are known, and the oxide V_2O_3. However, a large number of complexes can be isolated from aqueous as well as nonaqueous solutions. In many respects the chemistry of vanadium(III) closely resembles that of titanium(III).

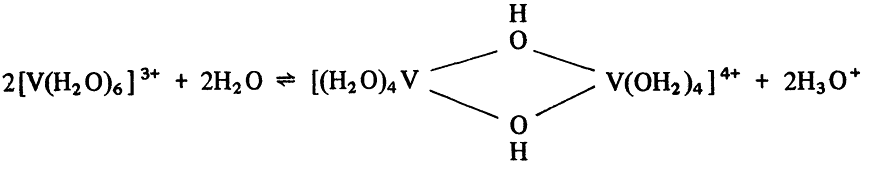
12.4.1 Aqueous Chemistry

Solutions containing the blue $[V(H_2O)_6]^{3+}$ ion are obtained by dissolution of the black basic oxide V_2O_3 in noncomplexing acids or by electrolytic reduction of V(IV) or V(V) in sulphate media. The V(III) state can also be obtained in aqueous solution by reduction of the higher states with an excess of bromide ions or by dissolution of the halides VX_3.

The hexaquo-ion is acidic and can exist only in aqueous solutions under acid conditions

$$[V(H_2O)_6]^{3+} + H_2O \rightleftharpoons [V(OH)(H_2O)_5]^{2+} + H_3O^+ \quad (pK_1 = 2.9)$$

It occurs in the solid state in the blue-violet alums such as $NH_4V(SO_4)_2.12H_2O$ which can be crystallised from sulphuric acid solutions. The olation reaction



$$2[V(H_2O)_6]^{3+} + 2H_2O \rightleftharpoons [(H_2O)_4V\begin{matrix}\overset{H}{O}\\ \underset{H}{O}\end{matrix}V(OH_2)_4]^{4+} + 2H_3O^+$$

for which $pK = 3.9$, is characterised by a strong charge-transfer band at 22 930 cm^{-1} (compare the spectrum of $[V(H_2O)_6]^{3+}$ in figure 6.8). This same binuclear vanadium(III) species is formed as an intermediate in the reaction between V^{II} and V^{IV} in acid perchlorate solutions. In alkaline solutions the hydrous oxide V_2O_3.aq precipitates; V^{III} complexes with nitrogen donors similarly give V_2O_3.aq when they are hydrolysed in water.

Vanadium(III) solutions are unstable to aerial oxidation especially under alkaline conditions; the reduction potential in acid solutions is given by

$$VO^{2+} + 2H^+ + e \rightarrow V^{3+} + H_2O \quad (E^\circ = 0.36\ V)$$

In the presence of added ligands, cationic complexes are more commonly formed than anionic ones. The halide hydrates $VCl_3.6H_2O$ and $VBr_3.6H_2O$, which can be crystallised from strongly acidic solutions, contain the $[VX_2(H_2O)_4]^+$ cations (compare their Ti analogues), and even complex halides such as $Cs_2VBr_5.5H_2O$ probably contain this cation, that is $[VBr_2(H_2O)_4]^+$, $2Cs^+$, $3Br^-$, H_2O. In alcohols too, cations of the type $[VX_2(ROH)_4]^+$ predominate. Other cationic complexes include those with urea, such as $V[OC(NH_2)_2]_6{}^{3+}$, while typically anionic complexes include the octahedral oxalate $[V(C_2O_4)_3]^{3-}$ and thiocyanate $[V(NCS)_6]^{3-}$ complexes. The addition of an excess of potassium cyanide to aqueous V^{III} solutions results in the formation of an intense blue colour; on standing in the absence of air at room temperature, the deep blue solution changes to a wine-red colour. From the red solution, red crystals of the potassium salt $K_4\,V(CN)_7.2H_2O$ can be precipitated by the addition of methanol. This complex contains seven-co-ordinate vanadium(III), the $[V(CN)_7]^{4-}$ ion having the pentagonal bipyramidal structure. The deep-blue complex has been isolated at low temperatures and is believed to contain vanadium in two different oxidation states, one of which is V^{II}.

12.4.2 *Vanadium*(III) *Halides*

All four halides are thermally stable solids at room temperature. The yellow-green fluoride VF_3 is particularly stable; it is insoluble in water and melts without decomposition at 1400°. The other halides VCl_3 (violet), VBr_3 (black), and VI_3 (black) are hydrolysed in water and undergo hydrolysis and oxidation in moist air. They are unstable at elevated temperatures, for example

$$2VCl_3 \xrightarrow{400^\circ} VCl_2 + VCl_4$$

$$2VI_3 \xrightarrow{300^\circ} 2VI_2 + I_2$$

With the exception of the fluoride, these halides dissolve in co-ordinating solvents such as alcohol or acetonitrile with the formation of complexes, but unlike the V^{IV} halides they are insoluble in nonpolar solvents. Co-ordination compounds (figure 12.4) are thus prepared by direct reaction or by ligand exchange on, for example, $VCl_3.3MeCN$. Cationic complexes are formed only rarely in these reactions. Ethylenediamine forms $[V(en)_3]Cl_3$ which is probably cationic, but the compounds originally believed to be hexammines, for example $[V(NH_3)_6]Cl_3$, are in fact mixtures such as $VCl_2(NH_2).4NH_3 + NH_4Cl$. Neutral complexes are very similar to the analogous compounds of titanium(III), being either five or six-co-ordinate. As well as the octahedral $VX_6{}^{3-}$ ions,

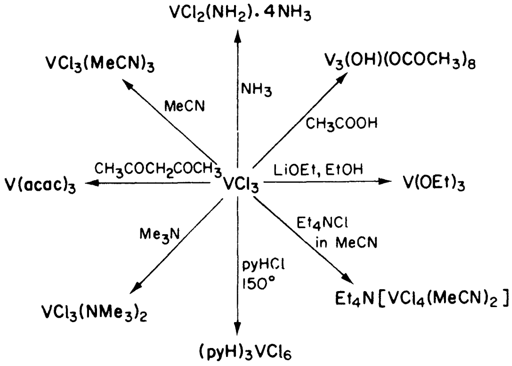


Figure 12.4 Complexes derived from VCl_3

which must be prepared in the absence of ligands other than X^-, complex salts containing anions of the type $[VX_4L_2]^-$ ($L = MeCN, CH_3COOH$) can be isolated from the solvents denoted by L; these evolve the solvent molecules when heated to above 100° in a vacuum, to give salts of the tetrahedral VCl_4^- or VBr_4^- ions.

12.5 Compounds of Vanadium(II) (d^3)

Compounds of vanadium(II) are strong reducing agents and difficult to work with in aqueous solution because of their rapid oxidation. The oxide VO is a basic oxide with the rock-salt structure; it is usually not stoichiometric. It dissolves in acids to give the $[V(H_2O)_6]^{2+}$ ion. This ion is also obtained as the final product in the reduction of NH_4VO_3 by zinc and acid. In this interesting reaction the colours of each oxidation state can be observed in turn; for example, if HCl is used, we have vanadate(V) yellow, $[VO(H_2O)_5]^{2+}$ blue, V^{3+} (for example $[VCl_2(H_2O)_4]^+$) green, and $[V(H_2O)_6]^{2+}$ violet. If sulphuric acid is used and the final solution evaporated in a vacuum over phosphorus pentoxide, the violet sulphate $VSO_4.6H_2O$ is obtained. This liberates hydrogen from water but is stable in acid solutions. The double sulphates $M_2V(SO_4)_2.6H_2O$ (Tutton's salts) contain the regularly octahedral $[V(H_2O)_6]^{2+}$ ion; they are somewhat more stable to oxidation than the simple sulphate. Electrolytic reduction from hydrochloric acid solutions of V(IV) gives $VCl_2(H_2O)_4$ which has the *trans*-octahedral (that is tetragonal) structure; $VBr_2(H_2O)_6$, $VI_2(H_2O)_6$, and $RbVCl_3.6H_2O$ contain the hexaquo-cations.

Cationic complexes containing, for example, $[V(bipy)_3]^{2+}$ are obtained from $VSO_4.7H_2O$ by the addition of a methanolic solution of the ligand, using KI or NH_4ClO_4 to precipitate the cation as the iodide or perchlorate salt. They arise also in the reactions of bases with vanadium hexacarbonyl, in which vanadium undergoes disproportionation, for example

$$3V(CO)_6 + 6CH_3COCH_3 \rightarrow [V^{II}(CH_3COCH_3)_6][V^{-I}(CO)_6]_2 + 6CO$$

Anionic complexes like the orange $K_4V(CN)_6$ (which contains octahedral

$[V(CN)_6]^{4-}$ ions) crystallise from solutions saturated in the anion.

The anhydrous halides VCl_2, VBr_2, and VI_2 are obtained by thermal decomposition or disproportionation of the higher halides. The chloride dissolves in hot pyridine to form $VCl_2(py)_4$ and reacts slowly with monomethylamine to form $VCl_2(MeNH_2)_6$. Complex chloride species such as VCl_3^-, VCl_4^{2-}, and VCl_6^{4-} are formed in melts of VCl_2 with alkali metal chlorides.

12.6 Compounds of Vanadium-(I), -(0), and -(−I)

12.6.1 Carbonyl and Nitrosyl Complexes

Vanadium hexacarbonyl $V(CO)_6$ forms blue-green sublimable crystals (for preparation see section 3.1.6). It is air-sensitive and decomposes above 60° with evolution of carbon monoxide. Being a monomeric molecule one electron short of the inert-gas configuration, it is paramagnetic ($\mu_{eff} = 1.7$ B.M. at room temperature) both in the solid state and in benzene solution. The ease of formation of the hexacarbonylvanadate(−I) ion $[V(CO)_6]^-$, which has the noble-gas configuration, is a characteristic feature of its chemistry. Thus, with many oxygen and nitrogen bases the vanadium carbonyl disproportionates to give $[VL_6]^{2+}$ cations and $[V(CO)_6]^-$anions (compare with section 12.5). However, some substitution products can be obtained. Phosphines give red-brown monomeric complexes of the type $V(CO)_4(PR_3)_2$ which are paramagnetic and, on the basis of their infrared spectra, are assigned the *trans* configuration.

The violet-red unstable nitrosyl carbonyl $V(CO)_5(NO)$ is formed when nitrogen monoxide is passed through a cyclohexane solution of the carbonyl at 0°; the orange diamagnetic $[V(CO)_4(NO)(PPh_3)]$ is similarly obtained by starting from $V(CO)_4(PPh_3)$. The nitrosyl cyanide complex $K_3[V(CN)_5NO].2H_2O$ contains discrete distorted octahedral $[V(CN)_5NO]^{3-}$ anions; the N—O stretching frequency occurs at 1530 cm^{-1}, indicating that NO is present as NO^+ and hence the oxidation state of vanadium is formally +1 in this ion.

12.6.2 Other Low Oxidation-state Complexes

2,2′-Bipyridyl and 1,10-phenanthroline form compounds of V(0) and V(−I) that are analogous to the Ti—bipy complexes. $V(bipy)_3$ and $V(phen)_3$ have magnetic moments indicating the presence of one unpaired electron, that is they are low-spin complexes. The lithium salts $Li[V(bipy)_3]$.4THF and $Li[V(phen)_3]$.3.5THF are diamagnetic and also low-spin therefore; they are highly air-sensitive. Metal-to-ligand d_π—p_π bonding is probably important in the stabilisation of these low oxidation state compounds. The phosphine $Me_2PCH_2CH_2PMe_2$ is also capable of stabilising V(0); black $V(Me_2PCH_2CH_2PMe_2)_3$ has $\mu_{eff} \approx 2.1$ B.M., and oxidises rapidly in air.

Bidentate sulphur donors form an interesting series of compounds of the types $[VS_6C_6R_6]^z$ (for example R = CN, $z = -1$ or -2 ; R = C_6H_5, $z = -2, -1$, or 0). These compounds have the trigonal prismatic six-co-ordinate structure around vanadium (see section 4.2.4); this has been established with certainty in the X-ray crystal structure determination on $[VS_6C_6Ph_6]$. The oxidation state formalism cannot be applied satisfactorily to these complexes; neither the +6 state (the vanadium being assumed to be bonded to $[S_2C_2Ph_2]^{2-}$ anions) nor the 0 state (with vanadium bonded to the neutral ligand PhCSCSPh) provides a reasonable explanation of the properties of these complexes. Vanadium is probably in some intermediate oxidation state with the ligands bonded as radical anions.

12.7 Organometallic Compounds of Vanadium

The most stable organovanadium compounds are the π-bonded, cyclopentadienyls. The violet-black vanadocene $V(C_5H_5)_2$ (m.p. 167°) has the 'sandwich' structure with the metal atom lying between the two cyclopentadienyl rings (as in ferrocene, chapter 15). Bis(benzene)vanadium $V(C_6H_6)_2$ (m.p. 277°) similarly has the π-bonded sandwich structure [as in $Cr(C_6H_6)_2$, chapter 13]. These compounds are fairly stable thermally, not decomposing below their melting points, but are unstable to aerial oxidation. σ-Bonded aryls are obtained by reactions of cyclopentadienylvanadium halides with lithium aryls in ether solvents at low temperatures, for example

$$(\pi\text{-}C_5H_5)_2VCl + LiPh \rightarrow (\pi\text{-}C_5H_5)_2VPh + LiCl$$

Treatment of $VCl_3.3\text{THF}$ with a tenfold excess of lithium phenyl in ether gives the remarkable purple complex $Li_4[VPh_6].3.5Et_2O$. This has a magnetic moment of 3.85 B.M., consistent with V(II); it is decomposed by water.

Organovanadium compounds are less effective as catalysts for polymerisation reactions than their titanium analogues, and consequently have received considerably less attention.

13 Chromium

13.1 The Element

Like vanadium, chromium shows a wide range of oxidation states and colours of compounds; its name derives from the Greek 'chromos' meaning colour. The green colour of emeralds is due to the presence of chromium in the mineral beryl, and the colour of ruby is due to the substitution of Cr^{III} ions for Al^{III} ions in the structure of α-Al_2O_3. Chromium is the first element of group VIA, lying above molybdenum and tungsten. The ground state outer electronic configuration is $3d^5\ 4s^1$, and like Ti and V it shows the highest oxidation state corresponding to the loss of all these outer electrons, that is +6 for Cr. Like V(V), however, Cr(VI) is a strongly oxidising state, chromium being bonded to fluorine or oxygen in its compounds. All oxidation states down to −2 are known in chromium compounds but the +3 state is by far the most stable and common.

Chromium (atomic number 24) is a light silvery grey lustrous metal that has considerable inertness to chemical attack. It is therefore widely used to plate other metals to give them a shiny corrosion-resistant coating. Another important use is in stainless steel, which contains 12–15 per cent chromium. Chromium is inert to attack by nitric acid, phosphoric acid, and aqua regia at room temperature; these reagents render the metal passive. However, it dissolves in nonoxidising acids such as dilute hydrochloric and sulphuric acids. When not in the passive state, chromium readily enters solution in salts of copper, tin, and nickel with precipitation of these metals. However, since many oxidising agents including oxygen of the air passivate the metal to some extent, the reactivity of any chromium sample is difficult to predict. At high temperatures the element reacts with alkali metal hydroxides, hydrogen halides, water, and many nonmetals including oxygen and the halogens.

13.2 Compounds of Chromium(VI) (d^0)

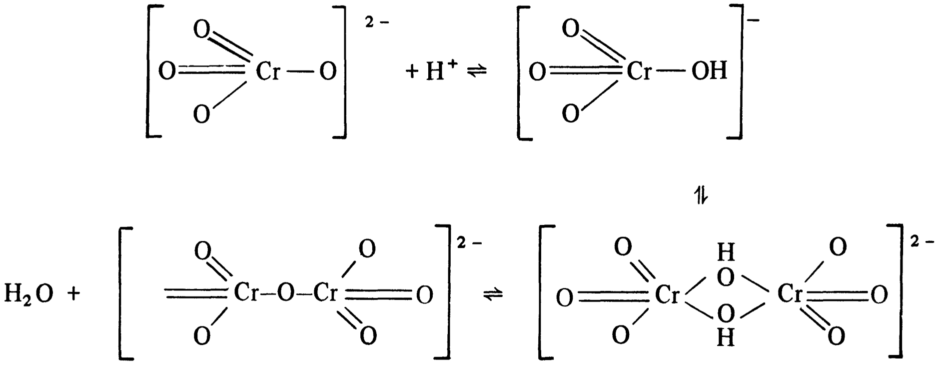
In the +6 oxidation state chromium has the $3d^0$ configuration; however, the compounds are usually yellow or red because of charge-transfer absorption. This is a strongly oxidising and acidic state; its complexes are predominantly anionic.

13.2.1 Aqueous Chemistry

The most important chromium(VI) compounds are the chromates and dichromates. The chromates are produced commercially by the oxidation of chromite by air at above 1000° in the presence of sodium carbonate

$$2FeO.Cr_2O_3 + 4Na_2CO_3 + \tfrac{7}{2}O_2 \rightarrow 4Na_2CrO_4 + Fe_2O_3 + 4CO_2$$

The +6 oxidation state is formed in aqueous solution by the oxidation of Cr(III) with, for example, peroxide in alkaline solution. The poisonous yellow chromate CrO_4^{2-} and orange dichromate $Cr_2O_7^{2-}$ ions are the species present in aqueous solutions containing no added ligands. These two ions coexist in equilibrium over quite a wide pH range, the chromate species being predominant in alkaline solution. When acid is added to a solution of chromate ions, protonation and olation occur



The $CrO_4{}^{2-}$ ion is tetrahedral while the $Cr_2O_7{}^{2-}$ ion is composed of two tetrahedral CrO_4 groups joined by a common oxygen atom with the $Cr\widehat{O}Cr$ angle of 115°. The addition of solutions of Ag^+, Pb^{2+}, or Ba^{2+} ions to solutions of potassium dichromate causes complete precipitation of these metals as chromates since these are insoluble and because the $CrO_4{}^{2-}$–$Cr_2O_7{}^{2-}$ equilibrium is so quickly re-established once disturbed. In the presence of high concentrations of complexing anions such as $SO_4{}^{2-}$ or Cl^-, substitution products of the chromate ion are formed

$$[CrO_3(OH)]^- + H^+ + Cl^- \rightleftharpoons [CrO_3Cl]^- + H_2O$$

A surprising feature of Cr^{VI} chemistry is the stability of these oxo-halo-compounds, especially $[CrO_3Br]^-$ and $[CrO_3I]^-$, which we might expect to undergo internal redox; the stability may be due to the kinetically slow reaction between Cr(VI) and halide ions.

The addition of concentrated sulphuric acid to a solution of a dichromate results in precipitation of the red crystalline CrO_3. This is a very water-soluble acidic oxide which acts as a powerful oxidising agent. It reacts explosively with some organic substances, being reduced to Cr_2O_3.

The addition of hydrogen peroxide solutions to acid dichromate solutions gives a deep violet-blue colour, which rapidly fades with evolution of oxygen. However, if ether is added, the blue colour becomes concentrated in the ether layer where it is more stable; this is the basis of the so-called 'blue lake' qualitative test for chromium. If pyridine is added to the ethereal solution, the explosive solid 'pyridine perchromate' $(py)CrO(O_2)_2$ is obtained. The structure of this compound (figure 13.1) has been determined by X-ray crystallography. The chromium atom is in the centre of an approximately pentagonal pyramid in which the oxide oxygen occupies the apical position. The blue compounds are thus all believed to be adducts (with water, ether, or pyridine) of the chromium(VI) peroxide $CrO(O_2)_2$. Its formation in water can be represented thus

$$[CrO_3(OH)]^- + 2H_2O_2 + H^+ \rightarrow CrO(O_2)_2 + 3H_2O$$

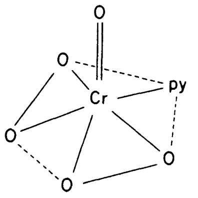


Figure 13.1 The structure of (py)Cr$(O_2)_2$

Many other peroxochromium species are known. Among these are the red-brown peroxochromates $M^I_3CrO_8$ formed in alkaline solution. These are paramagnetic (with one unpaired electron per chromium atom) and form mixed crystals with the niobium(v) and tantalum(v) compounds $M^I_3M^VO_8$; they are thus formulated as containing chromium(v), that is $[Cr(O_2)_4]^{3-}$.

13.2.2 Halides and Oxide Halides

The only known hexahalide is the unstable lemon-yellow CrF_6 prepared from the elements at 400° and 200 atm; at low pressures it decomposes above −100° into CrF_5 and fluorine.

The 'chromyl' halides CrO_2X_2 (X = F, Cl, Br) are dark liquids or low-melting solids rapidly hydrolysed in water, for example

$$CrO_2Cl_2 + 2H_2O \rightarrow H_2CrO_4 + 2HCl$$

Their thermal stability decreases in the order $F^- > Cl^- > Br^-$; the bromide is unstable at room temperature and the iodide has not been isolated. The chloride is readily prepared by the addition of concentrated sulphuric acid to a mixture of potassium dichromate and potassium chloride

$$K_2Cr_2O_7 + 4KCl + 6H_2SO_4 \rightarrow 2CrO_2Cl_2 + 6KHSO_4 + 3H_2O$$

The evolution of the red-brown vapour on heating this mixture has been used as a distinguishing test between chloride and bromide ions, since CrO_2Br_2 is unstable under these conditions. CrO_2Cl_2 is a covalent, roughly tetrahedral, monomer in the vapour and in most nonpolar solvents. It is a violent oxidising agent with some organic compounds; however, some apparently Lewis base adducts have been isolated, for example $CrO_2Cl_2.2D$ (D = acetone or Me_2SO), but these have been shown to contain chromium(iv). Reaction with N_2O_4 gives $Cr(NO_3)_3.2N_2O_4$, but with N_2O_5 chromyl nitrate is formed as a brown volatile liquid

$$CrO_2Cl_2 + 2N_2O_5 \rightarrow CrO_2(NO_3)_2 + 2NO_2Cl$$

This is a violent oxidising agent, causing benzene to inflame on contact.

13.3 Compounds of Chromium(v) (d^1) and Chromium(iv) (d^2)

The +4 and +5 oxidation states are relatively rarely found in chromium compounds. In most of these compounds, which usually undergo ready disproportionation, chromium is bound to oxygen only or to a mixture of oxygen and halide ligands.

The pentafluoride CrF_5 is a red solid (m.p. 30°) formed in the direct reaction between the elements at 400° in a flow system. The green solid CrF_4 is obtained at a slightly lower temperature. Both fluorides are rapidly hydrolysed by water but, while the pentafluoride is a very reactive oxidising agent, the tetrafluoride is rather inert and does not react with, for example, NH_3, SO_2, or BrF_3 at room temperature. Evidence for the presence of $CrCl_4$ in the vapour phase (for example over $CrCl_3$ by disproportionation) has been presented but no other CrX_5 or CrX_4 compounds have been isolated. The oxochloride $CrOCl_3$ is a dark red solid made by the reaction of CrO_3 with thionyl chloride. From concentrated hydrochloric acid, complexes $M^I_2[CrOCl_5]$ can be crystallised starting from CrO_3 and M^ICl.

Some dark blue solid alkali metal chromates(V), for example Na_3CrO_4, are known. These are paramagnetic and believed to contain discrete tetrahedral anions. In water they disproportionate to Cr^{III} and Cr^{VI}. Ca_2CrO_4Cl is known to contain distorted CrO_4 tetrahedra. Chromium(V) species have been shown to be present in solutions of CrO_3 in phosphoric acid and of chromates(VI) in 65 per cent oleum. Some simple chromium(IV) compounds include the green $Cr(NEt_2)_4$ (prepared from $CrCl_3$ and $LiNEt_2$) and the blue alkoxides $Cr(OR)_4$ obtained by alcoholysis of the tetrakis(diethylamide). The alkoxides are paramagnetic ($\mu_{eff} \approx 2.8$ B.M.), monomeric, and tetrahedral.

13.4 Compounds of Chromium(III) (d^3)

This is the most common and stable oxidation state of chromium especially in aqueous solution. Complexes of chromium(III) have the d^3 configuration and are kinetically inert (see chapter 8), undergoing only slow ligand substitution reactions. This has resulted in the study and isolation of a very large number of these complexes, virtually all of which possess octahedral co-ordination, which is a characteristic feature of chromium(III) chemistry. Three, four, and five-co-ordination do occur rarely as in, for example, $Cr(NPr^i_2)_3$, $Li[Cr(OBu^t)_4]$, and $CrCl_3(NMe_3)_2$.

13.4.1 Aqueous Chemistry

The violet hexaquo-ion $[Cr(H_2O)_6]^{3+}$ occurs in the solid state in salts such as $Cr_2(SO_4)_3.18H_2O$ and chrome alum $KCr(SO_4)_2.12H_2O$, as well as in solutions of $Cr(OH)_3$ in noncomplexing acids. The green chromium(III) salts, for example $Cr_2(SO_4)_3.6H_2O$, do not contain the hexaquo-ion; rather, they have anions in the co-ordination sphere of the metal. The acidity of the aquo-ion, that is

$$[Cr(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Cr(OH)(H_2O)_5]^{2+} + H_3O^+ \qquad (pK_1 = 1.6)$$

$$2[Cr(OH)(H_2O)_5]^{2+} \rightleftharpoons [(H_2O)_4Cr(OH)_2Cr(OH_2)_4]^{4+} + 2H_2O \; (K \approx 10^4)$$

prohibits the formation of salts of weak acids such as $CO_3{}^{2-}$ and S^{2-}in aqueous solution. The addition of alkali results in the precipitation of the green $Cr(OH)_3aq$. This is soluble in an excess of alkali to give species that may be $[Cr(OH)_6]^{3-}$. In ammonia, solution of the hydroxide is slow but soluble ammines are eventually formed. A very large number of these ammines have been characterised, ranging through $[Cr(NH_3)_6]^{3+}$ to $[Cr(NH_3)_2(H_2O)_4]^{3+}$, and with anionic substitution products such as $[Cr(NH_3)_5X]^{2+}$ and $[Cr(NH_3)_2(H_2O)_3X]^{2+}$ (X = univalent anion). Reinecke's salt $NH_4[Cr(NH_3)_2(NCS)_4].H_2O$ as often been used as a source of a large univalent anion in the precipitation of large cations as 'reineckates'. Complete replacement of co-ordinated water or ammonia molecules by anions leads to complexes of the types $[CrX_6]^{3-}$, such as $[CrF_6]^{3-}$ and $[Cr(CN)_6]^{3-}$, and $[Cr(AA)_3]^{3-}$ such as $[Cr(C_2O_4)_3]^{3-}$. Many polynuclear complexes are also known. These are usually hydroxo-bridged, for example $[(NH_3)_5Cr(OH)Cr(NH_3)_5]^{5+}$ (the so-called normal rhodo-ion), or oxo-bridged as in the basic rhodo-ion, that is $[(NH_3)_5CrOCr(NH_3)_5]^{4+}$. Trinuclear chromium(III) complexes also occur commonly. In the basic acetates, which contain, for example, the ion $[Cr_3O(O_2CCH_3)_6(H_2O)_3]^+$, the oxygen atom is at the centre of an equilateral triangle of chromium atoms each pair of which is bridged by two acetate groups, the octahedron around each chromium being completed by a terminal water molecule.

13.4.2 Chromium(III) *Oxide*

The green Cr_2O_3 results when chromium is burned in air, when dichromates are reduced by heating with, for example, carbon or sulphur, and in the spectacular thermal decomposition of ammonium dichromate (in which reaction the ammonium ion acts as the reducing agent)

$$(NH_4)_2Cr_2O_7 \rightarrow Cr_2O_3 + N_2 + 4H_2O$$

The crystallised form, made at high temperatures, is black with a metallic lustre. It has the corundum structure; indeed, isomorphous replacement of Al^{III} by Cr^{III} in corundum gives the mineral ruby. When Cr_2O_3 is ignited strongly, that is in its preparation from '$Cr(OH)_3$', it becomes inert to acids and bases. On fusion with basic oxides, compounds of the spinel type, that is $M^{II}O.Cr_2O_3$, are obtained. Cr_2O_3 has been used in a variety of green pigments.

13.4.3 Chromium(III) *Halides*

All four halides have been prepared, the green fluoride by the high-temperature reaction of the metal with HF, and the violet $CrCl_3$, black $CrBr_3$, and CrI_3 by direct combination of the elements at various temperatures. Only the chemistry of the chloride has been studied in any detail. A large number of adducts are known with donor molecules; these are usually of the six-co-ordinate type, for example $CrCl_3.3py$ and $CrCl_3.3THF$. The trimethylamine adduct $CrCl_3.2NMe_3$ has the five-co-ordinate *trans*-trigonal bipyramidal structure. With alkali metal chlorides in melts, two series of complex halides arise, $M^I_3CrCl_6$ and $M^I_3Cr_2Cl_9$; the latter series of compounds are also conveniently prepared in thionyl chloride. These halides are magnetically dilute; in $Cr_2Cl_9^{3-}$ each chromium ion is bonded to three terminal chloride ions and shares three bridging chloride ions in an approximately octahedral array about each chromium.

Chromium(III) chloride dissolves at a negligible rate in water but becomes rapidly soluble in the presence of Cr^{II} or a reducing agent capable of producing Cr^{II} in the solution. The Cr^{II} ions can undergo electron-transfer reactions with the inert Cr^{III} ions in the solid $CrCl_3$ via a chloride bridge, thus enabling Cr^{II} sites to be formed which can leave the solid and cause further solubilisation of the $CrCl_3$. The hexahydrate $CrCl_3.6H_2O$ exists in three isomeric forms; the normally purchased green form has the formula $[CrCl_2(H_2O)_4]Cl.2H_2O$, while the less common violet and pale green isomers have the formulae $[Cr(H_2O)_6]Cl_3$ and $[CrCl(H_2O)_5]Cl_2$ respectively.

13.5 Compounds of Chromium(II) (d^4)

The +2 state is a strongly reducing one for chromium. Aqueous solutions of chromium(II) are best obtained by dissolving pure chromium in dilute nonoxidising mineral acids such as HCl. They are also readily obtained by the reduction of dichromate by zinc and acid. These preparations must be carried out under a protective atmosphere. The aquo-ion $[Cr(H_2O)_6]^{2+}$ is very readily oxidised to the green $[Cr(H_2O)_6]^{3+}$ in air

$$Cr^{3+} + e \rightarrow Cr^{2+} \qquad (E^\circ = -0.41 \text{ V})$$

Several hydrated salts can be obtained from aqueous solution; these frequently contain the hexaquo-ion in the solid state. The sulphates resemble those of iron(II). The blue $CrSO_4.7H_2O$ is isomorphous with $FeSO_4.7H_2O$, and double salts of the formula $M^I{}_2Cr(SO_4)_2.6H_2O$ can be crystallised from solutions containing the alkali metal sulphates. Other hydrates include $Cr(ClO_4)_2.6H_2O$, $CrCl_2.4H_2O$, and $CrBr_2.6H_2O$.

The red crystalline acetate $Cr(OCOCH_3)_2.2H_2O$ is readily prepared in the laboratory. A chromium(II) solution is forced under hydrogen into a concentrated solution of sodium acetate. The chromium(II) acetate precipitates; it is much less readily oxidised than solutions of Cr^{II} but is nevertheless unstable in air. Figure 13.2 shows the dimeric structure of this acetate. In this structure each Cr atom is surrounded by an approximately square planar array of oxygen atoms from the two bridging acetate groups. The short Cr—Cr distance found (246 pm) implies a strong interaction between the two metal atoms. The compound is in fact diamagnetic, so the four metal electrons on each chromium are fully paired. Copper(II) acetate dihydrate has a similar structure although the Cu—Cu distance is larger (264 pm) and the spin moment is not completely quenched at room temperature.

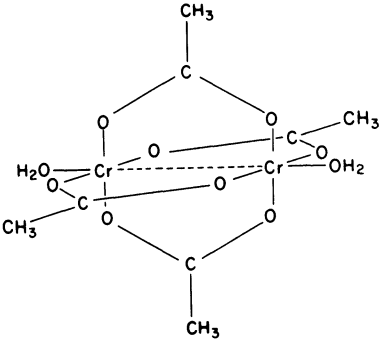


Figure 13.2 The structure of $Cr(OCOCH_3)_2.2H_2O$

Especially air-stable chromium(II) complexes are formed by hydrazine. The pale violet $CrCl_2(N_2H_4)_2$ precipitates when a chromium(II) chloride solution is passed into an excess of aqueous hydrazine. This complex has the polymeric hydrazine-bridged structure found for all $MX_2(N_2H_4)_2$ compounds of the first transition series (figure 13.3); it is paramagnetic, with $\mu_{eff} = 4.9$ B.M. The $[Cr(N_2H_4)_6]^{2+}$ complex has not been prepared but 2,2′-bipyridyl forms $[Cr(bipy)_3]^{2+}$ which in alkaline solution undergoes disproportionation

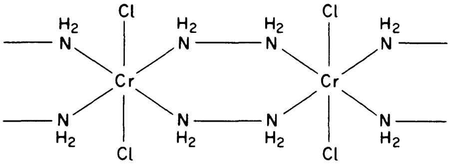


Figure 13.3 The structure of $CrCl_2(N_2H_4)_2$

$$2[Cr(bipy)_3]^{2+} \rightarrow [Cr(bipy)_3]^{+} + [Cr(bipy)_3]^{3+}$$

Anionic complexes containing the ions $[Cr(NCS)_6]^{4-}$ and $[Cr(CN)_6]^{4-}$ are also known. The common features of chromium(II) complexes are that they have the preferred co-ordination number of six and are usually high-spin ($t_{2g}{}^3 e_g{}^1$); the hexacyanide complex is low-spin ($t_{2g}{}^4$) with $\mu_{eff} = 3.2$ B.M.

The anhydrous halides CrX_2 (X = F, Cl, Br) are prepared by the reactions of the metal with the hydrogen halides at around 700°. The iodide is prepared by direct combination of the elements at around 600°. With donor molecules such as pyridine and triphenylphosphine oxide, tetragonal polymeric complexes $CrX_2.2L$ are formed. Complex halides of the types $M^I{}_2CrCl_4$ and M^ICrCl_3 have been obtained in melts.

13.6 Compounds of Chromium in Low Oxidation States

The hexacarbonyl $Cr(CO)_6$ has the noble-gas configuration and is a white crystalline diamagnetic air-stable solid. It has the octahedral structure. A large number of derivatives have been prepared in which one or more of the carbonyl groups are replaced by ligands such as pyridine, tertiary phosphines, tertiary arsines, etc. Halide ions similarly displace carbon monoxide, for example

$$Cr(CO)_6 + Et_4NI \xrightarrow{THF} Et_4N[Cr(CO)_5I] + CO$$

The $[Cr(CO)_5I]^-$ ion can be oxidised by, for example, Fe^{3+} to the deep blue $Cr(CO)_5I$ which is one of the best-known octahedral chromium(I) compounds. Reduction of $Cr(CO)_6$ by sodium in liquid ammonia affords the trigonal bipyramidal chromium(–II) anion $[Cr(CO)_5]^{2-}$. If the reduction is carried out using sodium borohydride in boiling THF, the anion $[HCr_2(CO)_{10}]^-$ is obtained in which the hydrogen atom bridges two $Cr(CO)_5$ groups. Many olefin and arene complexes, such as $C_6H_6Cr(CO)_3$, are obtained by heating the carbonyl with the hydrocarbon.

Other ligands capable of stabilising low oxidation states on chromium are the isocyanides as in $Cr(CNPh)_6$, cyanide ion as in $K_6Cr(CN)_6$, and 2,2′-bipyridyl which gives compounds analogous to those described for titanium and vanadium.

13.7 Organometallic Compounds of Chromium

The organometallic chemistry of chromium dates from 1919 when Hein prepared what were called polyphenyl chromium compounds; these had the general formula Ph_xCr and Ph_xCrI where $x = 2, 3, 4$, or 5. A reinvestigation of these compounds in 1954 by Zeiss showed that they are in fact sandwich compounds of chromium with the metal sandwiched between aromatic rings such as benzene and biphenyl. At about the same time, Fischer deduced that $Cr(C_6H_6)_2$ might be stable, by analogy with the known structure of ferrocene, and he proceeded successfully to synthesise dibenzenechromium (chapter 3).

While many olefin, cyclopentadienyl, and a few π-allyl and σ-bonded organochromium compounds are now known, the most celebrated organochromium compound is still dibenzenechromium. In this black diamagnetic solid the chromium atom is sandwiched between two benzene rings (figure 13.4). Since the rings are uncharged, the compound contains chromium(0) and is isoelectronic with ferrocene. Unlike ferrocene, however, it does not undergo electrophilic substitution reactions in the aromatic rings; rather, oxidation occurs to the $(\pi\text{-}C_6H_6)_2Cr^+$ cation. Some ligands completely replace both benzene rings in their reaction with dibenzenechromium, for example

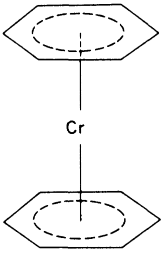


Figure 13.4 Dibenzenechromium

$$Cr(C_6H_6)_2 + 6PF_3 \rightarrow Cr(PF_3)_6 + 2C_6H_6$$

14 Manganese

14.1 The Element

Manganese is the third most abundant transition metal, being widely distributed in the earth's crust. It heads group VIIA of the periodic table, lying above technetium and rhenium. The maximum oxidation state +7 is shown in the permanganates, and all oxidation states from +7 to –3 are known; this is the widest range shown by a first-row transition element. Pure manganese is largely produced by electrolysis from aqueous solutions containing manganese(II) sulphate.

The metal resembles iron in appearance. Four allotropic modifications are known; the α-form, the stable form at room temperature, is hard and brittle. The largest use of manganese is in ferroalloys. Manganese is an electropositive metal, being attacked slowly by water and dissolving readily in dilute acids to form Mn^{2+}.aq with evolution of hydrogen. It differs from the earlier transition elements in the great stability of the +2 oxidation state, which for manganese corresponds to the d^5 completely half-filled shell. Thus Mn^{II} compounds are formed also when the metal combines with chlorine, bromine, iodine, and nitrogen; with fluorine, MnF_3 and MnF_4 are the major products.

14.2 Compounds of Manganese(VII) (d^0), Manganese(VI) (d^1), and Manganese(V) (d^2)

The best-known manganese(VII) species is the permanganate ion MnO_4^-. Potassium permanganate is manufactured by fusing the dioxide (pyrolusite) with potassium hydroxide in air to form the manganate

$$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$

The manganate is then oxidised electrolytically to permanganate

$$MnO_4^{2-} - e \rightarrow MnO_4^-$$

$KMnO_4$ forms dark purple crystals with a solubility in water at room temperature of 63 g l^{-1}. The lithium and sodium salts are considerably more soluble, while the rubidium and caesium salts are only sparingly soluble in water. The permanganate ion is a strong oxidising agent and is widely used for this purpose in the laboratory. Solutions of the ion slowly decompose on standing, with the formation of brown MnO_2

$$4MnO_4^- + 4H^+ \rightarrow 4MnO_2 + 2H_2O + 3O_2$$

This reaction is catalysed by light. In acid solution, reducing agents cause reduction to Mn^{2+}.aq

$$MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O \quad (E^\circ = +1.51\ V)$$

The reaction with reducing agents is initially slow, but it is catalysed by the presence of Mn^{2+} so proceeds quickly once Mn^{2+} has been formed, or if it is deliberately added. Permanganate is widely used for the volumetric estimation of other transition metal ions, for example Ti^{3+}, VO^{2+}, and Fe^{2+}, as well as for hydrogen peroxide, oxalates, formates, and nitrites. In alkaline or neutral solution reduction to MnO_2 occurs

$$MnO_4^- + 2H_2O + 3e \rightarrow MnO_2 + 4OH^- \ (E^\circ = +0.588 \text{ V})$$

The addition of concentrated alkali to $KMnO_4$ results in the formation of the green manganate ion

$$4MnO_4^- + 4OH^- \rightarrow 4MnO_4^{2-} + 2H_2O + O_2$$

This reaction can be reversed by passing chlorine or carbon dioxide through the manganate solution

$$MnO_4^{2-} + \tfrac{1}{2}Cl_2 \rightarrow MnO_4^- + Cl^-$$

The manganate ion is the only stable representative of the manganese(VI) state.

The oxide Mn_2O_7 behaves as the anhydride of permanganic acid. It is prepared as a dark heavy oil by the action of concentrated sulphuric acid on potassium permanganate

$$2KMnO_4 + 2H_2SO_4 \rightarrow Mn_2O_7 + 2KHSO_4 + H_2O$$

This oxide decomposes explosively on heating, and in water it gives permanganic acid solution.

Permanganic acid and its dihydrate can be isolated as purple solids $HMnO_4$ and $HMnO_4.2H_2O$ by low-temperature evaporation of its frozen aqueous solutions. It is a violent oxidant, causing ignition of hydrocarbons on contact and decomposing (often explosively) above 3°.

No simple halides of manganese(VII) are known but two oxyhalides exist. MnO_3F is prepared by the reaction of potassium permanganate with anhydrous hydrogen fluoride, iodine pentafluoride, or fluorosulphonic acid. It is a dark green liquid (m.p. −78°), instantly hydrolysed by moisture and decomposing explosively above room temperature to MnF_2, MnO_2, and O_2. The molecule is tetrahedral in the vapour phase. MnO_3Cl is similar; it is formed together with brown MnO_2Cl_2 and green $MnOCl_3$ in the reaction of Mn_2O_7 with HSO_3Cl; these oxyhalides can be handled more safely in carbon tetrachloride solution.

Manganates(V) containing the blue MnO_4^{3-} ion can be isolated from fused or concentrated aqueous sodium hydroxide. Magnetic susceptibility measurements confirm the +5 (d^2) oxidation state in these compounds; $Na_3MnO_4.10H_2O$ is isomorphous with Na_3VO_4.

14.3 Compounds of Manganese(IV) (d^3)

Manganese occurs naturally in this oxidation state as pyrolusite MnO_2. Its stability lies partly in its insolubility in water. Solutions of manganese(IV) compounds undergo ready oxidation to manganese(VI) in alkaline solution, and reduction to manganese(II) in acid solution. Manganese(IV) therefore has not an extensive aqueous solution chemistry.

MnO_2 is a black powder when anhydrous; the aquated form prepared in aqueous solution (by reduction of MnO_4^- or oxidation of $[Mn(H_2O)_6]^{2+}$) is brown. It evolves oxygen when heated to above 500° in air or when treated with hot concentrated sulphuric acid; it acts as a catalyst in the decomposition of hydrogen peroxide and potassium chlorate, and in the oxidation of carbon monoxide by copper(II) oxide. In cold concentrated hydrochloric acid, the hexachloromanganate(IV) ion is formed

$$MnO_2 + 6HCl \rightarrow MnCl_6{}^{2-} + 2H^+ + 2H_2O$$

In hot acid, reduction to manganese(II) occurs

$$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$$

The only known binary halide of manganese(IV) is the fluoride MnF_4. This is a blue hygroscopic solid which decomposes slowly at room temperature into MnF_3 and fluorine. It obeys the Curie–Weiss Law with $\mu_{eff} = 3.84$ B.M. at room temperature. Complex halides such as K_2MnF_6 and K_2MnCl_6 are known, but the latter salt liberates chlorine in dry air at room temperature. The hexacyanomanganate(IV) $K_2Mn(CN)_6$ has been prepared by the oxidation of $K_3Mn(CN)_6$ with nitrosyl chloride in dimethylformamide. A series of complex iodates $M^I{}_2Mn(IO_3)_6$ is also known.

14.4 Compounds of Manganese(III) (d^4)

Manganese(III) is still an oxidising state and is also unstable with respect to disproportionation in aqueous solution

$$2Mn^{3+}.aq + 2H_2O \rightarrow Mn^{2+}.aq + MnO_2 + 4H^+$$

The manganese(III) state can be stabilised by using acidic solutions, increasing the Mn^{2+} concentration, or by complex formation. It is prepared in aqueous solution by chemical or electrolytic oxidation of Mn^{II}, or by reduction of Mn^{IV} or Mn^{VII}. The aquo-ion $[Mn(H_2O)_6]^{3+}$ occurs in the alum $CsMn(SO_4)_2.12H_2O$; it is strongly acidic

$$[Mn(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Mn(OH)(H_2O)_5]^{2+} + H_3O^+ \quad (pK_1 \approx 0.9)$$

Hydrolysis of the aquo-ion is thus considerable even at high acidity. The electronic spectrum of this ion shows a single band with Jahn–Teller distortion at around 21 000 cm^{-1} corresponding to the $^5E_g \rightarrow {}^5T_{2g}$ transition in the octahedral d^4 ion.

Aerial oxidation of $Mn(OH)_2$ gives the brown hydrous oxide $Mn_2O_3.aq$ which upon drying at 100° gives $MnO(OH)$ (this also occurs naturally, as manganite). Mn_2O_3 also occurs in nature (braunite); it arises in the thermal decomposition of MnO_2 above 500°, and in the ignition of manganese(II) salts in air. Above 940°, Mn_2O_3 evolves oxygen, giving the manganese(II, IV) oxide Mn_3O_4.

The only thermally stable halide is MnF_3. This is a red-purple solid with $\mu_{eff} = 5.0$ B.M. at room temperature. It is instantly hydrolysed by moisture but has been extensively used as a fluorinating agent in organic chemistry. The crystal structure consists of distorted ($t_{2g}{}^3e_g{}^1$ ground state) MnF_6 octahedra which share corners. The black $MnCl_3$ has been obtained by the reaction of manganese dioxide with hydrogen chloride in ethanol at –63° followed by precipitation with carbon tetrachloride. It decomposes above –40° but with amines it forms 1 : 3 complexes which are thermally stable at room temperature but extremely sensitive to moisture. Complexes with halides are similarly more thermally stable; these include K_3MnF_6 (prepared in melts), $K_2[MnF_5(H_2O)]$ (prepared in aqueous HF), and the tris-(1,2-propanediamine)cobalt(III) salt of the $MnCl_6^{3-}$ ion.

One of the most stable Mn^{III} salts is the acetate $Mn(OCOCH_3)_3.2H_2O$. This is prepared by the oxidation of a solution of manganese(II) acetate in acetic acid with, for example, permanganate. Similarly, the acetylacetonate $Mn(acac)_3$ is obtained by the oxidation of manganese(II) solutions containing an excess of acetylacetone. The red sulphate $Mn_2(SO_4)_3.H_2SO_4.4H_2O$ crystallises from solutions of Mn_2O_3 in cold moderately concentrated sulphuric acid.

The hexacyano-complex $K_3Mn(CN)_6$ is obtained by treatment of manganese(III) acetate with an excess of aqueous potassium cyanide followed by precipitation with ethanol. The $[Mn(CN)_6]^{3-}$ ion is also readily formed by oxidation of Mn^{II} salts in an excess of cyanide ions; it is, unlike all the other Mn^{III} complexes we have mentioned, low-spin.

14.5 Compounds of Manganese(II) (d^5)

This is the most common oxidation state shown by manganese. Because of the high-spin d^5 configuration in most of its compounds, the salts of manganese(II) are a very pale pink colour (see section 6.2.7). The aquo-ion $[Mn(H_2O)_6]^{2+}$ is barely acidic, so manganese(II) forms an extensive series of salts with common anions; the carbonate $MnCO_3$ is even found in the natural state as manganese spar. Many of the hydrated salts, for example $MnSO_4.7H_2O$ and $Mn(ClO_4)_2.6H_2O$, contain the $[Mn(H_2O)_6]^{2+}$ ion. The addition of hydroxide ions to solutions of these salts causes precipitation of the white $Mn(OH)_2$; this is a true hydroxide and is largely basic. In the presence of air, alkaline suspensions of $Mn(OH)_2$ oxidise rapidly to the brown Mn_2O_3.aq. Oxidation of the Mn^{II} to permanganate can be achieved by periodate or persulphate ions in acid solution

$$2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \rightarrow 2MnO_4^- + 10SO_4^{2-} + 16H^+$$

The halides MnX_2 are pink crystalline solids which form hydrates in water and a large number of adducts with organic molecules, for example octahedral polymeric $MnCl_2.2py$ and tetrahedral $MnCl_2.2(OPPh_3)$. Complex halides are readily prepared in nonaqueous media; they are of two types. In the M^IMnX_3 type the manganese is octahedrally co-ordinated by halide ions while in the $M^I_2MnX_4$ type tetrahedral MnX_4^{2-} ions are present.

A large variety of complexes and stereochemistries are exhibited by Mn^{II}. Since these are mostly d^5, that is high-spin complexes, crystal-field stabilisation energies make no contribution to their overall thermodynamic stability. Octahedral and tetrahedral stereochemistries are common, and in $MnCl_2(DMSO)_3$ (DMSO = dimethyl sulphoxide) are found manganese ions in both stereochemistries, that is $[Mn(DMSO)_6]^{2+}[MnCl_4]^{2-}$. Ammonia forms octahedral $[Mn(NH_3)_6]^{2+}$ cations in its reactions with the anhydrous salts, while some terdentate amines such as 2,2′,2″-terpyridyl (terpy) form five-co-ordinate complexes, for example

MnI_2(terpy). Dodecahedral eight-co-ordination occurs in the tetranitratomanganate(II) anion in $[Ph_4As]_2Mn(NO_3)_4$.

Low-spin complexes are formed by cyanide ion and isonitriles, for example $[Mn(CN)_6]^{4-}$and $[Mn(CNR)_6]^{2+}$. These are more readily oxidised than the high-spin complexes, probably because of increased CFSE in the more highly charged Mn^{III} derivatives (the CFSE in the Mn^{II} complexes is only slightly greater than the pairing energy).

14.6 Compounds of Manganese in Low Oxidation States

The manganese atom requires eleven electrons in order to achieve the stable noble-gas configuration. The carbonyl $Mn(CO)_5$ has seventeen outer electrons and exists as the dimer $Mn_2(CO)_{10}$ in which each manganese atom has the required share in eighteen electrons. In the $Mn(CO)_5^-$ anion, however, the eighteen electron rule is again upheld and this is in fact a stable species.

$Mn_2(CO)_{10}$ has a metal–metal bond joining the two $Mn(CO)_5$ fragments; it forms yellow crystals that are slowly oxidised by the air. Reduction by sodium amalgam in tetrahydrofuran gives sodium pentacarbonylmanganate(−I) $NaMn(CO)_5$ which can be used to prepare a variety of compounds by reaction with organic halides

$$NaMn(CO)_5 + RX \rightarrow RMn(CO)_5 + NaX$$

If phosphoric acid is used in place of RX, the volatile liquid hydride $HMn(CO)_5$ is obtained. The carbonyl halides $Mn(CO)_5X$ are obtained in the reactions of the halogens with $Mn_2(CO)_{10}$ or $NaMn(CO)_5$. Thermal decomposition of the $Mn(CO)_5X$ compounds at 100° gives the halogen-bridged binuclear carbonyl halides $(CO)_4MnX_2Mn(CO)_4$. Many substitution products of these carbonyls with ligands are known, including two volatile nitrosyl carbonyls, the red $Mn(CO)_4NO$ and the green $Mn(CO)(NO)_3$.

As well as in carbonyl halides, Mn^I occurs in the $[Mn(CN)_6]^{5-}$ ion (obtained by Al/NaOH reduction of $[Mn(CN)_6]^{4-}$) and in the $[Mn(CNR)_6]^+$ cations that arise in the reactions of MnI_2 with RNC.

14.7 Organometallic Compounds of Manganese

The pure σ-bonded alkyls and aryls of manganese are unstable in air; dimethylmanganese is a polymeric powder which catches fire on exposure to the atmosphere. In contrast, alkyls containing π-acceptor groups are considerably more stable; the diamagnetic $CH_3Mn(CO)_5$, for example, is stable to air and water.

The unusual stability of the d^5 Mn^{2+} state results in manganese forming an ionic bis(cyclopentadienide) $Mn^{2+}(C_5H_5^-)_2$ rather than the covalent sandwich structured type shown by the other M^{2+} ions in the first transition series. Thus $Mn(C_5H_5)_2$ reacts with water to give cyclopentadiene and MnO (π-bonded cyclopentadienyls do not react with water). In the presence of other π-bonding ligands, however, manganese does form π-cyclopentadienyl complexes, for example $(\pi\text{-}C_5H_5)Mn(CO)_3$ and $(\pi\text{-}C_6H_6)Mn(\pi\text{-}C_5H_5)$.

15 Iron

15.1 The Element

Iron is the fourth most abundant element in the earth's crust; in the elemental form it occurs only rarely but in the combined state it is universally common. Iron has a very ancient history; it was probably first used by man nearly 6000 years ago (iron from meteorites), iron production beginning around 1200 B.C. Iron is the first member of the group VIII triad, lying above ruthenium and osmium. Unlike all the elements we have so far considered, iron does not show the maximum oxidation state corresponding to the removal of all (eight) of its valence electrons. The maximum oxidation state shown is +6 but states above +3 are all relatively unimportant; notice that with iron it is the +3 state that has the completely half-filled ($3d^5$) shell. As with manganese, however, the predominance of the +2 oxidation state continues to assert itself, and in the elements to follow, that is Co, Ni, and Cu, compounds in this state assume even greater preponderance.

Pure iron finds no great industrial use; it can be prepared by thermal decomposition of iron pentacarbonyl, by hydrogen reduction of pure iron oxides, or by aqueous electrolysis of pure iron salts. Two structural types of iron occur in the solid state. The α-form, stable at room temperature, has a body-centred cubic lattice. At about 910° the α-form is transformed into the γ-form which has a cubic close-packed structure. Iron is ferromagnetic up to 768° (the Curie point); thereafter it is paramagnetic. The magnetic and other physical properties of iron are dependent on the purity of the iron and the nature of its impurities. A very large number of steels and other iron alloys are produced for specific purposes.

Iron combines with most nonmetals on heating. The finely divided metal is pyrophoric in air at room temperature, the massive metal forming Fe_2O_3 and Fe_3O_4 in air above 150°. Steam reacts above 500°, forming Fe_3O_4 and FeO with liberation of hydrogen. Iron dissolves in dilute mineral acids to form iron(II) solutions; the dissolution of impure iron in dilute sulphuric acid is accompanied by the evolution of a gas with a characteristic odour. The hydrogen evolved contains traces of the hydrides of other elements (for example C and S) present as impurities in the iron. Concentrated nitric acid has (after a momentary reaction) a passivating effect on the iron owing to the formation of an oxide film layer on the surface of the metal. Even passivated iron dissolves in reducing acids such as dilute hydrochloric acid.

Rusting. The most economically important reaction of iron is the formation of hydrated oxide in the presence of oxygen and water, that is rusting. For this corrosion to occur at room temperature, oxygen, water, and an electrolyte all appear to be essential. The mechanism of rusting is electrochemical, the rate being governed by processes occurring at the water–iron interface. At this interface oxygen is reduced by a stepwise cathodic reaction that can be summarised by the equation

$$O_2 + 2H_2O + 4e \rightarrow 4OH^-$$

Iron enters solution as Fe^{2+} in an anodic reaction that provides the four electrons required above

$$2Fe \rightarrow 2Fe^{2+} + 4e$$

Thus Fe^{2+} and OH^- ions are present in solution, and in the presence of air the yellow-brown hydrated iron(III) oxide (rust) precipitates.

The Mössbauer effect. Iron compounds are particularly suitable for study by Mössbauer spectroscopy. The nuclide ^{57}Fe, daughter of ^{57}Co, has an excited state ($t_{1/2} = 1.0 \times 10^{-7}$ s) at 14.4 keV above the ground state. If an iron compound is irradiated with γ-rays from a ^{57}Co source, resonant absorption of γ-rays will occur if the iron nuclei in the compound are in an environment identical to that of the nuclei in the source. No absorption will occur if the source and compound nuclei are in different environments. The resonant absorption of γ-rays can be made to occur by giving the absorbing compound a velocity relative to that of the source. This velocity changes the energy of the incident quanta until, at a particular velocity, the energy corresponds to that required for resonant absorption. The positions of the absorption peaks are thus usually expressed in velocities (m s^{-1}), and shifts are related to some standard, for example sodium pentacyanonitrosylferrate(II) or stainless steel, arbitrarily taken as zero. These *isomer shifts* are directly proportional to the total s electron density at the nucleus. Thus iron(II) compounds give larger shifts than iron(III) compounds, since the 4s electrons in Fe^{2+} are more strongly screened by the extra 3d electron. This is particularly true of high-spin complexes, for which isomer shifts are of the order +1.0 to +1.8 mm s^{-1} for Fe^{2+} and +0.4 to +0.9 mm s^{-1} for Fe^{3+} ($Na_2[Fe(CN)_5(NO)]$ standard). Further information can be obtained when a splitting of the absorption peak occurs; splittings occur when there is an asymmetric electronic charge distribution, for example in high-spin $Fe^{2+}(d^6)$ but not in Fe^{3+} (d^5), or when magnetic dipole interactions occur as in ferro- and antiferro-magnetic compounds.

15.2 Compounds of Iron in High Oxidation States

Compounds of iron in +4, +5, and +6 oxidation states are known with iron in combination with oxygen but, rather surprisingly, not with fluorine.

The alkali metal ferrates(VI) K_2FeO_4 and Na_2FeO_4 are obtained by oxidation of a suspension of hydrous iron(III) oxide in concentrated alkali with hypochlorite

$$2Fe(OH)_3 + 3ClO^- + 4OH^- \rightarrow 2FeO_4{}^{2-} + 3Cl^- + 5H_2O$$

The deep-red $FeO_4{}^{2-}$ ions are most stable in alkali; in neutral or acid solution, decomposition to iron(III) is rapid

$$2FeO_4{}^{2-} + 10H^+ \rightarrow 2Fe^{3+} + 5H_2O + {}^3/{}_2O_2$$

Ferrates(VI) are very strong oxidising agents; ammonia is oxidised to nitrogen at room temperature. They contain the discrete tetrahedral $FeO_4{}^{2-}$ ion, the potassium salt being isomorphous with K_2SO_4 and K_2CrO_4. The magnetic moments of ferrates(VI) are in the range 2.8–3.1 B.M., in accord with magnetically dilute d^2 systems.

Potassium ferrate(V) K_3FeO_4 can be prepared by thermal decomposition of K_2FeO_4 at 700°; above this temperature it decomposes into $KFeO_2$, potassium oxide, and oxygen.

Ferrates(IV) of three types are known, that is $FeO_3{}^{2-}$, $FeO_4{}^{4-}$, and $FeO_5{}^{6-}$. The strontium and barium salts of the $FeO_4{}^{4-}$ ion are prepared as fine black crystals by oxidation of a mixture of hydrous iron(III) oxide and the alkaline earth metal oxide or hydroxide with oxygen at 700–800°

$$Sr_3[Fe(OH)_6]_2 + Sr(OH)_2 + \tfrac{1}{2}O_2 \rightarrow 2Sr_2FeO_4 + 7H_2O$$

The sodium salt is obtained similarly; it undergoes immediate disproportionation in dilute alkali

$$3Na_4FeO_4 + 8H_2O \rightarrow Na_2FeO_4 + 2Fe(OH)_3 + 10NaOH$$

These ferrates(IV) do not contain discrete $FeO_4{}^{4-}$ ions and are best regarded as mixed oxides. A compound FeO_2 ($\mu_{eff} = 4.91$ B.M.), which may be iron(IV) oxide, has been obtained by thermal decomposition of the reaction product obtained in the reaction of iron pentacarbonyl with dinitrogen tetroxide ($[FeNO_3]O$).

The only non-oxo compounds of iron in high oxidation states are the diarsine complexes $[Fe(diars)_2X_2]^{2+}$ (X = Cl or Br). These arise in the oxidation of the iron(III) complexes $[Fe(diars)_2X_2]^+$ with concentrated nitric acid. The magnetic moments of the iron(IV) compounds are in agreement with a low-spin d^4 configuration; Mössbauer studies support a tetragonal (D_{4h}) structure with the low-spin ground state ($d_{xy}{}^2$, $d_{xz}{}^1$, $d_{yz}{}^1$).

15.3 Compounds of Iron(III) (d^5)

In this oxidation state, iron forms mainly octahedral complexes. It resembles the d^5 Mn^{II} state in forming predominantly high-spin complexes; these have magnetic moments close to the spin-only value of 5.9 B.M. The few low-spin complexes, that is with CN^-, bipy, and phen as ligands, have moments in excess of the spin-only value (1.73 B.M.) because of orbital contribution arising from the $t_{2g}{}^5\ e_g{}^0$ ground state. Iron(III) tends to be stabilised [relative to iron(II)] by anionic ligands, having its greatest affinity for oxygen donors such as phosphates, tartrate, citrate, oxalate, and EDTA. These complexes are usually pale in colour as a result of the ${}^6A_{1g}$ ground state and the occurrence of spin-forbidden bands only in the visible.

15.3.1 Aqueous Chemistry

The pale violet hexaquo-ion occurs in the solid state in, for example, iron(III) alums as well as in acidic solutions of iron(III) containing anions of low co-ordinating ability. The acidity of the $[Fe(H_2O)_6]^{3+}$ ion has been considered in detail in section 3.1.2. The very pale hydrates $Fe(ClO_4)_3.10H_2O$, $Fe(NO_3)_3.6H_2O$, and $Fe_2(SO_4)_3.9H_2O$ (as well as others) can be crystallised from aqueous solution. These salts all undergo hydrolysis in water with the formation of a brown colour;

this colour disappears if the solution is acidified with the appropriate noncomplexing acid, the hexaquo-ion being re-formed.

In the presence of co-ordinating anions, substitution at the hexaquo-ion occurs. Thus, in hydrochloric acid various chloro-complexes are formed ranging from $[FeCl(H_2O)_5]^{2+}$ to $FeCl_4{}^{2-}$. With thiocyanate the complex ion $[Fe(SCN)(H_2O)_5]^{2+}$ is produced; its well-known blood-red colour is utilised in the qualitative detection of iron(III); however, if hydrous iron(III) oxide is dissolved in aqueous thiocyanic acid containing an alkali metal cation, salts of the $[Fe(SCN)_6]^{3-}$ ion can be isolated. Cyanide ion gives the species $[Fe(CN)_5(H_2O)]^{2-}$ and $[Fe(CN)_6]^{3-}$. Salts of the latter ion, the hexacyanoferrates(III) or ferricyanides, are most usually prepared by oxidation of the $[Fe(CN)_6]^{4-}$ salts. Potassium hexacyanoferrate(III) forms red poisonous crystals having $\mu_{eff} = 2.25$ B.M. at room temperature. In hot dilute sulphuric acid, hydrogen cyanide is evolved; the concentrated acid liberates carbon monoxide.

Very stable anionic complexes are formed by oxo-anions. Thus iron(III) chloride solutions (coloured yellow because of charge-transfer absorptions) are decolorised by the addition of phosphoric acid; the stability and colourless nature of the iron(III) phosphate complexes is used in the Zimmermann–Reinhardt method for estimating iron(II) with permanganate in the presence of chloride ions. The exact nature of the complexes is a matter of some dispute; in equimolar mixtures of $FeCl_3$ and H_3PO_4 the cationic species $[Fe(HPO_4).aq]^+$ is important, whereas solutions of iron(III) phosphate in phosphoric acid contain the anions $[Fe(PO_4)_3]^{6-}$ and $[Fe(HPO_4)_3]^{3-}$. The green tris(oxalato)-complexes containing the $[Fe(C_2O_4)_3]^{3-}$ ion are readily prepared by the addition of an excess of an alkali metal oxalate to an iron(III) salt solution. The ion can be resolved into its optical isomers but these racemise in less than one hour at room temperature. Citrate and tartrate complexes are similar; their formation is often used to prevent the precipitation of iron(III) in alkaline solution. EDTA (H_4Y) gives the seven-co-ordinate complex $[FeY(H_2O)]^-$ which in the rubidium salt has the roughly pentagonal bipyramidal arrangement of the donor atoms about the metal.

Stable neutral iron(III) complexes are formed by chelating oxygen and sulphur ligands. The red acetylacetonate $Fe(acac)_3$ is prepared by the aqueous reaction of iron(III) chloride with acetylacetone in the presence of a base (for example sodium acetate). It is high-spin, a nonelectrolyte in water, and has a fairly regular octahedral arrangement of oxygen atoms about iron. The dialkyldithiocarbamates $Fe(S_2CNR_2)_3$ are similarly prepared from aqueous iron(III) chloride and the sodium salt of the dialkyldithiocarbamate. They have interesting magnetic properties (see section 7.3.1), with a thermal equilibrium between high and low-spin states. When treated with concentrated hydrohalic acids the black compounds $FeX(S_2CNR_2)_2$ are formed. These constitute examples of five-co-ordinate iron(III); they have the square pyramidal structure (figure 15.1) with the iron atom 63 pm above the plane of the four sulphur atoms. They have magnetic moments around 3.9–4.0 B.M. corresponding to the three unpaired electrons (and no orbital contribution) expected for this stereochemistry.

Cationic complexes containing unidentate nitrogen donors are unstable in aqueous solution. The hexammines $[Fe(NH_3)_6]X_3$ are formed in anhydrous ammonia but are decomposed in water, the liberated ammonia enhancing the hydrolysis of

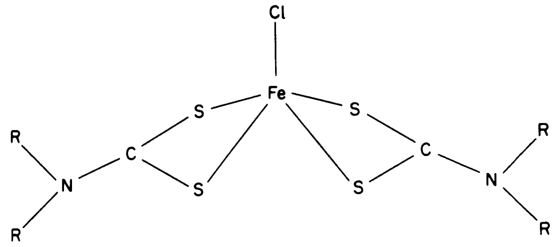


Figure 15.1 Chlorobis-(N,N-dialkyldithiocarbamato)iron(III)

the aquo-ion, so FeO(OH) . aq precipitates. Chelating ligands form water-stable complexes such as $[Fe(bipy)_3]^{3+}$ and $[Fe(phen)_3]^{3+}$; these strong-field ligands form low-spin complexes that are fairly inert to ligand substitution reactions. Oxygen donors form some stable cationic species, for example $Fe[OC(NH_2)_2]_6{}^{2+}$ and $[Fe_3O(OCOR)_6(H_2O)_3]^+$.

15.3.2 Simple Compounds

Iron(III) *oxides and hydroxides.* Treatment of aqueous iron(III) solutions with alkali leads to the precipitation of the red-brown hydrous iron(III) oxide. The hydroxide $Fe(OH)_3$ is not known, and this precipitate is believed to be best formulated as FeO(OH). On ignition above 200° the red-brown α-Fe_2O_3 is formed. This oxide occurs in nature as haematite; it is used in red pigments and as a polishing agent in rouge. It is paramagnetic and has the corundum (Al_2O_3) structure. A second form of the oxide, γ-Fe_2O_3, is obtained by careful oxidation of Fe_3O_4 or by heating lepidocrocite γ-FeO(OH); it is ferromagnetic and has a spinel-like structure with the iron atoms distributed randomly over the tetrahedral and octahedral sites.

The black Fe_3O_4 is a mixed iron(II, III) oxide occurring naturally as magnetite. It is strongly ferromagnetic and is oxidised to Fe_2O_3 on heating in air.

Iron(III) *halides.* Only FeF_3, $FeCl_3$, and $FeBr_3$ are known in the solid state; the iodine–iron reaction produces merely FeI_2. Even in aqueous solution, iron(III) oxidises iodide ions quantitatively to iodine. The brown-black $FeBr_3$ is difficult to obtain pure because it decomposes into $FeBr_2$ and bromine at temperatures only slightly in excess of those required for its preparation (200°). Aqueous solutions of $FeBr_3$ decompose on boiling, with evolution of bromine.

The black crystalline $FeCl_3$ has a semicovalent layer structure in which each iron atom is octahedrally surrounded by chlorines. In the vapour phase at 400°, Fe_2Cl_6 dimers occur, with tetrahedral co-ordination around iron. When heated in a vacuum to above 500°, chlorine is evolved and $FeCl_2$ formed. The reaction with Fe_2O_3 at 350° in a sealed tube produces the little-studied oxide chloride FeOCl. Iron(III) chloride fumes with hydrolysis in moist air and is very soluble in water. This solution is strongly acidic; crystallisation of the solution gives the yellow-brown 'hexahydrate' which has the structure *trans*-$[FeCl_2(H_2O)_4]Cl.2H_2O$. Iron(III) chloride reacts with a wide range of organic ligands to produce what appear to be addition compounds. Such compounds are formed, for example, by alcohols, ethers, aldehydes, ketones, and amines. The structures of many of these compounds are unknown; some which appear to be adducts have been shown to contain ionic species, for example $FeCl_3$ (DMSO)$_2$ and $Fe(NO_3)_3.N_2O_4$ in figure 15.2. With phenols, iron(III) chloride usually forms charge-transfer complexes but in some instances the phenol is oxidised to a coloured derivative; for example, β-naphthol gives β-dinaphthol. As well as adduct formation, iron(III) chloride undergoes redox and substitution reactions with ligands, examples of which are to be found in figure 15.2.

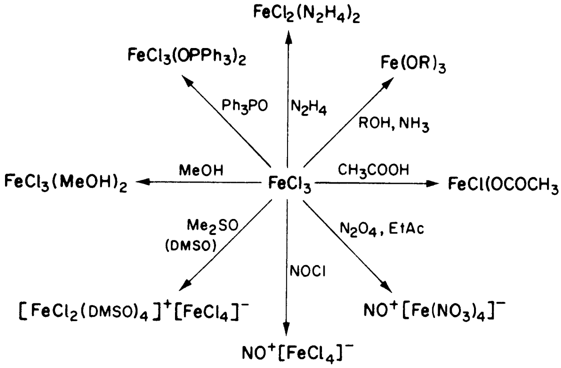


Figure 15.2 Some reactions of $FeCl_3$

Complex halides of iron(III) resemble the simple halides in their thermal stability. Thus no complex iodides are known, and the complex bromides that have been reported are thermally unstable with respect to evolution of bromine and formation of iron(II). The fluoride and chloride complexes are of three principal types: $M^I_3FeX_6$, $M^I_2FeX_5(H_2O)$, and M^IFeX_4. While it is doubtful if $FeCl_6{}^{3-}$ exists in solution, the pale yellow hexachloroferrates can be isolated from solution by using large cations having the same charge as the anion, for example $[Co(NH_3)_6]^{3+}$. The yellow tetrachloroferrates(III) are more readily obtained with a variety of cations and from a variety of solvents. The $FeCl_4{}^-$ ion is extractable from hydrochloric acid into ether, and this is of use in separations by solvent extraction. The crystal structure determination on $Ph_4As[FeCl_4]$ has confirmed that the $FeCl_4{}^-$ ion is roughly tetrahedral.

15.4 Compounds of Iron(II) (d^6)

The +2 state is in general a reducing state for iron; most iron(II) salts oxidise slowly in air although double salts (with alkali metal or ammonium salts) are more stable. The hydrated salts are pale green, these salts being known with all the common anions. They are often isomorphous with the same salts of other transition metals in the +2 oxidation state. The solubilities of iron(II) salts also resemble those of other M^{2+} ions in the first-row transition elements, that is the halides, nitrate, sulphate, and perchlorate are soluble, while the hydroxide, carbonate, phosphate, and oxalate are relatively insoluble.

15.4.1 *Aqueous Chemistry*

In the absence of other ligands, solutions of iron(II) in water contain the pale green $[Fe(H_2O)_6]^{2+}$ ion. This ion is present in many salt hydrates in the solid state, for example $FeSO_4.7H_2O$ and $(NH_4)_2SO_4.FeSO_4.6H_2O$. There is considerable distortion from octahedral symmetry for this ion; in iron(II) ammonium sulphate hexahydrate, for example, the tetragonal and slight rhombic distortions give $Fe{-}OH_2$ distances of 214, 188, and 185 pm. The aquo-ion is barely acidic, so $FeCO_3$ and $Fe(OH)_2$ can be prepared as discrete species from aqueous solution. The hydroxide is somewhat soluble in strong caustic soda solution, with the probable formation of $[Fe(OH)_4]^{2-}$ ions.

The dissolution of iron in nonoxidising acids gives Fe^{2+}.aq. This Fe^{2+} state is thermodynamically unstable to atmospheric oxidation

$$Fe^{3+} + e \rightarrow Fe^{2+} \qquad (E^\circ = +0.771\ V)$$

$$O_2 + 4H^+ + 4e \rightarrow 2H_2O \qquad (E^\circ = +1.229\ V)$$

This oxidation occurs only slowly in acid solution. Strong oxidising agents such as H_2O_2 readily oxidise Fe^{2+} in acid solution, the reactions with permanganate and dichromate ions being used in the volumetric estimation of iron. In alkaline solution, $Fe(OH)_2$ precipitates and the Fe^{II}/Fe^{III} potential changes dramatically

$$Fe(OH)_3 + e \rightarrow Fe(OH)_2 + OH^- \qquad (E^\circ = -0.877\ V)$$

The reducing power of iron(II) is thus enormously increased; one of the contributing factors to this greater ease of oxidation is the lower solubility of '$Fe(OH)_3$' compared with that of $Fe(OH)_2$. In alkaline solution therefore oxidation by air is rapid; precipitates of $Fe(OH)_2$ (white when pure) darken rapidly as they oxidise on standing in air.

As well as changes in pH, changes in the ligands have a marked effect on the redox potentials of the Fe^{II}/Fe^{III} system. The Fe^{2+} ion (d^6) is a good π-donor, and it might be expectedly stabilised in combination with π-acceptor ligands such as 2,2′-bipyridyl and 1,10-phenanthroline which have low-lying vacant π* orbitals. The Fe^{3+} ion (d^5) is a poorer π-donor, largely because of its higher charge. The potentials for these low-spin systems are

$$[Fe(bipy)_3]^{3+} + e \rightarrow [Fe(bipy)_3]^{2+} \qquad (E^\circ = +0.96\ V)$$

$$[Fe(phen)_3]^{3+} + e \rightarrow [Fe(phen)_3]^{2+} \qquad (E^\circ = +1.12\ V)$$

The tris-(1,10-phenanthroline)iron(II) sulphate is widely used in volumetric analysis as the indicator *ferroin;* with strong oxidising agents the colour change is quite striking

$$\underset{\text{deep red}}{[Fe(phen)_3]^{2+}} \rightarrow \underset{\text{pale blue}}{[Fe(phen)_3]^{3+}} + e$$

15.4.2 *Some Simple Compounds*

Iron(II) halides. The pale iron(II) halides (FeF_2 white, $FeCl_2$ and $FeBr_2$ pale yellow, FeI_2 grey) do not melt until red heat and are deliquescent in moist air. They crystallise from aqueous solution as hydrates. The tetrahydrate $FeCl_2(H_2O)_4$ which separates from solution above 12.3°, has discrete $FeCl_2(H_2O)_4$ units, and

$FeCl_2.6H_2O$, which crystallises below 12.3°, contains *trans*-$[FeCl_2(H_2O)_4]^+$ units. Nitrogen, phosphorous, and arsenic ligands react with iron(II) halides to give complexes of three general types; FeX_2L_2 (often tetrahedral), FeX_2L_4 (tetragonal), and $FeL_6{}^{2+}$ (octahedral). Some of these, as well as examples of those formed by other ligands, are illustrated in figure 15.3.

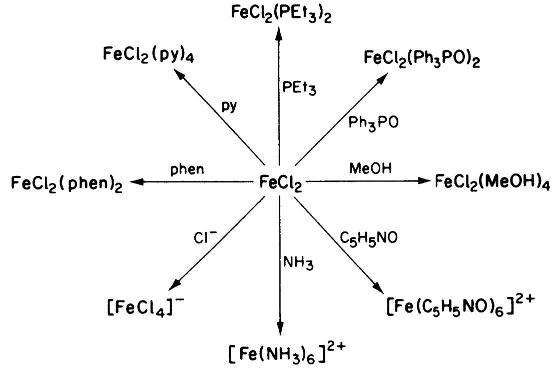


Figure 15.3 Some reactions of $FeCl_2$

Iron(II) *sulphides.* The brassy-yellow FeS_2 occurs in two forms, *pyrites* and *marcasite.* Pyrites can be regarded as having a rock-salt like arrangement of Fe^{2+} and $S_2{}^{2-}$ ions. Both sulphides are diamagnetic and thus contain spin-paired Fe^{2+} ($t_{2g}{}^6$). The grey FeS can be prepared directly from the exothermic reaction between the elements, or by reaction of aqueous solutions of iron(II) salts with alkali metal sulphides. It is antiferromagnetic; it finds use in the laboratory preparation of crude hydrogen sulphide.

Iron(II) *sulphate.* The heptahydrate $FeSO_4.7H_2O$ forms green crystals, which are very soluble in water. The white monohydrate and anhydrous $FeSO_4$ can be obtained by thermal dehydration. At red heat decomposition occurs

$$2FeSO_4 \rightarrow Fe_2O_3 + SO_2 + SO_3$$

The double salts (Tutton salts) $M^I{}_2SO_4.FeSO_4.6H_2O$ can be crystallised from solutions containing the alkali metal sulphates. The ammonium salt, commonly known as ferrous ammonium sulphate or Mohr's salt, finds extensive use in volumetric analysis where its greater stability to aerial oxidation both in the solid state and in acid solution is advantageous over the simple salt $FeSO_4.7H_2O$.

15.4.3 Complexes

Cationic complexes. These arise in the substitution reactions of the aquo-ion and in the disproportionation reactions of iron carbonyls in inert solvents

$$[Fe(H_2O)_6]^{2+} + 3en \rightarrow [Fe(en)_3]^{2+} + 6H_2O$$

$$5Fe(CO)_5 + 6py \rightarrow [Fe(py)_6][Fe_4(CO)_{13}]$$

Most of these cations are octahedral but the bidentate ligand 1,8-naphthyridine (figure 15.4) forms the eight-co-ordinate complex $[Fe(LL)_4](ClO_4)_2$. Most of the

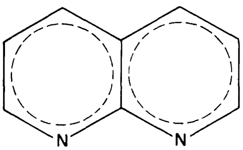


Figure 15.4 1,8-Naphthyridine

octahedral cations are high-spin ($t_{2g}^4\ e_g^2$); the strong-field ligands bipy, phen, and diars give low-spin (t_{2g}^6) diamagnetic $[Fe(LL)_3]^{2+}$ complexes.

Neutral complexes. Examples of these formed by the iron(II) halides have already been given. Several crystalline complex hydrides exist, for example the octahedral *trans*-$FeH_2(diphos)_2$ and *trans*-$FeHCl(diphos)_2$ [diphos = *o*-$C_6H_4(PEt_2)_2$]. These are prepared by the reaction of lithium aluminium hydride on the bis(phosphine)iron(II) halides in tetrahydrofuran. They are sensitive to oxidation but are thermally stable up to their melting points (>230°).

β-Diketones readily form complexes with iron(II) in aqueous solution, especially in the presence of tertiary nitrogen bases (which neutralise the liberated protons). Acetylacetone forms $Fe(acac)_2(py)_2$ and $Fe(acac)_2.1.5H_2O$, which are believed to contain high-spin six-co-ordinate iron(II) ($\mu_{eff} \approx 5.4$ B.M.), while dipivaloylmethane (DPMH) forms tetrahedral $Fe(DPM)_2$, which is high-spin with $\mu_{eff} = 5.0$ B.M.

Perhaps the most important iron complex is haem. Haemoglobin containing the iron in blood consists of haem bound to a protein called globin. Haem (figure 15.5) is an iron(II) complex of porphyrin in which the six-co-ordinate iron atom is bonded to four nitrogen atoms from pyrrole rings in a plane, and to a nitrogen atom in globin perpendicular to this plane. The sixth position is occupied by a water molecule. It is at this position that reversible uptake of oxygen can occur, and this

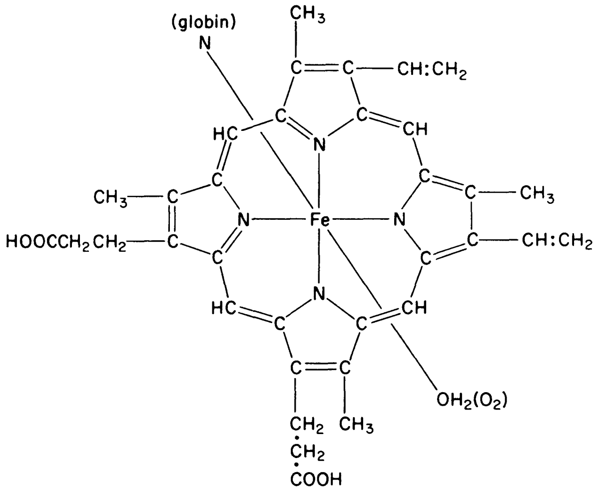


Figure 15.5 Haem

enables the red blood cells to transport oxygen from one part of the body to another. Haem has an even greater affinity for carbon monoxide than for oxygen, and it is the irreversibility of the formation of carboxyhaemoglobin that makes carbon monoxide poisonous.

Anionic complexes. Salts containing the tetrahedral $FeX_4{}^{2-}$ ions can readily be isolated from alcoholic mixtures of iron(II) halides and quaternary ammonium halides. The most important anionic complexes, however, are those with cyanide ions. The octahedral hexacyanoferrate(II) ion is readily formed by the addition of an excess of cyanide ions to an aqueous solution of an iron(II) salt. It is a stable nonpoisonous diamagnetic anion which forms salts with many cations. The alkali metal salts crystallise as hydrates, for example $K_4Fe(CN)_6.3H_2O$. The free acid $H_4Fe(CN)_6$ can be obtained as an etherate by treatment of the potassium salt with a strong acid such as HCl in ether; the ether can be removed in a stream of hydrogen at 80° to leave the acid as white crystals. Many substitution products of the $[Fe(CN)_6]^{4-}$ ion are known, for example $[Fe(CN)_5(H_2O)]^{3-}$ and $[Fe(CN)_5NO]^{2-}$. However, the best-known reaction of the ion is that with an iron(III) salt.

The reaction between $[Fe(CN)_6]^{4-}$ and an excess of Fe^{3+}.aq produces a blue precipitate called *Prussian blue.* Similarly, the reaction between $[Fe(CN)_6]^{3-}$ and Fe^{2+}.aq produces a blue precipitate known as *Turnbull's blue.* These compounds give the same Mössbauer spectrum and X-ray powder diffraction pattern, and are formulated as $Fe_4[Fe(CN)_6]_3$, that is iron(III) hexacyanoferrate(II). *Soluble Prussian blue* $KFe^{III}[Fe^{II}(CN)_6]$ is formed in the reaction between 1:1 molar proportions of Fe^{3+} and $[Fe(CN)_6]^{4-}$. Its electronic and Mössbauer spectra indicate that it contains high-spin iron(III) octahedrally surrounded by six nitrogen atoms and low-spin iron(II) having six carbon atoms as nearest neighbours. The intense colour of the compound is due to intravalence electron transfer (section 6.1.3).

15.5 Compounds of Iron in Low Oxidation States

Iron has a fairly extensive chemistry with π-acceptor ligands such as CO, NO, phosphines, bipyridyl, and bidentate sulphur ligands. We shall concern ourselves here with the carbonyl and nitrosyl complexes; these are the most extensive, and the other complexes in low oxidation states are similar to those discussed previously for other metals.

15.5.1 Iron Carbonyls

Iron forms three well-known carbonyls: $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$. The pentacarbonyl is a yellow liquid insoluble in water but soluble in organic solvents such as benzene. It thus behaves as a covalent monomer and has the trigonal bipyramidal structure. Some of its very extensive chemistry is illustrated in figure 3.2. When solutions of the pentacarbonyl are exposed to sunlight or ultraviolet radiation, dark yellow platelets of the enneacarbonyl $Fe_2(CO)_9$ are formed. The dodecacarbonyl $Fe_3(CO)_{12}$ is obtained from the pentacarbonyl by treatment with aqueous triethylamine to form $[Et_3NH][Fe_3(CO)_{11}H]$ which is then acidified and the carbonyl extracted into petroleum ether. $Fe_3(CO)_{12}$ forms green diamagnetic crystals that decompose at 140°.

In $Fe_2(CO)_9$ (figure 15.6) the iron atoms are surrounded in an approximately octahedral fashion by carbon monoxide molecules. Since the compound is diamagnetic it must contain a metal–metal bond. The Mössbauer spectrum of $Fe_3(CO)_{12}$ shows the presence of two types of iron atom; two of these atoms show quadrupole splitting and have isomer shifts similar to those in $Fe_2(CO)_9$ while the third iron atom shows little splitting, as would be expected for an octahedral environment. Such a structure (figure 15.7) is confirmed by the X-ray data. The anion $[Fe_3(CO)_{11}H]^-$ has a similar structure in which one of the bridging carbonyl groups is replaced by a bridging hydrogen atom.

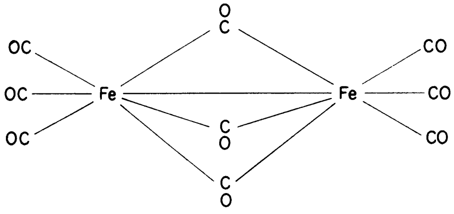


Figure 15.6 The structure of $Fe_2(CO)_9$

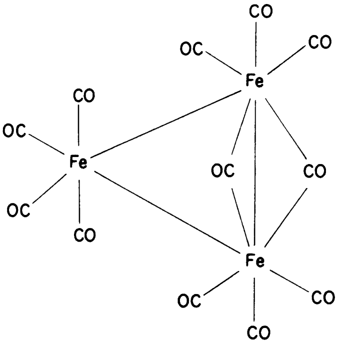


Figure 15.7 The structure of $Fe_3(CO)_{12}$

Carbonylate anions containing iron(–I) and iron(–II) are obtained in the reactions of bases with these carbonyls. For example, the reaction of aqueous alkali with $Fe(CO)_5$ gives yellow solutions containing the $[Fe(CO)_3H]^-$ ion; in the presence of air or oxidising agents, oxidation to the anions $[Fe_2(CO)_8]^{2-}$ and $[Fe_3(CO)_{11}]^{2-}$ occurs. The $[Fe(CO)_4]^{2-}$ ion is also formed in these reactions, as well as in disproportionation reactions of $Fe(CO)_5$ with ligands, for example

$$2Fe(CO)_5 + 3en \xrightarrow{145°} [Fe^{II}(en)_3]\,[Fe^{-II}(CO)_4] + 6CO$$

As well as the simple carbonyls, there are a variety of carbonyl halides and hydrides. The $Fe(CO)_4X_2$ (X = Cl, Br, I) compounds are probably octahedral; they are hydrolysed by water with evolution of carbon monoxide. The unstable gaseous hydride $H_2Fe(CO)_4$ is evolved when solutions of $[HFe(CO)_4]^-$ are acidified.

Similarly, polynuclear hydrides such as $H_2Fe(CO)_8$ and $H_2Fe_3(CO)_{11}$ are obtained by acidification of solutions of the polynuclear carbonylate anions.

15.5.2 Nitrogen Monoxide Complexes of Iron

Iron tetranitrosyl $Fe(NO)_4$ is obtained as black crystals when the pentacarbonyl is heated to 45° with nitrogen monoxide in an autoclave. It is an involatile and very reactive substance. Its infrared spectrum shows N–O stretching frequencies at 1810, 1730, and 1140 cm^{-1}, that is in both the NO^+ and NO^- regions, so the structure $Fe(NO^+)_3(NO^-)$ has been suggested for the tetranitrosyl. Nitrosyl halides, for example $Fe(NO)_3Cl$, and nitrosyl carbonyls, for example $Fe(NO)_2(CO)_2$, are also known.

Perhaps the best-known iron–nitrosyl compounds are the 'brown-ring compounds' observed in the qualitative test for the nitrate ion. Iron(II) sulphate solution absorbs nitrogen monoxide reversibly up to Fe : NO = 1 : 1. The magnetic susceptibility of these solutions indicates that the complex has three unpaired electrons, while the infrared spectra show absorptions in the 1730–1850 cm^{-1} region, that is characteristic of NO^+. The complex cation present is thus best formulated as $[Fe^I(NO)(H_2O)_5]^{2+}$ in which NO donates three electrons.

The nitrosylpentacyanoferrate(II) or nitroprusside ion $[Fe(NO)(CN)_5]^{2-}$ is also a well-known species. It arises in the reactions of nitric acid with $[Fe(CN)_6]^{3-}$ or $[Fe(CN)_4]^{4-}$ ions, for example

$$[Fe(CN)_6]^{4-} + 4H^+ + NO_3^- \rightarrow [Fe(NO)(CN)_5]^{2-} + CO_2 + NH_4^+$$

The red sodium salt $Na_2[Fe(NO)(CN)_5].2H_2O$ is diamagnetic, with the N–O stretching frequency at 1944 cm^{-1}. It is therefore formulated as containing Fe^{II} and NO^+.

15.6 Organometallic Compounds of Iron

Iron has played a very important role in the development of organometallic chemistry. Following the pioneering work of Reppe in 1949, the reaction of iron pentacarbonyl with acetylenes is now known to lead to an enormous variety of organic and organometallic compounds. The field of transition-metal organometallic compounds containing π-bonded aromatic rings began, however, in 1951 when two different groups of workers somewhat accidentally discovered ferrocene, bis-(π-cyclopentadienyl)iron $Fe(\pi\text{-}C_5H_5)_2$.

Ferrocene is an orange crystalline air-stable solid; it is insoluble in water but soluble in organic solvents. It is readily prepared by the reaction of sodium cyclopentadienide with iron(II) chloride in tetrahydrofuran

$$2NaC_5H_5 + FeCl_2 \rightarrow Fe(C_5H_5)_2 + 2NaCl$$

X-ray diffraction studies have established that in ferrocene the iron atom is sandwiched between two cyclopentadienyl rings, these rings being staggered relative to each other (figure 15.8). The bonding between the $C_5H_5^-$ rings and the Fe^{2+} ion consists principally of a π bond formed by overlap of the d_{xz} and d_{yz} orbitals on the metal with the π molecular orbitals on the rings that have the correct symmetry for overlap.

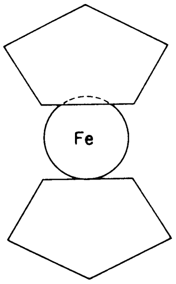
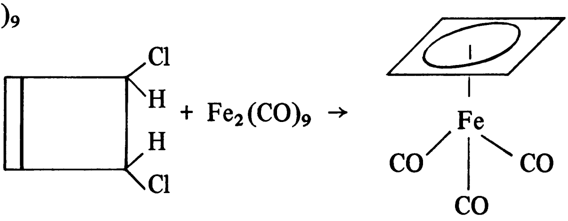


Figure 15.8 Ferrocene

The reactions of ferrocene are largely those of the aromatic rings; a very extensive organic chemistry of ferrocene is now known. Thus it undergoes Friedel–Crafts acylation and alkylation reactions but does not undergo the Diels–Alder reaction characteristically shown by conjugated dienes. Nitration and halogenation of the rings cannot be carried out because of oxidation to the ferricenium ion $Fe(C_5H_5)_2^+$.

Iron also forms arene complexes, the bis(benzene)iron(II) cation $[Fe(C_6H_6)_2]^{2+}$ being isoelectronic with ferrocene. Most interesting is the formation of cyclobutadiene complexes when the ligand itself is unstable. Much organic chemistry has been carried out on cyclobutadiene; it is stabilised in bonding, for example, to an $Fe(CO)_3$ group. Butadieneiron tricarbonyl is a pale yellow crystalline solid prepared by the reaction of *cis*- or *trans*-3,4-dichlorocyclobutene with $Fe_2(CO)_9$



16 Cobalt

16.1 The Element

Cobalt compounds have been used in coloured glass for at least 4000 years but the metal has been produced industrially only during this century. It is a widely distributed but relatively uncommon element in the earth's crust. It occurs biologically in vitamin B_{12}, which contains Co^{3+} bonded octahedrally to five nitrogen atoms (four from pyrroline rings and one from a benzimidazole ring) and the carbon atom of a CN^- group. The industrial extraction of the metal is usually an ancillary process to the extraction of other metals such as copper and lead.

Cobalt ($4s^2$ $3d^7$) stands between iron and nickel in group VIII and above rhodium and iridium. It shows high oxidation states even less willingly than iron, +3 being the highest oxidation state of any significance. Cobalt resembles iron and nickel in appearance, and like these metals it is ferromagnetic; it finds uses in a variety of steels designed to have specific magnetic properties. The massive metal is oxidised in air above 300° with the formation of Co_3O_4 and CoO. Steam forms CoO at red heat. Many nonmetals react when heated with cobalt; fluorine gives CoF_3, the other halogens giving CoX_2. Cobalt is more resistant than iron to attack by mineral acids, and it is not attacked by dilute alkalis.

16.2 Compounds of Cobalt(III) (d^6)

The important oxidation states of cobalt in aqueous solution are +3 and +2. The nature of the ligand bonded to cobalt has a dramatic effect on the stabilities of these oxidation states. Simple compounds of cobalt(III) are strong oxidising agents, and in water the $[Co(H_2O)_6]^{3+}$ ion is a very powerful oxidising agent; it oxidises water to oxygen

$$[Co(H_2O)_6]^{3+} + e \rightarrow [Co(H_2O)_6]^{2+} \qquad (E^\circ = +1.84\ V)$$

However, other ligands, for example ammonia, stabilise the cobalt(III) state to varying extents in aqueous solution

$$[Co(NH_3)_6]^{3+} + e \rightarrow [Co(NH_3)_6]^{2+} \qquad (E^\circ = +0.11\ V)$$

With some ligands, for example CN^-, the stabilisation of the +3 state is so great that the cobalt(II) complex reduces water to hydrogen

$$[Co(CN)_6]^{3-} + e \rightarrow [Co(CN)_5]^{3-} + CN^- \quad (E^\circ = -0.8\ V)$$

Further, the cobalt(II)–cyanide complex will even react with hydrogen to produce what is regarded as a cobalt(III) complex

$$2[Co(CN)_5]^{3-} + H_2 \rightarrow 2[Co(CN)_5H]^{3-}$$

There is thus no simple aqueous chemistry of cobalt(III) but there is an extensive range of complexes. For cobalt(II) the reverse is true; simple salts and aquo-complexes are stable in aqueous solution but the addition of other ligands makes for more facile conversion into the +3 state.

16.2.1 Simple Compounds

Cobalt(III) *fluoride.* CoF_3 is a light-brown powder which reacts violently with water with evolution of oxygen. It is obtained by the action of fluorine on the heated cobalt(II) halides CoF_2 or $CoCl_2$. It is a useful fluorinating agent; for example, it converts hydrocarbons into fluorocarbons

$$4CoF_3 + -CH_2- \rightarrow -CF_2- + 4CoF_2 + 2HF$$

With N_2O_5 the green crystalline nitrate $Co(NO_3)_3$ is formed.

A blue hydrate $CoF_3.3.5H_2O$ has been prepared by electrolytic oxidation of CoF_2 in 40 per cent HF. It oxidises water like the simple fluoride.

The other cobalt(III) halides are unknown, cobalt(III) being too strong an oxidising agent to exist solely with chloride, bromide, or iodide ions.

Cobalt(III) *oxide.* The oxidation of $Co(OH)_2$ in alkaline media gives a brown precipitate of uncertain structure; it is best written as Co_2O_3.aq. When this is dried at 150° the composition $Co_2O_3.H_2O$ is formed, which is probably CoO(OH). On further heating to 300°, oxygen begins to be evolved (as well as water) and black Co_3O_4 is formed. The dark-brown CoO(OH) is formed when $Co(OH)_2$ is heated in air at 100°; it has a layer lattice in which each cobalt is surrounded octahedrally by oxygen atoms.

Cobalt(III) *sulphate.* This is the most readily available cobalt(III) salt. The hydrate $Co_2(SO_4)_3.18H_2O$ is prepared by oxidation of cobalt(II) sulphate in 8N H_2SO_4 either electrolytically or with ozone or fluorine. It is stable in the dry state but liberates oxygen from water. Some alums, for example $KCo(SO_4)_2.12H_2O$, can be crystallised from sulphuric acid solutions; they, like the hydrated sulphate, are believed to contain the $[Co(H_2O)_6]^{3+}$ ion. As well as being acidic (hydrolysis to $[Co(OH)(H_2O)_5]^{2+}$ occurs in 0.1M perchloric acid), this ion is a strong oxidising agent. Therefore no salts of organic anions such as formate, tartrate, and citrate can be obtained since these anions are oxidised to carbon dioxide and water by $[Co(H_2O)_6]^{3+}$. However, cobalt(III) acetate is believed to be present in dilute acetic acid solutions of cobalt(II) acetate that have been oxidised with ozone.

16.2.2 Complex Compounds

We discussed in chapter 1 the part played by cobalt(III) complexes in the historical development of co-ordination chemistry. The fact that cobalt(III) forms an enormous number of octahedral complexes having the inert $t_{2g}{}^6$ configuration has resulted in these being used extensively for rate and mechanistic studies on octahedral substitution reactions (chapter 8).

Cobalt(III) has a great affinity for nitrogen donors especially ammonia, amines, nitro $-NO_2$, and $-NCS$ groups. Other ligands such as water molecules, halide, hydroxide, or carbonate ions may also be present in these complexes with nitrogen donors, and various stereoisomers can often be isolated from such mixed ligand systems. The preparation of these complexes usually involves the addition of the nitrogen donor to a cobalt(II) solution followed by oxidation with air or hydrogen peroxide. Perhaps the most famous of these compounds are the cobaltammines. The orange hexammines, containing the $[Co(NH_3)_6]^{3+}$ ion, are obtained from solutions of cobalt(II) salts in aqueous ammonia in the presence of added ammonium salts containing the required anion of the cobaltammine, for example

$$4[Co(H_2O)_6]Cl_2 + 4NH_4Cl + 20NH_3 + O_2 \rightarrow 4[Co(NH_3)_6]Cl_3 + 26H_2O$$

The hexammines are formed preferentially in the presence of a charcoal catalyst and by using air as oxidant. When charcoal is absent and oxidation is carried out by hydrogen peroxide, the aquopentammine species predominates. Treatment of this with concentrated hydrochloric acid gives the red chloropentamminecobalt(III) chloride

$$2[Co(H_2O)_6]Cl_2 + 2NH_4Cl + 8NH_3 + H_2O_2 \rightarrow 2[Co(NH_3)_5(H_2O)]Cl_3 + 12H_2O$$

$$[Co(NH_3)_5(H_2O)]Cl_3 \rightarrow [Co(NH_3)_5Cl]Cl_2 + H_2O$$

Other cobaltammines can be prepared similarly, as well as by ligand exchange with these cobaltammines; thus, for example, the chloropentammine reacts with hot aqueous ethylenediamine to give $[Co(en)_3]Cl_3$.

In addition to these mononuclear ammines, the uptake of molecular oxygen by cobalt(II)–ammonia solutions leads to polynuclear cobaltammines containing the peroxo –O–O– bridge. Two types of these complexes exist. There are diamagnetic, red or brown complexes containing the unit $[Co^{III} - O_2 - Co^{III}]$ as in, for example, $[(NH_3)_5Co{-}O{-}O{-}Co(NH_3)_5]^{4+}$. There are also the paramagnetic, green complexes, for example $[(NH_3)_5Co(O_2)Co(NH_3)_5]^{5+}$, which is believed to contain two octahedrally co-ordinated cobalt(III) ions bridged by the superoxide (O_2^-) ion. These compounds arise in the one-electron oxidation of the diamagnetic species.

The most important neutral cobalt(III) complexes of the $[CoL_3]$ type are those with β-diketones. The green acetylacetonate $Co(acac)_3$ is insoluble in water but soluble, and monomeric, in organic solvents. When it is reduced by aluminium alkyls in the presence of triphenylphosphine and under a nitrogen atmosphere, the orange molecular nitrogen complex $CoH(N_2)(PPh_3)_3$ is produced. This has an approximately trigonal bipyramidal structure with the Co atom slightly above the plane of the three phosphorus atoms. One of the apical positions is occupied by the N–N group, the atoms Co–N–N being almost collinear; hydrogen occupies the other apical position.

The more important anionic cobalt(III) complexes are those with F^-, CN^-, and NO_2^- as ligands. The fluorides $M^I_3CoF_6$ are obtained as blue solids from hydrofluoric acid solutions of CoF_3 and alkali metal fluorides. They constitute rare examples of high-spin cobalt(III) complexes $(t_{2g}^4\, e_g^2)$, having magnetic moments around 5.4 B.M.; their crystal structures contain octahedral CoF_6^{3-} units. The electronic spectra of these compounds show two bands around 14 500 and 11 800 cm^{-1} corresponding to the Jahn–Teller states of the $^5T_{2g} \rightarrow {}^5E_g$ transition.

The yellow cyanides $[Co(CN)_6]^{3-}$ are diamagnetic and low-spin. They give precipitates of hexacyanocobaltates(III) with heavy metals, and are generally inert to attack by reagents such as chlorine, hydrochloric acid, and alkalis. The well-known orange hexanitrocobaltate(III) ion, as found in 'sodium cobaltinitrite', is also low-spin and is used to precipitate potassium ions from aqueous solution as $K_3Co(NO_2)_6$. The sodium salt is prepared by blowing air through an aqueous mixture of a cobalt(II) salt and an excess of sodium nitrite in the presence of acetic acid

$$2[Co(H_2O)_6]^{2+} + 12NO_2^- + 2CH_3COOH + \tfrac{1}{2}O_2 \rightarrow 2[Co(NO_2)_6]^{3-} + 2CH_3COO^- + 13H_2O$$

It is precipitated by the addition of ethanol. The nitro groups are bound to cobalt via nitrogen and surround the cobalt octahedrally. In acid solution the $[Co(NO_2)_6]^{3-}$ ion is decomposed with the formation of cobalt(II) salts.

16.3 Compounds of Cobalt(II) (d^7)

16.3.1 Aqueous Chemistry

Like iron(II), cobalt(II) shows an extensive range of hydrated salts, which can be crystallised from aqueous solution. The pink aquo-ion $[Co(H_2O)_6]^{2+}$ occurs (together with small amounts of $[Co(H_2O)_4]^{2+}$) in solutions which are free of complexing anions, as well as in several solid salts, for example $Co(NO_3)_2.6H_2O$, $CoSO_4.7H_2O$, and $Co(ClO_4)_2.6H_2O$. The aquo-ion is barely acidic, and the carbonate can be precipitated as $CoCO_3.6H_2O$ by alkali metal carbonate solutions, so long as a pressure of carbon dioxide is maintained over the solution. In the absence of added ligands the aquo-ion is not a strong reducing agent like $[Fe(H_2O)_6]^{2+}$.

16.3.2 Simple Salts

Cobalt(II) halides. The pink CoF_2 is conveniently prepared by heating the double salt $CoF_2.2NH_4F$; ammonium fluoride sublimes. The blue $CoCl_2$, green $CoBr_2$, and blue-black CoI_2 are obtained by direct combination of the elements or by dehydration of their hydrates.

Crystalline $CoCl_2$ contains octahedrally co-ordinated cobalt; in the pink hydrate $CoCl_2.6H_2O$ each cobalt is surrounded by four water molecules at the corners of a distorted square with two chloride ions making up the distorted octahedron. $CoCl_2$ is very soluble in water, giving a pink-red solution, and in ethanol giving a blue solution. The addition of ligands to these solutions gives complexes that either precipitate directly or can be crystallised; some of these are mentioned under cobalt(II) complexes.

Cobalt(II) hydroxide. The addition of ammonia or alkali metal hydroxides to cobalt(II) solutions results in the precipitation of either the pink or the blue form of $Co(OH)_2$. The pink form is the more stable and is formed when a suspension of the blue form is warmed or allowed to stand. $Co(OH)_2$ is amphoteric; it dissolves in an excess of alkali to form blue solutions of the $[Co(OH)_4]^{2-}$ ion. In slightly alkaline solution $Co(OH)_2$ suspensions are rapidly oxidised by air to brown $CoO(OH)$. An excess of aqueous ammonia converts $Co(OH)_2$ into cobalt(II) ammines such as $[Co(NH_3)_6]^{2+}$ which again are rapidly oxidised by air, to the cobaltammines.

Solutions of $Co(OH)_2$ in aqueous acids give solutions of cobalt(II) salts which can be crystallised as hydrates. These are usually red or pink, containing octahedrally co-ordinated cobalt, often as the hexaquo-ion.

16.3.3 Complexes

Complexes of cobalt(II) are very numerous. They fall into two general groups; there are the pink or red basically octahedral complexes, and the intensely blue basically tetrahedral complexes. Cobalt(II) forms more tetrahedral complexes than any other transition metal ion (see the CFSE argument in section 5.5.5). In aqueous solution the equilibrium

$$\underset{\text{pale pink; octahedral}}{[Co(H_2O)_6]^{2+}} \underset{H_2O}{\overset{Cl^-}{\rightleftharpoons}} \underset{\text{intensely blue; tetrahedral}}{[CoCl_4]^{2-}}$$

has been of historical importance in our understanding of the curious problem of the formation of pink and blue compounds of cobalt(II). Donnan and Bassett in 1902 correctly identified the blue species as anionic, and even considered $CoCl_4{}^{2-}$ as a likely species. The connection between colour and stereochemistry is of much more recent origin. However, a word of warning is necessary. While the majority of cobalt(II) complexes fall within the categories pink–octahedral and blue–tetrahedral, there are many that have neither of these stereochemistries, and some for which the colours are reversed. We saw, for example, that anhydrous $CoCl_2$ is blue yet contains octahedrally co-ordinated cobalt(II).

Octahedral complexes of cobalt(II) may be either high-spin $t_{2g}{}^5\ e_g{}^2$ or low-spin $t_{2g}{}^6\ e_g{}^1$. In fact, rather high values of the ligand-field splitting parameter *Dq* are required to cause spin pairing, so only a few low-spin octahedral complexes occur (that is with the strongest ligand fields). Tetrahedral complexes are high-spin with the $e^4\ t_2{}^3$ configuration.

Cationic complexes. Anhydrous cobalt(II) salts react with ammonia to form ammines, for example $CoX_2.6NH_3$ (X = Cl, Br, I, ClO_4, BF_4, etc), which contain the octahedral $[Co(NH_3)_6]^{2+}$ ion. These ammines can be prepared in aqueous ammonia but they are readily oxidised in this medium; the $[Co(NH_3)_6]^{2+}$ ion is decomposed in pure water. Other octahedral cations are formed in the reactions of cobalt(II) salts with bases, for example $[Co(N_2H_4)_6]^{2+}$, $[Co(en)_3]^{2+}$, and in the disproportionation reactions of cobalt carbonyls, such as

$$3Co_2(CO)_8 + 12MeNH_2 \rightarrow 2[Co(MeNH_2)_6][Co(CO)_4]_2 + 8CO$$

Sometimes auto-complex formation occurs when a cobalt(II) salt is dissolved in a donor solvent. Two examples of this are

$$2CoCl_2 + 6Me_2SO \rightarrow [Co(OSMe_2)_6]^{2+} + [CoCl_4]^{2-}$$

$$2CoI_2 + 6MeCN \rightarrow [Co(NCMe)_6]^{2+} + [CoI_4]^{2-}$$

Some tetrahedral cationic species are known, for example in the blue $[Co(OAsPh_3)_4]I_2$ and $Co[SC(NH_2)_2]_4(ClO_4)_2$.

Neutral complexes. The reactions of cobalt(II) salts with ligand molecules give rise to a very large number of complexes; the principal types can be illustrated by the formulae CoX_2L, CoX_2L_2, and CoX_2L_4, where X is a univalent anion. Because of the small stability difference between the octahedral and tetrahedral stereochemistries for cobalt(II), it frequently happens that a given salt plus ligand combination gives complexes of both stereochemistries, and sometimes these exist together in equilibrium. Complexes of pyridine have been extensively studied and serve to illustrate these points.

Cobalt(II) chloride forms violet and blue forms of the complex $CoCl_2(py)_2$. The violet form is stable at room temperature; it contains octahedrally co-ordinated cobalt in a polymeric chlorine-bridged structure. The blue form is metastable at room temperature and has a monomeric tetrahedral structure. The reactions of pyridine with $CoBr_2$ and CoI_2 result in the tetrahedral $CoX_2(py)_2$ species only, while $Co(SCN)_2$ and $Co(SeCN)_2$ form only the octahedral $CoX_2(py)_2$ complexes. However, when dissolved in organic solvents, all these complexes give tetrahedral species; with added pyridine a tetrahedral–octahedral equilibrium occurs

$$CoX_2(py)_2 + 2py \rightleftharpoons CoX_2(py)_4$$

In a few cases complexes that do not have even approximately tetrahedral or octahedral stereochemistry arise. In the purple $Co(NO_3)_2(Me_3PO)_2$, for example, the nitrate ions are bidentate and the cobalt is six-co-ordinate in a highly irregular structure. High-spin five-co-ordinate complexes are formed by a few ligands, for example $NH(CH_2CH_2NH_2)_2$(den) which gives CoX_2–(den) complexes with cobalt(II) halides. Square planar complexes are formed by several bidentate anions such as dimethylglyoximate and similar ions.

Anionic complexes. The solid complex halides $M^I_2CoX_4$(X = Cl, Br, I) are readily prepared from aqueous or (for organic base cations) alcoholic solutions of M^IX and CoX_2. The $[CoCl_4]^{2-}$ ion is tetrahedral with some angular distortion the extent of which varies with the cation present. Hydrochloric acid solutions of $CoCl_2$ contain $[Co(H_2O)_6]^{2+}$ and $[CoCl(H_2O)_5]^+$ ions when the acid concentration is below 3M; above 8M the principally occurring species are $[CoCl_3(H_2O)]^-$ and $[CoCl_4]^{2-}$. Complex thiocyanates resemble the complex halides. The tetrahedral $[Co(NCS)_4]^{2-}$ ion is almost quantitatively precipitated as the mercury salt $HgCo(NCS)_4$ by the addition of a solution of a mercury(II) salt to a solution containing cobalt(II) and an excess of thiocyanate ions. The blue crystalline salt is used as a calibrant in the Gouy method for the determination of magnetic susceptibility. In the tetranitratocobaltate(II) $(Ph_4As)_2[Co(NO_3)_4]$, the cobalt atom is eight-co-ordinate with bidentate nitrate groups.

When cobalt(II) cyanide dissolves in aqueous potassium cyanide, an olive-green solution is formed which is rapidly oxidised by air. The addition of ethanol precipitates the violet $K_6[Co_2(CN)_{10}].4H_2O$, which is diamagnetic and probably has the cobalt–cobalt bonded structure $[(NC)_5Co{-}Co(CN)_5]^{6-}$ in the anion. The green solution (which contains either $[Co(CN)_5]^{3-}$ or $[Co(CN)_5(H_2O)]^{3-}$) absorbs molecular hydrogen to form $[Co(CN)_5H]^{3-}$ ions. This activation of molecular hydrogen has been useful in a variety of reduction processes. Thus the $Co(CN)_2$–KCN solutions are homogeneous catalysts for the hydrogenation of unsaturated organic compounds; for example, styrene is reduced to ethylbenzene and benzil to benzoin. When oxygen is passed through the $K_3Co(CN)_5$ solution, the peroxo-anion $[(CN)_5Co^{III}OOCo^{III}(CN)_5]^{6-}$ is formed; this diamagnetic anion is oxidised by bromine in alkaline solution to the red paramagnetic $[(CN)_5CoOOCo(CN)_5]^{5-}$ ion. Other molecules such as SO_2, $SnCl_2$, C_2F_4, and

C_2H_2 also give insertion products of the type $[(CN)_5CoSO_2Co(CN)_5]^{6-}$ in their reactions with $K_3Co(CN)_5$.

16.4 Compounds of Cobalt in Low Oxidation States

16.4.1 Cobalt Carbonyls

The simple carbonyls of cobalt are $Co_2(CO)_8$, $Co_4(CO)_{12}$, and $Co_6(CO)_{16}$. Dicobalt octacarbonyl is a brown diamagnetic solid having two bridging CO groups and a cobalt–cobalt bond (figure 16.1). Tetracobalt dodecacarbonyl is a black solid having the structure shown in figure 16.2. It consists of a tetrahedron of cobalt atoms three of which are bonded to two terminal CO and two bridging CO groups while the third is bonded to three terminal CO groups and the other three cobalt atoms.

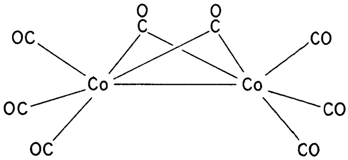


Figure 16.1 Dicobalt octacarbonyl

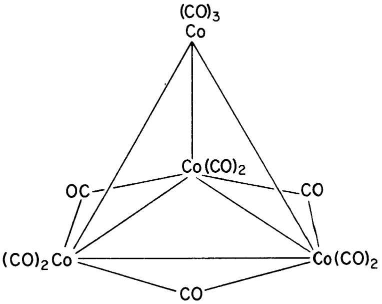


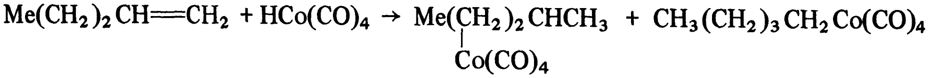
Figure 16.2 Tetracobalt dodecacarbonyl

All three carbonyls are air-sensitive. They undergo both substitution and disproportionation reactions with bases, for example

$$Co_2(CO)_8 + 2PPh_3 \rightarrow 2[Co(CO)_3(PPh_3)]_2 + 2CO$$

$$Co_2(CO)_8 + 12NH_3 \rightarrow 2[Co(NH_3)_6][Co(CO)_4]_2 + 8CO$$

In the dimeric substitution products it is the bridging CO groups that are replaced by the ligands. Carbonylate anions such as $[Co(CO)_4]^-$ are formed in aqueous alkali or by alkali metal reduction of the carbonyls in tetrahydrofuran or liquid ammonia. Acidification of solutions containing the tetracarbonylcobaltate(–I) ion yields the yellow volatile hydride $HCo(CO)_4$. This undergoes interesting reactions with unsaturated organic molecules; for example with olefins σ-bonded alkyl cobalt carbonyls result



$$Me(CH_2)_2CH{=}CH_2 + HCo(CO)_4 \rightarrow Me(\underset{\underset{Co(CO)_4}{|}}{C}H_2)_2CHCH_3 + CH_3(CH_2)_3CH_2Co(CO)_4$$

16.4.2 *Cobalt Nitrosyls*

No simple nitrosyl of cobalt is known. The dark-red diamagnetic $Co(NO)(CO)_3$ is obtained in the reaction of nitrogen monoxide with $Co_2(CO)_8$ at 40°. It is monomeric in the vapour phase and has the tetrahedral structure. In its reactions with donor molecules it is the CO groups that are replaced, illustrating that NO is one of the most powerful π-acceptor molecules. Nitrosyl halides $[Co(NO)_2X]_2$, nitrosyl cyanides $[Co(NO)(CN)_5]^{3-}$, and nitrosyl ammines, for example $[Co(NO)(NH_3)_5]^{2+}$ are also known.

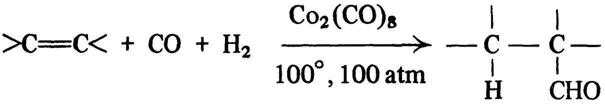
16.4.3 *Other Low Oxidation-state Compounds*

Complex cyanides of cobalt(0), that is $K_4Co(CN)_4$, and cobalt(I), that is $K_3Co(CN)_4$, are formed in the reduction of $K_3Co(CN)_6$ with potassium in liquid ammonia. These compounds are rapidly oxidised in air; $K_4Co(CN)_4$ liberates hydrogen from water. The crystalline cobalt(I) salts $[Co(CNR)_5]X$ are prepared by heating a cobalt(II) salt with the isocyanide in alcohol. The cation has the trigonal bipyramidal structure in $[Co(CNR)_5]ClO_4$. Five-co-ordinate cobalt(I) cations are also formed in an unusual disproportionation reaction of cobalt(II). When heated with strongly π-acidic polycyclic phosphite ligands such as $P(OCH_2)_3CMe$. (L), the reaction is

$$2[Co(H_2O)_6]^{2+} + 11L \rightarrow [Co^{I}L_5]^{+} + [Co^{III}L_6]^{3+} + 12H_2O$$

16.5 Organometallic Chemistry of Cobalt

The extensive organometallic chemistry of cobalt has been developed in part from the use of dicobalt octacarbonyl as a catalyst in a variety of organic syntheses. In the hydroformylation (oxo) reaction, aldehydes are prepared from alkenes, carbon monoxide, and hydrogen



$$>C{=}C< + CO + H_2 \xrightarrow[100^\circ,\,100\,atm]{Co_2(CO)_8} -\underset{\underset{H}{|}}{\overset{|}{C}}-\underset{\underset{CHO}{|}}{\overset{|}{C}}-$$

As a further example of the catalytic use of cobalt carbonyls, we may quote the conversion of alkyl halides into esters by using tetracarbonylcobaltate(–I) ions as catalyst

$$RX + CO + [Co(CO)_4]^- \rightarrow RCOCo(CO)_4 + X^-$$

$$RCOCo(CO)_4 + R'OH \rightarrow RCOOR' + HCo(CO)_4$$

The process is catalytic in cobalt if a tertiary amine is present to regenerate the $[Co(CO)_4]^-$ ion

$$HCo(CO)_4 + R_3N \rightarrow [R_3NH]^+ [Co(CO)_4]^-$$

No simple alkyls or aryls of cobalt exist. However, they can be stabilised with

π-bonding ligands such as CO, CN^-, PR_3, or π-C_5H_5. One cobalt alkyl occurs naturally in the coenzyme of vitamin B_{12} (cobalamin). Vitamin B_{12} (cyanocobalamin) can be reduced and then alkylated to give synthetic alkyl cobalamins.

Cobalt forms many π-cyclopentadienyl complexes including the paramagnetic cobaltocene $Co(\pi\text{-}C_5H_5)_2$, as well as arene complexes such as that with hexamethylbenzene, $[Co(C_6Me_6)]^+$.

17 Nickel

17.1 The Element

Nickel derives its name from the ore kupfernickel which was at one time believed to be an ore of copper. While nickel is not an uncommon element in the earth's crust, there are relatively few known deposits of nickel ores that are capable of being worked economically. One such deposit is that of pentlandite $(Ni, Fe)_9S_8$ at Sudbury, Ontario. The metal is extracted either electrolytically or by the Mond carbonyl process (section 10.2.2).

Nickel ($3d^8\ 4s^2$) continues to show the trend in decreasing stability of the high oxidation states as we pass along the first transition series. Unlike cobalt, the +3 state is relatively unimportant; for nickel only the +2 state is of importance in aqueous solution. The metal is ductile and resistant to corrosion; it is used in food handling and pharmaceutical plant wherever a nonpoisonous noncorrosive metal is required. It also finds use in catalysts for industrial processes, for example in the hydrogenation of unsaturated organic compounds. Raney nickel is a catalyst prepared by dissolving away the aluminium from the alloy $NiAl_3$ with alkali, thus leaving a porous and highly active form of the metal. The massive metal is attacked by dilute mineral acids but is resistant to attack by caustic alkalis and liquid hydrogen fluoride. It finds uses therefore in plant for handling caustic soda and in valves on cylinders of gases such as the hydrogen halides. The metal is readily dissolved in dilute nitric acid. Many nonmetals combine with heated nickel; steam reacts with red-hot nickel to give NiO and hydrogen. Carbon monoxide reacts at relatively low temperatures to give the carbonyl $Ni(CO)_4$.

17.2 Compounds of Nickel in High Oxidation States

The only important simple compound of nickel in an oxidation state above +2 is the hydrous nickel(III) oxide NiO(OH). No simple halides are known in oxidation states above +2.

The oxidation of alkaline nickel(II) solutions with chlorine, bromine, persulphate ions, or electrochemically, results in the formation of a black precipitate of β-NiO(OH). This evolves oxygen and water vapour at 140° leaving NiO. A separate phase γ-NiO(OH) is produced when nickel is added to a melt of sodium peroxide and sodium hydroxide at 600° and the cooled melt is treated with ice–water. It dissolves in sulphuric acid with evolution of oxygen.

Complexes of the unknown nickel(III) halides are sometimes obtained in the oxidation of the nickel(II) complexes. Thus the complexes $NiX_3(PR_3)_2$ result from the oxidation of $NiX_2(PR_3)_2$ compounds with the corresponding nitrosyl halides. $NiBr_3(PEt_3)_2$ has a magnetic moment of 1.72 B.M. at room temperature, and is believed to have a *trans*-trigonal bipyramidal structure. The hexafluoronickelates-(III) and -(IV), containing the $NiF_6{}^{3-}$ and $NiF_6{}^{2-}$ ions, are obtained by fluorination of melts of $KCl–NiCl_2$ mixtures at moderate temperatures and pressures of fluorine. The violet K_3NiF_6 evolves oxygen from water and undergoes disproportionation in liquid hydrogen fluoride

$$2K_3NiF_6 \rightarrow 6K^+ + NiF_6{}^{2-} + NiF_2 + 4F^-$$

The nickel(IV) complex K_2NiF_6 is diamagnetic having the low-spin $t_{2g}{}^6$ ground state. It evolves oxygen from water but forms bright-red solutions in hydrogen fluoride. When it is heated to 350° in a vacuum, fluorine is evolved.

$$3K_2NiF_6 \rightarrow 2K_3NiF_6 + NiF_2 + F_2$$

17.3 Compounds of Nickel(II) (d^8)

17.3.1 Aqueous Chemistry

The hexaquo-ion $[Ni(H_2O)_6]^{2+}$ is green, and this colour is shown by most hydrated simple salts and their aqueous solutions. Many salts crystallise with this ion, for example $Ni(NO_3)_2.6H_2O$, $NiSO_4.7H_2O$, and $NiSO_4.6H_2O$. The hexaquo-ion is barely acidic; no hydroxo- or oxo-nickelates(II) are known. The carbonate $NiCO_3.6H_2O$ is precipitated by sodium bicarbonate solution. The aquo-ion is also labile; a large number of complexes can be obtained by substitution reactions. Because of the great stability of the +2 oxidation state, redox reactions are uncommon in aqueous nickel(II) solutions.

17.3.2 Simple Compounds

Nickel(II) *halides.* Nickel is unique among the elements of the first transition series in forming simple halides in the +2 oxidation state only. The yellow NiF_2, $NiCl_2$, and $NiBr_2$, and black NiI_2 are high-melting solids. They give green solutions in water from which hydrates can be crystallised. The hexahydrate $NiCl_2.6H_2O$ contains *trans*-$[NiCl_2(H_2O)_4]$ units while the dihydrate $NiBr_2.2H_2O$ has nickel atoms in an environment of 4Br and $2H_2O$.

Nickel(II) *hydroxide and oxide.* The hydroxide $Ni(OH)_2$ is precipitated as a finely divided green powder by the addition of an alkali metal hydroxide solution to an aqueous solution of a nickel(II) salt. It is notoriously difficult to filter but becomes more crystalline on standing. Basic salts, for example $NiCl_2 . Ni(OH)_2$, may precipitate if very strong solutions of nickel(II) salts are used. The oxide NiO is produced in the thermal decomposition of the hydroxide, carbonate, or hydrated nitrate; it has the rock-salt structure.

Nickel(II) *cyanide.* The pale blue hydrated cyanide is precipitated by the addition of potassium cyanide solution to aqueous nickel(II) salt solutions. The structure of the hydrate may be $[Ni(H_2O)_x]^{2+}$ $[Ni(CN)_4]^{2-}$; it can be dehydrated at 140° to the yellow anhydrous $Ni(CN)_2$. A very interesting reaction of nickel cyanide is that with aqueous ammonia in the presence of benzene (or a similar molecule). Pale-violet clathrate compounds of the type $Ni(CN)_2.NH_3.C_6H_6$ are precipitated. In this compound, the benzene is trapped in the crystal structure as shown in figure 17.1*a*. As can be seen by studying figure 17.1*b*, the Ni and CN groups in this compound form layers with ammonia molecules bonded above and below the planes of the layers on alternate nickel atoms. Half the nickel atoms are thus octahedrally co-ordinated to nitrogen, while the other half are bonded to carbon atoms in a square plane. The average magnetic moment per nickel atom is 2.2 B.M. in accord

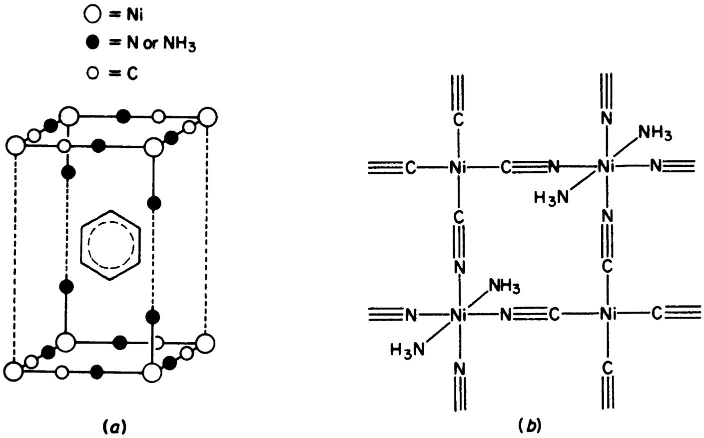


Figure 17.1 The benzene ammine nickel(II) cyanide clathrate

with the mixture of diamagnetic square nickel(II) and paramagnetic octahedral nickel(II) ions. Many other organic molecules, including pyridine, aniline, pyrrole, and thiophen, may be similarly trapped between the layers of the Ni–CN groups. The infrared spectra of the clathrates show absorptions similar to those of the free organic molecules, indicating that no bonding occurs between the aromatic molecule and the nickel atom.

17.3.3 Complexes

These are exceedingly numerous. The maximum co-ordination number shown is six in the octahedral and tetragonal complexes. Nickel(II) also forms many five-co-ordinate as well as square and tetrahedral four-co-ordinate complexes. However, it should be pointed out that tetrahedral complexes of nickel(II) are considerably less common than those of cobalt(II); this is to be expected in terms of the CFSE argument (section 5.5). A characteristic feature of nickel(II) chemistry is the low energy difference between these stereochemistries, which often results in equilibria between various structural types occurring in solution, as well as in the crystallisation of complexes containing nickel in two different stereochemistries. These various equilibria and 'anomalous' nickel(II) complexes have been discussed in section 7.3.2. We shall consider here those complexes that occur predominantly in one stereochemical form.

Cationic complexes. The substitution of water molecules in $[Ni(H_2O)_6]^{2+}$ by nitrogen donor molecules usually results in a colour change from green to violet as a result of the new ligand field present. In strong ammonia solutions the violet and octahedral hexammine $[Ni(NH_3)_6]^{2+}$ is formed, and salts of this ion can be precipitated with anions such as Br^- and I^-. Ethylenediamine forms octahedral chelated complexes containing the $[Ni(en)_3]^{2+}$ ion. There are also many octahedral cations containing a mixture of ligands, for example $[Ni(en)_2(NO_2)]BF_4$ which contains a polymeric distorted octahedral cation having bridging NO_2 groups. The monomeric cation $[Ni(diars)_2Cl_2]^+$, which has the four arsenic atoms in the square plane around nickel, is probably a nickel(II) complex containing a diarsine radical cation (diars$^+$).

Co-ordination numbers other than six are rare in cationic complexes. There are several five-co-ordinate cations such as $[NiLCl]^+$ in which L is a tetradentate ligand, but tetrahedral cations are rare and occur only with bulky ligands such as hexamethylphosphoramide which forms $[Ni(HMPA)_4](ClO_4)_2$.

Neutral complexes. The reactions between nickel(II) salts and donor molecules, particularly those containing nitrogen or phosphorus as the donor atom, give rise to a large number of neutral complexes (in addition to the cationic complexes illustrated above). Most commonly these are of the type NiX_2L_2 (which may be octahedral, square planar, or tetrahedral), but NiX_2L_4 and NiX_2L (L = unidentate ligand, X = univalent anion) also occur commonly. These complexes can be prepared by direct reaction between the salt and the ligand, or by thermal decomposition of $[NiL_6]X_2$ complexes which frequently proceeds via the stages NiL_4X_2, NiL_2X_2, and $NiLX_2$. The pyridine complexes will serve to illustrate these compound types. The direct reaction between nickel(II) chloride and pyridine produces the blue $Ni(py)_4Cl_2$ which has the *trans*-octahedral structure. On thermal decomposition above 110°, pyridine is evolved and the yellow-green $Ni(py)_2Cl_2$ is formed; at 170° this decomposes into pyridine and $Ni(py)Cl_2$. Both this and the bis(pyridine)-complex contain six-co-ordinate nickel. The hexa(pyridine)nickel(II) cations are formed only in the presence of weakly co-ordinating anions; for example, nickel(II) nitrate gives $[Ni(py)_6](NO_3)_2$.

Phosphorus ligands frequently give four-co-ordinate complexes. Trialkylphosphines give square planar $NiX_2(PR_3)_2$ compounds while the aryl phosphines give tetrahedral $NiX_2(PAr_3)_2$ complexes. The unusual $NiBr_2(PhCH_2PPh_2)_2$ complexes have been discussed in section 7.3.2.

Numerous neutral nickel(II) chelates are formed with chelating anionic ligands; the β-keto-enolates, salicylaldimine, and *vic*-dioxime complexes (section 7.3.2) are examples of this type. The best-known chelate is the bright-red bis(dimethylglyoximato)nickel(II) (figure 17.2). This precipitates quantitatively when a neutral or ammoniacal solution of a nickel(II) salt is treated with an alcoholic solution of dimethylglyoxime; the reaction is used in the gravimetric estimation of nickel. The structure has some interesting features. The nickel atom is at the centre of a square plane of nitrogen atoms. These planes are stacked one above the other in the crystal, alternate molecules being twisted through 90°, so the nickel

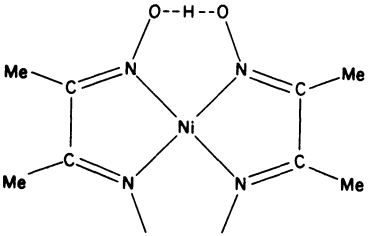


Figure 17.2 Bis(dimethylglyoximato)nickel(II)

atoms form chains with a Ni–Ni distance of 325 pm. There are strong intramolecular hydrogen-bonds within each molecule. The diamagnetic complex may thus be regarded as containing either square planar or tetragonally co-ordinated nickel (with metal–metal bonding).

Anionic complexes. The tetrahedral $M^I_2NiX_4$ (X = Cl, Br, I) complexes are readily prepared from the nickel(II) halide and a quaternary ammonium or phosphonium salt in nitromethane or ethanol; they are not easily obtained from aqueous solution. Substituted tetrahalonickelates(II) such as $[NiBr_3(PPh_3)]^-$ are similarly prepared in the presence of the added ligand; they have a distorted tetrahedral structure. These complexes have the intense blue colour and the high magnetic moments (3.5–4.1 B.M.) expected of tetrahedral d^6 complexes; the electronic spectrum of the $[NiCl_4]^{2-}$ ion is shown in figure 6.10. The tetrafluoronickelates(II) $[NiF_4]^{2-}$ and the trihalonickelates(II) M^INiX_3 (X = F, Cl, Br) contain octahedrally co-ordinated nickel.

The tetracyanonickelate(II) ion $[Ni(CN)_4]^{2-}$ is formed when nickel(II) cyanide is dissolved in an excess of aqueous potassium cyanide; the potassium salt crystallises from the orange-red solution as the orange $K_2Ni(CN)_4 . H_2O$. This salt is diamagnetic and contains square planar $[Ni(CN)_4]^{2-}$ ions. These ions are extremely stable with an overall stability constant β around 10^{30}; even chelates such as bis(dimethylglyoximato)nickel(II) dissolve in potassium cyanide solution (compare the stability constants for $Ni^{2+} - NH_3$ and Ni^{2+} – EDTA complexes in tables 3.1 and 3.2). There is some evidence for the formation of diamagnetic $[Ni(CN)_5]^{3-}$ ions in the presence of an excess of cyanide ions; no evidence has been found for $[Ni(CN)_6]^{4-}$ species.

17.4 Compounds of Nickel in Low Oxidation States

17.4.1 Nickel Carbonyl

The tetracarbonyl $Ni(CO)_4$ was the first metal carbonyl to be discovered (Mond, 1890). It is produced industrially as the intermediate in nickel refining (see section 10.2.2). Nickel carbonyl is a very toxic, diamagnetic liquid (b.p. 42°); it is insoluble in water but soluble in organic solvents. Electron diffraction studies on the vapour, and X-ray diffraction studies on the solid, show the molecule to be tetrahedral with linear Ni–C–O units. The stability of the molecule cannot be understood if the sole bonding involves a σ bond formed by overlap of a filled carbon σ orbital with a vacant σ orbital on nickel. The Ni–C bond is thus believed to consist of a σ bond and a π bond. The π bond is formed by overlap of a filled d_π orbital on nickel with a vacant p antibonding orbital on carbon monoxide. Such bonding is synergic since the donation of metal electron density into the carbon monoxide orbitals will enhance the σ-donor power of the latter while at the same time increasing the acceptor power of the nickel atom along the σ bond.

Nickel carbonyl is inflammable in air; its solutions oxidise slowly in air. Reduction by alkali metals in tetrahydrofuran gives carbonylate anions, for example

$$4Ni(CO)_4 + 2Na \rightarrow Na_2[Ni_4(CO)_9] + 7CO$$

In liquid ammonia the thermally unstable carbonyl hydride can be isolated as a tetra-ammoniate

$$2Ni(CO)_4 + 2Na + 6NH_3 \rightarrow [NiH(CO)_3]_2.4NH_3 + 2CO + 2NaNH_2$$

With donor molecules, disproportionation reactions are common, especially with nitrogen donors

$$3Ni(CO)_4 + 6py \rightarrow [Ni(py)_6][Ni_2(CO)_6] + 6CO$$

Phosphorus, arsenic, and antimony donors, as well as isonitriles and unsaturated organic molecules, give substitution products that are stable with respect to disproportionation, for example

$$Ni(CO)_4 \xrightarrow{PPh_3} Ni(CO)_3(PPh_3) \xrightarrow{PPh_3} Ni(CO)_2(PPh_3)_2$$

17.4.2 Nickel Nitrosyls

No simple nitrosyl of nickel is known, the reaction of the carbonyl with NO in the absence of a donor solvent proceeding according to

$$Ni(CO)_4 + 4NO \rightarrow Ni(NO)(NO_2) + 4CO + N_2O$$

The blue air-sensitive $Ni(NO)NO_2$ ignites on contact with water; it is believed to be polymeric, resembling the nitrosyl halides Ni(NO)X. Substituted nickel carbonyls with NO give nitrosyl complexes such as $Ni(NO)_2(PPh_3)_2$. Two series of nitrosyl halides are known. When nickel(II) halides react with NO in the presence of a halogen acceptor such as zinc, the nitrosyl monohalides Ni(NO)X are formed. The dihalides $Ni(NO)X_2$ arise in the reactions of nickel carbonyl with nitrosyl halides. The structures of these presumably polymeric compounds are unknown; both types show infrared absorptions in the NO^+ region.

17.4.3 Other Low Oxidation-state Compounds

The fairly extensive chemistry of nickel(0) includes compounds in which nickel is bonded to CN^-, acetylide ion, phosphines, aryl isocyanides, and acrylonitrile, as well as to those ligands such as 2,2′-bipyridyl and 1,10-phenanthroline which stabilise the zero oxidation states of all the first-row elements that we have so far considered.

The reduction of $K_2Ni(CN)_4$ in aqueous solution with, for example, sodium amalgam gives Bellucci's salt $K_4[Ni_2(CN)_6]$ containing nickel(I). This compound is diamagnetic, the anion being binuclear with a nickel–nickel bond. With potassium in liquid ammonia the reduction of $[Ni(CN)_4]^{2-}$ proceeds via this red nickel(I) complex to the yellow precipitate of $K_4Ni(CN)_4$ containing nickel(0). The $[Ni(CN)_4]^{4-}$ anion is isoelectronic with $Ni(CO)_4$ and is believed to have the tetrahedral structure. Other nickel(0) compounds can be obtained by substitution reactions on this cyano-complex

$$Ni(SbPh_3)_4 \xleftarrow{SbPh_3} K_4Ni(CN)_4 \xrightarrow{CO} K_2[Ni(CO)_2(CN)_2]$$

Nickel reacts with many phosphines directly, for example

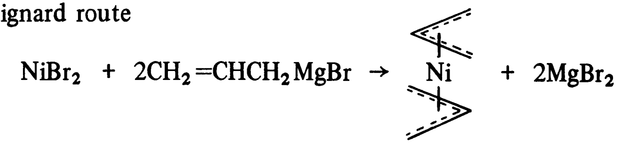
$$Ni + 4PF_3 \xrightarrow[35\ MPa]{100^\circ} Ni(PF_3)_4$$

$Ni(PCl_2Me)_4$ and $Ni(Ph_2PCH_2CH_2PPh_2)_4$ can be prepared under less extreme conditions; all these phosphine–nickel(0) compounds are believed to have the tetrahedral structure.

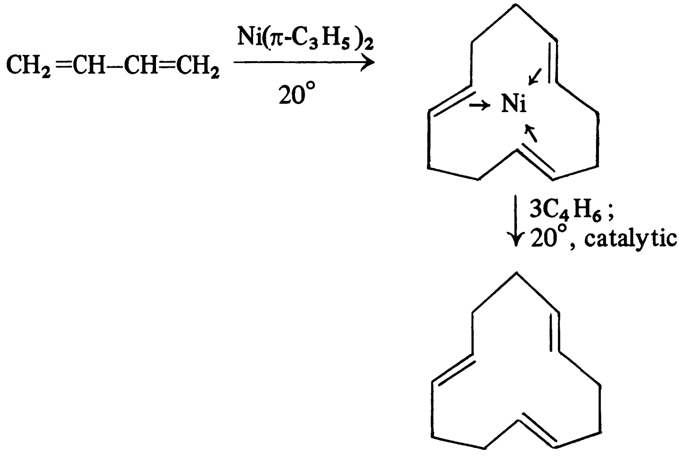
17.5 Organometallic Compounds of Nickel

Simple alkyls and aryls of nickel are usually too unstable to be isolated on their own. However, ligand-stabilised aryls can be made from square $(R_3P)_2NiX_2$ complexes and aryl Grignard reagents. Such compounds as $(R_3P)_2NiAr_2$ are yellow or brown and diamagnetic with the *trans*-square planar structure.

Nickel forms olefin and acetylene complexes as well as cyclobutadienyl and cyclopentadienyl derivatives. Perhaps the most important of the π-bonded organometallic compounds of nickel are the π-allyls. Bis-(π-allyl)nickel is obtained by the Grignard route



This sandwich-structured compound is pyrophoric in air but its ethereal solutions are stable to deoxygenated water. It is a very active catalyst for the cyclotrimerisation of butadiene to cyclododeca-1,5,9-triene



18 Copper

18.1 The Element

Copper has an ancient history, being used extensively in the Bronze Age. Its compounds are widely distributed in the earth's crust, and occasionally it occurs naturally as the element. It is the last member of the first transition series; the configuration $3d^{10}\ 4s^1$ gives rise to an extensive chemistry of the +1 oxidation state. In this respect it differs from all the other members of the first transition series. The next element, zinc with the $3d^{10}\ 4s^2$ configuration, shows the +2 state almost exclusively and does not have the transition-metal properties associated with the variable oxidation states.

Copper is a soft reddish metal noted for its high termal and electrical conductivities. The pure metal is used extensively in, for example, electrical equipment, as well as in alloys such as brass (Cu–Zn), bronze (Cu–Sn), and monel metal (Cu–Ni). The metal oxidises in air at red heat to CuO; at higher temperatures Cu_2O is formed. In dry atmospheres at room temperature little corrosion occurs; in moist atmospheres a green film of basic carbonate coats the metal. Copper is readily attacked by the halogens and by sulphur at relatively low temperatures. It dissolves in oxidising acids such as HNO_3, concentrated H_2SO_4, or dilute H_2SO_4 in the presence of air but is resistant to reducing acids such as dilute HCl, in accord with its noble position in the electrochemical series.

$$Cu^{2+} + 2e \rightarrow Cu \qquad (E^\circ = +0.34\ V)$$

18.2 Compounds of Copper(III) (d^8)

Copper(III) is isoelectronic with nickel(II) but only a few compounds of copper in this oxidation state have been characterised (no compounds of copper in oxidation states greater than +3 are known). There are no simple halides CuX_3 but fluorination of a 3 : 1 mixture of KCl and $CuCl_2$ in a flow system at 250° gives the pale green K_3CuF_6. This reacts violently with water and has a magnetic moment of 2.8 B.M. as expected of a $t_{2g}{}^6\ e_g{}^2$ configuration.

Oxidation of $Cu(OH)_2$ in alkaline solution with chlorine gives a strongly oxidising solution which evolves oxygen on acidification. The solid cuprates(III) can be obtained by heating mixtures of CuO and alkali metal superoxides in oxygen. The steel-blue $KCuO_2$ is diamagnetic and may therefore have a square planar structure in the anion. A few other complex salts such as the diamagnetic $Na_7[Cu(IO_6)_2].12H_2O$ and $Na_9[Cu(TeO_6)_2].16H_2O$ can be obtained by oxidation of copper(II) salts in alkaline solutions of the alkali metal periodate or tellurate.

18.3 Compounds of Copper(II) (d^9)

Copper(II) is the most stable state in aqueous solution. Its d^9 configuration gives rise to Jahn–Teller distortions (see sections 5.5.6 and 6.2.4) both in its simple compounds and in complexes. A wide range of stereochemistries are exhibited by copper(II) compounds, with four, five, and six-co-ordination predominating; in each structure variations from idealised geometries occur through bond length and bond angle distortions. The distorted octahedral compounds have magnetic moments in excess of the spin-only moment, being usually around 1.9 B.M. (section 7.2.1).

18.3.1 Aqueous Chemistry

The blue aquo-ion $[Cu(H_2O)_6]^{2+}$ is formed when copper(II) salts are dissolved in an excess of water. It is tetragonally distorted, with two water molecules further away from copper than the other four, which are in the square plane around the metal. The mild acidity of the ion results in the frequent precipitation of basic salts from aqueous solution. Thus the addition of sodium carbonate solution causes precipitation of the green basic carbonate $CuCO_3.Cu(OH)_2.aq$

$$[Cu(H_2O)_6]^{2+} + H_2O \rightleftharpoons [Cu(OH)(H_2O)_5]^+ + H_3O^+$$

$$2[Cu(OH)(H_2O)_5]^+ + CO_3^{2-} \rightarrow [Cu(OH)(H_2O)_5]_2CO_3$$

that is $CuCO_3.Cu(OH)_2.aq$

In neutral or acid solution, the copper(II) ion is a mild oxidant

$$Cu^{2+} + e \rightarrow Cu^+ \qquad (E^\circ = +0.15\ V)$$

The oxidation of iodide ions to iodine is used in the volumetric estimation of copper(II) with thiosulphate. This oxidation of iodide ions by Cu^{2+} proceeds despite the potential

$$\tfrac{1}{2}I_2 + e \rightarrow I^- \qquad (E^\circ = +0.54\ V)$$

because of the insolubility of the copper(I) product, CuI. The potential for the system

$$Cu^{2+} + I^- + e \rightarrow CuI \qquad (E^\circ = +0.86\ V)$$

thus shows that the oxidation of iodide ions according to the equation

$$Cu^{2+} + 2I^- \rightarrow CuI + \tfrac{1}{2}I_2$$

is thermodynamically favourable.

Substitution reactions of $[Cu(H_2O)_6]^{2+}$ with added ligands give rise to a large number of co-ordination compounds. With concentrated aqueous ammonia, the substitution proceeds as far as $[Cu(NH_3)_4(H_2O)_2]^{2+}$ (sections 3.1.1. and 3.1.2). Similarly, bidentate ligands such as ethylenediamine readily form the intensely blue complexes of the type $[Cu(en)_2(H_2O)_2]^{2+}$, with completely substituted compounds such as $[Cu(en)_3]^{2+}$ formed only in the highest concentrations of ethylenediamine. Cations such as $[Cu(NH_3)_6]^{2+}$ are readily formed under anhydrous conditions. Some neutral ligands such as hydrazine and methylhydrazine cause reduction of Cu^{II} in aqueous solution.

With chloride and bromide ions the blue $[Cu(H_2O)_6]^{2+}$ solution becomes yellow and brown respectively, and from such solutions a variety of halo-complexes have been isolated with different cations. The yellow $[CuCl_4]^{2-}$ ion is planar in $(NH_4)_2[CuCl_4]$, but with larger cations, such as $Cs_2[CuCl_4]$, the anion adopts a flattened tetrahedral structure. The red trichlorocuprates(II) $[CuCl_3]^-$ also show two distinct structural types. The potassium and ammonium salts contain planar binuclear anions $[Cu_2Cl_6]^{2-}$, which are stacked in the crystal lattice in such a manner that there is an elongated tetrahedral co-ordination about each copper atom. In $CsCuCl_3$ there are square planar $CuCl_4$ units linked by a single bridging atom; two terminal chlorines complete the distorted octahedral array around each copper atom. Cyanide ions cause precipitation of brownish-yellow $Cu(CN)_2$ which decomposes at room temperature with evolution of cyanogen (compare the reaction of Cu^{2+} with I^-). In an excess of cyanide the colourless $[Cu(CN)_4]^{2-}$ and $[Cu(CN)_4]^{3-}$ species are formed.

18.3.2 Simple Compounds

Copper(II) oxide and hydroxide. The black CuO results from thermal decomposition of the basic carbonate, hydroxide, or nitrate. It is readily reduced to the metal by hydrogen or carbon monoxide at around 300°, and is used as an oxidant in organic microanalysis for carbon and hydrogen.

The blue hydroxide $Cu(OH)_2$ is obtained (often contaminated with basic salts) on the addition of an alkali metal hydroxide solution to an aqueous copper(II) solution. It darkens on standing, becoming black above 30° as dehydration to the oxide takes place. In concentrated alkalis $Cu(OH)_2$ shows amphoteric character, forming deep-blue solutions of hydroxocuprates(II); in ammonia the soluble deep-blue $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ion is formed.

Copper(II) halides. The fluoride CuF_2 is a white hygroscopic solid, the chloride is yellow, and the bromide black; CuI_2 cannot be prepared because of the reduction of Cu^{2+} by iodide ions. The crystal structure of $CuCl_2$ consists of infinite chains of planar $CuCl_4$ groups (Cu–Cl = 230 pm), with two chlorine atoms from other chains completing (Cu–Cl = 295 pm) the tetragonally elongated octahedral environment around each copper atom. In the dihydrate $CuCl_2.2H_2O$, the square plane around copper is composed of two Cl at 228 pm and two H_2O at 193 pm, with the two further chlorine atoms completing the distorted octahedral structure at Cu–Cl = 295 pm.

Many complexes of copper(II) halides have been prepared. Nitrogen donors frequently form tetragonal CuX_2L_2 complexes, for example $CuCl_2(py)_2$, but some tertiary amines, phosphines, and arsines cause reduction to copper(I) complexes. With phosphine oxide ligands, tetrahedral complexes are formed as in $CuCl_2(Ph_3PO)_2$. 2,2′-Bipyridyl forms $CuX_2(bipy)_2$ adducts which contain the trigonal bipyramidal cations $[Cu(bipy)_2X]^+$.

Copper(II) sulphate. The blue pentahydrate $CuSO_4.5H_2O$ has copper co-ordinated to four water molecules in a plane with the tetragonal structure completed by two oxygen atoms from sulphate ions. The fifth water molecule is hydrogen-bonded as shown diagrammatically in the representation of part of the giant structure in figure 18.1. The pentahydrate is readily dehydrated thermally to the white $CuSO_4$; the d–d transition in the anhydrous salt has moved into the infrared as a result of the weaker (spectrochemical sense) ligand field.

From solutions of copper(II) sulphate saturated with ammonia, the dark blue ammine $CuSO_4.4NH_3.H_2O$ can be crystallised. This compound has a square pyramidal structure around copper, with the metal atom lying 20 pm out of the

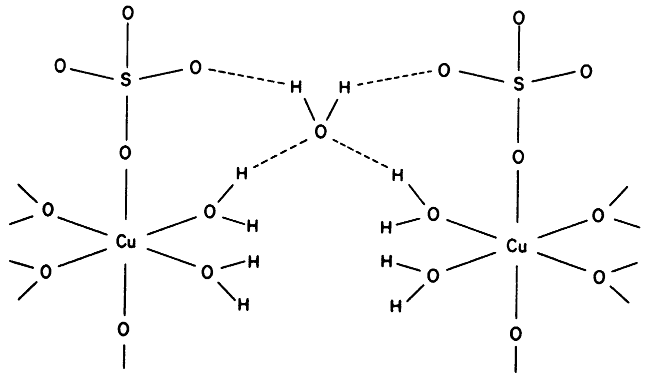


Figure 18.1 Representation of part of the structure of $CuSO_4.5H_2O$

plane of the four nitrogen atoms. With gaseous ammonia, $CuSO_4$ forms the violet pentammine $CuSO_4.5NH_3$.

Copper(II) nitrate. The anhydrous $Cu(NO_3)_2$ (section 10.3.2) exists in two crystal forms; these have complex structures in which copper ions are linked in infinite array by nitrate ions. The nitrate can be sublimed in a vacuum without decomposition. Discrete $Cu(NO_3)_2$ molecules occur in the vapour, in which the copper atoms are four-co-ordinated by oxygen atoms from bidentate nitrate groups. The deep-blue hydrate $Cu(NO_3)_2.3H_2O$ crystallises from aqueous solutions; it is very soluble in water.

Copper(II) acetate. Copper(II) carboxylates frequently have dimeric structures giving rise to anomalous magnetic properties. The acetate $[Cu_2(OCOCH_3)_4].2H_2O$ has the same structure as the chromium(II) analogue (figure 13.2). The Cu—Cu interaction gives rise to incomplete quenching of the spin moments of the ions, so low magnetic moments are observed in this type of carboxylate.

18.4 Compounds of Copper(I) (d^{10})

Copper(I) has the closed-shell $3d^{10}$ configuration, so its compounds are diamagnetic and colourless (except for those salts having coloured anions or in which charge-transfer transitions are of low energy). In solid compounds, copper(I) is often the thermodynamically stable state at moderate temperatures; for example, CuO and $CuBr_2$ give Cu_2O and CuBr on heating.

18.4.1 Aqueous Chemistry

If the potentials

$$Cu^+ + e \rightarrow Cu \qquad (E^\circ = +0.52\ V)$$

$$Cu^{2+} + e \rightarrow Cu^+ \qquad (E^\circ = +0.15\ V)$$

are compared we see that the Cu^+ ion (in the first equation) is capable of oxidising the Cu^+ ion (in the second equation) according to

$$Cu^+ + Cu^+ \rightarrow Cu + Cu^{2+} \quad (E^\circ = +0.37\ V)$$

That is, disproportionation of copper(I) aquo-ions occurs. Of course, in the presence of added ligands, the potentials are considerably affected, so the relative stabilities of Cu^I and Cu^{II} do depend on the nature of such ligands. The surprising instability of Cu^I in aqueous solution is probably connected with the low hydration energy of the Cu^+ ion (which may form $[Cu(H_2O)_2]^+$) compared with that of the Cu^{2+} ion which has the higher charge and co-ordination number.

Only the insoluble salts of copper(I) are stable in water, that is salts such as CuCl, CuI, and CuCN. Those that dissolve undergo disproportionation; thus Cu_2SO_4, prepared for example from Cu_2O and dimethyl sulphate, reacts immediately with water

$$Cu_2SO_4 + 6H_2O \rightarrow Cu + [Cu(H_2O)_6]^{2+} + SO_4{}^{2-}$$

Several water-soluble copper(I) complex species are stable with respect to disproportionation in aqueous solution. The complexes of copper(I) resemble those of silver(I) in having a preferred co-ordination number of two; however, three and four-co-ordination also occur. In aqueous ammonia, CuCl dissolves to form the colourless $[Cu(NH_3)_2]^+$ ion (compare Ag^I). This is readily oxidised in air to the blue $[Cu(NH_3)_4(H_2O)_2]^{2+}$ species; however, it is stable to disproportionation, the reaction

$$[Cu(NH_3)_4(H_2O)_2]^{2+} + Cu \rightarrow 2[Cu(NH_3)_2]^+ + 2NH_3 + 2H_2O$$

proceeding from left to right in the absence of air. Chloro-species of copper(I) are similarly prepared from copper(II) chloride solutions in hydrochloric acid

$$[CuCl_4]^{2-} + Cu \rightarrow 2[CuCl_2]^-$$

These two-co-ordinate complexes are linear like their silver(I) analogues. Complexes such as $[Cu(CN)_4]^{3-}$ and $[CuCl_3]^{2-}$ (in solid K_2CuCl_3) contain tetrahedrally co-ordinated copper(I) while planar three-co-ordination occurs in $K[Cu(CN)_2]$ (section 4.2.1).

18.4.2 Simple Compounds

Copper(I) oxide. The red Cu_2O occurs naturally in *cuprite;* it is precipitated as a finely divided orange form when alkaline solutions of copper(II) are treated with mild reducing agents such as glucose. In Fehling's solution the $[Cu(H_2O)_6]^{2+}$ ion is converted into a tartrate complex so that no $Cu(OH)_2$ is precipitated when alkali is added. In dilute sulphuric acid Cu_2O undergoes disproportionation

$$Cu_2O + 2H_3O^+ + 3H_2O \rightarrow Cu + [Cu(H_2O)_6]^{2+}$$

However, in solutions of co-ordinating agents, for example concentrated hydrochloric acid or concentrated aqueous ammonia, it dissolves to give solutions of copper(I) complexes.

Copper(I) halides. The fluoride is not known as a stable species at room temperature. The white CuCl, CuBr, and CuI are prepared by aqueous methods. The chloride is most easily prepared by reduction of a copper(II) salt solution in hydrochloric acid with copper metal or sulphur dioxide. The resulting solution of chloro-complexes such as $CuCl_2^-$ is poured into a large volume of water, and the CuCl precipitates. The iodide CuI precipitates when iodide ions are added to copper(II) salt solutions. In the solid state these halides have copper ions tetrahedrally surrounded by halide ions; in the vapour, CuCl forms principally a trimeric species, which is believed to have a puckered cyclic structure.

These halides are very insoluble in water but dissolve readily in solutions of ligands such as Cl^-, CN^-, $S_2O_3^{2-}$, and NH_3. Solutions of CuCl in hydrochloric acid contain the various $CuCl_2^-$, $CuCl_3^{2-}$, and $CuCl_4^{3-}$ ions depending on the chloride ion concentration.

Complexes of copper(I) halides with neutral donor molecules can be prepared by direct reaction or, often more conveniently, by reduction of copper(II) halides with ligands. Such complexes are often polymeric. In the azomethane complex $(CuCl)_2MeN{=}NMe$, the copper atoms are tetrahedrally co-ordinated by two chloride ions and two nitrogen atoms from the bridging *trans*-azomethane molecules. Complexes of CuCl with azo- and diazo-compounds have found use in organic chemistry. In the Sandmeyer reaction an $-NH_2$ group attached to an aromatic ring is replaced by a –Cl group when the amine is diazotised and treated with copper(I) chloride; the intermediate CuCl–diazonium salt complex decomposes evolving nitrogen. Azobenzene is converted into benzidine by treatment with CuCl in hydrochloric acid.

The iodide gives 1 : 1 adducts with phosphines and arsines CuI.L. Molecular weight measurements indicate some of these to be tetrameric, and the crystal structure determination on $CuI(AsMe_3)$ shows the presence of a tetrahedral array of copper atoms linked together by bridging iodine atoms. Each copper is tetrahedrally co-ordinated to one terminal arsenic atom and three shared iodine atoms.

18.4.3 Carbonyl and Organometallic Compounds

Solutions of copper(I) halides in hydrochloric acid or ammonia absorb carbon monoxide to form colourless complexes, the halogen-bridged dimer $[CuCl(CO)]_2$ can be isolated as colourless crystals.

Copper(II) forms no σ-bonded alkyls or aryls, Grignard reactions causing reduction to copper(I). The copper(I) alkyls and aryls, CuR, are thermally unstable and probably have polymeric structures. The only organometallic compounds of copper of any significance are those with acetylenes and olefins. Solutions of CuCl in hydrochloric acid absorb acetylene in forming complexes such as $CuCl.C_2H_2$ and $[CuCl_2(C_2H_2)]^-$. The explosive orange and diamagnetic acetylides $CuC{\equiv}CR$ and Cu_2C_2 are formed by using ammoniacal solutions of CuCl or with potassium acetylide in liquid ammonia. The insolubility of these acetylides suggests that they are polymeric, the copper atoms forming both σ and π bonds to the acetylide groups.

Copper(I)–olefin complexes are prepared by the reduction of alcoholic solutions of copper(II) halides with sulphur dioxide in the presence of the olefin. The most stable complexes are formed by chelating diolefins such as cyclo-octa-1,5-diene and norbornadiene. In the complex of cyclo-octa-1,5-diene $[C_8H_{12}CuCl]_2$, each copper atom is tetrahedrally surrounded by two bridging chlorine atoms and two olefinic double bonds.

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