Comprehensive Inorganic Chemistry

The Chemistry of

IRON, COBALT AND NICKEL

D. Nicholls

Chapters 40, 41 and 42 of
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PREFACE

The excellent reception that has been accorded to *Comprehensive Inorganic Chemistry* since the simultaneous publication of the five volumes of the complete work has been accompanied by the plea that sections should be made available in a form that would enable specialists to purchase copies for their own use. To meet this demand the publishers have decided to issue selected chapters and groups of chapters as separate editions. These chapters will, apart from the corrections of misprints and the addition of prefatory material and individual indices, appear just as they did in the main work. Extensive revision would delay publication and greatly raise the cost, so limiting the circulation of these definitive reviews.

A. F. TROTMAN-DICKENSON
Executive Editor

40. IRON

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1. THE ELEMENT

1.1. HISTORY

Iron was probably first used nearly 6000 years ago. There is little doubt that the earliest iron beads dating from this time were of meteoric origin—the production of iron from iron ores probably began around 1200 B.C. The earliest furnaces consisted of an oval hollow in the ground where the ore was ignited with wood charcoal and air blown in by bellows. These hearth furnaces gradually evolved into the blast furnace and by the 14th century these furnaces were able to reach the temperature required for the production of cast iron. Further advances came as the invention of the steam engine provided a source of more powerful blowing machinery and simultaneously created (via the railways) a demand for much increased production. Abraham Darby introduced coke as the reducing agent in the early 1730's. In the 19th century the whole steel manufacturing process was revolutionized by the inventions of the Bessemer process (1855), the Siemans–Martin process (1865) and the Thomas Gilchrist process (1878). For further details of the history of iron, the reader should consult Mellor's *Treatise*[1].

1.2. OCCURRENCE AND DISTRIBUTION

Iron is the fourth most abundant element in the earth's crust occurring to the extent of some 5·1%. It is believed that the earth's core consists mainly of iron. Elemental iron occurs only very rarely in the crust, but in the combined state it is universally common; indeed many minerals owe their tints to the presence of iron compounds. The most important ores are the oxides and carbonates. *Magnetite* (Fe_3O_4) constitutes the richest ore of iron; it is black and magnetic, one variety being called "lodestone". *Hematite* (Fe_2O_3) contains about 70% of iron and is reddish-brown; *limonite* is a variety of iron(III) oxide ore containing varying amounts of water but usually of approximate composition $2Fe_2O_3 . 3H_2O$. The carbonate $FeCO_3$ occurs as *siderite* (spathic iron ore); frequently carbonate ores are associated with clay or coal and these are called ironstones. *Iron pyrites* (FeS_2) is a common vein mineral, but is not directly worked as an ore of iron on account of its high sulphur content. Various silicates of iron also occur naturally.

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[1] J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. XII, p. 482, Longmans Green and Co., London (1932).

1.3. IRON AND STEEL MANUFACTURE

Iron and steel making is an extremely complex process and for a fuller account than is presented here the reader is referred to the textbooks on the subject[2]. Very useful summaries are to be found in Remy[3] and in Thomas's article[4].

Production of Pig Iron

The first stage in the extraction of iron from its ores involves the production of pig (cast) iron in the blast furnace. This furnace consists of a vertical shaft nearly 100 ft high and about 22 ft in diameter constructed of refractory bricks. Preheated compressed air (or oxygen-enriched air plus fuel oil) is blown in at the base of the furnace through "tuyeres" and the ground, often presintered, mixture of the iron oxide and coke (usually with added limestone) is fed in at the top. The coke burns in the air providing heat and carbon monoxide. The lower portion of the furnace thus becomes very hot and the iron produced by reduction of the oxide is molten and it runs down to the bottom of the furnace. Further mixture of ore and carbon then sinks down into the hot zone. The molten iron is tapped from the base of the furnace every few hours; slag is removed from above the molten iron at a separate tapping point. Blast furnaces are run continuously; the excess carbon monoxide from the top of the furnace can be used to heat the air which is blasted into the furnace at around 800°C. The slag finds uses in building materials ("breeze blocks") and in "iron portland cement".

Ore containing iron as carbonate must first be roasted to convert it into oxide:

$$2FeCO_3+{}^1/_2O_2 \rightarrow Fe_2O_3+2CO_2$$

Most ores contain impurities (gangue), either acidic (silica, alumina) or basic (limestone), and in order that these shall form fusible slags which can be removed easily from the furnace, it is necessary to add, for example, limestone if the gangue is acidic and acidic materials (slate or granite) if the gangue is basic.

A complete analysis of all the kinetic and thermodynamic aspects of the processes occurring in the furnace is not possible here, but some of the important principles are worthy of mention. Whilst much of the process can be understood thermodynamically, the role of kinetics is important since under the blast conditions the time spent by gases in the various temperature zones of the furnace is of the order of seconds. Temperatures in the furnace vary from around 200°C at the top to something near 2000°C at the bottom where the coke is burning fiercely in the blast from the tuyeres. In the upper levels of the furnace, the ore is reduced by carbon monoxide, since below about 700°C carbon monoxide is a better reducing agent than carbon. Typical exothermic reactions occurring in this region then are:

$$\begin{gathered}3Fe_2O_3+CO \rightarrow 2Fe_3O_4+CO_2\\ Fe_3O_4+4CO \rightarrow 3Fe+4CO_2\\ Fe_2O_3+CO \rightarrow 2FeO+CO_2\end{gathered}$$

so that some of the ore is already reduced at this stage to spongy iron. The carbon dioxide is removed upwards in the gas stream thus preventing the reverse reactions which might occur at higher temperatures. Because of the thermodynamic instability of carbon monoxide

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[2] R. G. Ward, *An Introduction to the Physical Chemistry of Iron and Steel Making*, Edward Arnold, London (1962); C. Bodsworth, *Physical Chemistry of Iron and Steel Manufacture*, Longmans, London (1963).

[3] H. Remy, *Treatise on Inorganic Chemistry*, Vol. II, p. 253, Elsevier (1956).

[4] R. W. Thomas, *Education in Chemistry*, **2** (1965) 167.

below 700°C, some decomposition into carbon and carbon dioxide occurs in these cooler regions especially upon contact with the freshly produced iron, the carbon produced being deposited on the iron. In the lower, hotter zones reduction by carbon effectively occurs, although of course carbon monoxide is the reactive intermediate:

$$FeO+C \rightarrow Fe+CO$$

Above 1000°C the iron can react with carbon to form the carbide Fe_3C. As the iron sinks into the hotter regions it takes up more carbon, its melting point is thus lowered and the liquid iron has a chance to pick up more carbon as it trickles down over the hot coke.

Much chemical reaction occurs in the slag which is largely calcium silicate, $CaSiO_3$. Sulphur from the coke is transferred to the iron as FeS, but can be removed to the slag under basic conditions and high temperature:

$$FeS+CaO+C \rightarrow CaS+Fe+CO$$

This sulphur removal is also aided by the presence of manganese, the manganese compounds entering the slag and reacting as follows:

$$FeS+Mn \rightarrow Fe+MnS$$
$$MnS+CaO \rightarrow CaS+MnO$$
$$MnO+C \rightarrow Mn+CO$$

In the high temperature zones (>1500°C) phosphates in the ores are reduced to phosphorus which combines with the iron as Fe_3P. Silica which is always present is reduced to silicon which becomes ferrosilicon. Thus a typical pig iron contains some 4% carbon, and up to 2·5% manganese, 2·5% silicon, 2% phosphorus and 0·1% sulphur, these figures of course being dependent upon the operating conditions and ores used. Pig iron is brittle and has a sharp melting point; nearly all of it (about 85%) is converted into steel.

Steel Production

The basic process in the refining of pig iron involves removal of oxidizable impurities in air or oxygen. The oxygen may be introduced into the molten pig iron in various ways. In the Bessemer Converter process the air is blown in through holes at the bottom of the converter and the heat of oxidation of the impurities is sufficient to keep the metal molten. More recently oxygen diluted with steam has been used instead of air thereby avoiding contamination of the iron with nitrogen. Alternatively the air or oxygen may be blown into the molten metal through steel pipes (Rotor process) or just blown on to the surface of the metal (LD process) or a combination of both. These operations are effective in removing carbon as carbon monoxide as well as silicon and manganese as oxides which float out and enter the slag phase above the iron. Sulphur and phosphorus, however, are not easily removed in this way because their oxides are not more stable than iron oxides at the temperature used and a basic slag must be used. Phosphorus will dissolve in a basic slag having excess oxide ions forming the phosphate; sulphur transfer from metal to slag is largely as sulphide ions. Originally this was effected by using a lining of calcined dolomite to the converter. In the Kaldo process (1956) a converter is charged with lime as well as the molten pig iron and scrap iron and rotated while oxygen is blown over the surface of the iron; the slag can be removed by tilting the converter and a second "blow" with fresh lime carried out.

The removal of gaseous and non-metallic impurities in the steel can be carried out by vacuum degassing. In this treatment the steel is melted in a high vacuum; the process is particularly useful for producing forging quality and high-alloy steels.

Steel usually has between 0·5 and 1·5% combined carbon. An important property of steel is that it may be "hardened" by heating to redness followed by quenching in water or oil. This produces a hard but brittle steel; the brittleness may be removed by heating (tempering) it for a short time at around 300°C. There are many special steels. Those containing about 2·5% silicon are hard and elastic and are used in springs. Manganese steels (0·4–1·6% Mn) are also elastic and have high tensile strength. Stainless steels contain about 12–15% chromium and may also contain other metals such as nickel and niobium. Steels containing tungsten and vanadium (usually as well as chromium) retain their hardness at high temperatures and are used in high-speed cutting machinery.

1.4. PREPARATION OF PURE IRON

Pure iron is very much a laboratory material and finds no great industrial use. Pure iron may be obtained by hydrogen reduction of its pure oxides or hydroxides. In one method precipitated iron(III) hydroxide is heated in a stream of pure hydrogen while the temperature is raised slowly from 400° to 700°C and maintained at 700° until reduction is complete. The uptake of hydrogen by the iron as it cools is negligible. The iron obtained by hydrogen reduction of oxides at relatively low temperatures (360–530°C) is in powdered form and frequently pyrophoric in air.

In the carbonyl process, iron is heated to 100–200°C under 50–200 atm of carbon monoxide to form the pentacarbonyl, $Fe(CO)_5$. The carbonyl is vaporized and decomposed at around 250°C to give iron as a fine powder free from most impurities. Iron prepared in this way, however, still contains some carbon and oxygen, but these can be removed by sintering the iron in a vacuum when they are removed as carbon monoxide.

Chemically pure iron can also be prepared by electrolysis of pure iron(II) salts. The best electrolytes are iron(II) chloride or iron(II) ammonium sulphate; details of the laboratory preparation may be found in Brauer[5].

1.5. ALLOTROPY OF IRON

Two structural types of iron occur in the solid state[6]. At room temperature iron has a body-centered cubic lattice (the α form). At about 910°C the α form is transformed into the γ allotrope which has a cubic close-packed structure. Around 1390°C a body-centred cubic lattice is reformed—the δ form. Thus the allotropy of iron is unusual in that it can exist with the same crystal form in two distinct temperature ranges which are separated by a range within which a different form is stable. The α and δ forms have similar lattice parameters—the differences between them being expected in view of thermal expansion which increases the size of the unit cell of the δ allotrope.

A further modification of iron, the β form, is commonly referred to, but this is not a true allotrope. Iron is ferromagnetic up to the Curie point at 768°C. Thereafter iron becomes paramagnetic, but no change of crystal form occurs until 910°. Between these two temperatures iron is called the β form.

[5] G. Brauer, *Handbuch der Präparativen Anorganischen Chemie*, Vol. 2, p. 1299, Ferdinand Enke, Stuttgart (1962).

[6] W. E. Addison, *The Allotropy of the Elements*, p. 75, Oldbourne Press, London (1964).

1.6. NUCLEAR PROPERTIES

The natural and artificial radioactive isotopes of iron are listed in Table 1; for fuller details of the radiochemistry of iron including particle energies and alternative modes of preparation of nuclides, the sources from which the table was compiled[7, 8] should be consulted. The nuclides ^{55}Fe and ^{59}Fe are the ones measured in neutron activation studies and are the most commonly used isotopes for tracer studies. ^{59}Fe has the advantage that it can be readily estimated by β- or γ-ray counting, but the longer half-life and softer radiation (X-rays with maximum energy of 5·6 keV) of ^{55}Fe make it the preferred isotope for biological work.

The Mössbauer Effect[9]

A relatively newly discovered type of nuclear resonance spectroscopy "Mössbauer spectroscopy" is particularly useful in the study of iron compounds. The nuclide ^{57}Fe, daughter of ^{57}Co, has an excited state ($t_{1/2} = 1{\cdot}0 \times 10^{-7}$ sec) at 14·4 keV above the ground state. If γ-radiation from a ^{57}Co source falls on an iron compound, then resonant absorption of γ-rays will occur if the iron nuclei are in an environment identical with that of the nuclei in the source. If, however, the source and absorber nuclei are in different environments, no absorption will occur. This resonant absorption of γ-rays can be made to occur, however, by imparting a velocity to the absorber relative to 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 position of the absorption peaks are thus usually expressed in velocities (cm/sec) rather than energies and shifts related to some standard, e.g. sodium pentacyanonitrosylferrate(II) or a stainless steel taken arbitrarily as zero. These "isomer shifts" are directly proportional to the total *s* electron density at the nucleus. Iron(II) compounds give more positive shifts than iron(III) compounds since the 4*s* electrons in Fe^{2+} are more strongly screened by the extra 3*d* electron. This is particularly true of high

TABLE 1. ISOTOPES OF IRON

Isotope	% nat. abundance	Atomic mass	Half-life	Decay mode	Preparation
^{52}Fe			8·3 h	β^+, EC	^{52}Cr(α, 4n)
^{53}Fe			8·9 m	β^+	^{50}Cr(α, n)
^{54}Fe	5·82	53·9396			
^{55}Fe			2·7 y	EC	^{54}Fe(n, γ)
^{56}Fe	91·66	55·9349			
^{57}Fe	2·19	56·9354			
^{58}Fe	0·33	57·9333			
^{59}Fe			45 d	β^-	^{58}Fe(n, γ)
^{60}Fe			3×10^5 y	β^-	Cu(400 MeV p)
^{61}Fe			6·0 m	β^-	^{64}Ni(n, α)

Symbols used: β^+ = positron emission; β^- = negative beta emission; EC = orbital electron capture; m = minutes; h = hours; d = days; y = years.

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[7] B. J. Wilson, Ed., *The Radiochemical Manual*, 2nd edition, The Radiochemical Centre, Amersham (1966).

[8] J. M. Nielson, *The Radiochemistry of Iron*, NAS–NRC No. 3017, Nuclear Science Series, Washington (1960).

[9] P. J. Danon, in *Chemical Applications of Mössbauer Spectroscopy*, p. 160, Eds. V. I. Goldanskii and R. H. Herber, Academic Press, N.Y. (1968).

spin iron complexes in which typical magnitudes of the isomer shift (sodium pentacyanonitrosylferrate(II) standard) are +0·10 to +0·18cm/sec for Fe^{2+} and +0.04 to +0·09 cm/sec for Fe^{3+}.

Splitting of the resonance peak may provide further structural information. For the Fe^{2+} ion (d^6) a quadrupole splitting occurs even if all the iron(II) nuclei are in an identical environment, but in $[Fe(CN)_6]^{4-}$ or for Fe^{3+} (d^5), for example, no splitting occurs. The splitting occurs because of an interaction between the electric field gradient at the nucleus (which depends upon the asymmetry of the electronic charge distribution) and the nuclear quadrupole. Splitting of the peak can also occur due to magnetic dipole interactions and Mössbauer spectroscopy is thus a sensitive tool for detecting ferro- and antiferromagnetic states. Examples of its use will be dealt with under specific iron compounds.

1.7. PHYSICAL PROPERTIES

Pure iron is a silvery-white, rather soft metal which is both malleable and ductile at room temperature. Its physical properties, however, are profoundly altered by the presence of trace amounts of other elements, and since pure iron finds little industrial use, the physical properties of the numerous steels are in many respects more important. The detailed properties of these materials can be found in the metallurgical works of reference[10, 16]. Table 2 summarizes the physical properties of iron having a purity of better than 99·9%[11].

TABLE 2. PHYSICAL PROPERTIES OF IRON

Atomic number	26
Electronic configuration	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$
M.p. (°C)	1535
ΔH fusion (cal/g)	65
B.p. (°C)	3000
ΔH vaporization (cal/g)	1598
Vapour pressure (at 1600°, atm)	$8{\cdot}0 \times 10^{-5}$
Density, (g/cm^3), 20°C	7·873
1564°C	7·00
Atomic weight	55·847
Atomic volume (cm^3/g atom, 25°C)	7·094
Electrical resistivity (microhm-cm), 20°C	9·71
1535°C, liquid	139
Ionization potential (eV), 1st	7·896
2nd	16·18
3rd	30·64
Heat capacity, C_p (cal/g-atom/°C), at 25°C	5·98
at m.p.	9·60
Thermal conductivity (cal/cm/sec/°C), 0°C	0·2
Linear coefficient of thermal expansion (micro-in/in/°C)	
alpha (20–100°C)	12·3
gamma (916–1388°C)	23·04
delta (1388–1502°C)	23·6
Magnetic properties of 99·99% Fe:	
permeability	88,400
induction (gauss), saturation	21,580
residual	11,830

[10] R. B. Ross, *Metallic Materials*, Chapman and Hall, London (1968).

[11] G. A. Moore and T. R. Shives, *Metals Handbook*, 8th edition, p. 1206, American Society for Metals, Metals Park, Ohio (1961).

The magnetic properties of iron are very dependent upon the presence of impurities and are often changed by annealing. Pure (99·9%) iron is ferromagnetic up to the Curie point at 768°C where it changes endothermically into the paramagnetic (β) form. The higher the purity of iron, the greater its permeability and the lower its hysteresis loss. Steels and other alloys principally of iron with cobalt are used in permanent magnets and many alloys[12] have been designed with specific magnetic properties. Alloys of iron with the other ferromagnetic metals cobalt and nickel are commonly used; alloys such as "hypernik" FeNi and permalloy $FeNi_3$ have exceedingly high permeabilities. Silicon added to steel has quite a different effect; it improves the hysteresis and eddy losses so that silicon steels are useful for electric motors and transformers where rapid fluctuations in the magnetism of the iron must occur. Iron alloys high in silicon are paramagnetic; usually, however, when iron is present as a minor constituent in an alloy with non-ferromagnetic materials, the alloy is ferromagnetic.

1.8. CHEMICAL PROPERTIES

Reactions with Elements

Iron absorbs hydrogen especially at high temperatures to form solid solutions. Similarly it absorbs small amounts of nitrogen above 800°C, reacting only slowly; ammonia, however, reacts readily above 400°C to form the nitride Fe_2N. This latter reaction is used for forming hard nitride surfaces on steel. Iron combines with most other non-metals directly at moderate temperatures to form binary compounds. The reaction with oxygen is dependent upon the conditions. Some forms of finely divided iron are pyrophoric in air at room temperature. Massive iron begins to oxidize in dry air above 150°C, Fe_2O_3 and Fe_3O_4 being the major products in excess of oxygen. Above 575°C and under low oxygen pressures, FeO is the major product. With sulphur and phosphorus exothermic reactions occur, crude FeS and Fe_3P being formed. The halogens react at relatively low temperatures ($\sim$ 200°C) to give the iron(III) halides with the exception of iodine which gives iron(II) iodide.

Reactions with Compounds

Steam reacts rapidly with iron above 500°, liberating hydrogen, the predominant oxide formed being Fe_3O_4 below 570°C and FeO above this temperature. Carbon dioxide reacts similarly in forming these two oxides (depending upon the temperature), itself being reduced to carbon monoxide. Carbon monoxide reacts with iron powder at 100–200°C and 200 atm pressure to form iron pentacarbonyl.

In accordance with its place in the electrochemical series (the redox potential for the Fe/Fe^{2+} couple is 0·440 V at 25°C), iron displaces copper from solutions of copper(II) salts and displaces hydrogen from dilute non-oxidizing acids such as hydrochloric and sulphuric acids with the formation of iron(II) salts. When ordinary (impure) iron dissolves in dilute sulphuric acid, the gas evolved has a very characteristic smell; this is due to contamination of the hydrogen with traces of hydrides of the elements (e.g. carbon and sulphur) present as impurities in the iron. Cold dilute nitric acid similarly gives a solution of iron(II), but with hot or strong acid a solution of the iron(III) salt is obtained. When immersed in concentrated nitric acid, iron, after a momentary reaction, becomes resistant to further attack and is said to have become passive. It will no longer then dissolve in dilute nitric acid or displace

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[12] K. Hoselitz, *Ferromagnetic Properties of Metals and Alloys*, Oxford University Press, London (1952).

copper from copper(II) salt solutions, but it will dissolve in reducing acids, e.g. dilute hydrochloric acid. The passivity is due to an oxide film layer on the surface of the iron and can be produced also using other oxidizing agents, e.g. chromic acid.

Rusting[13]

The rusting of iron, that is the formation of hydrated oxide in the presence of oxygen and water, is a special case of corrosion which, because of its enormous economic importance, has received much attention. For rusting to occur at room temperature, the presence of water, an electrolyte and oxygen all appear to be essential. Carbon dioxide is not necessary and at high concentrations may even have a protective effect. Iron completely immersed in fresh or salt water with air above the water surface undergoes slow rusting. The rusting is more rapid if the iron is only partially immersed since oxygen is rapidly replenished at the iron–water interface. In air, a humidity of some 50% (this corresponds to a partial pressure of water vapour of about 6 mm at room temperature) is necessary before rusting sets in, but at 80% humidity the corrosion is severe.

The mechanism of rusting is undoubtedly electrochemical. The corrosion rate is largely governed by processes occurring at the water–iron interface. At this junction, oxygen is reduced by a stepwise cathodic reaction which can be summarized as:

$$O_2+2H_2O+4e \rightarrow 4OH^-$$

The four electrons required for this process are supplied by iron entering the solution as iron(II) cations in an anodic reaction which may be summarized:

$$2Fe \rightarrow 2Fe^{2+}+4e$$

We now have Fe^{2+} and OH^- ions in solution in the presence of oxygen so that yellow-brown rust of hydrated iron(III) oxide precipitates.

Atmospheric rusting is greatly enhanced by the presence of dust particles and sulphur dioxide. Near the sea, airborne particles contain salt, and where there are no other factors to consider the rate of corrosion decreases as the distance from the sea increases. In urban and industrial areas, however, sulphur dioxide is the main cause of corrosion; in the presence of air and water sulphuric acid is formed which attacks the iron. When once iron(II) sulphate has appeared on the surface of iron or steel, rusting can continue in a moist atmosphere even in the absence of sulphur dioxide.

Iron objects can be protected from rusting by using inhibitors such as sodium hydroxide, sodium phosphate or potassium chromate solutions which superficially coat the iron. In "phosphatizing", a coat of iron(II) phosphate is placed upon the iron by immersing it in a bath of acid manganese(II) or zinc(II) phosphates. Other methods of protection involve covering the iron with another metal, e.g. zinc in galvanizing, tin for cans or with red lead paint.

1.9. BIOLOGICAL IMPORTANCE OF IRON COMPOUNDS[14]

Iron is an extremely important constituent of the blood and tissues of the animal body. Most of the iron in the body is present as iron porphyrin or heme proteins which include hemoglobin in the blood, myoglobin and the heme enzymes. Hemoglobin consists of a

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[13] U. R. Evans, *Quart. Revs. (London)* **21** (1967) 29.

[14] C. A. Johnson, in C. A. Hampel, *The Encyclopedia of the Chemical Elements*, p. 310, Reinhold (1968).

protein called globin bound to an iron-containing prosthetic group called heme. Heme is an iron(II) complex of porphyrin, in which the iron atom has a coordination number of six (Fig. 1) and is bonded to four nitrogens of pyrrole rings in a plane and to globin perpendicular to this plane via a nitrogen atom of the imidazole group in histidine. The sixth position is probably occupied by a water molecule. This configuration permits the reversible combination with molecular oxygen at this sixth coordination site and it is by this mechanism that the red blood cells carry oxygen from one part of the body to another. The affinity of heme for carbon monoxide is much greater than that for oxygen and it is this formation of carboxyhemoglobin irreversibly that makes carbon monoxide so poisonous.

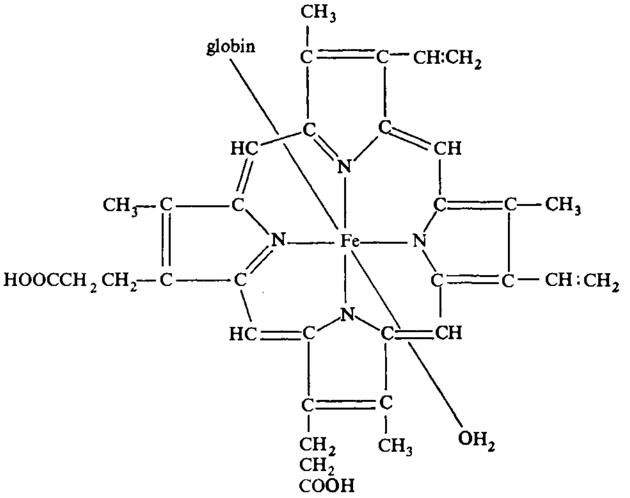

FIG. 1. Heme

Iron is also present in the body in non-heme proteins such as transferrin, ferritin and hemosiderin. In ferritin, iron is believed to be present as iron(III) hydroxide micelles or clusters.

1.10. ANALYTICAL CHEMISTRY OF IRON

Qualitative Detection of Iron

Iron(II) salts usually have a pale green colour in aqueous solution. With alkalis, pale green (white when pure) iron(II) hydroxide is precipitated; this darkens upon exposure to the air owing to oxidation. Potassium hexacyanoferrate(III) gives a deep blue colour or precipitate with iron(II) salts, but potassium thiocyanate gives no coloration.

Iron(III) salts are normally yellow or violet in aqueous solution and give a reddish-brown precipitate of hydrous iron(III) oxide with alkalis. Potassium hexacyanoferrate(II) gives a blue coloration or precipitate (Prussian blue) with iron(III) salts and potassium hexacyanoferrate(III) gives a brown or green colour. Potassium thiocyanate gives the blood red coloration of $[Fe(SCN)(H_2O)_5]^{2+}$ and this is an exceedingly delicate test for iron(III), one part per million being detectable.

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[15] N. H. Furman (Ed.), *Standard Methods of Chemical Analysis*, 6th edition, pp. 529–55, D. van Nostrand Co. Ltd. (1962).

Quantitative Determination of Iron[15]

The gravimetric estimation of iron is usually carried out by precipitating the iron with ammonia as hydrous iron(III) oxide, igniting this precipitate to constant weight and weighing as Fe_2O_3. Alternatively, to increase the bulk of the precipitate, the iron can be precipitated with 8-hydroxyquinoline or α-nitroso-β-naphthol and these ignited to Fe_2O_3. Volumetric methods usually involve reduction of iron(III) to iron(II) using for example tin(II) chloride or the Jones reductor, followed by titration of the iron(II) with dichromate, permanganate or cerium(IV). Alternatively iron(III) can be estimated iodometrically (Fe^{3+} liberates iodine from iodide ions) or by titration with a standard reducing agent such as titanium(III) solution.

Rapid colorimetric methods for iron use either iron(III) with thiocyanate ions or iron(II) with 1,10-phenanthroline. Solvent extraction techniques, e.g. of $HFeCl_4$ from hydrochloric acid by diethyl ether, enable removal of iron from solutions containing many other metal ions.

1.11. ALLOYS OF IRON

The Iron–Carbon Alloys

Carbon may be present in steels in three principal ways: it can occur in the uncombined state as graphite, in solid solution as or the compound Fe_3C—*cementite*. The phase diagram for Fe–C as well as those for many other binary alloys of iron can be found elsewhere[16]. The carbon in pig (cast) iron may be present in the form of cementite or graphite. The eutectic mixture containing 4·3% C at 1150°C consists of a mixture of cementite with *austenite* which is a solid solution of carbon in γ-Fe. When austenite is cooled slowly, cementite forms because the solubility of carbon in γ-Fe decreases with temperature. At around 690°C, because γ-Fe can no longer be stabilized by the presence of carbon, a eutectoid mixture of cementite and ferrite (α-iron) is formed; this is known as *pearlite*. If austenite is cooled rapidly by quenching to below 150°C, a supersaturated solution of carbon in α-Fe forms; this is known as *martensite* and is an extremely hard but brittle steel. By tempering (i.e. reheating to 200–300°C) to remove the brittleness, the solid solution is converted into a mixture of cementite and ferrite.

In austenite there are insufficient carbon atoms to form a regular structure and they probably occupy octahedral holes in the γ-Fe lattice. Cementite[17] is orthorhombic; the carbon atoms are at the centres of nearly regular trigonal prisms of iron atoms.

Other Iron Alloys

Silicon also forms solid solutions with iron, but other non-metals can enter solution only in very small amounts. There are, however, a considerable number of ferro-alloys with metals[18]. The main uses of these alloys are as additives to molten steel and cast iron in the preparation of special steels. Ferromanganese alloys (spiegeleisen) are added to steels as deoxidizing agents as well as to raise the manganese content. Ferrovanadium, ferrotungsten, ferrochromium and ferrosilicon are useful for imparting different properties to steels which may be required for special purposes. Some nickel–steel alloys (e.g. invar steel ~ 36% Ni) have very low coefficients of expansion; others higher in nickel content

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[16] C. J. Smithells, *Metals Reference Book*, Butterworths, London (1955).

[17] R. W. G. Wyckoff, *Crystal Structures*, Vol. 2, 2nd edition, p. 112, Interscience (1964).

[18] W. H. Dennis, *Metallurgy of the Non-Ferrous Metals*, p. 410, Pitman, London (1961).

(permalloys having 70–80% Ni) have high magnetic permeability and find uses in electromagnetic devices. There are a multitude of many-component alloys based upon iron, details of which are to be found elsewhere[11, 12].

2. COMPOUNDS OF IRON IN LOW OXIDATION STATES (−2, −1, 0, +1)

2.1. IRON CARBONYLS

Iron Pentacarbonyl, $Fe(CO)_5$

Pentacarbonyl iron is obtained as a yellow liquid in the direct reaction between iron and carbon monoxide. Finely divided iron will react slowly at ordinary temperatures and pressures, but for good yields, temperatures around 200°C and pressures of 50–200 atm are used. The complete absence of oxygen and the presence of traces of sulphur or selenium improve the yield.

Some physical properties of iron pentacarbonyl are listed in Table 3. The trigonal bipyramidal structure has been preferred to the square pyramidal one in the interpretation of electron diffraction[19], Raman and infrared[20] and thermodynamic[21] data; the apparently contradictory dipole moment of 0·8 *D* being attributed[22] to atom polarization. A single crystal X-ray structure determination at −80°C has confirmed[23] the trigonal bipyramidal

TABLE 3. PHYSICAL PROPERTIES OF IRON PENTACARBONYL

M.p.[a] (°C)	−20
ΔH_{fusion}[a] (cal/mole)	3161
B.p.[a] (°C)	103
$\Delta H_{\text{vap.}}$[a] (cal/mole)	9600
Vapour pressure equation for liquid[a]	$\log P_{\text{mm}} = 8{\cdot}514 - \frac{2105}{T}$
Heat capacity[a] C_p (cal/mole/deg)	
−206°C	20·9
14°C	56·9
$\Delta H_{\text{form.}}$[b] (kcal/mole)	−182·6
$\Delta H_{\text{comb.}}$[b] (kcal/mole)	−386·9
M–C mean bond dissociation energy[b] (kcal)	27·7
Density[c] (0°C)	1·4937
Infrared bands (cm^{-1})	
ν(M–C)[d]	432, 474
ν(C–O)[e]	2014, 2034

[a] A. J. Leadbetter and J. E. Spice, *Can. J. Chem.* **37** (1959) 1923.

[b] F. A. Cotton, A. K. Fischer and G. Wilkinson, *J. Am. Chem. Soc.* **81** (1959) 800.

[c] J. Dewar and H. O. Jones, *Proc. Roy. Soc.* (*London*) **A76** (1905) 563.

[d] W. F. Edgell, W. E. Wilson and R. Summitt, *Spectrochim. Acta*, **19** (1963) 863.

[e] G. Bor, *Spectrochim. Acta*, **18** (1962) 817.

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[19] R. V. G. Ewens and M. W. Lister, *Trans. Faraday Soc.* **35** (1939) 681.

[20] H. Stammreich, O. Sala and Y. Tavares, *J. Chem. Phys.* **30** (1959) 856; T. S. Piper and G. Wilkinson, *Naturwissenschaften*, **43** (1956) 15.

[21] A. J. Leadbetter and J. E. Spice, *Can. J. Chem.* **37** (1959) 1923.

[22] W. Hieber and E. Weiss, *Z. anorg. u. allgem. Chem.* **287** (1956) 223.

[23] A. W. Hanson, *Acta Cryst.* **15** (1962) 930.

structure. Some distortion is observed, however, the oxygen atoms being displaced by up to 0·13 Å and this is believed to allow closer packing in the crystal. Some authors[24], however, have suggested that the X-ray results cannot be taken to indicate any significant differences in the lengths of the axial and trigonal Fe–C bonds. Electron diffraction studies[25] on the vapour give the Fe–C axial distances of 1·797±0·015 Å and the Fe–C trigonal distances of 1·842±0·015 Å.

Iron pentacarbonyl is soluble in organic solvents, e.g. benzene, petroleum ether, but insoluble in water. Upon thermal decomposition at 250° it yields pure iron. In sunlight or under ultraviolet irradiation it evolves carbon monoxide and dark yellow platelets of iron enneacarbonyl, $Fe_2(CO)_9$, form. The pentacarbonyl (in ethereal solution) is attacked by mineral acids with evolution of carbon monoxide and hydrogen and the formation of iron(II) salts. In liquid hydrogen chloride, however, it is protonated[26] to give the $[Fe(CO)_5H]^+$ cation and the salt $[Fe(CO)_5H]^+PF_6$ can be isolated at low temperatures; it decomposes fairly rapidly at room temperature. Aqueous or alcoholic alkalis convert the pentacarbonyl to carbonylate anions, e.g.

$$Fe(CO)_5+3OH^- \rightarrow [HFe(CO)_4]^-+CO_3^{2-}+H_2O$$

These will be discussed separately as will be the carbonyl halides—the reaction products of the pentacarbonyl with the halogens under controlled conditions. The pentacarbonyl is completely oxidized by copper(II) chloride in acetone:

$$Fe(CO)_5+2CuCl_2 \rightarrow FeCl_2+2CuCl+5CO$$

but reacts with mercury(II) salts to form an air-stable, yellow insoluble compound $Fe(CO)_4Hg$:

$$Fe(CO)_5+HgSO_4+H_2O \rightarrow Fe(CO)_4Hg+H_2SO_4+CO_2$$

This compound can also be prepared from solutions of iron carbonyl hydride:

$$Fe(CO)_4H_2+HgCl_2 \rightarrow Fe(CO)_4Hg+2HCl$$

It decomposes at 150°C into mercury, iron and carbon monoxide. With iodine the carbonyl iodide is formed:

$$Fe(CO)_4Hg+2I_2 \rightarrow Fe(CO)_4I_2+HgI_2$$

Iron pentacarbonyl is a useful dehalogenating and carbonylating agent. Tungsten(VI) chloride is converted into tungsten hexacarbonyl and tin(II) chloride forms $Sn[Fe(CO)_4]_4$. It thus provides a route to polynuclear carbonyls having another metal present as well as iron. The reaction of iron pentacarbonyl with $[Ru(CO)_3Cl_2]_2$ or $Ru_3(CO)_{12}$ at 90–100°C affords[27] $H_2FeRu_3(CO)_{13}$, $Fe_2Ru(CO)_{12}$ and $Ru_2Fe(CO)_{12}$ (in addition to $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$). The photochemical reactions between iron pentacarbonyl and the carbonyls of group VIIA metals produce[28] the neutral linear trinuclear species $M_2Fe(CO)_{14}$ and the triangular anionic species $[MFe_2(CO)_{12}]^{2-}$. The infrared spectrum of the latter in the carbonyl stretching region is very similar to that of $Fe_3(CO)_{12}$ so that a similar structure

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[24] J. Donohue and A. Caron, *J. Phys. Chem.* **70** (1966) 603.

[25] M. I. Davis and H. P. Hanson, *J. Phys. Chem.* **69** (1965) 3405.

[26] Z. Iqbal and T. C. Waddington, *J. Chem. Soc.* (A) (1968) 2958.

[27] D. B. W. Yawney and F. G. A. Stone, *Chem. Communs.* (1968) 619; J. Knight and M. J. Mays, *Chem. and Ind.* (*London*) (1968) 1159.

[28] M. W. Lindauer, G. O. Evans and R. K. Sheline, *Inorg. Chem.* **7** (1968) 1249.

(viz. Fig. 9) is proposed in which the apical *cis*-$Fe(CO)_4$ moiety is replaced by a *cis*-$[M(CO)_4]^-$ group.

Substitution Reactions of Iron Carbonyls

The reactions of iron carbonyls with neutral Lewis bases are exceedingly numerous and fall into two main categories. Strong σ-donors such as nitrogen and oxygen bases cause disproportionation of the iron and the formation of carbonylate anions, e.g.

$$5Fe(CO)_5 + 6py \rightarrow [Fe(py)_6][Fe_4(CO)_{13}] + 12CO$$

Substitution reactions occur, however, predominantly with ligands capable of stabilizing the zero oxidation state of the iron, i.e. with those ligands having both σ-donor and π-acceptor properties. Such substitution reactions are brought about either thermally at temperatures up to 200° or photochemically. These reactions have been extensively

TABLE 4. SOME SUBSTITUTION PRODUCTS OF IRON CARBONYLS

Compound	Colour	ν(C–O), cm^{-1}
$Fe(CO)_4PPh_3$[a, b]	pale yellow	2055, 1978, 1943
$Fe(CO)_4AsPh_3$[b]	yellow	2054, 1977, 1945
$Fe(CO)_4SbPh_3$[b]	yellow-brown	2048, 1975, 1942
$Fe(CO)_4PF_3$[c]	yellow	2101, 2094, 2021, 2004, 1996, 1970, 1960
$Fe(CO)_4TePh_2$[d]	brown	2096, 2030, 2000, 1968
$Fe(CO)_4(CNMe)$[a, e]	pale yellow	2072, 1996, 1967
$Fe(CO)_4$(butadiene)[f]	orange	2084, 2004, 1981
$Fe(CO)_4$(ethylene)[g]	yellow-orange	2088, 2013, 2007, 1986
$Fe(CO)_3(PPh_3)_2$[a, b]	yellow	1885
$Fe(CO)_3(AsPh_3)_2$[b]	yellow	1884
$Fe(CO)_3$(Diars)[h]	golden-yellow	1996, 1916, 1877
$Fe(CO)_3(CNCMe_3)_2$[a]	yellow	2006 vw, 1923 s
$Fe(CO)_3(SbPh_3)_2$[b]	brown	1882
$Fe(CO)_3$(butadiene)[i]	pale yellow	2053, 1985, 1975
$Fe(CO)_3$(cyclo-octatetraene)[j]	red	2061, 1993, 1976, 1942, 1895, 1845
$Fe_2(CO)_6P_2Me_4$[k]	yellow	2047, 2009, 1976, 1963
$Fe_2(CO)_6S_2$[l]	red	2081, 2042, 2005
$[Fe(CO)_3SPh]_2$[m]	brick red	2073, 2038, 2003, 1957
$Fe_3(CO)_9S_2$[l]	red	2062, 2045, 2024, 1985
$Fe_2(CO)_8$(hexatriene)[g]	yellow	2085, 2075, 2014, 1994, 1965, 1950

[a] F. A. Cotton and R. V. Parish, *J. Chem. Soc.* (1960) 1440.
[b] A. F. Clifford and A. K. Mukherjee, *Inorg. Chem.* **2** (1963) 151; *idem, Inorganic Syntheses* **8** (1966) 185.
[c] R. J. Clark, *Inorg. Chem.* **3** (1964) 1395.
[d] W. Hieber and T. Kruck, *Chem. Ber.* **95** (1962) 2027.
[e] W. Hieber and D. von Pigenot, *Chem. Ber.* **89** (1956) 193.
[f] H. D. Murdoch and E. Weiss, *Helv. Chim. Acta*, **45** (1962) 1156; K. Noack, *ibid.* 1847.
[g] H. D. Murdoch and E. Weiss, *Helv. Chim. Acta*, **46** (1963) 1588.
[h] J. Lewis, R. S. Nyholm, S. S. Sandhu and M. H. B. Stiddard, *J. Chem. Soc.* (1964) 2825.
[i] B. F. Hallam and P. L. Pauson, *J. Chem. Soc.* (1958) 642; K. Noack, *Helv. Chim. Acta*, **45** (1962) 1847.
[j] R. T. Bailey, E. R. Lippincott and D. Steele, *J. Am. Chem. Soc.* **87** (1965) 5346.
[k] J. Chatt and D. A. Thornton, *J. Chem. Soc.* (1964) 1005.
[l] W. Hieber and J. Gruber, *Z. anorg. u. allgem. Chem.* **296** (1958) 91.
[m] W. Hieber and W. Beck, *Z. anorg. u. allgem. Chem.* **305** (1960) 265.

reviewed[29] and the photochemical methods surveyed[30]. Table 4 summarizes some of the products obtainable. It can be seen that substitution reactions occur with phosphorus, arsenic, antimony, sulphur and selenium donors as well as with unsaturated organic molecules and isocyanides; the products are generally of the mono- and di-substituted types. The compounds of general formulae $Fe(CO)_4L$ and $Fe(CO)_3L_2$ (L = unidentate ligand) are in general believed to possess trigonal bipyramidal configurations on the basis of their infrared spectra; the disubstituted products having the *trans*- configuration with only one infrared active vibration in the carbonyl stretching region[31]. Chelating ligands form *cis*-$[Fe(CO)_3(LL)]$ for example with *o*-phenylene-bisdimethyl-arsine (Diars) and 1,2-bis(diphenylphosphino)ethane. One mono-carbonyl complex is known, namely Fe(CO) $(Diars)_2$.

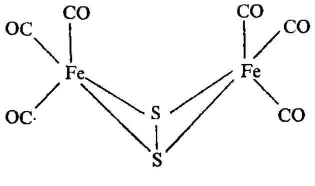

FIG. 2. $Fe_2(CO)_6S_2$.

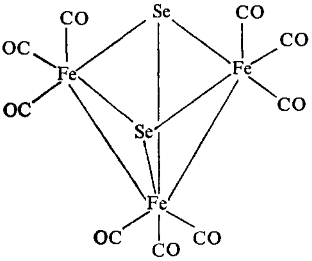

FIG. 3. $Fe_3(CO)_9Se_2$.

The elements of group VI, S, Se and Te, form a large variety of compounds derived from iron carbonyls; interest in these species has been of obvious importance in view of the known role of these elements as promoters in the synthesis of iron pentacarbonyl. The compounds $Fe_2(CO)_6S_2$ and $Fe_3(CO)_9X_2$ (X = S, Se, Te)[32] have interesting structures (Figs. 2 and 3).

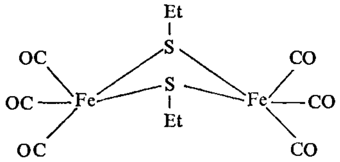

FIG. 4. $Fe_2(CO)_6(SEt)_2$.

The X-ray structure of $Fe_2(CO)_6S_2$[33] shows it to contain two bridging sulphur atoms, these being at a bonding distance to each other of 2·01 Å. In $Fe_2(CO)_9Se_2$[34] two of the iron atoms are bonded together via selenium bridges while the third iron atom is bonded to all four of these heavy atoms. The compounds are obtained by reactions of the tetracarbonylferrate anion with polysulphide or hyposulphite ions (for $Fe_2(CO)_6S_2$) or with sulphurous, selenious

[29] F. Calderazzo, R. Ercoli and G. Natta, in *Organic Synthesis via Metal Carbonyls*, pp. 109–28, I. Wender and P. Dino, Eds., Interscience (1968); M. Dub (Ed.) *Organometallic Compounds*, Vol. 1, Springer-Verlag (1966).

[30] W. Strohmeier, *Angew. Chem. Intern. Ed.* **3** (1964) 730.

[31] F. A. Cotton and R. V. Parish, *J. Chem. Soc.* (1960) 1440; A. Reckziegel and M. Bigorgne, *J. Organometallic Chem.* **3** (1965) 341.

[32] W. Hieber and J. Gruber, *Z. anorg. u. allgem. Chem.* **296** (1958) 91.

[33] C. H. Wei and L. F. Dahl, *Inorg. Chem.* **4** (1965) 1.

[34] L. F. Dahl and P. W. Sutton, *Inorg. Chem.* **2** (1963) 1067.

or tellurious acid (for $Fe_3(CO)_9X_2$). Similar compounds are obtained with alkyl sulphides; they are of the general formula $[Fe(CO)_3SR]_2$. The crystal structure[35] of the ethyl derivative, $[Fe(CO)_3SEt]_2$ (Fig. 4), shows it to consist of two sulphur bridged iron atoms; stereoisomers are possible depending upon the relative orientations of the ethyl groups with respect to the rest of the molecule. Such isomers have been obtained for the methyl compound and these have been designated[36] *syn*-$[Fe(CO)_3SMe]_2$ and *anti*-$[Fe(CO)_3SMe]_2$.

A further important group of substituted iron carbonyl complexes is that formed by unsaturated organic ligands; compounds formed from iron carbonyls and olefins or acetylenes are exceedingly numerous[29, 37] and cannot be dealt with in any detail here. The first of these was prepared by Reihlen[28] in 1930 by the reaction of butadiene with iron pentacarbonyl. The structure of the product, $C_4H_6Fe(CO)_3$, has caused much discussion; the location of the atoms was finally settled by Mills and Robinson[39] in 1960. The carbon atoms of the butadiene are *cis* and co-planar (Fig. 5); the iron atom lies approximately equidistantly (2·10±0·4 Å) from these four carbon atoms and the C–C distances are identical (1·45 and 1·46 Å) within experimental error. The exact nature of the bonding between the iron atoms and the butadiene moiety is, however, still not settled. In view of the equidistant carbon atoms it has been assumed that the π-electrons of butadiene are completely delocalized. However, it has been pointed out[40] that complete delocalization would lead to unequal bond lengths; it is still not certain whether or not there is σ-bonding between the iron atom and the terminal carbon atoms of the C_4H_6 group. In a similar complex, however, namely octafluorocyclohexa-1,3-diene iron tricarbonyl (Fig. 6), the iron

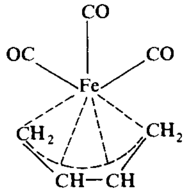

FIG. 5. Butadiene iron tricarbonyl.

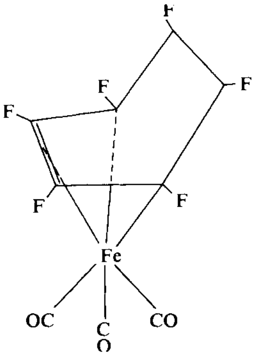

FIG. 6. Octafluorocyclohexa-1,3-diene iron tricarbonyl.

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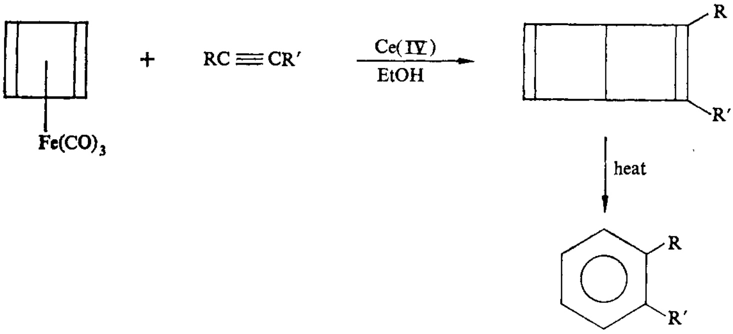
[35] L. F. Dahl and C. H. Wei, *Inorg. Chem.* **2** (1963) 328.
[36] R. B. King and M. B. Bisnette, *Inorg. Chem.* **4** (1965) 1663.
[37] R. Pettit and G. F. Emerson, in *Advances in Organometallic Chem.* **1** (1964) 1.
[38] H. Reihlen, A. Gruhl, G. von Hessling and O. Pfrengle, *Ann. Chem.* **482** (1930) 161.
[39] O. S. Mills and G. Robinson, *Acta Cryst.* **16** (1963) 758.
[40] M. R. Churchill and R. Mason, *Proc. Chem. Soc.* (1964) 226.

atom has been found[40] to be in a pseudo-octahedral environment and bonded to the planar C_4 unit through one π- and two σ-bonds.

Many interesting derivatives of cyclic systems have been prepared. With cyclopentadiene iron pentacarbonyl yields ferrocene $Fe(C_5H_5)_2$. The first cyclobutadiene complex, tricarbonylcyclobutadiene iron, was prepared[41] by the dehalogenation of *cis*-3,4-dichlorocyclobutene with iron enneacarbonyl. When reacted with an acetylenic compound in the presence of cerium(IV) ions, Dewar benzene derivatives are formed[42]:



Cyclo-octatetraene forms $Fe(CO)_3C_8H_8$, $Fe_2(CO)_6C_8H_8$ and $Fe_2(CO)_7C_8H_8$ in its reactions with iron pentacarbonyl and iron dodecacarbonyl. The X-ray structures of the first two compounds have been elucidated[43]; in these the cyclo-octatetraene rings are not planar; the $Fe(CO)_3$ groups, however, are associated with four nearly planar carbon atoms in an arrangement similar to that in butadiene iron tricarbonyl.

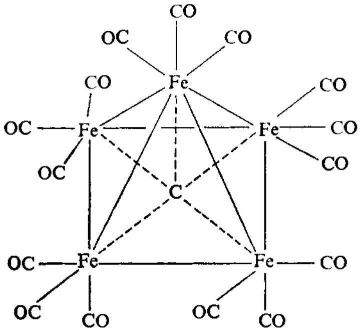


FIG. 7. $Fe_5(CO)_{15}C$.

Acetylenes react with iron enneacarbonyl at room temperature, with the dodecacarbonyl at 60–100° and with the pentacarbonyl at around 150° or under ultraviolet irradiation to give a host of complexes of different types[44]. The reactions are complicated and the products

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[41] G. F. Emerson, L. Watts and R. Pettit, *J. Am. Chem. Soc.* **87** (1965) 131.

[42] L. Watts, J. D. Fitzpatrick and R. Pettit, *J. Am. Chem. Soc.* **87** (1965) 3253.

[43] B. Dickens and W. N. Lipscomb, *J. Am. Chem. Soc.* **83** (1961) 489, 4862; *idem*, *J. Chem. Phys.* **37** (1962) 2084.

[44] W. Hubel, in *Organic Syntheses via Metal Carbonyls*, pp. 284–96, I. Wender and P. Pino, Eds., Interscience (1968).

very dependent upon the conditions of temperature and pressure used. Reppe[45] reacted iron pentacarbonyl with acetylene in aqueous ethanol under pressure and obtained a product which upon hydrolysis with water at 80° yielded hydroquinone and a compound $C_8H_4O_4Fe$ which is now known to be cyclopentadienone iron tricarbonyl. One particularly interesting compound is the carbonyl carbide $Fe_5(CO)_{15}C$, formed in small amounts when the dodecacarbonyl reacts with methylphenylacetylene or n-propylacetylene. Its structure[46] (Fig. 7) consists of a tetragonal pyramid of iron atoms with terminal carbonyl groups on each atom and a penta-coordinated carbon atom situated just below the centre of the basal plane of iron atoms and being approximately equidistant from all five iron atoms.

Di-iron Enneacarbonyl, $Fe_2(CO)_9$

This carbonyl is obtained as dark yellow platelets by exposing solutions of the pentacarbonyl in organic solvents to sunlight or ultraviolet irradiation. The quantum yield for the reaction is 2 and the following mechanism has been proposed[47]:

$$Fe(CO)_5 \rightarrow {}^*Fe(CO)_5$$
$$Fe(CO)_5 + {}^*Fe(CO)_5 \rightarrow Fe_2(CO)_9 + CO$$

Iron enneacarbonyl decomposes at 100°, but can be sublimed at 35°C in a high vacuum. It is insoluble in aliphatic hydrocarbons and reacts with many organic solvents to form mainly the pentacarbonyl or its substituted derivatives. These properties have considerably hindered structural studies; the infrared spectrum[48], for example, can only be measured in the solid. The X-ray crystal structure determination[49] shows it to have the structure shown in Fig. 8 in which six carbon monoxide molecules are arranged around each iron atom in a slightly distorted octahedral array. The Fe–Fe distance is 2·46 Å, whilst the Fe–C distances are all around 1·85 Å. The Mössbauer spectrum[50] also suggests that the iron atoms are in an octahedral environment. However, since the compound is diamagnetic it must contain an Fe–Fe bond as well as the three bridging carbonyl groups.

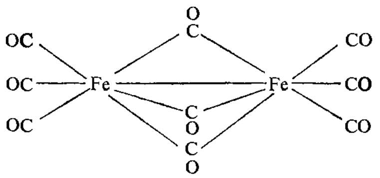

FIG. 8. Di-iron enneacarbonyl.

Whilst iron enneacarbonyl is a relatively reactive carbonyl, no disproportionation reactions have been observed with nitrogen or oxygen bases. Carbonylate anions are obtained in its reactions with alkalis or sodium in ammonia solutions:

$$Fe_2(CO)_9 + 4Na \rightarrow 2Na_2Fe(CO)_4 + CO$$

Substitution reactions occur readily and have already been discussed. In its reaction with

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[45] W. Reppe and H. Vetter, *Ann.* **582** (1953) 1, 38, 72, 87, 133.

[46] E. H. Braye, L. F. Dahl, W. Hubel and D. L. Wampler, *J. Am. Chem. Soc.* **84** (1962) 4633.

[47] G. Eyber, *Z. Physik. Chem.* **144A** (1929) 1.

[48] R. K. Sheline and K. S. Pitzer, *J. Am. Chem. Soc.* **72** (1950) 1107.

[49] H. M. Powell and R. V. G. Ewens, *J. Chem. Soc.* (1939) 286.

[50] R. H. Herber, W. R. Kingston and G. K. Wertheim, *Inorg. Chem.* **2** (1963) 153.

liquid sulphur dioxide, the enneacarbonyl yields $Fe_2(CO)_8SO_2$ which is believed to possess a structure having a sulphur dioxide bridge between the two iron atoms[51].

Tri-iron Dodecacarbonyl, $Fe_3(CO)_{12}$

This carbonyl was first obtained by thermal decomposition of non aqueous solutions of the enneacarbonyl at 100°C:

$$6Fe_2(CO)_9 \rightarrow 2Fe_3(CO)_{12}+6Fe(CO)_5$$

but is now usually prepared from solutions of carbonylferrate anions. One method[52] uses the oxidation of these ions with manganese(IV) oxide followed by acidification and extraction of the carbonyl into petroleum ether. In another method[53, 54] iron pentacarbonyl is treated with aqueous triethylamine to form the dark red $[Et_3NH][Fe_3(CO)_{11}H]$ which is then acidified and the carbonyl extracted into petroleum ether. Tri-iron dodecacarbonyl forms deep green, diamagnetic crystals which decompose at 140°C, but which can be sublimed slowly *in vacuo*. It dissolves in organic solvents and in pentacarbonyl iron in which its molecular weight corresponds to $Fe_3(CO)_{12}$.

The structure[55] of $Fe_3(CO)_{12}$ (Fig. 9) is related to that of $Fe_2(CO)_9$ in that it can be described as a triangular metal cluster in which one bridging group of the $Fe_2(CO)_9$ system is replaced by an $Fe(CO)_4$ group. This X-ray data is in agreement with the Mössbauer spectrum[56] which shows the presence of two types of iron atom; two of the iron atoms show substantial quadrupole splitting and have isomer shifts similar to those of the iron atoms in $Fe_2(CO)_9$, while the other iron atom shows little splitting as might be expected for an octahedral environment. A similar structure is possessed by the $[Fe_3(CO)_{11}H]$ anion in which one of the bridging carbonyl groups is replaced by a bridging hydrogen atom.

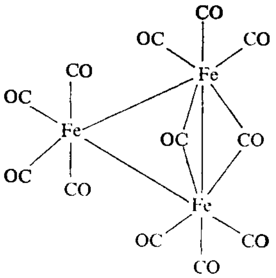

FIG. 9. Tri-iron dodecacarbonyl.

Unlike the enneacarbonyl, $Fe_3(CO)_{12}$ undergoes disproportionation reactions with bases and its reactivity is greater than that of the pentacarbonyl. The dodecacarbonyl reacts with methanol at room temperature, for example[57], and the pentacarbonyl is thereby produced:

$$3Fe_3(CO)_{12}+nMeOH \rightarrow [Fe(MeOH)_n][Fe_3(CO)_{11}]+5Fe(CO)_5$$

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[51] E. H. Braye and W. Hubel, *Angew. Chem.* **75** (1963) 345.

[52] W. Hieber and G. Brendel, *Z. anorg. u. allgem. Chem.* **289** (1957) 324; R. B. King and F. G. A. Stone, *Inorg. Syntheses*, **7** (1963) 193.

[53] M. Heintzler, Ger. Pat. 928,044 (1955); W. McFarlane and G. Wilkinson, *Inorg. Syntheses*, **8** (1966) 181.

[54] J. R. Case and M. C. Whiting, *J. Chem. Soc.* (1960) 4632.

[55] C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc.* **88** (1966) 1821.

[56] N. E. Ericksen and A. W. Fairhall, *Inorg. Chem.* **4** (1965) 1320.

[57] W. Hieber and G. Brendel, *Z. anorg. u. allgem. Chem.* **289** (1957) 338.

With a variety of nitrogen bases, iron(II) salts of the anions $[Fe_2(CO)_8]^{2-}$ and $[Fe_3(CO)_{11}]^{2-}$ are formed.

Carbonylferrates(-I) and (-II)

By the reactions of bases with iron carbonyls, any of the carbonylate anions $[Fe(CO)_4]^{2-}$, $[Fe_2(CO)_8]^{2-}$, $[Fe_3(CO)_{11}]^{2-}$ and $[Fe_4(CO)_{13}]^{2-}$ can result depending upon the base and the conditions used. These anions are interconvertible and their formation is dependent upon pH and temperature. The uninegative anions $[Fe(CO)_4H]^-$, etc., containing an added proton are also known. The identification of these various ions in solution has often been through the measurement of their electronic spectra; the colour of the ions varies from pale yellow to deep red as they become more complex. Agreement between various workers is not good, however; an excellent summary of these spectra can be found elsewhere[29].

The reaction of iron pentacarbonyl with aqueous or alcoholic alkalis gives yellow solutions containing the $[Fe(CO)_4H]^-$ ion; in the presence of air or oxidizing agents, oxidation occurs to form successively salts of $H_2Fe_2(CO)_8$ and $H_2Fe_3(CO)_{11}$, e.g.

$$2[Fe(CO)_4H]^- \rightarrow H_2 + [Fe_2(CO)_8]^{2-}$$

The binuclear anion is stable above pH 10, but in the presence of acid (pH 5) it is converted reversibly to the trinuclear species. The nature of the carbonylate anions formed in the disproportionation reactions of the carbonyls is very dependent upon the reaction temperature. When ethylenediamine reacts with $Fe_3(CO)_{12}$, salts of the $[Fe(en)_3]^{2+}$ cation are formed; if the reaction is carried out at 40°, the $[Fe_3(CO)_{11}]^{2-}$ anion predominates, at 90° the $[Fe(CO)_4H]^-$ anion forms and at 145° $[Fe(CO)_4]^{2-}$ is the predominant species. The nature of the base also determines which anion is formed. With iron pentacarbonyl, benzidine forms the $[Fe(CO)_4]^{2-}$ salt, while under comparable conditions picolines, *o*-phenanthroline and triphenylphosphine oxide favour the binuclear species, 2,2′-dipyridyl the trinuclear species and pyrrolidine the tetranuclear species. A third route to the carbonylate anions involves the reduction of the carbonyls or carbonyl halides with sodium in liquid ammonia, e.g.[58]

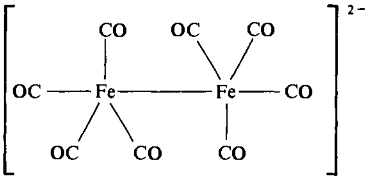

FIG. 10. The octacarbonyl diferrate(-I) anion.

$$Fe_3(CO)_{12} + 6Na \rightarrow 3Na_2[Fe(CO)_4]$$

The $[Fe(CO)_4]^{2-}$ ion is isoelectronic and isostructural with nickel carbonyl. The Mössbauer spectrum of $Na_2[Fe(CO)_4]$ at 25°C shows[56] the single resonance line expected for the tetrahedral anion, the isomer shift being one of the most negative so far observed. The $[Fe(CO)_8]^{2-}$ ion has only terminal carbonyl groups and is believed[59] to have the metal–metal bonded structure shown in Fig 10. In the $[Fe_2(CO)_7H]^-$ anion, however[60], the infrared spectrum indicates bridging carbonyl groups to be present and the Mössbauer

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[58] H. Behrens and R. Weber, *Z. anorg. u. allgem. Chem.* **281** (1955) 190.

[59] E. W. Abel, *Quart. Revs.* (*London*), **17** (1963) 155.

[60] K. Farmery, M. Kilner, R. Greatrex and N. N. Greenwood, *Chem. Communs.* (1968) 593.

spectrum shows the two iron atoms to be in equivalent environments. Its structure is thus probably analogous to that of $Fe_2(CO)_9$ with one bridging carbonyl group replaced by a hydrogen atom. The $[Fe_3(CO)_{11}]^{3-}$ ion is believed[59] to have a structure (Fig. 11) in which two of the carbonyl groups are each situated equidistant from the three iron atoms.

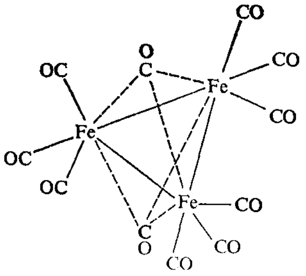

FIG. 11. The undecacarbonyl triferrate(-I) anion.

Iron Carbonyl Hydrides

Acidification of solutions of the $[Fe(CO)_4H]^-$ ion liberates the unstable, gaseous iron carbonyl hydride $H_2Fe(CO)_4$. This hydride can also be prepared by borohydride reduction of the carbonyl iodide $Fe(CO)_4I_2$ in tetrahydrofuran. It melts at −70°C to a pale yellow liquid which decomposes rapidly above −10°C into hydrogen and as yet uncharacterized products. With carbon monoxide it regenerates iron pentacarbonyl with liberation of hydrogen. Iron carbonyl hydride is a weak acid[61] ($K_1 = 4 \times 10^{-5}$; $K_2 = 4 \times 10^{-14}$) and many salt-like derivatives have been prepared. Calcium and magnesium hydroxides form salts of the type $M^{II}[Fe(CO)_4H]_2$ and crystalline compounds $[M(NH_3)_6]^{2+}[Fe(CO)_4H]_2$ can be precipitated from solutions of the $[HFe(CO)_4]^-$ anion by the hexammine metal(II) cations. The hexammine cobalt(III) cation, however, causes oxidation to $Fe_3(CO)_{12}$. The redox potential[62] for the reaction

$$3[Fe(CO)_4H]^- \rightarrow Fe_3(CO)_{12} + 3H^+ + 6e$$

is −0·35 V at 20°. The hydride is readily oxidized to the dodecacarbonyl with manganese(IV) oxide:

$$3Fe(CO)_4H_2 + 3MnO_2 + 6H^+ \rightarrow Fe_3(CO)_{12} + 6H_2O + 3Mn^{2+}$$

The structure of $H_2Fe(CO)_4$ is not yet known for certain despite broad line proton magnetic resonance and infrared studies. The environment of the iron atom could be essentially octahedral with the carbonyl groups slightly distorted towards the sterically smaller hydrogen atoms[63].

The chemistry of the polynuclear hydrides, i.e. the red-brown $H_2Fe_2(CO)_8$, red $H_2Fe_3(CO)_{11}$ and red $H_2Fe_4(CO)_{13}$, is less well studied. These hydrides are obtained by acidification of the polynuclear carbonylate anions and several of their salts, e.g. $[Me_4N]_2[Fe_4(CO)_{13}]$[64] and $[Ni(phen)_3][Fe_2(CO)_8]$[57], have been isolated.

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[61] P. Krumholz and H. M. A. Stettiner, *J. Am. Chem. Soc.* **71** (1949) 3035.

[62] W. Hieber and W. Hubel, *Z. Elektrochem.* **57** (1953) 331.

[63] M. L. H. Green and D. J. Jones, *Advances in Inorg. Chem. Radiochem.* **7** (1965) 149.

[64] W. Hieber and R. Werner, *Chem. Ber.* **90** (1957) 286.

Iron Carbonyl Halides

The reactions of iron pentacarbonyl with the halogens give rise to the unstable compounds $Fe(CO)_5X_2$ which decompose below 0°C with evolution of carbon monoxide and formation of the tetracarbonyl halides $Fe(CO)_4X_2$. These are also formed in the direct reactions between the iron(II) halides and carbon monoxide under pressure. The tetracarbonyl halides are non-electrolytes, soluble in inert organic solvents but hydrolysed by water with evolution of carbon monoxide. Their thermal and hydrolytic stability increases in the order $Cl < Br < I$, the thermal decomposition products being the lower carbonyl halides, $Fe(CO)_2X_2$ and $Fe(CO)_2X$; the existence of the intermediate tricarbonyl halides is doubtful. The red iron tetracarbonyl iodide is sufficiently stable to be sublimed *in vacuo*; in hydrogen it is converted into the bright red $Fe(CO)_2I_2$. Sometimes the lower carbonyl halide can be obtained directly; the reaction of the pentacarbonyl with iodine in boiling benzene, for example, yields $Fe(CO)_2I_2$. Thermal decomposition of this iodide yields first $Fe(CO)_2I$ and then the red unstable FeI.

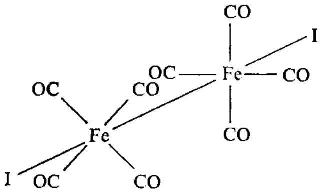

FIG. 12. Octacarbonyl di-iron(I) di-iodide.

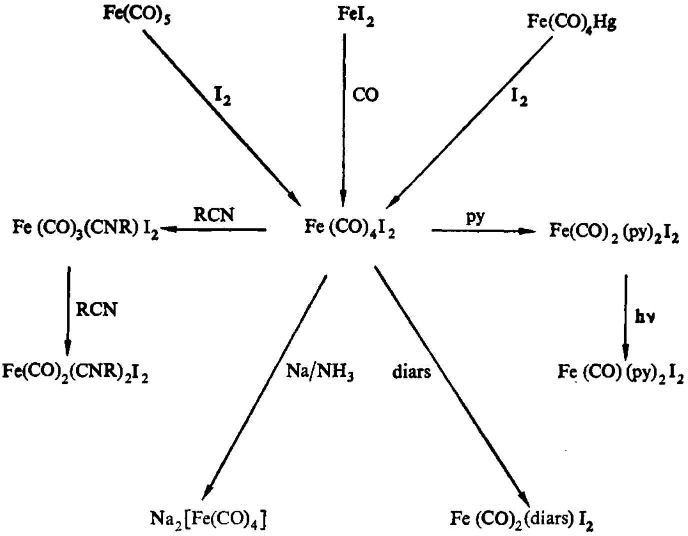

FIG. 13. Some chemistry of iron tetracarbonyl iodide.

The structures of most of the carbonyl halides are unknown. The infrared spectra of the tetracarbonyl halides have been recorded[29] and the iodide found[22] to have a dipole moment of 3·60±0·50 *D* so that it is probably *cis*-octahedral. The $[Fe(CO)_4I]^-$ anion is probably trigonal bipyramidal with the iodine atom in an apical position[65]. The reaction of iodine with tri-iron dodecacarbonyl in tetrahydrofuran gives $Fe_2I_2(CO)_8$, a colourless solid below its melting point (−5°C). The staggered D_{4d} structure (Fig. 12) has been proposed for this molecule.

The reactions of the tetracarbonyl halides with excess of bases leads to complete substitution (as with water), but displacement of carbonyl groups may proceed stepwise if the base is not in excess. The thermal stability of the substituted carbonyl halides increases with successive replacement of the carbonyl groups. Some reactions of the tetracarbonyl iodide are summarized in Fig. 13.

2.2. NITRIC OXIDE COMPLEXES OF IRON

For many nitric oxide complexes of iron there is some doubt about the magnitude of the oxidation state of the iron atom and so for convenience they will all be considered here despite the fact that some of the compounds certainly do not contain iron in a low oxidation state.

Iron Tetranitrosyl, $Fe(NO)_4$

This is obtained as black crystals when iron pentacarbonyl is heated to 45°C with nitrogen monoxide in an autoclave. It is involatile and very reactive, being oxidized in air and aqueous acids. Some of its reactions[66] are summarized in Fig. 14.

The structure of the tetranitrosyl is unknown. Its infrared spectrum shows N–O stretching frequencies at 1810, 1730 and 1140 cm^{-1} and the structure $Fe(NO^+)_3(NO^-)$ analogous to that of $Fe(NO^+)_3Cl$ has been proposed. Other structures suggested have been $(NO^+)[Fe(NO_3)]^-$ and $(NO^+)_3Fe{-}ON{=}NO{-}Fe(NO^+)_3$[67].

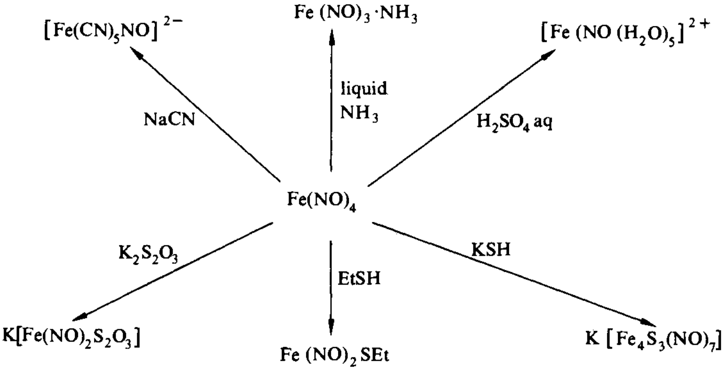

FIG. 14. Reactions of iron tetranitrosyl.

Iron Nitrosyl Carbonyls

By the reaction of nitrogen monoxide with iron pentacarbonyl at 95°C or with $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$, iron dicarbonyl dinitrosyl $Fe(NO)_2(CO)_2$ is formed. This can alternatively

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[65] E. W. Abel, I. S. Butler and C. R. Jenkins, *J. Organometallic Chem.* 8 (1967) 382.

[66] C. C. Addison and J. Lewis, *Quart. Revs. (London)*, 9 (1955) 138.

[67] B. F. G. Johnson and J. A. McCleverty, *Progress in Inorganic Chemistry*, 7 (1966) 280.

be prepared by treating a solution of $Na[Fe(CO)_4H]$ with sodium nitrite and acetic acid or by the action of nitrosyl chloride on the pentacarbonyl. It forms deep red crystals (m.p. 18·4°C) which are soluble in organic solvents and oxidized in air.

An early electron diffraction study[68] indicated that the carbon monoxide and nitrogen monoxide groups are arranged tetrahedrally around the iron atom with Fe–C = 1·84±0·02 Å, Fe–N = 1·77±0·02 Å, C–O = 1·15±0·03 Å and N–O = 1·12±0·03 Å. In this compound then the N–O distance is slightly shorter than that in nitrogen monoxide (1·15 Å) and the C–O distance is slightly longer than that in free carbon monoxide (1·128 Å). The infrared spectrum[69] shows the two N–O stretching vibrations (1810 and 1766 cm^{-1}) and the two C–O stretching vibrations (2083 and 2034 cm^{-1}) expected for C_{2v} symmetry. Its dipole moment[70] is 0·95 *D* and it has been suggested that two mesomeric forms of N–O are present, $M^{2-}{=}N{=}O^{+}$ and $M^{-}{-}N{\equiv}O$.

TABLE 5. SOME SUBSTITUTED IRON NITROSYLS

Compound	Colour	M.p. (°C)	ν(N–O) (cm^{-1})	Dipole moment (*D*)
$Fe(NO)_2(PF_3)_2$[a]	red-brown	liquid	1838, 1788	
$Fe(NO)_2(PPh_3)_2$[b, e, g]	brown	194	1723, 1679	
$[Fe(NO)_2(P_2Me_2)]_2$[c]	dark red	201–203	1753, 1733	
$[Fe(NO)_2(AsMe_2)]_2$[c]	dark red	227–230	1757, 1727	
$Fe(NO)_2(p\text{-}Me.C_6H_4.NC)_2$[d]	red	180–182		6·09
$Fe(NO)_2(p\text{-}MeO.C_6H_4.NC)_2$[d]	red-brown	197–199		6·52
$[Fe_2(NO)_4P_2Me_4]_2$[c]	dark purple	285	1705, 1684, 1650	
$Fe(NO)_2(CO)(PPh_3)$[b, e]	red	138–140d	1766, 1721	
$Fe(NO)_2(CO)(TePh_2)$[f]	red	—	1764, 1727	
$Fe(NO)_2(CO)(SbPh_3)$[b, e, g]	orange-red	105–115d	1773, 1730	

[a] T. Kruck and W. Lang, *Angew. Chem.* **76** (1964) 787.
[b] W. Beck and K. Lottes, *Chem. Ber.* **98** (1965) 2657.
[c] R. G. Hayter and L. F. Williams, *Inorg. Chem.* **2** (1963) 717.
[d] L. Malatesta and A. Sacco, *Z. anorg. u. allgem. Chem.* **274** (1953) 341.
[e] D. W. McBride, S. L. Stafford and F. G. A. Stone, *Inorg. Chem.* **1** (1962) 386.
[f] W. Hieber and T. Kruck, *Chem. Ber.* **95** (1962) 2027.
[g] L. Malatesta and A. Areneo, *J. Chem. Soc.* (1957) 3803.

Many substitution reactions occur with $Fe(NO)_2(CO)_2$, the substituting ligand invariably replacing the carbonyl groups. These derivatives (Table 5) are prepared by direct reaction with the ligand in an inert solvent, e.g.

$$Fe(NO)_2(CO)_2 + PPh_3 \rightarrow Fe(NO)_2(CO)(PPh_3) + CO$$

They are obtained with but a few exceptions as stable, diamagnetic crystalline solids.

The reaction of $Fe(NO)_2(CO)_2$ with alkali in methanol or with sodium amalgam in tetrahydrofuran leads to the formation of the $[Fe(NO)(CO)_3]^-$ anion. This anion is also formed in the reaction of iron pentacarbonyl with nitrite ion, viz.

$$Fe(CO)_5 + KNO_2 \rightarrow K[Fe(NO)(CO)_3] + CO + CO_2$$

It is isoelectronic and isostructural with $Co(NO)(CO)_3$; its infrared spectrum[71] has ν(N–O) at 1651 cm^{-1} and ν(C–O) at 1984 and 1881 cm^{-1}. By reaction with aqueous mercury(II)

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[68] L. O. Brockway and J. S. Anderson, *Trans. Faraday Soc.* **33** (1937) 1233.
[69] C. G. Barraclough and J. Lewis, *J. Chem. Soc.* (1960) 4842.
[70] E. Weiss and W. Hieber, *Z. anorg. u. allgem. Chem.* **287** (1956) 223.

cyanide, the mercury salt $Hg[Fe(NO)(CO)_3]_2$ can be obtained[72]; this readily disproportionates into $Hg[Fe(CO)_4]$ and $Fe(NO)_2(CO)_2$. With triphenylphosphine at room temperature, however, it undergoes a simple substitution reaction[73]:

$$Hg[Fe(NO)(CO)_3]_2 + 2PPh_3 \rightarrow Hg[Fe(NO)(CO)_2(PPh_3)]_2 + 2CO$$

Iron Nitrosyl Halides

The reaction of nitrogen monoxide with iron(II) chloride in the presence of iron powder at 70° gives the very unstable $Fe(NO)_3Cl$ as dark brown needles[74]. It sublimes at 110°C and readily evolves nitrogen monoxide. The trinitrosyl bromide and iodide are conveniently prepared from the tetracarbonyl halides by the reaction:

$$Fe(CO)_4X_2 + Fe + 6NO \rightarrow 2Fe(NO)_3X + 4CO$$

The dinitrosyl halides $Fe(NO)_2X$ are more stable and thought to be dimeric. The iodide $[Fe(NO)_2I]_2$ is prepared by reaction of nitric oxide with iron(II) iodide at 100°C or by the reaction of iodine on iron nitrosyl carbonyl:

$$2Fe(NO)_2(CO)_2 + I_2 \rightarrow [Fe(NO)_2I]_2 + 4CO$$

These brown-black nitrosyl halides are non-polar and soluble in organic solvents; they react with a variety of ligands to form black paramagnetic (and presumably tetrahedral) complexes of the type $Fe(NO)_2XL$. Some properties of the nitrosyl halides and some of their derivatives are listed in Table 6. In molten triphenylphosphine, $[Fe(NO)_2Br]_2$ undergoes disproportionation to give $Fe(NO)_2(PPh_3)_2$ and $Fe(NO)Br_2(PPh_3)_2$.

TABLE 6. SOME PROPERTIES OF IRON NITROSYL HALIDES AND THEIR DERIVATIVES

Compound	M.p. (°C)	ν(N–O) cm^{-1}	Dipole moment (*D*)	Magnetic moment (BM)
$Fe(NO)_3Cl$[a, b]	—	1826, 1763		
$Fe(NO)_3Br$[a, b]	—	1821, 1764	3·7	
$Fe(NO)_3I$[a, b]	—	1809, 1763	3·5	diamagnetic
$[Fe(NO)_2I]_2$[a, b]	—	1818, 1771		
$Fe(NO)_2Br(PPh_3)$[c, d]	160–163	1790, 1734	6·94	1·92
$Fe(NO)_2I(PPh_3)$[c, d]	127–130	1789, 1738	7·12	1·90
$Fe(NO)_2Br(AsPh_3)$[c, d]	140–143	—		1·84
$Fe(NO)_2I(SbPh_3)$[c, d]	74–76	1811, 1764		1·90
$Fe(NO)_2Br(C_5H_{11}N)$[c, d]	—	1797, 1731		1·82

[a] W. Hieber and W. Beck, *Z. Naturforsch.* **13b** (1958) 194.
[b] A. Jahn, *Z. anorg. u. allgem. Chem.* **301** (1959) 301.
[c] W. Hieber and R. Kramolowsky, *Z. Naturforsch.* **16b** (1961) 555; *Z. anorg. u. allgem. Chem.* **321** (1963) 94.
[d] W. Beck and K. Lottes, *Chem. Ber.* **98** (1965) 2657.

Sulphur Nitrosyl Complexes

Compounds containing sulphur as well as nitrogen monoxide bonded to iron have been known for a long time. The best known are the Roussin "red" and "black" salts of

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[71] W. Beck, *Chem. Ber.* **94** (1961) 1214.
[72] W. Hieber and H. Beutner, *Z. anorg. u. allgem. Chem.* **320** (1963) 101.
[73] R. B. King, *Inorg. Chem.* **2** (1963) 1275.
[74] W. Hieber and R. Nast, *Z. anorg. u. allgem. Chem.* **244** (1940) 23.

formulae $K[Fe(NO)_2S]$ and $K[Fe_4(NO)_7S_3]$ respectively. These are readily prepared[75] from iron(II) sulphate, sodium nitrite and ammonium sulphide.

The red salt is diamagnetic and presumably dimeric. Many esters of this salt, i.e. $[Fe(NO)_2SR]_2$, are known; they can be obtained from aqueous solution[75], e.g.

$$2FeSO_4+4KOH+EtSH+2NO \rightarrow Fe(NO)_2SEt+Fe(OH)_3+2K_2SO_4+H_2O$$

as well as from substitution reactions of iron nitrosyls and nitrosyl carbonyls with mercaptans[67]. These esters are dark red, diamagnetic and soluble in organic solvents. Molecular weight measurements confirmed the dimeric formulation and the structure of the ethyl ester has been elucidated by single crystal X-ray studies[76]. Each iron atom (Fig. 15) is tetrahedrally surrounded by two NO groups and two sulphur atoms; the ethyl groups are arranged *anti* to each other. The bond lengths are Fe–Fe, 2·720±0·003 Å, Fe–S, 2·270±0·004 av., Fe–N, 1·66, N–O, 1·17. The dipole moment[77] of this ester is 1·88±0·05 *D*.

Roussin's black salts contain the diamagnetic and monomeric anion $[Fe_4(NO)_7S_3]^-$. The structure of the caesium salt has been elucidated by single crystal X-ray diffraction[78].

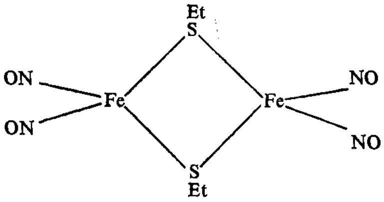

FIG. 15. Roussin's red ester $[Fe(NO)_2SEt]_2$.

It consists of a trigonal pyramid of iron atoms; each basal iron atom has two terminal NO groups and the apical iron atom just one, the three sulphur atoms lying above each vertical triangular face of the pyramid.

Two other types of compound[67], the dithiocarbamato complexes $Fe(NO)(S_2CNR_2)_2$ and the thiosulphato complexes $[Fe(NO)_2(S_2O_3)]^-$, contain iron atoms bonded to both sulphur and nitrogen monoxide. The dithiocarbamato complex $Fe(NO)(S_2CNMe_2)_2$ is believed to possess a tetragonal pyramidal structure with a bent Fe–N–O bond (vertical), the four sulphur atoms lying in the basal plane. A six-coordinate complex, $Fe(NO)_2(S_2CNMe_2)_2$, can be obtained by reaction of the mononitrosyl complex with nitrogen monoxide in chloroform. The thiosulphate complex anion $[Fe(NO)_2(S_2O_3)]^-$ is obtained in the reactions of potassium thiosulphate with $Fe(NO)_4$ or $[Fe(NO)_2I]_2$. Little structural data is available on the thiosulphate complexes; the compounds are diamagnetic and the N–O stretching frequencies are in the region expected for NO^+. A dimeric formulation with unidentate thiosulphate groups and a structure analogous to that of Roussin's red ester (Fig. 15) seems likely.

Cationic Nitrosyl Complexes, Brown Ring Compounds

The familiar brown-ring test for the nitrate ion using iron(II) sulphate and concentrated sulphuric acid involves the formation of a cationic iron nitrosyl species. Iron(II) sulphate

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[75] G. Brauer, *Handbuch der Präparativen Anorganischen Chemie*, Vol. II, p. 1526, Ferdinand Enke, Stuttgart (1962).

[76] J. T. Thomas, J. H. Robertson and E. G. Cox, *Acta Cryst.* **11** (1958) 599.

[77] W. Hieber and W. Beck, *Z. anorg. u. allgem. Chem.* **305** (1960) 274.

[78] G. Johannson and W. N. Lipscomb, *Acta Cryst.* **11** (1958) 594.

solutions absorb nitrogen monoxide reversibly up to a ratio Fe^{2+} : NO of 1 : 1. The hydrated salt $2Fe(NO)SO_4.13H_2O$ can be isolated[79] by adding a concentrated aqueous solution of iron(II) sulphate containing nitrogen monoxide to ice cold concentrated sulphuric acid saturated with nitrogen monoxide. The selenate and phosphate salts can also be isolated and are somewhat more stable. Little information, however, has been forthcoming concerning the structure of these solids. Solution studies, however, have given some information concerning the structure of the species present. Absorption spectra measurements show that the species responsible for the colour is independent of the anion and electrolysis shows that the nitrogen monoxide is associated with the cation. Studies on the magnetic susceptibility of the solutions of the $FeSO_4$–NO complex, over a temperature range[80], have shown that the complex has three unpaired electrons. The infrared spectra show frequencies in the 1730–1850 cm^{-1} region characteristically of coordinated NO^+. The complex cation is therefore best formulated as $[Fe^I(NO)(H_2O)_5]^{2+}$ in which NO donates three electrons. The brown colour is believed to be charge-transfer in origin.

The analogous pentammine complexes $[Fe(NO)(NH_3)_5]^{2+}$ have been reported[81], but they are very unstable; solutions of $[Fe(NH_3)_6]^{2+}$ do not absorb nitrogen monoxide. Solutions of iron(III) chloride in absolute ethanol do absorb the gas, however, and the reaction has been represented by[80]:

$$[Fe(EtOH)_6]^{3+} + NO \rightleftharpoons [Fe(NO)(EtOH)_5]^{3+} + EtOH$$

Nitrosyl Cyanides

The nitroprusside ion $[Fe(CN)_5NO]^{2-}$ has been known for over a century. It arises in the reaction of nitric acid with either of the ions $[Fe(CN)_6]^{4-}$ or $[Fe(CN)_6]^{3-}$, e.g.

$$[Fe(CN)_6]^{4-} + 4H^+ + NO_3 \rightarrow [Fe(CN)_5NO]^{2-} + CO_2 + NH_4^+$$

and in the reaction of iron(II) salts with potassium cyanide and sodium nitrite:

$$[Fe(CN)_6]^{4-} + NO_2^- \rightleftharpoons [Fe(CN)_5NO_2]^{4-} + CN^-$$
$$[Fe(CN)_5NO_2]^{4-} + H_2O \rightleftharpoons [Fe(CN)_5NO]^{2-} + 2OH^-$$

Salts of the nitroprusside ion are usually hydrated, e.g. Na, $2H_2O$; K, $1H_2O$; NH_4, $1H_2O$; their conductivities are as expected for three ions. The red sodium salt is diamagnetic with v(N–O) at 1944 cm^{-1} and it is thus formulated as containing NO^+ and Fe^{II}. The crystal structure of this salt has been determined[82]; the nitroprusside ion has C_{4v} symmetry, the iron atom being surrounded pseudo-octahedrally by five carbon atoms at $1{\cdot}90 \pm 0{\cdot}05$ Å and one nitrogen at $1{\cdot}63 \pm 0{\cdot}02$ Å. The Fe–N–O and Fe–C–N portions of the ion are linear, but the iron atom lies 0·2 Å above the plane of the four carbon atoms. The electronic spectrum of the nitroprusside ion has been studied both in solution and as a single crystal and a molecular orbital bonding scheme proposed in which a π^* NO level separates the e_g and t_{2g} levels[83]. Whilst back bonding from Fe(II) to CN^- is believed to be slight, back bonding from Fe(II) to NO^+ is believed to be substantial. Mössbauer studies[84] show that in this ion there is a very high s-electron density at the iron nucleus and this may be considered as an indication of a strong π-bond which delocalizes the t_{2g} electrons of the iron.

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[79] W. Manchot and F. Huttner, *Annalen*, **372** (1910) 153.

[80] W. P. Griffith, J. Lewis and G. Wilkinson, *J. Chem. Soc.* (1958) 3993.

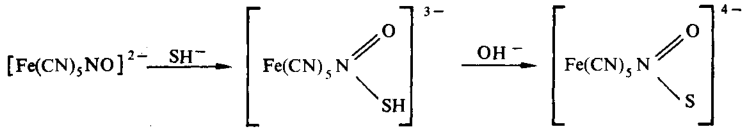
[81] E. Weitz and H. Muller, *Angew. Chem.* **62** (1950) 221.

[82] P. T. Manoharan and W. C. Hamilton, *Inorg. Chem.* **2** (1963) 1043.

[83] H. B. Gray, P. T. Manoharan, J. Pearlman and R. F. Riley, *Chem. Communs.* (1965) 62.

[84] J. Danon, *J. Chem. Phys.* **41** (1964) 3378.

The reactions of the nitroprusside ion with sulphur compounds have considerable importance in analytical chemistry. The detection of sulphur in organic compounds by the Lassaigne test uses the observation that nitroprusside solutions become violet in the presence of sulphides (Gmelin reaction). If alcoholic solutions are used the violet solid $Na_4[Fe(CN)_5N(:O)S]$ can be isolated; this is believed to be formed in the two-stage reaction:



Sulphites give a deep red colour with sodium nitroprusside solutions (Bodeker's reaction) due to the formation of the $[Fe(CN)_5N(O)SO_3]^{4-}$ ion.

Treatment of sodium nitroprusside with alkali causes the formation of the $[Fe(CN)_5NO_2]^{4-}$ ion; with ammonia the species $[Fe(CN)_5(NH_3)]^{4-}$ is formed. When the barium salt is treated with sulphuric acid, barium sulphate precipitates and red-brown leaflets of the unstable nitroprussic acid $H_2[Fe(CN)_5NO]$ can be isolated from the solution.

2.3. OTHER COMPOUNDS OF IRON IN LOW OXIDATION STATES

Amongst the compounds of iron of formally zero oxidation state are complexes with phosphines and 2,2′-dipyridyl (dipy). The reaction of iron pentacarbonyl with phosphorus trifluoride produces pentakis(trifluorophosphine)iron(0), $Fe(PF_3)_5$[85], as one of the substitution products of the carbonyl. This compound is a pale yellow solid (m.p. 44°C), soluble and stable in inert solvents but attacked by ethanol and acetone; it is believed to be monomeric.

The black tris(2,2′-dipyridyl)iron(0) has been synthesized by the reaction of iron(III) chloride with bipyridyl and its lithium salt in tetrahydrofuran[86]:

$$FeCl_3 + 3dipy + 1{\cdot}5Li_2dipy \rightarrow Fe(dipy)_3 + 3LiCl + 1{\cdot}5dipy$$

It is very sensitive to air and water, giving the $[Fe(dipy)_3]^{2+}$ cation in dilute acids. At 145°C *in vacuo* it decomposes into iron and 2,2′-dipyridyl. Whilst this compound formally contains iron(0) it is not known just how meaningful this assignment is. One possibility is that the dipyridyl is acting as a π-acceptor and receiving electrons into the vacant π^*-orbitals of the ring system from filled orbitals on the metal.

3. COMPOUNDS OF IRON(II)

3.1. GENERAL AND REDOX CONSIDERATIONS

In aqueous solution, the principally occurring oxidation states of iron are +2 and +3. In the absence of other complexing agents, solutions of iron(II) contain the pale green hexaquo ion, $[Fe(H_2O)_6]^{2+}$. The hydrated salts of iron(II) are also pale green; they are often isomorphous with the same salts of other transition metals in the +2 oxidation state. The

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[85] R. J. Clark, *Inorg. Chem.* 3 (1964) 1395.

[86] S. Herzog and H. Praekel, *Z. Chem.* 5 (1965) 469.

solubilities of iron(II) salts are also similar to those of other divalent ions of the first row transition elements, i.e. the halides, nitrate and sulphate soluble, the hydroxide, sulphide, phosphate and oxalate relatively insoluble. Most iron(II) salts are unstable with respect to oxidation in air, but the double salts with the alkali metal and ammonium salts tend to be the most stable. The standard electrode potentials for some iron couples are listed in Table 7; the values quoted are taken from the standard sources[87, 88] but the convention used is that recommended by the Commission on Physico-chemical Symbols and Terminology of the International Union of Pure and Applied Chemistry in 1953, i.e. the sign of the electrode potential is the same as the electrostatic charge on the electrode relative to the standard hydrogen electrode.

TABLE 7. STANDARD ELECTRODE POTENTIALS FOR SOME IRON COUPLES AT 250°C

Couple	Volts
Acid solution	
Fe^{2+}/Fe	-0·440
$Fe(C_2O_4)_3^{3-}/Fe(C_2O_4)_2^{2-}, C_2O_4^{2-}$	+0·02
$Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$	+0·36
Fe^{3+}/Fe^{2+}	+0·771
$Fe(dipy)_3^{3+}/Fe(dipy)_3^{2+}$	+0·96
$Fe(phen)_3^{3+}/Fe(phen)_3^{2+}$	+1·1
$FeO_4^{2-}, 8H^+/Fe^{3+}, 4H_2O$	+1·9
Basic solution	
$FeS(\alpha)/Fe, S^{2-}$	-0·95
$Fe(OH)_2/Fe, 2OH^-$	-0·877
$Fe_2S_3/2FeS(\alpha), S^{2-}$	-0·715
$Fe(OH)_3/Fe(OH)_2, OH^-$	-0·56
$FeO_4^{2-}, 4H_2O/Fe(OH)_3, 5OH^-$	+0·72

The dissolution of iron in non-oxidizing acids (and even oxidizing acids such as nitric and perchloric if they are cold and dilute) results in the formation of Fe^{2+}aq. In acid solutions this hydrated iron(II) cation is thermodynamically unstable with respect to atmospheric oxidation (viz. the $O_2,4H^+/2H_2O(l)$ couple $= +1{\cdot}229$ V), but oxidation occurs only slowly. The solutions are readily oxidized by strong oxidizing agents including acidified permanganate, dichromate, persulphate, hydrogen peroxide and cerium(IV). The standard potential for the Fe^{2+}/Fe^{3+} couple remains constant over a range of pH values at which precipitation of the hydrous oxide does not occur. When this pH is reached, however, the couple involved becomes

$$Fe(OH)_3 + e \rightarrow Fe(OH)_2 + OH^-$$

and the potential changes abruptly and markedly. The reducing power of iron(II) is enormously increased in alkaline solution due largely[89] to the greater solubility of its hydroxide compared to that of $Fe(OH)_3$. Thus in alkaline solution, iron(II) is readily oxidized by oxygen of the air, precipitates of white $Fe(OH)_2$ rapidly darkening through oxidation. Under alkaline conditions, iron(II) will also reduce nitrate and nitrite ions to ammonia, and copper(II) salts to the metal.

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[87] W. M. Latimer, *The Oxidation States of the Elements and their Potentials in Aqueous Solutions*, 2nd edition, Prentice Hall (1952).

[88] A. J. Bethune, in *The Encyclopedia of Electrochemistry*, p. 415, C. A. Hampel (Ed.), Reinhold (1964).

[89] N. V. Sidgwick, *The Chemical Elements and their Compounds*, Vol. II, p. 1349, Oxford (1950).

As well as changes in pH, changes in the ligands around the iron atoms have a marked effect upon the values of the electrode potentials[90]. Anionic ligands stabilize iron(III) rather than iron(II), anionic complexes being oxidized more readily than cationic complexes containing uncharged ligands. The highest potentials in the iron(II)/iron(III) system are those of cationic complexes having π-acceptor ligands. The Fe^{2+} ion (d^6) is a good π-donor cation and might be expected to be stabilized by ligands such as 2,2′-dipyridyl (dipy) and 1,10-phenanthroline (phen) which have low lying vacant π^*-orbitals. Poorer π-donor properties are shown by Fe^{3+} because of its higher charge and this applies irrespective of whether the complexes are of high or low spin. Normally, however, such π-acid ligands give low spin iron(II) complexes. Of the anions, the cyanide ion produces the highest potential, differing from, for example, oxalate in being a π-acceptor and forming low spin complexes with iron(II) and iron(III).

3.2. SIMPLE SALTS OF IRON(II)

Iron(II) halides. Some of the properties of the iron(II) halides are listed in Table 8. The hydrates are prepared by crystallization of solutions of iron or basic iron compounds in the corresponding hydrohalic acid. The many complexes which these halides form with anionic and neutral ligands will be described in section 3.3.

Iron(II) fluoride. This can be prepared by passing hydrogen fluoride over iron at red heat or over iron(II) chloride at a somewhat lower temperature. It is sparingly soluble in water with some hydrolysis, and is insoluble in alcohol, ether and benzene. The boiling point is about 1100°C and the melting point only a little below this temperature. It crystallizes in the rutile structure, the iron atom being surrounded tetragonally[91] by $4F^-$ at 2·12 Å and $2F^-$ at 1·99 Å. Iron(II) fluoride is reduced to iron by hydrogen at red heat, but is stable to hydrogen at 400°—and can be prepared by reduction of iron(III) fluoride with hydrogen at this temperature. It reacts violently when heated with metals such as sodium and aluminium, but undergoes no visible reaction with bromine, iodine or sulphur. The ammoniates $FeF_2.5NH_3.H_2O$, $FeF_2.NH_3.H_2O$ and $FeF_2.0{\cdot}5NH_3.H_2O$ are obtained in the reactions of gaseous ammonia with the tetrahydrate at various temperatures.

TABLE 8. IRON(II) HALIDES

Property	FeF_2	$FeCl_2$	$FeBr_2$	FeI_2
Colour	white	pale yellow-grey	yellow-green	grey
M.p. (°C)[a]	1000	670–674	684	red heat
Density[a]	4·09	3·16	4·64	5·32
$-\Delta H_f$ (kcal mole^{-1})[b]		81·5	60·02	29·98
Hydrates	4,8	1,2,4,6	2,4,6,9	2,4,6,9
$-\Delta H_{f\,aq}$(kcal mole^{-1})[b]	177·8	101·0	79·1	49·03

[a] R. C. Weast (Ed.), *Handbook of Chemistry and Physics*, 49th edition, The Chemical Rubber Company (1968).

[b] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, *Selected Values of Chemical Thermodynamic Properties*, National Bureau of Standards (1952).

Iron(II) chloride. This is prepared by the action of hydrogen chloride on heated iron,

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[90] C. S. G. Phillips and R. J. P. Williams, *Inorganic Chemistry*, Vol. 2, p. 312, Oxford (1966).

[91] W. H. Bauer, *Acta Cryst.* **11** (1958) 488.

by the reduction of iron(III) chloride with hydrogen or by dehydration of the hydrates. A convenient laboratory preparation[92] involves heating iron(III) chloride under reflux in chlorobenzene:

$$C_6H_5Cl+2FeCl_3 \rightarrow 2FeCl_2+C_6H_4Cl_2+HCl$$

It forms rhombohedral crystals with the $CdCl_2$ type structure. The magnetic moment $\mu_{eff} = 5{\cdot}87$ B.M. at 300°K, it is probably antiferromagnetic below 24°K[94]. The heat of fusion is 10·28 kcal $mole^{-1}$ and of vaporization is 30·21 kcal $mole^{-1}$; it is largely monomeric in the vapour. In moist air it is deliquescent and is very soluble in water (685 g $litre^{-1}$ at 20°C) and ethanol. The blue-green tetrahydrate, $FeCl_2.4H_2O$, separates from aqueous solution above 12·3°; below this temperature, $FeCl_2.6H_2O$ separates out. The tetrahydrates $FeCl_2.4H_2O$ and $FeF_2.4H_2O$ contain discrete $MX_2(H_2O)_4$ units and $FeCl_2.6H_2O$ contains *trans*-$[FeCl_2(H_2O)_4]$ units and not the hexaquo ion. The almost white, monoclinic $FeCl_2.2H_2O$ is obtained[93] by crystallization from solutions at above 72·6°C; at 120°C it decomposes to the monohydrate.

Iron(II) bromide. This can be prepared by the direct reaction of bromine or hydrogen bromide with iron at red heat; in contrast to the chloride, iron(III) bromide is unstable under these conditions. The hydrated bromide can be dehydrated in a stream of hydrogen bromide at 400°C. Iron(II) bromide forms a layer lattice of the CdI_2 type. It has a magnetic moment, $\mu_{eff} = 5{\cdot}71$ B.M. at 295°K[94]. It is deliquescent and very soluble in water; the pale green hexahydrate crystallizes at room temperature, the tetrahydrate above 49°C and the dihydrate above 83°C. A 9-hydrate forms below −29·3°C[95]. The anhydrous salt is also soluble in ether, ethanol and acetonitrile.

Iron(II) iodide. This is readily prepared by direct interaction between the elements since iron(III) iodide does not exist. Iron dissolves in a solution of iodine in water and evaporation of the resulting solution leads to a deposit of green crystals of the tetrahydrate. The anhydrous salt has a CdI_2 type lattice and is paramagnetic, $\mu_{eff}(295°K) \doteq 5{\cdot}75$ B.M. It is very soluble in water with slight hydrolysis and also soluble in ether and ethanol.

Iron(II) cyanide. This cannot be obtained from aqueous solution. The thermal decomposition of ammonium hexacyanoferrate(II) at 320° results in evolution of ammonium cyanide and the formation of a pale green residue of empirical formula $Fe(CN)_2$. This may have the structure $Fe_2[Fe(CN)_6]$; with aqueous potassium hydroxide it forms $Fe(OH)_2$ and $K_4[Fe(CN)_6]$.

Iron(II) thiocyanate. The green trihydrate $Fe(SCN)_2.3H_2O$ can be crystallized from solutions of iron in thiocyanic acid and from the filtrate of the barium thiocyanate–iron(II) sulphate aqueous reaction. A solution of the anhydrous salt in liquid ammonia is obtained when iron wire reacts with mercury(II) thiocyanate in ammonia. It is readily oxidized in air; the iron(III) thiocyanate can be reduced to the iron(II) salt with sulphite, arsenite, mercury(I) or tin(II) ions.

Iron(II) oxide. When iron is heated in a low partial pressure of oxygen above 575°C, FeO is formed. However, this is only stable at high temperatures and decomposes into iron and Fe_3O_4 when it is cooled slowly. To obtain crystalline FeO the high temperature product must be quenched rapidly to stop this disproportionation. Iron(II) oxide can be prepared

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[92] P. Kovacic and N. O. Brace, *Inorg. Syntheses*, 6 (1960) 172.

[93] K. H. Gayer and L. Woontner, *Inorg. Syntheses*, 5 (1957) 179.

[94] B. N. Figgis and J. Lewis, *Progress in Inorganic Chemistry*, 6 (1964) 176.

[95] *Gmelins Handbuch der Anorganischen Chemie, Eisen* Teil B (1932) p. 324.

in the laboratory as a black pyrophoric powder by thermally decomposing iron(II) oxalate *in vacuo*. Crystalline FeO (wustite) melts at 1368°C with a heat of fusion $\Delta H = 7{\cdot}5$ kcal mole^{-1}. It has a heat of formation of $-63{\cdot}7$ kcal mole^{-1} at 25° and a density of 5·7. Below 198°K (the Néel temperature) FeO is antiferromagnetic. It crystallizes with the rock salt structure having four Fe^{2+} and four O^{2-} ions per unit cell. However, it is always deficient in iron, the formula approximating to $Fe_{0{\cdot}93}O$ at 575°C. The deviation from the ideal stoichiometry of FeO is caused by the replacement of some of the Fe^{2+} ions by Fe^{3+} ions. In order to maintain neutrality, however, only two-thirds as many Fe^{3+} ions as Fe^{2+} ions are required so that the crystal becomes deficient in iron. Continued removal of Fe^{2+} and replacement by Fe^{3+} (i.e. oxidation) leads to Fe_3O_4 and eventually γ-Fe_2O_3.

Iron(II) hydroxide. This is formed as a white flocculent precipitate when iron(II) salts are treated with alkali under air-free conditions. In the presence of air it rapidly darkens to a dark green and thence to an almost black colour; at this stage iron(II) and iron(III) are both present in the precipitate. With excess of oxygen the red-brown iron(III) hydrous oxide is formed. Ammonia incompletely precipitates iron(II) hydroxide due, at least in part, to the formation of iron(II) ammonia complexes.

Iron(II) hydroxide crystallizes with the CdI_2 layer structure in which every iron atom is surrounded by six OH groups. It has a density of 3·40 and a heat of formation from the elements at 25°C of $-135{\cdot}8$ kcal mole^{-1}; its magnetic moment at room temperature is $\mu_{eff} = 5{\cdot}22$ B.M. It is a much stronger reducing agent than the Fe^{2+} ion and is unstable[96] even at room temperature with respect to decomposition into Fe_3O_4, water and hydrogen. Iron(II) hydroxide is more basic than acidic. In hydrochloric and sulphuric acids iron(II) salts are formed. In concentrated sodium hydroxide there is some solution and the tetrahydroxoferrate(II) $Na_2[Fe(OH)_4]$ may be obtained[97] by dissolving finely divided iron in boiling 50% sodium hydroxide; it forms fine blue-green crystals on cooling.

Iron sulphides. The iron–sulphur system has been very extensively studied[98] but is not yet completely characterized. The sulphide FeS_2 occurs in two forms, *pyrites* and *marcasite*, both of which have a brassy yellow colour. *Pyrites* is the more stable form at all temperatures and occurs widely in nature. It has a cubic lattice[99] with what may be regarded as a rock salt like arrangement of Fe^{2+} and $S_2{}^{2-}$ ions; each iron is octahedrally surrounded by sulphur while each sulphur atom has another sulphur and three iron atoms as nearest neighbours. *Marcasite* has a rather similar structure[98, 99]; it is orthorhombic with a less symmetrical arrangement of the same Fe^{2+} and $S_2{}^{2-}$ units. Whilst *pyrites* can be prepared thermally, *marcasite* can only be obtained by aqueous methods. Both forms are diamagnetic indicating the Fe^{2+} ions to be spin-paired ($t_{2g}{}^6$).

Pyrites is a very unreactive substance at room temperature but is more reactive at elevated temperatures. When heated in air it forms iron(III) oxide and sulphur dioxide and is consequently a source of sulphur for sulphuric acid manufacture. When heated in a vacuum it begins to evolve sulphur above 600°.

The grey monosulphide FeS can be prepared by the exothermic reaction between the elements or by aqueous methods from solutions of iron(II) salts and alkali metal sulphides. It occurs naturally as *pyrrhotite* which is usually deficient in iron and in meteorites as *froilite*. The structure is of the NiAs type; it has a density around 4·7, melting point 1193°

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[96] R. Fricke and S. Rihl, *Z. anorg. u. allgem. Chem.* **251** (1943) 414.

[97] H. Remy, *Treatise on Inorganic Chemistry*, Vol. 2, p. 272, Elsevier (1956).

[98] F. Jellinek, in *Inorganic Sulphur Chemistry*, p. 715, G. Nickless (Ed.), Elsevier (1968).

[99] A. F. Wells, *Structural Inorganic Chemistry*, 3rd edition, Oxford (1962).

and a heat of formation of $-22{\cdot}8$ kcal mole^{-1}. It is antiferromagnetic with a Néel point of 325°.

Iron monosulphide is insoluble in water but soluble in aqueous acids with evolution of hydrogen sulphide. When heated in a vacuum, sulphur is evolved above 1100° and iron remains at 1600°. It is readily oxidized when warmed in air.

The phases slightly deficient in iron are the monoclinic pyrrhotite Fe_7S_8 (or $Fe_{0{\cdot}877}S$) which is related to the NiAs structure but has one-eighth of the metal positions unoccupied, and hexagonal pyrrhotite $Fe_{0{\cdot}90-0{\cdot}94}S$. The phase Fe_7S_8 is ferromagnetic, but the magnetic properties of the hexagonal phase are very complex varying with composition and temperature.

Iron nitrides. Many nitrides of iron are described in the literature[95], but only two are worthy of description as definite compounds. The reaction of ammonia with iron at 400–500° gives the grey, orthorhombic nitride Fe_2N. This when heated in a vacuum at 440–550° evolves nitrogen and leaves Fe_4N (face-centred cubic). Both nitrides evolve nitrogen when heated above 600°. The Fe–N phase diagram is very complex but as well as these two compounds, phases formed include[99] (i) a solid solution—about 1·1 at. % nitrogen at 500° (α-phase), (ii) a γ-phase stable only above 600° and corresponding approximately to $Fe_{10}N$ and (iii) a hexagonal close-packed (ϵ-phase) whose composition varies considerably with temperature but extends from about Fe_3N to Fe_2N at low temperatures.

Of the iron phosphide and arsenide phases, FeP_2 and $FeAs_2$ have the marcasite structure and FeP and FeAs the NiAs structure. The phase Fe_2As has the C38 structure which is related to that of PbO[99].

Iron(II) carbonate. This occurs naturally as $FeCO_3$, *siderite* or *spathic iron ore*; it is formed as a white precipitate when an iron(II) solution is treated with an alkali metal carbonate. Whilst being insoluble in water, it dissolves in water containing carbon dioxide with the formation of the bicarbonate $Fe(HCO_3)_2$. This solution rapidly becomes oxidized in air and deposits hydrated iron(III) oxide. Upon thermal decomposition, $FeCO_3$ begins to evolve carbon dioxide at 200° and leave a residue of FeO.

Iron(II) carboxylates. With monobasic acids relatively simple carboxylate salts are formed. Iron(II) formate crystallizes as the green dihydrate; the white acetate $Fe(OCOCH_3)_2.4H_2O$ is very soluble in water with some hydrolysis, the solution being readily oxidized.

Iron(II) oxalate, $FeC_2O_4.2H_2O$, is precipitated as yellow crystals from solutions containing iron(II) and oxalate ions; in the presence of excess alkali metal oxalate, however, soluble oxalato complexes $M^I_2[Fe(C_2O_4)_2]$ are formed which can be precipitated by the addition of alcohol. The oxalate is paramagnetic with $\mu_{eff} = 5{\cdot}2$ B.M. at room temperature.

Iron(II) silicates. These occur naturally and are very widely distributed. They are usually present in the form of isomorphous mixtures with silicates of other metals, e.g. *olivine* $(Fe,Mg)_2[SiO_4]$ and *hypersthene* $(Fe,Mg)_2[SiO_6]$.

Iron(II) nitrate. This is obtained in hydrated form by crystallization from solutions of iron in cold dilute nitric acid,

$$4Fe + 10HNO_3 \rightarrow 4Fe(NO_3)_2 + NH_4NO_3 + 3H_2O$$

or from the filtrate in the iron(II) sulphate–lead nitrate reaction. At room temperature it crystallizes as the green hexahydrate; a 9-hydrate is stable below −10°. Solutions of the nitrate are unstable to heat, nitric oxide being evolved and the iron being oxidized to iron(III).

Iron(II) phosphate. Hydrated iron(II) phosphate $Fe_3(PO_4)_2.8H_2O$ occurs naturally as *vivianite*.. It can be prepared in the laboratory by precipitation from iron(II) sulphate solution with sodium phosphate at 60–80°; it is white when pure but becomes blue upon exposure to air. Several acid phosphates are known, e.g. $FeHPO_4.H_2O$ and $2H_2O$, and $Fe(H_2PO_4)_2.2H_2O$.

The arsenate $Fe_3(AsO_4)_2.8H_2O$ also occurs naturally (*symplesit*) and is precipitated from aqueous solutions.

Iron(II) sulphate. Green vitriol, $FeSO_4.7H_2O$, has been known since the thirteenth century; it crystallizes from solutions of iron or iron bases in dilute sulphuric acid. The heptahydrate forms green monoclinic crystals of density 1·88, very soluble in water (296 g litre^{-1} $FeSO_4$ at 25°C). By precipitating the aqueous solution with ethanol, heating the heptahydrate to 140° *in vacuo* or by crystallizing it from 50% sulphuric acid, the white monohydrate is obtained. This can be further dehydrated to the white, amorphous $FeSO_4$ by heating to 300° in a current of hydrogen. At red heat the sulphate decomposes:

$$2FeSO_4 \rightarrow Fe_2O_3+SO_2+SO_3$$

A tetrahydrate, $FeSO_4.4H_2O$, crystallizes from aqueous solutions above 56°.

Iron(II) sulphate readily forms double salts (*Tutton* salts) with alkali metal sulphates of formula $M^I_2SO_4.FeSO_4.6H_2O$. The ammonium salt commonly known as ferrous ammonium sulphate or *Mohr's salt* finds extensive use in volumetric analysis since it is stable in air and slightly acidified solutions do not deteriorate rapidly. It is soluble to the extent of about 350 g $(NH_4)_2SO_4.FeSO_4$ per litre at 25°. The magnetic properties of these salts have been extensively studied[94]; Mohr's salt has been used as the paramagnetic substance in the production of very low temperatures by the method of adiabatic demagnetization. The magnetic moments for these salts at 299°K are Rb, 5·41 B.M., Cs, 5·39 B.M., and Tl, 5·46 B.M.; the normal anhydrous sulphate has a magnetic moment of 4·90 B.M. (290°K) while for $FeSO_4.7H_2O$ the moment is 5·22 B.M. at the same temperature. They contain the $[Fe(H_2O)_6]^{2+}$ ion.

3.3. ORGANOMETALLIC COMPOUNDS OF IRON

Iron has played a very special part in the development of organometallic chemistry. The use of iron pentacarbonyl in organic synthesis from acetylene was developed by Reppe[100] as early as 1949. The now very extensive field of transition metal organometallic compounds containing π-bonded aromatic ring systems began, however, with the discovery of ferrocene in 1951. The independent discovery of ferrocene by two sets of workers was in both cases somewhat accidental. Kealy and Pauson[101] treated cyclopentadienyl magnesium bromide with iron(III) chloride in an attempt to couple the cyclopentadienyl radicals. Miller, Tebboth and Tremaine[102] passed cyclopentadiene and nitrogen at 300° over a reduced iron catalyst of the type used in the Haber process. In both cases one of the reaction products was biscyclopentadienyliron, $Fe(C_5H_5)_2$—ferrocene. The realization that in this compound the iron atoms were bound to the cyclopentadiene rings in some hitherto unknown way was quick to follow and the correct structure for ferrocene was proposed by Wilkinson, Rosen-

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[100] W. Reppe, *Neue Entwicklungen auf dem Gebiet der Chemie des Acetylens und Kohlenozyds*, Springer-Verlag (1949).

[101] T. J. Kealy and P. L. Pauson, *Nature*, **168** (1951) 1039.

[102] S. A. Miller, J. A. Tebboth and J. F. Tremaine, *J. Chem. Soc.* (1952) 632.

blum, Whiting and Woodward[103] only a year after its discovery. An enormous number of compounds are now known in which cyclopentadiene is π-bonded to a transition metal, and since a large proportion of the organometallic compounds of iron contain at least one aromatic ring system the chemistry of ferrocene will be described in some detail.

TABLE 9. SOME PHYSICAL PROPERTIES OF FERROCENE[a]

M.p. (°C)	173
$\Delta H_{\mathrm{fusion}}$ (kcal/mole)	5·5
B.p. (°C)	230
$\Delta H_{\mathrm{vaporization}}$ (kcal/mole)	11·3
$\Delta H_{\mathrm{sublimation}}$ (kcal/mole)	16·29
Vapour pressure equation	
for liquid	$\log P_{\mathrm{mm}} = 7{\cdot}615 - \frac{2470}{T}$
for solid	$\log P_{\mathrm{mm}} = 10{\cdot}27 - \frac{3680}{T}$
$\Delta H_{\mathrm{formation}}$ (kcal/mole) at 298°K	33·8
E_0, $(C_5H_5)_2Fe/(C_5H_5)_2Fe^+$ (volts)	−0·56
Molar susceptibility	-125×10^{-6}
Dipole moment (D)	0
Density (g/cm^3)	1·49
Molecular volume (cm^3/g)	124·7
Electronic spectrum in 95% ethanol	30·8 (52)
(band positions in kK, ϵ in parentheses)	22·7 (91)
Infrared spectrum (cm^{-1})	
C–H stretch	3085
antisymmetric C–C stretch	1411
antisymmetric ring breathing	1108
C–H bending modes	1002, 811
antisymmetric ring tilt	492
antisymmetric ring–Fe stretch	478
ring–Fe bend	170
NMR spectrum	
chemical shift (τ) of ring protons	5·96
Mössbauer spectrum	
isomer shift (mm/sec) 78°K	0·68
quadrupole splitting (mm/sec)	2·37
Crystallographic data, (space group $P2_1/a$)	
a (Å)	10·561
b (Å)	7·597
c (Å)	5·952
Interatomic distances	
Fe–C (Å)	2·045±0·01
C–C (Å)	1·403±0·02
Inter-ring (Å)	3·32

[a] Selected values from M. Rosenblum, *Chemistry of the Iron Group Metallocenes*, Part 1, Interscience New York (1965), and G. Wilkinson and F. A. Cotton, *Progress in Inorg. Chem.* 1 (1959) 1.

Bis(π-cyclopentadienyl)iron, "Ferrocene", $Fe(\pi\text{-}C_5H_5)_2$

Preparation. Ferrocene may be prepared by a variety of ways. Detailed laboratory instructions have been given[104] for its preparation from sodium cyclopentadienide and iron(II) chloride in tetrahydrofuran or ethylene glycol dimethyl ether:

$$FeCl_2+2C_5H_5Na \rightarrow (C_5H_5)_2Fe+2NaCl$$

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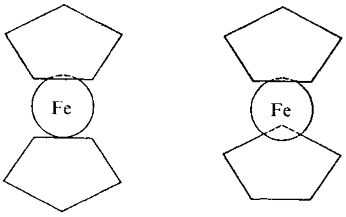
[103] G. Wilkinson, M. Rosenblum, M. C. Whiting and R. B. Woodward, *J. Am. Chem. Soc.* **74** (1952) 2125.

An alternative laboratory method involves the reaction of cyclopentadiene with iron(II) chloride in the presence of a base, e.g. diethylamine:

$$FeCl_2+2C_5H_6+2Et_2NH \rightarrow (C_5H_5)_2Fe+2Et_2NH_2Cl$$

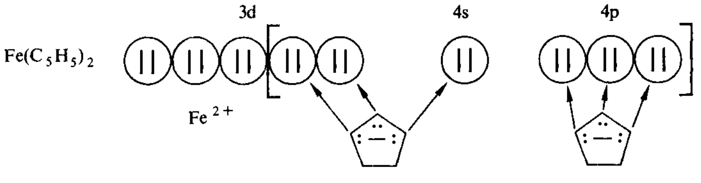
Physical properties, structure and bonding. Ferrocene is an orange crystalline solid, insoluble in water but soluble in most organic solvents. Its principal physical properties are listed in Table 9. X-ray diffraction studies show that in crystalline ferrocene (and in its substituted derivatives) the iron atom is "sandwiched" between the two cyclopentadienyl rings, these rings having the staggered configuration relative to each other (Fig. 16). The rings are parallel plane regular pentagons, all the C–C and Fe–C distances being equal. Electron diffraction studies[106] show, however, that ferrocene has the eclipsed configuration in the vapour state. In view of the relatively high symmetry of the ferrocene molecule and because it has been the most widely studied of the metal π-cyclopentadienyls, much interest has developed concerning the nature of the bonding in ferrocene. It will be possible here to give only the briefest summary of the theoretical treatments which have been evolved concerning the electronic structure of this compound; more detailed accounts are to be found elsewhere[105, 107].



staggered eclipsed

FIG. 16. Ferrocene.

A very simple valence-bond description of ferrocene has been proposed by Fischer[108]. In this description each of the cyclopentadiene rings ($C_5H_5^-$) donates three pairs of electrons into a vacant set of d^2sp^3 hybrid orbitals on Fe^{2+}. The configuration thus becomes:



Whilst this description is an oversimplification it did account for the diamagnetism of ferrocene, illustrate the stability of the molecule via the 18-electron rule and lead to the

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[104] G. Wilkinson, *Organic Syntheses*, **36** (1956) 31.

[105] M. Rosenblum, *Chemistry of the Iron Group Metallocenes*, Part 1, p. 30, Interscience, New York (1965)

[106] R. K. Bohn and A. Haaland, *J. Organometallic Chem.* **5** (1966) 470.

[107] F. A. Cotton, *Chemical Applications of Group Theory*, Wiley-Interscience, New York, second edition 1971.

[108] E. O. Fischer and H. P. Fritz, *Advances in Inorganic Chemistry and Radiochemistry*, **1** (1959).

correct prediction that bis(benzene)chromium(0) should be capable of existence (Cr^0 having six valency electrons and each benzene providing six electrons to the molecule).

Many attempts have been made to achieve a satisfactory molecular orbital description of ferrocene. The most recent of these are the treatments of Shustorovich and Dyatkina[109] and of Dahl and Ballhausen[110]. The ring carbon to carbon and carbon to hydrogen σ-bonds can be assumed to be unaffected by the metal–ligand bonding. In order to construct a molecular orbital energy level scheme, it is necessary first to know the symmetry properties of the molecular orbitals of the cyclopentadiene rings and of the atomic orbitals of the metal so that it can be seen which orbitals may overlap. Considering the individual cyclopentadienyl rings first: the five $2p\pi$ atomic orbitals on the carbon atoms combine to form five π molecular orbitals. These molecular orbitals fall into three groups which differ in their symmetry properties with respect to rotation about the molecular axis (which passes through the iron atom and the centre of each ring). The lowest energy molecular orbital is the symmetric one having no nodal plane perpendicular to the plane of the ring; it has the symmetry designation A_1. The next lowest energy orbitals are a degenerate set E_1 each

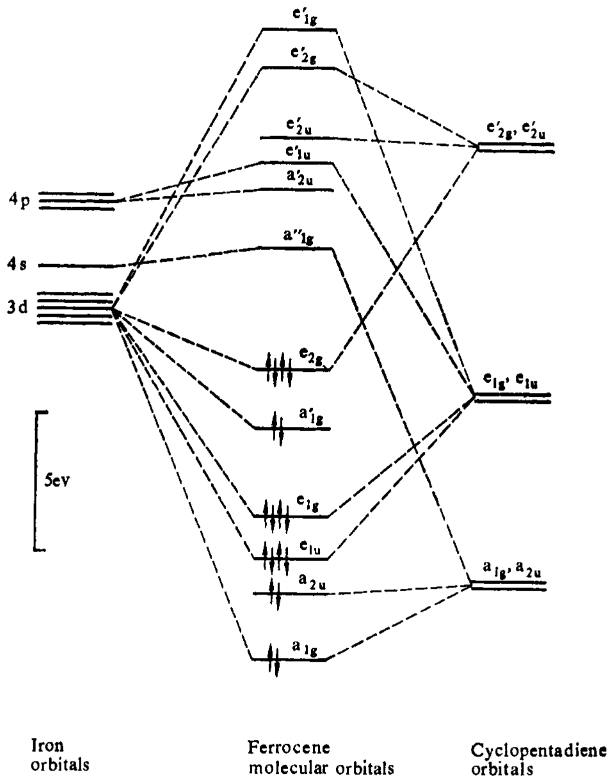

FIG. 17. Molecular orbital energy levels for ferrocene.

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[109] E. M. Shustorovich and M. E. Dyatkina, *Doklady Akad. Nauk SSSR*, **128** (1959) 1234; ibid. **133** (1960) 141.

[110] C. J. Ballhausen, *Introduction to Ligand Field Theory*, p. 218, McGraw-Hill, New York (1962). J. P. Dahl and C. J. Ballhausen, *Kgl. Danske Videnskab, Selskab, Mat-fys. Medd.* No. 5, **33** (1961).

having one nodal plane perpendicular to the ring; the highest energy orbitals are the E_2 set each of which has two such nodal planes. Excellent diagrammatic representations of these orbitals can be found in Green's book[111]. These localized molecular orbitals are then

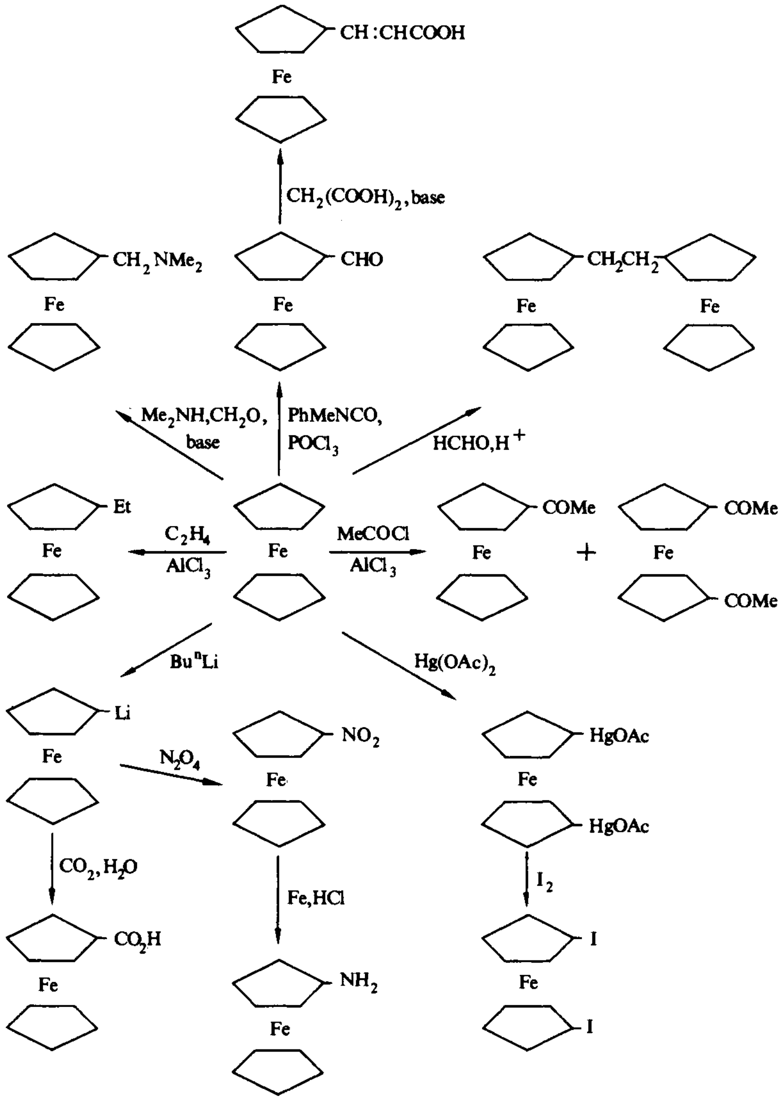


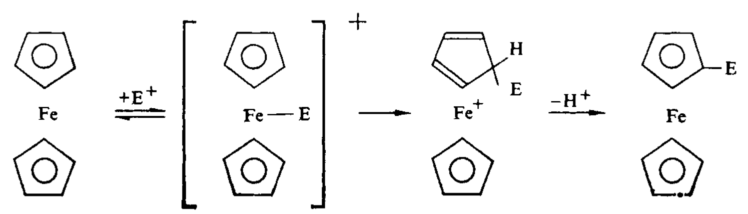
FIG. 18. Some organic chemistry of ferrocene.

combined linearly to give a set of ten new molecular orbitals encompassing both rings. In the D_{5d} point group (to which ferrocene belongs) these new orbitals have the symmetry symbols A_{1g}, A_{2u}, E_{1g}, E_{1u}, E_{2g} and E_{2u}. For the system of two rings then, we require two of each class of orbitals, one of each being symmetric (g) with respect to inversion through the centre and the other antisymmetric (u).

The atomic orbitals on the iron atom, i.e. $3d$, $4s$ and $4p$, have the following representations in D_{5d} symmetry (see Rosenblum[105] for good diagrams): A_{1g} ($4s$, $3d_{z^2}$), A_{2u} ($4p_z$), E_{1g} ($3d_{xz}$, $3d_{yz}$), E_{2g} ($3d_{xy}$, $3d_{x^2-y^2}$) and E_{1u} ($4p_x$, $4p_y$). Now only these orbitals on the rings and on the metal having the same representations can give rise to net overlap and the problem now resolves itself into determining the relative contribution of each possible overlap to the total metal–ring bond. The calculations of Schustorovich and Dyatkina lead to the molecular orbital energies for ferrocene shown in Fig. 17. By feeding the eighteen electrons of ferrocene into the lowest energy molecular orbitals, the nine bonding orbitals are filled. Note that twelve of the electrons are in strongly bonding orbitals while of the other six, two are in the non-bonding d_{z^2} orbital and four in the weakly bonding E_{2g} orbitals (derived from metal d_{xy} and $d_{x^2-y^2}$ orbitals). Thus as would be expected from purely symmetry considerations, of the metal orbitals it is the $3d_{xy}$ and $3d_{yz}$ which contribute most to the metal–ring bonding.

Chemical properties. Ferrocene is thermally stable and melts without decomposition. It is also stable to hydrolysis, but is quite readily oxidized. It is stable in air at room temperature but in acid solutions oxidation affords the ferricenium ion $[(C_5H_5)_2Fe]^+$. This cation can be isolated as salts with anions such as BF_4^- and $FeCl_4^-$ but is unstable in alkaline solution (ferrocene being regenerated).

The chemical reactions of ferrocene are largely those arising from the aromatic properties of the cyclopentadienyl rings and indeed the organic chemistry of ferrocene is now extremely extensive[105, 111]. Ferrocene is resistant to catalytic hydrogenation and does not undergo the Diels–Alder reaction characteristic of conjugated dienes. It does, however, readily undergo Friedel–Crafts acylation and alkylation reactions and also metallation reactions with, for example, butyl lithium or mercury(II) acetate. The products of these reactions are extremely useful intermediates in the synthesis of other organic derivatives of ferrocene. Nitration and halogenation of the rings cannot be carried out directly because of oxidation, but sulphonation can be effected using concentrated sulphuric acid in acetic anhydride. Some organic chemistry of ferrocene is summarized in Fig. 18. Whilst many of the reactions of substituted ferrocenes are similar to those of aromatic hydrocarbons, there are some reactions in which it is apparent that the iron atom plays a vital role. In electrophilic substitution reactions, for example, the attacking electrophile is believed to interact first with the iron atom, viz.[112]



and in Friedel–Crafts alkylation reactions, protonation of the iron may occur, the salt $[C_5H_5)_2FeH]^+AlCl_4^-$ having been isolated. A further reaction in which the iron atom plays a direct part is in the formation of stable α-carbonium ions in ferrocene[113]. Thus the vinyl group in vinylferrocene displays an unusual reactivity in being readily protonated by weak

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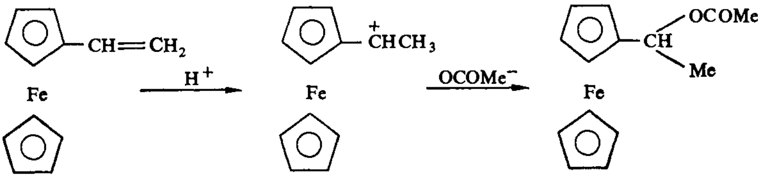
[111] M. L. H. Green, *Organometallic Compounds*, Vol. 2, p. 99, Methuen (1968).

[112] M. Rosenblum, J. O. Santer and W. G. Howells, *J. Am. Chem. Soc.* **85** (1963) 1450.

acids such as acetic and hydrazoic; with acetic acid the end product is α-ferrocenylethyl acetate[113], viz.



Just how the iron atom stabilizes the carbonium ions in the α-position is not yet fully understood.

Cyclopentadienyl Iron Carbonyls

Iron pentacarbonyl reacts with cyclopentadiene at 135° in an autoclave to give the binuclear complex $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ as deep reddish-purple crystals which are stable to air and water. The crystal structure determination[114] shows this molecule to be centrosymmetric with two bridging carbonyls forming a plane with the two iron atoms [Fig. 19(a)]. The rather short Fe–Fe distance of 2·49 Å and the diamagnetism of the compound indicate the presence of the Fe–Fe bond. In solution, however, it tautomerizes to the structure

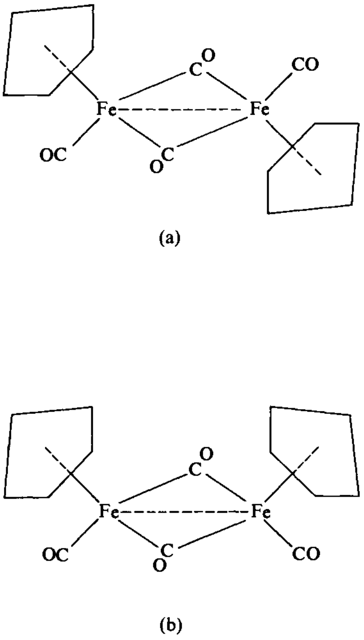


FIG. 19. (a) Crystal structure of $[\pi\text{-}C_5H_5)Fe(CO)_2]_2$. (b) Proposed structure in solution.

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[113] G. R. Buell, W. E. McEwen and J. Kleinberg, *J. Am. Chem. Soc.* **84** (1962) 40.

[114] O. S. Mills, *Acta Cryst.* **11** (1958) 620.

believed[115] to be that shown in Fig. 19(b), in which the two rings lie on one side of the mean plane formed by the bridging carbonyl groups and the iron atoms and the two terminal CO groups lie on the other side. In view of its ease of preparation and handling a large number of reactions of this cyclopentadienyl carbonyl have been studied and some of these are summarized in Fig. 20.

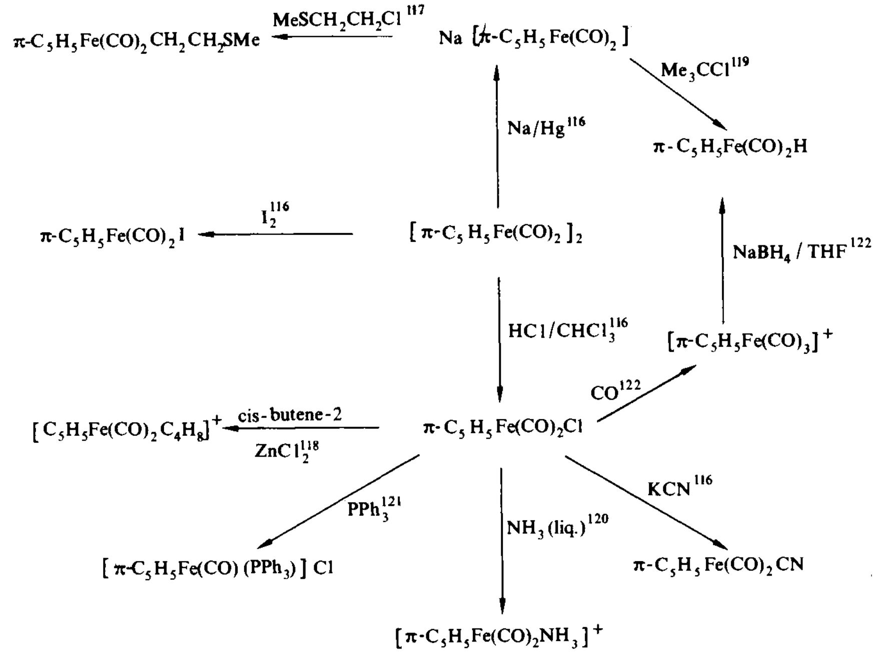

FIG. 20. Some reactions of π-cyclopentadienyl iron carbonyl complexes.

Upon prolonged refluxing in benzene $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ is converted to the compound $[\pi\text{-}C_5H_5FeCO]_4$ in which the iron atoms are believed to form a tetrahedron with a bridging carbonyl group above each of the four faces[123]. A somewhat similar iron cluster $[\pi\text{-}C_5H_5FeS]_4$ is obtained in the reactions of $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ with sulphur or cyclohexene sulphide. It crystallizes in both orthorhombic and monoclinic phases; the crystal structures of both have been determined[124].

Iron Complexes with Other Cyclic π-bonding Ligands

Arenes[125]. The bis(benzene)iron(II) cation $[Fe(C_6H_6)_2]^+$ is isoelectronic with ferrocene and might be expected to show considerable stability. However, the bis(benzene)- and

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[115] F. A. Cotton and G. Yagupsky, *Inorg. Chem.* **6** (1967) 15.

[116] T. S. Piper and G. Wilkinson, *J. Inorg. and Nuclear Chem.* **1** (1955) 165; ibid. **3** (1956) 104.

[117] R. B. King and M. B. Bisnette, *J. Am. Chem. Soc.* **86** (1964) 1267.

[118] E. O. Fischer and K. Fichtel, *Chem. Ber.* **95** (1962) 2063.

[119] M. L. H. Green and P. L. I. Nagy, *J. Organomet. Chem.* **1** (1963) 58.

[120] E. O. Fischer and E. Moser, *J. Organomet. Chem.* **5** (1966) 63.

[121] P. M. Treichel, R. L. Shubkin, K. W. Barnett and D. Reichard, *Inorg. Chem.* **5** (1966) 1177.

[122] A. Davison, M. L. H. Green and G. Wilkinson, *J. Chem. Soc.* (1961) 3172.

[123] R. B. King, *Inorg. Chem.* **5** (1966) 2227.

[124] R. A. Schunn, C. J. Fritchie and C. T. Prewitt, *Inorg. Chem.* **5** (1966) 892. C. H. Wei, G. R. Wilkes, P. M. Treichel and L. F. Dahl, *ibid.* 900.

bis(toluene)-iron(II) cations are rather susceptible to hydrolysis; with increased alkyl substitution, however, the arenes become more stable. Bis-arene complexes of xylenes, mesitylene and hexamethylbenzene are readily prepared direct from iron(II) halides[126]:

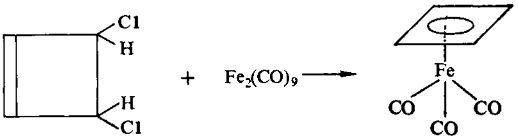
$$\mathrm{FeBr_2+2\ Arene} \xrightarrow{\mathrm{AlCl_3}} \mathrm{[Fe(Arene)_2]Br_2}$$

These iron(II) derivatives can be reduced to iron(I) and iron(0) compounds by dithionite ions in buffered and alkaline conditions respectively. The bis(hexamethylbenzene)iron(I) cation is deep violet, while bis(hexamethylbenzene)iron(0) is black, paramagnetic and extremely sensitive to air and light[127]. The compounds $Fe(C_6Me_6)_2$ and $Cr(C_6Me_6)_2$ are isomorphous[128] and these iron arenes are believed to have sandwich structures similar to that of bis(benzene)chromium. Indeed the sandwich-structured cation $[(\pi\text{-}C_5H_5)Fe(\pi\text{-}C_6H_6)]^+$ can be isolated as the air-stable, yellow hexafluorophosphate from the reaction of ferrocene with benzene in the presence of aluminium powder and aluminium chloride[129]. Reduction of this cation with lithium aluminium hydride gives orange-red $(\pi\text{-}C_6H_6)Fe(C_5H_6)$ in which the benzene is π-bonded and the cyclopentadiene molecule bound as a di-olefin.

Unlike the cyclopentadienyl iron carbonyls, arene iron carbonyl compounds are not readily obtained. Direct reactions between tri-iron dodecacarbonyl and alkylated benzenes do not yield π-complexes. With *m*- or *p*-divinylbenzenes, however, reaction proceeds to give the mono(arene)hexacarbonyl di-iron complexes. Other seemingly arene complexes, e.g. anthracene iron tricarbonyl, are probably best considered as possessing a localized di-ene bond to the iron atom.

Cyclobutadiene complexes. Despite the instability of cyclobutadiene itself, Longuet-Higgins and Orgel[130] suggested in 1956 that stable metal–cyclobutadiene complexes might exist. Today not only are many such compounds known particularly with iron, but they possess some fascinating organic chemistry[131]. The most readily available and hence the most studied of these compounds is cyclobutadiene iron tricarbonyl.

The reaction of either *cis*- or *trans*-3,4-dichlorocyclobutene with di-iron enneacarbonyl gives cyclobutadiene iron tricarbonyl as a stable, pale yellow crystalline solid (m.p. 26°):



Electron diffraction studies [131] have yielded the bond distances Fe–C (ring) = 2·07 Å; Fe–C (CO) = 1·82 Å; C–C (ring) = 1·46 Å; C–O = 1·13 Å. The compound shows aromatic properties—it readily undergoes electrophilic substitution reactions to yield

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[125] H. Zeiss, P. J. Wheatley and H. J. S. Winkler, *Benzenoid-Metal Complexes*, The Ronald Press Co., New York (1966).

[126] E. O. Fischer and R. Bottcher, *Chem. Ber.* **89** (1956) 2397; *idem*, *Z. anorg. u. allgem. Chem.* **291** (1957) 305.

[127] E. O. Fischer and E. Rohrscheid, *Z. Naturforsch.* **17b** (1962) 483.

[128] B. J. Nicholson and H. C. Longuet-Higgins, *Mol. Phys.* **9** (1965) 461.

[129] J. J. Eisch and R. B. King, *Organometallic Syntheses*, **1** (1965) 138.

[130] H. C. Longuet-Higgins and L. E. Orgel, *J. Chem. Soc.* (1956) 1969.

substituted cyclobutadiene iron tricarbonyl complexes. In the Friedel–Crafts acylation reaction, for example, cyclobutadiene iron tricarbonyl is almost as reactive as ferrocene and considerably more reactive than benzene. Some of its organic chemistry is illustrated in Fig. 21[131].

The oxidation of cyclobutadiene iron tricarbonyl with mild oxidants (Fe^{3+}, Ce^{4+}) was attempted in the hope that the free ligand might be liberated (as in the case with butadiene iron tricarbonyl). The products of the oxidation are syn- and anti-tricyclo-octadiene arising from a Diels–Alder type dimerization of cyclobutadiene:

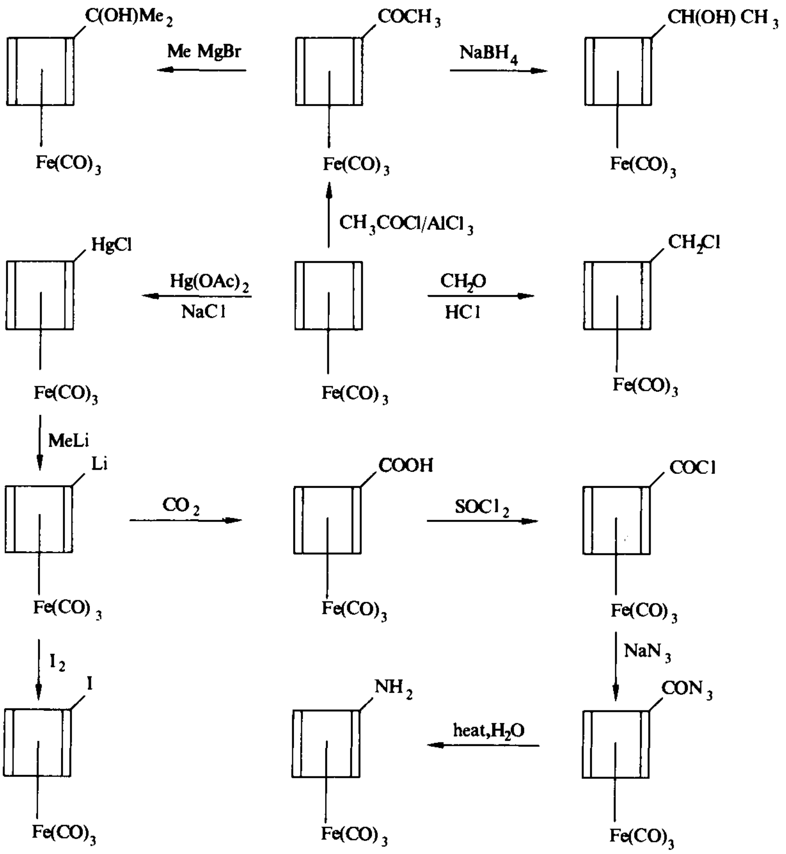
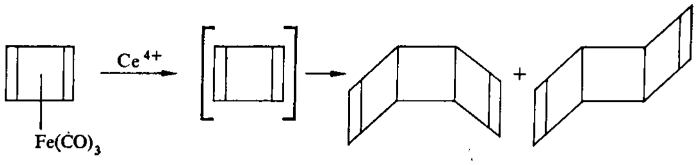


FIG. 21. Some chemistry of cyclobutadiene iron tricarbonyl.



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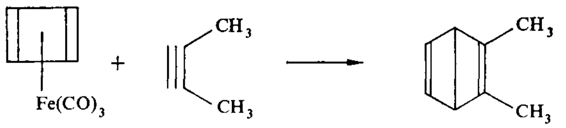
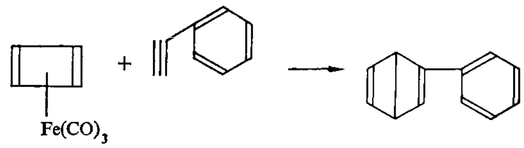
[131] R. Pettit, *Planary Lectures presented at the I.U.P.A.C. Third International Symposium on Organometallic Chemistry*, p. 253, Butterworths, London (1968).

In the presence of dienophilic reagents, the liberated cyclobutadiene reacts to produce Dewar benzene derivatives in a fairly general route, e.g.



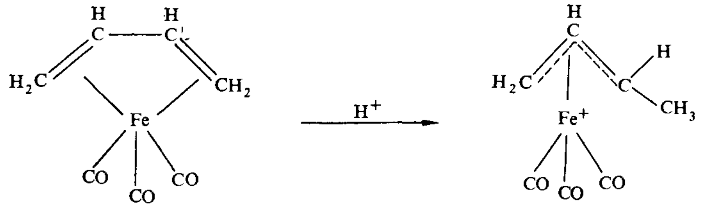
Starting from phenylacetylene, the end product is a molecule having one ring with the Dewar structure and the other ring with the Kekulé structure!



Benzocyclobutadiene iron tricarbonyl has a similarly interesting organic chemistry[131] which cannot be dealt with here.

Olefin, acetylene and π-allyl complexes. Most of the iron olefin complexes contain a mono- or di-olefin bonded to an $Fe(CO)_3$ group and some of these have been discussed in section 2.1. Further details can be found in the extensive review articles[132-4].

π-Allyl complexes of iron are of more recent discovery. They arise in the protonation of diene iron tricarbonyls, e.g. of butadiene iron tricarbonyl.



The π-allyl produced in this example is hydrolysed by water at room temperature giving methyl ethyl ketone, carbon monoxide and iron hydroxides. An alternative method of preparation is by reaction of iron pentacarbonyl with an allyl halide[135]—it has been found convenient to prepare $(\pi\text{-}C_3H_5)Fe(CO)_3I$ by this means and react this with tetra-alkylammonium salts in order to obtain the corresponding chloride and bromide. The chloride has also been prepared by the reaction[136]:

$$\tfrac{1}{2}[C_3H_5PdCl]_2 + Fe_2(CO)_9 \rightarrow C_3H_5Fe(CO)_3Cl + Fe(CO)_5 + Pd + CO$$

The X-ray crystal structure of π-allyliron tricarbonyl iodide has established[137] the structure shown in Fig. 22. The differences observed in the C–C bond lengths only slightly exceed

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[132] R. Pettit and G. F. Emerson, *Advances in Organometallic Chem.* **1** (1964) 1.

[133] R. G. Guy and B. L. Shaw, *Advances in Inorg. Chem. Radiochem.* **4** (1962) 77.

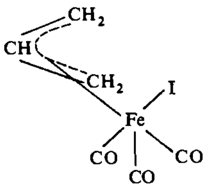
[134] F. Calderazzo, R. Erdi and G. Natta, also W. Hubel, in *Organic Syntheses via Metal Carbonyls* (I. Wender and P. Pino Ed.), Interscience, New York (1968).

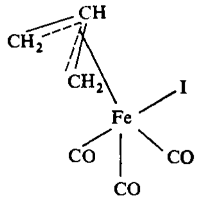
[135] A. N. Nesmeyanov and I. I. Kritskaya, *J. Organomet. Chem.* **14** (1968) 387.

[136] A. N. Nesmeyanov, A. Z. Rubezhov and S. P. Gubin, *Izv. Akad. Nauk SSSR Ser. Khim.* (1966) 194.

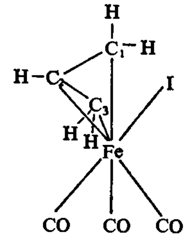
[137] M. Kh. Minasyan, Yu. T. Struchkov, I. I. Kritskaya and R. L. Avoyan, *Zh. Strukt. Khim.* **7** (1966) 903.

the experimental error in their measurement. In solution the nuclear magnetic resonance spectrum is consistent[138] with the existence of rotational isomers having different orientations of the allyl group with respect to the halogen:





By reduction with sodium amalgam $(\pi\text{-}C_3H_5)Fe(CO)_3I$ yields the carbonylate anion $Na[Fe(\pi\text{-}C_3H_5)(CO)_3]$; addition of allyl bromide to this yields the bis(π-allyl) compound $(\pi\text{-}C_3H_5)_2Fe(CO)_3$. The tris($\pi$-allyl), $Fe(\pi\text{-}C_3H_5)_3$, has been briefly reported as golden-orange, decomposing at -40°C. It is prepared by Grignard reaction of allyl magnesium chloride on an iron halide at low temperatures[139].



C_1—Fe = 2·26 Å
C_2—Fe = 2·09 Å
C_3—Fe = 2·34 Å
C_1—C_2 = 1·43 Å
C_2—C_3 = 1·35 Å
Fe—I = 2·75 Å
$C_1\hat{C}_2C_3 = 131°$

FIG. 22. Structure of π-allyliron tricarbonyl iodide.

The reactions of iron carbonyls with acetylenes lead to an enormous variety of organic and organometallic compounds. The original discoveries of Reppe[100] that alkaline solutions of iron pentacarbonyl convert acetylenes into hydroquinones at moderate temperatures have been followed by intensive investigations on the nature of the organo-iron intermediates. Of the iron carbonyls, the dodecacarbonyl usually gives the greatest number of complexes in its reactions with acetylenes at 60–100°; the enneacarbonyl reacts at as low as room temperature, but the pentacarbonyl usually requires ultraviolet irradiation or temperatures above 100°. Most of the compounds formed in these reactions do not contain an acetylene bonded to the metal, but frequently contain ring systems bonded to the iron. Some typical products are illustrated in Fig. 23[111, 134]. The less stable intermediate acetylene

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[138] A. N. Nesmeyanov, Yu. A. Ustynynk, I. I. Kritskaya and G. A. Shchembelov, *J. Organometal. Chem.* **14** (1968) 395.

[139] G. Wilke, *Angew. Chem. Intern. Ed.* **5** (1966) 151.

complexes can be isolated when bulky substituents (e.g. Ph, Me_3C, Fig. 23) are present on the acetylene. The reaction between the dodecacarbonyl and diphenylacetylene in petroleum ether at 90° leads to at least half a dozen different iron complexes of which only three are shown in Fig. 23. In the formation of these compounds the organic moiety is built up during the reaction by linkage of several acetylenes with or without uptake of carbon monoxide, most probably via a multicentre mechanism[140]. The nature of the products depends not only upon the starting carbonyl but also upon the reaction conditions and cyclic organic products such as cyclopentadienones, quinones and hydroquinones are also isolable from the reaction mixtures. One or two of the more interesting products of these reactions will now be discussed.

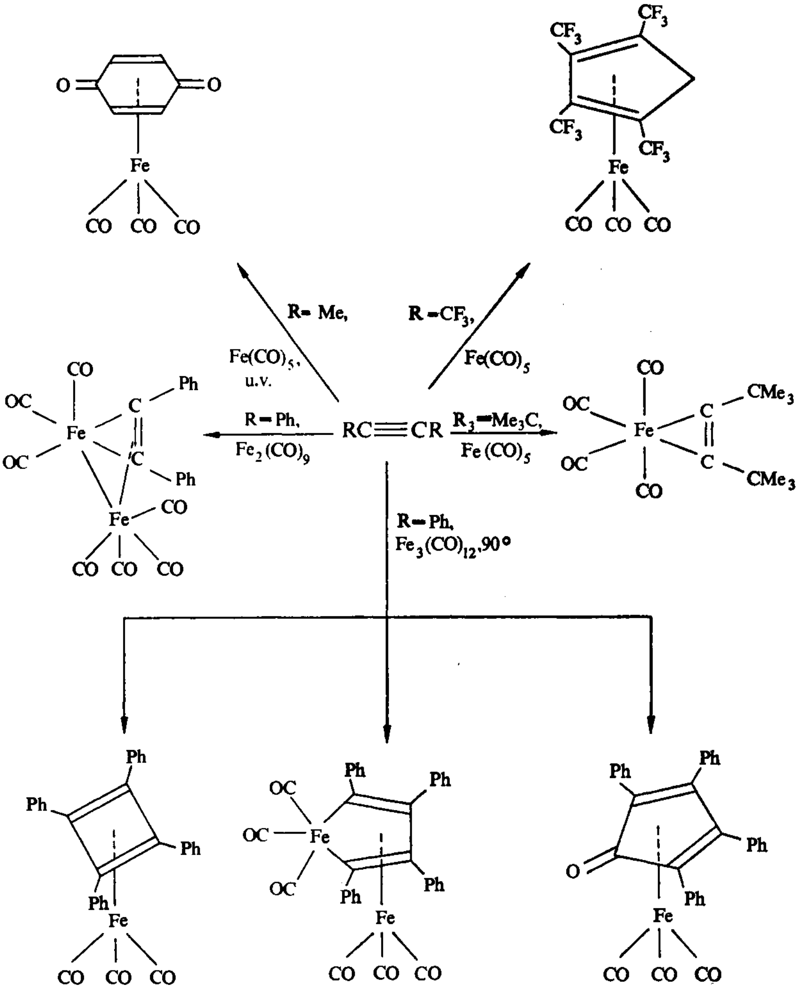

FIG. 23. Some products of iron carbonyl-acetylene reactions.

The violet complex of empirical formula $(PhC_2Ph)_2Fe(CO)_8$ is precipitated when iron dodecacarbonyl reacts with diphenylacetylene in hot methanol; in boiling benzene or

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[140] G. N. Schrawzer, *Chem. Ber.* **94** (1961) 1403.

petroleum ether, however, this complex undergoes rearrangement to a black isomer. The structures of both isomers have been determined by X-ray studies[141]; they are illustrated in Fig. 24. The less stable violet isomer has three iron atoms in a triangular plane with an acetylene bonded one on either side. In the isomerization to the black form, the two acetylenes join with an iron atom in the formation of the ferracyclopentadiene ring. Upon thermal decomposition at 150° the black isomer loses an $Fe(CO)_2$ group and forms the ferracyclopentadiene complex shown in Fig. 23. The unusual pentanuclear iron carbonyl carbide, $Fe_5(CO)_{15}C$, formed in the reaction of the dodecacarbonyl with certain alkynes has been illustrated earlier (Fig. 7).

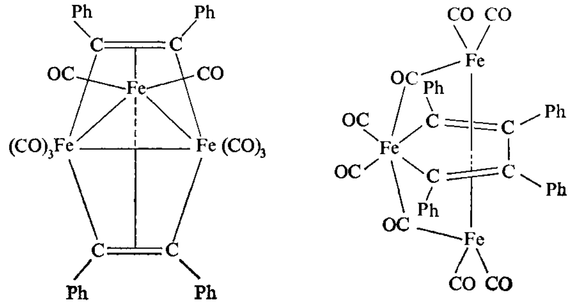

FIG. 24. Structures of violet and black forms of $Fe_3(CO)_8(PhC_2Ph)_2$.

σ-Bonded Organometallic Compounds of Iron

The σ-bonded organometallic compounds of iron (in which iron is bonded to a specific carbon atom by a σ-bond) are far less numerous than the π-complexes. The simple alkyls and aryls of iron are too unstable to exist on their own, but many compounds are known containing π-bonding ligands such as carbon monoxide, a tertiary phosphine, or π-cyclopentadienyl in addition to the Fe–C σ-bond. In general with the other transition elements it is found that Fe–C σ-bonded compounds have their stability increased if electronegative alkyl or aryl groups are used[142], and perfluoroalkyls or iron are fairly well characterized, but again these usually contain carbon monoxide or other π-bonding ligand. We shall look at the general methods of preparation of these compounds[111, 134, 142] and then some of their properties rather than single out particular compounds for detailed discussion.

Preparation methods

(a) *Use of Grignard reagents.* Perhaps the most general preparative route is the reaction of Grignard reagents with cyclopentadienyl or carbonyl iron halides, e.g.

$$(\pi\text{-}C_5H_5)Fe(CO)_2Br + MeMgBr \rightarrow (\pi\text{-}C_5H_5)Fe(CO)_2Me + MgBr_2$$

Alkyl or aryl lithiums can be similarly used as in, for example, the preparations of pentafluorophenyliron tetracarbonyl iodide and vinyl(π-cyclopentadienyl)iron dicarbonyl:

$$C_6F_5Li + Fe(CO)_4I_2 \rightarrow (C_6F_5)Fe(CO)_4I + LiI$$

$$CH_2{=}CHLi + C_5H_5Fe(CO)Cl \rightarrow (C_5H_5)Fe(CO)_2(CH{=}CH_2) + LiCl$$

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[141] R. P. Dodge and V. Schomaker, *J. Organomet. Chem.* **3** (1965) 274.

[142] P. M. Treichel and F. G. A. Stone, *Advances in Organomet. Chem.* **1** (1964) 143.

(b) *From carbonylferrate anions.* The anions formed when iron carbonyls or cyclopentadienyl iron carbonyls are treated with sodium amalgam in tetrahydrofuran can be reacted *in situ* with an alkyl or aryl halide to form an Fe–C bond, viz.

$$\mathrm{Na[(\pi\text{-}C_5H_5)Fe(CO)_2]+RX \rightarrow (\pi\text{-}C_5H_5)Fe(CO)_2R+NaX}$$

A similar reaction with acyl halides often leads to the isolation of the alkyl through decomposition of the intermediate acyl derivative, e.g.

$$\mathrm{Na_2[Fe(CO)_4]+C_2F_5COCl \rightarrow (C_2F_5)_2Fe(CO)_4+CO+NaCl}$$

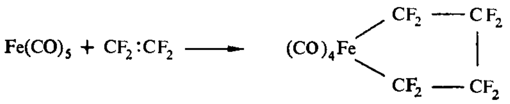
(c) *Addition of olefins to iron hydride complexes.* Cyclopentadienyliron dicarbonyl hydride readily adds across olefins such as perfluoroethylene and butadiene:

$$\mathrm{(C_5H_5)Fe(CO)_2CF_2CF_2H \xleftarrow{CF_2\,:\,CF_2} (C_5H_5)Fe(CO)_2H \xrightarrow{CH_2\,:\,CH.CH\,:\,CH_2} (C_5H_5)Fe(CO)_2CH_2CH : CHCH_3}$$

Iron tetracarbonyl hydride similarly adds across perfluoroethylene to give the *cis*-octahedral $\mathrm{(HCF_2CF_2)Fe(CO)_4}$.

(d) *Other routes.* There are several other ways of preparing compounds with Fe–C σ-bonds; some of these have been mentioned in earlier sections, e.g. in the reactions of acetylenes with iron carbonyls. Other methods include the reactions of perfluoralkyl iodides and of perfluoro-olefins with iron carbonyls, e.g.

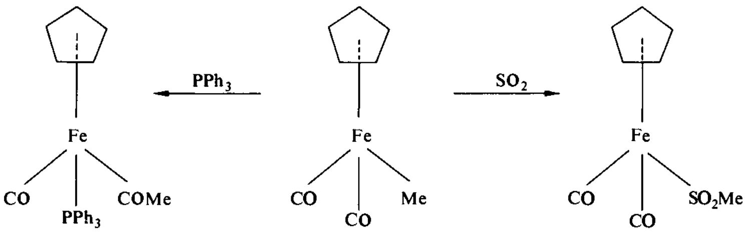
$$\mathrm{Fe(CO)_5+CF_3I \rightarrow (CF_3)Fe(CO)_4I+[(CF_3)Fe(CO)_3I]_2}$$



The reactions of sodium acetylides with liquid ammonia solutions of iron(II) salts lead to the formation of explosive σ-bonded acetylide complexes:

$$\mathrm{6NaC : CMe+[Fe(NH_3)_6](SCN)_2 \rightarrow Na_4[Fe(C : CMe)_6]+2NaCN+6NH_3}$$

Properties. The thermal, oxidative and hydrolytic stabilities of these σ-bonded derivatives depend to a very large extent upon the nature and number of the π-bonding ligands also attached to the iron, so that generalizations are not possible. The π-cyclopentadienyl iron dicarbonyl derivatives $\mathrm{(C_5H_5)Fe(CO)_2R}$ are perhaps the most studied σ-bonded organo iron compounds because of their ease of preparation and handling. The alkyl compounds are stable to hydrolysis and to dilute acids; their thermal stability decreases as the size of the alkyl group increases, the propyl compounds decomposing at 60° *in vacuo*. The Fe–C sigma bond is readily carbonylated and even sulphur dioxide insertion occurs[143]:



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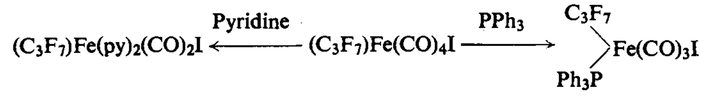
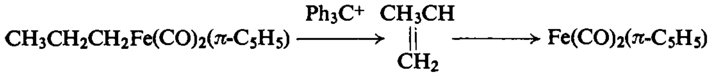
[143] J. P. Bibler and A. Wojcicki, *Inorg. Chem.* **5** (1966) 889; *J. Am. Chem. Soc.* **86** (1964) 5051.

With the perfluoro-alkyl derivatives, however, such insertion reactions do not readily occur. Instead replacement of carbon monoxide occurs when perfluoroalkyl iron carbonyls and carbonyl halides are treated with Lewis bases[144]:



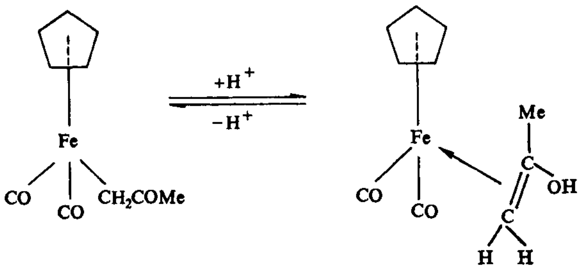
$$(C_3F_7)Fe(py)_2(CO)_2I \xleftarrow{\text{Pyridine}} (C_3F_7)Fe(CO)_4I \xrightarrow{PPh_3} \overset{C_3F_7}{\underset{Ph_3P}{>}}Fe(CO)_3I$$

Several of these σ-alkyls can be converted to olefin π-complexes by hydride abstraction,



$$CH_3CH_2CH_2Fe(CO)_2(\pi\text{-}C_5H_5) \xrightarrow{Ph_3C^+} \begin{matrix}CH_3CH\\ \|\\ CH_2\end{matrix} \longrightarrow Fe(CO)_2(\pi\text{-}C_5H_5)$$

or in the case of functionally substituted alkyls by reversible protonation of the ligand:



The phosphine stabilized aryls (i.e. those containing only a tertiary phosphine as π-bonding ligand) are far less stable than the carbonyl or π-cyclopentadienyl iron compounds. The golden yellow pentachlorophenyl complex $[Fe(C_6Cl_5)_2(PEt_2Ph)_2]$ decomposes in benzene solution at 25°. It has a magnetic moment of 3·6 B.M. and is believed to contain iron in a *trans*- square planar configuration.

3.4. COMPLEXES OF IRON(II)

For the purpose of describing the preparation and properties of iron(II) complexes, the latter will be classified according to whether they contain cationic, neutral (uncharged) or anionic iron species. On page 1033, where the electronic structure of the complexes is considered, they will be classified according to their structural type.

Cationic Iron(II) Complexes

The hexaquo ion, $[Fe(H_2O)_6]^{2+}$. This ion is present in the crystal structures of several hydrated iron(II) salts[145]. The octahedral $[Fe(H_2O)_6]^{2+}$ unit in the Tutton salt $(NH_4)_2SO_4.FeSO_4.6H_2O$ has a distinct tetragonal and slight rhombic distortion, the Fe–O distances being 2·14, 1·88 and 1·85 Å. In $FeSiF_6.6H_2O$ the $[Fe(H_2O)_6]^{2+}$ octahedra are trigonally distorted. The hexaquo ion is also present in $FeSO_4.7H_2O$, $Fe(ClO_4)_2.6H_2O$ (but not in $FeCl_2.6H_2O$) and in aqueous solutions of Fe^{2+} containing no other donor molecules or ions. Complexes containing this ion have a pale blue-green colour; their redox properties have been discussed in section 3.1.

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[144] R. A. Plowman and F. G. A. Stone, *Inorg. Chem.* **1** (1962) 518.

[145] R. W. G. Wyckoff, *Crystal Structures*, 2nd edition, Vol. 3, Interscience (1965).

Solutions of the hexaquo ion are barely acidic; for the equilibrium[146]

$$[Fe(H_2O)_6]^{2+} + H_2O \rightleftharpoons [Fe(H_2O)_5(OH)]^{+} + H_3O^{+}$$

$K_1 = 10^{-9 \cdot 5}$. The addition of sodium carbonate solution, therefore, results in the precipitation of iron(II) carbonate with no evolution of carbon dioxide (contrast the reaction of the hexaquo iron(III) cation). With strong alkalis the hydroxide $Fe(OH)_2$ is precipitated.

Cations containing other bases. Most of the other cationic iron(II) complexes contain unidentate or bidentate nitrogen donor molecules. The reactions of ammonia with iron(II) halides lead to products containing up to ten molecules of ammonia per iron atom. The thermally stable ammoniates at room temperature however are the hexa-ammoniates, e.g. $FeCl_2 . 6NH_3$ and $FeBr_2 . 6NH_3$. The crystal structure of these[145] shows them to contain the $[Fe(NH_3)_6]^{2+}$ ion. The hexammine iron(II) bromide is conveniently prepared in the laboratory[147] by saturating a solution of iron in hydrobromic acid (under an atmosphere of hydrogen) with ammonia; it forms pale blue-grey crystals which decompose upon exposure to the atmosphere.

With unidentate nitrogen donors other than ammonia the $FeL_6{}^{2+}$ cations are not readily formed in aqueous solution. They are available, however, through the general route involving the disproportionation of iron carbonyls. Thus reaction of iron pentacarbonyl with pyridine at 85° and in the presence of ultraviolet light takes place according to

$$5Fe(CO)_5 + 6py \rightarrow [Fe(py)_6][Fe_4(CO)_{13}] + 12CO$$

and these reactions give cationic iron(II) complexes with a wide variety of nitrogen bases usually in benzene as solvent (viz. page 997) as well as a few oxygen bases, e.g. dimethyl sulphoxide $[Fe(DMSO)_6]^{2+}$. This green dimethyl sulphoxide cation as well as the yellow-green pyridine-N-oxide complex $[Fe(C_5H_5NO)_6]^{2+}$ can also be obtained, however, starting from iron(II) salts.

The chelating ligands, 1,10-phenanthroline, 2,2′-dipyridyl and diamines form complex octahedral cations of the types $[Fe(phen)_3]^{2+}$, $[Fe(dipy)_3]^{2+}$ and $[Fe(en)_3]^{2+}$ both in aqueous solution and by disproportionation reactions of iron carbonyls in inert solvents. The dipyridyl and phenanthroline complexes can be isolated as salts, e.g. $[Fe(dipy)_3]Cl_2 . 7H_2O$, and their solutions find use in volumetric analysis as redox indicators (see section 3.1 for standard potentials). Tris(1,10-phenanthroline)iron(II) sulphate is widely used as *ferroin*; the colour change with strong oxidizing agents is quite striking:

$$\underset{\text{deep red}}{[Fe(phen)_3]^{2+}} \rightarrow \underset{\text{pale blue}}{[Fe(phen)_3]^{3+}} + e^-$$

The stepwise replacement of water molecules from the hexaquo iron(II) cation leads to all members of the series, e.g. with ethylenediamine the stepwise stability constants are[148]

$$\begin{aligned}
&[Fe(H_2O)_6]^{2+} + en \rightarrow [Fe(H_2O)_4(en)]^{2+} + 2H_2O, && K_1 = 10^{4 \cdot 34}\\
&[Fe(H_2O)_4(en)]^{2+} + en \rightarrow [Fe(H_2O)_2(en)_2]^{2+} + 2H_2O, && K_2 = 10^{3 \cdot 31}\\
&[Fe(H_2O)_2(en)_2]^{2+} + en \rightarrow [Fe(en)_3]^{2+} + 2H_2O, && K_3 = 10^{2 \cdot 05}
\end{aligned}$$

The multidentate nitrogen ligands show even larger stability constants. For diethylenetriamine ($NH_2C_2H_4NHC_2H_4NH_2$) complexes with Fe(II), $K_1 = 1 \cdot 7 \times 10^6$ and $K_2 = 10^6$,

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[146] L. G. Sillen, *Quart. Revs.* (*London*), **13** (1959) 153.

[147] G. W. Watt and W. A. Jenkins, *Inorg. Syntheses*, **4** (1953) 161.

[148] *Stability Constants of Metal-Ion Complexes*, Chemical Society (London) Special Publication No. 17 (1964).

and for triethylenetetramine ($NH_2C_2H_4NHC_2H_4NHC_2H_4NH_2$) a tetradentate ligand, $K_1 = 10^8$.

Some interesting complex cations containing alkyl cyanides and isocyanides have been described. When iron reacts with chlorine or bromine in methyl cyanide[149], the complexes produced contain octahedral iron(II) cations and tetrahedral iron(III) anions, e.g. $[Fe(MeCN)_6][FeBr_4^-]_2$. Similar reactions in ethyl acetate and nitromethane give products which have been formulated as $[Fe(EtAc)_6][FeX_4]_2$ and $[Fe(MeNO_2)_6][FeX_4]_2$. The isocyanides also form octahedral iron(II) cations[150]; the reaction of potassium hexacyanoferrate(II) with dimethyl sulphate at the temperature of reflux yields crystals of $[Fe(CNMe)_6](HSO_4)_2$ on cooling. In the chloride $[Fe(CNMe)_6]Cl_2$, the Fe–C distance is 1·85 Å—very similar to that in iron carbonyl. The Fe–C–N–C atoms are not colinear, the C–N–C angle being 173°. Upon thermal decomposition at 130–150° under reduced pressure, dicyanotetrakis(methyl isocyanide)iron(II) is formed:

$$[Fe(CNMe)_6]Cl_2 \rightarrow Fe(CN)_2(CNMe)_4 + 2MeCl$$

Neutral Iron(II) Complexes

Complex hydrides. Whilst no simple molecular hydride of iron exists, there are several complexes containing the Fe–H bond. The hydridocarbonyls and hydridocarbonylate anions have been considered in section 2.1. Table 10 lists some properties of some phosphine-stabilized hydrides. These hydrides are prepared by reaction of lithium aluminium hydride with the bis(phosphine)iron(II) halides in tetrahydrofuran. The only stable dihydride, $FeH_2[C_6H_4(PEt_2)_2]_2$, can also be prepared directly from the reaction of finely divided iron with the diphosphine under hydrogen. The hydrides are sensitive to oxidation, especially when in solution; they show surprising thermal stability, decomposing at the melting points given in Table 10. Dipole moment measurements have confirmed the *trans*-structure for the octahedral complexes.

TABLE 10. SOME PHOSPHINE-STABILIZED IRON HYDRIDES

Hydride	Colour	M.p. (°C)	ν(M–H) (cm^{-1})	M–H proton resonance τ(ppm)
trans-FeH_2 (diphos I)$_2$[a]	orange	248–249·5	1726	23·1
trans-FeHCl (diphos I)$_2$[b]	red	230·5–231·5	1870	40·5
trans-FeHCl (diphos II)$_2$[b]	red	180	1810	
trans-FeHCl (diphos III)$_2$[b]	red	154·5–155·5	1849	
trans-FeHI (diphos III)$_2$[b]	red-brown	173	1872	
$Fe_2H(C_5H_5)_2(CO)_2(\mu\text{-}PMe_2)$[c]	dark brown	137–140		28·73
$Fe_2H(C_5H_5)_2(CO)_2(\mu\text{-}PPh_2)$[c]	dark brown	153–157		28·67

diphos I = $o\text{-}C_6H_4(PEt_2)_2$; diphos II = $C_2H_4(PMe_2)_2$; diphos III = $C_2H_4(PEt_2)_2$.

[a] J. Chatt, F. A. Hart and D. T. Rosevear, *J. Chem. Soc.* (1961) 5504.

[b] J. Chatt and R. G. Hayter, *J. Chem. Soc.* (1961) 5507; *ibid.* (1963) 6017.

[c] R. G. Hayter, *J. Am. Chem. Soc.* **85** (1963) 3120.

Nitrogen, phosphorous and arsenic ligands. With these ligands the iron(II) halides form complexes of two principal types, FeX_2L_4 and FeX_2L_2. With some ligands, complexes of both types can be prepared. Tetra(pyridine)iron(II) chloride is prepared[151] as yellow crystals

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[149] B. J. Hathaway and D. G. Holah, *J. Chem. Soc.* (1964) 2408.

[150] L. Malatesta, *Progress in Inorg. Chem.* **1** (1959) 328.

[151] O. Bandish and W. H. Hartung, *Inorg. Syntheses*, **1** (1939) 184.

by the addition of a saturated solution of iron(II) chloride to excess pyridine; it is considerably more stable in air than simple iron(II) salts and is a useful starting material for synthetic work. Other compounds of this type are formed by tertiary aromatic amines, e.g. $FeBr_2$(isoquinoline)$_4$, FeI_2(γ-picoline)$_4$ and isocyanides, e.g. $FeI_2(CNCH_3)_4$. Primary amines tend to form compounds of the types $[FeL_6]Cl_2$ and $FeCl_2L_2$. Thus $FeCl_2(NH_3)_2$ and $FeCl_2(MeNH_2)_2$ are the thermal decomposition products of the hexammine complexes. Aromatic amines form the bis complexes at or near room temperature, e.g. yellow $FeCl_2(PhNH_2)_2$. Hydrazine forms tetragonal complexes of this type, $FeX_2(N_2H_4)_2$, which contain bridging and bidentate hydrazine groups. Similar types of complexes are formed with other iron(II) salts.

Tertiary phosphines give complexes with the formula $FeX_2(PR_3)_2$, but they tend to dissociate in solution and are particularly unstable in hydroxylic solvents[152]. The colourless spin-free tetrahedral complexes $FeCl_2L_2$ ($L = PEt_3$, PEt_2Ph, $PEtPh_2$ and PPh_3) can be prepared using benzene as solvent. Primary and secondary phosphines appear to form a variety of different types of complex. Dicyclohexylphosphine forms the colourless and tetrahedral $FeCl_2L_2$ type of complex while diethylphosphine gives the red and probably square planar complex $FeCl_2(PHEt_2)_2$. Monophenylphosphine forms cationic complexes of the type $[Fe(PH_2Ph)_4]X_2$. Chelating diphosphines and diarsines form diamagnetic complexes of the type FeX_2(chelate)$_2$ having the *trans*-octahedral configurations. The tetratertiary phosphine tris-(*o*-diphenylphosphinophenyl)phosphine (QP) gives diamagnetic six-coordinate complexes $FeX_2(QP)$ ($X = NCS^-$ and CN^-) and trigonal bipyramidal cations $[FeX(QP)]^+$ ($X = Cl^-, Br^-, I^-$) which have μ_{eff} about 3 B.M.

Oxygen and sulphur ligands. Complexes of iron(II) chloride with alcohols and organic esters contain one, two or four molecules of the ligand, e.g. $FeCl_2(EtOH)$, $FeCl_2(MeCOOMe)$, $FeCl_2(MeOH)_2$ and $FeCl_2(MeOH)_4$. They form colourless crystals which rapidly turn yellow under aerial oxidation. Tetrahedral complexes are formed by the tertiary phosphine and arsine oxides; these are of the types $FeX_2.(Ph_3PO)_2$, $FeX_2[(Me_2N)_3PO]_2$ and $FeX_2(Ph_3AsO)_2$. Picolinic acid N-oxide (pico $= C_5H_4(COO^-)NO$) forms, however, a deeply coloured (magenta) octahedral complex $Fe(pico)_2(H_2O)_2$ and pyridine N-oxide forms cation species $[Fe(C_5H_5NO)_6]^{2+}$.

Chelating oxygen ligands, e.g. diketones, readily form complexes with aqueous iron(II) solutions especially in the presence of tertiary nitrogen bases which neutralize the liberated protons. Acetylacetone forms six-coordinate complexes having only two chelate rings, e.g. $Fe(acac)_2(py)_2$. In the absence of coordinating nitrogen donors the hydrated acetylacetonate $Fe(acac)_2.1{\cdot}5H_2O$ forms; this is easily dehydrated to the orange-red $Fe(acac)_2$. This anhydrous compound is probably polymeric; it has a magnetic moment $\mu_{eff} = 5{\cdot}4$ B.M. at room temperature, characteristic of octahedrally coordinated iron(II). With dipivaloylmethane (DPMH), however, the tetrahedral $Fe(DPM)_2$ is formed; it is high spin with $\mu_{eff} = 5{\cdot}0$ B.M. at room temperature. These compounds are all very sensitive to aerial oxidation; the hexafluoroacetylacetonate $Fe(F_6acac)_2.2H_2O$ is the most stable.

The most interesting complexes with sulphur ligands are those of the 1,2-dithiols and related types[154]. These compounds are of the neutral and anionic types and they present similar problems of oxidation state assignment as, for example, the 2,2-dipyridyl complexes. For simplicity they will all be considered here. The reaction of the sodium salt of the

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[152] G. Booth, *Advances Inorg. Chem. Radiochem.* **6** (1964) 13.

[153] J. P. Fackler, *Progress in Inorg. Chem.* **7** (1966) 404.

[154] J. A. McCleverty, *Progress in Inorg. Chem.* **10** (1968) 49.

maleonitriledithiolate anion, $Na_2S_2C_2(CN)_2$, with iron(II) salts gives either the dimeric dianion $[FeS_4C_4(CN)_4]_2^{2-}$ (dark red-brown) or the trisubstituted complex $[FeS_6C_6(CN)_6]^{2-}$ (green) depending upon the type of cation used as precipitant (the former being obtained with tetra-alkyl-ammonium salts, the latter with tetra-aryl-phosphonium or arsonium salts). In the $[FeS_4C_4(CN)_4]_2^{2-}$ anion each iron atom is surrounded by five sulphur atoms in a distorted square pyramidal arrangement; for the tetrabutylammonium salt the bond lengths are Fe–S (basal plane) $= 2{\cdot}23 \pm 0{\cdot}01$ Å, Fe–S (apical) $= 2{\cdot}46 \pm 0{\cdot}01$ Å, C–C $= 1{\cdot}39 \pm 0{\cdot}03$ Å, C–S $= 1{\cdot}73 \pm 0{\cdot}03$ Å. Similar dimeric dianions are obtained in the ethanolic reactions of iron(II) salts with the disodium salts of benzene-1,2-dithiol, and some of its methyl substituted derivatives and of tetrachlorobenzene-1,2-dithiol. The neutral polymeric complex $[Fe(S_2C_6Cl_4)_2]$ is produced when iron powder, hexachlorobenzene and sodium sulphide react in dimethyl formamide; upon dissolution in acetone–dimethyl formamide mixtures the dimeric dianion $[Fe(S_2C_6Cl_4)_2]_2^{2-}$ is produced. Other neutral types of complex known include the diamagnetic $[FeS_4C_4(CF_3)_4]_2$ and $[FeS_4C_4R_4]$ ($R = H$, Ph, etc.). The interest in these neutral and anionic complexes is centred partly on their easy interconversion by one electron transfer reactions. Thus voltammetric and polarographic studies on the complex $[FeS_4C_4(CF_3)_4]_2$ have shown two reversible one-electron reduction waves and one reversible two-electron reduction wave corresponding to the processes:

$$[MS_4]_2 \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [MS_4]_2^{1-} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [MS_4]_2^{2-} \underset{-2e^-}{\overset{+2e^-}{\rightleftharpoons}} [MS_4]^{2-}$$

For a fuller discussion of the properties of these complexes the reader is referred to the recent excellent review article[154].

Anionic Iron(II) Complexes

Complex halides. The cream coloured, tetrahedral tetrahaloferrates(II) $[FeX_4]^{2-}$ can be readily prepared[155] from the iron(II) halide and a quarternary ammonium or arsonium halide in ethanol. They usually precipitate upon mixing the solutions; recrystallization is not possible because of their decomposition in hot alcohol. These compounds are isomorphous with the $[MX_4]^{2-}$ complexes of other divalent first row transition metal ions. They are unibivalent electrolytes in nitrobenzene, but some decomposition occurs in organic solvents.

Complex cyanides[156]. The hexacyanoferrate(II) (ferrocyanide) ion is a stable, non-poisonous and well-known complex iron(II) anion; it forms a large number of salts with various cations. The free acid, $H_4Fe(CN)_6$ (ferrocyanic acid), can be obtained as an etherate by the reaction of the potassium salt with hydrogen chloride (or cold sulphuric acid) in the presence of ether. The ether is readily removed at 80–90° in a stream of hydrogen to leave the acid as white crystals. It can also be obtained in aqueous solution by ion exchange on the potassium salt, and is precipitated when concentrated hydrochloric acid is added to an aqueous solution of this salt. The acid dissociation constants in water are[157] $K_1 > K_2$; $K_3 = 6 \pm 2 \times 10^{-3}$; $K_4 = 6{\cdot}7 \pm 0{\cdot}3 \times 10^{-5}$, so that only the first two are typical of a strong acid. The infrared spectrum shows broad absorption in the 3300–2300 cm^{-1} region which shifts on deuteration and two ($C \equiv N$) stretching frequencies; all four hydrogen atoms are believed to be hydrogen bonded to cyanide ions in a *trans*-arrangement[189].

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[155] N. S Gill, *J. Chem. Soc.* (1961) 3512.

[156] B. M. Chadwick and A. G. Sharpe, *Advances in Inorg. Chem., Radiochem.* **8** (1966) 114.

[157] J. Jordan and G. J. Ewing, *Inorg. Chem.* **1** (1962) 587.

[158] A. P. Ginsberg and E. Koubek, *Inorg. Chem.* **4** (1965) 1186.

The alkali and alkaline earth metal salts of ferrocyanic acid crystallize from aqueous solution as hydrates; e.g. Na, $10H_2O$, K, $3H_2O$, Rb, $2H_2O$, Cs, $3H_2O$, Ca, $11H_2O$, Ba, $6H_2O$. These salts are all water-soluble, whereas salts of other cations are usually insoluble. The copper(II) salt has been used as a semi-permeable membrane since a film of it is permeable to water but not to certain solutes. The potassium salt is the most important and we shall deal with its chemistry in detail as illustrative of the others.

Potassium hexacyanoferrate(II), $K_4Fe(CN)_6.3H_2O$, is obtained commercially from gasworks spent oxide (which contains Prussian blue) by treatment with lime and subsequent treatment of the solution with a soluble potassium salt; the less soluble potassium hexacyanoferrate(II) can be crystallized from this mixture. In the laboratory it is readily prepared by treating aqueous iron(II) sulphate with an excess of potassium cyanide; the initially precipitated iron(II) cyanide dissolves upon boiling in the excess of potassium cyanide solution and the ferrocyanide crystallizes on cooling. The trihydrate is diamagnetic and dimorphic existing in monoclinic (pseudotetragonal) and tetragonal forms. Its infrared spectrum in solution[159] shows a single $\nu(C \equiv N)$ at 2044 cm^{-1}, but in the solid state a large number of bands are observed[160]; $\nu(Fe–C)$ occurs at 416 cm^{-1}. White, anhydrous $K_4Fe(CN)_6$ is obtained by dehydrating the trihydrate at 100°.

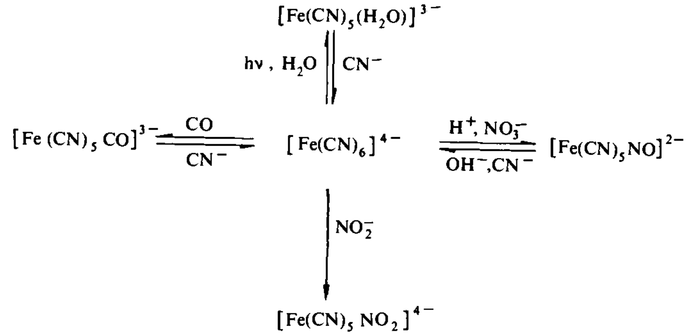

FIG. 25. Substitution products of $[Fe(CN)_6]^{4-}$.

The $[Fe(CN)_6]^{4-}$ ion is oxidized to Prussian blue by oxygen in acidic but not significantly in neutral or alkaline solutions. Many oxidizing agents will, however, effect the oxidation to $[Fe(CN)_6]^{3-}$, e.g. Ce^{4+}, MnO_4^-, $Cr_2O_7^{2-}$ and $S_2O_8^{2-}$. Dilute sulphuric acid liberates hydrogen cyanide when heated with ferrocyanide; concentrated sulphuric acid liberates carbon monoxide:

$$K_4Fe(CN)_6+6H_2SO_4+6H_2O \rightarrow 6CO+2K_2SO_4+3(NH_4)_2SO_4+FeSO_4$$

Alkalis have little effect upon the $[Fe(CN)_6]^{4-}$ ion. Prolonged boiling of aqueous solutions, especially in the presence of light, leads to the reversible production of the $[Fe(CN)_5(H_2O)]^{3-}$ ion. The basicity of the nitrogen atoms in the cyanide groups has been demonstrated by the observation that potassium hexacyanoferrate(II) absorbs six molecules of boron trifluoride[161].

The monosubstitution products of the hexacyanoferrate(II) ion are exemplified[156] in Fig. 25.

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[159] L. H. Jones, *Inorg. Chem.* **2** (1963) 777.

[160] I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta,* **18** (1962) 101.

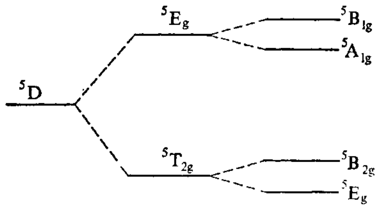
[161] D. F. Shriver, *J. Am. Chem. Soc.* **85** (1963) 1405.

The mono-aquo species is normally prepared by the action of an alkaline hydroxylamine solution upon the nitroprusside:

$$[Fe(CN)_5NO]^{2-} + NH_2OH + OH^- \rightarrow [Fe(CN)_5(H_2O)]^{3-} + N_2O + H_2O$$

It reacts with concentrated aqueous ammonia to give the pale yellow $[Fe(CN)_5(NH_3)]^{3-}$ ion from which many amines will displace ammonia and form the aminopentacyanoferrates(II). The chemistry of the nitrosylpentacyanoferrates(II) has already been discussed (page 1004). The carbonylpentacyano complexes are prepared by reaction of the hexacyanoferrates(II) with carbon monoxide under pressure at above 130°.

Perhaps the most well-known reaction of the hexacyanoferrate(II) is that with an excess of an iron(III) salt. This reaction produces a blue precipitate which has been long known as *Prussian blue*. The reaction of hexacyanoferrates(III) with an excess of an iron(II) salt also produces a blue precipitate known as *Turnbull's blue*. These two compounds give the same X-ray powder diffraction pattern and Mössbauer spectrum[162] and both are formulated as iron(III) hexacyanoferrate(II), $Fe_4[Fe(CN)_6]_3$. If 1:1 molar proportions of an iron(III) salt and the hexacyanoferrate(II) are reacted together then *soluble Prussian blue* is formed. This has the composition $KFe[Fe(CN)_6].H_2O$ with a variable water content and a magnetic moment of 5·7 B.M. The electronic[163] and Mössbauer spectra[164] indicate a formulation as $KFe^{III}[Fe^{II}(CN)_6]$ with high spin iron(III) surrounded octahedrally 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 electron transfer from iron(II) to iron(III). The reaction between iron(II) and hexacyanoferrate(II) ions leads to a white precipitate of $K_2Fe[Fe(CN)_6]$ containing only iron(II). *Berlin green*, on the other hand, contains only iron(III); it is obtained using an iron(III) salt and a hexacyanoferrate(III) and is usually formulated as $Fe[Fe(CN)_6]$. The basic structural[99] unit for all these compounds seems to be a cubic array of iron atoms with cyanide ions along cube edges between these atoms. This is the structure of $Fe[Fe(CN)_6]$; in $KFe[Fe(CN)_6]$ and $K_2Fe[Fe(CN)_6]$ the cubes contain potassium atoms in the centre of every other, and every, cube of iron atoms respectively.



(a) O_h (b) D_{4h}

FIG. 26. Weak field states for Fe^{2+} in (a) octahedral, and (b) tetragonal symmetry.

Other anionic complexes. Thiocyanate complexes with the $[Fe(SCN)_6]^{4-}$ anion can be prepared by dissolving iron(II) hydroxide in thiocyanic acid and adding an alkali metal thiocyanate. The colourless complexes are readily oxidized in air and are decomposed by aqueous ammonia, iron(II) hydroxide being precipitated.

Ato complexes of iron(II) are rather unstable. Whilst oxyanions frequently form weak

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[162] E. Fluck, W. Kerler and W. Neuwirth, *Angew. Chem. Intern. Ed.* **2** (1963) 277.

[163] M. R. Robin, *Inorg. Chem.* **1** (1962) 337.

[164] J. F. Duncan and P. W. R. Wigley, *J. Chem. Soc.* (1963) 1120.

complexes with aqueous iron(II), only a few salts containing such complex ions have been isolated. These include oxalato complexes $[Fe(C_2O_4)_2]^{2-}$ and nitro complexes $[Fe(NO_2)_6]^{4-}$. Ethylenediaminetetraacetic acid (EDTA) forms a 1 : 1 complex $[Fe(EDTA)]^{2-}$ ($K = 10^{14 \cdot 33}$); this is readily oxidized to the much more stable iron(III) complex.

Spectral and Magnetic Properties of Iron(II) Complexes

High spin octahedral and tetragonal complexes. Most iron(II) complexes are of the high spin type, quite strong ligand fields being required to cause the formation of spin-paired complexes. Iron(II) has the $3d^6$ configuration with a free ion ground term ${}^5D$, this being the only quintet state. For the weak field octahedral limit the ground state is $t_{2g}^4 \, e_g^2$ and the ${}^5D$ term is split[165] (Fig. 26) into ${}^5E_g$ and ${}^5T_{2g}$. Only one spin-allowed transition is thus expected in the electronic spectra of the weak field complexes (the complete energy level diagram for d^6 showing the higher energy triplet and singlet spin states can be seen in the standard

TABLE 11. ELECTRONIC SPECTRA OF SOME OCTAHEDRAL AND TETRAGONAL SPIN-FREE IRON(II) COMPLEXES

Octahedral complexes	${}^5T_{2g} \rightarrow {}^5E_g$ (cm^{-1})	
$[Fe(H_2O)_6]^{2+}$ in water[a]	10,400	8300
in $Fe(NH_4)_2(SO_4)_2 . 6H_2O$[a]	10,800	8400
in $FeSiF_6 . 6H_2O$[a]	10,700	8300
FeF_2[b]	10,660	6990
$FeCl_2$[c]	7600	5800
$FeBr_2$[c]	6800	5400
FeI_2[c]	6100	4900
$Fe(MeCN)_6^{2+}$ [d]	11,000	
$Fe(NCSe)_6^{4-}$ [e]	11,150	9760
Tetragonal complexes	${}^5E_g \rightarrow {}^5B_{1g}$	${}^5E_g \rightarrow {}^5A_{1g}$
$FeF_2 . 4H_2O$[f]	10,150	
$FeCl_2 . 4H_2O$[f]	11,000	6800
$FeBr_2 . 4H_2O$[f]	11,000	6150
$FeBr_2 . 6H_2O$[f]	11,000	6200
$FeCl_2(phen)_2$[g]	10,510	8470
$FeCl_2(py)_4$[h]	10,300	8550
$FeBr_2(py)_4$[h]	10,650	7750
$FeCl_2(isoquin)_4$[h]	10,950	9100
$FeBr_2(isoquin)_4$[h]	11,450	7800
$FeI_2(isoquin)_4$[h]	11,750	5900
$FeCl_2 . 2H_2O$[f]	9800	5750
$FeCl_2(py)_2$[h]	9900	5850
$FeCl_2(4\text{-cyanopyridine})_2$[h]	9850	6250

phen = 1,10-phenanthroline, py = pyridine, isoquin = isoquinoline.

[a] F. A. Cotton and M. D. Meyers, *J. Am. Chem. Soc.* **82** (1960) 5023.
[b] W. E. Hatfield and T. S. Piper, *Inorg. Chem.* **3** (1964) 1295.
[c] G. Winter, *Austral. J. Chem.* **21** (1968) 2859.
[d] B. J. Hathaway and D. G. Holah, *J. Chem. Soc.* (1964) 2408.
[e] D. Forster and D, M. L. Goodgame, *Inorg. Chem.* **4** (1965) 1712.
[f] C. D. Burbridge and D. M. L. Goodgame, *J. Chem. Soc.* (A) (1968) 1410.
[g] K. Madeja and E. Konig, *J. Inorg. and Nuclear Chem.* **25** (1963) 377.
[h] D. M. L. Goodgame, M. Goodgame, M. Hitchman and M. Weeks, *Inorg. Chem.* **5** (1966) 635.

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[165] C. J. Ballhausen, *Introduction to Ligand Field Theory*, McGraw-Hill, New York (1962).

texts[166, 167]). In practice, octahedral iron(II) complexes usually exhibit a broad absorption band which is frequently split into two components (Table 11). This splitting is probably due[168] to the Jahn–Teller effect at least in solutions of $[Fe(H_2O)_6]^{2+}$, since it is much larger than that which might arise through spin-orbit coupling. In the crystals, however, tetragonal distortion is sometimes present—iron(II) ammonium sulphate hexahydrate contains the tetragonally (and slightly rhombically) distorted $[Fe(H_2O)_6]^{2+}$ ion. In the iron(II) halides, however, the crystal structures show only trigonal distortion to be possible; this would cause a small splitting of the ${}^5T_{2g}$ level into ${}^5E_g$ and ${}^5A_{1g}$[165] and would not account for the splitting of the ${}^5T_{2g} \rightarrow {}^5E_g$ band. In the complexes which do not have six identical ligands around the iron atom the ${}^5E_g$ level undergoes a more pronounced splitting. The crystal structures of $FeCl_2.4H_2O$[169] and $FeCl_2.2H_2O$[170] are known to be considerably distorted from octahedral; in the dihydrate the structure consists of planar chains of iron and chlorine atoms separated by water molecules. In general for these complexes of FeX_2L_4 type, the greater the dissimilarity of the ligand field strengths of X and L the greater is the separation between the observed bands. In view of the similarity between the spectra of $FeBr_2.4H_2O$ and $FeBr_2.6H_2O$ it is concluded that the latter contains *trans*-$[FeBr_2(H_2O)_4]$ units rather than $[Fe(H_2O)_6]^{2+}$ ions. The band assignments in tetragonal symmetry (Table 11, Fig. 26) are those of Lever[171] to whom the reader should refer for a full discussion. Suffice it to say here that absolute proof that the ground state is ${}^5E_g$ (rather than ${}^5B_{2g}$) is lacking.

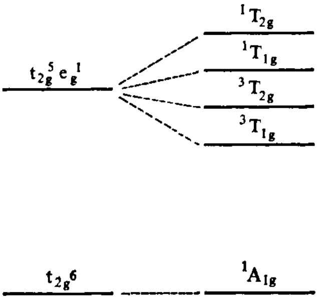

FIG. 27. Strong field octahedral states for Fe^{2+}.

For octahedral high spin complexes of iron(II) with the ${}^5T_2$ ground term, the magnetic moment is expected to be[94] about 5·5 B.M. at room temperature; the spin-orbit coupling constant, $\lambda = -100\ cm^{-1}$, and the moment is not expected to vary much with temperature. In complexes whose symmetry deviates from pure octahedral a reduction in this moment towards the spin only value for four unpaired electrons (4·8 B.M.) is expected. In practice most octahedral iron(II) complexes have magnetic moments μ_{eff} in the range 5·3–5·5 B.M.

Low spin octahedral complexes. With strong field ligands spin-pairing occurs and low spin octahedral iron(II) complexes have the electron configuration t_{2g}^6; this configuration gives rise to the ${}^1A_{1g}$ ground state. Electronic excitation to the e_g orbitals leads to the configuration $t_{2g}^5e_g^1$ which gives rise to the spin triplet and spin singlet states shown in

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[166] A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, London (1968).
[167] B. N. Figgis, *Introduction to Ligand Fields*, Interscience, New York (1966).
[168] F. A. Cotton and M. D. Myers, *J. Am. Chem. Soc.* **82** (1960) 5023.
[169] B. R. Penfold and J. A. Grigov, *Acta Cryst.* **12** (1959) 850.
[170] B. Morosin and J. E. Graeber, *J. Chem. Phys.* **42** (1965) 898.
[171] A. B. P. Lever, *Co-ordination Chem. Revs.* **3** (1968) 119.

Fig. 27. Two spin allowed bands are to be expected, i.e. from the $^1A_{1g}$ ground state to the $^1T_{1g}$ and $^1T_{2g}$ states, as well as two weaker spin forbidden bands. The assignment of these bands (Table 12) has presented considerable difficulty and must be regarded as tentative. The $^1A_{1g} \rightarrow {}^3T_{2g}$ transition is not usually observed for d^6 ions since it has a very low intensity and is normally obscured by the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition.

TABLE 12. ELECTRONIC SPECTRA (cm^{-1}) OF SOME SPIN-PAIRED IRON(II) COMPLEXES

Complex	$^1A_{1g} \rightarrow {}^3T_{1g}$	$^1A_{1g} \rightarrow {}^3T_{2g}$	$^1A_{1g} \rightarrow {}^1T_{1g}$	$^1A_{1g} \rightarrow {}^1T_{2g}$
$[Fe(dipy)_3]Br_2 . 6H_2O$[a]	11,500			
$[Fe(phen)_3]^{2+}aq.$[b]	12,260			
$Fe(phen)_2(CN)_2$[b]	12,500			
[Fe(*cis*-edas)$_3$](ClO$_4$)$_2$[c]	14,700		21,500	27,400
$[Fe(diars)_3](ClO_4)_2$[c]	14,500		21,400	26,600
$[Fe(CN)_6]^{4-}$[d]	23,700		31,000	37,040
$[Fe(CNO)_6]^{4-}$[e]	20,000		25,870	32,000

dipy = 2,2′-dipyridyl, phen = 1,10-phenanthroline
edas = 1,2-bis(dimethylarsino)ethylene
diars = *o*-phenylenebis(dimethylarsine).

[a] R. A. Palmer and T. S. Piper, *Inorg. Chem.* **5** (1966) 864.

[b] E. Konig, *Co-ordination Chem. Revs.* **3** (1968) 485.

[c] R. D. Feltham, H. G. Metzger and W. Silverthorn, *Inorg. Chem.* **7** (1968) 2003.

[d] E. Konig and H. L. Schlafer, *Z. Physik. Chem.* **34** (1962) 355.

[e] W. Beck and K. Feldt, *Z. anorg. u. allgem. Chem.* **341** (1965) 113.

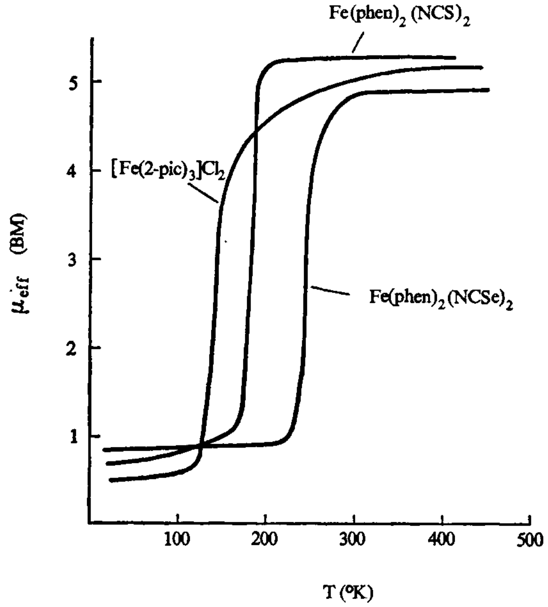

FIG. 28. Variation of magnetic moment, μ_{eff}, with temperature for some iron(II) complexes.

These complexes are of course diamagnetic; very low magnetic moments for salts of $[Fe(dipy)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$ have been reported, but these may be due to the presence of iron(III) impurities.

Magnetic properties near the $^5T_2$*–*$^1A_1$ *"crossover".* The change from high spin to low spin configurations for iron(II) is expected (from ligand field theory) to occur abruptly at a certain value of the ligand field splitting parameter, Δ. When the energy separation between the low spin and high spin ground states for a complex is only a few hundred reciprocal centimetres, then both states may be exhibited for the complex at different temperatures. Iron(II) is a particularly useful system for studying this magnetic crossover since the low spin state is diamagnetic and the change in the number of unpaired electrons is four. The magnetic properties of several iron(II) complexes have been studied in detail and the variation in magnetic moment of some complexes with temperature is shown in Fig. 28.

The complexes $Fe(phen)_2(NCS)_2$ and $Fe(phen)_2(NCSe)_2$ exist in the high spin $^5T_2$ ground state at room temperature with magnetic moments in excess of 5 B.M. and absorption spectra having bonds at 11,900 cm^{-1} assignable to the $^5T_{2g} \rightarrow {}^5E_g$ transition[172]. At 174°K the magnetic moment of $Fe(phen)_2(NCS)_2$ suddenly decreases to below 1 B.M.; for $Fe(phen)_2(NCSe)_2$ this drop occurs at 232°K. Below these temperatures the complexes have the $^1A_{1g}$ ground state and the electronic spectra are shifted accordingly, the $^1A_{1g} \rightarrow {}^3T_{1g}$ band occurring for both compounds at 10,400 cm^{-1}. Some cationic iron(II) complexes also exhibit this phenomenon. With the tris(2-aminomethylpyridine)iron(II) cation $[Fe(2\text{-pic})_3]^{2+}$ the chloride salt shows a marked crossover (Fig. 28), but the bromide and iodide show a progressively less marked effect[173]. Other examples include the complexes $[Fe(BR_3H)_3]$ (R=1-pyrazolyl[174]) and $[Fe(triL)_2]X_2$ [triL=2-(2-pyridylamino)-4-(2-pyridyl)-1,3-thiazole][175]. Confirmation of the high spin–low spin transformations has come from Mössbauer spectra where values of the isomer shift and quadrupole splitting at high temperatures are characteristic of the high spin state while at low temperatures they are characteristic of the low spin state[172, 176].

Tetrahedral complexes. In a tetrahedral field the ^5D ground term of the Fe^{2+} free ion in split into an upper $^5T_2$ and a lower ^5E state. Spin-orbit coupling effects are small, the overall spread of sub-levels due to this effect being about 500 cm^{-1} for $^5T_2$ and less than this for the ^5E ground state[177]. Thus in tetrahedral fields only one band, i.e. the spin allowed $^5E \rightarrow {}^5T_2$, is expected for iron(II). This band is in fact found in the near infrared region (Table 13); it has an intensity of some 10–100 times that of the octahedral spin free iron(II) complexes. Many of the compounds in Table 13 show in addition some much weaker bands in the 11,000–20,000 cm^{-1} region, these usually appearing as shoulders on the strong charge-transfer absorptions; they are probably due to spin-forbidden transitions. In complexes of the type FeX_2L_2 the effects of low symmetry components of the ligand field on the orbital degeneracy of the $^5T_2$ state become evident. Three bands might be expected since in C_{2v} symmetry $T_2 \rightarrow A_1+B_1+B_2$; only two are observed, however.

The magnetic moments of tetrahedral iron(II) complexes are surprisingly high in view of the ^5E ground term; even the mixing in of orbital contribution from the first excited state would only be expected to raise the moment from the spin only value of 4·9 to around 5·1–5·2 B.M. The moments are, however, as large as those of spin free octahedral complexes and do not vary much over the temperature range 95–295°K. For the FeX_4^{2-} ions

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[172] E. Konig and K. Madeja, *Inorg. Chem.* **6** (1967) 48.
[173] G. A. Renovitch and W. A. Baker, *J. Am. Chem. Soc.* **89** (1967) 6377.
[174] J. P. Jesson, S. Trofimenko and D. R. Eaton, *J. Am. Chem. Soc.* **89** (1967) 3158.
[175] R. N. Sylva and H. A. Goodwin, *Austral. J. Chem.* **20** (1967) 479.
[176] I. Dezsi, B. Molnar, T. Tarnoczi and K. Tompa, *J. Inorg. Nuclear Chem.* **29** (1967) 2490.
[177] C. Furlani, E. Cervone and V. Valenti, *J. Inorg. Nuclear Chem.* **25** (1963) 159.

it has been suggested that the high magnetic moments arise from a contribution from a ${}^7S(3d^5\,4s)$ term[178].

TABLE 13. ELECTRONIC SPECTRA (d–d) AND MAGNETIC MOMENTS OF SOME TETRAHEDRAL IRON(II) COMPLEXES

Complex	${}^5E \rightarrow {}^5T_2$ (cm^{-1})	μ_{eff} B.M.(~ 20°C)[a]
$(Et_4N)_2FeCl_4$[b]	4050	5·39
$(Et_4N)_2FeBr_4$[c]	3000	5·44
$(Bu_4{}^nN)_2FeI_4$[a]	2500	
$(Et_4N)_2Fe(NCO)_4$[e]	5000	
$(Et_4N)_2Fe(NCS)_4$[d]	5900; 4600	5·42
$M^*_2Fe(NCSe)_4$[e]	6050; 4750	
$Fe(Ph_3AsO)_2Br_2$[c]	5000	
$Fe(Ph_3PO)_2Cl_2$[c]	4550	
$Fe(quin)_2Cl_2$[a]	5780; 4950	5·20
$Fe(quin)_2Br_2$[a]	5560; 4650	5·19
$Fe(quin)_2I_2$[a]	5810	5·28
$Fe(quin)_2(NCS)_2$[a]	6100; 4950	
$(Et_4N)Fe(quin)Cl_3$[a]	4930; <4000	5·30
$(Et_4N)Fe(quin)Br_3$[a]	4840	5·35
$(Bu_4N)Fe(quin)I_3$[a]	4400	

*M = [*p*-xylylenebis(triphenylphosphonium)]$^{2+}$

[a] C. D. Burbridge and D. M. L. Goodgame, *J. Chem. Soc.* (A) (1968) 1074.

[b] C. Furlani, E. Cervone and V. Valenti, *J. Inorg. Nuclear Chem.* 25 (1963) **159**.

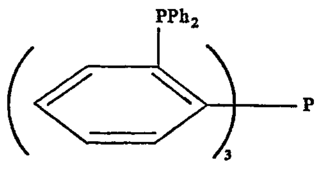
[c] D. Forster and D. M. L. Goodgame, *J. Chem. Soc.* (1965) 454.

[d] *Idem, ibid.*, p. 268.

[e] *Idem, Inorg. Chem.* 4 (1965) 1712.

Other symmetries. The electronic spectra of square planar iron(II) complexes are not yet characterized. Iron(II) phthalocyanine is planar with a room temperature magnetic moment $\mu_{\text{eff}} = 3{\cdot}96$ B.M. and bis(pentachlorophenyl)bis(Et_2PPh)Fe has a similar magnetic moment, $\mu_{\text{eff}} = 3{\cdot}6$ B.M.

Trigonal bipyramidal iron(II) complexes of high spin type are formed by the polyamine $N(CH_2CH_2NMe_2)_3$[179] while the phosphorus and arsenic ligands tris(*o*-diphenylphosphinophenyl)-phosphine (QP)



QP

and its arsenic analogue QAs give low spin complexes of the type $[FeX(QP)]^+$ with magnetic moments in the region of 3·05 B.M.[180]

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[178] R. J. H. Clark, R. S. Nyholm and F. B. Taylor, *J. Chem. Soc.* (*A*) (1967) 1802.

[179] M. Ciampolini, N. Nardi and G. P. Speroni, *Co-ordination Chem. Revs.* 1 (1966) 222.

[180] M. J. Norgett, J. H. M. Thornley and L. M. Venanzi, *Co-ordination Chem. Revs.* **2** (1967) 99.

4. COMPOUNDS OF IRON(III)

4.1. SIMPLE COMPOUNDS AND SALTS OF IRON(III)

Iron(III) halides. The thermal stability of these halides decreases markedly along the series $F^- > Cl^- > Br^- > I^-$. The fluoride FeF_3 is sufficiently stable to be sublimed at above 1000° whereas the iodide FeI_3 has not been isolated uncontaminated with FeI_2. Iron(III) is too powerful an oxidizing agent to exist in conjunction with iodide ions; aqueous routes to iron(III) iodide result in the liberation of iodine and reduction of the iron to iron(II). Some physical properties of these halides are given in Table 14.

TABLE 14. PHYSICAL PROPERTIES OF IRON(III) HALIDES

	FeF_3	$FeCl_3$	$FeBr_3$
Colour[a]	green	black	dark red-brown
M.p. (°C)[a]	1000	306	
ΔH_{fusion}(kcal mole^{-1})[b]		10·3	
$\Delta H_{\text{formation}}$(kcal mole^{-1})[b]		−96·8	
Density[a]	3·52	2·898	
Hydrates[c]	$4\frac{1}{2}$, 3	6, $3\frac{1}{2}$, $2\frac{1}{2}$, 2	6

[a] *Handbook of Chemistry and Physics*, 49th edition, The Chemical Rubber Co., Ohio (1968).

[b] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, *Selected Values of Chemical Thermodynamic Properties*, National Bureau of Standards Circular 500 (1952).

[c] N. V. Sidgwick, *The Chemical Elements and Their Compounds*, Oxford University Press (1950).

Iron(III) fluoride, FeF_3. This can be prepared by the action of fluorine on the metal, iron(II), or iron(III) chloride or by dehydration of the hydrate (obtained from aqueous solution) by heating in a current of hydrogen fluoride. A convenient laboratory preparation[181] involves the reaction of hydrogen fluoride with anhydrous iron(III) chloride at room temperature:

$$FeCl_3 + 3HF \rightarrow FeF_3 + 3HCl$$

When crystallized from aqueous solution (iron(III) "hydroxide" and aqueous hydrofluoric acid) it forms the pale pink $4\frac{1}{2}$-hydrate (room temperature evaporation) and the pink 3-hydrate (evaporation by heating).

Iron(III) fluoride is only sparingly soluble in water and insoluble in alcohol and ether. When heated in hydrogen it is reduced to iron(II) fluoride and thence to the metal. In aqueous solution the hydrolysis appears to be very slight; in the presence of alkali metal fluorides, complex fluorides of types $MFeF_4$, $M_2FeF_5.xH_2O$ and M_3FeF_6 can be crystallized. The magnetic behaviour of FeF_3 is complicated[182]; between 63° and 293°K the susceptibility is field strength dependent. The trihydrate has a magnetic moment $\mu_{\text{eff}} = 2{\cdot}25$ B.M. at 300°K.

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[181] G. Brauer, *Handbuch der Präparativen Anorganischen Chemie*, p. 244, Ferdinand Enke, Stuttgart (1960).

[182] B. N. Figgis and J. Lewis, *Progress in Inorg. Chem.* 6 (1964) 167.

[183] B. R. Tarr, *Inorg. Syntheses*, 3 (1950) 191.

[184] E. R. Epperson, S. M. Horner, K. Knox and S. Y. Tyree, *Inorg. Syntheses*, 7 (1963) 163.

[185] A. R. Pray, *Inorg. Syntheses*, 5 (1957) 153.

Iron(III) chloride, $FeCl_3$. This halide can be condensed as black crystals from the reaction of gently heated iron with dry chlorine[183], by heating together iron(III) oxide and carbon tetrachloride under pressure[184] or by dehydrating the hexahydrate with thionyl chloride under reflux[185]. It sublimes above 300°; vapour density measurements show it to be dimeric, i.e. Fe_2Cl_6, at 400° but monomeric at 750° (an excess of chlorine must be present to stop its decomposition). When heated *in vacuo* above 500°, decomposition into iron(II) chloride and chlorine occurs.

Iron(III) chloride is very soluble in water (about 480 g/litre at room temperature) and undergoes hydration in moist air to the yellow-brown hexahydrate. This hydrate can be prepared by crystallization from a solution of iron in hydrochloric acid which has been oxidized to iron(III) with chlorine. In the solid state, the hexahydrate has the structure *trans*-$[FeCl_2(H_2O)_4]Cl.2H_2O$. Aqueous solutions of iron(III) chloride are strongly acidic through hydrolysis; they dissolve electropositive metals, e.g. magnesium, with evolution of hydrogen and liberate carbon dioxide from alkali metal carbonates, hydrous iron(III) oxide being precipitated in both cases. In dilute solution the acidity can be represented[186] as the protonation of a water molecule by the hexaquo ion; addition

$$[Fe(H_2O)_6]^{3+}+H_2O \rightleftharpoons [Fe(OH)(H_2O)_5]^{2+}+H_3O^+, \; K_1 = 10^{-3\cdot5}$$

of base then removes H_3O^+ so that this equilibrium and the subsequent equilibria (see section 4.2) move to the right and "$[Fe(OH)_3(H_2O)_3]$", i.e. $FeO(OH)+4H_2O$, hydrous iron(III) oxide precipitates. In stronger solutions of iron(III) chloride, chloride ions enter the coordination sphere of the iron and octahedral species such as $[FeCl_4(OH_2)_2]^-$ predominate. When hydrochloric acid is added to these strong solutions, however, a polymeric species is formed which consists of alternating $FeCl_4$ (tetrahedral) and $FeCl_4(OH_2)_2$ (octahedral) units with adjacent units sharing a chloride ion[187]. Dilute solutions (0·68 M) of iron(III) chloride in concentrated hydrochloric acid contain[188] principally the tetrahedral tetrachloroferrate(III) anion, $FeCl_4^-$. Iron(III) chloride is also soluble in other donor solvents such as alcohols, ethers, ketones, nitriles and amines with the formation of complexes; it is relatively insoluble in non polar solvents such as benzene.

The crystalline solid has a semicovalent layer structure with hexagonal packing of chloride ions, each iron atom being surrounded octahedrally by six chlorines in a BiI_3 type structure[189]. The dimers in the vapour phase have a structure similar to that of Al_2Cl_6 with the iron atoms surrounded by chlorines in a roughly tetrahedral fashion[190]. The magnetic properties of iron(III) chloride in its different environments have been investigated extensively[182]. The magnetic moment at 290°K is 5·73 B.M. and is independent of the field strength. In aqueous hydrochloric acid the room temperature moment is 5·94 B.M. and the hexahydrate has a similar moment (5·95 B.M.).

Iron(III) bromide, $FeBr_3$. This is prepared[181] by the reaction of iron or iron(II) bromide with bromine at 170–200°. It is difficult to obtain pure since it decomposes at slightly above these temperatures even in the presence of bromine, the bromide ions being oxidized by the Fe^{3+}. Such an oxidation occurs when an aqueous solution of iron(III) bromide is boiled, iron(II) and bromine being formed. Iron(III) bromide is very soluble in water from which it can be crystallized at room temperature as the dark green hexahydrate $FeBr_3.6H_2O$.

[186] L. G. Sillén, *Quart. Revs. (London)*, **13** (1959) 146.

[187] G. W. Brady, M. B. Robin and J. Varimbi, *Inorg. Chem.* **3** (1964) 1168.

[188] G. L. Standley and R. F. Kruh, *J. Chem. Phys.* **34** (1961) 1450.

[189] A. F. Wells, *Structural Inorganic Chemistry*, 3rd edition, Oxford University Press (1962).

[190] E. Z. Zasorin, N. G. Rambidi and P. Akishin, *Zhur. Strukt. Khim.* **4** (1963) 910.

It is also soluble in donor solvents such as alcohol ether and acetic acid but less soluble in hydrocarbons. The solid has a similar structure to that of $FeCl_3$.

Iron oxide chloride, FeOCl. This is formed[191] when a mixture of iron(III) oxide and iron(III) chloride is heated in a sealed tube to 350°. It is also formed in the heated bomb reaction between iron(III) chloride and water and in the reaction of hydrogen chloride with iron(III) oxide at above 289°. It forms rhombic leaflets with a metallic lustre appearing red by transmitted light. With aluminium trichloride at around 300° it forms aluminium oxide chloride:

$$AlCl_3 + FeOCl \rightarrow AlOCl + FeCl_3$$

It is unaffected by water at room temperature, but in boiling water it slowly hydrolyses to γ-FeO(OH). Similarly, prolonged reaction with gaseous or liquid ammonia produces the maroon coloured amide, $FeO(NH_2)$.

Iron(III) thiocyanate, $Fe(SCN)_3$. Though the simple cyanide $Fe(CN)_3$ is unknown, the thiocyanate is prepared as dark violet crystals by reaction of thiocyanogen with iron or by extracting a mixture of potassium thiocyanate and an iron(III) salt with ether, followed by evaporation of the ether. It is very soluble in water from which it crystallizes as the red trihydrate $Fe(SCN)_3.3H_2O$. The blood-red colour developed when dilute solutions of iron(III) salts and thiocyanate ions are mixed is due largely to the $[Fe(SCN)(H_2O)_5]^{2+}$ ion; this reaction finds extensive use in the qualitative and quantitative determination of iron.

Iron(III) oxides and hydroxides. Treatment of iron(III) solutions with alkali leads to precipitation of the red-brown hydrated iron(III) oxide which when ignited above 200° leaves the red-brown oxide α-Fe_2O_3. This oxide occurs naturally as haematite; it finds uses in red pigments (ochre, Venetian red) and as a polishing agent in rouge. It has a melting point of 1565°, density of 5·24 and heat of formation of $-196{\cdot}5$ kcal mole^{-1}. α-Fe_2O_3 has the corundum (Al_2O_3) structure in which each iron atom is surrounded octahedrally by six oxygen atoms, the latter being in hexagonal close-packed array.

A second form of iron(III) oxide, γ-Fe_2O_3, does not occur naturally, but can be prepared by careful oxidation of Fe_3O_4 or by heating γ-FeO(OH) (*lepidocrocite*). It has a spinel-like structure[189] with a cubic closed-packed array of oxygen atoms and the iron atoms distributed randomly over the tetrahedral and octahedral sites. Unlike the paramagnetic α-form, γ-Fe_2O_3 is ferromagnetic. Upon heating in air to above 400° it is converted into α-Fe_2O_3, but when heated *in vacuo* above 250° it yields Fe_3O_4.

Black Fe_3O_4 is a mixed iron(II)–iron(III) oxide also obtained when iron is oxidized in a limited supply of air. It melts at 1538°, has a density of 5·2 and a heat of formation of $-267{\cdot}0$ kcal mole^{-1}. It occurs naturally as magnetite (*lodestone* or *magnetic iron ore*), is strongly ferromagnetic and has a fairly high electrical conductivity. Magnetite has the inverse spinel structure[189] in which the Fe^{2+} ions are in octahedral sites and the Fe^{3+} ions are half in octahedral and half in tetrahedral sites in a cubic close-packed array of oxide ions. It is insoluble in aqueous acids; it can be slowly oxidized to Fe_2O_3 by heating in air.

The hydroxide $Fe(OH)_3$ is not known. The red-brown precipitate obtained by the action of ammonia or alkalis on solutions of iron(III) is amorphous to X-rays and has a variable water content. This precipitate is believed to consist of FeO(OH) which is known to exist in at least two different crystalline forms depending upon the method of preparation; these are the α-FeO(OH) (*goethite*) and the γ-FeO(OH) (*lepidocrocite*). The γ-form is produced during the normal rusting of iron. The freshly precipitated hydrated iron(III) oxide is

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[191] H. Schafer, *Z. anorg. u. allgem. Chem.* **259** (1949) 265; *ibid.* **260** (1949) 127, 279; *ibid.* **261** (1950) 142.

readily soluble in mineral acids and slightly soluble in alkalis to form ferrates(III), e.g. $NaFeO_2$. These ferrates(III) are more easily obtained from molten mixtures of iron(III) oxide with an alkali metal oxide, hydroxide or carbonate; they are decomposed in water.

Iron peroxo-species. Treatment of an alcoholic suspension of iron(II) hydroxide with 30% hydrogen peroxide at −20° to −60° yields a red product believed to be of formula $Fe(O_2)$[192]. Peroxo derivatives of iron are probably formed as intermediates in the catalytic decomposition of hydrogen peroxide by iron(II) or iron(III) salts; spectrophotometric studies indicate that the hydroperoxo ion $[Fe(OOH)]^{2+}$ is formed. Many compounds of iron(II) take up molecular oxygen; the so called oxygen carriers include haemoglobin (section 1.9) and bis(dimethylglyoximato)iron(II) which reversibly take up oxygen. Simple iron(II) species take up oxygen in neutral and alkaline solution and become oxidized to iron(III) via FeO_2^+ and $[Fe(OOH)]^{2+}$.

Iron(III) alkoxides. Iron(III) chloride reacts with primary, secondary and tertiary alcohols in the presence of ammonia according to [193]

$$FeCl_3 + 3ROH + 3NH_3 \rightarrow Fe(OR)_3 + 3NH_4Cl$$

The alkoxides can be separated from the ammonium chloride by extraction of the mixture with benzene. These alkoxides are orange or brown crystalline solids readily hydrolysed in water. The primary alkoxides are trimeric in boiling benzene and many are stable enough to be sublimed *in vacuo*. These trimers probably contain triangular clusters of spin-free Fe^{3+} ions.

Iron(III) carboxylates. The iron(III) carboxylates are not well characterized. The reactions of aliphatic carboxylic acids with hydrous iron(III) oxide or iron(III) salt hydrates yield basic carboxylates[194]. Similarly the reaction of acetic anhydride with iron(III) nitrate nonahydrate gives basic complexes similar to those obtained with chromium(III), i.e. $[Fe_3(OCOR)_7OH]NO_3$. The Mössbauer spectra[195] of complexes containing the $[Fe_3(OCOR)_6(OH)_2]^+$ ion provide evidence for only one type of iron atom and magnetic studies[196] indicate that the trinuclear species persists for some time in aqueous solution. These complexes are therefore believed to possess not linear structures but trinuclear structures similar to those elucidated by X-ray studies[197] on the analogous chromium(III) complexes, and they may be better formulated as containing the $[Fe_3O(RCO_2)_6(H_2O)_3]^+$ cation.

Iron(III) chloride and bromide are solvolysed by acetic acid, but only as far as the $FeX(OCOCH_3)_2$ species ($X = Cl, Br$).

Iron(III) nitrate. The adduct $Fe(NO_3)_3 . N_2O_4$ is obtained when iron(II) chloride, iron(III) chloride or iron pentacarbonyl react with dinitrogen tetroxide in an appropriate organic solvent[198]. On the basis of spectroscopic, magnetic and conductivity studies this adduct is formulated as the nitrosonium salt $NO^+[Fe(NO_3)_4]^-$. When heated *in vacuo* this salt gives a sublimate of $NO_2^+[Fe(NO_3)_4]^-$; the unsolvated nitrate $Fe(NO_3)_3$ has not yet been isolated.

Crystallization of solutions of iron or hydrous iron(III) oxide in moderately strong

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[192] J. A. Connor and E. A. V. Ebsworth, *Advances in Inorg. Chem. Radiochem.* **6** (1964) 279.

[193] D. C. Bradley, R. K. Multani and W. Wardlaw, *J. Chem. Soc.* (1958) 126, 4153.

[194] C. Oldham, *Progress in Inorg. Chem.* **10** (1968) 242.

[195] J. F. Duncan, R. M. Golding and K. F. Mok, *J. Inorg. Nuclear Chem.* **28** (1966) 1114.

[196] A. Earnshaw, B. N. Figgis and J. Lewis, *J. Chem. Soc.* (A) (1966) 1656.

[197] B. N. Figgis and G. B. Robertson, *Nature*, **205** (1965) 694.

[198] C. C. Addison, P. M. Boorman and N. Logan, *J. Chem. Soc.* (1965) 4978.

nitric acid gives two hydrates depending upon the acid strength and concentration of the solution. The enneahydrate $Fe(NO_3)_3.9H_2O$ forms pale violet monoclinic crystals which dissolve in water to give a brown solution owing to hydrolysis. The cubic hexahydrate $Fe(NO_3)_3.6H_2O$ crystallizes from more concentrated solutions.

Iron(III) phosphate. This is precipitated as yellowish-white $FePO_4.2H_2O$ when a solution of disodium phosphate is added to a solution of an iron(III) salt. It is soluble in mineral acids and decomposed by hot aqueous ammonia. The decolorization of iron(III) chloride solutions by phosphoric acid is due to the formation of colourless phosphato complexes, e.g. $[Fe(PO_4)_3]^{6-}$.

Iron(III) sulphate. Anhydrous $Fe_2(SO_4)_3$ is obtained as an almost white powder by boiling anhydrous iron(II) sulphate with concentrated sulphuric acid or by careful heating of the hydrated salt. Solutions of iron(III) sulphate prepared, for example, by oxidizing solutions of iron(II) sulphate with nitric acid yield a series of hydrates upon crystallization; the common hydrates have 12, 9 (the common, violet crystals), 6 and 3 molecules of water. When thermally decomposed, iron(III) oxide and sulphur trioxide are formed:

$$Fe_2(SO_4)_3 \rightarrow Fe_2O_3+3SO_3$$

The anhydrous salt is rather reluctant to dissolve in water unless a trace of iron(II) sulphate is present (cf. $CrCl_3$). Hydrolysis occurs in such solutions (unless sufficient acid is present to preserve the $[Fe(H_2O)_6]^{3+}$ ion) and a series of basic sulphates can be isolated. Some of these occur naturally, e.g. $Fe_2O_3.2SO_3.7H_2O$ (*amaranthite*) and $2Fe_2O_3.5SO_3.17H_2O$ (*copiapite*). Iron(III) sulphate finds uses as a mordant and in the preparation of iron(III) alum and Prussian blue.

The iron(III) alums have the general formula $M^IFe(SO_4)_2.12H_2O$. Ammonium iron alum and potash iron alum are used as mordants; they are prepared by crystallization from solutions of iron(III) sulphate to which ammonium or potassium sulphates have been added. They are pale violet, containing the $[Fe(H_2O)_6]^{3+}$ ion, but turn brown in aqueous solution owing to hydrolysis.

Iron(III) perchlorate. This crystallizes as the pale pink decahydrate $Fe(ClO_4)_3.10H_2O$ from solutions of iron(III) chloride or hydrous iron(III) oxide in perchloric acid. Upon standing over phosphorus pentoxide the decahydrate becomes the hexahydrate; a 9-hydrate crystallizes from solution above 42°. This salt has been important in the study of the hydrated Fe^{3+} ion since perchlorate ions have only very low coordinating ability.

4.2. COMPLEX COMPOUNDS OF IRON(III)

Cationic Complexes

The hexaquo ion $[Fe(H_2O)_6]^{3+}$. This pale violet ion occurs in the solid state in iron(III) alums and in acidic solutions of iron(III) salts having anions of low coordinating ability. Its chemistry is dominated by its high acidity and consequent hydrolysis in aqueous solution and has been a topic of much investigation[199]. The hydrolytic equilibria of the first stages of hydrolysis are as follows:

$$[Fe(H_2O)_6]^{3+}+H_2O \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+}+H_3O^+; \; K_1 = 10^{-3\cdot05}$$
$$[Fe(H_2O)_5(OH)]^{2+}+H_2O \rightleftharpoons [Fe(H_2O)_4(OH)_2]^{+}+H_3O^+; \; K_2 = 10^{-3\cdot26}$$

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[199] L. G. Sillen, *Quart. Revs. (London)* **13** (1959) 146.

The olation reaction

$$2[Fe(H_2O)_6]^{3+}+2H_2O \rightleftharpoons [Fe_2(OH)_2(H_2O)_8]^{4+}+2H_3O^+;\ K = 10^{-2\cdot91}$$

is also important in which the binuclear cation is believed to have the structure shown in Fig. 29. These solutions are thus strongly acidic; if the pH of the solution is raised much above pH 2 then larger aggregates (i.e. more highly condensed species) form until eventually colloidal gels are formed and hydrous iron(III) oxide precipitates. Magnetic studies on iron(III) perchlorate solutions over a pH range have shown[200] that the $[Fe(H_2O)_6]^{3+}$ ion is paramagnetic with $\mu_{eff} = 5\cdot82$ B.M. while the binuclear cation is diamagnetic as a result of exchange interaction between adjacent iron atoms. The yellow colour of the partially hydrolysed cation, e.g. $[Fe(H_2O)_5(OH)]^{2+}$, is due to charge transfer absorption tailing into the visible region; it can be discharged by the addition of sulphuric or perchloric acids. In the presence of coordinating anions, however, the charge transfer spectrum is due to the new complexes formed by replacement of one or more water molecules, e.g. iron(III) chloride solution is yellow due to chloro complexes and in the presence of thiocyanate ions blood red $[Fe(H_2O)_5SCN]^{2+}$ is formed.

Other cationic species. Urea forms hexacoordinate iron(III) cations $[Fe(NH_2CONH_2)_6]^{3+}$ which can be isolated as salts with, for example, chloride and perchlorate anions. These compounds are high spin with magnetic moments in the region of 5·95 B.M. at room temperature. The urea is coordinated via the oxygen atoms. Unidentate nitrogen donors do not form very stable complexes in aqueous solution. The ammines $[Fe(NH_3)_6]X_3$ are formed in ammonia gas, but these have high dissociation pressures of ammonia at room temperature and are immediately decomposed by water with the formation of the hydrous oxide. Chelating nitrogen ligands form more stable complexes, e.g. $[Fe(bipy)_3]^{3+}$, $[Fe(phen)_3]^{3+}$; these strong field ligands form low spin complexes which are fairly inert to substitution by other ligands and can be crystallized from solution with large anions such as perchlorate. Several mixed cationic complexes containing these ligands and cyanide ions are known[201], e.g. $[Fe(phen)_2(CN)_2]ClO_4$ and $[Fe(bipy)_2(CN)_2]NO_3$. These again are low spin with magnetic moments of about 2·35 B.M. at room temperature. The chelating diarsine, *o*-phenylenebis(dimethylarsine) forms similar compounds but with halide ions, viz. $[Fe(diars)_2Cl_2]ClO_4$[202]. Iron forms most stable complexes, however, with oxygen donors; most of these are anionic in type, the trinuclear carboxylato complexes are however cationic, viz. $[Fe_3O(OCOR)_6(H_2O)_3]^+$.

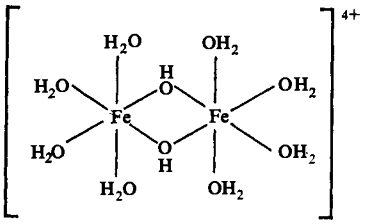

FIG. 29. ol-bridged dimer, $[Fe_2(OH)_2(H_2O)_8]^{4+}$.

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[200] L. N. Mulay and P. W. Selwood, *J. Am. Chem. Soc.* 77 (1955) 2693.

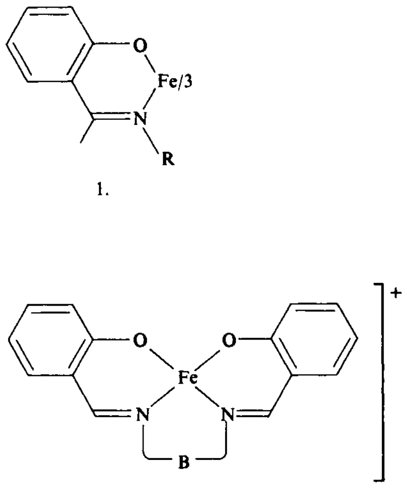
[201] A. A. Schilt, *J. Am. Chem. Soc.* **82** (1960) 3000.

[202] R. S. Nyholm, *J. Chem. Soc.* (1950) 851.

[203] G. Booth, *Advances in Inorg. Chem. Radiochem.* **6** (1964) 13.

Neutral Complexes

Iron(III) halide complexes. Iron(III) chloride forms complexes with a wide range of organic molecules having oxygen or nitrogen donor atoms. Most of these are regarded as addition compounds and their structures are usually unknown. Alcohols form compounds of the formula $FeCl_3.2ROH$ and ethers give $FeCl_3.R_2O$ and $FeCl_3.2R_2O$. In the presence of hydrogen chloride these latter compounds form oxonium salts, e.g. $[Me_2OH]FeCl_4$ (from $FeCl_3.Me_2O$). Similar adducts are formed by aldehydes and ketones. These adducts are prepared by direct interaction often in a solvent such as benzene; they are usually very susceptible to hydrolysis. Phosphine oxides and sulphides also form complexes with iron(III) chloride, e.g. yellow, $FeCl_3.2Ph_3PO$. The colour reactions of iron(III) chloride with phenols have long been used as tests for phenolic character; whilst charge-transfer complexes are usually formed, in some cases the phenol is oxidized to a coloured derivative, e.g. β-naphthol gives green β-dinaphthol.



1.

2.

FIG. 30. Schiff base complexes of iron(III).

Nitrogen donors usually form cationic complexes, hydrazine and 1,1-dimethylhydrazine being exceptional in causing reduction to iron(II). Triphenyl phosphine and arsine form the complexes $[FeCl_3(EPh_3)_2]_2$ when the chloride reacts with these ligands in ethyl acetate; with methanol as solvent, however, the tetrachloroferrate(III) $[MePPh_3][FeCl_4]$ is formed[203]. The complexes with substituted arsines, $[FeCl_3(arsine)_2]_2$, may also perhaps be better formulated as containing the tetrachloroferrate anion, i.e. $[FeCl_2(arsine)_4][FeCl_4]$.

Iron(III) chelates of oxygen and sulphur ligands. Stable complexes are formed between iron(III) and chelating oxygen ligands such as β-diketones and salicylic acid derivatives. Iron(III) acetylacetonate $[Fe(CH_3COCHCOCH_3)_3]$ is prepared by the aqueous reaction between iron(III) chloride, acetylacetone and a base (usually sodium acetate) or by heating iron pentacarbonyl under reflux with acetylacetone[204]. It crystallizes from alcohol as red prisms (m.p. 179°C); it is soluble also in ether and benzene, but less soluble in water and

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[204] T. G. Dunne and F. A. Cotton, *Inorg. Chem.* **2** (1963) 263.

n-heptane. A crystal structure determination[205] shows the iron atom to be surrounded by the six oxygen atoms from the three chelate molecules in a fairly regular octahedral arrangement, the Fe–O distances being 1·95 Å. It is spin-free with a magnetic moment $\mu_{eff} = 5{\cdot}90$ B.M. between 82° and 302°K, the Curie law being obeyed; the electronic spectrum is discussed elsewhere[206]. Aqueous solutions of tris(acetylacetonato)-iron(III) are non-conductors of electricity and are decomposed on boiling or upon treatment with alkalis when hydrous iron(III) oxide is precipitated; they are much more stable to acids, however. With phenylhydrazine reduction occurs and $Fe^{II}(acac)_2(PhNHNH_2)_2$ formed.

Several complexes of iron(III) with Schiff bases have been described[207]. These salicylaldimine complexes are of two types (Fig. 30). They are prepared either by direct reaction of the Schiff base with an iron(III) salt in ethanolic solution or by reaction of tris-(salicylaldehydato)iron(III) with the amine (RNH_2 for type 1 in Fig. 30 and $B(NH_2)_2$ for type 2). These complexes are high spin. There are, however, some binuclear complexes exemplified by the formula [Fe sal$_2$ en]$_2$O (the formula in the square brackets indicates two units as in Fig. 30 (2) in which $B = CH_2CH_2$) which have magnetic moments ranging from about 0·6 B.M. at 80°K to about 1·9 B.M. at 298°K. These compounds are believed to contain a linear Fe–O–Fe system through which magnetic exchange interaction is occurring[208].

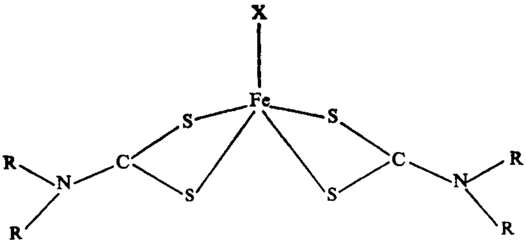

FIG. 31. Halogenobis(N,N-dialkyldithiocarbamato)iron(III) (X = Cl, Br, I).

Iron(III) chelates of bidentate sulphur donors are interesting from several points of view. The iron(III) dialkyldithiocarbamates $[Fe(S_2CNR_2)_3]$ are obtained as black crystals by the aqueous reaction between an iron(III) salt and the sodium salt of the dialkyldithiocarbamic acid[209]. They have magnetic moments at room temperature which lie between those expected for high and low spin octahedral complexes and which depend upon the chemical nature of the R substituents. The anomalous magnetic moments persist in benzene solution in which solvent the complexes are monomeric so that these moments cannot arise through antiferromagnetic exchange interactions. A thermal equilibrium between spin states $S = {}^1/_2$ and $S = {}^5/_2$ is thus invoked for these compounds. When these complexes (dissolved in benzene) are treated with concentrated halogen hydracids the black compounds $[FeX(S_2CNR_2)_2]$ are formed. These compounds (Fig. 31) are examples of five-coordinate iron(III) having the square pyramidal configuration[210]. The iron atom lies 0·63 Å above the plane of the sulphur atoms. The compounds are monomeric in the solid state and in

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[205] R. B. Roof, *Acta Cryst.* **9** (1956) 781.
[206] J. P. Fackler, *Progress in Inorg. Chem.* **7** (1966) 361.
[207] R. H. Holm, G. S. Everett and A. Chakravorty, *Progress in Inorg. Chem.* **7** (1968) 83.
[208] J. Lewis, F. Mabbs and A. Richards, *J. Chem. Soc.* (A) (1967) 1014.
[209] A. H. White, R. Roper, E. Kokot, H. Waterman and R. L. Martin, *Austral. J. Chem.* **17** (1964) 294.
[210] R. L. Martin and A. H. White, *Inorg. Chem.* **6** (1967) 712.

solution; their magnetic moments vary between 3·88 and 4·05 B.M. for different compounds at room temperature, that is they show the three unpaired electrons and no orbital contribution as is expected for this stereochemistry.

Anionic Complexes

Halide complexes. The stability of the halide complexes of iron(III) decreases as the ease of oxidation of the halide ion increases. Thus there are no complex iodides and such complex bromides as have been reported are thermally unstable with respect to evolution of bromine and formation of iron(II).

The fluoride complexes are of three principal types, $M_3^IFeF_6$, $M_2^IFeF_5.H_2O$ and M^IFeF_4. The reactions between iron(III) hydrous oxide and alkali metal fluorides in aqueous hydrofluoric acid yield principally the aquopentafluoroferrates(III), e.g. $Na_2FeF_5.H_2O$ [211]. The aquo complexes can be converted into the hexafluoroferrates(III) by treatment with molten potassium hydrogen difluoride[212]. The ammonium salt $(NH_4)_3FeF_6$ is cubic[213], while the potassium salt K_3FeF_6 has a slightly distorted cubic unit cell; these compounds are magnetically dilute high spin complexes with room temperature magnetic moments of around 5·9 B.M. The tetrafluoroferrates(III) are obtained from aqueous hydrofluoric acid solutions using 1 : 1 mole ratios of the univalent cation and iron(III) fluoride.

As with fluoride complexes, the principal chloro complex anions are $FeCl_6^{3-}$, $[FeCl_5.H_2O]^{2-}$ and $FeCl_4^-$. However, unlike the fluoride complexes, it is the tetrahedral species which is most readily available, iron(III) chloride being, in contrast to the fluoride, very soluble in water and ethanol. A large number of yellow tetrachloroferrates(III) $(BH)FeCl_4$ have been prepared from ethanolic solutions of iron(III) chloride and the organic base hydrochlorides. The $FeCl_4^-$ ion is also formed in aqueous hydrochloric acid and is extractable into ether—a property which has proved valuable in a variety of solvent extraction procedures. In chloride-containing non-aqueous solvents too, this ion is formed; sometimes direct reaction produces a solid tetrachloroferrate, e.g.

$$NOCl + FeCl_3 \rightarrow NO^+FeCl_4^-$$

The crystal structure determination[214] on $Ph_4As[FeCl_4]$ has confirmed that the $FeCl_4^-$ ion is tetrahedral. In this compound it is somewhat flattened, the Cl–Fe–Cl angles being 114·5° and 107°; the Fe–Cl distances are 2·19±0·03 Å. The pale yellow hexachloro-complexes $FeCl_6^{3-}$ can be obtained[215] from aqueous solution using large cations having the same charge as the anion, e.g. $[Co(pn)_3]^{3+}$ (pn = 1,2-propanediamine) and $[Co(NH_3)_6]^{3+}$. It is doubtful if the $FeCl_6^{3-}$ ion exists in solution. From concentrated aqueous solutions of ammonium and iron(III) chlorides, however, crystals of the hydrated pentachloro species $(NH_4)_2FeCl_5.H_2O$ can be grown.

The brown tetrabromoferrates(III), e.g. $Et_4N[FeBr_4]$, can be prepared in alcoholic solution from iron(III) bromide[216]. The $FeBr_4^-$ ion also arises in the unusual reaction between iron and bromine in methyl cyanide, the product obtained having the formulation $[Fe^{II}(MeCN)_6{}^{2+}][FeBr^{III}{}_4{}^-]_2$.

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[211] B. Cox and A. G. Sharpe, *J. Chem. Soc.* (1954) 1798.
[212] R. D. Peacock, *J. Chem. Soc.* (1957) 4684.
[213] R. W. G. Wyckoff, *Crystal Structures*, 2nd edition, Vol. 3, p. 373, Interscience (1965).
[214] B. Zaslow and R. E. Rundle, *J. Phys. Chem.* **61** (1957) 490.
[215] W. E. Hatfield, R. C. Fay, C. E. Pfluger and T. S. Piper, *J. Am. Chem. Soc.* **85** (1963) 265.
[216] N. S. Gill, *J. Chem. Soc.* (1961) 3512.

Cyanide complexes[217]. The most important iron(III) cyanide complex is the hexacyanoferrate(III) anion $[Fe(CN)_6]^{3-}$. The potassium salt (potassium ferricyanide) is invariably prepared by oxidation of the hexacyanoferrate(II) with, for example, chlorine or electrolytically. It forms anhydrous red orthorhombic crystals having a magnetic moment $\mu_{eff} = 2{\cdot}25$ B.M. at 300°K and exhibiting a single cyanide stretching band at 2125 cm^{-1}; ν(M–C) is located at 389 cm^{-1}. Unlike the iron(II) complex, $K_3Fe(CN)_6$ is poisonous and aquation (to the $[Fe(CN)_5(H_2O)]^{2-}$ ion) occurs more readily than with the $[Fe(CN)_6]^{4-}$ ion. In alkaline solution it is a strong oxidizing agent, chromium(III) being oxidized to chromate. With hot dilute sulphuric acid hydrogen cyanide is evolved; the concentrated acid liberates carbon monoxide.

The alkali and alkaline earth metal hexacyanoferrates(III) give yellow solutions in water. Some of these crystallize as yellow hydrates, viz. Li $4H_2O$, Na $2H_2O$, NH_4 $3H_2O$, Ca $10H_2O$ and $12H_2O$. The silver salt and heavy metal salts are generally insoluble; the iron(II) salt has been discussed on page 1032. The free acid $H_3Fe(CN)_6$ can be obtained from the potassium salt and concentrated hydrochloric acid. It behaves as a strong tribasic acid in aqueous solution.

Several substitution products of the type $[Fe(CN)_5L]^{2-}$ are known. The aquopentacyano complexes $[Fe(CN)_5H_2O]^{2-}$ are readily obtained as deep violet crystals by the action of heat, light or dilute acid on the hexacyanoferrates(III). Oxidation of the $[Fe(CN)_5NH_3]^{3-}$ ion with nitrous acid or hypobromite yields the $[Fe(CN)_5NH_3]^{2-}$ ion. This amminepentacyanoferrate(III) anion gives the intensely purple complex $[Fe(CN)_5N_3]^{3-}$ with azide ions and the intensely blue $[Fe(CN)_5SCN]^{3-}$ with thiocyanate ions[218].

Thiocyanate complexes. Apart from the cationic aquothiocyanato species, there are the hexathiocyanatoferrates(III) $[Fe(SCN)_6]^{3-}$ which can be isolated as alkali metal salts from solutions of hydrous iron(III) oxide in aqueous thiocyanic acid to which an alkali metal thiocyanate is added. These salts are bright red, very soluble in water from which they crystallize as hydrates Na $12H_2O$, K $4H_2O$, NH_4 $4H_2O$ and Ca $2H_2O$. The complex ion undergoes dissociation in aqueous solution unless an excess of thiocyanate ions is present.

Ato complexes. Iron(III) cations very readily form complexes with oxygen donor anions such as phosphate, carboxylates, hydroxy carboxylates and phenoxides.

The decolorizing effect of phosphoric acid on iron(III) chloride solutions has been the subject of numerous investigations. Phosphate complexes are undoubtedly formed, but their nature has been a matter of some dispute. In equimolar mixtures of iron(III) chloride and phosphoric acid the cationic complex $[FeHPO_4]^+$ is present; in solutions of iron(III) phosphate in phosphoric acid, however, the $[Fe(PO_4)_3]^{6-}$ or $[Fe(HPO_4)_3]^{3-}$ anions are present[219]. Pyrophosphate also gives strong complexes with iron(III); these are of the type[220] $[Fe(P_2O_7)_2]^{5-}$.

The green tris(oxalato) complexes containing the $[Fe(C_2O_4)_3]^{3-}$ ion are readily prepared by the addition of excess of an alkali metal or ammonium oxalate to an iron(III) salt solution. A convenient laboratory preparation of $K_3Fe(C_2O_4)_3.3H_2O$ involves[221] suspending iron(II) oxalate in potassium oxalate solution and treating the mixture with hydrogen peroxide and oxalic acid. The green crystals are photosensitive, the trivalent

[217] B. M. Chadwick and A. G. Sharpe, *Advances in Inorg. Chem. Radiochem.* **8** (1966) 83.

[218] B. Jaselkis, *J. Am. Chem. Soc.* **83** (1961) 1082.

[219] J. E. Salmon, *J. Chem Soc.* (1952) 2316; *ibid.* (1953) 2644.

[220] L. B. Rogers and C. A Reynolds, *J. Am. Chem. Soc.* **71** (1949) 2081.

[221] W. G. Palmer, *Experimental Inorganic Chemistry*, p. 521, Cambridge University Press (1954).

iron oxidizing the oxalate ion to carbon dioxide and leaving a yellow deposit of iron(II) oxalate:

$$2K_3Fe(C_2O_4)_3 \rightarrow 2FeC_2O_4 + 2CO_2 + 3K_2C_2O_4$$

The complex is high spin having a magnetic moment $\mu_{eff} = 5{\cdot}90$ at 300°K. The tris-(oxalato)ferrate(III) ion can be resolved into optical isomers, but these racemize in less than 1 hr at room temperature. Tartrato-, malonato- and catechol anionic complexes are also known, the latter giving violet $M^I[Fe(cat)_2]$ and red $M_3{}^I[Fe(cat)_3]$ complexes (H_2 cat = catechol).

Ethylenediaminetetraacetic acid (EDTA = H_4Y) gives the seven-coordinate $[Fe(Y)H_2O]^-$ ion in solution and this is also present in the crystal structure of the amber rubidium salt $Rb[Fe(Y)H_2O]$[222]

$$[Fe(H_2O)_6]^{3+} + Y^{4-} \rightarrow [FeY(H_2O)]^- + 5H_2O$$

the shape is roughly pentagonal bipyramidal for the five oxygen and two nitrogen nearest neighbours to iron.

4.3. ELECTRONIC STRUCTURES OF IRON(III) COMPLEXES

High spin complexes. Iron(III) has the free ion electronic configuration in the ground state of $3d^5$. In high spin complexes ($S = {}^5/_2$) this gives rise to a ^6S free ion ground term. Since this is the only sextuplet term arising from d^5 and since this is not split in a crystal field all the terms of higher energy are of a different spin multiplicity to the ground term.

TABLE 15. ELECTRONIC SPECTRA (in cm^{-1}) OF HIGH SPIN IRON(III) COMPLEXES

Complex	$^6A_1 \rightarrow {}^4T_1(G)$	$^4T_2(G)$	$^4A_1, {}^4E(G)$	$^4T_2(D)$	$^4E(D)$
$[Fe(H_2O)]_6{}^{3+}$ [a]	12,600	18,500	24,300 24,600		
$[Fe(NH_2CONH_2)_6]^{3+}$ [a]	12,500	17,100	23,100 23,400		
$[Fe(C_2O_4)_3]^{3-}$ [a]	10,700	15,200			
$FeF_6{}^{3-}$ [a]	14,200	19,700	25,400	28,800	30,200
$FeCl_6{}^{3-}$ [b]		18,730	22,080		
$FeCl_4{}^-$ [e]	13,700		14,500	16,100	16,600
$FeBr_4{}^-$ [c]	11,700	12,700	13,200	14,100	14,500

[a] C. K. Jorgensen, *Absorption Spectra and Chemical Bonding in Complexes*, p. 292, Pergamon (1962).

[b] W. E. Hatfield, R. C. Fay, C. E. Pfluger and T. S. Piper, *J. Am. Chem. Soc.* **85** (1963) 265.

[c] B. J. Hathaway and D. G. Holah, *J. Chem. Soc.* (1964) 2408; A. P. Ginsberg and M. B. Robin, *Inorg. Chem.* **2** (1963) 817.

All the electronic transitions are thus spin forbidden (as well as Laporte forbidden) so that the ligand field bands in the spectra of these complexes are very weak. The complete energy level (Tanabe–Sugano) diagram for the d^5 ion can be seen in the standard texts[223-5]; this diagram is the same for octahedral and tetrahedral fields. Suffice it to state here that there is a total of ten transitions possible; Table 15 lists some spectra of high spin complexes with the lowest energy assignments. These assignments must be regarded as tentative; the

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[222] M. D. Lind and J. L. Hoard, *Inorg. Chem.* **3** (1964) 34.

[223] T. M. Dunn in *Modern Co-ordination Chemistry*, p. 229, Ed. Lewis and Wilkins, Interscience (1960).

[224] A. B. Lever, *Inorganic Electronic Spectroscopy*, p. 109, Elsevier (1968).

[225] B. N. Figgis, *Introduction to Ligand Fields*, p. 163, Interscience (1966).

spectra are frequently not well resolved and complicated by the presence of charge transfer bands which obscure the higher energy spin forbidden bands. In iron(III) chloro complexes, for example, the charge transfer bands begin in the 22,000–23,000 cm^{-1} region and in bromo complexes they occur as low as 17,000–18,000 cm^{-1}. The tetrahedral species such as $FeCl_4^-$ have narrow bands in the visible region and several broader bands in the ultraviolet[226]; these latter intense bands are at 41,300, 31,700 and 27,500 cm^{-1}, they have been used for the detection and estimation of this ion.

The magnetic properties of high spin iron(III) complexes of cubic symmetry are fairly straightforward. As the ground term is $^6A_1$ the magnetic moments are expected to be close to the spin only value of 5·92 B.M. and to be independent of temperature and this is found to be the case experimentally for magnetically dilute complexes.

Low spin complexes. With strong field ligands (CN^-, phen, dipy) octahedral iron(III) complexes are of the low spin type (t_{2g}^5) and the ground term is then $^2T_{2g}$. This ground term is orbitally degenerate so that magnetic moments exceed the spin only value for one unpaired electron (1·73 B.M.) and are typically in the region of 2·3 B.M. at room temperature. These moments also vary with temperature, such variations being useful in determining the contributions of low symmetry components to the ligand field[227].

In the interesting intermediate field case where the ligand field strength is of the same order of magnitude as the mean pairing energy for the d^5 configuration, then the two different spin states are present in thermal equilibrium. Such a situation occurs when iron(III) is octahedrally surrounded by six sulphur atoms as in the dialkyldithiocarbamates $[Fe(S_2CNR_2)_3]$; it must be distinguished from that in which iron has a quartet ground term ($S = {}^3/_2$) through square pyramidal coordination (section 4.2).

The electronic spectra of low spin iron(III) complexes have not been adequately characterized. The spectrum of $K_3Fe(CN)_6$ has been measured[228] but the band assignments are in some doubt because of the presence of some very strong charge transfer bands.

5. COMPOUNDS OF IRON IN HIGH OXIDATION STATES (+4, +5, +6)

Rather surprisingly the higher oxidation states of iron Fe(IV) d^4, Fe(V) d^3 occur when iron is in combination with oxygen but not with fluorine.

5.1. IRON(IV) COMPOUNDS

Ferrates(IV). Various ferrates(IV) have been reported containing the anions[229] $[FeO_3]^{2-}$, $[FeO_4]^{4-}$ and $[FeO_5]^{6-}$. The strontium and barium salts, Sr_2FeO_4 and Ba_2FeO_4, are prepared by oxidation of a mixture of hydrous iron(III) oxide and the alkaline earth metal oxide or hydroxide with oxygen at 700–800°, e.g.

$$Sr_3[Fe(OH)_6]_2+Sr(OH)_2+{}^1/_2O_2 \rightarrow 2Sr_2FeO_4+7H_2O$$

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[226] P. A. McCusker and S. M. S. Kennard, *J. Am. Chem. Soc.* **81** (1959) 2976.

[227] B. N. Figgis, J. Lewis, F. E. Mabbs and G. A. Webb, *J. Chem. Soc.* (A) (1966) 422.

[228] C. S. Naiman, *J. Chem. Phys.* **35** (1961) 323.

[229] R. Scholder, H. V. Bunsen and W. Zeiss, *Z. anorg. u. allgem. Chem.* **283** (1956) 330; R. Scholder, F. Kindervater and W. Zeiss, *ibid.* 338.

The ferrate is isolated from the reaction mixture as fine black crystals by extraction of the excess strontium or barium oxide with methanol. The sodium salt Na_4FeO_4 is similarly prepared by heating a 4:1 mixture of sodium oxide and iron(III) oxide to 450° in an oxygen gas stream. It disproportionates immediately 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 better regarded as mixed oxides. It is interesting to note that a compound FeO_2 which may be iron(IV) oxide has recently been prepared[230]. The vapour phase reaction of iron pentacarbonyl with nitrogen dioxide gives a yellow-brown powder formulated as $(FeNO_3)O$; upon thermal decomposition to 400° this gives a residue of FeO_2. The magnetic moment of FeO_2 is 4·91 B.M. which is close to the spin only value expected for four unpaired electrons in Fe^{4+}.

Ditertiary arsine complexes of iron(IV). The octahedral complexes $[Fe(diars)_2X_2]^{2+}$ (diars = *o*-phenylenebisdimethylarsine; X = Cl, Br) are obtained by oxidation of the corresponding iron(III) complexes $[Fe(diars)_2X_2]^+$ with concentrated nitric acid[231]. The magnetic properties of these cations when in conjunction with diamagnetic anions (such as BF_4^-) have been studied over the temperature range 80–300°K; the magnetic moments indicate two unpaired electrons and are consistent with a low-spin (t_{2g}^4) configuration having a large tetragonal distortion. The far infrared spectra are in accord with the halogen atoms being in *trans*-positions. The salt $[Fe(diars)_2Cl_2](BF_4)_2$ is a black powder (m.p. 190° decomp.) very hygroscopic, but may be kept for a short time *in vacuo* in the absence of light. It is insoluble in non-polar solvents but sparingly soluble in nitromethane in which it is a uni-bivalent electrolyte, the solution decomposing over some 30 min.

5.2. IRON(V) COMPOUNDS

This oxidation state is only known in the ferrates(V)[232]. The potassium salt K_3FeO_4 can be prepared by thermal decomposition of the ferrate(VI) K_2FeO_4 at 700° or by the reaction of K_2FeO_4 with KOH at 600–700°. Above 700° it decomposes into $KFeO_2$, potassium oxide and oxygen. The reaction of iron(III) oxide with rubidium hydroxide in a stream of oxygen at 600° gives a product containing some 90% Rb_3FeO_4; when this is heated in a stream of nitrogen at 350° the pure Rb_3FeO_4 is obtained. The sodium ferrate(V) Na_3FeO_4 is obtained in an impure state when Na_3FeO_3 is heated under a high pressure (120 atm) of oxygen.

5.3. IRON(VI) COMPOUNDS

The ferrates(VI) have been studied in more detail because they are available from aqueous solution as well as from high temperature routes. The alkali metal ferrates(IV) K_2FeO_4 and Na_2FeO_4 are best prepared[232] by oxidizing 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 red-purple ferrate(VI) ion also forms in the anodic oxidation of iron in alkaline solution. Small yields of potassium ferrate(VI) are formed in the fusion of iron filings and potassium

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[230] C. C. Addison, B. F. G. Johnson and N. Logan, *J. Chem. Soc.* (1965) 4490.

[231] G. S. F. Hazeldean, R. S. Nyholm and R. V. Parish, *J. Chem. Soc.* (A) (1966) 162.

[232] R. Scholder, *Bull. Soc. Chim. France*, (1965) 1112.

nitrate, and a solution of sodium ferrate(VI) can be obtained by fusing iron(III) oxide with sodium peroxide and extracting the product with ice cold water.

The alkali metal salts give deep red solutions from which the calcium, strontium and barium salts can be precipitated by metathesis. The ferrate(VI) solutions are most stable in alkali where although slow decomposition occurs,

$$4FeO_4^{2-}+4H_2O \rightarrow 2Fe_2O_3+8OH^-+3O_2$$

it can be stabilized for many hours by the addition of periodate. In neutral or acidic solution the decomposition to iron(III) is rapid:

$$2FeO_4^{2-}+10H^+ \rightarrow 2Fe_3^+ + 5H_2O+{}^3/_2O_2$$

Ferrates(VI) are thus very strong oxidizing agents, e.g. they oxidize ammonia to nitrogen at room temperature. Thermal decomposition of solid ferrates(VI) gives eventually iron(III) oxide, the metal oxide and oxygen, but the intermediate ferrates(V) and ferrates(IV) can be obtained at lower temperatures.

The ferrates(VI) contain the discrete tetrahedral FeO_4^{2-} ion; the potassium salt is isomorphous with potassium sulphate and potassium chromate. The magnetic susceptibility of the potassium[233] and caesium ferrates(VI)[234] have been measured and magnetic moments in the range 2·8–3·06 B.M. obtained as expected for a magnetically dilute d^2 system. The electronic spectrum[235] shows two broad bands (with some fine structure) at 12,720 and 19,600 cm^{-1}; these are assigned to the $^3A_2 \rightarrow {}^3T_1$ and $^3A_2 \rightarrow {}^3T_1$ transitions.

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[233] H. J. Hrostowski and A. B. Scott, *J. Chem. Phys.* **18** (1950) 105.

[234] W. Klemm, C. Brendel and G. Wehrmeyer, *Chem. Ber.* **93** (1960) 1506.

[235] A. Carrington, D. Schonland and M. C. R. Symons, *J. Chem. Soc.* (1957) 659; A. Carrington and M. C. R. Symons, *ibid.* (1960) 889.

41. COBALT

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1. THE ELEMENT

1.1. HISTORY

Cobalt compounds have been used for colouring glass for at least 4000 years, but prior to 1914 virtually no cobalt metal was produced[1]. The metal was first isolated and recognized as an element by the Swedish chemist Brandt in 1735. Electroplating of cobalt onto metals began around the mid-nineteenth century; by the first decade of the twentieth century the usefulness of cobalt in steels and other alloys was becoming apparent. In 1917, Honda announced the discovery of a cobalt containing magnet steel and in 1935 the Alnico series of magnet alloys (Al, Ni, Fe, Co) were developed.

1.2. OCCURRENCE AND DISTRIBUTION[2]

Cobalt constitutes about 0·001% of the earth's crust. It is widely distributed, but the principal ores capable of being commercially exploited are the arsenides, the sulphides and the oxides. These ores are nearly always associated with ores of other metals, especially with those of nickel. *Smaltite*, $CoAs_2$, containing up to 28% cobalt and *Skutterudite*, $(Co, Ni)As_3$, containing up to 21% cobalt are the principal arsenides. Some sulphide ores are *Carrollite*, $CuS.Co_2S_3$, *Linnaeite*, Co_3S_4, and *Cattierite*, CoS_2. *Cobaltite* (cobalt glance) is a sulpharsenide, CoAsS, which frequently contains up to 10% of iron. The "oxidized" cobalt minerals, as the oxides are called, include *Asbolite*, a cobaltiferous mixture of manganese and iron oxides having a very variable cobalt content; *Heterogenite*, a black hydrated cobalt oxide usually containing copper and the red *Erythrite*, of approximate formula $3CoO.As_2O_5.8H_2O$.

1.3. INDUSTRIAL PRODUCTION OF COBALT

The extraction of cobalt is usually a process somewhat ancillary to the more major operation of extracting other metals such as copper and lead. Various treatments are used depending upon the nature of the original ore[1, 3], but these usually involve a combination

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[1] *Cobalt Monograph*, Edited by Centre d'Information du Cobalt, Brussels (1960).

[2] R. S. Young, *Cobalt*, A.C.S. Monograph No. 108, Reinhold, New York (1948).

[3] W. H. Dennis, *Metallurgy of the Non-Ferrous Metals*, 2nd edition, Pitman, London (1961).

of furnace, chemical and thermal or electrolytic reduction processes. The first step involves the smelting of the purified ore in an electric furnace; this concentrates the metal in a speiss, matte or alloy. The furnace product is then dissolved in sulphuric acid and this solution chemically treated to separate cobalt from other metals present. Processes vary, but in a typical one, silver is removed by precipitation with salt, iron by precipitation with lime and then cobalt is precipitated from the cobalt and nickel containing solution as $Co(OH)_3$ by the addition of sodium hypochlorite. This precipitate can be converted to Co_2O_3 by heating to about 800°C and this oxide reduced with charcoal at 1000–1100°C to give granules of cobalt which are magnetically separated from excess charcoal. Alternatively the cobalt solution purified from other metals is electrolysed in lead-lined cells with lead anodes and mild steel cathodes. Both this and the thermal reduction give cobalt of purity exceeding 99%, the chief impurity being nickel.

Hydrogen reduction of Co_2O_3 has also been used industrially, particularly for the production of cobalt powders in powder metallurgy. The reduction is rapid above 700°C; the cobalt so produced is preferably cooled in a hydrogen atmosphere to avoid oxidation.

1.4. ALLOTROPY OF COBALT

At ordinary temperatures, cobalt exists as a hexagonal close-packed (α) form, but above 417°C it undergoes an endothermic and rather sluggish transformation to a face-centred cubic (β) form. Whilst the α-form is the more stable allotrope under normal conditions, the β-form can exist at room temperature and can be stabilized by the inclusion of about 6% of iron.

The very low free energy change (~ 100 cal/g atom) associated with the α–β transformation enables the small energy changes which are associated with many metallurgical processes to have a significant effect upon the allotropic transformation. Thus upon moderate deformation at room temperature, the β-form is converted to the hexagonal close-packed form, and recrystallization of hexagonal cold-worked cobalt results in the formation of a certain amount of the cubic phase which does not return to the hexagonal form at room temperature.

1.5. NUCLEAR PROPERTIES[4,5]

The naturally occurring and artificially-radioactive isotopes of cobalt are listed in Table 1. The natural isotope ^{59}Co is converted to the isomeric ^{60}Co nuclei by bombardment with thermal neutrons in a reactor. Both isomers decay to a non-radioactive isotope of nickel, ^{60}Ni, by emission of β-rays and γ-rays. Cobalt-60 is a widely used source of radioactivity; it is used as a concentrated source of γ-rays in radiation chemistry research. It has been widely used in biological work (activation analysis), in tracer studies in such fields as metal plating, corrosion and catalysis and in medicine in the distant therapy treatment of malignancies.

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[4] L. C. Bate and G. W. Leddicotte, *The Radiochemistry of Cobalt*, NAS–NRC Nuclear Science Series No. 3041, Washington (1961).

[5] *Handbook of Chemistry and Physics*, 49th edition, The Chemical Rubber Company, Cleveland (1968).

TABLE 1. ISOTOPES OF COBALT

Isotope	% natural abundance	Atomic mass	Half-life	Decay mode	Preparation (example)
^{54}Co			0·18 s	β^+	^{54}Fe (p, n)
^{55}Co			18·2 h	β^+, EC	^{55}Fe (p, γ)
^{56}Co			77·3 d	EC, β^+	^{56}Fe (d, 2n)
^{57}Co			270 d	EC	^{60}Ni (p, α)
^{58m}Co			9·0 h	IT	^{58}Fe (p, n)
^{58}Co			71 d	EC, β^+	^{58}Ni (n, p)
^{59}Co	100	58·9332			
^{60m}Co			10·5 m	IT, β^-	^{59}Co (n, γ)
^{60}Co			5·27 y	β^-	^{59}C (n, γ)
^{61}Co			9·90 m	β^-	^{64}Ni (p, α)
^{62m}Co			1·9 m	β^-	^{64}Ni (d, α)
^{62}Co			13·9 m	β^-	^{62}Ni (n, p)
^{63m}Co			1·4 h		
^{63}Co			52 s	β^-	
^{64m}Co			2 m	IT	
^{64}Co			7·8 m	β^-	^{64}Ni (n, p)

EC = orbital electron capture; IT = isomeric transition from upper to lower isomeric state; s = seconds, m = minutes, h = hours, d = days, y = years. Isomers designated by superscript m.

1.6. PHYSICAL PROPERTIES[1,6]

Cobalt is a silvery white metal resembling pure iron and nickel in appearance. Cobalt is harder than iron, electrodeposited cobalt being harder than the ordinary metal produced thermally. The presence of small amounts of carbon (up to 0·3%) increases the tensile and compressive strength and does not affect the hardness. Cobalt can be machined, but is somewhat brittle. The physical properties of cobalt (Table 2) are very dependent not only upon its purity but also upon the allotropic form (or mixture of forms) present. The sluggish transformation between the two allotropes probably accounts for the variation in physical properties reported for cobalt of purity greater even than 99·9%.

Like iron and nickel, cobalt is ferromagnetic. Although iron has the highest saturation magnetization of the ferromagnetic elements, cobalt is the only element capable of

TABLE 2. PHYSICAL PROPERTIES OF COBALT

Atomic number	27
Electronic configuration	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^7\ 4s^2$
M.p. (°C)	1493
ΔH—fusion (cal/g)	62
Vapour pressure equation for solid	$\log_{10}P(\text{atm}) = -\frac{22{,}209}{T} - 0{\cdot}223 \times 10^{-3}T + 8{\cdot}036$
B.p. (°C)	3100
ΔH—vaporization (cal/g)	1500
Density (g/cm^3)	8·90
Electrical resistivity (microhm-cm), 0°C	5·68
Thermal conductivity (cal/sec/cm^2/°C/cm), 0–100°C	0·165
Specific heat (cal/g/°C), 15–100°C	0·1056
liquid	0·141
Ionization potential (eV), First	7·86
Second	17·05
Heat capacity (cal/°C/g atom), 25°C.	5·98

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[6] C. A. Hampel (Editor), *The Encyclopedia of the Chemical Elements*. Reinhold (1968).

increasing this magnetization, a maximum of 24,300 gauss being obtained for a composition 65% Fe, 35% Co as compared with 21,500 gauss for pure iron. Cobalt has a further outstanding magnetic property, that of having the highest-known Curie temperature (1121)°C. A large variety[1] of cobalt steels and alloys have been developed for specific purposes.

1.7. CHEMICAL PROPERTIES

Reactions with Elements

Cobalt absorbs very little hydrogen even at high temperatures and nitrogen is practically insoluble up to 1200°C. Finely divided cobalt is pyrophoric in air, but the massive metal is scarcely attacked below 300°C. The oxide scale on cobalt heated in air or oxygen up to 900° consists of an outside layer of Co_3O_4 and a layer of CoO next to the metal; above 900°, Co_3O_4 decomposes and the scale consists of CoO only. Cobalt reacts with many non-metals when heated, e.g. the halogens, boron, sulphur, phosphorus, arsenic and antimony, the reactions often proceeding with incandescence. Fluorine forms CoF_3, while the other halogens give the cobalt(II) halide.

Reactions with Compounds

Cobalt is oxidized to CoO by steam at red heat. In ammonia at 470°, the nitride Co_2N is formed, but this decomposes at 600°. Carbon monoxide combines with finely divided cobalt at 200° and 100 atm pressure to form the carbonyl $Co_2(CO)_8$, but above 225° and at atmospheric pressure the carbide Co_2C is formed.

Cobalt is more resistant to attack by mineral acids than iron; this is expected from the value of the Co/Co^{2+} potential of $-0{\cdot}27$ V (Fe/Fe^{2+} potential $= -0{\cdot}44$ V). It dissolves in dilute hydrochloric and sulphuric acids with evolution of hydrogen. Concentrated nitric acid rapidly attacks cobalt at room temperature, but renders it passive at about $-10°$. Hydrofluoric and phosphoric acids also attack the metal, but it is unattacked by dilute alkalis.

Hydrogen chloride reacts with cobalt at 450°, forming cobalt(II) chloride; hydrogen sulphide forms Co_3S_4 when passed over cobalt powder at around 400° and CoS at 700°. Carbon dioxide reacts above 700° according to the equilibrium:

$$Co+CO_2 \rightleftharpoons CoO+CO$$

1.8. BIOLOGICAL IMPORTANCE OF COBALT COMPOUNDS

Cobalt is a vital trace element in animal nutrition. Ruminants grazing upon cobalt-deficient pastures exhibit retarded growth, loss of appetite and anaemia; rapid recovery from these symptoms occurs upon feeding the animals with a cobalt-supplemented diet. Cobalt salts are not therefore considered to be particularly toxic to animals, but to man they can in sufficiently large doses irritate the gastro-intestinal tract and cause nausea, vomiting and diarrhoea[7]. Small amounts of cobalt, however, are invaluable in the treatment of pernicious anaemia. The discovery in 1926 of the antipernicious anaemia factor in liver led to the discovery in 1948 of vitamin B_{12}, which was very soon after shown to contain cobalt.

Vitamin B_{12}, cyanocobalamin (Fig. 1), contains cobalt in oxidation state +3. It resembles a porphyrin, but differs in having four pyrroline rings instead of four pyrrole rings. The

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[7] C. Weissbecker, *Kobalt als Spurenelement und Pharmakon*, Wissenschaftliche Verlagges., Stuttgart (1950).

cobalt atom is surrounded octahedrally by five nitrogen atoms (four from the pyrroline rings and one from the benzimidazole ring) and one carbon atom of a cyanide group. The cyanide group can be replaced by other anions, e.g. vitamin B_{12a} is hydroxocobalamin and vitamin B_{12c} is nitritocobalamin.

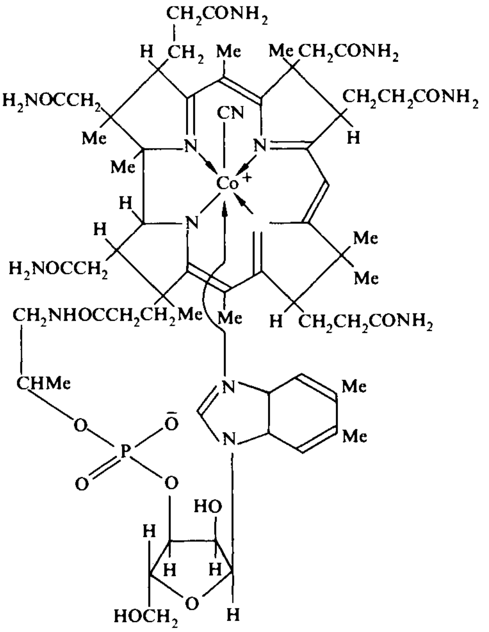

FIG. 1. Vitamin B_{12}.

Cobalt compounds also have some synergic effects on certain antibiotics, notably penicillin; cobalt is added to penicillin in the treatment of mastitis (an udder inflammation in cattle) where large doses of penicillin alone result in the presence of the antibiotic in the milk.

1.9. THE ANALYTICAL CHEMISTRY OF COBALT[8]

Qualitative Detection

Salts containing the aquocobalt(II) cation give no precipitate with hydrogen sulphide in acid solution, but precipitate black cobalt(II) sulphide in ammoniacal solution. With alkalis, the pink hexaquocobalt(II) cation gives a pale blue precipitate of the hydroxide; with excess of ammonia this precipitate dissolves and slowly gives a brown solution through oxidation. The addition of potassium nitrite to a neutral or acetic acid solution of Co^{2+} saturated with potassium chloride quickly results in the formation of a yellow precipitate of potassium hexanitrocobaltate(III). Concentrated ammonium thiocyanate solution gives a blue solution of the $[Co(SCN)_4]^{2-}$ anion which can be precipitated by adding Hg^{2+} ions. Dithiooxamide (rubeanic acid), in alcoholic solution, added to ammoniacal cobalt solutions gives a brown precipitate; this reaction is used in paper chromatography to distinguish cobalt from nickel (which gives a blue-violet colour).

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[8] R. S. Young, *The Analytical Chemistry of Cobalt*, Pergamon (1966).

Quantitative Determination

Cobalt may be determined gravimetrically by a variety of methods. For the determination of cobalt in ferrous alloys, iron is first removed by precipitation either with zinc oxide suspension or with trisodium phosphate. The cobalt is then usually precipitated with α-nitroso-β-naphthol and the precipitate ignited to constant weight as Co_3O_4. Other gravimetric procedures involve precipitation and weighing as $Hg[Co(SCN)_4]$ or as the anthranilate $Co(C_7H_6O_2N)_2$. A rapid method[9] which can be completed in 30 min involves the precipitation of cobalt with pyridine in thiocyanate media and weighing as $[Co(C_5H_5N)_4](SCN)_2$. Cobalt can also be determined gravimetrically by electrolysis. Platinum gauze electrodes are used in an electrolyte of cobalt(II) sulphate and ammonium sulphate. The cathode is washed with cold water, alcohol dried at 100° and weighed.

Volumetrically cobalt(II) salts may be estimated by potentiometric titration with standard potassium hexacyanoferrate(III) in the presence of high concentrations of ammonium citrate and ammonia solution. Alternatively the cobalt(II) solution may be treated with a known excess of potassium cyanide solution and the excess of cyanide ions titrated potentiometrically with standard silver nitrate. In this titration $[Co(CN)_5]^{3-}$ is formed so that $Co^{2+} \equiv 5CN^-$.

Colorimetric methods for estimating cobalt use the blue colour developed by chloride ions or thiocyanate ions; when only small amounts of cobalt are present, nitroso-R-salt, sodium 1-nitroso-2-hydroxynaphthalene-3,6-disulphonate $C_{10}H_4OH.NO(SO_3Na)_2$, may be used to give a red cobalt complex which is stable in nitric acid (a useful distinction from many other elements).

Polarographic methods usually use the reduction of cobalt(III) ammines; this method allows the determination of cobalt in a one-thousand-fold excess of nickel.

1.10. ALLOYS OF COBALT

The chief outlet for cobalt metal is as an alloying element in the production of high speed steels—"hard alloys" for cutting tools and in magnetic alloys. Two of the important cobalt containing hard alloys are *Widia* and *Stellite*. Widia metal comprises about 13% Co, 84% W and 3% C and is one of the hardest alloys known. The Stellite alloys contain around 50% Co and 3% Cr, the rest being made up from tungsten, iron, carbon and silicon. Depending upon their hardness, these stellites find uses in valves, dies, facing alloys and cutting tools. Cobalt alloys are also important because of their oxidation and corrosion resistance and, where elevated temperatures must be used, e.g. in gas turbines and jet engines, they are superior to many other alloys in stress-to-rupture strength and creep properties. *Vitallium* containing 65% Co and 25% Cr is used as a dental and surgical alloy being unattacked by body fluids.

Magnetic alloys consume about 20% of cobalt production and a large number[1] of such alloys are available for specific purposes. Among the permanent magnetic materials are the high cobalt (30–50%) steels and the *Alnico* type ferrous alloys containing about 12% Al, 20% Ni and 5–25% Co. Magnetically soft alloys (i.e. those characterized by their inability to retain induced magnetism once the external field is removed) using cobalt include the *Supermendurs* which contain 49% Co, 49% Fe and 2% V and the *Perminvars* which are ternary alloys having about 25% Co, 45% Ni and 30% Fe.

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[9] A. I. Vogel, *Quantitative Inorganic Analysis*, 3rd edition, p. 531, Longmans (1961).

2. COMPOUNDS OF COBALT IN LOW OXIDATION STATES (-1, 0, +1)

2.1. COBALT CARBONYLS

Preparation of Cobalt Carbonyls

Dicobalt octacarbonyl $Co_2(CO)_8$ and tetracobalt dodecacarbonyl $Co_4(CO)_{12}$ have been known for over sixty years[10], but a new carbonyl, hexacobalt hexadecacarbonyl $Co_6(CO)_{16}$, has been described only recently[11].

The direct reaction between cobalt metal and carbon monoxide produces $Co_2(CO)_8$; typical reaction conditions are 100 atm pressure and 200°, but a variety of combinations of high pressure and temperature have been employed[12]. Formation of the carbonyl is favoured by the presence of sulphur or iodine but inhibited by oxygen. Cobalt halides and sulphides can be carbonylated under conditions similar to those used for the metal in the presence of a reducing metal such as copper, e.g.

$$2CoI_2+8CO+4Cu \rightarrow Co_2(CO)_8+4CuI$$

A convenient laboratory preparation[13] involves the hydrogen reduction of cobalt carbonate in petroleum ether under a pressure of carbon monoxide:

$$2CoCO_3+2H_2+8CO \rightarrow Co_2(CO)_8+2CO_2+2H_2O$$

This carbonyl can also be prepared from aqueous solutions of cobalt(II) salts[14]. Under alkaline conditions carbon monoxide is absorbed and the tetracarbonylcobaltate(−1) anion $[Co(CO)_4]^-$ formed; when the solution is acidified, the hydride $CoH(CO)_4$ is formed and this spontaneously decomposes at room temperature:

$$2Co(NO_3)_2+12KOH+11CO \rightarrow 2KCo(CO)_4+4KNO_3+3K_2CO_3+6H_2O$$
$$KCo(CO)_4+HCl \rightarrow HCo(CO)_4+KCl$$
$$2HCo(CO)_4 \rightarrow Co_2(CO)_8+H_2$$

Tetracobalt dodecacarbonyl is most conveniently prepared by thermal decomposition of the octacarbonyl at 50° in an inert atmosphere[15]:

$$2Co_2(CO)_8 \rightarrow Co_4(CO)_{12}+4CO$$

at present it cannot be prepared direct from cobalt(II) salts and carbon monoxide. Treatment of $Co_4(CO)_{12}$ with alkali metals in tetrahydrofuran gives the green-yellow $[Co_6(CO)_{15}]^{2-}$ ion which is slowly transformed into the red-brown $[Co_6(CO)_{14}]^{4-}$ anion; these ions are oxidized in aqueous solution by iron(III) chloride to a mixture of carbonyls from which the black $Co_6(CO)_{16}$ can be extracted[11].

Physical Properties and Structure of Cobalt Carbonyls

Some of the physical properties of the carbonyls are given in Table 3. Dicobalt octacarbonyl sublimes readily and is soluble in hydrocarbon solvents, but the other carbonyls

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[10] L. Mond, H. Hirtz and M. D. Cowap, *J. Chem. Soc.* (1910) 798.

[11] P. Chini, *Chem. Communs.* (1967) 440.

[12] F. Calderazzo, R. Ercoli and G. Natta, in *Organic Syntheses via Metal Carbonyls*, I. Wender and P. Pino (Eds.), Interscience (1968).

[13] I. Wender, H. W. Sternberg, S. Metlin and M. Orchin, *Inorg. Syntheses*, **5** (1957) 190.

[14] P. Gilmont and A. A. Blanchard, *Inorg. Syntheses*, **2** (1946) 238.

[15] J. C. Hileman, *Preparative Inorganic Reactions*, W. L. Jolly (Ed.), Vol. 1, p. 101, Interscience (1964).

TABLE 3. PHYSICAL PROPERTIES OF COBALT CARBONYLS

Property	$Co_2(CO)_8$	$Co_4(CO)_{12}$	$Co_6(CO)_{16}$[a]
Colour	orange-brown	black	black
M.p. (°C)[b]	51	60d	100–110d
Density[b]	1·73		2·36[f]
Vapour pressure (mm Hg at 15°)[c]	0·07		
Dipole moment (D)[c]	1·29		
U.V. spectrum (cm^{-1})[d]	35,700; 28,600	26,800	
I.R. spectrum, ν(C–O) cm^{-1} [e]	2112, 2071, 2059, 2044, 2031, 2001, 1886, 1857	2104·4, 2063·2, 2054·5, 2048, 2037·9, 2027·5, 1898·4, 1867	2103, 2061, 2057, 2026, 2020, 2018, 1806, 1772

[a] P. Chini, *Chem. Communs.* (1967) 440.

[b] J. C. Hileman, *Preparative Inorganic Reactions*, Ed. W. L. Jolly, Vol 1. p. 101, Interscience (1964).

[c] F. Calderazzo, R. Ercoli and G. Natta, in *Organic Syntheses via Metal Carbonyls*, I. Wender and P. Pino (Eds.), Interscience (1968).

[d] R. A. Friedel, I. Wender, S. L. Shufler and H. W. Sternberg, *J. Am. Chem. Soc.* **77** (1955) 3951.

[e] D. M. Adams, *Metal Ligand and Related Vibrations*, p. 123, Arnold (1967).

[f] V. Albano, P. Chini and V. Scatturin, *Chem. Communs.* (1968) 163.

are only sparingly soluble. Cryoscopic molecular weight determinations indicate the dimeric and tetrameric formulations for $Co_2(CO)_8$ and $Co_4(CO)_{12}$. The X-ray crystal structure[16] of $Co_2(CO)_8$ shows the cobalt atoms to be bonded via two bridging CO groups (Fig. 2). The diamagnetism of the molecule and the closeness of the cobalt atoms (Co–Co = 2·52 Å) indicates the presence of a cobalt-cobalt bond; the mean Co–C (bridging) distance = 1·92 Å, Co–C (terminal) distance = 1·80 Å, C–O (bridging) = 1·21 Å and C–O (terminal) = 1·17 Å. Infrared studies[17, 18] on solutions of this carbonyl have established the presence of two isomeric forms in solution; one form has the structure as in the crystal and the infrared spectrum as recorded in Table 3. The other isomer has no bridging carbonyl groups and probably has either a trigonal bipyramidal arrangement (D_{3d} symmetry) or a square pyramidal arrangement (C_{2v} symmetry) around each cobalt atom. This isomer is favoured at higher temperatures; the equilibrium

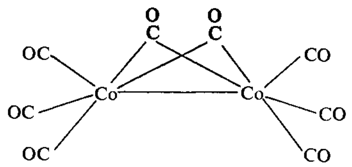
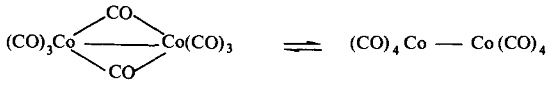


FIG. 2. Molecular structure of dicobalt octacarbonyl.



$$(CO)_3Co(\mu\text{-}CO)_2Co(CO)_3 \rightleftharpoons (CO)_4Co—Co(CO)_4$$

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[16] G. G. Sumner, H. P. Klug and L. E. Alexander, *Acta Cryst.* **17** (1964) 732.

[17] K. Noack, *Spectrochim. Acta*, **19** (1963) 1925.

[18] G. Bor, *Spectrochim. Acta*, **19** (1963) 2065.

involves[19] an entropy change (from left to right) of 5 eu and an enthalpy change of −1·30 kcal mole^{-1} so that this is an "entropy driven" reaction.

The X-ray structural study[20] on $Co_4(CO)_{12}$ has established the structure shown in Fig. 3. It consists of a tetrahedron of cobalt atoms; three of these have two terminal CO groups and are bridged by CO groups, the other cobalt atom is bonded to three terminal CO groups and the other three cobalt atoms only. The infrared spectrum is considerably simpler than would be expected theoretically for such a structure and consequently a different structure has been proposed for $Co_4(CO)_{12}$ in solution[21]. The carbonyl $Co_6(CO)_{16}$ has a similar infrared spectrum to, and is isomorphous[22] with, $Rh_6(CO)_{16}$ so that it probably has the same structure.

Chemical Properties of Cobalt Carbonyls

All three carbonyls are air sensitive both in the solid state and in solution. They are decomposed by reaction with halogens (no stable carbonyl halides being known), cobalt(II) halides and carbon monoxide being formed; oxidizing acids similarly give cobalt(II) salts.

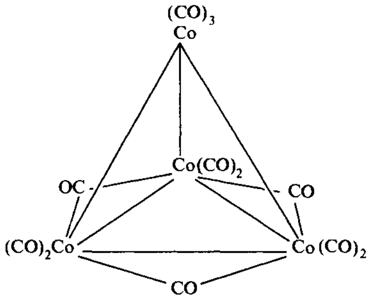

FIG. 3. Tetracobalt dodecacarbonyl.

In strongly alkaline solutions, $Co_2(CO)_8$ is reduced to the tetracarbonylcobaltate(−I), $[Co(CO)_4]^-$. This tetrahedral carbonylate anion is a very common feature of cobalt carbonyl chemistry; it is also formed when solutions of $Co_2(CO)_8$ or $Co_4(CO)_{12}$ are reduced by sodium amalgam in inert solvents or by sodium in liquid ammonia at below −75°:

$$Co_2(CO)_8+2Na \rightarrow 2Na[Co(CO)_4]$$

as well as in numerous disproportionation reactions of the carbonyls. The reduction of $Co_4(CO)_{12}$ with sodium or lithium in tetrahydrofuran at room temperature produces the carbonylate anions $[Co_6(CO)_{15}]^{2-}$ and $[Co_6(CO)_{14}]^{4-}$ as well as $[Co(CO)_4]^-$. The green-black caesium salt $Cs_2[Co_6(CO)_{15}].3H_2O$ and the red-black potassium salt $K_4[Co_6(CO)_{14}].8H_2O$ have been isolated. The crystal structure of the caesium salt shows[22] the cluster of cobalt atoms to form a distorted octahedron with a mean Co–Co distance of 2·49 Å; nine CO groups are terminal, three are bridged to edges of the octahedron and three bridged on faces. Dicobalt octacarbonyl finds extensive use as a catalyst in a large variety of organic transformations[23]; the detailed chemistry of the alkyl and acylcobalt

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[19] K. Noack, *Helv. Chim. Acta*, **47** (1964) 1064.

[20] C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc.* **88** (1966) 1821.

[21] D. L. Smith, *J. Chem. Phys.* **42** (1965) 1460.

[22] V. Albano, P. Chini and V. Scatturin, *Chem. Communs.* (1968) 163.

[23] A. J. Chalk and J. F. Harrod, *Advances in Organomet. Chem.* **6** (1968) 119.

carbonyls which are frequently intermediates in these reactions has been reviewed[24]. We shall here consider the chemistry of the carbonyls under the headings of disproportionation reactions and substitution reactions.

Disproportionation reactions. These are of two types: strong bases with nitrogen or oxygen donor atoms cause disproportionation into cobalt(II) and cobaltate(–I), e.g.

$$3Co_2(CO)_8+12NH_3 \rightarrow 2[Co(NH_3)_6][Co(CO)_4]_2+8CO$$
$$3Co_2(CO)_8+6\ \text{phen} \rightarrow 2[Co(\text{phen})_3][Co(CO)_4]_2+8CO$$
$$3Co_4(CO)_{12}+24\ \text{py} \rightarrow 4[Co(\text{py})_6][Co(CO)_4]_2+4CO$$

These products are typically pink or red, air-sensitive solids and are formed by a wide range of organic nitrogen bases as well as by oxygen donors such as water, alcohols, ketones, amides and ethers; the cation is normally hexacoordinate.

With isocyanides, phosphines, arsines and stibines, however, the disproportionation reaction yields low spin pentacoordinate cobalt(I) cations:

$$Co_2(CO)_8+5RNC \rightarrow [Co(CNR)_5][Co(CO)_4]+4CO$$

The ionic products formed by the group V donors contain only partially substituted cations and the salts readily decompose into normal substitution products of the carbonyl:

$$\begin{array}{l} Co_2(CO)_8+2L \rightarrow [Co(CO)_3L_2][Co(CO)_4]+CO \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\qquad\quad [Co(CO)_3L]_2+CO \\ (L = PR_3,\ AsR_3,\ SbR_3) \end{array}$$

Substitution reactions. These occur with tertiary phosphines, arsines and stibines, with sulphur compounds and with unsaturated organic molecules. The compounds $[Co(CO)_3L]_2$ ($L = PR_3$, AsR_3, SbR_3) formed by reaction between the ligand and $Co_2(CO)_8$ in inert solvents show no infrared bands attributable to bridging CO groups and so probably contain $Co(CO)_3L$ groups joined only by a cobalt–cobalt bond. This bond is broken in the reactions of these substitution products with sodium amalgam when the corresponding anions are formed, e.g. $Na[Co(CO)_3PR_3]$. These anions are useful starting materials in the synthesis of cobalt carbonyl hydrides[25] and carbonyl halides[26], e.g.

$$[CoH(CO)_3PPh_3] \xleftarrow{H^+} Na[Co(CO)_3PPh_3] \xrightarrow{CF_3I} Co(CO)_3PPh_3I$$

Mercaptans react with $Co_2(CO)_8$ to give sulphur bridged complexes of the type $[CoSR(CO)_3]_2$ as crystalline air-stable solids. Some rather more complicated reaction products have also been isolated from these systems, however; these include $Co_4(CO)_4(EtS)_7$ and $Co_4(CO)_7(EtS)_3$[27]. Elemental sulphur and hydrogen sulphide react with $Co_2(CO)_8$ in hydrocarbon solvents yielding[28] carbonyl sulphides of types $[Co_2S(CO)_5]_n$, $Co_3S(CO)_9$ and $Co_3S_2(CO)_7$.

Whilst $Co_2(CO)_8$ does not readily form substitution products with mono-olefins, tetra-

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[24] R. F. Heck in *Organic Syntheses via Metal Carbonyls*, p. 373, I. Wender and P. Pino (Eds.), Interscience (1968).

[25] W. Hieber and E. Lindner, *Z. Naturforsch.* **16b** (1961) 137; *idem, Chem. Ber.* **94** (1961) 1417.

[26] W. Hieber and E. Lindner, *Chem. Ber.* **95** (1962) 273.

[27] E. Klumpp, L. Marko and G. Bor, *Chem. Ber.* **97** (1964) 926.

[28] T. A. Manuel, *Advances in Organomet. Chem.* **3** (1965) 181.

fluoroethylene gives the orange crystalline derivative $(CO)_4CoCF_2CF_2Co(CO)_4$ at room temperature; this is believed to contain Co–C σ-bonds[29]. Di-olefins give a variety of derivatives, the structures of which are mostly unknown. Butadiene forms $[Co(CO)_2C_4H_6]_2$, which has a dipole moment of 3·02*D* and contains bridging CO groups. Cyclopentadiene reacts readily to form $C_5H_5Co(CO)_2$ as a red oil; this does not undergo Friedel–Crafts acylation so that the aromaticity of the C_5H_5 group is not yet proven in this compound.

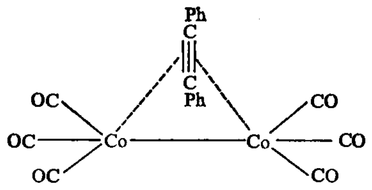


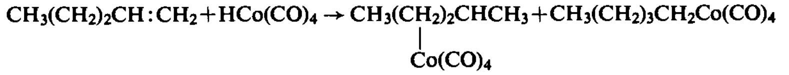
FIG. 4. Structure of $Co_2(CO)_6PhC_2Ph$.

Acetylenes react fairly readily with $Co_2(CO)_8$ to give deeply coloured, diamagnetic complexes $Co_2(CO)_6RC{\vdots}CR'$. X-ray studies on the diphenylacetylene compound[30] have revealed the structure shown in Fig. 4, in which the acetylenic C–C bond is nearly perpendicular to the Co–Co bond (Co–Co distance = 2·47 Å).

Cobalt Carbonyl Hydride[31]

The hydride $Co(CO)_4H$ can be prepared as a yellow liquid (m.p. −26°) by acidification of tetracarbonylcobaltate(–I) solutions (followed by sweeping out the volatile hydride), or by treating cobalt with carbon monoxide and hydrogen at 150° and 50 atm. The highly toxic, foul-smelling liquid decomposes at room temperature into $Co_2(CO)_8$ and hydrogen, but is relatively more suitable in the gaseous phase especially when diluted with carbon monoxide. It is readily oxidized in air and is sparingly soluble in water (3×10^{-3} moles/litre) in which it behaves as a strong acid ($K \sim 1$). The location of the hydrogen atom has provoked much discussion and the problem is still unsolved. It is now certain, however, that the hydrogen is bonded directly to cobalt. The infrared spectrum[32] shows carbonyl stretching frequencies at 2121, 2062 and 2043 cm^{-1} and ν(M–H) at 1934 cm^{-1}; it is most readily interpreted in terms of a molecule with C_{3v} symmetry. The structure may be trigonal bipyramidal with three equatorial CO groups displaced downwards towards the axial hydrogen atom. The hydrogen atom is detected by proton magnetic resonance; it shows a chemical shift $\tau = 20{\cdot}7$ ppm.

Cobalt carbonyl hydride undergoes interesting reactions with unsaturated organic molecules and epoxides[24]. With olefins, instead of substitution reactions, the hydride adds across the double bond with the production of a mixture of σ-bonded alkyl cobalt carbonyls, e.g.



$$CH_3(CH_2)_2CH{:}CH_2 + HCo(CO)_4 \rightarrow CH_3(CH_2)_2\underset{\substack{|\\ Co(CO)_4}}{CH}CH_3 + CH_3(CH_2)_3CH_2Co(CO)_4$$

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[29] H. H. Hoehn, L. Pratt, K. F. Watterson and G. Wilkinson, *J. Chem. Soc.* (1961) 2738.

[30] W. G. Sly, *J. Am. Chem. Soc.* **81** (1959) 18.

[31] M. L. H. Green and D. J. Jones, *Advances Inorg. Chem. Radiochem.* 7 (1965) 115.

[32] D. M. Adams, *Metal Ligand and Related Vibrations*, p. 123, Arnold (1967).

Conjugated dienes undergo 1:4 addition to give 2-butenylcobalt tetracarbonyl derivatives:

$$CH_2{:}CH.CH{:}CH_2 + HCo(CO)_4 \rightarrow CH_3CH{:}CHCH_2Co(CO)_4$$

These derivatives are thermally unstable, however, and evolve carbon monoxide near room temperature to form π-allyl cobalt carbonyls. Butadiene gives a mixture of two isomers of formula $[Co(C_4H_7)(CO)_3]$ which have been shown by their n.m.r. spectra[33] to be geometrical isomers of π-crotyltricarbonylcobalt (Fig. 5). The addition of cobalt carbonyl hydride to epoxides occurs in dilute solution at or below room temperature with the formation of β-hydroxyalkylcobalt tetracarbonyls which are conveniently converted into the more stable β-hydroxyacylcobalt complexes if the reaction is carried out under a carbon monoxide atmosphere:

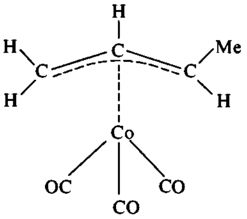
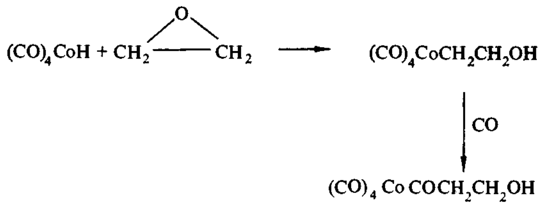


FIG. 5. π-Crotyltricarbonylcobalt.



Cobalt Carbonyl Halides

The only unsubstituted carbonyl halide reported[34] is the unstable, brown-black iodide $Co(CO)I_2$ prepared by the reaction of cobalt(II) iodide with carbon monoxide under 250 atm pressure at room temperature.

Phosphine substituted carbonyl halides are prepared[26, 35] by halogenation of the phosphine substituted carbonylate anion $[Co(CO)_3PPh_3]^-$. Thus the cobalt(I) compounds $XCo(CO)_3(PPh_3)$ ($X = Cl$, Br, I) are prepared by reaction of this anion with phosphorus oxytrichloride, *N*-bromosuccinimide and trifluoroiodomethane in tetrahydrofuran at low temperatures. These halides react with triphenylphosphine to give the disubstituted derivatives $XCo(CO)_2(PPh_3)_2$. These carbonyl halides are non-polar and soluble in tetrahydrofuran; $ClCo(CO)_2(PPh_3)_2$ is diamagnetic.

2.2. COBALT NITROSYLS

No simple nitrosyls of cobalt are known, but many complexes containing coordinated nitrogen monoxide have been studied (Table 4).

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[33] D. W. Moore, H. B. Jonassen, T. B. Joyner and A. Bertrand, *Chem. and Ind.* (1960) 1304.

[34] W. Hieber and H. Schulten, *Z. anorg. u. allgem. Chem.* **243** (1939) 145.

[35] W. Hieber and H. Duchatsch, *Chem. Ber.* **98** (1965) 2530.

Cobalt Nitrosyl Carbonyl, $CoNO(CO)_3$

This nitrosyl is most readily obtained[36] by the action of nitrogen monoxide on dicobalt octacarbonyl at 40°:

$$Co_2(CO)_8 + 2NO \rightarrow 2Co(NO)(CO)_3 + 2CO$$

If the carbonyl is unavailable, then the tetracarbonylcobaltate(-I) ion can be prepared by treating an alkaline solution of a cobalt(II) salt in the presence of cyanide ions with carbon monoxide and this gives the nitrosyl when the solution is shaken with nitrogen monoxide at room temperature[14]:

$$KCo(CO)_4 + NO + H_2O \rightarrow Co(NO)(CO)_3 + CO + KOH + \tfrac{1}{2}H_2$$

The nitrosyl carbonyl is a dark red diamagnetic liquid (b.p. 78·6°) soluble in organic solvents but insoluble in water; it is monomeric in the vapour phase. It is isoelectronic with nickel carbonyl and $Fe(NO)_2(CO)_2$ and electron diffraction studies[37] confirm the tetrahedral structure. The bond lengths are: Co–C, 1·83±0·02; C–O, 1·14±0·03; Co–N, 1·76±0·02 and N–O, 1·10±0·04 Å. The N–O bond length is thus somewhat shorter than in NO (1·18 Å) and on the basis of dipole moment measurements[38] ($\mu_D = 0{\cdot}72D$) it has

TABLE 4. SOME COBALT NITROSYL COMPOUNDS

Compound	Colour	ν(N–O) cm⁻¹	ν(C–O) cm⁻¹	Other data
$Co(NO)(CO)_3$[a, c]	red	1806	2100, 2033	m.p. −11°
$Co(NO)(CO)_2(PPh_3)$[a, b]	red	1761	2035, 1981	m.p. 130°
$Co(NO)(CO)_2(PCl_3)$[a]	red	1805	2073, 2030	
$Co(NO)(CO)(PPh_3)_2$[a, b]	red-brown	1717	1957	m.p. 177°d
$Co(NO)(CO)(SbPh_3)_2$[b]	brown-black	1719	1962, 1950	m.p. 119°d
$Co(NO)(PPh_3)_3$[c]	violet	1738		m.p. 175°
$Co(NO)[P(OPh)_3]_3$[c]	orange	1640		m.p. 195°
$Co(NO)(p\text{-}MeC_6H_4.NC)_3$[d]	red			dip. mom. = 5·29D
$[Co(NO)_2Cl]_2$[e]	black-brown	1859, 1790		dip. mom. = 1·04D
$Co(NO)_2Cl(PPh_3)$[f]	black	1829, 1776		dip. mom. = 6·72D
$Co(NO)I_2(PEt_3)_2$[g]	brown	1744, 1690		m.p. 98°
$[Co(NO)_2SEt]_2$[e]	black	1807, 1759		
$[Co(NO)(PPh_3)SEt]_2$[h]	black	1670		m.p. 142°
$Co(NO)_2(PPh_3)SEt$[i, j]	brown			m.p. 68–70°
$[Co(NO)_2SCN]_2$[i, j]	black	1855, 1825		m.p. 89–90°
$K_3[Co(NO)_2(S_2O_3)_2]$[e]	green	1827, 1730		
$Co(NO)(S_2CNMe_2)_2$[k]	black	1626		m.p. 125–130°
$K_3[Co(NO)(CN)_5].2H_2O$[k, l]	yellow	1120		diamagnetic
$C_2F_5Co(NO)_2(PPh_3)$[m]	brown-violet	1829, 1774		m.p. 65°

[a] W. D. Horrocks and R. C. Taylor, *Inorg. Chem.* **2** (1963) 1723.
[b] W. Hieber and J. Ellerman, *Chem. Ber.* **96** (1963) 1643.
[c] W. Beck and K. Lottes, *Chem. Ber.* **98** (1965) 1657.
[d] L. Malatesta and A. Sacco, *Z. anorg. u. allgem. Chem.* **274** (1953) 341.
[e] A. Jahn, *Z. anorg. u. allgem. Chem.* **301** (1959) 301.
[f] W. Hieber and K. Heinecke, *Z. anorg. u. allgem. Chem.* **316** (1962) 305.
[g] G. Booth and J. Chatt, *J. Chem. Soc.* (1962) 2099.
[h] W. Hieber and J. Ellerman, *Chem. Ber.* **96** (1963) 1650.
[i] W. Hieber, I. Bauer and G. Neumair, *Z. anorg. u. allgem. Chem.* **325** (1965) 250.
[j] W. Beck and K. Lottes, *Z. anorg. u. allgem. Chem.* **335** (1965) 258.
[k] J. Lewis, R. J. Irving and G. Wilkinson, *J. Inorg. Nuclear Chem.* **7** (1958) 32.
[l] W. P. Griffith, J. Lewis and G. Wilkinson, *J. Chem. Soc.* (1961) 775.
[m] W. Hieber and E. Lindner, *Chem. Ber.* **95** (1962) 2042.

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[36] R. L. Mond and A. F. Wallis, *J. Chem. Soc.* (1922) 32.
[37] L. O. Brockway and J. S. Anderson, *Trans. Farad. Soc.* **33** (1937) 1233.
[38] E. Weiss and W. Hieber, *Z. anorg. u. allgem. Chem.* **287** (1956) 223.

been suggested that two mesomeric forms of NO are present, $M^{2-} = N = O^{+}$ and $M^{-} - N \equiv O$. The infrared spectrum of $Co(NO)(CO)_3$ and its substituted derivatives have been studied in some detail (refs. Table 4) and the general conclusion has been reached that nitric oxide is one of the most powerful π-acceptors. In its reactions with donor molecules such as amines, phosphines, arsines and stibines (usually in inert solvents), it is the carbon monoxide groups which are replaced, derivatives with one, two or three molecules of ligand (Table 4) having been prepared.

Cobalt Nitrosyl Halides

The dinitrosyl halides $[Co(NO)_2X]_2$ (X = Cl, Br, I) are formed[39] in the direct reactions between nitrogen monoxide and the anhydrous cobalt(II) halides at atmospheric pressure and temperatures in the region of 70–120°; the presence of cobalt powder as a halogen acceptor is necessary in the preparation of the chloro- and bromo-nitrosyls. They are dimeric, diamagnetic solids believed to be halogen bridged; the infrared spectra (Table 4) show two N–O stretching frequencies in the region typified by NO^{+} and exclude structures involving NO bridges. They react with donor molecules to give monomeric complexes $Co(NO)_2XL$.

Triethylphosphine complexes of cobalt(II) halides readily absorb nitrogen monoxide in benzene solution and the diamagnetic mono-nitrosyl halide complexes $Co(NO)X_2(PEt_3)$ are formed.

Cobalt Nitrosyl–Sulphur Compounds

The cobalt analogue of Roussin's red salt (see chapter on Iron, page 1002) $K[Co(NO)_2S]$ is obtained in the reaction of $[Co(NO)_2Cl]_2$ and potassium sulphide[39]; it is probably dimeric like the esters $[Co(NO)_2SR]_2$ which are obtained using alkali metal mercaptides instead of sulphides. These esters react with donor molecules forming $Co(NO)_2(SR)L$. Compounds of the type $[Co(NO)PR_3(SR)]_2$, formed in the reactions of $Co(NO)(CO)_2PR_3$ with thioethers or disulphides, are diamagnetic probably having sulphur bridges and a tetrahedral distribution of NO, PR_3, and two S atoms around each cobalt.

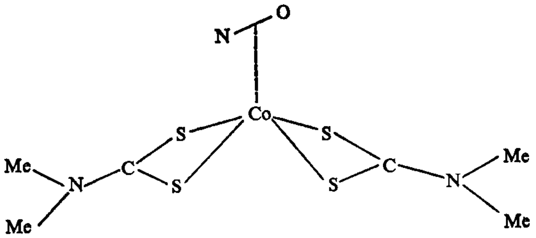

FIG. 6. $Co(NO)(S_2CNMe_2)_2$.

The dithiocarbamato complexes $Co(NO)(S_2CNR_2)_2$ (R = Me, Et) prepared[40] by saturating a mixture of the sodium dialkyldithiocarbamate and a cobalt(II) salt in methanol with nitrogen monoxide are readily oxidized in air. An X-ray diffraction study[41] of $Co(NO)(S_2CNMe_2)_2$ has shown that the coordination around the cobalt is that of a rectangular-based pyramid with the cobalt atom on the pyramidal axis 0·54 Å above the plane

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[39] W. Hieber and R. Marin, *Z. anorg. u. allgem. Chem.* **240** (1939) 241.

[40] R. L. Carlin, F. Canziani and W. K. Bratton, *J. Inorg. Nuclear Chem.* **26** (1964) 898.

[41] P. R. H. Alderman, P. G. Owston and J. M. Rowe, *J. Chem. Soc.* (1962) 668.

of the four sulphur atoms. The point of intersection of the pyramidal axis with the N–O bond is not well defined but appears to be at the mid point of this bond rather than at the nitrogen atom (Fig. 6).

Other sulphur-bonded nitrosyls are the thiosulphato complexes $[Co(NO)_2(S_2O_3)_2]^{3-}$ and the thiocyanate $[Co(NO)_2SCN]_2$, which presumably has –SCN– bridges.

Nitrosyl Cyanides

The yellow nitrosyl cyanide $K_3[Co(NO)(CN)_5].2H_2O$ is prepared by reaction of the $[Co(NH_3)_5(NO)]^{2+}$ cation with excess potassium cyanide and hydroxide. It is diamagnetic, very soluble and stable in water and on the basis of its infrared spectrum appears (unlike all the complexes we have thus far considered) to contain NO^-.

A series of carbonyl nitrosyl cyanides are obtained when potassium cyanide reacts with cobalt nitrosyl carbonyl[42]:

$$\begin{array}{lcl} Co(NO)(CO)_3 & \xrightarrow{KCN} & K[Co(NO)(CO)_2CN] \\ & & \downarrow \\ & & K_2[Co(NO)(CO)(CN)_2] \\ & & \downarrow \\ & & K_3[Co(NO)(CN)_3] \end{array}$$

These compounds presumably have tetrahedral anions; $[CoNO(CO)_2CN]^-$ is diamagnetic and isoelectronic with $[Co(CO)_4]^-$.

Other Cobalt Nitrosyl Compounds

The cationic $[Co(NO)(NH_3)_5]^{2+}$ complex has been known in two isomeric forms for many years. The black salt $[Co(NO)(NH_3)_5]Cl_2$ has been shown crystallographically[43] to contain a monomeric cation of roughly octahedral shape. The Co–N–O bond is apparently linear, but there is disagreement over the N–O bond distance. The salt is diamagnetic, unstable in aqueous acids and is considered as containing NO^- and Co(III). The red isomeric cation gives salts which are considerably more stable in aqueous solution; the nitrate is a 4:1 electrolyte in aqueous solution and thus contains a dimeric cation. Infrared evidence suggests that this cation should be formulated as containing a bridging hyponitrite, $[Co(NH_3)_5ONNOCo(NH_3)_5]^{4+}$.

Several five-coordinated cobalt cations containing nitrogen monoxide are known; these are of the type $[Co(NO)L_2]^{2+}$ where L is a bidentate ligand such as ethylenediamine, *o*-phenylenebis(dimethylarsine); six-coordinate complexes $[Co(NO)L_2X]X$ ($X = Cl$, Br, I or NCS) are also formed by the same ligands; these are formulated as containing Co(III) and NO^-.

2.3. OTHER COMPLEXES OF COBALT IN LOW OXIDATION STATES

Complex Cyanides

The reduction of potassium hexacyanocobaltate(III) with excess of potassium in liquid ammonia gives the brown-violet $K_8[Co_2(CN)_8]$. This compound liberates hydrogen from water, shows only two $C \equiv N$ stretching frequencies (at 2120 and 2062 cm^{-1}) and has a

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[42] R. Nast and M. Rohmer, *Z. anorg. u. allgem. Chem.* **285** (1956) 271.

[43] D. Hall and A. A. Taggart, *J. Chem. Soc.* (1965) 1359; D. Dale and D. C. Hodgkin, *ibid.* 1364.

magnetic moment $\mu_{\text{eff}} = 0{\cdot}6$ B.M.[44]. When the reduction is carried out using only 2·3 mole ratios of potassium per $K_3Co(CN)_6$, then the pale yellow cobalt(I) cyano complex $K_3[Co(CN)_4]$ is formed[45]; this turns red-brown upon warming to room temperature and is rapidly oxidized in air.

Whilst no pure carbonylcyano complex of cobalt(0) has been isolated, the cobalt(I) anion $[Co(CN)_3CO]^{2-}$ is formed in the reaction of carbon monoxide and potassium hydroxide with $K_3[Co(CN)_5]$ and can be isolated as the tris-*o*-phenanthroline iron(II) salt[46].

Isocyanide Complexes[47]

The crystalline yellow to brown cobalt(I) salts $[Co(CNR)_5]X$ are obtained when cobalt(II) salts are heated with an excess of an isocyanide in alcohol. For convenience a mild reducing agent such as hydrazine or dithionite is often added to a cobalt(II) isocyanide complex such as $Co(CNR)_4I_2$. The $[Co(CNR)_5]^+$ cation is also formed in the disproportionation reactions of cobalt carbonyls with isocyanides. Salts of this cation are quite stable in air, soluble in organic solvents and insoluble in water. They are diamagnetic and by analogy with the isoelectronic iron pentacarbonyl molecule the cation would be expected to be trigonal bipyramidal. Indeed in the perchlorate $[Co(CNMe)_5]ClO_4$ this structure has been confirmed for the cation[48].

Cobalt(I) Complexes of 2,2′-Dipyridyl, 1,10-Phenanthroline and Polycyclic Phosphites

The cobalt(III) cations $[Co(dipy)_3]^{3+}$ and $[Co(phen)_3]^{3+}$ can be reduced by sodium borohydride in aqueous ethanol to the dark blue[49] $[Co(dipy)_2]^+$ and the brown-black[50] $[Co(phen)_3]^+$ complexes which have been isolated as the perchlorate salts. Dipyridyl also forms $[Co(dipy)_3]ClO_4$ as a blue-black precipitate in the reduction of $[Co(dipy)_3](ClO_4)_3$ with sodium amalgam[51]. These dipyridyl complexes of cobalt(I) are diamagnetic, insoluble in water but soluble in nitrobenzene and readily oxidized in air.

The polycyclic phosphite ligands, $P(OCH_2)_3CMe$, $P(OCH_2)_3CEt$ and $P(OCH)_3(CH_2)_3$ have strong π-acidity and cause disproportionation of the hexa-aquo cobalt(II) cation into cobalt(I) and cobalt(III) cations containing these ligands[52]:

$$2[Co(H_2O)_6](ClO_4)_2 + 11L \rightarrow [CoL_5]ClO_4 + [CoL_6](ClO_4)_3 + 12H_2O$$

Several cobalt(I) complexes of these ligands have been isolated as diamagnetic yellow powders; the $[CoL_5]^+$ cation has the trigonal bipyramidal structure.

3. COMPOUNDS OF COBALT(II)

3.1. GENERAL AND REDOX CONSIDERATIONS

The principally occurring oxidation states of cobalt in aqueous solutions are +2 and +3. In the absence of ligands other than water, solutions of cobalt(II) contain the pink

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[44] W. Hieber and C. Bartenstein, *Z. anorg. u. allgem. Chem.* **276** (1954) 12.
[45] G. W. Watt and R. J. Thompson, *J. Inorg. Nuclear Chem.* **9** (1959) 311.
[46] W. Hieber and C. Bartenstein, *Z. anorg. u. allgem. Chem.* **276** (1954) 1.
[47] L. Malatesta, *Progress in Inorg. Chem.* **1** (1959) 283.
[48] F. A. Cotton, T. G. Dunne and J. S. Wood, *Inorg. Chem.* **4** (1965) 318.
[49] A. A. Vlcek, *Nature*, **180** (1957) 753.
[50] N. Maki, M. Yamagami and H. Itatani, *J. Am. Chem. Soc.* **86** (1964) 514.
[51] G. M. Waind and B. Martin, *J. Inorg. Nuclear Chem.* **8** (1958) 551; *Proc. Chem. Soc.* (1958) 169.
[52] T. J. Huttermann, B. M. Foxman, C. R. Sperati and J. G. Verkade, *Inorg. Chem.* **4** (1965) 950.

hexa-aquo ion $[Co(H_2O)_6]^{2+}$ and this is the thermodynamically stable state. The cobalt(III) ion $[Co(H_2O)_6]^{3+}$ is a very powerful oxidizing agent—it will in fact oxidize water to oxygen. Thus in the absence of complexing agents simple cobalt(III) salts are not stable in aqueous solution. In the presence of ligands, e.g. ammonia, which stabilize the cobalt(III) state, however, the oxidation of cobalt(II) to cobalt(III) becomes very much more favourable and may even be brought about by atmospheric oxygen. With some ligands, e.g. cyanide, the stabilization is so pronounced that the cobalt(II) complex reduces water to hydrogen, and even reacts with hydrogen to produce what is regarded as a cobalt(III) complex:

$$2[Co(CN)_5]^{3-} + H_2 \rightarrow 2[Co(CN)_5H]^{3-}$$

The standard electrode potentials for some cobalt couples are listed in Table 5; the data are taken from standard sources[53, 54], the sign convention being as defined in the chapter on Iron, Section 3.1. As a result of these potentials, cobalt(II) forms a large number of simple salts which are stable in neutral or acidic aqueous solutions, whereas simple salts of cobalt(III) are uncommon and unstable in aqueous solution. The complex compounds of cobalt(III) are, however, numerous and stable and have played an important rôle in the development of coordination chemistry.

TABLE 5. STANDARD ELECTRODE POTENTIALS FOR SOME COBALT COUPLES AT 25°

Couple	Potential (volts)
Acid solution	
Co^{2+}/Co	−0·277
Co^{3+}/Co^{2+}	+1·842
Basic solution	
$CoS(\beta)/Co,S^{2-}$	−1·07
$CoS(\alpha)/Co,S^{2-}$	−0·90
$Co(CN)_6^{3-}/Co(CN)_5^{3-}$	−0·8
$Co(OH)_2/Co,2OH^-$	−0·73
$CoCO_3/Co,CO_3^{2-}$	−0·64
$Co(NH_3)_6^{2+}/Co,6NH_3$	−0·422
$Co(NH_3)_6^{3+}/Co(NH_3)_6^{2+}$	+0·108
$CoO(OH)/Co(OH)_3,OH^-$	+0·17

3.2. SIMPLE COMPOUNDS OF COBALT(II)

Cobalt(II) halides. Some of the properties of the cobalt(II) halides are listed in Table 6. The hydrates are obtained by crystallization of solutions of the metal, oxide or carbonate in the corresponding hydrohalic acid. The halides form very many complex compounds; these are described in Section 3.3.

Cobalt(II) fluoride. This can be prepared by heating the double salt $CoF_2.2NH_4F$ (when ammonium fluoride sublimes) or by heating cobalt(II) oxide or chloride in a stream of hydrogen fluoride. Finely divided cobalt reacts with fluorine at 500° to form a mixture of CoF_2 and CoF_3. Cobalt(II) fluoride crystallizes in the rutile structure. It is only sparingly soluble in water; it reacts with steam at red heat (giving cobalt(II) oxide and hydrogen fluoride) and is reduced by hydrogen above 300°.

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[53] W. M. Latimer, *The Oxidation States of the Elements and their Potentials in Aqueous Solutions*, 2nd edition, Prentice-Hall (1952).

[54] A. J. Bethune, in *The Encyclopedia of Electrochemistry*, p. 415 (C. A. Hampel, Ed.) Reinhold (1964).

Cobalt(II) chloride. This is the sole product when cobalt is heated in chlorine. It is readily prepared by dehydration of the pink hexahydrate either at 150° *in vacuo* or by treatment with thionyl chloride. In the crystal, each cobalt is surrounded octahedrally by six chloride ions in a $CdCl_2$ type structure[55, 56]. The magnetic moment is 5·47 B.M. at 293°K[57]. It is readily soluble in water to give a pink solution and in alcohol giving a deep blue solution. The anhydrous salt turns pink in moist air due to hydration; this property has led to extensive use of cobalt chloride as an indicator in desiccants such as silica gel. At room temperature, the orange-pink hexahydrate crystallizes from aqueous solutions, the violet dihydrate crystallizes above 52° and the blue-violet monohydrate above 90°.

The hexahydrate $CoCl_2.6H_2O$ forms monoclinic crystals in which each cobalt atom is surrounded by four water molecules at the corners of a distorted square ($Co–H_2O =$ 2·12 Å) and by two chlorine atoms ($Co–Cl = 2·43$ Å) to form a distorted octahedron.[58]

TABLE 6. COBALT(II) HALIDES

Property	CoF_2	$CoCl_2$	$CoBr_2$	CoI_2
Colour	pink	blue	green	blue-black
M.p. (°C)	1200	724[a]	678[b]	515[c]
Density	4·46	3·356	4·909	5·68
$-\Delta H_f$ (kcal mole^{-1})	159	77·8	55·5	24·4
$-\Delta H_f$ (aq) (kcal mole^{-1})	173·6	96·1	73·9	42·8
Hydrates	2, 3, 4	1, 2, 4, 6	2, 6	2, 4, 6

[a] In HCl gas. [b] In N_2. [c] In vacuum.

The other two water molecules are not bonded directly to cobalt. In the monoclinic dihydrate $CoCl_2.2H_2O$, the octahedral symmetry around the cobalt atom is maintained by the sharing of chlorine atoms between two cobalt atoms. In the flattened octahedral structure[58] there are two Co–Cl distances of 2·450 Å, two of 2·478 Å and two $Co–H_2O$ distances of 2·040 Å.

Some basic chlorides are known[59]; the pink, rhombohedral $Co_2(OH)_3Cl$ has a structure containing cobalt atoms in two different environments. One cobalt is surrounded by six hydroxyl groups each at 2·12 Å and the other by four hydroxyl groups at 2·16 Å and two chlorines at 2·53 Å.

Cobalt(II) bromide. The green anhydrous salt is prepared by dehydration of the red hexahydrate or by the action of bromine on heated cobalt. It is very soluble in water and soluble in many polar organic solvents; it deliquesces in moist air to a red solution. The hexahydrate crystallizes from aqueous solution at room temperature; it melts at 100°, evolving water and forming the purple dihydrate.

Cobalt(II) iodide. Two isomeric forms of this are known. The data in Table 6 refer to the almost black (α) form prepared by the reaction of hydrogen iodide with finely divided cobalt at 400–500°. When this material is sublimed in a high vacuum some yellow (β) CoI_2 sublimes (0·8 g β-CoI_2 from 10 g α-CoO_2)[60]. The black α-form gives a pink solution in

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[55] A. F. Wells, *Structural Inorganic Chemistry*, 3rd edition, Oxford University Press (1962).

[56] R. W. G. Wyckoff, *Crystal Structures*, 2nd edition, Vol. 1, Interscience (1963).

[57] B. N. Figgis and J. Lewis, *Progress in Inorganic Chemistry*, **6** (1964) 37.

[58] R. W. G. Wyckoff, *Crystal Structures*, 2nd edition, Vol. 3, Interscience (1965).

[59] H. Remy, *Treatise on Inorganic Chemistry*, Vol. II, p. 298, Elsevier (1956).

[60] G. Brauer, *Handbuch der Präparativen Anorganischen Chemie*, Vol. II, p. 1323, Ferdinand Enke (1962).

water whilst the β-form gives a colourless solution which turns pink upon warming. The crystal structures of these two forms are unknown.

From solutions of cobalt bases in hydriodic acid can be crystallized the dark red hexahydrate. The hexagonal crystals have, unlike the chlorides, cobalt atoms surrounded by six water molecules at 2·30 Å. The concentrated aqueous solution is dark red below 20° and green above 35°. The green $CoI_2.4H_2O$ and $CoI_2.2H_2O$ separate from the aqueous solutions at higher temperatures.

Cobalt(II) cyanide. A light brown precipitate of $Co(CN)_2.2$ or $2{\cdot}5H_2O$ can be obtained from cobalt(II) chloride and potassium cyanide solutions[61]. This can be dehydrated at 250° in a stream of nitrogen to the blue anhydrous cyanide. Both the hydrated and the anhydrous compounds have magnetic moments (3·27 and 3·12 B.M. respectively) which are much lower than is expected for three unpaired electrons. The crystal structures of these compounds have been interpreted as being that of soluble Prussian blue (see chapter on Iron, page 1032) with one cobalt atom being low spin (one unpaired electron) surrounded by six carbon atoms while the other is high spin (three unpaired electrons) being surrounded by six nitrogen atoms as nearest neighbours.

In excess of potassium cyanide cobalt(II) cyanide gives an olive-green solution which is rapidly oxidized by air and probably contains the five-coordinate $[Co(CN)_5]^{3-}$ species.

Cobalt(II) thiocyanate. This deep red-violet salt is obtained as the tetrahydrate by crystallization of an aqueous solution of cobalt carbonate in thiocyanic acid. It is very deliquescent and gives a dark blue concentrated solution which turns pink upon dilution. It gives blue solutions in many organic solvents.

Cobalt(II) oxide. This is obtained as an olive-green powder by heating the metal in air or steam or by thermal decomposition of the hydroxide, carbonate or nitrate. It has the sodium chloride lattice and is antiferromagnetic below 292°K. When heated in oxygen above 400° the black oxide Co_3O_4 is obtained. This oxide is isomorphous with magnetite Fe_3O_4, and has tetrahedrally surrounded cobalt(II) ions and octahedrally surrounded cobalt(III) ions. Both these oxides are readily reduced to the metal by heating in hydrogen or with carbon. The reactions of CoO with silica, alumina and zinc oxide are used to form pigments in the ceramic industry.

Cobalt(II) hydroxide. The addition of alkali metal hydroxides to solutions of cobalt(II) salts results in the precipitation of cobalt(II) hydroxide in either a blue or pink form depending upon the conditions. The pink form is the more stable of the two and is obtained when a suspension of the blue form is allowed to stand or is warmed. Cobalt(II) hydroxide is amphoteric, dissolving in alkalis to form blue solutions of the $[Co(OH)_4]^{2-}$ ions. In the presence of alkali, suspensions of $Co(OH)^8$ are oxidized by air to the brown CoO(OH), this oxidation being brought about rapidly by oxidants such as hypochlorite, bromine water or hydrogen peroxide. The pink $Co(OH)_2$ (density 3·597) has the brucite $(Mg(OH)_2)$ structure in which the cobalt atoms are surrounded by six hydroxides. The blue form is more disordered, but its structure is not known for certain.

Cobalt sulphides[62]. The black precipitate (so-called α-CoS) obtained from cobalt(II) solutions by treatment with sodium sulphide has the composition $Co(SH,OH)_2$, the hydroxide content depending upon the alkalinity of the precipitation medium. When freshly precipitated, this composition is soluble in acids, but upon standing, this amorphous precipitate changes to a mixture containing crystalline $Co_{1-x}S$ and Co_9S_8 which is insoluble

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[61] B. M. Chadwick and A. G. Sharpe, *Advances in Inorg. Chem. Radiochem.* **8** (1966) 83.

[62] F. Jellinek, in *Inorganic Sulphur Chemistry*, p. 669 (G. Nickless, Ed.), Elsevier (1968).

in dilute acids. In the cobalt–sulphur system, sulphides identified are CoS_2 (with the pyrites structure), Co_3S_4 (with a spinel-type structure) and the cobalt-deficient $Co_{1-x}S$ (with the NiAs structure). Cobalt disulphide is ferromagnetic below 120°K; above this temperature the paramagnetism is that of the low spin configuration $t_{2g}{}^6e_g{}^1$. The phase Co_3S_4 (which occurs naturally as *linnaeite*) is stable up to about 650°; thereafter CoS_2 and $Co_{1-x}S$ are formed. It is readily prepared by the action of hydrogen sulphide on cobalt powder at 400°. The phase Co_9S_8 is peritectically formed around 835°; its structure is remarkable in that eight of the cobalt atoms occupy tetrahedral holes in a cubic close packing of sulphur while the ninth cobalt atom is in an octahedral environment.

Cobalt nitrides. These are not formed by direct combination of the elements. The nitrides Co_2N and Co_3N are formed when ammonia reacts with freshly prepared cobalt powder at 380°. The thermal decomposition of cobalt(III) amide (prepared by the reaction of hexaammine cobalt(III) nitrate with potassium amide in liquid ammonia) at 40–50° gives CoN as a black, pyrophoric and amorphous powder.

Phosphorus and arsenic combine directly when heated with cobalt. In the Co–P system three phosphides are known: Co_2P, CoP and CoP_3, all being obtained by direct synthesis. The arsenides $CoAs_2$ (*smaltite*) and $CoAs_3$ occur naturally.

Cobalt(II) carbonate. This occurs naturally as *sphaerocobaltite.* It can be precipitated as the violet-red hexahydrate $CoCO_3.6H_2O$ from aqueous solutions of cobalt(II) salts and an alkali metal bicarbonate if the reaction is carried out under an atmosphere of carbon dioxide. In the absence of carbon dioxide basic salts are precipitated in these reactions. The hydrate is dehydrated to the $CoCO_3$ at 140° and at 350° *in vacuo* CoO is formed.

Cobalt(II) carboxylates. The red acetate $Co(OCOCH_3)_2.4H_2O$ can be crystallized from solutions of cobalt bases in acetic acid. It finds uses as a catalyst in auto-oxidation reactions, frequently in acetic acid solutions; the reactive species in these solutions are[63] $Co(OCOCH_3)_2$ and $[Co(OCOCH_3)_4]^{2-}$. It is also used as a bleaching and drying agent for varnishes and lacquers. The dihydrate $Co(OCOCH_3)_2.2H_2O$ contains octahedrally coordinated cobalt with unidentate acetate groups each being hydrogen bonded to a coordinated water molecule[64]. The anhydrous acetate forms bis-adducts $Co(OCOCH_3)_2.2L$ with ligands such as pyridine and hydrazine.

Cobalt(II) oxalate precipitates as a pink powder of formula $CoC_2O_4.2H_2O$ when oxalate ions are added to a solution of a cobalt(II) salt. It is readily soluble in aqueous ammonia. The yellowish-pink tetrahydrate is used in the preparation of catalysts and of cobalt metal for powder-metallurgical applications.

Cobalt(II) nitrate. The red hygroscopic hexahydrate $Cu(NO_3)_2.6H_2O$ crystallizes from aqueous solutions of cobalt bases in dilute nitric acid at room temperature. It becomes the trihydrate when heated at 56°; at higher temperatures decomposition occurs. The anhydrous nitrate can, however, be obtained by condensation of dinitrogen pentoxide onto a solution of the hydrated nitrate in nitric acid, or by dissolution of cobalt in a mixture of equal volumes of dinitrogen tetroxide and ethyl acetate[65]. From this latter medium the deep purple adduct $Co(NO_3)_2.2N_2O_4$ separates; this becomes $Co(NO_3)_2.N_2O_4$ at 50° *in vacuo* and the pale purple $Co(NO_3)_2$ at 120°. The dinitrogen tetroxide adducts have been formulated as containing coordinated nitrate groups, e.g. $NO^+[Co(NO_3)_3]^-$. It is remarkable that no oxidation to cobalt(III) occurs in any of these reactions.

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[63] P. J. Proll, L. H. Sutcliffe and J. Walkley, *J. Phys. Chem.* **65** (1961) 455.

[64] C. Oldham, *Progress in Inorg. Chem.* **10** (1968) 223.

[65] C. C. Addison and D. Sutton, *J. Chem. Soc.* (1964) 5553.

Cobalt(II) phosphate. The anhydrous $Co_3(PO_4)_2$ is obtained when cobalt(II) salts are heated with phosphoric acid. The octahydrate $Co_3(PO_4)_2.8H_2O$ is precipitated when aqueous solutions of cobalt(II) chloride and potassium hydrogen phosphate are mixed. As it is a brilliant lavender colour it is used in artists' paints and as a pigment in ceramics. The pyrophosphate $Co_2P_2O_7.8H_2O$ is similarly precipitated using sodium pyrophosphate and a cobalt(II) solution.

Cobalt(II) sulphate. From aqueous solutions the orange-pink heptahydrate $CoSO_4.7H_2O$ crystallizes; this is isomorphous with $FeSO_4.7H_2O$. Crystallization at 30° or by heating the heptahydrate at 41·5° yields the orange-red hexahydrate; the monohydrate is formed above 70° and the anhydrous sulphate above 250°. This cubic anhydrous salt decomposes at 735°; it is less deliquescent than the chloride or nitrate and is the salt used for many commercial purposes. Its solubility in water (about 36 g $CoSO_4$ in 100 g H_2O at 20°) increases with temperature; it is insoluble in alcohol. The hydrates are magnetically dilute, having magnetic moments around 4·75 B.M. at room temperature.

Double sulphates crystallize from solutions of cobalt(II) sulphate to which alkali metal or ammonium sulphates have been added, e.g. $(NH_4)_2SO_4.CoSO_4.6H_2O$, which forms red crystals isomorphous with the iron analogue (Mohr's salt). Some basic sulphates, e.g. blue $CoSO_4.3Co(OH)_2$ and violet $2CoSO_4.3Co(OH)_2.5H_2O$, are known.

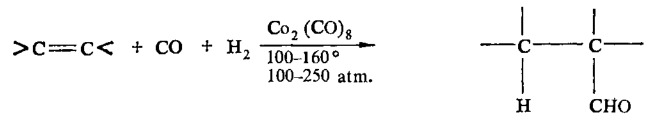
Cobalt(II) sulphite. Reddish granular crystals of $CoSO_3.5H_2O$ are obtained when sulphur dioxide is passed through an aqueous suspension of cobalt(II) hydroxide. It is sparingly soluble in water and readily forms double salts with alkali metal sulphites.

Cobalt(II) halates and perhalates. The very soluble chlorate $Co(ClO_3)_2.6H_2O$ can be prepared by crystallization from the filtrate of the cobalt(II) sulphate–barium chlorate reaction. It is thermally unstable, but the anhydrous salt can be obtained from the hydrate at 60° *in vacuo*. The bromate and iodate are similar, but the iodate is only sparingly soluble in water.

The red perchlorate $Co(ClO_4)_2.6H_2O$ crystallizes from solutions of cobalt bases in perchloric acid. It is extremely soluble in water (about 254 g per 100 g H_2O at 26)°, the solutions containing the $[Co(H_2O)_6]^{2+}$ ion.

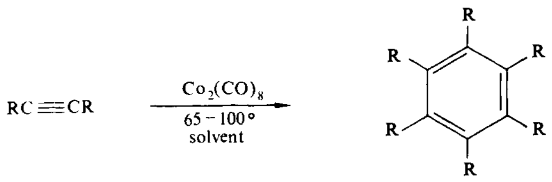
3.3. ORGANOMETALLIC COMPOUNDS OF COBALT

The use of dicobalt octacarbonyl as a catalyst in a variety of organic syntheses has led to the study of an extensive and important organometallic chemistry of cobalt. As examples of the use of a cobalt carbonyl catalyst we may quote the hydroformylation (OXO) reaction which enables the preparation of aldehydes from alkenes, carbon monoxide and hydrogen:



$$>C{=}C< + CO + H_2 \xrightarrow[\substack{100\text{–}160^\circ \\ 100\text{–}250\text{ atm.}}]{Co_2(CO)_8} -\underset{H}{\overset{|}{\underset{|}{C}}}-\underset{CHO}{\overset{|}{\underset{|}{C}}}-$$

and the cyclic trimerization of alkynes:



Several excellent reviews of organocobalt chemistry are available[66–69]. We shall here consider the compounds according as to whether they contain Co–C σ-bonds or cobalt π-bonded to a system of carbon atoms and for simplicity will deal here with all organocobalt compounds irrespective of the oxidation state of cobalt.

σ-Bonded Organometallic Compounds of Cobalt

The simple alkyls and aryls of cobalt are too unstable to exist on their own; in the presence of π-bonding ligands, however, such as carbon monoxide, tertiary phosphines, π-cyclopentadienyl or cyanide ion, stable Co–C σ-bonded complexes can be isolated. The preparative methods used include[70] those starting from Grignard reagents, carbonylcobaltate anions or cobalt carbonyl hydride and can be exemplified by the equations:

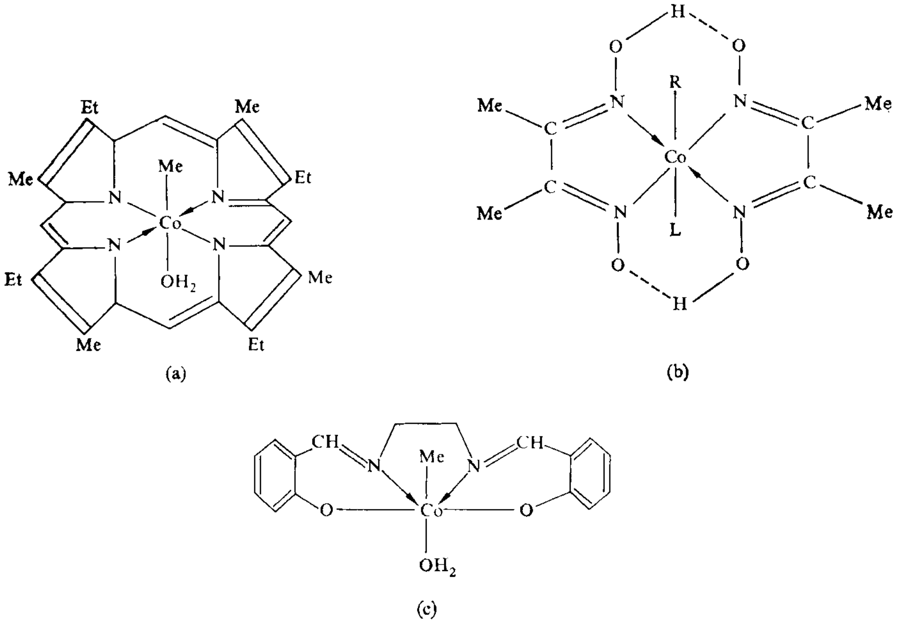
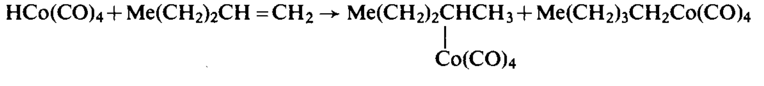


Fig. 7. Some "model" vitamin B$_{12}$ complexes.

$$(\pi\text{-}C_5H_5)(PPh_3)CoI_2 + MeMgI \rightarrow MeCoI(PPh_3)(\pi\text{-}C_5H_5) + Me_2Co(PPh_3)(\pi\text{-}C_5H_5)$$

$$Na[Co(CO)_4] + MeI \rightarrow MeCo(CO)_4 + NaI$$



$$HCo(CO)_4 + Me(CH_2)_2CH{=}CH_2 \rightarrow Me(CH_2)_2\underset{\displaystyle Co(CO)_4}{\underset{|}{C}}HCH_3 + Me(CH_2)_3CH_2Co(CO)_4$$

Vitamin B$_{12}$ (Fig. 1) can be regarded as a naturally occurring cobalt alkyl; in this, cobalt

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[66] G. E. Coates, M. L. H. Green and K. Wade, *Organometallic Compounds*, Vol. 2, Methuen (1968).

[67] R. F. Heck, Organic syntheses via alkyl- and acylcobalt tetracarbonyls, in I. Wender and P. Pino (Eds.), *Organic Syntheses via Metal Carbonyls*, Vol. 1, p. 373, Interscience (1968).

[68] W. Hubel, Organometallic derivatives from metal carbonyls and acetylene compounds, *ibid.*, p. 273.

[69] A. J. Chalk and J. F. Harrod, *Advances in Organomet. Chem.* **6** (1968) 119.

[70] G. W. Parshall and J. J. Mrowca, *Advances in Organomet. Chem.* **7** (1968) 157.

is bonded to an adenosyl group via a Co–C σ-bonded linkage. Alkyl cobalamins can be prepared by the action of alkyl halides, olefins or acetylenes on the reduced form of cyanocobalamin (vitamin B_{12_s}). A number of cobalt complexes with systems rather resembling that of vitamin B_{12} have been investigated. These include the aetioporphyrin complexes[71] (Fig. 7a), the dimethylglyoxime complexes[72] (Fig. 7b) and the Schiff base complexes[73] (Fig. 7c).

The alkyl cobalt carbonyls are an important group of compounds particularly as far as synthetic organic chemistry is concerned[67]. The light yellow methyl cobalt tetracarbonyl melts at −44° and is thermally unstable above −35°. The perfluoroalkyls, e.g. $C_6F_5Co(CO)_4$, have higher melting points and greater thermal stability and phosphine substituted derivatives, e.g. $C_2F_5Co(CO)_3(PPh_3)$, are fairly high melting solids. The most important reaction of this type of compound is the reversible carbonylation to acylcobalt carbonyls:

$$RCo(CO)_4 + CO \rightleftharpoons RCOCo(CO)_4$$

These acyls react with alcohols at about 50° to give esters, thus enabling the preparation of esters from alkyl halides by means of the readily carried out reactions:

$$RX + CO + [Co(CO)_4]^- \rightarrow RCOCo(CO)_4 + X^-$$

$$RCOCo(CO)_4 + R'OH \rightarrow RCOOR' + HCo(CO)_4$$

The process is catalytic in cobalt if a tertiary amine is present because the carbonylcobaltate(–I) is regenerated:

$$RCOCo(CO)_4 + R'OH + R_3''N \rightarrow RCOOR' + [R_3''NH][Co(CO)_4]$$

Some unusual alkylcobalt carbonyls of the general formula $Co_3(CO)_9CR$ have been prepared from cobalt carbonyl acetylene complexes $Co_2(CO)_6RC_2H$ by treatment with dilute sulphuric acid. The chloride (R = Cl) can be prepared directly from dicobalt octacarbonyl and carbon tetrachloride. These compounds are purple solids showing no infrared absorptions due to bridging carbonyl groups; X-ray studies[74] on the methyl compound show it to have the structure shown in Fig. 8.

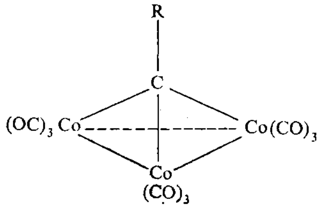

FIG. 8. Structure of $Co_3(CO)_9CMe$.

Another group of cobalt alkyls worthy of mention are the cobalt(III) derivatives

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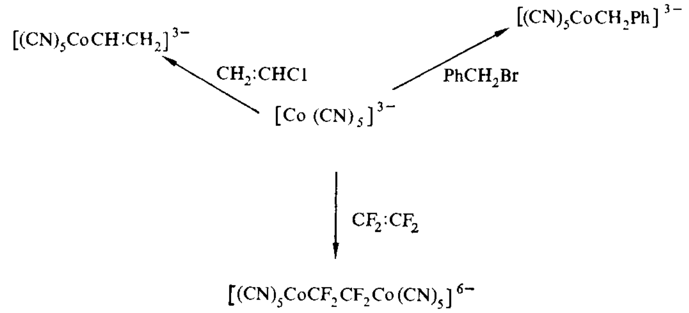
[71] D. A. Clarke, R. Grigg, A. W. Johnson and H. A. Pinnock, *Chem. Communs.* (1967) 309.

[72] G. N. Schrauzer and R. J. Windgassen. *J. Am. Chem. Soc.* **88** (1966) 3738; *ibid.* **89** (1967) 143, 1999, 3607.

[73] G. Costa, G. Mestroni and L. Stefani, *J. Organometal. Chem.* 7 (1967) 493.

[74] P. W. Sutton and L. F. Dahl, *J. Am. Chem. Soc.* **89** (1967) 261.

$[(CN)_5CoR]^{3-}$. These relatively non-labile, low spin, d^6 complexes are prepared by direct reaction between the pentacyanocobaltate(II) and organic halides:



Aqueous solutions of salts of these anions are stable in the absence of oxygen but are decomposed by acids.

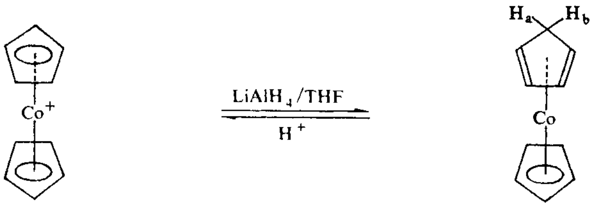
The σ-bonded acetylides $Na_4[Co(C \vdots CR)_6]$ are obtained[75] in the liquid ammonia reaction (R = H, Me):

$$6NaC \vdots CR + [Co(NH_3)_6](SCN)_2 \rightarrow Na_4[Co(C \vdots CR)_6] + 2NaSCN + 6NH_3$$

The salt $Na_4[Co(C \vdots CMe)_6]$ is green and paramagnetic (low spin); it is oxidized readily to the more stable yellow cobalt(III) salt $Na_3[Co(C \vdots CMe)_6]$.

Some π-Bonded Organometallic Compounds of Cobalt

Olefin, allyl and acetylene complexes. Cobalt does not readily form complexes with mono-olefins, but several compounds with di-olefins have been described. The reactions of dicobalt octacarbonyl with olefins and acetylenes have been mentioned on page 1063. Hydride addition to the cobaltocenium ion results in the formation of a cyclopentadiene complex:



The chemical properties of this olefin complex indicate some unusual degree of reactivity of the endo hydrogen atom (H_a nearer to cobalt). It is easily removed by protons to form the cobaltocenium ion and hydrogen or by carbon tetrachloride:

$$Co(C_5H_5)(C_5H_6) + CCl_4 \rightarrow [Co(C_5H_5)_2]Cl + CHCl_3$$

The infrared spectrum of this diamagnetic olefin complex shows[76] an unusually low C–H stretching frequency at 2750 cm^{-1}; this has been attributed to interaction between the

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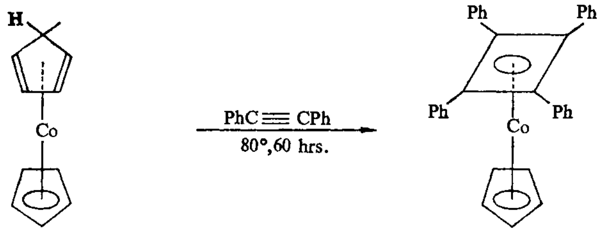
[75] R. Nast and H. Lewinsky, *Z. anorg. u. allgem. Chem.* **282** (1955) 210.

[76] M. L. H. Green, L. Pratt and G. Wilkinson, *J. Chem. Soc.* (1959) 3753.

endo-C-H_a and the cobalt atom. By reaction with diphenylacetylene a cyclobutadiene derivative is obtained:



Cyclic diolefin complexes are formed when (π-C_5H_5)Co(CO)$_2$ is reacted with unsaturated ligands, carbon monoxide being completely displaced (Fig. 9).

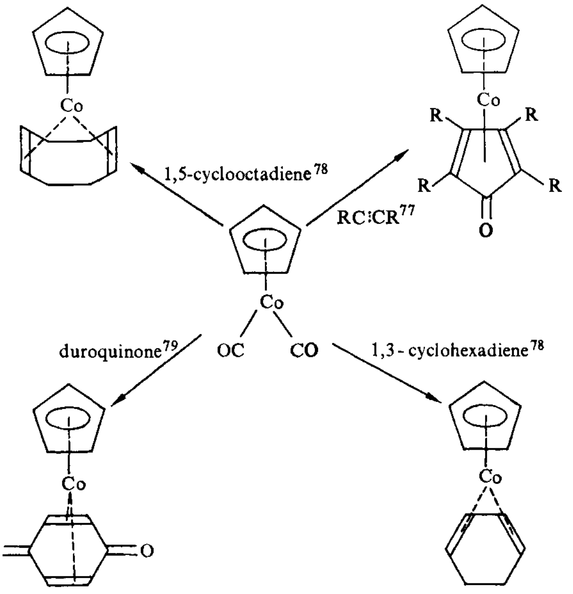


FIG. 9. Cyclic diolefin complexes from (C_5H_5)Co(CO)$_2$.

π-Allyl complexes of cobalt are obtained either from cobalt carbonyl hydride (page 1064) or by treatment of an allyl halide with a cobalt complex (Fig. 10). Such π-allyl complexes are readily oxidized and are usually yellow or red solids. Reaction of Co(π-C_3H_5)(CO)$_3$ (yellow liquid, m.p. −32 to −33°) with triphenylphosphine results in replacement of carbonyl groups rather than allyl groups; the resulting derivative Co(π-C_3H_5)(CO)$_2$(PPh$_3$) is considerably more stable, melting with decomposition at 132°.

π-Cyclopentadienyl complexes. Bis(π-cyclopentadienyl)cobalt (cobaltocene) (π-C_5H_5)$_2$Co. Cobaltocene, the cobalt analogue of ferrocene, can be prepared in a variety of ways, but is

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[77] R. Markby, H. W. Sternberg and I. Wender, *Chem. and Ind. (London)* (1959) 1381.

[78] R. B. King, P. M. Treichel and F. G. A. Stone, *J. Am. Chem. Soc.* **83** (1961) 3593.

[79] G. N. Schrauzer and H. Thyret, *Angew Chem.* **75** (1963) 641.

most usually prepared from stoichiometric amounts of sodium cyclopentadienide and anhydrous cobalt(II) chloride in tetrahydrofuran. The reaction[83] is exothermic and the mixture becomes dark purple as the reaction proceeds; after heating under reflux to ensure completion of reaction, the solvent is removed and the cobaltocene purified by sublimation at 0·1 mm above 60°. Other preparative routes have involved the reaction between sodium cyclopentadienide and cobalt(II) thiocyanate in liquid ammonia[84] and reduction of the $[Co(C_5H_5)_2]^+$ cation with lithium aluminium hydride[85].

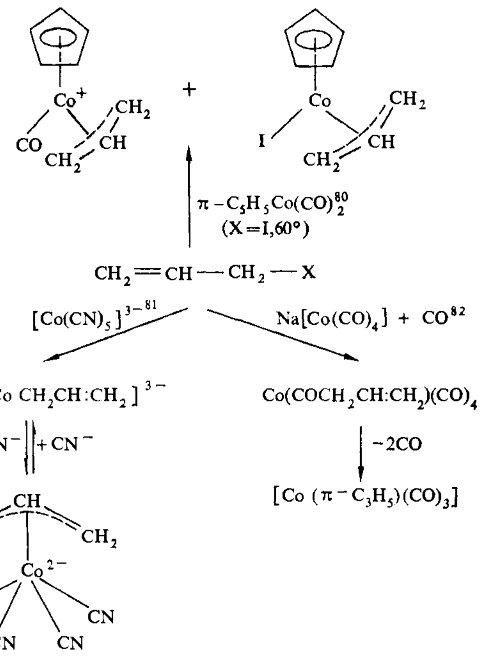

FIG. 10. π-Allyl complexes of cobalt.

Cobaltocene forms purple-black, air-sensitive crystals which melt at 173°. They are readily oxidized to the more stable cobaltocenium ion, $[Co(C_5H_5)_2]^+$. Having one more electron than ferrocene, cobaltocene is paramagnetic with $\mu = 1{\cdot}76$ B.M. at room temperature; the electronic configuration of the molecule thus becomes (see chapter on Iron, Fig. 17) $a_{1g}^2\ a_{1u}^2\ e_{1u}^4\ e_{1g}^4\ a'_{1g}{}^2\ e_{2g}^4\ a''_{1g}{}^1$. The ready loss of this electron to gain the more stable 18-electron structure is thus not surprising. The diamagnetic cobaltocenium salts can be prepared directly from a cobalt(III) salt and cyclopentadienyl magnesium bromide. The cation is stable in concentrated nitric acid, but like ferrocene is susceptible to attack by nucleophiles.

Cobaltocene is thermally stable up to 250°, is insoluble in water and liquid ammonia but gives purple-red solutions in organic solvents. With carbon monoxide under moderate

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[80] R. F. Heck, *J. Org. Chem.* **28** (1963) 604.

[81] J. Kwiatek and J. K. Seyler, *J. Organomet. Chem.* **3** (1965) 421.

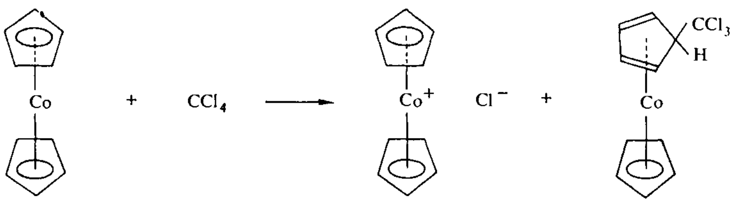
[82] R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.* **83** (1961) 1097; *ibid.* **82** (1960) 750.

[83] R. B. King, *Organometallic Syntheses*, Vol. 1, p. 70, Academic Press (1965).

[84] E. O. Fischer and R. Jira, *Z. Naturforsch.* **8b** (1953) 327.

[85] G. Wilkinson, *Naturwiss.* **42** (1955) 96.

pressures and temperatures the cyclopentadienylcobalt dicarbonyl, $(\pi\text{-}C_5H_5)Co(CO)_2$, is formed. One of the more interesting reactions is that with carbon tetrachloride in which the ionic cobaltocenium chloride is precipitated[86]



π-Cyclopentadienyl cobalt dicarbonyl. This is prepared either by the reaction of cyclopentadiene with dicobalt octacarbonyl[87] or by reaction of bis(π-cyclopentadienyl)cobalt with carbon monoxide under moderate pressures and temperatures[88]. It is a dark red oily liquid, b.p. 75°/22 mm, m.p. −22°. It is somewhat air-sensitive and best stored under nitrogen; it is soluble in organic solvents and has a dipole moment of $2{\cdot}87 \pm 0{\cdot}1 D$.

The carbonyl groups in $(\pi\text{-}C_5H_5)Co(CO)_2$ are readily displaced by a number of ligands (see Fig. 9). With iodine the di-iodide $(\pi\text{-}C_5H_5)Co(CO)I_2$ is formed from which the carbon monoxide can be displaced by ligands:

$$[(\pi\text{-}C_5H_5)Co(dipy)I]^+I^- \xleftarrow{\text{dipy}} (\pi\text{-}C_5H_5)Co(CO)I_2 \xrightarrow{Ph_3P} (\pi\text{-}C_5H_5)Co(PPh_3)I_2$$

When the cyclopentadienyl dicarbonyl is irradiated with ultraviolet light in hexane solution, a black crystalline diamagnetic trimer $[C_5H_5CoCO]_3$ is obtained[89]; this may exist in two isomeric forms.

Arene complexes of cobalt. The general route to metal arenes via aluminium, aluminium chloride, a hydrocarbon and the metal chloride produces the bis(hexamethylbenzene)-cobalt(I) cation when hexamethylbenzene and cobalt(II) chloride are used[90]:

$$3CoCl_2 + Al + 3AlCl_3 + 6Me_6C_6 \xrightarrow{100^\circ} 3[(Me_6C_6)_2Co][AlCl_4]$$

The yellow, paramagnetic (the PF_6^- salt has $\mu_{\text{eff}} = 2{\cdot}95$ B.M.) cation can be isolated as a variety of salts; it is isoelectronic with the corresponding iron(O) complex. In the absence of aluminium powder the above reaction produces the cobalt(II) cation

$$CoCl_2 + 2AlCl_3 + 2Me_6C_6 \rightarrow [Co(Me_6C_6)_2][AlCl_4]_2$$

which can be isolated as the paramagnetic ($\mu_{\text{eff}} = 1{\cdot}73$ B.M.) hexachloroplatinate. In neutral or strongly acidic solution this cation undergoes disproportionation:

$$2[Co^{II}(C_6Me_6)_2]^{2+} \rightarrow [Co^{I}(C_6Me_6)_2]^+ + [Co^{III}(C_6Me_6)_2]^{3+}$$

No salts of the cobalt(III) cation have, however, been isolated.

Reduction of the bis(hexamethylbenzene)cobalt(I) and cobalt(II) cations with sodium

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[86] S. Katz, J. F. Weiher and A. F. Voight, *J. Am. Chem. Soc.* **80** (1958) 6459.

[87] T. S. Piper, F. A. Cotton and G. Wilkinson, *J. Inorg. Nuclear Chem.* **1** (1955) 313.

[88] R. B. King, P. M. Treichel and F. G. A. Stone, *J. Am. Chem. Soc.* **83** (1961) 3600; *idem, Inorg. Syntheses,* **7** (1963) 112.

[89] R. B. King, *Inorg. Chem.* **5** (1966) 2227.

[90] E. O. Frischer and H. H. Lindner, *J. Organometallic Chem.* **1** (1964) 307.

in liquid ammonia at −78° yields bis(hexamethylbenzene)cobalt(0) as dark red-brown needles:

$$[Co(C_6Me_6)_2]PF_6 + Na \rightarrow Co(C_6Me_6)_2 + NaPF_6$$

This compound is very air-sensitive and soluble in non-polar solvents. In the solid state and in solution it is paramagnetic ($\mu_{eff} = 1{\cdot}86$ B.M.); this result is somewhat surprising as the compound has three electrons in excess of the inert gas structure. This compound is thus not satisfactorily described by the molecular orbital schemes which have been proposed for bis(benzene)chromium (see, for example, ref. 66). Further, it has a dipole moment of $1{\cdot}78 \pm 0{\cdot}07D$ in benzene and so this compound probably does not have the highly symmetric sandwich structure of bis(benzene)chromium.

An unusual trinuclear arene carbonyl cation $[(C_6H_6)_3Co_3(CO)_2]^+$ is obtained[91] when mercury tetracarbonylcobaltate(–I) is heated with benzene in the presence of aluminium chloride:

$$3C_6H_6 + 2Hg[Co(CO)_4]_2 \rightarrow [(C_6H_6)_3Co_3(CO)_2][Co(CO)_4] + 2Hg + 10CO$$

The structure of this cation is not known for certain, but is believed to contain a triangle of cobalt atoms, each cobalt being π-bonded to a benzene ring, with carbon monoxide molecules forming a trigonal bipyramid by being one above and one below the triangle of cobalt atoms.

3.4. COMPLEXES OF COBALT(II)

Cobalt(II) complexes are very numerous and a comprehensive coverage of those known up to about 1962 can be found in Gmelin[92]. Most of these complexes have a basically octahedral or tetrahedral structure having usually orange-pink or blue-violet colours respectively. Cobalt(II) forms more tetrahedral complexes than any other transition metal ion; the relatively low difference in crystal field stabilization energies between octahedral and tetrahedral cobalt(II) (d^7) complexes (as compared with that for other d^n configurations) is at least partly responsible for this[93]. The relationship between the colour of the complexes and their stereochemistry, e.g.

$$[Co(H_2O)_6]^{2+} \underset{H_2O}{\overset{Cl^-}{\rightleftharpoons}} [CoCl_4]^{2-}$$

pale pink intense blue
octahedral tetrahedral

is of relatively recent understanding. Historically important was Donnan and Bassett's paper[94] in 1902. These workers observed the migration of the blue colour in a cobalt(II) chloride solution to the anode during electrolysis. Their conclusion that the species responsible for the blue colour must carry a negative charge (and they correctly assumed $CoCl_4^{2-}$ as a possible species) and that conversely cationic divalent cobalt is pink was still the prevalent belief at the time of Sidgwick's writing[95] in 1950.

In the following account we shall consider the complexes according as to whether they contain cationic, neutral (uncharged) or anionic species for the purposes of describing their

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[91] P. Chini and R. Ercoli, *Gazz. Chim. Ital.* **88** (1958) 1170; E. O. Fischer and O. Beckert, *Angew. Chem.* **70** (1958) 744.

[92] *Gmelins Handbuch der Anorganischen Chemie*, System Number 58, B, Verlag Chemie (1963).

[93] A. B. Blake and F. A. Cotton, *Inorg. Chem.* **3** (1964) 5.

[94] F. G. Donnan and H. Bassett, *J. Chem. Soc.* **81** (1902) 939.

[95] N. V. Sidgwick, *The Chemical Elements and Their Compounds*, Vol. II, p. 1392, Oxford (1950).

preparation and chemistry; then on pages 1087–93, where the electronic structure of the complexes is considered, they will be classified according to their structural type.

Cationic Cobalt(II) Complexes

The hexa-aquo ion $[Co(H_2O)_6]^{2+}$. This pink ion is present in the crystal structures of $Co(ClO_4)_2.6H_2O$, $Co(NO_3)_2.6H_2O$, $CoSO_3.6H_2O$ and $CoSO_4.7H_2O$; it is also present in aqueous solutions of cobalt(II) salts of non-complexing anions, together with smaller amounts of the tetrahedral $[Co(H_2O)_4]^{2+}$ ion[96]. Solutions of the hexa-aquo ion are barely acidic, the carbonate $CoCO_3$ being precipitated by alkali metal carbonate solutions as long as a pressure of carbon dioxide is maintained over the solution. The redox properties of this ion have been considered in Section 3.1.

Other $[CoL_x]^{2+}$ *cations.* Many cobalt(II) salts react with ammonia to form ammoniates, six molecules of ammonia usually combining with the salt. Whilst these ammines can be prepared in aqueous solution in the presence of excess of ammonia they are readily oxidized in this medium; the $[Co(NH_3)_6]^{2+}$ ion is decomposed by pure water. The crystal structures[6] of $CoX_2.6NH_3$ ($X = Cl$, Br, I, ClO_4, BF_4, PF_6 and SO_3F) possess cobalt atoms octahedrally surrounded by ammonia molecules in a K_2PtCl_6 structure. There is one example of the tetrahedral cation $[Co(NH_3)_4]^{2+}$—that in the perrhenate $[Co(NH_3)_4](ReO_4)_2$.

Hexacoordinate species are formed in many reactions between cobalt(II) salts and donor solvents and also in the disproportionation reactions of dicobalt octacarbonyl:

$$CoCl_2+6N_2H_4 \rightarrow [Co(N_2H_4)_6]^{2+}+2Cl^-$$
$$CoI_2+6Me_2SO \rightarrow [Co(Me_2SO)_6]^{2+}+2I^-$$
$$3Co_2(CO)_8+12MeNH_2 \rightarrow 2[Co(MeNH_2)_6][Co(CO)_4]_2+8CO$$

In some solvents and with some cobalt(II) salts autocomplex formation occurs, e.g.[97]

$$2CoCl_2+6Me_2SO \rightarrow [Co(Me_2SO)_6]^{2+}+[CoCl_4]^{2-}$$
$$2CoI_2+6MeCN \rightarrow [Co(MeCN)_6]^{2+}+[CoI_4]^{2-}$$

Bidentate ligands frequently form octahedral cations, e.g. $[Co(dipy)_3]^{2+}$, $[Co(phen)_3]^{2+}$, $[Co(en)_3]^{2+}$ both in aqueous solution and by disproportionation reactions with cobalt carbonyls. Some of these ligands, however, give square planar complexes, e.g. $[Co(en)_2](AgI_2)_2$[98], $[Co(MeSCH_2CH_2SMe)_2](ClO_4)_2$[99], $[CoA_2]^{2+}$ (A = dimethyl-*o*-methylthiophenylarsine)[100] and $[Co(diars)_2](ClO_4)_2$[101].

Tetrahedral cations are also formed by some unidentate ligands. Cobalt is tetrahedrally coordinated by oxygen in $[Co(Ph_3AsO)_4]I_2$ and $[Co(HMPA)_4](ClO_4)_2$ (HMPA = hexamethylphosphoramide); these compounds are readily prepared as blue solids by reaction of the cobalt salt with excess of the ligand. Thiourea forms $[Co(tu)_4](ClO_4)_2$ containing tetrahedral cations in which the thiourea molecules are bonded to cobalt via sulphur. The benzimidazole complex $[Co(BZDH)_4]^{2+}$ is a further example of a tetrahedral cation with a nitrogen donor ligand.

A few five-coordinate cations are formed with the quadridentate ligand $N(CH_2CH_2NMe_2)_3$ (trenMe); these are of the type [Co(trenMe)X]X (X = Cl, Br, I). These

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[96] T. J. Swift, *Inorg. Chem.* 3 (1964) 526.
[97] V. Gutmann, *Coordination Chem. Revs.* 2 (1967) 239.
[98] A. B. P. Lever, J. Lewis and R. S. Nyholm, *J. Chem. Soc.* (1963) 2552.
[99] F. A. Cotton and D. L. Weaver, *J. Am. Chem. Soc.* 87 (1965) 4189.
[100] B. Chiswell and S. E. Livingstone, *J. Chem. Soc.* (1960) 97.
[101] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.* (1959) 338.

compounds are high spin ($\mu_{eff} \sim 4{\cdot}5$ B.M.) and are uni-univalent electrolytes in nitrobenzene. They have the trigonal bipyramidal structure; a crystal field energy level diagram has been devised for cobalt in this stereochemistry and the spectral properties of these compounds have been discussed[102]. The methyl isonitrile complexes are interesting in that two compounds of formula $Co(CNMe)_5(ClO_4)_2$ can be obtained. The yellow, diamagnetic form contains the dimeric cation $[(MeNC)_5Co–Co(CNMe)_5]^{4+}$ being isoelectronic and isostructural with $Mn_2(CO)_{10}$. The blue form is paramagnetic with one unpaired electron and presumably has a five-coordinate structure.

Neutral Cobalt(II) Complexes

Complexes with nitrogen, phosphorus and arsenic ligands. The cobalt(II) halides and other simple salts form a very large number of complexes with ligands having these donor atoms. Complexes can usually be prepared by direct reaction of an aqueous or ethanolic solution of the cobalt salt with the ligand and are generally of the types CoX_2L, CoX_2L_2 and CoX_2L_4 where X = univalent anion and L = ligand. Whilst the pink complexes are frequently octahedral and the blue ones tetrahedral the stereochemistry cannot be assumed from the colour alone since there are several well-documented contradictory examples. It should be noted also here that the words octahedral and tetrahedral imply roughly these stereochemistries in these discussions as there are few if any complexes with symmetries high enough to justify these words in their true sense.

Nitrogen donors form by far the largest number of complexes of this group and it will be possible to mention but a few examples only. Because of the small stability difference between the octahedral and tetrahedral complexes, it is common to find both stereochemistries with a given cobalt salt and ligand and indeed to sometimes find the two complexes in equilibrium. One of the most studied series of complexes is that of the compounds $CoX_2(py)_2$[103]. The chloride complex $CoCl_2(py)_2$ can exist at room temperature as a violet (stable) form and as a blue (unstable) form. The violet form is octahedral with chlorine bridges[104] (it has cobalt surrounded by four chlorines at 2·49 Å and two nitrogens at 2·14 Å) and the blue form tetrahedral and monomeric. The bromide and iodide and cyanate form only blue tetrahedral $CoX_2(py)_2$ while the thiocyanate and selenocyanate form only purple-red octahedral complexes $Co(NCS)_2(py)_2$ and $Co(NCSe)_2(py)_2$. All of these complexes, however, give tetrahedral species when dissolved in organic solvents such as nitrobenzene. The addition of more pyridine to such solutions leads to a tetrahedral–octahedral equilibrium:

$$CoX_2(py)_2 + 2py \rightleftharpoons CoX_2(py)_4$$

and such systems enable the study of the importance of electronic and steric effects in determining these stereochemistries[105]. In general the more readily the σ-pair of electrons on the ligand is polarizable, the fewer the molecules of the ligand are required to effect electroneutrality. So that for complexes with a given nitrogen ligand and various halide ions, a change from octahedral to tetrahedral stereochemistry sometimes occurs in going from the chloride to the iodide. This occurs with pyridine as we have seen already and with

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[102] M. Ciampolini, N. Nardi and G. Speroni, *Coordination Chem. Revs.* **1** (1966) 222.

[103] N. S. Gill, R. S. Nyholm, G. A. Barclay, T. I. Christie and P. J. Pauling, *J. Inorg. Nuclear Chem.* **18** (1961) 88.

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ligands such as pyrazine and substituted pyrazines[106]. Steric effects are observed when the ligand has alkyl groups which would interfere with other groups in an octahedral structure. Thus pyrazine forms octahedral $CoI_2(pyz)_2$, but 2,6-dimethylpyrazine forms tetrahedral $CoI_2(2,6\text{-}dmp)_2$; also hydrazine forms octahedral $CoCl_2(N_2H_4)_2$ with hydrazine bridges while unsymmetrical dimethylhydrazine forms only tetrahedral $CoCl_2(Me_2NNH_2)_2$[107].

For many nitrogen ligands both tetrahedral CoX_2L_2 and octahedral CoX_2L_4 complexes can be prepared by using the appropriate metal-to-ligand ratio. With phosphines and arsines, however, a preference for tetrahedral stereochemistry is found even in excess of the ligand, examples being[108] $CoX_2(EtPH_2)_2$, $CoX_2(Et_3P)_2$ and $CoX_2(Et_3As)_2$ ($X = Cl$, Br, I). Exceptions, however, are the green complexes with diethylphosphine $CoX_2(Et_2PH)_4$ which have magnetic moments around 2·0 B.M. and may be spin-paired octahedral. The existence of a high spin–low spin equilibrium has been established in solutions of $Co(PEt_3)_2(NCS)_2$[109]; the high spin form is monomeric and tetrahedral while the low spin form is dimeric with pentacoordination around the cobalt.

Neutral tetrahedral complexes in which nitrogen is the only donor atom can be prepared from heterocyclic nitrogen bases such as pyrazole, imidazole and benzimidazole. Whilst in neutral solution these ligands give the usual variety of octahedral and tetrahedral complexes, in slightly alkaline solution a proton is removed from a ligand atom and compounds such as purple bis(pyrazolato)cobalt(II) $Co(C_3H_3N_2)_2$ precipitate. These compounds are believed to possess polymeric structures with cobalt tetrahedrally surrounded by four nitrogen atoms from two bidentate heterocyclic anions.

Planar complexes are formed by the tetradentate ligands bis(salicylaldehydeethylenediminato) ion[110] and the porphyrins. Cobalt phthalocyanine[111] is formed when etched cobalt metal is heated with phthalonitrile; it can be sublimed to dark blue needles which have a reddish-purple lustre and a magnetic moment of 2·73 B.M. at room temperature.

Some ligands give rise to five-coordinate cobalt(II) complexes. Schiff bases of formula $ClC_6H_3(OH)CH{:}NCH_2CH_2NEt_2$ (Cl–Salen–NEt_2) give rise, among other complexes, to the five-coordinate complex (5-Cl–Salen–$NEt_2)_2Co$ which has a distorted square pyramidal structure[112]. Bis(*N*-methylsalicylaldiminato)-cobalt(II) forms a dimer[113] in which each cobalt is surrounded by a distorted trigonal bipyramid of ligand atoms. The tridentate ligand $HN(CH_2CH_2NH_2)_2$ (den) forms five-coordinate complexes[102] $[Co(den)X_2]$ ($X = Cl$, Br, I or NCS); these are spin free and are non-conductors in nitrobenzene.

Complexes with oxygen and sulphur ligands. Cobalt(II) salts form a large number of complexes with alcohols, thioalcohols, ethers, ketones and thio compounds[92]; we shall consider but a few of these complexes here. As with nitrogen donors, the stereochemistry of the complexes frequently varies with only minor changes in the ligands. Ethylenethiourea, for example, forms tetrahedral complexes[114] with cobalt(II) halides $Co(etu)_2X_2$; the bidentate ligand dimethylmercaptoethane, however, forms octahedral $Co(MeSCH_2CH_2SMe)_2X_2$ complexes[115].

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[107] D. Nicholls, M. Rowley and R. Swindells, *J. Chem. Soc.* (*A*) (1966) 950.
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The cobalt(II) nitrate complexes of phosphine oxide and arsine oxide ligands are interesting because at first sight the compounds $Co(R_3MO)_2(NO_3)_2$ appear to be tetrahedral on the basis of their magnetic and spectroscopic data. The molecular structure of $Co(Me_3PO)_2(NO_3)_2$ has been determined[116] by a single crystal X-ray study and shown to contain hexacoordinate cobalt atoms with each nitrate ion being bidentate. The arrangement of the six oxygen atoms around the cobalt is, however, a highly irregular one, the molecule having no true symmetry elements whatsoever.

The 1,3-diketones form well-studied neutral crystalline derivatives with cobalt(II) salts[117]. Cobalt(II) acetylacetonate $Co(acac)_2.2H_2O$ is readily precipitated as orange needles by the addition of an alkaline solution of acetylacetone to a cobalt(II) chloride solution. This dihydrate has the *trans*-octahedral structure[118]. When dehydrated *in vacuo* at 58° the purple anhydrous compound $Co(acac)_2$ is obtained; other anhydrous β-diketonates are prepared similarly. In the solid state $Co(acac)_2$ is tetrameric[119]; the metal atoms are in a pseudo-octahedral environment, there being bridging and non-bridging acetylacetonate units present in the structure. In solution too oligomers are found, the molecular weight being a function of concentration and solvent. In coordinating solvents, the solvent fills the two available sites around the four-coordinate $Co(acac)_2$. The dipivaloylmethane analogue $Co[CH(COCMe_3)_2]$ has a distorted tetrahedral arrangement of oxygen atoms around cobalt[120], thus explaining the differences observed in its electronic spectrum[121] as compared with other tetrahedral cobalt(II) complexes.

The most interesting complexes with bidentate sulphur donors are those with the 1,2-dithiols and related types[122]. These complexes are of neutral and anionic types and present problems of oxidation state assignment; for simplicity they will all be considered here. The neutral complex $[CoS_4C_4(CF_3)_4]$ is obtained as shiny black plates in the reaction of dicobalt octacarbonyl with bis(perfluoromethyl)dithietene, $S_2C_2(CF_3)_2$. It is diamagnetic and dimeric in solution. The crystal structure determination[123] has verified the dimeric structure in the solid; the coordination around cobalt is best described as square pyramidal in which the four basal sulphur atoms of each unit are in a plane from which the cobalt atom is displaced by 0·37 Å towards one (apical) sulphur atom of the other unit. The average Co–S(basal) distance is $2{\cdot}16 \pm 0{\cdot}02$ Å and the Co–S(apical) distance 2·38 Å. By reaction of cobalt(II) salts in aqueous or alcoholic solutions with the sodium salts $Na_2S_2C_2(CN)_2$ or $Na_2S_2C_2H_2$, the anionic species $[CoS_4C_4(CN)_4]^{2-}$ and $[CoS_4C_4H_4]^-$ are obtained, and the sodium salts of benzene-1,2-dithiol (and its methyl substituted derivatives) and tetrachlorobenzene-1,2-dithiol give the anions $[Co(S_2C_6H_4)]^-$ and $[Co(S_2C_6Cl_4)_2]^-$. Many of these apparently monoanionic species are in fact dimeric dianions, i.e. $[Co\text{–}S_4]_2^{2-}$, and such complexes as are dimeric in the solid state and in non-coordinating solvents are diamagnetic. In dimethyl sulphoxide the tetrachlorobenzene and dicyanodithiolene complexes have magnetic moments of 2·37 and 2·81 B.M. respectively and this may indicate dissociation of the dimers into monomers having spin-triplet ground states. The arene-dithiolene complexes apart from the tetrachlorobenzene dithiolate are high spin ($S = 1$)

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in the solid state and in solution. Oxidation of the dimeric dianions gives the paramagnetic monoanions $[Co–S_4]_2^-$ and the diamagnetic neutral complexes $[Co–S_4]_2^0$. The ease of interconversion of these various species is illustrated by the dimeric species $[CoS_4C_4(CF_3)_4]_2$, which under polarographic study[124] reveals two reversible one-electron reduction waves and one reversible two-electron reduction wave corresponding to the processes:

$$[MS_4]_2 \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [MS_4]_2^{1-} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [MS_4]_2^{2-} \underset{-2e^-}{\overset{+2e^-}{\rightleftharpoons}} [MS_4]^{2-}$$

Anionic Cobalt(II) Complexes

Complex halides. The complex chlorides, bromides and iodides of formula M_2CoX_4 are readily prepared by evaporation of aqueous solutions containing stoichiometric proportions of the alkali metal and cobalt(II) chlorides. In the case of organic base cations, the reaction of the organic base hydrohalides with cobalt(II) halide hexahydrates in ethanol leads to precipitation of the tetrahalocobaltates; the green iodide $[Et_4N]_2CoI_4$ is best prepared in glacial acetic acid[125]. When prepared in aqueous solution the salts are sometimes isolated as hydrates, e.g. $(NH_4)_2CoCl_4.2H_2O$. Complex fluorides are less well characterized, but compounds such as $(NH_4)_2CoF_4.2H_2O$ and K_2CoF_4 can be crystallized.

The $CoCl_4^{2-}$ ion is tetrahedral; the tetrahedron of chloride ions is not perfectly regular, however, because although the cobalt–chlorine bond distances are all equal, there is angular distortion. In Cs_2CoCl_4[126] the angles are 107°20′, 108°50′, 109°20′ and 116°20′ while in $[Me_4N]_2CoCl_4$[127] they are 108°18′, 109°6′, 110°24′ and 111°42′. Caesium also forms Cs_2CoCl_5, which contains the distorted tetrahedral $CoCl_4^{2-}$ ion[128].

Solutions of cobalt(II) chloride in hydrochloric acid contain a variety of chloro complexes as illustrated by the equations:

$$[Co(H_2O)_6]^{2+} + Cl^- \rightleftharpoons [CoCl(H_2O)_5]^+ + H_2O$$
$$[CoCl(H_2O)_5]^+ + Cl^- \rightleftharpoons [CoCl_2(H_2O)_2] + 3H_2O$$
$$[CoCl_2(H_2O)_2] + Cl^- \rightleftharpoons [CoCl_3(H_2O)]^- + H_2O$$
$$[CoCl_3(H_2O)]^- + Cl^- \rightleftharpoons [CoCl_4]^{2-} + H_2O$$

In dilute (3 M) hydrochloric acid, $[Co(H_2O)_6]^{2+}$ and $[CoCl(H_2O)_5]^+$ are the principally occurring species whilst above 8 M acid the anionic species $[CoCl_3(H_2O)]^-$ and $CoCl_4^{2-}$ predominate. In concentrated acid electronic spectral studies[129] indicate that $[CoCl_3(H_2O)]^-$ is the principal species whilst n.m.r. spectra[130] of ^{17}O and ^{35}Cl in such solutions indicate $[CoCl_4]^{2-}$ to predominate. In $ZnCl_2$–KCl melts, cobalt(II) chloride is present solely as $CoCl_4^{2-}$, but in $ZnCl_2$–$AlCl_3$ melts there is an octahedral–tetrahedral equilibrium, higher temperatures favouring the tetrahedral species[131].

Whilst octahedral complex halides are rare for cobalt with chloride bromide and iodide ions (except in melts), the red fluoride $KCoF_3$ crystallizes with the cubic perovskite structure[132] in which each cobalt is surrounded octahedrally by six fluoride ions; a small

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tetragonal distortion occurs at 114°K. In Ba_2CoF_6[133] the CoF_6 octahedron is tetragonally elongated.

Complex cyanides. When cobalt(II) cyanide is dissolved in aqueous potassium cyanide, an olive-green solution is formed which is rapidly oxidized by air. This solution has been the subject of a great deal of study[134]; it has a Co : CN^- ratio of 1 : 5 and is paramagnetic with a moment of 1·72 B.M. per cobalt. Upon the addition of ethanol to this solution, a violet salt of probable formula[134] $K_6[Co_2(CN)_{10}].4H_2O$ is precipitated; this can be dehydrated over phosphorus pentoxide *in vacuo* at room temperature. This violet salt is diamagnetic and shows three strong bands in the cyanide stretching region[135] at 2133, 2090 and 2079 cm^{-1} and is believed to have a cobalt–cobalt bonded structure $[(NC)_5Co{-}Co(CN)_5]^{6-}$ analogous to $Mn_2(CO)_{10}$.

No monomeric anion can be isolated from the green solution. Interpretation of the e.s.r.[136] and ligand field spectra[137] have been based on C_{4v} symmetry for the anion. The most likely structure is the square pyramidal one for the $[Co(CN)_5]^{3-}$ ion but some authors[138] prefer the six-coordinate structure $[Co(CN)_5(H_2O)]^{3-}$. The solutions are difficult to study because not only do they oxidize readily, but they age as well, the solutions being "fresh" for a matter of seconds only. The fresh solutions absorb molecular hydrogen with the formation of a hydride complex which cannot be isolated, but which on the basis of proton magnetic resonance and ultraviolet spectra is believed[135, 139] to be $[Co(CN)_5H]^{3-}$. This colourless complex undergoes only slow decomposition in the absence of oxygen at room temperature. The oxidation probably occurs via the scheme[140]:

$$[Co(CN)_5H]^{3-} \xrightarrow{O_2} [Co(CN)_5OOH]^{3-} \xrightarrow{H^+} [Co(CN)_5(H_2O)]^{2-}$$

The formation of this hydride complex is a convenient way to activate molecular hydrogen for a variety of reduction processes. Thus cobalt(II) cyanide solutions in potassium cyanide act as homogenous catalysts for the hydrogenation of unsaturated organic compounds[141, 142]; styrene is reduced to ethylbenzene, 1,3-cyclohexadiene to cyclohexane, benzil to benzoin and nitrobenzene to aniline.

Treatment of the green $K_3[Co(CN)_5]$ solution with sulphur dioxide yields a red solution from which methanol precipitates the diamagnetic $K_6[(CN)_5CoSO_2Co(CN)_5].4H_2O$[143]. Similar insertion reactions are observed with $SnCl_2$, C_2F_4 and C_2H_2. Whilst slow oxidation of cobalt(II) cyanide complexes gives the $[Co(CN)_5(H_2O)]^{2-}$ ion, the passage of a rapid stream of oxygen through $[Co(CN)_5]^{3-}$ species at 0° yields[144] largely the dimer $[CN_5Co^{III}OOCo^{III}(CN)_5]^{6-}$; the potassium salt of this peroxo anion can be isolated as a monohydrate. This diamagnetic peroxo species can be oxidized by bromine in alkaline solution to the red paramagnetic ion $[(CN)_5CoOOCo(CN)_5]^{5-}$ which contains cobalt in the formal oxidation states +3 and +4.

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Complex thiocyanates. These resemble the complex halides in being blue tetrahedral complexes. The alkali metal salts crystallize as hydrates, e.g. $K_2[Co(NCS)_4].4H_2O$ and $Na_2[Co(NCS)_4].8H_2O$; they give blue solutions in many organic solvents but turn pink with decomposition in dilute aqueous solution. The extraction of $(NH_4)_2[Co(NCS)_4]$ from aqueous solution by amyl alcohol and ether is the basis of a colorimetric method for estimating cobalt[145]. The mercury salt $Hg[Co(NCS)_4]$ is precipitated almost quantitatively by the addition of mercury(II) chloride to a solution containing cobalt(II) and excess thiocyanate ions. This salt finds uses in the gravimetric estimation of cobalt[146] and as a calibrant for magnetic susceptibility measurements by the Gouy method. The gram susceptibility is[57] $16{\cdot}44 \pm 0{\cdot}08$ cg mole^{-1} at 293°K.

Similar tetrahedral species, i.e. $[Co(NCO)_4]^{2-}$ and $[Co(NCSe)_4]^{2-}$, are formed by cyanate and selenocyanate ions.

Complex nitrates and nitrites. Tetranitratocobaltates(II) are formed by reaction of cobalt(II) salts with tetramethylammonium nitrate in nitromethane[147] or with methyltriphenylarsonium iodide and silver nitrate in acetonitrile[148]. Pale red alkali metal salts $K_2Co(NO_3)_4$ and $Na_2Co(NO_3)_4$ are rather surprisingly prepared in the reactions of the hexanitrocobaltates(III) with dinitrogen pentoxide[149]. These salts of the $[Co(NO_3)_4]^{2-}$ ion are hygroscopic; their magnetic and spectroscopic properties resemble those of tetrahedral cobalt(II) complexes. The X-ray structure determination on the tetraphenylarsonium salt[150] shows that the cobalt is eight-coordinate with bidentate nitrate ions, the eight oxygen atoms lying at the vertices of an irregular dodecahedron. If the nitrate ions are regarded as occupying only a single coordination site, then the coordination around cobalt does approximate to tetrahedral.

The cubic hexanitrocobaltates(II), $K_2Ba[Co(NO_2)_6]$ and $K_2Pb[Co(NO_2)_6]$ are examples of low spin octahedral complexes[151]; their room temperature magnetic moments are 1·88 and 1·81 B.M. respectively.

Other anionic complexes. Other unidentate anions such as OH^-, N_3^-, acetate[63] and trifluoroacetate[152] form tetrahedral complexes with cobalt(II). Formato complexes appear to be of the type $[Co(OCOH)_6]^{4-}$ and oxalato complexes $[Co(OX)_2]^{2-}$; like the carbonato salts, e.g. $K_2[Co(CO_3)_2].4H_2O$, they are decomposed in water.

Spectral and Magnetic Properties of Cobalt(II) Complexes

The Co^{2+} ion has the $3d^7$ electronic configuration which in octahedral fields may give rise to either high spin $t_{2g}^5\ e_g^2$, or low spin $t_{2g}^6\ e_g^1$, complexes. Rather high values of the ligand field splitting parameter ($Dq > 1500$ cm^{-1})[153] are in fact required to cause spin pairing with cobalt(II) so that a few complexes only (with the strongest field ligands) are encountered. Tetrahedral complexes are high spin with the $e^4t_2^3$ configuration.

High spin octahedral complexes. The ground term arising from the $t_{2g}^5\ e_g^2$ configuration

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[145] N. H. Furman (Ed.), *Standard Methods of Chemical Analysis*, 6th edition, Vol. I, p. 389, D. Van Nostrand (1962).

[146] A. I. Vogel, *Quantitative Inorganic Analysis*, 3rd edition, p. 529, Longmans (1962).

[147] F. A. Cotton and T. G. Dunne, *J. Am. Chem. Soc.* **84** (1962) 2013.

[148] D. K. Straub, R. S. Drago and J. T. Donoghue, *Inorg. Chem.* **1** (1962) 848.

[149] R. J. Fereday and D. Sutton, *Chem. Communs.* (1966) 510.

[150] F. A. Cotton and J. G. Bergman, *Inorg. Chem.* **5** (1966) 1208.

[151] J. G. Schmidt, W. S. Brey and R. C. Stoufer, *Inorg. Chem.* **6** (1967) 268.

[152] J. G. Bergman and F. A. Cotton, *Inorg. Chem.* **5** (1966) 1420.

[153] C. J. Ballhausen, *Introduction to Ligand Field Theory*, p. 255, McGraw-Hill (1962).

in an octahedral field is ${}^4T_{1g}$; the other quartet terms arising are shown in Fig. 11 together with the ${}^2E_g$ term which at the strongest fields becomes the ground term (corresponding to $t_{2g}^6\ e_g^1$). The more complete energy level diagram of Tanabe and Sugano[154] can be found in the spectroscopic texts[155, 156]. The most complete calculation of the energy levels with respect to the ligand field coulombic (Dq), spin-orbit (λ) and electron correlation parameters (Racah B and C) for both octahedral and tetrahedral cobalt(II) is that of Liehr[157]; the results are presented graphically in Liehr's paper and elsewhere[158]. The interpretation of the spectra of six-coordinate cobalt(II) compounds is, however, still a matter of some difficulty. Some typical spectra are presented in Table 7 together with probable assignments.

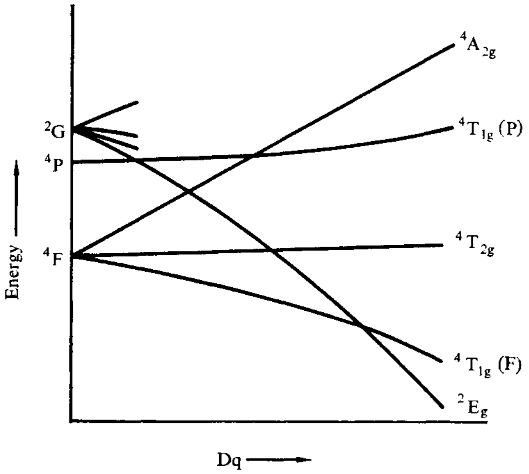

FIG. 11. Partial energy level diagram for the Co^{2+} ion in an octahedral field.

TABLE 7. ELECTRONIC SPECTRA (cm^{-1}) OF HIGH SPIN SIX-COORDINATE COBALT(II) COMPOUNDS*

Compound	${}^4T_{1g} \rightarrow {}^4T_{2g}$	${}^4T_{1g} \rightarrow {}^4A_{2g}$	${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$	Dq	B
$[Co(H_2O)_6]^{2+}$[a]	8100	16,000	19,400	920	825
$[Co(DMSO)_6]^{2+}$[a]	7410	14,600	18,700	848	824
$[Co(PyO)_6]^{2+}$[a]	9090		19,470	1020	766
$[Co(NH_3)_6]^{2+}$[a]	9000		21,100	1020	885
$[Co(bipy)_3]^{2+}$[b]	11,300		22,000	1267	791
$KCoF_3$[c]	7,340	15,010	19,490	770	880
$CoCl_2$[c]	6600	13,300	17,250	690	780
$CoBr_2$[c]	6200	12,000	16,800	640	760
Co^{2+} in MgO[d]	8390		20,280	927	945

* Centres of gravity of composite bands quoted.

[a] A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier (1968).
[b] R. A. Palmer and T. S. Piper, *Inorg. Chem.* **5** (1966) 864.
[c] J. Ferguson, D. L. Wood and K. Knox, *J. Chem. Phys.* **39** (1963) 881.
[d] R. Pappalardo, D. L. Wood and R. C. Linares, *J. Chem. Phys.* **35** (1961) 2041.

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[154] Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, **9** (1954) 753, 766.
[155] A. B. P. Lever, *Inorganic Electronic Spectroscopy*, p. 112, Elsevier (1968).
[156] B. N. Figgis, *Introduction to Ligand Fields*, p. 165, Interscience (1966).
[157] A. D. Liehr, *J. Phys. Chem.* **67** (1963) 1314.
[158] R. L. Carlin, *Transition Metal Chemistry*, **1** (1965) 1.

In general it can be seen that the spectra consist of a band in the near infrared which is assigned to the lowest energy transition $^4T_{1g} \rightarrow {}^4T_{2g}$ and a band in the visible near 20,000 cm^{-1} which is assigned to the $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ transition. The $^4T_{1g} \rightarrow {}^4A_{2g}$ transition is frequently not observed. Whilst the other two transitions have the normal intensities of octahedral spin-allowed Laporte forbidden bands, this latter transition involves a two-electron process for strong fields (the $^4A_{2g}$ state is derived from a $t_{2g}{}^3\,e_g{}^4$ configuration while the $^4T^1{}_g(F)$ state is derived largely from the $t_{2g}{}^5\,e_g{}^2$ configuration) and is expected to be very much weaker. The visible band frequently has a shoulder or fine structure to it; this has been sometimes attributed to the $^4T_{1g} \rightarrow {}^4A_{2g}$ transition but it may alternatively have its origin in spin–orbit coupling, vibrational broadening, low symmetry components to the ligand field or transitions to doublet states. A typical spectrum showing this asymmetric band is that of anhydrous cobalt(II) chloride[159] shown in Fig. 12. In this case the shoulder and peaks on the high energy side of the $^4T_{1g}(P)$ level are assigned to spin forbidden transitions to doublet states. It is interesting to note that cobalt(II) chloride is blue at room temperature and yet contains octahedrally surrounded cobalt(II)—a simple illustration of the fact that colour is not an infallible guide to stereochemistry.

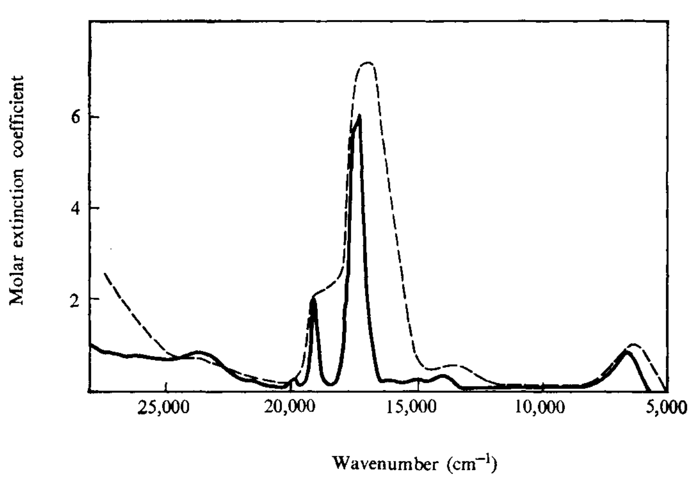

FIG. 12. Electronic spectrum of $CoCl_2$ at room temperature (broken line) and at −253°K (full line).

The magnetic properties of high spin octahedral cobalt(II) complexes are governed by the orbitally degenerate ground term $^4T_{1g}$; this provides an orbital contribution to the magnetic moment so that room temperature moments are experimentally found to be in the range 4·7 – 5·2 B.M. The spin–orbit coupling constant for the Co^{2+} ion is $\lambda = -178$ cm^{-1}. The magnetic moments of some high spin complexes are given in Table 8 together with values of the Curie–Weiss constant θ. As expected, the magnetic moments of these complexes vary considerably with temperature. Low spin octahedral cobalt(II) complexes have the ^2E_g ground term arising from the $t_{2g}{}^6\,e_g{}^1$ electronic configuration. The magnetic moment of these compounds is expected to be invariant with temperature and to be given by[57] $1{\cdot}73(1-2\lambda/10Dq)$. In practice the moments for complexes such as those containing $[Co(NO_2)_6]^{4-}$ are in the range 1·70 – 1·85 B.M.

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[159] J. Ferguson, D. L. Wood and K. Knox, *J. Chem. Phys.* **39** (1963) 881.

TABLE 8. MAGNETIC PROPERTIES OF SOME HIGH SPIN COBALT(II) COMPLEXES

Complex	μ_{eff} (B.M.)	T, °K	θ°
Octahedral:			
$CoCl_2.6H_2O$[a]	4·82	293	30
$Co(NH_3)_6Cl_2$[b]	5·21	293	40
$Co(NO_3)_2.6H_2O$[c]	4·84	300	25
$Rb_2Co(SO_4)_2.6H_2O$[d]	4·91	298	30
$Co(OCOCH_3)_2$[e]	5·13	293	34
$Co(N_2H_4)_2Cl_2$[f]	4·79	298	-9
$Co(phen)_2(ClO_4)_2$[g]	4·70	297	11
Tetrahedral:			
$[Ph_4As]_2CoCl_4$[h]	4·73	295	8
$[pyH]_2CoBr_4$[h]	4·80	298	7
$CoCl_2(quin)_2$[i]	4·63	297	12
$[Co(Ph_3PO)_4](ClO_4)_2$[i]	4·67	300	6
$[Ph_4As]_2Co(N_3)_4$[j]	4·39	299	6
$K_2[Co(NCO)_4]$[j]	4·26	300	8
$[Me_4N]_2Co(NCSe)_4$[k]	4·45	295	8

[a] R. B. Flippen and S. A. Friedberg, *J. Appl. Phys.* **31** (1960) 3385.

[b] R. B. Janes, *Phys. Rev.* **48** (1935) 78.

[c] A. Lallemand, *Ann. Phys. (Paris)*, **3** (1935) 97.

[d] B. C. Guha, *Proc. Roy. Soc.* A. **206** (1951) 353.

[e] S. S. Bhatnagar, M. L. Khanna and M. B. Nevgi, *Phil. Mag.* **25** (1938) 234.

[f] S. Datta, *Phil. Mag.* **17** (1934) 585.

[g] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.* (1959) 338.

[h] F. A. Cotton and R. H. Holm, *J. Chem. Phys.* **31** (1959) 788.

[i] *Ibid.* **32** (1960) 1168.

[j] F. A. Cotton and M. Goodgame, *J. Am. Chem. Soc.* **83** (1961) 1777.

[k] F. A. Cotton, D. M. L. Goodgame, M. Goodgame and T. E. Haas, *Inorg. Chem.* **1** (1961) 565.

Tetrahedral complexes. Again three quartet–quartet transitions are possible, but the ordering of the levels is now inverted as compared with the octahedral case; a simple ordering of the levels is shown in Fig. 13.

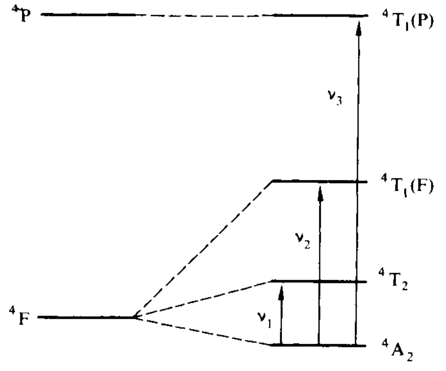

FIG. 13. Energy levels for tetrahedral cobalt(II) complexes.

TABLE 9. SOME SPECTRA (cm^{-1}) OF TETRAHEDRAL COBALT(II) COMPLEXES

Complex	$^4A_2 \rightarrow {}^4T_1(F)$	$^4A_2 \rightarrow {}^4T_1(P)$	Dq	B
$CoCl_4^{2-}$[a]	5460	14,700	312	710
$CoBr_4^{2-}$[a]	4980	14,000	285	695
CoI_4^{2-}[a]	4600	13,250	265	665
$[Co(OH)_4]^{2-}$[a]	7300	16,600	423	747
$[Co(N_3)_4]^{2-}$[b]	6750	14,900	392	658
$[Co(NCO)_4]^{2-}$[b]	7150	16,100	415	720
$[Co(NCS)_4]^{2-}$[c]	7780	16,250	455	691
$[Co(Ph_3PO)_4]^{2+}$[a]	6240	16,300	368	787
$[Co(Ph_3AsO)_4]^{2+}$[d]	6450	16,000	372	754
$[Co(etu)_4]^{2+}$[e]	6480	14,600	378	651
$[Co(tu)_4]^{2+}$[f]	7200	14,500	425	600

etu = ethylenethiourea; tu = thiourea.

[a] F. A. Cotton, D. M. L. Goodgame and M. Goodgame, *J. Am. Chem. Soc.* **83** (1961) 4690.

[b] F. A. Cotton and M. Goodgame, *J. Am. Chem. Soc.* **83** (1961) 1777.

[c] F. A. Cotton, D. M. L. Goodgame, M. Goodgame and A. Sacco, *J. Am. Chem. Soc.* **83** (1961) 4157.

[d] M. Goodgame, D. M. L. Goodgame and F. A. Cotton, *Inorg. Chem.* **1** (1962) 239.

[e] R. Pappalardo, D. L. Wood and R. C. Linares, *J. Chem. Phys.* **35** (1961) 2041.

[f] F. A. Cotton, O. D. Faut and J. T. Mague, *Inorg. Chem.* **3** (1964) 17.

The lowest energy band ν_1 should give Dq directly since $E(^4T_2)-E(^4A_2)=10Dq$. This band is not often observed, however, since it is weak, the transition being forbidden for electric dipole absorption in pure tetrahedral symmetry; also it lies in the infrared (3000–5000 cm^{-1} region) where it is frequently overlapped by vibrational bands. The $\nu_2[^4A_2 \rightarrow {}^4T_1(F)]$ and $\nu_3[^4A_2 \rightarrow {}^4T_1(P)]$ bands lie in the near infrared and visible regions respectively. They differ most significantly from the octahedral absorptions in their much greater intensities, thus allowing a ready distinction between the two stereochemistries; the molar extinction coefficients are in the range $10–10^2$ for ν_2 and $10^2-2\times10^3$ for ν_3. Thus tetrahedral complexes are frequently an intensely blue colour. Some typical spectra are listed in Table 9 together with derived values[154] for the paramets Dq and B. Both the ν_2 and ν_3 bands have considerable breadth and show fine structure; Figure 14 shows typical

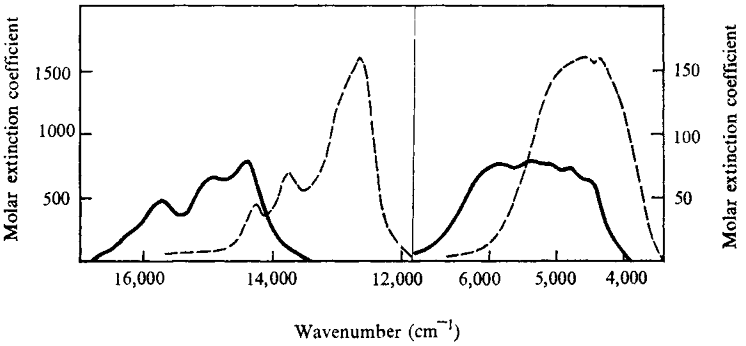

FIG. 14. Spectra of $[Bu_4^nN]CoCl_4$ in CH_2Cl_2 containing 0·1 M Bu_4^nNCl (———) and of $[Bu_4^nN]CoI_4$ in $CHCl_3$ containing 0·1 M Bu_4^nNI (- - - - - -).

spectra, those of $CoCl_4^{2-}$ and CoI_4^{2-}. The origin of the fine structure has been attributed to spin–orbit coupling[160, 161], but this alone, however, cannot account for the breadth of the bands since the first order spin–orbit splitting is only 6λ[161] and the band widths are of the order of 2000 cm^{-1}. Whilst vibrational broadening may be important in some complexes it seems unlikely to be the major reason for the band breadths. Low temperature crystal studies[162] on $CoCl_4^{2-}$ show relatively little narrowing of the bands at low temperatures (20°K). Low symmetry components of the crystal field[162] and transitions to the doublet states[161] are probably the main causes of the multiple absorption bands.

Complexes of lower symmetry than tetrahedral, e.g. CoX_2L_2 and $[CoX_3L]^-$ species, show spectra rather similar to those of the CoX_4^{2-} species. The near infrared band (ν_2) in these complexes is, however, usually broadened and the lower symmetry components are more pronounced. In the CoX_2L_2 complexes of C_{2v} symmetry the ${}^4A_2 \rightarrow {}^4T_1(F)$ band should be split into three transitions ${}^4A_2 \rightarrow {}^4B_2$, ${}^4A_2 \rightarrow {}^4A_2$ and ${}^4A_2 \rightarrow {}^4B_1$ and the ${}^4A_2 \rightarrow {}^4T_1(P)$ band should be similarly split. Such splittings are in fact observed[163] in a large number of these complexes of cobalt(II) halides with nitrogen and phosphorus donors, the bands occurring at 8000–10,200 cm^{-1}, ~ 7000 cm^{-1} and ~ 6000 cm^{-1}.

The magnetic moments of some tetrahedral complexes are listed in Table 8. Since the ground term is ${}^4A_2$ the magnetic moments are expected to follow the equation

$$\mu_{\text{eff}} = 3{\cdot}87\left(1 - \frac{4\lambda}{10Dq}\right)$$

where μ_{eff} is corrected for temperature independent paramagnetism (T.I.P. $= 2{\cdot}09/10Dq$ cgs) and 3·87 is the spin only moment. With $10Dq$ values around 4000 cm^{-1} this equation gives values of between 4·4 and 4·8 B.M. for the magnetic moment and the experimental moments for most "tetrahedral" complexes lie within this range. A distinction from octahedral complexes is that the tetrahedral moments are essentially independent of temperature. A summary of electron spin resonance data on cobalt(II) complexes has been given by Carlin[158] and by McGarvey[164].

Square-planar complexes. This stereochemistry is rare for cobalt(II). It is well authenticated by X-ray structural analysis in bis(dithioacetylacetonato)cobalt(II) $[Co(MeCS.CH.CSMe)_2]$[165], the bis(maleonitriledithiolate) anion[166] $[Co(MNT)_2]^{2-}$, *trans*-dimesitylbis(diethylphenylphosphine)cobalt(II)[167] and cobalt(II) phthalocyanine[168]. The square complexes so far investigated are all of the low spin type with room temperature magnetic moments in the range 2·1–2·8 B.M. On a simple crystal field ordering of the d orbitals the configuration becomes (in order of increasing energy), $d_{z^2}{}^2$, $(d_{xz}, d_{yz})^4$, $d_{xy}{}^1$, $d_{x^2-y^2}{}^0$. The pink $[Co(en)_2](AgI_2)_2$ has $\mu_{\text{eff}} = 2{\cdot}46$ B.M. at room temperature and is

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[160] F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 2nd edition, Interscience (1966).
[161] H. A Weakliem, *J Chem. Phys.* **36** (1962) 2117.
[162] J. Ferguson, *J. Chem. Phys.* **39** (1963) 116.
[163] A. B. P. Lever and S. M. Nelson, *J. Chem. Soc.* (A) (1966) 859.
[164] B. R. McGarvey, *Transition Metal Chemistry*, 3 (1966) 90.
[165] R. Beckett and B. F. Hoskins, *Chem. Communs.* (1967) 909; R. L. Martin and I. M. Stewart, *Nature*, **210** (1966) 522.
[166] J. D. Forrester, A. Zalkin and D. Templeton, *Inorg. Chem.* **3** (1964) 1500.
[167] P. G. Owston and J. M. Rowe, *J. Chem. Soc.* (1963) 3411.
[168] R. P. Linstead and J. M. Robertson, *J. Chem. Soc.* (1936) 1736.

isomorphous with the copper analogue and therefore probably contains square planar cobalt[169]. Other planar complexes are certain of the bis(salicylal)ethylene diimine cobalt(II) derivatives. These exhibit a narrow absorption band around 8500 cm^{-1} and a stronger broader band near 20,000 cm^{-1}; as yet, however, the spectra of these square complexes is not fully understood. Some of these β-ketoamine complexes are planar in the solid state but in solution behave in accordance with the equilibrium[170]

$$\text{planar}(S = \tfrac{1}{2}, \mu \sim 2{\cdot}2 \text{ B.M.}) \rightleftharpoons \text{tetrahedral}(S = \tfrac{3}{2}, \mu \sim 4{\cdot}4 \text{ B.M.})$$

4. COMPOUNDS OF COBALT(III)

4.1. SIMPLE COMPOUNDS AND SALTS OF COBALT(III)

Cobalt(III) fluoride. The reaction of fluorine with cobalt(II) chloride or fluoride proceeds rapidly and exothermically at 250° to give CoF_3 as a light brown powder[171]. Alternatively cobalt(III) fluoride can be prepared by fluorinating cobalt metal with chlorine trifluoride. It forms hexagonal crystals of density 3·89, isomorphous with iron(III) and aluminium(III) fluorides, the cobalt atoms being octahedrally surrounded by fluorine atoms[172]. The heat of formation is -187 kcal $mole^{-1}$ and the magnetic moment is 1·60 B.M. at 90°K rising to 2·46 B.M. at 293°K[173]; it is thus a high spin compound but not magnetically dilute.

Anhydrous cobalt(III) fluoride turns dark in the presence of traces of water and reacts violently with the liquid-evolving oxygen. When heated in an inert atmosphere above 350°, cobalt(II) fluoride is formed. It reacts vigorously with many elements, e.g. Al, P, As, S, I, being reduced to cobalt(II) fluoride. It is insoluble in alcohol, ether and benzene and is a useful fluorinating agent in organic chemistry[174]. At 400° all the hydrogen of hydrocarbons can be replaced by fluorine and addition of fluorine to unsaturated linkages occurs:

$$4CoF_3 + {-}CH_2{-} \rightarrow {-}CF_2{-} + 4CoF_2 + 2HF$$
$$2CoF_3 + {>}C{=}C{<} \rightarrow {>}CF{-}CF{<} + 2CoF_2$$

The blue hydrate $CoF_3.3{\cdot}5H_2O$ is prepared[175] by electrolytic oxidation of a saturated solution of cobalt(II) fluoride in 40% hydrofluoric acid. This compound is also decomposed in water and is insoluble in organic solvents. The magnetic susceptibility[176] obeys the Curie–Weiss law with a θ value of 60°; the magnetic moment at room temperature is 4·47 B.M., so that like the anhydrous salt it is probably not magnetically dilute. Little is known of its structure; if the water is coordinated to the cobalt as, for example, $[CoF_3(H_2O)_3]0{\cdot}5H_2O$, it is rather surprising that the water molecules do not cause spin pairing on the cobalt(III) ion—the analogous $CoF_3(NH_3)_3$ is diamagnetic.

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[169] A. B. P. Lever, J. Lewis and R. S. Nyholm, *J. Chem. Soc.* (1963) 2552.

[170] G. W. Everett and R. H. Holm, *J. Am. Chem. Soc.* **87** (1965) 5266.

[171] H. F. Priest, *Inorg. Syntheses*, **3** (1950) 175.

[172] R. W. G. Wyckoff, *Crystal Structures*, Vol. 2, Interscience (1964).

[173] B. N. Figgis and J. Lewis, *Progress in Inorg. Chem.* **6** (1964) 37.

[174] M. Stacey and J. C. Tatlow, *Advances in Fluorine Chemistry*, **1** (1960) 166.

[175] B. Cox and A. G. Sharpe, *J. Chem. Soc.* (1954) 1798.

[176] H. C. Clark, B. Cox and A. G. Sharpe, *J. Chem. Soc.* (1957) 4132.

Cobalt(III) chloride is of very dubious existence and the bromide and iodide have never been prepared. These halides are expectedly redox unstable, the Co^{3+} ion being a strong oxidant. Dissolution of cobalt(III) oxide in hydrochloric acid leads to evolution of chlorine. Indeed cobalt(III) compounds are estimated volumetrically as a result of their liberation of iodine from potassium iodide in acid solution.

Cobalt(III) oxide. Neither the oxide Co_2O_3 nor the hydroxide $Co(OH)_3$ is definitely established. The oxidation of cobalt(II) hydroxide in aqueous suspension with, for example, peroxides, or the destruction of a cobalt(III) complex with alkali gives a brown or black powder $Co_2O_3.aq$ which upon drying at 150° yields the monohydrate $Co_2O_3.H_2O$; this is probably best formulated as CoO(OH). When heated further in attempts to dehydrate it, the "monohydrate" begins to evolve oxygen (as well as water) at 300° with the formation of black Co_3O_4. When heated to 100° in air cobalt(II) hydroxide is converted to dark brown CoO(OH).

Cobalt(III) oxide hydroxide CoO(OH) is hexagonal with a layer lattice[177], having the $NaHF_2$ structure. The cobalt is surrounded octahedrally by oxygen atoms and there is hydrogen bonding between the O^{2-} and OH^- ions forming nearly symmetrical O_2H^{3-} groups.

Cobalt(III) amide. The reaction between hexamminecobalt(III) salts and potassium amide in liquid ammonia gives the brown amorphous amide $Co(NH_2)_3$[178]. This is soluble in excess of potassium amide solution with the probable formation of a binuclear amide complex anion $K_3[Co_2(NH_2)_9]$; with ammonium nitrate solutions (in an autoclave at 100°) the hexammine salt is re-formed:

$$Co(NH_2)_3 + 3NH_4NO_3 \rightarrow [Co(NH_3)_6](NO_3)_3$$

Cobalt(III) amide slowly evolves ammonia at room temperature, forming the nitride CoN.

Cobalt(III) acetate. The electrolytic oxidation of cobalt(II) acetate in glacial acetic acid containing 2% of water gives an apple-green solid which is probably a hydroxy bridged cobalt(III) acetate[179], although earlier authors[180] had described it as the trimeric acetate $Co_3(OCOCH_3)_9$. Cobalt(III) acetate is believed to be present in dilute acetic acid solutions of cobalt(II) acetate which have been oxidized with ozone.

Cobalt(III) nitrate. Anhydrous $Co(NO_3)_3$ can be prepared[181] as green hygroscopic crystals by the reaction of dinitrogen pentoxide on cobalt(III) fluoride. It is volatile at fairly low temperatures (e.g. 40° and 10^{-2} mm Hg) and reacts vigorously with a range of organic solvents. A crystal structure determination[182] shows the nitrate groups to be bidentate and the coordination around cobalt to be basically octahedral. All the Co–O bonds are equivalent, being $1{\cdot}90 \pm 0{\cdot}02$ Å, but the O–Co–O angle for each bidentate ligand is only 68°.

Aqueous solutions of cobalt(III) nitrate have been prepared electrolytically, but no solid hydrates isolated.

Cobalt(III) sulphate. The blue, crystalline hydrate $Co_2(SO_4)_3.18H_2O$ is prepared by the oxidation of cobalt(II) sulphate in 8N sulphuric acid either electrolytically or chemically with ozone or fluorine. It is stable in the dry state, but is decomposed by water with evolution of oxygen; it is fairly stable in solution in dilute sulphuric acid. Cobalt(III) alums

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[177] Yu. D. Kondrashev and N. N. Fedorova, *Doklady Akad. Nauk SSSR*, **94** (1954) 229.

[178] O. Schmitz-Dumont, H. Broja and H. F. Piepenbrink, *Z. anorg. u. allgem. Chem.* **253** (1947) 118.

[179] J. A. Sharp and A. G. White, *J. Chem. Soc.* (1952) 110.

[180] C. Schall and C. Thiemewiedtmarcker, *Z. Electrochem.* **35** (1929) 337.

[181] R. J. Fereday, N. Logan and D. Sutton, *Chem. Communs.* (1968) 271.

[182] J. Hilton and S. C. Wallwork, *Chem. Communs.* (1968) 871.

$MCo(SO_4)_2.12H_2O$ ($M = K$, Rb, Cs or NH_4) can be isolated as blue crystals from the mixed cooler solutions of the two sulphates in dilute sulphuric acid. The potassium alum is diamagnetic, the rubidium salt has a magnetic moment less than 1 B.M. and the ammonium alum has a moment of 2·1 B.M. at 304°K[183]. The hydrated sulphate also has a small positive magnetic susceptibility. The sulphate is believed like the alums to contain the $[Co(H_2O)_6]^{3+}$ ion.

Cobalt(III) sulphate is the most readily available cobalt(III) salt and has been used in investigations into the reactions of the Co^{3+}aq. ion. By reaction with barium perchlorate in perchloric acid solution, a solution of cobalt(III) perchlorate is obtained. The rate of decomposition of cobalt(III) perchlorate solutions depends in a rather complex manner upon the hydrogen ion concentration[184]. Electronic spectral studies[185] indicate that hydrolysis of the $[Co(H_2O)_6]^{3+}$ ion to $[Co(OH)(H_2O)_5]^{2+}$ occurs in 0·1N perchloric acid. Solutions of cobalt(III) in sulphuric acid polymerize aqueous acrylonitrile and methyl methacrylate and cause the oxidation of a wide variety of organic compounds. Formic, tartaric, malic and citric acids, for example, are oxidized to carbon dioxide so that no cobalt(III) salts of these anions have been prepared.

4.2. COMPLEX COMPOUNDS OF COBALT(III)

Historical Importance

Since cobalt(III) complexes have played such a very important part in the development of coordination chemistry, some brief history[186] is relevant here. B. M. Tassaert in 1798 was probably the first to observe that a solution of a cobalt(II) salt in aqueous ammonia turns brown upon exposure to the air, the colour changing to wine red on boiling. Some decades later, Frémy showed that the cobalt had been oxidized to cobalt(III) and that the new salt is associated with up to six ammonia molecules, e.g. $CoCl_3.6NH_3$. This compound stimulated interest because it was difficult to see how two compounds, $CoCl_3$ and NH_3, both with their valencies satisfied, could combine together to form a stable compound. Further, a range of compounds could be isolated, e.g. $CoCl_3.6NH_3$, $CoCl_3.5NH_3$ and $CoCl_3.4NH_3$; these were named after their respective colours, i.e. luteocobaltic chloride, purpureocobaltic chloride and the green isomer of $CoCl_3.4NH_3$, praseocobaltic chloride.

It was Alfred Werner who in the last decade of the nineteenth century unravelled the mysteries of the bonding in these compounds—which are known under the collective name of cobaltammines. Amongst the experimental evidence available were the facts that silver nitrate solution precipitated three chloride ions immediately from $CoCl_3.6NH_3$ but only two from $CoCl_3.5NH_3$ and one from $CoCl_3.4NH_3$. Also conductivity studies on these compounds and on a similar series of ammines formed by platinum indicated different numbers of ions to be present in aqueous solutions of the different ammines. Not only did Werner propose our present-day formulations of these ammines (below), but he went on to propose a theory which has been applicable without essential alteration up to the present day. Werner's postulates can be summarized as three main points. Firstly, metals possess two types of valency, a primary valency (known as oxidation state today) and a secondary valency (coordination number today). Secondly, metals tend to satisfy both types of

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[183] B. N. Figgis and J. Lewis, *Progress in Inorg. Chem.* 6 (1964) 37.

[184] C. E. H. Bawn and A. G. White, *J. Chem. Soc.* (1951) 331.

[185] J. H. Baxendale and C. F. Wells, *Trans. Farad. Soc.* 53 (1957) 800.

[186] J. R. Partington, *A History of Chemistry*, Vol. 4, p. 918, Macmillan (1964).

valency and thirdly, the secondary valencies are directed to fixed positions in space about the central metal ion. Thus in the cobaltammines the primary valency is three and the secondary valency is six and we get the formulations:

$$CoCl_3.6NH_3 = [Co(NH_3)_6]Cl_3$$
$$CoCl_3.5NH_3 = [Co(NH_3)_5Cl]Cl_2$$
$$CoCl_3.4NH_3 = [Co(NH_3)_4Cl_2]Cl$$

Werner's third postulate was perhaps the most significant and yet most difficult to prove. It predicted the occurrence of various types of isomer and took Werner nearly twenty years to prove. Before the advent of direct methods of structural determination Werner was able to prove the octahedral structure for these compounds by the resolution of the $[Co(en)_3]^{3+}$ ion into its predicted optical isomers. Cobalt(III) complexes have thus made a significant contribution to the development of inorganic stereochemistry.

The number of cobalt(III) complexes now known is exceptionally large. Virtually all of these have the octahedral structure. They undergo ligand exchange reactions at conveniently measurable rates and have therefore been extensively studied. Much of our knowledge of octahedral substitution reactions is based upon such rate studies on cobalt(III) complexes.

The Cobaltammines

Cobalt(III) has a great affinity for nitrogen ligands and forms an enormous number[187] of complexes in which cobalt is bonded to ammonia, an amine, nitro groups or the nitrogen atom in NCS groups often in addition to water molecules, halide, carbonate, or hydroxide ions. Several stereoisomers are often possible for one particular compound and *cis–trans* isomers can frequently be isolated. The preparation of these complexes normally involves the addition of ammonia or other nitrogen donor to a cobalt(II) solution followed by oxidation with, for example, hydrogen peroxide or by bubbling air through the mixture in the presence of an activated charcoal catalyst.

The orange hexammines containing the $[Co(NH_3)_6]^{3+}$ ion are prepared[188] using charcoal and a high concentration of the ammonium salt, e.g.

$$4CoCl_2+4NH_4Cl+20NH_3+O_2 \rightarrow 4[Co(NH_3)_6]Cl_3+2H_2O$$

In the absence of charcoal and using hydrogen peroxide as oxidant the aquopentammine salt is formed; upon treatment with concentrated hydrochloric acid the red chloropentammine cobalt(III) chloride forms[189]:

$$2CoCl_2+2NH_4Cl+8NH_3+H_2O_2 \rightarrow 2[Co(NH_3)_5(H_2O)]Cl_3$$
$$[Co(NH_3)_5(H_2O)]Cl_3 \rightarrow [Co(NH_3)_5Cl]Cl_2+H_2O$$

Other complexes, e.g. $[Co(dipy)_3]^{3+}$ and *trans*-$[Co(en)_2Cl_2]^+$, can be prepared by routes similar to those used for the hexammine and chloropentammine respectively. An alternative preparative route involves ligand exchange with another cobaltammine. Thus the chloropentammine reacts with hot aqueous ethylenediamine to give $[Co(en)_3]Cl_3$ with evolution of ammonia. The interconversion of *cis–trans* isomers is frequently straightforward; the *trans*-$[Co(en)_2Cl_2]Cl$ is converted to the *cis* form merely by evaporating a neutral aqueous

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[187] *Gmelins Handbuch der Anorganischen Chemie*, **58** Cobalt, part B, Verlag Chemie (1964).

[188] J. Bjerrum and J. P. McReynolds, *Inorg. Syntheses*, **2** (1946) 216.

[189] G. G. Schlessinger, *Inorg. Syntheses*, **9** (1967) 160.

solution of the *trans* form to dryness on a water bath[190]. Aquation occurs when $[Co(NH_3)_5Cl]^{2+}$ or *cis*- or *trans*-$[Co(en)_2Cl_2]^+$ is heated in water:

$$[Co(en)_2Cl_2]^+ + H_2O \rightarrow [Co(en)_2Cl(H_2O)]^{2+} + Cl^-$$
$$[Co(en)_2Cl(H_2O)]^{2+} + H_2O \rightarrow [Co(en)_2(H_2O)_2]^{3+} + Cl^-$$

and ligand exchange occurs also with anions, e.g.

$$[Co(en)_2Cl_2]^+ + 2NCS^- \rightarrow [Co(en)_2(NCS)_2]^+ + 2Cl^-$$

Detailed accounts of the preparation of some carbonatopentammine complexes $[Co(NH_3)_5CO_3]^+$ and of some nitroethylenediamine complexes $[Co(en)_2(NO_2)_2]^+$ are given elsewhere[191, 192].

The octahedral structure of the mononuclear cobaltammines has been confirmed by crystallographic studies[193]. The orthorhombic $[Co(NH_3)_5Cl]Cl_2$ has what may be considered as a fluorite-like arrangement of $[Co(NH_3)_5Cl]^{2+}$ and Cl^- ions; in each $[Co(NH_3)_5Cl]^{2+}$ ion the cobalt is "octahedrally" surrounded with one ammonia at a Co–N distance of 1·91 Å, four ammonias at Co–N distances 1·97–1·98 Å and one chlorine at 2·27 Å. The anionic chloride ions are at their closest 3·29 Å from the coordinated ammonia groups and some of these may involve hydrogen bonding. In trinitrotriamminecobalt(III) $[Co(NH_3)_3(NO_2)_3]$, the cobalt is at the centre of an only slightly distorted octahedron, the Co–N distances being between 1·96 and 1·99 Å, two of the NO_2 groups being *trans* to each other. The tris(ethylenediamine)cobalt(III) ion $[Co(en)_3]^{3+}$ has an overall D_3 symmetry; the six nitrogen atoms are at Co–N distances of 1·991 ± 0·009 Å and are only slightly displaced from the octahedral positions, the N–Co–N angle averaging 85·5°. It is important to note here that normal X-ray methods do not elucidate the absolute configuration for these optically active complexes with chelate rings. The absorption edge (Bijvoet[194]) technique with X-rays does, however, lead to an unambiguous determination of absolute configuration and this technique has been used on $[Co(en)_3]^{3+}$ [195] and $[CoX_2(en)_2]^+$ (X = Cl[196], Br[197]). The ethylenediamine chelate rings in these complexes are not planar but puckered. The arrangement in *trans*-$[Co(en)_2Cl_2]^+$ is shown in Fig. 15; the ion is centrosymmetric, possessing the two different conformations (δ and λ) of the puckered rings which are possible (δ and λ

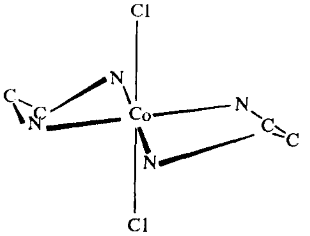

FIG. 15. The *trans*-$[Co(en)_2Cl_2]^+$ ion.

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[190] J. C. Bailar, *Inorg. Syntheses*, **2** (1946) 223.

[191] F. Basolo and R. K. Murmann, *Inorg. Syntheses*, **4** (1953) 171.

[192] H. F. Holtzclaw, D. P. Sheetz and B. D. McCarty, *Inorg. Syntheses*, **4** (1953) 176.

[193] R. W. G. Wyckoff, *Crystal Structures*, 2nd edition, Vol. 3, Interscience (1965).

[194] J. M. Bijvoet, A. F. Peerdeman and A. J. Bommel, *Nature*, **168** (1951) 271.

[195] Y. Saito, *I.U.P.A.C. Xth International Conference on Co-ordination Chemistry, Japan 1967*, p. 21, Butterworths (1968).

[196] A. Nakahara, Y. Saito and H. Kuroya, *Bull. Chem. Soc. Japan*, **25** (1952) 331.

[197] S. Ooi, Y. Komiyama, Y. Saito and H. Kuroya, *Bull. Chem. Soc. Japan*, **32** (1959) 263.

forms are mirror images of each other). In $[Co(en)_3]Cl_3 \cdot 3H_2O$, the $[Co(en)_3]^{3+}$ ion has the "lel" form (Corey and Bailar's nomenclature[198]); in this form (Fig. 16 shows the "lel" and "ob" forms) the direction of the C–C bond in an ethylenediamine molecule is approximately parallel to the three-fold axis of the ion. The two optical isomers of these forms are labelled Δ and Λ; once the absolute configuration of one of these isomers, e.g. $(+)_D[Co(en)_3]^{3+}(\Delta)$, has been determined by X-rays, the configurations of other similar Δ and Λ isomers, e.g. of $[Co(pn)_3]^{3+}$, can be determined by comparison of the optical rotatory dispersion and circular dichroism curves. For detailed discussion of these techniques the reader is referred to Gillard[199].

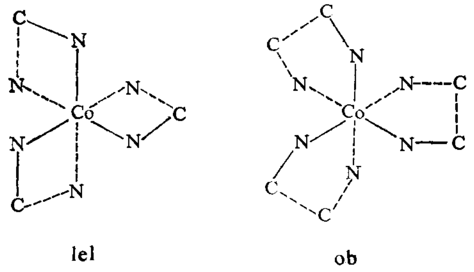

FIG. 16. "Lel" and "ob" forms of $[Co(en)_3]^{3+}$.

In their reactions the cobaltammines are inert, that is their reactions with other ligands are slow—often taking hours, days or even weeks to reach the equilibrium position. By far the most important substitution reaction is that of aquation:

$$[Co(NH_3)_5X]^{2+} + H_2O \rightleftharpoons [Co(NH_3)_5(H_2O)]^{3+} + X^-$$

Extremely extensive studies have been made of these reactions and the accumulated evidence points[200, 201] to them occurring via a dissociation process in which breaking of the Co–X bond is more important than the formation of the new Co–H_2O bond. This does not necessarily imply that a five-coordinate reactive intermediate, e.g. $[Co(NH_3)_5]^{3+}$, is formed which can discriminate between competing nucleophiles, indeed it has been shown[202] that no intermediate of sufficient stability to be selective in its reactions is formed along the reaction pathway of the $[Co(NH_3)_5NO_3]^{2+}$–SCN^- reaction. However, all these aquation reactions do not involve a common intermediate and at the extreme where N_2 or CO_2 is the leaving group a genuine intermediate may be formed[203]. The anation reaction, i.e. the reverse of the aquation reaction, appears to take place via the rapid equilibration to an ion pair followed by a slow rearrangement to the acido product:

$$[Co(NH_3)_5(H_2O)]^{3+} + X^- \rightleftharpoons [Co(NH_3)_5(H_2O)]^{3+}X^-$$
$$[Co(NH_3)_5(H_2O)]^{3+}X^- \rightleftharpoons [Co(NH_3)_5X]^{2+}H_2O$$

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[198] E. J. Corey and J. C. Bailar, *J. Am. Chem. Soc.* **81** (1959) 2620.

[199] R. D. Gillard, *Progress in Inorg. Chem.* 7 (1966) 215.

[200] F. Basolo, *I.U.P.A.C. Xth International Conference on Co-ordination Chemistry, Japan 1967*, p. 37, Butterworths (1968).

[201] C. H. Langford and H. B. Gray, *Ligand Substitution Processes*, Benjamin (1965).

[202] R. G. Pearson and J. W. Moore, *Inorg. Chem.* 3 (1964) 1334.

[203] G. E. Dolbear and H. Taube, *Inorg. Chem.* 6 (1967) 60.

The rates of hydrolysis of cobalt(III) complexes are pH dependent and in molar alkali the rates of base hydrolysis exceed the rates of acid hydrolysis by up to eight orders of magnitude. The rates of base hydrolysis in reactions of the type:

$$[Co(NH_3)_5Cl]^{2+} + OH^- \rightarrow [Co(NH_3)_5OH]^{2+} + Cl^-$$

are second order; this might be taken to imply that they involve a simple S_N2 process. However, whilst the hydroxide ion may be a privileged nucleophile[204] in aqueous solution, this mechanism is regarded as unlikely by other workers[200, 205] because one might expect some other nucleophiles to behave in this way. An alternative mechanism for base hydrolysis is that originally proposed by Garrick[205], i.e. the S_N1CB mechanism:

$$[Co(NH_3)_5Cl]^{2+} + OH^- \overset{\text{fast}}{\rightleftharpoons} [Co(NH_3)_4(NH_2)Cl]^+ + H_2O$$
$$[Co(NH_3)_5(NH_2)Cl]^+ \xrightarrow{\text{slow}} [Co(NH_3)_4(NH_2)]^{2+} + Cl^-$$
$$[Co(NH_3)_4(NH_2)]^{2+} + H_2O \xrightarrow{\text{fast}} [Co(NH_3)_5(OH)]^{2+}$$

This mechanism requires that the reacting complex possess at least one protonic hydrogen on a non-leaving ligand; in complexes having no such protonic hydrogen acceleration by base should not be observed. This is in fact generally found to be so, e.g. for *trans*-$[Co(bipy)_2(NO_2)_2]^+$ and *trans*-$[Co(diars)_2Cl_2]^+$. There are, however, more compelling lines of evidence in support of the S_N1 mechanism. Reactions of the type:

$$[Co(en)_2(NO_2)Cl]^+ + Y^- \rightarrow [Co(en)_2(NO_2)Y]^+ + Cl^-$$

carried out in dimethyl sulphoxide solution are very slow but in the presence of added base become fast[206]. Since the reaction of $[Co(en)_2(NO_2)(OH)]^+$ with Y^- is slow, an S_N2 mechanism with this as intermediate is eliminated; presumably the five-coordinate conjugate base $[Co(en)(en\text{-}H)(NO_2)]^+$ is the active intermediate which readily reacts with Y^- and becomes protonated to give the final product, thereby regenerating the catalyst base. In aqueous solution, studies with labelled ^{18}O have shown in some cases[207] that hydroxide ion is not the entering group and hence the S_N2 process is not occurring.

In addition to these mononuclear ammines, cobalt forms numerous polynuclear cobaltammines in which cobalt atoms are bridged by groups such as OH^-, NH_2^- and NH^{2-}. The cobaltammine octahedra can be joined at a corner as in $[(NH_3)_5Co\text{–}NH_2\text{–}Co(NH_3)_5]Cl_5$ or along an edge as in $[(NH_3)_4Co(OH)_2Co(NH_3)_4]Cl_4$, or at a face as in $[(NH_3)_3Co(OH)_3Co(NH_3)_3]Cl_3$. Larger units can also be formed, e.g. $[(NH_3)_3Co(OH)_3Co(OH)_3Co(NH_3)_3]Cl_3$ and $[Co\{(OH)_2Co(NH_3)_4\}_3]Cl_6$.

Perhaps the most interesting group of these polynuclear complexes, however, are those containing the peroxy bridge –O–O–[208]. Two series of these complexes exist; there are the diamagnetic complexes, which are usually red or brown, and there are paramagnetic complexes, which are usually green. The diamagnetic salts contain the unit $[Co^{III}\text{–}O_2\text{–}Co^{III}]$ in which two cobalt(III) atoms are linked by a peroxide ion; examples of these are:

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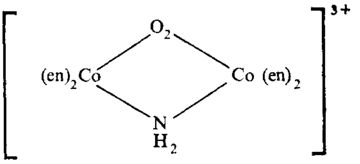
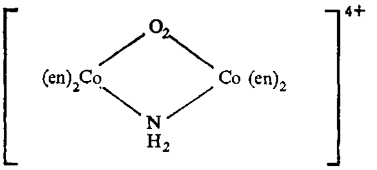
[204] M. L. Tobe, *Sci. Progr.* (*London*), **48** (1960) 483.
[205] F. J. Garrick, *Nature*, **139** (1937) 507.
[206] R. G. Pearson, H. H. Schmidtke and F. Basolo, *J. Am. Chem. Soc.* **82** (1960) 4434.
[207] M. Green and H. Taube, *Inorg. Chem.* **2** (1963) 948.
[208] J. A. Connor and E. A. V. Ebsworth, *Advances Inorg. Chem. Radiochem.* **6** (1964) 279.

$[(NH_3)_5Co(O_2)Co(NH_3)_5]^{4+}$ and



They are prepared (e.g.) by aerial oxidation of ammoniacal solutions of cobalt(II) salts. The paramagnetic complexes (μ_{eff} = 1·6–1·8 B.M.) can frequently be obtained as one-electron oxidation products of the diamagnetic derivatives; examples are:

$[(NH_3)_5Co(O_2)Co(NH_3)_5]^{5+}$ and



They are preferably prepared, however, by oxidation of cobalt(II) salts in the presence of the ligands, with ozone, hydrogen peroxide or ammonium persulphate. Both series of salts are most stable when dry, but they all decompose slowly at room temperature and are usually decomposed in water or dilute acids.

The structures and formulations of the paramagnetic species have aroused much discussion. Werner regarded them as containing cobalt(III) and cobalt(IV) with a bridging peroxide ion, i.e. $[Co^{III}–O_2–Co^{IV}]$; e.s.r. studies, however[209], showed them to contain equivalent cobalt atoms. An X-ray study[210] on $[(NH_3)_5CoO_2Co(NH_3)_5]SO_4(HSO_4)_3$ has

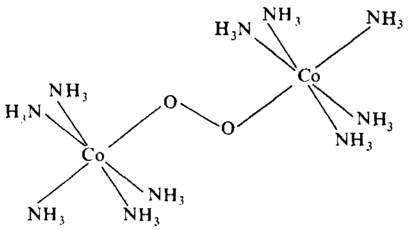


FIG. 17. The geometry of the $[(NH_3)_5CoO_2(NH_3)_5]^{5+}$ cation.

revealed the geometry of the cation (Fig. 17). The five ammonia molecules and an oxygen atom from the bridging group surround each cobalt octahedrally, the Co–N distances being 1·95±0·02 Å. The bridging O_2 group joins the octahedra in the staggered position as shown, each oxygen being σ-bonded to a cobalt atom. The O–O distance is 1·31±0·02 Å, only slightly longer than that found in alkali metal superoxides (1·28 Å). The most reasonable formulation for this cation then is that it contains two cobalt(III) atoms bridged by a superoxide (O_2^-) ion.

Neutral Complexes of Cobalt(III)

There are, of course, many uncharged species of the cobaltammine types $[CoX_3(NH_3)_3]$ where X = Cl^-, NO_3^-, NO_2^-, N_3^-, etc., and $[CoX_3(NH_3)L_2]$, where L is a unidentate ligand such as pyridine or where L_2 represents a bidentate nitrogen ligand such as ethylene-

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[209] I. Bernal, E. A. V. Ebsworth and J. A. Weil, *Proc. Chem. Soc.* (1959) 57.
[210] W. P. Schaefer and R. E. Marsh, *J. Am. Chem. Soc.* **88** (1966) 178.

diamine. These compounds are detailed in Gmelin[187] and will not be discussed further here. The most important complexes of the type [CoL_3] are those with β-diketones.

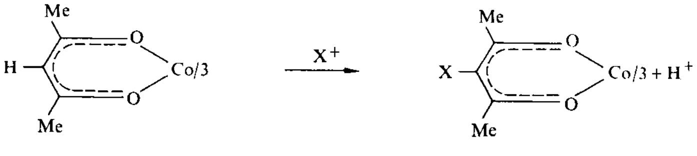
Cobalt(III) acetylacetonate $Co(CH_3COCHCOCH_3)_3$ is prepared[211] as dark green crystals (m.p. 241°) by the oxidation of a cobalt(II) solution in the presence of acetylacetone. It is only sparingly soluble in water but soluble in organic solvents[212] and is monomeric in the vapour as well as in benzene. The crystals are isomorphous with the monoclinic tris(acetylacetonates) of aluminium, manganese(III) and chromium(III); they are diamagnetic $\chi_M = -59{\cdot}4 \times 10^{-6}$ c.g.s. units at 27·4°C. Partial resolution of $Co(acac)_3$ into its optical isomers has been effected by zone melting in dibenzoyl-*d*-tartaric acid[213] and by chromatographing with optically active absorbants[214]. The cobalt(III) complexes with unsymmetrical β-diketones—for example, the benzoylacetonate and the trifluoroacetylacetonate can be separated into their *cis–trans* isomers; the kinetics of the *cis* to *trans* isomerization of the trifluoroacetylacetonate has been studied by ^{19}F magnetic resonance spectroscopy[215].

The reactions of $Co(acac)_3$ have provided some interesting products. Reducing agents frequently produce cobalt(II) species—for example, hydrazine by reaction with the coordinated ligand gives the mauve bis(3,5-dimethylpyrazolato)cobalt(II), although if the hydrazine is in excess, reduction to cobalt occurs. In the presence of triphenylphosphine the reduction of the acetylacetonate by aluminium alkyls in a nitrogen atmosphere produces the orange molecular nitrogen complex $CoH(N_2)(PPh_3)_3$ [216]. This same complex is produced in the reaction of the trihydride $CoH_3(PPh_3)_3$, produced by the reaction of $CoX_2(PPh_3)_2$ (X = Cl, Br, I) with borohydride, with nitrogen at room temperature and atmospheric pressure[217].

$$CoH_3(PPh_3)_3 + N_2 \rightleftharpoons CoH(N_2)(PPh_3)_3 + H_2$$

The complex is moderately stable in air and soluble in non-polar solvents. The infrared spectrum shows a strong absorption at 2080–2084 cm^{-1} assignable to the coordinated N–N stretch, but the Co–H stretch has not been detected. Preliminary X-ray studies[216] suggest that the coordination about cobalt may be best described as trigonal bipyramidal with the Co atom 0·3 Å above the trigonal plane of the three phosphorus atoms. One apical position is occupied by the N–N group, Co–N–N being almost colinear, and the other may contain the hydrogen atom.

The central hydrogen atom on the chelate rings in $Co(acac)_3$ can be replaced by several groups under apparently electrophilic conditions, e.g.[218]



X = Cl, Br, I, SCN, SAr, SCl, NO_2, CH_2Cl, CH_2NMe_2, COR, CHO.

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[211] B. E. Bryant and W. C. Fernelius, *Inorg. Syntheses*, **5** (1957) 188.
[212] *Ibid.* 105.
[213] V. F. Doron and S. Kirschner, *Inorg. Chem.* **1** (1962) 542.
[214] T. Moeller and E. Gulyas, *J. Inorg. Nuclear Chem.* **5** (1958) 245.
[215] R. C. Fay and T. S. Piper, *Inorg. Chem.* **3** (1964) 348.
[216] J. H. Enemark, B. R. Davies, J. A. McGinnety and J. A. Ibers, *Chem. Communs.* (1968) 96.
[217] A. Sacco and M. Rossi, *Chem. Communs.* (1967) 316.
[218] J. P. Collman, *Angew. Chem. Intern. Ed.* **4** (1965) 132.

and mixed ring complexes are frequently obtained when mono- or disubstitution (i.e. on one or two rings) occurs in a limited concentration of the electrophilic reagent.

Neutral complexes of the type [Co(acac)$_2$(NO$_2$)L] in which L is an amine have been prepared by the reactions[219]:

$$[Co(acac)_2(NO_2)_2]^- + L \rightarrow [Co(acac)_2(NO_2)L] + NO_2^-$$

They are red, water-insoluble solids, inert to further substitution by amines; their spectroscopic properties indicate that they have the *trans* structure.

Anionic Complexes of Cobalt(III)

Complex fluorides. The blue alkali metal salts M_3CoF_6 have been prepared from cobalt(III) fluoride in hydrofluoric acid and the potassium salt by the action of fluorine on $K_3Co(NO_2)_6$ or a 3 : 1 mixture of potassium and cobalt(II) chlorides at 400°. Alternatively the salt of the $[Co(CN)_6]^{3-}$ ion can be fluorinated to CoF_6^{3-} by elemental fluorine at around 300°. These compounds have magnetic moments in the range 5·2–5·6 B.M. and are thus rare examples of high spin cobalt(III) complexes. The crystal structures of these salts containing the octahedral CoF_6^{3-} ions are closely related to the cubic $(NH_4)_3FeF_6$ structure[220]. Whilst K_2NaCoF_6 is strictly cubic there is some distortion in Na_3CoF_6 and K_3CoF_6; Li_3CoF_6 and $Ba_3(CoF_6)_2$ have lattices considerably distorted from cubic.

Complex cyanides. Cobalt(III) cyanide is believed to be obtained as a dark blue solid when the aquated acids $H[Co(CN)_4]$ and $H_2[Co(CN)_5]$ are heated. When cobalt(II) cyanide is dissolved in potassium cyanide solution and the deep red solution is boiled in air the yellow hexacyanocobaltate(III) is formed[221]. The diamagnetic $K_3Co(CN)_6$ is very soluble in water at room temperature, only sparingly soluble in liquid ammonia at the boiling point and insoluble in ethanol. The ordinary product possesses four known crystalline forms, three of which are monoclinic and one orthorhombic[222]. A neutron diffraction study[223] on the monoclinic form with the smallest unit cell has established that the Co–C–N unit is linear with Co–C = 1·89 Å and C–N = 1·15 Å.

The $[Co(CN)_6]^{3-}$ ion is inert to attack by chlorine, hydrogen peroxide, alkalis and hydrochloric acid; concentrated sulphuric acid liberates carbon monoxide. It gives precipitates of hexacyanocobaltates(III) with heavy metals. Exchange with labelled cyanide proceeds very slowly, but the rate is increased by light when aquation takes place as the rate-determining step[224]:

$$[Co(CN)_6]^{3-} + H_2O \rightarrow [Co(CN)_5(H_2O)]^{2-} + CN^-$$

The free acid $H_3Co(CN)_6$ can be isolated as the colourless pentahydrate from solutions prepared by passage of $K_3Co(CN)_6$ down a cation exchange column (H$^+$ form); it can be dehydrated by heating. Alternatively it can be prepared using hydrochloric acid and ether on the potassium salt. Its infrared spectrum[225] shows a single $\nu(C{\equiv}N)$ at 2202 cm^{-1} and a broad band at 750 cm^{-1} which has been assigned to a superposition of hydrogen-bonded N–H stretching and deformation modes; symmetrical hydrogen bonds are believed to be

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[219] L. J. Boucher and J. C. Bailar, *J. Inorg. Nuclear Chem.* **27** (1965) 1093.

[220] R. W. G. Wyckoff, *Crystal Structures*, 2nd edition, Vol. 3, Interscience (1965).

[221] J. H. Bigelow, *Inorg. Syntheses*, **2** (1946) 225.

[222] J. A. Kohn and W. D. Townes, *Acta Cryst.* **14** (1961) 617.

[223] N. A. Curry and W. A. Runciman, *Acta Cryst.* **12** (1959) 674.

[224] A. G. MacDiarmid and N. F. Hall, *J. Am. Chem. Soc.* **76** (1954) 4222.

[225] D. F. Evans, D. Jones and G. Wilkinson, *J. Chem. Soc.* (1964) 3164.

present. The acid is a strong tribasic acid extremely stable, being only slowly decomposed by boiling in water. It thus resembles $H_3Fe(CN)_6$ and is non-toxic. It can be methylated with diazomethane in methanol to give $Co(CN)_3(MeNC)_3$ and has been esterified with numerous alcohols.

A variety of substituted cyanide complexes are known[226]: these include $[Co(CN)_5(H_2O)]^{2-}$, $[Co(CN)_5Br]^{3-}$, $[Co(CN)_5NO]^{3-}$ and $[Co(CN)_5(SCN)]^{3-}$. The brown peroxy complex $K_6[(CN)_5Co(O_2)Co(CN)_5].H_2O$ is obtained when oxygen is rapidly bubbled through a solution containing Co(II) and CN^- in a 1 : 5 mole ratio. This complex anion oxidizes the pentacyanocobaltate(II) anion according to

$$[(CN)_5Co(O_2)Co(CN)_5]^{6-}+2[Co(CN)_5]^{3-}+6H_2O \rightarrow 4[Co(CN)_5(H_2O)]^{2-}+4OH^-$$

so that slow aerial oxidation of $[Co(CN)_5]^{3-}$ produces mainly the aquopentacyanocobaltate(III).

Nitrocomplexes. Sodiumhexanitrocobaltate(III) ("sodiumcobaltinitrite") $Na_3Co(NO_2)_6$ is a well-known orange solid which precipitates potassium ions from aqueous solution as $K_3Co(NO_2)_6$. It is prepared[227] by blowing air through a mixture of cobalt(II) nitrate and sodium nitrite solutions in the presence of acetic acid:

$$2[Co(H_2O)_6]^{2+}+12NO_2^-+2CH_3COOH+\tfrac{1}{2}O_2 \rightarrow 2[Co(NO)_2)_6]^{3-}+2CH_3COO^-+13H_2O$$

after filtration of any precipitated potassium or ammonium salts, the sodium salt is precipitated by the addition of ethanol. The hexanitrocobaltates(III) of potassium, rubidium and caesium have cubic structures[220], the NO_2 groups being octahedrally distributed about the cobalt atoms, each *trans*-$[O_2N\text{–}Co\text{–}NO_2]$ unit being planar. In $K_3Co(NO_2)_6$, the bond lengths are Co–N = 2·04 Å, N–O = 1·11 Å and O–O = 2·10 Å. No structural analysis has been carried out on the sodium salt but on the basis of its infrared spectrum it has been concluded that it does not have the T_h symmetry of the other salts but rather the anion has S_6 site symmetry[228].

The $[Co(NO_2)_6]^{3-}$ ion is decomposed in acidic solution with the formation of cobalt(II) salts. One of its more remarkable reactions is that with the acetylacetonate ion in which four of the nitro groups only are replaced:

$$[Co(NO_2)_6]^{3-}+2acac^- \rightarrow [Co(acac)_2(NO_2)_2]^-+4NO_2^-$$

The sparingly soluble sodium, potassium, thallium(I) and silver salts of this anion can be isolated. On the basis of infrared evidence[219] the anion is believed to possess the *trans* structure; the rapid replacement of one NO_2 group in this anion by an amine can be explained by invoking the *trans* effect.

Carbonato complexes. There are a large number of carbonato complexes of the substituted cobaltammine type: these may contain unidentate carbonate ions, e.g. $[Co(NH_3)_5(CO_3)]^+$, or bidentate carbonate ions as in $[Co(NH_3)_4(CO_3)]^+$ [229]. Anionic carbonato complexes have been known for some years and many different formulae have been proposed for them. The oxidation of cobalt(II) salts by hydrogen peroxide or hypochlorite in the presence of potassium bicarbonate gives a deep green solution. Using a saturated bicarbonate solution at 0° the sodium salt $Na_3[Co(CO_3)_3].3H_2O$ precipitates as

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[226] B. M. Chadwick and A. G. Sharpe, *Advances Inorg. Chem. Radiochem.* **8** (1966) 83.

[227] G. Brauer, *Handbuch der Präparativen Anorganischen Chemie*, Vol. II, p. 1341, Ferdinand Enke (1962).

[228] I. Nakagawa, T. Shimanouchi and K. Yamasaki, *Inorg. Chem.* **3** (1964) 772.

[229] C. R. Piriz Mac-Coll, *Co-ordination Chem. Revs.* **4** (1969) 147.

an olive-green powder[230]. When dry this complex is stable in a stoppered bottle at room temperature; it decomposes at 90° without melting. Because this compound contains six base equivalents per molecule the addition of ligands in their acid form results in the formation of the cobalt(III) complex of the ligand; thus with *o*-aminophenol hydrochloride, for example, tris(*o*-aminophenolato)cobalt(III) is formed. The structure of the carbonato complex is not yet definitely established and it may, for example, be formulated as $Na_3[Co(HCO_3)_3(OH)_3]$. The potassium salt has the same empirical formula; it is, unlike the sodium salt, water-soluble. The reaction with nitrite ion[231], i.e.

$$[Co(CO_3)_3]^{3-} + 2KNO_2 \rightarrow trans\text{-}[Co(CO_3)_2(NO_2)_2]^{3-} + K_2CO_3$$

involves opening two of the carbonato-cobalt rings. All attempts to resolve $[Co(CO_3)_3]^{3-}$ into optical isomers have so far failed.

Carboxylato complexes. Like the carbonato ammine complexes, carboxylate anions form cobaltammines, e.g. $[Co(NH_3)_5(ox)]^+$ (ox = oxalate), in which they are unidentate and also those, e.g. $[Co(NH_3)_4(ox)]^+$, in which they are bidentate. Pure anionic carboxylato complexes are largely limited to the oxalatocobaltates(III). The potassium salt $K_3[Co(C_2O_4)_3] \cdot 3H_2O$ is best prepared[232] by the oxidation of a solution of cobalt(II) oxalate in potassium oxalate with lead dioxide. The excess lead salt is filtered off and the emerald green needles of the oxalatocobaltate(III) are precipitated by the addition of ethanol. Below 13·2°, the potassium salt crystallizes as the racemate, but above this temperature the optical isomers crystallize individually and the crystals can be separated mechanically. The pure *d*- and *l*-forms can readily be obtained[233] using a chemical separation at 0°; both isomers racemize rapidly in solution, about 24 hr being sufficient for complete racemization. The other alkali metals similarly form hydrated tris(oxalato)cobaltates(III). These are all hydrated, the lithium and sodium salts being isomorphous with the corresponding oxalato complexes of chromium(III) and aluminium(III).

Hydroxy-bridged oxalato complexes of the type $[(C_2O_4)_2Co(OH)_2Co(C_2O_4)_2]^{4-}$ are prepared from cobalt(II) salts and potassium oxalate in the presence of hydrogen peroxide at 55°. The potassium forms dark green crystals of the trihydrate. The barium and sodium salts are prepared from it by metathetic reactions[234]. The sodium salt is decomposed in the solid state by heat or light; in acid solution decomposition occurs rapidly

$$[(C_2O_4)_2Co(OH)_2Co(C_2O_4)_2]^{4-} \xrightarrow{2H^+} 2Co^{2+} + 2CO_2 + 3C_2O_4^{2-} + 2H_2O$$

Spectroscopic and Magnetic Properties of Cobalt(III) Complexes

The Co^{3+} ion is isoelectronic with Fe^{2+} (d^6 systems) and qualitatively the same energy level diagram applies to both species. In contrast to iron(II), however, almost all cobalt(III) complexes are low spin (t_{2g}^6 configurations) with the ${}^1A_{1g}$ ground state. Only with fluoride ions as ligands are high spin complexes of the $t_{2g}^4\,e_g^2$ configuration and ${}^5T_{2g}$ ground state found.

High spin complexes. The electronic spectra of various CoF_6^{3-} salts show[235] two bands at around 14,500 and 11,800 cm^{-1} which are assigned to the ${}^5T_{2g} \rightarrow {}^5E_g$ transition, the

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[230] H. F. Bauer and W. C. Drinkard, *Inorg. Syntheses*, **8** (1966) 202; *J. Am. Chem. Soc.* **82** (1960) 5031.
[231] V. A. Golovnya, L. A. Kokh and S. K. Sokol, *Zh. Neorg. Khim.* (English Edn.) **4** (1965) 448.
[232] J. C. Bailar and E. M. Jones, *Inorg. Syntheses*, **1** (1939) 37.
[233] G. B. Kauffman, L. T. Takahashi and N. Sugisaka, *Inorg. Syntheses*, **8** (1966) 207.
[234] A. M. Sargeson and I. K. Read, *Inorg. Syntheses*, **8** (1966) 204.
[235] F. A. Cotton and M. D. Meyers, *J. Am. Chem. Soc.* **82** (1960) 5023.

splitting being due to the dynamic Jahn Teller effect. The potassium salt has a magnetic moment of 5·63±0·05 B.M. with a Curie–Weiss constant $\theta = -10\pm2$°K; $Ba_3(CoF_6)_2$ also obeys the Curie–Weiss law but has $\mu_{eff} = 5{\cdot}27\pm0{\cdot}08$ B.M. and $\theta = -39\pm5$°; it is believed that the CoF_6 octahedra may be considerably distorted in this compound. The expected magnetic moment for an octahedral high spin complex (Co^{3+} has $\lambda = -145$ cm^{-1}) is about 5·8 B.M. at 300°K, falling somewhat with temperature[173].

Low spin complexes. Two absorption bands are expected in these complexes corresponding to the spin allowed transitions from the ${}^1A_{1g}$ ground state (see chapter on Iron, Fig. 26) to the ${}^1T_{1g}$ and ${}^1T_{2g}$ states; these transitions are usually observed (Table 10) in the visible and ultraviolet. The two spin forbidden bands to the triplet states are located in the near infrared and visible, but have not often been found. A more complete list of spectra than those presented here, particularly of substituted cobaltammines, can be found in Jorgensen's book[236]. The energies of the transitions are given by[237]

TABLE 10. ELECTRONIC SPECTRA (cm^{-1}) OF SOME SIX-COORDINATE COBALT(III) COMPLEXES

Complex	${}^1A_{1g}\rightarrow{}^3T_{1g}$	${}^1A_{1g}\rightarrow{}^3T_{2g}$	${}^1A_{1g}\rightarrow{}^1T_{1g}$	${}^1A_{1g}\rightarrow{}^1T_{2g}$
$[Co(CO_3)_3]^{3-}$ [a]			15,700	22,800
$[Co(H_2O)_6]^{3+}$ [b]	8000	12,500	16,500	24,700
$[Co(ox)_3]^{3-}$ [b]	8500	12,000	16,700	23,800
$Co(acac)_3$ [c]	9100	12,500	16,900	25,000
$[Co(NH_3)_6]^{3+}$ [a]	13,000	17,200	21,000	29,500
$[Co(en)_3]^{3+}$ [a]	13,700	17,500	21,400	29,500
$[Co(CNO)_6]^{3-}$ [d]			25,000	31,500
$Co[P(OCH_2)_3CMe]_6^{3+}$ [e]			30,800	35,700
$[Co(CN)_6]^{3-}$ [a]			32,400	39,000
cis-$[Co(en)_2Cl_2]^+$ [a]			18,900	25,600
trans-$[Co(en)_2Cl_2]^+$ [a]			16,200 22,000	25,800

[a] C. K. Jørgensen, *Absorption Spectra and Chemical Binding in Complexes*, Pergamon (1962).

[b] D. A. Johnson and A. G. Sharpe, *J. Chem. Soc.* (A) (1966) 798.

[c] D. W. Barnum, *J. Inorg. Nuclear Chem.* **21** (1961) 221.

[d] W. Beck and K. Feldt, *Z. anorg. u. allgem. Chem.* **341** (1965) 113.

[e] J. G. Verkade and T. S. Piper, *Inorg. Chem.* **2** (1963) 944.

$$E[{}^1A_{1g}\rightarrow{}^1T_{1g}] = 10Dq-C$$
$$E[{}^1A_{1g}\rightarrow{}^1T_{2g}] = 10Dq+16B-C$$
$$E[{}_1A_{1g}\rightarrow{}^3T_{1g}] = 10Dq-3C$$
$$E[{}^1A_{1g}\rightarrow{}^3T_{2g}] = 10Dq+8B-3C$$

In these equations contributions from $kB^2/10Dq$ have been ignored since for cobalt(III) complexes $10Dq$ is large and B small.

The spectrum of $[Co(H_2O)_6]^{3+}$ (Table 10) was measured in caesium cobalt(III) alum; the four bands are fitted with the parameters $10Dq = 20{,}800$, $B = 513$ and $C = 4250$ cm^{-1}. The polarized absorption spectrum of Co^{3+} in corundum at 77°K shows[238] the ${}^1T_{1g}$ level at 15,560 cm^{-1} and the ${}^1T_{2g}$ level at 22,980 cm^{-1}; these bands are split by a trigonal field

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[236] C. K. Jørgensen, *Absorption Spectra and Chemical Binding in Complexes*, Pergamon (1962).

[237] A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier (1968).

[238] N. S. Hush and R. J. M. Hobbs, *Progress in Inorg. Chem.* **10** (1968) 259.

by 360 and 370 cm^{-1}. The intensities of these spin allowed bands in cobalt(III) complexes are relatively high with ε of the order 10–10^2 l. cm^{-1} mole^{-1}. Studies[239] on the polarized crystal spectrum of $[Co(en)_3]^{3+}$ at low temperature indicate that the spectra are almost entirely dipole in nature and that the observed intensities are predominantly due to vibronic coupling involving the t_{1u} and t_{2u} vibrations of the CoN_6 octahedron.

In the six-coordinate complexes of lower symmetry such as CoL_4X_2, CoL_4XY and CoL_3X_3 splitting of one or both bands may be observed. For the *cis*- and *trans*-isomers of CoL_4X_2 and CoL_4XY complexes, the electronic spectra can usually be used to diagnose which isomer is present. The *cis* complexes are not centrosymmetric and their spectra are usually more intense than those of the corresponding *trans*-isomers. Further, the lowest energy band is split to a much greater extent in the *trans*- than in the *cis*-isomers. Typical spectra[240], i.e. those of *cis*- and *trans*-$[Co(en)_2F(H_2O)]^+$, are illustrated in Fig. 18. The splitting of the $^1T_1$ state in *trans*-CoL_4X_2 is expected theoretically to be twice as great as that in the *cis*-isomers. In the tetragonal field the $^1T_1$ state splits into the $^1A_2$ and ^1E components and the $^1T_2$ state into $^1B_2$ and $^1E(T_2)$; the transition energies to these components in a tetragonal field are given by[237]:

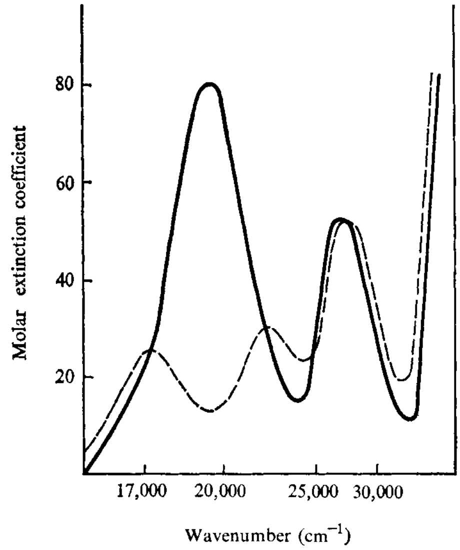

FIG. 18. Absorption spectra of *cis*-$[Co(en)_2F(H_2O)]^+$ (———) and *trans*-$[Co(en)_2F(H_2O)]^+$ (– – – –).

$$
\begin{aligned}
E[^1A_1 \rightarrow {}^1A_2] &= 10Dq - C \\
E[^1A_1 \rightarrow {}^1E] &= 10Dq - C - \tfrac{35}{4}Dt \\
E[^1A_1 \rightarrow {}^1B_2] &= 10Dq + 16B - C - 4Ds - 5Dt \\
E[^1A_1 \rightarrow {}^1E(T_2)] &= 10Dq + 16B - C + 2Ds - \tfrac{25}{4}Dt
\end{aligned}
$$

The splitting of the $^1T_{1g}$ level under the tetragonal field is thus $\frac{35}{4}Dt$ and whilst this can readily yield values of Dt the splitting of the $^1T_{2g}$ level is usually not sufficiently resolved to enable calculation of Ds.

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[239] R. Dingle, *Chem. Communs.* (1965) 304.

[240] S. C. Chan and C. K. Poon, *J. Chem. Soc.* (A) (1966) 146.

Complexes of low spin cobalt(III) are expected to be diamagnetic with a small temperature-independent paramagnetism associated with the $^1A_1$ ground term. Whilst they are in practice mostly diamagnetic some simple salts are reportedly paramagnetic; this paramagnetism may, however, be due to the presence of cobalt(II) impurities. Few examples are yet known of cobalt(III) complexes near the $^1A_1 \rightarrow {}^5T_2$ crossover point. Studies of cobalt(III) in oxide systems have shown that in $LaCoO_3$ having the perovskite structure with a Co^{3+}–O^{2-} distance of 1·91 Å, the $^5T_2$ ground state prevails, whilst in spinels such as Co_3O_4 having a Co^{3+}–O^{2-} distance of 2·0–2·1 Å the $^1A_1$ ground state is predominant[241].

Five-coordinate complexes. The tetrahedral cobalt(II) complexes $CoX_2(PR_3)_2$ have the remarkable property that they give five-coordinate cobalt(III) complexes upon oxidation. These $CoX_3(PR_3)_2$ complexes have two unpaired spins, are monomeric and presumably have a trigonal bipyramidal structure. The compounds $CoBr_3(PEt_3)_2$ and $CoCl_3(PEt_3)_2$ show absorption bands at 17,000 and 18,000 cm^{-1} respectively, which, despite their high intensity, may be *d–d* bands[242].

5. COMPOUNDS OF COBALT IN HIGH OXIDATION STATES (+4, +5)

Compounds of cobalt in oxidation states greater than +3 are rare and often poorly characterized. They occur only in compounds of cobalt bonded to fluorine or oxygen.

The yellow hexafluorocobaltate(IV) Cs_2CoF_6 is formed when Cs_3CoCl_4 is fluorinated at 300°; it has the cubic K_2SiF_6 structure[243]. The reported magnetic moment of 2·97 B.M. is, however, not what would be expected for a Co^{4+} ion with five or one unpaired electrons.

The oxidation of strongly alkaline cobalt(II) solutions with hypochlorite, persulphate or permanganate ions gives a precipitate believed to be a mixture of Co_2O_3 aq and CoO_2 aq[244]. At high temperatures and oxygen pressures alkali and alkaline earth metal cobaltates(IV) and (V) are believed to be formed. A mixture of $2Ba(OH)_2$ and $2Co(OH)_2$ yields red-brown Ba_2CoO_4 at 1150°. Impure Na_3CoO_4 has been prepared from Co_3O_4 and sodium oxide at 450° and 100 atm pressure[245]. The potassium salt K_3CoO_4 is similarly prepared[246]; it has two crystalline modifications. One form has an X-ray diffraction pattern resembling those of K_3PO_4 and K_3FeO_4; this form changes in two days to a more stable form. The oxidizing powder and magnetic studies on mixed crystals with K_3PO_4 indicate the presence of Co(V) in these compounds.

[241] R. L. Martin and A. H. White, *Transition Metal Chemistry*, **4** (1968) 113.

[242] K. A. Jensen and C. K. Jørgensen, *Acta Chem. Scand.* **19** (1965) 451.

[243] R. Hoppe, *Rec. trav. chim.* **75** (1956) 569.

[244] J. Besson, *Ann. Chim.* **2** (1947) 527, 547.

[245] R. Scholder, *Bull. Soc. Chim. France* (1965) 1112.

[246] C. Brendel and W. Klemm, *Z. anorg. u. allgem. Chem.* **320** (1963) 59.

42. NICKEL

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1. THE ELEMENT

1.1. HISTORY[1,2]

Although an alloy of nickel ("packfong") has been known to the Chinese for over 2000 years, the isolation of nickel metal was first achieved only some 200 years ago. In Germany during the late seventeenth century a heavy reddish-brown ore was used to colour glass green. The Saxon miners believed that this was an ore of copper but never succeeded in isolating copper from it. As a result of these futile attempts the ore became known as "Kupfernickel" (Old Nick's copper).

In 1751, Cronstedt investigated a new mineral from the cobalt mines in Helsingland, Sweden. Upon calcining the green crystals which covered the surface of the weathered ore and reducing the oxide so formed, Cronstedt obtained a white, hard and brittle metal bearing no resemblance to copper. He also demonstrated that the new metal was the dominant base in Kupfernickel and so proposed the name "nickel" for this metal. The first sample of pure nickel was prepared by Bergmann in 1775, and by 1805 Richter and others had described its physical properties.

1.2. OCCURRENCE AND DISTRIBUTION[2,3]

Nickel occurs to an estimated 0.016% in the 10-mile depth of the earth's crust, ranking twenty-fourth in the order of abundance of the elements in this crust. The total amount of nickel is greater than that of copper, zinc and lead combined, but there are relatively few known nickel deposits that are capable of being economically worked. Nickel ores fall into three main classes—sulphides, oxides and silicates, and arsenides.

One of the world's largest nickel deposits is at Sudbury, Ontario. Here the principal nickel-containing ore is *pentlandite* $(Ni,Fe)^9S^8$; it occurs along with iron sulphide, copper minerals such as chalcopyrite and also minerals of the platinum group. Similar deposits occur in South Africa, the USSR and Minnesota. The oxide ores are principally of two types. In the silicate type (New Caledonian and Oregon ores) the nickel occurs mainly in hydrous magnesium silicate, e.g. *garnierite* $(Ni,Mg)_6Si_4O_{10}(OH)_8$. The other oxide type (Cuban ore) is of high iron content and the nickel is associated mainly with *limonite*, e.g. $(Ni,Fe)O(OH)\cdot nH_2O$. Although the oxide ores account for the largest proportion of the

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[1] J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. XV, Longmans (1936).

[2] *Gmelins Handbuch der Anorganischen Chemie, Nickel,* 57 Teil A1, Verlag Chemie, 1967.

[3] C. A. Hampel (ed.), *The Encyclopaedia of the Chemical Elements*, Reinhold (1968).

earth's nickel content, they are widely distributed (occurring in the USSR, the Philippines, Indonesia, New Guinea, Greece, the Caribbean area and Brazil) and nickel production from them accounts for only about one-third of the total. The arsenide ores are the least important occurring mainly in Spain, Canada and Germany. The principal ones are *niccolite* (Kupfernickel) NiAs, *chloanthite* $NiAs_2$, *nickel glance* NiAsS, *annabergite* $Ni_3As_2O_8 \cdot 8H_2O$ and *smaltite* $(Ni,Co,Fe)As_2$.

1.3. INDUSTRIAL PRODUCTION OF NICKEL[4]

The ore is first crushed and concentrated by a flotation process which separates out the rock particles and separates the sulphide ores into a nickel–copper concentrate, a copper concentrate and a nickeliferous iron sulphide concentrate. The nickel–copper concentrate is roasted and smelted to form a matte; the nickel and copper sulphides present can be separated by a regulated slow cooling of the matte from 926° to 520°. Under these conditions, crystals of Cu_2S and Ni_3S_2 form chemically free from one another and can be mechanically separated by grinding and flotation. Alternatively, the sulphides can be separated by heating the matte with sodium bisulphate and coke (Orford process); two layers are formed in the melt, the sodium and copper sulphides unite in a solution lighter than the nickel and so the two can be separated by the "tops and bottoms" process. The nickel sulphide is sintered to the oxide; this oxide can be used as such in the manufacture of nickel steels, but for nickel production it has to be reduced and then refined. Two methods are used—the Mond process in Wales and an electrolytic process in Canada.

Mond process. This process is based upon the formation of volatile nickel carbonyl $Ni(CO)_4$, which is stable below 60° but decomposes into nickel and carbon monoxide at 180°. The nickel oxide is reduced to crude metal by water gas consisting of some 52% hydrogen and 36% carbon monoxide at 400°. Under these conditions the reduction is effectively carried out by hydrogen so that after removal of water (formed by $NiO + H_2 \rightarrow Ni + H_2O$) the exit gases are enriched in carbon monoxide. This gas is passed over the nickel at 50° and the carbonyl (b.p. 43°) decomposed at 180°, the nickel being deposited on nickel shot and the carbon monoxide being recycled for the preparation of more carbonyl.

Electrolytic refining. The oxide is reduced to crude metal by heating with coke in reverberatory furnaces. The crude metal (about 95% Ni, 2% Cu) is cast into anodes and these used in electrolytic cells containing a nickel sulphate and chloride solution as electrolyte and a pure nickel sheet cathode. Upon electrolysis the nickel dissolves from the anodes and plates out on the cathode; if special precautions are taken to prevent iron and copper depositing also (e.g. purification of the anolyte) the deposited nickel has a purity of 99.9%.

1.4. PREPARATION OF PURE NICKEL

The carbonyl process is most commonly employed when very pure nickel is required. The impure metal is reacted with pure carbon monoxide at 50° and the carbonyl produced fractionated several times prior to pyrolysis at around 200°. The nickel thus obtained has a purity of 99.90–99.99% depending upon the materials used.

Electrolytic methods for producing high purity nickel depend upon the production

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[4] W. H. Dennis, *Metallurgy of the Non-ferrous Metals*, 2nd edn., Pitman (1961).

of high purity nickel salts. The nickel obtained by the electrolysis of pure nickel chloride solution with inert platinum–iridium anodes is 99.99% pure.

1.5. NUCLEAR PROPERTIES[5, 6]

Nickel occurs naturally as a mixture of five stable isotopes. Table 1 lists these with their percentage abundances and atomic masses based on ^{12}C. Many preparative methods have been used[2] for the artificially radioactive isotopes; an example of the preparation together with the half-life and decay mode are given in the table for each isotope.

TABLE 1. ISOTOPES OF NICKEL

Isotope	% natural abundance	Atomic mass	Half-life	Decay mode	Preparation (example)
^{56}Ni			6.4 d	EC	^{54}Fe (α, $2n$)
^{57}Ni			36 h	EC, β^+	^{58}Ni (γ, n)
^{58}Ni	67.88	57.9353			
^{59}Ni			8×10^4 y	EC	^{58}Ni (n, γ)
^{60}Ni	26.23	59.9332			
^{61}Ni	1.19	60.9310			
^{62}Ni	3.66	61.9283			
^{63}Ni			92 y	β^-	^{63}Cu (n, p)
^{64}Ni	1.08	63.9280			
^{65}Ni			2.56 h	β^-	^{64}Ni (n, γ)
^{66}Ni			55 h	β^-	^{68}Zn (p, $3p$)
^{67}Ni			50 s		^{70}Zn (n, α)

EC = orbital electron capture; s = seconds; h = hours; d = days; y = years.

1.6. PHYSICAL PROPERTIES

Some of the important physical properties of nickel are listed in Table 2. It is a silvery white metal capable of taking a high polish. In its commercially pure form (99.5%) it has wide and important industrial applications. It can be forged, welded, machined, and rolled into sheets. Nickel is ductile, moderately strong, and highly resistant to corrosion in many media. It retains its strength at high temperatures and its ductility as well as its strength at sub-zero temperatures. Fabricated nickel has mechanical properties resembling those of mild steel; it is, however, unlike steel, resistant to corrosion, and this fact, together with the fact that it is non-toxic, leads to its use in the manufacture of plant for food handling and pharmaceutical processing.

Nickel is ferromagnetic below the Curie point 357°C; its saturation induction is approximately 6000 gauss. It ordinarily has a face-centred cubic lattice with a cell edge $a = 3.5239$ Å [7]. A hexagonal form ($a = 2.65$, $c = 4.33$ Å) is also known; this is not ferromagnetic and changes into the cubic form at 250°.

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[5] R. L. Heath, in *Handbook of Chemistry and Physics*, 49th ed., Chemical Rubber Company, Cleveland (1968), p. B. 4.

[6] L. J. Kirby, *The Radiochemistry of Nickel*, NAS–NRC Nuclear Science Series No. 3051, Washington (1961).

[7] R. W. G. Wyckoff, *Crystal Structures*, 2nd ed., Vol. 1 (1963).

The most important use of nickel is in austenitic chromium—nickel steels which are renowned for their resistance to corrosion; nickel alloys are described in section 1.9. Nickel also finds use as a catalyst in industrial processes, e.g. in the hydrogenation of unsaturated organic compounds (manufacture of fats), and in oil refining. Raney nickel is a widely used catalyst prepared by dissolving away the aluminium from $NiAl_3$ with alkali thereby leaving a porous highly active form of the metal.

TABLE 2. PHYSICAL PROPERTIES OF NICKEL[3, 5]

Atomic number	28
Electronic configuration	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8\ 4s^2$
Atomic weight	58.71
M.p. (°C)	1453
ΔH_{fusion} (cal g^{-1})	73.8
B.p. (°C)	2732
$\Delta H_{\text{vaporization}}$ (cal g^{-1})	1487
Vapour pressure (mm Hg):	
1000°C	1.2×10^{-6}
m.p.	9.4×10^{-3}
2000°C	213
Density (g cm^{-3}):	
20°C	8.908
Liquid	7.9
Electrical resistivity (microhm-cm) 20°C	6.844
Thermal conductivity (cal cm^{-1} $°C^{-1}$ sec^{-1}), 100°C	0.198
Specific heat (cal g^{-1}) 200°C	0.1225
Ionization potential (eV):	
First	7.633
Second	18.15
Third	35.16
Specific heat (cal g^{-1}):	
25°C	0.1061
100°K	0.232

1.7. CHEMICAL PROPERTIES

1.7.1. Reaction with Elements

Nickel absorbs hydrogen especially when finely divided, the hydrogen absorption increasing with temperature. Even at room temperature a considerable occlusion of hydrogen is observed when hydrogen ions are discharged at a porous nickel electrode. No definite hydrides, however, have been characterized. Nitrogen is not absorbed by nickel nor does it combine directly with it. Finely divided nickel may be pyrophoric in air under certain conditions; nickel wire burns brilliantly in oxygen and sheet nickel tarnishes like steel when it is heated in air. Binary compounds are formed directly when nickel is heated with sulphur, boron, silicon, and phosphorus. Heated nickel burns in chlorine and bromine forming the yellow nickel(II) halides; nickel and iodine react similarly when heated together in a sealed tube. Finely divided nickel is attacked by fluorine above 400°. Molten nickel takes up carbon (up to 6.25%), but upon solidification most of this separates out as graphite; up to 0.5% C can be held in solid solution at 1315°C. Nickel combines vigorously with aluminium forming NiAl ($NiAl_2$ and $NiAl_3$ decompose above their melting points).

1.7.2. Reaction with Compounds

Nickel is attacked by steam at red heat with the formation of the oxide and hydrogen. Ammonia is decomposed by nickel at moderate temperatures (above 300°); formation of the nitride Ni_3N occurs around 445°. Hydrogen fluoride reacts with nickel powder at 225° to form NiF_2 and the other hydrogen halides react similarly although the massive metal is only slowly attacked at temperatures below 500°. Nickel is a suitable metal for containing these hydrogen halides (when they are dry) below 200° and is used in valves on cylinders of these gases. Hydrogen sulphide corrodes nickel at moderate temperatures forming the black sulphide NiS. A mixture of NiS and Ni_2S is formed when carbon disulphide is passed over nickel filings above 350°. The oxides of nitrogen all react with heated nickel to some extent forming nickel(II) oxide and nitrogen; carbon monoxide reacts at relatively low temperatures (50°) to form the carbonyl $Ni(CO)_4$.

Nickel is fairly electropositive, its electrode potential for the reaction

$$Ni \rightarrow Ni^{2+}+2e \quad (E^\circ = -0.250\ V)$$

being similar to that for the analogous cobalt reaction. It dissolves in dilute mineral acids rather more slowly than does iron. Hydrogen is liberated from non-oxidizing acids, including sulphurous, sulphuric, hydrochloric, and phosphoric acids. Dilute nitric and nitrous acids dissolve the metal rapidly, oxides of nitrogen being evolved. Concentrated nitric acid renders the metal passive. An outstanding property of nickel is its resistance to attack by caustic alkalis, and the metal has found widespread use in the production and handling of caustic soda. The metal is, however, attacked by aqueous ammonia.

1.8. ANALYTICAL CHEMISTRY

1.8.1. Qualitative Detection

Solutions of nickel(II) salts in water are normally green. Black nickel sulphide is precipitated from faintly alkaline solutions of its salts by hydrogen sulphide, no precipitation occurring under acid conditions. Nickel salts are readily distinguished from cobalt salts by reaction with dimethylglyoxime (dissolved in ethanol) in dilute ammonia solution; the nickel ions give a bright red precipitate of bis(dimethylglyoximato)nickel(II), but cobalt ions merely give a brown coloration. Furildioxime $(C_4H_3O)_2C_2(NOH)_2$ gives a similar precipitate with nickel ions; this reagent, however, will detect one part of nickel in 6 million[8]. Dithiooxamide (rubeanic acid) $(CSNH_2)_2$ gives a blue–violet precipitate in ammoniacal solutions of nickel(II) salts; copper and cobalt salts interfere with this test, but this reagent finds uses as a developer in paper chromatography where a separation of the metals has already been achieved.

1.8.2. Quantitative Estimation

The most frequently used gravimetric method for determining nickel in its salts uses dimethylglyoxime[9]; the dimethylglyoximate is dried at 110–120° and weighed as $Ni(C_4H_7O_2N_2)_2$. Cobalt does not interfere in the determination, but if iron is present, e.g. in steel analysis, then sufficient citrate or tartrate ions must be added to keep the iron(III) in solution. A more rapid gravimetric method involves precipitation of nickel ions with pyridine and thiocyanate ions as $[Ni(C_5H_5N)_4](SCN)_2$—a complete determination

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[8] A. I. Vogel, *Macro and Semimicro Qualitative Inorganic Analysis*, Longmans (1953).

[9] A. I. Vogel, *A Text-book of Quantitative Inorganic Analysis*, Longmans (1961).

being completed in about 30 min[9]. Nickel can also be determined gravimetrically by electrolysis of nickel salts in strong ammonia solution containing ammonium sulphate, nickel being deposited on the weighed cathode.

Volumetrically, nickel(II) salts may be estimated by titration with potassium cyanide in slightly ammoniacal solution in the presence of a turbidity due to silver iodide. The nickel ions form $[Ni(CN)_4]^{2-}$ ions until at the end point the turbidity clears due to dissolution of the silver iodide as $[Ag(CN)_2]^-$. Alternatively, the nickel can be precipitated with 8-hydroxyquinoline and the precipitated oxinate $Ni(C_9H_9ON)_2 \cdot 2H_2O$ filtered off and titrated with standard potassium bromate.

A colorimetric method for nickel involves the addition of dimethylglyoxime to an alkaline solution of the nickel salt which has been treated with bromine (or other oxidizing agent). The red solution thus formed is measured at 445 mμ.

1.9. ALLOYS OF NICKEL[4]

Nickel is an important component of many alloys, about 85% of nickel production being used in alloy form. These alloys can be conveniently divided into ferrous and non-ferrous.

1.9.1. Ferrous Alloys

The presence of small amounts of nickel in steel lead to improved mechanical properties, facilitate heat treatment, and give greater reliability and regularity of the properties of the steel. *Stainless steel* contains 18% chromium and up to 8% nickel; it is well known for its resistance to corrosion coupled with strength and toughness. *Nickel cast-iron*, formed when nickel is added to white or grey cast-iron, is denser, stronger, and more readily machined than cast-iron; it is used in engine cylinder blocks and heads. *Nickel–iron alloys* contain in excess of 25% nickel; alloys having this proportion of nickel are frequently no longer ferromagnetic. The exact amount of nickel required to give non-magnetic properties is, however, very dependent upon the impurities present. Examples of non-magnetic ferrous alloys are *Ni-Resist* (Ni 14%, Cu 6%, Cr 2%, C 3%) and *Nomag* (Ni 11%, Mn 6%). These materials are used in electrical engineering as they combine non-magnetic properties with high electrical resistance. Alloys having 35–80% nickel have a high magnetic permeability. *Permalloy* (Ni 78.5%, Fe 21.5%) was developed especially for use in telegraph cables; the addition of molybdenum to such alloys gives *Supermalloy* which has a very high initial permeability, and is used in the construction of magnetic screens. Permanent magnets can be produced by special treatment of steels containing aluminium, nickel, and cobalt (*Alnico*); these have about twenty-five times the magnetic strength of the best carbon–steel magnets.

1.9.2 Non-ferrous Alloys

Nickel and copper are mutually soluble in all proportions, the strength of the alloy increasing up to 60–70% nickel in which composition range the alloys combine high mechanical properties with exceptional corrosion resistance and ready workability. The outstanding example of this type of alloy is *Monel*, which has about 68% nickel, 32% copper, with trace amounts of manganese and iron. *Cupro-nickels* have up to 80% copper; the "silver" coins used in Britain and the American "nickel" are made of approximately

75% copper and 25% nickel. *Nickel silver* (*German silver*) contains some 10–30% nickel, 55–65% copper, and the balance zinc; when electroplated with pure silver, the material is known as EPNS. Nickel–chromium alloys find extensive uses as electric resistance materials, e.g. *Nichrome* wire (Ni 60%, Cr 40%) and *Iconel* (Ni 76%, Cr 5%, balance mainly Fe); they have oxidation resistance up to 1200°C and good high temperature mechanical properties which prevent heating elements from sagging.

2. COMPOUNDS OF NICKEL IN LOW OXIDATION STATES (−I, 0, +I)

2.1. NICKEL CARBONYL, $Ni(CO)_4$

Nickel tetracarbonyl was discovered in 1890 by Mond, Langer, and Quincke[10] by the reaction of carbon monoxide with nickel powder at atmospheric pressure and temperatures below 100°. It is a colourless liquid at room temperature. A great number of variations on Mond's original preparation have been described, most of them using the reduction of nickel ores, oxides, or salts followed by reaction with carbon monoxide at temperatures below 150° and pressures of 1–150 atm. Nickel carbonyl is produced industrially on a large scale as the intermediate in nickel refining. A convenient laboratory preparation[11] involves the preparation of finely divided nickel by thermal decomposition of nickel(II) formate; this nickel in the presence of a little mercury reacts with carbon monoxide at room temperature and atmospheric pressure.

Nickel carbonyl can also be synthesized in aqueous media in the presence of sulphur compounds. The passage of carbon monoxide through an alkaline nickel(II) sulphate solution in the presence of ethyl mercaptan gives good yields of the carbonyl. Nickel sulphide is quantitatively transformed into the carbonyl by reaction with carbon monoxide in alkaline solution[12]:

$$NiS + 5CO + 4OH^- \rightarrow Ni(CO)_4 + S^{2-} + CO_3^{2-} + 2H_2O$$

Under more severe conditions, e.g. 120° and 50 atm of carbon monoxide, even the hexammine $[Ni(NH_3)_6]^{2+}$ is converted to the carbonyl.

2.1.1. Physical Properties and Structure

Nickel carbonyl is a very toxic mobile liquid with a high vapour pressure at room temperature. Some of its physical properties are listed in Table 3. It is diamagnetic, insoluble in water, but soluble in many organic solvents. Electron diffraction studies on the vapour[13] and X-ray diffraction studies on the solid (bond lengths in Table 3) show the molecule to be regular tetrahedral with linear Ni–C–O units. Since the donor power of the lone pair electrons on the carbon atom in carbon monoxide is not great, the formation of four Ni–C σ-bonds only, does not adequately explain the stability of the carbonyl. The Ni–C bond is thus believed to consist of a σ-bond formed by overlap of a filled carbon σ-orbital with a vacant σ-orbital on nickel and a π-bond formed by overlap of a filled $d\pi$ nickel orbital with an empty $p\pi$ antibonding orbital on carbon monoxide. This bonding

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[10] L. Mond, C. Langer and F. Quincke, *J. Chem. Soc.* (1890) 749.

[11] W. L. Gilliland and A. A. Blanchard, *Inorg. Syntheses*, **2** (1946) 234.

[12] H. Behrens and E. Eisenmann, *Z. anorg. u. allgem. Chem.* **278** (1955) 155.

[13] L. O. Brockway and P. C. Cross, *J. Chem. Phys.* **3** (1935) 828.

is synergic since the feeding of metal electrons into carbon monoxide orbitals will tend to increase the σ-donor power of the latter while at the same time the donation of electrons from carbon to the metal along the σ-bond renders the carbon monoxide more positive and ready to accept electrons from the metal into its π orbitals. This type of bonding should be evidenced by shorter M–C and longer C–O bonds as compared to M–C single and C≡O triple bonds respectively. The bond length in carbon monoxide is 1.128 Å, i.e. shorter than in the carbonyl (1.15 Å), but unfortunately the uncertainties in these distances are of the order 0.2–0.3 Å so that no significance can be attached to this bond "lengthening". The infrared spectra, however, do support this reduction in C–O bond order, the (C–O) stretching frequency in carbon monoxide (2143 cm^{-1}) being reduced to 2057 cm^{-1} in the gaseous carbonyl. Further, it is found that if some of the CO ligands are replaced with other ligands of low acceptor power, then the increase in the M–C back bonding is reflected in even lower values of the C–O stretching frequency.

TABLE 3. PHYSICAL PROPERTIES OF NICKEL CARBONYL

M.p. (°C)[a]	−19.3
B.p. (°C)[b]	42.2
Vapour pressure equation[c] (−35 to 45°C)	$\log p = 7.690-1519/T$
ΔH_{fusion}[a] (kcal $mole^{-1}$)	3.306
$\Delta H_{\text{vaporization}}$[a] (kcal $mole^{-1}$)	6.50
Heat capacity[a], C_p (cal $mole^{-1}$) 270°K	48.23
ΔH for reaction[d] $Ni(s)+4CO(g) \rightarrow Ni(CO)_4(g)$ (kcal $mole^{-1}$)	−39.1
$\Delta H_{\text{combustion}}$[d] to NiO and CO_2 (kcal $mole^{-1}$)	−282.2
Mean dissociation energies of M–C bond[e] (kcal)	35.2
Infrared spectrum of gas (cm^{-1}):[f]	
ν (C–O)	2057
δ(C–M–C)	64–68
δ(M–C–O)	459
γ(M–C)	422
δ(C–M–C)	74
Density 20°C[g] (g cm^{-3})	1.3103
Dipole moment[h] (D)	0.3
Interatomic distances[i] (Å):	
Ni–C	1.84±0.03
C–O	1.15±0.03

[a] J. E. Spice, L. A. K. Staveley and G. A. Harrow, *J. Chem. Soc.* (1955) 100.
[b] B. Suginuma and K. Satozaki, *Bull. Inst. Phys. Chem. Res. Tokyo* **21** (1942) 432.
[c] J. S. Anderson, *J. Chem. Soc.* (1930) 1653.
[d] A. K. Fischer, F. A. Cotton and G. Wilkinson. *J. Am. Chem. Soc.* **79** (1957) 2044.
[e] *Ibid.*, **81** (1959) 800.
[f] D. M. Adams, *Metal Ligand and Related Vibrations*, Arnold (1967) p. 84.
[g] F. W. Laird and M. A. Smith, *J. Am. Chem. Soc.* **57** (1935) 266.
[h] L. E. Sutton, R. G. A. New and J. B. Bentley, *J. Chem. Soc.* (1933) 652.
[i] J. Ladell, B. Post and I. Fankuchen, *Acta Cryst.* **5** (1952) 795.

2.1.2. Chemical Properties[14]

Nickel carbonyl is stable in a sealed vessel at room temperature. It burns in air with a bright luminous flame and forms explosive mixtures with air. It is very poisonous—considerably more so than that expected of its carbon monoxide content. Just as the vapour

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[14] F. Calderazzo, R. Ercoli and G. Natta, in *Organic Syntheses via Metal Carbonyls* (I. Wender and P. Pino, eds.), Interscience (1968).

is decomposed thermally above 50° into nickel and carbon monoxide, so, too, is a benzene solution of the carbonyl when heated under reflux. Reactions of the carbonyl must therefore be carried out at low temperatures. Dilute aqueous acids or alkalis have no effect upon nickel carbonyl.

Oxidation and reduction reactions. Nickel carbonyl is readily oxidized by air; its solutions in organic solvents develop a pale green gelatinous precipitate as the oxidation proceeds. Such solutions are also readily oxidized to nickel(II) salts by the halogens (no carbonyl halides are formed) by cyanogen and by sulphur. Hydrogen chloride and hydrogen sulphide decompose the solutions slowly with evolution of hydrogen and carbon monoxide.

Nitrogen dioxide reacts with nickel carbonyl to produce a mixture of nickel(II) nitrite and nitrate; nitrogen monoxide reacts with the carbonyl in an inert solvent under pressure to give $Ni(NO)NO_2$ [15]. In the gas phase, carbon disulphide reacts according to

$$CS_2+2Ni(CO)_4 \rightarrow 2NiS+C+8CO$$

and a black crystalline phosphide NiP is obtained in the vapour phase reaction with phosphorus or phosphine at 50°. With many halogenated organic compounds, nickel(II) halides are produced; thus acetyl chloride gives biacetyl, carbon monoxide, and nickel chloride, and Grignard reagents give organic carbonyl compounds[16].

Nickel carbonyl can be reduced to a carbonyl hydride by reaction with alkali metals in liquid ammonia[17]:

$$2Ni(CO)_4+2Na+2NH_3 \rightarrow [NiH(CO)_3]_2+2CO+2NaNH_2$$

This hydride is isolated as the red tetraammoniate $[NiH(CO)_3]_2 . 4NH_3$. At temperatures above −30°C it decomposes into the tetracarbonyl, ammonia, and hydrogen. The tetraammoniate reacts with water to form the carbonylate anions $[Ni_4(CO)_9]^{2-}$ and $[Ni_4H(CO)_9]^-$.

When the tetracarbonyl is reduced by sodium, potassium or magnesium amalgams in tetrahydrofuran the enneacarbonyltetranickelates are formed[18].

$$4Ni(CO)_4+2Na \rightarrow Na_2[Ni_4(CO)_9]+7CO$$

These salts are extremely air sensitive; they crystallize from solution as solvates, e.g. $Na_2[Ni_4(CO)_9]4.5THF$ and $K_2[Ni_4(CO)_9]1.5THF$. In water these salts form the $[Ni_4H(CO)_9]^-$ ion which can be precipitated as the $[Ni(phen)_3]^{2+}$ salt:

$$[Ni_4(CO)_9]^{2-}+H_2O \rightarrow [HNi_4(CO)_9]^-+OH^-$$

When these solutions are treated with phosphoric acid, black violet crystals of $H_2Ni_4(CO)_9$ can be obtained. The reduction of nickel carbonyl with lithium amalgam proceeds slightly differently, producing the octacarbonyltrinickelate anion

$$3Ni(CO)_4+2Li \rightarrow Li_2[Ni_3(CO)_8]+4CO$$

The dark red pyrophoric salt crystallizes with 7 THF molecules. This anion is also formed[19] when nickel carbonyl is allowed to react with saturated methanolic solutions of sodium hydroxide over many hours.

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[15] R. D. Feltham and J. T. Cariel, *Inorg. Chem.* **3** (1964) 121.

[16] F. L. Benton, S. M. C. Voss and P. A. McCusker, *J. Am. Chem. Soc.* **67** (1945) 82.

[17] H. Behrens and F. Lohofer, *Chem. Ber.* **94** (1961) 1391; H. Behrens, H. Zizlsperger and R. Rauch, *ibid.*, p. 1497.

[18] W. Hieber and J. Ellerman, *Z. Naturforsch.* **18b** (1963) 595.

[19] H. W. Sternberg, R. Markby and I. Wender, *J. Am. Chem. Soc.* **82** (1960) 3638.

Disproportionation reactions. Nitrogen donor molecules frequently causes disproportionation of nickel carbonyl into carbonyl free cations and polynuclear carbonylnickelates. With pyridine, morpholine, α-picoline, and piperidine[20], unstable substitution products such as $Ni(CO)_3L$ are formed and decompose with disproportionation of the nickel:

$$3Ni(CO)_3L + 3L \rightarrow [NiL_6]^{2+}[Ni_2(CO)_6]^{2-}$$

With 1,10-phenanthroline and 2,2′-dipyridyl the substitution products are isolated because the $[Ni_2(CO)_6]^{2-}$ anion reduces the cations, e.g.

$$[Ni(phen)_3]^{2+} + [Ni_2(CO)_6]^{2-} \rightarrow 3Ni(CO)_2phen$$

Ethylenediamine gives the disproportionation reaction with the formation of the $[Ni_4(CO)_9]^{2-}$ ion. Liquid ammonia forms substitution products[12] $[Ni(CO)_3(NH_3)_3]$ and $[Ni(CO)_2(NH_3)_2]$ both of which disproportionate above −60°.

Substitution reactions[22]. These occur in the reactions of nickel carbonyl with phosphorus, arsenic, and antimony donors as well as with isonitriles and unsaturated organic molecules. Mono- and di-substituted products are easily obtained, but tri- and tetrasubstituted products are obtained more rarely; some examples of substitution products prepared by direct reaction between nickel carbonyl and the ligand are given in Table 4.

TABLE 4. SOME SUBSTITUTION PRODUCTS OF NICKEL CARBONYL

Compound	Colour	M.p.(°C)	Reference
$Ni(CO)_3PPh_3$	Cream	126	L. S. Meriwether and M. L. Fiene, *J. Am. Chem. Soc.* **81** (1959) 4200
$Ni(CO)_2(PPh_3)_2$	Pale yellow	212*d*	*Ibid.*
$Ni(CO)_3PF_3$	White	—	R. J. Clark and E. O. Brimm, *Inorg. Chem.* **4** (1965) 651.
$Ni(CO)_2(PF_3)_2$	White	-93	*Ibid.*
$Ni(CO)_2[o\text{-}C_6H_4(PMe_2)_2]$	White	121–125	J. Chatt and F. A. Hart, *J. Chem. Soc.* (1970) 1378.
$Ni(CO)[P(OPh)_3]_3$	White	98·5	L. Malatesta and A. Sacco, *Ann. Chim.* (*Rome*) **44** (1954) 134.
$Ni(CO)[PhP(o\text{-}C_6H_4PEt_2)_2]$	Orange	189–191·5	J. Chatt and F. A. Hart, *J. Chem. Soc.* (1965) 812.
$Ni(CO)_3AsPh_3$	White	105	W. Reppe and W. J. Schweckendiek, *Ann. Chem.* **560** (1948) 104.
$Ni(CO)_3SbPh_3$		96–100	*Ibid.*
$Ni(CO)_3SbCl_3$	Pale buff		G. Wilkinson, *J. Am. Chem. Soc.* **73** (1951) 5502.
$Ni(CO)_3(CNMe)$	Colourless		M. Bigorgne, *J. Organomet. Chem.* **1** (1963) 101.

The reactions often proceed in an inert solvent at room temperature, but sometimes heating under reflux in a low boiling solvent is necessary. The reactions of the phosphorus halides are interesting in that completely substituted derivatives can be obtained; phosphorus trichloride gives $Ni(PCl_3)_4$ from which $Ni(PBr_3)_4$ and $Ni(PF_3)_4$ can be obtained by reaction with the appropriate phosphorus trihalide[23]. Phenyl isonitrile

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[20] W. Hieber, J. Ellermann, and E. Zahn, *Z. Naturforsch.* **18b** (1963) 589.

[21] H. Behrens and H. Zizlsperger, *J. Prakt. Chem.* **14** (1961) 249.

[22] T. A. Manuel, *Advances Organomet. Chem.* **3** (1965) 181.

[23] G. Wilkinson, *J. Am. Chem. Soc.* **73** (1951) 5501.

similarly gives complete replacement of carbonyl groups in forming $Ni(CNPh)_4$[24]. The disubstituted phosphine complexes have been used as catalysts in the trimerizations of acetylenic compounds[25, 26]; $Ni(CO)_2(PPh_3)_2$ catalyses the conversion of propargyl alcohol to a mixture of 1,2,4- and 1,3,5,-tri(hydroxymethyl)benzene and of phenylacetylene into 1,2,4-triphenylbenzene.

Many of these substituted carbonyls have been prepared primarily for use in infrared studies[22] and some for mechanistic studies[27]. The exchange reactions between complexes of the types $Ni(CO)_3PR_3$ or $Ni(CO)_2(PR_3)_2$ and other phosphines proceed by an S_N1 mechanism, the rates depending upon the strength of the Ni–CO or Ni–P bond which dissociates to give the 3-coordinate intermediate. The σ-bonding ability of the phosphines seems to be most important in determining the Ni–P bond strength, while the π-bonding ability of the phosphines is more important in determining the Ni–CO bond strength.

When nickel carbonyl reacts with unsaturated organic molecules, complete replacement of the carbonyl groups is usually observed[28]. Thus cyclopentadiene reacts with the carbonyl in *n*-hexane at 70° to give π-cyclopentadienyl–π-cyclopentenyl–nickel(II), i.e. $(\pi\text{-}C_5H_5)Ni(\pi\text{-}C_5H_7)$. Allyl iodide reacts under similar conditions to form the deep red π-allyl complex $Ni(C_3H_5I)_2$, and compounds of the type NiL_2 (L = acrylonitrile, acrylaldehyde, or duroquinone) are also formed by direct reaction of the ligand with nickel carbonyl. Diphenylacetylene undergoes a more profound reaction when heated with the carbonyl in petroleum ether in a sealed tube at 110°; the product is the same as that obtained from tetraphenylcyclopentadienone and nickel carbonyl, i.e. bis(tetraphenylcyclopentadienone)nickel[29].

2.2. NICKEL NITROSYLS[30]

No simple nitrosyl of nickel is known, but a variety of substituted nitrosyls exist examples of which are given in Table 5.

The reaction of nickel carbonyl with nitrogen monoxide has been studied by many workers[30]; in the absence of water or other coordinating solvent the blue air-sensitive solid $Ni(NO)(NO_2)$ is obtained.

$$Ni(CO)_4 + 4NO \rightarrow Ni(NO)NO_2 + 4CO + N_2O$$

This compound ignites with a yellow flame upon contact with water. It is believed to be polymeric and similar in this respect to the nitrosyl halides $[Ni(NO)X]_n$. The infrared spectrum of $Ni(NO)NO_2$ shows in addition to the strong nitrosyl band, bands typical of nitrito and bridging nitrito groups. It gives a blue solution in ethanol which reacts with triphenylphosphine to form $Ni(NO)(NO_2)(PPh_3)_2$. In the presence of traces of water, nickel carbonyl and nitrogen monoxide form a blue compound which is formulated as $Ni(NO)(OH)_3$ containing tetrahedral nickel(II). In methanol as solvent this reaction produces $Ni(NO)(OH)(OMe)_2$. This compound is converted into a green compound

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[24] F. Klages and K. Monkemeyer, *Naturwiss.* **37** (1950) 210; W. Hieber, *Z. Naturforsch.* **5b** (1950) 129.
[25] W. Reppe and W. J. Schweckendiek, *Ann. Chem.* **560** (1948) 104.
[26] J. D. Rose and F. S. Statham, *J. Chem. Soc.* (1950) 69.
[27] L. S. Meriwether and M. Fiene, *J. Am. Chem. Soc.* **81** (1959) 4200.
[28] G. N. Schrauzer, *Advances Organomet. Chem.* **2** (1964) 1.
[29] E. Weiss and W. Hubel, *J. Inorg. Nucl. Chem.* **11** (1959) 42.
[30] B. F. G. Johnson and J. A. McCleverty, *Progress Inorg. Chem.* **7** (1966) 277.

on standing, the NO^+ band at 1820 cm^{-1} disappearing and new bands, believed to be due to bridging nitro groups, appearing; the transformation is thus represented:

$$2Ni(NO)(OH)(OMe)_2 \rightarrow [Ni(NO_2)(OMe)(MeOH)]_2$$

In the presence of an amine and cyclopentadiene, the nickel carbonyl–nitrogen monoxide reaction yields the stable, volatile liquid $(\pi\text{-}C_5H_5)NiNO$; this diamagnetic compound is obtained also in the direct reaction between nickelocene and nitrogen monoxide[31]. Since the infrared spectrum indicates the presence of NO^+, this compound is formulated as containing nickel(0), $(C_5H_5^-)Ni^0(NO^+)$. The microwave spectrum[32] shows the Ni–N–O atoms to be colinear, and the infrared spectrum[33] has confirmed the open sandwich type of structure and the overall C_{5v} symmetry for the molecule. The reactions of substituted nickel carbonyls with nitrogen monoxide give nickel nitrosyl complexes such as $Ni(NO)_2(PPh_3)_2$.

TABLE 5. SOME NITROSYL COMPLEXES OF NICKEL

Compound	Colour	ν(N–O) (cm^{-1})	Other properties
$Ni(NO)(NO_2)$[a]	Light blue	1845	
$Ni(NO)(OH)_3$[b]	Blue	1825	μ_{eff} = 2.97 BM
$Ni(NO)(OH)(OMe)_2$[b]	Blue	1820	μ_{eff} = 2.8 BM
$Ni(NO)_2(PPh_3)_2$[c]	Purple	1745	Dip. mom., 4.26 *D*
$Ni(NO)_2[P(OPh)_3]_2$[c]	Purple	1710	
$[Ni(NO)Br]_n$[d]	Blue–black	1870[c]	
$[Ni(NO)I]_n$[d]	Blue–black	1855[e]	
$Ni(NO)Br(PPh_3)_2$[e]	Blue	1735	Dip. mom., 6.28 *D*
$Ni(NO)(NO_3)(PPh_3)_2$[e]	Blue	1725	
$Ni(NO)(NO_2)(PEt_3)_2$[f]	Violet-brown	1705	Dip. mom., 7.1 *D*
$Ni(NO)I(AsPh_3)_2$[g]	Blue	—	m.p., 168–169°
$Ni(NO)Br(SbPh_3)_2$[g]	Blue	—	m.p., 104–106°
$Ni(NO)Cl(PEt_3)_2$[g]	Dark brown	1706	m.p., 53–54°
$Ni(NO)(\pi\text{-}C_5H_5)$[a]	Red–brown	1843	m.p., −41°
$[Ni(NO)Cl_2]_n$[h]	Dark green	1870, 1835	
$[Ni(NO)Br_2]_n$[h]	Dark green	1865, 1830	
$[Ni(NO)(SEt)]_n$[i]	Green	1760	
$[Ni\cdot(NO)SCN]_n$[j, k]	Blue	1853	m.p., 75°
$Ni(NO)(NCS)(PPh_3)_2$[j, k]	Violet	1754	m.p., 179–186°
$Ni(NO)(PPh_3)_2SPh$[j]	Violet–black	—	m.p., 180–184°
$K_2[Ni(NO)(CN)_3]$[l]	Red	1780[m]	ν(C–N), 2133, 2118 cm^{-1}

[a] R. D. Feltham and J. T. Carriel, *Inorg. Chem.* **3** (1964) 121.
[b] W. P. Griffith, J. Lewis, and G. Wilkinson, *J. Chem. Soc.* (1959) 1775.
[c] *Ibid.* (1961) 2259.
[d] W. Hieber and R. Nast, *Z. anorg. u. allgem. Chem.* **244** (1940) 23.
[e] R. D. Feltham, *Inorg. Chem.* **3** (1964) 116.
[f] G. Booth and J. Chatt, *J. Chem. Soc.* (1962) 2099.
[g] W. Hieber and I. Bauer, *Z. Naturforsch.* **16б** (1961) 556; *Z. anorg. u. allgem. Chem.* **321** (1963) 107.
[h] C. C. Addison and B. F. G. Johnson, *Proc. Chem. Soc.* (1962) 305.
[i] J. Lewis, R. J. Irving and G. Wilkinson, *J. Inorg. Nuclear Chem.* **7** (1958) 32.
[j] W. Hieber, I. Bauer and G. Neumair, *Z. anorg. u. allgem. Chem.* **325** (1965) 250.
[k] W. Beck and K. Lortes, *Z. anorg. u. allgem. Chem.* **325** (1965) 250.
[l] R. Nast and E. Proeschel, *Z. anorg. u. allgem. Chem.* **256** (1948) 145.
[m] W. P. Griffith and G. Wilkinson, *J. Inorg. Nuclear Chem.* **7** (1958) 295.

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[31] T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nuclear Chem.* **1** (1955) 165.
[32] A. P. Cox, L. F. Thomas and J. Sheridan, *Nature*, **181** (1958) 1157.
[33] R. D. Feltham and W. G. Fately, *Spectrochimica Acta*, **20** (1964) 1081.

Nickel nitrosyl monohalides Ni(NO)X are prepared by reactions of the nickel(II) halides with nitrogen monoxide in the presence of a halogen acceptor such as zinc:

$$2NiI_2+Zn+2NO \xrightarrow{150^\circ} 2Ni(NO)I+ZnI_2$$

These compounds are volatile and non-polar but only slightly soluble in organic solvents. They oxidize readily in air and are decomposed by acids. The strong single absorption band in the 1800–1900 cm^{-1} region confirms the presence of NO^+ so that these compounds are formulated as containing nickel(0). They are almost certainly polymeric; a tetrameric structure with iodide bridges has been proposed for Ni(NO)I. A large number of derivatives of these halides of formula $Ni(NO)XL_2$ are obtained by direct reaction with ligands; in addition to these monomeric derivatives, some halogen bridged dimers, e.g. $[Ni(NO)I(PPh_3)]_2$, are known.

The dark green nitrosyl dihalides $Ni(NO)X_2$ are obtained in the reactions of nickel carbonyl with nitrosyl chloride or bromide. These compounds are involatile, insoluble in non-polar solvents, and dissolve in donor solvents with evolution of nitrogen monoxide. They are thermally stable up to above 150° when they evolve nitrogen monoxide leaving the nickel(II) halide. Their infrared spectra show two strong bands in the NO^+ region and their room temperature magnetic moments are 3.7 and 3.2 BM for the chloride and bromide respectively, indicating two unpaired electrons per nickel atom. Their structures are unknown but again they are almost certainly polymeric.

The purple crystalline cyanonitrosyl $K_2[Ni(CN)_3(NO)]$ is obtained by treating $K_4[Ni_2(CN)_6]$ in liquid ammonia with nitrogen monoxide. It is diamagnetic, contains a mononuclear anion and has the single N–O and the two C–N stretching frequencies expected for the tetrahedral (C_{3v}) symmetry.

2.3. COMPLEX CYANIDES AND ISOCYANIDES

Solutions of potassium tetracyanonickelate(II) are readily reduced by potassium in liquid ammonia firstly to the red $K_4[Ni_2(CN)_6]$ and thence to a yellow precipitate of $K_4Ni(CN)_4$ [34]. This complex cyanide of nickel(O) is thermally stable up to 160° but is rapidly oxidized in air and evolves hydrogen in aqueous solution. The $[Ni(CN)_4]^{4-}$ anion is isoelectronic with $Ni(CO)_4$ and is believed to have the tetrahedral structure; its infrared spectrum[35] shows only one C–N stretching band at 1985 cm^{-1}. When $K_4[Ni(CN)_4]$ is treated with carbon monoxide in liquid ammonia the yellow $K_2[Ni(CN)_2(CO)_2]$ is obtained[36] and complete replacement of cyanide groups occurs in the reactions with triphenylphosphine, triphenylarsine and triphenylstibine, e.g.

$$K_4[Ni(CN)_4]+4Ph_3Sb \rightarrow Ni(SbPh_3)_4+4KCN$$

The nickel(I) complex $K_4[Ni_2(CN)_6]$, sometimes known as Bellucci's salt[37], is obtained in the reduction of aqueous $K_2[Ni(CN)_4]$ with sodium or potassium amalgam (or electrolytically) under an atmosphere of hydrogen; the dark red nickel(I) complex is precipitated by the addition of ethanol. It is also formed as an intermediate in the alkali-metal in

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[34] J. W. Eastes and W. M. Burgess, *J. Am. Chem. Soc.* **64** (1942) 1187, 2715; J. J. Burbage and W. C. Fernelius, *ibid.* (1943) 1484.

[35] M. F. Amr El Sayed and R. K. Sheline, *J. Am. Chem. Soc.* **80** (1958) 2047.

[36] R. Nast and H. Roos, *Z. anorg. u. allgem. Chem.* **272** (1953) 242.

[37] I. Bellucci and R. Corelli, *Z. anorg. u. allgem. Chem.* **86** (1914) 88.

ammonia reductions of $K_2[Ni(CN)_4]$. The nickel(I) salt is diamagnetic both in the solid state and in solution, and the anion has been shown to be binuclear by a cryoscopic method[38]. It is evident, therefore, that the anion has a nickel–nickel bond, but other features of its structure are not yet fully resolved. From preliminary X-ray studies[39] the presence of bridging cyanide groups was inferred, and the Ni–Ni distance estimated at 2.6 Å; infrared evidence, however[40], suggests that the anion is planar with no bridging cyanide groups, i.e. $[(CN)_3Ni\text{–}Ni(CN)_3]^{4-}$.

Aqueous solutions of the $[Ni_2(CN)_6]^{4-}$ ion slowly become oxidized in the presence of cyanide ion:

$$[Ni_2(CN)_6]^{4-}+2H_2O+2CN^- \rightarrow 2[Ni(CN)_4]^{2-}+H_2+2OH^-$$

Carbon monoxide is absorbed by the aqueous solutions, an orange solution of $K_4[Ni(CN)_6(CO)_2]$ being formed[41]. This salt can readily be isolated if liquid ammonia is used as the reaction medium. The structure of the anion is not yet known for certain; cryoscopy and the diamagnetism of the compound confirm the dimeric formulation for both the solid and the solutions, but the infrared spectrum has been interrupted on the basis of both bridged[42] and non-bridged[43] structures.

The monomeric anion $[Ni(CN)_4]^{3-}$ is reported[44] to be formed by reduction of nickel(II) cyanide in an alkaline solution of $K_2[Ni(CN)_4]$ with hydrazine. It has a magnetic moment of 1.73 BM and is oxidized rapidly in moist air:

$$2K_3[Ni(CN)_4]+H_2O+\tfrac{1}{2}O_2 \rightarrow 2K_2[Ni(CN)_4]+2KOH$$

The aryl isocyanide derivatives of nickel(0), $Ni(CNR)_4$, are formed by the reaction

$$Ni(CO)_4+4CNR \rightarrow Ni(CNR)_4+4CO$$

under mild conditions[45]. Tetrasubstitution of the carbonyl is the rule with the aryl isocyanides but mono- (viz. Table 4) and trisubstituted derivatives have been obtained with methyl isocyanide. The tetra(arylisocyanide)nickel(0) compounds can also be prepared from alkaline solutions of nickel(II) salts; alcoholic suspensions of nickel(II) hydroxide react slowly with the isocyanides according to

$$Ni(OH)_2+5CNR \rightarrow Ni(CNR)_4+RNCO+H_2O$$

These complexes are yellow crystalline solids, soluble in organic solvents to give solutions which are quite stable in the absence of air. The infrared spectra[46] of the tetraarylisonitriles show two N–C stretching frequencies; these are believed to arise as a result of departure from strict T_d symmetry by bending at the nitrogen atoms. In $(MeNC)_3Ni(CO)$, ν(C–O) occurs at 1923 cm^{-1}; this very low frequency is interpreted as indicating a considerable degree of back donation to the carbonyl group, at the expense of the nitrile groups (whose mean frequency is only slightly less than that in the free ligand).

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[38] R. Bast and W. Pfab, *Z. Naturforsch.* **12b** (1957) 122.
[39] W. Pfab and R Nast, *Z. Krist.* **111** (1959) 259.
[40] W. P. Griffith and G. Wilkinson, *J. Inorg. Nuclear Chem.* **7** (1958) 295.
[41] R. Nast and T. von Krakkay, *Z. anorg. u. allgem Chem.* **272** (1953) 233.
[42] R. Nast and H. Kasperl, *Chem. Ber.* **92** (1959) 2135.
[43] W. P. Griffith, F. A. Cotton and G. Wilkinson, *J. Inorg. Nuclear Chem.* **10** (1959) 23.
[44] R. Nast and T. von Krakkay, *Z. Naturforsch.* **9b** (1954) 798.
[45] L. Malatesta, *Progress Inorg. Chem.* **1** (1959) 283.
[46] F. A. Cotton and F. Zingales, *J. Am. Chem. Soc.* **83** (1961) 351.

2.4. PHOSPHINE COMPLEXES

The completely substituted nickel(0) phosphine complexes $Ni(PX_3)_4$ can be prepared (in addition to the nickel carbonyl route, pp. 1118–19) by direct reaction of phosphines with finely divided nickel, e.g.[47]

$$Ni + 4PF_3 \xrightarrow[350\text{ atm.}]{100^\circ} Ni(PF_3)_4$$

Methyldichlorophosphine reacts with nickel at the temperature of reflux to give $Ni(PCl_2Me)_4$[48] and the aromatic diphosphines o-$C_6H_4(PEt_2)_2$ and $Ph_2PCH_2CH_2PPh_2$ similarly give $Ni(diphosphine)_2$ [49]. These diphosphine complexes can also be prepared by, for example, borohydride reduction of the nickel(II) complexes, $NiX_2(diphosphine)_2$. Tetrakis(triethylphosphine)nickel(0) has been prepared from bis(π-allyl)nickel[50] and nickelocene reacts with trialkyl- and triaryl-phosphites to give good yields of $Ni[P(OR)_3]_4$ [51].

These phosphine complexes are all believed to have tetrahedral structures and the Raman spectrum[52] of $Ni(PF_3)_4$ is in agreement with this stereochemistry. The triphenylphosphine complex reacts in solution with molecular oxygen to give the adduct $Ni(O_2)(PPh_3)_2$ [53] which is stable in solution below −35°. Upon hydrolysis with water saturated ether and acetylacetone at −78°, hydrogen peroxide is liberated in 83.5% yield along with triphenylphosphine.

A few phosphine complexes of nickel(I) are known. The compounds $NiX(PPh_3)_3$ (X = Cl, Br, I) are obtained[54] as yellow or orange solids by the reaction of the π-allyl nickel halides with triphenylphosphine in the presence of norbornene at room temperature in a benzene–ether solvent. These complexes slowly decompose in air but are stable at room temperature under nitrogen. They are paramagnetic in the solid state (magnetic moments in the range 1.9–2.0 BM) and are believed to be tetrahedral. The complexes of the diphosphines $Ph_2P(CH_2)_{3\text{ or }4}(PPh_2)$, [(diphos)(CN)Ni(diphos)Ni(CN)(diphos)] are believed to be square planar nickel(I) complexes; their magnetic moments are in the range 2.0–2.3 BM at room temperature[55].

The room temperature reaction between nickel(II) acetylacetonate and Et_2AlOEt in the presence of triphenylphosphine gives yellow crystals of the ethylene complex $(PPh_3)_2NiC_2H_4$[56]. In this complex there is a small deviation from strictly planar arrangement of the two phosphorus and two carbon atoms around nickel, mean Ni–P and Ni–C distances being 2.19 and 2.01 Å respectively[57]. The olefin in this complex is readily replaced by other donors such as styrene, dimethyl- and diphenyl-acetylenes.

2.5. OTHER COMPOUNDS OF NICKEL IN LOW OXIDATION STATES

Liquid ammonia is a very convenient medium for preparing low oxidation state nickel complexes. Alkali metals and alkali metal acetylides are soluble without reaction in this

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[47] T. Kruck and K. Baur, *Chem. Ber.* **98** (1965) 3070.
[48] L. D. Quin, *J. Am. Chem. Soc.* **79** (1957) 3681.
[49] J. Chatt and F. A. Hart, *J. Chem. Soc.* (1960) 1398.
[50] G. Wilke and B. Bogdanovic, *Angew. Chem.* **73** (1961) 756.
[51] J. R. Olechowski, C. G. McAlister and R. F. Clark, *Inorg. Chem.* **4** (1965) 246.
[52] L. A. Woodward and J. R. Hall, *Nature*, **181** (1958) 831.
[53] G. Wilkie, H. Schott and P. Heimbach, *Angew. Chem., Int. Ed.* **6** (1967) 92.
[54] L. Porri, M. C. Gallazzi and G. Vitulli, *Chem. Communs.* (1967) 228.
[55] B. Corain, M. Bressan, P. Rigo and A. Turco, *Chem. Communs.* (1968) 509.
[56] G. Wilke and G. Herrmann, *Angew. Chem. Int. Ed.* **1** (19623 549.
[57] C. D. Cook, C. H. Koo, S. C. Nyburg and M. T. Shiomi, *Chem. Communs.* (1967) 426.

medium, so that syntheses of nickel(I) and nickel(0) acetylides have been made possible by the reactions[58].

$$K_4[Ni_2(CN)_6(CO)_2]+8KC\vdots CR \rightarrow K_6[Ni_2(C\vdots CR)_8]+6KCN+2CO$$
$$K_4[Ni_2(C\vdots CH)_4]+2K \rightarrow K_4[Ni(C\vdots CH)_4]$$

The yellow nickel(I) and the orange–brown nickel(0) complexes are diamagnetic so that the former is probably nickel–nickel bonded; the nickel(0) acetylide is pyrophoric in air. A few nitrogen bonded nickel(0) compounds can be prepared by reaction of the ligands with the tetracyanonickelate(0) in ammonia[59]:

$$K_4Ni(CN)_4+2D \rightarrow NiD_2+4KCN$$
$$(D = 2,2'\text{-dipyridyl; } 1,10\text{-phenanthroline})$$

Bis(acrylonitrile)nickel(0) $[Ni(CH_2{:}CHCN)_2]$ is a product of the reaction between nickel carbonyl and acrylonitrile[60]. It is co-ordinatively unsaturated and very unstable; with triphenylphosphine more stable derivatives, i.e. $[Ni(CH_2{:}CHCN)_2PPh_3]$ and $[Ni(CH_2{:}CHCN)_2(PPh_3)_2]$, are formed. The infrared spectrum of $Ni(CH_2{:}CHCN)_2$ indicates that the nitrile group is not involved in bonding to nickel and that the metal is bonded to the ligand through the π electrons of the olefinic double bond. It is slightly paramagnetic ($\mu_{\text{eff}} = 0.66$ BM) and has been used as a catalyst in the oligomerization of acetylenes and olefins. Acetylene is converted into cyclo-octatetraene along with benzene and styrene diphenylacetylene into hexaphenylbenzene and but-2-yne into hexamethylbenzene; the catalytic activity of $Ni(CH_2{:}CHCN)_2$ is not high, however (judging by the yields of products per gram of catalyst)[61].

The cyclopentadienyl nickel carbonyls of formally low oxidation states are considered in section 3.

3. COMPOUNDS OF NICKEL(II)

3.1. GENERAL AND REDOX CONSIDERATIONS

Unlike iron and cobalt, nickel commonly shows only the +2 oxidation state in aqueous solution. The hexaquo ion $[Ni(H_2O)_6]^{2+}$ is green and aqueous solutions of nickel(II) salts usually have this colour as do most of the hydrated salts. The $[Ni(H_2O_6]^{2+}$ ion has been shown crystallographically[62] to be present in $Ni(NO_3)_2{\cdot}6H_2O$, $NiSO_3{\cdot}6H_2O$, $(NH_4)_2Ni(SO_4)_2{\cdot}6H_2O$, $NiSO_4{\cdot}6H_2O$ and $NiSO_4{\cdot}7H_2O$, but $NiCl_2{\cdot}6H_2O$ contains *trans*-$[NiCl_2(H_2O)_4]$ units. The hexaquo ion is quite labile and barely acidic; no hydroxo or oxonickelates(II) are known. Some standard electrode potentials for some nickel couples are given in Table 6; the data are from standard sources[63, 64], the sign convention being as defined under iron, Section 3.1. The great stability of the +2 oxidation in aqueous solution extends to the solid simple compounds; nickel is unique amongst the first-row transition elements in forming simple halides

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[58] R. Nast, *Chemical Society Special Publication* No. 13 (1959) 103.

[59] H. Behrens and A. Muller, *Z. anorg. u. allgem. Chem.* **341** (1965) 124.

[60] G. N. Schrauzer, *J. Am. Chem. Soc.* **81** (1959) 5310; **82** (1960) 1008.

[61] *Idem, Chem. Ber.* **94** (1961) 1403.

[62] R. G. W. Wyckoff, *Crystal Structures*, 2nd ed., Interscience, Vol. 3 (1965).

[63] W. M. Latimer, *The Oxidation States of the Elements and their Potentials in Aqueous Solutions*, 2nd ed., Prentice Hall (1952).

[64] A. J. Bethune, in *The Encyclopedia of Electrochemistry* (C. A. Hampel, ed.), Reinhold (1964) p. 415.

in one oxidation state only. In its complex compounds nickel(II) is peculiar in that stereochemical transformations occur rather easily, the free energy differences between the various stereochemistries being rather small. Indeed, in some complexes two different isomers having, for example, tetrahedral and square planar structures, occur together in the crystalline unit cell. These statements are elaborated in section 3.4.

TABLE 6. STANDARD ELECTRODE POTENTIALS FOR SOME NICKEL COUPLES AT 25°

Couple	Potential (V)
Acid solution	
Ni^{2+}/Ni	-0.25
$NiO_2, 4H^+/Ni, 2H_2O$	+1.678
Basic solution	
$NiS(\gamma)/Ni, S^{2-}$	-1.04
$NiS(\alpha)/Ni, S^{2-}$	-0.83
$Ni(OH)_2/Ni, 2OH^-$	-0.72
$[Ni(NH_3)_6]^{2+}/Ni, 6NH_3(aq)$	-0.476
$NiCO_3/Ni, CO_3^{2-}$	-0.45
$NiO_2, 2H_2O/Ni(OH)_2, 2OH^-$	+0.490

3.2. SIMPLE COMPOUNDS OF NICKEL(II)

Nickel(II) halides[65]. Some of the physical properties of these halides are given in Table 7. The hydrated halides are crystallized from solutions of the metal, its oxide, hydroxide, or carbonate in the hydrohalic acids. These halides form a very large number of complex compounds particularly with nitrogen and phosphorus bases; these are reviewed in section 3.3.

TABLE 7. NICKEL(II) HALIDES

Property	NiF_2	$NiCl_2$	$NiBr_2$	NiI_2
Colour	Yellow	Yellow	Yellow	Black
M.p.(°C)	1450[a]	1001[a]	965[a]	780[b]
$-\Delta H_f$ (kcal mole^{-1})	157.2[a]	74.5[a]	54.2[c]	20.5[c]
$-\Delta H_f$(aq) (kcal mole^{-1})[c]	171.5	95.1	73.1	42.0
μ_{eff}(BM at 20°C)[a]	2.85	3.32	3.0	3.25
Density[b]	4.63	3.55	5.098	5.83
Hydrates[d]	4	2, 4, 6, 7	2, 3, 6	4, 6

[a] R. Colton and J. H. Canterford, *Halides of the First Row Transition Metals*, Wiley, Interscience, (1969).

[b] R. C. Weast (Ed.), *Handbook of Chemistry and Physics*, 49th Ed. Chemical Rubber Company (1968).

[c] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, *Selected Values of Chemical Thermodynamic Properties*, National Bureau of Standards (1952).

[d] *Gmelins Handbuch der Anorganischen Chemie*, Nickel B, 2, Verlag Chemie (1966).

Nickel(II) fluoride. This is formed only slowly in the reaction of the metal with fluorine

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[65] R. Colton and J. H. Canterford, *Halides of the First Row Transition Metals*, Wiley-Interscience (1969), p. 406.

at 550° or hydrogen fluoride in a bomb at 225° (hence the use of nickel alloys, e.g. monel in the handling of fluorine and corrosive fluorides). Nickel(II) fluoride is best prepared[66] by fluorination of nickel(II) chloride with elemental fluorine at 350° or by heating the ammonium fluoride double salt. Other reactions which have been used are the reactions of nickel(II) chloride with hydrogen fluoride above 500° or chlorine trifluoride at 250° and dehydration of $NiF_2{\cdot}4H_2O$ in a stream of hydrogen fluoride at 350–400°.

Nickel(II) fluoride has the tetragonal rutile structure with only slightly tetragonally compressed NiF_6 octahedra[67]; the Ni–F distances being 2.01 and 1.98 Å. Above the melting point it sublimes as a linear gaseous molecule[68]. The anhydrous fluoride is rather unreactive towards concentrated acids; it is only slightly soluble in anhydrous hydrogen fluoride and is not attacked by electronegative elements such as chlorine, sulphur and phosphorus. The pale green tetrahydrate is slightly soluble in water; when heated, several intermediate hydrates are formed prior to NiF_2.

Nickel(II) chloride. This can be obtained by reaction of the elements either in a flow system at high temperatures or by reaction in ethanol at 20° [69]. It is readily prepared in the laboratory by dehydration of the hexahydrate with thionyl chloride[70].

Nickel(II) chloride is isomorphous with the chlorides of iron(II), cobalt(II) and manganese(II), having the cadmium chloride lattice. It vaporizes over the temperature range 440–700° as monomeric and dimeric species the vapour pressure being given by[71]

$$\log P_{\mathrm{mm}} = 12.051 - 11{,}499/T$$

The pure sublimed chloride dissolves in water only slowly and is much less soluble in organic solvents than the corresponding cobalt(II) salt. It is paramagnetic above about 50°K with $\theta = 67°$.

From aqueous solution nickel(II) chloride crystallizes as the green hexahydrate; this begins to evolve water above 50°. The crystal structure[72] of $NiCl_2{\cdot}6H_2O$ contains *trans*-$[NiCl_2(H_2O)_4]$ units, the Ni–Cl and Ni–O bond lengths being 2.38 and 2.10 Å respectively. The hexahydrate obeys the Curie–Weiss law above 6°K with θ approximately 10°. Evaporation of aqueous nickel(II) chloride solutions at above 40° gives crystals of the tetrahydrate $NiCl_2{\cdot}4H_2O$; this is also obtained when saturated aqueous solutions are treated with hydrogen chloride. The dihydrate $NiCl_2{\cdot}2H_2O$ is best prepared by evaporation of nickel(II) chloride solutions at above 75°. It has a rather complicated structure[73] consisting of polymeric chains in which the nickel atoms are surrounded by four chlorines in a distorted square plane and two water molecules; the polymeric chains are connected together with hydrogen bonds.

Nickel(II) bromide. Anhydrous $NiBr_2$ is most conveniently prepared by the action of bromine on nickel, either at red heat or in ethereal solution at room temperature[74] or by dehydration of the hexahydrate at about 140°. It crystallizes with the $CdCl_2$ type structure,

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[66] H. F. Priest, *Inorg. Syntheses*, **3** (1950) 173.

[67] H. M. Haendler, W. L. Patterson and W. J. Bernard, *J. Am. Chem. Soc.* **74** (1952) 3167; W. H. Bauer, *Acta Cryst.* **11** (1958) 488.

[68] T. C. Ehlert, R. A. Kent and J. L. Margrave, *J. Am. Chem. Soc.* **86** (1964) 5093.

[69] R. C. Osthoff and R. C. West, *J. Am. Chem. Soc.* **76** (1954) 4732.

[70] A. R. Pray, *Inorg. Syntheses*, **5** (1957) 153.

[71] H. Schafer, L. Bayer, G. Briel, K. Etzel and K. Krehl, *Z. anorg. u. allgem. Chem.* **278** (1959) 300.

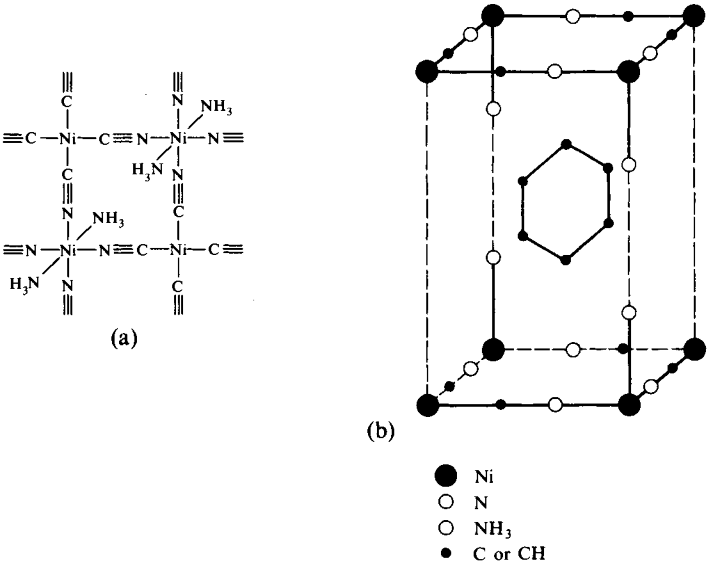
[72] J. Mizuno, *J. Phys. Soc. Japan*, **16** (1961) 1574.

[73] B. Morosin, *Acta Cryst.* **23** (1967) 630.

[74] G. Brauer, *Handbuch der Präparativen Anorganischen Chemie*, Ferdinand Enke (1962), Vol. II, p. 1345.

the nickel atoms being surrounded octahedrally by bromine atoms at 2.57 Å. It resembles the chloride also in its magnetic properties; it is, however, magnetically anisotropic with $g_{\parallel} = 2.16$ and $g_{\perp} = 2.23$ at 300°K[75].

The green hexahydrate $NiBr_2{\cdot}6H_2O$ readily evolves water; crystallization from aqueous solutions above 29° yields the trihydrate $NiBr_2{\cdot}3H_2O$. The hexahydrate can be dehydrated to a dihydrate over concentrated sulphuric acid at 5°. The environment of the nickel atoms in $NiBr_2{\cdot}6H_2O$ is 2Br and $4H_2O$ and in $NiBr_2{\cdot}2H_2O$ 4Br and $2H_2O$; in both cases the Ni–Br distance is 2.6 and the Ni–O distance 2.0 Å[76].



(a) (b)

FIG. 1. The benzene ammine nickel(II) cyanide clathrate.

Nickel(II) iodide. This can be prepared by dehydration of the hexahydrate or by the metathetic reaction between sodium iodide and nickel(II) chloride or nitrate in ethanol[77]. It has the $CdCl_2$ type lattice and is paramagnetic down to 75°K. Only one hydrate is well characterized—the blue-green $NiI_2{\cdot}6H_2O$; unlike the other halide hexahydrates, this contains $[Ni(H_2O)_6]^{2+}$ cations[76, 78].

Nickel(II) cyanide. The addition of potassium cyanide to aqueous nickel(II) salt solutions results in the precipitation of grey-blue, hydrated, nickel(II) cyanide. The brownish-yellow anhydrous compound is obtained by heating the hydrate to above 140°; it is probably diamagnetic[79]. Tracer studies on the hydrate suggest[80] that two different types of nickel atom are present, so that its structure may be $[Ni(H_2O)_x]^{2+}[Ni(CN)_4]^{2-}$. It is soluble in excess of potassium cyanide solution to give an apricot-yellow solution from which crystals of $K_2Ni(CN)_4{\cdot}H_2O$ can be obtained.

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[75] J. S. Wells and D. R. Winder, *J. Chem. Phys.* **45** (1966) 410.

[76] D. Weigel, *Bull. Soc. Chim. France*, (1963) 2087.

[77] A. B. P. Lever, *J. Inorg. Nuclear Chem.* **27** (1965) 149.

[78] M. Gewdin-Louer and D. Weigel, *Compt. Rend.* **264B** (1967) 895.

[79] B. M. Chadwick and A. G. Sharpe, *Advances Inorg. Chem. Radiochem.* **8** (1966) 147.

[80] F. A. Long, *J. Am. Chem. Soc.* **73** (1951) 537.

This most interesting reaction of nickel(II) cyanide is the formation of clathrate compounds in the presence of ammonia. When a solution of $Ni(CN)_2$ in aqueous ammonia is shaken with benzene, a pale violet precipitate of the benzene clathrate $Ni(CN)_2 \cdot NH_3 \cdot C_6H_6$ is obtained. In this compound[81] the Ni and CN groups form layers with ammonia molecules bonded above and below the planes of the layers on alternate nickel atoms. Thus half the nickel atoms are octahedrally surrounded by nitrogen (Ni–N = 2.15 Å, $Ni\text{–}NH_3 = 2.06$ Å) and half are planar 4-coordinated by carbon (Ni–C = 1.76 Å) (Fig. 1a). The benzene molecules occupy the holes (cages) formed between the layers (Fig. 1b). The average magnetic moment per nickel atom is 2.2 BM[82], and it has thus been established that the 4-coordinate nickel atoms are diamagnetic while the 6-coordinate atoms are paramagnetic with two unpaired electron spins.

The benzene content of this clathrate compound varies in different preparations, the maximum uptake corresponding to $Ni:C_6H_6$ of 1:1; water is probably present up to a maximum of $Ni:H_2O$ of 1:0.33 in these preparations. Many other organic molecules can be entrapped by the ammine nickel(II) cyanide, e.g. thiophen, pyrrole, aniline and pyridine, but larger molecules such as the methyl benzenes are not trapped. The clathrate compounds regenerate the trapped molecule upon heating or when the complex is broken down in aqueous solution. The infrared spectra[83] of the clathrates show absorptions similar to those of the liquid organic molecules, and the clathrates can often be made to burn with a smoky flame due to the entrapped molecule. Similar clathrates are formed by tetracyanonickelates(II) of metal ammine cations, e.g. $[Cu(NH_3)_4][Ni(CN)_4]$ and $[Cd(NH_3)_6][Ni(CN)_4]$[84].

Nickel(II) thiocyanate. This is obtained by dissolving nickel(II) carbonate in thiocyanic acid or by metathesis from nickel(II) sulphate and barium thiocyanate. It gives a green solution in water from which it separates below 15° as the tetrahydrate; above 25°, yellow $Ni(SCN)_2 \cdot 0.5H_2O$ separates, and the brown amorphous anhydrous salt is obtained when this is dehydrated at 150°.

Nickel(II) oxide. The oxidation of nickel with oxygen produces mainly NiO, but some Ni_2O_3 may also be formed under some conditions. The thermal decomposition of the hydroxide, carbonate, or nitrate produces NiO as a green powder. It is isomorphous with CoO having the NaCl-type lattice. At room temperature it is antiferromagnetic with a magnetic moment near 1.3 BM[85]. The melting point is $1955 \pm 20°$ and density 6.82 g cm^{-3}.

Nickel(II) oxide is insoluble in water but soluble in acids as long as it has not been ignited at a high temperature (under these latter conditions it is converted into grey–black octahedra having a metallic lustre). It reacts reversibly with hydrogen, the reaction

$$NiO + H_2 \rightleftharpoons Ni + H_2O$$

proceeding from left to right at relatively low temperatures in a stream of hydrogen.

Nickel(II) hydroxide. This is precipitated as finely divided green powder when an alkali metal hydroxide solution is added to an aqueous solution of a nickel(II) salt. It is frequently difficult to filter at first but becomes more crystalline upon prolonged standing. If the nickel salt is incompletely precipitated, especially if very strong solutions of nickel(II) are used, then

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[81] J. H. Rayner and H. M. Powell, *J. Chem. Soc.* (1952) 319.

[82] R. S. Drago, J. T. Kwon and R. D. Archer, *J. Am. Chem. Soc.* **80** (1958) 2667.

[83] V. M. Bhatnagar, *Chemie Analytique*, **49** (1967) 563.

[84] R. Baur and G. Schwarzenbach, *Helv. Chim. Acta*, **43** (1960) 842.

[85] B. N. Figgis and J. Lewis, *Progress Inorg. Chem.* **6** (1964) 37.

the precipitate may be a basic salt. This is particularly true of the halides, in which case compounds such as $NiCl_2 \cdot 3Ni(OH)_2$ and $NiCl_2 \cdot Ni(OH)_2$ have been characterized[86].

Nickel(II) hydroxide crystallizes (density, 4.15 g cm^{-3}) with the CdI_2 layer structure in which every nickel atom is surrounded by six hydroxides. It begins to decompose to the oxide above 200°. It is insoluble in sodium hydroxide solution but dissolves readily, giving a blue–violet solution in concentrated ammonia; this solution contains cationic nickel(II) ammine complexes.

Nickel sulphides[87]. The black nickel sulphide precipitated from nickel(II) salt solutions by ammonium sulphide in neutral but not strongly acid solution is the so-called α-NiS; it consists largely of amorphous $Ni(SH,OH)_2$ when first precipitated. At low pH this crystallizes to give mainly the rhombohedral γ-NiS, while at higher pH the hexagonal β-NiS ($Ni_{1-x}S$) crystallizes. In the nickel–sulphur system there exists NiS_2 with pyrites structure, Ni_3S_4 with the spinel structure and the dimorphic NiS. The low temperature form, the naturally occurring millerite, is rhombohedral (density 5.3–5.9 g cm^{-3}), the nickel atoms being surrounded by five sulphur atoms (Ni–S ~2.18 Å) in a tetragonal pyramid. The high temperature form of NiS has a NiAs type structure with the nickel in an octahedral co-ordination site, and this structure extends over a nickel deficient range $Ni_{1-x}S$. Other sulphides occurring are Ni_3S_2 and Ni_7S_6; details of these phases can be found in Gmelin[86].

Nickel(II) amide. The liquid ammonia reaction between soluble nickel(II) salts and potassium amide in stoichiometric amounts results in the precipitation of red nickel(II) amide diammoniate, $Ni(NH_2)_2 \cdot 2NH_3$. This amide is soluble in liquid ammonia solutions of ammonium iodide:

$$Ni(NH_2)_2.2NH_3 + 2NH_4I \rightarrow [Ni(NH_3)_6]I_2$$

and decomposes at 585° *in vacuo* to nickel metal via the scheme[88]:

$$Ni(NH_2)_3.2NH_3 \xrightarrow{42.3^\circ} Ni(NH_2)_3 \xrightarrow{119.3^\circ} Ni_3N_2 \xrightarrow{362^\circ} Ni_3N \xrightarrow{585^\circ} Ni$$

The phosphorus analogue $Ni(PH_2)_2$ has been prepared similarly using a solution of KPH_2[89]. It decomposes at 0° evolving phosphine and hydrogen and dissolves in a liquid ammonia solution of KPH_2 to form probably $K_2[Ni(PH_2)_4]$.

Nickel(II) carbonate. Basic carbonates are precipitated when alkali metal carbonate solutions react with nickel(II) salts. When bicarbonates are used, however, or if the precipitation is carried out under an atmosphere of carbon dioxide, a pale green, finely crystalline precipitate of $NiCO_3 \cdot 6H_2O$ is obtained. When this is heated to 140°, basic carbonates are formed and soon thereafter nickel(II) oxide formation begins. The anhydrous carbonate appears to exist in two forms[90], one green and the other yellow. Both are prepared from nickel(II) chloride and sodium bicarbonate solutions in an autoclave under a pressure of carbon dioxide, the green form at 250° and the yellow form at 180°.

Nickel(II) carboxylates. Nickel(II) formate can be crystallized as the green dihydrate $Ni(HCOO)_2 \cdot 2H_2O$ from solutions of nickel bases in formic acid. The crystal structure[91] of this shows the nickel atoms to be octahedrally surrounded by oxygen atoms; one set of

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[86] Gmelin's *Handbuch der Anorganischen Chemie*, Nickel (B, 2), Verlag Chemie (1966).

[87] F. Jellinek, in *Inorganic Sulphur Chemistry* (G. Nickless, ed.), Elsevier (1968), p. 669.

[88] G. W. Watt and D. D. Davies, *J. Am. Chem. Soc.* **70** (1948) 3753.

[89] O. Schmitz-Dumont, F. Nagel and W. Schaal, *Angew. Chem.* **70** (1958) 105.

[90] G. Brauer, *Handbuch der Präparativen Anorganischen Chemie*, Ferdinand Enke (1962), Vol. II, p. 1354.

[91] K. Korgmann and R. Mattes, *Z. Krist.* **118** (1963) 291.

nickel atoms is bonded to six oxygens from formate groups, while another set are bonded to four water molecules in a plane with oxygen atoms from formate groups above and below the plane. There are thus formate bridges between nickel atoms building up an infinite polymer network. Anhydrous nickel(II) formate has been prepared by reaction of hexammine nickel(II) chloride with sodium ethoxide and formic acid in ethanol when sodium chloride precipitates[92].

Nickel(II) acetate crystallizes from solutions of the hydroxide in acetic acid at room temperature as the green tetrahydrate. This is isomorphous with the cobalt(II) salt having a distorted octahedral structure with the nickel atoms surrounded by four water molecules and two oxygens from two acetato groups which are *trans* to each other[93]. Its magnetic moment is 3.30 BM at room temperature. The hygroscopic anhydrous acetate is obtained by dehydration of the tetrahydrate *in vacuo* or by heating the tetrahydrate under reflux with acetic anhydride[94]. Like the tetrahydrate it is magnetically dilute at room temperature. Upon thermal decomposition in nitrogen (or *in vacuo*) at 300° it evolves acetone, acetic acid, carbon monoxide, carbon dioxide and water leaving nickel and Ni_3C[95].

Nickel(II) oxalate precipitates as $NiC_2O_4{\cdot}2H_2O$ when oxalic acid is added to nickel salt solutions. It is isomorphous with the oxalates of magnesium, zinc and iron(II), and has $\mu_{eff} = 2.95$ BM. When heated *in vacuo* it decomposes evolving water above 150° and carbon dioxide above 300° leaving finely divided nickel suitable for catalytic purposes or reacting to form the carbonyl. The oxalate dissolves in acids with decomposition and in ammonia with ammine formation.

Nickel(II) silicate. Stoichiometric quantities of NiO and SiO_2 heated to 1500° combine to give green Ni_2SiO_4 with the olivine structure; a green transparent spinel phase is obtained from this at higher temperatures and under pressure. A green hydrated silicate $NiSiO_3{\cdot}xH_2O$ ($x = 1$–3) is precipitated from nickel(II) solutions by Na_2SiO_3.

Nickel(II) nitrate. Emerald green crystals of the hexahydrate $Ni(NO_3)_2{\cdot}6H_2O$ crystallize from aqueous solutions at room temperature. These are isomorphous with the corresponding cobalt(II) salt containing the regular octahedral $[Ni(H_2O)_6]^{2+}$ ions with Ni–O distances = 2.03 Å[96]. The tetrahydrate crystallize above 54° and the dihydrate above 85.4°. The pale green anhydrous nitrate[97] can be obtained by dehydration of the hydrate with dinitrogen pentoxide in fuming nitric acid or by the liquid phase reaction of dinitrogen tetroxide with nickel carbonyl [the gas phase reaction gives the nitrite $Ni(NO_2)_2$]

$$Ni(CO)_4 + 2N_2O_4 \rightarrow Ni(NO_3)_2 + 2NO + 4CO$$

The first product of this latter rather violent reaction is the adduct $Ni(NO_3)_2{\cdot}N_2O_4$ from which the nitrogen tetroxide is removed by heating *in vacuo*. It can also be prepared by the reaction of dinitrogen tetroxide–ethyl acetate mixtures with nickel(II) chloride. The infrared spectrum shows it to be a typical covalent nitrate. It is involatile and decomposes upon heating in nitrogen to give the nitrite $Ni(NO_2)_2$ above 260°.

Thermal decomposition of the hexahydrate gives basic nitrates as does treatment of its saturated solutions with sodium hydroxide. A typical example is $Ni(NO_3)_2{\cdot}Ni(OH)_2{\cdot}6H_2O$

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[92] P. Dupuy and C. Moreau, *Compt. Rend.* **242** (1956) 2242; **243** (1956) 1635.

[93] J. N. van Niekerk and F. R. L. Schoening, *Acta Cryst.* **6** (1963) 609.

[94] H.-D. Hardt and H. Pohlmann, *Z. anorg. u. allgem. Chem.* **343** (1966) 92.

[95] J. -L. Doremieux, *Compt. Rend.* **261** (1965) 4426; J. Leicester and M. J. Redmann, *J. Applied Chem.* **12** (1962) 357.

[96] D. Weigel, B. Imelik and P. Laffite, *Bull. Soc. Chim. France* (1962) 544.

[97] C. C. Addison and N. Logan, *Advances Inorg. Chem. Radiochem.* **6** (1964) 71.

which is believed not to have a layer lattice, like most basic nickel(II) salts, but to have a complex ionic lattice, i.e. $[Ni(H_2O)_6][Ni(NO_3)_2(OH)_2]$[98].

Nickel(II) phosphates. Nickel forms a large number of phosphates of various types[86]. Disodium hydrogen phosphate precipitates the green flocculent orthophosphate $Ni_3(PO_4)_2 \cdot 8H_2O$ from nickel(II) solutions, and the green acid phosphate $Ni(H_2PO_4)_2 \cdot 2H_2O$ crystallizes from solutions of nickel(II) carbonate in aqueous phosphoric acid at 80°. Ammonium phosphate precipitates $Ni(NH_4)PO_4 \cdot 6H_2O$ from nickel(II) solutions; this when ignited yields the pyrophosphate, $Ni_2P_2O_7$.

Nickel(II) sulphate. All the hydrates from $NiSO_4 \cdot 7H_2O$ to $NiSO_4 \cdot H_2O$ have been reported. At 15–20° the orthorhombic heptahydrate crystallizes, at slightly higher temperatures, two different $NiSO_4 \cdot 6H_2O$ phases crystallize from aqueous solution, the blue–green α-phase up to 53.3° and thereafter the green β-phase. The lower hydrates are thermal decomposition products of the heptahydrate. The crystal structure[62] of the heptahydrate is built up of $[Ni(H_2O)_6]^{2+}$ octahedra, SO_4^{2-} tetrahedra with the extra water molecule being hydrogen-bonded with oxygen atoms of sulphate ions and hydrogen atoms of co-ordinated water molecules. The tetragonal α-$NiSO_4 \cdot 6H_2O$ also contain $[Ni(H_2O)_6]^{2+}$ octahedra with Ni–O distances of 2.02 and 2.04 Å.

Anhydrous nickel(II) sulphate, prepared by dehydration of the hydrates at above 300°, is a yellow powder which is rather reluctant to dissolve in cold water. It forms a series of double salts $M_2^I[Ni(H_2O)_6](SO_4)_2$ (M^I = K, Rb, Cs, NH_4, Tl) which are isomorphous with other Tutton salts of divalent transition metal ions.

All of these sulphates are magnetically dilute and have magnetic moments in the range 3.08–3.26 BM[85]. The anhydrous sulphate becomes antiferromagnetic near 13°K.

Nickel(II) sulphite and thiosulphate. The sulphite forms hexa- and tetrahydrates from solutions of freshly precipitated nickel(II) hydroxide in aqueous sulphur dioxide. Hexagonal and tetragonal forms of $NiSO_3 \cdot 6H_2O$ occur. The thiosulphate $NiS_2O_3 \cdot 6H_2O$ has been obtained[99] by metathesis using barium thiosulphate and nickel(II) sulphate; it is orthorhombic and isomorphous with $MgS_2O_3 \cdot 6H_2O$.

Nickel(II) halates and perhalates. The halates $Ni(XO_3)_2$ (X = Cl, Br, I) are obtained as hydrates by crystallization of the filtrates from the reactions of nickel(II) sulphate with the barium halates. Nickel(II) perchlorate crystallizes as the very hygroscopic hexahydrate; it is very soluble in water (259 g $NiClO_4 \cdot 6H_2O$ per 100 g H_2O) and soluble in alcohol and acetone. The yellow–green anhydrous salt has been prepared[100] from nickel(II) trifluoroacetate and perchloric acid in trifluoroacetic acid at 25°.

3.3. ORGANOMETALLIC COMPOUNDS OF NICKEL[101, 102]

3.3.1. σ-Bonded Nickel Alkyls and Aryls

The stability of σ-bonded nickel organo derivatives increases in the order alkyls < phenyls < *ortho*-substituted phenyls ∼ alkynyls with, of course, the usual increased stability of the perfluoro-alkyls and -aryls. Simple alkyls and aryls of nickel are usually too unstable to

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[98] W. Feitknecht and A. Collett, *Helv. Chim. Acta*, **23** (1940) 180.

[99] D. Weigel, B. Imelik and M. Prettre, *Bull. Soc. Chim. France* (1962) 1427.

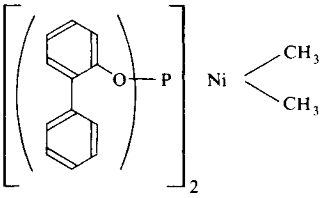
[100] G. S. Fujioka and G. H. Cady, *J. Am. Chem. Soc.* **79** (1957) 2451.

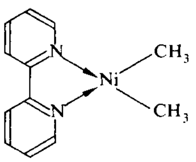
[101] G. E. Coates, M. L. H. Green and K. Wade, *Organometallic Compounds*, Vol. 2, Methuen (1968).

[102] G. N. Schrauzer, *Advances Organomet. Chem.* **2** (1964) 1.

exist on their own; even in the presence of tertiary phosphines the alkyls, e.g. $(R_3P)_2NiMe_2$, are too unstable to isolate. Many stable aryl derivatives have, however, been isolated from the reactions between the square $(R_3P)_2NiX_2$ complexes (X = halogen) and the aryl Grignard reagents; they are of the types $(R_3P)_2NiX(Ar)$ and $(R_3P)_2Ni(Ar)_2$[103]. These compounds are yellow to brown in colour, diamagnetic, and have the *trans* square planar configuration. In order for these compounds to have any great stability it has been found that the aryl group should be *ortho*-substituted, e.g. the compounds $(PR_3)_2NiX(Ar)$ where Ar = *o*-tolyl, *o*-chlorophenyl, *o*-methoxyphenyl, mesityl and 1-naphthyl are high melting point (75–160°) solids, indefinitely stable in air and in boiling ethanol and benzene. This "ortho-effect" is believed to result from a combination of steric and electronic factors[103]. The ortho substituents prevent rotation of the aryl group by steric interactions and the aryl group is held with its plane perpendicular to that of the complex. In this position (z-plane) its π-orbitals interact specifically with the nickel d_{xy} orbital thus increasing the energy separation between the d_{xy} and the $d_{x^2-y^2}$ levels in the square-planar scheme $d_{z^2} < d_{xz}$, $d_{yz} < d_{xy} < d_{x^2-y^2}$. The compound is thus stabilized with respect to a dissociative mechanism and the steric effect of the ortho-substituents is such as to stabilize the complexes to attack along the z-axis. It would thus be expected that the most inert complexes are those possessing two *ortho*-substituents on the aryl group, e.g. $(PR_3)_2NiX$(mesityl), and this is, in fact, found to be the case.

Whilst nickel alkyls cannot be stabilized by phosphines they can be stabilized by tri(2-biphenylyl)phosphite and 2,2′-dipyridyl as well as by π-bonded organic systems. Dimethyl nickel is formed[104] in the reaction of nickel(II) acetylacetonate with aluminium trimethyl; in the absence of stabilizing ligands it decomposes into nickel and methyl radicals. In the presence of the phosphite and dipyridyl ligands already mentioned, the following derivatives are obtained[105]:





The dipyridyl compound forms green crystals which can be recrystallized from boiling benzene. The methyl groups are quantitatively evolved as methane upon treatment of the complex with 5 N hydrochloric acid or primary alcohols. The reaction between π-allyl nickel bromide and methyl magnesium chloride in ether at −78° yields violet crystals of methyl(π-allyl)nickel. This decomposes above −40° yielding nickel and various hydrocarbons[106].

Bis(trityl)nickel $(Ph_3C)_2Ni$, unlike other alkyls and aryls is a stable violet crystalline solid which can be prepared by the reaction of nickel(II) bromide with tritylsodium in ether at −78° as well as by other routes[107]. This compound decomposes in argon at about 120°

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[103] J. Chatt and B. L. Shaw, *J. Chem. Soc.* (1960) 1718.

[104] G. Wilkie, *IUPAC Third International Symposium on Organometallic Chemistry* 1967, *Plenary Lectures*, Butterworths (1968) p. 181.

[105] G. Wilkie and G. Herrmann, *Angew. Chem., Int. Ed.* **5** (1966) 581.

[106] B. Bogdanovic, H. Bonnemann and G. Wilke, *ibid.*, p. 582.

[107] G. Wilke and G. Schott, *ibid.*, p. 583.

and reacts with molten triphenylphosphine at 80° to give $Ni(PPh_3)_4$:

$$Ni(CPh_3)_2+4PPh_3 \rightarrow Ni(PPh_3)_4+Ph_3C.CPh_3$$

In concentrated hydrochloric acid, the blue trityl nickel chloride is slowly formed.

Nickel forms several σ-bonded acetylene derivatives, e.g. by the reactions[108]

$$\begin{tikzcd}
\mathit{trans}\text{-}(Et_3P)_2NiCl_2 + NaC\vdots CR \arrow[r] & \mathit{trans}\text{-}(Et_3P)_2\,Ni(C\vdots CR)Cl \arrow[d, "NaC\vdots CR"] \\
 & \mathit{trans}\text{-}(Et_3P)_2\,Ni(C\vdots CR)_2
\end{tikzcd}$$

These ethynyls melt without decomposition. The reaction between alkali metal acetylides and nickel(II) salts in liquid ammonia has been used to prepare tetraethynylnickelates(II)[109]:

$$KC\vdots CR+[Ni(NH_3)_6](SCN)_2 \rightarrow K_2[Ni(C\vdots CR)_4].2NH_3+2KSCN+4NH_3$$

These compounds are yellow and diamagnetic resembling the cyanide $K_2[Ni(CN)_4]$. They are readily de-ammoniated but are sensitive to shock and tend to decompose spontaneously. With potassium in ammonia the tetraethynylnickelate(0) complexes $[Ni(C:CR)_4]^{4-}$ are obtained. The unsubstituted ethynyls are produced in the liquid ammonia reaction:

$$[Ni(NH_3)_6](SCN)_2+Na_2[Ni(C\vdots CR)_4] \rightarrow 2Ni(C\vdots CR)_2.4NH_3+2NaSCN$$

Upon de-ammoniation *in vacuo* the polymeric acetylides $[Ni(C:CR)_2]_n$ are produced.

3.3.2. Olefin, Acetylene and π-allyl Derivatives

Although the catalytic effect of nickel carbonyl and its phosphine derivatives on the polymerization and other reactions of olefins have been extensively studied[102, 110], relatively few complexes of nickel with olefins have been isolated. Some have been prepared from nickel carbonyl[102]; these include the red diamagnetic complexes $Ni(olefin)_2$, where olefin = duroquinone, CH_2:CHCN, NCCH:CHCN and CH_2CHCHO. Some reactions of

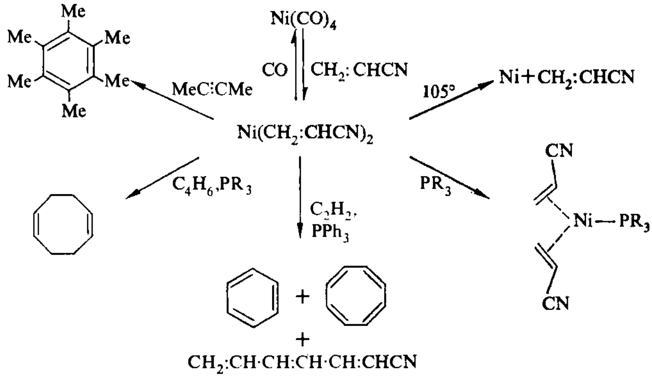

Fig. 2. Some reactions of bis(acrylonitrile)nickel.

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[108] J. Chatt and B. L. Shaw, *J. Chem. Soc.* (1961) 285.

[109] R. Nast and K. Vester, *Z. anorg. u. allgem. Chem.* **279** (1955) 146.

[110] C. Hoogzand and W. Hubel, in *Organic Synthesis via Metal Carbonyls* (I. Wender and P. Pino, eds.) Interscience (1968), p. 343.

bis(acrylonitrile)nickel including some of its acetylene polymerization reactions are given in Fig. 2. A number of mixed olefin complexes have been prepared by reaction of duroquinone with nickel carbonyl in the presence of a polyolefin. These compounds, Ni(duroquinone)(olefin) (olefin = cyclooctatetraene, cyclooctatriene, cycloocta-1,5-diene, bicyclo(2,2,1)-heptadiene, cyclooctatrienone, etc.), are dark red water-soluble crystals whichd ecompose at 120–200°. An X-ray structural determination[111] on (cycloocta-1,5-diene)Ni(duroquinone) has revealed the structure shown in Fig. 3. The nickel atom is sandwiched between a duroquinone ring and the boat form cycloocta-1,5-diene ring; the two sets of parallel double bonds in the olefin rings are perpendicular to each other and the nickel atom is in an approximately tetrahedral arrangement of these double bonds. In the duroquinone fragment, the two carbonyl groups are bent back away from the nickel and the four methyl carbons bent slightly towards the metal. Similar structures are expected for the other duroquinone–nickel–polyolefin complexes. The triphenylphosphine complex $(Ph_3P)_2NiC_2H_4$ and its analogues with other unsaturated molecules have already been discussed in section 2.4. The bis(cycloocta-1,5-diene)- and bis(cyclooctatetraene)nickel complexes can be similarly prepared by the aluminium alkyl reduction of nickel(II) acetylacetonate in the presence of the olefin; with these chelating olefins no other stabilizing ligand is required[112].

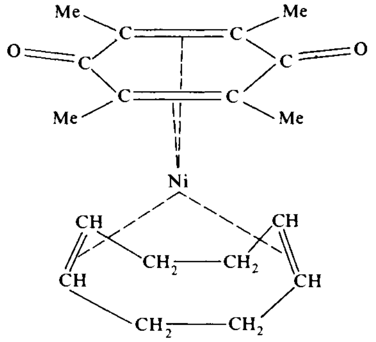
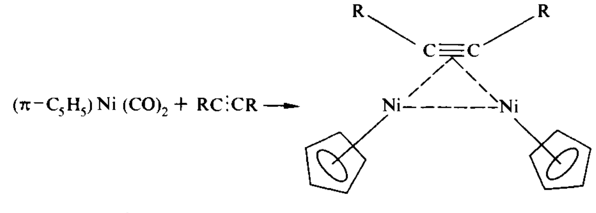


Fig. 3 (Cycloocta-1,5-diene)Ni(duroquinone).

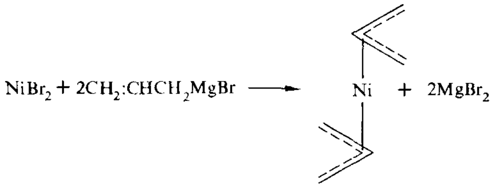
Acetylene nickel complexes of the π-bonded type are also rather rare. Diphenylacetylene reacts with nickel carbonyl in petroleum ether in a sealed vessel at 110° to give[113] bis(tetraphenylcyclopentadienone)nickel. The π-cyclopentadienyl nickel dicarbonyl however does give [as well as does $(\pi\text{-}C_5H_5)_2Ni$] acetylene complexes by direct reaction[114]:



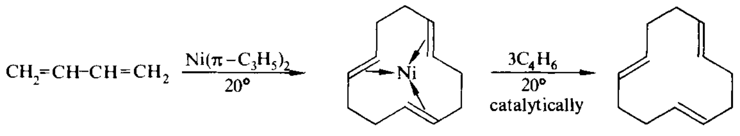
These complexes are green in solution and are slowly oxidized by air.

[111] M. D. Glick and L. F. Dahl, *J. Organomet. Chem.* **3** (1965) 200.
[112] B. Bogdanovic, M. Kroner and G. Wilke, *Annalen*, **699** (1966) 1.
[113] E. Weiss and W. Hubel, *J. Inorg. Nuclear. Chem.* **11** (1959) 42.
[114] J. F. Tilney-Bassett, *J. Chem. Soc.* (1961) 577.

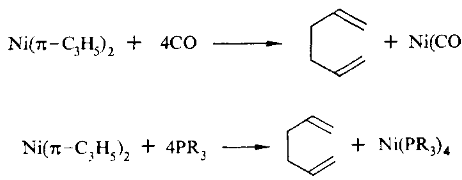
Perhaps the most important group of π-bonded organo nickel compounds are the π-allyls[115]. Bis(π-allyl)nickel is best prepared by the reaction of nickel(II) bromide with allyl magnesium bromide in ether at −10°:



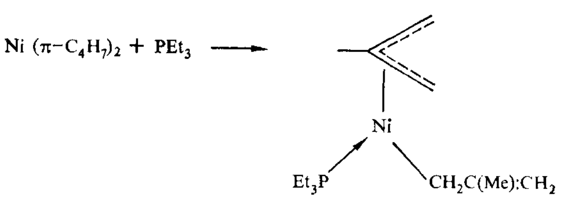
The sandwich structure has been confirmed by X-ray analysis of the more stable bis(π-2-methylallyl)nickel complex[116]. In this compound the methyl groups are *trans* to one another and the other three carbon atoms in each methylallyl group are situated at about the same distance from the central nickel atom. Bis(π-allyl)nickel is volatile in ether and crystallizes below 1°C forming long yellow needles; it is pyrophoric but its ethereal solutions are unaffected by deoxygenated water. It is a very active catalyst for the cyclotrimerisation of butadiene to cyclododeca-1,5,9-triene:



The π-allyl is converted in this reaction to the volatile blood red crystalline cycloocta-dodecatriene-nickel, the allyl groups combining to form hexa-1,5-diene as they do also in the reactions with carbon monoxide and with tertiary phosphines:



A 1:1 complex of bis(π-methylallyl)nickel and triethylphosphine can, however, be isolated in the crystalline state, but on the basis of its infrared spectrum it is formulated as containing one Ni–C σ-bond:



π-Allyl nickel halides are obtained in the reactions of nickel carbonyl[117] or better[102]

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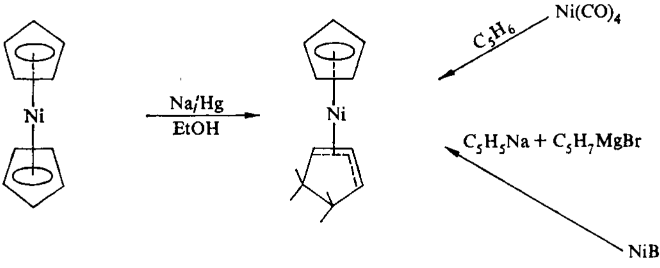
[115] G. Wilke, B. Bogdanovic, P. Hardt, P. Heimbach, W. Keim, M. Kroner, W. Oberkirch, K. Tanaka, E. Steinrucke, D. Walter and H. Zimmermann, *Angew. Chem. Int. Ed.* **5** (1966) 151.

[116] R. Uttech and H. Dietrich, *Z. Krist.* **122** (1965) 60.

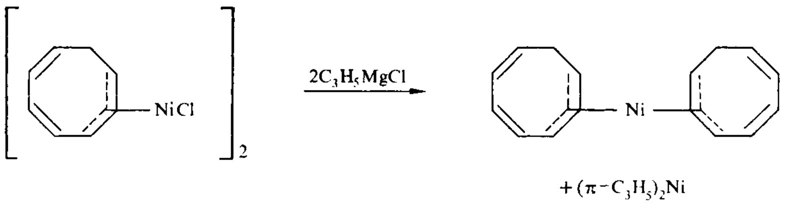
[117] E. O. Fischer and G. Burger, *Z. Naturforsch.* **16b** (1961) 77.

bis(cycloocta-1,5-diene)nickel with allyl halides as well as in the reactions of the bis(π-allyls) with anhydrous hydrogen halides in ether. These dark red compounds have the dimeric formula $[(\pi\text{-allyl})NiX]_2$ with halogen bridges. They react with phosphines to form monomeric adducts such as $(C_3H_5)NiBr\cdot(1\text{–}3)PEt_3$. Whilst the ^1H NMR spectrum of the 1:1 adduct is characteristic of a π-allyl group, the 1:2 adduct gives a spectrum of a dynamic allyl system and the 1:3 adduct (as the complex $[(CH_2{:}CHCH_2)Ni(PEt_3)_3]AlBr_4$) shows the σ-bonded allyl type of spectrum.

Several cyclic bis(π-allyl)nickel compounds are known. Bis-(π-cyclohexenyl)- and bis(π-cycloheptenyl)nickel decompose above −40° and at room temperature respectively but bis(π-cyclo-octenyl)nickel is stable at room temperature. The (π-cyclopentenyl) compounds have been prepared by numerous routes[118], viz.:

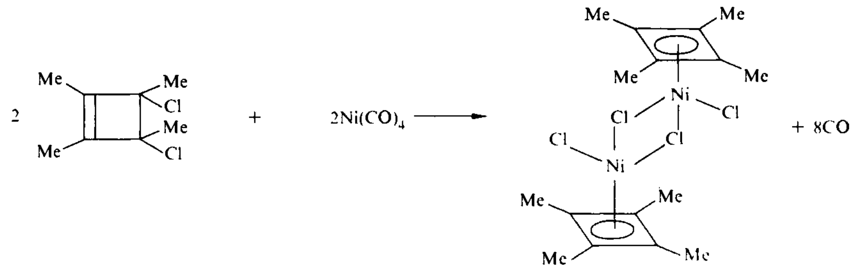


and the bis(π-cyclooctatrienyl)nickel arises from the reaction of π-cyclooctatrienyl nickel chloride (from the reaction of cyclooctatetraene-nickel with hydrogen chloride at −80°) with allyl magnesium chloride:



3.3.3. Cyclobutadienyl and Cyclopentadienyl Complexes

Cyclobutadienyl compounds. The reaction between dichlorotetramethylcyclobutene and nickel carbonyl produced one of the first known π-cyclobutadiene complexes[119]:



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[118] M. L. H. Green and P. L. I. Nagy, *Advances Organomet. Chem.* **2** (1964) 325.

[119] R. Criegee and G. Schroder, *Annalen*, **623** (1959) 1.

The structure of this compound has been established by X-ray diffraction[120]. The C–C distances in the planar rings are in the range 1.40–1.45 Å, the methyl substituents being displaced out of the plane of the ring away from the metal atom; two of the chlorine atoms are bridging (Ni–Cl = 2.35 Å) and two bound only to one nickel atom (Ni–Cl = 2.26 Å). The infrared spectrum of $C_4Me_4NiCl_2$ has been assigned[121] on the basis of the crystal structure symmetry. This compound is a red–violet solid soluble in methylene chloride and in water. The aqueous solutions contain chloride ions and π-cyclobutadiene-nickel-aquo complexes. Other similar compounds which have been prepared include the dark blue $C_4(Ph)_4NiCl_2$ and $C_4(Ph)_4NiBr_2$.

Cyclopentadienyl complexes; *bis(π-cyclopentadienyl)nickel*, (*nickelocene*) $Ni(\pi\text{-}C_5H_5)_2$. Nickelocene can be prepared by many methods[122, 123] analogous to those used for ferrocene.

TABLE 8. SOME PHYSICAL PROPERTIES OF NICKELOCENE

Magnetic moment[a] μ_{eff} (BM)	2.86
Dipole moment[b] (*D*)	0
Electronic spectrum[b, c] (cm^{-1})	32,500; 14,300
Heat of formation[b] ΔH_f (kcal $mole^{-1}$):	
(i) From elements	62.8
(ii) From Ni(g) + C_5H_5 radicals	123
Lattice constants[d] (Å):	
a	5.88
b	7.86
c	10.68
Principal infrared bands[e] (cm^{-1})	3052, 2891, 1421, 1109, 1002, 839, 772, 355

[a] E. O. Fischer and H. P. Fritz *Advances Inorg. Chem. Radiochem.* **1** (1959) 55.

[b] G. Wilkinson P. L. Pauson and F. A. Cotton, *J. Am. Chem. Soc.* **76** (1954) 1970.

[c] E. O. Fischer and R. Jira, *Z. Naturforsch.* **8b** (1953) 217.

[d] W. Pfab and E. O. Fischer, *Z. anorg. u. allgem. Chem.* **274** (1953) 317.

[e] H. P. Fritz, *Advances Organomet. Chem.* **1** (1964) 239.

Nickel(II) acetylacetonate is usefully soluble in organic solvents and is therefore used in the Grignard synthesis of nickelocene from cyclopentadienyl magnesium halides. More ionic nickel(II) salts such as the thiocyanate can be reacted with potassium cyclopentadienide in liquid ammonia. The simplest laboratory method, however, involves[124] the addition of a dimethyl sulphoxide solution of hydrated nickel(II) chloride to potassium hydroxide and cyclopentadiene (i.e. potassium cyclopentadienide) in 1,2-dimethoxyethane:

$$10KOH + 2C_5H_6 + NiCl_2 \cdot 6H_2O \rightarrow Ni(C_5H_5)_2 + 2KCl + 8KOH \cdot H_2O$$

Nickelocene forms dark emerald green crystals which melt in nitrogen in 173–174° with some decomposition but which can be sublimed *in vacuo* above 80°. In air slow oxidation occurs but water neither attacks nor dissolves it; nickelocene is, however, soluble

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[120] J. D. Dunitz, H. C. Mez, O. S. Mills and H. M. M. Shearer, *Helv. Chim. Acta*, **45** (1962) 647.

[121] H. P. Fritz, *Advances Organomet. Chem.* **1** (1964) 239.

[122] R. B. King, *Organomet. Syntheses*, **1** (1965) 71.

[123] J. M. Birmingham, *Advances Organomet. Chem.* **2** (1964) 365.

[124] W. L. Jolly and D. J. Chazan, *Inorg. Syntheses*, **11** (1968) 122.

in most organic solvents. Some of its physical properties are given in Table 8. It has the sandwich structure being isomorphous with ferrocene; the Ni–C distance is 2.20 Å and the inter ring distance 3.4 Å. The paramagnetism indicates the electron assignment (see chapter on Iron, Fig. 17) $a_{1g}^2\ a_{1u}^2\ e_{1u}^4\ e_{1g}^4\ a'_{1g}^2\ e_{2g}^4\ e'_{1g}^2$.

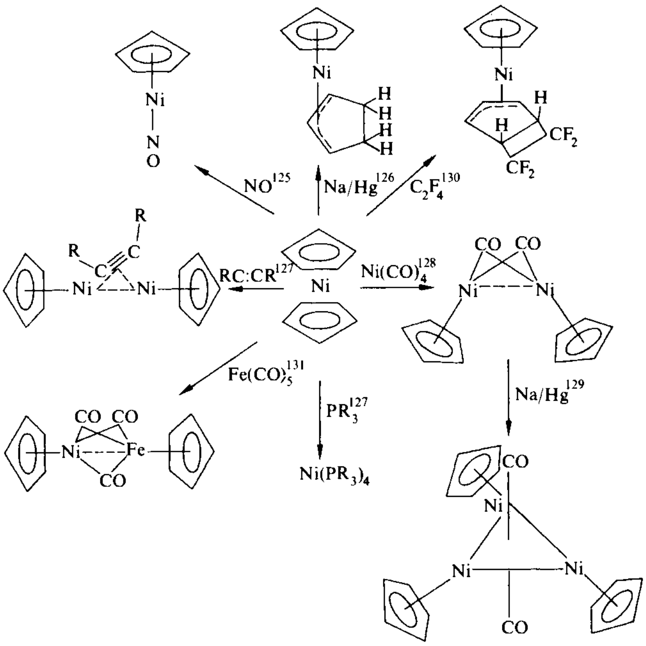

FIG. 4. Some reactions of nickelocene.

Nickelocene is a fairly reactive molecule. The oxidation product is the orange–yellow paramagnetic $(\pi\text{-}C_5H_5)_2Ni^+$ cation; this is rather unstable and decomposes in solution, but it may be precipitated as the reineckate or tetraphenylborate. Some reactions of nickelocene are shown in Fig. 4. Two cyclopentadienyl carbonyls can be obtained from the reaction with nickel carbonyl. The red diamagnetic $[(\pi\text{-}C_5H_5)NiCO]_2$ shows two carbonyl stretching bands (at 1897 and 1838 cm^{-1}) in the solid and the structure has been shown by X-rays[132] to have the folded configuration for the carbonyl groups as shown in Fig. 4. In solution, however, only a very small dipole moment is observed, and the vapour shows only one carbonyl stretching frequency; a centrosymmetric structure may thus exist in these phases[129, 133]. The carbonyl groups in $[(\pi\text{-}C_5H_5)NiCO]_2$ are readily replaced by acetylenes[114], diphosphines, and diarsines[134] to give compounds containing carbon, phosphorus, and arsenic bridges respectively. The green paramagnetic $(\pi\text{-}C_5H_5)_3Ni_3(CO)_2$

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[125] E. O. Fischer and R. Jira, *Z. Naturforsch.* **9b** (1954) 618.

[126] M. Dubeck and A. H. Filbey, *J. Am. Chem. Soc.* **83** (1961) 1257.

[127] H. Behrens and K. Meyer, *Z. Naturforsch.* **21b** (1966) 489.

[128] M. Dubeck, *J. Am. Chem. Soc.* **82** (1960) 502.

[129] E. O. Fischer and C. Palm, *Chem. Ber.* **91** (1958) 1725.

[130] D. W. McBride, R. L. Pruett, E. Pitcher and F. G. A. Stone, *J. Am. Chem. Soc.* **84** (1962) 497.

[131] J. F. Tilney-Bassett, *Proc. Chem. Soc.* (1960) 419.

[132] J. P. Nice and O. S. Mills, *J. Organomet. Chem.* **10** (1967) 337.

[133] H. P. Fritz and C. G. Kreiter, *Chem. Ber.* **96** (1963) 2008.

[134] R. G. Hayter, *Inorg. Chem.* **2** (1963) 1031.

has one unpaired electron and zero dipole moment; the X-ray structure[135] shows the three nickel atoms to occupy the corners of an equilateral triangle with the two carbon monoxide groups symmetrically arranged above and below the plane of the nickel atoms.

Several analogous of nickelocene have been prepared; these include the red-brown bis(indenyl)nickel[135] and the green bis(methylcyclopentadienyl)nickel[136] (m.p. 39–40°).

3.4. COMPLEXES OF NICKEL(II)

Coordination compounds of nickel(II) are exceedingly numerous[137]. The maximum coordination number shown is six and whilst octahedral or distorted octahedral complexes are the most numerous, nickel(II) also forms many 5-coordinate (square pyramidal and trigonal bipyramidal) and 4-coordinate (tetrahedral and square planar) complexes. One of the most remarkable facts about the stereochemistry of nickel(II) complexes is that equilibria between the different structural types often exist in solution and these equilibria are frequently temperature dependent and often concentration dependent. We shall discuss here firstly the preparation and properties of these compounds which exist practically completely in one stereochemical form, classifying them according as to whether they contain cationic, neutral or anionic nickel(II). Then in section 3.4.4 those complexes which participate in the stereochemical interconversions will be considered. In section 3.4.5 the spectral and magnetic properties of the complexes are discussed according to stereochemical types.

3.4.1. Cationic Nickel(II) Complexes

The fairly regular octahedral cation $[Ni(H_2O)_6]^{2+}$ gives the green colour to many nickel(II) salt hydrates and to their solutions. The water molecules are readily replaced by other neutral or anionic ligands and many of these new complexes can be crystallized from solution. Alcohols thus displace water molecules in a stepwise fashion and by reaction of anhydrous nickel(II) bromide with silver nitrate or perchlorate in ethanolic solution, green crystals of the $[Ni(EtOH)_6]^{2+}$ salts can be obtained by evaporation, after filtering off the silver bromide. The substitution of water molecules in the hexaquo ion by nitrogen

TABLE 9. STABILITY CONSTANTS OF SOME NICKEL(II) COMPLEXES

Ligand	Temp. (°C)	log K_1	log K_2	log K_3	log K_4	log K_5	log K_6
NH_3	25	2.36	1.90	1.55	1.23	0.85	0.42
N_2H_4	20	2.76	2.44	2.15	1.85	1.55	1.24
py	25	1.78	1.05	0.31			
en	30	7.66	6.40	4.55			
pn	25	8.04	6.37	4.24			
dipy	25	6.80	6.46	5.20			
phen	25	8.60	8.10	7.55			
EDTA	30	17.5					

py = pyridine; en = ethylenediamine; pn = propylenediamine; dipy = 2,2′-dipyridyl; phen = 1,10-phenanthroline; EDTA = ethylenediaminetetraacetic acid.

[135] E. O. Fischer, D. Seus and R. Jira, *Z. Naturforsch.* **8b** (1953) 692.

[136] L. T. Reynolds and G. Wilkinson, *J. Inorg. Nuclear Chem.* **9** (1959) 86.

[137] Gmelin's *Handbuch der Anorganischen Chemie*, **57** (C, 1), Verlag Chemie (1968).

donors usually leads to a colour change from green to violet as a result of the stronger ligand field now present. Some stepwise stability constants of nickel(II) complexes are listed in Table 9 [138]. In strong ammonia solution, complete replacement of coordinated water molecules occurs with the formation of the violet hexammine $[Ni(NH_3)_6]^{2+}$. Salts of this ion can be precipitated by concentrated ammonia solution from strong solutions of nickel(II) salts—as, for example, in the preparations of $[Ni(NH_3)_6]Br_2$ and $[Ni(NH_3)_6]I_2$[139]. These hexaammoniates are also obtained in the direct reaction between ammonia and nickel(II) salts at or below room temperature. They dissolve without decomposition in water containing ammonia. In these nickel(II) halide hexaammoniates, the nickel is surrounded octahedrally by the ammonia molecules in fluorite-type structures[140]. Hydrazine acts as a unidentate ligand showing formation constants similar to those for ammonia. Solid complexes isolated from aqueous hydrazine solutions, however, contain the polymeric NiN_6 structure of empirical formula $[Ni(N_2H_4)_3]^{2+}$; methylhydrazine, however, yields the hexahydrazine cation $[Ni(MeNHNH_2)_6]^{2+}$, salts of which can be precipitated from ethanolic solution[141]. Pyridine addition to nickel(II) salt solutions usually causes the precipitation or formation of neutral complexes but with weakly coordinating anions the dark blue hexapyridine salts, e.g. $[Ni(py)_6](NO_3)_2$ [137], can be isolated. A great increase in stability of the complexes is observed (viz. Table 9) with the chelating ligands. The tris(ethylenediamine)- and tris(propylenediamine)-nickel(II) chlorides are readily prepared as dihydrates from aqueous solution[142]. In $[Ni(en)_3](NO_3)_2$ [143] the nickel atoms are octahedrally surrounded by nitrogen atoms at distances of 2.12 Å. Some other NiL_6^{2+} cations prepared by direct reaction include those with pyridine-N-oxide[144], acetamide[145], dimethyl sulphoxide[146] and methyl cyanide[147]. The crystal structure of hexakis(thiourea)-nickel(II) bromide consists[148] of $Ni[SC(NH_2)_2]_6{}^{2+}$ and Br^- ions, the nickel atoms being surrounded by six sulphur atoms from the ligand in a distorted octahedral environment. Alternatively, these NiL_6^{2+} cations arise in the disproportionation reactions of nickel carbonyl (Section 2.1.2), e.g.

$$5Ni(CO)_4 + 3en \rightarrow [Ni(en)_3][Ni_4(CO)_9] + 11CO$$

There are many octahedral nickel(II) cations containing a mixture of ligands[137]; most of these contain a bidentate ligand such as ethylenediamine. The complex $[Ni(en)_2(NO_2)]BF_4$, for example, contains a polymeric distorted octahedral cation with bridging NO_2 groups[149]. Similarly, $[Ni(en)_2(NCS)]I$ contains NCS bridges in a dimeric octahedral structure[150]. The nickel(II) complexes of *o*-phenylenebis(dimethylarsine) (diars) have presented some interesting problems. The oxidation of the neutral complex

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[138] *Stability Constants of Metal-Ion Complexes*, Special Publication No. 17, Chemical Society, London (1964).

[139] G. W. Watt, *Inorg. Syntheses*, **3** (1950) 194.

[140] R. G. W. Wyckoff, *Crystal Structures*, 2nd edn., Vol. 3, Interscience (1965).

[141] D. Nicholls and R. Swindells, *J. Inorg. Nuclear Chem.* **30** (1968) 2211.

[142] H. M. State, *Inorg. Syntheses*, **6** (1960) 200.

[143] L. N. Swink and M. Atoji, *Acta Cryst.* **13** (1960) 639.

[144] R. L. Carlin and M. J. Baker, *J. Chem. Soc.* (1964) 5008.

[145] R. S. Drago, D. W. Meek, M. D. Joesten, and L. La Roche, *Inorg. Chem.* **2** (1963) 124.

[146] D. W. Meek, R. S. Drago and T. S. Piper, *Inorg. Chem.* **1** (1962) 285.

[147] B. J. Hathaway and D. G. Holah, *J. Chem. Soc.* (1964) 2400.

[148] M. S. Weininger, J. E. O'Connor and E. L. Amma, *Inorg. Chem.* **8** (1969) 424.

[149] M. G. B. Drew, D. M. L. Goodgame, M. A. Hitchman and D. Rogers, *Chem. Communs.* (1965) 477.

[150] A. E. Shvelashvili, M. A. Porai-Koshits and A. S. Antsyshkina, *Zh. Strukt. Khim.* **5** (1964) 797.

$Ni(diars)_2Cl_2$ by oxygen in the presence of excess chloride ion gives the brown paramagnetic (one unpaired electron) compound $[Ni(diars)_2Cl_2]Cl$ [157]; this was regarded for many years as containing nickel(III). A crystal structure study[152] has confirmed the presence of the monomeric cation $[Ni(diars)_2Cl_2]^+$ which has the four arsenic atoms in an approximately square planar arrangement around nickel, the two chlorine atoms completing the slightly elongated octahedral structure. The Ni–As distances are significantly greater in $[Ni(diars)_2Cl_2]^+$ (2.34–2.37 Å) than in the neutral $Ni(diars)_2I_2$ (2.28–2.30 Å) and this fact coupled with evidence from the electron spin reasonance spectrum on $[Ni(diars)_2Cl_2]^+$ and the diarsine radical cation, has led to the new formulation containing nickel(II), i.e. $(Ni^{II}Cl_2(diars^+{}_2))^+$. The reported diamagnetism of the complex presumed to be $[Ni(diars)_3](ClO_4)_2$ [151, 153] was difficult to comprehend until X-ray diffraction studies[154] revealed the compound to be $[Ni(diars)(triars)](ClO_4)_2$ (triars = bis(*o*-dimethylarsinophenyl)methylarsine) in which the nickel atom is in a tetragonal pyramid of the five arsenic atoms. The diamagnetic nickel(II) complexes of the terdentate triarsines $[Ni(triars)_2](ClO_4)_2$ have spectra similar to that of the mixed arsine cation and may have nickel atoms which experience a tetragonal pyramidal field of five of the arsenics with the sixth either uncoordinated or very loosely bound.

Whilst there are a fair number of 5-coordinate nickel(II) cationic complexes of the type $[Ni\ L\ Cl]^+$, where L is a tetradentate ligand (viz. section 3.4.5), tetrahedral cations are rare, occurring only in complexes of bulky ligands, e.g. $[Ni(HMPA)_4](ClO_4)_2$ [155] (HMPA= hexamethylphosphoramide) and $[Ni(Me_3NO)_4](ClO_4)_2$ [156].

3.4.2. Neutral Nickel(II) Complexes

Complexes of nickel(II) halides with neutral donor molecules. Nickel(II) halides and other simple nickel(II) salts form a very large number of complexes with ligands having, in particular, nitrogen or phosphorus donor atoms [137, 138]. Only the halide complexes will be treated here, since the halides form more complexes than the salts of other anions and illustrate the diversity of stereochemistry of these complexes; for the similar neutral complexes of other salts, e.g. nitrate and thiocyanate, the reader should consult Gmelin[137]. These complexes are most commonly of the types NiX_2L_2 (which may be tetrahedral, square, or octahedral) but NiX_2L and NiX_2L_4 (usually octahedral) also occur frequently when L is a unidentate ligand. The complexes are prepared by direct reaction either of the solid salt with the ligand or of solutions of the salt and ligand in ethanol or even water. Frequently the thermal decomposition of $[NiL_6]X_2$ complexes proceeds via the stable phases NiL_4X_2, NiL_2X_2 and $NiLX_2$. It will be possible to discuss only a few well studied compounds here but some examples of typical complexes of nickel(II) halides are given in Table 10. This table shows the variation in stereochemistries shown by these complexes and the lack of correlation between colour and stereochemistry shown by them.

One of the largest groups of complexes of nickel(II) halides studied is that with pyridine, substituted pyridines and related ligands. Direct reaction between nickel(II) chloride

[151] R. S. Nyholm, *J. Chem. Soc.* (1950) 2061.
[152] P. Kreisman, R. Marsh, J. R. Preer and H. B. Gray, *J. Am. Chem. Soc.* **90** (1968) 1067.
[153] B. Bosnich, R. Bramley, R. S. Nyholm and M. L. Tobe, *J. Am. Chem. Soc.* **88** (1966) 3926.
[154] B. Bosnich, R. S. Nyholm, P. J. Pauling and M. L. Tobe, *J. Am. Chem. Soc.* **90** (1968) 4741.
[155] J. T. Donoghue and R. S. Drago, *Inorg. Chem.* **1** (1962) 866.
[156] R. S. Drago, J. T. Donoghue and D. W. Herlocker, *Inorg. Chem.* **4** (1965) 836.
[157] R. Colton and J. H. Canterford, *Halides of the First Row Transition Metals*, Wiley–Interscience (1969).

and pyridine produces the blue $NiCl_2(py)_4$. This has the *trans*-octahedral structure with Ni–Cl = 2.39 Å and Ni–N = 2.00 Å[158]; above 110° it decomposes into pyridine and $NiCl_2(py)_2$. The amine $NiCl_2(NH_3)_2$ is similarly obtained from $Ni(NH_3)_6Cl_2$ at 120°; the magnetic and spectral data indicate that both this and the pyridine complex contain octahedrally coordinated nickel.

TABLE 10. SOME COMPLEXES OF NICKEL(II) HALIDES

Complex	Colour	Stereochemistry	Properties
$NiCl_2(aniline)_2$[a]	Green	Octahedral	μ = 3.36 BM
$NiBr_2(pyridine)_2$[b]	Yellow–green	Octahedral	μ = 3.30 BM
$NiBr_2(pyridine)_4$[b]	Light-blue	Octahedral	
$NiCl_2(quinoline)_2$[c]	Yellow	Octahedral	μ = 3.41 BM
$NiCl_2(quinoline)_2$[c]	Blue	Tetrahedral	μ = 3.54 BM
$NiI_2(quinoline)_2$[c]	Green	Square planar	Diamagnetic
$NiCl_2(dipy)_2$[d]	Green	Octahedral	μ = 3.20 BM
$NiCl_2(dipy)$[d]	Yellow	Octahedral	μ = 3.38 BM
$NiCl_2(PMe_3)_2$[e]	Red	Square planar	Diamagnetic
$NiCl_2(PPh_3)_2$[f]	Blue	Tetrahedral	μ = 3.07 BM
$NiBr_2(PPh_3)_2$[g]	Green	Tetrahedral	μ = 2.97 BM
$NiCl_2(PHPh_2)_3$[h]	Brown	Five-coordinate	m.p. 98°C
$NiI_2(PMePh_2)_2$[i]	Red–brown	Tetrahedral	μ = 3.32 BM
$NiBr_2[P(C_6H_{11})_3]_2$[j]	Green	Square planar	Diamagnetic
$NiBr_2(TAS^*)$[k]		Square pyramidal	Diamagnetic
$NiBr_2(diars)$[l]	Red	Square planar	Diamagnetic
$NiI_2(diars)_2$[m]	Brown	Octahedral	
$NiCl_2(Et_3PO)_2$[n]	Violet	Tetrahedral	m.p. 93°C
$NiCl_2(Ph_3AsO)_2$[o]	Blue	Tetrahedral	μ = 3.95 BM
$NiBr_2(1,4\text{-dioxan})_2$[p]	Yellow	Octahedral	μ = 3.35 BM
$NiCl_2[SC(NH_2)_2]_4$[q]	Yellow	Octahedral	

* TAS = methyl bis(3-propanedimethylarsino)arsine.

[a] I. S. Ahuja, D. H. Brown, R. H. Nuttall and D. W. A. Sharp, *J. Inorg. Nuclear Chem.* **27** (1965) 1105.

[b] J. R. Allan, D. H. Brown, R. H. Nutall and D. W. A. Sharp, *J. Inorg. Nuclear Chem.* **27** (1965) 1529.

[c] D. M. L. Goodgame and M. Goodgame, *J. Chem. Soc.* (1963) 207.

[d] R. H. Lee, E. Griswold and J. Kleinberg, *Inorg. Chem.* **3** (1964) 1278.

[e] K. A. Jensen, P. H. Nielsen and C. T. Pedersen, *Acta Chem. Scand.* **17** (1963) 1115.

[f] G. Garton, D. H. Henn, H. M. Powell and L. M. Venanzi, *J. Chem. Soc.* (1963) 3625.

[g] L. M. Venanzi, *J. Chem. Soc.* (1958) 719.

[h] R. G. Hayter, *Inorg. Chem.* **2** (1963) 932.

[i] R. G. Hayter and F. S. Humiec, *Inorg. Chem.* **4** (1965) 1701.

[j] K. Issleib and A. Brack, *Z. anorg. u. allgem. Chem.* **277** (1954) 258.

[k] G. A. Mair, H. M. Powell and D. E. Henn, *Proc. Chem. Soc.* (1960) **415**.

[l] M. J. Hudson, R. S. Nyholm and M. H. B. Stiddard, *J. Chem. Soc.* (A) (1968) 40.

[m] N. C. Stephenson, *Acta Cryst.* **17** (1964) 592.

[n] K. Issleib and B. Mitscherling, *Z. anorg. u. allgem. Chem.* **304** (1960) 73.

[o] D. M. L. Goodgame and M. Goodgame, *Inorg. Chem.* **4** (1965) 139.

[p] G. W. A. Fowles, D. A. Rice and R. A. Walton, *J. Chem. Soc.* (A) (1968) 1842.

[q] A. Lopez-Castro and M. R. Turner, *J. Chem. Soc.* (1963) 1309.

In general, phosphines give 4-coordinate complexes, the trialkyl phosphine complexes

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[158] M. A. Porai-Koshits, E. K. Yukhno, A. S. Antsishkina and L. M. Dikareva, *Kristallografiya*, **2** (1957) 371.

are square planar both in the solid state and in solution while the triarylphosphines give tetrahedral complexes. The tetrahedral structure in these complexes is favoured in the order $PEt_3 < PEt_2Ph < PEtPh_2 < PPh_3$ and also in the order $Cl < Br < I$, i.e. in order of decreasing ligand field strength. A single crystal X-ray study on $NiCl_2(PPh_3)_2$ shows the nickel to be in a pseudo tetrahedral environment with Ni–Cl = 2.27 Å, Ni–P = 2.28 Å and the angles Cl–N–Cl and P–Ni–P, 123° and 117° respectively. The compound of empirical formula $NiBr_2[P(Ph_2)CH_2Ph]_2$ occurs in two forms, one red and one green. While this is certainly not unusual for such nickel(II) complexes, the remarkable green form contains three molecules in the triclinic unit cell; one molecule has the *trans*-square planar configuration while the other two molecules contain tetrahedrally coordinated nickel [159]. The red form of this compound is diamagnetic and presumably square planar; the triethylphosphine complex $NiBr_2(PEt_3)_2$ has been shown to be *trans*-square planar with Ni–P and Ni–Br dstancse of 2.26 and 2.30 Å respectively[160]. The analogous arsine and stibine complexes

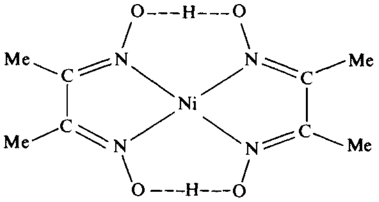


FIG. 5. Bis(dimethylglyoximato)nickel(II).

are considerably less stable than their phosphine analogues, but $NiI_2(AsEt_3)_2$ has been isolated. Chelating arsines readily form complexes with nickel(II) salts, however; $NiBr_2(TAS)$ has the distorted square pyramidal structure with an apical bromine atom and the other bromine atom at about 20° below the plane of the nickel and arsenic atoms.

Complexes of chelate anionic ligands. There are a large number of nickel(II) chelates such as β-keto-enolates and salicylaldimine complexes which are discussed along with the interesting complexes of nickel(II) salts with *N*-substituted di-amines in section 3.4.4. The complexes of *vic*-dioximes have long been important as analytical reagents for nickel(II) ions.

Bis(dimethylglyoximato)nickel(II) $[Ni(DMG)_2]$ is obtained quantitatively as a red flocculent precipitate when an alcoholic solution of dimethylglyoxime is added to a neutral or ammoniacal solution of a nickel(II) salt and this reaction is thus used in the gravimetric estimation of nickel. The structure of the diamagnetic $Ni(DMG)_2$ [161] (Fig. 5) shows several interesting features. The nickel atoms are surrounded by four nitrogen atoms at 1.85 Å in a square plane. The planar molecules (Fig. 5) stack one above another, alternate molecules being twisted through 90°, so that the nickel atoms form chains with a Ni–Ni distance of 3.25 Å. Each molecule contains strong intramolecular hydrogen bonds, the O–O distances being only 2.40 Å. The infrared spectrum[162] shows an O–H stretching frequency in the 2350 cm^{-1} region, an O–H deformation mode at 1780 cm^{-1} and the out-of-plane O–H vibration at 900–950 cm^{-1}. In bis(ethylmethylglyoximato)nickel(II)[163]

[159] B. T. Kilbourn, H. M. Powell and J. A. C. Darbyshire, *Proc. Chem. Soc.* (1963) 207.

[160] V. Scatturin and A. Turco, *J. Inorg. Nuclear Chem.* **8** (1958) 447.

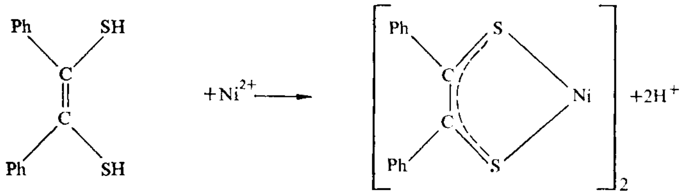
[161] L. E. Godycki and R. E. Rundle, *Acta Cryst.* **6** (1953) 457.

[162] R. Blinc and D. Hadzi, *J. Chem. Soc.* (1958) 4536.

[163] E. Frasson and C. Panattoni, *Acta Cryst.* **13** (1960) 893.

the O–O distance is even shorter at 2.33 Å, but the shortest Ni–Ni distance is 4.75 Å, so that this can be regarded as a square planar complex.

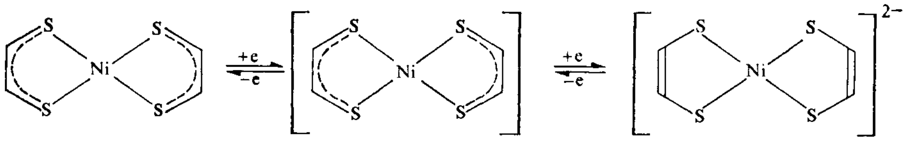
Like iron and cobalt, nickel forms numerous complexes with bidentate sulphur donors such as the 1,2-dithiols and 1,2-dithioketones[164, 165]. The neutral complexes $NiS_4C_4R_4$ (R = alkyl, aryl, CF_3 or H) form blue or green crystals which are stable to aqueous acids and bases and also to air. One method of preparation of these complexes involves the preparation of the dithiols (e.g. via acyloins and P_4S_{10}) and reaction of these with nickel(II) salts:



The trifluoromethyl analogue is best prepared from nickel carbonyl and the dithietene;

$$Ni(CO)_4 + 2(CF_3)_2C_2S_2 \rightarrow [NiS_4C_4(CF_3)_4] + 4CO$$

while the anionic cyano analogues $[NiS_4C_4(CN)_4]^{n-}$ are readily prepared starting from the sodium salt $Na_2S_2C_2(CN)_2$ [166]. The uncharged complexes are diamagnetic; the square planar structure of $[NiS_4C_4Ph_4]$ has been established by X-ray analysis[167]. The C–C and C–S bond lengths are intermediate between those expected for single and double bonds. The anions $[NiS_4C_4(CN)_4]^{1-}$ and $[NiS_4C_4(CN)_4]^{2-}$ similarly have the planar structure[168, 169]. The monoanions are paramagnetic in the solid state as well as in solution and give a single line in the electron spin resonance spectrum[170] with $< g > = 2.08$ for $[NiS_4C_4(CN)_4]^-$. It is believed that the unpaired electron occupies a π-molecular orbital which is delocalized over the whole complex rather than that these complexes contain nickel(III). The dianions are diamagnetic and seem on the basis of bond lengths to be best regarded as nickel(II) complexes of dithiolate ligands. These compounds can thus be approximately represented by the formulae:



Like their iron and cobalt analogues they readily undergo the electron transfer reactions represented by the above equations. The stable neutral complex $[NiS_4C_4Ph_4]$ shows a surprising reactivity towards unsaturated organic molecules reacting for example with

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[164] G. N. Schrauzer, *Transition Metal Chemistry* (R. L. Carlin, ed.), Vol. 4 (1968), p. 299.
[165] J. A. McCleverty, *Progress Inorg. Chem.* **10** (1968) 49.
[166] A. Davison and R. H. Holm, *Inorg. Syntheses*, **10** (1967) 8.
[167] D. Sartain and M. Truter, *Chem. Communs.* (1966) 382.
[168] C. J. Fritchie, *Acta Cryst.* **20** (1966) 107.
[169] R. Eisenberg, J. A. Ibers, R. J. H. Clark and H. B. Gray, *J. Am. Chem. Soc.* (1964) 113.
[170] H. B. Gray, *Transition Metal Chemistry* (R. S. Carlin, ed.), Vol. 1 (1965), p. 239.

phenylacetylene at room temperature, and with norbornadiene and norbornene to form addition compounds from which the olefins can be recovered by heating under reduced pressure. With phosphines the substitution of one of the bidentate ligands by two phosphine ligands often occurs giving complexes of the type $(R_3P)_2Ni(S_2C_2R_2)$ but bis-adducts, e.g. $NiS_4C_4Ph_4.2P(Bu^n)_3$ are also formed in certain cases.

3.4.3. Anionic Nickel(II) Complexes

Complex halides. Complex salts containing the NiX_4^{2-} anions (X = Cl, Br, I) are readily prepared from the appropriate nickel(II) halides and quaternary ammonium, phosphonium or arsonium salts in ethanol or nitromethane[171, 172]; only rarely have they been obtained from aqueous solution. The yellow tetrafluoronickelates(II) are most conveniently prepared by fusion of nickel(II) fluoride with the stoichiometric amount of an alkali metal or alkaline earth metal fluoride *in vacuo* or in an atmosphere of hydrogen fluoride.

The $NiCl_4^{2-}$, $NiBr_4^{2-}$ and NiI_4^{2-} ions have tetrahedral structures; their salts are frequently isostructural with the cobalt analogues, and distortions from tetrahedral symmetry of the anions vary slightly with different cations due to crystal packing effects. In $(Me_4N)_2NiCl_4$ [173] the $NiCl_4^{2-}$ anions are somewhat flattened with Cl–Ni–Cl bond angles of 107.8° and 114.4° and Ni–Cl bond lengths varying from 2.256 to 2.283 Å. A similar distortion of the $NiCl_4^{2-}$ ions occurs in the tetraethylammonium salt [174], but in the triphenylmethylarsonium compound the $NiCl_4^{2-}$ ion is perfectly tetrahedral within experimental error, the mean Ni–Cl distance being 2.692 Å and the Cl–Ni–Cl angle 109°28′. These blue salts dissolve largely unchanged in nitromethane, but in dimethyl sulphoxide, dimethyl formamide and water, solvation occurs and species in the series $[NiX_nL_{6-n}]^{2-n}$ are formed. The NiX_4^{2-} salts (X = Cl, Br, I) are magnetically dilute and have room temperature magnetic moments in the range 3.5–4.1 BM[174] expected for tetrahedral complexes. Substituted tetrahalogenonickelates(II) such as $(Et_4N)[NiBr_3.PPh_3]$ are readily prepared as for the NiX_4^{2-} salts but in the presence of the substituting ligand; magnetic and spectral data on these complexes indicate a distorted tetrahedral structure for the $[NiX_3L]^-$ anions[175–177]. This structure has been confirmed by a crystal structure determination on tetra-n-butylammonium tribomo(quinoline)nickelate(II)[178]. The blue pentachloronickelate(II), Cs_3NiCl_5, is obtained by rapid quenching of $CsCl–NiCl_2$ melts of the correct stoichiometry[179]. It is isostructural with the cobalt analogue and contains tetrahedrally coordinated nickel; its electronic spectrum in the molten state has been recorded[180].

The tetrafluoronickelates(II) contain octahedrally coordinated nickel(II); the potassium, rubidium, ammonium and thallium(I) salts are tetragonal[181], Li_2NiF_4 is cubic[177] and $BaNiF_4$ is orthorhombic[182]. Apart from the lithium salt ($\mu_{eff} = 3.8$ BM at room temperature

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[171] N. S. Gill and R. S. Nyholm, *J. Chem. Soc.* (1959) 3997.

[172] N. S. Gill and F. B. Taylor, *Inorg. Syntheses* **9** (1967) 140.

[173] J. R. Weisner, R. C. Srivastava, C. H. L. Kennard, M. Di Vaira and E. C. Lingafelter, *Acta Cryst.* **23** (1967) 565.

[174] D. M. L. Goodgame, M. Goodgame and F. A. Cotton, *J. Am. Chem. Soc.* **83** (1961) 4161.

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[177] D. H. Brown, K. P. Forrest, R. H. Nuttall and D. W. A. Sharp, *J. Chem. Soc.* (A) (1968) 2146.

[178] W. De W. Horrocks, D. H. Templeton and A. Zalkin, *Inorg. Chem.* **7** (1968) 2303.

[179] E. Iberson, R. Gut and D. M. Gruen, *J. Phys. Chem.* **66** (1962) 65.

[180] C. R. Boston, J. Brynestead and G. P. Smith, *J. Chem. Phys.* **47** (1967) 3193.

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[182] J. C. Cousseins and M. Samouel, *Compt. Rend.* **265C** (1967) 1121.

these compounds are antiferromagnetic showing room temperature moments around 2.0 BM. The reflectance spectra of Ni_2NiF_4, K_2NiF_4 and Rb_2NiF_4 have been assigned on O_h symmetry[181].

The trihalonickelates(II) $MNiX_3$ (X = F, Cl, Br) are obtained when a nickel(II) halide and an alkali metal halide are reacted in 1 : 1 stoichiometry either in the melt or in methanol or for the fluorides, in boiling water[157]. They all contain octahedrally coordinated nickel. The potassium salt $KNiF_3$ (m.p. 1130°) has the perovskite-type structure with the Ni–F distance of 2.01 Å, while the sodium and rubidium salts occur in two different modifications (Na, cubic and orthorhombic, Rb cubic and hexagonal). The single crystal study of $(Me_4N)[NiBr_3]$[183] shows the anion to adopt a polymeric chain structure having $NiBr_6$ octahedra which share opposite faces. Whilst the trifluoronickelates(II) are antiferromagnetic[184] at room temperature, the trichloronickelates(II) show magnetic moments in the range 3.1–3.5 BM[185, 186] expected for magnetically dilute octahedral nickel(II) complexes.

A hexafluoronickelate(II), Ba_2NiF_6, has been obtained as a yellow solid by fusing a 2 : 1 mixture of barium fluoride and nickel(II) fluoride at 1200° [187]. The $NiF_6{}^{4-}$ octahedra are tetragonally elongated with Ni–F distances of 2.03 and 1.97 Å. This compound has a room temperature magnetic moment of 3.76 BM and becomes antiferromagnetic at low temperatures.

Complex cyanides[188]. Potassium tetracyanonickelate(II) can be crystallized as orange crystals of formula $K_2Ni(CN)_4.H_2O$ from the orange–red solution of nickel(II) cyanide in aqueous potassium cyanide[189]. It can be dehydrated at 100°. The alkali metal and alkaline earth metal tetracyanonickelates(II) are water soluble and crystallize as hydrates, e.g. $Na_2Ni(CN)_4.3H_2O$, $Ba[Ni(CN)_4].4H_2O$ and $Sr(Ni(CN)_4.5H_2O$. In all of these compounds the $[Ni(CN)_4]^{2-}$ ions are square planar; in the potassium salt[190] the Ni–C distances are 1.87 Å. The salts are diamagnetic; the infrared spectra of the sodium and barium salts have been studied in detail and the force constants calculated[191].

The tetracyanonickelate(II) ion is extremely stable with the very high formation constant[192] $K = 10^{30.1\pm0.2}$ at 25°; even bis(dimethylglyoximato)nickel(II) is soluble in aqueous potassium cyanide. An aqueous solution of the free acid, $H_2Ni(CN)_4$, can be obtained by the use of a cation exchange resin in H^+ form; it decomposes fairly rapidly into hydrated nickel(II) cyanide and hypocyanic acid[185]. Hypobromite oxidation of $Ni(CN)_4{}^{2-}$ solutions yields a black precipitate of hydrated NiO_2. With boron trifluoride[193] $K_2[Ni(CN)_4]$ acts as a Lewis base forming $K_2Ni(CN)_4.4BF_3$, the $C{\equiv}N$ stretching frequency in the new complex being 2245 cm^{-1} as compared to 2130 cm^{-1} in $K_2[Ni(CN)_4]$. In liquid ammonia, $K_2[Ni(CN)_4]$ is reduced to $K_4Ni(CN)_4$ by potassium (see Section 2.3) and converted into $K_2[Ni(C \vdots CR)_4]$ by potassium acetylides[194].

In the deep-red solutions of $[Ni(CN)_4]^{2-}$ in excess of cyanide there is considerable

[183] G. Stucky, S. D. Agostino and G. McPherson, *J. Am. Chem. Soc.* **88** (1966) 4828.

[184] D. J. Machin, R. L. Martin and R. S. Nyholm, *J. Chem. Soc.* (1963) 1490; D. J. Machin and R. S. Nyholm, *ibid.*, p. 1500.

[185] R. W. Asmussen and H. Soling, *Z. anorg. u. allgem. Chem.* **283** (1956) 3.

[186] D. M. L. Goodgame, M. Goodgame and M. J. Weeks, *J. Chem. Soc.* (1964) 5194.

[187] H. G. Schrering, *Z. anorg. u. allgem. Chem.* **353** (1967) 1, 13.

[188] B. M. Chadwick and A. G. Sharpe, *Advances in Inorg. Chem. Radiochem.* **8** (1966) 83.

[189] W. C. Fernelius and J. J. Burbage, *Inorg. Syntheses* **2** (1946) 225.

[190] N. G. Vannerberg, *Acta Chem. Scand.* **18** (1964) 2385.

[191] R. L. McCullough, L. H. Jones and G. A. Crosby, *Spectrochim. Acta* **16** (1960) 929.

[192] J. T. Christensen, R. M. Izatt, J. D. Hale, R. T. Pack and G. D. Watt, *Inorg. Chem.* **2** (1963) 337.

[193] D. F. Shriver, *J. Am. Chem. Soc.* **84** (1962) 4610; **85** (1963) 1405.

[194] R. Nast and H. Kasperl, *Z. anorg. u. allgem. Chem.* **295** (1958) 227.

evidence for the formation of diamagnetic $[Ni(CN)_5]^{3-}$ which has[195] $\nu(C{\equiv}N)$ at 2103 cm^{-1} as compared to $[Ni(CN)_4]^{2-}$ in aqueous solution which has $\nu(C{\equiv}N)$ at 2124 cm^{-1}. The salt $[Cr(en)_3][Ni(CN)_5]\cdot 1.5H_2O$ contains[196] two kinds of nickel(II) anions; one has a tetragonal pyramidal structure having Ni–C (apical) = 2.14 Å and Ni–C (basal) = 1.87 Å while the other has a distorted trigonal bipyramidal structure with Ni–C (apical) = 1.80 Å and Ni–C (equatorial) = 1.88–2.00 Å. There is no evidence for the formation of $[Ni(CN)_6]^{4-}$ ions or $[Ni(CN)_5F]^{4-}$ in the $[Ni(CN)_4]^{2-}$–CN^- systems with added cyanide or fluoride respectively; with added iodide and thiocyanate, however, the complexes $[Ni(CN)_4I]^{3-}$ and $[Ni(CN)_4(SCN)]^{3-}$ are formed[197].

Complex isothiocyanates and isocyanates. Salts of the hexaisothiocyanatonickelate(II) ion can be isolated from aqueous solutions of nickel(II) thiocyanate in alkali metal thiocyanate solutions. They are usually hydrated, e.g. green $K_4[Ni(NCS)_6].4H_2O$[198]. This trigonal potassium salt contains octahedrally coordinated nickel ions with nickel bonded to nitrogen so that it is an isothiocyanate complex. There are several substituted isothiocyanates e.g. $[Ni(NH_3)_2(NCS)_4]^{2-}$ and $[Ni(NH_3)_3(NCS)_3]^-$, which have co-linear Ni–N–C groups. The mercury(II) salt $Hg[Ni(H_2O)_2(NCS)_4]$ has a *trans*-octahedral anion[199] with Ni–N = 2.05 Å.

Tetrahedral nickel(II) complexes of thiocyanate and cyanate ions are also well characterized[200]. Tetraethylammonium tetraisocyanatonickelate(II), $(Et_4N)_2[Ni(NCO)_4]$, is obtained as deep-blue hygroscopic crystals by reaction of $(Et_4N)_2NiBr_4$ with silver cyanate in acetone; the precipitate is filtered off and the complex precipitated by the addition of ether. The complex is isomorphous with the cobalt(II) analogue and the tetrahedral stereochemistry of the anion is supported by magnetic and spectral data.

Complex nitrites. The brownish-red anhydrous nitro complexes $M_4^I[Ni(NO_2)_6]$ contain octahedral anions[201] with Ni–N distances of 2.15 Å. The potassium salt is precipitated from mixed ice cold saturated solutions of nickel(II) nitrate and potassium nitrite. It is paramagnetic and gives green solutions in water.

Carboxylato complexes. While monocarboxylic acid anions do not form strong complexes with nickel(II) ions, bidentate carboxylate anions do form complexes. The stepwise formation constants[202] of $[Ni(C_2O_4)_3]^{4-}$ are $K_1 = 10^{4\cdot 10}$, $K_2 = 10^{3\cdot 05}$, and $K_3 = 10^{1\cdot 36}$; the green salt $K_2[Ni(C_2O_4)_2].6H_2O$ crystallizes from aqueous solutions of nickel(II) oxalate in potassium oxalate[203].

3.4.4. The "Anomalous" Behaviour of Nickel(II) Complexes

Most of the complexes which we have so far discussed can be isolated purely in one stereochemical form or another although many of them can be isolated in a pure form as two different stereochemical isomers. However, there are a considerable number of nickel(II) complexes which do not behave under all conditions as typical of any one stereochemical form. These compounds have for long been known as "anomalous", so we

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[195] R. A. Penneman, R. Bain, G. Gilbert, L. H. Jones, R. S. Nyholm and G. K. N. Reddy, *J. Chem. Soc.* (1963) 2266.

[196] K. N. Raymond and J. A. Ibers, quoted in L. Sacconi, *Transition Metal Chem.* **4** (1968) 199.

[197] J. S. Coleman, H. Petersen and R. A. Penneman, *Inorg. Chem.* **4** (1965) 135.

[198] J. Lewis, R. S. Nyholm and P. W. Smith, *J. Chem. Soc.* (1961) 4594.

[199] K. H. Chou and M. A. Porai-Koshits, *Kristallografiya*, **5** (1960) 462.

[200] D. Forster and D. M. L. Goodgame, *J. Chem. Soc.* (1964) 2790; *Inorg. Chem.* **4** (1965) 715, 823.

[201] A. Ferrari, L. Cavalca and M. Nardelli, *Gazz. Chim. Ital.* **81** (1951) 945.

[202] J. I. Watters and R. De Witt, *J. Am. Chem. Soc.* **82** (1960) 1333.

[203] D. P. Graddon, *J. Inorg. Nuclear Chem.* **3** (1956) 308.

retain the nomenclature here although these so-called anomalies are now largely resolved. It will be convenient to disuss these complexes under separate headings.

Octahedral-square-planar equilibria in solution. A surprisingly large number of nickel(II) complexes give solutions in organic solvents having magnetic moments whose magnitude depends upon such factors as solvents, concentration and temperature. In donor solvents, square complexes are frequently interconvertible with octahedral complexes by way of the equilibrium

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

With strong donors such as water or pyridine the equilibrium usually lies well to the right, the octahedral complexes being readily isolated. When L=dipivaloylmethanido, $[(Me_3CCO)_2CH]^-$, for example, the nickel β-diketonate is normally isolated as a green, paramagnetic dihydrate or alcoholate from which the red diamagnetic and planar complex is isolated by heating to remove the added ligands[204]. Certain of the much studied[205] nickel(II) salicylaldimine complexes also exemplify this equilibrium. Thus the diamagnetic solids $Ni(HO\text{-}sal)_2$ and $Ni(Me\text{-}sal)_2$ (i.e. Fig. 6, R = OH and Me respectively) dissolve in chloroform giving partially paramagnetic solutions (μ in the range 1.1–2.2 BM per nickel atom) and in pyridine giving fully paramagnetic solutions (μ=3.1 BM per nickel atom) from which the bis(pyridine) adducts can be isolated as stable octahedral complexes.

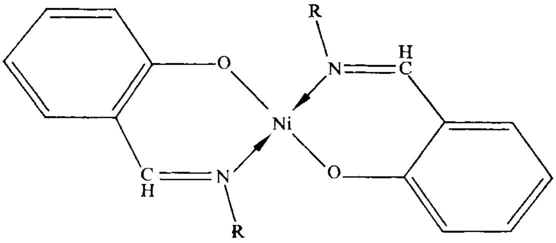

FIG. 6. Bis(N-alkylsalicylaldiminato)nickel(II).

The Lifschitz salts[206]—nickel(II) complexes of substituted ethylenediamines, particularly the stilbenediamines, have the general formula $[NiL_2X_2]$ where X is an anion. These compounds often occur in hydrated form and are of two types, the yellow diamagnetic and the blue paramagnetic types. Which of these types is formed depends upon many factors such as temperature, nature of the anion, the nature of the diamine, and also of the solvent in which the complex was prepared. For the anhydrous compounds, yellow complexes are formed when the anion X is derived from a strong mineral acid, e.g. ClO_4^-, NO_3^-, SO_4^{2-}, Cl^- and both blue and yellow complexes are obtained when X is the anion of an organic acid, e.g. acetate, benzoate, cinnamate. The results of spectroscopic and magnetic studies[207, 208] and of X-ray studies[209] have established that, at least in many cases, the yellow salts are square while the blue salts are tetragonal complexes derived from the square ones by coordination of, for example, two water molecules or anions. The blue

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[204] F. A. Cotton and J. P. Fackler, *J. Am. Chem. Soc.* **83** (1961) 2818.

[205] R. H. Holm, G. W. Everett and A. Chakravorty, *Progress Inorg. Chem.* **7** (1966) 83.

[206] I. Lifschitz, J. G. Bos and K. M. Dijkema, *Z. anorg. u. allgem. Chem.* **242** (1939) 97; I. Lifschitz and J. G. Bos, *Rec. Trav. Chim.* **59** (1940) 407.

[207] W. C. E. Higginson, S. C. Nyburg and J. S. Wood, *Inorg. Chem.* **3** (1964) 463.

[208] C. J. Ballhausen and A. D. Liehr, *J. Am. Chem. Soc.* **81** (1959) 538.

[209] S. C. Nyburg and J. S. Wood, *J. Am. Chem. Soc.* **81** (1959) 468.

complex formed by meso-stilbenediamine and dichloroacetate ions is isolated as a tetrahydrate having $\mu = 3.16$ BM; this has an octahedral structure with two water molecules occupying apical positions. The yellow complex formed with these ligands is unusual in that it contains in each crystal cell two molecules with the octahedral structure and one with the planar structure. In the octahedral molecules the octahedra are completed by oxygen atoms of the dichloroacetate ions with Ni–O distances of 2.08 and 2.16 Å.

Monomer–polymer equilibria. The origin of the paramagnetism of the bis(*N*-alkylsalicylaldimine)nickel(II) complexes in non-coordinating solvents (when they are diamagnetic in the solid state) was at first more difficult to explain but is now attributed to association into species in which the nickel atom becomes 5- or 6-coordinate. The magnetic moment of Ni(Me–sal)$_2$ in chloroform and benzene solutions has been found to increase with concentration; the values of the susceptibility measured over a temperature range cannot be fitted to an equation which gives the susceptibility for a system distributed over singlet and triplet states. It has thus been concluded that the magnetic behaviour of this compound is due to an equilibrium between the planar form and an associated species containing paramagnetic nickel ions[210]. It is necessary to invoke a structure for this paramagnetic species in which the nickel becomes at least 5-coordinate in order to stabilize a triplet ground state. The square Ni(Me–sal)$_2$ complex also becomes converted to a paramagnetic isomer when heated to above 180° and again a polymeric structure is believed to be responsible for the paramagnetism[211].

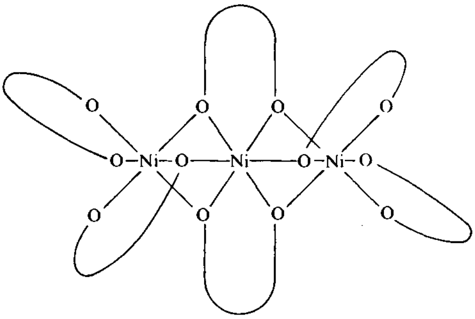

FIG. 7. Trimeric structure of nickel(II) acetylacetonate.

A further example of this kind of equilibrium is shown by the nickel(II) β-diketonates. Nickel(II) acetylacetonate is isolated as the dihydrate Ni(acac)$_2$.2H$_2$O from aqueous solutions of nickel(II) salts in the presence of acetylacetone and a weak base such as sodium acetate; it is readily dehydrated to the green anhydrous compound at 50° *in vacuo*[212]. From ammoniacal solutions of nickel(II) salts the diammoniate Ni(acac)$_2$.2NH$_3$ precipitates; this also readily evolves the two extra ligands to give the green acetylacetonate[213]. This compound (m.p. 229–230°) can be sublimed at 170–210° and a pressure of 0.2–0.4 mm. In the crystalline state the molecule is trimeric with a slightly distorted octahedral coordination about the nickel atoms in the trimer[214]; in Fig. 7 only the nickel and oxygen

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[210] R. H. Holm, *J. Am. Chem. Soc.* **83** (1961) 4683.

[211] L. Sacconi, P. Paoletti and R. Chini, *J. Inorg. Nuclear Chem.* **8** (1958) 429; *J. Am. Chem. Soc.* **80** (1958) 3583.

[212] R. G. Charles and M. A. Pawlikowski, *J. Phys. Chem.* **62** (1958) 440.

[213] M. M. Jones, *J. Am. Chem. Soc.* **81** (1959) 3188.

[214] G. J. Bullen, R. Mason and P. Pauling, *Inorg. Chem.* **4** (1965) 456.

atoms are shown, the curved lines representing the rest of the chelate rings. In the vapour state, however, the molecule is most probably monomeric, and in solution (10^{-2} M) in chloroform the electronic spectrum indicates it to be planar[215]. With more bulky β-ketoenolate groups, red diamagnetic and presumably planar compounds can be prepared. With the exception of the dipivaloylmethane complex described earlier, these other β-ketoenolates dissolve in organic solvents to give solutions in which the red monomer–green polymer equilibrium exists. The colours of the solutions are thus dependent upon concentration, temperature, and the nature of the solvent.

The octahedral structure of nickel(II) acetylacetonate is readily preserved in the presence of donor molecules or solvents, complexes of the type $\mathrm{Ni(acac)_2.2L}$ being formed. The *trans*-octahedral arrangement has been confirmed for $\mathrm{Ni(acac)_2.2H_2O}$[216] and $\mathrm{Ni(acac)_2.2py}$[217].

Tetrahedral–square planar equilibria. The formation of both tetrahedral and square complexes of the type $\mathrm{NiL_2X_2}$, where L is a phosphine has been mentioned in section 3.4.2. With some particular phosphines these complexes exist in solution in a tetrahedral–square planar equilibrium. Thus benzene solutions of mixed alkyl–aryl phosphine complexes contain mixtures of diamagnetic and paramagnetic forms[218] and it is often possible to isolate the two isomers (one red or brown and diamagnetic and one green or blue and paramagnetic)[219]. The planar $\mathrm{NiBr_2[(Pr^i)P(Ph)_2]_2}$ can be stored for long periods at 0° but isomerizes to the tetrahedral form in about one day at 25°. Similar solution equilibria are shown by complexes of the diphosphine $\mathrm{Ph_2P(CH_2)_3PPh_2}$ [220].

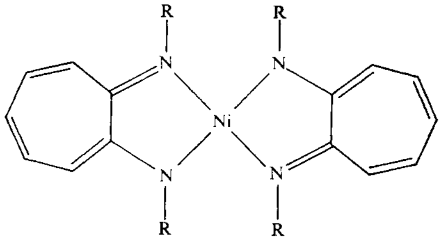

FIG. 8. Troponeiminato-nickel(II) complexes.

The complexes of the sec-alkylsalicylaldiminato[205] (Fig. 6, R = sec-alkyl) and the aminotroponeiminato[221] (Fig. 8) types are the most thoroughly investigated examples of this type of equilibrium. The tetrahedral bis(*N*-sec-alkylsalicylaldiminato)-nickel(II) complexes were in fact the first tetrahedral chelate complexes of nickel(II) to be recognized. Those complexes of these chelates, which are diamagnetic in the solid state, dissolve in organic solvents such as chloroform and toluene becoming paramagnetic with magnetic moments usually in the range 0.8–2.3 BM. The magnetic and spectral properties of the

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[215] J. P. Fackler, *Progress Inorg. Chem.* **7** (1966) 361.

[216] H. Montgomery and E. C. Lingafelter, *Acta Cryst.* **17** (1964) 1481.

[217] J. T. Hashagen and J. P. Fackler, *J. Am. Chem. Soc.* **87** (1965) 2821.

[218] M. C. Browning, R. F. B. Davies, D. J. Morgan, L. E. Sutton and L. M. Venanzi, *J. Chem. Soc.* (1961) 4186; M. C. Browning, J. R. Mellor, D. J. Morgan, S. A. J. Pratt, L. E. Sutton and L. M. Venanzi, *ibid.* (1962) 693.

[219] R. G. Hayter and F. S. Humiec, *Inorg. Chem.* **4** (1965) 1701.

[220] G. R. VanHecke and W. De W. Horrocks, *Inorg. Chem.* **5** (1966) 1968.

[221] D. R. Eaton, W. D. Phillips and D. J. Caldwell, *J. Am. Chem. Soc.* **85** (1963) 397; D. R. Eaton and W. D. Phillips, *J. Chem. Phys.* **43** (1965) 392.

solutions are temperature dependent, the equilibrium being shifted towards the tetrahedral form as the temperature rises. The position of the equilibrium depends to some extent upon steric factors. The stable planar form of a bis(bidentate) salicylaldimine complex is *trans*. When, however, the alkyl chain is branched at the α-carbon, there is steric crowding in the *trans*-planar structure and the tetrahedral structure becomes more favoured. Thus when $R = Bu^t$ (Fig. 6) the solution magnetic moment is greater than 3.2 BM so that the complex is present almost entirely in the tetrahedral isomeric form and in the solid state the complexes $(Bu^t\text{-sal})_2Ni$ are tetrahedral irrespective of any substituents in the ring (which normally contribute an electronic effect to the position of the equilibrium). The magnetic moments of the paramagnetic isomers are in the region of 3.3±0.1 BM at room temperature, i.e. well below the expected value (3.9–4.2 BM) for tetrahedral stereochemistry. The lower orbital contributions in these complexes are almost certainly a consequence of the lowering of the ligand field symmetry from T_d to pseudo C_{2v}.

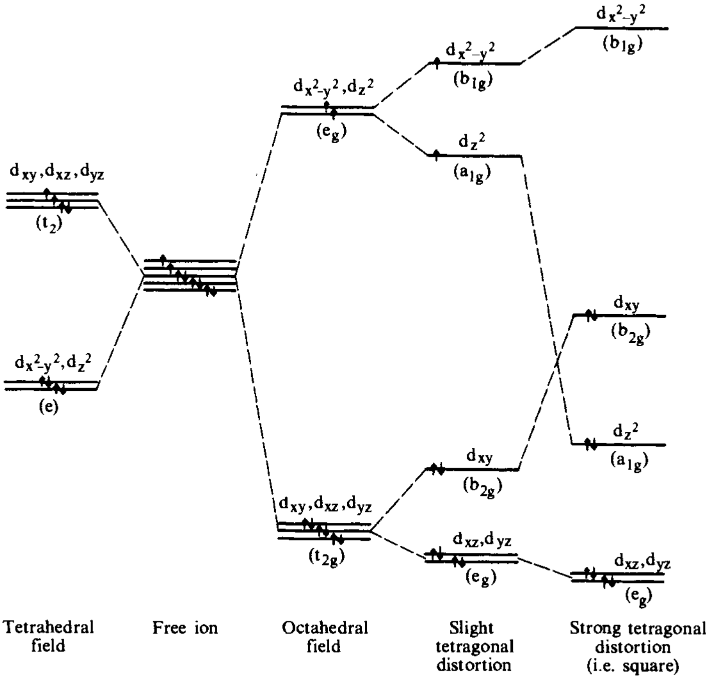

FIG. 9. Simple crystal field splitting diagrams for nickel(II) ions in various crystal fields.

The bis(*N*,*N*′-disubstituted-aminotroponeiminato)nickel(II) complexes also exhibit the planar–tetrahedral equilibrium in solution, and their proton magnetic resonance spectra show large isotropic proton hyperfine contact shifts. These have been used to calculate the thermodynamic parameters of the equilibria[222]. The high and low field shifts observed are a result of the unpaired electron spin density on the nickel atoms being introduced into the ligand π-system. The two unpaired electrons on the nickel are in the t_2 orbitals which have the correct symmetry for π-bonding with the p_π orbitals on the nitrogen atoms

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[222] D. R. Eaton, A. D. Josey, W. D. Phillips and R. E. Benson, *J. Chem. Phys.* 37 (1962) 347.

containing the lone pairs of electrons. The p.m.r. results indicate that the extent of this Ni–N π-bonding is fairly constant with changes in the substituent on the nitrogen.

3.4.5 Spectral and Magnetic Properties of Nickel(II) Complexes

The Ni^{2+} ion has the $3d^8$ outer electron configuration which gives rise to the triplet and singlet terms (in order of increasing energy) ^3F, ^1D, ^3P, ^1G, ^1S. The simple crystal field diagrams for this ion in tetrahedral, octahedral and tetragonal fields are shown in Fig. 9. It can be readily seen from these diagrams that in octahedral and slightly tetragonally distorted octahedral fields, two unpaired electrons are present; the ground state makes no orbital contribution to the magnetic moment so that these moments are expected to be not greatly different from the "spin only" moment (2.83 BM). In tetrahedral fields, again, two unpaired electrons are present, but there is now orbital contribution to the magnetic moment through the equivalence and degeneracy of the incompletely filled t_2 orbitals; magnetic moments are thus expected to be well in excess of the spin only value, and typically lie in the range 3.2–4.0 BM. In strong tetragonal and square crystal fields the electrons pair and the complexes become diamagnetic. We shall now consider the magnetic and spectral properties of nickel(II) complexes in these various stereochemistries in turn dealing first with the 6-coordinate compounds. Several excellent reviews on this subject are available[223, 224].

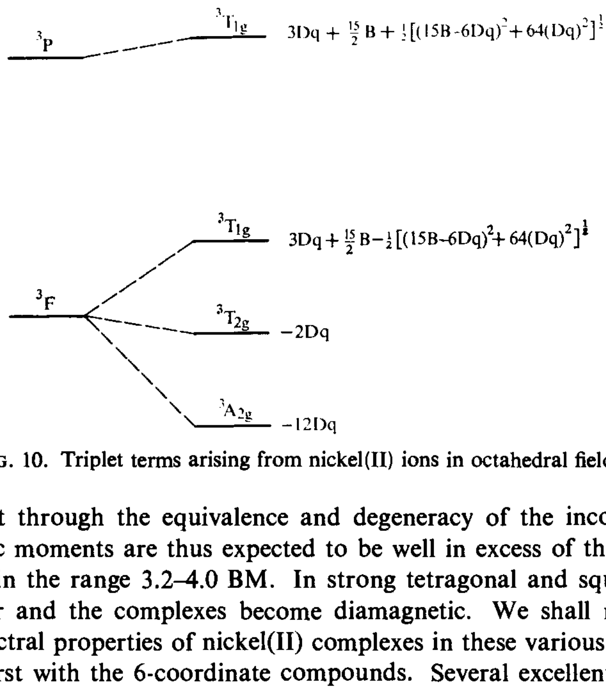

FIG. 10. Triplet terms arising from nickel(II) ions in octahedral fields.

Six-coordinate complexes. Nickel(II) complexes with this coordination number are almost always high spin complexes having either regular or distorted octahedral stereochemistries. The ^3F ground term is split in an octahedral field giving rise to the triplet terms with the energies shown in Fig. 10[225]. Thus three spin allowed transitions are expected having the energies

$$^3A_{2g} \rightarrow {}^3T_{2g},\ \nu_1 = 10Dq,$$

$$^3A_{2g} \rightarrow {}^3T_{1g}(F),\ \nu_2 = 15Dq + {}^{15}/_2B - {}^1/_2[(15B-6Dq)^2+64(Dq)^2]^{1/2}.$$

$$^3A_{2g} \rightarrow {}^3T_{1g}(P),\ \nu_3 = 15Dq + {}^{15}/_2B + {}^1/_2[(15B-6Dq)_2+64(Dq)^2]^{1/2}.$$

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[223] L. Sacconi, *Transition Metal Chem.* **4** (1968) 199.

[224] A. B. P. Lever, *Inorganic Electronic Spectroscopy,* Elsevier (1968).

[225] C. J. Ballhausen, *Introduction to Ligand Field Theory,* McGraw-Hill, New York (1962).

These three transitions are observed (viz. Table 11) in the regions 7000–13,000, 11,000–20,000, and 20,000–28,000 cm^{-1}. The values of $10Dq$ can be seen to vary from about 6800 to 12,700 cm^{-1}, while values of the Racah parameter B found in the complexes are usually some 70–90% of the free ion value, 1041 cm^{-1}. Transitions to spin singlet levels are sometimes observable, the $^3A_{2g} \rightarrow {}^1E_g$ band being in the 11,000–15,000 cm^{-1} region and the $^3A_{2g} \rightarrow {}^1T_{1g}$ band in the 17,000–22,000 cm^{-1} region. Whilst the ν_1 and ν_3 bands are normally symmetrical, the ν_2 band often shows a shoulder or appears as a doublet especially when Dq/B is near unity (viz. Fig. 11). This doublet structure has been ascribed to a gaining of intensity of the $^3A_{2g} \rightarrow {}^1E_g$ transition through configurational interaction with the $^3T_{1g}(F)$ level[226, 227] and also to spin-orbit coupling[228]. The complete energy level diagram for d^8 ions in cubic fields can be seen in Tanabe and Sugano's paper[229] and in many texts[224, 230, 231]. The energy level diagram for octahedral nickel(II) complexes inclusive of spin-orbit coupling has been presented by Liehr and Ballhausen[232].

TABLE 11. ELECTRONIC SPECTRA (CM^{-1}) OF SOME OCTAHEDRAL NICKEL(II) COMPLEXES

Complex	$^3A_{2g} \rightarrow {}^3T_{2g}$	$^3A_{2g} \rightarrow {}^3T_{1g}$	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$
$NiBr_2$ [a]	6,800	11,800	20,600
$NiCl_2$ [a]	7,200	11,500	21,900
$KNiF_3$ [b]	7,250	12,530	23,810
$[Ni(DMSO)_6]^{2+}$ [c]	7,728	12,970	24,038
$[Ni(MeOH)_6]^{2+}$ [d]	8,430	14,226	25,000
$[Ni(H_2O)_6]^{2+}$ [e, f]	8,500	13,800	25,300
$[Ni(etu)_6]^{2+}$ [g]	8,000	13,500	19,100
$[Ni(NCS)_6]^{2-}$ [h]	9,600	15,950	25,800
$[Ni(MeNH_2)_6]^{2+}$ [i]	10,000	16,779	27,322
$[Ni(NH_3)_6]^{2+}$ [e]	10,750	17,500	28,200
$[Ni(MeCN)_6]^{2+}$ [j]	10,700	17,400	27,810
$[Ni(en)_3]^{2+}$ [k]	11,200	18,350	29,000
$[Ni(dipy)_3]^{2+}$ [k]	12,650	19,200	
$[Ni(phen)_3]^{2+}$ [k]	12,700	19,300	

DMSO = dimethylsulphoxide; etu = ethylenethiourea.

[a] A. Ludi and W. Feitknecht, *Helv. Chim. Acta*, **46** (1963) 2226.
[b] R. G. Schulman, S. Sugano and K. Knox, *Phys. Rev.* **130** (1963) 512.
[c] D. W. Meek, R. S. Drago and T. S. Piper, *Inorg. Chem.* **1** (1962) 285.
[d] V. Imhof and R. S. Drago, *Inorg. Chem.* **4** (1965) 427.
[e] O. Bostrup and C. K. Jorgensen, *Acta Chem. Scand.* **11** (1957) 1223.
[f] A. Bose and R. Chatterjee, *Proc. Phys. Soc.* **83** (1963) 23.
[g] S. L. Holt and R. L. Carlin, *J. Am. Chem. Soc.* **86** (1964) 3017.
[h] D. Forster and D. M. L. Goodgame, *Inorg. Chem.* **4** (1965) 823.
[i] R. S. Drago, D. W. Meek, R. Longhi and M. D. Joesten, *Inorg. Chem.* **2** (1963) 1056.
[j] B. J. Hathaway and D. G. Holah, *J. Chem. Soc.* (1964) 2400.
[k] C. K. Jorgensen, *Acta Chem. Scand.* **9** (1955) 1362.

The 6-coordinate complexes of the type NiL_4X_2, NiL_2X_2, and $NiLX_2$ have spectra typical of octahedral nickel(II) complexes. The ν_2 and ν_3 bands are not greatly affected

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[226] C. K. Jorgensen, *Acta Chem. Scand.* **9** (1955) 1362.
[227] O. G. Holmes and D. S. McClure, *J. Chem. Phys.* **26** (1957) 1686.
[228] A. D. Liehr and C. J. Ballhausen, *Ann. Phys.* **6** (1959) 134; *Mol. Phys.* **2** (1959) 123.
[229] Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, **9** (1954) 753, 766.
[230] B. N. Figgis, *Introduction to Ligand Fields*, Interscience (1966).
[231] T. M. Dunn in *Modern Co-ordination Chemistry* (J. Lewis and R. G. Wilkins, eds.), Interscience (1960)
[232] A. D. Liehr and C. J. Ballhausen, *Ann. Phys.* (*N.Y.*) **6** (1969) 134.

by the lower symmetry, but the ν_1 band is frequently split into two components which are assigned to the transitions from $^3B_{1g}$ to the $^3B_{2g}$ and ^3E_g (components of $^3T_{2g}$ in O_h) levels in *trans*-NiL_4X_2 complexes of D_{4h} symmetry. The extent of the splitting is about 2000–2500 cm^{-1}; a typical spectrum, that of $Ni(py)_4Cl_2$,[233] is illustrated in Fig. 11. For *cis*-octahedral complexes the band splitting is expected to be smaller. The effects of these distortions from octahedral symmetry on the energy levels of nickel(II) complexes have been illustrated by Furlani[234].

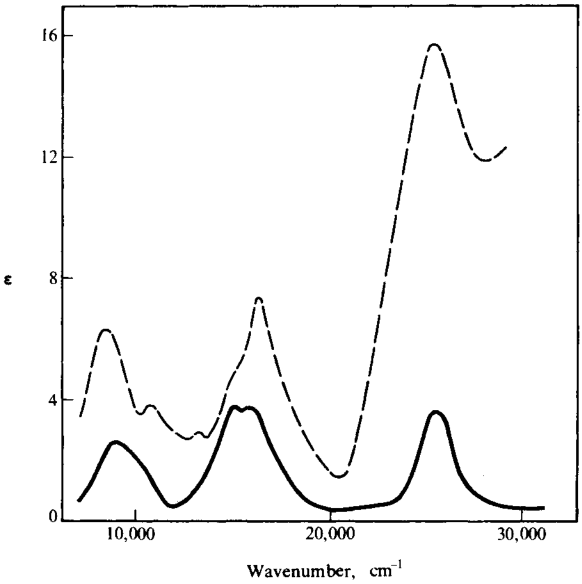

FIG. 11. Electronic spectra of $[Ni(H_2O)_6]^{2+}$ (——) and $Ni(py)_4Cl_2$ (– – – –).

Regular octahedral complexes of nickel(II) are always paramagnetic, the ground state being $^3A_{2g}$ and no singlet state from a d configuration is able to cross it. The magnetic moments are expected to be given[235] by the term $2.83\ (1-4\lambda/10Dq)$; $\lambda = -315\ cm^{-1}$ for Ni^{2+} so that the moments are expectedly some 10% above the spin only value. The experimental magnetic moments lie usually within the range 2.9–3.3 BM; they are independent of temperature and of small departures from octahedral symmetry. There are a few complexes which are both diamagnetic and 6-coordinate, the most thoroughly studied of these is the nickel(II) iodide–*o*-phenylenebisdimethylarsine complex $NiI_2(diars)_2$. In this compound the iodine atoms are *trans* to each other and the Ni–I distance (3.21 Å) is greater than the sum of the covalent radii (2.67 Å)[236]; this fact coupled with the very different positions of iodide ions and the diarsine in the spectrochemical series results in a strong tetragonal ligand field in this compound. It thus behaves similarly to the square complexes (viz. Fig. 9). The halide complexes of *N,N'*-diethylthiourea $NiX_2(detu)_4$ are interesting in that the iodide and bromide complexes are sufficiently tetragonal to be

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[233] S. M. Nelson and T. M. Shepherd, *J. Chem. Soc.* (1965) 3276.
[234] C. Furlani, *Gazz. Chim. Ital.* **88** (1958) 279.
[235] B. N. Figgis and J. Lewis, *Progress Inorg. Chem.* **6** (1964) 37.
[236] N. C. Stephenson, *Acta Cryst.* **17** (1964) 592.

diamagnetic; the chloride is diamagnetic at −196°, but thence shows a reversible increase in magnetic moment with increasing temperature[237]. This is attributed to the thermal population of a triplet state lying very close to the singlet ground state.

Tetrahedral complexes. In tetrahedral fields the outer electronic configuration becomes $e^4t_2^4$ and the splitting of the free ion terms becomes that shown in Fig. 12. A more sophisticated energy level diagram which includes the quantitative effects of spin-orbit coupling has been presented by Liehr and Ballhausen[225 232]. Three spin-allowed transitions are expected from the $^3T_1$ ground state, but because the tetrahedral crystal field splitting is only four-ninths that in an octahedral field, the absorption bands are shifted towards the infrared as compared to the octahedral bands. The tetrahedral bands also differ in being more intense (by a factor of about ten times) as a result of the absence of a centre of symmetry in these complexes. In general the spectra (Table 12) show a very broad band in the 15,000 cm^{-1} region containing the $^3T_1 \rightarrow {}^3T_1(P)$ transition with weaker bands on either side of this transition being assigned to spin-forbidden bands. The near infrared band around 7000 cm^{-1} is assigned to the $^3T_1 \rightarrow {}^3A_2$ transition; the lowest energy band, corresponding to the $^3T_1 \rightarrow {}^3T_2$ transition, is not frequently observed.

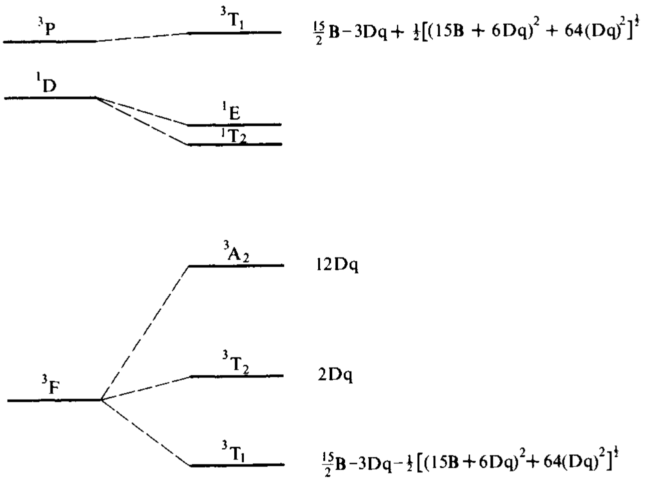

FIG. 12. Energies of triplet terms for tetrahedral nickel(II) complexes.

Since the ground term $^3T_1$ in tetrahedral nickel(II) complexes is orbitally degenerate, the magnetic moment is expected to be raised considerably over the spin only value through orbital contribution. The experimental moments lie within the range 3.2–4.1 BM and are dependent upon temperature. If the ligand field departs from tetrahedral symmetry or if electron delocalization occurs, then the moment becomes closer to the spin only value, and shows less variation with temperature.

Square-planar complexes. Nickel(II) forms a surprisingly large number of square complexes. The tetrahedral configuration is favoured as compared to the planar one by the spin pairing energy and by the minimization of electrostatic repulsion energy. The planar configuration is stabilized by strong nickel–ligand covalent bonding (both σ- and π-bonding) and short nickel–ligand bond lengths are frequently observed in planar

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[237] S. L. Holt, R. J. Bouchard and R. L. Carlin, *J. Am. Chem. Soc.* **86** (1964) 519.

complexes. The electronic ground state of a planar complex may be either $e_g^4a_{1g}^2b_{2g}^2$ (Fig. 9), i.e. a spin singlet state $^1A_{1g}$, or $e_g^4a_{1g}^2b_{2g}^1b_{1g}^1$, i.e. a spin triplet state $^3A_{2g}$ and an excited state $^1A_{2g}$. The low spin state is favoured[208] if the separation between the $d_{x^2-y^2}$ and d_{xy} orbitals is more than 10,000 cm^{-1}.

Square planar nickel(II) complexes are commonly orange or red, but a few have purple or green colours. Their spectra frequently consist[224] of a strong ($\epsilon = 50$–500 l cm^{-1} mole^{-1}) band around 15,000–23,000 cm^{-1} with a second band in the range 23,000–27,000 cm^{-1}. These bands are commonly assigned to the transitions $^1A_{1g} \rightarrow {}^1A_{2g}$ $(b_{2g} \rightarrow b_{1g})$ and $^1A_{1g} \rightarrow {}^1B_{1g}$ $(a_{1g} \rightarrow b_{1g})$. A further weaker band is sometimes observed in the 11,000–15,000 cm^{-1} region and this is probably a spin forbidden band. The major difference between the spectra of square complexes and those of octahedral or tetrahedral complexes is the absence of any bands below 10,000 cm^{-1}. The absence of such bands confirms that the $d_{x^2-y^2}$—d_{xy} separation is invariably greater than this figure and accordingly these planar complexes are all diamagnetic. While energy level diagrams have been constructed[238] for nickel(II) complexes in planar D_{4h} symmetry, no unique interpretation of the spectra is yet possible. For a detailed discussion of the structure and bonding in square nickel(II) complexes the reader is referred to Gray's article[170].

TABLE 12. ELECTRONIC SPECTRA (CM^{-1}) OF SOME TETRAHEDRAL NICKEL(II) COMPLEXES

Complex	$^3T_1 \rightarrow {}^3A_2$	$^3T_1 \rightarrow {}^3T_1(P)$	10*Dq*[d]
$NiCl_4^{2-}$ [a]	7549 8700 (sh)	14,250 15,240 15,950 (sh)	4090
$NiBr_4^{2-}$ [a]	6995	13,230 14,140 15,200 (sh) 16,700 (sh)	3790
NiI_4^{2-} [a]	7042 8330 (sh)	11,480 (sh) 12,800 (sh) 14,030 14,530 (sh)	3820
$Ni(Ph_3PO)_2Br_2$ [a]	7250	14,290 (sh) 15,580	3950
$[Ni(NCO)_4]^{2-}$ [b]	9460	15,600 16,800	5060
$Ni[OP(NMe_2)_3]_4^{2+}$ [c]	8000	14,000 15,800	4370

[a] M. Goodgame, D. M. L. Goodgame and F. A. Cotton, *J. Am. Chem. Soc.* **83** (1961) 4161.

[b] D. Forster and D. M. L. Goodgame, *J. Chem. Soc.* (1964) 2790; (1965) 268.

[c] J. T. Donoghue and R. S. Drago, *Inorg. Chem.* **1** (1962) 866.

[d] A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier (1968).

Five-coordinate complexes. Nickel(II) complexes in this stereochemistry are uncommon and occur only when particular steric requirements and donor power of the ligand stabilize this geometry. These complexes are of two types, high spin ($S = 1$) and low spin ($S = 0$). In the diamagnetic compounds the donor atoms are usually those of low electronegativity, especially phosphorus and arsenic, which are usually involved in π-bonding to the nickel.

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[238] G. Maki, *J. Chem. Phys.* **28** (1958) 651; **29** (1958) 162, 1129.

The high spin complexes have magnetic moments in the range 3.2–3.4 BM and have the electronegative elements nitrogen or oxygen as donor atoms. In many cases, one or two halide ions complete the 5-coordination in both high and low spin types.

The crystal field splitting diagram for the *d* orbitals in trigonal bipyramidal (D_{3h}) and square pyramidal (C_{4v}) configurations is shown in Fig. 13. These are the two limiting

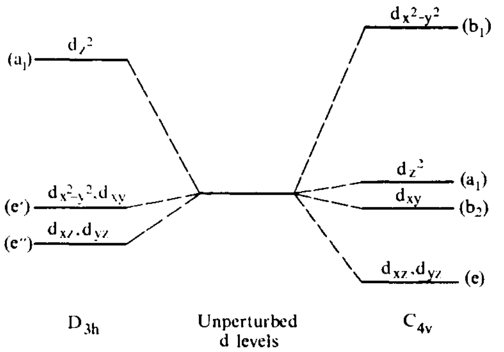

FIG. 13. Splitting of the *d*-orbitals in 5-co ordination

configurations to which the structures of the complexes tend. There is little to choose energetically between them so that the particular stereochemistry adopted by any complex is mainly determined by the steric requirements of the ligands and crystal lattice energies. The energy levels for both stereochemistries have been calculated and the energy level

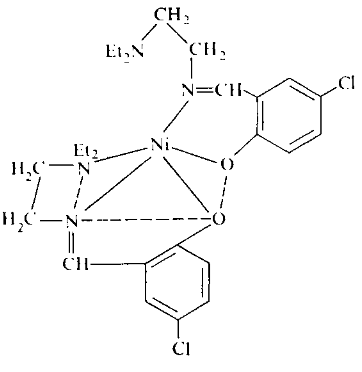

FIG. 14. Five-coordination in Ni[5Cl-sal-en-NEt$_2$]$_2$.

diagrams constructed[239]. Only for large field strengths or with extensive nephelauxetic effects are diamagnetic compounds expected.

In C_{4v} symmetry the free ion ^3F is split into five levels $^3B_1 < {^3E} < {^3A_2}, {^3B_2} < {^3E}$ and the ^3P term into ^3E and $^3A_2$ so that a large number of spin allowed bands are expected. These are, indeed, found in, for example, Ni[5Cl-sal-en-NEt$_2$]$_2$ [240] which has the irregular square pyramidal structure shown in Fig. 14[241]. In this compound the spectrum has been

[239] M. Ciampolini, *Inorg. Chem.* **5** (1966) 35.

[240] L. Sacconi, P. Nannelli, N. Nardi and U. Campigli, *Inorg. Chem.* **4** (1965) 943.

[241] P. L. Orioli, M. Di Vaira and L. Sacconi, *J. Am. Chem. Soc.* **88** (1966) 4383.

assigned locating the ^3E level at 7500 cm^{-1}, $^3A_2$ at 9900 cm^{-1}, $^3B_2$ at 12,600 cm^{-1} and the upper $^3E(F)$ level at 16,500 cm^{-1}, the states derived from the ^3P term being obscured by ligand absorption. The paramagnetic methyldiphenylarsine oxide complex [Ni(OAsPh$_2$Me)$_4$ClO$_4$]ClO$_4$ [242] is interesting in that it is believed to be square pyramidal with the four arsine oxide ligands in a plane below the metal atom and a perchlorate group bonded via oxygen in the apical position. It is also unusual that other high spin 5-coordinate nickel(II) complexes contain, as a rule, polydentate ligands.

In complexes of D_{3h} symmetry several spin allowed bands are again expected in their electronic spectra. These are indeed found in, for example, [Ni(Me$_6$tren)Br]Br[243] [Me$_6$tren = N(CH$_2$CH$_2$NMe$_2$)$_3$], the structure of which is illustrated in Fig. 15. The (distorted) trigonal bipyramidal structure has also been proven[244] in the salicylaldimine complex [Ni(H-sal-MeDPT)] where MeDPT = bis(salicylaldiminotrimethylene)methylamine. In this the pentadentate ligand surrounds the nickel with two oxygen and one nitrogen atom in the trigonal plane and two nitrogen atoms in the apical positions.

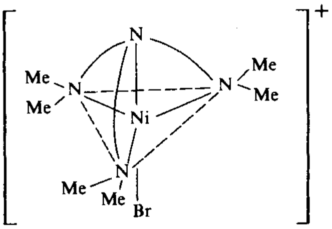

FIG. 15. The bromo[tris(2-dimethylaminoethyl)-amine]nickel(III) cation.

Low spin 5-coordinate nickel(II) complexes have absorption spectra showing much more intense bands than the high spin compounds. For the diamagnetic trigonal bipyramidal complexes the configuration (Fig. 13) is $(e'')^4(e')^4$ or $^1A_1'$. The other terms arising from the ^1D free ion term are shown in Fig. 16. A more complete and quantitative diagram has been presented elsewhere[245] along with the spectra of many trigonal bipyramidal complexes. Two spin-allowed bands are to be expected, labelled ν_1 and ν_2 in Fig. 16. The complexes [NiX(QP)]$^+$ [X = Cl, Br, I, NCS, NO$_3$, ClO$_4$ and CN; QP = tris(*o*-diphenylphosphinophenyl)phosphine] show a strong band ($\epsilon \sim$ 5000 l cm^{-1}mole^{-1}) in the 17,000 cm^{-1}

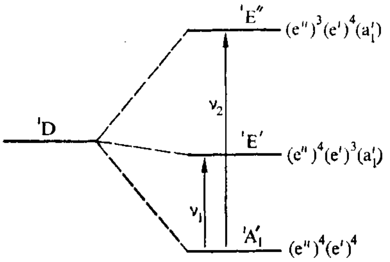

FIG. 16. Simple energy level diagram for low spin trigonal bipyramidal nickel(II) complexes.

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region and a weaker band ($\epsilon \sim 2100$ l cm^{-1} mole^{-1}) in the 26,000 cm^{-1} region; these bands are assigned to the ν_1 and ν_2 transitions.

Low spin complexes with monodentate ligands include the phosphine complexes of types NiL_3X_2, where $L = PEt_2Ph$[246] or $PHPh_2$[247]. These dissociate in solution, but in the solid state the compound $NiBr_2(PHPh_2)_3$ is isostructural with its cobalt analogue and so has a structure intermediate between square planar and trigonal bipyramidal. The low magnetic moment of the iodo complex $NiI_2(PHPh_2)_3$ has been explained by assuming a thermal population of singlet and triplet states, the ground state being close to the crossover point. In saturated solutions of potassium cyanide, the $[Ni(CN)_5]^{3-}$ ion exists and is believed to have the square pyramidal structure. The solid compounds $[Cr(NH_3)_6][Ni(CN)_5].2H_2O$ and $[Cr(en)_3][Ni(CN)_5].2H_2O$[248] appear to contain[196] two $[Ni(CN_5]^{3-}$ ions per unit cell, one of which has the tetragonal pyramidal and the other a distorted trigonal bipyramidal structure. Five-coordinate low spin complexes of bidentate ligands include those of diarsines $[Nidiars_2X]^+$ [249], *o*-phenylenediphenylarsine-diphenylphosphine $[Ni(AP)_2X]^+$[250]. Tridentate ligands give even more stable 5-coordinate complexes. The bis(3-dimethylarsinopropyl)methylarsine complex $Ni(TAS)Br_2$ has a very distorted square pyramidal structure[251].

4. COMPOUNDS OF NICKEL IN HIGH OXIDATION STATES (+3, +4)

4.1. SIMPLE COMPOUNDS OF NICKEL(III) AND NICKEL(IV)

Scarcely any simple compounds of nickel in high oxidation states are known; such compounds as are known are the hydrous oxides and mixed metal oxides of nickel(III) and nickel(IV). There are no simple halides in these oxidation states.

The most thoroughly studied oxide system is β-NiO(OH) which is obtained[252] as a black precipitate when nickel(II) salt solutions are oxidized by chlorine, bromine or by persulphate ions in alkaline solution. It is soluble in acids; in hot water a nickel(II, III) hydroxide $Ni_3O_2(OH)_4$ is formed[252]. At 140° it is decomposed into NiO, water and oxygen. A separate black phase, known as γ-NiO(OH), is obtained by adding nickel to a melt of sodium peroxide and sodium hydroxide at 600° and treating the cooled product with ice-water[253]. This phase dissolves in sulphuric acid with evolution of oxygen and decomposes upon heating to above 138°.

The oxide $NiO_2.nH_2O$ is also obtained by persulphate oxidation of $Ni(OH)_2$[254]. The electrochemical oxidation of $Ni(OH)_2$ produces firstly β-NiO(OH) and after prolonged oxidation a phase with an average oxidation state per nickel atom of about 3.3[255]. A

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variety of mixed oxides of the types $K_2NiO_{2.5}$ and K_2NiO_3 have been obtained by heating nickel(II) oxide with alkali metal oxides in a stream of oxygen[256]; the former compound has a magnetic moment of 1.67 BM while the latter has a moment of about 2 BM.

4.2. COMPLEXES OF NICKEL(III)

Complexes of nickel(III) halides can sometimes be prepared by oxidation of the corresponding nickel(II) halide complex. However, relatively few complexes are definitely characterized as containing nickel(III); the problems of oxidation state assignment of $[NiCl_2diars_2]^+$ have been discussed in section 3.4.1. The triethylphosphine complex $NiBr_3(PEt_3)_2$ can be prepared either by oxidation of $NiBr_2(PEt_3)_2$ with bromine in benzene solution[257] or by its reaction with nitrosyl bromide[258]. The chloride $NiCl_3(PEt_3)_2$ is less stable and can only be prepared by the nitrosyl chloride route. Tribromobis(triethylphosphine)nickel(III) is a black crystalline solid, m.p. 83–84°; it is soluble in pentane giving an intensely green solution in which the complex is monomeric and has zero dipole moment. The magnetic moment of $NiBr_3(PEt_3)_2$ is 1.72 BM at room temperature. A *trans*-trigonal bipyramidal structure is favoured for this compound. Similar complexes of nickel(III) with bidentate phosphines, e.g. $[NiBr_3(Me_2PCH_2CH_2PMe_2)]$, $[NiBr_2(Me_2PCH_2CH_2PMe_2)_2][Br_3]$[259] and $[NiBr_3(Ph_2PCH_2CH_2PPh_2)]$[260] have been characterized. Ethylenediamine complexes of the type $[Ni(en)_2X_2]^+$ are obtained by halogen oxidation of the nickel(II) complexes dissolved in ethanol. Again, the compounds are paramagnetic with one unpaired electron per nickel atom[262].

The hexafluoronickelates(III) containing the NiF_6^{3-} anion are obtained when, for example, a 3 : 1 mixture of potassium chloride and nickel(II) chloride is fluorinated at 300° under a 300 mm pressure of fluorine[263]. The violet crystalline K_3NiF_6 has a face-centred cubic lattice. It evolves oxygen from water being reduced to nickel(II), but is stable *in vacuo* at 450°. In liquid hydrogen fluoride partial disproportionation occurs:

$$2K_3NiF_6 \rightarrow 6K^+ + NiF_6^{2-} + NiF_2 + 4F^-$$

The electronic spectrum[263] of K_3NiF_6, shows only one band at about 19,500 cm^{-1}; its magnetic moment is reported to be 2.54 BM[264].

4.3. COMPLEXES OF NICKEL(IV)

The red hexafluoronickelate(IV), K_2NiF_6, is more easily prepared than the nickelate(III) complex, a 2 : 1 mixture of KCl : $NiCl_2$ being fluorinated[263]. Complexes of the other alkali metal cations have been prepared also from the alkali metal tetrachloronickelates(II)[265] or by fluorination of nickel(II) fluoride and an alkali metal halide in a bomb at 350° and

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350 atm.[266]. The compounds are diamagnetic, having the low spin $t_{2g}{}^6$ ground state; their infrared spectra show metal–fluorine stretching frequencies at around 655 and 350 cm^{-1}. The electronic spectrum shows two fairly strong *d–d* transitions at 19,000 and 25,300 cm^{-1} which are assigned to the $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions; spin forbidden bands to the $^3T_{1g}$ and $^3T_{2g}$ states are observed with very low intensity at 12,900 and 16,000 cm^{-1}. These data can be fitted to the Tanabe–Sugano strong field matrices using $Dq = 2010$ cm^{-1} and $B = 515$ cm^{-1}. These salts exhibit extremely large diamagnetic ^{19}F n.m.r. shifts (+253 ppm) which are temperature independent[268].

Potassium hexafluoronickelate(IV) evolves oxygen from water but gives bright red solutions in anhydrous hydrogen fluoride. Above 350° *in vacuo* it decomposes according to[263]

$$3K_2NiF_6 \rightarrow 2K_3NiF_6 + NiF_2 + F_2$$

The sodium and potassium nickel(IV) paraperiodates $NaNiIO_6 . H_2O$ and $KNiIO_6 . \frac{1}{2}H_2O$ are obtained by persulphate oxidation of nickel(II) in the presence of the alkali metal periodate[269]. They are dark purple crystalline solids, insoluble in cold water and decompose readily upon heating. In contact with air they emit an odour of ozone.

Nickel(IV) also occurs in the purple, diamagnetic heteropoly salts such as $3BaO \cdot NiO_2 \cdot 9MoO_3 \cdot 12H_2O$ and $Na_{12}NiNb_{12}O_{38} \cdot (48\text{–}50)H_2O$[270]. These compounds are stable in the solid state but decompose slowly in solution.

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INDEX

- Brown ring compounds 1003

- Cobalt
  - allotropy 1054
  - alloys 1058
  - analysis 1057
  - carbonyls 1059
    - halides 1064
    - hydride 1063
    - preparation 1059
    - properties 1059, 1060
    - structure 1059
  - complexes
    - cyanide 1067
    - isocyanide 1068
  - history 1053
  - industrial production 1053
  - nitrosyls 1064
    - –carbonyl 1065
    - cyanides 1067
    - halides 1066
    - –sulphur compounds 1066
  - occurrence 1053
  - properties
    - biological 1056
    - chemical 1056
    - nuclear 1054
    - physical 1054
- Cobalt(I) complexes 1068
- Cobalt(II) 1068
  - bromide 1070
  - carbonate 1072
  - carboxylates 1072
  - chloride 1070
  - complexes 1080
    - anionic 1085
    - cationic 1081
    - magnetic properties 1087
    - neutral 1082
    - spectra 1087
  - cyanide 1071
  - fluoride 1069
  - halates 1073
  - hydroxide 1071
  - iodide 1070
  - nitrate 1072
- Cobalt(II) (*cont.*)
  - nitrides 1072
  - organometallic compounds 1073
    - π-bonded 1076
    - σ-bonded 1074
  - oxide 1071
  - perhalates 1073
  - phosphate 1073
  - sulphate 1073
  - sulphides 1071
  - sulphite 1073
  - thiocyanate 1071
- Cobalt(III) 1093
  - acetate 1094
  - amide 1094
  - complexes 1095
    - anionic 1102
    - magnetic properties 1104
    - neutral 1100
    - spectra 1104
  - fluoride 1093
  - nitrate 1094
  - oxide 1094
  - sulphate 1094
- Cobalt(IV) 1107
- Cobalt(V) 1107
- Cobaltammines 1095
- Cobaltocene 1077

- Iron 979
  - allotropy 982
  - alloys 988
  - analysis 987
  - carbonyls
    - dodeca- 996
    - ennea- 995
    - ferrates 997
    - halides 999
    - hydrides 998
    - penta- 989
    - substitution reactions 991
  - history 979
  - manufacture 980
    - pig iron 980
    - pure iron 982
  - nitrosyls 1000

Iron (*cont.*)
    carbonyls 1000
    cyanides 1004
    halides 1002
    sulphur complexes 1002
    tetra- 1000
  occurrence 979
  properties
    biological 986
    chemical 985
    nuclear 983
    physical 983
Iron(II) 1005
  bromide 1008
  carbonate 1010
  carboxylates 1010
  chloride 1007
  complexes 1026
    anionic 1030
    arsenic ligands 1028
    cationic 1026
    cyanides 1030
    halides 1030
    hydrides 1028
    magnetic properties 1033
    neutral 1028
    nitrogen ligands 1028
    oxygen ligands 1029
    phosphorus ligands 1028
    spectra 1033
    sulphur ligands 1029
  cyanide 1008
  fluoride 1007
  hydroxide 1009
  iodide 1008
  nitrate 1010
  nitrides 1010
  organometallic compounds 1011
    acetylene 1021
    alkyls 1024
    arenes 1017
    aryls 1024
    cyclobutadienyl carbonyls 1019
    cyclopentadienyl 1012
    cyclopentadienyl carbonyls 1017
    ferrocene 1012
    olefin 1021
    π-allyl 1021
  oxide 1008
  phosphate 1011
  silicates 1010
  sulphate 1011
  sulphides 1009
  thiocyanate 1008
Iron(III) compounds 1038
  alkoxides 1041
  bromide 1039
  carboxylates 1041
  chloride 1039
  complexes 1042
    anionic 1046
    cationic 1042
    cyanides 1047
Iron(III) compounds (*cont.*)
    electronic structures of 1048
    halides 1046
    neutral 1044
  fluoride 1038
  hydroxides 1040
  nitrate 1041
  oxides 1040
  oxidechloride 1040
  perchlorate 1042
  peroxo-species 1041
  phosphate 1042
  sulphate 1042
  thiocyanate 1040
Iron(IV) 1049
Iron(V) 1050
Iron(VI) 1050

Mossbauer effect 983

Nickel
  alloys 1114
  analysis 1113
  high oxidation states 1159
  industrial production 1110
  low oxidation states 1115
    carbonyl 1115
    complex cyanides 1121
    complex isocyanides 1121
    phosphine complexes 1123
  occurrence 1109
  organometallic compounds 1131
    acetylene 1133
    alkyls 1131
    aryls 1131
    cyclobutadienyl 1136
    cyclopentadienyl 1137
    olefin 1133
    π-allyl 1133
  preparation 1110
  properties
    chemical 1112
    nuclear 1111
    physical 1111
Nickel(II) 1124
  amide 1129
  bromide 1126
  carbonate 1129
  carboxylates 1129
  chloride 1126
  complexes 1139
    anionic 1145
    anomalous behaviour of 1147
    cationic 1139
    five-coordinate 1156
    magnetic properties 1152
    neutral 1141
    octahedral 1153
    spectra 1152
    square-planar 1155
    tetrahedral 1155
  cyanide 1127
  fluoride 1125

Nickel(II) (*cont.*)
  halides 1125
  hydroxide 1128
  iodide 1127
  nitrate 1130
  oxide 1128
  phosphates 1131
  silicate 1130
  sulphate 1131
Nickel(II) (*cont.*)
  sulphides 1129
  thiocyanate 1128
Nickel(III) complexes 1160
Nickel(IV) complexes 1160

Steel manufacture 981

Werner theory 1095

Contents of Comprehensive Inorganic Chemistry

VOLUME 1

The element Hydrogen, ortho- and para-Hydrogen, atomic Hydrogen
K M MACKAY *University of Waikato*

Hydrides
K M MACKAY *University of Waikato*

Deuterium and Tritium
K M MACKAY *University of Waikato* & M F A DOVE *University of Nottingham*

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F O SLADKY *University of Innsbruck*

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W A HART & O F BEUMEL Jr *Foote Mineral Co, Pennsylvania*

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T P WHALEY *International Minerals and Chemical Corp, Illinois*

Beryllium
D A EVEREST *National Physical Laboratory, Teddington*

Magnesium, Calcium, Strontium, Barium and Radium
R D GOODENOUGH & V A STENGER *The Dow Chemical Co, Michigan*

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N N GREENWOOD *University of Leeds*

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K WADE & A J BANISTER *University of Durham*

Carbon
A K HOLLIDAY, G HUGHES & S M WALKER *University of Liverpool*

An introduction to the organic chemistry of the metallic elements
M L H GREEN *University of Oxford* & P POWELL *Royal Holloway College*

Silicon
E G ROCHOW *Harvard University*

Index

VOLUME 2

Germanium
E G ROCHOW, *Harvard University*

Tin
E W ABEL *University of Exeter*

Lead
E W ABEL *University of Exeter*

Nitrogen
K JONES *University of Manchester Inst. of Science & Technology*

Phosphorus
A D F TOY *Stauffer Chemical Co, New York*

Arsenic, Antimony and Bismuth
J D SMITH *University of Sussex*

Oxygen
E A V EBSWORTH *University of Edinburgh,*
J A CONNOR *University of Manchester,* &
J J TURNER *Newcastle on Tyne University*

Sulphur
M SCHMIDT & W SIEBERT *University of Wurzburg*

Selenium, Tellurium and Polonium
K W BAGNALL *University of Manchester*

Fluorine
T A O'DONNELL *University of Melbourne*

Chlorine, Bromine, Iodine and Astatine
A J DOWNS & C J ADAMS *University of Oxford*

Index

VOLUME 3

Copper
A G MASSEY *University of Technology, Loughborough*

Silver
N R THOMPSON *ICI, Runcorn Heath Laboratory, Cheshire*

Gold
B F G JOHNSON *University of Cambridge*
& R DAVIS *Kingston Polytechnic*

Group IIB
B J AYLETT *Westfield College, London*

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Zirconium and Hafnium
D C BRADLEY & P THORNTON *Queen Mary College, London*

Vanadium
R J H CLARK, *University College, London*

The chemistry of Niobium and Tantalum
D BROWN *Atomic Energy Research Establishment, Harwell*

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C L ROLLINSON *University of Maryland*

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R D W KEMMITT *University of Leicester*

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Rhenium
R D PEACOCK *University of Leicester*

Iron
D NICHOLLS *University of Liverpool*

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D NICHOLLS *University of Liverpool*

Nickel
D NICHOLLS *University of Liverpool*

The 2nd and 3rd row elements of group VIIIA, B and C
S E LIVINGSTONE *University of New South Wales*

Index

VOLUME 4

The Lanthanides
T MOELLER *Arizona State University*

Carbonyls, Cyanides, Isocyanides and Nitrosyls
W P GRIFFITH *Imperial College of Science & Technology London*

Compounds of the transition elements involving metal-metal bonds
D L KEPERT *University of Western Australia*
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Transition metal hydrogen compounds
J C GREEN & M L H GREEN *University of Oxford*

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D J M BEVAN *The Flinders University of South Australia*

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P HAGENMULLER *University of Bordeaux*

Isopolyanions and heteropolyanions
D L KEPERT *University of Western Australia*

Transition metal chemistry
B F G JOHNSON *University of Cambridge*

Organo-transition metal compounds and related aspects of homogeneous catalysis
B L SHAW & N I TUCKER *University of Leeds*

Index

VOLUME 5

The Actinides
J A LEE & J A MARPLES
G W C MILNER & G PHILLIPS
P G MARDON
Atomic Energy Research Establishment, Harwell
C KELLER *Kernforschungszentrum, Karlsruhe*
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Nottingham

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Sussex

Volume 5 635 pp + Master index

"Volume 5 is devoted to the Actinides (635 pp) and the Master Index (78 pp). The latter serves little purpose since it merely indicates the subsections of CIC, and thus repeats the indexes in each individual volume. Indeed, as the treatment of each element or series of elements follows a standard pattern, the volumes are essentially self-indexing anyway. A one-page table of contents at the beginning of Volume 5 would have been more helpful and is a curious omission. The running headings at the top of each double page are also singularly uninformative, only three being used: 'The Elements' for 102 pages, 'Compounds' for 361 pages and 'Solution Chemistry' for the remaining 171 pages.

The treatment of actinium and the actinides (elements 89–103) is both readable and authoritative. Nine of the contributors are from AERE, Harwell, and the other five (with one exception) are from nuclear chemistry institutes in Sweden and Germany. In reviewing these 5f elements it is salutary to recall that the majority have been synthesized for the first time within the last 30 years—yet the number of compounds known and the amount of information on them has already outstripped the more limited chemistry of their 4f congeners, the lanthanides. The authors have done a magnificent job in assembling, collating, assessing, and systematizing a vast amount of data on the physical and chemical properties of these elements and their numerous compounds. The work, which is extensively referenced, will undoubtedly remain the standard first source of information in this area for many years to come."

Professor N. N. Greenwood FRIC
Leeds

INDEPENDENT OPINION

Volume 1 1467 pp + index

"This covers the chemistry of hydrogen, the noble gases, and of the elements of Groups IA, IIA, IIIB, carbon and silicon. The first three chapters deal with hydrogen, hydrides, deuterium and tritium and the fourth is an interesting discussion of the proton, protonic acids and the hydrogen bond. Two chapters follow on the inert gases, including interesting and extensive recent knowledge about their compounds set out by N. Bartlett and F. O. Sladky. Four chapters on the alkalis and alkaline earths contain a wealth of detail, although perhaps along traditional lines. N. N. Greenwood has written an excellent account on boron chemistry of book length in itself, and another chapter deals at length with much new informationabout aluminium, gallium, indium and thallium. Chapters 13 and 15 deal with carbon and silicon. Here it might have been expected that more would have been included on the high pressure chemistry of carbon and silicates, and mineral chemistry. Chapter 14 by M. L. H. Green and P. Powell is a useful introduction to the organic chemistry of the metallic elements, along modern lines of ligand field theory and ideas about metal complexes.

Throughout this volume, with its different authors, it is perhaps inevitable that there is some lack of uniformity in the extent of detail given. There are also a few lapses in symbolism, notation, and uniformity of units. Yet the whole must be regarded as a highly commendable collection of material which will be valuable to chemists of all kinds."

Professor Sir Harold Thompson FRS
Oxford

Volume 2 1594 pp + index

"Volume 2 is concerned with the chemistry of the elements of Groups IV, V, VI, VII. The general impression on reading the various chapters of this volume is the great effectiveness in reporting a considerable amount of chemistry in a very digestible form. The systematic presentation applied to each chapter allows a rapid assessment of the appropriate chemical information, and the text is well documented with reference to the original literature plus good review articles for a more detailed coverage. Perhaps a minor criticism of this work lies in the indexing; the subject index is relatively sparse for a text of such magnitude and it would have been of considerable utility to have a formulae index to the text.

The area of chemistry covered by this work is obviously very great, but it does appear to have dealt with it in a very succinct manner for the majority of the text, which extends to approximately 1500 pages. The two major chapters in the book are associated with the chemistry of nitrogen, approximately 240 pages, and the chemistry of the halogens (excepting fluorine), approximately 500 pages. The book thus encompasses in one volume what would normally be a series of books. Both of the above mentioned chapters are admirable and the authors, K. Jones on nitrogen with A. J. Downs and C. J. Adams on the halogens, are to be commended on both the presentation and coverage. The chapter on the halogens illustrates the real strength of the series, in that detailed chemical information is not only presented but discussed in physico-chemical theoretical terms. A scientific compendium of this size often suffers from the "catalogue" approach, but the present text presents the chemistry in critical mode with a realistic assessment of the various physical methods used in property determination. Thus the properties of the halogens are discussed in terms of bond energies, bond lengths, vibrational properties, e.s.r., n.m.r., n.q.r. and Mossbauer spectroscopy, electronic and magnetic properties and dipole moments allowing a detailed appraisal of the use of various modern methods in studying the chemical properties reviewed.

Considering the magnitude of the task undertaken, it is extremely pleasing to note the number of chapters referring to papers in the 1971 period—a truly great commendation on the overall editorship of these volumes. Perhaps a general note in each volume stating the period covered by the references would have been of help. In general this work provides a welcome and unique addition to the inorganic literature."

Professor J. Lewis FRS
Cambridge

Volume 3 1370 pp + index

"This volume covers the chemistry of the elements of the d-block of the Periodic Table (the transition elements), with the exception of the Lanthanide elements (Vol. 4), the Actinide elements (Vol. 5) and some special aspects which are common to many of the transition elements (Vol. 4). The volume is therefore concerned specifically with the three elements which characterize each of the ten transition groups, and the chapters are mostly grouped in this way. However, the six platinum metals are treated in one chapter which is the best way to fit these similar elements into the overall scheme which is standard for all five volumes. There are altogether 17 chapters, written by 14 authors who are internationally