of HI on the heated metal. The fluoride is only slightly soluble in water but the others dissolve readily to give solutions from which pink or red hexahydrates can be crystallized. These solutions can alternatively and more conveniently be made by dissolving the metal, oxide or carbonate in the appropriate hydrohalic acid. The chloride is widely used as an indicator in the desiccant, silica gel, since its blue anhydrous form turns pink as it hydrates (see p. 1131).

The disinclination of these metals to form oxoanions has already been remarked and the same is evidently true of oxohalides: none have been authenticated.

26.3.3 Complexes

The chemistry of oxidation states above IV is sparse. Apart from RhF_6 and IrF_6, such chemistry as there is, is mainly confined to salts of $[RhF_6]^-$ and $[IrF_6]^-$. These are prepared respectively by the action of F_2 on $RhCl_3$ and KF under pressure,[9] and by fluorinating a lower halide of iridium with BrF_3 in the presence of a halide of the counter cation. Hydrido complexes of iridium in the formal oxidation state V are obtained by the action of $LiAlH_4$ or $LiBH_4$ on Ir^{III} compounds in the presence of phosphine or cyclopentadienyl ligands. $[IrH_5(PR_3)_2]$, in which the five hydrogens lie equatorially in a pentagonal bipyramid, and the "half sandwich", $[(\eta^5-C_5Me_5)IrH_4]$, are examples.

Oxidation state IV (d^5)

Cobalt provides only a few examples of this oxidation state, namely some fluoro compounds and mixed metal oxides, whose purity is questionable and, most notably, the thermally stable, brown, tetraalkyl, $[Co(1-norbornyl)_4]$. Prepared by the reaction of $CoCl_2$ and Li(1-norbornyl), it is the only one of a series of such compounds obtained for the first row transition metals Ti to Co which has been structurally characterized.[10] It is tetrahedral and, with a d^5 configuration, its room-temperature magnetic moment of 1.89 BM indicates that it is low-spin; the first example to be authenticated for a tetrahedral complex of a first row transition metal. Rhodium(IV) complexes are confined to salts of the oxidizing and readily hydrolysed $[RhX_6]^{2-}$ (X = F, Cl), the green solid $Cs_2[RhCl_6]$ being one of the few to be confirmed.[11] Only iridium(IV) shows appreciable stability.

The salts of $[IrX_6]^{2-}$ (X = F, Cl, Br) are comparatively stable and their colour deepens from red, through reddish-black to bluish-black with increasing atomic weight of the halogen. $[IrF_6]^{2-}$ is obtained by reduction of $[IrF_6]^-$, $[IrCl_6]^{2-}$ by oxidation of $[IrCl_6]^{3-}$ with chlorine, and $[IrBr_6]^{2-}$ by Br^- substitution of $[IrCl_6]^{2-}$ in aqueous solution. The hexachloroiridates in particular have been the subject of many magnetic investigations. They have magnetic moments at room temperature somewhat below the spin-only value for the t_{2g}^5 configuration (1.73 BM), and this falls with temperature. This has been interpreted as the result of antiferromagnetic interaction operating by a superexchange mechanism between adjacent Ir^{IV} ions via intervening chlorine atoms. More importantly, in 1953 in a short but classic paper,[12] J. Owen and K. W. H. Stevens reported the observation of hyperfine structure in the esr signal obtained from solid solutions of $(NH_4)_2[IrCl_6]$ in the isomorphous, but diamagnetic, $(NH_4)_2[PtCl_6]$. This arises from the influence of the chlorine nuclei and, from the magnitude of the splitting, it was inferred that the single unpaired electron, which is ostensibly one of the metal d^5 electrons, in fact spends only 80% of its time on the metal, the rest of the time being divided equally between the 6 chlorine ligands. This was the first unambiguous evidence that metal d electrons are able to move in molecular

[9] A. K. BRISDON, J. H. HOLLOWAY, E. G. HOPE and W. LEVASON, *Polyhedron* 11, 7–11 (1992).

[10] E. K. BYRNE, D. S. RICHESON and K. H. THEOPOLD, *J. Chem. Soc., Chem. Commun.*, 1491–2 (1986).

[11] I. J. ELLISON and R. D. GILLARD, *Polyhedron* 15, 339–48 (1996).

[12] J. OWEN and K. W. H. STEVENS, *Nature* 171, 836 (1953).

Table 26.4 E° for some Co^{III}/Co^{II} couples in acid solution

Couple	E°/V
$[Co(H_2O)_6]^{3+} + e^- \rightleftharpoons [Co(H_2O)_6]^{2+}$	1.83
$[Co(C_2O_4)_3]^{3-} + e^- \rightleftharpoons [Co(C_2O_4)_3]^{4-}$	0.57
$[Co(edta)]^- + e^- \rightleftharpoons [Co(edta)]^{2-}$	0.37
$[Co(bipy)_3]^{3+} + e^- \rightleftharpoons [Co(bipy)_3]^{2+}$	0.31
$[Co(en)_3]^{3+} + e^- \rightleftharpoons [Co(en)_3]^{2+}$	0.18
$[Co(NH_3)_6]^{3+} + e^- \rightleftharpoons [Co(NH_3)_6]^{2+}$	0.108
$[Co(CN)_6]^{3-} + H_2O + e^- \rightleftharpoons [Co(CN)_5(H_2O)]^{3-} + CN^-$	-0.8
$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O$	1.229

Figure 26.1 Trinuclear structure of (i) $[Ir_3O(SO_4)_9]^{10-}$ and (ii) $[Ir_3N(SO_4)_6(H_2O)_3]^{4-}$.

orbitals over the whole complex, and implies the presence of π as well as σ bonding.

In aqueous solution, the halide ions of $[IrX_6]^{2-}$ may be replaced by solvent and a number of aquo substituted derivatives have been reported. Other Ir^{IV} complexes with O-donor ligands are $[IrCl_4(C_2O_4)]^{2-}$, obtained by oxidizing Ir^{III} oxalato complexes with chlorine, and Na_2IrO_3, obtained by fusing Ir and Na_2CO_3.

Two interesting trinuclear complexes must also be mentioned. They are $K_{10}[Ir_3O(SO_4)_9].3H_2O$, obtained by boiling Na_2IrCl_6 and K_2SO_4 in conc sulfuric acid, and $K_4[Ir_3N(SO_4)_6(H_2O)_3]$, obtained by boiling Na_3IrCl_6 and $(NH_4)_2SO_4$ in conc sulfuric acid. They have the structure shown in Fig. 26.1, analogous to that of the basic carboxylates, $[M_3^{III}O(O_2CR)_6L_3]^+$ (see Fig. 23.9). The oxo species formally contains 1 Ir^{IV} and 2 Ir^{III} ions and the nitride species 2 Ir^{IV} ions and 1 Ir^{III} ion, but in each case the charges are probably delocalized over the whole complex.

Oxidation state III (d^6)

For all three elements this is the most prolific oxidation state, providing a wide variety of kinetically inert complexes. As has already been pointed out, these are virtually all low-spin and octahedral, a major stabilizing influence being the high CFSE associated with the t_{2g}^6 configuration ($\frac{12}{5}\Delta_o$, the maximum possible for any d^x configuration). Even $[Co(H_2O)_6]^{3+}$ is low-spin but it is such a powerful oxidizing agent that it is unstable in aqueous solutions and only a few simple salt hydrates, such as the blue $Co_2(SO_4)_3.18H_2O$ and $MCo(SO_4)_2.12H_2O$ (M = K, Rb, Cs, NH_4), which contain the hexaaquo ion, and $CoF_3.3\frac{1}{2}H_2O$ can be isolated. This paucity of simple salts of cobalt(III) contrasts sharply with the great abundance of its complexes, expecially with N-donor ligands[13], and it is evident that the high CFSE is not the only factor affecting the stability of this oxidation state.

Table 26.4 illustrates the remarkable sensitivity of the reduction potential of the Co^{III}/Co^{II} couple to different ligands whose presence renders Co^{II} unstable to aerial oxidation. The extreme effect of CN^- can be thought of as being due, on the one hand, to the ability of its empty π^* orbitals to accept "back-donated" charge from the metal's filled t_{2g} orbitals and, on the other, to its effectiveness as a σ donor (enhanced partly by its negative charge). The magnitudes of the

---

13 P. HENDRY and A. LUDI, *Adv. Inorg. Chem.* **35**, 117–98 (1990).

changes in $E°$ are even greater than those noted for the Fe^{III}/Fe^{II} couple (p. 1093), though if the two systems are compared it must be remembered that the oxidation state which can be stabilized by adoption of the low-spin t_{2g}^6 configuration is +3 for cobalt but only +2 for iron. Nevertheless, the effect of increasing pH is closely similar, the M^{III} "hydroxide" of both metals being far less soluble than the M^{II} "hydroxide". In the case of cobalt this reduces $E°$ from 1.83 to 0.17 V:

$$Co^{III}O(OH) + H_2O + e^- \rightleftharpoons Co^{II}(OH)_2 + OH^-;$$
$$E° = 0.17 \text{ V}$$

thereby facilitating oxidation to the +3 state.

Complexes of cobalt(III), like those of chromium(III) (p. 1027), are kinetically *inert* and so, again, indirect methods of preparation are to be preferred. Most commonly the ligand is added to an aqueous solution of an appropriate salt of cobalt(II), and the cobalt(II) complex thereby formed is oxidized by some convenient oxidant, frequently (if an *N*-donor ligand is involved) in the presence of a catalyst such as active charcoal. Molecular oxygen is often used as the oxidant simply by drawing a stream of air through the solution for a few hours, but the same result can, in many cases, be obtained more quickly by using aqueous solutions of H_2O_2.

The cobaltammines, whose number is legion, were amongst the first coordination compounds to be systematically studied[†] and are undoubtedly the most extensively investigated class of cobalt(III) complex. Oxidation of aqueous mixtures of CoX_2, NH_4X and NH_3 (X = Cl, Br, NO_3, etc.) can, by varying the conditions and particularly the relative proportions of the reactants, be used to prepare complexes of types such as $[Co(NH_3)_6]^{3+}$, $[Co(NH_3)_5X]^{2+}$ and $[Co(NH_3)_4X_2]^+$. The range of these compounds

is further extended by the replacement of X by other anionic or neutral ligands. The inertness of the compounds makes such substitution reactions slow (taking hours or days to attain equilibrium) and, being therefore amenable to examination by conventional analytical techniques, they have provided a continuing focus for kinetic studies. The forward (aquation) and backward (anation) reactions of the pentaammines:

$$[Co(NH_3)_5X]^{2+} + H_2O \rightleftharpoons$$
$$[Co(NH_3)_5(H_2O)]^{3+} + X$$

must be the most thoroughly studied substitution reactions, certainly of octahedral compounds. Furthermore, the isolation of *cis* and *trans* isomers of the tetraammines (p. 914) was an important part of Werner's classical proof of the octahedral structure of 6-coordinate complexes. The kinetic inertness of cobalt(III) was also exploited by H. Taube to demonstrate the inner-sphere mechanism of electron transfer (see Panel on p. 1124).

Compounds analogous to the cobaltammines may be similarly obtained using chelating amines such as ethythenediamine or bipyridyl, and these too have played an important role in stereo-chemical studies. Thus *cis*-$[Co(en)_2(NH_3)Cl]^{2+}$ was resolved into $d(+)$ and $l(-)$ optical isomers by Werner in 1911 thereby demonstrating, to all but the most determined doubters, its octahedral stereochemistry.[‡] More recently, the absolute configuration of one of the optical isomers of $[Co(en)_3]^{3+}$ was determined (see Panel on p. 1125).

Another *N*-donor ligand, which forms extremely stable complexes, is the NO_2^- ion: its best-known complex is the orange "sodium cobaltinitrite", $Na_3[Co(NO_2)_6]$, aqueous solutions of which were used for the quantitative precipitation of K^+ as $K_3[Co(NO_2)_6]$ in classical analysis. Treatment of this with fluorine yields

---

[†] The observation by B. M. Tassaert in 1798 that solutions of cobalt(II) chloride in aqueous ammonia gradually turn brown in air, and then wine-red on being boiled, is generally accepted as the first preparation of a cobalt(III) complex. It was realized later that more than one complex was involved and that, by varying the relative concentrations of ammonia and chloride ion, the complexes $CoCl_3.xNH_3$ ($x = 6, 5$ and 4) could be separated.

[‡] So deep-seated at that time was the conviction that optical activity could arise only from carbon atoms that it was argued that the ethylenediamine must be responsible, even though it is itself optically inactive. The opposition was only finally assuaged by Werner's subsequent resolution of an entirely inorganic material (p. 915).

Electron Transfer (Redox) Reactions

Two mechanisms exist for the transfer of charge from one species to another:

1. *Outer-sphere*. Here, electron transfer from one reactant to the other is effected without changing the coordination sphere of either. This is likely to be the case if both reactants are coordinatively saturated and can safely be assumed to be so if the rate of the redox process is faster than the rates observed for substitution (ligand transfer) reactions of the species in question. A good example is the reaction,

$$[Fe^{II}(CN)_6]^{4-} + [Ir^{IV}Cl_6]^{2-} \rightleftharpoons [Fe^{III}(CN)_6]^{3-} + [Ir^{III}Cl_6]^{3-}$$

The observed rate law for this type of reaction is usually first order in each reactant. Extensive theoretical treatments have been performed, most notably by R. A. Marcus and N. S. Hush, details of which can be found in more specialized sources[14]

2. *Inner-sphere*. Here, the two reactants first form a bridged complex (*precursor*); intramolecular electron transfer then yields the *successor* which in turn dissociates to give the products. The first demonstration of this was provided by H. Taube. He examined the oxidation of $[Cr(H_2O)_6]^{2+}$ by $[CoCl(NH_3)_5]^{2+}$ and postulated that it occurs as follows:

$$[Cr^{II}(H_2O)_6]^{2+} + [Co^{III}Cl(NH_3)_5]^{2+} \rightleftharpoons [(H_2O)_5Cr^{II}-Cl-Co^{III}(NH_3)_5]^{4+}$$

precursor

electron transfer

$$[Cr^{III}(H_2O)_5Cl]^{2+} + [Co^{II}(NH_3)_5H_2O]^{2+} \xleftarrow{\ H_2O\ } [(H_2O)_5Cr^{III}-Cl-Co^{II}(NH_3)_5]^{4+}$$

successor

$$\downarrow H_2O, H^+$$

$$[Co^{II}(H_2O)_6]^{2+} + 5NH_4^+$$

The superb elegance of this demonstration lies in the choice of reactants which permits no alternative mechanism. Cr^{II} (d^4) and Co^{II} (d^7) species are known to be substitutionally labile whereas Cr^{III} (d^3) and Co^{III} (low-spin d^6) are substitutionally inert. Only if electron transfer is preceded by the formation of a bridged intermediate can the inert cobalt reactant be persuaded to release a Cl^- ligand and so allow the quantitative formation of the (then inert) chromium product. Corroboration that electron transfer does not occur by an outer-sphere mechanism followed by loss of Cl^- from the chromium is provided by the fact that, if $^{36}Cl^-$ is added to the solution, none of it finds its way into the chromium product.

Demonstration of ligand transfer is crucial to the proof that *this particular reaction* proceeds via an inner-sphere mechanism, and ligand transfer is indeed a usual feature of inner-sphere redox reactions, but it is not an *essential* feature of *all* such reactions.

The observed rate law for inner-sphere, as for outer-sphere, reactions is commonly first order in each reactant but this does not indicate which step is rate-determining. Again, details should be obtained from more extensive accounts.[14]

For their work in this field, Taube and Marcus were awarded Nobel Prizes for Chemistry in 1983 and 1992 respectively.

$K_3[CoF_6]$, whose anion is notable not only as the only hexahalogeno complex of cobalt(III) but also for being high-spin and hence paramagnetic with a magnetic moment at room temperature of nearly 5.8 BM.

[14] R. G. WILKINS, *Kinetics and Mechanism of Reactions of Transition Metal Complexes*, 2nd edn., VCH, Weinhein, 1991, 465 pp. T. J. MEYER and H. TAUBE, Chap. 9 in *Comprehensive Coordination Chemistry*, Vol. 1, pp. 331–84, Pergamon Press, Oxford, 1987.

$[Co(CN)_6]^{3-}$ has already been mentioned and is extremely stable, being inert to alkalis and, like $[Fe(CN)_6]^{4-}$, which likewise involves the t_{2g}^6 configuration, it is reportedly nontoxic.

Complexes of cobalt(III) with O-donor ligands are generally less stable than those with N-donors although the dark-green $[Co(acac)_3]$ and $M_3^I[Co(C_2O_4)_3]$ complexes, formed from the chelating ligands acetylacetonate and oxalate, are stable. Other carboxylato complexes such as those of

Determination of Absolute Configuration

Because they rotate the plane of polarized light in opposite directions (p. 919) it is a relatively simple matter to distinguish an optical isomer from its mirror image. But to establish their absolute configurations is a problem which for long defeated the ingenuity of chemists. Normal X-ray diffraction techniques do not distinguish between them, but J. M. Bijvoet developed the absorption edge, or anomalous, diffraction technique which does. In this method the wavelength of the X-rays is chosen so as to correspond to an electronic transition of the central metal atom, and under these circumstances phase changes are introduced into the diffracted radiation which are different for the two isomers. An understanding of the phenomenon not only allows the isomers to be distinguished but also their configurations to be identified. Once the absolute configuration of one complex has been determined in this way, it can then be used as a standard to determine the absolute configuration of other, similar, complexes by the relatively simpler method of comparing their *optical rotary dispersion* (ORD) and *circular dichroism* (CD) curves.[15]

Normal measurements of optical activity are concerned with the ability of the optically active substance to rotate the plane of polarization of plane polarized light, its specific optical rotatory power (α_m) being given by

$$\alpha_m = \frac{\alpha V}{m \, l} \text{ rad m}^2 \text{ kg}^{-1}$$

where α is the observed angle of rotation, V is the volume, m is the mass, and l is the path length.

The reason why this phenomenon occurs is that plane polarized light can be considered to be made up of left- and of right-circularly polarized components, and the nature of an optically active substance is such that, in passing through it, one component passes through greater electron density than does the other. As a result, that component is slowed down relative to the other and the two components emerge somewhat out-of-phase, i.e. the plane of polarization of the light has been rotated. If the wavelength of the polarized light is varied, and α_m then plotted against wavelength, the result is known as an *optical rotary dispersion* curve. For those wavelengths at which the substance is transparent, α_m is virtually constant, which is to say the ORD curve is flat. But what happens when the wavelength of the light is such that it is absorbed by the substance in question?

In absorbing light the molecules of a substance undergo electronic excitations which involve displacement of electron charge. Because of their differing routes through the molecules, the two circularly polarized components of the light produce these excitations to different extents and are consequently absorbed to different extents. The difference in extinction coefficients, $\epsilon_{\text{left}} - \epsilon_{\text{right}}$, can be measured and is known as the *circular dichroism*. If the CD is plotted against wavelength it is therefore zero at wavelengths where there is no absorption but passes through a maximum, or a minimum, where absorption occurs. Accompanying these changes in CD it is found that the ORD curve is like a first derivative, passing through zero at the absorption maximum (Fig. A). Such a change in sign of α_m highlights the importance of quoting the wavelength of the light used when classifying optical isomers as ($+$) or ($-$), since the classification could be reversed by simply using light of a different wavelength.[†]

Figure A   Diagrammatic representation of the Cotton effect (actually "positive" Cotton effect. The "negative" effect occurs when the CD curve shows a minimum and the ORD curve is the reverse of the above).

Panel continues

[†]The situation is perhaps not quite so bad as is implied here, since *single* measurements of α_m are usually made at the sodium D line, 589.6 nm. Nevertheless, it is clearly better to state the wavelength than to assume that this will be understood.

---

[15]R. D. GILLARD, *Prog. Inorg. Chem.* **7**, 215–76 (1966).

The behaviours of CD and ORD curves in the vicinity of an absorption band are collectively known as the *Cotton effect* after the French physicist A. Cotton who discovered them in 1895. Their importance in the present context is that molecules with the same absolute configuration will exhibit the same Cotton effect for the same d-d absorption and, if the configuration of one compound is known, that of *closely similar* ones can be established by comparison.

The optical isomer of $[Co(en)_3]^{3+}$ referred to in the main text is the $(+)_{NaD}$ isomer, which has a left-handed *(laevo)* screw axis as shown in Fig. Ba, and according to the convention recommended by IUPAC is given the symbol Λ. This is in contrast to its mirror image (Fig. Bb) which has a right-handed *(dextro)* screw axis and is given the symbol Δ.

(a) Λ configuration   (b) Δ configuration

Figure B The absolute configuration of the optical isomers of a metal tris-chelates complex such as $[Co(en)_3]^{3+}$. (a) Λ configuration and (b) Δ configuration.

the acetate are, however, less stable but are involved in the catalysis of a number of oxidation reactions by Co^{II} carboxylates.

A noticeable difference between the chemistries of complexes of chromium(III) and cobalt(III) is the smaller susceptibility of the latter to hydrolysis, though limited hydrolysis, leading to polynuclear cobaltammines with bridging OH^- groups, is well known. Other commonly occurring bridging groups are NH_2^-, NH^{2-} and NO_2^-, and singly, doubly and triply bridged species are known such as

the bright-blue $[(NH_3)_5Co-NH_2-Co(NH_3)_5]^{5+}$,

garnet-red $[(NH_3)_4Co\overset{\displaystyle OH}{\underset{\displaystyle OH}{\diagup\diagdown}}Co(NH_3)_4]^{4+}$,

and red $[(NH_3)_3Co\overset{\displaystyle NH_2}{\underset{\displaystyle OH}{\diagup\diagdown}}OH-Co(NH_3)_3]^{3+}$

But probably the most interesting of the polynuclear complexes are those containing $-O-O-$ bridges (see also p. 616).

In the preparation of cobalt(III) hexaammine salts by the aerial oxidation of cobalt(II) in aqueous ammonia it is possible, in the absence

of a catalyst, to isolate a brown intermediate, $[(NH_3)_5Co-O_2-Co(NH_3)_5]^{4+}$. This is moderately stable in conc aqueous ammonia and in the solid, but decomposes readily in acid solutions to Co^{II} and O_2, while oxidizing agents such as $(S_2O_8)^2$ convert it to the green, paramagnetic $[(NH_3)_5Co-O_2-Co(NH_3)_5]^{5+}(\mu_{300} \sim 1.7\,BM)$. The formulation of the brown compound poses no problems. The 2 cobalt atoms are in the $+3$ oxidation state and are joined by a peroxo group, O_2^2, all of which accords with the observed diamagnetism; moreover, the stereochemistry of the central $Co-O-O-Co$ group (Fig. 26.2a) is akin to that of H_2O_2 (p. 634). The green compound is less straightforward. Werner thought that it too involved a peroxo group but in this instance bridging Co^{III} and Co^{IV} atoms.

Figure 26.2 O_2 bridges in dinuclear cobalt complexes: (a) peroxo (O_2^{2-}) bridge, and (b) superoxo (O_2^-) bridge.

Table 26.5 Spectra of octahedral low-spin complexes of cobalt(III)

Complex	Colour	ν_1/cm^{-1}	ν_2/cm^{-1}	$10Dq$/cm^{-1}	B/cm^{-1}
$[Co(H_2O)_6]^{3+}$	Blue	16 600	24 800	18 200	670
$[Co(NH_3)_6]^{3+}$	Golden-brown	21 000	29 500	22 900	620
$[Co(C_2O_4)_3]^{3-}$	Dark green	16 600	23 800	18 000	540
$[Co(en)_3]^{3+}$	Yellow	21 400	29 500	23 200	590
$[Co(CN)_6]^{3-}$	Yellow	32 400	39 000	33 500	460

This could account for the paramagnetism, but esr evidence shows that the 2 cobalt atoms are actually equivalent, and X-ray evidence shows the central Co–O–O–Co group to be planar with an O–O distance of 131 pm, which is very close to the 128 pm of the superoxide, O_2^-, ion. A more satisfactory formulation therefore is that of 2 Co^{III} atoms joined by a superoxide bridge. Molecular orbital theory predicts that the unpaired electron is situated in a π orbital extending over all 4 atoms. If this is the case, then the π orbital is evidently concentrated very largely on the bridging oxygen atoms.

If $[(NH_3)_5Co-O_2-Co(NH_3)_5]^{4+}$ is treated with aqueous KOH another brown complex, $[(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}O_2)Co(NH_3)_4]^{3+}$ is obtained and, again, a 1-electron oxidation yields a green superoxo species, $[(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}O_2)Co(NH_3)_4]^{4+}$ The sulfate of this latter is actually one component of Vortmann's sulfate — the other is the red $[(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(NH_3)_4](SO_4)_2$. They are obtained by aerial oxidation of ammoniacal solutions of cobalt(II) nitrate followed by neutralization with H_2SO_4.

Apart from the above green superoxo-bridged complexes and the blue fluoro complexes, $[CoF_6]^{3-}$ and $[CoF_3(H_2O)_3]$, octahedral complexes of cobalt(III) (being low-spin) are diamagnetic. Their magnetic properties are therefore of little interest but, somewhat unusually for low-spin compounds, their electronic spectra have received a good deal of attention[16] (see Panel on p. 1128). Data for a representative sample of complexes are given in Table 26.5

Complexes of rhodium(III) are usually derived, directly or indirectly, from $RhCl_3.3H_2O$ and those of iridium(III) from $(NH_4)_3[IrCl_6]$. All the compounds of Rh^{III} and Ir^{III} are diamagnetic and low-spin, the vast majority of them being octahedral with the t_{2g}^6 configuration. Their electronic spectra can be interpreted in the same way as the spectra of Co^{III} complexes, though the second d–d band, especially in the case of Ir^{III}, is frequently obscured by charge-transfer absorption. The d–d absorptions at the blue end of the visible region are responsible for the yellow to red colours which characterize Rh^{III} complexes.

Similarity with cobalt is also apparent in the affinity of Rh^{III} and Ir^{III} for ammonia and amines. The kinetic inertness of the ammines of Rh^{III} has led to the use of several of them in studies of the *trans* effect (p. 1163) in octahedral complexes, while the ammines of Ir^{III} are so stable as to withstand boiling in aqueous alkali. Stable complexes such as $[M(C_2O_4)_3]^{3-}$, $[M(acac)_3]$ and $[M(CN)_6]^3$ are formed by all three metals. Force constants obtained from the infrared spectra of the hexacyano complexes indicate that the M–C bond strength increases in the order Co < Rh < Ir. Like cobalt, rhodium too forms bridged superoxides such as the blue, paramagnetic, $[Cl(py)_4Rh-O_2-Rh(py)_4Cl]^{5+}$ produced by aerial oxidation of aqueous ethanolic solutions of RhCl$_3$ and pyridine.[17] In fact it seems likely that many of the species produced by oxidation of aqueous solutions of Rh^{III} and presumed to contain the metal in higher oxidation states, are actually superoxides of Rh^{III}.[18]

[16] A. B. P. LEVER, *Inorganic Electronic Spectroscopy*, 2nd edn., pp. 473–7, Elsevier, Amsterdam, 1984.

[17] N. S. A. EDWARDS, I. J. ELLISON, R. D. GILLARD and B. MILE, *Polyhedron* **12**, 371–4 (1993).

[18] I. J. ELLISON and R. D. GILLARD, *J. Chem. Soc., Chem. Commun.*, 851–3 (1992).

Electronic Spectra of Octahedral Low-spin Complexes of Co(III)

It is possible to observe spin-allowed, d–d bands in the visible region of the spectra of low-spin cobalt(III) complexes because of the small value of $10Dq$, (Δ), which is required to induce spin-pairing in the cobalt(III) ion. This means that the low-spin configuration occurs in complexes with ligands which do not cause the low-energy charge transfer bands which so often dominate the spectra of low-spin complexes.

In practice two bands are generally observed and are assigned to the transitions: $\nu_1 = {}^1T_{1g} \leftarrow {}^1A_{1g}$ and $\nu_2 = {}^1T_{2g} \leftarrow {}^1A_{1g}$ (see Fig. A)

Figure A   Simplified Energy Level diagram for d^6 ions showing possible spin-allowed transitions in complexes of low-spin cobalt(III).

These transitions correspond to the electronic promotion $t_{2g}^6 \rightarrow t_{2g}^5 e_g^1$ with the promoted electron maintaining its spin unaltered. The orbital multiplicity of the $t_{2g}^5 e_g^1$ configuration is 6 and so corresponds to two orbital triplet terms ${}^1T_{1g}$ and ${}^1T_{2g}$. If, on the other hand, the promoted electron changes its spin, the orbital multiplicity is again 6 but the two T terms are now spin triplets, ${}^3T_{1g}$ and ${}^3T_{2g}$. A weak band attributable to the spin-forbidden ${}^3T_{1g} \leftarrow {}^1A_{1g}$ transition is indeed observed in some cases in the region of $11\,000-14\,000\,\mathrm{cm}^{-1}$.

Data for some typical complexes are given in Table 26.5. The assignments are made, producing values of the inter-electronic repulsion parameter B as well as of the crystal-field splitting, $10Dq$.

The colours of *cis* and *trans* isomers of complexes $[CoL_4X_2]$ or $[Co(L-L)_2X_2]$ frequently differ and, although simple observation of colour will not alone suffice to establish a *cis* or *trans* geometry, an examination of the electronic spectra does have diagnostic value. Calculations of the effect of low-symmetry components in the crystal field show that the *trans* isomer will split the excited terms appreciably more than the *cis*, and the effect is most marked for ${}^1T_{1g}$, the lowest of the excited terms. In practice, if L-L and X are sufficiently far apart in the spectrochemical series (e.g. L-L = en and X = F which has been thoroughly examined), the ν_1 band splits completely, giving rise to three separate bands for the *trans* complex whereas the *cis* merely shows slight asymmetry in the lower energy band. Furthermore, because (like tetrahedral complexes) a *cis* isomer lacks a centre of symmetry, its spectrum is more intense than that of the centrosymmetric *trans* isomer.

It is relevant to note at this point that, because the metal ions are isoelectronic, the spectra of low-spin Fe^{II} complexes might be expected to be similar to those of low-spin Co^{III}. However, Fe^{II} requires a much stronger crystal field to effect spin-pairing and the ligands which provide such a field also give rise to low-energy charge-transfer bands which almost always obscure the d–d bands. Nevertheless, the spectrum of the pale-yellow $[Fe(CN)_6]^{4-}$ shows a shoulder at $31\,000\,\mathrm{cm}^{-1}$ on the side of a charge transfer absorption and this is attributed to the ${}^1T_{1g} \leftarrow {}^1A_{1g}$ transition.

Despite the above similarities, many differences between the members of this triad are also to be noted. Reduction of a trivalent compound, which yields a divalent compound in the case of cobalt, rarely does so for the heavier elements where the metal, univalent compounds, or M^{III} hydrido complexes are the more usual products. Rhodium forms the quite stable, yellow $[Rh(H_2O)_6]^{3+}$ ion when hydrous Rh_2O_3 is dissolved in mineral acid, and it occurs in the solid state in salts such as the perchlorate, sulfate and alums. $[Ir(H_2O)_6]^{3+}$ is less readily obtained but has been shown to occur in solutions of Ir^{III} in conc $HClO_4$.

There is also clear evidence of a change from predominantly class-a to class-b metal charactristics (p. 909) in passing down this group. Whereas cobalt(III) forms few complexes with the heavier donor atoms of Groups 15 and 16, rhodium(III), and more especially iridium (III), coordinate readily with *P*-, *As*- and *S*-donor ligands. Compounds with *Se*- and even *Te*- are also known.[19] Thus infrared, X-ray and ^{14}N nmr studies show that, in complexes such as $[Co(NH_3)_4(NCS)_2]^+$, the NCS^- acts as an *N*-donor ligand, whereas in $[M(SCN)_6]^{3-}$ (M = Rh, Ir) it is an *S*-donor. Likewise in the hexahalogeno complex anions, $[MX_6]^{3-}$, cobalt forms only that with fluoride, whereas rhodium forms them with all the halides except iodide, and iridium forms them with all except fluoride.

Besides the thiocyanates, just mentioned, other *S*-donor complexes which are of interest are the dialkyl sulfides, $[MCl_3(SR_2)_3]$, produced by the action of SR_2 on ethanolic $RhCl_3$ or on $[IrCl_6]^{3-}$. Phosphorus and arsenic compounds are obtained in similar fashion, and the best known are the yellow to orange complexes, $[ML_3X_3]$, (M = Rh, Ir; X = Cl, Br, I; L = trialkyl or triaryl phosphine or arsine). These compounds may exist as either *mer* or *fac* isomers, and these are normally distinguished by their proton nmr spectra (a distinction previously made by the measurement of dipole moments). An especially

interesting feature of their chemistry is the ease with which they afford hydride and carbonyl derivatives. For instance, the colourless, air-stable $[RhH(NH_3)_5]SO_4$ is produced by the action of Zn powder on ammoniacal $RhCl_3$ in the presence of $(NH_4)_2SO_4$:

$$[RhCl(NH_3)_5]Cl_2 \xrightarrow[SO_4^{2-}]{Zn} [RhH(NH_3)_5]SO_4$$

Ternary hydrides of Rh and Ir containing the octahedral $[MH_6]^{3-}$ anions have been prepared[20] by the reaction of LiH and the metal under a high pressure of H_2. It is however unusual for hydrides of metals in such a high *formal* oxidation state as +3 to be stable in the absence of π-acceptor ligands and, indeed, in the presence of π-acceptor ligands such as tertiary phosphines and arsines, the stability of rhodium(III) hydrides is enhanced. Thus H_3PO_2 reduces $[RhCl_3L_3]$ to either $[RhHCl_2L_3]$ or $[RhH_2ClL_3]$, depending on L; and the action of H_2 on $[Rh^I(PPh_3)_3X]$ (X = Cl, Br, I) yields $[RhH_2(PPh_3)_3X]$ which is, formally at least, an oxidation by molecular hydrogen. However, it is iridium(III) that forms more hydrido-phosphine and hydrido-arsine complexes than any other platinum metal. Using $NaBH_4$, $LiAlH_4$, EtOH or even $SnCl_2 + H^+$ to provide the hydride ligand, complexes of the type $[MH_nL_3X_{3-n}]$ can be formed for very many of the permutations which are possible from L = trialkyl or triaryl phosphine or arsine; X = Cl, Br or I. Many polynuclear hydride complexes are also known.[21]

Oxidation state II (d⁷)

There is a very marked contrast in this oxidation state between cobalt on the one hand, and the two heavier members of the group on the other. For cobalt it is one of the two most stable oxidation states, whereas for the others it is of only minor importance.

[19] A. Z. AL-RUBAIE, Y. N. AL-OBAIDI and L. Z. YOUSIF, *Polyhedron* **9**, 1141–6 (1990).

[20] W. BRONGER, M. GEHLEN and G. AUFFERMANN, *Z. anorg. allg. Chem.* **620**, 1983–5 (1994).

[21] T. M. G. CARNEIRO, D. MATT and P. BRAUNSTEIN, *Coord. Chem. Revs.* **96**, 49–88 (1989).

Many early reports of Rh^{II} and Ir^{II} complexes have not been verified and in some cases may have involved M^{III} hydrides. Monomeric compounds require stabilization by ligands such as phosphines or $C_6Cl_5^-$. Thus, the action of LiC_6Cl_5 on $[L_2M-Cl-ML_2]$, where $L_2 = 2[P(OPh)_3]$, cyclooctene or cycloocta-1,5-diene, affords *trans* square planar products of the type $[M^I(\eta^1-C_6Cl_5)_2(L_2)]^-$, oxidation of which yield monomeric paramagnetic compounds such as $[M^{II}(\eta^1-C_6Cl_5)_2(L_2)]$ and, in the case of iridium, square planar $[Ir^{II}(\eta^1-C_6Cl_5)_4]^{2-}$ isolated as its $(NBu_4)^+$ salt.[22] Rhodium(II) is somewhat more common than iridium(II). Paramagnetic, *trans* square planar phosphines $[RhCl_2L_2]$ and the alkyl $(RhR_2(tht)_2)$, $(R = 2,4,6-Pr^i_3C_6H_2$; tht = tetrahydrothiophene) have been characterized.[23] Also, depending on temperature and relative concentrations, the reaction of $Rh(NO)Cl_2(PPh_3)_2$ and $Na(S_2CNR_2)$ in benzene yields either $Rh(S_2CNR_2)_2$ or $Rh(S_2CNR_2)(PPh_3)$, characterized by spectroscopic methods as square planar and square pyramidal respectively.[24]

Rhodium(II), however, is most familiar in a series of green dimeric diamagnetic compounds.[25] If hydrous Rh_2O_3, or better still $RhCl_3.3H_2O$ and sodium carboxylate, is refluxed with the appropriate acid and alcohol, green or blue solvated $[Rh(O_2CR)_2]_2$ is formed. Compounds of this type are generally air-stable and have the same bridged structure as the carboxylates of Cr^{II}, Mo^{II} and Cu^{II}; in the case of the acetate this involves a Rh–Rh distance of 239 pm which is consistent with a Rh–Rh bond. If rhodium acetate is treated with a strong acid such as HBF_4, whose anion has little tendency to coordinate, green solutions apparently containing the diamagnetic Rh_2^{4+} ion are obtained but no solid salt of this has been isolated. Why no comparable Ir^{II} carboxylates, and very few other dimeric species stabilized by metal–metal bonding, have yet been prepared is not clear.

By contrast, Co^{II} carboxylates such as the red acetate, $Co(O_2CMe)_2.4H_2O$, are monomeric and in some cases the carboxylate ligands are unidentate. The acetate is employed in the production of catalysts used in certain organic oxidations, and also as a drying agent in oil-based paints and varnishes. Cobalt(II) gives rise to simple salts with all the common anions and they are readily obtained as hydrates from aqueous solutions. The parent hydroxide, $Co(OH)_2$, can be precipitated from the aqueous solutions by the addition of alkali and is somewhat amphoteric, not only dissolving in acid but also redissolving in excess of conc alkali, in which case it gives a deep-blue solution containing $[Co(OH)_4]^{2-}$ ions. It is obtainable in both blue and pink varieties: the former is precipitated by slow addition of alkali at $0°C$, but it is unstable and, in the absence of air, becomes pink on warming (cf. p. 1131).

Complexes of cobalt(II) are less numerous than those of cobalt(III) but, lacking any configuration comparable in stability with the t_{2g}^6 of Co^{III}, they show a greater diversity of types and are more labile. The redox properties have already been referred to and the possibility of oxidation must always be considered when preparing Co^{II} complexes. However, providing solutions are not alkaline and the ligands not too high in the spectrochemical series, a large number of complexes can be isolated without special precautions. The most common type is high-spin octahedral, though spin-pairing can be achieved by ligands such as CN^- (p. 1133) which also favour the higher oxidation state. Appropriate choice of ligands can however lead to high-spin-low-spin equilibria as in $[Co(terpy)_2]X_2.nH_2O$ and some 5- and 6-coordinated complexes of Schiff bases and pyridines.[26]

Many of the hydrated salts and their aqueous solutions contain the octahedral, pink

[22] M. P. GARCIA, M. V. JIMENEZ, L. A. ORO and F. J. LAHOZ, *Organometallics* **12**, 4660–3 (1993).

[23] R. S. HAY-MOTHERWELL, S. U. KOSCHMIEDER, G. WILKINSON, B. HUSSAIN-BATES and M. B. HURSTHOUSE, *J. Chem. Soc., Dalton Trans.*, 2821–30 (1991).

[24] K. K. PANDEY, D. T. NEHETE and R. B. SHARMA, *Polyhedron* **9**, 2013–18 (1990).

[25] F. A. COTTON and R. A. WALTON, *Multiple Bonds Between Metal Atoms*, Clarendon Press, Oxford, 1993, 787 pp.

[26] P. THUERY and J. ZARAMBOWITCH, *Inorg. Chem.* **25**, 2001–8 (1986).

Figure 26.3 The tetrameric structure of $[Co(acac)_2]_4$.

Table 26.6 CFSE values[†] for high-spin complexes of d^0 to d^{10} ions

No. of d electrons	0	1	2	3	4	5	6	7	8	9	10
CFSE(oct)/(Δ_o)	0	$\frac{2}{5}$	$\frac{4}{5}$	$\frac{6}{5}$	$\frac{3}{5}$	0	$\frac{2}{5}$	$\frac{4}{5}$	$\frac{6}{5}$	$\frac{3}{5}$	0
CFSE(tet)/(Δ_t)	0	$\frac{3}{5}$	$\frac{6}{5}$	$\frac{4}{5}$	$\frac{2}{5}$	0	$\frac{3}{5}$	$\frac{6}{5}$	$\frac{4}{5}$	$\frac{2}{5}$	0

[†]The Crystal Field Stabilization Energy (CFSE) is the additional stability which accrues to an ion in a complex, as compared to the free ion, because its d-orbitals are split. In an octahedral complex a t_{2g} electron increases the stability by $2/5\Delta_o$ and an e_g electron decreases it by $3/5\Delta_o$. In a tetrahedral complex the orbital splitting is reversed and an e electron therefore increases the stability by $3/5\Delta_t$ whereas a t_2 electron decreases it by $2/5\Delta_t$.

$[Co(H_2O)_6]^{2+}$ ion, and bidentate *N*-donor ligands such as en, bipy and phen form octahedral cationic complexes $[Co(L-L)_3]^{3+}$, which are much more stable to oxidation than is the hexaammine $[Co(NH_3)_6]^{2-}$. Acac yields the orange $[Co(acac)_2(H_2O)_2]$ which has the *trans* octahedral structure and can be dehydrated to $[Co(acac)_2]$ which attains octahedral coordination by forming the tetrameric species shown in Fig. 26.3. This is comparable with the trimeric $[Ni(acac)_2]_3$ (p. 1157), like which it shows evidence of weak ferromagnetic interactions at very low temperatures. $[Co(edta)(H_2O)]^{2+}$ is ostensibly analogous to the 7-coordinate Mn^{II} and Fe^{II} complexes with the same stoichiometry, but in fact the cobalt is only 6-coordinate, 1 of the oxygen atoms of the edta being too far away from the cobalt (272 compared to 223 pm for the other edta donor atoms) to be considered as coordinated.

Tetrahedral complexes are also common, being formed more readily with cobalt(II) than with the cation of any other truly transitional element (i.e. excluding Zn^{II}). This is consistent with the CFSEs of the two stereochemistries (Table 26.6). Quantitative comparisons between the values given for CFSE(oct) and CFSE(tet) are not possible because of course the crystal field splittings, Δ_o and Δ_t differ. Nor is the CFSE by any means the most important factor in determining the stability of a complex. Nevertheless, where other factors are comparable, it can have a decisive effect and it is apparent that no configuration is more favourable than d^7 to the adoption of a tetrahedral as opposed to

an octahedral stereochemistry. Thus, in aqueous solutions containing $[Co((H_2O)_6]^{2+}$ there are also present in equilibrium, small amounts of tetrahedral $[Co(H_2O)_4]^{2+}$, and in acetic acid the tetrahedral $[Co(O_2CMe)_4]^2$ occurs. The anionic complexes $[CoX_4]^{2-}$ are formed with the unidentate ligands, $X = Cl$, Br, I, SCN and OH, and a whole series of complexes, $[CoL_2X_2]$ (L = ligand with group 15 donor atom; X = halide, NCS), has been prepared in which both stereochemistries are found. $[CoCl_2py_2]$ exists in two isomeric forms: a blue metastable variety which is monomeric and tetrahedral, and a violet, stable form which is polymeric and achieves octahedral coordination by means of chloride bridges. Ligand polarizability is an important factor determining which stereochemistry is adopted, the more polarizable ligands favouring the tetrahedral form since fewer of them are required to neutralize the metal's cationic charge. Thus, if $L = py$, replacement of Cl^- by I^- makes the stable form tetrahedral and if L = phosphine or arsine the tetrahedral form is favoured irrespective of X.

The most obvious distinction between the octahedral and tetrahedral compounds is that *in general* the former are pink to violet in colour whereas the latter are blue, as exemplified by the well-known equilibrium:

$$[Co(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CoCl_4]^{2-} + 6H_2O$$

<div align="center">pink   blue</div>

This is not an infallible distinction (as the blue but octahedral $CoCl_2$ demonstrates) but is a useful

Electronic Spectra and Magnetic Properties of High-spin Octahedral and Tetrahedral Complexes of Cobalt(II)

Cobalt(II) is the only common d^7 ion and because of its stereochemical diversity its spectra have been widely studied. In a cubic field, three spin-allowed transitions are anticipated because of the splitting of the free-ion, ground ^4F term, and the accompanying ^4P term. In the octahedral case the splitting is the same as for the octahedral d^2 ion and the spectra can therefore be interpreted in a semi-quantitative manner using the same energy level diagram as was used for V^{3+} (Fig. 22.9, p. 997). In the present case the spectra usually consist of a band in the near infrared, which may be assigned as $\nu_1 = {}^4T_{2g}(F)\leftarrow{}^4T_{1g}(F)$, and another in the visible, often with a shoulder on the low energy side. Since the transition $^4A_{2g}(F)\leftarrow{}^5T_{1g}(F)$ is essentially a 2-electron transition from $t_{2g}^5 e_g^2$ to $t_{2g}^3 e_g^4$ it is expected to be weak, and the usual assignment is

$$\nu_2(\text{shoulder}) = {}^4A_{2g}(F)\leftarrow{}^4T_{1g}(F)$$

$$\nu_3 = {}^4T_{1g}(P)\leftarrow{}^4T_{1g}(F)$$

Indeed, in some cases it is probable that ν_2 is not observed at all, but that the fine structure arises from term splitting due to spin-orbit coupling or to distortions from regular octahedral symmetry.

In tetrahedral fields the splitting of the free ion ground term is the reverse of that in octahedral fields so that, for d^7 ions in tetrahedral fields $^2A_{2g}(F)$ lies lowest but three spin-allowed bands are still anticipated. In fact, the observed spectra usually consist of a broad, intense band in the visible region (responsible for the colour and often about 10 times as intense as in octahedral compounds) with a weaker one in the infrared. The only satisfactory interpretation is to assign these, respectively, as, $\nu_3 = {}^4T_1(P)\leftarrow{}^4A_2(F)$ and $\nu_2 = {}^4T_1(F)\leftarrow{}^4A_2(F)$ in which case $\nu_1 = {}^4T_2(F)\leftarrow{}^4A_2(F)$ should be in the region $3000–5000\,\text{cm}^{-1}$. Examination of this part of the infrared has sometimes indicated the presence of a band, though overlying vibrational bands make interpretation difficult.

Table 26.7 gives data for a number of octahedral and tetrahedral complexes, the values of $10Dq$ and B having been derived by analysis of the spectra.[27] It is clear from these data that the "anomolous" blue colour of octahedral $CoCl_2$ arises because 6 Cl^- ions generate such a weak crystal field that the main band in its spectrum is at an unusually low energy, extending into the red region (hence giving a blue colour) rather than the green-blue region (which would give a red colour) more commonly observed for octahedral Co^{II} compounds.

Magnetic properties provide a complementary means of distinguishing stereochemistry. The T ground term of the octahedral ion is expected to give rise to a temperature-dependent orbital contribution to the magnetic moment whereas the A ground term of the tetrahedral ion is not. As a matter of fact, in a tetrahedral field the excited $^4T_2(F)$ term is "mixed into" the ground $^4A_2$ term because of spin–orbit coupling and tetrahedral complexes of Co^{II} are expected to have magnetic moments given by $\mu_e = \mu_{\text{spin-only}}(1 - 4\lambda/10Dq)$, where $\lambda = -170\,\text{cm}^{-1}$ and $\mu_{\text{spin-only}} = 3.87\,\text{BM}$.

Thus the magnetic moments of tetrahedral complexes lie in the range $4.4–4.8\,\text{BM}$, whereas those of octahedral complexes are around $4.8–5.2\,\text{BM}$ at room temperature, falling off appreciably as the temperature is reduced.

empirical guide whose reliability is improved by a more careful analysis of the electronic spectra[27] (see Panel). Data for some octahedral and tetrahedral complexes are given in Table 26.7.

Square planar complexes are also well authenticated if not particularly numerous and include [Co(phthalocyanine)] and [Co(CN)4]⁻ as well as [Co(salen)] and complexes with other Schiff bases. These are invariably low-spin with magnetic moments at room temperature in the range 2.1–2.9 BM, indicating 1 unpaired electron. They are primarily of interest because

of their oxygen-carrying properties, discussed already in Chapter 14 where numerous reviews on the subject are cited. The uptake of dioxygen, which bonds in the bent configuration,

$$Co-O \overset{\diagup O}{\diagdown}\quad,$$

is accompanied by the attachment of a solvent molecule *trans* to the O_2 and the retention of the single unpaired electron. There is fairly general agreement, based on esr evidence, that electron transfer from metal to O_2 occurs just as in the bridged complexes referred to on

27 pp. 480–504 of ref. 16.

Table 26.7   Electronic spectra of complexes of cobalt(II)

(a) Octahedral

Complex	ν_1/cm^{-1}	ν_2/cm^{-1} (weak)	ν_3/cm^{-1} (main)	$10Dq/cm^{-1}$	B/cm^{-1}
$[Co(bipy)_3]^{2+}$	11 300		22 000	12 670	791
$[Co(NH_3)_6]^{2+}$	9000		21 100	10 200	885
$[Co(H_2O)_6]^{2+}$	8100	16 000	19 400	9200	825
$CoCl_2$	6600	13 300	17 250	6900	780

(b) Tetrahedral

Complex	ν_2/cm^{-1}	ν_3/cm^{-1} (main)	$10Dq/cm^{-1}$	B/cm^{-1}
$[Co(NCS)_4]^{2-}$	7780	16 250	4550	691
$[Co(N_3)_4]^{2-}$	6750	14 900	3920	658
$[CoCl_4]^{2-}$	5460	14 700	3120	710
$[CoL_4]^{2-}$	4600	13 250	2650	665

p. 1126, producing a situation close to the extreme represented by low-spin Co^{III} attached to a superoxide ion, O_2^-. (The opposite extreme, represented by Co^{II}–O_2, implies that the unpaired electron resides on the metal with the dioxygen being rendered diamagnetic by the loss of the degeneracy of its π^* orbitals with consequent spin pairing.) However, the precise extent of the electron transfer is probably determined by the nature of the ligand *trans* to the O_2.

The difficulty of assigning a formal oxidation state is more acutely seen in the case of 5-coordinate NO adducts of the type $[Co(NO)(salen)]$. These are effectively diamagnetic and so have no unpaired electrons. They may therefore be formulated either as Co^{III}–NO^- or Co^I–NO^+. The infrared absorptions ascribed to the N–O stretch lie in the range 1624–$1724\,cm^{-1}$, which is at the lower end of the range said to be characteristic of NO^+. But, as in all such cases which are really concerned with the differing polarities of covalent bonds, such formalism should not be taken literally.

Other 5-coordinate Co^{II} compounds which have been characterized include $[CoBr\{N(C_2H_4NMe_2)_3\}]^+$, which is high-spin with 3 unpaired electrons and is trigonal bipyramidal (imposed by the "tripod" ligand), and

$[Co(CN)_5]^{3-}$, which is low-spin with 1 unpaired electron and is square pyramidal. The latter complex is isolated from solutions of $Co(CN)_2$ and KCN as the yellow $[NEt_2Pr_2^i]^+$ salt, an extremely oxygen-sensitive and hygroscopic material. A further difficulty which hindered its isolation is its tendency to dimerize to the more familiar deep-violet, $[(CN)_5Co$–$Co(CN)_5]^{6-}$. The absence of a simple hexacyano complex is significant as it seems to be generally the case that ligands such as CN^-, which are expected to induce spin-pairing, favour a coordination number for Co^{II} of 4 or 5 rather than 6; the planar $[Co(diars)_2](ClO_4)$ is a further illustration of this. Presumably the Jahn–Teller distortion, which is anticipated for the low-spin $t_{2g}^6 e_g^1$ configuration is largely responsible.

Oxidation state I (d⁸)

Oxidation states lower than $+2$ normally require the stabilizing effect of π-acceptor ligands and some of these are appropriately considered along with organometallic compounds in Section 26.3.5. Exceptions are the square pyramidal anion of the black, $Mg_2[CoH_5]$ (obtained by prolonged heating of the powdered metals under high

pressure of H_2) and the linear anion of the garnet red $CsK_2[CoO_2]^{(27a)}$ (see p. 1166). However, although $+1$ is not a common oxidation state for cobalt, it is one of the two most common states for both rhodium and iridium and as such merits separate consideration.

Simple ligand-field arguments, which will be elaborated when M^{II} ions of the Ni, Pd, Pt triad are discussed on p. 1157, indicate that the d^8 configuration favours a 4-coordinate, square-planar stereochemistry. In the present group, however, the configuration is associated with a lower oxidation state and the requirements of the 18-electron rule,[†] which favour 5-coordination, are also to be considered. The upshot is that most Co^I complexes are 5-coordinate, like $[Co(CNR)_5]^+$, and square-planar Co^I is apparently unknown. On the other hand, complexes of Rh^I and Ir^I are predominantly square planar, although 5-coordination does also occur.

These complexes are usually prepared by the reduction of compounds such as $RhCl_3.3H_2O$ and K_2IrCl_6 in the presence of the desired ligand. It is often unnecessary to use a specific reductant, the ligand itself or alcoholic solvent being adequate, and not infrequently leading to the presence of CO or H in the product. A considerable proportion of the complexes of Rh^I and Ir^I are phosphines and of these, two in particular demand attention. They are Wilkinson's catalyst, $[RhCl(PPh_3)_3]$, and Vaska's compound, *trans*-$[IrCl(CO)(PPh_3)_2]$, both essentially square planar.

Wilkinson's catalyst, $[RhCl(PPh_3)_3]$. This red-violet compound[(28)], which is readily obtained by refluxing ethanolic $RhCl_3.3H_2O$ with an excess of PPh_3, was discovered[(29)] in 1965. It undergoes a variety of reactions, most of which involve either replacement of a phosphine ligand (e.g. with CO, CS, C_2H_4, O_2 giving *trans* products) or oxidative addition (e.g. with H_2, MeI) to form Rh^{III}, but its importance arises from its effectiveness as a catalyst[(30)] for highly selective hydrogenations of complicated organic molecules which are of great importance in the pharmaceutical industry. Its use allowed, for the first time, rapid *homogeneous* hydrogenation at ambient temperatures and pressures:

The precise mechanism is complicated and has been the subject of much speculation and controversy, but Fig. 26.4 shows a simplified but reasonable scheme. The essential steps in this are the oxidative addition of H_2 (if the hydrogen atoms are regarded as "hydridic", i.e. as H^-, the metal's oxidation state increases from $+1$ to $+3$); the formation of an alkene complex; alkene insertion and, finally, the reductive elimination of the alkane (i.e. the metal's oxidation state reverting to $+1$). The rhodium catalyst is able to fulfil its role because the metal is capable of changing its coordination number (loss of phosphine from the dihydro complex being encouraged by the large size of the ligand) and it possesses oxidation states ($+1$ and $+3$) which differ by 2 and are of comparable stability.

The discovery of the catalytic properties of $[RhCl(PPh_3)_3]$ naturally brought about a widespread search for other rhodium phosphines with catalytic activity. One of those which was found, also in Wilkinson's laboratory, was *trans*-$[Rh(CO)H(PPh_3)_3]$ which can conveniently be

---

[†] The filling-up of the bonding MOs of the molecule may be regarded, more simply, as the filling of the outer 9 orbitals of the metal ion with its own d electrons plus a pair of σ electrons from each ligand. A 4-coordinate d^8 ion is thus a "16-electron" species and is "coordinatively unsaturated". Saturation in this sense requires the addition of 10 electrons, i.e. 5 ligands, to the metal ion. By contrast rhodium(III) is a d^6 ion and so can expand its coordination sphere to accommodate 6 ligands with important consequences in catalysis which will be seen below.

27a F. BERNHARD and R. HOPPE, *Z. anorg. allg. Chem.* **620**, 187–91 (1994).

28 The paramagnetic impurity which invariably accompanies Wilkinson's catalyst has proved difficult to identify. It is probably the air-stable, green, *trans*- $[RhCl(CO)(PPh_3)_2]$. see K. R. DUNBAR and S. C. HAFFNER, *Inorg. Chem.* **31**, 3676–9 (1992).

29 J. F. YOUNG, J. A. OSBORN, F. H. JARDINE, and G. WILKINSON, *J. Chem. Soc., Chem. Commun.*, 131 2 (1965).

30 R. S. DICKSON, *Homogeneous Catalysis with Compounds of Rhodium and Iridium*, D. Reidel, Dordrecht, 1985, 278 pp.

Figure 26.4   The catalytic cycle for the hydrogenation of an alkene, catalysed by $[RhCl(PPh_3)_3]$ in benzene; possible coordination of solvent molecules has been ignored and the ligand PPh_3 has been represented as P throughout, for clarity.

dealt with here. It was found that, for steric reasons, it selectively catalyses the hydrogenation of alk-1-enes (i.e. terminal olefins) rather than alk-2-enes and it has been used in the *hydroformylation* of alkenes, (i.e. the addition of H and the formyl group, CHO) also known as the OXO process because it introduces oxygen into the hydrocarbon. This is a process of enormous industrial importance, being used to convert alk-1-enes into aldehydes which can then be converted to alcohols for the production of polyvinylchloride (PVC) and polyalkenes and, in the case of the long-chain alcohols, in the production of detergents:

$$RCH{=}CH_2 + H_2 + CO \xrightarrow{\text{catalyst}} RCH_2CH_2CHO$$

A simplified reaction scheme is shown in Fig. 26.5 Again, the ability of rhodium to change its coordination number and oxidation state is crucial, and this catalyst has the great advantage over the conventional cobalt carbonyl catalyst that it operates efficiently at much lower temperatures and pressures and produces straight-chain as opposed to branched-chain products.

The reason for its selectivity lies in the insertion step of the cycle. In the presence of the two bulky PPh_3 groups, the attachment to the metal of $-CH_2CH_2R$ (anti-Markovnikov addition, leading to a straight chain product) is easier than the attachment of $-CH(CH_3)R$ (Markovnikov addition, leading to a branched-chain product).

Vaska's compound, trans-$[IrCl(CO)(PPh_3)_2]$. This yellow compound can be prepared by the reaction of triphenylphosphine and $IrCl_3$ in a solvent such as 2-methoxyethanol which acts both as reducing agent and supplier of CO. It was discovered in 1961 by L. Vaska and J. W. di Luzio[31] and recognized as an ideal material for the study of oxidative addition reactions, since its products are generally stable and readily characterized. It is certainly the most thoroughly investigated compound of Ir^I. It forms octahedral Ir^{III} complexes in oxidative addition reactions with H_2, Cl_2, HX, MeI and RCO_2H, and ^1H nmr shows that in all cases the phosphine ligands are *trans* to each other. The 4 remaining ligands (Cl,

[31] L. Vaska and J. W. Di Luzio, *J. Am. Chem. Soc.* **83**, 2784–5 (1961).

Figure 26.5　　The catalytic cycle for the hydroformylation of an alkene catalysed by *trans*-[RhH(CO)(PPh$_3$)$_3$]. The tertiary phosphine ligand has been represented as P throughout.

CO and two components of the reactant) therefore lie in a plane and 3 isomers are possible:

There is apparently no simple way of predicting which of these will be formed and each case must be examined individually. The situation is further complicated by the fact that, when the Cl of Vaska's compound is replaced by H, Me or Ph, addition of H$_2$ gives products in which the phosphines are now *cis*. Various

theoretical models have been suggested to account for this.[32]

Addition reactions with ligands such as CO and SO$_2$ (the addition of which as an uncharged ligand is unusual) differ in that no oxidation occurs and 5-coordinate 18-electron Ir^I products are formed.

The facile absorption of O$_2$ by a solution of Vaska's compound is accompanied by a change in colour from yellow to orange which may be reversed by flushing with N$_2$. This

---

[32] M. J. Burk, M. P. McGrath, R. Wheeler and R. H. Crabtree, *J. Am. Chem. Soc.* **110**, 5034–9 (1988).

is one of the most widely studied synthetic oxygen-carrying systems and has been discussed earlier (p. 615). The O−O distance of 130 pm in the oxygenated product (see Fig. 14.5b, p. 617) is rather close to the 128 pm of the superoxide ion, O_2^-, but this would imply Ir^{II} which is paramagnetic whereas the compound is actually diamagnetic. The oxygenation is instead normally treated as an oxidative addition with the O_2 acting as a bidentate peroxide ion, O_2^{2-}, to give a 6-coordinate Ir^{III} product. However, in view of the small "bite" of this ligand the alternative formulation in which the O_2 acts as a neutral unidentate ligand giving a 5-coordinate Ir^I product has also been proposed.

Oxygen-carrying properties are evidently critically dependent on the precise charge distribution and steric factors within the molecule. Replacement of the Cl in Vaska's compound with I causes loss of oxygen-carrying ability, the oxygenation being irreversible. This can be rationalized by noting that the lower electronegativity of the iodine would allow a greater electron density on the metal, thus facilitating $M \rightarrow O_2$ π donation: this increases the strength of the $M−O_2$ bond and, by placing charge in antibonding orbitals of the O_2, causes an increase in the O−O distance from 130 to 151 pm.

Lower oxidation states

Numerous complexes of Co, Rh and Ir are known in which the formal oxidation state of the metal is zero, −1, or even lower. Many of these compounds contain CO, CN^- or RNC as ligands and so are more conveniently discussed under organometallic compounds (Section 26.3.5). However, other ligands such as tertiary phosphines also stabilize the lower oxidation states, as exemplified by the brown, tetrahedral, paramagnetic complex $[Co^0(PMe_3)_4]$: this is made by reducing an ethereal solution of $CoCl_2$ with Mg or Na amalgam in the presence of PMe_3. Further treatment of the product with Mg/thf in the presence of N_2 gives $[Mg(thf)_4][Co^{-II}(N_2)(PMe_3)_4]$. Similar

reactions with $P(OMe)_3$ and $P(OEt)_3$ give both paramagnetic monomers $[Co^0\{P(OR)_3\}_4]$, and diamagnetic dimers $[Co_2^0\{P(OR)_3\}_8]$, whereas the more bulky $P(OPr^i)_3$ yields only the orange-red monomeric product. With an excess of sodium amalgam as reducing agent the product with this latter ligand is the white-crystalline $Na[Co^{-I}\{P(OPr^i)_3\}_5]$. In view of the ready solubility of this compound in pentane and the d^{10} configuration of Co^{-1} it may be that only 4 of the phosphite ligands are directly coordinated to the metal centre: one possible formulation would be

With the terdentate *P*-donor ligand, MeC-$(CH_2PPh_2)_3$, (tppme) excess sodium amalgam and an atmosphere of N_2 yields the deep-brown $[(tppme)Co−N−N−Co(tppme)]$ which, unusually for a dimer, is paramagnetic.[33] The N−N distance in the linear bridge is 118 pm compared with 109.8 pm in N_2 (p. 412).

Another technique for obtaining low oxidation states is by electrolytic reduction using cyclic voltametry. Some spectacular series can be achieved of which, perhaps, the most notable is based on $[Ir^{III}(bipy)_3]^{3+}$: this, when dissolved in MeCN, can be oxidized to $[Ir^{IV}(bipy)_3]^{4+}$ and reduced in successive 1-electron steps to give every oxidation state down to $[Ir^{-III}(bipy)_3]^{3-}$, a total of 8 interconnected redox complexes. However, by no means all have been isolated as solid products from solution. Many other

[33] F. CECCONI, C. A. GHILARDI, S. MIDOLLINI, S. MONETI, A. ORLANDINI and M. BACCI, *J. Chem. Soc., Chem. Commun.*, 731–3 (1985).