

the action of various fluorinating agents on OsO_4 but they are subject to disproportionation and not easily prepared in pure form.

25.3.4 Complexes^(10,11,21,22,23)

Oxidation state VIII (d^0)

Iron forms barely any complexes in oxidation states above +3, and in the +8, +7 and +6 states those of ruthenium are less numerous than those of osmium. Ru^{VIII} complexes are confined to a few unstable (sometimes explosive) amine adducts of RuO_4 . The “perosmates” (p. 1082) are, of course, adducts of OsO_4 , but the most stable Os^{VIII} complexes are the “osmiamates”, $[\text{OsO}_3\text{N}]^-$ (p. 419). Pale-yellow crystals of $\text{K}[\text{OsO}_3\text{N}]$ are obtained when solutions of OsO_4 in aqueous KOH (i.e. the perosmate) are treated with ammonia: the compound has been known since 1847 and A. Werner formulated it correctly in 1901. The anion is isoelectronic with OsO_4 and has a distorted tetrahedral structure (C_{3v}), while its infrared spectrum shows $\nu_{\text{Os-N}} = 1023 \text{ cm}^{-1}$, consistent with an $\text{Os}\equiv\text{N}$ triple bond. Hydrochloric and hydrobromic acids reduce $\text{K}[\text{OsO}_3\text{N}]$ to red, $\text{K}_2[\text{Os}^{\text{VI}}\text{NX}_5]$.

Oxidation state VII (d^1)

Fluorides and oxo compounds of Ru^{VII} and Os^{VII} have already been mentioned, and salts such as $(\text{R}_4\text{N})[\text{RuO}_4]$, ($\text{R} = n$ -propyl, n -butyl) are useful reagents to oxidize a variety of organic materials without attacking double or allylic bonds.⁽²⁴⁾

²¹ P. N. HAWKER and M. V. TWIGG, *Iron(II) and Lower States*, Chap. 44.1, pp. 1179–288; S. M. NELSON, *Iron(III) and Higher States*, Chap. 44.2, pp. 217–76; M. SCHRÖDER and T. A. STEPHENSON, *Ruthenium*, Chap. 45, pp. 277–518; W. P. GRIFFITH, *Osmium*, Chap. 46, pp. 519–633 in *Comprehensive Coordination Chemistry*, Vol. 4, Pergamon Press, Oxford, 1987.

²² C.-M. CHE and V. W.-W. YAM, High valent compounds of Ruthenium and Osmium, *Adv. Inorg. Chem.* **39**, 233–325 (1992).

²³ P. A. LAY and W. D. HARMAN, Recent advances in osmium chemistry, *Adv. Inorg. Chem.* **37**, 219–380 (1991).

²⁴ W. P. GRIFFITH, *Platinum Metals Rev.* **33**, 181–5 (1989).

Oxidation state VI (d^2)

The most important members of this class are the osmium nitrido, and the “osmyl” complexes. The reddish-purple $\text{K}_2[\text{OsNCl}_5]$ mentioned above is the result of reducing the osmiamate. The anion has a distorted octahedral structure with a formal triple bond $\text{Os}\equiv\text{N}$ (161 pm) and a pronounced “*trans*-influence” (pp. 1163–4), i.e. the $\text{Os}-\text{Cl}$ distance *trans* to $\text{Os}-\text{N}$ is much longer than the $\text{Os}-\text{Cl}$ distances *cis* to $\text{Os}-\text{N}$ (261 and 236 pm respectively). The anion $[\text{OsNCl}_5]^{2-}$ also shows a “*trans*-effect” in that the Cl opposite the N is more labile than the others, leading, for instance, to the formation of $[\text{Os}^{\text{VI}}\text{NCl}_4]^-$, which has a square-pyramidal structure with the N occupying the apical position.

The osmyl complexes, of which the osmate ion $[\text{Os}^{\text{VI}}\text{O}_2(\text{OH})_4]^{2-}$ may be regarded as the precursor, are a series of diamagnetic complexes containing the linear $\text{O}=\text{Os}=\text{O}$ group together with 4 other, more remote, donor atoms which occupy the equatorial plane. That the $\text{Os}-\text{O}$ bonds are double (i.e. 1σ and 1π) is evident from the bond lengths of 175 pm — very close to those of 172 pm in OsO_4 . The diamagnetism can then be explained using the MO approach outlined in Chapter 19, but modified to allow for the tetragonal compression along the axis of the osmyl group (taken to define the z -axis). On this model, the effect of 6 σ interactions produces the molecular orbitals shown in Fig. 19.14 (p. 922). The tetragonal compression then splits the essentially metallic t_{2g} and e_g^* sets, as shown to the left of Fig. 25.4b. Two 3-centre π bonds are then formed, one by overlap of the metal d_{xz} orbital with the p_x orbitals of the 2 oxygen atoms (Fig. 25.4a), the second similarly by d_{yz} and p_y overlap. Each 3-centre interaction produces 1 bonding, 1 virtually nonbonding, and 1 antibonding MO, as shown. The metal d_{xy} orbital remains unchanged and, in effect, the two d electrons of the Os are obliged to pair-up in it since other empty orbitals are inaccessible to them.

The $\{\text{Os}^{\text{VI}}\text{O}_2\}^{2+}$ group has a formal similarity to the more familiar uranyl ion $[\text{UO}_2]^{2+}$ and is present in a variety of octahedral complexes

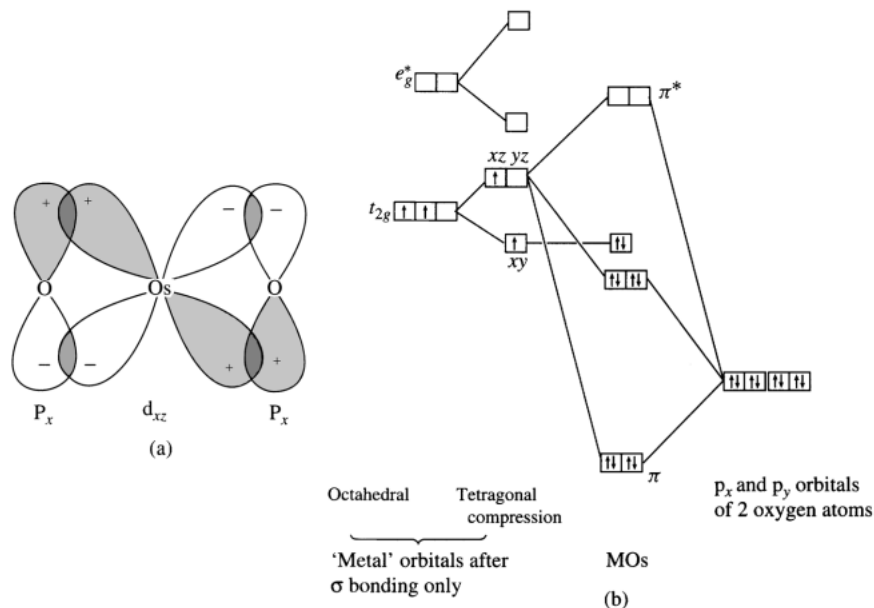


Figure 25.4 Proposed π bonding in osmyl complexes: (a) 3-centre π bond formed by overlap of ligand p_x and metal d_{xz} orbitals (a similar bond is produced by p_y and d_{yz} overlap), and (b) MO diagram (see text).

in which the 4 equatorial sites are occupied by ligands such as OH^- , halides, CN^- , $(\text{C}_2\text{O}_4)^{2-}$, NO_2^- , NH_3 and phthalocyanine. These are obtained from OsO_4 or potassium osmate.

A few analogous but less stable trans-dioxoruthenium(VI) compounds such as the bright yellow $[\text{RuO}_2(\text{O}_2\text{CCH}_3)_2\text{py}_2]$ ($\text{Ru}-\text{O} = 172.6\text{ pm}$) are also known.⁽²⁵⁾

Oxidation state V (d^3)

This is not a very stable state for this group of metals in solution, $[\text{MF}_6]^-$ and $[\text{OsCl}_6]^-$ being amongst the few established examples. It is, however, well-characterized and stable in numerous solid-state oxide systems (p. 1082).

Oxidation state IV (d^4)

Under normal circumstances this is the most stable oxidation state for osmium and the

$[\text{OsX}_6]^{2-}$ complexes ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$) are particularly well known. $[\text{RuX}_6]^{2-}$ ($X = \text{F}, \text{Cl}, \text{Br}$) are also familiar but can more readily be reduced to Ru^{III} . All these $[\text{MX}_6]^{2-}$ ions are octahedral and low-spin, with 2 unpaired electrons. Their magnetic properties are interesting and highlight the limitations of using "spin-only" values of magnetic moments in assessing the number of unpaired electrons (see Panel).

The action of hydrochloric acid on RuO_4 in the presence of KCl produces a deep-red crystalline material, of stoichiometry $\text{K}_2[\text{RuCl}_5(\text{OH})]$, but its diamagnetism precludes this simple formulation. The compound is in fact $\text{K}_4[\text{Cl}_5\text{Ru}-\text{O}-\text{RuCl}_5]$ and is of interest as providing an early application of simple MO theory to a linear $\text{M}-\text{O}-\text{M}$ system (not unlike the later treatment of the osmyl group). If the $\text{Ru}-\text{O}-\text{Ru}$ axis is taken as the z -axis and each Ru^{IV} is regarded as being octahedrally coordinated, then the low-spin configuration of each Ru^{IV} ion is $d_{xy}^2 d_{xz}^1 d_{yz}^1$. The diamagnetism is accounted for on the basis of two 3-centre π bonds, one arising from overlap

²⁵ S. PERRIER, T. C. LAU and J. K. KOCHI, *Inorg. Chem.* **29**, 4190–5 (1990).

Magnetic Properties of Low-spin, Octahedral d^4 Ions

That halide ligands should cause spin-pairing may in itself seem surprising, but this is not all. The regular, octahedral complexes of Os^{IV} have magnetic moments at room temperature in the region of 1.48 BM and these decrease rapidly as the temperature is reduced. Even the moments of similar complexes of Ru^{IV} (which at around 2.9 BM are close to the "spin-only moment" expected solely from the angular momentum of 2 unpaired electrons) fall sharply with temperature. In the first place, low-spin configurations are much more common for the second- and third-row than for first-row transition elements and this is due to (a) the higher nuclear charges of the heavier elements which exert stronger attractions on the ligands so that a given set of ligands produces a greater splitting of the metal d orbitals, and (b) the larger sizes of 4d and 5d orbitals compared to 3d orbitals, with the result that interelectronic repulsions, which tend to oppose spin-pairing, are lower in the former cases. These factors explain why the halide complexes of Os^{IV} and Ru^{IV} are low-spin but what of the temperature dependence and their magnetic behaviour? This arises from the effect of "spin-orbit coupling" which can be summarized in a plot of μ_e versus $kT/|\lambda|$ (Fig. A). λ is the spin-orbit coupling constant for a particular ion and is indicative of the strength of the coupling between the angular momentum vectors associated with S and L , and also of the magnitude of the splitting of the ground term of the ion (3T , in the case of low-spin d^4). When $|\lambda|$ is of comparable magnitude to kT , $\mu_e \sim 3.6$ BM, which is the spin-only moment (2.83 BM) plus a contribution from the orbital angular momentum. Thus, Cr^{III} ($\lambda = -115 \text{ cm}^{-1}$) and Mn^{III} ($\lambda = -178 \text{ cm}^{-1}$) at room temperature ($kT \sim 200 \text{ cm}^{-1}$), lie on the flat portion of the curve and so have magnetic moments of about 3.6 BM which only begin to fall at appreciably lower temperatures. On the other hand, Ru^{IV} ($\lambda = -700 \text{ cm}^{-1}$) and Os^{IV} ($\lambda \sim -2000 \text{ cm}^{-1}$) have moments which at room temperature are already on the steep portion of the curve and so are extremely dependent on temperature. In each case, as the temperature approaches 0 K so also $\mu_e \rightarrow 0$, corresponding to a coupling of L and S vectors in opposition and their associated magnetic moments therefore cancelling each other.

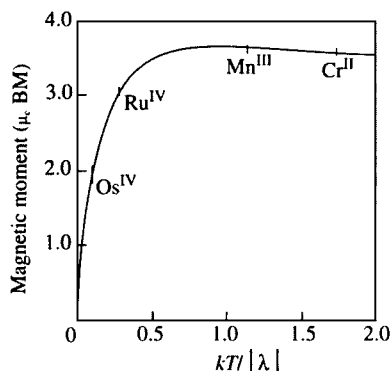


Figure A The variation with temperature and spin-orbit coupling constant, of the magnetic moments of octahedral, low-spin, d^4 ions. (The values of μ_e at 300 K are marked for individual ions).

All d^n configurations with T ground terms give rise to magnetic moments which are lower for second- and third-row than for first-row transition elements and are temperature dependent, but in no case so dramatically as for low-spin d^4 .

of the oxygen p_x orbital and the two d_{xz} orbitals of the Ru ions, and the other similarly from p_y and d_{yz} overlap (Fig. 25.5). The bromo analogue apparently does not exist.⁽²⁶⁾

Ruthenium(IV) produces few other complexes of interest but osmium(IV) yields several sulfite complexes (e.g. $[\text{Os}(\text{SO}_3)_6]^{8-}$ and substituted derivatives) as well as a number of complexes, such as $[\text{Os}(\text{bipy})\text{Cl}_4]$ and $[\text{Os}(\text{diars})_2\text{X}_2]^{2+}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), with mixed halide and Group 15 donor atoms. The iron analogues of the latter complexes (with $\text{X} = \text{Cl}, \text{Br}$), are obtained by oxidation of

²⁶ D. APPLEBY, R. I. CRISP, P. B. HITCHCOCK, C. L. HUSSEY, T. A. RYAN, J. R. SANDERS, K. R. SEDDON, J. E. TURP and J. A. ZORA, *J. Chem. Soc., Chem. Commun.*, 483-5 (1986).

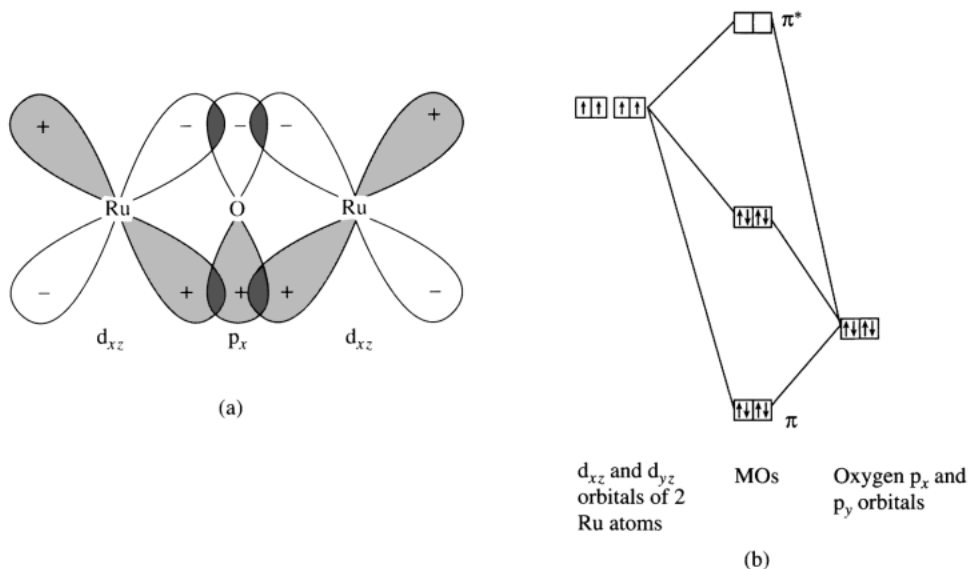


Figure 25.5 π bonding in $[\text{Ru}_2\text{OCl}_{10}]^{4-}$: (a) 3-centre π bond formed by overlap of an oxygen p_x and ruthenium d_{xz} orbitals (another similar bond is produced by p_y and d_{yz} overlap), and (b) MO diagram.

$[\text{Fe}(\text{diars})_2\text{X}_2]^+$ with conc HNO_3 and provide rare examples of complexes containing iron in an oxidation state higher than +3. The halide ions are *trans* to each other and a reduction in the magnetic moment at 293 K from a value of ~ 3.6 BM (which might have been expected, since $\lambda = -260 \text{ cm}^{-1}$ for Fe^{IV} — see Panel) to 2.98 BM is explained by a large tetragonal distortion.

Oxidation state III (d^5)

Ruthenium(III) and osmium(III) complexes are all octahedral and low-spin with 1 unpaired electron. Iron(III) complexes, on the other hand, may be high or low spin, and even though an octahedral stereochemistry is the most common, a number of other geometries are also found. In other respects, however there is a gradation down the triad, with Ru^{III} occupying an intermediate position between Fe^{III} and Os^{III} . For iron the oxidation state +3 is one of its two most common and for it there is an extensive, simple, cationic chemistry (though the aquo

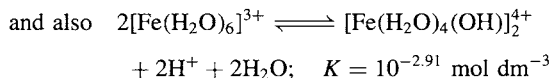
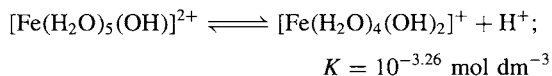
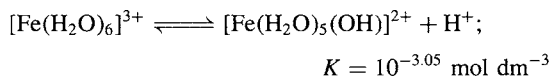
ion, $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, is too readily hydrolysed to be really common). For ruthenium it is the best-known oxidation state and $[\text{Ru}(\text{H}_2\text{O})_6]^{3+}$, which can be obtained by oxidation of the divalent ion (p. 1095), has been characterized⁽²⁷⁾ in the toluene sulfonate, $[\text{Ru}(\text{H}_2\text{O})_6](\text{tos})_3$ and the caesium alum (see below). For osmium, however, Os^{III} is a distinctly less-common oxidation state, being readily oxidized to Os^{IV} or even, in the presence of π -acceptor ligands such as CN^- , reduced to Os^{II} . There is no evidence of a simple aquo ion of osmium in this or indeed in any other oxidation state.

Except with anions such as iodide (but see p. 1084) which have reducing tendencies, iron(III) forms salts with all the common anions, and these may be crystallized in pale-pink or pale-violet hydrated forms. These presumably contain the $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ cation, and the iron alums certainly do. These alums have the composition $\text{Fe}_2(\text{SO}_4)_3\text{M}_2^{\text{I}}\text{SO}_4 \cdot 24\text{H}_2\text{O}$ and can be formulated $[\text{M}^{\text{I}}(\text{H}_2\text{O})_6][\text{Fe}^{\text{III}}(\text{H}_2\text{O})_6][\text{SO}_4]_2$.

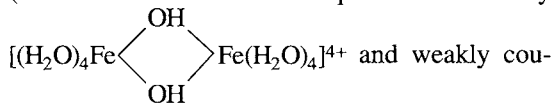
²⁷ F. JOENSEN and C. E. SCHAFFER, *Acta. Chem. Scand. Ser. A*, **38**, 819–20 (1984).

Like the analogous chrome alums they find use as mordants in dyeing processes. The sulfate is the cheapest salt of Fe^{III} and forms no less than 6 different hydrates (12, 10, 9, 7, 6 and 3 mols of H_2O of which $9\text{H}_2\text{O}$ is the most common); it is widely used as a coagulant in the treatment not only of potable water but also of sewage and industrial effluents.

In the crystallization of these hydrated salts from aqueous solutions it is essential that a low pH (high level of acidity) is maintained, otherwise hydrolysis occurs and yellow impurities contaminate the products. Similarly, if the salts are redissolved in water, the solutions turn yellow/brown. The hydrolytic processes are complicated, and, in the presence of anions with appreciable coordinating tendencies, are further confused by displacement of water from the coordination sphere of the iron. However, in aqueous solutions of salts such as the perchlorate the following equilibria are important:



(The dimer in the third equation is actually



pled electron spins on the 2 metal ions reduce the magnetic moment per iron below the spin-only value for 5 unpaired electrons.)

It is evident therefore that Fe^{III} salts dissolved in water produce highly acidic solutions and the simple, pale-violet, hexaquo ion only predominates if further acid is added to give pH ~ 0 . At somewhat higher values of pH the solution becomes yellow due to the appearance of the above hydrolysed species and if the pH is raised above 2–3, further condensation occurs, colloidal gels begin to form, and eventually a

reddish-brown precipitate of hydrous iron(III) oxide is formed (see p. 1080).

The colours of these solutions are of interest. Iron(III) like manganese(II), has a d^5 configuration and its absorption spectrum might therefore be expected to consist similarly of weak spin-forbidden bands. However, a crucial difference between the ions is that Fe^{III} carries an additional positive charge, and its correspondingly greater ability to polarize coordinated ligands produces intense, charge-transfer absorptions at much lower energies than those of Mn^{II} compounds. As a result, only the hexaquo ion has the pale colouring associated with spin-forbidden bands in the visible region of the spectrum, while the various hydrolysed species have charge transfer bands, the edges of which tail from the ultraviolet into the visible region producing the yellow colour and obscuring weak d–d bands.⁽²⁸⁾ Even the hexaquo ion's spectrum is dominated in the near ultraviolet by charge transfer, and a full analysis of the d–d spectrum of this and of other Fe^{III} complexes is consequently not possible.

Iron(III) forms a variety of cationic, neutral and anionic complexes, but an interesting feature of its coordination chemistry is a marked preference (not shown by Cr^{III} with which in many other respects it is similar) for *O*-donor as opposed to *N*-donor ligands. Ammines of Fe^{III} are unstable and dissociate in water; chelating ligands such as bipy and phen which induce spin-pairing produce more stable complexes, but even these are less stable than their Fe^{II} analogues. Thus, whereas deep-red aqueous solutions of $[\text{Fe}(\text{phen})_3]^{2+}$ are indefinitely stable, the deep-blue solutions of $[\text{Fe}(\text{phen})_3]^{3+}$ slowly turn khaki-coloured as polymeric hydroxo species form. By contrast, the intense colours produced when phenols or enols are treated with Fe^{III} , and which are used as characteristic tests for these organic materials, are due to the formation of Fe–O complexes. Again, the addition of phosphoric acid to yellow, aqueous solutions of FeCl_3 , for instance, decolourizes them because

²⁸ A. B. P. LEVER, *Inorganic Electronic Spectroscopy*, 2nd edn., pp. 329–34 and 452–3, Elsevier, Amsterdam, 1984.

of the formation of phosphato complexes such as $[\text{Fe}(\text{PO}_4)_3]^{6-}$ and $[\text{Fe}(\text{HPO}_4)_3]^{3-}$. The deep-red $[\text{Fe}(\text{acac})_3]$ and the green $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ are other examples of complexes with oxygen-bonded ligands although the latter, whilst very stable towards dissociation, is photosensitive due to oxidation of the oxalate ion by Fe^{III} and so decomposes to $\text{Fe}(\text{C}_2\text{O}_4)$ and CO_2 .

Complexes with mixed *O*- and *N*-donor ligands such as edta and Schiff bases are well known and $[\text{Fe}(\text{edta})(\text{H}_2\text{O})]^-$ and $[\text{Fe}(\text{salen})\text{Cl}]$ are examples of 7-coordinate (pentagonal bipyramidal) and 5-coordinate (square-pyramidal) stereochemistries respectively.

As in the case of Cr^{III} , oxo-bridged species with magnetic moments reduced below the spin-only value (5.9 BM in the case of high-spin Fe^{III}) are known. $[\text{Fe}(\text{salen})_2\text{O}]$, for instance, has a moment of 1.9 BM at 298 K which falls to 0.6 BM at 80 K and the interaction between the electron spins on the 2 metal ions is transmitted across an Fe–O–Fe bridge, bent at an angle of 140° . Trinuclear, basic carboxylates, $[\text{Fe}_3\text{O}(\text{O}_2\text{CR})_6\text{L}_3]^+$, are, however, entirely analogous to their Cr^{III} counterparts (p. 1030).⁽²⁹⁾

Halide complexes decrease markedly in stability from F^- to I^- . Fluoro complexes are quite stable and in aqueous solutions the predominant species is $[\text{FeF}_5(\text{H}_2\text{O})]^{2-}$ while isolation of the solid and fusion with KHF_2 yields $[\text{FeF}_6]^{3-}$. Chloro complexes are appreciably less stable, and tetrahedral rather than octahedral coordination is favoured.[†] $[\text{FeCl}_4]^-$ can be isolated in yellow salts with large cations such as $[\text{RN}_4]^+$ from ethanolic solutions or conc HCl. $[\text{FeBr}_4]^-$ and $[\text{FeI}_4]^-$ are also known but are readily reduced to Fe^{II} either by internal

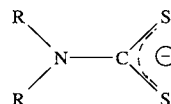
oxidation–reduction or by the action of excess ligand.⁽³⁰⁾

The blood-red colour produced by mixing aqueous solutions of Fe^{III} and SCN^- (and which provides a well-known test for Fe^{III}) is largely due to $[\text{Fe}(\text{SCN})(\text{H}_2\text{O})_5]^{2+}$ but, in addition to this, the simple salt $\text{Fe}(\text{SCN})_3$ and salts of complexes such as $[\text{Fe}(\text{SCN})_4]^-$ and $[\text{Fe}(\text{SCN})_6]^{3-}$ can also be isolated.

The high-spin d^5 configuration of Fe^{III} , like that of Mn^{II} , confers no advantage by virtue of CFSE (p. 1131) on any particular stereochemistry. Some examples of its consequent ability to adopt stereochemistries other than octahedral have just been mentioned and further examples are given in Table 25.3 (p. 1078). These cover the range of coordination numbers from 3 to 8.

Further similarity with Mn^{II} may be seen in the fact that the vast majority of the compounds of Fe^{III} are high-spin. Only ligands such as bipy and phen (already mentioned) and CN^- , which are high in the spectrochemical series, can induce spin-pairing. The low-spin $[\text{Fe}(\text{CN})_6]^{3-}$, which is best known as its red, crystalline potassium salt, is usually prepared by oxidation of $[\text{Fe}(\text{CN})_6]^{4-}$ with, for instance, Cl_2 . It should be noted that in $[\text{Fe}(\text{CN})_6]^{3-}$ the CN^- ligands are sufficiently labile to render it poisonous, in apparent contrast to $[\text{Fe}(\text{CN})_6]^{4-}$, which is kinetically more inert. Dilute acids produce $[\text{Fe}(\text{CN})_5(\text{H}_2\text{O})]^{2-}$, and other pentacyano complexes are known.

Fe^{III} complexes in general have magnetic moments at room temperature which are close to 5.92 BM if they are high-spin and somewhat in excess of 2 BM (due to orbital contribution) if they are low-spin. A number of complexes, however, were prepared in 1931 by L. Cambi and found to have moments intermediate between these extremes. They are the iron(III)-*N,N*-dialkyldithiocarbamates, $[\text{Fe}(\text{S}_2\text{CNR}_2)_3]$, in which the ligands are:



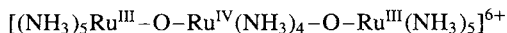
²⁹ R. D. CANNON and R. P. WHITE, *Prog. Inorg. Chem.* **36**, 195–298 (1988).

[†] In the compound, previously assumed to be $(\text{pyH})_3[\text{Fe}_2\text{Cl}_9]$ with the anion composed of a pair of face-sharing octahedra, the iron is in fact coordinated tetrahedrally and the correct formulation is, $[(\text{pyH})_3\text{Cl}][\text{FeCl}_4]_2$, see R. SHAVIV, C. B. LOWE, J. A. ZORA, C. B. AAKERÖY, P. B. HITCHCOCK, K. R. SEDDON and R. L. CARLIN, *Inorg. Chim. Acta* **198–200**, 613–21 (1992).

³⁰ S. POHL, U. BIERBACH and W. SAAK, *Angew. Chem. Int. Edn. Engl.* **28**, 776–7 (1989).

so that the Fe^{III} is surrounded octahedrally by 6 sulfur atoms. They provide well documented examples of high-spin/low-spin crossover (i.e. spin equilibria) (see Panel p. 1096).

Ruthenium(III) forms extensive series of halide complexes, the aquo-chloro series being probably the best characterized of all its complexes. The $\text{Ru}^{\text{III}}/\text{Cl}^-/\text{H}_2\text{O}$ system has received extensive study, especially by ion-exchange techniques. The ions $[\text{RuCl}_n(\text{H}_2\text{O})_{6-n}]^{(n-3)-}$ from $n = 6$ to $n = 0$ have all been identified in solution and a number also isolated as solids. $\text{K}_3[\text{RuF}_6]$ can be obtained from molten $\text{RuCl}_3/\text{KHF}_2$. Several bromo complexes have been reported amongst them the dimeric anion $[\text{Ru}_2\text{Br}_9]^{3-}$ which, like its chloro analogue, is composed of a pair of face-sharing octahedra. There are, however, no iodo complexes and, whilst $[\text{Os}(\text{CN})_6]^{3-}$ as well as the Fe^{III} analogue are known and some substituted cyano complexes of Ru^{III} have been prepared, the parent $[\text{Ru}(\text{CN})_6]^{3-}$ has only recently been isolated as the brilliant yellow $(\text{Bu}^n_4\text{N})^+$ salt by aerial oxidation of dmf solution of $[\text{Ru}(\text{CN})_6]^{2+}$.⁽³¹⁾ Ru^{III} is much more amenable to coordination with *N*-donor ligands than is Fe^{III} , and forms ammines with from 3 to 6 NH_3 ligands (the extra ligands making up octahedral coordination are commonly H_2O or halides) as well as complexes with bipy and phen. Treatment of “ RuCl_3 ” with aqueous ammonia in air slowly yields an extremely intense red solution (ruthenium red) from which a diamagnetic solid can be isolated, apparently of the form:



Its diamagnetism can be explained on the basis of π overlap, producing polycentre molecular orbitals essentially the same as used for $[\text{Ru}_2\text{OCl}_{10}]^{4-}$ (see Fig. 25.5). It is stable in either acid or alkali and its acid solution can be used as an extremely sensitive test for oxidizing agents since even such a mild reagent as iron(III) chloride oxidizes the red, 6+ cation to a yellow, paramagnetic, 7+ cation of the same constitution (a change which is detectable in solutions containing less than 1 ppm Ru).

Trinuclear basic acetates $[\text{Ru}_3\text{O}(\text{O}_2\text{CMe})_6\text{L}_3]^+$ have also been prepared apparently with the same constitution as the analogous Fe^{III} and Cr^{III} compounds (p. 1030).

For osmium, halogeno complexes are less diverse but the reaction of acetic acid/acetic anhydride with $[\text{OsCl}_6]^{2-}$ yields brown $\text{Os}_2(\text{O}_2\text{CMe})_4\text{Cl}_2$ which, if treated as a suspension in anhydrous ethanol with gaseous HX ($\text{X} = \text{Cl}, \text{Br}$), yields $[\text{Os}_2\text{X}_8]^{2-}$. These diamagnetic ions are notable for the presence of the $\text{Os}\equiv\text{Os}$ triple bond unsupported by bridging ligands. The triply bridged $[\text{Os}_2\text{Br}_9]^{3-}$ is also known.⁽³²⁾

Oxidation state II (d^6)

This is the second of the common oxidation states for iron and is familiar for ruthenium, particularly with Group 15-donor ligands (Ru^{II} probably forms more nitrosyl complexes than any other metal). Osmium(II) also produces a considerable number of complexes but is usually more strongly reducing than Ru^{II} .

Iron(II) forms salts with nearly all the common anions.[†] These are usually prepared in aqueous solution either from the metal or by reduction of the corresponding Fe^{III} salt. In the absence of other coordinating groups these solutions contain the pale-green $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ ion which is also present in solids such as $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and the well-known “Mohr’s salt”, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ introduced into volumetric analysis by K. F. Mohr in the 1850s.[‡]

³¹ S. ELLER and R. D. FISCHER, *Inorg. Chem.*, **29**, 1289–90 (1990).

³² G. A. HEATH and D. G. HUMPHREY, *J. Chem. Soc., Chem. Commun.*, 672–3 (1990).

[†] An exception is NO_2^- which instantly oxidizes Fe^{II} to Fe^{III} and liberates NO. $\text{Fe}(\text{BrO}_3)_2$ and $\text{Fe}(\text{IO}_3)_2$ also are unstable.

[‡] K. F. Mohr (1806–79) was Professor of Pharmacy at the University of Bonn. Among his many inventions were the specific gravity balance, the burette, the pinch clamp, the cork borer, and the use of the so-called Liebig condenser for refluxing. In addition to his introduction of iron(II) ammonium sulfate as a standard reducing agent he devised Mohr’s method for titrating halide solutions with silver ions

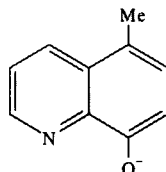
The Fe^{III}/Fe^{II} Couples

A selection of the standard reduction potentials for some iron couples is given in Table A, from which the importance of the participating ligand can be judged (see also Table 25.8 for biologically important iron proteins). Thus Fe^{III}, being more highly charged than Fe^{II} is stabilized (relatively) by negatively charged ligands such as the anions of edta and derivatives of 8-hydroxyquinoline, whereas Fe^{II} is favoured by neutral ligands which permit some charge delocalization in π -orbitals (e.g. bipy and phen).

Table A E° at 25°C for some Fe^{III}/Fe^{II} couples in acid solution

Fe ^{III}	Fe ^{II}	E°/V
[Fe(phen) ₃] ³⁺ + e ⁻	\rightleftharpoons [Fe(phen) ₃] ²⁺	1.12
[Fe(bipy) ₃] ³⁺ + e ⁻	\rightleftharpoons [Fe(bipy) ₃] ²⁺	0.96
[Fe(H ₂ O) ₆] ³⁺ + e ⁻	\rightleftharpoons [Fe(H ₂ O) ₆] ²⁺	0.77
[Fe(CN) ₆] ³⁻ + e ⁻	\rightleftharpoons [Fe(CN) ₆] ⁴⁻	0.36
[Fe(C ₂ O ₄) ₃] ³⁻ + e ⁻	\rightleftharpoons [Fe(C ₂ O ₄) ₂] ²⁻ + (C ₂ O ₄) ²⁻	0.02
[Fe(edta)] ⁻ + e ⁻	\rightleftharpoons [Fe(edta)] ²⁻	-0.12
[Fe(quin) ₃] + e ⁻	\rightleftharpoons [Fe(quin) ₂] + quin ^{-(a)}	-0.30

^(a)quin⁻ = 5-methyl-8-hydroxyquinolate.



The value of E° for the couple involving the simple aquated ions, shows that Fe^{II}(aq) is thermodynamically stable with respect to hydrogen; which is to say that Fe^{III}(aq) is spontaneously reduced by hydrogen gas (see p. 435). However, under normal circumstances, it is not hydrogen but atmospheric oxygen which is important and, for the process $\frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2\text{O}$, $E^\circ = 1.229\text{ V}$, i.e. oxygen gas is sufficiently strong an oxidizing agent to render [Fe(H₂O)₆]²⁺ (and, indeed, all other Fe^{II} species in Table A) unstable wrt atmospheric oxidation. In practice the oxidation in acidic solutions is slow and, if the pH is increased, the potential for the Fe^{III}/Fe^{II} couple remains fairly constant until the solution becomes alkaline and hydrous Fe₂O₃ (considered here for convenience to be Fe(OH)₃) is precipitated. But here the change is dramatic, as explained below.

The actual potential E of the couple is given by the Nernst equation,

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[\text{Fe}^{\text{II}}]}{[\text{Fe}^{\text{III}}]}$$

where $E = E^\circ$ when all activities are unity. However, once precipitation occurs, the activities of the iron species are far from unity; they are determined by the solubility products of the 2 hydroxides. These are:

$$[\text{Fe}^{\text{II}}][\text{OH}^-]^2 \sim 10^{-14} (\text{mol dm}^{-3})^3 \text{ and } [\text{Fe}^{\text{III}}][\text{OH}^-]^3 \sim 10^{-36} (\text{mol dm}^{-3})^4$$

Therefore when $[\text{OH}^-] = 1 \text{ mol dm}^{-3}$, $\frac{[\text{Fe}^{\text{II}}]}{[\text{Fe}^{\text{III}}]} \sim 10^{22}$

Hence $E \sim 0.771 - 0.05916 \log_{10}(10^{22}) = 0.771 - 1.301 = -0.530\text{ V}$

Thus by making the solution alkaline the sign of E has been reversed and the susceptibility of Fe^{II}(aq) to oxidation (i.e. its reducing power) enormously increased. This is why white, precipitated Fe(OH)₂ and FeCO₃ are rapidly darkened by aerial oxidation and why Fe^{II} in alkaline solution will reduce nitrates to ammonia and copper(II) salts to metallic copper.

Addition of $K_4[Fe^{II}(CN)_6]$ to aqueous Fe^{III} produces the intensely blue precipitate, Prussian blue.^(32a) The X-ray powder pattern and Mössbauer spectrum of this are the same as those of Turnbull's blue which is produced by the converse addition of $K_3[Fe^{III}(CN)_6]$ to aqueous Fe^{II} . By varying the conditions and proportions of the reactants, a whole range of these blue materials can be produced of varying composition with some, which are actually colloidal, described as soluble Prussian blue. They have found application as pigments in the manufacture of inks and paints since their discovery in 1704 and, in 1840, their formation on sensitized paper was utilized in the production of blueprints. It appears that all these materials have the same basic structure. This consists of a cubic lattice of low-spin Fe^{II} and high-spin Fe^{III} ions with cyanide ions lying linearly along the cube edges, and water molecules situated inside the cubes. The intense colour is due to charge-transfer from Fe^{II} to Fe^{III} . Unfortunately, detailed characterizations are bedevilled by difficulties in obtaining satisfactory single crystals and reproducible compositions. Good quality single crystals formulated as $Fe_4[Fe(CN)_6]_3 \cdot xH_2O$ ($x = 14-16$) can be produced by the slow diffusion of H_2O vapour into a solution of Fe^{III} and $[Fe(CN)_6]^{4-}$ in conc HCl. This has the same basic lattice but with some of the Fe^{II} and CN^- sites occupied by water. Less delicate methods lead to the absorption of alkali metal ions (particularly K^+) and to formulations such as $M^I Fe^{II} Fe^{III} (CN)_6 \cdot xH_2O$. The same structure motif is found in $Fe^{III} Fe^{III} (CN)_6$ and in the virtually white, readily oxidizable $K_2 Fe^{II} Fe^{II} (CN)_6$, the former having no counter cations while the K^+ ions of the latter fill all the lattice cubes. Having all their iron atoms in a uniform oxidation state, however, these two compounds lack the intense colour of the Prussian blues.

It is possible to replace 1 CN^- in the hexacyanoferrate(II) ion with H_2O , CO , NO_2^- , and, most importantly, with NO^+ . The "nitroprusside" ion $[Fe(CN)_5NO]^{2-}$ can be produced by the

action of 30% nitric acid on either $[Fe(CN)_6]^{4-}$ or $[Fe(CN)_6]^{3-}$. That it formally contains Fe^{II} and NO^+ (rather than Fe^{III} and NO) is evident from its diamagnetism, although Mössbauer studies indicate that there is appreciable π delocalization of charge from the t_{2g} orbitals of the Fe^{II} to the nitrosyl and cyanide groups. The red colour of $[Fe(CN)_5(NOS)]^{4-}$, formed by the addition of sulfide ion, is used in a common qualitative test for sulfur. Another qualitative test involving an iron nitrosyl is the "brown ring" test for NO_3^- , using iron(II) sulfate and conc H_2SO_4 in which NO is produced. The brown colour, which appears to be due to charge-transfer, evidently arises from a cationic iron nitrosyl complex which has a magnetic moment ~ 3.9 BM; it is therefore formulated as $[Fe(NO)(H_2O)_5]^{2+}$ in which the iron can be considered formally to be in the +1 oxidation state.

Roussin's "red" and "black" salts, formulated respectively as $K_2[Fe_2(NO)_4S_2]$ and $K[Fe_4(NO)_7S_3]$, are obtained by the action of NO on Fe^{II} in the presence of S^{2-} and are structurally interesting. In both cases the iron atoms are pseudo-tetrahedrally coordinated (Fig. 25.6) and, though the assignment of formal oxidation states has only doubtful significance, their diamagnetism and the presence of rather short $Fe-Fe$ distances are indicative of some direct metal-metal interaction. The $[NEt_4]^+$ black salt in acetonitrile solution has been reversibly reduced electrochemically⁽³³⁾ to $[Fe_4(NO)_7S_3]^{n-}$ ($n = 1-4$), the $n = 2$ and 3 compounds being isolated and shown to retain essentially the same structure, though somewhat expanded, as expected with the extra charge.

These, and related, iron nitrosyl compounds have excited considerable interest because of their biological activity.⁽³⁴⁾ Nitroprusside induces muscle relaxation and is therefore used to control high blood pressure. Roussin's black salt has antibacterial activity under conditions relevant to

³³ S. D'ADDARIO, F. DEMARTIN, L. GROSSI, M. C. IAPALUCCI, F. LASCHI, G. LONGONI and F. ZANELLO, *Inorg. Chem.* **32**, 1153-60 (1993).

³⁴ A. R. BUTLER, C. GLIDEWELL and S. M. GLIDEWELL, *Polyhedron*, **11**, 591-6 (1992).

^{32a} K. R. DUNBAR and R. A. HEINTZ, *Prog. Inorg. Chem.* **45**, 283-391 (1997).

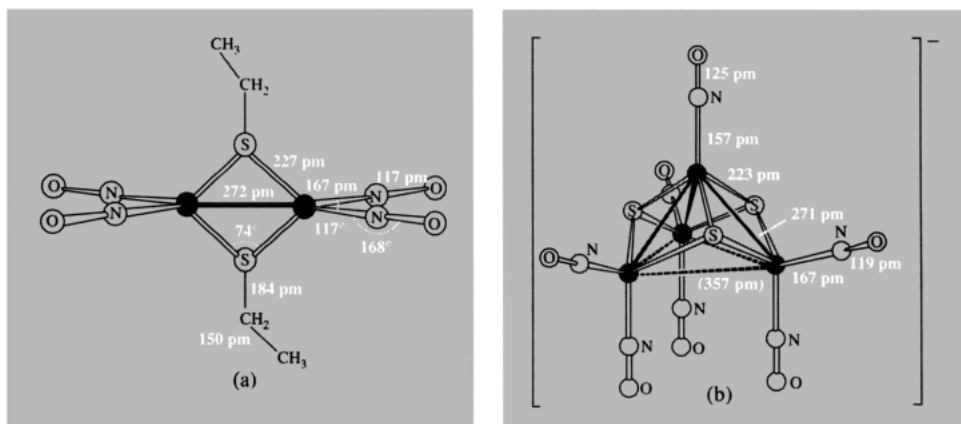
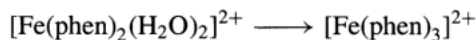


Figure 25.6 The structure of Roussin's salts: (a) the ethyl ester $[\text{Fe}(\text{NO})_2\text{SET}]_2$ of the red salt showing pseudo-tetrahedral coordination of each iron ($\text{Fe}-\text{Fe} = 272 \text{ pm}$), and (b) the anion of the black salt $\text{Cs}[\text{Fe}_4(\text{NO})_7\text{S}_3] \cdot \text{H}_2\text{O}$ showing a pyramid of 4 Fe atoms with an S atom above each of its three non-horizontal faces ($\text{Fe}_{\text{apex}}-\text{Fe}_{\text{base}} = 271 \text{ pm}$, $\text{Fe}_{\text{base}} \cdots \text{Fe}_{\text{base}} 357 \text{ pm}$). (The anion may alternatively be viewed as an Fe_3S_3 ring with the "chair" conformation.) Note that even the short Fe-Fe distances are appreciably greater than the Fe-Fe "single-bond" distance of $\sim 250 \text{ pm}$.

food-processing, while some of the red esters promote the activity of certain environmental carcinogens.

In addition to high-spin octahedral complexes with magnetic moments in excess of 5 BM, and diamagnetic, low-spin octahedral complexes, Fe^{II} affords further examples of high-spin/low-spin transitions within a given compound (see Panel, p. 1096). It has already been noted that a change from high-spin to low-spin accompanies the change,



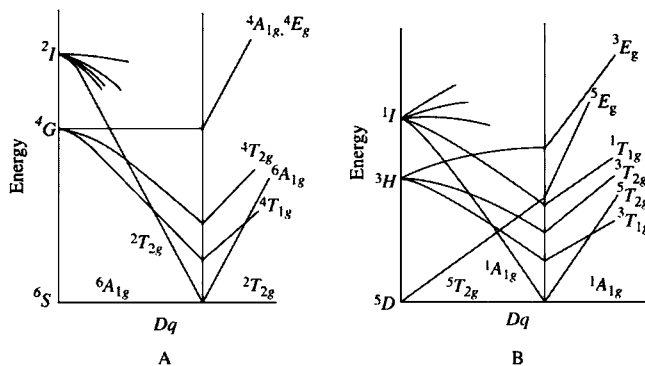
so it is no great surprise that spin transitions have been found in $[\text{Fe}(\text{phen})_2\text{X}_2]$ ($\text{X} = \text{NCS}$, NCS_e) complexes and their bipy analogues. These evidently lie just to the high-field side of the crossover since at temperatures below -125°C the compounds are almost diamagnetic (what paramagnetism there is is probably due to impurity), while at some temperature between -125°C and -75°C depending on the compound, the moment quite suddenly rises to over 5 BM. Confirmation of the transition in these and other Fe^{II} complexes has been provided by electronic and Mössbauer spectroscopy.

Apart from compounds such as $[\text{RuCl}_2\text{-(PPh}_3)_3]$, which is square pyramidal because the sixth coordinating position is stereochemically blocked, Ru^{II} compounds (and also Os^{II} compounds) are octahedral and diamagnetic. $[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$ can be prepared in aqueous solution by electrolytic reduction of $[\text{RuCl}_5(\text{H}_2\text{O})]^{2-}$ using Pt/H_2 and, though readily oxidized to Ru^{III} (p. 1088), has been isolated and characterized⁽²⁷⁾ in the pink $[\text{Ru}(\text{H}_2\text{O})_6](\text{tos})_2$ and the sulfates $\text{M}_2[\text{Ru}(\text{H}_2\text{O})_6](\text{SO}_4)_2$ ($\text{M} = \text{Rb}$, NH_4). The cyano complexes $[\text{Ru}(\text{CN})_6]^{4-}$ and $[\text{Ru}(\text{CN})_5\text{NO}]^{2-}$, analogous to their iron counterparts, are also known but the most notable compounds of Ru^{II} are undoubtedly its complexes with Group 15 donor ligands, such as the amines and nitrosyls.

$[\text{Ru}(\text{NH}_3)_6]^{2+}$ and corresponding tris chelates with en, bipy and phen, etc., are obtained from " RuCl_3 " with Zn powder as a reducing agent. The hexammine is a strongly reducing substance and $[\text{Ru}(\text{bipy})_3]^{2+}$, although thermally very stable, is capable of photochemical excitation involving the promotion of an electron from a molecular orbital of essentially metal character to one of an essentially ligand character, after which its oxidation is possible. A number of similar

Spin Equilibria^(35–38)

Because the d-orbitals of a metal in an octahedral complex split into t_{2g} and e_g^* sets (p. 922), each of the d^4 – d^7 configurations can exist in either high-spin or low-spin configurations, depending on whether the energy (P) required to force spin-pairing is greater or smaller than the orbital splitting (Δ_0 or $10Dq$). This is illustrated in the energy level diagrams (Figs. A and B) for d^5 and d^6 ions where in each case at a critical value of Δ_0 (the crossover point), the ground terms of the high- and low-spin configurations (${}^6A_{1g}$ and ${}^2T_{2g}$ respectively for d^5 , ${}^5T_{2g}$ and ${}^1A_{1g}$ for d^6) are equal. Close to the crossover point both terms are thermally accessible and a Boltzmann distribution of molecules between the two states can be envisaged.



Energy level diagrams for, A d^5 ions and B d^6 ions.

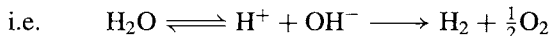
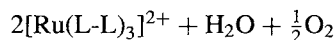
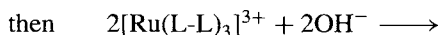
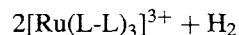
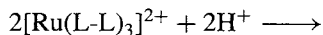
This simple explanation accounts quite well for a variety of dithiocarbamate complexes of iron(III) whose magnetic moments rise gradually from about 2.3 BM (corresponding to low-spin d^5) at very low temperatures to > 4 BM (corresponding to roughly equal populations in the two states) above room temperature.

However, the emptying of the e_g^* orbitals in changing from high- to low-spin allows a shortening of metal-ligand distances with a corresponding increase in Δ_0 . Such a situation does not correspond to the crossover point since the two isomers occupy different positions on the Δ_0 axis. In solutions, conversion of one isomer to the other is usually facile and equilibrium readily established. In solids, on the other hand, molecules are coupled by lattice vibrations and the conversion is often accompanied by a change of phase. The iron(II) compound $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ is a good example of this, the change in magnetic moment being far too abrupt to be accounted for by a simple Boltzmann distribution between thermally accessible spin states.

Spin equilibria have been investigated by bulk magnetic measurements, X-ray crystallography, vibrational, electronic, Mössbauer, esr and nmr spectroscopy and also at high pressures. Besides their obvious intrinsic interest, they have biological relevance because of the change in spin when haemoglobin is oxygenated (p. 1099). Geologically, the high-spin iron(II) in minerals such as olivine (p. 347) becomes low-spin under high pressure in the earth's mantle. Since some spin-transitions can be induced optically, there are also possible light storage applications.

complexes with substituted bipyridyl ligands luminesce in visible light,⁽³⁹⁾ and considerable effort is being devoted to preparing suitable derivatives which could be used to catalyze the

photolytic decomposition of water, with a view to the conversion of solar energy into hydrogen fuel.



³⁵ L. L. MARTIN, R. L. MARTIN and A. M. SARGESON, *Polyhedron* **13**, 1969–80 (1994).

³⁶ E. KÖNIG, *Structure and Bonding* **76**, 51–152 (1991).

³⁷ H. TOFLUND, *Coord. Chem. Revs.* **94**, 67–108 (1989).

³⁸ J. K. BEATTY, *Adv. Inorg. Chem.* **32**, 1–53 (1988).

³⁹ E. KRAUSZ and J. FERGUSON, *Prog. Inorg. Chem.* **37**, 293–390 (1989).

The pentaammine derivative, $[\text{Ru}(\text{NH}_3)_5\text{N}_2]^{2+}$, when prepared in 1965 by the reduction of aqueous RuCl_3 with N_2H_4 , was the first dinitrogen complex to be produced (p. 414). It contains the linear Ru–N–N group ($\nu_{(\text{N}-\text{N})} = 2140 \text{ cm}^{-1}$). The dinuclear derivative $[(\text{NH}_3)_5\text{Ru}-\text{N}-\text{N}-\text{Ru}(\text{NH}_3)_5]^{4+}$ with a linear Ru–N–N–Ru bridge ($\nu_{(\text{N}-\text{N})} = 2100 \text{ cm}^{-1}$ compared to 2331 cm^{-1} for N_2 itself) is also known (see pp. 414 and 1035 for a fuller discussion of the significance of N_2 complexes).

The nitrosyl complex $[\text{Ru}(\text{NH}_3)_5\text{NO}]^{3+}$, which is obtained by the action of HNO_2 on $[\text{Ru}(\text{NH}_3)_6]^{2+}$, is isoelectronic with $[\text{Ru}(\text{NH}_3)_5\text{N}_2]^{2+}$ and is typical of a whole series of Ru^{II} nitrosyls.^(11,21) They are prepared using reagents such as HNO_3 and NO_2^- and are invariably mononitrosyls, the 1 NO apparently sufficing to satisfy the π -donor potential of Ru^{II} . The RuNO group is characterized by a short Ru–N distance in the range 171–176 pm, and a stretching mode $\nu_{(\text{N}-\text{O})}$ in the range 1930–1845 cm^{-1} , consistent with the formulation $\text{Ru}^{\text{II}}=\overset{+}{\text{N}}=\text{O}$. The other ligands making up the octahedral coordination include halides, O-donor anions, and neutral, mainly Group 15 donor ligands.

The stability of ruthenium nitrosyl complexes poses a practical problem in the processing of wastes from nuclear power stations. ^{106}Ru is a major fission product of uranium and plutonium and is a β^- and γ emitter with a half-life of 1 year (374d). The processing of nuclear wastes depends largely on the solvent extraction of nitric acid media, using tri-*n*-butyl phosphate (TBP) as the solvent (p. 1261). In the main, the uranium and plutonium enter the organic phase while fission products such as Cs, Sr and lanthanides remain in the aqueous phase. Unfortunately, by this procedure Ru is less effectively removed from the U and Pu than any other contaminant. The reason for this problem is the coordination of TBP to stable ruthenium nitrosyl complexes which are formed under these conditions. This confers on the ruthenium an appreciable solubility in the organic phase, thereby necessitating several extraction cycles for its removal.

Osmium(II) forms no hexaaquo complex and $[\text{Os}(\text{NH}_3)_6]^{2+}$, which may possibly be present in potassium/liquid NH_3 solutions, is also unstable. $[\text{Os}(\text{NH}_3)_5\text{N}_2]^{2+}$ and other dinitrogen complexes are known but only ligands with good π -acceptor properties, such as CN^- , bipy, phen, phosphines and arsines, really stabilize Os^{II} , and these form complexes similar to their Ru^{II} analogues.

Mixed Valence Compounds of Ruthenium⁽⁴⁰⁾

Ruthenium provides more examples of dinuclear compounds in which the metal is present in a mixture of oxidation states (or in a non-integral oxidation state) than any other element.

Heating $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ in acetic acid/acetic anhydride under reflux yields brown $[\text{Ru}_2(\text{O}_2\text{CCH}_3)_4]\text{Cl}$ (*cf* Os p. 1091) in which the metals are linked by four acetate bridges in the manner of Cr^{II} and Mo^{II} carboxylates (p. 1033). In this and analogous carboxylates, Ru = Ru 224–230 pm with magnetic moments indicative of three unpaired electrons; this can be explained by the assumption that the π^* and δ^* orbitals (see Fig. 23.14) are close enough in energy to afford the $\pi^*\delta^*$ configuration.⁽⁴¹⁾ Treatment of $[\text{Ru}(\text{NH}_3)_6]^{2+}$ in conc. HCl produces the intensely coloured *ruthenium blue*, $[(\text{NH}_3)_5\text{Ru}(\mu\text{-Cl})_3\text{Ru}(\text{NH}_3)_5]^{2+}$ (Ru–Ru 275.3 pm). In all these cases the metal atoms are indistinguishable and are assigned an oxidation state of 2.5.

The “Creutz–Taube” anion, $[(\text{NH}_3)_5\text{Ru}\{\text{N}(\text{CH}=\text{CH})_2\text{N}\}\text{Ru}(\text{NH}_3)_5]^{5+}$ displays more obvious redox properties, yielding both 4+ and 6+ species, and much interest has focused on the extent to which the pyrazine bridge facilitates electron transfer. A variety of spectroscopic studies supports the view that low-energy electron tunnelling across the bridge delocalizes the charge, making the 5+ ion symmetrical. Other complexes, such as the anion $[(\text{CN})_5\text{Ru}^{\text{II}}(\mu\text{-CN})\text{Ru}^{\text{III}}(\text{CN})_5]^-$, are asymmetric

⁴⁰ R. J. CRUTCHLEY, *Adv. Inorg. Chem.* **41**, 273–325 (1994).

⁴¹ F. A. COTTON and R. A. WALTON, pp. 399–430 *Multiple Bonds between Metal Atoms*, Clarendon Press, Oxford (1993).