

Table 25.4 Electronic spin-states of iron

Spin quantum number (S)	Ion	Electronic configuration	Typical compounds
0 (diamagnetic)	Low-spin Fe <sup>II</sup>	$t_{2g}^6$	K <sub>4</sub> [Fe(CN) <sub>6</sub> ].3H <sub>2</sub> O HbO <sub>2</sub> (oxygenated haemoglobin)
$\frac{1}{2}$ (1 unpaired e <sup>-</sup> )	Low-spin Fe <sup>III</sup>	$t_{2g}^5$	K <sub>3</sub> [Fe(CN) <sub>6</sub> ], HbCN [Fe(diars)(CO) <sub>2</sub> I] [Fe(diars) <sub>2</sub> Cl <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub> Ba[FeO <sub>4</sub> ] [Fe(S <sub>2</sub> CNR <sub>2</sub> ) <sub>2</sub> Cl]
	Low-spin Fe <sup>I</sup>	$t_{2g}^6 e_g^1$	
1 (2 unpaired e <sup>-</sup> )	Low-spin Fe <sup>IV</sup>	$t_{2g}^4 e_g^2$	Ba[FeO <sub>4</sub> ] [Fe(S <sub>2</sub> CNR <sub>2</sub> ) <sub>2</sub> Cl]
	Tetrahedral Fe <sup>VI</sup>	$e^3$	
$\frac{3}{2}$ (3 unpaired e <sup>-</sup> )	Distorted square pyramidal Fe <sup>III</sup>	$d_{x^2-y^2}^2 d_{yz}^1 d_{xz}^1 d_{z^2}^1$	
	High-spin Fe <sup>II</sup>	$t_{2g}^4 e_g^2$	[Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup> , deoxyhaemoglobin
$\frac{5}{2}$ (5 unpaired e <sup>-</sup> )	High-spin Fe <sup>III</sup>	$t_{2g}^3 e_g^2$	[Fe(acac) <sub>3</sub> ], iron-transport proteins

a remarkably wide range of oxidation states, particularly for Ru and Os, and, although it is now evident that as the size of the atoms decreases across each period the tendency to form compounds with high coordination numbers is diminishing, Os has a greater tendency than Ru to adopt a coordination number of 6 in the higher oxidation states. Thus OsO<sub>4</sub> expands its coordination sphere far more readily than RuO<sub>4</sub> to form complexes such as [OsO<sub>4</sub>(OH)<sub>2</sub>]<sup>2-</sup>, and Os has no 4-coordinate analogue of [RuO<sub>4</sub>]<sup>2-</sup>.

Iron is notable for the range of electronic spin states to which it gives rise. The values of *S* which are found include every integral and half-integral value from 0 to  $\frac{5}{2}$  i.e. every value possible for a d-block element (Table 25.4).

## 25.3 Compounds of Iron<sup>(10)</sup>, Ruthenium<sup>(11)</sup> and Osmium

The borides (p. 145), carbides (pp. 297, 1074), and nitrides (p. 417) have been discussed previously. Binary hydrides are not formed but prolonged heating of powdered Mg and Fe under a high pressure of H<sub>2</sub> yields MgFeH<sub>6</sub> containing the octahedral hydrido anion, [FeH<sub>6</sub>]<sup>4-</sup> which satisfies the 18-electron rule.

### 25.3.1 Oxides and other chalcogenides

The principal oxides of the elements<sup>(12)</sup> of this group are given in Table 25.5.

Table 25.5 The oxides of iron, ruthenium and osmium

Oxidation state	+8	+4	+3	+2
Fe			Fe <sub>2</sub> O <sub>3</sub>	FeO
Ru		RuO <sub>4</sub>	RuO <sub>2</sub>	
Os		OsO <sub>4</sub>	OsO <sub>2</sub>	

Three oxides of iron may be distinguished, but are all subject to nonstoichiometry. The lowest is FeO which is obtained by heating iron in a low partial pressure of O<sub>2</sub> or as a fine, black pyrophoric powder by heating iron(II) oxalate *in vacuo*. Below about 575°C it is unstable towards disproportionation into Fe and Fe<sub>3</sub>O<sub>4</sub> but can be obtained as a metastable phase if cooled rapidly. It has a rock-salt structure but is always deficient in iron, with a homogeneity range of Fe<sub>0.84</sub>O to Fe<sub>0.95</sub>O. Treatment of any aqueous solution of Fe<sup>II</sup> with alkali produces a flocculent precipitate. If air is rigorously excluded this is the virtually white Fe(OH)<sub>2</sub> which is almost entirely basic in character, dissolving readily in non-oxidizing acids to give Fe<sup>II</sup> salts but

<sup>10</sup> *Chemistry of Iron* (J. SILVER, ed.), Blackie, London, 1993, 306 pp.

<sup>11</sup> E. A. SEDDON and K. R. SEDDON, *The Chemistry of Ruthenium*, Elsevier, Amsterdam, 1984, 1374 pp.

<sup>12</sup> U. SCHWERTMANN and R. M. CORNELL, *Iron Oxides in the Laboratory*, VCH, Weinheim, 1991, 137 pp.

showing only slight reactivity towards alkali. It gradually decomposes, however, to  $\text{Fe}_3\text{O}_4$  with evolution of hydrogen and in the presence of oxygen darkens rapidly and eventually forms the reddish-brown hydrated iron(III) oxide.  $\text{Fe}_3\text{O}_4$  is a mixed  $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$  oxide which can be obtained by partial oxidation of  $\text{FeO}$  or, more conveniently, by heating  $\text{Fe}_2\text{O}_3$  above about  $1400^\circ\text{C}$ . It has the inverse spinel structure. Spinel is of the form  $\text{M}^{\text{II}}\text{M}_2^{\text{III}}\text{O}_4$  and in the normal spinel (p. 247) the oxide ions form a ccp lattice with  $\text{M}^{\text{II}}$  ions occupying tetrahedral sites and  $\text{M}^{\text{III}}$  ions octahedral sites. In the inverse structure half the  $\text{M}^{\text{III}}$  ions occupy tetrahedral sites, with the  $\text{M}^{\text{II}}$  and the other half of the  $\text{M}^{\text{III}}$  occupying octahedral sites.<sup>†</sup>  $\text{Fe}_3\text{O}_4$  occurs naturally as the mineral magnetite or lodestone. It is a black, strongly ferromagnetic substance (or, more strictly, "ferromagnetic" — see p. 1081), insoluble in water and acids. Its electrical properties are not simple, but its rather high conductivity may be ascribed to electron transfer between  $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$ .

$\text{Fe}_2\text{O}_3$  is known in a variety of modifications of which the more important are the  $\alpha$ - and  $\gamma$ -forms. When aqueous solutions of iron(III) are treated with alkali, a gelatinous reddish-brown precipitate of hydrated oxide is produced (this is amorphous to X-rays and is not simple  $\text{Fe}(\text{OH})_3$ , but probably  $\text{FeO}(\text{OH})$ ); when heated to  $200^\circ\text{C}$ , this gives the red-brown  $\alpha$ - $\text{Fe}_2\text{O}_3$ . Like  $\text{V}_2\text{O}_5$  and  $\text{Cr}_2\text{O}_3$  this has the corundum structure (p. 243) in which the oxide ions are hcp and the metal ions occupy octahedral sites. It occurs naturally as the mineral haematite and, besides its overriding importance as a source of the metal (p. 1072), it is used (a) as a pigment, (b) in the preparation of rare earth/iron garnets and

other ferrites (p. 1081), and (c) as a polishing agent — jewellers' rouge. The second variety  $\gamma$ - $\text{Fe}_2\text{O}_3$  is metastable and is obtained by careful oxidation of  $\text{Fe}_3\text{O}_4$ , like which it is cubic and ferrimagnetic. If heated *in vacuo* it reverts to  $\text{Fe}_3\text{O}_4$  but heating in air converts it to  $\alpha$ - $\text{Fe}_2\text{O}_3$ . It is the most widely used magnetic material in the production of magnetic recording tapes.

The interconvertibility of  $\text{FeO}$ ,  $\text{Fe}_3\text{O}_4$  and  $\gamma$ - $\text{Fe}_2\text{O}_3$  arises because of their structural similarity. Unlike  $\alpha$ - $\text{Fe}_2\text{O}_3$ , which is based on a hcp lattice of oxygen atoms, these three compounds are all based on ccp lattices of oxygen atoms. In  $\text{FeO}$ ,  $\text{Fe}^{\text{II}}$  ions occupy the octahedral sites and nonstoichiometry arises by oxidation, when some  $\text{Fe}^{\text{II}}$  ions are replaced by two-thirds their number of  $\text{Fe}^{\text{III}}$  ions. Continued oxidation produces  $\text{Fe}_3\text{O}_4$  in which the  $\text{Fe}^{\text{II}}$  ions are in octahedral sites, but the  $\text{Fe}^{\text{III}}$  ions are distributed between both octahedral and tetrahedral sites. Eventually, oxidation leads to  $\gamma$ - $\text{Fe}_2\text{O}_3$  in which all the cations are  $\text{Fe}^{\text{III}}$  which are randomly distributed between octahedral and tetrahedral sites. The oxygen lattice remains intact throughout but contracts somewhat as the number of iron atoms which it accommodates diminishes.

Ruthenium and osmium have no oxides comparable to those of iron and, indeed, the lowest oxidation state in which they form oxides is +4.  $\text{RuO}_2$  is a blue to black solid, obtained by direct action of the elements at  $1000^\circ\text{C}$ , and has the rutile (p. 961) structure. The intense colour has been suggested as arising from the presence of small amounts of Ru in another oxidation state, possibly +3.  $\text{OsO}_2$  is a yellowish-brown solid, usually prepared by heating the metal at  $650^\circ\text{C}$  in NO. It, too, has the rutile structure.

The most interesting oxides of Ru and Os, however, are the volatile, yellow tetroxides,  $\text{RuO}_4$  (mp  $25^\circ\text{C}$ , bp  $130^\circ\text{C}^{(13)}$ ) and  $\text{OsO}_4$  (mp  $40^\circ\text{C}$ , bp  $130^\circ\text{C}$ ). They are tetrahedral molecules and the latter is perhaps the best-known compound of osmium. It is produced by aerial oxidation of the heated metal or by oxidizing other compounds of osmium with

<sup>†</sup> Although  $\text{Fe}_3\text{O}_4$  is an inverse spinel it will be recalled that  $\text{Mn}_3\text{O}_4$  (pp. 1048–9) is normal. This contrast can be explained on the basis of crystal field stabilization. Manganese(II) and  $\text{Fe}^{\text{III}}$  are both  $d^5$  ions and, when high-spin, have zero CFSE whether octahedral or tetrahedral. On the other hand,  $\text{Mn}^{\text{III}}$  is a  $d^4$  and  $\text{Fe}^{\text{II}}$  a  $d^6$  ion, both of which have greater CFSEs in the octahedral rather than the tetrahedral case. The preference of  $\text{Mn}^{\text{III}}$  for the octahedral sites therefore favours the spinel structure, whereas the preference of  $\text{Fe}^{\text{II}}$  for these octahedral sites favours the inverse structure.

<sup>13</sup> Y. KODA, *J. Chem. Soc., Chem. Commun.*, 1347–8 (1986).

nitric acid. It dissolves in aqueous alkali to give  $[\text{Os}^{\text{VIII}}\text{O}_4(\text{OH})_2]^{2-}$  and oxidizes conc (but not dil) hydrochloric acid to  $\text{Cl}_2$ , being itself reduced to  $\text{H}_2\text{OsCl}_6$ . It is used in organic chemistry to oxidize  $\text{C}=\text{C}$  bonds to *cis*-diols and is also employed as a biological stain. Unfortunately, it is extremely toxic and its volatility renders it particularly dangerous.  $\text{RuO}_4$  is, appreciably less stable and will oxidize dil as well as conc  $\text{HCl}$ , while in aqueous alkali it is reduced to  $[\text{Ru}^{\text{VI}}\text{O}_4]^{2-}$ . If heated above  $100^\circ\text{C}$  it decomposes explosively to  $\text{RuO}_2$  and is liable to do the same at room temperature if brought into contact with oxidizable organic solvents such as ethanol. Its preparation obviously requires stronger oxidizing agents than that of  $\text{OsO}_4$ ; nitric acid alone will not suffice and instead the action of  $\text{KMnO}_4$ ,  $\text{KIO}_4$  or  $\text{Cl}_2$  on acidified solutions of a convenient Ru compound is used.

The sulfides are fewer in number than the oxides and favour lower metal oxidation states. Iron forms 3 sulfides (p. 680).  $\text{FeS}$  is a grey, nonstoichiometric material, obtained by direct action of the elements or by treating aqueous  $\text{Fe}^{\text{II}}$  with alkali metal sulfide. It has a NiAs structure (p. 679) in which each metal atom is octahedrally surrounded by anions but is also quite close to 2 other metal atoms. It oxidizes readily in air and dissolves in aqueous acids with evolution of  $\text{H}_2\text{S}$ .  $\text{FeS}_2$  can be prepared by heating  $\text{Fe}_2\text{O}_3$  in  $\text{H}_2\text{S}$  but is most commonly encountered as the yellow mineral pyrites. This does not contain  $\text{Fe}^{\text{IV}}$  but is composed of  $\text{Fe}^{\text{II}}$  and  $\text{S}_2^{2-}$  ions in a distorted rock-salt arrangement, its diamagnetism indicating low-spin  $\text{Fe}^{\text{II}}(d^6)$ . It is very unreactive unless heated, when it gives  $\text{Fe}_2\text{O}_3 + \text{SO}_2$  in air, or  $\text{FeS} + \text{S}$  in a vacuum.  $\text{Fe}_2\text{S}_3$  is the unstable black precipitate resulting when aqueous  $\text{Fe}^{\text{III}}$  is treated with  $\text{S}^{2-}$ , and is rapidly oxidized in moist air to  $\text{Fe}_2\text{O}_3$  and  $\text{S}$ .

Ruthenium and osmium form only disulfides. These have the pyrite structure and are diamagnetic semiconductors; this implies that they contain  $\text{M}^{\text{II}}$ .  $\text{RuSe}_2$ ,  $\text{RuTe}_2$ ,  $\text{OsSe}_2$  and  $\text{OsTe}_2$  are very similar. All 6 dichalcogenides are obtained directly from the elements.

### 25.3.2 Mixed metal oxides and oxoanions<sup>(14)</sup>

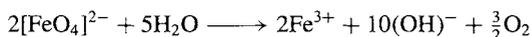
The “ferrites” and “garnets” of iron are mixed metal oxides of considerable technological importance. They are obtained by heating  $\text{Fe}_2\text{O}_3$  with the carbonate of the appropriate metal. The ferrites have the general form  $\text{M}^{\text{II}}\text{Fe}_2^{\text{III}}\text{O}_4$ . Some adopt the *normal* spinel structure and others the *inverse* spinel structure (p. 248) as just described for  $\text{Fe}_3\text{O}_4$  (which can itself be regarded as the ferrite  $\text{Fe}^{\text{II}}\text{Fe}_2^{\text{III}}\text{O}_4$ ). In inverse spinels the unpaired electrons of all the cations in octahedral sites ( $\text{M}^{\text{II}}$  and half the  $\text{M}^{\text{III}}$ ) are magnetically coupled parallel to give a ferromagnetic sublattice, while the unpaired electrons of all the cations in tetrahedral sites (the remaining  $\text{M}^{\text{III}}$ ) are similarly but independently coupled parallel to give a second ferromagnetic sublattice. The spins of one sublattice, however, are antiparallel to those of the other. If the cations in the octahedral sites have the same total number of unpaired electrons as those in the tetrahedral sites, then the effects of 2 ferromagnetic sublattices are mutually compensating and “antiferromagnetism” results; but where the sublattices are not balanced then a type of ferromagnetism known as ferrimagnetism results, the explanation of which was first given by L. Néel in 1948 (Nobel Prize for Physics, 1970). Important applications of inverse spinel ferrites are as cores in high-frequency transformers (where they have the advantage over metals of being free from eddy-current losses), and in computer memory systems.

So-called “hexagonal ferrites” such as  $\text{BaFe}_{12}\text{O}_{19}$  are ferrimagnetic and are used to construct permanent magnets. A third type of ferrimagnetic mixed oxides are the garnets,  $\text{M}_3^{\text{III}}\text{Fe}_5\text{O}_{12}$ , of which the best known is yttrium iron garnet (YIG) used as a microwave filter in radar.

Mixed oxides of  $\text{Fe}^{\text{IV}}$  such as  $\text{M}_4^{\text{I}}\text{FeO}_4$  and  $\text{M}_2^{\text{II}}\text{FeO}_4$  can be prepared by heating  $\text{Fe}_2\text{O}_3$  with the appropriate oxide or hydroxide in

<sup>14</sup> A. F. WELLS, *Structural Inorganic Chemistry*, 5th edn., Complex oxides, pp. 575–625, Oxford University Press, Oxford, 1984.

oxygen. These do not contain discrete  $[\text{FeO}_4]^{4-}$  anions and, as was seen above, mixed oxides of  $\text{Fe}^{\text{III}}$  are generally based on close-packed oxide lattices with no iron-containing anions. However, oxoanions of iron are known and are usually based on the  $\text{FeO}_4$  tetrahedron.<sup>†</sup> Thus for iron(III),  $\text{Na}_5\text{FeO}_4$ ,  $\text{K}_6[\text{Fe}_2\text{O}_6]$  (2 edge-sharing tetrahedra), and  $\text{Na}_{14}[\text{Fe}_6\text{O}_{16}]$  (rings of 6 corner-sharing tetrahedra), have been prepared and more recently, for iron(V),  $\text{K}_3[\text{FeO}_4]$ .<sup>(15)</sup> But the best-known oxoanion of iron is the ferrate(VI) prepared by oxidizing a suspension of hydrous  $\text{Fe}_2\text{O}_3$  in conc alkali with chlorine, or by the anodic oxidation of iron in conc alkali. The tetrahedral  $[\text{FeO}_4]^{2-}$  ion is red-purple and is an extremely strong oxidizing agent. It oxidizes  $\text{NH}_3$  to  $\text{N}_2$  even at room temperature and, although it can be kept for a period of hours in alkaline solution, in acid or neutral solutions it rapidly oxidizes the water, so liberating oxygen:



The distinction between the first member of the group and the two heavier members, which was seen to be so sharp in the early groups of transition metals, is much less obvious here. The only unsubstituted, discrete oxoanions of the heavier pair of metals are the tetrahedral  $[\text{Ru}^{\text{VII}}\text{O}_4]^-$  and  $[\text{Ru}^{\text{VI}}\text{O}_4]^{2-}$ . This behaviour is akin to that of iron or, even more, to that of manganese, whereas in the osmium analogues the metal always increases its coordination number by the attachment of extra  $\text{OH}^-$  ions. If  $\text{RuO}_4$  is dissolved in cold dilute  $\text{KOH}$ , or aqueous  $\text{K}_2\text{RuO}_4$  is oxidized by chlorine, virtually black crystals of  $\text{K}[\text{Ru}^{\text{VII}}\text{O}_4]$  ("perruthenate") are deposited. These are unstable unless dried and are reduced by water, especially if alkaline, to the orange

$[\text{Ru}^{\text{VI}}\text{O}_4]^{2-}$  ("ruthenate") by a mechanism which is thought to involve octahedral intermediates of the type  $[\text{RuO}_4(\text{OH})_2]^{3-}$  and  $[\text{RuO}_4(\text{OH})_2]^{2-}$ .  $\text{K}_2[\text{RuO}_4]$  is obtained by fusing  $\text{Ru}$  metal with  $\text{KOH}$  and  $\text{KNO}_3$ .

By contrast, dissolution of  $\text{OsO}_4$  in cold aqueous  $\text{KOH}$  produces deep-red crystals of  $\text{K}_2[\text{Os}^{\text{VIII}}\text{O}_4(\text{OH})_2]$  ("perosmate"), which is easily reduced to the purple "osmate",  $\text{K}_2[\text{Os}^{\text{VI}}\text{O}_2(\text{OH})_4]$ . The anions in both cases are octahedral with, respectively, *trans*  $\text{OH}$  and *trans*  $\text{O}$  groups.

By heating the metal with appropriate oxides or carbonates of alkali or alkaline earth metals, a number of mixed oxides of  $\text{Ru}$  and  $\text{Os}$  have been made. They include  $\text{Na}_5\text{Os}^{\text{VII}}\text{O}_6$ ,  $\text{Li}_6\text{Os}^{\text{VI}}\text{O}_6$  and the "ruthenites",  $\text{M}^{\text{II}}\text{Ru}^{\text{IV}}\text{O}_3$ , in all of which the metal is situated in octahedral sites of an oxide lattice.  $\text{Ru}^{\text{V}}$  (octahedral) has now also been established by  $^{99}\text{Ru}$  Mössbauer spectroscopy as a common stable oxidation state in mixed oxides such as  $\text{Na}_3\text{Ru}^{\text{V}}\text{O}_4$ ,  $\text{Na}_4\text{Ru}^{\text{V}}\text{O}_7$ , and the ordered perovskite-type phases  $\text{M}_2^{\text{II}}\text{Ln}^{\text{III}}\text{Ru}^{\text{V}}\text{O}_6$ .

### 25.3.3 Halides and oxohalides

The known halides of this group are listed in Table 25.6. As in the preceding group the highest halide is a heptafluoride, but  $\text{OsF}_7$  (unlike  $\text{ReF}_7$ ) is thermally unstable. It was for many years thought that  $\text{OsF}_8$  existed but the yellow crystalline material to which the formula had been ascribed turned out to be  $\text{OsF}_6$ , the least unstable of the platinum metal hexafluorides. (In view of the propensity of higher fluorides to attack the vessels containing them, to disproportionate and to hydrolyse, it is not surprising that early reports on them sometimes proved to be erroneous.) The highest chloride is  $\text{OsCl}_5$  and, rather unexpectedly perhaps, neither ruthenium nor iron form a chloride in an oxidation state higher than +3. Iron in fact does not form even a fluoride in an oxidation state higher than this and its halides are confined to the +3 and +2 states.

$\text{OsF}_7$  has been obtained as a yellow solid by direct action of the elements at  $600^\circ\text{C}$

<sup>†</sup> An exception is  $\text{K}_3[\text{FeO}_2]$  which contains the linear  $[\text{O}-\text{Fe}^{\text{I}}-\text{O}]^{3-}$  anion (see p. 1166). It is surprisingly prepared as garnet-red crystals when a mixture of  $\text{K}_6[\text{CdO}_4]$  and  $\text{CdO}$  is subjected to prolonged heating at  $450^\circ\text{C}$  in a closed iron cylinder and reacts with the cylinder walls! F. BERNARD and R. HOPPE, *Z. anorg. allg. Chem.* **619**, 969–75 (1993).

<sup>15</sup> R. HOPPE and K. MADER *Z. anorg. allg. Chem.* **586**, 115–24 (1990).

Table 25.6 Halides of iron, ruthenium and osmium (mp/°C)

Oxidation state	Fluorides	Chlorides	Bromides	Iodides
+7	OsF <sub>7</sub> yellow			
+6	RuF <sub>6</sub> dark brown (54°) OsF <sub>6</sub> yellow (33°)			
+5	RuF <sub>5</sub> dark green (86.5°) OsF <sub>5</sub> blue (70°)	OsCl <sub>5</sub> black (d > 160°)		
+4	RuF <sub>4</sub> yellow OsF <sub>4</sub> yellow (230°)	OsCl <sub>4</sub> red (also black form)	OsBr <sub>4</sub> black (d 350°)	
+3	FeF <sub>3</sub> pale green (>1000°) RuF <sub>3</sub> dark brown (d > 650°)	FeCl <sub>3</sub> brown-black (306°) RuCl <sub>3</sub> black (α) dark brown (β) OsCl <sub>3</sub> dark grey (d 450°)	FeBr <sub>3</sub> red-brown (d > 200°) RuBr <sub>3</sub> dark brown (d > 400°)	FeI <sub>3</sub> black RuI <sub>3</sub> black
+2	FeF <sub>2</sub> white (>1000°)	FeCl <sub>2</sub> pale yellow (674°) RuCl <sub>2</sub> brown	FeBr <sub>2</sub> yellow-green (d 684°) RuBr <sub>2</sub> black	OsI <sub>3</sub> black FeI <sub>2</sub> grey RuI <sub>2</sub> blue OsI <sub>2</sub> black
+1				OsI metallic grey

and a pressure of 400 atm, but under less drastic conditions OsF<sub>6</sub> is produced, as is RuF<sub>6</sub>. This latter pair are low-melting, yellow and brown solids, respectively, hydrolysing violently with water and with a strong tendency to disproportionate into F<sub>2</sub> and lower halides. The pentafluorides are both polymeric, easily hydrolysed solids obtained by specific oxidations or reduction of other fluorides, and their structures involve [MF<sub>5</sub>]<sub>4</sub> units in which 4 corner-sharing MF<sub>6</sub> octahedra form a ring (Fig. 25.3).

The tetrafluorides are yellow solids, probably polymeric, and are obtained by reducing RuF<sub>5</sub> with I<sub>2</sub>, and OsF<sub>6</sub> with W(CO)<sub>6</sub>. The tetrachloride and tetrabromide of osmium require pressure as well as heat in their preparations from the

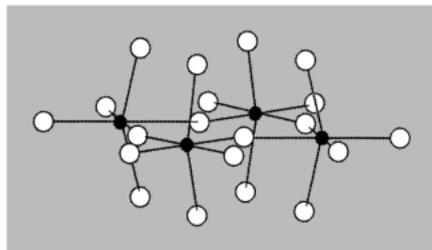
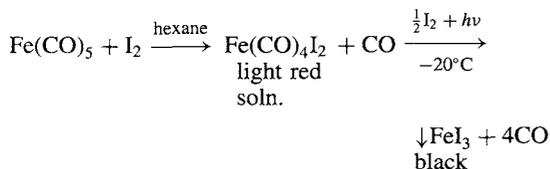


Figure 25.3 Tetrameric pentafluorides of Ru and Os, [M<sub>4</sub>F<sub>20</sub>]. Their structures are similar to, but more distorted than, those of the pentafluorides of Nb and Ta (see Fig. 22.4).

elements and are black solids, the bromide consisting of OsBr<sub>6</sub> octahedra connected by shared edges.

In the +3 and +2 oxidation states those halides of osmium which have been reported are poorly characterized, grey or black solids. The compound obtained by thermal decomposition of  $\text{OsBr}_4$  and previously thought to be  $\text{OsBr}_3$  has since been shown<sup>(16)</sup> to be  $\text{Os}_2\text{OBr}_6$ , the chloride analogue of which is also known. For ruthenium,  $\text{RuCl}_3$  is well known and, as the anhydrous compound, exists in two forms: heating Ru metal at  $330^\circ\text{C}$  in CO and  $\text{Cl}_2$  produces the dark-brown  $\beta$ -form which if heated above  $450^\circ\text{C}$  in  $\text{Cl}_2$  is converted to the black  $\alpha$ -form which is isomorphous with  $\text{CrCl}_3$  (p. 1020). Evaporation of a solution of  $\text{RuO}_4$  in hydrochloric acid in a stream of HCl gas produces red  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ ; aqueous solutions contain both  $[\text{Ru}(\text{H}_2\text{O})_6]^{3+}$  and chloro-substituted species and are easily hydrolysed and oxidized to  $\text{Ru}^{\text{IV}}$ . Where impurities due to such reactions are suspected, conversion back to  $\text{Ru}^{\text{III}}$  chloride can be effected by repeated evaporations to dryness with conc HCl. This gives a uniform though rather poorly characterized product that is widely used as the starting material in ruthenium chemistry.

All the anhydrous +3 and +2 halides of iron are readily obtained, except for iron(III) iodide, where the oxidizing properties of  $\text{Fe}^{\text{III}}$  and the reducing properties of  $\text{I}^-$  lead to thermodynamic instability. It has, however, been prepared<sup>(17)</sup> in mg quantities by the following reaction, with air and moisture rigorously excluded,



The other anhydrous  $\text{FeX}_3$  can be prepared by heating the elements (though in the case of  $\text{FeBr}_3$  the temperature must not rise above  $200^\circ\text{C}$  otherwise  $\text{FeBr}_2$  is formed). The fluoride, chloride and bromide are respectively white, dark

brown and reddish-brown. The crystalline solids contain  $\text{Fe}^{\text{III}}$  ions octahedrally surrounded by halide ions and decompose to  $\text{FeX}_2 + \frac{1}{2}\text{X}_2$  if heated strongly under vacuum.  $\text{FeCl}_3$  sublimes above  $300^\circ\text{C}$  and vapour pressure measurements show the vapour to contain dimeric  $\text{Fe}_2\text{Cl}_6$ , like  $\text{Al}_2\text{Cl}_6$  consisting of 2 edge-sharing tetrahedra. The trifluoride is sparingly soluble, and the chloride and bromide very soluble in water and they crystallize as white  $\text{FeF}_3 \cdot 4\text{H}_2\text{O}$  (converting above  $50^\circ\text{C}$  to the pink trihydrate),<sup>(18)</sup> yellow-brown  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and dark-green  $\text{FeBr}_3 \cdot 6\text{H}_2\text{O}$ . The chloride is probably the most widely used etching material, being particularly important for etching copper in the production of electrical printed circuits. It is also used in water treatment as a coagulant (by producing a "ferric hydroxide" floc which removes organic matter and suspended solids) in cases where the  $\text{SO}_4^{2-}$  of the more widely used iron(III) sulfate is undesirable.

Of the anhydrous dihalides of iron the iodide is easily prepared from the elements but the others are best obtained by passing HX over heated iron. The white (or pale-green) difluoride has the rutile structure the pale-yellow dichloride the  $\text{CdCl}_2$  structure (based on ccp anions, p. 1212) and the yellow-green dibromide and grey diiodide the  $\text{CdI}_2$  structure (based on hcp anions, p. 1212), in all of which the metal occupies octahedral sites. All these iron dihalides dissolve in water and form crystalline hydrates which may alternatively be obtained by dissolving metallic iron in the aqueous acid.

Apart from the pale green  $\text{RuOF}_4$  and the oxochlorides already referred to, oxohalides are largely confined to the oxofluorides of osmium,<sup>(19)</sup>  $\text{OsO}_3\text{F}_2$ ,  $\text{OsO}_2\text{F}_3$ ,  $\text{OsOF}_5$ ,  $\text{OsOF}_4$  and the recently confirmed<sup>(20)</sup>  $\text{OsO}_2\text{F}_4$ , previously thought to be  $\text{OsOF}_6$ . The compounds of  $\text{Os}^{\text{VIII}}$  are orange and red solids and those of the lower oxidation states are yellow to green. Typical preparations involve

<sup>18</sup> D. G. KARRAKER and P. K. SMITH, *Inorg. Chem.* **31**, 1119–20 (1992).

<sup>19</sup> J. H. HOLLOWAY and D. LAYCOCK, *Adv. Inorg. Chem. Radiochem.* **28**, 73–99 (1984).

<sup>20</sup> K. O. CHRISTE and R. BOUGON, *J. Chem. Soc., Chem. Commun.*, 1056 (1992).

<sup>16</sup> H. SCHÄFER, *Z. anorg. allg. Chem.* **535**, 219–20 (1986).

<sup>17</sup> K. B. YOON and J. K. KOCHI, *Inorg. Chem.* **29**, 869–74 (1990).