

Table 22.4 Sulfides of vanadium, niobium and tantalum

V <sub>3</sub> S	Nb <sub>21</sub> S <sub>8</sub>	Ta <sub>6</sub> S	V <sub>2</sub> S <sub>3</sub>	—	—
—	—	Ta <sub>2</sub> S	V <sub>5</sub> S <sub>8</sub>	Nb <sub>1+x</sub> S <sub>2</sub>	Ta <sub>1+x</sub> S <sub>2</sub>
V <sub>5</sub> S <sub>4</sub>	—	—	—	NbS <sub>2</sub>	TaS <sub>2</sub>
VS	NbS <sub>1-x</sub>	TaS	—	NbS <sub>3</sub>	TaS <sub>3</sub>
V <sub>7</sub> S <sub>8</sub>	—	—	VS <sub>4</sub>	—	—
V <sub>3</sub> S <sub>4</sub>	Nb <sub>3</sub> S <sub>4</sub>	—			

Table 22.5 Selenides and tellurides of vanadium, niobium and tantalum

V <sub>2</sub> Se	—	—	—	—	—
V <sub>5</sub> Se <sub>4</sub>	Nb <sub>5</sub> Se <sub>4</sub>	—	V <sub>5</sub> Te <sub>4</sub>	Nb <sub>5</sub> Te <sub>4</sub>	—
VSe	NbSe	—	VTe <sub>1+x</sub>	—	TaTe
V <sub>7</sub> Se <sub>8</sub>	—	—	—	—	—
V <sub>3</sub> Se <sub>4</sub>	Nb <sub>3</sub> Se <sub>4</sub>	—	V <sub>3</sub> Te <sub>4</sub>	Nb <sub>3</sub> Te <sub>4</sub>	—
(V <sub>2</sub> Se <sub>3</sub> )	Nb <sub>2</sub> Se <sub>3</sub>	Ta <sub>2</sub> Se <sub>3</sub>	V <sub>2</sub> Te <sub>3</sub>	—	—
V <sub>5</sub> Se <sub>8</sub>	—	—	V <sub>5</sub> Te <sub>8</sub>	—	—
—	Nb <sub>1+x</sub> Se <sub>2</sub>	Ta <sub>1+x</sub> Se <sub>2</sub>	V <sub>1+x</sub> Te <sub>2</sub>	Nb <sub>1+x</sub> Te <sub>2</sub>	Ta <sub>1-x</sub> Te <sub>2</sub>
VSe <sub>2</sub>	NbSe <sub>2</sub>	TaSe <sub>2</sub>	VTe <sub>2</sub>	NbTe <sub>2</sub>	TaTe <sub>2</sub>
—	—	TaSe <sub>3</sub>	—	—	—
—	NbSe <sub>4</sub>	—	—	NbTe <sub>4</sub>	TaTe <sub>4</sub>

metallic conductivity and magnetic properties range from diamagnetic (e.g. VS<sub>4</sub>), through paramagnetic (VS, V<sub>2</sub>S<sub>3</sub>), to antiferromagnetic (V<sub>7</sub>S<sub>8</sub>). Selenides and tellurides show a similar profusion of stoichiometries and structural types (Table 22.5).

In addition to these binary chalcogenides, many of which exist over wide ranges of composition because of the structural relation between the NiAs and CdI<sub>2</sub> structure types (p. 556), several ternary phases have been studied. Some, like BaVS<sub>3</sub> and BaTaS<sub>3</sub> have three-dimensional structures in which the Ba and V(Ta) are coordinated by 12 and 6 S atoms respectively. Other compounds such as the easily hydrolysed (NH<sub>4</sub>)<sub>3</sub>VS<sub>4</sub>, which has been known for over a century, and M<sub>3</sub><sup>I</sup>VS<sub>4</sub> (M = Na, K, Tl) prepared by heating stoichiometric amounts of the elements under vacuum<sup>(21)</sup> contain the discrete, tetrahedral [VS<sub>4</sub>]<sup>3-</sup> anion. The cluster chemistry of the thiometallates of this group, however, is not comparable to that of the oxometallates. It is very limited and whereas, for instance, (Et<sub>4</sub>N)<sub>4</sub>[M<sub>6</sub>S<sub>17</sub>].3CH<sub>3</sub>CN (M = Nb,

Ta) contains a discrete [M<sub>6</sub>S<sub>17</sub>]<sup>4-</sup> anion,<sup>(22)</sup> the stoichiometrically analogous M<sub>4</sub><sup>I</sup>Nb<sub>6</sub>O<sub>17</sub>·0.3H<sub>2</sub>O has an extended structure.

### 22.3.4 Halides and oxohalides

The known halides of vanadium, niobium and tantalum, are listed in Table 22.6. These are illustrative of the trends within this group which have already been alluded to. Vanadium(V) is only represented at present by the fluoride, and even vanadium(IV) does not form the iodide, though all the halides of vanadium(III) and vanadium(II) are known. Niobium and tantalum, on the other hand, form all the halides in the high oxidation state, and are in fact unique (apart only from protactinium) in forming pentafluorides. However in the +4 state, tantalum fails to form a fluoride and neither metal produces a trifluoride. In still lower oxidation states, niobium and tantalum give a number of (frequently nonstoichiometric) cluster compounds which can be considered to involve fragments of the metal lattice.

<sup>21</sup> A. T. HARRISON and O. W. HAWORTH, *J. Chem. Soc., Dalton Trans.*, 1405-9 (1986).

<sup>22</sup> J. SOLA, Y. DO, J. M. BERG and R. H. HOLM, *Inorg. Chem.* **24**, 1706-13 (1985).

Table 22.6 Halides of vanadium, niobium and tantalum<sup>(a)</sup> (mp, bp/°C)

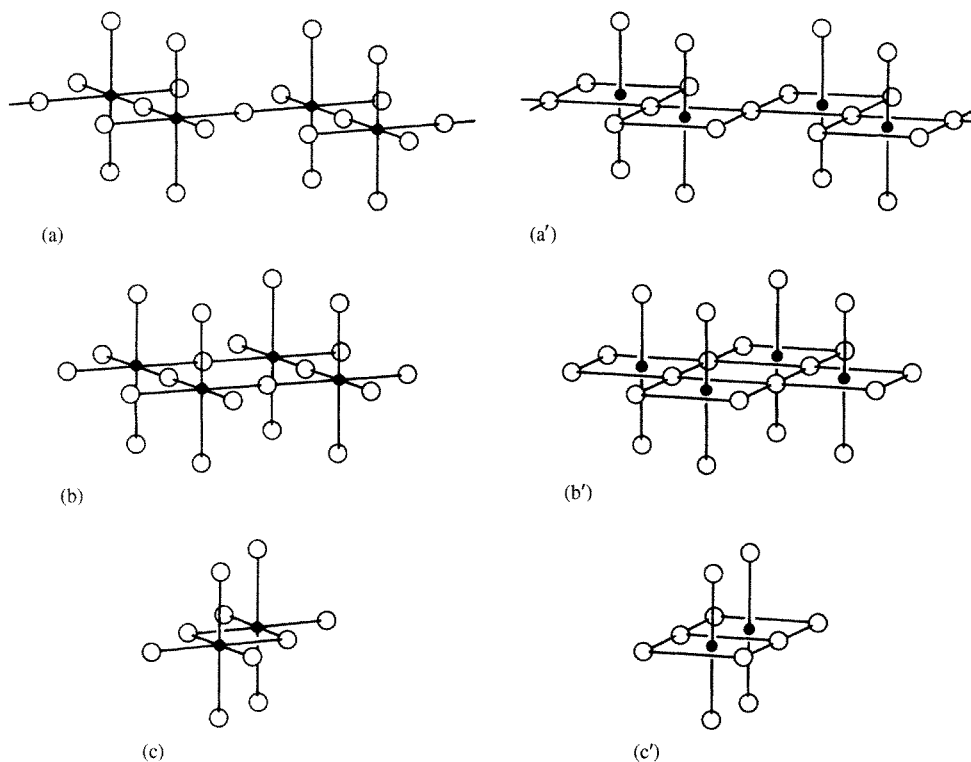
Oxidation state	Fluorides	Chlorides	Bromides	Iodides
+5	VF <sub>5</sub> colourless mp 19.5°, bp 48.3°	—	—	—
	NbF <sub>5</sub> white mp 79°, bp 234°	NbCl <sub>5</sub> yellow mp 203°, bp 247°	NbBr <sub>5</sub> orange mp 254°, bp 360°	NbI <sub>5</sub> brass coloured
	TaF <sub>5</sub> white mp 97°, bp 229°	TaCl <sub>5</sub> white mp 210°, bp 233°	TaBr <sub>5</sub> pale yellow mp 280°, bp 345°	TaI <sub>5</sub> black mp 496°, bp 543°
+4	VF <sub>4</sub> lime green (subl > 150°)	VCl <sub>4</sub> red-brown mp -26°, bp 148°	VBr <sub>4</sub> magenta (d - 23°)	—
	NbF <sub>4</sub> black (d > 350°)	NbCl <sub>4</sub> violet-black	NbBr <sub>4</sub> dark brown	NbI <sub>4</sub> dark grey mp 503°
+3	—	TaCl <sub>4</sub> black	TaBr <sub>4</sub> dark blue	TaI <sub>4</sub>
	VF <sub>3</sub> yellow-green mp 800°	VCl <sub>3</sub> red-violet	VBr <sub>3</sub> grey-brown	VI <sub>3</sub> brown-black
	NbF <sub>3</sub> (?) blue	NbCl <sub>3</sub> black	NbBr <sub>3</sub> dark brown	NbI <sub>3</sub>
+2	TaF <sub>3</sub> (?) blue	TaCl <sub>3</sub> black	TaBr <sub>3</sub>	—
	VF <sub>2</sub> blue	VCl <sub>2</sub> pale green (subl 910°)	VBr <sub>2</sub> orange-brown (subl 800°)	VI <sub>2</sub> red-violet

<sup>(a)</sup>Niobium and Ta also form a number of polynuclear halides in which the metal has non-integral oxidation states (see text).

VF<sub>5</sub> and all pentahalides of Nb and Ta can be prepared conveniently by direct action of the appropriate halogen on the heated metal. They are all relatively volatile, hydrolysable solids (indicative of the covalency to be anticipated in such a high oxidation state) in which the metals attain octahedral coordination by means of halide bridges (Fig. 22.4). VF<sub>5</sub> is an infinite chain polymer, whereas NbF<sub>5</sub> and TaF<sub>5</sub> are tetramers, and the chlorides and bromides are dimers. The colours vary from white fluorides, yellow chlorides, and orange bromides, to brown iodides. The decreasing energy of the charge-transfer bands responsible for these colours is a reflection of the increasing polarizability of the anions from F<sup>-</sup> to I<sup>-</sup>, and for each anion usually the least readily reduced Ta produces the palest colour. All the pentahalides can be

sublimed in an atmosphere of the appropriate halogen and they are then monomeric, probably trigonal bipyramidal. Potentially they are all Lewis acids but their ability to form adducts (LMX<sub>5</sub>) diminishes and the iodides rarely do so.

The tetrahalides can be prepared by direct action of the elements. However, whereas VF<sub>4</sub> tends to disproportionate into VF<sub>5</sub> + VF<sub>3</sub> and must be sublimed from them, VCl<sub>4</sub> and VBr<sub>4</sub> tend to dissociate into VX<sub>3</sub> +  $\frac{1}{2}$ X<sub>2</sub> and so require the presence of an excess of halogen. Even so, VBr<sub>4</sub> has only been isolated by quenching the mixed vapours at -78°C. VF<sub>4</sub> is a bright-green hygroscopic solid, probably consisting of fluorine-bridged VF<sub>6</sub> octahedra. VCl<sub>4</sub> is a red-brown oil, rapidly hydrolysed by water to give solutions of oxovanadium(IV) chloride, and magnetic and spectroscopic evidence indicate that

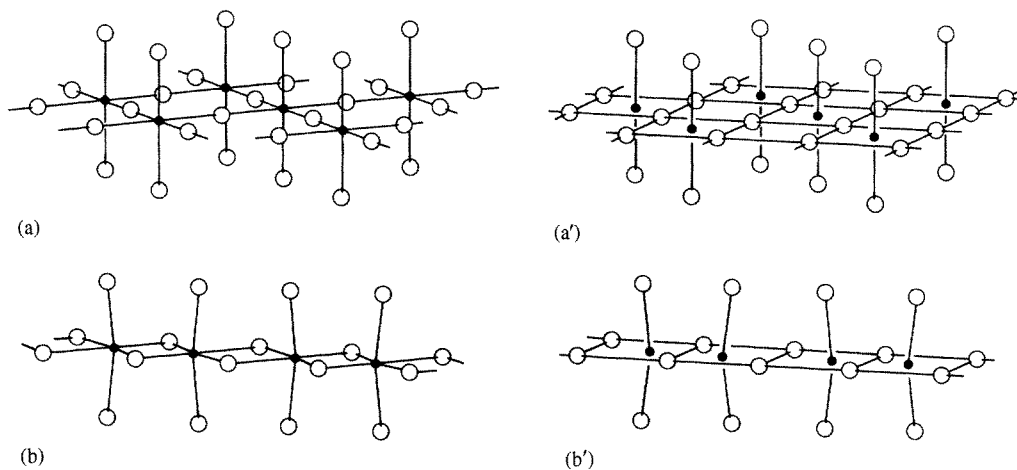


**Figure 22.4** Alternative representations of: (a) infinite chains of vanadium atoms in  $\text{VF}_5$ , (b) tetrameric structures of  $\text{NbF}_5$  and  $\text{TaF}_5$ , and (c) dimeric structure of  $\text{MX}_5$  ( $\text{M} = \text{Nb}, \text{Ta}$ ;  $\text{X} = \text{Cl}, \text{Br}$ ).

it consists of unassociated tetrahedral molecules. As far as its properties are known, the magenta-coloured  $\text{VBr}_4$  is similar.

The Nb and Ta tetrahalides (except  $\text{TaF}_4$  which is unknown, and  $\text{NbI}_4$  which is prepared by thermal decomposition of  $\text{NbI}_5$ ) are generally prepared by reduction of the corresponding pentahalide and are all readily hydrolysed.  $\text{NbF}_4$  is a black involatile solid and its low magnetic moment suggests extensive metal-metal interaction, presumably via the intervening  $\text{F}^-$  ions since it consists of infinite sheets of  $\text{NbF}_6$  octahedra (Fig. 22.5a). The chlorides, bromides and iodides are brown to black solids with a chain structure (Fig. 22.5b) in which pairs of metal atoms are displaced towards each other, so facilitating the interaction which leads to their diamagnetism.

The vanadium trihalides are all crystalline, polymeric solids in which the vanadium is 6-coordinate.  $\text{VF}_3$  is prepared by the action of HF on heated  $\text{VCl}_3$  and this, along with  $\text{VBr}_3$  and  $\text{VI}_3$ , can be prepared by direct action of the elements under appropriate conditions. They are coloured and have magnetic moments slightly lower than the spin-only value of 2.83 BM corresponding to 2 unpaired electrons. Apart from the trifluoride, which is not very readily oxidized nor very soluble in water, they are easily oxidized by air and are very hygroscopic, forming aqueous solutions of  $[\text{V}(\text{H}_2\text{O})_6]^{3+}$ . As with the other lower halides of Nb and Ta, the trihalides are obtained by reduction or thermal decomposition of their pentahalides. Despite claims for the existence of  $\text{NbF}_3$  and  $\text{TaF}_3$  it is probable that these blue materials are

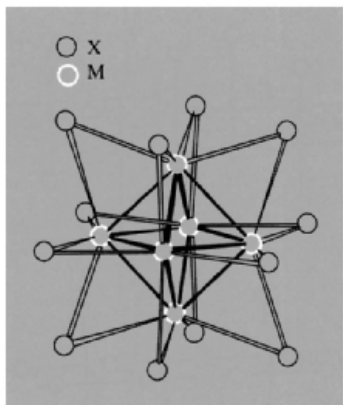


**Figure 22.5** Alternative representations of: (a) the sheet structure of  $\text{NbF}_4$  and (b) the chain structure of  $\text{MX}_4$  ( $M = \text{Nb, Ta}$ ;  $X = \text{Cl, Br, I}$ ) showing the displacement of the metal atoms which leads to diamagnetism.

actually oxide fluorides but, because  $\text{O}^{2-}$  and  $\text{F}^-$  are isoelectronic and very similar in size, they are difficult to distinguish by X-ray methods. The remaining 5 known trihalides of this pair of metals are dark coloured, rather unreactive materials. The  $\text{Nb}-\text{Cl}$  system has been the most thoroughly studied but the others appear to be entirely analogous. They are nonstoichiometric and the composition “ $\text{MX}_3$ ” is best considered as a single unexceptional point within a broad homogeneous phase based on hcp halide ions. At one extreme is  $\text{M}_3\text{X}_8$  (i.e.  $\text{MX}_{2.67}$ ) in which one-quarter of the octahedral sites are empty and the others occupied by triangular groups of metal atoms. Of the 15 valence electrons provided by the 3 metal atoms, 8 are lost by ionization and transfer to the 8 Cl atoms and, of the remaining 7 available for metal–metal bonding, 6 are considered to be in bonding orbitals and 1 in a nonbonding orbital. This accounts for the magnetic moment of 1.86 BM for each trinuclear cluster in  $\text{Nb}_3\text{Cl}_8$ . Metal deficiency then produces stoichiometries to somewhat beyond  $\text{MX}_3$  (i.e.  $\text{M}_{2.67-x}\text{X}_8$ ) after which the  $\text{MX}_4$  phase separates, containing pairs of interacting metal atoms, as already mentioned (i.e.  $\text{M}_2\text{X}_8$ ).

In the still lower oxidation state, +2, the halides of vanadium on the one hand, and niobium and tantalum, on the other, diverge still further. The dihalides of V are prepared by reduction of the corresponding trihalides and have simple structures based on the close-packing of halide ions: the rutile structure (p. 961) for  $\text{VF}_2$ , and the  $\text{CdI}_2$  structure (p. 1212) for the others. They are strongly reducing and hygroscopic, dissolving in water to give lavender-coloured solutions of  $[\text{V}(\text{H}_2\text{O})_6]^{2+}$ . By contrast, high-temperature reductions of  $\text{NbX}_5$  or  $\text{TaX}_5$  with the metals (or Na or Al) yield a series of phases based on  $[\text{M}_6\text{X}_{12}]^{n+}$  units consisting of octahedral clusters of metal atoms with the halogen atoms situated above each edge of the octahedra (Fig. 22.6). These may be surrounded by:

- Four similar units, with each of which a halogen atom is shared, producing a sheet structure with the composition  $[\text{M}_6\text{X}_{12}]\text{X}_{4/2} = \text{M}_6\text{X}_{14}$  (i.e.  $\text{MX}_{2.3}$ ). These compounds are diamagnetic as a result of the metal–metal bonding.
- Six similar units, with each of which a halogen atom is shared, producing a



**Figure 22.6**  $[M_6X_{12}]^{n+}$  cluster with X bridges over each edge of the octahedron of metal ions.

three-dimensional array with the composition  $[M_6X_{12}]X_{6/2} = M_6X_{15}$  (i.e.  $MX_{2.5}$ ). These have magnetic moments corresponding to 1 unpaired electron per hexamer and so indicate the same metal–metal bonding within the cluster as in (a).

By incorporation of alkali metal halides in the reaction mix, materials of composition  $M_4^- [M_6X_{18}]$  can be produced in which each  $M_6X_{12}$  unit has a further six X atoms attached to its apices, so forming discrete clusters.

Many of these cluster compounds are water-soluble and yield solutions in which the clusters are retained throughout chemical reactions. These reactions include attachment of a variety of ligands at the apical (or “terminal”) sites as well as reversible oxidations of the clusters. Thus, it has been possible<sup>(23)</sup> to isolate  $Rb_4[Nb_6Br_{12}(N_3)_6] \cdot 2H_2O$  from aqueous methanolic solutions, and from aqueous alcoholic solutions of  $[M_6X_{12}]X_2 \cdot 8H_2O$  ( $M = Nb, Ta; X = Cl, Br$ )<sup>(23a)</sup> the insoluble, diamagnetic compounds  $[M_6X_{12}(ROH)_6]X_2$ . In these compounds all the terminal coordination sites are occupied by azide groups and aliphatic alcohols respectively. In addition  $[M_6X_{12}]^{2+}$  (diamagnetic) can also be

oxidized to  $[M_6X_{12}]^{3+}$  (1 unpaired electron) and then to  $[M_6X_{12}]^{4+}$  (diamagnetic), and compounds such as  $M_6X_{14}$ ,  $M_6X_{15}$  and  $M_6X_{16}$ , usually with 7 or 8 molecules of  $H_2O$ , can be crystallized. Although terminal ligands are generally more labile than the bridging halogen atoms, isomers of the green  $[Ta_6Cl_{12}(\mu-Cl)_2(PR_3)_4]$  in which the terminal chlorines are either *cis* or *trans* have been isolated by column chromatography. The isomerism was then retained<sup>(24)</sup> when the individual isomers were oxidized by  $NOBF_4$  or  $AgBF_4$  to the orange to brown  $BF_4^-$  salts of  $[Ta_6Cl_{12}(\mu-Cl)_2(PR_3)_4]^{n+}$  ( $n = 1, 2$ ).

The  $[M_6X_8]$  cluster unit in which halogen atoms are situated above each *face* of the  $M_6$  octahedron is far less common here than in Group 6 (p. 1022) but does occur in the unusual compound,  $Nb_6I_{11}$ . This consists of a 3D array of six  $[Nb_6I_8]$  units joined by shared iodines:  $[Nb_6I_8]I_{6/2} = Nb_6I_{11}$ . It absorbs hydrogen and, in 1967, provided the first example of a metal atom cluster with an encapsulated H atom at its centre.<sup>(25)</sup> Both  $Nb_6I_{11}$  and  $HNb_6I_{11}$  exhibit a “spin-crossover”: 1 to 3 unpaired electrons at 274 K for the former, and diamagnetic to 2 unpaired electrons at 324 K for the latter.<sup>(26)</sup>

The cluster compounds of this group may be regarded as intermediate between the  $[M_6X_8]^{n+}$  type of Group 6 (p. 1022) which generally possess sufficient electrons (24) to allow M–M single bonds on each edge of the octahedron, and the comparatively electron-poor clusters of Groups 3 and 4 (p. 950 and 965) which generally require the presence of an interstitial atom to stabilize them.<sup>(27)</sup>

The known oxohalides are listed in Table 22.7. They are generally prepared from the oxides but are not particularly well known and, as can be seen, are limited almost entirely to the oxidation states of +4 and +5. Those in the

<sup>24</sup> H. IMOTO, S. HAYAKAWA, N. MORITA and T. SAITO, *Inorg. Chem.* **29**, 2007–14 (1990).

<sup>25</sup> A. SIMON, F. STOLLMAIER, D. GREGSON and H. FUESS, *J. Chem. Soc., Dalton Trans.*, 431–4 (1987).

<sup>26</sup> H. IMOTO and A. SIMON, *Inorg. Chem.* **21**, 308–19 (1982).

<sup>27</sup> A. SIMON, *Angew. Chem. Int. Edn. Engl.* **27**, 159–83 (1988).

<sup>23</sup> H.-J. MEYER, *Z. anorg. allg. Chem.* **621**, 921–4 (1995).

<sup>23a</sup> A. KASHTA, N. BRNICEVIC and R. E. MCCARLEY, *Polyhedron* **10**, 2031–6 (1991).

Table 22.7 Oxohalides of vanadium, niobium and tantalum<sup>(28)</sup>

Oxidation state	Fluorides		Chlorides		Bromides		Iodides	
+5	VOF <sub>3</sub> yellow mp 300° bp 480°	VO <sub>2</sub> F brown	VOCl <sub>3</sub> yellow mp -77° bp 127°	VO <sub>2</sub> Cl orange	VOBr <sub>3</sub> deep red (d 180°)			—
	TaOF <sub>3</sub>	NbO <sub>2</sub> F white TaO <sub>2</sub> F	NbOCl <sub>3</sub> white TaOCl <sub>3</sub> white	NbO <sub>2</sub> Cl white TaO <sub>2</sub> Cl white	NbOBr <sub>3</sub> yellow-brown TaOBr <sub>3</sub> pale yellow	NbO <sub>2</sub> Br brown TaO <sub>2</sub> Br orange-gold	NbOI <sub>3</sub> black TaOI <sub>3</sub>	NbO <sub>2</sub> I red TaO <sub>2</sub> I
+4	VOF <sub>2</sub> yellow		VOCl <sub>2</sub> green		VOBr <sub>2</sub> yellow-brown (d 180°)			
			NbOCl <sub>2</sub> black TaOCl <sub>2</sub>		NbOBr <sub>2</sub>  TaOBr <sub>2</sub> black		NbOI <sub>2</sub> black TaOI <sub>2</sub> black	
+3	—		VOCl yellow-brown bp 127°		VOBr violet (d 480°)			

former oxidation state are relatively stable but those in the latter are notably hygroscopic and hydrolyse vigorously to the hydrous pentoxides. The Nb(V) and Ta(V) compounds are rather volatile, though less so than the pentahalides. NbOCl<sub>3</sub> is the best known, mainly because of its propensity for occurring as an unwanted impurity in the preparation of VCl<sub>5</sub> if O<sub>2</sub> is not rigorously excluded or, more specially, if V<sub>2</sub>O<sub>5</sub> is used.

### 22.3.5 Compounds with oxoanions

The group oxidation state of +5 is too high to allow the formation of simple ionic salts even for Nb and Ta, and in lower oxidation states the higher sublimation energies of these heavier metals, coupled with their ease of oxidation, again militates against the formation of simple salts of the oxoacids. As a consequence the only simple oxoanion salts are the sulfates of vanadium in the oxidation states +3 and +2. These can be crystallized from aqueous solutions as hydrates and are both strongly

reducing. They give rise to blue-violet alums, MV(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O, the ammonium alum being air-stable when dry, and to the reddish-violet Tutton's salts, M<sub>2</sub>V(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, the ammonium analogue of which is again relatively more stable to oxidation.

In the higher oxidation states partially hydrolysed species dominate the aqueous chemistry, the most important being the oxovanadium(IV), or vanadyl, ion VO<sup>2+</sup>. This gives the sulfate VOSO<sub>4</sub>·5H<sub>2</sub>O, containing monodentate sulfate and octahedrally coordinated vanadium, and the polymeric VOSO<sub>4</sub>. Oxovanadium(V) species are not well characterized, outside the oxohalides VOX<sub>3</sub>, but in strongly acid solutions VO<sub>2</sub><sup>+</sup> is formed and reportedly gives the nitrate VO<sub>2</sub>(NO<sub>3</sub>). The VO<sub>2</sub><sup>+</sup> ion is also found in anionic complexes such as [VO<sub>2</sub>(oxalate)<sub>2</sub>]<sup>3-</sup> and in all cases the oxygens are mutually *cis* as they are in the isoelectronic MoO<sub>2</sub><sup>2+</sup> (p. 1024). Niobium and tantalum produce a variety of complicated and ill-defined, but probably polymeric, species which include the nitrates, MO(NO<sub>3</sub>)<sub>3</sub>, sulfates such as Nb<sub>2</sub>O(SO<sub>4</sub>), and double sulfates such as (NH<sub>4</sub>)<sub>6</sub>Nb<sub>2</sub>O(SO<sub>4</sub>)<sub>7</sub>, all of which are extremely readily hydrolysed.

<sup>28</sup> H. SCHÄFER, R. GERKEN and L. ZYLKA, *Z. anorg. allg. Chem.* **534**, 209–15 (1986).

### 22.3.6 Complexes<sup>(29,30)</sup>

#### Oxidation state V (d<sup>0</sup>)

Vanadium (V) has a great affinity for *O*-donors: the extensive chemistry of the polyoxometallates has already been discussed and complexes not involving oxygen, such as the white diamagnetic hexafluorovanadates, MVF<sub>6</sub>, are extremely susceptible to hydrolysis. If H<sub>2</sub>O<sub>2</sub> is added to aqueous solutions of [VO<sub>4</sub>]<sup>3-</sup> a series of substituted products is obtained depending on pH. Using Raman and <sup>51</sup>V nmr spectroscopy to compare the solutions with compounds of known compositions and structures, suggests<sup>(31)</sup> that the red-brown acidic solutions contain [VO(O<sub>2</sub>)(H<sub>2</sub>O)<sub>4</sub>]<sup>+</sup> and that in progressively more alkaline solutions, [VO(O<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)]<sup>-</sup>, [VO<sub>2</sub>(O<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)]<sup>3-</sup>, [VO(O<sub>2</sub>)<sub>3</sub>]<sup>3-</sup> and [V(O<sub>2</sub>)<sub>4</sub>]<sup>3-</sup> are among the species produced until, from strongly alkaline solutions, blue-violet crystals of M<sub>3</sub>[V(O<sub>2</sub>)<sub>4</sub>].*n*H<sub>2</sub>O (M<sup>I</sup> = Li, Na, K, NH<sub>4</sub>) are deposited. Like the corresponding Cr ion (p. 637), [V(O<sub>2</sub>)<sub>4</sub>]<sup>3-</sup> is 8-coordinate and dodecahedral, but such a high coordination number is not common for vanadium. Niobium and tantalum produce similar peroxy-compounds, e.g. pale yellow K<sub>3</sub>[Nb(O<sub>2</sub>)<sub>4</sub>] and white K<sub>3</sub>[Ta(O<sub>2</sub>)<sub>4</sub>].

However, most complexes of Nb<sup>V</sup> and Ta<sup>V</sup> are derived from the pentahalides. NbF<sub>5</sub> and TaF<sub>5</sub> dissolve in aqueous solutions of HF to give [MOF<sub>5</sub>]<sup>2-</sup> and, if the concentration of HF is increased, [MF<sub>6</sub>]<sup>-</sup>. This is normally the highest coordination number attained in solution though some [NbF<sub>7</sub>]<sup>2-</sup> may form, and [TaF<sub>7</sub>]<sup>2-</sup> definitely does form, in very high concentrations of HF. However, by suitably regulating the concentration of metal, fluoride ion and HF, octahedral

[MF<sub>6</sub>]<sup>-</sup>, capped trigonal prismatic [MF<sub>7</sub>]<sup>2-</sup>, and even square-antiprismatic [MF<sub>8</sub>]<sup>3-</sup> salts can all be isolated. By contrast with the fluorides, aqueous solutions of MCl<sub>5</sub> and MBr<sub>5</sub> (M = Nb, Ta) yield only oxochloro- and oxobromo-complexes, though the application of non-aqueous procedures allows their use as starting materials.

Niobium(V) is generally considered to be a class-a metal, but the SCN<sup>-</sup> ligand yields a series of both *N*-bonded thiocyanato and *S*-bonded isothiocyanato complexes, e.g. [Nb(NCS)<sub>*n*</sub>(SCN)<sub>6-*n*</sub>]<sup>-</sup> (*n* = 0, 2, 4, 5, 6). Furthermore, dithiocarbamates, dodecahedral [M(S<sub>2</sub>CNR<sub>2</sub>)<sub>4</sub>]<sup>+</sup>, and dithiolates,<sup>(32)</sup> [M(SCH<sub>2</sub>CH<sub>2</sub>S)<sub>3</sub>]<sup>-</sup> with stereochemistry midway between octahedral and trigonal-prismatic, are known for both Nb and Ta. The pentahalides of these two metals act as Lewis acids and form complexes of the type MX<sub>5</sub>L with *O*, *S*, *N*, *P*, and *As* donor ligands.

#### Oxidation state IV (d<sup>1</sup>)

The tetrahalides are Lewis acids and produce a number of adducts with a variety of donor atoms, the most common coordination number being 6. [VF<sub>4</sub>L] (L = NH<sub>3</sub>, py) are insoluble in common organic solvents, have magnetic moments of about 1.8 BM, and are thought to be fluorine-bridged polymers. [VCl<sub>4</sub>2L] (L = py, MeCN, aldehydes, etc.) and VCl<sub>4</sub>(L-L) (L-L = bipy, phen, diars) are brown paramagnetic, readily hydrolysed compounds assumed to be 6-coordinate monomers. Similar compounds of Nb and Ta are also paramagnetic and the metal-metal bonding which led to the diamagnetism of the parent tetrahalides is presumed to have been broken to give adducts which again are 6-coordinate monomers. Hexahalo-complexes [MX<sub>6</sub>]<sup>2-</sup> (M = V, X = F, Cl; M = Nb, Ta, X = Cl, Br) are known, the vanadium compounds being especially sensitive to moisture though stable to air.

<sup>29</sup> L. V. BOAS and L. C. PESSOA, Vanadium, Chap. 33, pp. 453-583, and L. G. HUBERT-PFALZGRAF, M. POSTEL and J. G. RIESS, Niobium and Tantalum, Chap. 34, pp. 585-697 in *Comprehensive Coordination Chemistry*, Vol. 3, Pergamon Press, Oxford, 1987.

<sup>30</sup> R. W. BERG, *Coord. Chem. Revs.* **113**, 1-130 (1992).

<sup>31</sup> N. J. CAMPBELL, A. C. DENGEL and W. P. GRIFFITH, *Polyhedron* **8**, 1379-86 (1989). See also A. BUTLER, M. J. CLAGUE and G. E. MEISTER, *Chem. Revs.* **94**, 625-38 (1994).

<sup>32</sup> K. TATSUMI, Y. SEKIGUCHI, A. NAKAMURA, R. E. CRAMER and J. J. RUPP, *Angew. Chem. Int. Edn. Engl.* **25**, 86-7 (1986).

Higher coordination numbers are also found. Vanadium and Nb produce the dodecahedral  $[\text{MCl}_4(\text{diars})_2]$  just like the Group 4 metals. This is probably the most common stereochemistry for this coordination number but others are possible; differences in energy are slight and this facilitates non-rigidity. For example the yellow-coloured solid  $\text{K}_4[\text{Nb}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$  contains dodecahedral niobium(IV) (like its molybdenum isomorph), whereas esr and infrared data suggest that, in solution, the anion has the square-antiprismatic configuration. Likewise, the deep-red niobium(III) complex  $\text{K}_5[\text{Nb}(\text{CN})_8]$  adopts a dodecahedral ( $D_{2d}$ ) configuration for the anion in the crystal whereas the single  $^{13}\text{C}$  nmr signal in aqueous solution implies either a square-pyramidal ( $D_{4d}$ ) or fluxional ( $D_{2d}$ ) structure.

The major contrast with the Group 4 metals is the stability of  $\text{VO}^{2+}$  complexes which are the most important and the most widely studied of the vanadium(IV) complexes, and are the usual products of the hydrolysis of other vanadium(IV) complexes.  $\text{VO}^{2+}$  behaves as a class-a cation, forming stable compounds with *F* (especially), *Cl*, *O*, and *N* donor ligands. These “vanadyl” complexes are generally blue to green and can be cationic, neutral or anionic. They are very frequently 5-coordinate in which case the stereochemistry is almost invariably square pyramidal.  $[\text{VO}(\text{acac})_2]$  (Fig. 22.7) is the archetypal example of this geometry in coordination compounds. In this and in similar compounds the  $\text{V}=\text{O}$  bond length is  $\sim 157\text{--}168$  pm which is about 50 pm shorter than the 4 equatorial  $\text{V}\text{--}\text{O}$  bonds. This, as well as spectroscopic evidence, is consistent with the

formulation of the bond as double. A sixth ligand may be weakly bonded *trans* to the  $\text{V}=\text{O}$  to produce a distorted octahedral structure; the concomitant reduction in the stretching frequency of the  $\text{V}=\text{O}$  bond generally within the range,  $985 \pm 50 \text{ cm}^{-1}$  has been interpreted in terms of electron donation from this sixth ligand, thereby making the vanadium atom less able to accept charge from the oxygen and so reducing the bond order. Tetradentate Schiff bases, produced for instance by the condensation of salicylaldehyde with primary diamines, in most cases give entirely analogous compounds, but some are yellow and may be polymeric with the vanadium attaining 6-coordination by “stacking” so that the sixth position of each vanadium is occupied by the oxygen from the  $\text{V}=\text{O}$  beneath. The black  $[\text{V}(\text{salen})_4(\mu\text{-O})_3](\text{BF}_4)_2$  [ $\text{H}_2\text{salen} = N,N'$ -ethylenebis(salicylideneimine), p. 907] has recently been shown to be tetrameric with a linear  $\text{V}\text{--}\text{O}\text{--}\text{V}\text{--}\text{O}\text{--}\text{V}\text{--}\text{O}\text{--}\text{V}$  chain.<sup>(33)</sup>

In spite of the evident proclivity of  $\text{VO}^{2+}$  to form square pyramidal or distorted octahedral complexes, it must not be assumed that 5-coordination inevitably results in the former shape.  $[\text{VOCl}_2(\text{NMe}_3)_2]$  is in fact trigonal bipyramidal (Fig. 22.8), no doubt because of a dominant steric effect of the bulky trimethylamine ligands rather than any electronic effect. Most oxovanadium(IV) complexes are magnetically simple, having virtually “spin-only” moments of 1.73 BM corresponding to 1 unpaired electron, but their electronic spectra are less easily understood. This is primarily due to the presence of a strong  $\pi$  contribution to the bond between the vanadium and the oxygen which makes it difficult to assign an unequivocal sequence to the molecular orbitals involved.<sup>(34)</sup>

Some square pyramidal derivatives of thiovanadyl,  $(\text{V}=\text{S})^{2+}$ , have also been prepared from the corresponding vanadyl complexes: deep magenta  $[\text{VS}(\text{salen})]$  and  $[\text{VS}(\text{acen})]$  [ $\text{H}_2\text{acen} = N,N'$ -ethylenebis(acetylacetylideneimine)] by

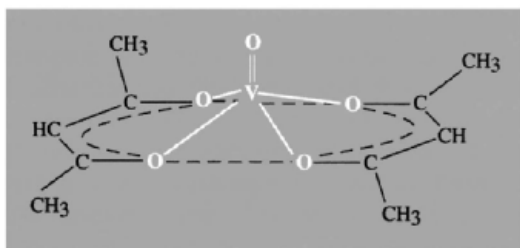
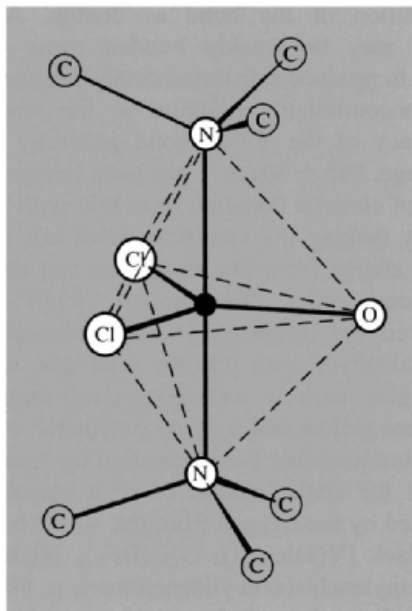


Figure 22.7 The square-pyramidal structure of  $[\text{VO}(\text{acac})_2]$ .

<sup>33</sup> A. HILLS, D. L. HUGHES, G. J. LEIGH and J. R. SANDERS *J. Chem. Soc., Chem. Commun.*, 827–9 (1991).

<sup>34</sup> A. B. P. LEVER, *Inorganic Electronic Spectra*, 2nd edn., pp. 384–91, Elsevier Amsterdam, 1984.





**Figure 22.8** The trigonal bipyramidal structure of  $[\text{VOCl}_2(\text{NMe}_3)_2]$ .

the action of  $\text{B}_2\text{S}_3$  in  $\text{CH}_2\text{Cl}_2$ ; brown  $[\text{VS}(\text{SCH}_2\text{-CH}_2\text{S})_2]^{2-}$  by the action of  $(\text{Me}_3\text{Si})_2\text{S}$  in  $\text{MeCN}$ .<sup>(35)</sup> The exclusion of air and moisture throughout these preparations is essential in order to avoid reversion to vandyl complexes.

### Oxidation state III ( $d^2$ )

Until comparatively recently only vanadium had a significant  $\text{M}^{\text{III}}$  coordination chemistry and even so the majority of its compounds are easily oxidized and must be prepared with air rigorously excluded. The usual methods are to use  $\text{VCl}_3$  as the starting material, or to reduce solutions of vanadium(V) or (IV) electrolytically. However, the reduction of pentahalides of Nb and Ta by Na amalgam or Mg, has facilitated the expansion of  $\text{Nb}^{\text{III}}$  and  $\text{Ta}^{\text{III}}$  chemistry particularly with *S*- and *P*-donor ligands.

The chemistry of vanadium(III) closely parallels that of titanium(III) and it likewise favours octahedral coordination. The interpretation of the electronic spectra of its complexes, as the prime examples of  $d^2$  ions in an octahedral field, provided the stimulus for early preparative work in this area. In general, the spectra are characterized by two bands in the visible region with a further much more intense absorption in the ultraviolet. The two former bands are believed to arise from *d*-*d* transitions and others from charge-transfer. Since the  $d^2$  configuration in a cubic field is expected to give rise to three spin-allowed transitions it is assumed that the most energetic of these is obscured by the charge-transfer band. Table 22.8 gives data for some octahedral vanadium(III) complexes (see also ref. 34, pp. 400–6). It turns out, on examination of data such as these, that a coherent interpretation of the spectra is only possible if the bands are assigned (Fig. 22.9) as:

$$\nu_1 = {}^3T_{2g}(F) \leftarrow {}^3T_{1g}(F)$$

$$\nu_2 = {}^3T_{1g}(P) \leftarrow {}^3T_{1g}(F)$$

and the third, obscured one, therefore as:

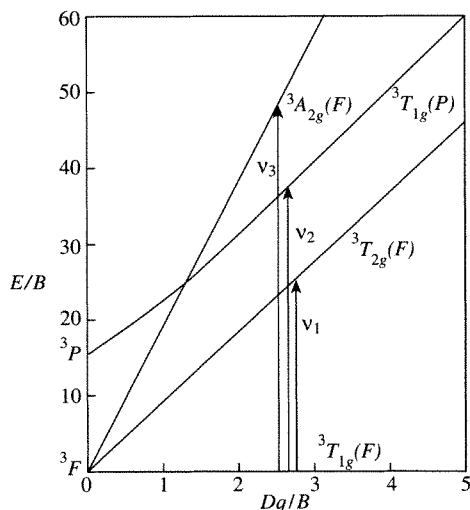
$$\nu_3 = {}^3A_{2g}(F) \leftarrow {}^3T_{1g}(F)$$

*B* is the Racah “interelectronic repulsion parameter”. It is included in Fig. 22.9 in order to retain generality and obviate the necessity of drawing separate diagrams for each  $d^2$  metal ion. The expansion of *d*-electron charge on complexation reduces its value as compared to the value for the free-ion ( $860\text{ cm}^{-1}$ ). In general the electronic spectra of these 6-coordinate complexes are accounted for moderately well on the assumption of basically octahedral crystal fields, but the inclusion of trigonal distortions gives more satisfactory results. The magnetic moments of  $d^2$  ions in perfectly octahedral fields are expected to involve “orbital contribution” which varies with temperature. In practice the moments at room temperature rarely exceed the spin-only value and their variation with temperature is less than anticipated for a *T* ground term. This also is in accord with the presence of some distortion which splits the

<sup>35</sup> G. CHRISTOU, D. HEINRICH, J. K. MONEY, J. R. RAMBO, J. C. HUFFMAN and K. FOLTING *Polyhedron*, **8**, 1723–7 (1989).

Table 22.8 Typical octahedral complexes of vanadium(III)

Complex	Colour	$\nu_1/\text{cm}^{-1}$	$\nu_2/\text{cm}^{-1}$	$10Dq/\text{cm}^{-1}$	$B/\text{cm}^{-1}$	$\mu/\text{BM}$ (room temperature)
$[\text{NH}_4][\text{V}(\text{H}_2\text{O}_6)[\text{SO}_4]_2 \cdot 6\text{H}_2\text{O}]$	Blue-violet	17 800	25 700	19 200	620	2.80
$[\text{VCl}_3(\text{MeCN})_3]$	Green	14 400	21 400	15 500	540	2.79
$[\text{VCl}_3(\text{thf})_3]$	Orange	13 300	19 900	14 000	553	2.80
$\text{K}_3[\text{VF}_6]$	Green	14 800	23 250	16 100	649	2.79
$[\text{pyH}]_3[\text{VCl}_6]$	Purple-pink	16 650	18 350	12 650	513	2.71

Figure 22.9 Energy Level diagram for a  $d^2$  ion in an octahedral crystal field.

${}^3T_{2g}$  ground term and so reduces the temperature dependence of the magnetic moment.

Cationic complexes of the type  $[\text{VL}_6]^{3+}$  of which  $[\text{V}(\text{H}_2\text{O}_6)]^{3+}$  is the best-known example are actually rather rare, the action of  $\text{NH}_3$  on  $\text{VX}_3$  for instance, causing ammonolysis of the  $\text{V}-\text{X}$  bond to produce  $\text{VX}_2(\text{NH}_2)_n\text{NH}_3$ . Anionic  $[\text{VX}_6]^{3-}$ ,  $[\text{VX}_5\text{L}]^{2-}$ ,  $[\text{VX}_4\text{L}_2]^-$  and neutral  $[\text{VCl}_3\text{L}_3]$  are more common. Dithiolates  $[\text{V}_2(\text{SCH}_2\text{CH}_2\text{S})_4]^{2-}$  with four sulfur atoms bridging the two vanadium atoms are also known (Fig. 22.10a), their diamagnetism and short  $\text{V}-\text{V}$  distances (260 pm) indicating  $\text{M}-\text{M}$  bonding.

In spite of the preponderance of 6-coordinate complexes, other coordination numbers are known: the ions  $[\text{VCl}_4]^-$  and  $[\text{VBr}_4]^-$  are tetrahedral and are notable in that 4-coordination

with ligands other than  $O$ -donors is common only later in the transition series. Their spectra exhibit two bands in the regions of  $9000\text{ cm}^{-1}$  and  $15000\text{ cm}^{-1}$  which are assigned to  ${}^3T_1(F) \leftarrow {}^3A_2$  and  ${}^3T_1(P) \leftarrow {}^3A_2$  transitions respectively, corresponding quite reasonably to values of  $\Delta_t$  of about  $5000$  to  $5500\text{ cm}^{-1}$ . Their magnetic moments too are about  $2.7\text{ BM}$  and independent of temperature, as expected.

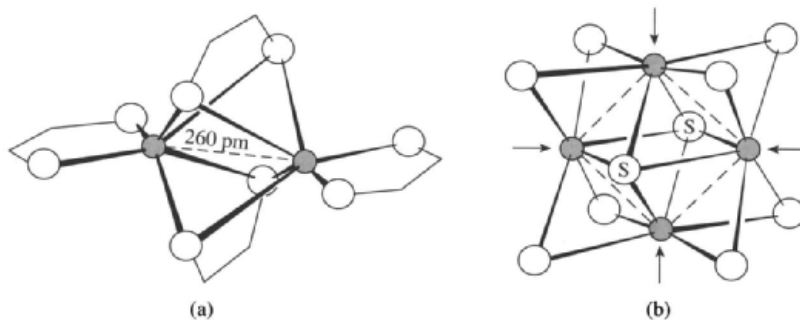
Neutral complexes of the type  $[\text{VX}_3(\text{NMe}_3)_2]$  ( $\text{X} = \text{Cl}, \text{Br}$ ) are trigonal bipyramidal with the trimethylamines occupying the axial positions. By contrast  $[\text{V}\{\text{N}(\text{SiMe}_3)_2\}_3]$  has a 3-coordinate, planar structure, presumably because the bis(trimethylsilyl)amido ligands are too big for the  $\text{V}^{\text{III}}$  to accommodate more. The 7-coordinate  $\text{K}_4[\text{V}(\text{CN})_7] \cdot 2\text{H}_2\text{O}$  has a pentagonal bipyramidal structure and is a rare example of a 7-coordinated transition metal complex which persists in solution and in which the ligand is not  $\text{F}^-$ .

A few trinuclear oxo-centred carboxylates  $[\text{V}_3\text{O}(\text{RCOO})_6\text{L}_3]^+$  of a type more common for later transition metals (see Fig. 23.9, p. 1030) have been obtained,<sup>(36)</sup> as well as  $[\text{Nb}_3\text{O}_2(\text{MeCOO})_6(\text{thf})_3]^+$  whose structure differs essentially only in that there are **two** bridging  $O$  atoms above and below the  $\text{Nb}_3$  plane.<sup>(37)</sup>

With  $S$ - and  $P$ - donor ligands such as  $\text{SMe}_2$  and  $\text{PMe}_3$ ,  $\text{M}_2\text{Cl}_6\text{L}_4$  ( $\text{M} = \text{Nb}, \text{Ta}$ ) consisting of a pair of edge-sharing octahedra are formed. For  $\text{Nb}$ , but interestingly not for

<sup>36</sup> F. A. COTTON, M. W. EXTINE, L. R. FALVELLO, D. B. LEWIS, G. E. LEWIS, C. A. MURILLO, W. SCHWOTZER, M. TOMAS and J. M. TROUP, *Inorg. Chem.* **25**, 3505-12 (1986).

<sup>37</sup> F. A. COTTON, M. P. DIEBOLD, R. LLUSAR and W. J. ROTH, *J. Chem. Soc., Chem. Commun.*, 1276-8 (1986).



**Figure 22.10** (a) dithiolates  $[V_2(SCH_2CH_2S)_4]^{2-}$ . (b)  $[Nb_4S_2(SPh)_{12}]^{4-}$  and  $[Nb_4S_2(SPh)_8(PMe_2R)_4]$  in which the four arrowed coordination sites are occupied by  $SPh^-$  and  $PMe_2R$  respectively. Unlabelled S atoms in (b) all have an attached Ph which is not shown. Nb–Nb(av)  $\sim 282$  pm.

Ta, tetranuclear, orange coloured derivatives  $Li_4[Nb_4S_2(SPh)_{12}]^{38}$  and  $[Nb_4S_2(SPh)_8(PMe_2R)_4]$  (R = Me, Ph)<sup>39</sup> have been shown to have a common and rather stable central unit of four Nb atoms in a square plane with two  $\mu_4$ -S atoms above and below it (Fig. 22.10b). The diamagnetism and average Nb–Nb separations of approx 282 pm are consistent with single bonds between adjacent Nb atoms.

### Oxidation state II ( $d^3$ )

The coordination chemistry of this oxidation state is not well-developed. Vanadium(II) complexes are usually prepared by electrolytic or zinc reduction of acidic solutions of vanadium in one of its higher oxidation states. The resulting blue-purple solutions are strongly reducing, and reduction of the water is, in general, only prevented by the presence of acid. Several salts and double sulfates which contain the  $[V(H_2O)_6]^{2+}$  ion are known and there are adducts of  $VCl_2$  of the type  $[VCl_2L_4]$ , where L is one of a number of *O*- or *N*-donor ligands. The spectroscopic and magnetic properties of these compounds are typical of a  $d^3$  ion and their interpretation follows closely that for the chromium(III) ion (p. 1028). Also

typical of a  $d^3$  ion is the fact that vanadium(II) is kinetically inert and undergoes substitution reactions only slowly.

Other complexes of the type  $[VCl_2L_2]$  are distinguished by their colour (green) and magnetic moment ( $\sim 3.2$  BM), well below the spin-only value for 3 unpaired electrons, and some at least are halogen-bridged oligomers. Carboxylate derivatives such as the trinuclear  $[V_3(RCOO)_6(Me_2NCHCHNMe_2)_2]$  have recently been prepared<sup>40</sup> as has the binuclear  $[V_2(RNCHNR)_4]$  (R = *p*-MeC<sub>6</sub>H<sub>4</sub>).<sup>41</sup> The former contains an almost linear chain of V atoms held together by carboxylate bridges and, in the latter, the pair of V atoms bridged by the four ligands, are so close (197.8 pm) that a  $V\equiv V$  bond is indicated (for single- and double-bonded V–V species, separations of approx. 260 and 220 pm, respectively, are common).

Organometallic compounds apart, oxidation states below +2 are best represented by complexes with tris-bidentate nitrogen-donor ligands such as 2,2'-bipyridyl. Reduction by  $LiAlH_4$  in thf yields tris(bipyridyl) complexes in which the formal oxidation state of vanadium is +2 to –1. Magnetic moments are compatible with low-spin configurations of the metal but,

<sup>38</sup> J. L. SEELA, J. C. HUFFMAN and G. CHRISTOU, *J. Chem. Soc., Chem. Commun.*, 1258–60 (1987).

<sup>39</sup> E. B. KIBALA, F. A. COTTON and P. A. KIBALA, *Polyhedron* **9**, 1689–94 (1990).

<sup>40</sup> J. J. H. EDEMA, S. GAMBAROTTO, S. HAO and C. BEN-SIMON, *Inorg. Chem.* **30**, 2584–6 (1991).

<sup>41</sup> F. A. COTTON, L. M. DANIELS and C. A. MURILLO, *Angew. Chem. Int. Edn. Engl.* **31**, 737–8 (1992).

as with the analogous compounds of titanium, it may well be that they would be better regarded as complexes with reduced, i.e. anionic, ligands.

### 22.3.7 The biochemistry of vanadium<sup>(41a)</sup>

Certain vertebrates have an astonishing ability to accumulate vanadium in their blood. For example, the ascidian seaworm *Phallusia mammilata* has a blood concentration of V up to 1900 ppm, which represents more than a millionfold concentration with respect to the sea-water in which it lives. The related organism *Ascidia nigra* has an even more spectacular accumulation with concentrations up to 1.45% V (i.e. 14 500 ppm) in its blood cells, which also contain considerable concentrations of sulfuric acid (pH ~ 0). One possibility that has been mooted is that the ascidia accumulates vanadate and polyvanadate ions in mistake for phosphate and polyphosphates (p. 528).

Indeed, the observation that vanadate is a potent inhibitor of phosphate-recognizing enzyme systems was a great stimulus to work in this area, but it now seems likely that its action is more complicated than simple mimicry of phosphates.<sup>(42)</sup> This is germane to obtaining an understanding of the antitumor activity of  $[V(\eta^5-C_5H_5)_2Cl_2]$ .

A number of nitrogen-fixing bacteria contain vanadium and it has been shown that in one of these, *Azotobacter*, there are three distinct nitrogenase systems based in turn on Mo, V and Fe, each of which has an underlying functional and structural similarity.<sup>(43)</sup> This discovery has prompted a search for models and the brown  $V^{-1}$  compound  $[Na(thf)]^+[V(N_2)_2(dppe)_2]$  (dppe =  $Ph_2PCH_2CH_2PPh_2$ ) has recently been prepared by reduction of  $VCl_3$  by sodium naphthalenide

in the presence of dppe.<sup>(44)</sup> Acidification achieves partial nitrogen fixation since one of the four N atoms is converted to  $NH_3$ .

### 22.3.8 Organometallic compounds<sup>(45)</sup>

The organometallic chemistry of this group developed rather slowly but there has been a surge of interest, especially in Nb and Ta, in the last decade or so. The chemistry of  $\sigma$  alkyls or aryls is less well developed than for many other elements but  $[V^{III}\{CH(SiMe_3)_2\}_3]$ ,  $[V^{IV}(CH_2SiMe_3)_4]$ , and  $[V^VO(CH_2SiMe_3)_3]$  have been isolated. In these compounds the possibility of decomposition by alkene elimination or other routes is circumvented by the absence of  $\beta$  hydrogen atoms (p. 926) and the bulkiness of the trimethylsilylmethyl groups. Complexes such as  $[MMe_5(dmpe)]$  ( $M = Nb, Ta$ ;  $dmpe = Me_2PCH_2CH_2PMe_2$ ) decompose spontaneously above room temperature and, although free  $TaMe_5$  has been isolated, it can explode spontaneously at room temperature even in the absence of air. Despite this instability, the Ta–Me bond itself is rather strong: thermochemical studies have shown that the mean bond dissociation energy  $D(Ta-Me)$  in  $TaMe_5$  is  $261 \pm 6 \text{ kJ mol}^{-1}$ , which is substantially greater than, for example, the mean dissociation energy  $D(W-CO)$  of  $178 \pm 3 \text{ kJ mol}^{-1}$  in the kinetically much more stable  $W(CO)_6$ . Expanding the coordination sphere of the metal by the addition of other ligands such as  $C_5H_5^-$ , halides and phosphines often increases the thermal stability.

Reduction of  $MCl_5$  or  $MCl_3$  under an atmosphere of CO yields salts of the  $[M(CO_6)]^-$  ions ( $M = V, Nb, Ta$ )<sup>(46)</sup> which have the noble gas electron configuration. Using Na as reductant

<sup>44</sup> D. REHDER, C. WOITHA, W. PRIEBSCHE and M. GAILUS *J. Chem. Soc., Chem. Commun.*, 364–5 (1992).

<sup>45</sup> M. G. CONNELLY, Vanadium, Chap. 24, pp. 648–704, and J. A. LABINGER, Niobium and Tantalum, Chap. 25, pp. 706–82 in *Comprehensive Organometallic Chemistry*, Vol. 3, Pergamon Press, Oxford, 1982.

<sup>46</sup> S. C. SRIVASTAVA and A. K. SHRIMAL, *Polyhedron* **7**, 1639–65 (1988).

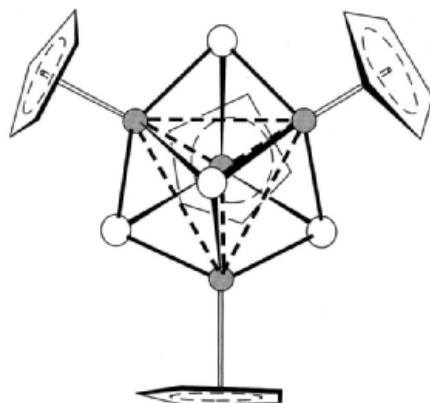
<sup>41a</sup> H. SIGEL and A. SIGEL (eds.), *Metal Ions in Biological Systems*, Vol. 31, Marcel Dekker, New York, 1995, 779 pp.

<sup>42</sup> A. BUTLER and C. J. CARRANO, *Coord. Chem. Revs.* **109**, 61–105 (1991).

<sup>43</sup> R. R. EADY, *Adv. Inorg. Chem.* **36**, 77–102 (1991).

with pyridine or diglyme as solvent requires high temperatures and pressures, but the application of high-energy ultrasound or the use of Mg/Zn as reductant allows less forcing conditions. In the case of the V salt, but not those of Nb and Ta, acidification and extraction with petroleum ether yields volatile, blue-green, pyrophoric crystals of  $V(CO)_6$ . Unlike other formally odd-electron transition metal carbonyls, this does not attain the noble gas configuration by dimerization and the formation of a M–M bond. It is in fact monomeric and isomorphous with Group 6 octahedral hexacarbonyls (p. 1037); it undergoes substitution reactions typical of metal carbonyls, but is unique amongst simple carbonyls in being paramagnetic with a moment at room temperature of 1.81 BM. Further reduction of  $[Na(diglyme)_2][M(CO)_6]$  with Na metal in liquid  $NH_3$  yields the super-reduced 18-electron species  $[M(CO)_5]^{3-}$  which contain M in their lowest known formal oxidation state (–3).<sup>(47)</sup> Although sensitivity is somewhat dependent on the counter-cation involved, several of the salts of these ions are hazardously shock and temperature sensitive. Direct synthesis of  $V(CO)_6$ ,  $V_2(CO)_{12}$  and  $M(CO)_n$  ( $M = V, n = 1-5$ ;  $M = Ta, n = 1-6$ ) by condensation of vanadium vapour with CO in a matrix of noble gases is possible. The same technique has also been used to prepare the hexakis(dinitrogen) compound,  $[V(N_2)_6]$  (p. 981) which is isoelectronic and probably isostructural with the hexacarbonyl.

With the cyclopentadienyl ligand, vanadium forms the simple “sandwich” compound, “vanadocene”.  $[V(\eta^5-C_5H_5)_2]$  which is dark violet, paramagnetic (3 unpaired electrons) and extremely air-sensitive. Oxidative addition reactions are possible and provide compounds such as  $[V(\eta^5-C_5H_5)_2Cl_n]$  ( $n = 1, 2, 3$ ) and  $[V(\eta^5-C_5H_5)_2R_2]$ , while its reaction with dithioacetic acid produces the dark-brown tetramer  $[V_4(\eta^5-C_5H_5)_4(\mu_3-S_4)]$ , Fig. 22.11.<sup>(48)</sup> With four  $V^{III}$  atoms, eight electrons are available for six V–V bonds and the implied bond order of 2/3

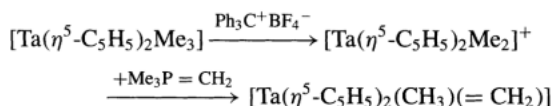


**Figure 22.11**  $[V_4(\eta^5-C_5H_5)_4(\mu_3-S)_4]$  the centre of which is a tetrahedron of V atoms face-capped by S atoms.

is consistent with the observed average V–V separation of 287.6 pm and magnetic moment of 2.65 BM at room temperature.

Niobium and tantalum do not form simple, thermally stable sandwich compounds. Niobocene is actually a dimer and a hydride (Fig. 22.12a). They do however form  $[M(\eta^5-C_5H_5)_4]$  (p. 940) in which two rings are  $\eta^5$ - and two  $\eta^1$ -bonded, and there are many bis(cyclopentadienyl) compounds of the types  $[M(\eta^5-C_5H_5)_2X_2]$  and  $[M(\eta^5-C_5H_5)_2R_2]$  in which, if the  $C_5H_5$  is taken as a single ligand, the coordination geometry is pseudo-tetrahedral.  $[M(\eta^5-C_5H_5)_2X_3]$  and  $[M(\eta^5-C_5H_5)_2R_3]$  are also known.

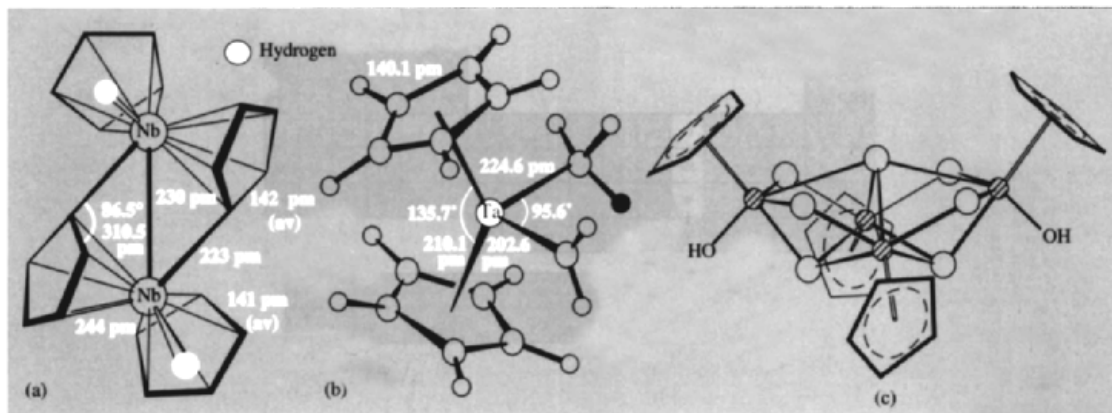
An important compound is the mixed methyl-methylene derivative of bis(cyclopentadienyl)tantalum(V) prepared by the following sequence of high-yield reactions:



The structure of the pale buff-coloured product is shown in Fig. 22.12b and this allows a direct comparison between the three Ta–C distances: Ta=CH<sub>2</sub> 203 pm, Ta–CH<sub>3</sub> 225 pm, and Ta–C(C<sub>5</sub>H<sub>5</sub>) 216 pm. It will also be noted that the two cyclopentadienyl rings are eclipsed and that the CH<sub>2</sub> group orients perpendicular to the C–Ta–C plane.

<sup>47</sup> J. E. ELLIS, *Adv. Organometallic Chem.* **31**, 1–52 (1990).

<sup>48</sup> S. A. DURAJ, M. T. ANDRAS and B. RIHTER, *Polyhedron* **8**, 2763–7 (1989).



**Figure 22.12** (a) The structure of dimeric  $[\text{Nb}(\eta^5\text{-C}_5\text{H}_5)\text{H}-\mu\text{-(}\eta^5,\eta^1\text{-C}_5\text{H}_4\text{)}]_2$ . The observed diamagnetism of this compound is consistent with the Nb–Nb bond shown. Each of the two bridging rings is  $\eta^5$ -bonded to one Nb and  $\eta^1$ -bonded to the other. (b) The structure of  $[\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_3)(=\text{CH}_2)]$ . (c) The structure of  $[\text{Ta}_4(\eta^5\text{-C}_5\text{Me}_5)_4(\mu_2\text{-O})_4(\mu_3\text{-O})_2(\mu_4\text{-O})(\text{OH})_2]$ .

Cationic cyclopentadienyl complexes are not common in this group, but recent examples whose structures have been determined include  $[\text{Nb}^{\text{V}}(\eta^5\text{-C}_5\text{H}_5)_2\text{Cl}_2]\text{BF}_4$ <sup>(49)</sup> and  $[\text{Nb}(\eta^5\text{-C}_5\text{H}_5)_2\text{L}_2](\text{BF}_4)_2$  (L = CNMe and NCMe),<sup>(50)</sup> which have pseudo-tetrahedral symmetry. Mono(cyclopentadienyl), or “half-sandwich” poly-oxo complexes are of interest as hydrocarbon-soluble models for oxide catalysts. The action of water on  $[\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)(\text{PMe}_3)_2]$  yields the colourless  $[\text{Ta}_4(\eta^5\text{-C}_5\text{Me}_5)_4\text{O}_7(\text{OH})_2]$  which has a tetranuclear “butterfly” core (Fig. 22.12c).<sup>(51)</sup>

<sup>49</sup>K. H. THIELE, W. KUBAK, J. SIELER, H. BORRMANN and A. SIMON, *Z. anorg. allgem. Chem.* **587**, 80–90 (1990).

<sup>50</sup>M. A. A. De C. T. CARRONDO, J. MORAIS, C. C. ROMAO and M. J. ROMAO, *Polyhedron* **12**, 765–70 (1993).

<sup>51</sup>V. C. GIBSON, T. P. KEE and W. CLEGG, *J. Chem. Soc., Chem. Commun.*, 29–30 (1990).

The chemistry of these metals with ring systems other than cyclopentadienyl has been little developed but, since larger rings afford more bonding electrons it would seem that the relatively electron-poor, early transition elements (see p. 941) should provide a field of study ripe for expansion. Reduction of  $\text{NbCl}_4$  by Na/Hg in thf in the presence of cycloheptatriene and  $\text{PMe}_3$  provides a convenient route and several  $\text{C}_7$ -ring compounds have been prepared<sup>(52)</sup> including the blue-green, 17-electron complex  $[\text{Nb}^{\text{II}}(\eta^7\text{-C}_7\text{H}_7)(\text{PMe}_3)_2\text{I}]$  which is isomorphous with the previously described Zr analogue (Fig. 21.10c).

<sup>52</sup>M. L. H. GREEN, P. MOUNTFORD, P. SCOTT and V. S. B. MTETWA, *Polyhedron* **10**, 389–92 (1991), and *J. Chem. Soc., Chem. Commun.*, 314–5 (1992).