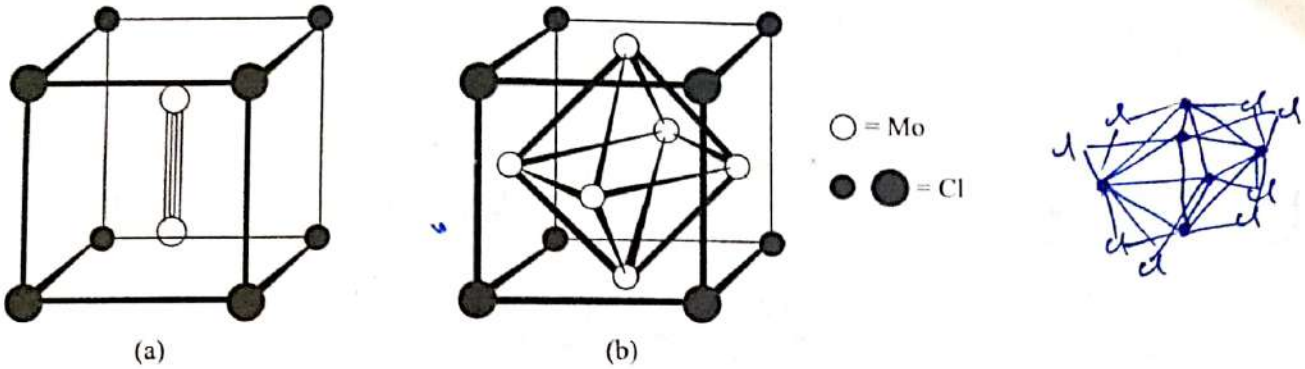

Fig. 13.18 A comparison of the two chloro complexes of Mo(II): (a) quadruply bonded $[Mo_2Cl_8]^{4-}$; (b) singly bonded $[Mo_6Cl_8]^{4+}$. [From Cotton, F. A. *Acc. Chem. Res.* **1969**, *2*, 240 Reproduced with permission.]

Hexanuclear Clusters

Clusters of six molybdenum, niobium, or tantalum atoms have been known for many years, predating the work with rhenium. There two types: In the first, an octahedron of six metal atoms is coordinated by eight chloride ligands, one on each face of the octahedron (Fig. 13.17a). This is found in "molybdenum dichloride," Mo_6Cl_{12}, better formulated as $[Mo_6Cl_8]Cl_4$. Each Mo(II) atom can use its four electrons to form four bonds with adjacent molybdenum atoms and can receive dative bonds from the four chloride ligands.[72]

Cotton has pointed out that a metal in a low oxidation state can adopt one of two strategies in forming clusters. It can form multiple bonds to another metal, as in $[Re_2X_8]^{2-}$, or it can form single bonds to several other metal atoms, as in the octahedral clusters. It is interesting that Mo(II) adopts both methods (Fig. 13.18) and that both structures have a cubic arrangement of chloride ions.

The second class of hexanuclear clusters also contains an octahedron of metal atoms, but they are coordinated by twelve halide ligands along the edges (Fig. 13.17b). Niobium and tantalum form clusters of this type. Here the bonding situation is somewhat more complicated: The metal atoms are surrounded by a very distorted square prism of four metal and four halogen atoms. Furthermore, these compounds are electron deficient in the same sense as the boranes—there are fewer pairs of electrons than orbitals to receive them and so fractional bond orders of $\frac{1}{2}$ are obtained.

Polyatomic Zintl Anions and Cations

It has been known for nearly 100 years that posttransition metals dissolve in liquid ammonia in the presence of alkali metals to give highly colored anions.[73] In the 1930s, polyatomic anions (Fig. 13.19a,b) such as Sn_9^{4-}, Pb_7^{4-}, Pb_9^{4-}, Sb_7^{3-}, and Bi_3^{3-} were identified but not structurally characterized. Attempts at isolating crystals were unsuccessful because they decomposed in solution. This problem was overcome in 1975 by stabilizing the cation of the salt as a cryptate (see Chapter 16), e.g., $[Na(crypt)]_2Pb_5$ and $[Na(crypt)]_4Sn_9$, which reduces the tendency of the salt to convert to a metal alloy.[74]

Salts of polyatomic cations, such as Bi_5^{5+} and Te_6^{4+}, are obtained from melts and stabilized by large weakly basic anions such as $AlCl_4^-$:

$$Bi + BiCl_3 + AlCl_3(\text{excess}) \longrightarrow Bi_5[AlCl_4]_3 \qquad \textbf{(13.59)}$$

Isopoly Anions

Transition metals in their higher oxidation states are formally similar to nonmetals with corresponding group numbers: V (VB) and P (VA) in VO_4^{3-} and PO_4^{3-}, Cr (VIB) and S (VIA) in CrO_4^{2-} and SO_4^{2-}, Mn (VIIB) and Cl (VIIA) in MnO_4^- and ClO_4^-. the analogy may be extended to polyanions, such as dichromate, $Cr_2O_7^{2-}$; however, the differences in behavior between the metal and nonmetal anions are often more important than their similarities. Whereas polyphosphoric acids and polysulfuric acids form only under rather stringent dehydrating conditions polymerization of some metal anions occurs spontaneously upon acidification. For example, the chromate ion is stable only at high pHs. As the pH is lowered, protonation and dimerization occur:

$$CrO_4^{2-} + H^+ \longrightarrow (HO)\,CrO_3^- \qquad \textbf{(13.44)}$$

$$(HO)\,CrO_3^- + H^+ \longrightarrow (HO)_2\,CrO_2 \qquad \textbf{(13.45)}$$

$$2(HO)_2CrO_2 \longrightarrow Cr_2O_7^{2-} + H_2O + 2H^+ \qquad \textbf{(13.46)}$$

Treatment with concentrated sulfuric acid completes the dehydration process and red chromium (VI) oxide ("chromic acid") precipitates:

$$\frac{n}{2}Cr_2O_7^{2-} + nH^+ \longrightarrow (CrO_3)_n + \frac{n}{2}H_2O \qquad \textbf{(13.47)}$$

The structure of CrO_3 consists of infinite linear chains of CrO_4 tetrahedra.

Other metals such as vanadium have more complicated chemistry. The vanadate ion, VO_4^{3-}, exists in extremely basic solution. Under *very* dilute conditions as the pH is lowered, protonation occurs to give monomers:

$$VO_4^{3-} \xrightarrow{+H^+} VO_3OH^{2-} \xrightarrow{+H^+} VO_2(OH)_2^- \xrightarrow{+H^+} VO(OH)_3(?) \longrightarrow VO_2^+ \qquad \textbf{(13.48)}$$

When solutions are more concentrated, however, protonation and dehydration occur to form $[V_2O_7]^{4-}$ and higher vanadates.[36] Further polymerization occurs unitil hydrous V_2O_5 precipitates at low pH. The precipitation of vanadium (V) oxide from aqueous solution as well as the similar behavior of other metal oxides, such as MoO_3 and WO_3, stands in sharp constrast to the extremely hygroscopic behavior of the analogous nonmetal compounds P_2O_5 and SO_3.

The polymerization of vanadate, molybdate, and tungstate ions forming isopoly anions has received a great deal of attention. Early in the condensation process the coordination number of the metals changes from 4 to 6, and the basic building unit in the polymerization process becomes an octahedron of six oxygen atoms surrounding each metal atom. Unlike tetrahedra, which can only link by sharing an apex, the resulting octahedra may link by sharing either an apex or edge (rarely a face) due to the relaxation of electrostatic repulsions in the larger octahedra. As a result, the structures tend to be small clusters of octahedra in the deiscrete polyanions, culminating in infinite structures in the oxides. When the edge sharing takes place, the structure may be stabilized (relative to electrostatic repulsions) if some distortion occurs such that the metal ions move away from each other. As the polymerization increases, it becomes more and more difficult to have all metal ions capable of moving to assist in this reduction in electrostatic repulsion. Ultimately the sharing of edges ceases since the requisite distorition becomes impossible. It might be expected that the smaller the metal ion, the less the repulsion and the larger the number of edge-sharing octahedra per unit. This expectation is borne out in a general way. For example, the metal radii (Table 4.4) are V^{5+} (68pm), Mo^{6+} (73pm), W^{6+} (74 pm), Nb^{5+} (78 pm) = Ta^{5+} (78 pm) and the most *common* corresponding edge-shared polyanions are $[V_{10}O_{28}]^{6-}$, $[Mo_7O_{24}]^{6-}$, $[Mo_8O_{26}]^{4-}$, $[W_6O_{19}]^{2-}$, $[W_7O_{24}]^{6-}$, $[Nb_6O_{19}]^{8-}$, and $[Ta_6O_{19}]^{8-}$.[37] To form larger polyanions such as $[W_{12}O_{42}]^{12-}$ or $[H_2W_{12}O_{40}]^{6-}$, edge sharing must give way to apex sharing.

The isopoly anions may be considered to be portions of a closest packed array of oxide ions with the metal ions occupying the octahedral holes. The edge-sharing array found in $[V_{10}O_{28}]^{6-}$ consists often octahedra stacked as shown in Fig. 13.3a. This seems to be the largest stacked-octahedral isopoly anion cluster compatible with metal–metal repulsions, and the remaining edge-shared structures represent portions of this unit.[38]

However, explanations for growth limitation based on repulsion of metal ions may be somewhat oversimplified. Elements other than vanadium, niobium, tantalum, molybdenum, and tungsten do not form isopoly anions. Other ions which have appropriate radii (e.g., Al^{3+}, 67 pm; Ga^{3+}, 76 pm; I^{7+}, 67 pm) for discrete isopoly anion formation instead form chains, sheets, or three-dimensional frameworks. Why does polymerization stop for isopoly anions? An oxygen atom in a terminal position in an isopoly anion is strongly π bonded to a transition metal such as Mo(VI) or W(VI). These terminal oxygen atoms are never found trans to one another because they avoid.

Although elucidation of various molybdate species continues, four appear to be most important: (1) the simple molybdate, MoO_4^{2-}, stable at high pH; (2) the heptamolybdate (also known as paramolybdate), $[Mo_7O_{24}]^{6-}$ (Fig. 13.3a), formed in equilibrium with molybdate down to pH 4–5; (3) octamolybdate, $[\beta\text{-}Mo_8O_{26}]^{4-}$(Fig. 13.3b),[39] formed in more acidic solutions; (4) $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$, the largest isopolyanion known, present in solutions at about pH 1.8. From strongly acidic solutions can be precipitated polymeric $MoO_3 \cdot 2H_2O$ consisting of sheets of corner-shared MO_6 octahedra.

---

[36] Pope, M. T. *Heteropoly and Isopoly Oxometalates*: Springer-Verlag: New York, 1983.

[37] The isolation of $[Nb_{10}O_{28}]^{6-}$ (Graeber, E.J. : Morrison, B. *Acta Crystallogr., Sect. B* **1977**, *33*, 2137–2143), which has a structure analogous to $[V_{10}O_{28}]^{6-}$, weakened the validity of this relationship.

[38] Kepert, D. L. *Inorg. Chem.* **1969**, *5*, 1556–1558.

[39] Both α and β isomers of $[Mo_8O_{26}]^{4-}$ are known and isomerize intramolecularly in solution. Klemperer, W. G.; Shum, W. *J. Am. Chem. Soc.* **1976**, *98*, 8291–8293. Masters, A. F.; Gheller, S. F.; Brownlee, R. T. C; O'Connor, M. J.; Wedd, A. G. *Inorg. Chem.* **1980**, *79*, 3866–3868. Klemperer, W. G.; Schwartz, C.; Wright, D. A. *J. Am. Chem. Soc.* **1985**, *107*, 6941–6950.