

Table 23.5 Oxohalides of Group 6 (mp/°C)

Oxidation state	Fluorides		Chlorides		Bromides		Iodides
+6	CrOF <sub>4</sub> red (55°)	CrO <sub>2</sub> F <sub>2</sub> violet (32°)		CrO <sub>2</sub> Cl <sub>2</sub> red (-96.5°) bp 117°		CrO <sub>2</sub> Br <sub>2</sub> red (d < rt)	
	MoOF <sub>4</sub> white (97°) bp 186°	MoO <sub>2</sub> F <sub>2</sub> white (subl 270°)	MoOCl <sub>4</sub> green (101°) bp 159°	MoO <sub>2</sub> Cl <sub>2</sub> pale yellow (175°) bp 250°		MoO <sub>2</sub> Br <sub>2</sub> purple-brown	
	WOF <sub>4</sub> white (101°) bp 186°	WO <sub>2</sub> F <sub>2</sub> white	WOCl <sub>4</sub> red (209°) bp 224°	WO <sub>2</sub> Cl <sub>2</sub> pale yellow (265°)	WOB <sub>4</sub> dark brown (277°) or black (321°)	WO <sub>2</sub> Br <sub>2</sub> red	WO <sub>2</sub> I <sub>2</sub> green
+5	CrOF <sub>3</sub>		CrOCl <sub>3</sub> dark red				
	MoOF <sub>3</sub> green, also dark blue		MoOCl <sub>3</sub> black (d > 200°)	MoO <sub>2</sub> Cl	MoOBr <sub>3</sub> black (subl 270° vac)		
+3			WOCl <sub>3</sub> olive green		WOB <sub>3</sub> dark brown		WO <sub>2</sub> I
			CrOCl green		CrOBr		

Cr<sup>IV</sup>OCl<sub>2</sub> has been observed in the gaseous phase by means of mass spectrometry.<sup>(29)</sup>

are prepared by a variety of oxygenation and halogenation reactions which frequently produce mixtures, and many specific preparations have therefore been devised.<sup>(28)</sup> They are possibly best known as impurities in preparations of the halides from which air or moisture have been inadequately excluded, and their formation is indicative of the readiness with which metal-oxygen bonds are formed by these elements in high oxidation states.

### 23.3.7 Complexes of chromium, molybdenum and tungsten<sup>(3,30,31)</sup>

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

No halogeno complexes of the type [MX<sub>6+x</sub>]<sup>x-</sup> are known and, although homoleptic imido

complexes, Li<sub>2</sub>[M(NBu<sup>t</sup>)<sub>4</sub>] (M = Cr, Mo, W), containing tetrahedrally coordinated M<sup>VI</sup> have been prepared,<sup>(32)</sup> the coordination chemistry of this oxidation state is centred mainly on oxo and peroxo complexes. The former class includes chromyl alkoxides<sup>(33)</sup> and adducts of tungsten oxohalides such as [WOX<sub>5</sub>]<sup>-</sup> and [WO<sub>2</sub>X<sub>4</sub>]<sup>2-</sup> (X = F, Cl), but most are octahedral chelates of

<sup>29</sup> V. PLIES, *Z. anorg. allg. Chem.* **602**, 97-104 (1991).

<sup>30</sup> L. F. LARKWORTHY, K. B. NOLAN and P. O'BRIEN, *Chromium*, Chap. 35, pp. 699-969, A. G. SYKES, G. J. HUNT, R. L. RICHARDS, C. D. GARNER, J. M. CHARNOCK and E. I. STIEFEL, *Molybdenum*, Chap. 36, pp. 1229-444, and Z. DORI, *Tungsten*, Chap. 37, pp. 973-1022, in *Comprehensive Coordination Chemistry*, Vol. 3, Pergamon Press, Oxford, 1987. For Chromium see also D. A. HOUSE, *Adv. Inorg. Chem.* **44**, 341-73 (1997).

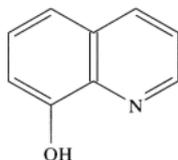
<sup>31</sup> R. COLTON, *Coord. Chem. Revs.* **90**, 1-109 (1988).

<sup>32</sup> A. A. DANOPOULOS and G. WILKINSON, *Polyhedron* **9**, 1009-10 (1990).

<sup>33</sup> S. L. CHADHA, V. SHARMA and A. SHARMA, *J. Chem. Soc., Dalton Trans.*, 1253-5 (1987).

<sup>28</sup> Ref. 2, pp. 275-81.

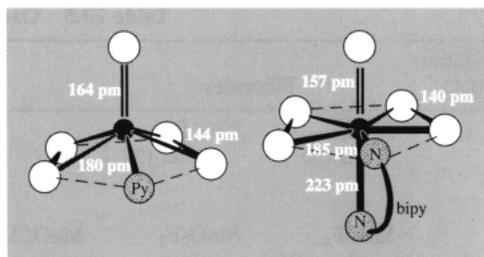
the types  $[\text{MO}_2\text{X}_2(\text{L-L})]^{(34)}$  and  $[\text{MO}_2(\text{L-L}^-)_2]$  ( $\text{M} = \text{Mo}, \text{W}$ ). In the  $\text{MO}_2^{2+}$  group of these compounds the oxygen atoms are mutually *cis*, thereby maximizing the  $\text{O}(\text{p}_\pi) \rightarrow \text{M}(\text{d}_\pi)$  bonding, and the group is reminiscent of the uranyl  $\text{UO}_2^{2+}$  ion (p. 1273), though its chemistry is by no means as extensive and the latter is a linear ion. The best-known example of this type of compound is  $[\text{MoO}_2(\text{oxinate})_2]$  used for the gravimetric determination of molybdenum; oxine is 8-hydroxyquinoline, i.e.



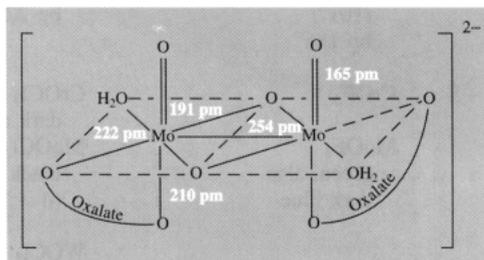
The peroxy-complexes provide further examples of the ability of oxygen to coordinate to the metals in their high oxidation states. The production of blue solutions when acidified dichromates are treated with  $\text{H}_2\text{O}_2$  is a qualitative test for chromium.<sup>†</sup> The colour arises from the unstable  $\text{CrO}_5$  which can, however, be stabilized by extraction into ether, and blue solid adducts such as  $[\text{CrO}_5(\text{py})]$  can be isolated. This is more correctly formulated as  $[\text{CrO}(\text{O}_2)_2\text{py}]$  and has an approximately pentagonal pyramidal structure (Fig. 23.6a). Bidentate ligands, such as phenanthroline and bipyridyl produce pentagonal bipyramidal complexes in which the second N-donor atom is loosely bonded *trans* to the  $=\text{O}$  (Fig. 23.6b). This 7-coordinate structure is favoured in numerous peroxy-complexes of Mo and W, and the dark-red peroxy anion  $[\text{Mo}(\text{O}_2)_4]^{2-}$  is 8-coordinate, with  $\text{Mo}-\text{O}$  197 pm and  $\text{O}-\text{O}$  155 pm.

### Oxidation state V ( $d^1$ )

This is an unstable state for chromium and, apart from the fluoride and oxohalides already



**Figure 23.6** Molecular structures of (a)  $[\text{CrO}(\text{O}_2)_2\text{py}]$  and (b)  $[\text{CrO}(\text{O}_2)_2(\text{bipy})]$ .



**Figure 23.7** The dimeric, oxygen bridged,  $[\text{Mo}_2\text{O}_4(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^{2-}$  showing the close approach of the 2 Mo atoms and unusually large range of  $\text{Mo}-\text{O}$  distances from 165 to 222 pm.

mentioned, it is represented primarily by the blue to black chromates of the alkali and alkaline earth metals and the red-brown tetraperoxo-chromate(V). The former contain the tetrahedral  $[\text{CrO}_4]^{3-}$  ion and hydrolyse with disproportionation to  $\text{Cr}(\text{III})$  and  $\text{Cr}(\text{VI})$ . The latter can be isolated as rather more stable salts from alkaline solutions of dichromate treated with  $\text{H}_2\text{O}_2$ . These red salts contain the paramagnetic 8-coordinate, dodecahedral,  $[\text{Cr}(\text{O}_2)_4]^{3-}$  ion, which is isomorphous with the corresponding complex ions of the Group 5 metals (p. 994). The  $\eta^2\text{-O}_2$  groups are unsymmetrically coordinated, with  $\text{Cr}-\text{O}$  185 and 195 pm and the  $\text{O}-\text{O}$  distance 141 pm.

The heavier elements have a much more extensive +5 chemistry including, in the case of molybdenum, a number of compounds of considerable biological interest which will be discussed separately (p. 1035). A variety of reactions involving fusion and nonaqueous

<sup>34</sup> K. DREISCH, C. ANDERSSON and C. STÄLHANDSKE, *Polyhedron* **11**, 2143–50 (1992).

<sup>†</sup> The acidity is important. In alkaline solution  $[\text{Cr}^{\text{V}}(\text{O}_2)_4]^{3-}$  is produced, but from neutral solutions explosive violet salts, probably containing  $[\text{Cr}^{\text{VI}}\text{O}(\text{O}_2)_2\text{OH}]^-$ , are produced.

solvents has been used to produce octahedral hexahalogeno complexes. These are very susceptible to hydrolysis, and the affinity of  $\text{Mo}^{\text{V}}$  for oxygen is further demonstrated by the propensity of  $\text{MoCl}_5$  to produce green oxomolybdenum(V) compounds by oxygen-abstraction from appropriate oxygen-containing materials. This leads to a number of well-characterized complexes of the type  $[\text{MoOCl}_3\text{L}]$  and  $[\text{MoOCl}_3\text{L}_2]$ . Oxomolybdenum(V) compounds are also obtained from aqueous solution and include monomeric species such as  $[\text{MoOX}_5]^{2-}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{NCS}$ ) and dimeric, oxygen-bridged complexes such as  $[\text{Mo}_2\text{O}_4(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^{2-}$  (Fig. 23.7) which may be considered to be derived from the orange-yellow aquo ion  $[\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6]^{2+}$ . Whereas the monomeric compounds are paramagnetic with magnetic moments corresponding to 1 unpaired electron, the binuclear compounds are diamagnetic, or only slightly paramagnetic, suggesting appreciable metal-metal interaction occurring either directly or via the bridging oxygens.

Also of interest are the octacyano complexes,  $[\text{M}(\text{CN})_8]^{3-}$  ( $\text{M} = \text{Mo}, \text{W}$ ), which are commonly prepared by oxidation of the  $\text{M}^{\text{IV}}$  analogues (using  $\text{MnO}_4^-$  or  $\text{Ce}^{\text{IV}}$ ) and whose structures apparently vary, according to the environment and counter cation, between the energetically similar square-antiprismatic and dodecahedral forms.<sup>(35)</sup>

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

As for the previous oxidation state, the chemistries of  $\text{Mo}^{\text{IV}}$  and  $\text{W}^{\text{IV}}$  are much more extensive than that of  $\text{Cr}^{\text{IV}}$  which is largely confined to peroxo- and fluoro- complexes.  $[\text{Cr}(\text{O}_2)_2(\text{NH}_3)_3]$ , which has a dark red-brown metallic lustre, may be obtained either by treating  $[\text{Cr}(\text{O}_2)_4]^{3-}$  with warm aqueous ammonia or by the action of  $\text{H}_2\text{O}_2$  on ammoniacal solutions of  $(\text{NH}_4)_2\text{CrO}_4$ . It has a pentagonal bipyramidal structure in which the peroxo- groups occupy

four of the planar positions, and the  $\text{NH}_3$  molecules are replaceable by other ligands. The very hydrolysable salts of  $[\text{CrF}_6]^{2-}$  are obtained by direct fluorination of anhydrous  $\text{CrCl}_3$  and an alkali metal chloride.

More or less hydrolysable hexahalogeno salts of  $[\text{MX}_6]^{2-}$  ( $\text{M} = \text{Mo}, \text{X} = \text{F}, \text{Cl}, \text{Br}; \text{M} = \text{W}, \text{X} = \text{Cl}, \text{Br}$ ) are also known and the yellow octacyano compounds have provided structural interest ever since the classical work of J. I. Hoard in 1939 established  $\text{K}_4[\text{Mo}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$  as the first example of an 8-coordinate complex. This and its W analogue have dodecahedral ( $D_{2d}$ ) structures and their diamagnetism arises from the splitting of their d-orbitals which stabilizes one (probably the  $d_{xy}$ ) to such an extent that the two d electrons pair in it. The energy barrier between dodecahedral and square antiprismatic ( $D_{4d}$ ) structures is, however, small and the latter is obtained if the  $\text{K}^+$  counter cations are replaced by  $\text{Cd}^{2+}$ .<sup>95</sup> Mo and  $^{14}\text{N}$  nmr studies show<sup>(35a)</sup> that the ion is dodecahedral in aqueous solution and that the equivalence of the eight CN groups (indicating the more symmetrical  $D_{4d}$  form), implied by earlier  $^{13}\text{C}$  work, arises from rapid tumbling of the ion rather than fluxional rearrangement. Photolysis of the otherwise stable  $[\text{M}(\text{CN})_8]^{4-}$  solutions causes loss of four  $\text{CN}^-$  ions to give octahedral oxo compounds such as  $\text{K}_4[\text{MO}_2(\text{CN})_4] \cdot 6\text{H}_2\text{O}$  ( $\text{M} = \text{Mo}, \text{W}$ ).

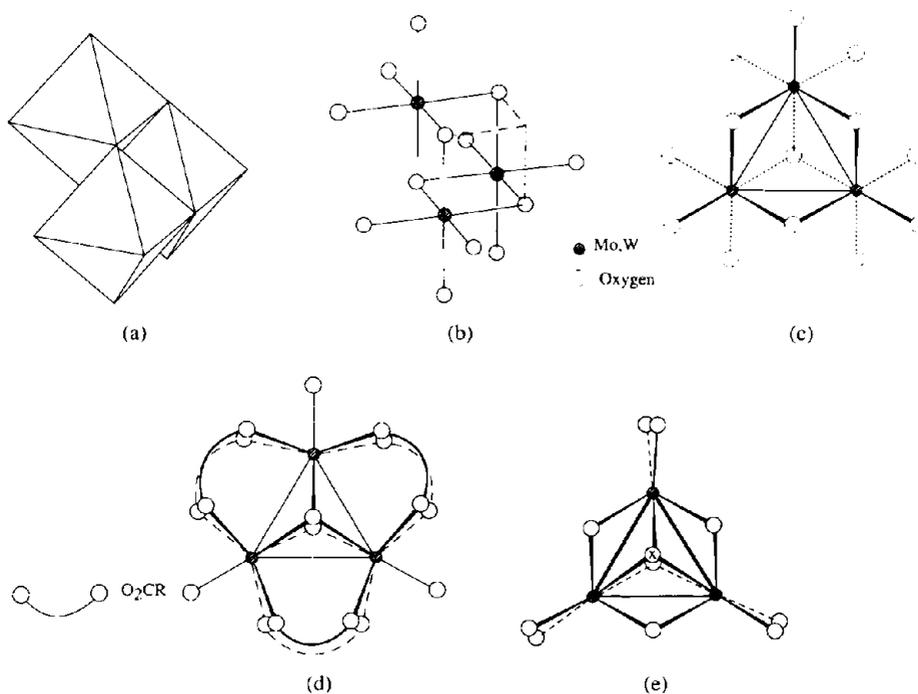
Other mononuclear complexes include the tetrahedral  $[\text{Mo}(\text{NMe}_2)_4]$  and the octahedral  $\text{Li}_2[\text{Mo}(\text{NMe}_2)_6] \cdot 2\text{thf}$ <sup>(36)</sup> but recent interest in the chemistry of the  $\text{M}^{\text{IV}}$  ion has centred on the trinuclear oxo and thio complexes of Mo and W, particularly the former. They are of three main types. The first may be conceptually based on the  $[\text{M}_3\text{O}_{13}]$  unit found in the aquo ions  $[\text{M}_3\text{O}_4(\text{H}_2\text{O}_9)]^{4+}$  ( $\text{M} = \text{Mo},$ <sup>(37)</sup> W). It contains a

<sup>35a</sup> R. T. C. BROWNLEE, B. P. SHEHAN and A. G. WEDD, *Inorg. Chem.* **26**, 2022-4 (1987).

<sup>36</sup> M. H. CHISHOLM, C. E. HAMMOND and J. C. HUFFMAN, *Polyhedron* **7**, 399-400 (1988).

<sup>37</sup> Preparations of the various aquo ions of Mo in oxidation states II to V are given in D. T. RICHENS and A. G. SYKES, *Inorg. Synth.* **23**, 130-40 (1985).

<sup>35</sup> J. G. LEIPOLDT, S. S. BASSON and A. ROODT, *Adv. Inorg. Chem.* **40**, 241-322 (1994).



**Figure 23.8** Trinuclear, M–M bonded species of Mo<sup>IV</sup> and W<sup>IV</sup>. (a) (b) and (c) are alternative representations of the M<sub>3</sub>O<sub>13</sub> unit: (a) emphasizes its relationship to the edge-sharing octahedra of the M<sub>3</sub> group in polymetallate ions; (b) shows the (μ<sub>3</sub>-O) (μ<sub>2</sub>-O)<sub>3</sub> bridges and M–M bonds of its M<sub>3</sub>O<sub>4</sub> “incomplete cubane” core; and (c) emphasizes its triangular centre by viewing from the unoccupied corner of the cuboid. (d) and (e) offer the same perspective as (c) but of [M<sub>3</sub>O<sub>2</sub>(O<sub>2</sub>CR)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]<sup>2+</sup> and [M<sub>3</sub>(μ<sub>3</sub>-X)(μ<sub>3</sub>-OR)(OR)<sub>9</sub>] structures respectively.

triangle of M–M bonded metals capped by a single oxygen on one side and on the other side three oxygens bridge each pair of metal atoms. It may be viewed either as a reduced form of the M<sub>3</sub> group found in polymetallate ions, or as an “incomplete cubane-type” of complex<sup>(38)</sup> (Fig. 23.8). Some, or all, of the nine water molecules of the aquo ion are replaceable by a variety of ligands including oxalate, edta and NCS<sup>-</sup>, and thio derivatives<sup>(38a)</sup> containing M<sub>3</sub>O<sub>3</sub>S, M<sub>3</sub>O<sub>2</sub>S<sub>2</sub>, M<sub>3</sub>OS<sub>3</sub> and M<sub>3</sub>S<sub>4</sub> cores have been prepared. In the mixed O/S species, S appears always to occupy the μ<sub>3</sub>-position. M–M bond lengths are about 250 pm for M<sub>3</sub>O<sub>4</sub> species increasing to 270–280 pm for M<sub>3</sub>S<sub>4</sub>, there

being very little difference between Mo and W compounds. Preparative routes vary but usually involve reduction from M<sup>VI</sup> or M<sup>V</sup>, often by the use of NaBH<sub>4</sub>. Se and Te analogues of the Mo compounds are also known and an Se analogue for W has recently been reported.<sup>(39)</sup>

The second type of trinuclear compounds containing [M<sub>3</sub>O<sub>2</sub>(O<sub>2</sub>CR)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]<sup>2+</sup> and obtained by the reaction of M(CO)<sub>6</sub> (M = Mo, W) with carboxylic acids, features a similar triangle of M–M bonded metal atoms but this time capped on *both* sides by μ<sub>3</sub>-O atoms (Fig. 23.8d). Complexes in which either one or both of these capping atoms are replaced by μ<sub>3</sub>-CR, alkylidene,

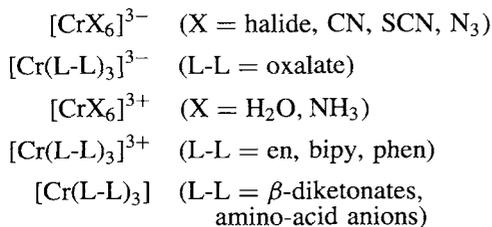
<sup>38</sup> T. SHIBAHARA, *Adv. Inorg. Chem.* **37**, 143–73 (1991).  
<sup>38a</sup> T. SAITO, *Adv. Inorg. Chem.* **44**, 45–92 (1997).  
<sup>39</sup> V. P. FEDIN, M. N. SOKOLOV, A. V. VIROVETS, N. V. POD-BEREZSKAY and V. Y. FEDEROV, *Polyhedron* **11**, 2973–4 (1992).

groups are also obtainable and all these biccapped species are notable for their kinetic inertness. The third trinuclear type is that of the alkoxides  $[M_3(\mu_3-X)(\mu_3-OR)(OR)_9]$  ( $M = Mo, W; X = O, NH$ )<sup>(40)</sup> which again are biccapped but with only single bridges spanning the M–M bonds (Fig. 23.8e).

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

This is by far the most stable and best-known oxidation state for chromium and is characterized by thousands of compounds, most of them prepared from aqueous solutions. By contrast, unless stabilized by M–M bonding, molybdenum(III) compounds are sparse and hardly any are known for tungsten(III). Thus Mo, but not W, has an aquo ion  $[Mo(H_2O)_6]^{3+}$ , which gives rise to complexes  $[MoX_6]^{3-}$  ( $X = F, Cl, Br, NCS$ ). Direct action of acetylacetonate on the hexachloromolybdate(III) ion produces the sublimable  $[Mo(acac)_3]$  which, however, unlike its chromium analogue, is oxidized by air to  $Mo^V$  products. A black  $Mo^{III}$  cyanide,  $K_4Mo(CN)_7 \cdot 2H_2O$ , has been precipitated from aqueous solution by the addition of ethanol. Its magnetic moment ( $\sim 1.75$  BM) is consistent with 7-coordinate  $Mo^{III}$  in which the loss of degeneracy of the  $t_{2g}$  orbitals has caused pairing of 2 of the three d electrons.

Chromium(III) forms stable salts with all the common anions and it complexes with virtually any species capable of donating an electron-pair. These complexes may be anionic, cationic, or neutral and, with hardly any exceptions, are hexacoordinate and octahedral, e.g.:



There is also a multitude of complexes with 2 or more different ligands, such as the pentaammines  $[Cr(NH_3)_5X]^{n+}$  which have been extensively used in kinetic studies. These various complexes are notable for their kinetic inertness, which is compatible with the half-filled  $t_{2g}$  level arising from an octahedral  $d^3$  configuration and is the reason why many thermodynamically unstable complexes can be isolated. Ligand substitution and rearrangement reactions are slow (half-times are of the order of hours), with the result that the preparation of different, solid, isomeric forms of a compound was the classical means of establishing stereochemistry and the reason why early coordination chemists devoted so much attention to  $Cr^{III}$  complexes. For precisely the same reason, however, the preparation of these complexes is not always straightforward. Salts such as the hydrated sulfate and halides, which might seem obvious starting materials, themselves contain coordinated water or anions and these are not always easily displaced. Simple addition of the appropriate ligand to an aqueous solution of a  $Cr^{III}$  salt is therefore not a usual preparative method, though in the presence of charcoal it is feasible in the case, for instance, of  $[Cr(en)_3]^{3+}$ . Some alternative routes, which avoid these pre-formed inert complexes, are:

- (i) *Anhydrous methods*: ammine and amine complexes can be prepared by the reaction of  $CrX_3$  with  $NH_3$  or amine, and salts of  $[CrX_6]^{3-}$  anions are best obtained by fusion of  $CrX_3$  with the alkali metal salt.
- (ii) *Oxidation of Cr(II)*: ammine and amine complexes can also be prepared by the aerial oxidation of mixtures of aqueous  $[Cr(H_2O)_6]^{2+}$  (which is kinetically labile) and the appropriate ligands.
- (iii) *Reduction of Cr(VI)*:  $CrO_3$  and dichromates are commonly used to prepare such complexes as  $K_3[Cr(C_2O_4)_3]$  and  $NH_4[Cr(NH_3)_2(NCS)_4] \cdot H_2O$  (Reinecke's salt).

<sup>40</sup> M. H. CHISHOLM, D. L. CLARK, M. J. HAMPDEN-SMITH and D. H. HOFFMAN, *Angew. Chem. Int. Edn. Engl.* **28**, 432–44 (1989).

The violet hexaquo ion,  $[Cr(H_2O)_6]^{3+}$ , occurs in the chrome alums,  $Cr_2(SO_4)_3 \cdot M_2SO_4 \cdot 24H_2O$

Table 23.6 Spectroscopic data for typical octahedral complexes of chromium(III)

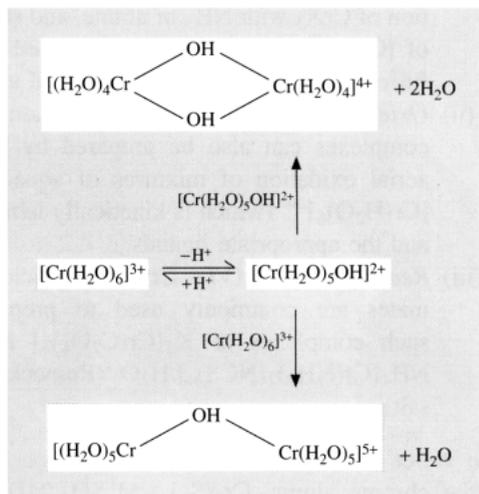
Complex	Colour	$\nu_1/\text{cm}^{-1}$	$\nu_2/\text{cm}^{-1}$	$\nu_3/\text{cm}^{-1}$	$10Dq/\text{cm}^{-1}$	$B/\text{cm}^{-1}$	$\mu_{\pi}/\text{BM}^{(a)}$
$\text{K}[\text{Cr}(\text{H}_2\text{O})_6][\text{SO}_4]_2 \cdot 6\text{H}_2\text{O}$	Violet	17 400	24 500	37 800	17 400	725	3.84
$\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$	Reddish-violet	17 500	23 900		17 500	620	3.84
$\text{K}_3[\text{Cr}(\text{NCS})_6] \cdot 4\text{H}_2\text{O}$	Purple	17 800	23 800		17 800	570	3.77
$[\text{Cr}(\text{NH}_3)_6]\text{Br}_3$	Yellow	21 550	28 500		21 550	650	3.77
$[\text{Cr}(\text{en})_3]\text{I}_3 \cdot \text{H}_2\text{O}$	Yellow	21 600	28 500		21 600	650	3.84
$\text{K}_3[\text{Cr}(\text{CN})_6]$	Yellow	26 700	32 200		26 700	530	3.87

<sup>(a)</sup>Room temperature value of  $\mu_e$ .

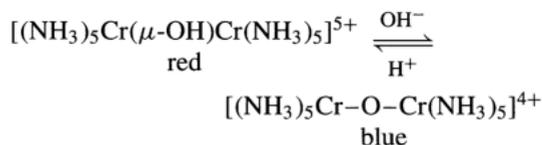
(e.g.  $[\text{K}(\text{H}_2\text{O})_6][\text{Cr}(\text{H}_2\text{O})_6][\text{SO}_4]_2$ ), but in hydrated salts and aqueous solutions, green species, produced by the replacement of some of the water molecules by other ligands, are more usual. So, the common form of the hydrated chloride is the dark-green *trans*- $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ , and other isomers are known (see p. 920).

Chromium(III) is the archetypal  $d^3$  ion and the electronic spectra and magnetic properties of its complexes have therefore been exhaustively studied<sup>(41)</sup> (see Panel). Data for a representative sample of complexes are given in Table 23.6.

One of the most obvious characteristics of  $\text{Cr}^{\text{III}}$  is its tendency to hydrolyse and form polynuclear complexes containing  $\text{OH}^-$  bridges. This is thought to occur by the loss of a proton from coordinated water, followed by coordination of the  $\text{OH}^-$  so formed to a second cation:



The ease with which the proton is removed can be judged by the fact that the hexaquo ion ( $\text{p}K_a \sim 4$ ) is almost as strong an acid as formic acid. Further deprotonation and polymerization can occur and, as the pH is raised, the final product is hydrated chromium(III) oxide or “chromic hydroxide”. Formation of this is the reason why amine complexes are not prepared by simple addition of the amine base to an aqueous solution of  $\text{Cr}^{\text{III}}$ . By methods which commonly start with  $\text{Cr}^{\text{II}}$ , binuclear compounds such as  $[(\text{en})_2\text{Cr}(\mu_2\text{-OH})_2\text{Cr}(\text{en})_2]$  and  $[(\text{NH}_3)_5\text{Cr}(\mu\text{-OH})\text{Cr}(\text{NH}_3)_5]\text{X}_5$  are obtained. These have temperature-dependent magnetic moments, somewhat lower than those usual for octahedral  $\text{Cr}^{\text{III}}$  and indicative of weak antiferromagnetic interaction via the bent  $\text{Cr}-\text{O}(\text{H})-\text{Cr}$  bridges. Stronger antiferromagnetic interaction (magnetic moment per metal atom at room temperature  $\sim 1.3 \text{ BM}$  falling to zero below 100 K) is found in the oxo-bridged derivative of the latter compound:



The linear  $\text{Cr}-\text{O}-\text{Cr}$  bridge evidently permits pairing of the  $d$  electrons of the 2 metal atoms via  $d_{\pi}-p_{\pi}$  bonds, much more readily than the bent  $\text{Cr}-\text{OH}-\text{Cr}$  bridge. Blue  $[\text{LCr}(\mu_2\text{-O})(\mu_2\text{-O}_2\text{CMe})_2\text{CrL}]$  ( $\text{L} = 1,4,7\text{-trimethyl-1,4,7-triazacyclononane}$ ), produced similarly by

<sup>41</sup> A. B. P. LEVER *Inorganic Electronic Spectroscopy*, (2nd edn.), pp. 417–28, Elsevier, Amsterdam, 1984.

### Electronic Spectra and Magnetic Properties of Chromium(III)

In an octahedral field the free-ion ground  $^4F$  term of a  $d^3$  ion is split into an  $A$  and two  $T$  terms which, along with the excited  $^4T(P)$  term (Fig. A), give rise to the possibility of three spin-allowed d-d transitions of which the one of lowest energy is a direct measure of the crystal field splitting,  $\Delta$  or  $10Dq$ :

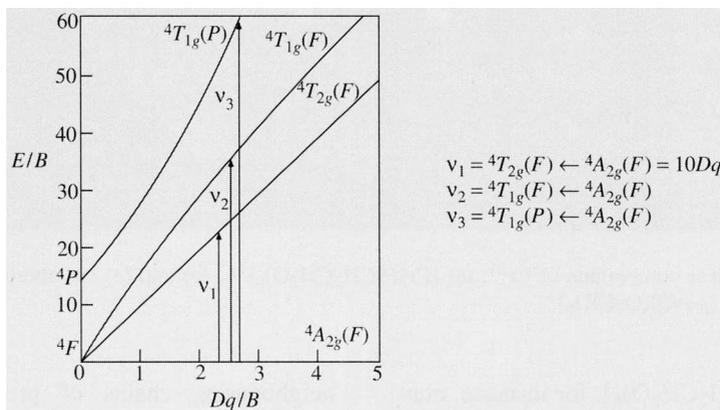


Figure A Energy Level diagram for a  $d^3$  ion in an octahedral crystal field.

Assignment of the observed bands to these transitions, provides an estimate of  $B$ , the Racah "interelectron repulsion parameter." Its value (Table 23.6) is invariably below that of the free-ion ( $1030\text{ cm}^{-1}$ ) because the expansion of d-electron charge on complexation reduces the interelectronic repulsions.

The magnetic moment arising from the ground  $^4A$  term is expected to be close to the spin-only value of  $3.87\text{ BM}$  and independent of temperature. In practice, providing the compounds are mononuclear, these expectations are realized remarkably well apart from the fact that, as was noted for octahedral complexes of vanadium(III), the third high-energy band in the spectrum is usually wholly or partially obscured by more intense charge-transfer absorption.

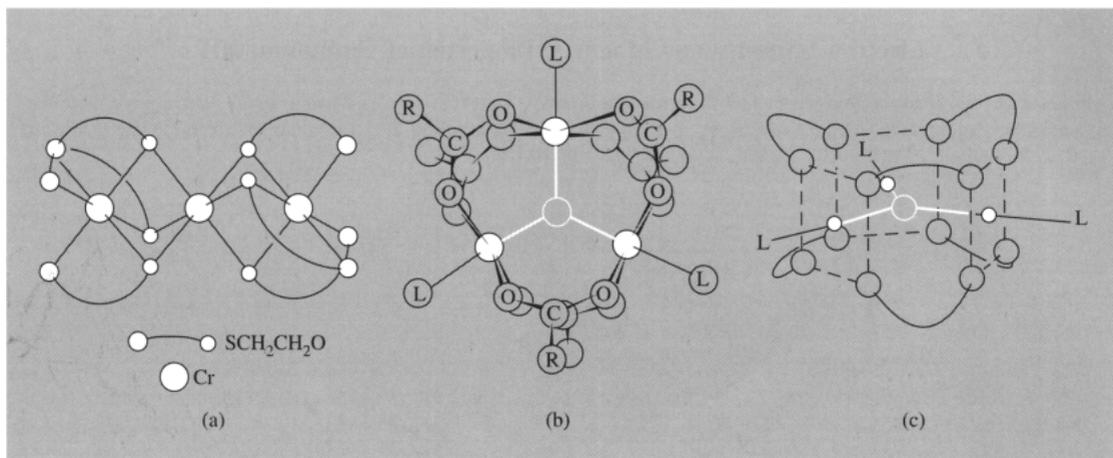
In addition to the terms so far mentioned there are a number of spin doublets and, in the  $\text{Cr}^{3+}$  ions of ruby ( $\alpha\text{-Al}_2\text{O}_3$ , corundum, in which a small proportion of  $\text{Al}^{3+}$  ions have been replaced by  $\text{Cr}^{3+}$ ), two of these ( $^2E_g$  and  $^2T_{1g}$ ) lie just below the  $^4T_{2g}$ . Ions excited to the  $^4T_{2g}$  may decay back to the ground level with *spontaneous emission* of radiation but some will decay instead to the doublets, the small energy difference being converted to lattice vibrations. The rate of decay by spontaneous emission from the doublets to the ground level is however slow, being spin-forbidden, but can be induced by interaction with photons of the same energy as those to be emitted (i.e. *stimulated emission*). This situation is exploited in the ruby laser,<sup>(42)</sup> in which a rod of ruby is irradiated by intense light of appropriate frequency to continually excite and re-excite the  $\text{Cr}^{3+}$  ions to the  $^4T_{2g}$  term. This *optical pumping* has the effect of steadily building up the population of the doublets. At suitable intervals the photons from the small proportion of ions which do spontaneously decay from the doublets are reflected by mirrors back through the rod where they interact with the excited ions, triggering their decay. This produces a burst of extremely intense radiation which is monochromatic, coherent and virtually non-divergent.

deprotonation of a pink, OH-bridged species but, crucially, with a  $120^\circ$  Cr-O-Cr bridge, shows only weak antiferromagnetic interaction.<sup>(43)</sup>

Examples of O atoms providing  $\pi$  pathways for antiferromagnetic interaction are also to be found among trinuclear compounds of  $\text{Cr}^{\text{III}}$ .

<sup>42</sup> J. A. DUFFY, *Bonding, Energy Levels and Bands*, pp. 72-7, Longman, Harlow, 1990.

<sup>43</sup> L. L. MARTIN, K. WIEGHARDT, G. BLONDIN, J.-J. GIRERD, B. NUBER and J. WEISS, *J. Chem. Soc., Chem. Commun.*, 1767-9 (1990).



**Figure 23.9** Trinuclear compounds of Cr<sup>III</sup>: (a)  $[\text{Cr}_3(\text{SCH}_2\text{CH}_2\text{O})_6]^{3-}$ . (b) and (c) are alternative representations of  $[\text{Cr}_3(\mu_3\text{-O})(\text{O}_2\text{CR})_6]^+$ .

( $\text{PPh}_4$ )<sub>2</sub>Na[Cr<sub>3</sub>(SCH<sub>2</sub>CH<sub>2</sub>O)<sub>6</sub>], for instance, consists of three face-sharing octahedra in which the Cr<sup>III</sup> atoms are linearly aligned and the *O*-, *S*-donor ligands are arranged so that all bridging atoms are oxygens<sup>(44)</sup> (Fig. 23.9a). A whole series of “basic” carboxylates of the general type  $[\text{Cr}_3\text{O}(\text{RCOO})_6\text{L}_3]^+$  show weak interactions and have the structure (Fig. 23.9b,c) common to carboxylates of other M<sup>III</sup> atoms and containing a central μ<sub>3</sub>-O.<sup>(45)</sup>

Hydrolysed, polynuclear Cr<sup>III</sup> complexes are of considerable commercial importance in the dyeing and tanning industries. In the former the role is that of a mordant to the dye. In leather production it is necessary to treat animal hides to prevent putrefaction and to render them supple when dry. Traditionally, tannin was used, hence the name of the process, but this was superseded towards the end of the nineteenth century by solutions of chromium(III) sulfate. After soaking in sulfuric acid the hides are impregnated with the Cr<sup>III</sup> solution. This is subsequently made alkaline, when the polynuclear complexes form and bridge

neighbouring chains of proteins, presumably by coordinating to the carboxyl groups of the proteins.

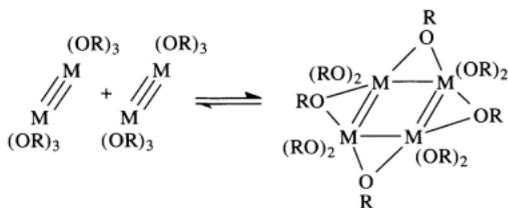
The bulk of the chemistry of Mo<sup>III</sup> and W<sup>III</sup> is associated with M≡M bonded species<sup>(46)</sup> which have been extensively studied for over a decade. M<sub>2</sub>X<sub>6</sub> compounds are commonly found with X = NR<sub>2</sub>, OR, CH<sub>2</sub>SiMe<sub>3</sub>, SAr and more recently SeAr,<sup>(47)</sup> and are generally both oxygen- and moisture-sensitive. The usual preparative route is by reacting metal halides with LiNR<sub>2</sub> followed by ligand substitution of the M<sub>2</sub>(NR<sub>2</sub>)<sub>6</sub> so obtained, and the products are of the type X<sub>3</sub>M≡MX<sub>3</sub> in which the two MX<sub>3</sub> halves are staggered with respect to each other. The σ<sup>2</sup>π<sup>4</sup> triple bond is readily understood from the MO diagram of Fig. 23.12 (p. 1033), given that the two d<sup>3</sup> metal ions contribute six electrons for M–M bonding. Neutral ligands can sometimes be added, to yield LX<sub>3</sub>M≡MX<sub>3</sub>L, and a series of tetranuclear products has been obtained by dimerization of M<sub>2</sub>(OR)<sub>6</sub>

<sup>44</sup> J. R. NICHOLSON, G. CHRISTOU, R.-J. WANG, J. C. HUFFMAN, H.-R. CHANG and D. N. HENDRICKSON, *Polyhedron* **19**, 2255–63 (1991).

<sup>45</sup> R. D. CANNON and R. P. WHITE, *Prog. Inorg. Chem.* **36**, 195–298 (1988).

<sup>46</sup> F. A. COTTON and R. A. WALTON, *Multiple Bonds between Atoms*, 2nd edn., Oxford Univ. Press, Oxford, 1993, 787 pp.

<sup>47</sup> M. H. CHISHOLM, J. C. HUFFMAN, I. P. PARKIN and W. E. STREIB, *Polyhedron* **9**, 2941–52 (1990).



The precise shape of the  $M_4$  core can be varied by partial substitution of OR with halide, and ranges from square to “butterfly” but apparently never tetrahedral<sup>(48)</sup>

Another type of triply bonded species is represented by the purple and unusually air-stable,  $Cs_2[Mo_2(HPO_4)_4(H_2O)_2]$ , prepared by the reaction of  $K_4MoCl_8 \cdot 2H_2O$  and  $CsCl$  in aqueous  $H_3PO_4$ . Here the cation has the dinuclear structure more commonly found in the divalent carboxylates (see below) and the  $M \equiv M$  bond is supported by phosphate bridges.

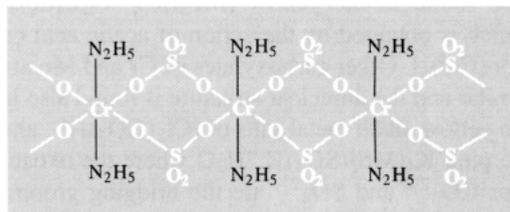
Although having formal oxidation states of  $2\frac{2}{3}$  per metal, it is opportune to mention here important molecular analogues of the Chevrel phases.<sup>(49)</sup>  $M_6S_8(PEt_3)_6$ , ( $M = Mo, W$ ) have the same octahedral  $[M_6S_8]$  core found in Chevrel phases (with the addition of terminal phosphines on each metal) but without the trigonal elongation found in the latter (p. 1018). That both are 20-electron clusters is compelling evidence that the distortion arises from intercluster interactions, which are absent in the molecular compounds, rather than because the number of cluster electrons is insufficient to form  $M-M$  bonds along all twelve edges of the octahedron.

### Oxidation state II ( $d^4$ )

For chromium, this oxidation state is characterized by the aqueous chemistry of the strongly reducing  $Cr^{II}$  cation, and a noticeable tendency to form dinuclear compounds with multiple metal-metal bonds. This tendency is even more

marked in the case of molybdenum but, perhaps surprisingly, is much less so in the case of tungsten,<sup>†</sup> though single  $M-M$  bonds are present in the  $[M_6X_8]^{4+}$  clusters of the dihalides of both Mo and W (p. 1022).

With the exception of the nitrate, which has not been prepared because of internal oxidation-reduction, the simple hydrated, sky-blue, salts of chromium(II) are best obtained by the reaction of the appropriate dilute acid with pure chromium metal, air being rigorously excluded. A variety of complexes is formed, especially with  $N$ -donor chelating ligands which commonly produce stoichiometries such as  $[Cr(L-L)_3]^{2+}$  and  $[Cr(L-L)_2X_2]$ . They (and other complexes of  $Cr^{II}$ ) are generally extremely sensitive to atmospheric oxidation if moist, but are considerably more stable when dry, probably the most air-stable of all being the pale-blue hydrazinium sulfate,  $(N_2H_5^+)_2Cr^{II}(SO_4)_2$ . In the solid state this consists of linear chains of  $Cr^{II}$  ions, bridged by  $SO_4^{2-}$  ions:



The majority of  $Cr^{II}$  complexes are octahedral and can be either high-spin ( $t_{2g}^3 e_g^1$ ) or low-spin ( $t_{2g}^4$ ). The former are characterized by magnetic moments close to 4.90 BM and visible/ultraviolet spectra consisting typically of a broad band in the region of  $16\,000\text{ cm}^{-1}$  with another band around  $10\,000\text{ cm}^{-1}$ . Since a  $d^4$  ion in a perfectly octahedral field can give rise to only one  $d-d$  transition it is clear that some lowering of symmetry has occurred. Indeed, this is expected as a consequence of the Jahn-Teller effect, even when the metal is surrounded by 6 equivalent donor atoms. The splitting of the free-ion  $^5D$

<sup>48</sup> M. H. CHISHOLM, C. E. HAMMOND, J. C. HUFFMAN and J. D. MARTIN, *Polyhedron* **9**, 1829-41 (1990).

<sup>49</sup> T. SAITO, N. YAMAMOTO, T. NAGASE, T. TSUBOI, K. KOBAYASHI, T. YAMAGATA, H. IMOTO and K. UNOURA, *Inorg. Chem.* **29**, 764-70 (1990).

<sup>†</sup> A major reason for their comparative paucity is that the dinuclear acetate, which in the case of Mo is the most common starting material in the preparation of quadruply bonded dimeric complexes, is unknown for W.

term is shown in Fig. 23.10 and the two observed bands are assigned to superimposed  ${}^5B_{2g} \leftarrow {}^5B_{1g}$  and  ${}^5E_g \leftarrow {}^5B_{1g}$  transitions and to the  ${}^5A_{1g} \leftarrow {}^5B_{1g}$  transition respectively. The low-spin, intensely coloured compounds such as  $K_4[Cr(CN)_6] \cdot 3H_2O$  and  $[Cr(L-L)_3]X_2 \cdot nH_2O$  (L-L = bipy, phen; X = Cl, Br, I) have magnetic moments in the range 2.74–3.40 BM and electronic spectra showing clear evidence of extensive  $\pi$  bonding, as is to be expected with such ligands.

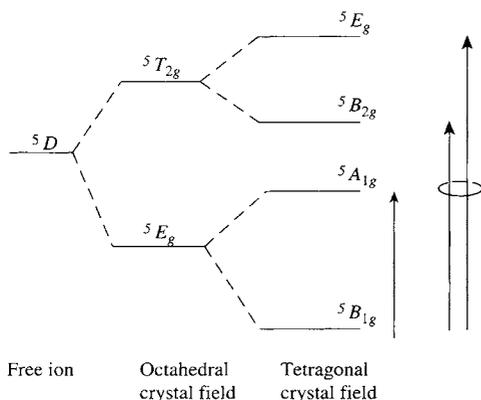
Although distorted octahedral geometry is certainly the most usual,  $Cr^{II}$  has a varied stereochemistry, as indicated in Table 23.2 (p. 1006).

One of the best known of  $Cr^{II}$  compounds, and one which has often been used as the starting material in preparations of other  $Cr^{II}$  compounds, is the acetate, itself obtained by addition of sodium acetate to an aqueous solution of a  $Cr^{II}$  salt. The red colour of the hydrated acetate is in sharp distinction to the blue of the simple salts — a contrast reflected in its dinuclear, bridged structure (Fig. 23.11a). This structure is also found in the yellow  $[Mo_2(\mu, \eta^2-O_2CMe)_4]$  which is obtained by the action of acetic acid on  $[Mo(CO)_6]$ . Other carboxylates of Cr and Mo are similar and the dinuclear structure is found also in the yellow alkali metal salts of  $[Cr_2(CO_3)_4]^{4-}$  and the pink  $K_4[Mo_2(SO_4)_4] \cdot 2H_2O$  where the oxoanions  $CO_3^{2-}$  and  $SO_4^{2-}$  are the bridging groups. Although an exact structure determination is lacking it is likely that the violet dihydrate,

obtained by partial dehydration of the blue “double sulphate”  $Cs_2SO_4 \cdot CrSO_4 \cdot 6H_2O$ , is of the same type in which case the formulation  $Cs_4[Cr_2(\mu, \eta^2-SO_4)_4(H_2O)_2] \cdot 2H_2O$  would be appropriate.  $[NBU_4]_2[Cr(NCS)_4]$  exists in two forms in which the usual correlation between structure and colour of  $Cr^{II}$  salts is reversed.<sup>(49a)</sup> The red form contains the mononuclear, planar  $[Cr(NCS)_4]^{2-}$  ion whereas the blue form contains the dinuclear  $[(NCS)_3Cr(\mu-NCS)_2Cr(NCS)_3]^{4-}$  ion featuring bridging thiocyanates (p. 324).

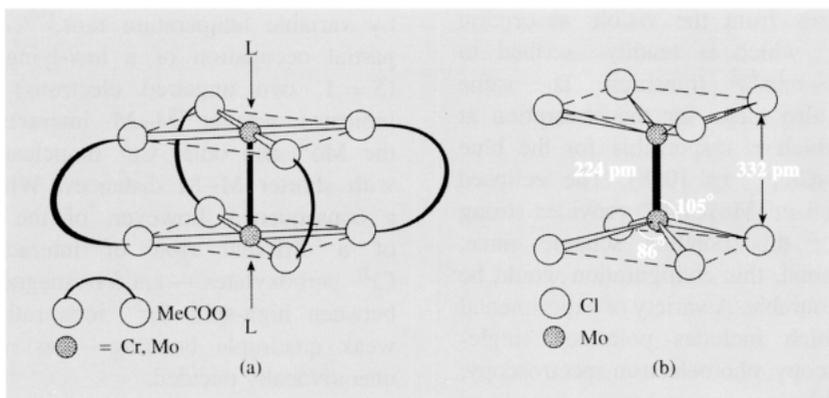
The reaction of conc HCl and molybdenum acetate at 0°C produces the diamagnetic red anion  $[Mo_2Cl_8]^{4-}$  (Fig. 23.11b) in which the 2  $MoCl_4$  are in the “eclipsed” orientation relative to each other and are held together solely by the Mo–Mo bond. At somewhat higher temperatures (~50°C) the above reactants also produce the  $[Mo_2Cl_8H]^{3-}$  ion which has the  $[M_2^{III}Cl_7]^{3-}$  structure (Fig. 23.4) but with one of the bridging Cl atoms replaced by a H atom.

An abundance of dinuclear compounds with a wide range of bridging groups involving not only the O–C–O unit of the carboxylates but also N–C–O, N–C–N, N–N–N and C–C–O, or like  $[Mo_2Cl_8]^{4-}$  with no bridging groups at all, are now known for  $Cr^{II}$  and  $Mo^{II}$ , particularly the latter.  $W^{II}$  also forms a comparatively small number and analogues of the isoelectronic  $Re^{III}$  and  $Tc^{III}$  are well-known (p. 1058–9). The  $Cr^{II}$  compounds apart, all these compounds whether bridged or not are diamagnetic, have very short M–M distances and clearly involve M–M bonds the precise nature of which has excited considerable attention<sup>(46)</sup>. The best simple description of the  $d^4$  systems is that shown in Fig. 23.12. The  $d_{x^2-y^2}$  orbital is assumed to have been used in  $\sigma$  bonding to the ligands and the four d electrons on each metal atom are then used to form a M–M quadruple bond ( $\sigma + 2\pi + \delta$ ) as originally proposed by B. N. Figgis and R. L. Martin for the bonding in dinuclear chromium(II) acetate (*J. Chem. Soc.* 3837–46 (1956)). The characteristic

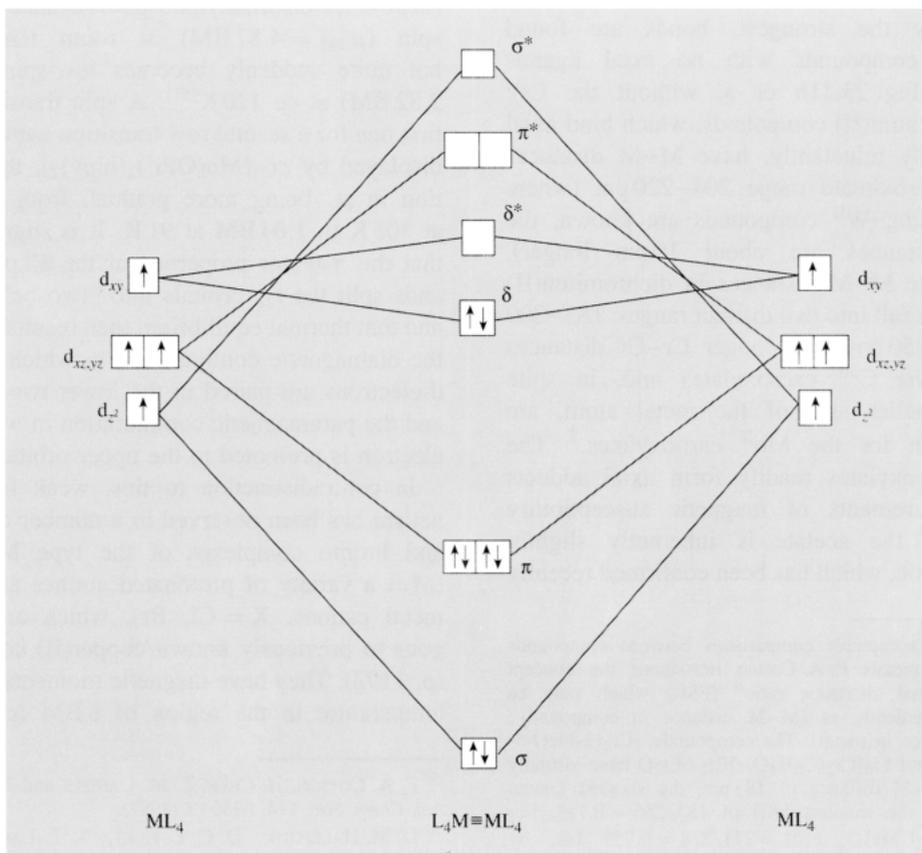


**Figure 23.10** Crystal field splitting of the  ${}^5D$  term of a  $d^4$  ion.

<sup>49a</sup> L. F. LARKWORTHY, G. A. LEONARD, D. C. POVEY, S. S. TANDON, B. J. TUCKER and G. W. SMITH, *J. Chem. Soc., Dalton Trans.*, 1425–8 (1994).



**Figure 23.11** (a)  $[M_2(\mu, \eta^2\text{-O}_2\text{CMe})_4]$ ,  $M = \text{Cr, Mo}$ . In the case of Cr, but not Mo, the hydrate and other adducts can be formed by attachment of  $\text{H}_2\text{O}$  (or in general,  $L$ ) molecules as arrowed. (b)  $[\text{Mo}_2\text{Cl}_8]^{4-}$ .



**Figure 23.12** Simplified MO diagram showing the formation of an M–M quadruple bond in  $M_2L_8$  systems of  $d^4$  metal ions giving a ground configuration of  $\sigma^2 \pi^4 \delta^2$  (the  $d_{x^2-y^2}$ , along with  $p_x$ ,  $p_y$  and  $s$  orbitals of the metal ions are assumed to be used in the formation of M–L  $\sigma$  bonds).

red colour arises from the visible absorption at  $19\,000\text{ cm}^{-1}$  which is readily ascribed to the  $\sigma^2\pi^4\delta\delta^* \leftarrow \sigma^2\pi^4\delta^2$  transition. The same assignment is also made for the absorption at  $14\,300\text{ cm}^{-1}$  which is responsible for the blue colour of  $[\text{Re}_2\text{Cl}_8]^{2-}$  (p. 1058). The eclipsed orientation noted in  $[\text{Mo}_2\text{Cl}_8]^{4-}$  provides strong confirmation of this bonding scheme since, without the  $\delta$  bond, this configuration would be sterically unfavourable. A variety of experimental techniques, which includes polarized single-crystal spectroscopy, photoelectron spectroscopy, and X-ray emission spectroscopy, has been used to further substantiate this view of the bonding. Accurately determined M–M distances provide the most readily available indication of bond strength. The shortest, and therefore presumably the strongest, bonds are found in those compounds with no axial ligands (i.e. like Fig. 23.11b or a, without the Ls). Dimolybdenum(II) compounds, which bind axial ligands only reluctantly, have M–M distances in the approximate range 204–220 pm (where corresponding W<sup>II</sup> compounds are known, the W–W distances are about 10 pm longer), whereas the M–M distances in dichromium(II) compounds fall into two distinct ranges: 183–200 and 220–250 pm. The longer Cr–Cr distances refer to the Cr<sup>II</sup> carboxylates and, in spite of the smaller size of the metal atom, are longer than for the Mo<sup>II</sup> carboxylates.<sup>†</sup> The Cr(II) carboxylates readily form axial adducts and measurements of magnetic susceptibility show that the acetate is inherently slightly paramagnetic, which has been confirmed recently

<sup>†</sup> To effect acceptable comparisons between compounds of different metals F. A. Cotton introduced the concept of the “formal shortness ratio” (FSR) which may be defined conveniently as (M–M distance in compound) : (M–M distance in metal). The compounds,  $[\text{Cr}_2(2\text{-MeO-5-MeC}_6\text{H}_3)_4]$  and  $\text{Li}_6[\text{Cr}_2(\text{C}_6\text{H}_4\text{O})_4]\text{Br}_2 \cdot 6\text{Et}_2\text{O}$  have virtually the same M–M distance of 183 pm, the shortest known and yielding the smallest FSR of  $183/256 = 0.715$ . For  $[\text{Mo}_2(\mu, \eta^2\text{-O}_2\text{CMe})_4]$ ,  $\text{FSR} = 211/278 = 0.759$  but, by contrast, for  $[\text{Cr}_2(\mu, \eta^2\text{-O}_2\text{CMe})_4] \cdot 2\text{H}_2\text{O}$   $\text{FSR} = 236/256 = 0.922$ . For comparison, the strongest homonuclear bonds for which bond energies are accurately known are  $\text{N}\equiv\text{N}$  and  $\text{C}\equiv\text{C}$  and their FSRs are  $110/140 = 0.786$  and  $120.6/154 = 0.783$  respectively.

by variable temperature nmr.<sup>(50)</sup> This implies partial occupation of a low-lying spin triplet ( $S = 1$ , two unpaired electrons) and clearly indicates weaker M–M interaction than in the Mo<sup>II</sup> and other Cr<sup>II</sup> dinuclear compounds with shorter M–M distances. Whether this is a consequence, however, of the involvement of a different *type* of interaction in the Cr<sup>II</sup> carboxylates — antiferromagnetic coupling between high-spin Cr<sup>2+</sup> ions rather than just weak quadruple bonding — has not yet been unequivocally decided.

Interesting spin transitions are also observed: Although the reddish-purple  $[\text{CrI}_2(\text{dmpe})_2]$ , (dmpe = 1,2-bis(dimethylphosphino)ethane) is low-spin, the purple-brown  $[\text{CrI}_2(\text{depe})_2]$ , (depe = 1,2-bis(diethylphosphino)ethane) is high-spin ( $\mu_{295} = 4.87\text{ BM}$ ) at room temperature but quite suddenly becomes low-spin ( $\mu_{90} = 2.82\text{ BM}$ ) at *ca* 170 K<sup>(51)</sup>. A spin transition, the first one for a second row transition metal, is also displayed by *cis*- $[\text{Mo}(\text{OPr}^i)_2(\text{bipy})_2]$ , the reduction in  $\mu_e$  being more gradual, from 1.96 BM at 305 K to 1.04 BM at 91 K. It is suggested<sup>(52)</sup> that the  $\pi$ -donor properties of the alkoxide ligands split the  $t_{2g}$  orbitals into “two below one” and that thermal equilibrium then results between the diamagnetic configuration in which the four d-electrons are paired in the lower two orbitals, and the paramagnetic configuration in which one electron is promoted to the upper orbital.

In contradistinction to this, weak ferromagnetism has been observed in a number of chloro and bromo complexes of the type  $\text{M}_2[\text{CrX}_4]$  (M = a variety of protonated amines and alkali metal cations, X = Cl, Br), which are analogous to previously known copper(II) complexes (p. 1192). They have magnetic moments at room temperature in the region of 6 BM (compared

<sup>50</sup> F. A. COTTON, H. CHEN, L. M. DANIELS and X. FENG, *J. Am. Chem. Soc.* **114**, 8980–3 (1992).

<sup>51</sup> D. M. HALEPOTO, D. G. L. HOLT, L. F. LARKWORTHY, G. J. LEIGH, D. C. POVEY and G. W. SMITH *J. Chem. Soc., Chem. Commun.*, 1322–3 (1989), *Polyhedron* **8**, 1821–2 (1989).

<sup>52</sup> M. H. CHISHOLM, E. M. KOBER, D. J. IRONMONGER and P. THORTON, *Polyhedron* **4**, 1869–74 (1985).