

Figure 24.4 (a) The tricapped trigonal prismatic structure of the $[\text{ReH}_9]^{2-}$ anion. (b) $[\text{Re}_2(\mu\text{-H})_3\text{H}_6\text{MeC}(\text{CH}_2\text{-PPh}_2)_3]^-$. For clarity, only the P atoms of the triphos ligand are shown.

known with certainty, but ReOCl_4 may be noted as an example of a square-pyramidal structure.

24.3.4 Complexes of manganese, technetium and rhenium^(3,10,11)

Oxidation state VII (d^0)

The coordination chemistry of this oxidation state is confined mainly to a few readily hydrolysed oxohalide complexes of Re such as KReO_2F_4 . Exceptions to this limitation are provided by the isomorphous hydrides K_2MH_9 of Tc and Re which formally involve M^{VII} and H^- . The rhenium analogue was the first to be prepared as the colourless, diamagnetic product of the reduction of KReO_4 by potassium in aqueous diaminoethane (ethylenediamine). The

elucidation of its structure (Fig. 24.4a) illustrates vividly the problems associated with identifying a novel compound when its isolation in a pure form is difficult and when conventional chemical analysis is unable to establish the stoichiometry with accuracy.[†] Several other hydrido complexes are known, of which the reddish-orange, dinuclear $(\text{Et}_4\text{N})[\text{Re}_2\text{H}_9(\text{triphos})]$ may be mentioned. This is obtained by treatment of $(\text{Et}_4\text{N})_2[\text{ReH}_9]$ with $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$ in

[†] Only by using a wide range of physical techniques were these difficulties surmounted. The product was first thought to be $\text{K}[\text{Re}(\text{H}_2\text{O})_4]$ containing Re^{-1} with a square-planar geometry, by analogy with the isoelectronic Pt^{II} . The nmr spectrum, however, indicated the presence of an Re-H bond so the compound was reformulated as $\text{KReH}_4 \cdot 2\text{H}_2\text{O}$. Fresh analytical evidence then suggested that earlier products had been impure and a further reformulation, this time as K_2ReH_8 , was proposed. The observed diamagnetism could then only be accounted for by assuming metal-metal bonding between the implied d^1 rhenium(VI) atoms, but X-ray analysis showing the Re atoms to be 550 pm apart, precluded this possibility. The problem was finally resolved when a neutron diffraction study established the formula as K_2ReH_9 and the structure is tricapped trigonal prismatic. The nmr spectrum actually shows only one proton signal in spite of the existence of distinct capping and prismatic protons, and this is thought to be due to rapid exchange between the sites.

¹⁰ B. CHISWELL, E. D. MCKENZIE and L. F. LINDOY, *Manganese*, Chap. 41, pp. 1–122; K. A. CONNER and R. A. WALTON, *Rhenium*, Chap. 43, pp. 125–213 in *Comprehensive Coordination Chemistry*, Vol. 4, Pergamon Press, Oxford, 1987.

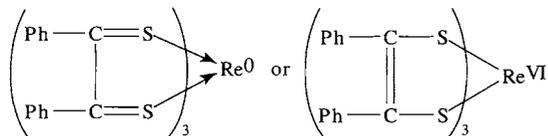
¹¹ J. BALDAS, *Adv. Inorg. Chem.* **41**, 2–123 (1994) and F. TISATO, F. REFOSCO and G. BANDOLI, *Coord. Chem. Revs.* **135/136**, 325–97 (1994) are devoted to technetium.

MeCN. The structure of the anion (Fig 24.4b) can be envisaged as a tridentate $[\text{ReH}_9]^{2-}$ ligand coordinated to $\text{Re}(\text{triphos})^+$, and, since the metal atoms are only 259.4 pm apart, is said to involve an $\text{Re}\equiv\text{Re}$ triple bond⁽¹²⁾ (in which case the $[\text{ReH}_9]^{2-}$ should be regarded as tetradentate and its Re atom as 10-coordinated).

Oxidation state VI (d^1)

Again, fluoro and oxo complexes of rhenium predominate. The reaction of KF and ReF_6 in an inert PTFE vessel yields pink $\text{K}_2[\text{ReF}_8]$, the anion of which has a square-prismatic structure; hydrolysis converts it to $\text{K}[\text{ReOF}_5]$.

An interesting compound which is usually included in discussions of Re^{VI} chemistry is the green crystalline dithiolate, $[\text{Re}(\text{S}_2\text{C}_2\text{Ph}_2)_3]$. This was the first authenticated example of a trigonal prismatic complex (Fig. 19.6, p. 915) but besides its structural interest it has, along with other complexes of such ligands, posed problems regarding the oxidation state of the metal. The ligand may be thought to coordinate in either of two extreme ways (or some intermediate state between them):



The difference between the two extremes is essentially that, in the former, the Re retains its valence electrons in its d orbitals whereas in the latter it loses 6 of them to delocalized ligand orbitals. In either case paramagnetism is anticipated since rhenium has an odd number of valence electrons. The magnetic moment of 1.79 BM corresponding to 1 unpaired electron, and esr evidence showing that this electron is situated predominantly on the ligands, indicates that an intermediate oxidation state is involved

¹² S. C. ABRAHAMS, A. P. GINSBERG, T. F. KOETZLE, P. MARSH and C. R. SPRINKLE, *Inorg. Chem.* **25**, 2500–10 (1986).

but does not specify which one. Because of this uncertainty, dithiolate ligands, and others like them, have been expressively termed “non-innocent” ligands by C. K. Jørgensen.⁽¹³⁾

Oxidation state V (d^2)

This oxidation state is sparse in the case of Mn but is important in the pharmaceutical applications of Tc, and an extensive chemistry has been developed. Some fluoro complexes of Tc and Re such as the salts of $[\text{MF}_6]^-$ are known, but oxo compounds predominate and, in $[\text{MOC}_5]^{2-}$ and $[\text{MOX}_4]^-$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) for instance, other halides are also able to coordinate. $[\text{MOX}_4]^-$ is square pyramidal with apical $\text{M}=\text{O}$ and the MO^{3+} moiety is reminiscent of VO^{2+} , being found in other compounds (particularly those containing phosphines) and labilizing whatever ligand is *trans* to it. The ir stretching frequency of the $\text{M}=\text{O}$ bond is conveniently used for its detection, lying in the range $890\text{--}1020\text{ cm}^{-1}$ for $\text{Tc}=\text{O}$ and generally about 20 cm^{-1} lower for $\text{Re}=\text{O}$. The $\text{M}\equiv\text{N}$ group also stabilizes the oxidation state, probably because the π bonds are able to reduce the charge on the M^{V} ; it is found in compounds such as $[\text{MNX}_2(\text{PR}_3)_3]$ and $[\text{MNX}_2(\text{PR}_3)_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) produced when $[\text{MO}_4]^-$ is reduced by hydrazine in the presence of appropriate ligands, of which phosphines are especially useful.⁽¹⁴⁾ The ir stretching frequency is again of diagnostic value being found in the approximate range of $1050\text{--}1100\text{ cm}^{-1}$ for $\text{Tc}\equiv\text{N}$ and 20 cm^{-1} or so lower for $\text{Re}\equiv\text{N}$. Eight-coordinate and probably dodecahedral $[\text{ReCl}_4(\text{diars})_2]\text{ClO}_4$ has been prepared and the Tc analogue is notable as the first example of 8-coordinate technetium.

¹³ C. K. JØRGENSEN, *Oxidation Numbers and Oxidation States*, Springer-Verlag, Berlin, 1969, 291 pp.

¹⁴ For other $\text{Tc}\equiv\text{N}$ compounds see for instance: G. A. WILLIAMS and J. BALDAS, *Aust. J. Chem.* **42**, 875–84 (1989); C. M. ARCHER, J. R. DILWORTH, J. D. KELLY and M. MCPARTLIN, *Polyhedron* **8**, 1879–81 (1989).

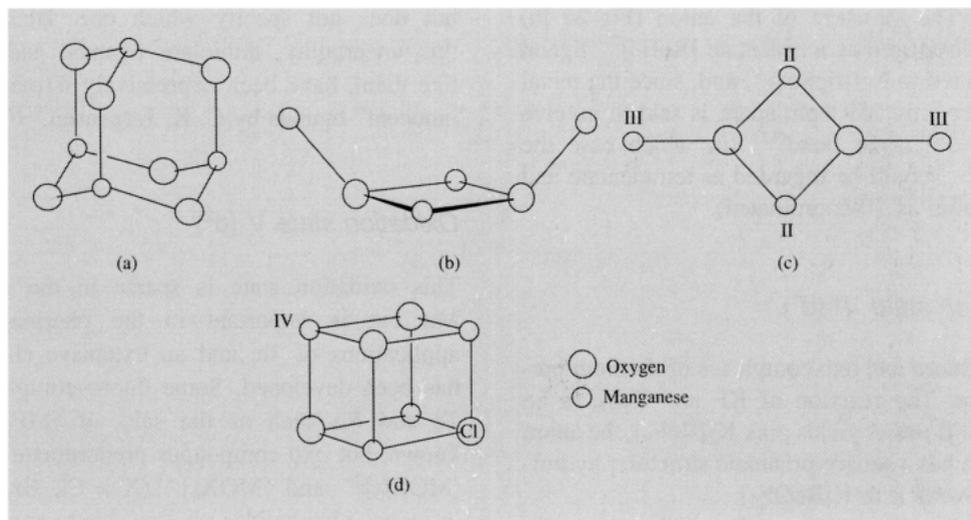


Figure 24.5 Cores of some Mn_4 complexes. (a) Adamantane $\{Mn_4^{IV}O_6\}$ in $[Mn_4O_6(tacn)_4]^{4+}$. (b) Butterfly $\{Mn_2^{III}O_2\}$ in $[Mn_4O_2(MeCOO)_7(bipy)_2]^+$. (c) Planar $\{Mn_2^{II}Mn_2^{III}O_2\}$ in $[Mn_4O_2(MeCOO)_6(bipy)_2]$. (d) Cubane $\{Mn_3^{III}Mn^{IV}O_3Cl\}$ in $[Mn_4O_3Cl_4(MeCOO)_3py_3]$.

Oxidation state IV (d^3)

This is apparently the highest oxidation state in which manganese is able to form complexes. Monomeric complexes are sparse, though $K_2[MnX_6]$, where $X = F, Cl, IO_3$ and CN are known, but di- and poly-meric compounds are more numerous and have received attention as models for the water-oxidizing enzyme, *Photosystem II*,⁽¹⁵⁾ important in plant photosynthesis. An $Mn(\mu-O)_2Mn$ core is thought to be involved and the redox behaviour of compounds such as $[(L-L)_2Mn(\mu-O)_2Mn(L-L)_2]^{n+}$ ($L-L = 1,10$ -phenanthroline, $2,2'$ -bipyridyl; $n = 2, 3, 4$, implying $Mn^{III}-Mn^{III}$, $Mn^{III}-Mn^{IV}$ and $Mn^{IV}-Mn^{IV}$ pairings) has been studied.⁽¹⁶⁾ Schiff bases and carboxylate ligands have also been used and complexes with OH bridges and also triply bridged complexes have been

produced. Fully oxidized $Mn^{IV}-Mn^{IV}$ species are often observed only electrochemically and not completely characterized. An exception is the Mn^{IV} tetramer, $[Mn_4O_6(tacn)_4]^{4+}$ prepared by aerial oxidation of Mn^{2+} in the presence of 1,4,7-triazacyclononane. The core of this has the adamantane structure, each Mn being facially coordinated to one tacn and three μ_2 -oxygens (Fig. 24.5a).

Relatively few compounds of Tc^{IV} have radiopharmaceutical use, and its chemistry in this oxidation state has therefore been comparatively neglected. For both the heavier elements the preference for oxo compounds is diminishing while the tendency to form $M-M$ multiple bonds has not yet acquired the importance to be found in more reduced states. The most important compounds are the salts of $[MX_6]^{2-}$ [$M = Tc, Re$; $X = F, Cl, Br, I$]. The fluoro complexes are obtained by the reaction of HF on one of the other halogeno complexes and these in turn are obtained by reducing $[MO_4]^-$ (commonly by using I^-) in aqueous HX. The corresponding Tc and Re complexes are closely similar, but an interesting difference between Tc^{IV} and Re^{IV} is found in their behaviour with CN^- . The reaction

¹⁵ V. K. YACHANDRA, K. SAUER and M. P. KLEIN, *Chem. Revs.* **96**, 2927–50 (1996); R. MANCHANDA, G. W. BRUDVIG, and R. H. CRABTREE, *Coord. Chem. Revs.* **144**, 1–38 (1995).

¹⁶ G. W. BRUDVIG and R. H. CRABTREE, *Prog. Inorg. Chem.* **37**, 99–142 (1989); J. B. VINCENT and G. CHRISTOU, *Adv. Inorg. Chem.* **33**, 197–258 (1989); K. WIEGHARDT, *Angew. Chem. Int. Edn. Engl.* **28**, 1153–72 (1989).

of KCN and K_2ReI_6 in methanol yields a mixture of $\text{K}_4[\text{Re}^{\text{III}}(\text{CN})_7] \cdot 2\text{H}_2\text{O}$ and $\text{K}_3[\text{Re}^{\text{VO}_2}(\text{CN})_4]$ whereas the analogous reaction of KCN and K_2TcI_6 produces a reddish-brown, paramagnetic precipitate, thought to be $\text{K}_2[\text{Tc}(\text{CN})_6]$.

Oxidation state III (d^4)

Nearly all manganese(III) complexes are octahedral and high-spin with magnetic moments close to the spin-only value of 4.90 BM expected for 4 unpaired electrons. The d^4 configuration is also expected to be subject to Jahn–Teller distortions (p. 1021). For reasons which are not obvious, the $[\text{Mn}(\text{H}_2\text{O}_6)]^{3+}$ ion in the alum $\text{CsMn}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ does not display the appreciable distortion from octahedral symmetry (elongation of two *trans* bonds) found, for instance, in solid MnF_3 , the octahedral Mn^{III} sites of Mn_3O_4 , $[\text{Mn}(\text{acac})_3]$ and in tris(tropolonato)manganese(III). Manganese(III) is strongly oxidizing in aqueous solution with a marked tendency to disproportionate into Mn^{IV} (i.e. MnO_2) and Mn^{II} (see Fig. 24.1). It is, however, stabilized by *O*-donor ligands, as evidenced by the way in which the virtually white $\text{Mn}(\text{OH})_2$ rapidly darkens in air as it oxidizes to hydrous Mn_2O_3 or $\text{MnO}(\text{OH})$, and by the preparation of $[\text{Mn}(\text{acac})_3]$ via the aerial oxidation of aqueous Mn^{II} in the presence of acetylacetonate. $\text{K}_3[\text{Mn}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ is also known, while the complexing oxoanions, phosphate and sulfate, have a stabilizing effect on aqueous solutions. The main preparative routes to Mn^{III} are by reduction of KMnO_4 or oxidation of Mn^{II} . The latter may be effected electrolytically but a common method is by way of the red-brown acetate. This is similar to the “basic” acetate of chromium(III) and so involves the $[\text{Mn}_3\text{O}(\text{MeCOO})_6]^+$ unit (see Fig. 23.9, p. 1030). The hydrate is prepared by oxidation of manganese(II) acetate with KMnO_4 in glacial acetic acid, and the anhydrous salt by the action of acetic hydride on hydrated manganese(II) nitrate.

The field of oxo-bridged polynuclear complexes of manganese, much of it involving mixed

oxidation states and facile redox behaviour, is expanding rapidly⁽¹⁶⁾. Oxidation of an ethanolic solution of Mn^{II} acetate by $(\text{Bu}_4\text{N})\text{MnO}_4$ in the presence of acetic acid and pyridine can yield either the Mn^{III} compound, $[\text{Mn}_3\text{O}(\text{MeCOO})_6\text{py}_3]^+$ or the $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}$ compound, $[\text{Mn}_3\text{O}(\text{MeCOO})_6\text{py}_3]$. Addition of bipyridyl to solutions of these in MeCN gives the tetranuclear, $[\text{Mn}_4\text{O}_2(\text{MeCOO})_7(\text{bipy})_2]^+$ and $[\text{Mn}_4\text{O}_2(\text{MeCOO})_6(\text{bipy})_2]$ respectively. The structures of the cores of these and other Mn_4 complexes⁽¹⁷⁾ are given in Fig. 24.5.

Still higher nuclearities, up to 12 in $[\text{Mn}_{12}\text{O}_{12}(\text{RCOO})_{16}(\text{H}_2\text{O})_4]$ ($\text{R} = \text{Me}, \text{Ph}$), have been reported.⁽¹⁸⁾ The cores of these two compounds, which are of interest as potential building blocks in the preparation of molecular ferromagnets, consist of a central $[\text{Mn}_4^{\text{IV}}(\mu\text{-O})_4]$ cubane linked by *O*-bridges to eight Mn atoms.

The most important low-spin octahedral complex of Mn^{III} is the dark-red cyano complex, $[\text{Mn}(\text{CN})_6]^{3-}$, which is produced when air is bubbled through an aqueous solution of Mn^{II} and CN^- . $[\text{MnX}_5]^{2-}$ ($\text{X} = \text{F}, \text{Cl}$) are also known; the chloro ion, at least when combined with the cation $[\text{bipyH}_2]^{2+}$, is notable as an example of a square pyramidal manganese complex.

Technetium(III) complexes are accessible especially if stabilized by back-bonding ligands, and are most commonly 6-coordinate. $[\text{TcCl}_2(\text{diars})_2]\text{ClO}_4$, prepared by the reaction of *o*-phenylenebisdimethylarsine and HCl with HTcO_4 in aqueous alcohol, is probably the best known. The rhenium(III) analogue is isomorphous but requires the help of a reducing agent such as H_3PO_2 to effect the reduction from $[\text{ReO}_4]^-$. Other examples are $[\text{Tc}(\text{NCS})_6]^{3-}$ and $[\text{Tc}(\text{thiourea})_6]^{3+}$. However, 7-coordinate compounds such as $[\text{M}(\text{CN})_7]^{4-}$ are also known and, more recently, it has been reported⁽¹⁹⁾ that the

¹⁷ V. MCKEE, *Adv. Inorg. Chem.* **40**, 323–410 (1994).

¹⁸ P. D. W. BOYD, Q. LI, J. B. VINCENT, K. FOLTING, H.-R. CHANG, W. E. STREIB, J. C. HUFFMAN, G. CHRISTOU and D. N. HENDRICKSON, *J. Am. Chem. Soc.* **110**, 8537–9 (1988).

¹⁹ C. M. ARCHER, J. R. DILWORTH, P. JOBANPUTRA, R. M. THOMPSON, M. MCPARTLIN, P. C. POVEY, G. W. SMITH and J. D. KELLY, *Polyhedron* **9**, 1497–1502 (1990).

reaction of $[\text{MOC}_2\text{Cl}_4]^-$ with excess arylhydrazine and PPh_3 in ethanol gives 5-coordinate, diamagnetic, $[\text{MCl}(\text{N}_2\text{Ar})_2(\text{PPh}_3)_2]$.

In general Re^{III} is readily oxidized to Re^{IV} or Re^{VII} unless it is stabilized by metal-metal bonding⁽²⁰⁾ as in the case of the trihalides already discussed. Rhenium(III) complexes with Cl^- and Br^- have been characterized and are of two types, $[\text{Re}_3\text{X}_{12}]^{3-}$ and $[\text{Re}_2\text{X}_8]^{2-}$, both of which involve multiple Re-Re bonds. If Re_3Cl_9 or Re_3Br_9 are dissolved in conc HCl or conc HBr respectively, stable, red, diamagnetic salts may be precipitated by adding a suitable monovalent cation. Their stoichiometry is $\text{M}^{\text{I}}\text{ReX}_4$ and they were formerly thought to be unique examples of low-spin, tetrahedral complexes. X-ray analysis, however, showed that the anions are trimeric with the same structure as the halides (Fig. 24.3) and likewise incorporating Re=Re double bonds. Their chemistry reflects their structure since 3 halide ions per trimeric unit can be replaced by ligands such as MeCN, Me_2SO , Ph_3PO and PEt_2Ph yielding neutral complexes $[\text{Re}_3\text{X}_9\text{L}_3]$.

The blue diamagnetic complexes $[\text{Re}_2\text{X}_8]^{2-}$ are produced when $[\text{ReO}_4]^-$ in aqueous HCl or HBr is reduced by H_3PO_2 and they can then be precipitated by the addition of a suitable cation. A more efficient method, which also yields a product soluble in polar organic solvents, is the reaction of $(\text{NBu}_4)\text{ReO}_4$ with refluxing benzoyl chloride followed by the addition of a solution of $(\text{NBu}_4)\text{Cl}$ in ethanol saturated with HCl. Salts of $[\text{Re}_2\text{X}_8]^{2-}$ are the starting points for almost all dirhenium(III) compounds and the ion provided one of the first examples of a quadruple bond in a stable compound (see pp. 1032, 1034). The structure of $[\text{Re}_2\text{Cl}_8]^{2-}$ is shown in Fig. 24.6 and, as in $[\text{Mo}_2\text{Cl}_8]^{4-}$ (Fig. 23.11, p. 1033), the chlorine atoms are eclipsed. In both ions the metal has a d^4 configuration which is to be expected if a δ -bond is present. $[\text{Re}_2\text{Cl}_8]^{2-}$ can be reduced polarographically to unstable $[\text{Re}_2\text{Cl}_8]^{3-}$ and $[\text{Re}_2\text{Cl}_8]^{4-}$, and also undergoes a variety of substitution reactions (Fig. 24.6b,c,d).

One Cl on each Re may be replaced by phosphines, while $\text{MeSCH}_2\text{CH}_2\text{SMe}$ (dth) takes up 4 coordination positions on 1 Re to give $[\text{Re}_2\text{Cl}_5(\text{dth})_2]$. In this case the average oxidation state of the rhenium has been reduced to +2.5. The reduction in bond order from 4 to 3.5, which the addition of a δ^* electron implies, causes some lengthening of the Re-Re distance and the configuration is staggered. Carboxylates are able to bridge the metal atoms forming complexes of the type $[\text{Re}_2\text{Cl}_2(\text{O}_2\text{CR})_4]$ which are clearly analogous to the dimeric carboxylates found in the previous group.

In the octachloro technetium system, by contrast, the paramagnetic $[\text{Tc}_2\text{Cl}_8]^{3-}$ is the most readily obtained species. The Tc has a formal oxidation state of +2.5 with a $d(\text{Tc-Tc})$ 210.5 pm and the configuration is eclipsed. The pale green $[\text{NBu}_4]_2^+[\text{Tc}_2^{\text{III}}\text{Cl}_8]^{2-}$ can be isolated from the products of reduction of $[\text{TcCl}_6]^{2-}$ with $\text{Zn}/\text{HCl}(\text{aq})$. The compound is strictly isomorphous with $[\text{NBu}_4]_2^+[\text{Re}_2\text{Cl}_8]^{2-}$ and has (Tc-Tc) 214.7 pm. The reason for the increase in Tc-Tc distance on removal of the δ^* electron, and the consequent increase in the presumed bond order from 3.5 to 4, is not clear, but has been ascribed to a decrease in the strength of σ and π bonding caused by orbital contraction occurring as the charge on the metal core (and hence the bond order) increases.⁽²¹⁾

Oxidation state II (d^5)

The chemistry of technetium(II) and rhenium(II) is meagre and mainly confined to arsine and phosphine complexes. The best known of these are $[\text{MCl}_2(\text{diars})_2]$, obtained by reduction with hypophosphite and Sn^{II} respectively from the corresponding Tc^{III} and Re^{III} complexes, and in which the low oxidation state is presumably stabilized by π donation to the ligands. This oxidation state, however, is really best typified by manganese for which it is the most thoroughly studied and, in aqueous solution, by far the most

²⁰ F. A. COTTON and R. A. WALTON, *Multiple Bonds between Atoms*, 2nd edn., Oxford University Press, Oxford, 1993, 787 pp.

²¹ p. 123 of ref. 20.

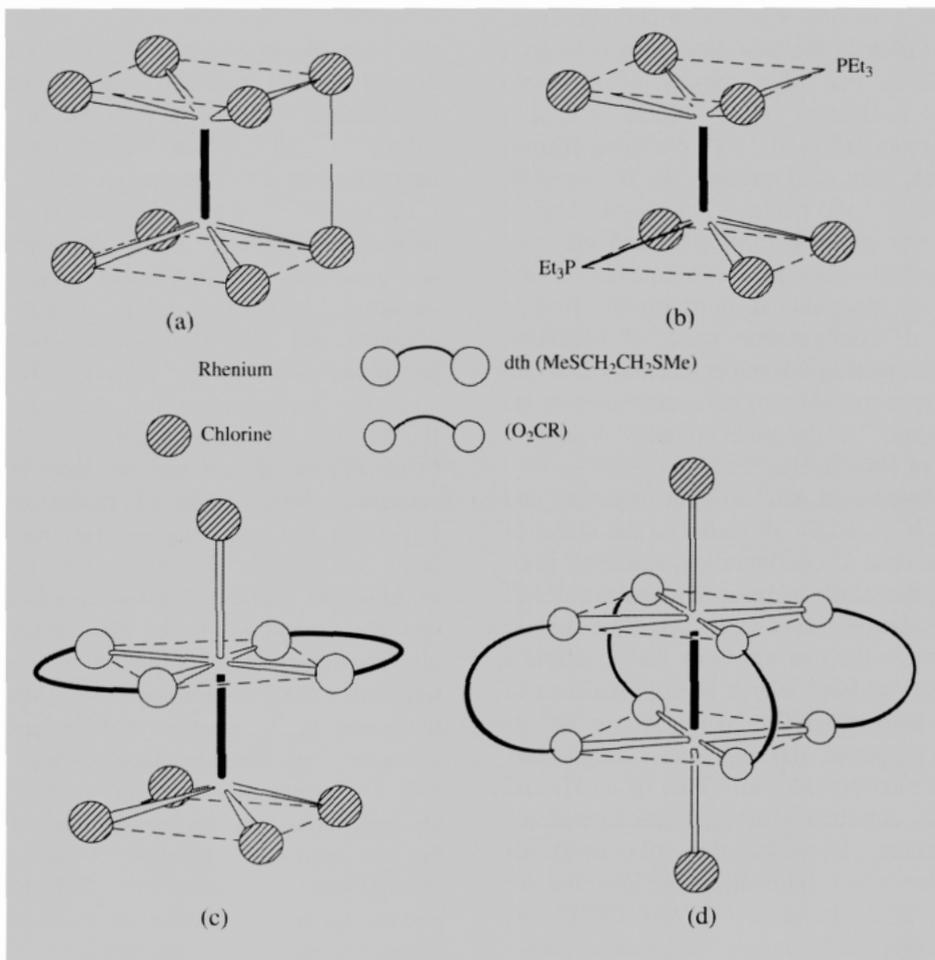
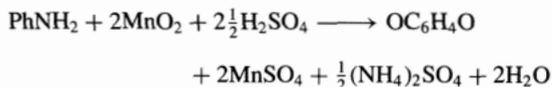


Figure 24.6 Some complexes of Re with multiple Re-Re bonds: (a) $[\text{Re}_2\text{Cl}_8]^{2-}$. (b) $[\text{Re}_2\text{Cl}_6(\text{PEt}_3)_2]$. (c) $[\text{Re}_2\text{Cl}_5(\text{dth})_2]$. (d) $[\text{Re}_2(\text{O}_2\text{CR})_4\text{Cl}_2]$.

stable; accordingly it provides the most extensive cationic chemistry in this group.

Salts of manganese(II) are formed with all the common anions and most are water-soluble hydrates. The most important of these commercially and hence the most widely produced is the sulfate, which forms several hydrates of which $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ is the one commonly formed. It is manufactured either by treating pyrolusite with sulfuric acid and a reducing agent, or as a byproduct in the production of hydroquinone (MnO_2 is used in the conversion of aniline to quinone):



It is the starting material for the preparation of nearly all manganese chemicals and is used in fertilizers in areas of the world where there is a deficiency of Mn in the soil, since Mn is an essential trace element in plant growth. The anhydrous salt has a surprising thermal stability; it remains unchanged even at red heat, whereas the sulfates of Fe^{II} , Co^{II} and Ni^{II} all decompose under these conditions.

Aqueous solutions of salts with non-coordinating anions contain the pale-pink, $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$, ion which is one of a variety of high-spin octahedral complexes ($t_{2g}^3 e_g^2$) which have been prepared more especially with chelating ligands such as en, edta, and oxalate. As is expected, most of these have magnetic moments close to the spin-only value of 5.92 BM, and are very pale in colour. This is a consequence of the fact that all electronic d-d transitions from a high-spin d^5 configuration must, of necessity, involve the pairing of some electrons and are therefore spin-forbidden. This is embodied in the interpretation⁽²²⁾ of the rather complex absorption spectrum of $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$.

The resistance of Mn^{II} to both oxidation and reduction is generally attributed to the effect of the symmetrical d^5 configuration, and there is no doubt that the steady increase in resistance of M^{II} ions to oxidation found with increasing atomic number across the first transition series suffers a discontinuity at Mn^{II} , which is more resistant to oxidation than either Cr^{II} to the left or Fe^{II} to the right. However, the high-spin configuration of the Mn^{II} ion provides no CFSE (p. 1131) and the stability constants of its high-spin complexes are consequently lower than those of corresponding complexes of neighbouring M^{II} ions and are kinetically labile. In addition, a zero CFSE confers no advantage on any particular stereochemistry which must be one of the reasons for the occurrence of a wider range of stereochemistries for Mn^{II} than is normally found for M^{II} ions.

Green-yellow salts of the tetrahedral $[\text{MX}_4]^{2-}$ ($X = \text{Cl}, \text{Br}, \text{I}$) ions can be obtained from ethanolic solutions and are well characterized. Furthermore, a whole series of adducts $[\text{MnX}_2\text{L}_2]$ ($X = \text{Cl}, \text{Br}, \text{I}$) are known where L is an N -, P - or As -donor ligand, and both octahedral and tetrahedral stereochemistries are found. Of interest because of the possible role of manganese porphyrins in photosynthesis is $[\text{Mn}^{\text{II}}(\text{phthalocyanine})]$ which is square planar. The reaction of aqueous edta with MnCO_3 yields

a number of complex species, amongst them the 7-coordinate $[\text{Mn}(\text{edta})(\text{H}_2\text{O})]^{2-}$ which has a capped trigonal prismatic structure. The highest coordination number, 8, is found in the anion $[\text{Mn}(\eta^2\text{-NO}_3)_4]^{2-}$ which, like other such ions, is approximately dodecahedral (p. 916).

A varied chemistry, centred on the phosphines $[\text{MnX}_2(\text{PR}_3)]$, is also developing. These are moisture sensitive and, frequently, air-sensitive, polymeric solids which can be obtained not only by the reaction of the phosphine with MnX_2 ($X = \text{Cl}, \text{Br}, \text{I}$), but also by the reaction of the phosphorane, R_3PX_2 , with powdered metal.⁽²³⁾ In the case of $[\text{MnI}_2(\text{PPhMe}_2)]$ two isomers have been characterised. Both consist of chains of $[\text{Mn}(\mu\text{-I})_2]$ units but whereas, in the one prepared from MnX_2 two phosphines are coordinated to alternate metals (4,6,4,6 coordination), in the one prepared from Mn metal, a single phosphine is coordinated to each metal (uniform 5,5,5,5 coordination).⁽²³⁾ $[\text{MnX}_2(\text{PR}_3)]$ have also been found to react reversibly with a variety of small molecules such as CO, NO, C_2H_4 and SO_2 (see for instance ref. 24). O_2 will also react reversibly in some cases but its controlled addition to the pale-pink $[\text{MnI}_2(\text{PMe}_3)]$ (obtained from PMe_3I_2 and Mn powder in dry ethyl ether as a 4,6,4,6 coordination polymer) yields successively⁽²⁵⁾ the dark-red dimer, $[\text{Mn}^{\text{III}}(\text{PMe}_3)_2(\mu\text{-I})\text{Mn}^{\text{II}}(\text{PMe}_3)_2\text{I}_2]$ (involving approximately tetrahedral Mn^{III} and trigonal bipyramidal Mn^{II}) and finally the dark-green, trigonal bipyramidal $[\text{Mn}^{\text{III}}(\text{PMe}_3)_2\text{I}_3]$.

Spin-pairing in manganese(II) requires a good deal of energy and is achieved only by ligands such as CN^- and CNR which are high in the spectrochemical series. The low-spin complexes. $[\text{Mn}(\text{CN})_6]^{4-}$ and $[\text{Mn}(\text{CNR})_6]^{2+}$ are presumed

²³ S. M. GODFREY, D. G. KELLY, A. G. MACKIE, P. P. MACRORY, C. A. MCAULIFFE, R. G. PRITCHARD and S. M. WATSON, *J. Chem. Soc., Chem. Commun.* 1447-9 (1991).

²⁴ D. S. BARRATT, G. A. GOTT and C. A. MCAULIFFE, *J. Chem. Soc., Dalton Trans.*, 2065-70 (1988).

²⁵ C. A. MCAULIFFE, S. M. GODFREY, A. G. MACKIE, and R. G. PRITCHARD, *J. Chem. Soc., Chem. Commun.* 483-5 (1992).

²² A. B. P. LEVER, *Inorganic Electronic Spectroscopy*, 2nd edn., pp. 448-52, Elsevier, Amsterdam, 1984.