Manganese: Inorganic & Coordination Chemistry

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1 BACKGROUND AND GENERAL CHEMISTRY

Manganese is a relatively abundant metal, constituting about 0.085% of the earth’s crust. Among the transition metals, only iron is more abundant. Manganese minerals are widely distributed; oxides, hydrous oxides, silicates, and carbonates are the most common. Large quantities (more than $10^{12}$ tons) of ‘manganese nodules’ that have been discovered on the floor of the oceans may become a source of manganese. These nodules contain about 24% of manganese together with many other metals in lesser abundance. Most manganese today is obtained from ores, pyrolusite (MnO$_2$) and rhodochrosite (MnCO$_3$) are the most common. The metal is produced by reduction of its oxides with sodium, magnesium, and aluminum, or by electrolysis. Nearly all manganese produced commercially is used in the steel industry as ferromanganese.

Manganese is roughly similar to iron (see Iron: Inorganic & Coordination Chemistry) in its physical and chemical properties but is harder and more brittle, though less refractory (mp 1247°C). At room temperature, manganese metal is not particularly reactive to air, despite it being quite electropositive; however it burns in O$_2$ to form the manganese oxide MnO$_2$, in N$_2$ to yield the nitride Mn$_3$N$_2$, and in Cl$_2$ to form MnCl$_2$, and reacts with Br$_2$, I$_2$, or Br$_2$ to form MnBr$_2$, MnI$_2$ and both MnF$_2$ and MnF$_3$, respectively. It dissolves readily in dilute nonoxidizing acids to form manganese (II) salts ([Mn(H$_2$O)$_6$]$^{2+}$) together with H$_2$ gas.

Manganese resembles Ti, V, and Cr in that the highest oxidation state, Mn$^{VII}$, corresponds to the loss of all the 3d and 4s electrons. In common with V and Cr, the higher oxidation states form Mn=O and Mn=NBu$_2$ multiple bond. The oxo species are strong oxidants and some are very unstable and explosive. In the oxidation state, the most stable is II, with the $+3$, $+4$, $+5$, and $+6$ states becoming increasingly less stable. The oxidation states and common stereochemistries are summarized in Table 1 (see Manganese: Organometallic Chemistry).

2 MANGANESE (II)

This is the dominant oxidation state and the most stable. In neutral or acidic aqueous solution, very pale pink [Mn(H$_2$O)$_6$]$^{2+}$ is present, which is resistant to oxidation, while in basic media, the hydroxide Mn(OH)$_2$ formed is easily oxidized by air (Figure 1).$^{1,2}$ Manganese (II) is a ‘hard’ acid and is quite distinctly a class (a) metal. This is manifest, for example, in the preference for O donors rather than N-donor

The standard reduction potentials (E°/V) are listed in Figure 1.

![Figure 1 Standard reduction potentials (E°/V)](image)
Table 1  The oxidation state and geometry of some manganese compounds

<table>
<thead>
<tr>
<th>Oxidation state</th>
<th>Coord. number</th>
<th>Geometry</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$^{II}$, d$^2$</td>
<td>2</td>
<td>Linear</td>
<td>Mn[$C(SiMe_3)3$]$_2$</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>Trig. Planar</td>
<td>Mn[N($N(SiMe_3)2$)]$_3$</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>Tet</td>
<td>Mn[Cl$_4$]$_2$</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>Square</td>
<td>Mn[$H_2O_4$]$SO_4$:$H_2O$</td>
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<tr>
<td></td>
<td>5</td>
<td>Tbp</td>
<td>Mn[$(trenMe_3)Br$]Br</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>Dist. Tbp</td>
<td>Mn[$(ntrMe_3)Cl$]Cl</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>Oct</td>
<td>Mn[$H_2O_6$]$_2$</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>Dist Oct</td>
<td>Mn[$(bipy)HCl$]$_2$</td>
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<tr>
<td></td>
<td>7</td>
<td>Pbp</td>
<td>Mn$_2$(N$_5$macrocycle)</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>Dist Pbp</td>
<td>Mn[$(dmu)H(NO_3)$]</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>Dod</td>
<td>Mn[$(NO_3)H$(N$_2$Schiff base)]</td>
</tr>
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<td>Mn$^{III}$, d$^4$</td>
<td>3</td>
<td>Trig. Planar</td>
<td>Mn[$N(SiMe_3)3$]</td>
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<td></td>
<td>4</td>
<td>Square</td>
<td>Mn[$S_2C_6H_3Me$]$_2$</td>
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<tr>
<td></td>
<td>5</td>
<td>Supy</td>
<td>Mn$_3$(PMe)$_2$</td>
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<td>6</td>
<td>Oct</td>
<td>Mn[acac]$_3$</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>Dist. Oct</td>
<td>Mn$_3$F$_3$, Mn$(terpy)F_3$</td>
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<td>Mn$^{IV}$, d$^3$</td>
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<td>Tet</td>
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<td></td>
<td>6</td>
<td>Oct</td>
<td>Mn$_2$O$_2$, MnCl$_2$</td>
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<tr>
<td>Mn$^{V}$, d$^2$</td>
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<td>Tet</td>
<td>MnO$_2$$_2$$_2$, [Mn(NBu$_2$)$_2$(µ-NBu$_2$)]$_2$</td>
</tr>
<tr>
<td>Mn$^{VI}$, d$^1$</td>
<td>4</td>
<td>Tet</td>
<td>MnO$_2$$_2$$_2$, [Mn(NBu$_2$)$_2$(µ-NBu$_2$)]$_2$</td>
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<tr>
<td>Mn$^{VII}$, d$^0$</td>
<td>3</td>
<td>Planar</td>
<td>MnO$_2$$_2$$_2$, MnCl(NBu$_2$)$_3$</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>Tet</td>
<td>MnO$_2$$_2$$_2$, Mn$_2$F$_3$, MnCl(NBu$_2$)$_3$</td>
</tr>
</tbody>
</table>

$^a$Oct, octahedral; Supy, square pyramidal; Tbp, trigonal bipyramidal; Tet, tetrahedral; Pbp, pentagonal bipyramidal; Dod, dodecahedral; Dist, distorted.

Magnetic susceptibilities are easily recorded and the high-spin configuration gives an essentially spin-only, temperature independent magnetic moment of 5.92µ$_B$. The strong paramagnetic behavior unfortunately renders NMR useless, giving broad signals. Single-crystal X-ray diffraction still provides the only unequivocal form of characterization and is now used more and more routinely. The studies in solution remain a major difficulty with these labile systems, and assumptions about the nature of the compounds in solution are often necessary.

Conventional X- and Q-band EPR spectra are generally complex and often difficult to interpret. The recent use of high-field and high-frequency EPR spectroscopy (HF-EPR) has led to simplified spectra with remarkable resolution and provides an accurate determination of the electronic parameters of the studied compounds. Therefore, with this technique, structural information can be afforded both on solid state and in solution.

2.1 Nitrogen Ligands

The solution structure of the Mn$^{2+}$ ion in CH$_3$CN and five other organic nitriles, as determined by EXAFS spectroscopy, is six-coordinate with Mn–N bond lengths of 2.21(1)Å, while the octahedral [Mn(CH$_3$CN)$_6$][MnI$_4$] crystals are obtained from CH$_3$CN solutions of MnI$_2$.
Amine complexes are not particularly stable\textsuperscript{2,4} but there are tertiary amine complexes, for example, [MnI\textsubscript{2}(NMe\textsubscript{3})]\textsuperscript{2-} and [Mn\textsubscript{2}(μ-1\textsubscript{2})I\textsubscript{2}(NMe\textsubscript{3})\textsubscript{2}]\textsuperscript{10}. The secondary amine can be three-coordinate\textsuperscript{11,12} as in [Mn(N(SiMe\textsubscript{3})\textsubscript{2})\textsubscript{2}]\textsuperscript{2-}. Amides can be also three-coordinate with bridges as in [Mn\textsubscript{2}(μ-1\textsubscript{2})O\textsubscript{2}(NPr\textsubscript{2})\textsubscript{2}]\textsuperscript{13} and four-coordinate\textsuperscript{14} in [Mn(NPr\textsubscript{2})\textsubscript{2}]\textsuperscript{2-}.

With higher multidentate N-donor ligands, manganese (II) compounds become rather more robust.

Bridging ligands such as cyano\textsuperscript{15,16} and azido\textsuperscript{17} are used to form one-, two-, and three-dimensional polymeric systems and represent a fast growing research field because of their interesting magnetic properties. In addition to the polymeric binary dicyanamide and azide systems, for example, [Mn(N(CN)\textsubscript{2})\textsubscript{2}]\textsuperscript{+}, [Mn(N(CN)\textsubscript{2})\textsubscript{3}]\textsuperscript{2-}, and [Mn(CH\textsubscript{3})\textsubscript{3}]\textsuperscript{20} ancillary organic ligands, such as pyrazine, 4,4′-bipy and 2,2′-bipy have been extensively used to create other lattice types.

![Diagram](Diagram.png)

Manganese (II) oxide, a dark green powder, has the rock salt structure and is insoluble in water. There is little doubt that the species formed when almost any MnX\textsubscript{2} salt is dissolved in water is [Mn(H\textsubscript{2}O)\textsubscript{6}]\textsuperscript{2+}. Most of the salts crystallize from water as hydrate; those with weakly coordinating anions, such as Mn(ClO\textsubscript{4})\textsubscript{2}·6H\textsubscript{2}O and Mn(SO\textsubscript{4})·7H\textsubscript{2}O, contain [Mn(H\textsubscript{2}O)\textsubscript{6}]\textsuperscript{2+}. Solutions of Mn\textsubscript{2} in alcohols give [Mn(ROH)\textsubscript{6}]\textsuperscript{2+} species or polymeric Mn\textsubscript{2}·ROH systems.\textsuperscript{4} Few alkoxides are known and are usually made by interaction of Mn\textsubscript{2} with LiOR in the alcohol. Use of bulky OR groups can give monomeric species or bridged dimers such as [Mn(OC\textsubscript{6}Cl\textsubscript{3}H\textsubscript{2})(μ-OC\textsubscript{6}Cl\textsubscript{3}H\textsubscript{2})(bipy)]\textsuperscript{2-}. Several tetrameric alkoxide are known to have the Mn\textsubscript{4}O\textsubscript{4} cubane cores (see Section 5). The typical tetranuclear clusters [Mn(OMe)(MeOH)L\textsubscript{4}] (L = dpm, dbm) have four μ\textsubscript{3}-OMe groups and four Mn\textsuperscript{II} atoms at alternating vertices of the cube with the chelate diketonate L and MeOH bound to the Mn atoms, which are thus octahedrally coordinated.\textsuperscript{57} The disc-like molecule [Mn\textsubscript{15}O\textsubscript{12}(moe)\textsubscript{4}(moe\textsubscript{2})\textsubscript{10}moeH (moe = O\textsubscript{2}C\textsubscript{2}H\textsubscript{2}OCH\textsubscript{3}) recently synthesized is the largest alkoxide molecule\textsuperscript{28} (others are heterometallic alkoxides containing Mn and Sn or Sb). In solvent ethers such as THF and dioxane, Mn\textsubscript{2} form stable species, which are probably polymeric chain structures such as [MnCl\textsubscript{2}(THF)\textsubscript{1.6}]\textsuperscript{29}.

2.3 Oxygen Ligands

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2.2 Phosphorus Ligands

Although complexes of stochiometry [MnX\textsubscript{2}(PR\textsubscript{3})\textsubscript{3}] are polymeric with halide bridges, there are also monomers found as the octahedral [MnX\textsubscript{2}(dmppe\textsubscript{2})], the distorted tetrahedral [Mn\textsubscript{3}L\textsubscript{2}(PEt\textsubscript{3})\textsubscript{2}], and a dinuclear [Mn\textsubscript{2}I\textsubscript{2}(μ-I)\textsubscript{2}(P(NMe\textsubscript{3})I\textsubscript{2})\textsubscript{2}]. The complexes [MnX\textsubscript{2}(PR\textsubscript{3})\textsubscript{n}] have the remarkable ability to reversibly bind O\textsubscript{2}, CO, NO, and ethylene in THF at low temperatures and irreversibly bind SO\textsubscript{2} under ambient conditions. The O\textsubscript{2} species are deep blue or purple and probably peroxy ones. Irreversible oxidation of R\textsubscript{2}P to R\textsubscript{3}PO also occurs slowly to give, for example, [MnI\textsubscript{2}(OPPh\textsubscript{2}Me)(PPh\textsubscript{2}Me)] and [MnI\textsubscript{2}(OPPh\textsubscript{2}Me\textsubscript{2})\textsubscript{2}], both of which have been structurally characterized.\textsuperscript{26}

Phosphine complexes with alkyl ligands are discussed in the chapter Manganese: Organometallic Chemistry.
2.3.1 Oxides of Phosphorus and Arsenic

The air stable tetrahedral [MnX₂(OEPH₃)₂] (E = P, As; X = Cl, Br, I, NCS, NO₃) and the octahedral [MnX₂(OEPH₃)₃] (X = I, NCS) complexes have been known for many years. Some compounds, such as [MnX₂(OEPH₃)₂] (X = Br, I), exhibit triboluminescence properties. Complexes of the type [Mn(NCS)₂(OPR₃)] (R = Ph, Et, n-Bu, n = 1–4) and [MnX₂(OPR₃)₃] (R = Et, n-Pr, n-Bu, X = Cl, Br, I) have also been synthesized. The new ‘Chinese lantern’ complexes [XMn₁₂(µ-dppO₂)₄]X± (X = Cl, Br, I) have been shown to have an increasing affinity for SO₂ across the series Cl < Br < I.22

2.3.2 Oxyanions

Crystalline borates, carbonates, and silicates of manganese (II) have been characterized for a long time. Manganese (II) nitrates are very hydroscopic. Hydrates are stable under ambient conditions although manganese(II) nitrites and iodates are only stable at low temperatures. Some compounds, such as [MnX₂(OPPh₃)₂](X = = Cl, Br, I, P, As; R = 4-MeC₆H₄, 2-ClPh, 3-ClPh, 4-ClPh, 2,4,6-Cl₃C₆H₂, 2,4,6-Cl₃C₅H₂, 2,4,6-Cl₃C₆H₃, 2,4,6-Cl₃C₅H₃) have been known for many years. Some examples are NaMnP₂O₇, sulfate

2.3.3 Monocarboxylates and Multidentate Oxygen Ligands

Mono and dicarboxylates are interesting ligands because of their biological relevance and because their wide variety of coordination modes make them key building blocks for the synthesis of one-, two- and three-dimensional polymeric networks in the presence of other organic nitrogen ligands. Compounds with manganese (II) can be also monomeric, dimeric, or clusters of higher nuclearity and can exist in mixed-valent species (see Section 5). Some examples with monocarboxylate ligands are [Mn₂(µ-O₂CR)₂(bipy)₄]²⁻, [Mn₂(µ-O₂CR)₃(bipy)₂], and [Mn(µ-O₂CR)₃(bipy)]⁺ with R = 2-CIPh, 3-CIPh, 4-CIPh.46

Dicarboxylates such as malonate, adipate, fumarate, and maleate generally produce polymeric compounds with a variety of bridging modes. Mono and binuclear malonate, and adipate complexes with bipy, phen, and a high nuclearity cluster with phthalate [Mn₁₀(OH)₃(phth)₄(bipy)₆][NH₂Et₂], with a pinwheel-shaped [Mn₁₀O₉] core, have also been reported.52

The oxalate [Mn₂(C₂O₄)₃]⁴⁻, like the catecholate [Mn(cat)₃]⁴⁻ compounds, can be readily oxidized to Mn⁴⁺ state. Otherwise, oxalate can form polymers and the combination of phosphate and oxalate in forming hybrid framework materials has been also explored.54 Several hydroxycarboxylates exist as monomers or polymers and the first mononuclear manganese citrate complex, (NH₄)₄[Mn(C₆H₅O₇)₂], has been recently isolated and crystallographically characterized.55

Multidentate oxygen ligands such as the symmetric tetraketo- (H₂L) give an asymmetric complex, [Mn₃L₃], which has been reported as the first asymmetric homometallic helicate formed from a symmetric ligand. A wide variety of compounds have been studied with the β-diketone monooanions such as acetylacetonate (acac) and hexafluoroacetylacetone (hfacac) that have been used as ligands in many polymeric systems.57

2.4 Sulfur Ligands

Structural data are available for a range of bitetra- and quaternary sulfides of manganese (II), which contain four-coordinate [MnS₄] tetrathedral and six-coordinate [MnS₆] octahedral; no other polyhedra have been detected. The thiolates may be tetrathedral complexes of the type [Mn(SR)₄]²⁻, [Mn₂(SR)₄(µ-SR)₂]²⁻, and [Mn₄(SRH)₄]²⁻. Thiolates with bulky aryl groups can stabilize low-coordination numbers as in the three-coordinate [(ArS)Mn⁴⁺(µ-SAR)₂], Ar = 2,4,6-Bu₃C₆H₂S. The crystal structure of a five-coordinated compound [Mn₂(C₃S₅)₄]⁴⁺, C₃S₅²⁻ = 4,5-dimercapto-1,3-dithiole-2-dithiole-2-thionate, has also been reported.59 There are dithiocarbamates, as well as the sulfido anion, [Mn(S₆)₂]²⁻, that are infinite polymers with bridging S atoms. Some Se and Te analogue compounds are also known.2

2.5 Halide Ligands

The halide complexes exhibit a wide structural diversity. Anhydrous MnF₂ and MnCl₂ have the tetragonally distorted (TiO₂) rutile and the hexagonal layer-type structures (defined first for CdCl₂) respectively, while both MnBr₂ and MnI₂ have the CdI₂ layer structure.4 The formation constants of Mn²⁺ with X⁻ in aqueous solution are very low, but when ethanol or acetic acid is used as a solvent, salts of complex anions of varying types may be isolated, such as MnX₃⁻ (octahedral with
perovskite structure), MnX₂^2− (tetrahedral or polymeric octahedral with halide bridges),³⁰ MnCl₆^4− (octahedral), Mn₂Cl₂^2− (octahedral),³⁰ ⁶⁰ and Mn₂Cl₃^3− (linear chain face-sharing MnCl₆ octahedra, also discrete MnCl₄^2−, tetrahedral). The precise nature of the product obtained depends on the cation used and also on the halide and the solvent. There is a variety of halide complexes containing other ligands present, such as MnI₂(THF)₃ trans-[MnCl₄(H₂O)₂]^4−, and amine and phosphine species.

2.6 Mixed-Donor Atom Ligands

For this area of chemistry, the use of X-ray diffraction is necessary to assign unambiguously which ligand donor atoms are bound. The preference of manganese(II) for O rather than N donors is seen in the amino acid complexes, in which the amino acids generally bind only through the O atoms of the carboxylic acid group. In polymeric species, for example, [Mn(gly)₃Cl₂]ₙ, the carboxylate acts as a bridge between adjacent manganese(II) atoms⁶¹ and in monomeric ones, only one of the O atoms is coordinated.⁴ Manganese(II) complexes of several amino acids catalytically disproportionate hydrogen peroxide in the presence of imidazole.⁶²

In several multidentate ligands associating one carboxylate and pyridine/imidazole moieties, the coordination involves both the N and O atoms. Dimeric,⁶³ but also trimeric,⁶⁴ or polymeric,⁶⁵,⁶⁶ complexes can be formed in which metal centers are linked by one or two oxygen of the carboxylate moiety of the ligand.

Manganese(II) compounds with several types of Schiff-base ligands are known. A linear tetranuclear [{Mn₂(L)₂O₂(C₂Me₅)(CH₃OH)}₂], where L is a N₂O₂ donor set, has an unprecedented arrangement of five N₂O₂ and six-coordinated O₆ manganese ions.⁶⁷ A (pyridylazo)oxime ligand forms the low-spin mononuclear [MnL³]₂(3) complex with the very rare mononuclear oximato-O coordination.⁶⁸

There is sound evidence that mixed O, S donors can bind both donor atoms to manganese(II), while there are few examples of N, S donors.⁶⁹,⁷⁰ A rare example of a complex with N, O, S donors is the octahedral low-spin thioether complexes [Mn(L₄)]⁺ that can be electrochemically oxidized to [Mn(L₄)]³⁺; one example of each has been structurally characterized.⁷¹

2.7 Macrocyclic Ligands

There has been a large number of studies involving coordination of Mn(II) by a wide variety of nitrogen and mixed-oxygen nitrogen macrocyclic ligands. Among them, as for the higher oxidation states of manganese, a significant number of investigations were made using pendant arm polyazamacrocycles. For the mixed-donor Schiff-base macrocycles, complexes are formed by a template reaction and the solution complexation properties (determination of the stability constant) of a large range of ligands have been reported. The main applications of those mixed-donor macrocycles and their resulting manganese (II) complexes concern the separation and analysis of Mn²⁺, the epoxidation of olefin, and modeling of biological redox processes (superoxide dismutase and catalase activities) (see Manganese Proteins with Mono- & Dinuclear Sites). All these studies are not detailed here and an extensive review of this topic can be found in Reference 1.

In manganese(II) compounds incorporating crown ether macrocycles, the metal is generally II-bonded to the crown via water molecules, although it has been possible to isolate some compounds such as [Mn(12-crown-4)]³⁺ and [Mn(15-crown-5)(CF₃SO₃)]₂, in which all the ether oxygen atoms of the crown bind directly to manganese(II).⁷²–⁷⁴

3 MANGANESE (III)

The aqua ion of manganese(III) can be obtained by electrolytic or peroxy sulfate oxidation of Mn³⁺ solutions, or by reduction of MnO₄⁻.² The ion plays a central role in the complex redox reactions of the higher oxidation states of manganese in aqueous solutions, although it is often subject to disproportionation into manganese(IV) (MnO₂) and manganese(II). It is more stable in acidic solution. The chemistry of manganese(III) is dominated by dinuclear, trinuclear, and tetranuclear complexes with o xo, alkoxo, and carboxylates bridges. The propensity of these complexes to be in mixed-valence states such as manganese(II,III) or manganese(III,IV)
require the confirmation of their structures by spectroscopic and X-ray structural methods (see Section 5). Mononuclear compounds can be stabilized by Schiff-base ligands, nitrogen-base ligands, and macrocyclic ligands. The most commonly observed coordination numbers of manganese(III) are 5 and 6. Few compounds are known with S and P donors ligands.

The electronic configuration of manganese(III) is $3d^4$, and therefore, the high-spin configuration in an octahedral field is subject to Jahn–Teller distortion like for Cu$^{II}$ and Cr$^{III}$ compounds. Such distortions often serve to identify the Mn$^{III}$ polyhedra in mixed oxidation state compounds (see Section 5). There are few examples of low-spin compounds, for example, [Mn(CN)$_6$]$^{3-}$, [MnH$_4$(dmpe)$_2$], and there are other examples among macrocyclic compounds. The electronic spectra of these $d^4$ systems have spin-allowed d-d transitions, and accordingly the compounds have more color than those of manganese(II). All high-spin manganese(III) complexes have magnetic moments very close to 4.9 $\mu_B$.

Recently developed techniques of HF-EPR have now proven to be effective at elucidating the electronic structure of integer-spin systems such as high-spin manganese(III) ($S=2$) compounds, which are usually EPR silent at X- and Q-band frequencies. Mononuclear complexes with axial $^{75,76}$ (macrocyclic ligands) and rhombic symmetries $^{77,78}$ have been studied and this technique has been proposed as a useful tool for the structural investigation of these complexes and also for mixed-valence clusters incorporating manganese (III) $^{79}$ (see Section 5).

### 3.1 Nitrogen Ligands

The chemistry of manganese(III) with nitrogen ligands, other than macrocycles or mixed N, O donors is still quite limited. Amido species include the three-coordinate planar [Mn(N(SiMe$_3$)$_2$)$_3$] and the trigonal pyramidal four-coordinate complex Mn(N$_3$N)$_3$, where N$_3$N = [Bu'Me$_2$Si]NCH$_2$CH$_2$N]. $^{2}$ The interaction of alkaline-earth nitrides and manganese nitride at high temperatures leads to compounds such as Ca$_2$Mn$_3$N or Ca$_2$Mn$_5$N$_3$ that have sheet structures involving the trigonal planar [Mn(N$_3$)$_3$]$^{6-}$ anion. $^{80}$ Octahedral mononuclear complexes with bi- or tridentate N-ligands and halides or pseudohalides have been structurally characterized such as [Mn(L)(X)$_3$(H$_2$O)$_n$] $^{81-83}$ (X = bipy, phen; X = Cl, F), [Mn(phen)$_2$(Cl)$_2$]$^{84}$ and [Mn(L)(X)$_3$]$^{77}$ (L = terpy, bpea; X = F, N$_3$). Tripodal N-ligands allowed the isolation and structural characterization of very rare mononuclear manganese(III) complexes: the side-on peroxo pyrazolate-pyrazolylborate, [Mn(n$_2$-O$_2$)(3,5-Pr$_2$pzH)BB(3,5-Pr$_2$-pz)$_2$], $^{85}$ the hydroxo, [Mn(LH$_2$)(OH)]$^{-}$ $^{5}$ (and the oxo, [Mn(LH$_2$)(O)]$^{2-}$ $^{6}$).

Various reactions with open-chain mono to hexadentate N-ligands have produced multinuclear $\mu$-alkoxo, oxo, and/or carboxylato bridged manganese(III) compounds and some examples are given in Section 5. $^{1}$

### 3.2 Oxygen Ligands

Manganese(III) complexes with a variety of oxygen ligands constitute the largest group next to those with mixed-donor ligands. The carboxylate chemistry of manganese(III) is mainly represented by monooxo-carboxylates compounds, such as acetate, benzoate, and their derivatives, while with bidentate carboxylates such as oxalate, malonate, and salicylate, there is a limited number of compounds. This chemistry can be extremely complicated and often has mixed valences (see Section 5). The chemistry of manganese(III) with monooxo-carboxylates is extensive and results in the formation of clusters with nuclearities of 2, 3, 4, 6, 7, 8, 9, 10, and 18, and polymers with or without coligands such as Schiff bases. $^{1}$ Examples of compounds are the elusive manganese(III) formate formed by the reaction of KMnO$_4$ and formic acid that has finally been crystallographically characterized as the polymeric Mn($\mu$-O$_2$CH)$_2$5CO$_2$·0.25HCO$_2$H·0.67H$_2$O with a carboxylate cage encapsulating the other molecules. $^{87}$ The ‘manganic acetate’ still often referred to as Mn(OCMe)$_2$:2H$_2$O has the well-known trinuclear oxocentered core [Mn$_6$($\mu$-O$_2$)O$_5$($\mu$-O$_2$)CMe$_6$]$^{9+}$. $^{88}$ Otherwise, the oxidation of Mn(OMe)$_2$:4H$_2$O with KMnO$_4$ in acetic acid gives the triply bridged polymer [Mn($\mu$-OH)(O$\mu$-OCMe)$_2$;MeCO$_2$H·H$_2$O]. $^{89}$

Mononuclear complexes are mostly obtained with hydroxo-carboxylate (e.g. (NH$_4$)$_3$[Mn(C$_6$H$_5$O$_7$)$_2$])$^{35}$ or $\beta$-diketones and related ligands. $^{1}$ Examples of carboxylate-free complexes of higher nuclearity with diketones are [Mn$_2$(OMe)$_2$(dmab)$_4$] and [NaMn$_6$(OMe)$_2$(dmb)$_6$]$,^{+}$ the latter displaying a 12-metallocrown-6 structure. $^{90}$ The nonalkoxo [Mn$_3$O$_5$X$_4$(Me$_2$ dbm)$_6$] (X = Cl, Br) has been also structurally characterized. $^{91}$ Detailed magnetic studies indicate that these three hexanuclear clusters have ground spin states of 12. 

Catechol$^{92,93}$ and other diphenolates form manganese(III) complexes.

A rare example of a manganese(III) cluster with phosphinate and phosphonate ligands is [Mn$_9$O$_2$(O$_2$PPh)$_2$(O$_2$PPh)$_2$(O$_2$CPPh)$_2$(py)$_2$] synthesized by the reaction of [Mn$_3$O(O$_2$CPH)$_2$(py)$_2$]$^{2-}$ with an equimolar quantities of phenylphosphonic acid. $^{94}$


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3.3 Phosphorus, Sulfur, and Halide Ligands

Phosphorus compounds of manganese (III), except for alkyl and hydride species, are still limited to [MnCl₂(diphos)₂]Cl₂ and [MnX₂(PMe₂)₂]X (X = Cl, Br, I, NCS). The tendency of manganese(III) to oxidize sulfur ligands results in the rarity of such compounds. Nevertheless, for simple thios, a new species has been isolated and characterized such as the dimer with asymmetric Mn–S bridges [Mn₂(pttd)₂]₂⁻ (pttd⁻ = propane-1,2,3-trithiol), which is very similar to the previously reported [Mn₂(edt)₄]²⁻ (edt²⁻ = ethane-1,2-dithiolate) species.

The only binary compound of manganese(III) with the halides stable at room temperature is MnF₃. Hydrated salts of the anions MnF₄⁻, MnF₃²⁻, and MnF₂³⁻ are known. The salt Tl₂MnF₃·H₂O has chains of (MnF₃)₂⁻ units, and some other fluoromanganese(III) complexes are [MnF₃(urea)]₃·H₂O, K₃[MnF₂(C₂H₅O)₂]·3H₂O and those with N-donor ligands (see Section 3.1). Although several methods of making MnCl₃ in solution are known, the best is the interaction of [Mn₂O₁₂(O₂CMe)₁₆(H₂O)₄]₁⁻ with acetonitrile or other solvents, with Me₃SiCl. The resulting purple solutions are useful starting materials for synthesis of [MnCl₄(NBu₂)₂]⁺ or amine complexes such as [MnCl₃(bipy)]⁺, [MnCl₄(H₂O)(bipy)]⁻, and the imido species MnCl(NBu₂)₃. Most of the polydentate ligands that stabilize manganese(III) are Schiff bases and their derivatives. Square planar and pyramidal mononuclear manganese(III) complexes with tetradentate Schiff bases have been extensively investigated for the epoxidation of olefins. Other types of mixed N, O-donor ligands form interesting compounds such as [MnCl₃(bipy)]⁺ and related macrocycles.

3.4 Mixed Donors and Macrocycles Ligands

Most of the polydentate ligands that stabilize manganese(III) are Schiff bases and their derivatives. Square planar and pyramidal mononuclear manganese(III) complexes with tetridentate Schiff bases have been extensively investigated for the epoxidation of olefins. Other types of mixed N, O-donor ligands form interesting compounds such as [MnCl₃(bipy)]⁺ and related macrocycles.

4 MANGANESE (IV)

In aqueous solution, the insoluble MnO₂ is formed readily. Much of the manganese (IV) chemistry involves O-donor ligands. The compounds are generally high-spin d³ (S = 3/2) species and many are octahedral showing magnetic moments close to the spin-only value of 3.87 &mu;B. In contrast, MnO₂ is an insulator with d⁰ magnetic moment.

4.1 Nonoxygen Containing Compounds

This class of compounds is relatively limited. Few examples of nonporphyrinic manganese(IV) complexes coordinated solely by nitrogen have been structurally characterized: [Mn(H₂bipy)₃]⁺, the water stable [Mn(biguaniade)₃]⁺ and Mn(bipy)(N₃)₄.

Compounds with dithiolates have been characterized. The only binary halide known is the unstable MnF₄ that decomposes to MnF₂ and F₂. Room temperature syntheses of MnF₂ and hexafluoromanganate(IV) of alkali cations A₂MnF₆ (A = Li–Cs) have been reported.

4.2 Oxygen-containing Compounds

These are of great variety and importance. A new tetrachlorocatecholate derivative [Mn(Cl₄cat)₂]⁻ has been isolated. A wide variety of compounds with various multidentate mixed-donor ligands have been synthesized, the majority of which contain N and O donor atoms (see Section 5). Several mononuclear manganese (IV) of the type Mn(L)₂ with tridentate O,N,O ligands and Mn(L)Cl₂ with tetradentate Schiff bases have been synthesized. Complexes with oxo bridges are very characteristic of manganese (IV) chemistry and some examples are given in Section 5. Many porphyrins have Mn=O bonds and have been much studied as oxygen transfer agents, for example, in the epoxidation of C=C bonds.

5 MIXED OXIDATION STATE (II–IV)

For about twenty years, there have been an increasing number of publications on mixed-valence manganese multinuclear complexes that are relevant to such diverse fields as metalloenzymes and single-molecule magnets (see Manganese Proteins with Mono- & Dinuclear Sites and Manganese: The Oxygen-evolving Complex & Models). Besides the small clusters, comprising two to four metal ions relevant to biological systems such as manganese catalases and the oxygen-evolving complex of Photosystem II, a large interest has been invested in larger clusters, not only for their biological relevance, but also for their interesting magnetic properties. Hundreds of new compounds have been made, those with carboxylate ligands being the most common. However, other ligands employed...
have been pyridine, polypyrrolid, pyrazolylborates, triazacyclonanes, and Schiff bases of various sorts. These have been obtained in oxidation states II–IV with both unitary and mixed valencies. The majority of mixed valency complexes form crystallographically valence-trapped species with distinct sites for each oxidation level. The electronic (EPR), magnetic, and electrochemical properties of these compounds have been largely investigated. Some of the core types are shown in Figure 2. The structures vary from quite simple to extremely complicated and the more complex species can have structures built up of different core units. This chemistry is too extensive to detail here and the reader should note the existence of several recent reviews, that cover this literature.1,79,113–116 Only some recent examples are given here.

5.1 Dinuclear Complexes

The majority of Mn$_2$(III,IV) and Mn$_2$(IV,IV) compounds have bis-µ-oxo or bis-µ-alkoxo mono-µ-carboxylato cores, for example, [Mn$_2$(III,IV)(O)$_2$(terpy)$_2$(X)$_2$]$^{2+}$ (X = H$_2$O or CF$_3$CO$_2$)$_{117,118}$ [Mn$_2$(IV)(O)$_2$(SO$_4$)$_2$]$_{119}$ and [Mn$_2$(IV)(O)$_2$(O$_2$CMe)(bpy)$_2$(Cl$_2$(H$_2$O))],$_{120}$ while for Mn$_2$(III,III) complexes, mono-µ-oxo bis-µ-carboxylato and bis-µ-alkoxo mono-µ-carboxylato cores are the most common, for example, [Mn$_2$(III)(O$_2$CMe)$_2$(HB(pz)$_2$)$_2$] and [Mn$_2$(III)(5-Br-salpn)$(OMe)$(O$_2$CMe)(MeOH)$_2$]$_{121}$ All complexes with a bis-µ-alkoxo mono-µ-carboxylato contain a Schiff-base coligand.1 The only example of a bis-µ-oxo bis-µ-carboxylato Mn$_2$(III,IV) complex is [Mn$_2$O$_2$(Ar$_{6}$CO$_2$)$_2$(bpy)$_2$]$^{2+}$.122 Few examples of tris-µ-oxo, di-µ-oxo mono-µ,1,2-peroxo, and mono-µ-oxo bridged dinuclear complexes are known. Examples are [Mn$_2$(IV)(O)$_2$(Me$_3$acn)$_2$]$^{2+}$,$_{123}$ [Mn$_3$(IV)(O$_2$)(Me$_3$acn)$_3$]$^{2+}$, and [Mn$_{111}$O$(L)_3$]$^{2+}$ with a Schiff-base pentadentate monoanionic ligand (L = N,N-bis(2-pyridylmethyl)-N$^\prime$-salicylidene-1,2-diaminobenzen)$_{124}$ The one-electron oxidized complex [Mn$_3$(III,IV)O$(L)_3$]$^{3+}$ has been electrochemically prepared and crystallized and is the only example of a structurally characterized mono-oxo bridged Mn$_2$(III,IV) complex.

Several Mn$_2$(II,II) complexes exist with different bridging patterns including solely carboxylates, or those associated with aqua, hydroxo, alkoxo, or phenoxy bridges.114 Conversely, mixed-valent Mn$_2$(III,II) derivatives have received much less attention.125

Among these numerous dimeric complexes that have been prepared using a variety of ligands, very few exist in more than two stable oxidation states. Examples of complexes with three stable oxidation states are di-µ-oxo bridged dinuclears with tetradentate N-donor ligands such as [Mn$_2$O$_2$(taa)$_2$]$^{2+}$,$_{3+}$,$_{4+}$ where the (III,III), (III,IV), and (IV,IV) states can be electrochemically generated. A rare example of complexes isolated and crystallographically characterized at the four oxidation states (II,II), (II,III), (III,III), and (III,IV) is the series [Mn$_2$(2-OHsalpn)$_2$]$_2$$^{2+}$,$_{3+}$,$_{4+}$,$_{126}$ Otherwise, core interconversions or changes in nuclearity have been observed for a series of compounds at different oxidation states. The complexes [Mn$_2$(III)(µ-O)(µ-O$_2$CMe)$_2$(bpea)$_2$]$^{2+}$ and [Mn$_2$(IV)(µ-O)(µ-O$_2$CMe)(bpea)$_2$]$^{3+}$ can be selectively and quantitatively electrogenerated from [Mn$_2$(II)(µ-O$_2$CMe)$_2$(bpea)$_2$]$^{2+}$ in acetoniitrile solution and it appears that each substitution of an acetate group by an oxo group is induced by a two-electron oxidation of the corresponding dinuclear complexes.24 Electrochemical oxidation of [Mn$_3$(III,IV)O$_2$(bipy)$_4$]$^{3+}$ in water leads to the stable, linear tetranuclear [Mn$_4$(IV)O$_6$(bipy)$_6$]$^{4+}$,127

5.2 Trinuclear and Tetranuclear Complexes

The number of trinuclear manganese(II) complexes with bridging carboxylates is limited and most possess the linear [Mn$_3$(µ-carboxylato)$_6$] core as in [Mn$_3$(O$_2$CMe)$_6$(bipy)$_2$] and there is only one example of a hydroxocentered complex$^{128}$ [ppy$_3$(Mn$_3$(µ$_2$-O$_2$CMe)$_2$(µ$_3$-OH)(catechol)) (Type I)]. Several mixed-valence Mn$_{111}$Mn$_{111}$Mn$_{111}$ or Mn$_{111}$Mn$_{111}$Mn$_{111}$ carboxylato compounds with open structures have been also isolated with Schiff-base ligands.$^{113}$ All the trinuclear manganese(III) carboxylato complexes possess the basic manganic acetocxocentered structure, for example, [Mn$_3$(O$_2$CMe)$_6$(HB(pz)$_2$)$_2$] and [Mn$_3$(O$_2$CMe)$_6$(py)$_3$]$^{2+}$, the latter is also crystallized in the Mn$_{111}$Mn$_{111}$Mn$_{111}$ oxidation state.$^{113}$ All trinuclear Mn$_3$(IV) complexes have the Mn$_3$O$_4$ core, for example, [Mn$_3$O$_4$(phen)$_4$(H$_2$O)$_2$]$^{4+}$ (Type II).$^{113}$

Examples of tetranuclear adamantane-shaped complexes (Type III) are [Mn$_4$(IV)O$_6$(bpea)$_4$]$^{4+}$ and its corresponding one-electron reduced species, while cubane cores (Type IV) are found in [Mn$_4$(IV)O$_6$(O$_2$PPh$_2$)$_4$] and its one-electron reduced species. A large family of tetranuclear clusters is
now known with the distorted cubane core [Mn$_{10}^{III}$Mn$_{4}^{IV}$O$_{6}$] (Ar$_{8}$CO$_{2}$)$_{2}$ Me$_{2}$bipy)$_{6}$] and the tetranuclear Mn$_{12}^{II}$O$_{12}$O(OCR)$_{16}$O(H$_{2}$O)$_{4}$ with an adamantine-like inner Mn$_{2}^{II}$Mn$_{4}^{III}$ core respectively.

5.3 Higher Nuclearity Clusters

A novel hexanuclear high-valent species, [Mn$_{10}^{III}$Mn$_{4}^{IV}$O$_{6}$] (Ar$_{8}$CO$_{2}$)$_{2}$ Me$_{2}$bipy)$_{6}$] and the tetranuclear Mn$_{12}^{II}$O$_{12}$O(OCR)$_{16}$O(H$_{2}$O)$_{4}$ with an adamantine-like inner Mn$_{2}^{II}$Mn$_{4}^{III}$ core respectively.

6 MANGANESE (V) (VI) AND (VII)

Most of the manganese compounds that have high oxidation states involve oxo compounds; however some other compounds in these oxidation states have been synthesized and characterized, especially those based on nitrodo and imido ligands.

6.1 Oxochemistry

Reduction of the tetraoxomanganates Mn$_{4}^{2-}$, Mn$_{2}^{2-}$, and MnO$_{4}^{3-}$ by pulse radiolytically—generated free organic radicals leads to the unstable [Mn$_{4}^{V}$O$_{3}$(OH)$_{5}$] and [Mn$_{2}^{IV}$O$_{3}$(OH)$_{5}$] species. They were characterized by their UV-visible spectra and their corresponding acid dissociation constants have been determined.

The permanganate anion is well-known as a convenient oxidizing agent in inorganic and organic chemistry. Its utilization for synthesis has been investigated following several procedures. The oxidizing properties of Mn$_{4}^{2-}$ have also been applied to the destruction of pollutants in groundwater or as a chemiluminescent analytical agent.

Crystals of Na$_{4}$Mn$_{3}$O$_{4}$P$_{2}$O$_{5}$, a mixed-metal Mn(VII)P(V) oxide, were synthesized via a sodium hydroxide flux. Manganese [Mn(V)O] complexes have drawn considerable attention over the past 15 years because they are generally accepted to be the key reactive intermediates in many catalytic oxide processes, especially those related with biomimicry. However, only a few Mn$_{o}$O species have been isolated and their structures resolved. Two well-characterized species involving the use of a tetraanionic ligand to stabilize the high-valent manganese center have been reported. The very short bond distance suggests a Mn$_{o}$O bond. One of these complexes can be activated for O-atom transfer by the addition of a secondary cation like Na$^+$. A major advance in this chemistry was made with the isolation and characterization of a porphyrin Mn$_{2}$O species. Besides studies in the porphyrin series, some oxomanganese (V) corrole complexes have been generated, characterized spectroscopically, and investigated in catalytic oxidations. Direct proof of the existence of discrete [Mn$_{2}^{V}$O(salen)]$^{+}$ complexes has been obtained by means of electrospray tandem mass spectrometry.

6.2 Nonoxo Chemistry

Nitrido macrocyclic complexes containing a terminal Mn$_{2}^{V}$≡N bond have proven to be versatile and effective aminating agents with a different class of olefins; an asymmetric version of this methodology was also reported. The complexes [L$_{n}$Mn$_{n}^{III}$N] are usually made by photolysis of azide precursors [L$_{n}$Mn$_{n}^{III}$(N$_{3}$)] (Arshankkow–Poznjak reaction). The ligands L$_{n}$ are the regular macrocycles: porphyrins, corroles, cyclams, salens. Alternative methods for their synthesis have been developed using an oxidizing agent (e.g. NaOCl), and some of these nitrido manganese complexes have been structurally characterized. An extremely short Mn≡N bond distance (1.50–1.55 Å) was observed. Since the manganese (V) species have a d$^3$ electron configuration,
they are nonmagnetic with a low-spin ground state. A terminal imido complex of a Mn(V), the postulated intermediate in amination and aziridination reactions with nitrido complexes, has been synthesized and fully characterized.\textsuperscript{147}

Ligand substitution by CN\textsuperscript{−} of nitrido complexes of Mn(V) leads to the simple nitrido cyanometalate of Mn(V): [Mn\textsuperscript{V}(N(CN))\textsubscript{5}]\textsuperscript{+}, which has been structurally characterized, together with an assignment of its electronic transitions and orbital energies.\textsuperscript{148}

The interaction of MnCl\textsubscript{3} with NBu\textsubscript{t}(SiMe\textsubscript{3}) gave the thermally and air stable Mn(VII) species [Mn(NBu\textsubscript{t})\textsubscript{3}Cl].\textsuperscript{149} tert-Butyl imido chemistry has been further developed and over 40 imido compounds are now known.\textsuperscript{150} The Cl atom of [Mn(NBu\textsubscript{t})\textsubscript{3}Cl] can be substituted by, for example, Br, O\textsubscript{2}CR, SC\textsubscript{6}F\textsubscript{5}, and NBu\textsubscript{t}; all these compounds are green. Reduction of [Mn(NBu\textsubscript{t})\textsubscript{3}Cl] can give the dimers [Mn\textsuperscript{IV}(NBu\textsubscript{t})\textsubscript{2}(\mu-NBu\textsubscript{t})\textsubscript{2}]\textsuperscript{2+} and [Mn\textsuperscript{VI}(NBu\textsubscript{t})\textsubscript{2}(\mu-NBu\textsubscript{t})\textsubscript{2}]. Another unusual anion is [Mn\textsuperscript{VII}(≡N)(NBu\textsubscript{t})\textsubscript{3}]\textsuperscript{2−}.

7 REFERENCES


