

GENERAL REVIEW

1.1 INTRODUCTION

The element manganese and its different ores have long been known mainly because of their use in the preparation of different coloured materials, like tinted glass, detergents and in alloying materials for steels, iron and other non-ferrous metals. Most recently, it has been proved that the element is essential for all types of living beings. It is also known that manganese deficiency inhibits growth and diminishes life expectancy. It is believed that manganese complexes are involved in photo-synthesis reactions. These complexes also activate many enzymatic and oxidative processes occurring in plants and animals. Now-a-days, manganese glycerophosphate, manganese hypophosphite etc., are used as essential nutrients in the formulations of many animal foods and vitamin tablets.

Although manganese is essential to man, it becomes poisonous when administered in high concentration.

It is worth-mentioning that India is one of the largest producers of manganese.

The study of the chemistry and technology of the element is, thus, of great importance and in recent years the chemistry of manganese has been receiving considerable attention to scientists.

Manganese with an outermost electronic configuration of $3d^54s^2$, probably exhibits a wider range of valencies than any other metal of the first transition series. Each metal preceding manganese, uses all its d and s electrons in exhibiting its highest covalency, usually, in oxo-compounds or fluorides; but in four succeeding elements, the d-electrons gradually appear to cease functioning as valency electrons, the range of stable valencies suddenly contracts and the highest is usually not more than three. Thus, manganese, among the first transition series, shows the highest oxidation state of seven (vii) in its oxo-compounds MnO_4^- and MnO_2F . The other known oxidation states of manganese are -(III), -(II), (0), + (I), +(II), +(III), +(IV), +(V), +(VI). Manganese (+II) is the most stable oxidation state because of the half-filled shell configuration. The lower oxidation states are usually found in the carbonyl, nitrosyl and organo-metallic derivatives of manganese.

Unfortunately, the chemistry of manganese(+III) is not extensive. Higher valent manganese compounds mainly in its +III, +IV or +V states are generally unstable, partly because of the readiness with which they hydrolyse and precipitate as insoluble manganese oxide and partly because they are easily reduced by oxidisable substances present in the solution. However, they may be stabilised to some extent by complex formation. The insolubility and high lattice energy of the complexes enhance the stability.



The energetics of the interconvertibility of different oxidation states of manganese at different pH (Table 1.1) will help in understanding their relative stabilities.

TABLE 1.1: Some oxidation potentials of manganese¹

		E ^o (V)
Mn(s)	= Mn ²⁺ (aq)+2e ⁻	1.20
Mn ²⁺ (aq)	= Mn ³⁺ (aq)+e ⁻	ca. -1.50
Mn ²⁺ (aq)+2H ₂ O(liq)	= MnO ₂ (s)+4H ⁺ (aq)+2e ⁻	-1.24
MnO ₂ (s)+4OH ⁻ (aq)	= MnO ₄ ⁻ (aq)+2H ₂ O(liq)+3e ⁻	-0.59
MnO ₄ ³⁻ (aq)	= MnO ₄ ²⁻ (aq)+e ⁻	ca. -0.30
Mn ²⁺ (aq)+4H ₂ O(liq)	= MnO ₄ ⁻ (aq)+8H ⁺ (aq)+5e ⁻	-1.51
MnO ₂ (s)+2H ₂ O(liq)	= MnO ₄ ⁻ (aq)+4H ⁺ (aq)+3e ⁻	-1.69
MnO ₂ (s)+2H ₂ O(liq)	= MnO ₄ ²⁻ (aq)+4H ⁺ (aq)+2e ⁻	-2.26
Mn(s)+2OH ⁻ (aq)	= Mn(OH) ₂ (s)+2e ⁻	1.58
Mn(OH) ₂ (s)+OH ⁻ (aq)	= Mn(OH) ₃ (s)+e ⁻	ca. 0.20
Mn(OH) ₃ (s)+OH ⁻ (aq)	= MnO ₂ (s)+2H ₂ O(liq)+e ⁻	ca. -0.10
Mn(OH) ₂ (s)+2OH ⁻ (aq)	= MnO ₂ (s)+2H ₂ O(liq)+2e ⁻	ca. 0.03
Mn(OH) ₂ (s)+6OH ⁻ (aq)	= MnO ₄ ⁻ (aq)+4H ₂ O(liq)+5e ⁻	-0.34
MnO ₂ (s)+4OH ⁻ (aq)	= MnO ₄ ³⁻ (aq)+2H ₂ O(liq)+e ⁻	ca. -0.90
MnO ₂ (s)+4OH ⁻ (aq)	= MnO ₄ ²⁻ (aq)+2H ₂ O(liq)+2e ⁻	-0.60

An excellent review² has recently been published on the chemistry of higher oxidation state of manganese by W. Levason and C.A. McAuliffe. This review deals with the chemistry of

manganese in oxidation states +III to +VII. Chemistry of manganese (+III) in aqueous solution has also been reviewed³. However, in the following few paragraphs, a brief description of the chemistry of manganese(III) and manganese(IV) has been reported.

1.2 CHEMISTRY OF MANGANESE(IV)

Manganese(IV) has a more extensive chemistry than any of its higher oxidation states; but in general, the compounds are not stable. Aside from MnO_2 , MnF_4 and $Mn(SO_4)_2$, the only stable compounds are a few complexes.

(i) Oxides containing manganese(IV):

There is an extensive literature on the simplest manganese(IV) oxide, MnO_2 . MnO_2 is usually non-stoichiometric and it exists in different forms, α , β , ν , δ , ϵ and η . The common form, β - MnO_2 (pyrolusite) is made by heating manganese(II) nitrate at $150-160^\circ$ and purifying it from its lower oxides⁴ by extracting it repeatedly with boiling nitric acid. Most of the other modifications of MnO_2 are said⁵ to be changed to the β -variety on heating in air at 400° . At this temperature, it has an ideal composition $MnO_{2.00}$ with the rutile structure $a = 4.38$, $c = 2.86 \text{ \AA}$. All forms of MnO_2 lose oxygen on heating strongly, eventually giving rise to Mn_2O_3 .

Some more oxides of manganese have been discovered, in which Mn^{IV} is suspected to be present in addition to other oxidation states. Compounds that do fit into the category of mixed-valence oxides⁶⁻⁹ containing Mn(IV) are Mn_3O_4 , Mn_5O_8 and the newly discovered $\text{Mn}_7\text{O}_{12} \cdot 6\text{H}_2\text{O}$ and $\text{Mn}_7\text{O}_{13} \cdot 5\text{H}_2\text{O}$. The purple-red powder of Mn_3O_4 form a distorted spinel structure $\text{Mn}^{\text{II}}\text{Mn}_2^{\text{III}}\text{O}_4$ (ref.10) and not $\text{Mn}_2^{\text{II}}\text{Mn}^{\text{IV}}\text{O}_4$ as reported earlier. The structural determination of Mn_5O_8 supports the formulation, $\text{Mn}_2^{\text{II}}\text{Mn}_3^{\text{IV}}\text{O}_8$ which contain a distorted octahedral arrangement of O-atoms around Mn^{IV} and a distorted trigonal prism around Mn^{II} (ref.11).

Recently, Giovanoli et al.^{8,9} found that $\text{Na}_4\text{Mn}_{14}\text{O}_{27} \cdot 9\text{H}_2\text{O}$ reacts with dilute nitric acid to produce manganese(III) manganate(IV), $\text{Mn}_7\text{O}_{13} \cdot 5\text{H}_2\text{O}$ and with $\text{Mn}(\text{NO}_3)_2$ solution to form manganese(II) manganate(IV), $\text{Mn}_7\text{O}_{12} \cdot 6\text{H}_2\text{O}$.

(ii) Other simple manganese(IV) compounds:

Two more simple manganese(IV) compounds are MnF_4 and $\text{Mn}(\text{SO}_4)_2 \cdot \text{MnF}_4$ may be prepared by fluorinating manganese powder in a fluidized bed at $600-700^\circ\text{C}$ ^{1,2}. It is a very hygroscopic blue solid slowly decomposing to manganese trifluoride and fluorine at room temperature^{12,13}.

It seems likely that manganese(IV) exists in concentrated sulphuric acid, though there is no definite evidence of solid complexes of manganese(IV) sulphates¹⁴.

(iii) Manganates and peroxomanganates(IV):

A large number of mixed oxides containing Mn^{IV} , often described as manganates(IV) are known. K_2MnO_3 , Rb_2MnO_3 , Na_4MnO_4 , Ba_2MnO_4 , Sr_2MnO_4 and Ba_3MnO_5 have been reported^{15,16} and some of their crystal structures have also been determined¹⁷.

A number of "mixed valence" manganates exists and will be dealt here briefly. $KMnO_2$ and $RbMnO_2$ oxidise readily in air to substances of empirical formulae $MMnO_{2.25}$ ($M=K, Rb$). These may be represented as $M_4Mn_2^{III}Mn_2^{IV}O_9$. Giovanoli et al.⁸ found that the oxidation of fresh $Mn(OH)_2$ in aqueous NaOH with molecular oxygen produced sodium manganese(II, III) manganate(IV), $Na_4Mn_{14}O_{27.9}H_2O$, and determined its structure. A phase $K_2Mn_4O_{7.8-8.0}$ was observed¹⁵ from the reaction of MnO_2 with 2KOH, which is close to the composition observed by Delano¹⁸ for the compound formed from a mixture of $4K_2CO_3 + MnO_2$. Recent studies of the decomposition products of $KMnO_4$ have shown¹⁹ that the water-insoluble products(s) have compositions approximating to " $K_4Mn_7O_{16}$ ", which may indicate that they are related to some of the compounds discussed above.

The peroxomanganate salt, $K_2H_2Mn(O)(O_2)_3$ was obtained as a dark red crystalline solid by reaction of $KMnO_4$ with H_2O_2 in 30% KOH at $-18^\circ C$. The salt decomposed to MnO_2 and O_2 in water, to Mn^{II} and O_2 in acids, and tended to explode on warming²⁰. The occurrence of $K_3HMn(O)(O_2)_3$ and $K_2H_2Mn(O_2)_4$ was also postulated.

(iv) Manganese(IV) complexes of oxygen and nitrogen donor ligands:

The sulphato-compound, $\text{Mn}(\text{SO}_4)_2$ may be considered as the simplest oxygen-donor complex of manganese(IV). It is obtained by oxidising MnSO_4 in hot concentrated H_2SO_4 with permanganate²¹, which hydrolyses to MnO_2 even in dilute sulphuric acid.

Other known complexes of this type are complexes with orthoperiodate, iodate, tellurate and rather surprisingly the oxalate. Solutions of manganese(IV) iodate are best prepared by dissolving freshly prepared manganese dioxide in iodic acid followed by careful oxidation of the manganese (III) formed with periodic acid²². These solutions invariably contain small amounts of manganese(III). Solutions of manganese(IV) periodate are amber or brown but over a period of days in the presence of air they become violet due to the formation of manganese(III). The solutions are stable in sealed quartz vessels, but in glass a red precipitate of the complex $\text{K}_2\text{Mn}(\text{IO}_3)_6$ is formed. Complexes of this type have also been prepared by the action of iodic acid and alkali iodate on MnO_2 suspended in water²³. The complexes are always contaminated with MnO_2 and the recorded magnetic moment of the potassium salt has been corrected for this impurity²⁴.

Complex periodates of manganese(IV) have been prepared by reacting sodium (or, potassium) hypochlorite and periodate with a solution of manganese(II) chloride^{25, 26}. The products have the stoichiometry $\text{Na}_7\text{H}_4\text{Mn}(\text{IO}_6)_3 \cdot 17\text{H}_2\text{O}$ and $\text{K}_7\text{H}_4\text{Mn}(\text{IO}_6)_3 \cdot 8\text{H}_2\text{O}$, and their redox behaviour and magnetic moments indicate that they are complexes of manganese(IV). In solution the complexes slowly decompose to permanganate and iodate. An X-ray structure analysis of the sodium complex shows that the manganese(IV) atom is at the centre of a regular octahedron formed by three bidentate periodate octahedra²⁷.

Reimer and Lister²⁸ also showed that the dark red crystals obtained from MnSO_4 and alkali periodate solutions in strong sulphuric acid solution are $\text{MMnIO}_6 \cdot 1/2\text{H}_2\text{O}$ ($\text{M} = \text{Na}, \text{K}$), not $\text{M}_2\text{Mn}_2\text{I}_2\text{O}_{11}$ as originally reported²⁹. They have $\mu_{\text{eff}} = 4.17$ B.M. (Na), 3.87 B.M.(K), and are remarkably stable, being insoluble in, and not hydrolysed by water.

Alkaline hypochlorite oxidises MnSO_4 mixed with an alkali metal tellurate to dark red complexes $\text{K}_6\text{H}_8\text{Mn}(\text{TeO}_6)_3 \cdot 5\text{H}_2\text{O}$ ($\mu_{\text{eff}} = 3.30$ B.M.) and $\text{Na}_7\text{H}_7\text{Mn}(\text{TeO}_6)_3 \cdot 3\text{H}_2\text{O}$ which are less stable in solution than the periodate analogues^{26, 30}.

Complex iodates, $\text{M}_2\text{Mn}(\text{IO}_3)_6$ ($\text{M} = \text{NH}_4, \text{K}$) and $\text{BaMn}(\text{IO}_3)_6$ are produced as brown-violet solids on boiling MnO_2 , iodic acid, and the metal iodate solutions³¹. The K-salt has $\mu_{\text{eff}} = 3.82$ B.M. and dissolves in water to give a brown

solution, which deposits a brown precipitate (MnO_2); its IR spectrum has been reported³².

A 12-heteropolytungstic acid with manganese(IV) as the central ion, and the corresponding potassium and ammonium salts have been reported³³. Spectral studies have confirmed that the manganese(IV) ion is in a tetrahedral environment. The 9-molybdomanganate(IV) anion $[\text{MnMo}_9\text{O}_{32}]^{6-}$, however, contains a trigonally distorted MnO_6 octahedron and the spectrum of the heteropoly-12-niobomanganate(IV) anion suggests that the trigonal distortion in the niobate is even more pronounced.

Dark olive-green crystals of $\text{K}_2\text{Mn}(\text{C}_2\text{O}_4)_2(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ have been obtained³⁴ by the interaction of potassium permanganate, oxalic acid and potassium oxalate at 0°C . This complex on microscopic examination, showed that it is a mixture of orange and green crystals, possibly due to cis-and trans-isomers. The green variety is only stable at 0°C or lower and in absence of light. It decomposes quickly in water forming tris-(oxolato)-manganate(III).

Other complexes include the red-brown formaldoxime $\text{Na}_2\text{Mn}(\text{CH}_2\text{NO})_6$, obtained on aerial oxidation of manganese(II) solutions containing formaldoxime³⁵; black crystalline $(\text{NH}_4)_2\text{H}_2\text{MnE}_2\text{O}_9$ ($\text{E} = \text{P}, \text{As}$)³⁶ and the yellow-red glycerylmanganates(IV) e.g. $\text{Na}_2\text{Mn}(\text{C}_3\text{H}_5\text{O}_3)_2$, formed on heating freshly precipitated MnO_2 with glycerol and aqueous alkali³⁷.

The complexes of manganese(IV) with biguanides³⁸ are presumably the first cationic complexes of manganese(IV) to be reported, and also the first instance of its affinity for nitrogen donor ligands. The compounds include $[\text{Mn}(\text{Etbig})_2(\text{OH})_2]$, $1.5\text{H}_2\text{O}$ and $[\text{Mn}(\text{Big})_2(\text{OH})_2]$, $2\text{H}_2\text{O}$ and the corresponding salts of the type $[\text{Mn}(\text{BigH})_2(\text{OH})_2]\text{X}_2$ where $\text{X} = \text{NO}_3$, IO_3 , $1/2(\text{SO}_4)$, $1/2(\text{CrO}_4)$, $1/2(\text{HPO}_4)$, $1/2(\text{C}_2\text{O}_4)$ and BF_4 . A similar complex base with hexamethylenedibiguanide has also been reported³⁹. Bright red crystals of $[\text{Mn}(\text{BigH})_2(\text{OH})_2](\text{OH})_2$ are formed on treatment of alkaline KMnO_4 with biguanide, or by oxidising Mn^{II} and biguanidine with alkaline persulphate. Other salts are prepared by metathesis. They have unusually low magnetic moments, in the range of 2.0-2.5 B.M.⁴⁰ and may be dimeric with either oxo- or hydroxy-bridges.

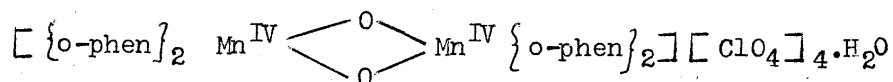
Phthalocyanine is known to form several manganese(IV) complexes with oxide, hydroxide or cyanide ligands in axial positions⁴¹. It is, however, noteworthy that some of these phthalocyanine complexes which were originally formulated as a manganese(IV) complex are now shown to be an oxygen-bridged complex of manganese(III). For example, solutions of MnPc in pyridine undergoes oxidation in presence of air to give a binuclear manganese oxygen-bridged complex. The product from this reaction was originally formulated as a manganese(IV) complex, $\text{Mn}(\text{Pc})(\text{py})\text{O}$ ⁴². But, an X-ray structure determination on this complex reveals that it is a manganese(III) complex, pyPcMn-O-Mn-PcPy ⁴³ containing a linear Mn-O-Mn bridge. When

(MnPcpy)₂O is heated, pyridine is lost and a polymeric oxymanganese(IV) complex is formed, PcMnO⁴¹. Another manganese(IV) phthalocyanine complex also results when manganese(II) formate is treated with 1,3-diiminoisoin-doline. The structure of this complex is not known for certain but it is possibly MnPc(OH)₂⁴¹. It reacts with alcoholic sodium hydroxide to give the trans dioxo complex Na₂[MnPcO₂] whose magnetic behaviour is consistent with a manganese(IV) complex.

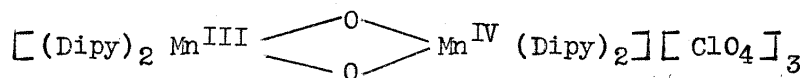
Similar complexes of manganese(IV) with porphyrin have been identified⁴⁴. In air, however, the stable oxidation state is +III and the complexes can be oxidised to the (IV) state. These complexes are of special interest since it is possible that similar complexes of manganese may be involved in certain biological oxidative processes e.g. photosynthesis and metabolism of human red blood cells⁴⁴.

The most important types of complexes are given by 2,2-bipyridyl and 1,10-phenanthroline. Mn(bipy)Cl₄ and [MnO{o-phen}₂][ClO₄]₂·0.5H₂O were obtained by Goodwin and Sylva^{45,46} as black and deep red-brown crystals. The high-spin complex MnCl₄dipy was prepared by the addition of dipyridyl to the brown solution prepared from KMnO₄ and hydrochloric acid. The formation of the second complex apparently involves disproportionation of [MnCl₃(H₂O)phen] in perchloric acid medium. The antiferromagnetic nature of the complex⁴⁷ suggests that it may possibly have a structure

such as

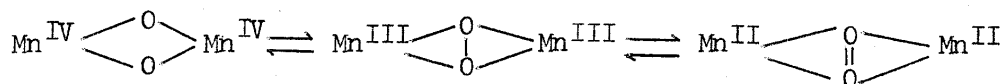


Another complex ion $\left[\text{Mn}_2\text{L}_4\text{O}_2 \right]^{+3}$ where L = 2,2-bipyridyl or 1,10-phenanthroline were initially studied by Nyholm and Turco⁴⁸, and recently by Rafael et al⁴⁹ with perdisulphate and perchlorate anions. In these complexes manganese exhibits a mixed oxidation state of +3 and +4 and they are expected to have similar structure to $\left[\text{Mn}_2(\text{o-phen})_4\text{O}_2 \right] \left[\text{ClO}_4 \right]_4 \cdot \text{H}_2\text{O}$ just shown above. For example, the structure^{48,49} of bipyridyl complex with the perchlorate ion can be shown below



The e.s.r.^{50,51} and magneto-chemical measurements have supported the distinct existence of Mn^{III} and Mn^{IV} states.

Another report⁵² of these e.s.r. spectra indicate presence of a Mn^{II} as impurity. That paper describes other reactions of these compounds and indicates the possibility of such species as shown below in tautomeric form. However, the



structure is not yet well established.

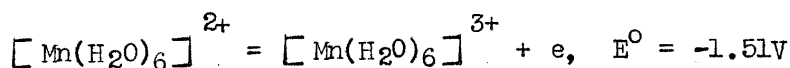
Another series of mixed thiocyanates of manganese(IV) have been prepared⁵³ by the action of liquid bromine on $\text{Mn}(\text{SCN})_2$ and fusing $\text{Mn}(\text{SCN})_2$ with iodine, sulphur, selenium or tellurium. The compounds include $\text{Mn}(\text{SCN})_2\text{X}_2$ (where X = Br, I, 1/2 Se or 1/2 Te) and also $\text{Mn}_5(\text{SCN})_9\text{Br}_{11}$, $\text{Mn}_2(\text{SCN})_3\text{Br}_5 \cdot 3\text{H}_2\text{O}$ etc. A few oxy- and halogene-sulphides e.g. MnSCl_2 , MnOS etc. have been reported⁵⁴.

(v) Halo-complexes:

A simple halo compound is MnF_4 . Barring the pentafluoride KMnF_5 , the halogeno complexes of manganese(IV) are all of the six-coordinate type, $[\text{MnX}_6]^{2-}$ represented by the fluoro⁵⁵ and chloro⁵⁶ salts. Fluoro compounds of the type MMnF_6 (M = Ba, Sr, Ca, or Mg) have been prepared by the direct fluorination of BaMnO_4 , SrMnO_4 or equimolar mixture of manganese (+2) and alkaline earth salts at various temperatures in the range of 150-550°C. Water decomposes the compounds forming dirty yellow to brown products.

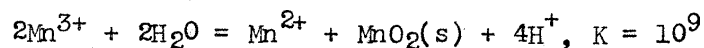
1.3 GENERAL CHEMISTRY OF MANGANESE(III)

The chemistry of Mn^{III} is not extensive. In aqueous solution, it is quite unstable like Co^{III} , being easily reduced to Mn^{II} , as shown by the potential



The practically instantaneous decomposition of manganese (III) compounds is attributed partly to hydrolysis with the

precipitation of hydrated manganese(III) oxide, and partly to disproportionation into Mn^{IV} and Mn^{II} , as the following equilibrium constant shows:



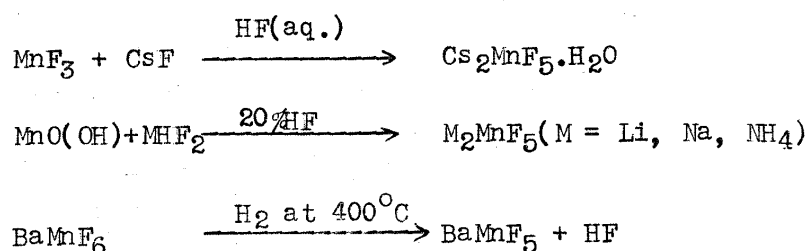
Manganese(III) due, partly, to its weakness as a base, has a fairly strong tendency to form complexes in which the trip-positive state of the element is somewhat stabilised. However, a very limited number of such complexes have been prepared, as the tendency to hydrolysis and dismutation prevails. The majority of the compounds of manganese(III) isolated so far are chelate complexes, and are of the anionic type.

(i) Halides and complex halides: A red purple trifluoride and a very unstable trichloride are known. MnF_3 is prepared⁵⁷ by fluorination of MnF_2 , MnCl_2 and various oxides or best by MnI_2 , or dissolving $\text{Mn}(\text{IO}_3)_2$ in BrF_3 and evaporating at 140°C . Ruby-red crystal of the hydrate $\text{MnF}_3 \cdot 2\text{H}_2\text{O}$ are obtained by dissolving Mn_2O_3 in $\text{HF}(\text{aq})$ or by oxidising $\text{Mn}(\text{II})$ in HF with KMnO_4 or electrolytically. The anhydrous compound is moisture sensitive, but the hydrate is not hydrolysed in water in presence of HF . An adduct $\text{MnF}_3 \cdot 4\text{XeF}_6$ or possibly $\text{MnF}_4 \cdot 4\text{XeF}_6$ is formed on heating Mn with Xe and excess fluorine under pressure⁵⁸. A black solid analysing as MnCl_3 is formed on suspending MnO_2 in dry ether at -78°C , saturating with dry HCl and precipitating with CCl_4 . The action of liquid HCl on $\text{Mn}(\text{Ac})_3$ at -100°C produces brown crystalline MnCl_3 soluble

in organic solvents to form green solution which loses Cl_2 readily above -35°C .

The halogeno-complexes of manganese(III) are mostly of $[\text{MnX}_5]^{+2}$ and $[\text{MnX}_6]^{+3}$ ions. The interaction of potassium permanganate, manganese(II) sulphate, hydrofluoric acid and potassium hydrogen fluoride yields pink crystals of $\text{K}_2[\text{MnF}_5] \cdot \text{H}_2\text{O}$. Water is not co-ordinated, as was thought previously, because the recent crystal structure determination⁵⁷ shows that the ion is 5-coordinated.

The complex of the formula K_3MnF_6 and K_2NaMnF_6 was obtained by fusing $\text{K}_2\text{MnF}_5 \cdot \text{H}_2\text{O}$ with MHF_2 ($\text{M} = \text{K}, \text{Na}$). Cs_2KMnF_6 was synthesised by direct fluorination method. K_3MnF_6 readily loses one fluoride ion in water giving $\text{K}_2\text{MnF}_5 \cdot \text{H}_2\text{O}$. Substitution of potassium by bulky cations like $[\text{M}(\text{NH}_3)_6]^{3+}$ ($\text{M} = \text{Co}, \text{Cr}, \text{Rh}$) have been performed by interaction of Mn(II) in 40% HF and KMnO_4 in presence of cations and NH_4F . I.R. spectra were examined and discussed in terms of distorted octahedral due to Jahn-Teller effect. A few other methods of synthesis are given below:



The brown violet MMnF_4 ($\text{M} = \text{Li}, \text{K}, \text{Rb}$) are formed by hydrogen reduction of corresponding MMnF_5 at $150-250^\circ\text{C}$.

Hexachloro-manganates are only formed by large cations.

$[M(Pc)_3][MnCl_6]$ ($M = Co, Rh$) are prepared by Hatfield et al⁶⁰ by oxidation of $MnSO_4$ in concentrated HCl with $NaClO_3$ in presence of $[M(Pc)_3]Cl_3$. $[Co(en)_3][MnCl_6] \cdot 2H_2O$ may similarly be obtained⁶¹ using $KMnO_4$ as oxidising agent. These compounds show high (Mn-Cl) compared to other $MnCl_6^{3-}$. $[MnCl_5]^{2-}$ is formed by reaction of MnO_2 with acetyl chloride in ether or by saturating MnO_2 suspended in CCl_4 with dry HCl and by extracting with ether. In both cases addition of NEt_4Cl precipitates the dark green pentachloro-manganates(III). Similarly (1,10 phenanthrolineH₂) $MnCl_5$ and (2,2' dipyridylH₂) $MnCl_5$ were prepared. The structure of $[MnCl_5]^{2-}$ is square pyramidal with distortion towards trigonal pyramidal. The green anion $[MnCl_2]^{2-}$ has distorted square pyramidal co-ordination in acetone solution.

A chloro-complex of composition $MnCl_3pyHCl$ has been prepared by interaction of pyridine hydrochloride and MnO_2 dissolved in acetic acid saturated with HCl. It is, however, worthwhile to examine whether the compound $(PyH)MnCl_4$ has tetrahedral configuration or not.

(ii) Oxides, Hydroxides and their complexes: Manganese(III) oxide exists in two forms referred to as $\alpha - Mn_2O_3$ and $\beta - Mn_2O_3$. The α -form has been prepared by the decomposition of commercial MnO_2 in air at $800^\circ C$ or by the decomposition of the nitrate, carbonate, oxalate or chloride hydrate of manganese(II) in air between $600-800^\circ C$. When $\alpha - Mn_2O_3$ is

heated in vacuum from 300° to 500°C, Mn_3O_4 is formed and it appears to be impossible to pump oxygen off the oxide without converting it to Mn_3O_4 .

γ - Mn_2O_3 has been prepared by heating the so-called γ - MnO_2 in vacuum at 500°C for about 78 hr⁶³ or by careful dehydration of γ - $MnOOH$. Prolonged heating of γ - MnO_2 in vacuum at 500°C gives, successively γ - Mn_2O_3 , Mn_3O_4 and finally MnO .

α - Mn_2O_3 is reported to have the distorted body centred cubic symmetry with orthorhombic unit cell ($a = 9.412$, $b = 9.418$, $c = 9.423 \text{ \AA}$). The distortion is probably a consequence of the Jahn-Teller effect of the high spin d^4 manganese(III) ion. The Neel temperature of α - Mn_2O_3 is about 82°K.

On the otherhand, γ - Mn_2O_3 is reported to have a tetragonal unit cell⁶⁴ ($a = 8.1$, $c = 9.4 \text{ \AA}$). The X-ray patterns of γ - Mn_2O_3 and Mn_3O_4 are nearly identical. The magnetic susceptibility of γ - Mn_2O_3 has been measured at 25°, -80° and -185°C and an appraisal of magnetic susceptibility measurements led to the conclusion that the vacant octahedral sites are disordered⁶⁵. When heated in vacuum at 500° for 48 hr, γ - Mn_2O_3 is transformed to α - Mn_2O_3 .

There is no good evidence of $Mn(OH)_3$ but occurrence of two forms of $Mn(O)(OH)$ seems to be well established, α - $Mn(O)(OH)$ and γ - $Mn(O)(OH)$ (groutite)(similar to natural

magnetite). A β -Mn(O)(OH) species was also reported to be formed. The manganite and groutite are both formed by the oxidation of Mn(OH)₂ under carefully controlled condition⁶⁶.

γ -MnOOH has a monoclinic, pseudo orthorhombic cell as shown by neutron and x-ray diffraction. The structure of the mineral groutite, which is designated as α -MnOOH, is almost the same as that of diaspore (α -AlOOH). It has an orthorhombic unit cell but accurate bond lengths are not known.

Although, there is no good evidence for Mn(OH)₃, complex hydroxides of manganese(III) e.g. Na₃Mn(OH)₆ are known⁶⁷.

Scholder and Kyri⁶⁸ found that Mn(OH)₂ in 50% sodium hydroxide is oxidised to NaMnO₂. They also obtained it by heating MnO₂ and Na₂CO₃ in air at 1000°C. LiMnO₂ is formed by fusion in argon atmosphere.

Besides these, a large number of complex oxide have also been reported and a review of those is beyond the scope of this thesis.

1.4 MANGANESE(III) COMPLEXES WITH OXYGEN DONOR LIGANDS:

Mn₂(SO₄)₃ is a well known compound which on dissolving in 70% sulphuric acid and cooling separates as red crystalline compound having composition HMn(SO₄)₂. 2H₂O⁶⁹ as one of the members of alums, M^IMn(SO₄)₂.12H₂O. It has effective magnetic moment value (4.9 B.M.) when M = K, Rb, NH₄. A similar alum has been reported by Mailhe⁴² having formula K₂SeO₄, Mn₂(SeO₄)₃.24H₂O.

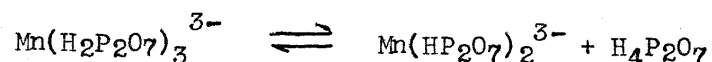
A grey green compound $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ known for a long time, was prepared by the oxidation of manganese(II) salts in H_3PO_4 . The addition of a solution of manganese(II) nitrate in nitric acid, and the reaction of manganese dioxide with phosphoric acid produces this compound. In general, olive green manganese(III) phosphate is precipitated from the purple solutions of manganese(III). $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ is insoluble in water and it is not attacked by dilute nitric or sulphuric acid. With concentrated hydrochloric acid it gives chlorine gas. In concentrated sulphuric acid, $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ gives a violet solution.

The violet solution obtained by dissolving manganese(III) acetate in concentrated phosphoric acid contains an acid phosphate complex of manganese(III). Transport experiments show that its formula may be written as $\text{H}_3[\text{Mn}(\text{PO}_4)_2] \cdot 3\text{H}_2\text{O}$. Only one of its hydrogen may be replaced by a cation to give salts of composition⁷⁰ $\text{MH}_2[\text{Mn}(\text{PO}_4)_2] \cdot 3\text{H}_2\text{O}$ ($\text{M} = \text{NH}_4$ or Na). The complexes $\text{M}[\text{Mn}(\text{HPO}_4)_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ probably have similar structures⁷⁰ to the corresponding diaquo-oxalato and diaquo-malonato manganese(III) complexes.

MnPO_4 is isostructural⁷¹ with FePO_4 . $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ follows a Curic-Weiss law between 93° and 350°K .

Manganese(III) forms stable complexes with pyrophosphate. Hydrated manganese(III) pyrophosphates, $\text{Mn}_4(\text{P}_2\text{O}_7)_3 \cdot \text{H}_2\text{O}$ have been prepared by a number of methods. The violet complex

ion $[\text{Mn}(\text{H}_2\text{P}_2\text{O}_7)_3]^{3-}$ has been widely used for analytical purposes³. The pK of the reaction³



has been found to be 4.25 at 25°C.

The oxidation potential for the reaction



is about 1.15V and the oxidation of many organic and inorganic compounds by manganese(III) pyrophosphate complexes have been effected⁷².

Manganese violet, a finely powdered pigment, has the formula $\text{NH}_4\text{MnP}_2\text{O}_7$. Thermal decomposition of $\text{NH}_4\text{MnP}_2\text{O}_7$ can give either manganese(II) trimetaphosphate or a mixture of manganese(II) tri- and tetra-metaphosphate⁷³.

$\text{NH}_4\text{MnP}_2\text{O}_7$ has a magnetic moment of 4.88 B.M. at 300°K and a θ value of 10° in the temperature range 93-473°K.

Many other manganese(III) pyrophosphate complexes are known such as $\text{NaMnP}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$, $\text{KMnP}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ and $\text{NH}_4\text{MnP}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$.⁷⁴

Manganese(III) perchlorate is not known but by electrolytic oxidation of manganese(II) salts in perchlorate media manganese(III) can be generated under nitrogen. The presence of both hexa-aquo and hydroxypenta-aquo-ion has been indicated by spectrophotometric study⁷⁵.

Manganese(III) iodate, $\text{Mn}(\text{IO}_3)_3$, is reported to be formed as a grey-lilac to brown violet powder on dissolving freshly precipitated manganese dioxide in iodic acid in the presence of manganese(II) iodate¹⁴. The complexes $\text{M}_2\text{Mn}(\text{IO}_3)_5$ ($\text{M} = \text{K}, \text{Rb}, \text{Cs}$ or NH_4) are also reported to be formed by the action of different iodates on the manganese(III) compound $\text{Mn}(\text{OCOCH}_3)_3 \cdot 2\text{H}_2\text{O} \cdot \text{HIO}_3$ ^{22, 23}. Kinetic studies of the disproportionation reaction of manganese(III) in various aqueous iodate systems show that the equilibrium

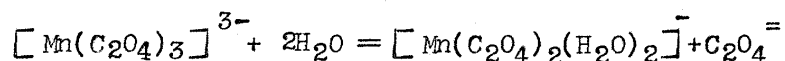
$\text{Mn}(\text{IV}) + \text{Mn}(\text{II}) \rightleftharpoons 2\text{Mn}(\text{III})$ is rapidly established.

Manganese(III) acetate, $\text{Mn}(\text{OCOCH}_3)_3 \cdot 2\text{H}_2\text{O}$ is one of the best known manganese(III) compounds since it is easy to prepare, relatively stable and serves as a convenient starting point for the synthesis of other manganese(III) compounds. It is obtained as red brown crystals by oxidising a solution of manganese(II) acetate in hot glacial acetic acid with permanganate or chlorine.

A manganese(III) formate was also prepared some years ago by the action of formic acid on manganese dioxide and was formulated as $[\text{Mn}_3(\text{OCOH})_6] [\text{OCOH}]_3 \cdot 2\text{H}_2\text{O}$. The compound is decomposed by water and ethanol but is soluble in acetic acid¹⁴.

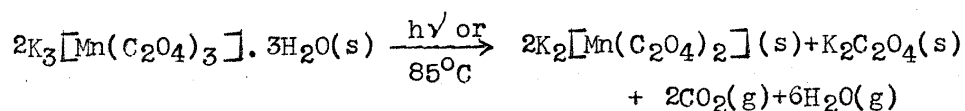
From the kinetic studies of the reaction between permanganate and oxalic acid, the formation of oxalato

complexes was postulated. The manganese(III) complex $K_3Mn(C_2O_4)_3 \cdot 3H_2O$ can be prepared by addition of $KMnO_4$ to a hot solution of oxalic acid followed by addition of K_2CO_3 ^{34, 76}. In absence of air and light this compound can be stored for long periods at 20°C. This compound is readily soluble in water and concentrated solutions are deep reddish brown. However, on dilution or acidification solutions become yellowish brown due to hydrolysis^{34, 76}.



The equilibrium of this reaction can be shifted towards left by the addition of excess oxalate ion. The kinetics of the rate of hydrolysis of $[Mn(C_2O_4)_3]^{3-}$ has been measured⁷⁷.

The $[Mn(C_2O_4)_3]^{3-}$ ion has been studied photochemically and thermo-chemically in both aqueous solutions and in solid states⁷⁸. The stoichiometry of the photo-chemical and thermal dissociation is



The analogous malonate complexes, tris (malonato) and diaquobismalonatomanganate(III) salts were first reported by Meyer and Schramm⁷⁹, but could not be obtained in sufficiently

pure states probably because of their instability towards heat, light and water. Cartledge and co-workers obtained^{34, 80} dark green crystals of $K[Mn(malonate)_2(H_2O)_2] \cdot 2H_2O$ and also the olive green anhydrous salt $K_3[Mn(malonate)_3]$ in absolute methanol. The electronic spectra⁸¹ and magnetic measurement of these complexes have been examined and interpreted.

A number of manganese complexes with polyamino carboxylic acids, trans - 1,2, cyclohexanediaminetetraacetic acid (cyDTA), ethylene diaminetetraacetic acid (EDTA) and hydroxy ethylenediamine tetraacetic acid (HEDTA) have been prepared and characterised⁸²⁻⁸⁴. The deep red compound of manganese (III) with EDTA obtained by reacting a suspension of MnO_2 with free ligand has been formulated as $K[Mn(EDTA-4H)H_2O]$, $1.5H_2O$ on the basis of ion exchange studies and pH titration. X-ray diffraction analysis proved that manganese(III) is seven-coordinated⁸⁵. The oxidation state was determined by iodometric titration⁸². The rate of decomposition of some manganese(III) polyamino carboxylates has been determined. The ruby-red manganese(III) chelates of EDTA formed in faintly acidic solution on oxidising the colourless manganese(II) chelates with lead dioxide or sodium bismuthate is of analytical importance⁸⁶.

One cationic complex species of manganese(III) with 2,2'- bipyridine N, N' - dioxide has been isolated as dark-red crystals of $[Mn(bipyO_2)_3](S_2O_8)_{1.5} \cdot 4H_2O$ and

$[\text{Mn}(\text{bipyO}_2)_3] (\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$. The persulphate was obtained by mixing together $\text{K}_2\text{S}_2\text{O}_8$, MnSO_4 and ligand in water at 80°C . The perchlorate was prepared by metathesis. The conductance and magnetic susceptibility values are consistent with the formulation⁸⁷.

Manganese(III) like many other tripositive ions forms neutral chelates with β -diketones. Tris (acetylacetonato) manganese(III) can be obtained in two forms. One form is brilliantly black and the other is greenish. β -diketonates of manganese(III) has been reviewed by Talkler⁸⁸ and the preparation of $\text{Mn}(\text{acac})_3$ was described by Fernelius and Bryant⁸⁹. However, the compound may be prepared by a variety of methods, viz. by (i) the action of acetylacetone on manganese(III) acetate; (ii) the reaction of an aqueous suspension Mn_2O_3 with the ligand and (iii) by oxidising manganese(II) ions with permanganate in presence of acetylacetone at pH 5-6.5. Molecular weight determination by cryoscopic methods has shown the chelate to be monomeric in both solid and vapour states. $\text{Mn}(\text{acac})_3$ is isomorphous with the aluminium(III), chromium(III) and cobalt(III) analogues.

In aqueous acetylacetone, the tris chelate $\text{Mn}(\text{acac})_3$ dissociates producing the cationic complex⁹⁰ $[\text{Mn}(\text{acac})_2(\text{H}_2\text{O})_2]^+$. The equilibrium constant of this reversible change has been determined spectro-photometrically. The result indicates that

in $\text{Mn}(\text{acac})_3$, the third ligand is appreciably more firmly bound than in the corresponding oxalato or malonato-chelate. The olive-green perchlorate and chloride salts of the cationic chelates were prepared by triturating the tris-complex with the respective acids until a permanent pH of 2 was attained. The salts decompose quickly in water alone with the precipitation of hydrated manganese(III) oxide and reduction to manganese(II) salts at higher acidity. Attempts have been made to prepare compounds of the type MXL_2 (L=acac, X=Cl, Br) in non-aqueous etherial benzene medium by passing HX through $\text{Mn}(\text{acac})_3$ ⁹¹. Spectral analysis shows it to be square pyramidal.

Acetylacetone reacting with MnCl_3 replaces one or two chloride atom(s) as was observed by Tung and Kries.⁹² When MnClL_2 is treated with HCl and pyridine oxide(Q) MnCl_2LQ_2 results. Similarly, reactions with carboxylic acid resulted⁹³ in $\text{MnL}_2(\text{RCO}_2)$. The absorption spectra at I.R.region, visible region and u.v.region revealed the geometry to be distorted octahedral. At higher pH values, the acidic ionisation of the coordinated water molecule in the bis-chelate has also been determined.

The other β -diketonato complexes of manganese(III) include tris-chelate with benzoylacetone and trifluoro-acetylacetone. $\text{Mn}(\text{bzac})_3$ has been obtained as green prism by interaction of benzoylacetone and manganese acetate⁹⁴.