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HIGHER OXIDATION STATE CHEMISTRY OF MANGANESE

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A. INTRODUCTION

In the higher oxidation states, manganese shows some resemblance to technetium and rhenium, and a more formal resemblance to chlorine, especially in the 7+ state Manganese chemistry is dominated by the very stable manganese (II) cation ($3d^5$), which is in marked contrast to technetium and rhenium where there is little evidence for any simple cations.

Apart from a review by Sidgwick over twenty years ago[1] and a recent review of the solution chemistry of manganese (III)[2], no comprehensive collation of the higher oxidation state chemistry of this important metal has appeared

Reference to Table 1 illustrates the multiplicity of oxidation states in which manganese exists, and it is the purpose of this review to describe the chemistry of Mn^{III}, Mn^{IV}, Mn^{V}, Mn^{VI}, and Mn^{VII}.

B MANGANESE (VII)

Manganese (VII) is found only in compounds containing oxide ligands. All Mn^{VII} compounds are very strongly oxidising, and with the exception of the permanganates, are thermally unstable, decomposing, often explosively, at or below room temperature.

TABLE 1

Redox potentials for manganese[3]

Reaction			Redox potential (*v*)
$MnO_2(s) + 4\,H^+(aq) + 2\,e^-$	→	$Mn^{2+}(aq) + 2\,H_2O$	1.239
$MnO_2(s) + 4\,OH^-(aq)$	→	$MnO_4^-(aq) + 2\,H_2O + 3\,e^-$	−0.588
$MnO_4^{3-}(aq)$	→	$MnO_4^{2-}(aq) + e^-$	−0.3
$Mn^{2+}(aq)$	→	$Mn^{3+}(aq) + e^-$	−1.5
$Mn^{2+}(aq) + 4\,H_2O$	→	$MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^-$	−1.51
$MnO_2(s) + 2\,H_2O$	→	$MnO_4^-(aq) + 4\,H^+(aq) + 3\,e^-$	−1.69
$MnO_2(s) + 2\,H_2O$	→	$MnO_4^{2-}(aq) + 4\,H^+(aq) + 2\,e^-$	−2.26
$Mn^{3+}(aq) + 2\,H_2O$	→	$MnO_2(s) + 4\,H^+(aq) + e^-$	−1.0
$Mn(OH)_2(s) + 2OH^-(aq)$	→	$MnO_2(s) + 2\,H_2O + 2\,e^-$	0.03
$Mn(OH)_2(s) + 6\,OH^-(aq)$	→	$MnO_4^-(aq) + 4\,H_2O + 5\,e^-$	−0.34
$MnO_2(s) + 4\,OH^-(aq)$	→	$MnO_4^{3-}(aq) + 2\,H_2O + e^-$	−0.9
$MnO_2(s) + 4\,OH^-(aq)$	→	$MnO_4^{2-}(aq) + 2\,H_2O + 2\,e^-$	−0.603
$Mn(OH)_2(s) + OH^-(aq)$	→	$Mn(OH)_3(s) + e^-$	0.2
$MnO_4^{2-}(aq)$	→	$MnO_4^-(aq) + e^-$	−0.56

(i) Oxide halides

MnO_3X (X = F, Cl) are obtained from the reaction of $KMnO_4$ with the appropriate halosulphonic acid[4,5] or [4,6,7] with anhydrous HX. MnO_3F is also formed[8] from $KMnO_4$ and IF_5. Manganese trioxide fluoride forms dark green crystals, which melt at −38° to a green liquid, which vaporises to a green gas (extrapolated b.p. +60°). Green-violet MnO_3Cl is similar but less stable. MnO_3F decomposes above 0°, often explosively, forming MnO_2, MnF_2, and O_2, and hydrolyses instantly in water to $HMnO_4$ and HF. Microwave spectroscopy[9] shows the structure to be tetrahedral, with Mn—F = 1.724 Å, Mn—O = 1.586 Å, and O—Mn—F = 108.5°. The IR and electronic spectra of both compounds have been reported[5,10].

(ii) Manganese heptoxide

Mn_2O_7 is an oily liquid, $D_4^{20} = 2.396$, which appears red by transmitted, green by reflected light; the vapour is purple. It freezes at 5.9° and can be distilled at low pressure[11]. It separates on standing[11–13] from $KMnO_4$ and cold, concentrated H_2SO_4. Mn_2O_7 decomposes slowly above 0° into MnO_2 and oxygen, at higher temperatures or in the presence of dust or organic matter, it explodes violently, forming Mn_2O_3 and oxygen[11]. It dissolves in water to form permanganic acid of which it is the anhydride, and is soluble without reaction in freons and SO_2Cl_2, and only slowly reacts with CCl_4; such solutions have been proposed as useful strong oxidising agents[5]. The structure is probably $O_3MnOMnO_3$ (cf. Cl_2O_7), a proposal supported by the small dipole moment[11].

(iii) Permanganic acid and the permanganates

A deep purple solution of $HMnO_4$ is obtained by adding the calculated quantity of sulphuric acid to saturated barium permanganate solution[14]. The dilute solution is stable but decomposes on concentration. Dubois[14] obtained a 24.5% solution which froze at −11° to a mass of ice and permanganic acid crystals, but these soon decomposed in diffuse daylight. By fractional vacuum sublimation of these crystals, anhydrous $HMnO_4$ and the dihydrate $HMnO_4 \cdot 2H_2O$ were obtained[15]. $HMnO_4$ forms deep violet rectangular crystals, very soluble in water, and slightly soluble in CCl_3CF_3 and perfluorodecalin. It explodes on contact with most organic materials, and on warming. The dihydrate is generally similar but reacts less violently.

$KMnO_4$ is extensively used as a strong oxidising agent, no attempt has been made to cover this aspect of its chemistry in this review. Dark purple, orthorhombic crystals of $KMnO_4$ are normally obtained from K_2MnO_4 by electrochemical oxidation, or by disproportionation with acids (usually CO_2). Barium permanganate results from passing CO_2 through an aqueous suspension of $BaMnO_4$ (ref. 16), and other permanganates are obtained from this by metathesis with the appropriate sulphate[17–19]. $AgMnO_4$, which crystallises on mixing saturated solutions of $KMnO_4$ and $AgNO_3$, can also be used with the appropriate chloride[20–23]. The sparingly soluble permanganates of NH_4^+, Rb, Cs, can be obtained directly from $KMnO_4$ and M_2SO_4 ($M = NH_4$, Rb, Cs)[24].

The permanganates of K, Rb, Cs, NH_4, Ba, Ag, crystallise anhydrous, but many of the others form hydrates, e.g. Li ($3H_2O$), Na ($2.1H_2O$) (ref. 25), Mg, Cd, Zn, Cu, Ni, (all $6H_2O$), Sr ($3H_2O$), Ca ($4H_2O$). The hydrated alkali and alkaline earth permanganates can be dehydrated without decomposition, but the others decompose[25].

The permanganate ion consists of a manganese atom surrounded by four oxygen atoms at the corners of a regular tetrahedron[26] with Mn–O (ave.) = 1.629 ± 0.008 Å, and O–Mn–O = 109.4 ± 0.7°. The electronic spectrum is discussed in Sect. E and the vibrational frequencies are recorded in Table 2. The IR spectra of a number of individual permanganates have been recorded, and discussed in terms of the site symmetry of the anion[25].

The thermal decomposition of $KMnO_4$ has been the subject of a great deal of work, but the nature of some of the products is still uncertain. The water-soluble decomposition product is K_2MnO_4, but the nature of the water-insoluble part has been disputed. Thermogravimetric and differential thermal analyses have been used to study the decomposition

TABLE 2

Vibrational spectra of the tetraoxoanions

	Frequency (cm^{-1})				
	$\nu_1(A_1)$	$\nu_2(E)$	$\nu_3(F_2)$	$\nu_4(F_2)$	Ref.
MnO_4^-	838	355	921	429	29
MnO_4^{2-}	810		862	328	30
MnO_4^{3-}	836		770	348	30

of the K and Rb salts[27,28]. Herbstein et al [28] propose the idealised decomposition equation

$$10\ KMnO_4 = 2\ 6\ K_2MnO_4 + (2\ 3\ K_2O,\ 7\ 3\ MnO_{2\ 05}) + 6\ O_2$$

at 250° in air The phase in parentheses is of unknown structure but may be related to the Mn^{IV}–Mn^{III} complex oxides prepared by Scholder and Protzer[51].

The structural parameters of some individual permanganates are given in Table 3

TABLE 3

Crystal structures of some permanganates

Compound	Type	Dimensions (A)			Ref
		a	*b*	*c*	
$KMnO_4$	Orthorhombic	9 105	5 720	7 425	26
$RbMnO_4$	Orthorhombic	7 65	9 55	5 74	31
$CsMnO_4$	Orthorhombic	7 96	10 06	5 80	31
NH_4MnO_4	Orthorhombic	7 58	9 33	5 78	32
$LiMnO_4\ 3H_2O$	Hexagonal	7 73		5 39	17,33
$Ba(MnO_4)_2$	Orthorhombic	14 71	11 86	7 39	34
$Sr(MnO_4)_2\ 3H_2O$	Cubic	9 61			22
$AgMnO_4$	Monoclinic	5 66	8 27	7 13	35
$Mg(MnO_4)_2\ 6H_2O$	Orthorhombic	7 81	13 56	5 28	31
$Zn(MnO_4)_2\ 6H_2O$	Orthorhombic	7 81	13 56	5 23	31
$Ni(MnO_4)_2\ 6H_2O$	Orthorhombic	7 75	13 45	5 20	31
$Cd(MnO_4)_2\ 6H_2O$	Orthorhombic	8 04	13 91	5 34	19

(iv) MnO_3^+ or O_3MnOSO_3H

The green solution formed on dissolving $KMnO_4$ in concentrated H_2SO_4 contains MnO_3^+ or O_3MnOSO_3H, or possibly both, depending upon concentration, and not $(MnO_3)_2SO_4$ as was assumed in the older literature[36,37] Cryoscopic, conductimetric, and electronic spectral studies were said to be consistent with the presence of a planar MnO_3^+ cation, formed by the reaction[36]

$$KMnO_4 + 3\ H_2SO_4 = K^+ + H_3O^+ + MnO_3^+ + 3\ HSO_4^-$$

In 100% sulphuric acid O_3MnOSO_3H is said to be present[37]

C MANGANESE (VI)

Mn^{VI} is confined to salts of the manganate (VI) ion, and MnO_2Cl_2 Mn^{VI} is stable only in basic solution, its most characteristic reaction being to disproportionate in acidic or neutral solution.

(i) Manganese dioxide dichloride

MnO_2Cl_2 is the only oxide halide of Mn^{VI} known, although presumably MnO_2F_2

could be prepared. Briggs[5] obtained MnO_2Cl_2 as a very unstable brown liquid, by reduction of $KMnO_4$ in HSO_3Cl with SO_2 at low temperatures. It begins to decompose at $-30°$, and hydrolyses to MnO_4^-, MnO_2, and Cl^-

(ii) "Manganese trioxide"

The early claims[38,39] to have prepared MnO_3 have not been substantiated by later work. Lankshear[40] showed that the red solid claimed as MnO_3 is really a mixture of $HMnO_4$ and some MnO_2, and it has since been demonstrated that Mn_2O_7 loses oxygen to form MnO_2 directly, with no evidence for any intermediate oxide[12]. Despite this, reports of a compound MnO_3 still appear in textbooks from time to time[7]

(iii) Manganates (VI)

The parent acid is unknown, acidification of manganate (VI) solutions resulting in disproportionation. Manganates (VI) are obtained by fusing MnO_2 with alkali metal hydroxides under oxidising conditions or by electrolytic oxidation of alkaline manganese (II) solutions[41]. Pure K_2MnO_4 was obtained by boiling $KMnO_4$ with concentrated KOH solution, and various hydrates of sodium manganate (VI) can be prepared similarly[42]. Alkali metal manganates (VI) are also formed by thermal decomposition of the corresponding permanganate[43], or by heating MnO_2 with the metal superoxide[44]. Barium manganate precipitates[16] on boiling $KMnO_4$ with a saturated aqueous solution of $Ba(NO_3)_2$ and $Ba(OH)_2$. Lithium manganate does not appear to have been reported, MnO_2 does not dissolve readily in fused LiOH, and $LiMnO_4$ decomposes to Li_2O and MnO_2 on heating[43]. A number of others manganates (VI) were reported in the older literature (see ref. 45), but these must be regarded as doubtful until reinvestigated.

Alkali metal manganates (VI) form deep green crystals, which often appear darker due to a superficial layer of permanganate. They dissolve in aqueous alkali to form green solutions, but in acidic, neutral, or even weakly basic solutions, they disproportionate

$$3\ M_2MnO_4 + 2\ H_2O = 2\ MMnO_4 + MnO_2 + 4\ MOH \quad (M = \text{alkali metal})$$

Thermal decomposition produces manganates (V) and other products, e.g., at 620° in nitrogen[28]

$$10\ K_2MnO = 5.7\ K_3MnO_4 + 0.5(2.9\ K_2O, 8.6\ MnO_{2.1}) + 3.40\ O_2$$

The electronic spectrum is discussed later (Section E) and the IR frequencies are shown in Table 2. $K_2MnO_4(d^1)$ has a magnetic moment of 1.73 B.M., and follows the Curie–Weiss law with $\theta \simeq 0°$ (ref. 46). The structure of K_2MnO_4 shows the MnO_4^{2-} ion to be tetrahedral with $Mn{-}O = 1.659$ Å, and $O{-}Mn{-}O = 109.5 \pm 0.7°$, which means that the Mn–O bond length is 0.03 Å longer than in the permanganate[47], in agreement with the predictions of molecular orbital theory. The structural parameters of the alkali manganates are reported in Table 4.

TABLE 4

Manganate (VI) crystal structures

Compound	Type	Dimensions (A)			Ref
		a	*b*	*c*	
K_2MnO_4	Orthorhombic	7 667	5 895	10 359	47
Rb_2MnO_4	Orthorhombic	7 997	10 670	6 044	44
Cs_2MnO_4	Orthorhombic	8 360	11 052	6 247	44

D MANGANESE (V)

Manganese (V), the rarest of the higher oxidation states, occurs in the manganate (V) anion, and in $MnOCl_3$ It is even more prone to disproportionation than manganese (VI), existing only in strongly basic solution.

(i) Manganese oxide trichloride

This is the only oxide halide, although as with MnO_2Cl_2 the fluorine analogue should be capable of existence $MnOCl_3$ is a mint-green liquid, with a deep yellow vapour, formed by reducing $KMnO_4$ dissolved in HSO_3Cl with $CHCl_3$, or better with sucrose[5]. The pure liquid decomposes above 0° to $MnCl_3$, and hydrolyses readily, MnO_4^{3-} being produced only if sufficient alkali is present to prevent its decomposition.

(ii) Manganates (V)

These were characterised by Lux[48] as recently as 1946, although other workers had previously obtained blue oxo-species of manganese without recognising their true nature Deep blue sodium manganate (V) is obtained[48-50] on reduction of $KMnO_4$ in concentrated aqueous NaOH, with Na_2SO_3, KI, or HCOONa, or by oxidation of manganese (II) or MnO_2 in an alkaline melt[48,49] A simple method for obtaining the Na, K, Rb compounds has recently been described[51] Pure anhydrous alkali manganates (V) (including Li_3MnO_4) are formed[50] by heating the permanganate with MOH

Lux[48] obtained a deep blue hydrate which he formulated as Na_3MnO_4 $10H_2O$, but Scholder et al.[50] suggested this was Na_3MnO_4 $\frac{1}{2}NaOH$ $12H_2O$, and found that on recrystallisation from cold concentrated NaOH, Na_3MnO_4 $7H_2O$ is produced A compound of limiting composition $Na_3MnO_4.0$ $25NaOH.12H_2O$, analogous to the corresponding vanadate, phosphate, and arsenate has been obtained[52]. Klemm showed that $Na_3MnO_4.10H_2O$ contains Mn^V and not Mn^{VI} and Mn^{IV} by magnetic analysis[53]

$Ba_3(MnO_4)_2$ (refs 53, 54), $Sr_2(MnO_4)(OH)$ (refs 54, 55), $Ba_5(MnO_4)_3Cl$ (ref. 56), and $Ba_5(MnO_4)_3(OH)$ (ref 53) have been reported.

Electronic (Sect E) and vibrational spectra (Table 2), have been reported, but no structural data are available for the MnO_4^{3-} ion. The magnetic moments of a number of Mn^V compounds have been reported by Klemm et al [57] as Na_3MnO_4 $10H_2O$ 2.8B M,

$Ba_5(MnO_4)_3(OH)$ 2 83B M., $Ba_3(MnO_4)_2$ 2 83B M , K_3MnO_4 2.68B M.*, Rb_3MnO_4 2 61B M * and Cs_3MnO_4 2 57B M *

In solution, manganates (V) disproportionate into MnO_4^{2-} and MnO_2, unless a large excess of alkali is present K_3MnO_4 is much more stable thermally than either $KMnO_4$ or K_2MnO_4, in dry air it appears to be stable up to at least 900°, but is decomposed rapidly by moisture[28]

A compound Na_5MnO_5 was reported in Scholder's review[54] but no details were given

E ELECTRONIC SPECTRA AND STRUCTURE OF THE TETRAOXOANIONS

The tetraoxoanions of manganese have provided fruitful discussion for workers interested in the energy levels and electronic spectra and structures of these tetrahedral $(XO_4)^{n-}$ species, which are characterised by strong visible and near-ultraviolet absorptions There have been many interpretations, and these frequently differ from one another

Wolfsberg and Helmholtz[58] (W–H) carried out some semi-empirical calculations on the permanganate ion, according to the molecular orbital scheme, and their most surprising result was the order of the first unfilled M O.'s ($3t_2 < 2e$) which is not in agreement with crystal field (C F) theory Subsequently, Ballhausen and Liehr[59] (B–L) proposed a different scheme which is in agreement with C F. theory and is justified by intensity calculations The latter proposals were supported by the studies of Carrington and coworkers[60–63], who showed on the basis of ESR measurements that the unpaired electron in the MnO_4^{2-} ion (d^1), occupied an e level More recently, Fenske and Sweeney[64] concluded that if the empirical parameters of the W–H calculations are substantially altered, any order of levels can be obtained, and, consequently, any transition assignment justified A calculation of Viste and Gray[65] (V–G) has confirmed the B–L order of levels, but with a different transition assignment.

Olcari et al.[66] have carried out an S.C.F –M O –L C A O. calculation for the MnO_4^- ion, and confirmed the order of levels previously assigned by B–L A new spectral assignment was presented, attributing to each observed absorption band two electronic transitions occurring between one of the occupied M O.'s ($t_1, 2t_2, 1t_2$) and the two lowest empty M O 's ($2e, 3t_2$). These workers subsequently extended their calculations to the MnO_4^{2-} and MnO_4^{3-} ions[67]

The spectra of the three ions are shown in Fig 1, and Table 5 contains the spectral assignments proposed by various workers.

F MANGANESE (IV)

Mn^{IV} has a more extensive chemistry than the higher oxidation states, but, in general, the compounds are not particularly stable The apparent exception, MnO_2, owes its "stability" to its insolubility; other Mn^{IV} compounds are readily hydrolysed and reduced There are few simple compounds, the majority of manganese (IV) compounds containing the element in a complex anion.

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*Low values may be due to the presence of some manganate (VI)

TABLE 5

Spectral assignments of tetraoxoanions

Anion	Band maxima (cm^{-1})	Wolfsberg–Helmholtz[58]	Ballhausen–Liehr[59]	Carrington–Jorgensen[63]	Carrington–Symons[60]	Viste–Gray[65]	Kingsley et al.[68]	Orgel[69]	Oleari et al.[66,67]
$[MnO_4]^-$		$t_1 \rightarrow 3t_2$	$t_1 \rightarrow 2e$	$t_1 \rightarrow 2e$		$t_1 \rightarrow 2e$			$t_1 \rightarrow 3t_2$
				$2t_2 \rightarrow 2e$					$t_1 \rightarrow 2e$
		$2t_2 \rightarrow 3t_2$	$t_1 \rightarrow 3t_2$	$t_1 \rightarrow 3t_2$					$2t_2 \rightarrow 2e$
				$2t_2 \rightarrow 3t_2$					$2t_2 \rightarrow 3t_2$
									$1t_2 \rightarrow 2e$
									$1t_2 \rightarrow 3t_2$
									$1e \rightarrow 3t_2$
$[MnO_4]^{2-}$	(12,000)				$2e \rightarrow 3t_2(^2T_2)$				$2e \rightarrow 3t_2(^2T_2)$
	16,580			$2e \rightarrow 3t_2(?)$	$t_1 \rightarrow 2e(^2T_2)$	$2e \rightarrow 3t_2$			$t_1 \rightarrow 2e(^2T_1)$
	22,830			$t_1 \rightarrow 2e$	$t_1 \rightarrow 2e(^2T_1)$	$t_1 \rightarrow 2e$			$t_1 \rightarrow 2e(^2T_1)$
	28,170			$2t_1 \rightarrow 2e(?)$	$t_1 \rightarrow 3t_2(^2T_2)$	$2t_2 \rightarrow 2e$			$2t_2 \rightarrow 2e(^2T_1)$
									$t_1 \rightarrow 3t_2(^2T_2)$
									$2t_2 \rightarrow 2e(2T_2)$
	33,200				$t_1 \rightarrow 3t_2(^2T_1)$				$2t_2 \rightarrow 3t_2(^2T_2)$
									$t_1 \rightarrow 3t_2(^2T_1)$
$[MnO_4]^{3-}$	11,000					$2e \rightarrow 3t_2(^3T_2)$	$2e \rightarrow 3t_2(^3T_2)$	$2e \rightarrow 3t_2(^3T_2)$	$2e \rightarrow 3t_2(^3T_2)$
	14,810			$2e \rightarrow 3t_2$	$t_1 \rightarrow 2e(^3T_1)$	$2e \rightarrow 3t_2(^3T_1)$	$t_1 \rightarrow 2e(^3T_1)$	$2e \rightarrow 3t_2(^3T_1)$	$2e \rightarrow 3t_2(^3T_1)$
	(16,700)						$2e \rightarrow 3t_2(^3T_1)$		
	30,800			$t_1 \rightarrow 2e$	$t_1 \rightarrow 3t_2(^3T_1)$	$t_1 \rightarrow 2e(^3T_1)$	$t_1 \rightarrow 3T_2(^3T_1)$	$t_1 \rightarrow 2e(^3T_1)$	$t_1 \rightarrow 3t_2(^3T_1)$

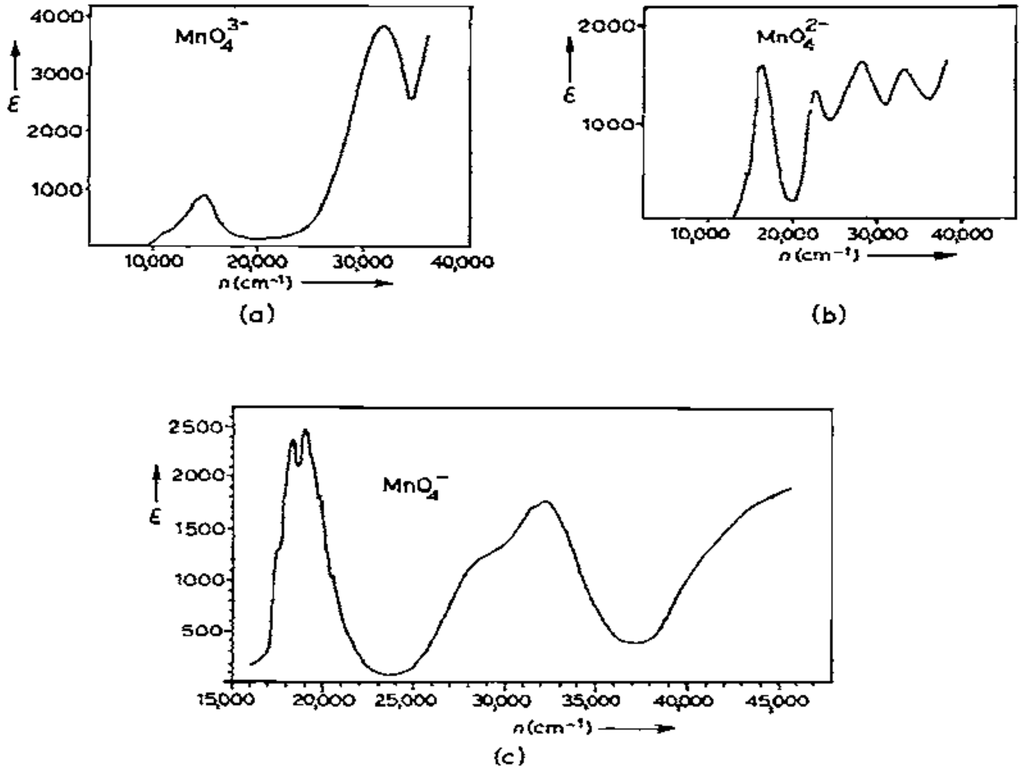


Fig 1 Electronic spectra of the tetraoxoanions (a), (b), Oleari et al [67], (c) G van den Boef, H J van der Beek and T. Braaf *Rec. Trav. Chim.*, 77 (1958) 1064 Reproduced by permission

(i) Halides

The only halide is the very reactive MnF_4, there is little evidence for $MnCl_4$ despite a number of claims in the older literature[70]. Sharpe and Woolf[71] were unable to isolate MnF_4 from the reaction of $Mn(IO_3)_2$ with BrF_3, although the solution obtained gave Mn^{IV} fluorocomplexes upon addition of KF. The blue, very hygroscopic, tetrafluoride is produced by fluorination of manganese powder in a fluidised bed[72] or of MnF_2, MnF_3, $LiMnF_5$, or Li_2MnF_6, at 550° (ref 73) It obeys the Curie–Weiss law with $\mu_{eff} = 3.48$ B.M. Fluorine is lost on standing, and it hydrolyses instantly in water. A small amount of red solid is produced from ClF and manganese powder in a fluidised bed[72], this may be a mixed halide, e g. $MnClF_3$. There appear to be no oxide halides known

(ii) Complex halides

Hexahalomanganates (IV), $MnX_6{}^{2-}$ (X = Cl, F), and pentafluoromanganates (IV), MnF_5^-, are known All attempts to prepare bromine analogues have failed.

Hexafluoromanganates (IV) are obtained by four basic methods.

(*a*) Direct fluorination of an intimate mixture of $MnSO_4$, $MnCl_2$, or NH_4MnF_3, and the chloride, sulphate, or carbonate of the desired cation.

(*b*) Fluorination of the corresponding permanganate, manganate (VI), or manganate (IV)

(*c*) Electrolytic oxidation of MnF_2 in 40% HF in the presence of the metal fluoride.

(*d*) Fluorination of the starting materials in (*a*) or (*b*) with BrF_3 (ref. 89).

Some properties of these compounds are reported in Table 6, and their structures in Table 7.

$(NO)_2MnF_6$ and the heavy metal hexafluoromanganates are instantly decomposed by water, the alkali metal compounds hydrolyse only slowly in the cold. The MnF_6^{2-} ion (d^3) is a regular octahedron[77,87], with Mn–F = 1.72–1.75 Å, and exhibits ν(Mn–F) at 625 cm^{-1} (ref. 81). Asprey et al.[97a] have recently studied the IR and Raman spectra of some hexafluoromanganates (IV).

The brick-red pentafluoromanganates (IV), formed on fluorination of $MMnF_3$ (M = K,Rb,Cs) at 450–500°, or of LiF + MnF_2 at 350°, are instantly decomposed by water[73,74]. They have magnetic moments in the range 3.7–3.9 B.M., and the Mn–F stretching frequency in $KMnF_5$ is at 617 cm^{-1} (ref. 81). Although the structures have not been determined, it seems probable that they contain condensed MnF_6 units.

The very dark red hexachloromanganates (IV) are prepared[88,90] by adding saturated alkali metal chloride solution to calcium permanganate in 40% hydrochloric acid at 0°. The potassium salt is also obtained from $KMnO_4$ and saturated aqueous HCl (ref. 88), or by the reaction of potassium acetate and manganese (III) acetate in the presence of a large excess of acetyl chloride[91]. They readily lose chlorine on standing. K_2MnCl_6 has μ_{eff} = 3.9B.M.[92] and ν(Mn–Cl) = 358 cm^{-1} (ref. 93).

The diffuse reflectance spectra of the hexafluoromanganates have been studied by a number of workers[94–96]. Allen et al.[94] found five bands in the spectrum of K_2MnF_6 at 14.0 kK ($^4A_{2g} \rightarrow {}^2E_g, {}^2T_{1g}, t_{2g}^3$) 29.3 kK ($^4A_{2g} \rightarrow {}^2T_{2g}, t_{2g}^3$), 22.2 kK ($^4A_{2g} \rightarrow {}^2T_{2g}, t_{2g}2e_g$), 28.6 kK ($^4A_{2g} \rightarrow {}^2T_{1g}, t_{2g}2e_g$), 38.8 kK ($\pi \rightarrow t_{2g}$). Novotny and Sturgeon[95] reported the spectra of the K, Rb, Cs and Ba compounds, and examined the effect of the method of preparation on the spectrum of the K salt. Moews[88] reported bands at 15.4, 16.6, 27.4, 33.3 kK for K_2MnCl_6, but this was disputed by other workers, who reported absorption at 17.8, 25.0, 43.5 kK, which they assigned as $^4t_2 \rightarrow {}^4t_5$, $^4t_2 \rightarrow {}^4t_4$, and charge transfer, respectively[97].

(iii) Manganese dioxide

There is an extensive literature on MnO_2, only a very small amount of which will be mentioned here[98–110]. The common form, β-MnO_2 (pyrolusite), is made by heating manganese (II) nitrate at 150–160°, extracting with water, drying at 200°, and repeatedly extracting with boiling nitric acid to remove lower oxides[105]. Several modifications of the basic method have been described[98] and most of the other forms of MnO_2 are said[102] to change into the β variety on heating in air at 400°. It has an ideal composition $MnO_{2.00}$, with the rutile structure a = 4.38, c = 2.86 Å, but it is usually oxygen deficient[98]. Reducing agents attack it readily in acid solution, alkalis cause disproportionation, whilst concentrated H_2SO_4 at 110° forms Mn^{III} sulphate and oxygen.

TABLE 6

Hexafluoromanganates (IV)

Compound	Preparation*	Colour	Magnetic moment (B.M.)	Ref
Li_2MnF_6	a	Yellow	3.85	74
Na_2MnF_6	a, c	Yellow		75
K_2MnF_6	a, c, d	Yellow	3.86	71, 75, 79, 82–84
Rb_2MnF_6	a, c	Yellow		75, 79
Cs_2MnF_6	a, c	Yellow		75, 79
$(NH_4)_2MnF_6$	c	Yellow		85
$CaMnF_6$	a	Yellow	3.87	78, 79, 87
$SrMnF_6$	a, b	Yellow	3.82	78–80
$BaMnF_6$	a, b	Yellow	3.90	78–80
$MgMnF_6$	a	Orange-yellow	3.9	78, 79, 87
$(NO)_2MnF_6$	d	Yellow		86
$CdMnF_6$	a	Yellow	3.78	87
$NiMnF_6$	a	Ochre-yellow	5.38	87
$ZnMnF_6$	a	Orange-yellow		87
$HgMnF_6$	a	Orange		87
$CuMnF_6$	a	Bright red	4.43	87
$AgMnF_6$	b	Dark brown	4.43	87

*Letters refer to methods a, b, c and d discussed in text

TABLE 7

Structural parameters of Mn^{IV} complex halides

Compound	Type		Parameters (Å)		Ref
			a	*c*	
Li_2MnF_6	Na_2SiF_6,	hexagonal	8.42	4.59	74
Na_2MnF_6	Na_2SiF_6,	hexagonal	9.03	5.13	75, 76
K_2MnF_6	"Rb_2MnF_6",	hexagonal	5.67	9.35	77
		trigonal	5.71	4.65	77
	K_2PtCl_6,	cubic	8.28		77
Rb_2MnF_6	"Rb_2MnF_6",	hexagonal	5.86	9.50	77
	K_2PtCl_6,	cubic	8.40		77
Cs_2MnF_6	K_2PtCl_6,	cubic	8.92		77
$(NH_4)_2MnF_6$	"Rb_2MnF_6",	hexagonal	5.91	9.55	85
$MgMnF_6$	$LiSbF_6$,	hexagonal	5.01	13.17	78, 79, 87
$CaMnF_6$	$LiSbF_6$,	hexagonal	5.21	14.17	78, 79, 87
$SrMnF_6$	$BaGeF_6$,	hexagonal	7.02	6.78	78, 79
$BaMnF_6$	$BaGeF_6$,	hexagonal	7.35	7.09	78, 79, 80
$CdMnF_6$	$LiSbF_6$,	hexagonal	5.08	14.00	87
$NiMnF_6$	VF_3,	hexagonal	4.91	13.16	87
$ZnMnF_6$	VF_3,	hexagonal	4.96	13.29	87
$HgMnF_6$	$LiSbF_6$,	hexagonal	5.08	14.12	87
K_2MnCl_6	K_2PtCl_6,	cubic	9.6445 ± 0.002		88
Rb_2MnCl_6	K_2PtCl_6,	cubic	9.82 ± 0.02		88
Cs_2MnCl_6	K_2PtCl_6,	cubic	10.17 ± 0.02		88
$(NH_4)_2MnCl_6$	K_2PtCl_6,	cubic	9.80 ± 0.02		88
$(NMe_4)_2MnCl_6$	K_2PtCl_6,	cubic	12.70 ± 0.02		88

A large number of varieties of MnO_2 have been reported, but despite a great deal of work, the nature of some of these is still in doubt. Many of them contain Mn^{III} ions, water, or other metal ions, and exist over a range of compositions. A brief discussion of some of these forms is given below (see refs. 102–104 for references to earlier work).

Glemser and coworkers[102–104] described six other varieties, α, γ, δ, ϵ, η, and the mineral ramsdellite. The latter is orthorhombic $a = 4.53$, $b = 9.27$, $c = 2.87$ Å. α-MnO_2 is related to the mineral cryptomelane, and always contains other large cations, it has been formulated as $A_xMn_8O_{16}$ (A = K, Ba, etc, $x < 1$)[101, 102]. All forms lose oxygen on heating, eventually forming Mn_2O_3. It has since been shown that δ-MnO_2 is a ternary oxide (see below). The phase $Mn(OH)_2 \cdot 2MnO_2$ is formed[106] upon wet oxidation of γ-Mn_2O_3 above $MnO_{1.4}$.

(iv) "Mixed-valence oxides"

The manganese–oxygen system, especially in the presence of other cations, and of water, is very complex, and a number of compounds have been discovered in addition to the simple oxides of Mn^{II}, Mn^{III}, and Mn^{IV}. The older literature contains several reports of oxides containing manganese in more than one oxidation state[45], many of these must be regarded as very doubtful and will not be discussed further. Compounds that do fit into the category of mixed-valence oxides are Mn_3O_4, Mn_5O_8, and the recently discovered $Mn_7O_{12} \cdot 6H_2O$, and $Mn_7O_{13} \cdot 5H_2O$.

α-Mn_3O_4 occurs as the mineral hausmannite, and is the product[98] of heating any oxide, and many manganese salts, in air at 1000°. The purple-red powder has a distorted spinel structure (distortion is caused by the d^4 Mn^{III} ions), $a = 8.13$ Å, $c/a = 1.16$. It is a normal spinel $Mn^{II}Mn_2^{III}O_4$ (ref. 111) not $Mn_2^{II}Mn^{IV}O_4$ as reported in some of the earlier work. It changes reversibly into a cubic modification β-Mn_3O_4 above 1170°. Concentrated H_2SO_4 produces Mn^{II} and Mn^{III} sulphates, and HNO_3 causes disproportionation

$$Mn_3O_4 + 4\ HNO_3 = 2\ Mn(NO_3)_2 + MnO_2 + 2\ H_2O$$

Mn_5O_8 is produced on oxidation of Mn_3O_4 in a nitrogen/oxygen stream at 250–500°, or by heating β-$MnO(OH)$ in air below 500° (ref. 113). It is a black powder, which loses oxygen above 550° to form α-Mn_2O_3. The structure determination supports the formulation $Mn_2^{II}Mn_3^{IV}O_8$, there is a distorted octahedral arrangement of oxygen atoms around Mn^{IV}, and a distorted trigonal prism around Mn^{II} (ref. 114).

Giovanoli et al.[108,109] found that $Na_4Mn_{14}O_{27} \cdot 9H_2O$, reacts with dilute nitric acid to produce manganese (III) manganate (IV) $Mn_7O_{13} \cdot 5H_2O$ (hexagonal $a = 2.84$, $c = 7.27$ Å), and with $Mn(NO_3)_2$ solution to form manganese (II) manganate (IV) $Mn_7O_{12} \cdot 6H_2O$. Prolonged digestion of $Mn_7O_{13} \cdot 5H_2O$ with nitric acid produces γ-MnO_2, upon heating $Mn_7O_{13} \cdot 5H_2O$, the first product is γ-MnO_2 and finally a distorted β-MnO_2 results. δ-MnO_2 seems to be related to these manganate (IV) species with some of the Mn^{III} replaced by Mn^{IV}, it also contains a fairly large amount of alkali metal ions[107,109]. The structural relationships of these compounds, and the reduction of $Mn_7O_{13} \cdot 5H_2O$ to γ-$MnO(OH)$ with cinnamyl alcohol, have been described[110].

(v) Manganates (IV)

A large number of mixed oxides containing Mn^{IV}, often described as manganates (IV) are known, but will not be described here.

On heating a mixture of MnO_2 + 2KOH, Scholder and Protzer[51] obtained a mixture of K_3MnO_4, $KMnO_2$, and K_2MnO_3. At 200° this contained 75 mole % of K_2MnO_3, whilst at 550° only 18 mole % was present. Similar results were obtained with MnO_2 + 2RbOH. Some Mn^{IV} always disproportionates and the authors report that the isolation of pure K_2MnO_3 is not possible.

Scholder[54] reported the compounds Na_4MnO_4, Ba_2MnO_4, Sr_2MnO_4, and Li_2MnO_3, but no details were given. The crystal structure of Ba_3MnO_5 was determined by Mansmann[115], who found it to be isostructural with Cs_3CoCl_5. $MMnO_3$ (M = Sr, Ba) and substances formulated $CaO.xMnO_2$ ($x = \frac{1}{2}$, 1, 2, 3, 5) have been reported[45].

A number of "mixed valence" manganates exist, and will be dealt with here for convenience. $KMnO_2$ and $RbMnO_2$ oxidise readily in air to substances of empirical formulae $MMnO_{2.25}$ (M = Rb, K). These were formulated[51] as $M_4Mn_2^{III}Mn_2^{IV}O_9$. Giovanoli et al.[108] found that the oxidation of fresh $Mn(OH)_2$ in aqueous NaOH with molecular oxygen produced sodium manganese (II, III) manganate (IV), $Na_4Mn_{14}O_{27}\cdot 9H_2O$, and determined its structure. It has a double-layer structure resembling chalcophanite. A phase $K_2Mn_4O_{7.8-8.0}$ was observed[51] from the reaction of MnO_2 with 2KOH, which is close to the composition observed by Delano[116] for the compound formed from a mixture of $4K_2CO_3 + MnO_2$. Recent studies of the decomposition products of $KMnO_4$ have shown[28] that the water-insoluble product(s) have compositions approximating to "$K_4Mn_7O_{16}$", which may indicate that they are related to some of the compounds discussed above. Further work is required, however, before any conclusion can be reached.

(vi) Peroxomanganates (IV)

By reaction of $KMnO_4$ with H_2O_2 in 30% KOH at −18°, Scholder obtained $K_2H_2Mn(O)(O_2)_3$ as a dark red crystalline solid, which decomposed to MnO_2 and O_2 in water, to Mn^{II} and O_2 in acids, and tended to explode on warming[117]. The occurrence of $K_3H\ Mn(O)(O_2)_3$ and $K_2H_2Mn(O_2)_4$ was also postulated.

(vii) Manganese (IV) compounds of oxygen donor ligands

The only simple compound appears to be the black crystalline $Mn(SO_4)_2$ obtained on oxidising $MnSO_4$ in hot concentrated H_2SO_4 with permanganate[119], which hydrolyses to MnO_2 even in dilute sulphuric acid. Anodic dissolution of manganese in 18–22 *N* sulphuric acid produces[118] a dark-coloured solution containing Mn^{IV}.

Complexes with orthoperiodate, iodate, tellurate, and rather surprisingly, oxalate, are probably the best known. Reimer and Lister[120] showed that the dark red crystals obtained from $MnSO_4$ and alkali periodate solutions, are $MMnIO_6\cdot\frac{1}{2}H_2O$ (M = Na, K), not $M_2Mn_2I_2O_{11}$ as originally reported[121]. They have μ_{eff} = 4.17 B.M. (Na), 3.87 B.M. (K), and are remarkably stable, being insoluble in, and not hydrolysed by water. On oxidising the mixture of $MnSO_4$ and periodate solutions with hypochlorite, two other compounds,

$Na_7H_4Mn(IO_6)_3.17H_2O$ and $K_7H_4Mn(IO_6)_3$ $8H_2O$ result[122] They are also red, but hydrolyse slowly in water to MnO_4^-, IO_3^-, and $H_3IO_6^{2-}$

Alkaline hypochlorite oxidises $MnSO_4$, mixed with an alkali metal tellurate, to dark red complexes. $K_6H_8Mn(TeO_6)_3$ $5H_2O$ (μ_{eff} = 3 30 B M) and $Na_7H_7Mn(TeO_6)_3$ $3H_2O$, (refs 123, 124) which are less stable in solution than the periodate analogues[125] The spectra and structures of a number of periodato-, and tellurato-manganese (IV) compounds have been determined[123,126,127]

Complex iodates, $M_2Mn(IO_3)_6$ (M = NH_4, K) and $BaMn(IO_3)_6$, are produced as brown-violet solids on boiling MnO_2, iodic acid, and the metal iodate solutions[128] The K salt has μ_{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 reported[129]

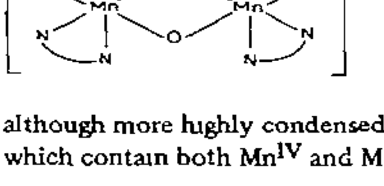
Dark olive-green crystals of $K_2Mn(C_2O_4)_2(OH)_2$ $2H_2O$, which on microscopic examination proves to be a mixture of orange and green crystals, possibly the *cis* and *trans* isomers, are formed[130] by the reaction of oxalic acid, potassium oxalate, and $KMnO_4$ in aqueous solution at 0°. The crystals decompose at room temperature, and the solutions slowly turn red-brown, indicating the formation of Mn^{III}.

Other complexes include the red-brown formaldoxime $Na_2Mn(CH_2NO)_6$, obtained on air oxidation of manganese (II) solutions containing formaldoxime[131], black crystalline $(NH_4)_2H_2MnE_2O_9$ (E = P, As)[132], and the curious yellow-red glycerylmanganates (IV), e g , $Na_2Mn(C_3H_5O_3)_2$, formed on heating freshly precipitated MnO_2 with glycerol and aqueous alkali[133]

(viii) Manganese (IV) complexes of N-donor ligands

These seem to be confined to biguanidine and 2,2'-bipyridyl complexes On treatment of alkaline $KMnO_4$ with biguanidine, or by oxidising Mn^{II} and biguanidine with alkaline persulphate, bright red crystals $[(OH)_2Mn(BigH)_2](OH)_2$ were formed, from which the NO_3^-, SO_4^{2-}, $C_2O_4^{2-}$, CrO_4^{2-}, and IO_3^-, can be obtained by metathesis. They have unusually low magnetic moments, in the range 2.0–2 5B.M.[134].

$Mn(bipy)Cl_4$ which is formed[135] as black crystals from the reaction of 2,2'-bipyridyl with $KMnO_4$ in concentrated HCl, loses chlorine on standing, and obeys the Curie–Weiss law with μ_{eff} = 3.82 B M. and θ = 8° (ref. 136) The *o*-phenanthroline analogue has not been obtained[135,137], but red-brown $[MnO(phen)_2](ClO_4)_2$ $\frac{1}{2}H_2O$ forms on treating $MnCl_3(phen)H_2O$ mixed with *o*-phenanthroline, with $HClO_4$.[136] It is antiferromagnetic, and may be an oxygen-bridged dimer, viz.



although more highly condensed structures are also possible. Some N-donor complexes which contain both Mn^{IV} and Mn^{III}, are discussed under Mn^{III}.

(ix) $K_2Mn(CN)_6$

Nitrosyl chloride oxidises $K_3Mn(CN)_6$ in DMF to canary yellow $K_2Mn(CN)_6$, μ_{eff} = 3.94 B.M., which is instantly decomposed by water[138]. Yakimach[139] claimed to have obtained $K_4Mn(CN)_8$ by reaction of $KMnO_4$ with alkaline KCN, but this was denied by Goldenberg[140], who could not repeat the preparation, and obtained a manganese (III) cyanocomplex contaminated with KOH. The $KMn^{II}Mn^{III}(CN)_6$ complex is similarly obtained[138] from NOCl and $K_2Mn^{II}Mn^{II}(CN)_6$.

(x) Heteropolyanions

Manganese (IV), like a number of other transition metal higher oxidation states, is stabilised by incorporation into a heteropolyanion. The 9-molybdomanganates (IV), e.g. $(NH_4)_6MnMo_9O_{32}\cdot 8H_2O$ (ref. 141) have been known for some time, and recently 12-niobomanganates (IV)[142,143] have been obtained, and the structure of $Na_{12}MnNb_{12}O_{38}\cdot 50H_2O$ determined[143]. Flynn and Stucky[144,145] have described three types of vanadomanganate (IV) – $K_5MnV_{11}O_{32}\cdot 10H_2O$, $K_5HMn_3V_{12}O_{39}\cdot 10H_2O$, and $K_7MnV_{13}O_{38}\cdot 16{-}18H_2O$.

G. MANGANESE (III)

Mn^{III} has a far more extensive chemistry than any of the other oxidation states discussed. There are relatively few simple compounds, but Mn^{III} is fairly stable in complexes, almost all of which are anionic, e.g. fluoro, chloro, cyano, or neutral β-diketonates; cationic species are rare. The complexes with oxygen donor ligands have been known for many years, but complexes with nitrogen donors have only recently been characterised. Sidgwick[1], for example, stated in 1950 that "trivalent manganese has no tendency to coordinate with nitrogen to form amines, nitrocomplexes, or in other ways". There is an almost total absence of complexes of the heavier Group V donors.

(i) Halides

A red-purple trifluoride, and a very unstable trichloride are known. MnF_3 is prepared[146–149] by fluorination of MnF_2, $MnCl_2$, various manganese oxides, or, best, MnI_2, or by dissolving $Mn(IO_3)_2$ in BrF_3 and evaporating at 140° (ref. 71, 150). Ruby-red crystals of the hydrate $MnF_3\cdot 2H_2O$ are obtained on dissolving Mn_2O_3 in aqueous HF, or by oxidising Mn^{II} in HF solution with $KMnO_4$, or electrolytically[151,152]. The anhydrous compound is moisture-sensitive, but the hydrate is not hydrolysed in water in the presence of HF (ref. 151). MnF_3 liberates fluorine on heating, although the dissociation pressure is less than 0.1 atm at 600° (ref. 153) and has been extensively studied as a fluorinating agent, especially in organic chemistry[147,154]. The structure is most unusual in that there are three different Mn–F distances. The lattice is monoclinic, a = 8.509, b = 5.037, c = 13.448 Å, and the structure consists[150] of distorted MnF_6 octahedra sharing corners with Mn–F 2.09, 1.92, 1.79 Å and Mn–F–Mn (ave.) 146°. The distortion has been discussed in terms of crystal field theory and the Jahn–Teller effect by Hepworth et al.[155]. Mass spectra[156] show that MnF_3 evaporates principally as the monomer, whilst the value for the heat of formation (−238 kcal. mole^{-1}) coupled with the heat of sublimation (68.0 ± 3 kcal. mole^{-1} at 298° K leads to a value for the average Mn–F bond energy of 97.9 ± 4 kcal mole^{-1}. The bond dissociation energies are D(Mn–F) = 101, D(FMn–F) = 119, $D(F_2Mn{-}F)$ = 74 kcal mole^{-1}. MnF_3 obeys the Curie–Weiss law with $\mu_{eff} = 5.0$ B.M. and $\theta = 8°$, and becomes antiferromagnetic at very low temperatures[157]. An adduct $MnF_3.4XeF_6$, or possibly $MnF_4.4XeF_6$, is formed on heating manganese with xenon and excess fluorine under pressure[158].

A black solid, analysing as $MnCl_3$ is formed[70] on suspending MnO_2 in dry ether at −78°, saturating with dry HCl, and precipitating with CCl_4. The action of liquid HCl on $Mn(OAc)_3$ at −100° produces brown crystalline $MnCl_3$, soluble in organic solvents to green solutions, and readily losing chlorine above about −35° (ref. 159).

(ii) Complex halides

Mn^{III} forms a number of complex anions with the halogens, *viz.* $MnF_6{}^{3-}$, $MnF_5{}^{2-}$, $MnF_4{}^{-}$, $MnCl_6{}^{3-}$, and $MnCl_5{}^{2-}$, but all attempts to prepare bromocomplexes have failed.

K_3MnF_6 and K_2NaMnF_6 are formed on fusing $K_2MnF_5.H_2O$ with MHF_2 (M = K, Na)[160,162] and Cs_2KMnF_6 has recently been obtained by direct fluorination[161]. K_3MnF_6 dissolves in aqueous HF to reform the $MnF_5.H_2O^{2-}$ ion, and is completely hydrolysed by water. $[M(NH_3)_6]MnF_6$ (M = Co, Cr, Rh) are obtained on oxidising Mn^{II} in 40% HF with $KMnO_4$ in the presence of the cation and NH_4F (ref. 163). The IR spectra of these compounds have been examined, and discussed in terms of the distorted $MnF_6{}^{3-}$ ion and the Jahn–Teller effect[163].

Pink crystals of $K_2MnF_5.H_2O$, which are hydrolysed by water, form[82,152] on oxidising MnF_2 in 40% HF followed by addition of KHF_2. $Cs_2MnF_5.H_2O$ was crystallised from mixed solutions of CsF and MnF_3 in aqueous HF, whilst M_2MnF_5 (M = Li, Na, NH_4) are formed[166,167] on adding MHF_2 to MnO(OH) in 20% HF. A substance which is probably $BaMnF_5$ is formed[79] on hydrogen reduction of $BaMnF_6$ at 400°. The "MnF_5" group in $(NH_4)_2MnF_5$ is actually a distorted MnF_6 octahedron, Mn–F = 1.84, 1.85, 2.12 Å, the octahedra being linked into infinite chains[167]. (Note added in proof: a crystal structure of $K_2MnF_5.H_2O$ has been determined by X-ray crystallography. The water molecule is not coordinated, and bridging fluorine atoms complete a distorted octahedron about the manganese. A. J. Edwards, *J. Chem. Soc. A*, (1971) 2653.)

The brown-violet $MMnF_4$ (M = Li, K, Rb) are formed[73,74] by hydrogen reduction of the corresponding $MMnF_5$ at 150–250°.

Hexachloromanganates (III) are only found with large cations. Hatfield et al.[168] prepared $[M(pn)_3]MnCl_6$ (M = Co, Rh) by oxidation of $MnSO_4$ in concentrated hydrochloric acid with $NaClO_3$ in the presence of $[M(pn)_3]Cl_3$. The Co compound, and the less stable $[Co(en)_3]MnCl_6.2H_2O$ may be obtained using $KMnO_4$ as the oxidising agent[169]. These compounds are instantly hydrolysed in water, decompose on keeping, and show rather high ν(Mn–Cl) frequencies compared with other hexachlorometallates (III)[93].

$(NEt_4)_2MnCl_5$ is formed by reaction of MnO_2 with acetyl chloride in ether[171], or by saturating MnO_2 suspended in CCl_4 with dry HCl and ether-extracting the black residue[170]. In both cases, addition of NEt_4Cl precipitates the dark green pentachloromanganate. Addition of the ligand to the dark brown solution of $KMnO_4$ in concentrated HCl precipitates

TABLE 8

Complex halides of manganese (III)

Compound	Colour	Structural data		Magnetic moment (B M)	Ref
K_3MnF_6	Blue-violet	Tetragonal,	a = 8 75	4 95	160
			c = 8 30 Å		
K_2NaMnF_6		Tetragonal,	a = 8 171		162
			c = 8 577		
Cs_2KMnF_6	Violet	Tetragonal,	a = 8 93	4 88	161
			c = 9 26		
$(NH_4)_3MnF_6$	Reddish				164
$[Co(NH_3)_6]MnF_6$	Orange-brown	Cubic,	a = 9 97	4 94	163
$[Cr(NH_3)_6]MnF_6$	Golden-brown	Cubic,	a = 10 06		163
$[Rh(NH_3)_6]MnF_6$	Violet	Cubic,	a = 10 05		163
K_2MnF_5 H_2O	Pink			3 32	82, 152, 165
Na_2MnF_5	Pink	Orthorhombic,	a = 6 08		
			b = 7 86		
			c = 9 28		167
Li_2MnF_5	Pink	Orthorhombic,	a = 5 46		
			b = 7 78		
			c = 8 81		167
$(NH_4)_2MnF_5$	Pink	Orthorhombic,	a = 6 20		
			b = 7 94		
			c = 10 72		167, 167a
$RbMnF_4$	Brown-violet			5 0	74
$KMnF_4$	Brown-violet			4 9	74
$LiMnF_4$	Brown			4 7	74
$[Co(pn)_3]MnCl_6$	Dark brown			4 91	168
$[Co(en)_3]MnCl_6$ $2H_2O$	Dark brown			4 94	169
$(NEt_4)_2MnCl_5$	Dark green			5 0	170, 171
$(phenH_2)MnCl_5$	Green-black			5 0	135, 136
$(bipyH_2)MnCl_5$	Green-black		a = 13 204	4 88	135, 136, 173
			b = 7 103		
			c = 15 339		

the green-black $(phenH_2)MnCl_5$ and $(bipyH_2)MnCl_5$ (ref 135) The structure of the latter has been determined, it contains discrete $MnCl_5^{2-}$ ions which are square pyramidal with a distortion towards trigonal bipyramidal, Mn—Cl = 2 53, 2 34 Å (ref 173) The alkali metal analogues have been described, but there is some doubt as to whether they are M_2MnCl_5 or M_2MnCl_5 H_2O, and they would repay further study[90,172]

(iii) Oxide

α-Mn_2O_3 is best prepared by decomposing manganese (II) nitrate at 150–200°, and then heating the product to constant weight at 600°, above this temperature the product obtained is not completely stoichiometric[98,105] It is the normal product of heating many manganese compounds in air between 600–800°, but above 900° oxygen is lost to form Mn_3O_4 The structure is body-centred cubic, a = 9 401 Å (c-sesquioxide type)[174]

γ-Mn_2O_3 was reported as a black powder obtained by careful dehydration of γ-MnO(OH) (ref 175), but recent work indicates that the γ-Mn_2O_3 phase exists only in the range $MnO_{1\ 33-1\ 40}$ and readily changes into α-Mn_2O_3 on heating[106]. The X-ray diffraction pattern is said to be similar to that of Mn_3O_4 to which it is related in the same way as γ-Fe_2O_3 is to Fe_3O_4.

There is much confusion in the literature about the nature of the various hydrated oxides of Mn^{III}. There is no good evidence for $Mn(OH)_3$, but two forms of MnO(OH) seem well-established α-MnO(OH) (manganite) and γ-MnO(OH) (groutite) are both formed by the oxidation of $Mn(OH)_2$ under carefully controlled conditions[100]. This reaction can also yield MnO_2 (various forms), manganates (III), manganates (IV), and a number of other products, so the confusion in the literature is not surprising! A β-MnO(OH) was also reported to be formed in this reaction[100,177] but this is now in doubt[106] Both α- and γ-MnO(OH) contain Mn^{III} surrounded octahedrally by oxygen atoms, with all the latter involved in hydrogen bonding[176] The difference in structures is in the extent of the distortion of the octahedron, in α-MnO(OH) this is quite small with average Mn—O = 1.89 Å, whilst in γ-MnO(OH) there are four oxygens at 1 88 Å, and two at 2 30 Å, a much more distorted structure[176]

(iv) Manganates (III)

The large number of complex oxides will not be discussed Scholder and Kyri[178] found that $Mn(OH)_2$ in 50% NaOH is oxidised to $NaMnO_2$, also obtained on heating Mn_2O_3 and Na_2CO_3 in air at 1000°, or along with the K, Rb analogues by heating a mixture of Mn_2O_3 and MOH in a 1 2 ratio in nitrogen[51] $LiMnO_2$ is formed by fusing the constituent oxides in argon[179] Scholder and Kyri[178] also reported $Na_3Mn(OH)_6.2\ 4H_2O$, $Na_4Mn(OH)_7\ 5H_2O$, and the Ba and Sr salts of the ions $Mn(OH)_5{}^{2-}$, $Mn(OH)_6{}^{3-}$, and $Mn(OH)_7{}^{4-}$.

$M_2Mn_4O_7$ (M = K, Rb) are formed on heating 1 1 mixtures of Mn_2O_3 and MOH[51].

(v) Manganese (III) compounds with oxygen donor ligands

Green $Mn_2(SO_4)_3$ is formed on dissolving $KMnO_4$, MnO_2, or Mn_2O_3 in hot concentrated sulphuric acid, and drying the product at 130°. It dissolves in 70% H_2SO_4 and on cooling red $HMn(SO_4)_2\ 2H_2O$ crystallises, but in more dilute acid, hydrolysis occurs[180,181] Violet solutions of Mn^{III} are formed by electrolysis of $MnSO_4$ in sulphuric acid solution[182] Alums are formed with alkali sulphates, there are double sulphates with Al, Cr^{III} and Fe^{III}. $CsMn(SO_4)_2\ 12H_2O$ is ruby-red, melts at 40°, and has μ_{eff} = 4.9B.M, the Rb, K, NH_4 analogues are known[183,184] but are less stable, and all are readily hydrolysed

Grey-green $MnPO_4.H_2O$ precipitates on oxidising Mn^{II} in phosphoric acid solution, but redissolves in concentrated H_3PO_4 to form a violet solution, said by Meyer and Marek[185] to contain $H_3Mn(PO_4)_2$, from which double salts with alkali phosphates, e g. $Na_2HMn(PO_4)_2.2H_2O$, can be isolated On dilution of the violet solution $MnPO_4\ H_2O$ is precipitated. Several Mn^{III} salts of the condensed phosphoric acids are known[45].

Manganese (III) acetate is one of the easiest Mn^{III} compounds to obtain, and is a convenient starting material for the synthesis of several others The cinnamon-brown anhydrous compound is produced in the violent reaction between $Mn(NO_3)_6.6H_2O$ and acetic anhydride[159], and the dihydrate by oxidation of the manganese (II) compound in glacial acetic acid with chlorine or $KMnO_4$ (ref 186)

Cartledge and Eriks[187] prepared the trisoxalato and bisoxalato complexes of Mn^{III} by oxidation of the corresponding Mn^{II} complexes with $KMnO_4$. When care was taken to isolate a pure product, the trisoxalatomanganate (III) could be stored at 20° in the absence of light with little decomposition, but the bisoxalatomanganate (III) was less stable, although it kept fairly well at 0°

Meyer and Schramm prepared several malonate complexes but it appears that these were impure in the majority of cases[188] Bullock et al. [189] have obtained and studied a large series of malonate complexes $M[MnL_2(H_2O)_2]$ (M = Cs, Tl, NH_4, Rb, NMe_4, NEt_4), $M[MnL_2(H_2O)_2].2H_2O$ (M = Na, K, C_5H_6N), $M[MnL_2(H_2O)_2]$ $3H_2O$ (M = Li), $M[MnL_2]$ (M = Na, K), $M_3[MnL_3]$ $3H_2O$ (M = K), $M_3[MnL_3]$ H_2O (M = K), and $[MnL_2(H_2O)_2]$ The effective magnetic moment for these complexes lay between 4.90 and 5.03 B M , and the visible spectra exhibited two absorption bands at 22,000 cm^{-1} and 13,000 – 16,000 cm^{-1}. Cartledge and Nichols[190] calculated the equilibrium constant for the reaction

$$[MnL_3]^{3-} + 2\,H_2O \rightleftharpoons [MnL_2(H_2O)_2]^- + L^{2-} \quad (L = C_3H_2O_4)$$

and obtained an average value of $K = 0.057$ at 0°

The solid EDTA complex of Mn^{III} was characterised by Yoshino et al [191] who found it was decomposed by light and heat, and was unstable at room temperature. They noted that in solution two forms existed depending on the pH of the solution, and suggested an equilibrium

$$[Mn(EDTA)(OH_2)]^- \rightleftharpoons [Mn(EDTA)(OH)]^{2-} + H^+$$

which leads to the conclusion that either EDTA is acting as a quinquedentate ligand, or that Mn^{III} is capable of forming seven-coordinate complexes The idea of seven-coordination is reasonable in the light of the crystallographic establishment of the Mn^{II}–EDTA complex as seven-coordinate[192]

The complexes $[Mn(bipyO_2)_3](ClO_4)_3$ $3H_2O$, $\mu_{eff} = 4.97$ B M.[193], and $[Mn(terpyO_3)_2](ClO_4)_3$ (ref 194) have been obtained. The latter contains $terpyO_3$ behaving as a tridentate ligand.

(vi) β-ketoenolates

Fackler[195] has reviewed the literature up to 1965. Fernelius and Bryant[196] have described the preparation of $Mn(acac)_3$, and the synthetic procedures have also been reviewed by Charles[197] Brown-black $Mn(acac)_3$, which is thermally less stable than the Cr, Ni, or Fe analogues, is most conveniently obtained by oxidising Mn^{II} with $KMnO_4$ in the presence of acetylacetone[198] The preparations of Mn^{III} complexes of diisobutyrylmethane[199], dipivaloylmethane[199], trifluoroacetylacetone[200,201], 1-phenyl-1,3-butanedione[201], hexafluoroacetylacetone[202], and 3-cyano-2,4-pentanedione[202] have been described

The standard heat of formation of $Mn(acac)_3$ at 25° has been determined by reaction calorimetry[203] to be –332.1 kcal $mole^{-1}$. Enthalpy changes at 25° for the hypothetical gaseous reactions

$$Mn^{3+}\,(g) + 3\,C_5H_7O_2^-\,(g) = Mn(C_5H_7O_2)_3\,(g) \quad \Delta H = -1475 \text{ kcal mole}^{-1}$$
$$Mn\,(g) + 3\,C_5H_7O_2\,(g) = Mn(C_5H_7O_2)_3\,(g) \quad \Delta H = -263 \text{ kcal mole}^{-1}$$

have been derived and thus the heterolytic bond energy = 246 kcal. mole^{-1}, and the homolytic bond energy = 44 kcal mole^{-1} for the Mn–O bond in Mn(acac)$_3$. The homolytic bond energy appears to provide the better basis for the comparison of M^{III}–O bond energies for the first transition series acetylacetonates[203].

Despite the high-spin d^4 electronic configuration of Mn^{III} in Mn(acac)$_3$, the room-temperature X-ray crystal structure indicates an almost regular octahedral arrangement about the metal[204] The distortion from D_3 symmetry is slight, but real, with Mn–O = 1 88 Å (deviation 0 03 Å) Forman and Orgel[205] have suggested that, because of the unusual infrared spectrum[206], Mn(acac)$_3$ is Jahn–Teller distorted Morosin and Brathovde[204]suggest that, because there are two types of O–Mn–O bond angles (96.9° and 87.8°) in the complex, the bands being observed include some coupling to an Mn–O bond. On the other hand, the crystal structure of acetylacetonatobis(*N*-phenylaminotroponiminato)manganese (III) has revealed[207] the first case of a distorted octahedral complex of high-spin Mn^{III}, where the distortion occurs because of different Mn–ligand bond lengths and not Mn–ligand bond angles. The Mn–O bond in the mixed-ligand complex, 1.96 Å, is significantly longer than in the acetylacetonate, this may be due to the presence of N donors in the complex The distortion takes the form of four short bonds and two long bonds, and Bartlett and Palenik[207] have suggested an empirical rule for predicting the final configuration of octahedral Mn^{III} complexes

Barnum has carried out some Huckel LCAO–MO calculations on Mn(acac)$_3$ and discussed the metal–ligand π-bonding[208]. Piper and Carlin[209] have studied the polarised visible spectrum of Al(acac)$_3$ isomorphously replaced in part with Mn^{3+} Electronic energy levels were assigned and interpretations of the spectral intensities and estimates of octahedral and trigonal field strengths were presented The trigonal field parameter, K, is 500 cm^{-1}

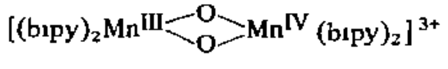
When Mn(acac)$_3$ is subjected to various acids in water, salts of type [Mn(acac)$_2$(H$_2$O)$_2$]$^+$ are formed[210] Manganese can be extracted quantitatively from alkaline peroxide solutions with acetylacetone and chloroform[211]

(vii) Schiff base complexes

There are not many reported investigations of Schiff base complexes of Mn^{III} Early work by Pfeiffer et al [212] and Tsumaki[213] on hydroxy compounds of the type Mn(salen)(OH) and Mn(sal-NR)$_2$OH, has recently been reinvestigated[214,216] Lewis et al [216] obtained two modifications of Mn(salen) (OH), one of which showed antiferromagnetic behaviour, possibly arising from an oxygen-bridged structure of the type [Mn$_2$(salen)$_2$O] H$_2$O Derivatives of the type Mn(salen)X (X = halogen, acetate, etc) have recently been studied and all display Curie–Weiss magnetic behaviour with small θ values[214]. Mn(salen) is oxidised by nitric oxide in ethanol to an Mn^{III} derivative[214], and it has been shown that three different complexes containing Mn^{III} and Mn^{IV} can be formed on oxidation under various conditions[215]. The six-coordinate [Mn(TS$_2$)] I H$_2$O (TS$_2$ = bissalicylaldehydetriethylenetetramine) was prepared[217] by reacting bissalicylaldehyde-Mn^{II} with triethylenetetramine, concentrated HCl, and KI, the magnetic moment is normal (5.05 B.M.). The complexes $Mn(sal\text{-}NR)_3$ and $Mn(sal\text{-}NR)_2X$ ($X = Cl, Br, OAc$) show high-spin magnetic behaviour ($\mu_{eff} = 4.80–5.04$ B.M.) with small deviations from the expected susceptibilities according to the Curie law[218]. The Curie–Weiss behaviour of the Mn(salen)X ($X = Br, I$) has been explained in terms of very weak antiferromagnetic interactions[218].

(viii) Manganese (III) complexes with nitrogen-donor ligands

Persulphate oxidation of $[Mn(bipy)_3]^{2+}$ produces a dark green complex[219], characterised as $[Mn(bipy)_2O]_2(S_2O_8)_{1.5}\cdot 3H_2O$ by Turco and Nyholm[220] who also obtained $[Mn(bipy)_2O]_2(ClO_4)_3\cdot 2H_2O$ by metathesis with $NaClO_4$. The effective magnetic moment is 1.7 B.M. indicating an average oxidation state of $Mn_{3.5}$, i.e. an Mn^{III}- and Mn^{IV}-containing molecule, for which the structure



$$[(bipy)_2Mn^{III}\langle{}^{O}_{O}\rangle Mn^{IV}(bipy)_2]^{3+}$$

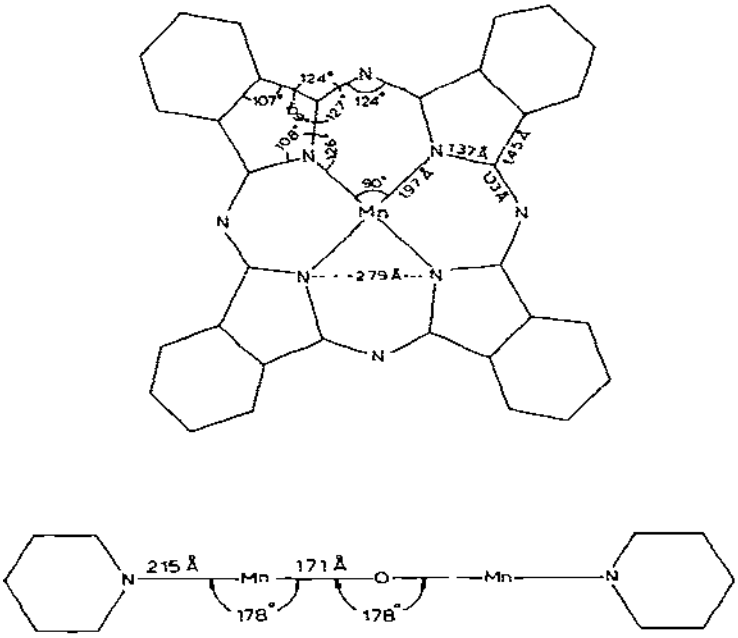
was postulated.

Goodwin and Sylva[135] found that *o*-phenanthroline and 2,2′-bipyridyl reacted with $KMnO_4$ in concentrated HCl, to produce pentachloromanganates (III), $[bipyH_2][MnCl_5]$ and $[phenH_2][MnCl_5]$. Solutions of lower acidity produced $[Mn(bipy)(H_2O)Cl_3]$ ($\mu_{eff} = 4.9$ B.M.) and $[Mn(phen)(H_2O)Cl_3]$ ($\mu_{eff} = 4.9$ B.M.). $[Mn(bipy)Cl_4]$ decomposes on heating to produce $[Mn(bipy)Cl_3]_2$, a chlorine-bridged dimer, with the rather low magnetic moment of 3.9 B.M., which can be obtained directly, along with $[Mn(phen)Cl_3]_2$, from the product of the interaction of MnO_2 and dry HCl in CCl_4 with either of these bidentate ligands[135]. The same workers[136] also prepared $[Mn(phen)(H_2O)F_3]$ and $[Mn(terpy)Cl_3]$ and studied the magnetic properties of a number of these complexes over the range ~ 100–300°K. The compounds $[MnL(H_2O)X_3]$ (L = phen, bipy, $X = F, Cl$) are simple paramagnetics, but $[MnLCl_3]$ are antiferromagnetic, in accordance with the dimeric, or possibly more highly polymeric, structures proposed. The tridentate ligand terpy forms $[MnLCl_3]$ (L = terpy) which is a normal, monomeric octahedral complex[136].

Funk and Kreis[221] reacted $MnCl_3$ with some simple amines and obtained mainly 1:3 adducts. The compounds were moisture-sensitive, but stable at room temperature, in contrast to the simple trichloride. With 2,2′-bipyridyl and *o*-phenanthroline, water-soluble complexes resulted in which the chloride could be substituted by other ions; similar addition compounds with ethers decomposed at room temperature. Reaction of $MnCl_3$ with acetylacetone caused substitution of one or two chlorides by the diketone. Among the complexes isolated were $MnLCl_3$ (L = bipy, phen, py), MnL_2Cl_3 (L = en, dioxan), and MnL_3Cl_3 ($L = NH_3, MeNH_2, EtNH_2, PrNH_2$, py), $MnCl_3\cdot 4THF$, and $Mn(acac)Cl_2$ and $Mn(acac)_2Cl$. Unfortunately, no measurements were carried out on this interesting series of complexes.

Ray and coworkers have prepared a number of interesting Mn^{III} complexes containing the biguanide ligand. The compound $[Mn_2(big)_4(OH)_2]\cdot H_2O$ becomes anhydrous on heating to 90° (ref. 222). $Mn(acac)_3$ reacts with biguanidine to yield[223] $[Mn(acac)(big)(OH)(H_2O)]$, which reacts further with H_2O to produce $[Mn(acac)(big\cdot H)(H_2O)]OH$. The mixed complex $[Mn(big)_2(benzoylacac)]$ has also been produced[224]. These workers have also prepared [Mn(pic)$_3$] (μ_{eff} = 4 9 B.M) and [Mn(oxin)$_3$] (μ_{eff} = 4 8 B M) (pic = anion of picolinic acid, oxin = anion of β-hydroxyquinoline). The latter complex reacts with bromine[225] to form [Mn(5,7-dibromoxin)$_3$]

Elvidge and Lever[226] found that the oxidation of pyridine solutions of phthalocyanatomanganese (II) with molecular oxygen resulted in precipitation of short, opaque crystals which they formulated as Mn^{IV}Pc py.O (Pc = phthalocyanato) An X-ray structure of this compound[227] showed it to be the more complicated phthalocyanatopyridinemanganese-(III)-μ-oxophthalocyanatopyridinemanganese (III) This novel molecule consists of two approximately flat and parallel manganese phthalocyanine ring systems, joined by an oxygen atom which is midway between the manganese atoms Each Mn also has a pyridine molecule coordinated opposite to the oxygen atom The crystals also contain molecules of pyridine of crystallisation



Average bond distances and angles

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Manganese has been implicated in oxygen formation which occurs during green plant photosynthesis[228] In fact, two Mn ions are found per photosynthetic unit in the chloroplast[229] Several suggestions have been made as to the function of the Mn ion in the liberation of O$_2$ by photosystem II. In these schemes the Mn^{II}–Mn^{III}–Mn^{IV} redox system is thought to take part in the electron-transfer chain from an electron donor to an electron acceptor[230]. Unfortunately, the metal atom binding sites and the ligands at these sites are not known Calvin[231] has suggested that a relevant model for the Mn in the chloroplast would be Mn complexes of porphyrin-like ligands. The photochemical behaviour of phthalocyanine[232], porphyrin[233], and chlorophyll[234] complexes of Mn have been extensively investigated In a detailed study of the photochemistry of phthalocyaninemanganese, it has been shown that the stable oxidation level of manganese may be shifted among the (II), (III), and (IV) oxidation states, depending on the nature of the fifth and sixth coordinating groups[235]. Furthermore, photochemical oxidation as well as photochemical reduction of the phthalocyaninemanganese (III) has been observed, and photochemical reduction of the manganese (IV) compound demonstrated. Mn^{III} etioporphyrins also are reduced to the (II)-oxidation state[235]. Some halide complexes of Mn^{III} protoporphyrin IX dimethyl ester have been prepared and studied[236]. A manganese (III) porphyrin was first prepared by Zaleski[237], and this mesoporphyrin IX was later studied by Taylor who examined its redox properties[238]. Also, the acetatoetioporphyrin II[232], acetatohematoporphyrin IX dimethyl ester, and chlorohematoporphyrin IX dimethyl ester[233], derivatives of Mn^{III} have been prepared. The reaction of Mn^{III} tetrapyridylporphines with various reducing agents has been studied[239].

(ix) Hexacyanomanganates (III)

$K_3Mn(CN)_6$ is prepared[241] by air oxidation of $K_4Mn(CN)_6$, or[83,240] by the action of excess aqueous KCN on a manganese (III) complex such as $MnPO_4$, $K_2MnF_5.H_2O$ or $Mn(CH_3COO)_3$. The Li, Na, Rb, NH_4 salts are also known. $K_3Mn(CN)_6$ forms red crystals, isomorphous with $K_3Fe(CN)_6$, $a = 13.59$, $b = 10.62$, $c = 8.52$ Å (ref. 243). The magnetic moment is 3.50 B.M., considerably higher than the "spin-only" value for a low spin d^4 compound (2.83 B.M.). The $Mn(CN)_6{}^{3-}$ ion is one of the few low-spin Mn^{III} compounds known (t_{2g}^4).

The yellow, dilute aqueous solution hydrolyses slowly to MnO(OH). Exchange between $Mn(CN)_6{}^{3-}$ and CN^- is very fast, first-order in $Mn(CN)_6{}^{3-}$ and zero-order in CN^-.

The standard potential for the reaction[242]

$$Mn(CN)_6{}^{3-} + e^- = Mn(CN)_6{}^{4-}$$

is −0.24V.

$K_3[Mn(CN)_5OH]$ has been reported[244,245]. The anion $[Mn(CN)_5NO]^{3-}$, although once regarded as an Mn^{III} compound, exhibits an N—O stretching frequency of 1730 cm^{-1} which indicates the presence of NO^+ and hence the oxidation state of the manganese is probably +1 (ref. 246).

Red-brown crystals of $1.2\,[K_4Mn(CN)_6].0.7\,[K_3Mn(CN)_6].H_2O$, a mixed Mn^{II}—Mn^{III} cyanocomplex is formed[247] by reaction between $K_4Mn(CN)_6$ and $K_3Mn(CN)_6$ under carefully controlled conditions. It has a magnetic moment of 1.04 B.M.

(x) Other Mn^{III} complexes

Nyholm and Sutton[248] were unable to oxidise $[Mn(DAS)_2X_2]$ (X = Cl, Br, I) to Mn^{III}, are found that DAS rapidly reduced $Mn(OAc)_3$ or $Mn(acac)_3$ to Mn^{II} under anhydrous conditions. In the presence of small amounts of water, the red-purple $[Mn(DAS)Cl_2.H_2O](ClO_4)$ was formed in low yield. The reaction can be represented

$$DAS + Mn(OAc)_3 + HClO_4 + \text{acetic anhydride} + H_2O \xrightarrow{\text{dry HCl gas}} [Mn(DAS)Cl_2.H_2O](ClO_4)$$

The complex has $\mu_{eff} = 5.13$ B.M. A green complex, probably the bromo analogue was isolated using HBr in place of HCl in the above reaction.

(xi) Manganese (III) in solution

A detailed review[2] is available, in which the generation of Mn^{III} in solution, its estimation, and the equilibria and kinetics of a large number of reactions are discussed.

Manganese (III) is a strongly oxidising species and is unstable with respect to disproportionation. Solutions of Mn^{III} in perchlorate media is generally produce solid hydrated MnO_2 on standing, instability increasing with increasing $[Mn^{III}]$ and decreasing acidity[249,250].

$$2\,Mn^{III} \rightarrow Mn^{IV} + Mn^{II}$$
$$Mn^{IV} + 2H_2O \rightarrow MnO_2 + 4\,H^+$$

Complexation of Mn^{III} with anions usually results in a reduction of the electrode potential of the Mn^{III}–Mn^{II} couple; for example, the electrode potential in the presence of EDTA is ca. −0.82V (ref. 251), while that in perchlorate media is ca. −1.58V. Moreover, the presence of a number of complexed Mn^{III} species complicates the interpretation of kinetic data. For example, Waters and Littler[252] have concluded that little information can be obtained from a study of the pH-dependence of reactions of manganese (III) pyrophosphate with organic reductants because of a lack of knowledge of oxidising species present in solution. An interesting observation regarding the magnitude of the effects of complexation on the oxidising power of Mn^{III} is that hydrogen peroxide is found as a product of the oxidation of oxalate by Mn^{III}CyDTA at low pH[253].

In an investigation of the analytical applications of the EDTA complex of Mn^{III}, Přibil et al.[254,255] found that the complex slowly decomposed. Yoshino et al.[256] isolated the complex and found decomposition was enhanced by heat, light, and traces of Mn^{II} ion. Tanaka et al.[257] have measured the standard oxidation–reduction potential of the Mn^{III} EDTA–Mn^{II}EDTA complex. Hamm isolated the complexes of Mn^{III} with EDTA, *trans*-1,2-diaminocyclohexane-tetraacetic acid (CyDTA), and hydroxyethylethylenediamine-tetraacetic acid (HEDTA), and established the rates of decomposition in acidic solution. The standard potentials for the reaction $Mn^{III}Y + e^- \rightleftharpoons Mn^{II}Y$ were determined, and all three complexes were equally good oxidising agents. Formation constants were calculated[251]. The products of the decomposition of the Mn^{III} complexes of CyDTA and EDTA were Mn^{II} complexes with oxidation of some of the ligand to formaldehyde, carbon dioxide, and the triacetate ligand[258]. The oxidation of oxalate with Mn^{III}CyDTA has been studied[253].

Important information concerning the stabilities of several Mn^{III} complexes has been obtained by a study of the Mn^{III}-catalysed oxidation of oxalic acid by chlorine[259] and bromine[260]. The rate-determining step in this reaction in the first-order decomposition of the monoxalate complex, viz.

$$MnC_2O_4^+ \xrightarrow{K_1} Mn^{2+} + C_2O_4^-$$

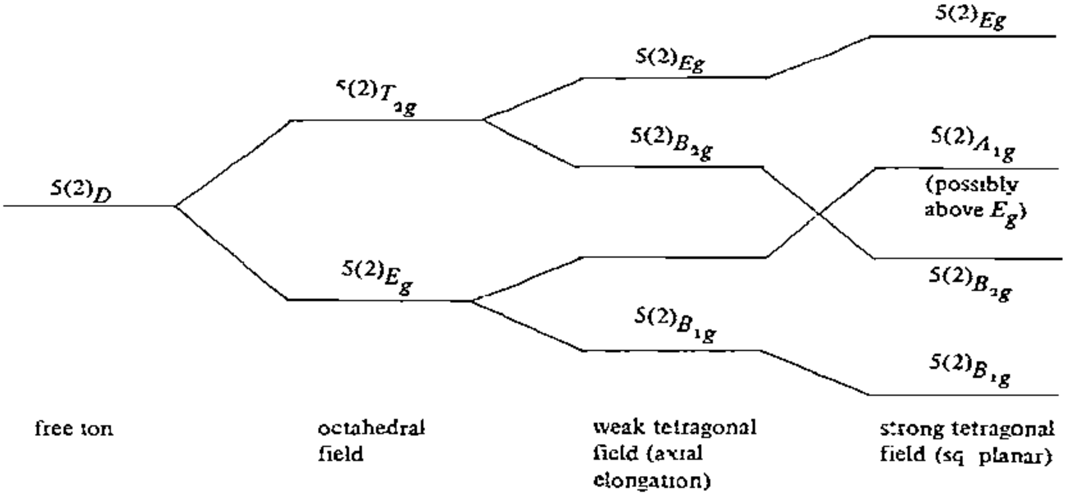
Studies of the oxalate complexes of Mn^{III} showed[259,261] that the decomposition was dependent on the concentrations of oxalate and H^+ ions. The decomposition of the tartrate[262] and glycolate[263] complexes was found to be first-order in the complex concentration in the presence of excess complexing agent, and to be inhibited by the addition of Mn^{II} ion.

Wells and coworkers have carried out spectrophotometric investigations of alcoholo-[264] and aquo-manganese (III)[265] species in perchlorate media. The reactions of aquomanganese (III) ions with bromide ion[266], hydrogen peroxide[267,268] hydrazoic acid[269,270] and hydroxylamine[271] in perchlorate media have been studied The species MnF(CH)$^+_{aq}$ has been postulated by Davies and Kustin[272]

Oxidation of organic compounds by Mn^{III} complexes in aqueous solution has been extensively studied[252], e g the oxidation of toluene by Mn(acetate)$_3$ in refluxing acetic acid yields benzyl acetate, *o*-methylbenzylacetate, and tolylacetic acid[273]. Most of these results have been successfully interpreted in terms of inner-sphere one-electron-transfer processes[274] The non-aqueous chemistry has been less extensively explored, and the oxidations reported have been interpreted as resulting from inner-[275] or outer-sphere[276] one-electron-transfer steps Manganese (III) acetate oxidises olefins to γ-lactones[277–280]

SPECTRA OF MANGANESE (III) COMPOUNDS

The electronic spectra of high-spin Mn^{III} compounds are of special interest because the ground electronic state anticipated in octahedral complex, ${}^5E_g$, is subject to strong Jahn–Teller forces[265,281] In general, three bands are observed in the visible region, and satisfactory assignment has been made in terms of D_{4h} symmetry[171,282] The two highest energy bands have been assigned to the transitions ${}^5B_{1g} \rightarrow {}^5B_{2g} \rightarrow {}^5E_g$



However, despite intensive work on the preparation and optical properties of Mn^{III} complexes[168,223,250,282–286], difficulties have arisen in assignment of the band in the near-infrared region. The relationship of the presence of this band to the structure of the complexes has not been clarified The band (which appears between 8 and 13kK has been variously assigned to a spin-forbidden transition[209,213] from the ground state to ${}^3T_{1g}$ (in O_h symmetry), as a low-energy charge-transfer transition[284,286] as a transition from the ${}^5E_g$ ground state to the trigonally split ${}^5T_{2g}$ excited state[287], and as a spin-allowed transition between components of the ^5E_g (in O_h symmetry) ground state split by Jahn–Teller forces[265,288]. Davis et al. have convincingly shown that this band can be assigned to the $^5B_{1g} \rightarrow {}^5A_{1g}$ transition in D_{4h} symmetry, and they formulated an interesting argument for this assignment[171]. The reflectance spectra of K_3MnF_6 (ref. 285) and $MnCl_6^{3-}$ (ref. 289) show the presence of a low-energy band at 9,000 cm^{-1} and 8,300 cm^{-1} respectively The single-crystal spectrum of $(NH_4)_2MnF_5$ shows a similar low-energy band at 12,750 cm^{-1} which can be assigned to the $^5B_{1g} \rightarrow {}^5A_{1g}$ transition on the basis of polarisation of the bands[167a] All other halide complexes for which there are data also show a low-energy band, e g Na_2MnF_5 (12,500 cm^{-1}) (ref 290), K_2MnCl_5 (12,000 cm^{-1}) (ref 289), K_2MnF_5 (12,100 cm^{-1}) (ref 289), $[(C_2H_5)_4N]_2MnCl_5$ (11,300 cm^{-1}) (refs. 135, 289), $[(bipy)H_2][MnCl_5]$ (11,500 cm^{-1}) (ref. 135), $[(phen)H_2][MnCl_5]$ (12,500 cm^{-1}) (ref 135) and MnF_3 (12,000 cm^{-1}) (ref 283) In the pentahalide species, the atom generally attains six-coordination by sharing axial ligands as in $(NH_4)_2MnF_5$ (refs 167, 291) In MnF_3, all fluorines are shared to complete the distorted octahedron about each Mn^{III} ion The shift in position of the low-energy band in going from the hexahalides to the pentahalides and MnF_3 is best understood on the basis of the Jahn–Teller effect In the hexahalides none of the ligand ions is shared, hence dynamic motion (minima exchange) of the tetragonally displaced ligands about the manganese may occur In the pentahalides and in MnF_3, where ligands are shared, the minima exchange should be decreased as stabilisation of the molecule in one tetragonally distorted form occurs A shift in the low-energy ($^5B_{1g} \rightarrow {}^5A_{1g}$) band to higher wave-numbers consistent with a statically distorted structure follows A similar argument[283] was presented for aqueous MnF^{2+}

(xiii) Low-spin compounds

The spectra of $Mn(CN)_6^{3-}$ and of $Mn(CN)_5(OH)^{3-}$ have been discussed by Chawla and Frank[292]. Earlier investigations[293,294] of the spectrum of the $Mn(CN)_6^{3-}$ ion in aqueous solution are of doubtful value, since it has been shown that hydrolysis in such solutions is not negligible, as had been earlier assumed[179,265]

The $Mn(CN)_6^{3-}$ ion[292] shows charge-transfer absorptions at 43,500, 21,800 cm^{-1}, with a spin-allowed transition at 27,000 cm^{-1} ($^3T_{1g} \rightarrow {}^3E_g$), and spin-forbidden transitions at 12,000 cm^{-1} ($^3T_{1g} \rightarrow {}^5E_g$), 12,500 cm^{-1} ($^3T_{1g} \rightarrow {}^1T_{2g}$), 13,500 cm^{-1}, ($^3T_{1g} \rightarrow {}^1E_g$), and 24,500 cm^{-1} ($^3T_{1g} \rightarrow {}^1A_{1g}$)

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