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8. MANGANESE

R.I. CRISP

CONTENTS

INTRODUCTION

The period of this review covers papers published in 1979 and 1980 and included in Volumes 92 and 93 of Chemical Abstracts. Some papers from Volume 91 are also included, where these were omitted from last year's review [1].

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The format is essentially the same as last year, but owing to the fact that much of the work concerned with porphyrin and phthalocyanine complexes cuts across the boundaries of oxidation state, a new section dealing with this work has been included. Once again, work of an essentially organometallic nature has been excluded, together with reports of purely kinetic or mechanistic interest. The photochemistry of manganese complexes has been adequately reviewed elsewhere [2].

8.1 HIGH OXIDATION STATES

A study of the decomposition of $A[MnO_4]$ (A = K, Rb or Cs), $K_2[MnO_4]$ and $NaK[MnO_4]$, using thermogravimetric and differential thermal analytical methods has been reported [3]. Solutions of $K[MnO_4]$ and $K_2[MnO_4]$ in chlorosulphonic acid have been shown to contain the heptavalent species $MnO_3.SO_3Cl$. Attempts to isolate such a species, however, result in reduction to $MnO.SO_3Cl$ [4]. The IR and Raman spectra of $K[MnO_4]$ in 18-crown-6-ether have been measured in terms of a lowering of the local symmetry of the $[MnO_4]^-$ ion due to $K^+/[MnO_4]^-$ ion pairing [5].

The reactions of manganate(VII) ion with several reducing agents have led to isolable complexes of Mn(III) and Mn(IV) [6,7,8].

8.2 MANGANESE(IV)

The salt $[NF_4]_2[MnF_6]$ has been prepared and characterised by X-ray powder diffractometry, ^{19}F NMR and IR spectroscopy [9]. The electron affinity of MnF_4 has been determined by an effusion method [10].

The properties of two kinds of hydrous manganese(IV) oxide, prepared by reduction of $K[MnO_4]$ or by disproportionation of $K_2[MnO_4]$ have been studied using X-ray, thermal, spectroscopic and magnetic measurements; also their chemical reactivity has been discussed [11]. IR spectral studies on the products of the reactions between manganese and dioxygen and manganese and dinitrogen monoxide in argon matrices have resulted in the identification of the species MnO_2 and $Mn(O_2)_n$ [12].

The preparation, and electrochemical and spectroscopic properties of tris(3,5-di-*tert*-butylcatecholate) complexes of Mn(IV), Mn(III) and Mn(II) have been reported. The Mn(IV) complex is observed to reversibly bind dioxygen at room temperature, the dioxygen being bound as the superoxide anion, $[O_2]^-$ [13]. A polarographic study of dihydroxobisbiguanidemanganese(IV) hydroxide has been reported [14].

8.3 MANGANESE(III)

8.3.1 Halides and pseudohalides

The crystal and magnetic structures of the planar ferromagnetic material $CsMnF_4$ have been determined by X-ray and neutron diffraction methods [15]. A low temperature study of the magnetic properties of $[phenH_2][MnCl_5]$ has been reported [16].

The electrochemical properties of $[Bu_4N]_3[Mn(CN)_6]$, in a variety of non-aqueous solvents, have been reported, and the relationship between the half-wave potentials and the solvent type discussed [17]. The magnetic structure of single crystals of low-spin $K_3[Mn(CN)_6]$ has been determined [18].

8.3.2 Oxides and hydroxides

The X-ray crystal structure of $Na_4Mn_2O_5$ reveals that the Mn^{3+} ion has a novel coordination number of five [19]. A neutron diffraction study of MnO(OH) was undertaken in order to determine its magnetic structure [20]. The thermal decomposition of two forms of MnO(OH) has been investigated: (i) γ-MnO(OH) decomposed *in vacuo* below 400 °C to a mixture of Mn_5O_8, α-Mn_3O_4 and water, above 400 °C, only α-Mn_3O_4 was formed; (ii) α-MnO(OH) decomposed at 250° to a new modification of Mn_2O_3 [21].

8.3.3 Complexes with Group VIB donor ligands

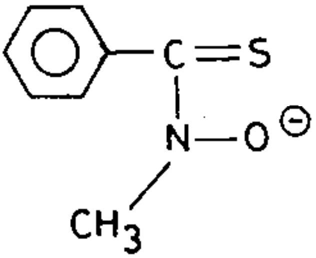
The X-ray crystal structure of $K_3[Mn(C_2O_4)_3].3H_2O$ has been determined and reveals that the complex contains discrete orthorhombically distorted $[Mn(C_2O_4)_3]^{3-}$ anions [22]. The photolyses of $K_3[Mn(C_2O_4)_3]$ and of $K[Mn(C_2O_4)_2(H_2O)_2]$ have been studied. The mechanism of the photolyses were discussed, and the electronic spectra of the photolysis products interpreted [23]. Mn(III) oxalate complexes have also been detected as intermediates in the reduction of $[MnO_4]^-$ by the oxalate ion [24].

A detailed study of the salt and solvent effects on the redox behaviour of $[Mn(acac)_3]$ has been reported. Polarographic and cyclic voltammetric methods were employed, together with UV-VIS-NIR spectroscopy and conductiometric measurements [25]. The temperature dependence of the CH_3 isotropic shift in the NMR spectrum of $[Mn(acac)_3]$ has been reported and two possible explanations proposed [26].

The X-ray crystal structure of the polymeric manganese(III) malonate salt $K[Mn(C_3H_2O_4)_2(CH_3OH)]$ shows that the compound contains two distinct octahedrally coordinated Mn^{3+} ions; one has two malonate ions and two methanol molecules involved in the coordination sphere, whereas the other has only malonate groups coordinated [27]. The autocatalytic oxidation of manganese(II) ethanoate by 3-chloroperbenzoic acid has been reported to proceed *via* a manganese(III) peracid complex [28].

A diphosphate complex of Mn(III) in sulphuric acid, and $[Mn(H_2O)_6]^{3+}$ in perchloric acid, have been generated coulometrically, and used for the determination of reducing species such as Fe(II) and 1,4-dihydroxybenzene [29]. $MnH_3P_2O_6.3H_2O$ has been studied in the solid state by a variety of physical and spectroscopic techniques and shown to contain coordinated $[HPO_3]^{2-}$ anions [30]. The preparations and spectral properties of the selenito manganese(III) complexes $A[Mn(SeO_3)_2].xH_2O$ {A = H, $[NH_4]$, K, Rb or Cs} have been reported; all the complexes possess a high spin d^4 configuration and probably have a polymeric octahedral geometry involving bridging oxygen atoms [31]. The thermal decomposition of several manganese(III) selenites has been studied [32,33].

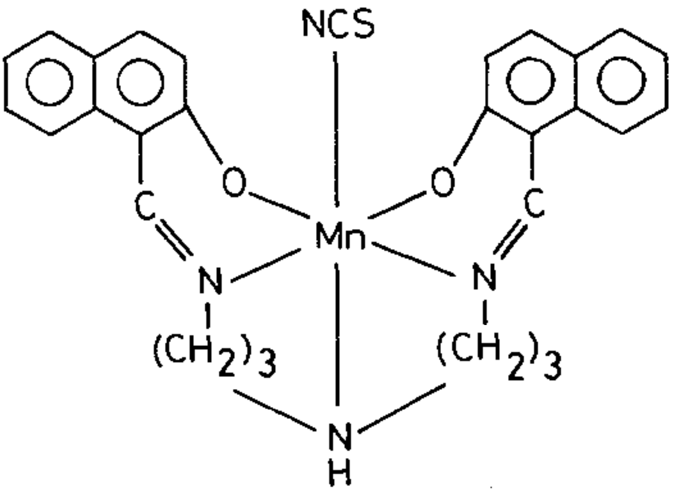
The X-ray crystal structure of the complex $[Mn(mtb)_3]$ {mtb = *N*-methylthiobenzohydroxamate (1)} has been determined. The complex shows a large tetragonal Jahn-Teller distortion, due to the high-spin d^4 state and has an $\{O_3S_3\}$ ligand environment [34].



(1)

8.3.4 Schiff base complexes

A correction to a paper included in last year's review [1; p. 171, ref. 37] has been published. The correct structure is shown in (2) [35]. An earlier paper [36], established a dependence of the reduction potential of Mn(III) complexes with pentadentate Schiff bases on the presence of electron withdrawing groups on the Schiff base and on the nature of the sixth ligand. It has now been shown that similar trends occur when the tetradentate Schiff bases (3) are used to prepare pentacoordinate complexes, although there is a marked steric effect for the ligand with Z = 3-MeO [37].



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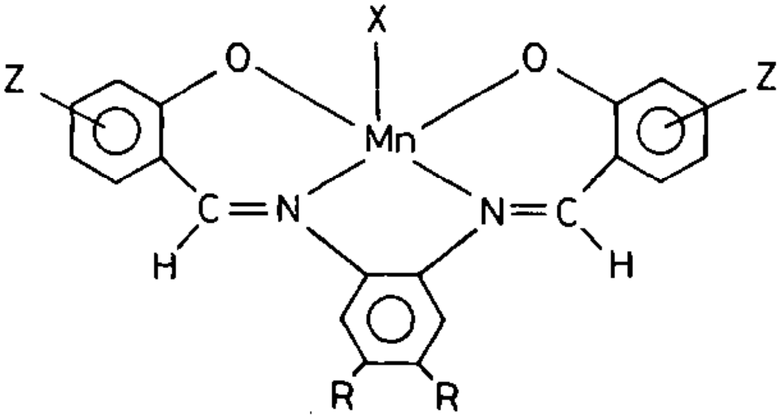
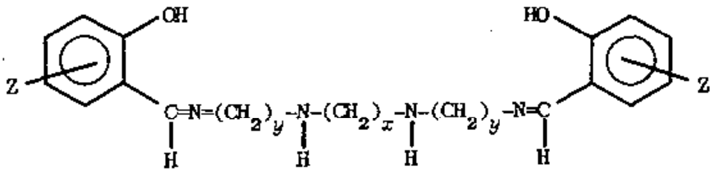
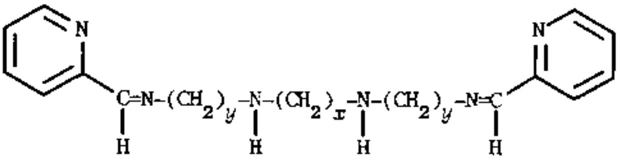


(3; X = NCS^-, I^-, NO_2^- or N_3^-; Z = 5-Cl,
3-MeO, H, 5-MeO or 4,6-$(MeO)_2$; R = H or CH_3)



(4; x = 2, y = 2, Z = H or 5-NO_2;
x = 2, y = 3, Z = H or 5-NO_2;
x = 3, y = 3, Z = H or 5-NO_2)

The reactivity of a series of manganese(III) and manganese(II) complexes with hexadentate ligands towards dioxygen and nitrogen oxide have been discussed; the complexes [Mn(L)][NCS], [Mn(L)] {H_2L = **(4)**} and [Mn(Q)]Y_2 {Q = **(5)**} have been considered in this respect, and only complexes of the ligands **(4)** promote the reactivity [38].

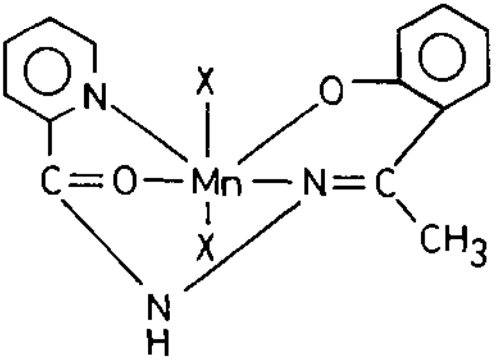


(5; *x* **= 2,** *y* **= 2, Y = NCS or I;**
x **= 2,** *y* **= 3, Y = NCS)**

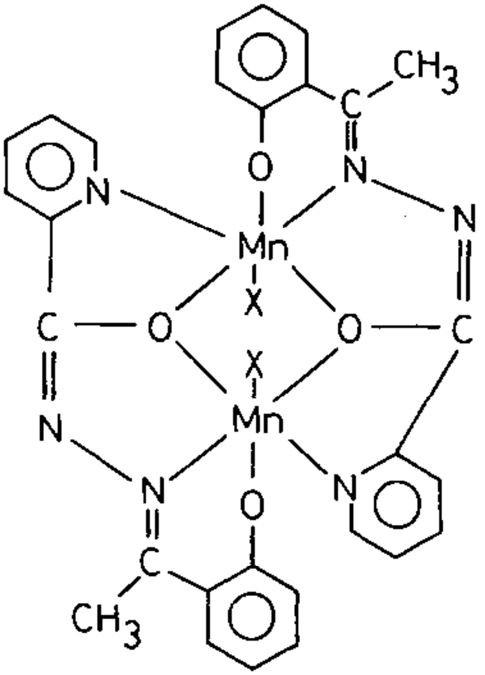
8.3.5 Complexes with nitrogen-oxygen or nitrogen-sulphur donor ligands

[Mn(edta)]$^-$ is reported to react with the superoxide ion in dmso to give [Mn(edta)]$^{2-}$. The reactions of this and of [Mn(cydta)]$^-$ {cydtaH_4 = diaminocyclohexane-*N*,*N*,*N*',*N*'-tetraacetic acid} with superoxide are also discussed. The X-ray crystal structure of K[Mn(edta)].2H_2O shows the manganese ion to be situated in a distorted octahedral {N_2O_4} environment [39]. The photolyses of K[Mn(edta)] and K[Mn(cydta)] in aqueous magnesium(II) perchlorate at 77 K have been studied and spectra of the photolysis products reported [40].

Orthohydroxyacetophenone-picoloyl hydrazone (H_2L) has been reported to react with Mn(O_2CMe)$_3$.3H_2O under conditions of low pH to give the tetragonal monomeric complex [Mn(HL)(O_2CMe)$_2$] **(6)**. Under conditions of high pH, a dimeric tetragonal complex [{Mn(L)(O_2CMe)}$_2$] **(7)** was formed, whereas with orthohydroxyacetophenone-isonicotinoyl hydrazone (H_2Q) under conditions of low pH, the trigonal bipyramidal monomeric complex [Mn(HQ)(O_2CMe)$_2$] **(8)** was formed and, under conditions of high pH, the square pyramidal dimer [Mn(Q)(O_2CMe)]$_2$ **(9)** was isolated.



(6; X = O_2CMe)

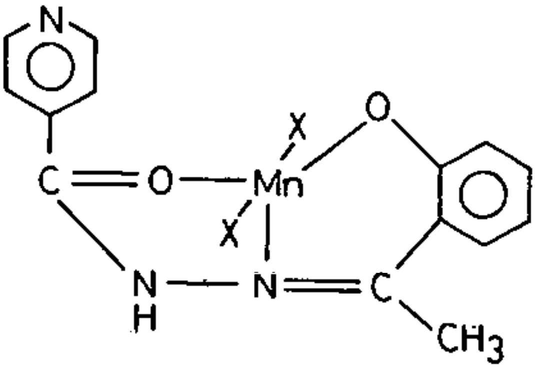


(7)

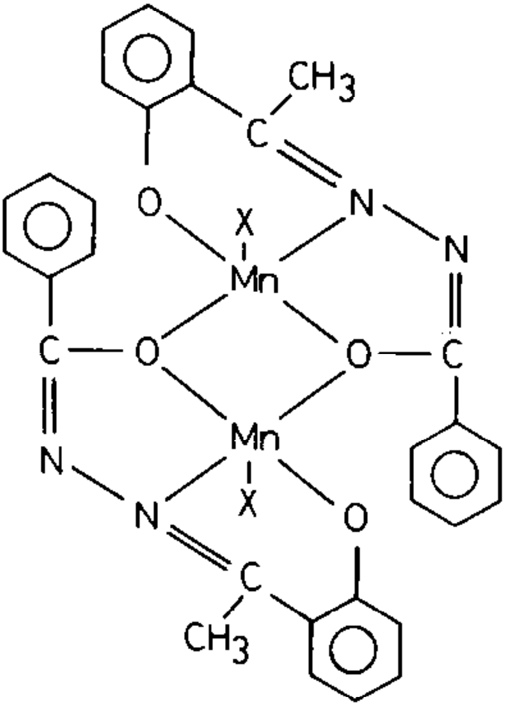
Spectral and magnetic properties of all four complexes have been reported [41].

The binuclear manganese(III) complexes $[\mathrm{Mn(L)(O_2CMe)}]_2$ and $[\mathrm{Mn(L)X(H_2O)}]_2$ $\{\mathrm{H_2L}$ = 3-salicylideneamino-1-propanol or its homologues; X = Cl, Br or $\mathrm{N_3}\}$ have been synthesised. These complexes are six coordinate with bridging L and bidentate $\mathrm{O_2CMe}$, or apical X and $\mathrm{H_2O}$ ligands [42]. Possible structures are shown in (10) and (11).

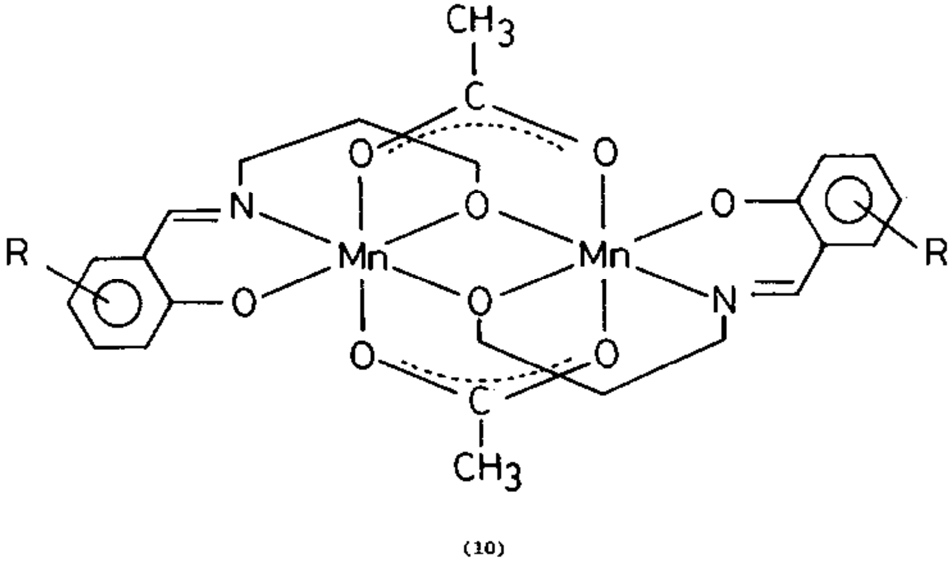
The X-ray crystal structure of a manganese(III) complex of the potentially septadentate trianionic ligand (12) has been determined. The manganese ion is



(8; X = $\mathrm{O_2CMe}$)



(9; X = O_2CMe)



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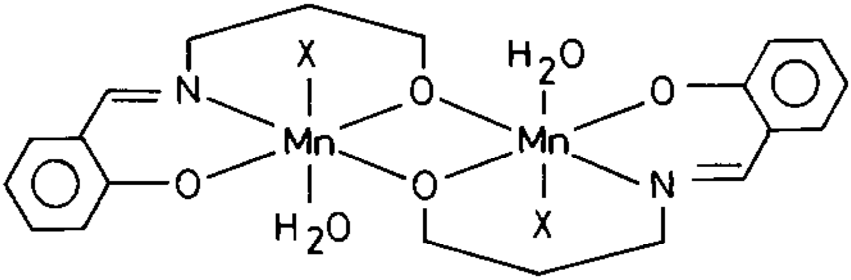
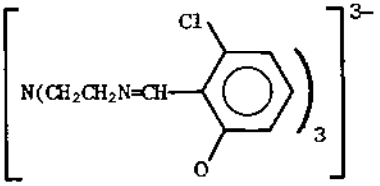


(11)

in an essentially octahedral $\{N_3O_3\}$ environment, the tertiary nitrogen atom of the ligand being uncoordinated [43].

The complexes $[Mn^{III}(sal_2en)(L)]$ (L = the semiquinone radical anion of 1,2-naphthaquinone, 3,5-di-*tert*-butyl-1,2-benzoquinone or 3,4,5,6-tetrachloro-1,2-benzoquinone) have been prepared [44]. $[Mn(pcd)_3]$ {pcd = 1-pyrrolidinecarbodithioate} has been studied in a variety of non-aqueous solvents by cyclic voltammetry [45].



(12)

8.4 MANGANESE(II)

8.4.1 Halides

8.4.1.1 Fluorides

A study of the critical behaviour of the magnetic susceptibility of MnF_2 near the Néel point has been undertaken and Fisher's relation between the magnetic specific heat and the magnetic parallel susceptibility was confirmed [46]. A differential thermal analytical study of MnF_2 has given temperatures of likely phase transitions and these data are compared with the results of X-ray studies [47].

Raman spectra of $KMnF_3$ near the cubic-tetragonal structural phase transition have been reported [48]. There has also been a detailed study of the IR spectra of $KMnF_3$ in both tetragonal phases (15 K and 110 K) [49]. First and second order Jahn-Teller coupling constants have been calculated for $RbMnF_3$ [50]. The structural phase transition in $BaMnF_4$ has been studied by linear dichroism [51] and its magnetic properties have also been studied [52].

8.4.1.2 Chlorides

The He(I) and He(II) PES of $MnCl_2$ have been measured and interpreted by means of SW-Xα and *ab initio* molecular orbital calculations [53]. A theoretical calculation of the electronic structure of $MnCl_2$ using the overlapping spheres model has given reasonable agreement with previous calculations and with experimental data [54]. The thermal conductivity of $MnCl_2.4H_2O$ has been measured as a function of temperature and applied magnetic field [55]. Changes in the visible absorption spectrum of aqueous $MnCl_2$ as a function of concentration have been recorded and the species $[MnCl(H_2O)_5]^+$ and $[MnCl_2(H_2O)_4]$ detected [56]. The transport properties of $MnCl_2(aq)$ have also been determined [57].

The crystal structure of $[CH_3NH_3](MnCl_3).2H_2O$ has been determined, and the compound shown to consist of linear chains of *cis*-$\{MnCl_4(H_2O)_2\}$ octahedra corner-linked by Cl atoms [58]. The crystal structure and magnetic properties of the $KCdCl_3$-type phase of $KMnCl_3$ have been reported [59] and the magnetic structure of the sodium salt has been determined by neutron diffraction [60]. The phase diagram of $CsMnCl_3.2H_2O$ near its bicritical point has been determined [61] and the effect of a strong magnetic field on its luminescence spectrum investigated [62]. The preparation of $A[MnCl_3]$ {A = 4-benzylpyridinium} has been reported; the complex exhibits a red luminescence [63]. The optical absorption spectra of the hexagonal and cubic phases of $RbMnCl_3$ have also been measured [64].

The magnetic phase diagram of the archetypal *quasi*-one-dimensional antiferromagnet $[NMe_4][MnCl_3]$ has been established [65]. EPR half-field transitions have been observed and analysed, the results being in accordance with theory [66]; low temperature measurements revealed two resonances, one due to Mn ions in the linear chains and a second of unknown origin [67].

Measurements of elastic constants for $[MeNH_3]_2[MnCl_4]$ have shown that certain anomalies occur at the phase transition temperatures [68]. Experimental evidence for spin diffusion in the *quasi*-two-dimensional Heisenberg magnet $[EtNH_3]_2[MnCl_4]$ has been presented [69,70]. The magnetic properties of $[PrNH_3]_2[MnCl_4]$, which behaves as a weak ferromagnet below 39.2 K, have been reported [71] and magnetic susceptibility measurements on $[4\text{-}XC_6H_4NH_3]_2[MnCl_4]$ {X = F, Cl, Br or Bu} between 4.2 and 160 K have shown these compounds to possess layer structures of the K_2NiF_4 type [72].

A magneto-optical investigation of $Rb_2[MnCl_4]$ has been undertaken [73]. The magnetic circular dichroism and linear magnetic dichroism of the $d\leftrightarrow d$ transitions in $[Et_4N]_2[MnX_4]$ (X = Cl, Br or I) have been determined [74]. The IR and Raman spectra of $[NH_3(CH_2)_3NH_3][MnCl_4]$ and its ND_3-deuterated analogue have been recorded over the temperature range 10-400 K. The spectra have been assigned and several phase transitions observed [75]. $A_2[MnCl_4]$ {A = 4-benzyl-pyridinium} has been prepared and shown to exhibit an orange luminescence [63]; the spectroscopic properties of $A_2[MnCl_4]$ {A = guanidinium} have also been studied [76].

The salt $[(CH_3)_3NH]_3[Mn_2Cl_7]$ has been observed to exhibit triboluminescence (the emission of light under an applied mechanical stress). Absorption and photoluminescence spectra have been measured and the relationship between pressure and the triboluminescence excitation discussed [77].

8.4.1.3 Bromides

The X-ray crystal structure of $RbMnBr_3$ has revealed that the Mn^{2+} ions are octahedrally coordinated by Br^- ions which reside in layers of composition $RbBr_3$ [78]. The optical absorption and luminescence spectra of Cs_3MnBr_5 have been reported to contain features characteristic of Mn^{2+} ions in a tetrahedral environment [79].

8.4.1.4 Iodides

The crystal and magnetic structures of the linear chain compound $CsMnI_3$ have been determined by measuring the Mössbauer spectrum of an ^{129}I labelled sample [80].

8.4.2 Oxides and hydroxides

Rotational and hyperfine structure has been observed in the electronic spectrum of MnO at *ca.* 550 nm [81]. The electrochemical oxidation of $Mn(OH)_2$ has been reported and two distinct stages observed, which were correlated with changes in crystal structure and composition [82].

X-ray powder diffraction and EPR analyses on a series of mixed oxide CaO-MnO samples, prepared by thermal decomposition of the mixed carbonates have shown the presence of a single phase, $(Ca_{1-x}Mn_x)O$ possessing the NaCl structure, across the whole composition range [83].

8.4.3 Carbonates, sulphates and phosphates

Two methods of preparation of $MnCO_3$ have been reported: from $Mn(OH)_2$ and CO_2 at 2400 atm and 160 °C [84] and by thermal decomposition of $Mn(C_2O_4).2H_2O$ at temperatures upto 420 °C under CO_2 at 2500 atm [85]. A detailed study of hydrated manganese(II) sulphites has identified two new species, $MnSO_3.2\frac{1}{2}H_2O$ and $MnSO_3.2H_2O$, which have been characterised by single-crystal X-ray studies [86]. Neutron diffraction studies on $MnSO_4$ have confirmed theoretical predictions that there are three successive magnetic phase transitions at 11.5, 10.5 and 7.2 K [87]. The reaction between SO_2 and MnO_2 has been studied: below 200 °C the products are a bidentate sulphato complex with C_{2v} symmetry and a tetrahedral sulphato complex; above 200 °C, $MnSO_4$ is formed [88]. The elastic properties of $K_2Mn_2(SO_4)_3$ have been measured [89]. Aqueous solutions of $MnSO_4$ have been characterised by measurements of their absorption spectra, osmotic coefficients [90], viscosity, vapour pressure and hydrogen solubility [91].

$Mn_3P_6O_{18}.9H_2O$ has been prepared by the reaction of $Mn(ClO_4)_2$ with $H_6P_6O_{18}$ in aqueous ethanol; the material was characterised by X-ray and IR measurements. Thermal decomposition of this material leads to the formation of $Mn_2P_4O_{12}$ [92]. The standard heat of formation of $Mn(H_2PO_4)_2.2H_2O$ has been calculated [93]. Manganese complexes with polymerised triallylphosphate have been prepared and their spectroscopic properties recorded [94].

8.4.4 Carboxylates

The magnetic properties of $Mn(O_2CMe)_2.4H_2O$ have been determined and analysed in terms of a theoretical model [95]. The co-crystallisation of Mn^{II} and M^{II} (M = Co, Ni or Zn) acetates from aqueous solutions has been reported to lead to the formation of a double salt, $Mn(O_2CMe)_2.M(O_2CMe)_2.2H_2O$, only in the case of zinc [96].

Spectral parameters of manganese(II) oxalates and their complexes with hydrazine have been determined [97] and their thermal decomposition studied [98].

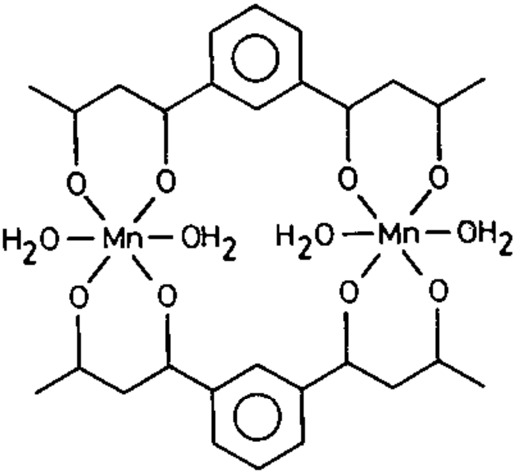
The complexes $[Mn(C_2O_4)L(H_2O)]$ {L = urea, thiourea, dmf, dmso, py, 4-Mepy, 3-Mepy, quin or morpholine} have also been investigated [99]. The preparation and characterisation of the complexes MnL_2 {HL = 2-oxocyclopentanoic acid [100] or phenoxyethanoic acid [101]} have been reported.

The complexes diaquabis(phenoxyethanoato)manganese(II) and diaquabis(4-chlorophenoxyethanato)manganese(II) have been shown by X-ray diffraction to be isostructural, with the water molecules mutually *trans* [102]. Complexes of manganese(II) with 1,2,4-benzenetricarboxylate have also been studied [103], and conductivity measurements have been made on solutions of $Mn(CF_3CO_2)_2$ in dmso [104].

8.4.5 Complexes with group VIB donor ligands

The preparations and properties of the complexes $Mn(thf)_2X_2$ {X = Cl, Br, I or NCS} have been reported by McAuliffe and coworkers. For X = Cl, Br or I, the complexes appear to be *pseudo*-octahedral polymers, whereas with $[NCS]^-$ a *pseudo*-tetrahedral monomer is formed. The reactions of the compounds with phosphines and subsequently with dioxygen have also been discussed [105] (see also section 8.12). $[Mn(4\text{-}CO_2\text{-}pyNO)_2(L)_2]$ {4-CO_2-pyNO = picolinate *N*-oxide; L = H_2O or D_2O} have been shown by IR spectroscopy to contain coordinated aqua-ligands and picolinate *N*-oxide coordinated *via* carboxyl and *N*-oxide atoms [106].

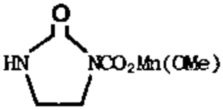
With nicotinic acid *N*-oxide (LH) or isonicotinic acid *N*-oxide (L'H) the pentacoordinate polymeric complexes $[Mn(LH_2)LCl]$ or $[Mn(L'H)L'Cl].4H_2O$ are formed, respectively [107,108]. On the basis of spectroscopic evidence, the complex $[Mn_2L_2(H_2O)_4]$ {L = 1,1-(1,3-phenylene)-bisdiene-1,3-butane} is believed to possess the structure (13) [109]. The powder diffraction pattern of



(13)

$[NH_4][MnL_3]$ {L = 4,4,4-trifluoro-1-(2-furyl)-1,3-butanedione} has shown it to be isomorphous with the corresponding cadmium complex, whose full structure was determined [110].

The salts $[Mn(acacH)_3][InCl_4]_2$ and $[Mn(etaaH)_3][InCl_4]_2$ {etaaH = ethyl 3-oxobutanoate}, containing cations in which the ligands are coordinated in their ketonic forms, have been prepared and characterised [111]. Wilkinson and coworkers have reported the preparations and properties of the polymeric complexes $[Mn(1\text{-ado})_2]_n$ and $[Mn(1\text{-admeo})_2]_n$ {1-ado = 1-adamantoxo; 1-admeo = 1-adamantylmethoxo} [112]. The X-ray crystal structure of the high-spin pentacoordinate complex $[Mn(dmu)Br_2]$ {dmu = *N*,*N'*-dimethylurea} has shown the complex to be trigonal pyramidal, with the bromo-ligands equatorial and with the equatorial dmu ligand being, unusually, linearly bonded ($Mn\hat{O}C$ = 180°) [113]. $[Mn(OMe)_2]$ is reported to react with imidazolidin-2-one and carbon dioxide to form the complex [114]. The compound $Mn\{OCH(CMe_3)_2\}_2$ has been prepared and its EPR and electronic

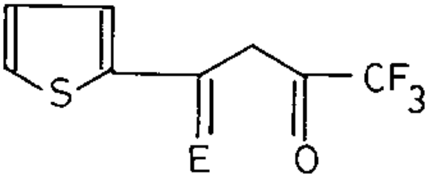


(14)

spectra recorded [115]. The 2,5-diphenyloxazole (PPO) complexes $[Mn(PPO)_nX_2]$ X = Cl, Br, I or SCN; n = 1,2 or 3 have been prepared and shown to be hexacoordinate and polymeric [116].

The X-ray crystal structure of hexaquamanganese(II) perchlorate 18-crown-6 has shown the Mn^{2+} ion to be in an octahedral aqua environment and to contain two crystallographically non-equivalent crown ether rings [117]. The crystal structure of the 12-crown-4 ether complex $[Mn(C_8H_{16}O_4)_2][Br_3]_2$ has also been reported. The manganese ion is found in a regular eight-coordinate square antiprismatic environment [118].

The preparations, spectral and magnetic properties of complexes $[Mn(acac)_2L_2]$ {L = H_2O, thiourea, phenylthiourea, benzoylthiourea, thiosemicarbazide, py, ½phen, ½bipy or ½(8-hydroxyquinoline)} have been reported [119], as have the complexes $[Mn(acac)_2L_x]$ {x = 1, L = py, 4-Mepy, pz, en, bipy or phen; x = 2, L = py, 4-Mepy, quinoxaline, quin or H_2O} [120]. The complexes $[MnL_2L'_2]$ {LH = thenoyltrifluoroacetone (15; E = O) or monothiothenoyltrifluoroacetone (15; E = S); L' = py or 4-Mepy} have been prepared [121]. The complexes of thiomalic acid (tmH_3), $A[Mn(tm)].nH_2O$ {A = Li; n = 3; A = Na or K; n = 2} and $[Mn(tmH)].2H_2O$ [122], have been prepared and characterised, stability constants have been calculated for a thiomalate complex [123] and for the cations $[Mn(tde)]^{2+}$ and $[Mn(tht)]^{2+}$ {tde = 2,2'-thiodiethanol; tht = tetrahydrothiophene} [124]. The thiourea complex $[Mn(tu)_4(H_2O)_2]Cl_2$ has also been studied [125]. Stability constants for the weak complexes formed by manganese(II) with 2,2'-thiodiethanol have been determined [126].



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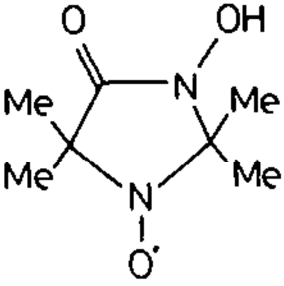
Complexes of manganese(II) with quinoline N-oxide [127], 4,6-dihydroxycoumaran-3-one [128], dihexylsulphoxide [129], 2- and 3-methylcyclohexanone α-hydroperoxides [130], hydroxycitronellal [131], 5-chloro-2-hydroxy-4-methylacetophenone [132], 2,6-dimethyl-4-pyrone [133], 4,5-dimethyl-2-hydroxyacetophenone and 3-bromo-2-hydroxy-5-methylacetophenone and their oximes [134], 8-caprylolactam [135], 6-caprolactam [136], 1,4-dioxane [137], 2,5-dihydroxybenzoic acid [138], di(2-ethylhexyl)phosphoric acid [139], trimorpholinophosphine oxide [140], 2-pyrrolidone [141] and phosphineacetic acids [142] have been studied, as have the complexes $[Mn(CF_3SO_3)_2]$ [143] and MnL_2 {HL = (16) [144], (17) or (18) [145]}.



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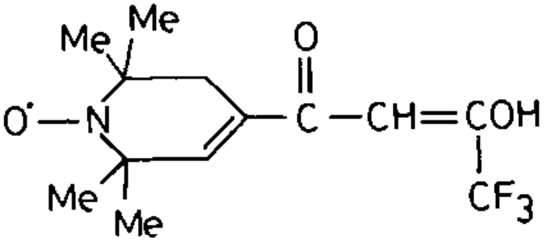

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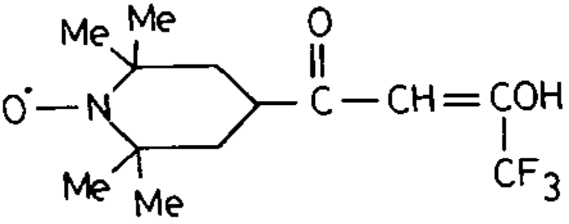

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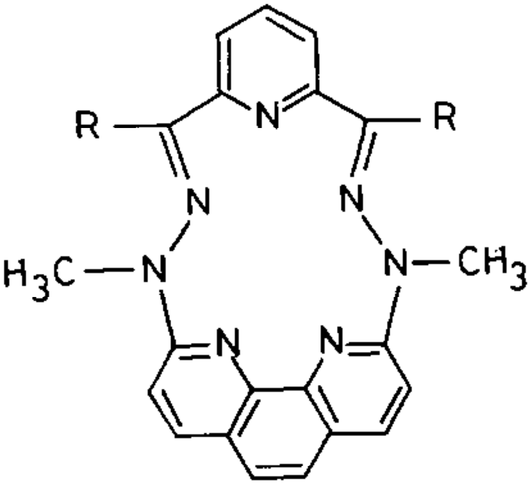
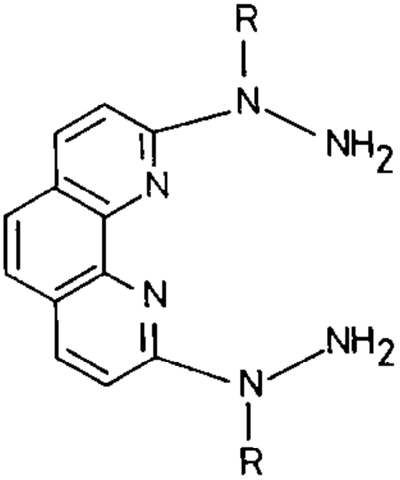
8.4.6 Complexes with nitrogen donor ligands

A series of manganese(II) complexes of the quinquedentate ligands (19) and their reduction products have been prepared and characterised by Lewis and coworkers. The crystal structure of [Mn(L)Cl][BF$_4$] {L = (19; R = Me)} shows this complex to be pentagonal pyramidal and that the ligand has a cavity size similar to that of porphyrins [146]. The same authors have also prepared complexes of



(19; R = H or Me)

the quadridentate ligands (20) [147].



(20; R = H or Me)

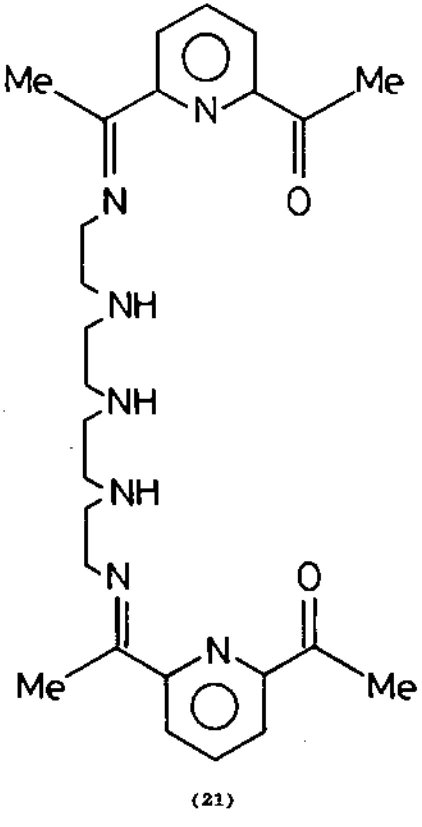
The crystal structure of $[Mn_2(L)_5(NCS)_4]$ {L = 4-methyltriazole} has been reported. Two Mn^{2+} ions are bridged by three methyltriazole groups, with two *N*-bonded $[NCS]^-$ ions and a monodentate methyltriazole group completing each $\{MnN_6\}$ octahedron [148]. The complex $[Mn(LL)_2(ClO_4)][ClO_4]$ {LL = bis(3,5-dimethylpyrazolyl)methane} has also been prepared and has one bidentate perchlorate anion in its coordination sphere [149]. Reaction of $[Mn_2(CO)_{10}]$ with a mixture of imidazole (imidH) and tetramethylimidazole has been reported to lead to formation of a compound 3Mn(imid)$_2$.2(imidH), whose crystal structure reveals a polymeric species containing both six- and four-coordinate Mn^{2+} ions [150]. The purine complex $[Mn(purH)_2(H_2O)_3]^{2+}$ has been prepared as its perchlorate salt; its structure is believed to be a linear oligomer involving unidentate terminal and bridging bidentate purine molecules, the octahedral coordination sphere about the manganese(II) being completed by three aqua ligands [151]. Liquid sulphur dioxide has been reported to stabilize the thiazyltrifluoride complex $[Mn(NSF_3)_4][AsF_6]_2$ [152].

The magnetic properties of the tetrameric fluoro-bridged species $[MnFL_3]_4[BF_4]_4$ {L = *N*-ethylimidazole} have been reported [153], as have those of $[Mn(4\text{-Ph-py})_2Cl_2]$ [154]. The electrochemical properties of $[Mn(L\text{-}L)_3]^{2+}$ {L-L = bipy, 4,4'-Ph$_2$bipy or 4,4'-Me$_2$bipy} have been investigated by AC and DC polarography and by DC cyclic voltammetry [155]. The thermal properties of the linear polymeric compound $[Mn(py)_2Cl_2]$ have been studied [156], as have the thermal decomposition of the complexes $[Mn(phen)_2X_2]$ {X = CN, CNO, NCS or NCSe} [157]. The far IR spectra of the complexes $[Mn(PhNH_2)_2X_2]$ (X = Cl or Br) have been reported [158].

Complexes of manganese(II) with 3,5-di(carboxymethylthio)-4-amino-4,1,2-triazole and 2,5-di(carboxymethylthio)-1,3,4-thiadiazole [159], 1-vinylimidazole [160], hexamethylenetetramine [161], 5-pyrazolone derivatives [162] and 3-methyl-2-hydrazinoquinoxaline [163] have been studied, as have the solution properties of some azide [164] and ethanenitrile [165] complexes. Some apparently dodecahedral complexes $[HR]_2[MnCl_4L_4]$ {R = *N*-cetylpyridine; L = a *N*-donor ligand} have been prepared [166].

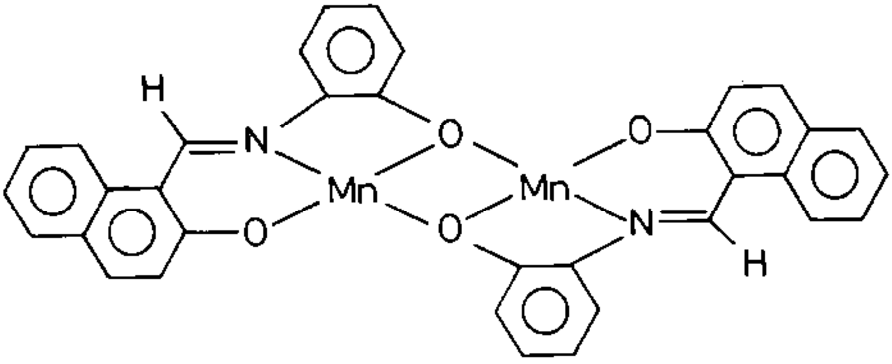
8.4.7 Complexes with mixed donor ligands

The preparation and properties of the eight-coordinate complex $[MnL][ClO_4]_2$ {L = **(21)**} have been reported [167]. The tridentate Schiff base ligand



(21)

N-(*o*-hydroxyphenyl)-5,6-benzosalicylideneimine (H_2nap) has been reported to form a binuclear square-planar complex $[\{Mn(nap)\}_2]$ **(22)** [168]. The ligand *N*-furfurylsalicylaldimine, which can exist in two isomeric forms **(23)** has been shown to complex with manganese(II) as **(23A)** [169]. $Mn(ClO_4)_2$ has been reported to react with *N*,*N*-bis(2-diethylaminoethyl)-2-hydroxyethylamine (bdhe) in



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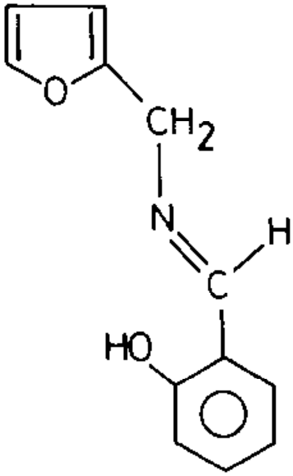

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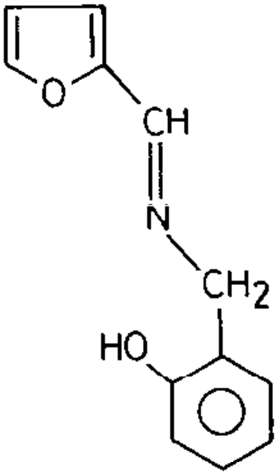


(23B)

propanone to give $[Mn_2(bdhe)_2][ClO_4]_2$, which contains a high-spin five-coordinate dimeric cation [170]. The crystal structures of $MnCl_2[NH_2CH_2P(O)(CH_3)OH]_2(H_2O)$ and $[Mn(NH_2CH_2P(O)(CH_3)OH)_2(H_2O)_2]Br_2.2H_2O$ have been published [171].

Other complexes of manganese(II) reported this year include, $A[MnL_3]$ {A = $[NBu_4]$ or $[PPh_4]$; HL = $CH_3C(NO)NOH$} [172] and those with the following ligands: benzaldehyde-, acetophenone- and benzophenone-(carbohydrazonemethyl) trimethylammonium chlorides [173], dibenzoylhydrazine [174], acetophenone- and anisaldehyde-hydrazones [175], α-benzoyl-β-phenylthiocarbamide [176], 5(3)-methylpyrazole-3(5)-carboxylic acid [177], L-hydroxyproline [178], orotic acid [179], salicylhydrazide and benzoylhydrazide [180], urotropine [181], Schiff bases derived from sulphamethoxypyridazine [182,183], 2-hydroxy-5-chlorobenzophenoneanil [184], *o*-(*N*-α-pyrrolylmethyleneamino)benzenesulphonic acid and 2-(*N*-α-pyrrolylmethyleneamino)ethanesulphonic acid [185], 8-furan-2-aldoxime [186], iso-nicotinic acid hydrazide [187], *o*-(*N*-α-furfuralideneimine)ethane [188] and benzene sulphonic acids [189], benzal-*o*-aminophenol derivatives [190], 2-benzofuran glyoxylaldehyde dioxime [191], α-amino-γ-methylthiobutyric acid [192], kojic acid [193], *N*-benzoyl-*N'*-phenylthiocarbamide derivatives [194], diethyldithiocarbamate with other *N*-donor ligands [195], the Schiff base derived from 2-hydroxy-5-methylacetophenone and *p*-toluidine [196], 5,5'-(4,4'-biphenydiylbisazo)bis(8-hydroxyquinoline) [197], thiodisuccinic acid [198], 4,6-dimethylpyrimidine-2-thione [199], iminodimethylphosphonic acid [200], *o*-(*N*-α-furfuralidenimino)benzoic acid and 3-(*N*-2-furfuralideneimino)propionic acid [201], 2-phenylacetohydroxamic acid [202], malonamide [203], sodium 1,2-naphthoquinone-4-sulphonate 2-semicarbazone [204], 1-phenyl-4-benzylamidothiosemicarbazone [205], *N*,*N'*-di(thiocarbamoyl)hydrazine [206], streptocide and albucid [207], isonicotine hydrazide [208], *N*-thiobenzoyl-*N*-phenylhydroxylamine [209], malonic acid diamide [210], pyrazine-2-carboxylic acid [211], 10-(2-pyridylazo)-9-phenanthrol [212], urazole [213], thiophene-2-aldoxime [214], ethyl xanthate [215], *p*-fluoro-, *p*-chloro, *p*-bromo, *p*-methylbenzoylacetones and 1-(4-fluorophenyl)-1,3-pentanedione [216], 3,5-diphenylisoxazole, 3-amino-5-methylisoxazole and 5-amino-3,4-dimethylisoxazole [217], 9-methylhypoxanthine [218], cinnamoylhydrazine [219], acrylamide [220], hydrazodithioamide [221], 2-hydroxymethylbenzimidazole [222], 2-hydroxy-5-chlorobenzophenone-*o*-tolil [223], cyclohexanonesemicarbazone and thiosemicarbazone [224], 1-(2-pyridylazo)-2-naphthol and 1-(2-pyridylazo)-2-phenanthrol [225], the Schiff base derived from *o*-aminobenzoic acid and terephthalaldehyde [226], tetramethyl ethylenediaminetetracetate [227], *N*-phenyl-2-furohydroxamic acid [228], hydrazodicarbonamide [229], and numerous sulpha-drugs [230].

8.5 MANGANESE(I)

Vibrational analysis of the isocyanide complexes $[Mn(RNC)_6]^+$ (R = CH_3, C_6H_5 or 4-Cl-C_6H_4) has provided evidence for distortion from the expected octahedral geometry [231].

8.6 CARBONYL COMPLEXES

8.6.1 Carbonyls and hydridocarbonyls

The photochemical reactions of $[Mn_2(CO)_{10}]$ with I_2, CH_3I, SnI_4, $CuCl_2.2H_2O$, HgX_2 (X = Cl, Br or I), C_6H_5HgI, $[(cp)Cr(NO)_2Cl]$, $[(cp)_2Cr_2(NO)_4]$ or $[Co_2(CNCH_3)_{10}][BF_4]_4$ have been studied in solution. The initial step of these reactions is the homolytic cleavage of the Mn-Mn bond to give the radical $[Mn(CO)_5]\cdot$. Isolable species include $[Mn(CO)_5X]$, $[Mn(CO)_5HgX]$, $[Mn(CO)_5]_2Hg$,

$[Mn(CO)_4(NO)]$, $[Mn_2(CO)_9(CNCH_3)]$ and $[Mn(CO)(CNCH_3)_5]^+$ [232].

$[HMn(CO)_5]$, when reacted with HO_3SCF_3, gives the coordinatively unsaturated cation $[Mn(CO)_5]^+$ with the evolution of dihydrogen, thus demonstrating the hydridic character of the hydrogen attached to the metal, well known to behave as a weak acid [233].

8.6.2 Halides

It has been shown that photolysis of $[Mn(CO)_5X]$ {X = Cl, Br or I} at high dilutions in argon or methane matrices at 12 K results in the formation of the new trigonal bipyramidal species $[Mn(CO)_4X]$, in which the halo-ligand is equatorial [234]. Adducts of the type $[Mn(CO)_8L_2(BR_2)_n]$ {n = 1 or 2} have been postulated as intermediates in the reaction of $[Mn_2(CO)_{10-n}L_n]$ {L = $P(OMe)_3$; n = 1 or 2} with bromine [235]. Bromination of $[(cp)Mn(CO)_2(PPh_3)]$ has been reported to produce the species $[(cp)Mn(CO)_2(PPh_3)Br][Br_3]$ [236].

8.6.3 Complexes with oxygen donor ligands

The compound $[Mn(CO)_5(H_2O)][BPh_4].nH_2O$ has been isolated by reaction of $[Mn(CO)_5(OClO_3)]$ with water in dichloromethane. The yellow crystalline compound is formed on addition of $Na[BPh_4]$, and although unstable at room temperature, has been characterised at low temperature by IR spectroscopy. It is reported that the aqua ligand is replaced by solvent in ethanenitrile and possibly also in propanone [237].

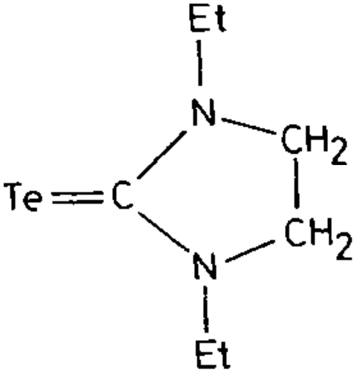
$[Mn_3(CO)_9(\mu_3\text{-}OEt)_2(\mu_2\text{-}OEt)]$, when reacted with BX_3 {X = F, Cl, Br or I} or with anhydrous HX {X = Cl or Br}, forms the corresponding $[Mn_3(CO)_9(\mu_3\text{-}OEt)_2(\mu_2\text{-}X)]$ complex. The crystal structures of these species and also of $[Mn_3(CO)_8(PMe_2Ph)(\mu_3\text{-}OEt)_2(\mu_2\text{-}OEt)]$ have been determined [238].

The products of thermal and photochemical reactions of $[Mn_2(CO)_{10}]$ with electron-acceptor molecules, such as acenaphthenquinone, 9,10-phenanthrenequinone, tetrachloro-1,2-benzoqninone, tetracyanoquinodimethane or 2,3-dichloro-5,6-cyano-1,4-benzoquinone, have been studied by EPR spectroscopy [239]. In a similar study, the reactions of quinones and α-diketones with $[Mn_2(CO)_{10}]$,$[(Me_3Sn)Mn(CO)_5]$, or $[(Me_2Sn)\{Mn(CO)_5\}_2]$ have been studied, and the mechanisms observed to be different for reaction with 1,4-quinones than for reaction with 1,2-quinones or α-diketones [240].

8.6.4 Complexes with sulphur or tellurium donor ligands

The bridged binuclear complex $A[(CO)_3Mn(\mu\text{-}mtb)_3Mn(CO)_3]$ {A = K or Cs; mtb = monothiobenzoate} has been prepared and characterised. The crystal structure of the rhenium analogue has octahedral coordination, with two octahedra sharing a common face. The mtb ligand only bonds *via* the sulphur atom [241].

The synthesis of a tellourea complex, *cis*[Mn(Br)(CO)$_4$L] {L = (24)}, has been reported [242].



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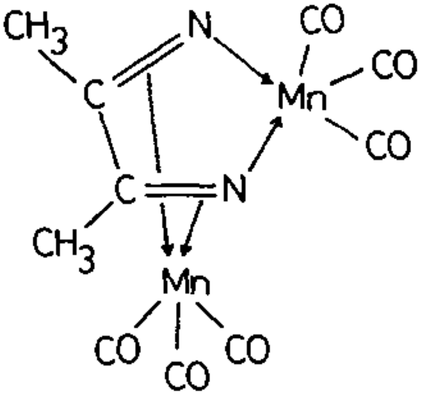
8.6.5 *Complexes with nitrogen donor ligands*

The crystal structure of [{(cp)Mn(CO)$_2$}$_2$(μ-N$_2$)] has been determined; the N-N distance of 0.1118 nm is the shortest so far recorded for a bridging dinitrogen moiety [243]. The crystal structures of the novel aryldiazenido complexes [(Mecp)Mn(CO)$_2$(N$_2$R)][BF$_4$] {R = 2-CF$_3$C$_6$H$_4$, 2-FC$_6$H$_4$ or C$_6$H$_5$} have also been determined. These compounds react with nucleophiles such as Cl$^-$, Br$^-$, I$^-$, CN$^-$ or SCN$^-$ to give the dinitrogen complex [(Mecp)Mn(CO)$_2$(N$_2$)] [244].

Reaction of [Mn(CO)$_4$(CNCH$_3$)]$^-$ with CH$_3$I gives the complex (25), whose crystal structure has been determined [245]. NCNSF$_2$ and NCNSOF$_2$ have been reported to yield *N*-bonded complexes [(CO)$_5$Mn(NCNSF$_2$)][AsF$_6$] and



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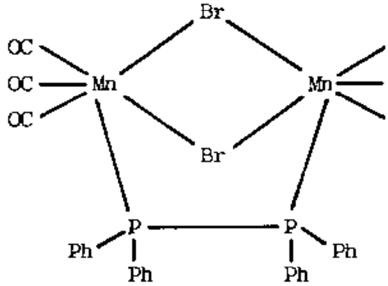
$[(CO)_5Mn(NCNSOF_2)][AsF_6]$, respectively, when reacted with $[(CO)_5Mn(SO_2)][AsF_6]$ [246].

The photolysis of $[Mn_2(CO)_{10}]$ in the presence of a variety of *N*–donor ligands has been studied [247]. Reaction of $[Mn(CO)_5(CH_3CN)][BF_4]$ with pyridine in nitromethane has been reported to yield $[Mn(CO)_3(py)_3]^+$ **(26)**, whereas in ethanenitrile $[Mn(CO)_5(py)]^+$ **(27)** is the principal product. **(27)** reacts with pyridine in nitromethane to yield **(26)** [248]. The complexes $A[Mn(CO)_5]_x$.bipy (A = Zn or Cd; x = 2; A = In; x = 3) have been prepared by the electrochemical oxidation of A in the presence of $[Mn_2(CO)_{10}]$ and bipy [249].

8.6.6 Complexes with phosphorus or arsenic donor ligands

$[Mn(CO)_5Br]$ has been reacted with P_2Ph_4 to form the complex **(28)**, whose



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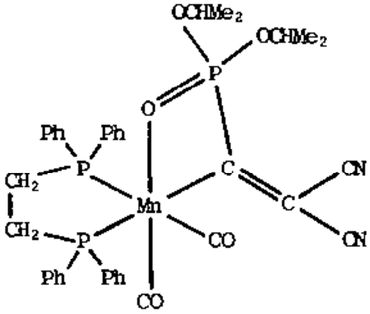
X-ray crystal structure has been determined [250]. The crystal structure of $[PPh_4][Mn(CO)_4(PPh_3)]$ has also been determined and the triphenylphosphine ligand shown to occupy an axial position in a distorted trigonal bipyramidal geometry [251].

$[Me_4N][cis\text{-}(CO)_4Mn(COCH_3)(COC_6H_5)]$ has been reported to decompose in the presence of triphenyl phosphine to give $[Me_4N][Mn(CO)_4(PPh_3)]$ and evidence presented for an $[Mn(CO)_4]^-$ intermediate; ^{13}C labelling experiments have enabled a mechanism to be postulated [252]. A study has been made of the effects of substituents on the strength of Mn–Mn bonds, by investigating the kinetics of thermal decomposition of some $[Mn_2(CO)_8L_2]$ {L = $PPhEt_2$, PPh_2Et, $PPh(OMe)_2$, $PPh_2(OMe)$ or $P(4\text{-}MeOC_6H_4)_3$} complexes; the data have been discussed in terms of both electronic and steric factors [253]. The potentially tridentate ligand $CH_3C(CH_2PPh_2)_3$ has been used to synthesise a variety of manganese(I) carbonyl phosphine complexes, which have been characterised by spectroscopic and conductivity measurements [254].

The reactions of (1-chloro-2,2-dicyanovinyl)manganese derivatives with trialkylphosphites lead to the formation of a series of 2,2-dicyanovinylphosphonato manganese complexes, whose spectroscopic properties suggest that the $(NC)_2C{=}CP(O)(OR)_2$ ligands are bidentate, coordinating *via* a vinylic carbon atom and a phosphoryl oxygen atom [255]. This has been confirmed by the determination of the crystal structure of the compound (29), a product of the reaction between *fac*-$[(NC)_2C{=}C(Cl)Mn(CO)_3(dppe)]$ and tris(isopropyl)phosphite [256]. The reactions of (1-chloro-2,2-dicyanovinyl)manganese derivatives with tris(dialkylamino)phosphines proceed by a very different route to those with trialkylphosphites. A novel dialkylamino transfer from phosphorus to carbon occurs giving dicyanoketeneimmonium derivatives. With secondary amines, novel dialkylcarbamoyl derivatives are formed [257].



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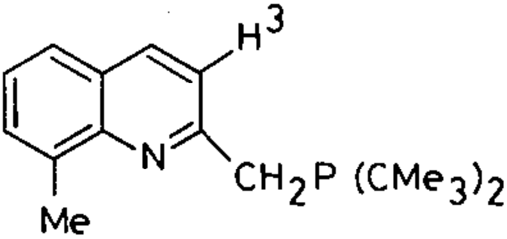
Two manganese complexes of the ligand mqp (30) have been isolated, and formulated as $[MnBr(CO)_4(mqp)]$, containing an unidentate mqp ligand, and $[Mn(CO)_4(mqp\text{-}H^3)]$, in which the mqp ligand is metallated at the 3-position [258]. The reaction of $[Mn_2(CO)_{10}]$ with the sterically constrained ligand $P(OCH_2)_3CEt$ (=L) has produced a mixture of isomers of the complexes $[Mn_2(CO)_{10-x}L_x]$ (x = 1,2,3 or 4). Reaction of $[Mn_2(CO)_6L_4]$ in xylene has produced the hydrides *mer-trans*-$[MnH(CO)_3L_2]$, *mer*-$[MnH(CO)_2L_3]$ and



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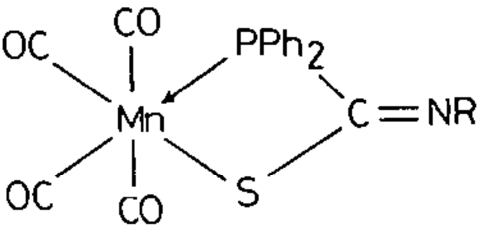
trans-[$MnH(CO)_2L_3$]. The complexes have been characterised by IR and ^1H n.m.r. spectroscopy [259]. Stepwise replacement of CO in [$MnH(CO)_5$] by L has led to the formation of the complex *cis*-[$MnH(CO)_4L$], as well as those described above. This method of preparation has also been utilised to prepare some of the corresponding deuteride complexes. The interconversion of *mer-trans-* and *mer-cis*-[$MnX(CO)_2L_3$] {X = H or D} has also been studied. Heating [$MnH(CO)_4L$] in solution gave either [{$Mn(CO)_4L_2$}] with hydrocarbon solvents or [$MnCl(CO)_4L$] with chlorinated solvents [260].

The reactions of [$Mn(CO)_5X$] (X = Cl, Br or I) with $Me_3SiN(R)C(S)PPh_2$ (R = Ph or Me), prepared from Me_3SiPPh_2 and RNCS, have been studied; when X = Cl and R = Me or Ph the complexes **(31)** are produced but when X = Br or I and R = Ph,



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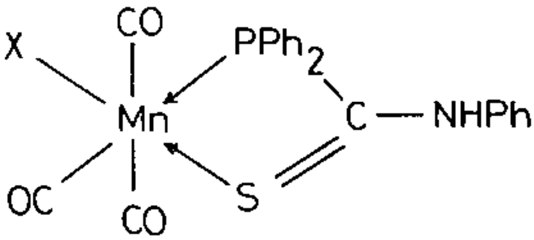


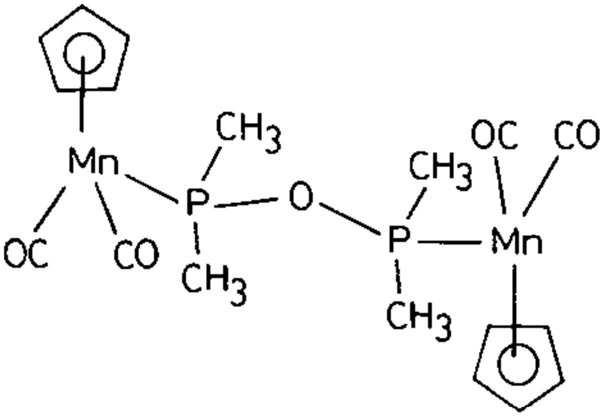
(32)

the complexes **(32)** are formed [261].

The structure of the first hexanuclear manganese complex [$Mn_6(CO)_9\{OP(OEt)_2\}_9$] has been determined [262]. The complex is paramagnetic and no evidence was obtained for metal-metal bonding interactions. There are two distinct types of manganese atom present: three are coordinated in approximately trigonal bipyramidal fashion by five oxygen atoms from the [$OP(OEt)_2$]$^-$ ligands, whilst the other three metal atoms are each coordinated by three phosphorus atoms and three carbonyl groups [262].

The crystal structure of μ-{oxybis(dimethylphosphane)bis-{dicarbonyl(η^5-cyclopentadienyl)manganese(I)} **(33)** has been determined [263]. Reaction of [$(Rcp)Mn(CO)_2(thf)$] (R = H or Me) with the phosphorins L, **(34)** and **(35)**, has led to the formation of the σ-phosphorin complexes [$(Rcp)Mn(CO)_2L$]. Irradiation of [$(cp)Mn(CO)_2$**(34)**] leads to formation of [$(cp)Mn\{\eta^6$-**(34)**$\}$], whilst irradiation of [$(Mecp)Mn(CO)_2$**(35)**] gives two products, one of which has been assigned the σ-π structure **(36)** [264]. Photochemical reaction of [$(Mecp)Mn(CO)_3$] with 2,4-dimethyl-2,3-diazaphosphole **(37**; L**)** in thf gives the complex [$(Mecp)Mn(CO)_2L$], in which the phosphole is coordinated *via* the non-basic phosphorus atom, rather than the basic nitrogen [265].

Reaction of [$HMn(CO)_5$] with triphenylarsine in the presence of dioxygen has been reported to lead to the formation of *cis*- and *trans*-isomers of


Mn
OC
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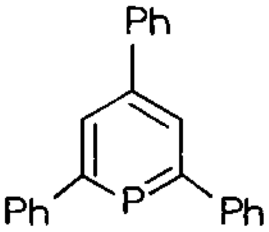
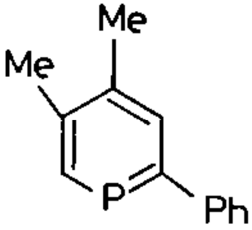
CH3
CH3
O
P
CH3
CH3
OC
CO
Mn

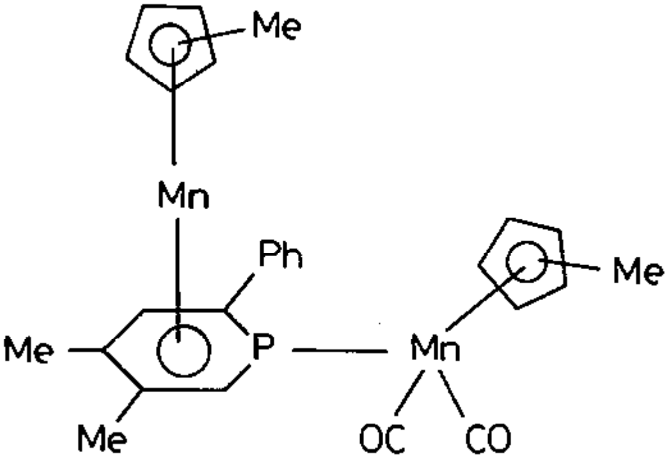
(33)


Ph
Ph
P
Ph

(34)


Me
Me
P
Ph

(35)


Me
Mn
Ph
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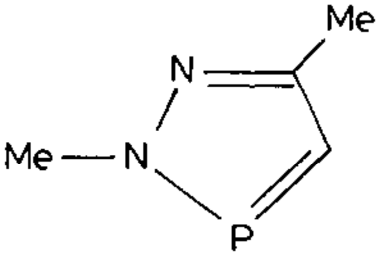
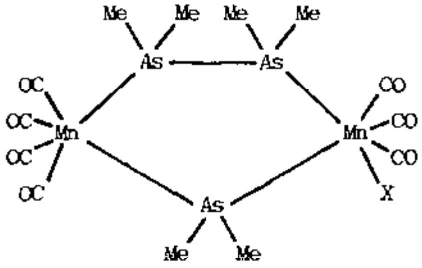
Mn
Me
Me
OC
CO

(36)



(37)

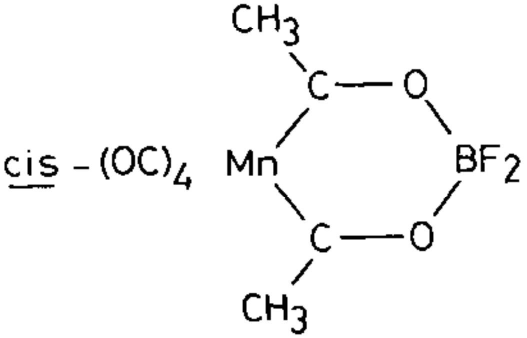
[Mn$_2$(CO)$_9$(AsPh$_3$)] [266]. Complexes of formulation [Mn$_2$(CO)$_7$X(AsMe$_2$)$_3$] (X = Cl or Br) have been prepared and identified crystallographically as having the inorganic five-membered heterocyclic structure (38) [267].



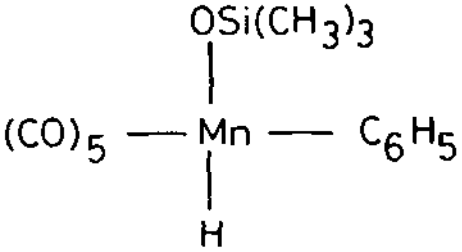
(38)

8.6.7 Organometallic complexes

Photolysis of [Mn(CO)$_5$R] (R = CH$_3$ or CH$_3$CO) at high dilutions in argon, methane or carbon monoxide matrices at 12 K has been shown by IR spectroscopy to yield the new pentacoordinate complexes [Mn(CO)$_4$R] [268]. The complex



(39)



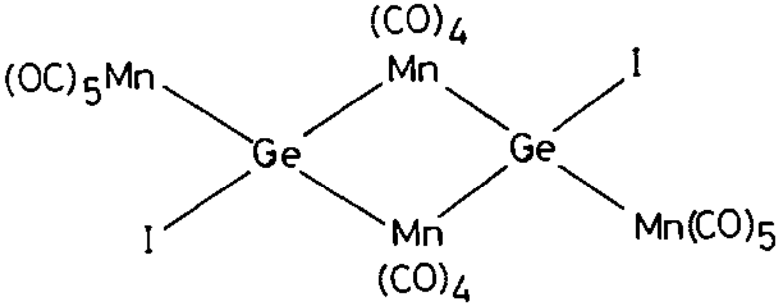
(40)

cis-$[(OC)_4Mn(CH_3CO)_2]Li$ is reported to react with BF_3 in dichloromethane at 0 °C to give the compound (39) [269]. Reaction of $[(OC)_5Mn\{Si(CH_3)_3\}]$ with benzaldehyde at 5 °C gives complex (40) which, on warming, decomposes to yield $[Mn_2(CO)_{10}]$ [270]. The acyloxymethyl complex $[(OC)_5MnCH_2OC(O)C(CH_3)_3]$ has been prepared from $Na[Mn(CO)_5]$ and used as a model for catalytic reactions converting synthesis gas into methanol and ethane-1,2-diol [271].

8.6.8 Germyl and stannyl complexes

It has been reported that the complex $[(Ph_2Sn)\{Mn(CO)_5\}_2]$ undergoes an insertion reaction with SO_2 to form the compound $[\{(PhSO_2)_2Sn\}\{Mn(CO)_5\}_2].SO_2$ which was characterised by IR spectroscopy [272]. Spectroscopic properties, and the photochemistry and electrochemistry of the complexes $[(Ph_3E)Mn(CO)_3(L\text{-}L)]$ {E = Sn or Ge; L-L = phen or biquinoline} have been reported [273].

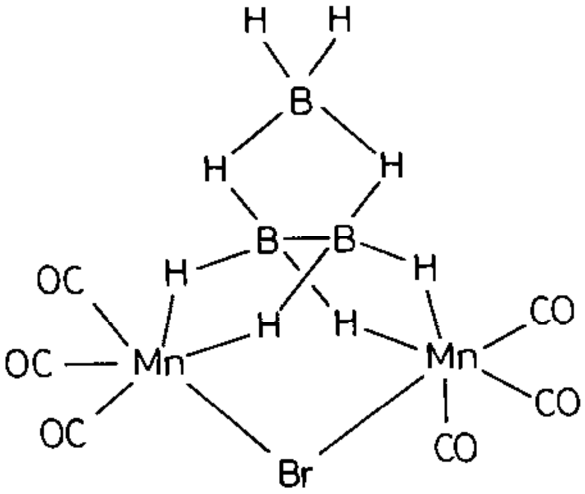
The polygermane manganese carbonyl complexes $[Mn(CO)_5GeX(GeH_3)_2]$ and $[Mn(CO)_5GeX_2GeX_2Mn(CO)_5]$ {X = H or Cl} have been synthesised and studied using the techniques of ^1H NMR, IR and Raman spectroscopy and mass spectrometry [274]. The X-ray crystal structure of the complex $[Mn_2(CO)_8\{\mu\text{-}GeMn(CO)_5I\}_2]$ (41) has been determined. The complex contains a planar Mn_2Ge_2 rhombus and has a Mn-Mn distance of 0.2934 nm [275].



(41)

8.6.9 Complexes with Group IIIB ligands

The crystal structure determination on $[(CO)_4Mn(B_3H_7Br)]$ at 173 K has revealed that the B_3H_7Br ligand coordinates by two Mn-H-B bridge bonds from different boron atoms [276]. The synthesis and characterisation of $[(\mu\text{-}X)Mn_2(CO)_6(B_3H_8)]$ (42) {X = Cl or Br} has been reported and the crystal structure of the bromo-compound determined [277]. The two Mn atoms are bridged by the bromine atom, and also by the bis(bidentate) $[B_3H_8]^-$ anion, giving a *pseudo*-octahedral environment about both metal centres. There



(42)

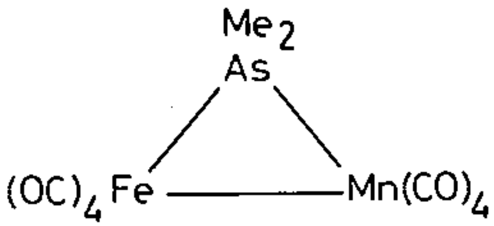
appears to be no metal-metal bond present. Reaction of [$HMn(CO)_5$] with B_5H_9 leads to formation of [$(OC)_3Mn(B_5H_{10})$]. This may, in turn, be converted to [$Br(OC)_3Mn(B_5H_9)$] or Na[$(OC)_3Mn(B_5H_9)$] by reaction with Br_2 or NaH, respectively [278].

The compound [NPr_4][$(Ph_3In)Mn(CO)_5$] has been prepared by reaction of [NPr_4][$Mn(CO)_5$] with Ph_3In in CH_2Cl_2. Analogous compounds with Ph_3Al and Ph_3Ga were found to be thermally unstable and could not be isolated [279].

8.6.10 Mixed-metal carbonyls

The reactions of [$MnRe(CO)_{10}$] with the phosphines Ph_3P, Bu_3P and $(PhO)_3P$ have been studied. The rhenium substituted products are formed almost exclusively, although under certain conditions the bis-substituted products are sometimes formed [280]. The mixed-metal carbon disulphide complexes [$(triphos)Co(\mu\text{-}CS_2)Mn(CO)_2Cp$] [281] and [$L_2(CO)_2Fe(\mu\text{-}CS_2)Mn(CO)_2Cp$] {L = $P(OMe)_3$, PMe_2Ph or PMe_3} [282] have been prepared. The crystal structure of the iron PMe_2Ph complex shows that the CS_2 ligand is η^2-bonded to the Fe atom and σ-bonded to Mn *via* the second S atom.

The compound **(43)** reacts with $Me_2E\text{-}NMe_2$ {E = P or As} to give [$(OC)_4Fe(\mu\text{-}AsMe_2)Mn(CO)_4(EMe_2NMe_2)$] **(44)**, which with HCl give [$(OC)_4Fe(\mu\text{-}AsMe_2)Mn(CO)_4(EMe_2Cl)$] **(45)**. **(43)** reacts with Me_2PCl to give **(45)** but with Me_2AsCl a rearrangement occurs, giving the ionic compound [$(OC)_4Fe(\mu\text{-}AsMe_2)_2Mn(CO)_4$]$^+$ [$(OC)_4Fe(\mu\text{-}AsMe_2)Mn(CO)_4Cl$]$^-$, whose crystal structure has been reported [283]. The complex [$(OC)_4Fe(\mu\text{-}AsMe_2)Mn(CO)_5$] can undergo



(43)

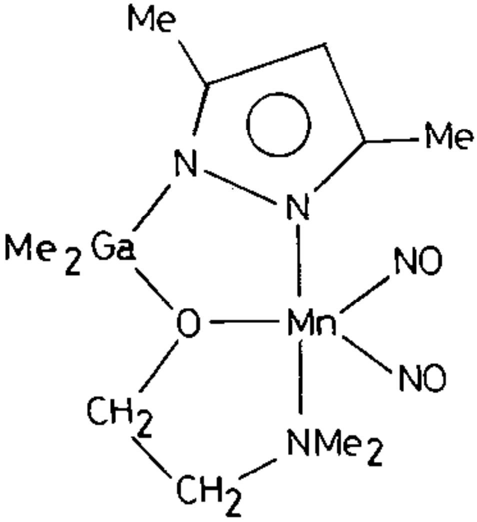
repeated metal-metal bond formation and cleavage by elimination of CO and addition of a phosphine ligand PR_3 {R = Me or OMe}. In each case, the phosphine ligand is added to the manganese atom but can be transferred to the iron atom by rearrangement. These reactions have allowed the preparation of forty one new complexes [284]. The metal-metal bonded species $[Cp(CO)_2Mn(\mu\text{-}AsMe_2)Co(CO)_3]$ (46) and compound (43) react with Me_2PCl or Me_2PPMe_2, respectively to give the non-metal-metal bonded species $[Cp(CO)_2Mn(\mu\text{-}AsMe_2)Co(CO)_3(PMe_2Cl)]$ or $[(OC)_4Fe(\mu\text{-}AsMe_2)Mn(CO)_4(PMe_2PMe_2)]$, respectively. Hydrolysis of the former leads to the tetranuclear species $[Cp(CO)_2Mn(\mu\text{-}AsMe_2)Co(CO)_3(\mu\text{-}PMe_2OPMe_2)Co(CO)_3(\mu\text{-}AsMe_2)Mn(CO)_2Cp]$, whilst the latter reacts with $[(nbd)Cr(CO)_4]$ or $[Fe(CO)_2(NO)_2]$ to give the pentanuclear species $[(OC)_4Fe(\mu\text{-}AsMe_2)Mn(CO)_4(\mu\text{-}PMe_2PMe_2)M(\mu\text{-}PMe_2PMe_2)Mn(CO)_4(\mu\text{-}AsMe_2)Fe(CO)_4]$ {M = $Cr(CO)_4$ or $Fe(NO)_2$} [285]. (46) or (43) also react with $[M(AsMe_2)]$ {M = $Fe(Cp)(CO)_2$, $Cr(Cp)(CO)_3$, $Mo(Cp)(CO)_3$, $W(Cp)(CO)_3$, $Fe(Cp)(CO)PMe_3$, $Cr(Cp)(CO)_2PMe_3$, $Mo(Cp)(CO)_2PMe_3$ or $W(Cp)(CO)_2PMe_3$}, to give the species $[Cp(CO)_2Mn(\mu\text{-}AsMe_2)Co(CO)_3(\mu\text{-}AsMe_2)M]$ or $[(OC)_4Fe(\mu\text{-}AsMe_2)Mn(CO)_4(\mu\text{-}AsMe_2)M]$, respectively [286].

The synthesis and crystal structure of the chiral complex $[Mn_2Pt(\mu_2\text{-}PPh_2)_2(CO)_9]$ have been reported. The compound has a non-linear metal skeleton with $Mn\text{-}\hat{Pt}\text{-}Mn = 159.56^\circ$ [287]. The series of heterobinuclear complexes $[Cp(CO)_2Mn(\mu\text{-}N_2H_4)Cr(CO)_5]$, $[Cp(CO)_2Mn(\mu\text{-}N_2H_2)Cr(CO)_5]$ and $[Cp(CO)_2Mn(\mu\text{-}N_2)Cr(CO)_5]$ have been prepared and characterised [288].

8.7 NITROSYL COMPLEXES

Hartree-Fock and configuration interaction calculations have been applied to the hypothetical linear species MnNO. The implications of the results have been examined with respect to the known molecule $[Mn(CO)_4(NO)]$ [289]. A molecular orbital study of the structure and reactivity of $[Mn(CN)_5(NO)]^{3-}$ has been described [290] and its thermal decomposition studied [291].

The crystal structure of $[Mn(NO)_3(PPh_3)]$ has been determined, this being the first such determination for a mononuclear metal trinitrosyl complex. The coordination geometry is tetrahedral, all of the NO groups are almost linearly bonded with Mn-$\hat{N}$-O = 177.2° [292]. The crystal structure of {2,12-di(2-pyridyl)-3,7,11-triazatrideca-2,11-diene}nitrosylmanganese diperchlorate has also been reported; it possesses approximately octahedral {MnN_6} coordination geometry [293]. The novel, five-coordinate, complex [$(Me_2Ga)(N_2C_5H_7)(OCH_2CH_2NMe_2)Mn(NO)_2$] has been synthesised. The crystal structure of the iron analogue indicates that it has the distorted trigonal bipyramidal geometry structure **(47)** [294].



(47)

The previously unknown iodonitrosyl complexes [(Rcp)Mn(CO)(NO)I] **(48**; R = H or Me**)** have been prepared, either by reaction of [{(Rcp)Mn(CO)(NO)}$_2$] **(49)** with I_2 or by reaction of [$(Rcp)Mn(CO)_2(NO)$][PF_6] with KI [295]. Complexes **(48)** react with Na[$AlH_2(OCH_2CH_2OCH_3)_2$] to form **(49)**, while [$(Mecp)Mn(NO)(PPh_3)I$] forms the hydridonitrosyl species [$(Mecp)Mn(NO)(PPh_3)H$] [296]. EPR spectra have been reported for the complexes [$Mn(NO)(dtc)_2Cl$] and [$Mn(NO)(dtc)_2(sa)$] (dtc = dithiocarbamate; sa = a thiourea derivative formed by partial decomposition of the dithiocarbamate in the reaction mixture) [297].

8.8 MIXED OXIDATION STATE COMPLEXES

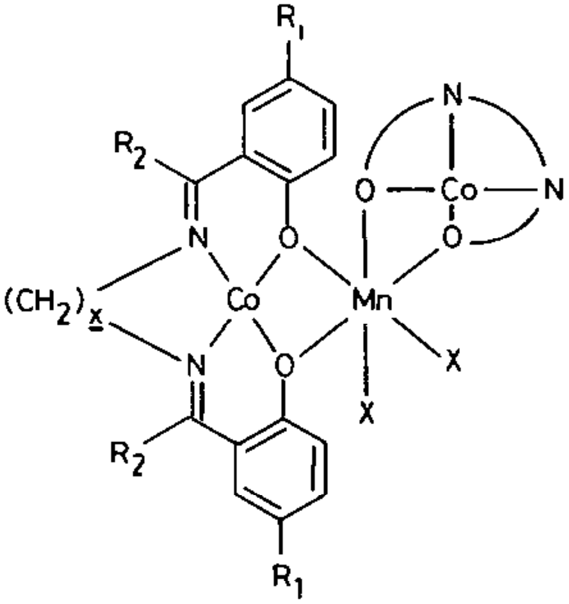
The complex [$Mn(H_2O)_2(O_2CMe)_3$] reacts with 3-chloropyridine to form the trinuclear mixed oxidation state complex [$Mn_3(3\text{-}Clpy)_3O(O_2CMe)_6$], in which the Mn(II) atom is crystallographically distinguishable from the two Mn(III) atoms [298]. Reaction of [$MnCl_3L_2$] {L = dioxane} with ligands L' {L' = 3-ethylpyridine *N*-oxide or 4-ethylpyridine *N*-oxide} in ethanol yields the mixed oxidation state complexes [$Mn_2Cl_5L'_4(EtOH)$]. It was proposed that the compound consists of Cl-bridged octahedral dimers in solution [299]. The photo-induced electron-transfer reactions of the mixed oxidation state complex $[(bipy)_2Mn(\mu\text{-}O)_2Mn(bipy)_2][ClO_4]_3$ in the presence of organic species such as anthracene have been studied; with 9,10-dicyanoanthracene photochemical oxidation of water was observed [300].

The final product of hydrolysis of $Na_3[Mn(CN)_6]$ in perchloric acid is reported to be the compound $Mn(CN)_3.0.57H_2O$. An analysis of structural, magnetic and spectroscopic data has shown that the compound is of Prussian blue type, containing six-fold *N*-coordinated Mn(II) and six-fold *C*-coordinated Mn(IV) in a cubic face-centred lattice and its magnetic properties were discussed in some detail [301].

Crystals of Mn_3O_4 have been grown in a $K_2[S_2O_7]$ flux [302].

8.9 HETERONUCLEAR COMPLEXES

The compounds $Cd(ECN)_4Mn$ (E = S or Se) have been prepared and characterised by X-ray powder diffraction, spectroscopic and magnetochemical measurements. The $[ECN]^-$ ligand is coordinated to cadmium *via S* or *Se*, and to manganese *via N* resulting in a high-spin tetrahedral complex [303]. The synthesis and magnetic properties of the complexes (50) have been reported [304].



(50; R_1, R_2 = H or CH_3; x = 2 or 3; X = Cl or Br)

The complexes $Mn_2^{II}[Fe(CN)_6]$ and $Mn_3^{II}[Fe(CN)_6]_2$ have been prepared and their magnetic and optical properties reported [305] and the materials $A_{18}Mn_{11}[Fe(CN)_6]_{10}$

(A = K or [NH_4]) also isolated [306]. The double fluoride heptahydrates $M^{II}M^{III}F_5.7H_2O$ {M^{II} = Mn, Fe, Co or Ni; M^{III} = Cr, V, Mn or Fe} have been prepared and their thermal decomposition studied [307]. The crystal structure of $MnUO_2(SO_4)_2.5H_2O$ has shown that the manganese atom is octahedrally coordinated, whilst the uranium atom is in a pentagonal bipyramidal environment [308]. The synthesis and magnetic properties of the μ-oxoiodoethanoate complex [$Fe_2MnO(ICH_2CO_2)_6(H_2O)_3$] have been reported [309]. A 2:1 adduct of chloro(*N*-{2-(dimethylamino)ethyl}salicylideneaminato)copper(II) with $MnCl_2$ has been isolated and characterised [310].

8.10 PORPHYRIN AND PHTHALOCYANINE COMPLEXES

It has been reported that reaction of Mn^{III}(TPP)Cl with iodosylbenzene in dichloromethane leads to the formation of a black microcrystalline solid which has been formulated as Mn^{V}(TPP)(O)Cl, containing occluded iodosylbenzene; its magnetic and spectral properties, together with some of its reactions have been studied [311].

The reactions of manganese(II) porphyrin complexes with dioxygen have been reviewed [312]. There is considerable controversy over whether the products of the reactions are best formulated as [Mn^{III}(porphyrin)(O_2^-)] or [Mn^{IV}(porphyrin)(O_2^{2-})]. EHMO calculations on both species have been performed, and they suggest that only the formulation [Mn^{IV}(porphyrin)(O_2^{2-})] gives agreement with observed optical parameters [313,314]. O = Mn^{IV}(TPP) has been prepared by oxygen transfer from iodosylbenzene to Mn^{II}(TPP); [Mn^{III}(TPP)][O_2CMe] is reported not to react under similar conditions. Spectral similarities suggest that Mn(IV) porphyrins prepared by other routes exist as oxo species in aqueous solution [315]. Mn^{III}(TPP)Cl, in conjunction with Na[BH_4] and air, has been shown to oxidise cyclohexene to give predominantly cyclohexanol (with some cyclohexenol). The active species was shown to be Mn(TPP) and two possible intermediates [Mn^{IV}(TPP)(O_2^{2-})] and [Mn^{III}(TPP)(O_2^-)] have been suggested [316]. The reactions of tetrabutylammonium imidazolate [Bu_4N][imid], with Mn(TPP) or $Mn(TPP)^+$ have been studied. By steric and stoicheiometric control, it has proved possible to isolate complexes with several different coordination numbers and spin states, including the first example of a low-spin manganese(III) porphyrin complex [Bu_4N][Mn(TPP)(imid)$_2$]. The crystal structure of polymeric $\{Mn(TPP)(imid)\}_n$ has also been determined [317], and the reactions of manganese(III) porphyrins with imidazole discussed [318].

Electron-transfer and ligand addition reactions of Mn^{II}(TPP) and Mn^{III}(TPP)Cl have been studied by cyclic voltammetry in dichloromethane. Six nitrogen donor ligands, L, were employed {L = py, 4-CNpyridine, 3-Brpyridine, 3-Mepy, 4-Mepy and 3,4-Me_2py} and in each case only five coordinate complexes of the types

[Mn(TPP)L] and $[Mn(TPP)L]^+$ were identified. There was found to be a relationship between complex stability and the basicity of the ligand L [319]. A detailed magnetic study of Mn(TPP)Cl and Mn(TPP)(py)Cl has been reported [320].

Theoretical calculations upon the hyperfine interaction in five-coordinate manganese porphyrin complexes Mn^{II}(porphyrin)(H_2O) and Mn^{III}(porphyrin)Cl have been performed [321]. The manganese 3*d* and 4*s* electron density distribution in (phthalocyaninato)manganese(II), $[(Pc)Mn^{II}]$, has been determined from X-ray diffraction data [322], and its electronic structure calculated by the CNDO/2 method [323]. The electronic properties of water soluble manganese(II) porphyrin complexes Mn(L) {L = tetra(4-pyridyl)porphine, tetra(*N*-methyl-4-pyridyl)porphine, tetra(4-sulphophenyl)porphine or tetra(4-carboxylphenyl)porphine}, the corresponding Mn(III) complexes, and their oxidation products have been reported, together with the results of electrophoretic experiments [324] and details of their photochemistry [325]. The electronic spectra of the charge-transfer complexes formed between $[(Pc)Mn^{II}]$ and SnX_4 {X = Cl, Br or I} have been reported [326].

8.11 COMPLEXES OF BIOCHEMICAL SIGNIFICANCE

This section contains only a brief resumé of some of the literature covering this area. For a more detailed review, please refer to the Chemical Society Specialist Periodical Reports upon Inorganic Biochemistry (ed. H.A.O. Hill).

A review of the reactivity of Mn(II) complexes towards dioxygen has been published [312].

The complexes formed between manganese(II) and the dinucleotides NADP [327,328] and NADPH [328] have been studied. The EPR spectrum of $[Mn(H_2O)_6]^{2+}$ in a hexadecyltrimethylammonium bromide/chloroform reversed micellar system shows distortions of the complex at low water concentrations. The significance of this with respect to Mn(II) catalysis of the hydrolysis of ATP has been discussed [329]. An X-ray scattering study upon amorphous $Na_2[Mn(ATP)(H_2O)_2].2H_2O$ has shown the ATP ligand to be tetradentate, *via* the N(7) atom of the purine ring and one oxygen atom from each of the three phosphate groups, octahedral coordination being completed by two *cis*-water molecules [330]. Other studies on adenosine-phosphate systems have been reported [331,332,333].

Complexes of manganese(II) with the following ligands have also been studied: histidine [334], histidine and 2-phenylacetohydroxamic acid [335], alanine [336], adenine [337], proline [338,339], glycine [339,340], 2-thiouracil [341], cycloserine [342], biuret [343], vitamin B_3 [344] and flavin mononucleotide [345]. The manganese(II) analogue of the blue copper protein azurin has also been prepared [346].

8.12 REVERSIBLE OXYGENATION OF MANGANESE(II) PHOSPHINE COMPLEXES

The controversy over the reactions of the manganese(II) phosphine complexes $MnLX_2$ {L = various tertiary phosphines and X = various anions} with dioxygen highlighted last year [1; p. 189] has continued. McAuliffe and coworkers, the authors of the original article claiming that the complexes mimic the behaviour of haemoglobin and myoglobin towards dioxygen [347], have published another short note, reporting [348] the results of experiments using labelled dioxygen. Samples of $^{16}O_2/^{18}O_2$ mixtures were analysed by mass spectrometry, subjected to repeated adsorption/desorption with both solid samples and thf solutions of some of the phosphine complexes, and the desorbed gas analysed. It was found that, within the limits of experimental error, the ratio of $^{16}O_2$ to $^{18}O_2$ remained unchanged and that there was no increase in the proportion of $^{16}O-^{18}O$ present in the mixture [348]. The significance of these results is not clear. The one important result, *viz.* what effect using $^{18}O_2$ had on the purported $\nu(O{-}O)$ stretching frequency of the complexes $[Mn(PR_3)X_2(O_2)]$ is not reported. The results, as reported, merely show that, whatever process is occurring in solution, the majority of the O_2 has not been involved in a reaction involving homolytic fission which produces O_2 as a product. In another brief report, the analogy of the behaviour of $[Mn(PBu_3)Br_2]$ in 1,2-dichloroethane with dioxygen, to that of myoglobin, is highlighted [349]. Full details of the all-important synthetic chemistry have not yet been published.

A full report of the independent investigation of these systems by Green and coworkers included last year has now appeared [350]. This report confirms the observation that solutions of MnX_2 in thf in the presence of PBu_3 give deeply coloured solutions, not only with dioxygen, but also upon electrochemical oxidation at a platinum electrode with the vigorous exclusion of dioxygen. The electronic spectra of these solutions prepared in the presence and absence of dioxygen are identical to each other, and also in peak position and spectral profile, to that reported [347] for the complex $[Mn(PBu_3)Br_2(O_2)]$. However, the spectrum of the species generated electrochemically [350] has extinction coefficients $>9000\ \ell\ mol^{-1}\ cm^{-1}$, compared with those reported for $[Mn(PBu_3)Br_2(O_2)]$ of $270\ \ell\ mol^{-1}\ cm^{-1}$. As $[Mn(PBu_3]Br_2(O_2)]$ can not be present in the electrochemically oxidised solution, the implications of this result are clear: the chromophore reported as $[Mn(PBu_3)Br_2(O_2)]$ does not contain dioxygen, and must be present in concentrations at least one, and possibly two, orders of magnitudes lower than has been assumed in the original work [347]. A possible reaction scheme, which gives the appearance of reversible dioxygen uptake has been suggested [350], involving the formation of a highly coloured, thermally unstable, manganese(III) or mixed-valence manganese(III,II) phosphine complex, stable in the presence of excess dioxygen, the colour being lost on removal of excess dioxygen and/or on warming the solution. In support of this postulate, tertiary phosphine oxides, the expected products of such reactions, were isolated from the oxidised solutions and characterised. The report [350] concludes that either the reports of reversible oxygen uptake are erroneous, or that the two related systems are different, but have coincidently identical spectroscopic properties.

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