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1. MANGANESE

C.P. WARRENS

CONTENTS

INTRODUCTION

This review covers papers published in the late 1981 and 1982 and included in volumes 96 and 97 of Chemical Abstracts. Some papers from volume 95 are also included, where they have not previously been reviewed.

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As usual, work of an essentially organometallic nature has been excluded, together with reports of purely kinetic or mechanistic interest.

1.1 HIGH OXIDATION STATES

The electronic energy levels in $[MnO_4]^-$ were evaluated by CNDO-SCF-MO calculations [1]. The crystal data and IR and Raman spectra of $Ba_5(MnO_4)_3F$ were reported [2].

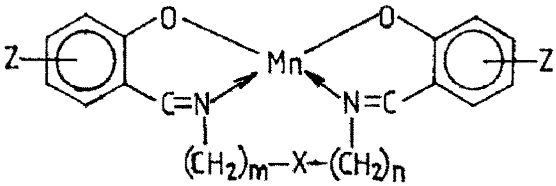
1.2 MANGANESE(IV)

The binding energies of electrons in the 2p and 3p levels of manganese in MnO_2, Mn_2O_3, Mn_3O_4 and MnO were determined by XPES. The energy of the 2p and 3p levels of manganese varies linearly with formal oxidation state [3,4]. The electrochemical reduction of suspended particles of MnO_2 in an acidic electrolyte, H_2SO_4, was studied at different values of pH [5]. The electrochemical reduction of MnO_2, suspended in an alkaline solution, KOH, was studied under an atmosphere of O_2, in which simultaneous reduction of MnO_2 and O_2 occurs [6].

The X-ray crystal structure and synthesis of the dipotassium salt of the tris(3,5-di-*t*-butylpyrocatecholato)manganese(IV) dianion was reported [7]. The complexes $[Mn(S_2CNR_2)_3]X$ (R = Et, X = BF_4 or ClO_4; R = cych, X = BF_4, ClO_4 or PF_6) were found to be irreversibly photodecomposed in solution [8].

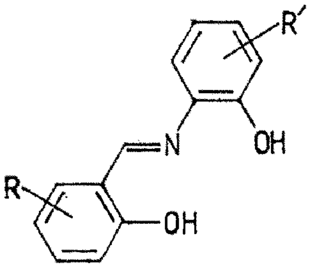
The XPES spectra of a series of manganese(IV), manganese(III), manganese(II) and manganese(I) complexes with the Schiff bases (*1*) were reported; the manganese $2p_{1/2}$ and $2p_{3/2}$ binding energies are relatively insensitive to changes in the ligand substituent, ligand donor groups and the oxidation state of manganese [9]. Some chloromanganese(III) Schiff base complexes react with HCl to give complexes of empirical formulae $[MnLCl_2]$ or $[MnL'_2Cl_2]$ (H_2L = sal_2en and its analogues; HL' = alkylsalicylideneamine; alkyl = Pr, Bu, CHMeEt, hexyl, cych, C_8H_{17}, $C_{12}H_{25}$, $C_{18}H_{37}$, Bz or $CH_2CH_2C_6H_5$). The magnetic properties of these complexes indicate an oxidation state of +4 for manganese [10,11].

Oxidation of the binuclear complexes $[Mn_2(R,R'\text{-sap})_2]$ (R,R'-sap = (*2*)) by tetrachloro-1,2-quinone gives the manganese(IV) complexes $[Mn(R,R'\text{-sap})_2]$. CV showed two redox steps due to $\mathrm{Mn(IV)} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} \mathrm{Mn(III)} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} \mathrm{Mn(II)}$. The redox potentials were dependent on R and R', with good correlation between the Hammet σ-values of R and R' to the phenolic oxygen and the redox potentials [12].



(1)

Z	m	n	X
H	1	1	-
H	3	3	-
H	1	2	-
H	3	3	NH
Me	3	3	NMe



(2)

R = R' = H
R' = H, R = 3-MeO, 5-Me or 5-Br
R = H, R' = 4'-Cl or 5'-NO_2

1.3 MANGANESE(III)

1.3.1 Halides and pseudohalides

The reaction of $[NH_4]MnF_3$ with XeF_2 to give $[NH_4]MnF_4$ was described [13], and the preparation of A_2MnF_5 (A = NH_4, Na, Cs, K or Li) was reported [14].

The energies of core and valence orbitals of $[Mn(CN)_6]^{3-}$ were calculated by discrete-variational Xα(DV-Xα) methods and correlated with XPES results. The calculated *d-d* excitation energies are in good agreement with Δ values obtained from the spectra [15].

1.3.2 Oxides and hydroxides

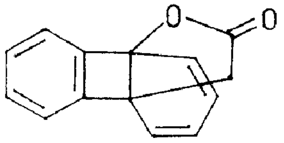
A fourth polymorph of MnO(OH), δ-MnO(OH), is prepared by bubbling air into a suspension of anhydrous MnO_2 at room temperature at pH ∿ 6. The compound is antiferromagnetic, T_N = 58.5 K, and is dehydrogenated to β-MnO_2 at 270 °C [16].

The reduction of the perovskite $LaMnO_3$ gave two new phases with ordered anion vacancies, $La_8Mn_8O_{23}$ and $La_4Mn_4O_{11}$ [17].

1.3.3 Complexes with Group VIB donor ligands

The direct synthesis of $[Mn(acac)_3]$ by the reaction of a concentrated solution of $K[MnO_4]$ with acacH in the absence of any buffer was reported: electron impact mass spectrometry showed the compound to be monomeric [18]. The effect of UV irradiation on an ethanolic solution of $[Mn(acac)_3]$ is to reduce the manganese to Mn(II), whilst the pentane-2,4-dionate anion is oxidised to ethanoate [19]. The electron transfer processes in mixtures of $[Mn(acac)_3]$ and RCO_2H (R = Me, Ph, CO_2H or vinyl) yield pentane-2,4-dionate or carboxyl radicals, part of which are stabilized by complexation with manganese(II) [20]. $[Mn(acac)_3]$ reacts with inorganic acids to give five-coordinate $[Mn(acac)_2X]$ (X = F, Cl, Br, I, NO_3 or SO_4) [21]. Powder magnetic measurements on the linear chain compounds $Mn(acac)_2X$ (X = $[N_3]$ or [NCS]) show the presence of antiferromagnetic interchain interaction [22]. The complexes $[Mn(LL)_3]$ (LL = acac, dbzm or S_2CNEt_2) react with NO_2 to give free iminoxy radicals. In contrast, $[Mn(LL)_3]$ (LL = S_2CNR_2, 8-quinolinethiolate or diethyldithiocarbonate) react with NO to give complexes of the type $[Mn(NO)(LL)_2]$ [23].

The value of the formal potential of the Mn(III)/Mn(II) ethanoate couple was determined potentiometrically at different concentrations of ethanoic acid [24]. The reaction of biphenylene with $[Mn(O_2CMe)_3]$ to give 2-acetoxy-, 2-formyl-, and 2-(acetoxymethyl)biphenylene and oxapropellane (*3*) was reported [25]. The synthesis and characterisation of the optically active complex $[Mn(L\text{-}moba)_3]$ (H-L-moba = 1-L-menthoxy-3-benzoylpropanone) was reported [26]. The stable chelate complexes of manganese, tris(pyridine-2-carboxylato)-manganese(III), bis(pyridine-2,6-dicarboxylato)manganese(III) and



(3)

bis(pyridine-2,4,6-tricarboxylato)manganese(III), prepared from MnO_2, $[Mn(O_2CMe)_3]$ or $K[MnO_4]$ and pyridine-2-carboxylic acid followed by treatment with the other pyridine carboxylic acids was reported [27].

The synthesis and X-ray structure of $[Mn(urea)_6][ClO_4]_3$ was reported. The cation has $\bar{3}$ symmetry, with all the Mn-O bonds equivalent, due to a dynamic Jahn-Teller distortion [28]. The reaction of MnO_2 with H_3PO_4 was studied by thermal methods. In the temperature range 150-335 °C, the main product is $Mn(PO_4)$, which reacts with H_3PO_4 at 300-450 °C to form $Mn_4(P_2O_7)_3$. This is stable up to 550-600 °C, but at higher temperatures decomposes releasing O_2 and forming manganese(II) and manganese(III) pyrophosphates [29]. The complex $[MnL_3]$ (L is the bidentate ligand *O,O*-diethylphosphonyldithiocarbamate) was also prepared and characterised [30].

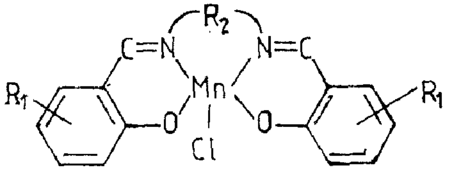
1.3.4 Complexes with Group VB donor ligands

Manganese(III) salts react with 2,6-diaminopyridine and pentane-2,4-dione to form distorted square pyramidal complexes [MnLX], where H_2L is a 16-membered N_6-tetradentate ligand, and X = Cl, Br, NO_3, NCS or O_2CMe: the pyridine nitrogen atoms take no part in the coordination [31].

1.3.5 Schiff base complexes

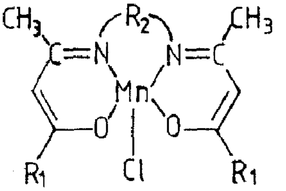
The reaction between Schiff base complexes of Mn(III) and $[O_2]^-$ was reported. For hexa- or penta-dentate Schiff base complexes, $Mn^{II}-O_2^{\cdot}$ complexes were produced. No reaction was observed for quadridentate Schiff base complexes, such as $[Mn(sal_2phen)(NCS)]$ or $[Mn(sal_2en)Cl]$. All the Schiff base complexes studied were reduced by $[HO_2]^-$ [32]. In an independent study, the reaction of manganese(III) chloride complexes of Schiff bases with $[O_2]^-$ was discussed and related to $-E_{\frac{1}{2}}\{Mn(III)/Mn(II)\}$ values. Compounds of the type (*4*) and (*5*), with $E_{\frac{1}{2}}$ less than 0.19 V, undergo oxidation, whereas complexes (*6*) and (*7*), with $E_{\frac{1}{2}}$ greater than 0.19 V were reduced to manganese(II) Schiff base complexes [33]. The crystal structure of *catena*-μ-ethanoato-*N*,*N*'-ethylenebis-[(2-hydroxy-1-napthyl)methaniminato]manganese(III) has been reported [34].

The catalytic decomposition of H_2O_2 by the binuclear complex $[Mn_2(salpa)_2]^{2+}$, (*8*), was compared to catalysis by mononuclear manganese(III) complexes [35]. The complexes $[\{MnL_2X\}_2]$ (HL = $BzNHN{=}CHC_6H_5OH\text{-}2$ or $2\text{-}HOC_6H_4C(O)NHN{=}CHC_6H_4OH\text{-}2$; X = O_2CMe or Cl) were also prepared and characterised [36], as were the complex $[Mn(LH)]Cl_2$ (H_2L = $2\text{-}HOC_6H_4CH{=}NCH_2C(O)NHCH_2CH_2NHC(O)N{=}CHC_6H_4OH\text{-}2$) [37], and the square pyramidal 1:1 complex of manganese(III) with the Schiff base prepared from 2-hydroxo-1-napthylmethylamine and salicylaldehyde [38].



(4)

R1	R2
H	C_6H_{10}
5-Me	CH_2CH_2
5,6-benzo	CH_2CH_2
H	CH_2CH_2

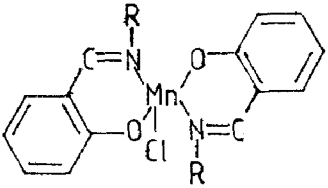


(5)

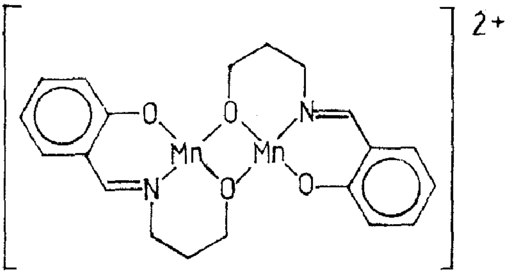
R1	R2
Me	CH_2CH_2
Me	$CH(Me)CH_2$
Ph	CH_2CH_2
Ph	$CH(Me)CH_2$

(6)

R1	R2
H	$CH(Me)CH_2$
3-OMe	CH_2CH_2
5-Br	CH_2CH_2
H	C_6H_4
5-NO_2	CH_2CH_2



(7; R = Bu, Pr or cych)



(8)

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

The preparation of *meso* and *rac*-isomers of Na[Mn(ehpg)] {ehpgH_4 = ethylenebis((o-hydroxyphenyl)glycine); ethylenediaminedi(o-hydroxyphenylacetate)} was reported [39] (see also Section 1.9).

The preparation and characterisation of a mixed piperidine pentamethylenedithiocarbamate complex of manganese(III) was reported; coordination occurs through the two thiocarbamate *S* atoms and the *N* atom of piperidine [40].

1.4 MANGANESE(II)

1.4.1 Halides and pseudohalides

1.4.1.1 Fluorides

The room temperature structure of MnF_2 was investigated by γ-ray diffraction [41], and an EPR study of the antiferromagnetic-ferromagnetic intermediate state of MnF_2 was reported [42]. Also reported was the reaction of MnF_2 with AsF_5 in anhydrous HF, which gave $MnF_2.2AsF_5$, which was studied by vibrational spectroscopy and X-ray powder diffraction [43].

The electronic energy levels in $[MnF_6]^{4-}$, obtained by CNDO-SCF-MO calculations were reported [1]. $[MnF_6]^{4-}$ was also the subject of calculations of the effect of charge transfer from ligand to manganese on parameters of two and three particle crystal field operators [44].

The isotropic and anisotropic electronic and magnetic electron nuclear interactions at ^{19}F and ^{23}Na in $NaMnF_3$ were studied by NMR [45]. The luminescence of $KMnF_3$ between 10 and 100 K was reported [46], as was its cubic to tetragonal phase transition [47]. The study of the weakly ferromagnetic compound $CsMnF_3$ by polarization and electronic spectroscopy was reported [48]. The first five *d-d* transitions in the spectra of $RbMnF_3$ and $CsMnF_3$ were observed [49]. The optical and EPR spectra for the antiferromagnetic complex $[NH_4]MnF_3$ above 80 K were reported [50].

1.4.1.2 Chlorides

The stability constants of $MnCl^+$ in dmso containing an equimolar mixture of $Co(ClO_4)_2$ and $Mn(ClO_4)_2$ were reported [51].

The antiferromagnetic hexagonal perovskite, $RbMnCl_3$, was studied by Raman scattering between 50 and 310 K; the fluorescence spectrum was also reported [52]. Also reported were the first five *d-d* transitions in the spectra of cubic and hexagonal $RbMnCl_3$ [49]. The luminescence and excitation spectra of antiferromagnetic $CsMnCl_3$ were reported [53].

The structural phase transitions of the layered compounds, $[C_nH_{2n+1}NH_3]_2MnCl_4$ (n = 1 or 2), studied by Brillouin scattering and linear birefringence methods from 0 to 500 K were reported [54]. The temperature dependence of the luminescence spectra of the Heisenberg-type two-dimensional antiferromagnets $[C_nH_{2n+1}NH_3]_2MnCl_4$ (n = 1, 2 or 3), measured between 4 and 300 K were reported [55]. The heat capacity of $[PrNH_3]_2MnCl_4$ was determined between 10 and 300 K; two phase transitions were observed, and the complex is magnetically ordered below 130 K [56]. The phase transitions of $[PrNH_3]_2MnCl_4$ between 0 and 450 K, studied by birefringence, were reported and compared to a similar study on $[EtNH_3]_2MnCl_4$ [57]. Also reported was an IR study of the phases of $[PrNH_3]_2MnCl_4$ occurring at room temperature and below [58]. The complexes $[R_3NH]_2MnCl_4$ and $[R'_3R''N]_2MnCl_4$ (R = octyl; R' = capryl and R" = methyl) were prepared and studied by DTA and thermogravimetry [59].

The study of the quasi-two-dimensional antiferromagnet $[H_2en]MnCl_4$ between 4.2 and 300 K by EPR was reported [60,61]. The phase changes which the complex $[NH_3C_3H_6NH_3]MnCl_4$ undergoes between 305 and 336 K were studied by determination of the crystal structures. Also reported was the study of phase changes by ^1H NMR spectroscopy between 78 and 336 K [62].

1.4.1.3 Bromides

An electron diffraction study of $MnBr_2$, carried out at 608 °C, was reported; a monomer and a bromine bridged four membered ring dimer are present [63]. Raman and far-IR spectra for a polycrystalline sample of $MnBr_2$ were reported [64].

The double perovskite-type structure of Rb_3MnBr_7, as determined by X-ray crystallography, was reported [65]. The perovskite-type structure of $RbMnBr_3$ was also determined by X-ray crystallography at room temperature [66].

The perovskite-type complexes $[C_nH_{2n+1}NH_3]_2MnBr_4$ (n = 11-16) were investigated by DSC, IR spectroscopy and X-ray diffraction, and compared to the corresponding chloro-complexes [67].

1.4.1.4 Pseudohalides

The analysis by semi-empirical methods of the electronic spectrum of $[Mn(CN)_6]^{4-}$ was reported [68].

1.4.2 Oxides

The reaction between Mn^+ and either O_2 or N_2O to form MnO^+ was examined in an ion beam apparatus; the bond energy from these studies was reported [69].

1.4.3 Carbonates, sulphates and phosphates

A study of the thermal stability of $MnCO_3$ in atmospheres of air, CO_2 and He was reported [70].

A study of $MnSO_4$ by XPES was reported [71]. Also reported was an X-ray analysis of $MnSO_4.5H_2O$, which was used to derive a model for aqueous $MnSO_4$, which was fitted to X-ray scattering intensities [72].

A structure of the complex $[MnL_3]$ (HL = bis(2-ethylhexyl)phosphoric acid) was proposed on the basis of IR spectroscopy, magnetic susceptibility and MWT data [73]. Also reported was the preparation and characterisation of $Mn_2L.xH_2O$ (H_4L = ethylenediphosphonic acid) [74].

1.4.4 *Carboxylates*

The crystal structure of the complex $[Mn(HCO_2)_2(H_2O)_2]$ was redetermined [75], and the EPR spectrum of the quasi-two-dimensional magnet $[Mn(HCO_2)_2(H_2O)_2]$ at room temperature indicated the presence of two types of Mn^{2+} ions [76].

The preparation of the complex $[AlMn(O_2CMe)_5]$ was reported [77]. The complex $Mn(O_2CMe)_2.MeOH.3H_2O$ was prepared, and X-ray diffraction and IR spectroscopy indicated that the methanol was coordinated to the manganese [78]. Also prepared and characterised were $Mn(O_2CMe)_2$.propionamide [79] and $Mn(O_2CMe)_2L$ (L = bipy or 4,4'-bipy) [80].

The study by DTA, TGA and DTGA of the thermal decomposition of the complexes $[NH_4]_2[Fe_2Mn(O_2CMe)_6(OH)_4]$, $[NH_4]_8[Fe_2Mn(C_2O_4)_8]$ and $[NH_4]_2[Fe_2Mn(C_2O_4)_2(OH)_6]$ was reported [81].

The crystal structure of tetraaquabis(2,4,5-trichlorophenoxyacetato)-manganese(II)-bis(2,4,5-trichlorophenoxyacetic acid)adduct was reported [82].

A study of the anhydrous complex $Mn(C_2O_4)$ by IR and electronic spectroscopy and X-ray diffraction was described [83] and the preparation and characterisation of the complex $[Mn(C_2O_4).2N_2H_4]$ was reported [84]. The thermal decomposition of the tetraaquabis(4-aminobenzoato)manganese(II), measured by TGA, DTA and DTGA was reported [85], as was the thermal behaviour of manganese(II) glycolate, as studied by TGA and DTA [86]. The preparation and characterisation of the complex MnL_2 (HL = antimonyhydrogenbis(thioglycolate)) was reported, in which carboxylate is a bidentate bridging ligand [87]. Also reported were the preparations of the complexes $Mn_2L.nH_2O$ (H_4L = 1,2,4,5-benzenetetracarboxylic acid) [88], MnL and MnL_2 (HL = 3-indoleacetic acid) [89], and $Mn(HL).nH_2O$ and $Mn(HL)_2.nH_2O$ (H_2L = pyrazine-2,3-dicarboxylic acid) [90].

1.4.5 *Complexes of Group VIB donor ligands*

The crystal structure of the 2:1 molecular complex of caffeine with hexaaquamanganese(II) was reported. In this complex,

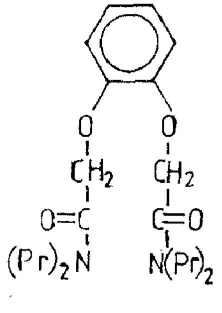
$[C_8H_{10}N_4O_2]_2[Mn(OH_2)_6]I[I_3]$, the caffeine molecules are uncoordinated [91]. A study of the magnetic properties of the weakly antiferromagnetic complexes $[Mn_2L(acac)_4]$ (L = dmf) and $[Mn_2L_2(acac)]$ (L = allylamine) in the range 4 to 300 K was described [92].

The preparation and characterisation of $[Mn(8\text{-}O\text{-}quin)(acac)].2H_2O$ was reported [93].

The preparation and characterisation of complexes with 1-ferrocenyl-1,3-pentanedione (HL), $[MnL_2(H_2O)_2]$ and $[MnL_2]$ were reported. In pyridine, $[MnL_2]$ is converted to $[MnL_2(py)_2]$ [94]. A potentiometric study of the complexes formed by manganese(II) with 1,5-dimethyl- and 1,5-diphenyl-1,3,5-pentanetriones was reported. The 1,5-dimethyltrione acts as a monobasic acid, whereas its 1,5-diphenyl analogue acts as a dibasic acid [95]. Also reported was the stability constant of the complex formed by Mn^{2+} with 5,5-dimethylcyclohexane-2-(2-hydroxyphenyl)hydrazono-1,3-dione [96].

The preparation and characterisation of the following complexes were reported; $[Mn(diglyme)_2][SbCl_6]_2$ and $[Mn(pentaglyme)_2][SbCl_6]_2$ [97]; $[Mn(triglyme)_2][SbCl_6]_2.2H_2O$ and $[Mn_2(triglyme)_2Cl_2][SbCl_6]_2$ [98]; and $[Mn(18\text{-}crown\text{-}6)MeNO_2][SbCl_6]_2$ [99].

The crystal structure of the complex formed between manganese(II) and the ligand (*9*, L), $[MnL_2][MnBr_4]$, was reported. The Mn^{2+} is coordinated to all eight *O* atoms of the two ligand molecules [100].



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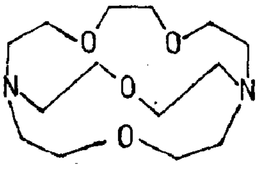
The determination by EPR spectroscopy of the formation constants of Mn^{2+} complexes with deprotonated and monoprotonated phosphonoethanoic acid and with phosphonomethanoic acid, 3-phosphonopropanoic acid, citric acid and the cryptand (*10*) were reported [101]. The heterotrinuclear complex bis[bis(μ-1-methylthyminato)-*cis*-diammineplatinum(II)]manganese(II) dichloridedecahydrate (*11*) was studied by EPR spectroscopy; the complex has a large zero field splitting due to tetragonal distortion of the Mn^{2+} [102].

The preparation and characterisation of complexes of manganese(II) picrates with 1,2-diaminobenzene, en, dien, bzd, hmta and 2-aminopyridine was reported



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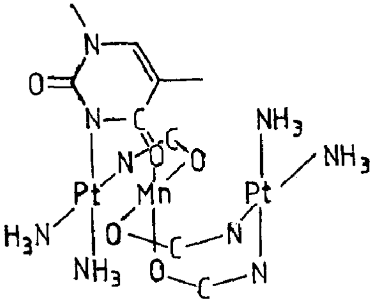


(11)

[103]. Also prepared and characterised were Mn(5'-AMP).$5H_2O$ [104] and $[MnL_6][BF_4]_2$ (L = 12-laurolactam) [105].

The preparation of the halogen-bridged complex of 2-pyridinecarboxamide-*N*-oxide, pco, $[Mn(pco)Cl_2]$ was described; pco acts as a bidentate oxygen donor [106]. Also reported was the preparation of a complex of 4-cyanopyridine-*N*-oxide, $[Mn(ONC_5H_4CN)_2(NCS)_2]$ [107].

The complexes $MnCl_2.2NH_2OH.H_2O$ and $MnSO_4.2NH_2OH.H_2O$ were prepared, in which the hydroxylammine coordinates to manganese through the oxygen atom [108]. The mechanoluminescence and electroluminescence of the non-photoluminescent complex $[Mn(OPPh_3)_2Cl_2]$ was reported [109]. The stability constants of the chelate complexes of manganese(II) with *N*,*N'*-bis(2-hydroxyethyl)aminomethylphosphonic acid [110] and with picolinic acid *N*-oxide [111] were reported. Also reported this year were complexes of manganese(II) with *o*-vanillinmonoxime [112] and *p*-quinonedioxime [113].

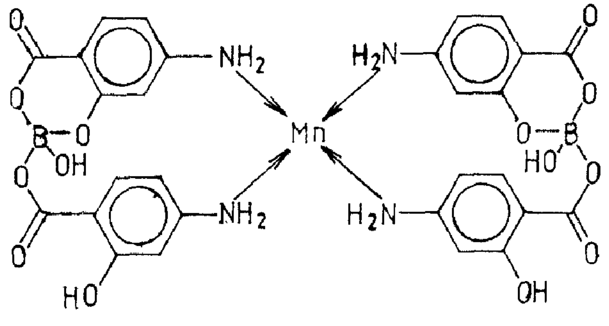
The determination of the standard free energy of formation, and from this the standard heat of formation, of MnS was reported [114]. A study of MnS by XPES spectroscopy was also described [71].

A study of the electronic structure of [MnLL'] (L = dimethyldithiocarbamate and L' = dithiophosphoric acid anion) by the CNDO/2 approximation was described [115]. The preparation and characterisation of square planar bimetallic complex [MnCd(dtc)$_4$] (H_2dtc = piperidine, or diethyl-dithiocarbamic acid) was reported [116]. The reaction of $MnCl_2$ with piperazine-*N*,*N*'-bis(dithiocarbamic acid) gives an infinitely chained planar polymer containing the $\{MnS_4\}$ chromophore [117]. The complex of $MnCl_2$ with thiosemicarbazide was studied by thermal analysis [118]. The octahedral complexes of 4-amino-3-(2-hydroxyphenyl)-1,2,4-triazoline-5-thione (hptt) and 3-(2-hydroxyphenyl)-4-(2-hydroxybenzylideneamino)-1,2,4-triazoline-5-thione (HOhbtt), [Mn(hptt)$_2X_2$] and [Mn(Ohbtt)$_2$] (X = Cl or NO_3) were prepared and characterised [119]. Also reported were the preparation and characterisation of [MnL_2X_2] (L = *N*-phenyl-*N*'-4-bromophenylthiourea; X = Cl, NCS or O_2CMe) [120], and the preparation of [MnL_2] (HL = $(4\text{-}EtC_6H_4)_2P(S)SH$; $(3,4\text{-}Cl_2C_6H_3)_2P(S)SH$ or $(2\text{-}Me\text{-}5\text{-}ClC_6H_3)_2P(S)SH$) [121].

The stability constant of the complex formed between manganese(II) and thiolhistidine was reported [122], as was the preparation and characterisation of [MnL_2] (L = 2-(2-hydroxyphenyl)benzothiazoline) [123].

1.4.6 Complexes of Group VB donor ligands

The preparation of $[Ph_4P]_2[Mn(NSOF_2)_4]$, from the reaction of $[Ph_4P]_2MnBr_4$ with Ag[$NSOF_2$] was reported. The complex was characterised by analysis, IR and ^{1}H and ^{19}F NMR spectroscopy [124]. The preparation of the complex (*12*) was reported; it was characterised by X-ray diffraction IR and ^{1}H NMR spectra and thermal decomposition studies [125].



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The reaction of 5-methylpyrazole with $Mn(BF_4)_2.H_2O$ to give the cubane-like tetrameric complex $[Mn_4F_4(5\text{-methylpyrazole})_{12}][BF_4]_4$ at room temperature was reported. Its structure was confirmed by X-ray powder diffraction and IR, UV and EPR spectroscopy. Low temperature magnetic susceptibility studies show that there is a weak antiferromagnetic interaction between the metal ions in the cluster [126].

The displacement of MeCN by $MeNH_2$ or $EtNH_2$ from manganese(II)-MECN complexes formed by dissolving $Mn(NO_3)_2.6H_2O$ in MeCN was reported [127].

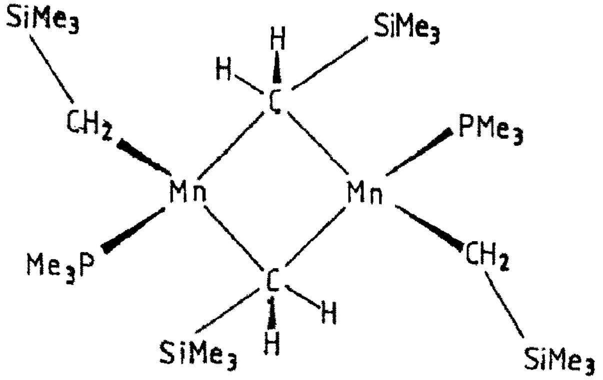
The preparation of complexes of hmta were reported, including $[Mn(NCS)_2(hmta)_2]$ and $[Mn(NCS)_2(hmta)_2(EtOH)_2]$ [128] and $Mn(hmta)SO_4$ [129]; in all of these cases hmta retains its chair configuration on complexation. Complexes of papaverine [130] and inosine [131] with manganese(II) were also reported.

The preparation and characterisation of the complexes $[MnL_2Q_2]$ (HL = pyridine-2-aldoxime or 6-methylpyridine-2-aldoxime; Q = py, 2-Mepy, 3-Mepy, 4-Mepy, 2-Etpy, 3-Etpy or 4-Etpy) were reported [132]. Also reported were the complex $[Mn(py)_4L_2]$ (HL = picric acid) [133], the complexes $[NH_4]_2[Mn(py)(SCN)_4]$ and $[NH_4]_2[Mn(phen)(SCN)_4]$ [134] and $\{Mn(bipy)\}^{2+}$ [135].

The preparation of the primary explosive $[Mn(N_2H_4)_3(NO_3)_2]$ was reported [136]. Also reported this year were complexes of manganese(II) with the following ligands: 2-aminopyrimidine [137], carbohydrazide [138,139], semicarbazidehydrochloride [140], sebacic acid hydrazide [141], isovalericacidhydrazide [142], oxalic aciddihydrazide, malonic acid dihydrazide and succinic acid dihydrazide [143], benzilphenylhydrazone [144], 1-ethyl- and 1-vinyl-2-(vinyloxymethyl)imidazole and analogous benzimidazole ligands [145], *N*-vinylimidazole [146], 5-methylimidazole [147], 1,2-dimethylbenzimidazole [148], benzotriazole [149] and sacchrinate [150].

The EXAFS spectrum of the layer compound $MnPS_3$ was recorded at 15 and 300 K [151].

The reaction of PMe_3 with $\{Mn(CH_2SiMe_3)_2\}_n$ to give the product $[Mn_2(CH_2SiMe_3)_4(PMe_3)_2]$ (*13*) was reported [152]. This complex was characterised by X-ray crystallography, and this represents the first crystal structure of a unidentate phosphine complex of manganese(II).



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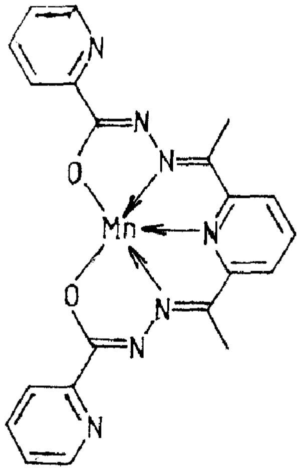
1.4.7 Mixed donor ligands

The preparation and X-ray diffraction analysis of diaqua[2,6-diacetylpyridinebis(picolinohydrazonato)-(2-)]manganese(II) (*14*) was reported [153].



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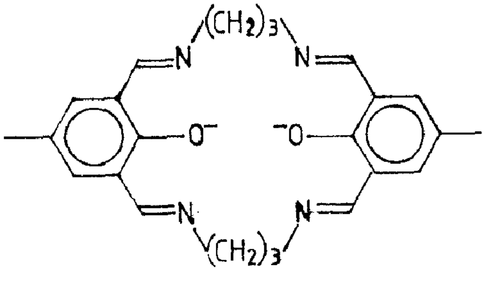
The preparation of manganese(II) chelate complexes of salicylaldazine, 5,5'-dichlorosalicylaldazine, 3,3'-dimethoxysalicylaldazine and salicylaldehydehydrazone was also reported [154]. The characterisation of the complex $LCuMnCl_2.H_2O$ {L^{2-} = (*15*)}, by variable temperature magnetic susceptibility measurements, was reported [155].



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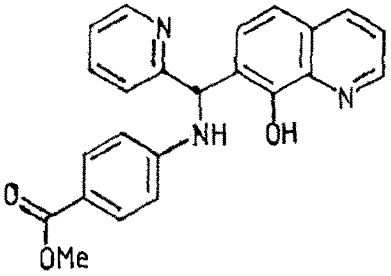
Also reported this year were complexes of manganese(II) with salicylamide, SaH, $[Mn(SaH)Cl_2(H_2O)]$ and $[Mn(Sa)_2]$ [156], of the Schiff bases prepared from 2-hydroxy-1-napthylmethylamine and salicylaldehyde [38], 4-cyanopyridine-*N*-oxide [157], the substituted 8-O-quin ligand (*16*) [158],



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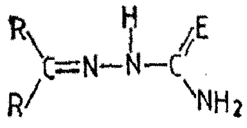
1-phenyl- and 1-(2-,3-,4-)-tolyl-violuric acid [159], *N*-2'-diphenylacetohydroxamic acid [160], *N*-phenylsalicylaldimine derivatives [161], 1,3-di(2-hydroxybenzyl)-2-phenylimidazoline [162], α-(1,3-dioxoindane-2-yl)ethylidene-4-toluidine [163], histidine [164], cytidine [165], iminodiacetic acid [166], *N*,*N*-dimethylacetamide [167], azodicarbonamide [168], heptanoylhydrazine [169], terephthaldehydebis(isonicotinic acid hydrazone) [170], salicylic acid-1-(1-hydroxy-2-napthyl)ethylidene hydrazide [171], 2-hydroxy-4-*N*-undecyl-3(H)-phenoxazone [172], substituted 4-oximino-2-pyrazolin-5-ones [173], 3-methyl-4-(2'-hydroxyphenylazo)2-pyrazolin-5-one [174], gallacetophenoneoximate [175], 3,5-dichloro-2-hydroxyacetophenoneoxime and 5-chloro-2-hydroxy-4-methylacetophenoneoxime [176], benzil monoxime [177], β-hydroxyethyliminodiacetate [178], 5-nitro- and 5-ammine-quinoline-8-carboxylic acid [179], 2-(thiophene-2-aldimino)benzene sulphonic acid and 2-(thiophene-2-aldimino)ethane sulphonic acid [180], Me, Ph, 3- and 4-pyridyl-thiazolidene hydrazone [181], 6-methyl-2-aminobenzothiazole [182], homocystine [183], sulfafurazole-2-hydroxyacetophenoneimine [184], the Schiff base derived from 1,2-phenylanediamine and 4,4'-bis(3-formyl-4-hydroxyphenylazo)biphenyl sulphone [185], and finally with the ligands (*17*; R = cycloheptyl or cyclopentyl) [186].



(17; E = O or S)

1.5 CARBONYL COMPLEXES

1.5.1 Carbonyls and hydridocarbonyls

The photolysis of $[Mn_2(CO)_{10}]$ in CH_2Cl_2 in the presence of quaternary ammonium halide to form the anions $[Mn(CO)_5]^-$ and $[Mn(CO)_4X_2]^-$ (X = Cl or Br) *via* the cleavage of the intermediate $[Mn_2(CO)_9X]^-$ was reported [187]. The reduction of $[Mn_2(CO)_{10}]$ and $[BrMn(CO)_5]$ by quaternary ammonium borohydrides gives $[Mn(CO)_5]$; this was isolated as $[(Ph_3Sn)Mn(CO)_5]$ by reaction with Ph_3SnCl. Similar reduction of *cis*-$[BrMn(CO)_4(PPh_3)]$ gives *cis*-$[HMn(CO)_4(PPh_3)]$ [188]. The production of the anions of $[Mn_2(CO)_{10}]$ and $[Mn_2(CO)_8(PR_3)_2]$ by exposure of dilute solutions to ^{60}Co γ-rays at 77 K, and their study by EPR spectroscopy, was reported [189]. A study of multiphoton-ionisation-generated Mn^+, produced by pulsed laser irradiation of gas phase $[Mn_2(CO)_{10}]$ by time of flight mass spectroscopy was reported [190]. It was also reported that laser photolysis of $[Mn_2(CO)_{10}]$ in cyclohexane solution produced $[Mn(CO)_5]^\cdot$, and a non-radical intermediate in a second primary photoprocess was determined to be $[Mn_2(CO)_9]$ [191]. X-ray diffraction data was obtained for $[Mn_2(CO)_{10}]$ at 74 K; no significant charge density accumulation was observed on the Mn-Mn bond. The molecular geometry is more distorted from ideal D_{4d} than at room temperature, and the axial carbonyls are more strongly bound than the equatorial [192]. The generation and characterisation by IR spectroscopy of $[Mn(CO)_5]^\cdot$, by photolysis of $[HMn(CO)_5]$ in a low temperature solid CO matrix, was reported [193]. The He(I) and He(II) photoelectron spectra of the complexes $[M\{Mn(CO)_5\}_2]$ (M = Zn, Cd or Hg) were reported [194].

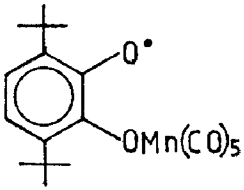
1.5.2 Halides

The reduction of $[MnBr(CO)_5]$ to $[Mn_2(CO)_{10}]$ by treatment with suspensions of either Li_2C_2 or Na_2C_2 was reported [195].

The IR reflectance and transmittance spectra for single crystals of $[Mn(CO)_5Br]$ and $[Mn_2(CO)_{10}]$ and the Raman spectrum of $[Mn(CO)_5Br]$ were obtained [196]. The reaction of $[Mn(CO)_5X]$ (X = Br or Cl) with Na or Ag atoms in a rotating cryostat gave $[Mn(CO)_5]^\cdot$, which was isolated in a C_6D_6 matrix at 77 K, and examined by EPR spectroscopy [197].

1.5.3 Oxygen donor ligands

3,6-di-*tert*-butylorthobenzoquinone reacts with $[Mn_2(CO)_{10}]$ at -80 °C to give the complex (*18*), which forms (*19*) on warming above -80 °C. Similarly,



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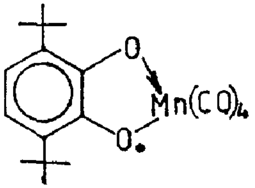


(19)

the reaction between $[Mn_2(CO)_{10}]$ and orthochloranil was reported [198].

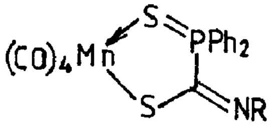
1.5.4 Sulphur donor ligands

The reaction of $[FeCp(CO)_2(CS_2)]^-$ with $[Mn(CO)_5Br]$ to give $[Cp(CO)_2FeC(=\overline{S)SMn}(CO)_4]$, which reacts with PPh_3 to give $[Cp(CO)_2FeC(=\overline{S)SMn}(CO)_3PPh_3]$ was reported [199].

The preparation of a variety of hydrogen sulphido-complexes of manganese carbonyls by treatment of the corresponding $-SSnMe_3$ compounds was reported. The complexes $[L_n(CO)_mMnSH]$ $\{L = PMe_3$ or $P(OMe)_3$; $n = 0$, $m = 4$; $n = 2$, $m = 3$; $n = 3$, $m = 2\}$ were prepared. $[(Me_3P)_2(CO)_3MnSH]$ reacts with RCl to give $[(Me_3P)_2(CO)_3MnSR]$ (R = Me_2As or CH_3CO) and with HgO to give $[\{(Me_3P)_2(CO)_3MnS\}_2Hg]$ [200].

The reaction of $Ph_2P(S)CSNHR$ (R = Me, Et or Ph) with $[ClMn(CO)_5]$ to give the complex (*20*) was reported. $Ph_2P(O)CSNHR$ and $[ClMn(CO)_5]$ react to give $[\{(CO)_3MnSC(=NR)P(O)Ph_2\}_2]$; the phosphine sulphide analogue of this is obtained by heating (*20*) in hexane [201].

The reaction of diphenylcyclopropenethione with $[CpMn(CO)_2(thf)]$ to give the complex (*21*) was reported [202].



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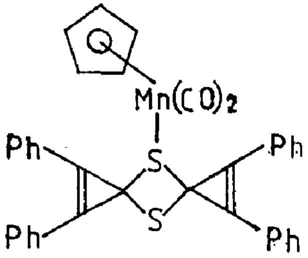

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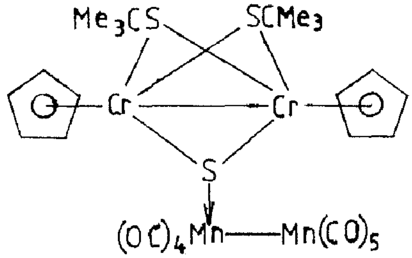
The preparation of the complexes *fac*-$[(CO)_3Mn^{\ominus}(X)S_2CCMe_2P^{\oplus}PPh_3]$ and $[(CO)_3Mn^{\ominus}(X)S_2CCMe_2P^{\oplus}PPh_3]_2$ from $Ph_3P^{\oplus}CMe_2CS_2^{\ominus}$ and $[XMn(CO)_5]$ or $[\{XMn(CO)_4\}_2]$ (X = Cl or Br) respectively was reported [203].

The X-ray structural determination of [Cp(CO)$_2$Mn←S=C(Ph)C$_5$H$_4$Mn(CO)$_3$] was reported [204], and the photochemical reaction of [{CpCrSCMe$_3$}$_2$S] with [Mn$_2$(CO)$_{10}$] in thf to give the complex (*22*) was also noted [205].



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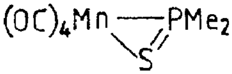
Treatment of the three-membered ring complexes (*23*), obtained from the dissociation of (*24*), with activated alkynes RC≡CR (R = CF$_3$, CO$_2$Me, CO$_2$Et or Co$_2$H) leads to the formation of the heterometallocyclopentadienes (*25*). The crystal structure of (*25*; R = CO$_2$Me) was reported [206]. The reaction of complexes (*25*) with either isocyanides RNC (R = CMe$_3$, cych or phenyl) or PPh$_3$ gives the substituted products (*26*) [207].

The complex (*25*; R = CO$_2$Me) cyclises with R'C≡CR" to give the complexes (*27*) (R' = R" = CO$_2$Et; R' = CO$_2$Me, R" = H) [208]. The complex (*27*) reacts with Raney nickel to eliminate sulphur, giving the complex (*28*), the crystal structure of which was also reported [209].



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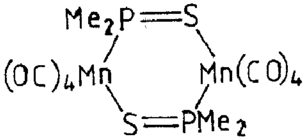

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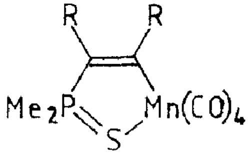

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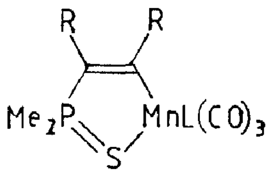
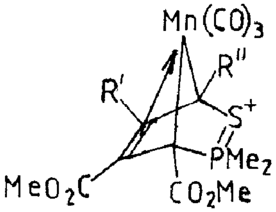


(26; L = PPh$_3$ or R'NC)



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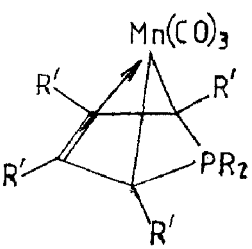

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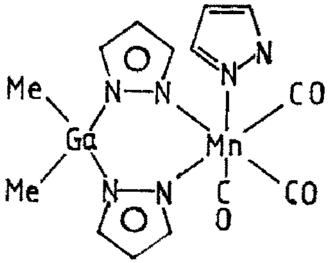
The X-ray structure of {dimethyl(3,5-dimethyl-1-pyrazolyl)(2-thiophenoxyethoxy)gallato(*N*(2),*O*,*S*)}tricarbonylmanganese(I) was reported [210].

1.5.5 Nitrogen donor ligands

The manganese(I) complexes of ureadiide, $M[Mn(CO)_5\{(RN)_2CO\}]$ and $M[Mn(CO)_4\{(RN)_2CO\}]$ (M = Li or K; R = Et, $CHMe_2$, cych, Bz, Ph, 4-biphenyl or 1-naphthyl) in which the ureadiide acts as a mono- or bidentate ligand respectively, were prepared [211].

The displacement of propanone from *fac*-$[Mn(CO)_3(chel)(OCMe_2)]^+$ or perchlorate from *fac*-$[Mn(CO)_3(chel)(OClO)_3]$ by bidentate ligands to give *fac*-$[Mn(CO)_3(chel)(L\text{-}L)]^+$ or $[\{fac\text{-}Mn(CO)_3(chel)_2\}(L\text{-}L)]^{2+}$ (chel = phen, bipy or dppe; L-L = dppm, dppe, dppb, succinonitrile or glutaronitrile) has been studied [212].

The reaction of $[Mn(CO)_5Br]$ with sodium dimethylbis(1-pyrazolyl)gallate and pyrazole to give the complex (*29*), the structure of which was ascertained by X-ray structural analysis, was reported [213].



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The complexes $[(O_3ClO)Mn(CO)_3(NN)]$ (NN = phen or bipy) react with excess ligands L (L = $P(OR)_3$ or $P(OR)_2Ph$; R = Me or Et) to give *cis,trans*-$[Mn(CO)_2(NN)L_2][ClO_4]$ or $[Mn(CO)(NN)L_3][ClO_4]$, if carried out under UV irradiation. The latter complexes are carbonylated to give *cis,cis*-$[Mn(CO)_2(NN)L_2][ClO_4]$ at normal pressure, and isomerise to *cis,trans*-isomers on heating in propanone. *fac*-$[(O_3ClO)Mn(CO)_3(dppe)]$ reacts with NN to give *cis*-$[Mn(CO)_2(NN)(dppe)]$, which on irradiation by UV in the presence of $P(OR)_3$ (R = Ph, Et or Me), gives $[Mn(CO)(NN)(dppe)\{P(OR)_3\}][ClO_4]$ [214].

1.5.6 Phosphorus and arsenic donors

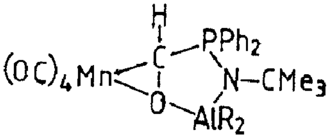
The crystal structure of *trans*-$[Mn_2(CO)_8(PEt_3)_2]$ was redetermined. The

Mn–Mn bond length of 2.9032(14) Å is indistinguishable from that in $[Mn_2(CO)_{10}]$ [215].

The reactions of photochemically prepared persistent radicals $[Mn(CO)_3L_2]^\bullet$ (L = PBu_3, $P(CHMeEt)_3$, $P(CHMe_2)_3$ or $P\{O(CHMe_2)\}_3$) with CCl_4, to give the corresponding chlorides, and with $HSnBu_3$ to give $[Mn(CO)_3L_2H]$ and $[Mn(CO)_3L_2(SnBu_3)]$ were reported [216].

The preparation of the complexes $[(CO)_4BrMn\{P(CMe_3)(M'Me_3)_2\}]$, $[(CO)_4BrMn\{P(M'Me_3)_3\}]$ and $[(CO)_8Mn(\mu\text{-}PRR')_2]$ (M' = Si, Ge or Sn; R = Me_3C or Me_3Ge; R' = Me_3C or Me_3M') from $[BrMn(CO)_5]$ and the corresponding phosphine was reported. The complexes containing μ-phosphido groups are formed by elimination of Me_3SiBr [217]. The treatment of $Na[Mn(CO)_5]$ with CH_2ClI to give $[Mn(CH_2Cl)(CO)_5]$, which reacts with Ph_3P to give $[Mn(CO)_3(PPh_3)_2Cl]$, was reported [218].

The reaction of $[HMn(CO)_5]$ with $Ph_2PN(CMe_3)\text{-}AlR_2$ (R = Me or Et) was studied by NMR spectroscopy: P–C bond formation occurs giving the complex (*30*). This reacts with further phosphine to give (*31*) and (*32*), or with $(PhO)_3P$ to substitute a carbonyl group [219].



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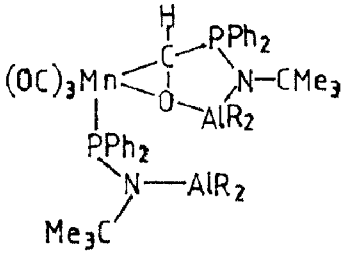

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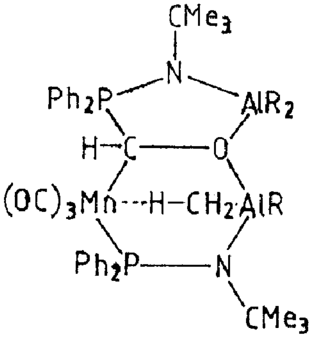

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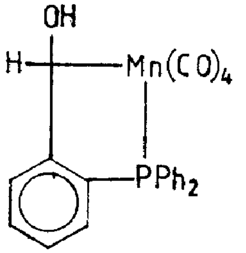
The fluxionality of the complexes $[Mn_2(CO)_6(dppm)_2]$ and $[Mn_2(CO)_5(dppm)]$ was studied by ^{13}C NMR spectroscopy [220].

Treatment of *fac*-$[MnBr(CO)_3(L\text{-}L)]$ (L-L = dppm or dppe) with phosphorus donors gives *cis,cis*-$[MnBr(CO)_2(L\text{-}L)L]$ (L = $P(OPh)_3$, L-L = dppm; L = $P(OPh)_3$, $P(OMe)_3$, $P(OEt)_3$, $PPh(OMe)_2$ or PEt_3, L-L = dppe). Oxidation with NO_2 or $[NO][PF_6]$ gives unstable cationic species isolable as hexafluorophosphate salts, which on reduction with hydrazine give *trans*-$[MnBr(CO)_2(L\text{-}L)L]$. Treatment of these complexes with $Tl[PF_6]$ in the presence of *N* or *P* donors, L', forms *cis,cis*- or *trans*-$[Mn(CO)_2(L\text{-}L)LL']$ or *mer*-$[MnCO_3(L\text{-}L)L][PF_6]$, if L' = CO [221].

The preparation of complexes of 2,2-dimethyl-dppp and 2,2-dimethyl-dpap (L-L), $[XMn(CO)_3(L\text{-}L)]$ (X = Cl, Br, I, CH_3 or CH_3CO) was reported [222]. The reaction of $[(\eta^5\text{-}RC_5H_4)Mn(CO)_3]$ (R = H or CH_3) with $Ph_3P{=}CH_2.LiBr$ to form $[(\eta^5\text{-}RC_5H_4)Mn(CO)_2(PPh_3)]$, $Ph_2P(C_6H_4\text{-}2\text{-}COCH_3)$ and $[(\eta^5\text{-}C_5H_4)Mn(CO)_2\{Ph_2P(C_6H_4\text{-}2\text{-}COCH_3)\}]$ was reported. The X-ray structure of the latter complex, with R = CH_3, was also reported [223].

The treatment of $[BrMn(CO)_4\{P(OMe)_3\}]$ or $[BrMn(CO)_3\{P(OMe_3)\}_2]$ with allyl bromide in the presence of a phase transfer catalyst, benzyltriethylammonium chloride, to give $[(\eta^3\text{-}C_3H_5)Mn(CO)_4\{P(OMe)_3\}]$ and $[(\eta^3\text{-}C_3H_5)Mn(CO)_3\{P(OMe)_3\}_2]$ was reported [224]. The complex $[(CO)_4BrMn\{PPh_2(CH_2)_nCl\}]$ undergoes reductive cyclo-elimination with sodium amalgam to give the complexes $[(CO)_4\overline{Mn(CH_2)_nP}Ph_2]$ (*n* = 1-4) [225]. This complex, with *n* = 4, undergoes ring contraction on heating to 200 °C in a sealed tube to give $[(CO)_4\overline{Mn\text{-}CH(Me)(CH_2)_2P}Ph_2]$: CO and SO_2 insert into the Mn-C bond of this complex [226].

The preparation of the α-hydroxyalkyl complex (*33*) from $[HMn(CO)_5]$ and $Ph_2P(2\text{-}C_6H_4CHO)$ was reported [227]. The reaction of $[Mn_2(CO)_{10}]$ with some arsine ligands at high temperatures to form $[Mn_2(CO)_8(\mu\text{-}AsR_2)_2]$ (R = Ph, $4\text{-}MeC_6H_4$, $4\text{-}MeOC_6H_4$, $4\text{-}FC_6H_4$ or $4\text{-}ClC_6H_4$) or with the arsines (*34*; R' = $PhCH_2$, C_6H_{11} or MeO) by loss of the non aryl groups was reported [228].



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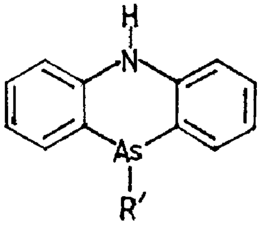


(34)

1.5.7 Organometallic complexes

The crystal and molecular structure of $[(\mu\text{-}CH_2)\{Mn(CO)_3(Mecp)\}_2]$ was reported [229], as was the experimental electron density distribution from single crystal X-ray data [230]. The He(I) PE spectrum of this complex below 11 eV was compared with ionisations of $[(Mecp)Mn(CO)_3]$ and $[(Mecp)Mn(CO)_2(C_2H_4)]$ [231].

The electrocatalytic ligand substitution reactions of [(Mecp)Mn(CO)$_2$L] by L' (L = MeCN or py, L' = PPh$_3$ or Me$_3$CNC) were studied, the reaction mechanism being by a cationic chain mechanism [232].

The reaction of ethanoic[^{13}C]methanoic anhydride with Na[Mn(CO)$_5$] to give ^{13}CO substituted [Mn(CO)$_5$H] was studied by mass spectroscopy. The reaction proceeded *via* a short-lived neutral formyl complex [(CO)$_5$Mn-^{13}CHO] [233].

An XPES study of [(cp)Mn(CO)$_2$(CS)] and [(cp)Mn(CO)$_3$] showed that the binding energies of the metal atom and carbonyl groups are approximately constant on replacing the CS group with CO [234].

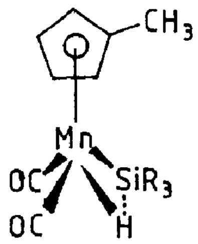
The photolysis of [Mn(cp)(CO)$_3$] in low temperature matrices (CH$_4$, Ar, CO or N$_2$) or in solution was studied by reaction of photogenerated species in either reactive matrices (^{13}CO or N$_2$) or coordinating solvents (thf or cyclooctene) [235].

Pentanuclear complexes containing bridging 4,4'-diisocyanobiphenyl linkages were prepared by reaction of [Mn(CO)$_5$Br] with 4-CNC$_6$H$_4$-C$_6$H$_4$-NC-4 followed by treatment with either [{Rh(CO)$_2$Cl}$_2$] or [{IrCl(cod)}$_2$] [236]. Non-chelating bidentate ligands (L-L), 1,3- and 1,4-diisocyanobenzene, 4,4'-diisocyanobiphenyl and 4,4'-diisocyanodiphenylmethane, react with [BrMn(CO)$_5$] to give [BrMn(CO)$_5$(L-L)], [BrMn(CO)$_4$(L-L)$_2$] and [{BrMn(CO)$_4$}$_2$(L-L)]. [(Rcp)Mn(CO)$_2$(NO)][PF$_6$] gives oligomers of the type [{(Rcp)Mn(NO)}$_n$(L-L)$_{n+1}$][PF$_6$]$_n$ [237].

The preparation and study by IR spectroscopy and mass spectrometry of [(cp)Mn(CO)$_2$(CNCOPh)] and [(Mecp)Mn(CO)$_2$(CNCOPh)] was described [238]. The energies of MO's were derived from empirically determined parameters and used to predict ionisation potentials and electrochemical oxidation data of the complexes [Mn(CO)$_x$(CNR)$_{6-x}$] (R = Me or Ph) [239]. The reaction between C$_6$H$_{11}$NC with [Mn$_2$(CO)$_{10}$] to give [Mn(CO)$_5$(CNC$_6$H$_{11}$)], catalysed by Pd/CaCO$_3$ or Pd/BaSO$_4$ was also reported [240].

1.5.8 Silyl and stannyl complexes

The reaction of Ph(H)$\overline{\mathrm{Si(CH_2)_4CH_2}}$ with [Mn$_2$(CO)$_{10}$] to give [Mn(CO)$_5${$\overline{\mathrm{Si(Ph)(CH_2)_4CH_2}}$}] and of Me(Cl)$\overline{\mathrm{Si(CH_2)_4CH_2}}$ with [Mn$_2$(CO)$_{10}$] to give [Mn(CO)$_5${$\overline{\mathrm{Si(Me)(CH_2)_4CH_2}}$}] was reported [241]. The neutron diffraction study of [(Mecp)Mn(CO)$_2$(H)(SiFPh$_2$)] was reported; values of both Mn-H and Si-H bond lengths were determined [242]. Similarly, a ^{1}H, ^{13}C and ^{29}Si NMR study of the complexes [(Mecp)Mn(CO)$_2$H(SiR$_3$)] (*35*) showed the possibility of a bonding interaction between Si and H, favouring a *cis*-geometry, whereas steric effects would favour a *trans* arrangement [243].



(35)

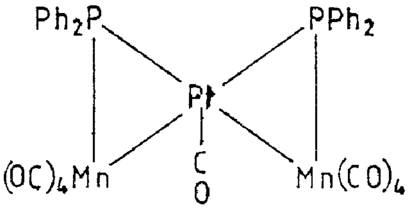
The reaction of the stannylene complexes $[M(CO)_5SnCl_2(thf)]$ (M = Cr or W) with $Na[Mn(CO)_5]$ to form tetrametallic heteronuclear cluster compounds $[(CO)_5MSn\{Mn(CO)_5\}_2]$ was observed [244]. Methyl-1-napthylphenylstannyltetracarbonyl(diphenyl-*N*-methyl-*N*-(S)-1-phenylethylaminophosphine)manganese(I) was prepared from racemic methyl-1-napthylphenyltinchloride, separated into two diastereomeric fractions by fractional crystallisation, and studied by NMR and IR spectroscopy [245].

1.5.9 Mixed metal carbonyls

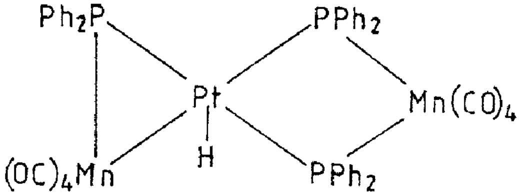
$[Mn_2(CO)_{10}]$ was reported to react with niobecene hydride to give $[(cp)_2Nb(CO)(\mu\text{-}CO)Mn(CO)_5]$, the structure of which was confirmed by X-ray analysis [246]. ^{17}O NMR spectra were recorded for the complexes $[MnR(CO)_5]$ (R = H, CH_3 or Br) and $[MnM(CO)_{10}]^{n-}$ (n = 0, M = Mn; n = 1, M = Cr, Mo or W) [247], and the preparation of $[H_2Os_3(CO)_{10}Mn(CO)_5]^-$ from $[H_2Os_3(CO)_{10}]$ and $K[Mn(CO)_5]$ was reported [248]. The reaction of $Na[Mn(CO)_5]$ with $[Rh(PPh_3)_3Cl]$ to give the heterobimetallic complex $[(Ph_3P)(CO)_2Mn(\mu\text{-}CO)_2Rh(PPh_3)_2]$ was reported; the structure postulated for this complex contains a double $Mn \leftarrow\!\!= Rh$ bond [249]. $[Mn(CO)_2(thf)(cp)]$ reacts with $[Rh(CO)_2(\eta^5\text{-}C_5Me_5)]$ to form the complex $[cp(CO)Mn(\mu\text{-}CO)_2Rh(CO)(\eta^5\text{-}C_5Me_5)]$, containing a donor $Mn \rightarrow Rh$ bond [250].

The preparation of $[BrPtL_2\{Mn(CO)_5\}]$ from L_3Pt (L = PPh_3) and $CuHgMn(CO)_5$ was reported, as was the reaction of L_4Pd with $[BrHgMn(CO)_5]$ to give $[Br_2L_2Pd\{Mn(CO)_5HgMn(CO)_5\}]$, and the reaction of PtL_3 and $[Hg\{Mn(CO)_5\}_2]$ to give $[L_2Pt\{Mn(CO)_5\}_2]$ [251]. The preparation of $[cp(CO)Mn(\mu\text{-}CS)(\mu\text{-}CO)Pt(PR_3)_2]$ (PR_3 = PMe_2Ph or $PMePh_2$) from $[Mn(CO)_2(CS)(cp)]$ and $[Pt(\eta^2\text{-}C_2H_4)(PR_3)_2]$ was reported. This complex reacts with $[Me_3O][BF_4]$ to give $[cp(CO)_2Mn\{=C(SMe)\}Pt(PR_3)_2][BF_4]$ [252,253].

The reaction of *cis*-$[PtCl_2(PPh_2Cl)_2]$ and $Na[Mn(CO)_5]$ to give $[Pt(CO)_2\{Mn(CO)_5\}_2]$ and three clusters (*36-38*) was reported [254].



(36)



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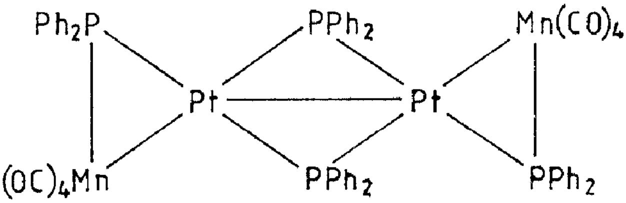

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1.6 NITROSYL COMPLEXES

The anisotropic EPR spectrum of $[Mn(CO)_4(NO)]^{\bullet}$ was detected in a γ-irradiated sample of $[Cr(CO)_6]$ doped with $[Mn(CO)_4(NO)]$ [255]. Manganese(II) reacts with N_2O_4 in ethylethanoate to give $[NO][Mn(NO_3)_3]$, which was characterised by IR, DTA and magnetic measurements [256].

^{119}Sn NMR chemical shifts as well as J(H-Sn) and J(P-Sn) were reported for the complexes $[Mn(NO)_3L]$, where L = $(Me_3Sn)_n(CMe_3)_{3-n}P$ (n = 1, 2 or 3) [257].

The reaction of $(C_6H_5CH_2)_2Mn$.dioxan with NO to give $[(C_6H_5CH_2)Mn(NO)]$ was also reported [258].

1.7 HETERONUCLEAR COMPLEXES

The perovskites La_2MnMO_6 (M = Cr, Co, Fe or Ni) were prepared by slowly heating in air co-precipitated basic carbonates, and were characterised by X-ray diffraction and magnetic susceptibility measurements [259]. The absorption spectra of the complexes $[M^{III}M^{III'}Mn(MeCO_2)_6(py)_3]$ ($M^{III} = M^{III'}$ = Fe; M^{III} = Fe, $M^{III'}$ = Cr) were reported [260].

The formation constants of the heterodinuclear complexes $[MnCuL_2L']^{2-}$ (L = phen or bipy; H_6L' = nitrilotrimethylenephosphonic acid) were determined. The complex with L = bipy is a catalyst for the oxidation of hydroquinone by

H_2O_2 [261].

1.8 PORPHYRIN AND PHTHALOCYANINE COMPLEXES

The X-ray crystal structure of nitrido{tetrakis(4-methoxyphenyl)porphinato}manganese(V), prepared from the addition of ammonia to the analogous manganese(III) porphyrin complex [Mn^{III}(porph)X] (X = Cl, Br or O_2CMe) and iodosylbenzene, was determined [262]. The crystal structure of the complex [$Mn^{IV}(MeO)_2$(TPP)], prepared by oxidation of [Mn^{III}(TPP)(O_2CMe)] by NaOCl or iodosylbenzene in basic methanol, was determined; the complex was studied by low temperature and room temperature magnetic susceptibility measurements [263]. [XMn^{III}(TPP)] reacts with iodosylbenzene to give [{XMn^{IV}(TPP)}$_2$O] (X = N_3 or OCN); the complex with X = N_3 was characterised by X-ray crystallography [264]. Oxidation of water-soluble manganese(III) porphyrins in alkaline solutions gives manganese(IV) complexes, which were proposed to be μ-oxo-dimers. Oxidation with hypochlorite was reported to give manganese(V) oxo-porphyrin [265]. Less efficient oxidation of manganese(III) porphyrins was observed in membranes and positively charged micelles, but in negatively charged micelles or microemulsions the oxidation was extremely inefficient and no manganese(V) complexes were observed. In CH_2Cl_2, the manganese(III) porphyrins reacted with phenoxathinylium hexachloroantimonate to give the manganese(III) porphyrin π-radical cation, whilst oxidation with iodosylbenzene gave the manganese(IV) porphyrin μ-oxo-dimer [266].

The cyclic voltammetry of [Mn^{III}(TPP)] with six different anions in twelve non-aqueous solvents was reported [267]. The use of [Mn^{III}(TPP)] as a model for cytochrome P-450, by the reaction of cyclohexane with (tosyliminoiodo) benzene and [Mn^{III}(TPP)] to give *N*-cyclohexyltoluene-4-sulphonamide, was reported [268].

The epoxidation of alkenes by sodium hypochlorite solution catalysed by [Mn(TPP)(O_2CMe)] in the presence of substituted pyridines was reported [269]. The electronic structure of manganese porphyrin was investigated by a CNDO/2 method [270]. It was also reported that irradiation by γ-rays at 77 K of [Mn^{III}(TPP)X] (X = Br or Cl) in 2-methyltetrahydrofuran gives two forms of [Mn^{II}(TPP)], depending on the halide used; these also differed from [Mn^{II}(TPP)] prepared chemically; these effects were attributed to solvent matrix effects [271]. Also reported was the preparation and study, by cyclic voltammetry, of [$RuCl_2$(nic_4TPP)MnCl] (nic_4TPPH_2 = *meso*-α,α,α,α-tetrakis(2-nicotinamidophenyl)-porphyrin) [272].

The complexes prepared from [Mn^{III}(porphyrin)Cl] and $[O_2]^-$ were studied by

NMR spectroscopy and solution magnetic susceptibilities, indicating a superoxomanganese(II) porphyrin configuration with coupling between the superoxide ligand and the manganese centre [273]. The IR spectra of [Mn(TPP)] and [Mn(TPP)(O_2)] were recorded in argon matrices at 15 K. Oxygen isotope scrambling experiments confirm that the O_2 is coordinated symmetrically side-on [274].

The complexing ability of [Mn(Pc)] in the solid state was studied by IR spectroscopy; the α form reacts with phenol, py and methanoic acid, whereas the β form does not [275]. The absorption spectral data for $[Mn(Pc)]^-$ were recorded, it forms complexes with thf, N_2H_4, py and *N*-methylpiperidine. At -60 °C in the presence of light and N_2H_4, [Mn(Pc)] is reduced to $[Mn(Pc)]^-$; in the presence of *N*-methylpiperidine reduction gives the dihydro and subsequently the tetrahydro derivative of [Mn(Pc)]. β-[Mn(Pc)] films on quartz are reduced by sodium vapour to $[Mn(Pc)]^{n-}$ (n = 1-4), whereas α-[Mn(Pc)] films form $[Mn(Pc)]^{2-}$ in the first stage [276]. The oxidation of [Mn(Pc)] films, and their reactions with py and HCl, were also reported [277]. The preparation of (tetra-1-phenylnapthalocyanine)manganese(II) was also reported this year [278].

1.9 COMPLEXES OF BIOCHEMICAL SIGNIFICANCE

The complexes *meso*- and *rac*-Na[Mn(ehpg)] (ehpg = ethylenebis{(2-hydroxyphenyl)glycine}) were prepared. Their optical, EPR and NMR spectra were compared to those of transferrin complexes and shown to be reasonable models for the metal binding in transferrin [39]. Also reported this year were complexes of manganese(II) with guanine [279] and adenine-*N*-oxide [280].

1.10 REVERSIBLE OXYGENATION COMPLEXES

The reversible dioxygenation of [Mn(PR_3)X_2] (R = pentyl or butyl; X = Cl, Br or I) was studied in solution by EPR spectroscopy and the claimed dioxygenated species [Mn(PR_3)(O_2)X_2] were proposed to have the unusual spin state, s = 5/2 [281].

The reported reversible binding of O_2 by $[Mn\{3,5-(CMe_3)_2Cat\}_2]^{2-}$ was claimed, however, to be due to oxidation of the ligand and subsequent reactions of the oxidation products, after a study of the system by optical spectroscopy [282]. The original workers, however, reported that oxidation of the ligand was not supported by redox thermodynamics, and the reaction was reinvestigated by spectrophotometry [283].

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