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1. Manganese 1992

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CONTENTS

INTRODUCTION

This review surveys the manganese literature for 1992 of interest to coordination chemists. It is based on a literature search of volumes 116, 117 and 118 (1 - 10) of *Chemical Abstracts*. Its format is in a similar vein to the 1991 review [1]. Additionally, major inorganic chemistry journals

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from January to December 1992 were searched separately. The assistance of Heidi Mercado of the Eastern Michigan University Library with a computer literature search is gratefully appreciated.

1.1 MANGANESE(VII)

A polarized neutron diffraction study of $K_3(MnO_4)_2$ has revealed strong localization of the electrons on two of the four manganese centres in each unit cell thereby confirming the compound as a mixed-valence double salt $K_3(Mn^{VII}O_4)K_3(Mn^{VI}O_4)_2$ [2].

1.2 MANGANESE(VI)

The salt $K_3(Mn^{VII}O_4)K_3(Mn^{VI}O_4)_2$ was mentioned in section 1.1. A new transition metal oxide $InMnO_3$ with an unusual ABO_3 structure has been synthesized [3]. The crystal structure shows it to consist of alternating layers of octahedrally coordinated indium and trigonal pyramidally coordinated manganese atoms.

1.3 MANGANESE(V)

1.31 Complexes with oxygen donor ligands

The vibrational and electrochemical properties of a series of stable manganese(V)-oxo complexes have been communicated [4]. Selective excitation studies indicate that the manganese to oxygen triple bond stretches are resonance enhanced while other modes are not. Cyclic voltammetric studies show that there is a substantial substituent effect manifested in the oxidation process which occurs over a range of 630 mV. Oxidation of the manganyl monoanions is facilitated by the non-innocent character of the aromatic-ring containing ligands.

1.3.2 Complexes with nitrogen donor ligands

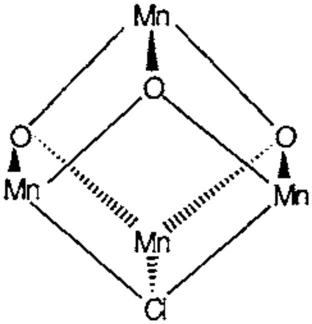
The synthesis and characterization of manganese(V)-nitridophthalocyanines(1–) and -(2–) have been reported [5]. The nitrido-metal stretching vibration is 1055 cm^{-1} and is independent of the oxidation state of the phthalocyanine ligand and is resonance Raman enhanced.

A communication of the first example of nitrogen atom transfer involving non-porphyrinic acceptors has appeared [6]. The manganese macrocyclic compounds nitrido[6,17-dihydro-6,8,15,17-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetrazacyclotetradecinato(2-)]manganese(V), ClMn(TMTAA), and chloro[bis-*N*,*N*'-(salicylaldehyde)ethylenediiminato]-manganese(III), $ClMn(Sal_2en)$ were found to undergo reversible reaction with nitrido[octaethylporphyrinato]manganese(V), Mn(N)(OEP), to give an equilibrium distribution of reactants and products even when the nitride acceptor was present in up to a two-fold excess. The reactions were monitored by visible spectroscopy.

1.4 MANGANESE(IV)

1.4.1 Complexes with oxygen donor ligands

Four $Mn^{IV}Mn_3^{III}$ complexes have recently been prepared as model complexes for the S_2 state of the water oxidation centre in PSII [7]. The complexes $(H_2Im)_2[Mn_4O_3Cl_6(O_2CCH_3)_3(HIm)]\cdot{}^3/_2CH_3CN$ and $[Mn_4O_3Cl_4(O_2CCH_3)_3(py)_3]\cdot{}^3/_2CH_3CN$ have pyramidal Mn_4O_3Cl cores (1) which are essentially superimposable. The Mn^{IV} ion is at the apex, a μ_3-Cl^- ion bridges the basal plane, and a μ_3-O^{2-} ion bridges each of the remaining three faces. The other complexes are $[Mn_4O_3Cl_4(O_2CCH_2CH_3)_3(py)_3]\cdot{}^3/_2CH_3CN$ and $[Mn_4O_3Cl_4(O_2CCH_2CH_3)_3(HIm)_3]\cdot{}^3/_2CH_3CN$. The $Mn^{IV}Mn_3^{III}O_3Cl$ core of these complexes is compared with the core of S_1 model complexes which have the $Mn_4^{III}(\mu_3\text{-}O)_2$ butterfly structure and it has been suggested that increasing the oxidation state from the S_1 to S_2 state is coupled with increasing oxide content. The nature of spin frustration in these complexes is analysed in detail.



(1)

An examination of the oxygenation chemistry of the complex (5-Cl-salen)Mn^{II}, (5-Cl-salen = 1,2-bis(5-chlorosalicylideneamino)ethane) has led to the synthesis of the bis(μ-oxo) dimer [(5-Cl-salen)$Mn^{IV}(\mu\text{-}O)]_2$ [8]. Cyclic voltammetry indicates that the dimer forms in less than 75 ms with oxygen binding by (salen)Mn^{II} most likely being the rate determining step. It was further characterized with UV, IR and ESR spectroscopies. In a related paper [9] cyclic voltammetry and UV-VIS spectroscopy were used to quantitatively monitor the reaction (equation 1, L and L' are appropriate Schiff's base ligands) which involves an unprecedented four electron two atom transfer reaction.

$$[LMn^{IV}(\mu\text{-}O)]_2 + 4L'Fe^{II} \rightarrow 2LMn^{II} + 2[L'Fe^{III}]_2(\mu\text{-}O) \qquad \text{equ. 1}$$

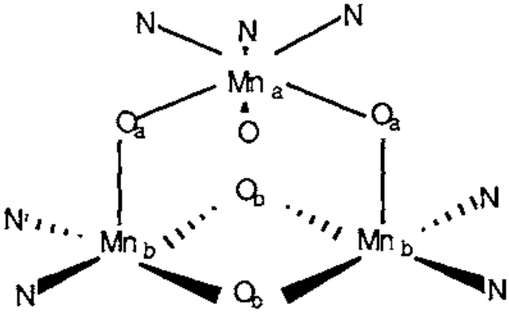
The first structurally characterized example of a coordinated $H_2IO_6^{3-}$ group has been reported recently [10]. The oxidation of a manganese(II) salt by NaOCl in alkaline solution in the presence of $NaIO_4$ gave soluble red crystals of $Na_7[Mn(H_2IO_6)(HIO_6)_2]\cdot18H_2O$. The structure of the anion shows an octahedrally coordinated Mn atom which is chelated by two $O_2IO_3(OH)^{4-}$ and one *trans* -$O_2IO_2(OH)_2^{3-}$.

The electronic and crystal structures of the heteropolymolybdates $[NH_4]_6[XMo_9O_{32}]\cdot 6H_2O$ where X = Mn or Ni have been described [11]. The Mn-O bond length is 1.897(3) Å while the low-temperature polarized electronic spectrum for Mn suggests a ligand field splitting parameter Δ = 22,500 cm^{-1} with the $^4T_2$ exited state exhibiting only a small trigonal splitting.

The conversion of an $\{Mn^{IV}(\mu_2\text{-}O)\}_2$ core to a stable $\{(Mn^{IV})_2(\mu_2\text{-}O)(\mu_2\text{-}OH)\}^+$ form exhibiting dramatically different activity towards hydrogen peroxide has been reported [12]. Protonation of $[(Mn^{IV}(saltn)\}_2(\mu_2\text{-}O)(\mu_2\text{-}OH)]ClO_4$, where H_2saltn = 1,3-bis(salicylideneaminato)propane, results in a significant change in the Mn-Mn separation of 0.1 Å concomitant with a decrease in catalase activity that reached a maximum rate of half of that of the unprotonated form.

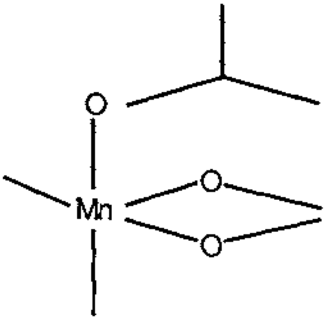
1.4.2 Complexes with oxygen and nitrogen donor ligands

The synthesis and properties of di- and trinuclear manganese oxo-complexes with the ligand *N,N*-bis(2-pyridylmethyl)ethylamine (bpea) has been reported [13]. Specifically, bond distances and angles for the dinuclear species $[Mn_2O_2(O_2CCH_3)(bpea)_2](ClO_4)$ are consistent with an Mn^{IV}_2 oxidation state assignment. Upon addition of an aqueous solution to an acetonitrile solution of this complex $[Mn_3O_4(OH)(bpea)_3](ClO_4)_3$ (2) was obtained. This complex comprises three Mn(IV) atoms two of which are coupled by doubly bridging oxo groups (Mn_b) while the third atom (Mn_a) is singly bridged to the other Mn atoms by oxo groups. Noteworthy is the fact that this complex possesses a terminally coordinated hydroxo group bound to the apical manganese, Mn-OH = 1.830(4) Å and is involved in a hydrogen-bonding interaction with an O_b group. This interaction results in a core distortion which brings Mn_a out of the plane of the two Mn_b and two O_b atoms. The EPR spectral properties are consistent with an $S = {}^3/_2$ ground state. These complexes were further characterized by UV-VIS and IR spectroscopic and electrochemical measurements. The relationship between the spin-state properties of the synthetic trinuclear aggregates and the proposed spin-state variability in Photosystem II manganese site has been noted.



(2)

In a related paper [14] $[Mn_2O_2(O_2CCH_3)(tpen)]^{2+}$, (tpen = *N,N,N',N'*-tetrakis(2-pyridylmethyl)-1,2-ethanediamine) was shown to react in aqueous solution depending on the pH of the medium. In acidic medium (3) is converted to the IV,IV product $[Mn_2O_2(O_2CCH_3)(tpen)]^{3+}$ while at a higher pH decomposition to the species $[\{Mn_3O_4(OH)(tpen)\}_2(\mu\text{-tpen})]^{6+}$ (4) was observed.



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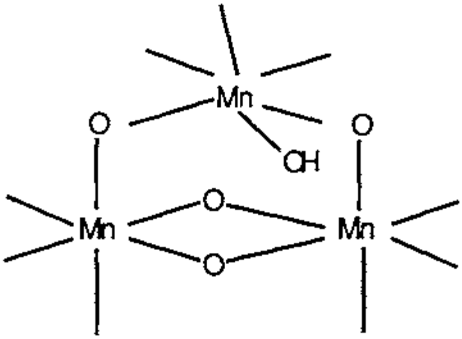

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The ground-state electronic structure of the dimer-of-dimers complex $[(Mn_2O_2)_2(tphpn)_2]^{4+}$, tphpn = *N,N,N',N'*-tetra(2-methylpyridyl)-2-hydroxypropanediamine was probed using magnetic susceptibility and isothermal saturation magnetization measurements [15]. This complex possesses structural features and a parallel polarization EPR spectrum which are similar to those observed for the S_1 state of photosystem II of the water oxidation catalyst. Results of this study are presented in light of their relevance to the manganese water oxidation catalyst.

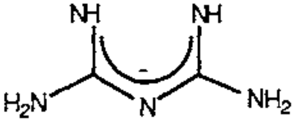
The synthesis, characterization and electrochemistry of Mn(IV) and Mn(III) complexes of hydroxamic acids which are well known for the siderophoric properties have been reported [16].

Two dimeric complexes $[Mn^{IV}(salpn)O]_2$ (salpn = 1,3-bis(salicylideneamino)propane] a bis(μ_2-oxo) complex and $[Mn^{IV}(salahp)Cl(CH_3OH)]_2$ the first example of a manganese dimer with unsupported alkoxide bridges (H_2salahap = 1-(salicylideneamino)-3-hydroxypropane), have been synthesized and characterized by X-ray crystallography [17]. These new dimers along with twenty other manganese complexes containing μ_2-oxo and μ_2-alkoxo groups have been used to develop a correlation between Mn-Mn separation and Mn-O-Mn bridge angle. Complexes containing μ_2-oxo bridges were found to conform to a law of cosines correlation between separation and bridge angle whereas when μ_2-alkoxo groups form a single-atom bridge marked deviation from the law of cosines behaviour was observed.

1.4.3 Complexes with nitrogen donor ligands

A rare example of a non-porphyrinic manganese(IV) complex coordinated solely through nitrogen atoms has been reported [18]. In particular, the tris-complex $[Mn(big)_3]^+$, (big =

biguanide) has been obtained as a red solid which decomposes in water but dissolves in Me_2SO and MeOH from which it crystallized readily. X-ray crystallography, IR spectroscopic and magnetic measurements indicate that $[Mn(big)_3]OAc{\cdot}2H_2O$ is comprised of a Mn(IV) centre bound to three deprotonated biguanide ligands (5) with octahedral MnN_6 coordination and an average Mn-N bond of 1.93 Å. Cyclic voltammetric scans indicate strong stabilization of Mn(IV) with respect to Mn(II).



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1.5 MANGANESE(III)

1.5.1 Complexes with halide ligands

An X-ray crystal structure of a new linear chain compound $Tl_2MnF_5{\cdot}H_2O$ has been obtained [19]. The manganese atom is located within elongated fluorine octahedra which share opposite corners forming infinite $(MnF_5)_n{}^{2n-}$ chains along the *c*-axis and being separated by Tl atoms and water molecules. The Mn-F bridging bonds are elongated in each chain 2.085 Å while the Mn-F terminal bonds are 1.818-1.845 Å. The compound has been characterized magnetically.

1.5.2 Complexes with oxygen donor ligands

An unusual example of multiple proton-coupled electron transfers in a single oxomanganese dimer $[(phen)_2Mn^{III}(O)_2Mn^{IV}(phen)_2](ClO_4)_3$ has been reported [20]. Two redox couples have been assigned to equations (2) and (3), the dimer is stable under experimental pH conditions and even after both bridges are protonated retains its solubility in solution.

$$[(phen)_2Mn^{III}(O)_2Mn^{IV}(phen)_2]^{3+} + H^+ + e^- \rightarrow$$
$$[(phen)_2Mn^{III}(O)(OH)Mn^{III}(phen)_2]^{3+} \qquad \text{equ.2}$$

$$[(phen)_2Mn^{III}(O)(OH)Mn^{III}(phen)_2]^{3+} + H^+ + e^- \rightarrow$$
$$[(phen)_2Mn^{III}(OH)_2Mn^{II}(phen)_2]^{3+} \qquad \text{equ.3}$$

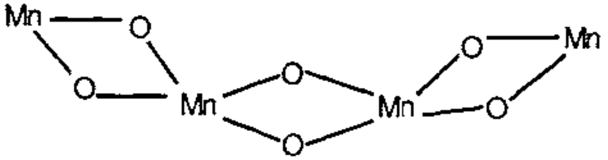
The first example of Br^- bridging high-oxidation state manganese centres has been reported [21]. The cubane complex $[Mn_4O_3Br(OAc)_3(dbm)_3]$, dbm = dibenzoylmethane, was synthesized by treating $[Mn_4O_2(OAc)_6(py)_2(dbm)_2]$ with either N^nBu_4Br in hot MeCN or Me_3SiBr in CH_2Br_2. Cyclic voltammetry and magnetic studies indicate that this complex displays similar reversible redox processes and similar magnetic exchange pathways to its Cl^- analogue, a finding of significant biological relevance to the photosynthetic water-oxidation enzyme.

A communication has appeared delineating how spin frustration can lead to appreciable numbers of unpaired electrons in a complex whose core results from the fusion of two Mn_4O_2 butterfly units. This has implications in that extrapolation of this effect to polymeric systems might be a viable route to molecular ferromagnets [22]. In particular, the preparation and characterization of $(NEt_4)[Mn_7O_4(OAc)_{10}(dbm)_4]\cdot 3CH_2Cl_2\cdot 2C_6H_{14}$ has been described and magnetic data indicate that the ground state is either $S = 3$ or $S = 4$.

The feasibility of altering the electron count of the complexes $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ (where R = Me or Ph) was investigated given their potential as building blocks to molecular ferromagnets [23]. Metal substitution and redox changes led to the preparation of the two compounds $[Mn_8Fe_4O_{12}(O_2CMe)_{16}(H_2O)_4]\cdot 4H_2O.2MeCO_2H$ and $[N^nPr_4][Mn_{12}O_{12}(O_2CPh)_{16}(H_2O)_4]\cdot H_2O$. Magnetic studies indicate that metal substitution or redox changes lead to major changes in the spin of the ground state species.

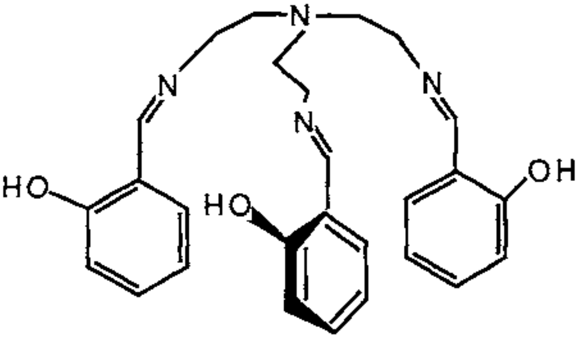
An attempt to synthesize model complexes for manganese catalase containing an asymmetric ligand environment has led to the complexes $[Mn^{IV}L(\mu\text{-}O)_2(\mu\text{-}MeCO_2)Mn^{III}(MeCO_2)_2]$ and $[Mn^{IV}L(\mu\text{-}O)_2(\mu\text{-}MeCO_2)Mn^{III}(bpy)MeOH)](ClO_4)_2\cdot MeOH$, L = 1,4,7-trimethyl-1,4,7-triazacyclononane [24]. Their structures have been obtained and their catalytic activity was found to be five orders of magnitude less than the native enzyme.

The synthesis, preliminary structural characterization and magnetic study of a new type of Mn_4-cluster with a linear $[Mn_4O_6]^{4+}$ chain structure have been described [25]. The cluster was synthesized by the condensation of $[Mn(bpy)Cl_3(H_2O)]$ (0.59 mmol) in 15 ml H_2O/HNO_3. Small amounts of NaOH were added during the addition to maintain a pH of 2. After recrystallization dark-brown crystals of $[Mn_4O_6(bpy)_6](ClO_4)_4\cdot 2H_2O$ were obtained. Preliminary X-ray data indicate that each cationic unit is composed of two-di-μ-oxo-dimanganese units linked by a di-μ-oxo bridge (6).



(6)

Complexes exhibiting a new geometry for tetramanganese namely, fused open cubanes, have been obtained [26]. By use of the podand ligand saltren H_3L (7) both template condensation of tris(2-aminoethyl)amine with salicylaldehyde and direct treatment of the neutral ligand with manganese(III) in MeOH–MeCN resulted in the deprotonation of phenolic groups and isolation of the tetranuclear di-μ-oxo cluster $[Mn_4O_2(L)_2]^{2+}$. The structure contains discrete $[Mn_4O_2(L)_2]^{2+}$ cations and $[MnCl_4]^{2-}$ anions. In the cation each manganese atom is six-coordinate with one having an NO_5-donor set while the other has a N_3O_3-set giving an Mn_4O_6 core consisting of two incomplete face-sharing cubanes, Mn-Mn distances are 2.898(2), 2,999(2) and 3.035(2) Å. Cyclic voltammetry and EPR spectroscopic studies have been conducted.



(7)

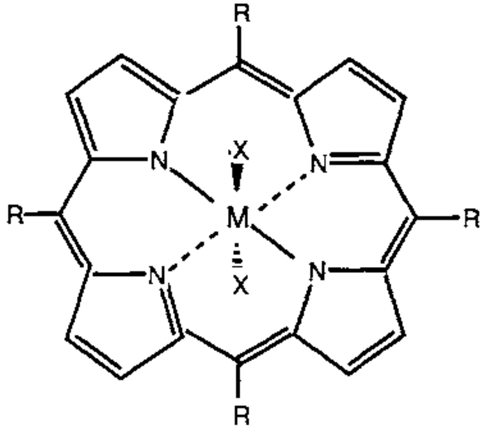
The kinetics and mechanism of the oxidation of hypophosphite ion by diaquobis(pentane-2,4-dionato)manganese(III) in aqueous perchlorate media have been investigated [27].

1.5.3 Complexes with oxygen and nitrogen donor ligands

The results of a study aimed at gaining an understanding of the mechanism of the O–O bond-breaking step in the decomposition of manganese(III) porphyrin-hydroperoxide complexes in water in the presence and absence of imidazole have been presented [28]. The kinetics and products of the reaction of [*meso*-tetrakis(2,6-dimethyl-3-sulfonatophenyl)porphinato]manganese(III) hydrate, $Mn^{III}(X)_2$ with ^tBuOOH and $(Ph)(Me)_2COOH$ in water (pH = 7.3-12.6, 30°C and $\mu = 0.2$ ($NaNO_3$); $X = H_2O$ or HO^-) have been studied. Results indicate that regardless of the pH, $Mn(X)_2$ catalyses the homolytic scission of hydroperoxides in the absence of imidazole. In its presence however, the mechanism was found to be pH dependent.

An investigation of the pH dependence of oxidation and reduction potentials and associated pK_a values for the water soluble and non-μ–oxo dimer-forming [5,10,15,20-tetrakis(2,6-dichloro-3-sulfonatophenyl)porphyrinato]Fe(III)$(X)_2$, Mn(III)$(X)_2$, and Cr(III)$(X)_2$, ($X = H_2O$ or HO^-) hydrates in aqueous solution has been undertaken [29]. A quantitative assessment of the influence of electronic effects of phenyl substituents of metallo-5,10,15,20-tetrakis(phenyl)porphyrins by comparison of the acid-base and electrochemical properties of (**8**)M(III)$(X)_2$, and (**9**)M(III)$(X)_2$ has been made and are thought to be due to inductive effects.

The preparation of two hexadentate ligands (H_2BBPEN and H_2BBPPN) (**10**,**11**) derived from alkyldiamines containing phenolate-type and α-pyridyl pendant arms has been described [30]. The Mn(III) complexes formed with these ligands have been characterized using spectral, solution electrical conductivity, magnetic and electrochemical techniques. An X-ray crystal structure was obtained for [Mn(BBPEN)][PF_6] and shows that this complex possesses short axial Mn-N(py) bond distances of 2.237(5) and 2.252(5) Å in comparison to those found in other "Jahn-Teller elongated" complexes. A relatively high redox potential for the Mn(IV)/Mn(III) couple ($E°$ = 0.90 V *vs* NHE) indicates that this complex is biomimetic of photosystem II.



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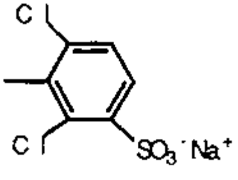

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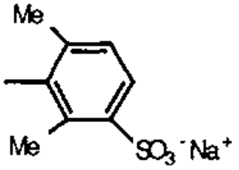

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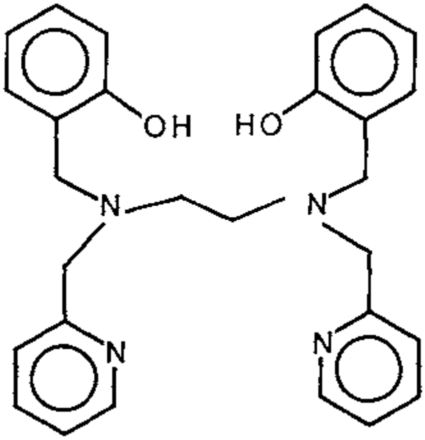

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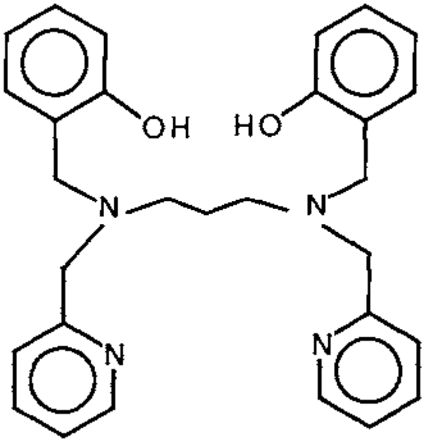


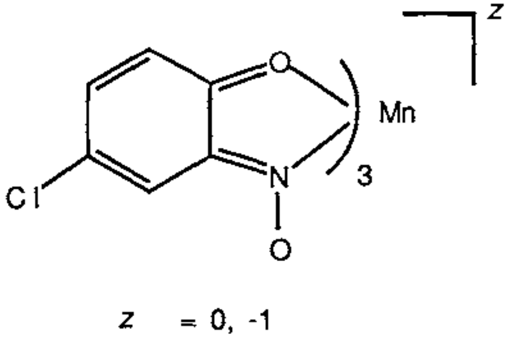
(11)

The preparation and isolation of the mononuclear complex $[Mn(salpn)(EtOH)_2](ClO_4)$, H_2salpn = *N,N'*-bis(salicylidene)-1,3-diaminopropane has been achieved [31]. X-ray crystallography indicates Mn-O and Mn-N distances are in good agreement with those for other Mn^{III} Schiff's base complexes. The complex was converted by air oxidation in basic methanol followed by recrystallization from dmf to $[Mn_2O_2(salpn)_2]$. These complexes were further characterized by magnetic susceptibility measurements and cyclic voltammetry.

Continuing studies on the assessment of the magnitude by which peripheral ligands may influence the structural, redox, magnetochemical and spectroscopic properties of a polynuclear oxide-bridged Mn aggregate have been conducted [32]. In particular, complexes employing the ligands 8-hydroxyquinoline, (hqnH), 5-chloro-8-hydroxyquinoline (Cl-hqnH) and 2-(hydroxylmethyl) pyridine (hmpH), have been synthesized. X-ray crystallography on $[Mn_4O_2(O_2CMe)_7(hqn)_2]$ and $[Mn_4O_2(O_2CMe)_7(hmp)_2]$ show a butterfly Mn_4O_2 core with seven carboxylate ligands bridging between two manganese ions and the hqn or hmp ligands deprotonated and chelating at the wingtips. Coordination about each manganese atom is elongated octahedral and NMR spectroscopic, conductivity and cyclic voltammetry studies were reported.

An attempt to model both manganese catalase and the oxygen evolving complex of Photosystem II has led to the synthesis of a manganese complex containing the ligand 3,5-bis(salicylideneamino)methylpyrazole [33]. The complex of formula $Mn_4(L)_2(CH_3O)_4(CH_3OH)_4]^{2+}$ comprises four linearly arranged Mn(III) ions with a terminal-internal Mn---Mn separation of 3.485Å and an internal-internal Mn---Mn separation of 3.127(2) Å. This complex exhibits high catalase activity in *N,N*-dimethylformamide.

The synthesis and isomerism of tris-chelated low-spin Mn(III) and Mn(II) complexes of the 4-chloro-*O*-benzoquinone oxime ligand (**12**) have been described [34]. The MnL_3 complex exhibits a preference for *mer*-geometry although *mer*- and *fac*-isomers coexist in solution as well as in the crystal lattice of the $[Et_4N]^+$ salt of $[MnL_3]^-$.



(12)

The first example of a polymer containing a dimeric repeat unit, with the structure $[Mn(salpn)\text{-}OAc\text{-}Mn(salpn)\text{-}OAc]_n$, salpn = *N,N'*-bis(salicylidene)-1,3-diaminopropane, and containing three hydrogen bonded water molecules per dimer has been reported [35]. The crystal structure of $[Mn(salpn)(OAc)]_2(H_2O)_3$ shows the Mn(salpn) units are bridged by the acetate groups in an *anti-anti* configuration while the two salpn ligands in each monomer are oriented 180° with respect to each other obviating any $\pi-\pi$ interaction. The manganese atoms are in distorted octahedral environments with elongation of the Mn-O bonds along the symmetry axis.

A communication has appeared describing the crystal structure and spectroscopy of two novel (formato)manganese tetraphenylporphyrin complexes $[(TPP)Mn(HCO_2)]_n$ and $[(TPP)Mn(HCO_2)]_3 \cdot 6CHCl_3$ (TPP = tetraphenylporphyrin) in which the manganese porphyrin moieties are linked by bridging formate ligands [36]. The former, a product of solvent oxidation, was obtained when a CH_2Cl_2 solution of (TPP)Mn(Cl) was washed several times with a 5% NaOH solution. The organic layer was separated and using a rotary evaporator its volume was repeatedly halved and then doubled by the addition of thf. Heptane was allowed to slowly infuse into the resultant solution over several weeks. The Mn-O(formate) bond length is 2.188(2) Å. It is built up from (tetraphenylporphinato)manganese(III) complexes linked by formate ligands, with one half of the formula unit comprising the asymmetric unit of the other. The manganese atom lies on a crystallographic inversion centre and the formate carbon atom sits on a two-fold axis as does the thf oxygen atom. The latter was prepared by dissolving (TPP)Mn(OH) in methanol and adding an equivalent of formic acid. Crystals were obtained by solvent stripping, redissolving in freshly distilled CH_2Cl_2, filtering, allowing hexane to infuse until the crystals began to deposit at the solution surface and the solution was allowed to stand overnight. This complex may be regarded as a fragment of a "fractured polymer" in which adjacent trimeric components of the "ruptured chain" have a longitudinal separation of 1.104 Å and a transverse displacement of 4.241 Å to give an overall distance of 8.565 Å between terminal Mn sites.

The synthesis and characterization of di-μ-oxodimanganese(III,IV) and (IV,IV) complexes containing the tetradentate ligand 1,4,7,10-tetraazacyclododecane (cyclen) has been achieved [37]. The crystal structure of $[(cyclen)Mn(III)O_2Mn(IV)(cyclen)]Cl_3 \cdot LiCl \cdot 5H_20$ has been obtained. The dimer which has a crystallographic inversion centre in the middle of the dimer gives rise to two crystallographic Mn atoms. The Mn-Mn separation is 2.694(1) Å while the average Mn-O distance is 1.818Å and $Mn\text{-}N(axial)_{avg} = 2.170(6)$ and $Mn\text{-}N(equatorial)_{avg} = 2.090(6)$Å. These complexes were characterized by EPR and electronic spectroscopies and magnetic measurements.

The kinetics and mechanism of the oxidation of *bis*(2,4,6-tripyridyl-1,3,5-triazine)iron(II) by *trans*-1,2-diaminocyclohexanetetraacetatomanganate(III) in acetate buffer have been monitored using stopped-flow spectrophotometry [38]. The reaction was found to be first order in substrate, and evidence for pre-complexation between the oxidant and substrate was obtained. The products were characterized by using ^{54}Mn and ^{59}Fe radiotracers.

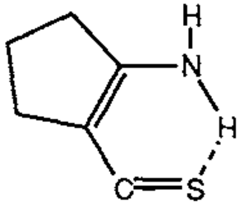
The crystal structure of the complex diaqua-*N*,*N*'-trimethylenebis(5'-chlorosalicyleneaminato)manganese(III) perchlorate monohydrate has been described [39]. The Schiff's base forms a square planar belt about the manganese atom with Mn-N bond lengths of 2.029(8) and 2.044(8) Å and Mn-O bond lengths of 1.894(6) and 1.866(6) Å. The distorted octahedral arrangement is completed by two capping water molecules at 2.230(6) and 2.206(7)Å. Infinite spirals of the complex which are generated by a screw axis along *c*, are linked by hydrogen bonds from the coordinated water to phenoxy oxygen and π-bonds between overlapping aromatic rings.

The use of the ligand *N,N,N',N'*-tetrakis(2-pyridylmethyl)-1,2-ethanediamime, tpen, in the synthesis of a complex containing an $[Mn_2O_2(O_2CCH_3)]^{2+}$ core and a spanning hexadentate ligand has been demonstrated [40]. A salient feature of the complex $[Mn_2O_2(O_2CCH_3)(tpen)](ClO_4)_2{\cdot}3H_2O$ is that the hexadentate tpen ligand spans the bis(oxo)-bridged dimer, its tripodal end binding facially to each Mn atom with the aliphatic nitrogen atoms situated trans to the Mn_2O_2 plane. The Mn(III) and Mn(IV) ions may be distinguished on the basis of metal-ligand distances and the $[Mn_2O_2]^{3+}$ core is not planar due to the bridging acetate group. This complex was characterized by electronic, IR and EPR spectroscopies, X-ray crystallography and magnetic susceptibility measurements.

The synthesis and characterization of a mononuclear Mn(III) hydroxide complex which displays stability with respect to condensation to μ-oxo species and which bears terminal hydroxide ligation has been described recently [41]. The requisite synthetic steps involved rapid stirring of a CH_2Cl_2 solution of [L'MnCl] where H_2L' = bis(2-hydroxy-5-nitrobenzylimino-propyliminopropyl)methylamine with an aqueous NaOH solution. After several minutes the yellow-green organic layer was transformed to a red-brown colour. Dark red crystals were used for X-ray structure determination. The Schiff's base is pentacoordinate with three nitrogen atoms coordinated meridionally and the phenolate oxygen atoms *cis* to each other. The proton of the coordinated hydroxide was located on a difference Fourier map (O-H = 1.0Å). The Mn-OH bond length is 1.827(6) Å and the complex was further characterized by ^1H NMR spectroscopy, magnetic susceptibility and UV-VIS spectroscopy.

1.5.4 Complexes with sulfur donor ligands

A report on the investigation of the coordination chemistry of the didentate donor (*S,S'*) 2-aminocyclopent-1-ene-1-carbodithioc acid (13) with Mn(III) and V(IV) has appeared [42]. The manganese complexes are high spin and exhibit two ligand-to-metal charge-transfer bands at 610 and 530 nm. Electrochemical studies have been carried out.



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1.5.5 Complexes with nitrogen donor ligands

Nuclear magnetic resonance dispersion (NMRD) has been used to study the ability of eight manganese porphyrins to enhance the longitudinal relaxation rate of water protons in aqueous solution [43]. Five of these porphyrins exhibited high relaxivities while the other three demonstrated much lower relaxivities. It was proposed that the latter exist as aggregates in solution while the former are monomeric. Addition of perdeuterated acetone to solutions of the latter caused them to attain relaxivities which are similar in magnitude to the others at all frequencies while the addition of acetone to solutions of the former caused no significant change.

A fundamentally new strategy for modelling the active site of cytochrome P-450 in asymmetric epoxidation of prochiral olefins has been proposed [44] Several new chiral metalloporphyrin catalysts which mediate asymmetric oxygen transfer have been prepared. They are derived from an enantiotopic porphyrin by introducing a strap on one side and have diastereotopic faces analogous to the chirally oriented protoheme in the active centre of cytochrome P-450(I) having enantiotopic protoporphyrin IX.

The surface enhanced resonance resonance Raman scattering spectra (SERRS) of adsorbates on a silver electrode for Mn(III) and Cr(III) tetraphenylporphines having an axially coordinated monoanion such as chloride and perchlorate in acetonitrile have been obtained [45]. In addition, a spectrum was also recorded for Mn(II)TPP which was electrochemically generated on the surface from the corresponding trivalent complexes. On adsorption to the electrode at 0 V, $(TPP)Mn^{III}Cl$ dissociates the fifth axial ligand forming the adsorbed species $[(TPP)Mn^{III}]^+$. The divalent complex is adsorbed as a four-coordinate species whereas in acetonitrile solution it is five-coordinate possessing an associated solvent molecule as the fifth ligand.

The effect of solution ionic strength on axial ligation in manganese(III) 5,10,15,20-tetraarylporphyrin chlorides has been quantified recently [46]. Tetrahydrofuran solutions of the metalloporphyrin (0.0 - 0.5M) in the electrolyte tetrabutylammonium tetrafluoroborate were studied by electronic absorption, resonance Raman spectroscopy and ultramicroelectrode voltammetry. Significant dissociation was found even at moderate electrolyte concentrations; this dissociation was promoted as the electrolyte concentration increased.

Studies on the ability of axial ligation to modulate redox potentials and electrode half-reactions by the coordination of methanol to Mn(TPP)Cl have been carried out [47]. The results of electrochemical and spectroscopic studies are presented and indicate that axial ligand preference for the Mn(III/II) oxidation states leads to biphasic behaviour in the $Mn^{III/II}$ reduction potentials.

Manganese(III) complexes of peripherally substituted dibenzotetraaza[14]annulenes were synthesized by the reaction of free ligand with $Mn(acac)_2NCS$ [48]. They were characterized by elemental analysis, magnetic moments, IR and FD-MS spectroscopy. Some of these complexes were found to be effective catalysts for mono-oxygenase-like oxidation of *p*-nitro-*N*,*N*-dimethylaniline by iodosylbenzene.

A potentiometric study of Mn(III) and Mn(II) complexes of 6-phenyl-2,2'-bipyridine and 2,2' : 6,2"-terpyridine in aqueous solutions has been reported [49].

1.6 MANGANESE(II)

1.6.1 Complexes with halide ligands

The complexes $MnI_2(CN^tBu)_n$ (n = 1, 1.5, 2), $MnI_2(PPh_3)(CN^tBu)_2$ and the mixed-valence isomeric complexes $[Mn(CN^tBu)_6][MnI_3(PPh_3)]$ and $[Mn(CN^tBu)_5(PPh_3)][MnI_3(CN^tBu)]$ have been prepared [50]. X-ray crystallography on the latter two complexes show them to have ion-pair structures. IR spectroscopic studies probing the nature of the Mn-C bond in these complexes is discussed.

1.6.2 Complexes with oxygen donor ligands

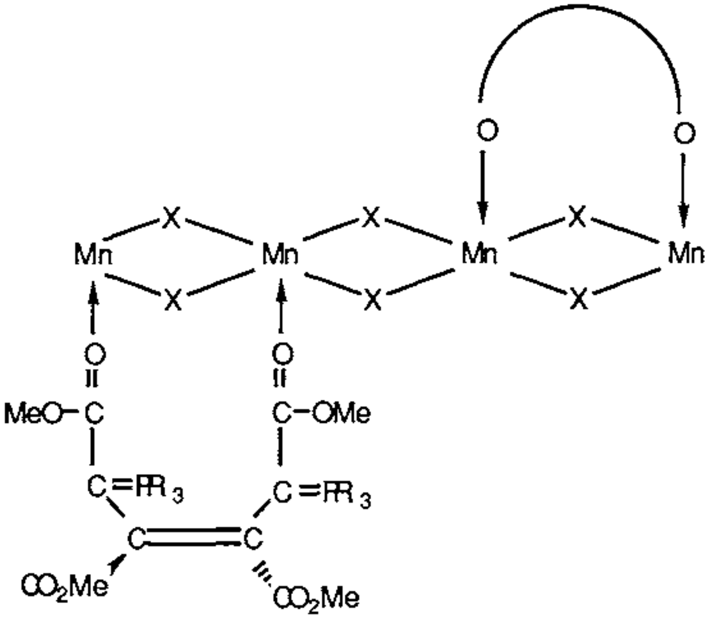
A new hexanuclear mixed-valence manganese cluster $[Mn_6O_2(O_2CPh)(EtOH)_4(H_2O)]\cdot EtOH$ has been synthesized in 40% yield [51]. In addition to terminal EtOH and H_2O groups it exhibits three different types of benzoate ligation namely μ_2-bridging, μ_2-bridging and monodentate terminal forms.

The redox chemistry of the ligand 4-methoxy-2-quinolinecarboxylic acid, its monoanion and its complexes with Mn(II) and Mn(III) has been studied in dmso using electrochemical, spectroscopic and magnetic measurements [52].

Using infrared spectroscopy the OD stretching vibration spectra of Mn^{2+} perchlorates in dilute (0.2-0.4M) aqueous solution were obtained [53]. Intensities, bandwidths and peak positions of the hydrated cation bands are reported. The OD stretching vibration band appears at 2427(2) cm^{-1}.

Adducts of the type $Mn(bR_3Pc)_nX_2$, (n = 1 or 2; X = I or NCS; bR_3Pc tetramethyl-2-butenediylidenebis(triorganophosphorane)-1,2,3,4-tetracarboxylate were prepared from the reaction of $Mn(phosphine)_nX_2$ with dimethylacetylenedicarboxylate or with the preformed bR_3Pc [54]. Elemental analysis, IR, ESR, and ^{13}C, ^{31}P were used to characterize intermediates and products. A structure is proposed in which carbonyl groups coordinate to manganese atoms (**14**).

Interest in the coordination of sulfur dioxide, an environmental hazard, to transition metal complexes has prompted thermodynamic studies on the reaction of sulfur dioxide with $[Mn(vppO_2)_2(NCS)_2]$, ($vppO_2$ = *cis*-$PPh_2(O)CHCHP(O)Ph_2$), in the solid state [55]. An adduct $Mn(vppO_2)_2(NCS)_2\cdot SO_2$ was produced; its structure is unconfirmed but sulfur dioxide is thought to be bound to a ligand. The mean standard enthalpy for the process was found to be -156.1 kJ mol^{-1} indicative of chemisorption. In related papers, the preparation, properties and reactions with sulfur dioxide in the solid state of complexes of the type $[MnL_2(H_2O)_2](ClO_4)$ where L = $Ph_2E(O)$-Y-$E(O)Ph_2$, E = P or As; Y = C_2H_4 or *cis*-C_2H_4 [56] or $[Mn\{OPPh_2(OPh)\}_2X_2]$, X = Cl, Br, I or NCS [57] have been described. These complexes react in the solid state with sulfur dioxide to produce bis-complexes which contain both weakly and strongly bound sulfur dioxide. Adsorption isotherms for the uptake of sulfur dioxide by these complexes have been obtained.



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The crystal structure of manganese(II) bis(phosphoenolpyruvate) dihydrate has been described [58]. The Mn atom is six coordinate being surrounded by two water and four phosphate oxygen atoms. Additionally, two terminal oxygen atoms of each phosphate group bridge pairs of manganese atoms forming linear chains along the *b* axis.

The production of hydrogen peroxide from dioxygen and hydroxylamine or hydrazine catalysed by manganese(II) catecholate complexes has been studied [59]. In this study the effect of variations in the substrate and ligand on H_2O_2 production was investigated.

1.6.3 Complexes with oxygen and nitrogen donor ligands

The synthesis and structures of the first neutral Mn(II) and Fe(II) catecholates, the dimers $Mn_2(DBCat)_4(py)_6$ and $Fe_2(DBCat)_2(py)_n$(n = 4,6) and $M_4(DBCat)_4(py)_6$ (M = Mn, Fe) and the first mixed-oxidation-state catecholate complex, the oxidation product $Mn_3(DBCat)_4(py)_4$, $DBCatH_2$ = 3,5-di-*tert*-butylcatechol and some of their spectroscopic properties are reported [60]. An X-ray crystal structure for $Mn_4(DBCat)_4(py)_6$ indicates an Mn_4O_6-core comprising four doubly bridging oxygens, two triply bridging oxygens, further coordination by pyridine ligands gives two Mn trigonal bipyramidal while the others are distorted octahedral giving a geometry which has a basket-like appearance. The structure of $Mn_3(DBCat)_4(py)_4$ comprises two five-coordinate Mn(III) one square pyramidal and one trigonal bipyramidal each bound by two doubly bridging catecholate oxygens to a central Mn(II) ion.

The synthesis, structure and characterization of a phenolate-bridged dimanganese(II) complex of a dinucleating phenol ligand has been reported [61]. The complex $[Mn_2(LO)(OAc)_2](ClO_4)$, (LOH = 2,6-bis((bis(2-(2-pyridyl)ethyl)amino)methyl)phenol) possesses two acetate ions and a phenoxy oxygen which bridge the manganese ions. Cyclic voltammetry in CH_3CN shows a reversible peak at 1.28 V (*vs* Ag/AgCl). The two redox potentials assigned to the $Mn^{II}_2/Mn^{II}Mn^{III}$ and the $Mn^{II}Mn^{III}/Mn^{III}_2$ redox processes are significantly higher than those potentials found for the same processes in analogous mixed-valence complexes indicating that the ligand LOH stabilizes lower oxidation states. This may be attributed to the six-membered chelate ring found in this complex. The EPR results are discussed.

Stereoselective trytophan 2,3-dioxygenase (TDO) model reactions with newly synthesized manganese chiral porphyrins have been reported recently [62]. The CD spectra of these porphyrins have been reported and reaction intermediates have been investigated by optical absorption, ESR and ^1H NMR spectroscopy.

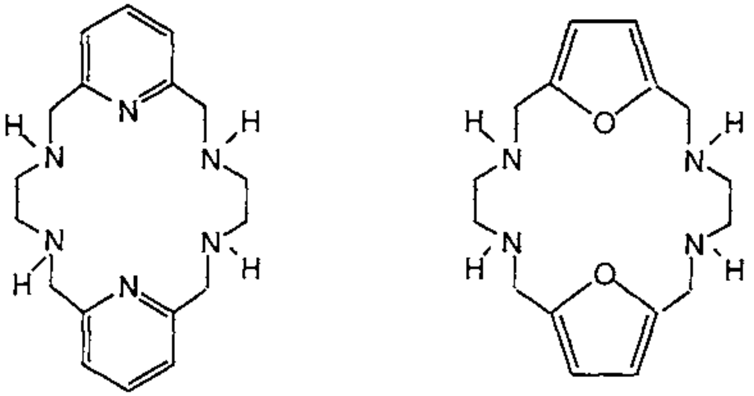
A re-examination of bulk magnetic susceptibility data in conjunction with variable-field magnetization and EPR studies has revealed a rare example of a triangular μ_3-oxide metal complex having an intermediate spin ground state [63]. Specifically, the mixed-valence complex $[Mn^{II}Mn^{III}_2O(O_2CCH_3)_6(py)_3](py)$ was found to have an $S = {}^3/_2$ ground state in contrast to a previous report of a ground state $S = {}^1/_2$. Susceptibility data for the related mixed-valence complex $[Mn^{II}Mn^{III}_2O(O_2CPh)_6(py)_2(H_2O)]\cdot{}^1/_2(CH_3CN)$ have been reanalysed and the ground state was determined to be $S = {}^1/_2$. The results for both complexes were discussed in terms of spin frustration within the Mn_3O core.

New 12- and 24-membered macrocycles with pendant acetato groups have recently been synthesized from a condensation reaction between ethylenediamine tetraacetic dianhydride and ethylenediamine [64]. The formation of the macrocycles $C_8H_{14}N_4O_2(CH_2CO_2H)_2$, $L(12)H_2$, and $C_{16}H_{28}N_8O_4(CH_2CO_2H)_4$, $L(24)H_2$ was confirmed by an X-ray crystal analysis of their complexes with Mn(II) and Cu(II). The structure of the $Mn_2L(24).8H_2O$ indicates that two manganese atoms are coordinated to four oxygen and two nitrogen atoms with Mn-O distances of 2.111 - 2.212 Å and Mn-N distances of 2.358 - 2.445 Å. Additionally, a weak bond is formed between an Mn atom and an oxygen atom (2.686 Å) establishing seven-coordination geometry about the Mn centre.

Two rare examples of water-bridged dinuclear Mn(II) complexes which exhibit properties similar to those of dimanganese centres in native proteins have been synthesized [65]. The preparation, structural characterization and magnetic properties of $[Mn_2(H_2O)(piv)_4(Me_2bpy)_2]$ and $[Mn_2(H_2O)(OAc)_4(tmeda)_2]$, piv = pivalate, Me_2bpy = 4,4'-dimethyl-2,2'-bipyridine, tmeda = *N,N,N',N'*-tetramethylethylenediamine have been documented. The molecular structures show both to comprise a core of two Mn(II) atoms bridged by a water molecule and two didentate carboxylate ligands. An additional carboxylate ligand is coordinated to each of the manganese atoms. The non-coordinating oxygen atoms on the latter carboxylates are strongly hydrogen bonded to the bridging water molecule with O····O distances of 2.498(4) and 2.539(4) Å and the O-H stretching frequency is shifted to 1965 cm^{1}. The Mn····Mn distances of 3.5950(9) and 3.621(2) Å are almost identical to the distance between two manganese atoms in a pseudocatalase of a *Lactobacillus* strain and ribonucleotide reductase of a *Micrococcus* strain.

The synthesis and characterization of low-spin tris(quinine oximates) of manganese(II) and (III), $[M(RQ)_3]^z$, (z = –1, O R = Cl, Br, Me, ^{t}Bu) have been described [66]. Geometrical isomerism has been observed although the isomer preferences of the two states are very different.

The preparation, characterization and metal binding properties of the ligands pyo$_2$[18]dieneN$_6$ and furo$_2$[18]aneN$_4$O$_2$, (**15**), have been reported [67] The stability constants for complexes of these ligands were compared with those of the saturated donor analogues [18]aneN$_6$ and [18]aneN$_4$O$_2$.



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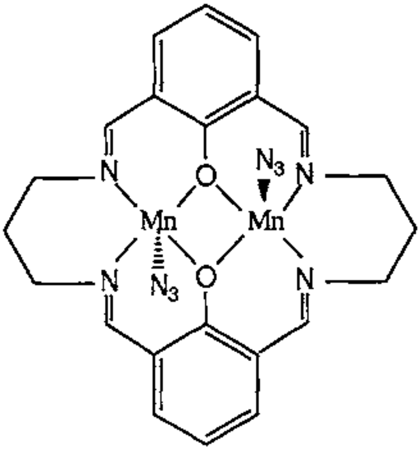
The reaction of manganese(II) alkyls with isocyanates and *tert*-butyl isocyanide has been described [68]. In particular, the reaction of Me_3SiNCO with $[Mn(CH_2{}^tBu)_2]_4$ yielded $Mn_3(CH_2{}^tBu)_2[\mu\text{-}OC(CH_2{}^tBu)N(SiMe_3)]_2(\mu\text{-}CH_2{}^tBu)_2$ and $Mn_4(CH_2{}^tBu)_2(\mu_3\text{-}NCO)_2[\mu\text{-}OC(CH_2{}^tBu)N(SiMe_3)]_4$. These complexes have been characterized by X-ray crystallography.

The synthesis, crystal and molecular structures of Mn(II) and Eu(II) complexes of the condensation product of benzoylacetone and benzoylhydrazine (H_2L) of composition $Mn(HL)_2$ and $[Eu(HL)_2(H_2L)H_2O]Cl$ have been reported [69].

The crystal structure of $[MnL(\alpha,\alpha'\text{-bpy}).H_2O].1.5H_2O$ where L is thiosemicarbazidediacetic acid has been determined [70]. The asymmetric unit contains two crystallographically non-equivalent $[MnL(\alpha,\alpha'\text{-bpy}).H_2O]$.complexes and three outer-sphere water molecules. The coordination environment about the Mn atom is a distorted seven-fold one.

A novel elimination reaction from a manganese(II) acetate tetrahydrate complex has led to the formation of a dinuclear complex with a Robson-type macrocyclic ligand [71] The reaction of 2,6-diformyl-4-methylphenol and 2-(3-aminopropylamino)ethanol with manganese(II) acetate tetrahydrate gave (**16**) by elimination of a hydroxylethyl group. Its crystal structure was determined, each Mn atom is coordinated by two bridging phenoxide oxygens and two imine nitrogens from the macrocycle with the coordination sphere being completed by an azide nitrogen yielding a square pyramidal geometry. The Mn atom is displaced by 0.67 Å on either side of the ligand plane, Mn-N(imine) distances are 2.153(6) and 2.192(5) Å while Mn-O(phenoxide) are 2.113(5) and 2.114(5) Å typical for Mn(II). The electronic spectrum and magnetic properties of this complex were studied.



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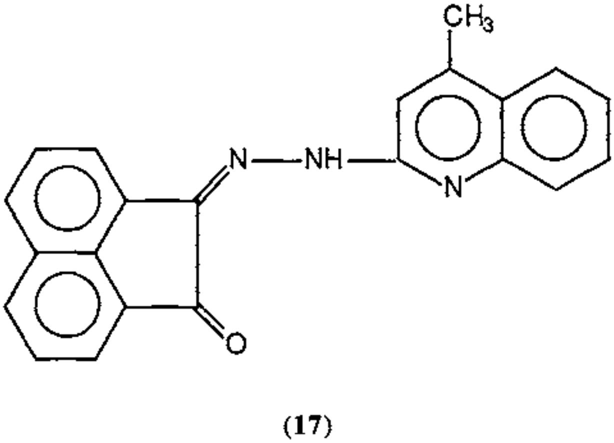
The synthesis, spectral and magnetic studies of manganese(II) complexes of substituted hydrazones have been documented [72]. The complexes have the general formula [MnL_2X_2] where L =ALH (**17**) and X = OAc and [MnL'_2X_2] where L' = ILH (**18**) and X = OAc, Cl.



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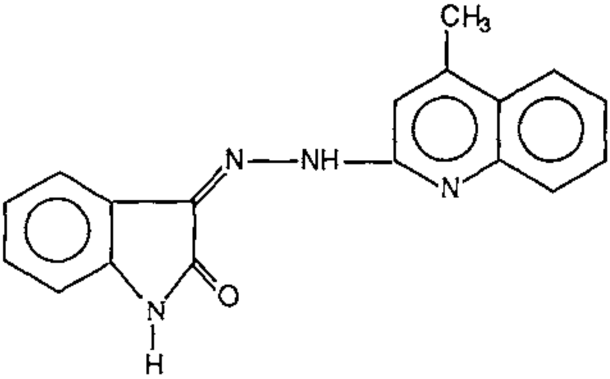

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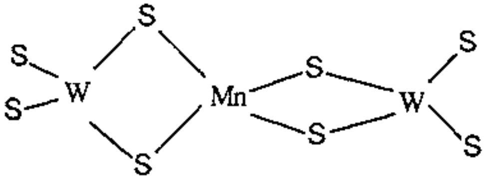
1.6.4 Complexes with sulfur donor ligands

The heterometallic complexes $(PPh_4)_2[Mn(MS_4)_2]$, (M = Mo or W) have been synthesized and characterized recently [73]. An X-ray analysis for the tungsten derivative (**19**) shows the four-membered rings to be strictly planar although strained as evidenced by the Mn-S bond distance of 2.452(7) Å and an Mn····W separation of 3.056(1) Å.



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1.6.5 Complexes with nitrogen donor ligands

Magnetic circular dichroism, MCD, in combination with matrix-isolation techniques was used recently in order to elucidate the ground state of manganese phthalocyanine [74]. The MCD and absorption spectra were studied in an Ar matrix at a temperature of approxiamately 5 K over the range 10000 to 33000 cm^{-1}. Absorption data point to a ^4E_g ground state whereas magnetic susceptibility measurements establish a $^4A_{2g}$ ground state, probably due to intermolecular interactions. The dispersion of the MCD permitted the assignment of an LMCT transition.

The magnetic field dependence of the aqueous proton NMR longitudinal relaxation rate has been studied in several Mn(II) nitrogen-containing macrocyclic complexes [75]. Structure-relaxivity relationships have been studied and show that when ring size is varied, relaxivity is correlated to first order with the number of coordinated water molecules whereas, when the degree of saturation in the ring is varied, relaxivity per coordinated water molecule decreases with increasing saturation in the ligand.

An eight-coordinate Mn(II) complex with a pyrazole-functionalized tetraazamacrocycle has been synthesized and characterized recently [76]. The complex $[MnL][PF_6]_2{\cdot}(CH_3)_2CO$ where L is 1,4,7,10-tetrazacyclodecane consists of an Mn^{2+} ion coordinated by four nitrogen atoms of the macrocycle and four nitrogen atoms of the dangling pyrazole groups which are arranged at the corners of a square prism. The basal faces of the prism are rotated by 24° with respect to each other about the pseudo-four-fold axis. Each set of nitrogen donor atoms is planar; Mn-N(macrocycle) distances average 2.500Å while the Mn-N(pyrazole) average 2.339 Å.

An electron-nuclear magnetic resonance method, ESEEM (electron spin-echo envelope modulation) has been used to probe the chemical constitution and structure of the GDP/GTP binding site in Mn^{2+} guanine nucleotide sequences of the protein p21 [77]. In particular, the observation and analysis from ^{31}P of GDP and from ^{15}N incorporated at the amide positions in the serine and glycine residues of the Mn^{2+} complexes are discussed.

The synthesis and characterization of complexes of the general formula $[M(bispicam)_2X_2$, bispicam = bis(2-pyridylmethyl)amine and M = Mn(II), Zn(II) and Cd(II) has been reported [78]. All of the complexes are facial isomers with $[Mn(bispicam)_2](ClO_4)_2$ crystallizing in the space group *C2/c*.

A mixed ligand complex of Mn(II) azide with picolinic acid has been synthesized [79]. In particular, the structure of catena-μ(1,3)azido-μ(*O,N*-picolinato)aquamanganese(II) indicates that the manganese atom is in a distorted octahedral environment being surrounded by a water molecule, the nitrogen (Mn-N 2.278(3) Å) and a carboxylato oxygen atom (Mn-O 2.218(3) Å) of the picolinato anion. Additionally, the carboxylato oxygen bridges another Mn atom giving rise to a centrosymmetric dimer. The dimeric units are connected to μ(1,3) bridging azido ligands (Mn-N 2.167(2) and 2.219(3) Å) thereby forming a two dimensional layer structure along the *ab* plane.

Complexes of Mn(II) with 2,6-bis-(benzimidazole-2'-yl)pyridine were synthesized and characterized by elemental analysis, electrical conductance, IR electronic spectroscopy and thermal analysis [80]. Complexes of this type have been demonstrated to possess a broad spectrum of biological activities. The crystal structure of $[MnLCl_2]{\cdot}$dmf was obtained, the Mn atom is in a distorted square pyramidal geometry with Mn-N(pyridine) = 2.2769(3) Å and Mn-N(benzimidazole) 2.229(3) and 2.258(3) Å.

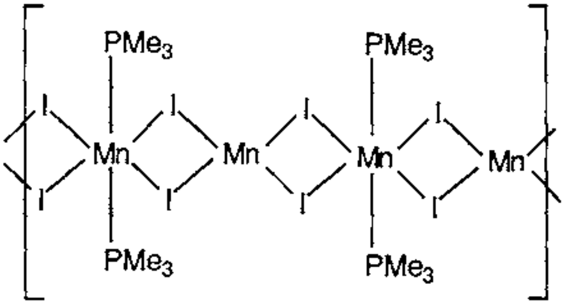
High spin manganese(II) bis-chelates using the tridentate 2,6-bis(pyrazol-1-ylmethyl)pyridine and its methyl substituted derivatives have been synthesized [81]. Cyclic voltammetry studies were undertaken in order to rationalize the electronic/steric effects of the ligands effects on redox potentials.

1.6.6 Complexes with nitrogen and phosphorus donor ligands

A new high-spin five-coordinate Mn(II) complex $[Mn(tdpea)I]BPh_4{\cdot}CH_2Cl_2$ where tdpea is the tripod ligand $N(CH_2CH_2PPh_2)$ has been synthesized and characterized [82]. This complex is exceptionally stable presumably due to the steric protection afforded by the tdpea ligand. The Mn atom is coordinated by one nitrogen and three phosphorus atoms of the tripod ligand and by an iodine atom. The Mn-N distance is 2.634(9) Å and the P-Mn-I angles average 104.3(5)° and the geometry may be considered as being halfway between a trigonal bipyramid and a tetrahedron.

1.6.7 Complexes with phosphorus donor ligands

The reaction of course-grain manganese powder with diiodotrimethylphosphorane in diethyl ether to form a polymeric complex $[Mn(PMe_3)I_2]_n$ **(20)** has been described [83]. This complex when treated with trace quantities of dioxygen gave $[Mn_2(PMe_3)_3I_5]\cdot PMe_3$ **(21)**, which is the first mixed valence Mn complex containing phosphine ligands. Both of these complexes react with excess dioxygen to give monomeric $[Mn_2(PMe_3)_2I_3]$, **(22)** .with **(21)** being representative of a transition state in the reaction of **(20)** with dioxygen to form **(22)**.



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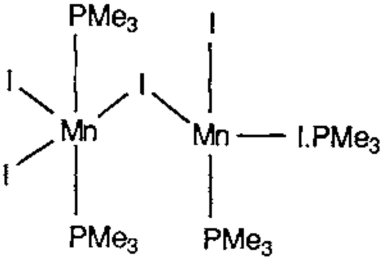

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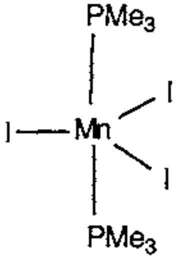

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A unique trinuclear complex $[\{MnI_2(PPhMe_2)_{1.33}\}_3]$ has been prepared and its crystal structure obtained [84]. It is comprised of a pseudo-octahedral MnI_4P_2 core sandwiched by two pseudo-tetrahedral MnI_3P units which are held together by bridging iodines. This complex reacts with anhydrous dioxygen in pentane giving a deep green complex $[Mn_4(\mu_4\text{-}O)I_6(PPhMe_2)_4]$ whose structure has also been determined.

Cyclic voltammetric studies on some Mn(II) tertiary arylphosphine complexes $[\{Mn[P(aryl)_3]X_2\}_n]$, [aryl = Ph, 4-ClC_6H_4, 4-MeC_6H_4, 4-$MeOC_6H_4$ or 2,4,6-$(MeO)_3C_6H_2$; X = Cl, Br, I or NCS] have been carried out [85]. A one-electron transfer process which becomes more reversible upon lowering the temperature is indicated implying an electrochemical-chemical mechanism.

The interaction between Mn(II) complexes containing $OPEt_3$, OP^nPr_3, and OP^nBu_3 ligands with sulfur dioxide in the solid state and in toluene slurries has been investigated [86]. Ligand-bound SO_2 complexes have been observed.

1.7 MANGANESE(I)

1.7.1 Complexes with halide ligands

Experiments on the photooxidation of $Mn(CO)_5Cl$ and $Re(CO)_5Cl$ in O_2-doped argon matrices have been reported [87]. Products include CO and CO_2 species and $MnO_nCl\cdots CO$ (n = 2 or 3). In the latter the ν(CO) is 2171 cm^{-1} indicative of a σ-bonded group.

1.7.2 Complexes with hydride ligands

The thermodynamics for the hydrogenation of dimanganese decacarbonyl according to equation 4 have been measured by *in situ* ^{59}Mn and ^{1}H NMR spectroscopies [88]. The results gave $\Delta H° = 8.7 \pm 0.3$ kcal mol^{-1} and $\Delta S° = 8.5 \pm 0.8$ cal $K^{-1}mol^{-1}$.

$$Mn_2(CO)_{10} + H_2 \rightarrow 2HMn(CO)_5 \qquad \text{equ. 4}$$

1.7.3 Complexes with oxygen donor ligands

The nature of manganese dioxolene bonding as a function of ligand oxidation state has been investigated [89]. The electronic absorption spectra are reported for all complexes and IR and resonance Raman spectroscopic studies have been carried out.

1.7.4 Complexes with sulfur donor ligands

The application of Fast Atom Bombardment Tandem Mass Spectrometry of dithioformate and thioformamide complexes has been reported [90]. The crystal structure of $[(\eta^5\text{-}C_6Me_6)Mn(CO)_2(SCHNEt_2)](BF_4)$ has also been reported. The spectral fragmentation patterns show simple bond cleavage with the thioformamide ligands.

A symmetrically bridged complex $\{(\eta^5\text{-}C_5H_5)(CO)_2Mn\}_2S$ has been synthesized from the reaction of $(\eta^5\text{-}C_5H_5)(CO)_2Mn(thf)$ with thirane, C_2H_4S [91]. Its X-ray crystal structure shows it to have an open form with 3-centre 4-electron bonding whereas the analogous rhenium complex has a closed form.

1.7.5 Complexes with phosphorus donor ligands

A study of the reaction of manganese and rhenium carbonyl cationic complexes with nucleophiles, equation 5, Nu^- = OEt^- or N_3^- has been documented [92]. The X-ray structures

$$[M(CO)_4(dppe)][BF_4] + Nu^- \rightarrow \textit{fac}\text{-}M(CO)_3(dppe)Z \qquad \text{equ. 5}$$

for Z = C(O)OEt and NCO have been obtained, both have *facial* octahedral geometries with the latter being the first example of a crystallographic analysis of a low-valent Mn(I) isocyanato complex

1.8 MANGANESE(0)

1.8.1 Complexes with phosphorus donor ligands

Crystal structure determinations on $MnRe(CO)_9(CN^tBu)$, $MnRe(CO)_9(CH_2C_6H_5)_3$ and $MnRe(CO)_8(CN^tBu)(PPh_3)$ have been performed. In all three structures the Mn-Re bond distance is found to be 2.963(7)Å indicating that site and degree of substitution on $MnRe(CO)_{10}$ do not influence the bond length value [93].

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