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Manganese 1995

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Introduction

This review surveys the advances in the coordination chemistry of manganese for the year 1995. It is based on a search of Chemical Abstracts, vols. 122, 123 and 124. An independent search of journals was also carried out.

An article describing how studies aimed towards an understanding of reactivity in metalloenzymes may lead to new aspects of chemistry extending beyond the scope of biological reactions has appeared [1]. Reviews on coordination chemistry with sterically hindered hydrotris(pyrazolyl)borate ligands from organometallic and bioinorganic perspectives [2] and the mechanistic and kinetic aspects of transition metal oxygen chemistry [3] have appeared.

1. Manganese(VI)

1.1. Complexes with oxygen donor ligands

The NIR luminescence of $[MnO_4]^{2-}$-doped crystals of K_2SO_4, K_2CrO_4 and K_2SeO_4 has been investigated [4]. Acidified manganese(VI) has been found to participate in remarkably fast oxidation processes with some alcohols and aldehydes [5]. The composition of the manganese species in the products was found to be dependent on the nature and concentration of the substrate and is governed by the rates of disproportionation and oxidation reactions involving both Mn(VI) and Mn(V). The high reactivity of Mn(V) and Mn(VI) towards alcohols has enabled the generation of alternative routes to hypomanganate and manganate esters.

1.2. Complexes with nitrogen donor ligands

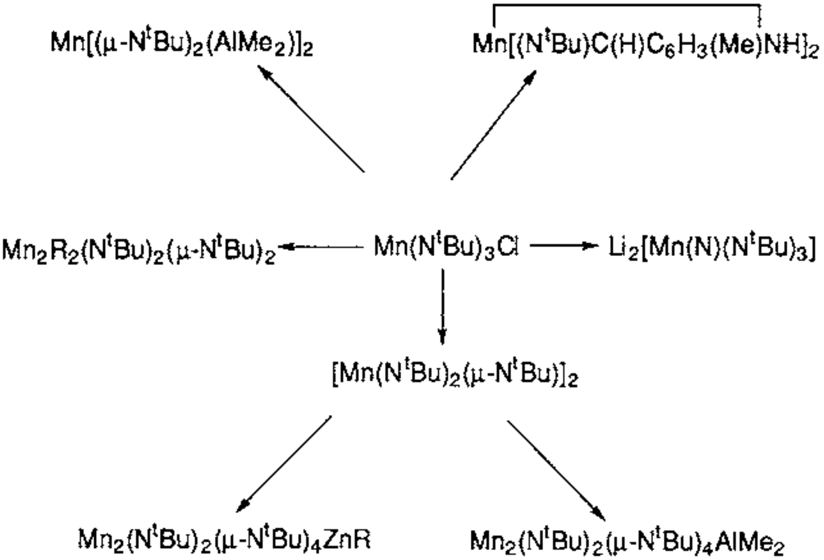
The syntheses and spectroscopic characterization of compounds derived from $Mn(N^tBu)_3Cl$ have been described [6]. The main reactions are delineated in scheme (**1**).

2. Manganese(V)

The theory of electronic emission spectroscopy from intraconfigurational transitions of tetrahedral d^2 complexes has been described [7]. It has been applied to the experimental emission spectra of Mn(V) ions in apatite and spodiosite lattices.

3. Manganese(IV)

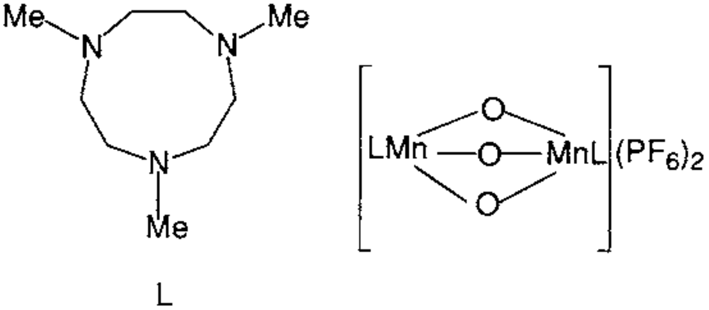
A novel dinuclear trapped valence complex of the tripodal *N,N*-bis(2-pyridylmethyl)ethylamine, (bpea), ligand possessing the $\{Mn_2O_2(O_2CCH_3)\}^{2+}$ core has been prepared recently [8]. The mixed-valence complex



(1)

$[\mathrm{Mn_2O_2(O_2CCH_3)(bpea)_2](ClO_4)_2}$ was obtained in 79% yield. Its crystal structure has been obtained which reveals it to possess an asymmetric dioxo-dimanganese(III,IV) core as a result of the different binding modes adopted by the bpea at the Mn(III) versus the Mn(IV) site. The complex was further characterized by EPR spectroscopy and CV. This compound was converted to $[\mathrm{Mn_2O_2(X_2)(bpea)_2](ClO_4)_2}$ upon addition of two equivalents of aqueous HX, X = F, Cl, in CH_3CN, presumably due to a disproportionation reaction. The yields of the halide compounds are consistent with a disproportionation process where half of the III,IV starting material was recovered in the IV,IV state and the other as the Mn(III) level. Of note is the fact that in the latter halide complexes, the bpea ligand adopts meridional coordination whereas in the acetate bridged structure it ligates in a facial fashion. Clearly, this ligand exhibits greater flexibility in this regard when compared to other ligands. The Mn–N distances in the acetate bridged complex are in the range 2.017(3)–2.137(3) Å while the Mn–O distances are in the range 1.772(2)–2.187(2) Å.

The pK_a value for $[\mathrm{Mn_2^{IV}}(\mu\text{-O})_3\mathrm{L_3}]^{2-}$ (**2**) where L = 1,4,7-trimethyl-1,4,7-triazacyclononane, was determined spectrophotometrically [9]. Its extremely low value of −2.0 suggests that the amount of electron density on oxygen is very small. Infrared and Raman spectroscopic studies reveal an asymmetric Mn–O–Mn vibration at 670 cm^{-1} while the symmetric Mn–O–Mn vibration is at 702 cm^{-1}. These high frequencies are due to the small value, 78°, of the Mn–O–Mn angle. Electrochemical studies in water and acetonitrile have been carried out and show that one-electron reduction of the complex is irreversible. Data from IR, EPR and UV–VIS spectroscopic studies on the reduced species suggest that it contains an $[Mn^{III}Mn^{IV}(\mu\text{-O})(\mu\text{-OH})]$ core which is susceptible to reaction with carboxylate groups.



L

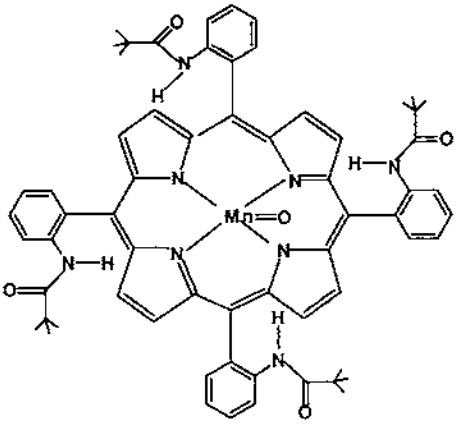
(2)

Valence tautomerism for quinone complexes of manganese has been studied [10]. In particular, intramolecular transfer has been investigated for members of the Mn(N-N)(3,6-DBQ)$_2$ series where DBQ = 3,6-di-*tert*-butyl-1,2-benzoquinone and N-N is a nitrogen-donor co-ligand and includes 2,2′-bpy, 4,4′-bpy, phen and 5-nitro-1,10-phenanthroline. The tautomers $[Mn^{IV}(bpy)(3,6\text{-}DBQ)_2]$, *trans*-$[Mn^{III}(4,4'\text{-}bpy)(3,6\text{-}DBSQ)(3,6DBcat)]$ and $[Mn^{II}(5\text{-nitro-}1,10\text{-phenanthroline})(3,6\text{-}DBQ)_2]$ result from differences in intramolecular Mn-quinone charge distribution. The complex [Mn(phen)(3,6-DBQ)$_2$] exists as an equilibrium mixture of Mn(IV) and Mn(III) tautomers in the solid state at room temperature. Overall the Mn(IV) tautomer is favoured at low temperatures for hard donor co-ligands.

The accessibility of higher oxidation states of manganese in "surface" sites of polyoxotungstate anions containing manganese(IV) has been reinvestigated [11]. Aqueous and non-aqueous soluble salts of Mn(IV)-containing Keggin polyoxotungstates $[(XO_4)W_{11}Mn^{IV}O_{36}H_X]^n$ (X = Si, B and Zn) were prepared by the chemical and electrolytic oxidation of the corresponding Mn(II) or Mn(III) anions. They were characterized by magnetic susceptibility, ESR and XANES. The crystal structure of $[(ZnO_4)W_{11}Mn^{IV}36Hx]\cdot 19H_2O$ indicates a disordered Keggin anion. An EXAFS investigation indicates the presence of an Mn^{IV} rather than $Mn^{IV}{=}O$.

A communication has appeared describing the characterization of an oxo(porphyrinato)manganese(IV) complex (3) by X-ray absorption spectroscopy; in particular, the Mn–O bond distance is now reported [12]. The Mn centre was found to be five-coordinate and the Mn–O distance was 1.69 ± 0.03 Å while the Mn–N distances were 2.00 ± 0.03 Å.

The first Mn-based halogenating system in which the reactive and final Mn-containing products are structurally characterized has been reported [13]. Specifically, dichloro(*N*,*N*′-(salicylidene)-1,3-propanediamino)manganese(IV) is the first moderate valent manganese complex that selectively *trans* chlorinates alkenes.



(3)

In both complexes their crystal structures reveal that the salen ligand binds to the manganese atom so that all four of its donor atoms are in the equatorial plane. In spite of the difference in manganese oxidation states, the equatorial metal–ligand distances are similar in both complexes. The Mn–Cl distances of 2.290(1) and 2.253(1) Å lengthen significantly upon reduction to the Mn^{III} complex where the Mn–Cl distance is 2.493(1) Å.

Manganese(IV) complexes with tridentate diacidic ligands have been synthesized [14]. The Mn(IV) chelates of salicylaldehyde benzoylhydrazone and salicylaldehyde salicylhydrazone were synthesized as a result of ligand exchange reactions involving bis(acetylacetonato)manganese(II), tris(acetylacetonato)manganese(III) and manganese(III) acetate. These complexes were characterized by mass spectrometry. The intermediate acetylacetonato-salicylaldehydebenzoylhydrazonato(2-)-methanol-manganese(III) was characterized by X-ray crystallography and has Mn–O distances ranging from 1.872(2) to 2.288(2) Å while the Mn–N distance was 1.970(2) Å.

4. Manganese(III)

4.1. Complexes with oxygen donor ligands

Novel decanuclear manganese mixed-valent manganese complexes have been synthesized and structurally characterized [15]. Complexes of formula $[Mn_{10}O_4(biphen)_4X_{12}]^{4-}$ (biphen = 2,2′-biphenoxide, $X = Cl^-$, Br^-) were obtained by simply treating biphen with manganese halide salts. The complexes $[Me_4N]_{10}[Mn_{10}O_4(biphen)_4Cl_{12}]$, $[Me_4N]_{10}[Mn_{10}O_4(biphen)_4Br_{12}]$ and $[Me_4N]_{10}$-$[Mn_{10}(CH_3CN)_4(H_2O)][EtNH]_2[Mn_{10}O_4(biphen)_4Cl_{12}]$ have been characterized by X-ray crystallography. They contain four Mn(II) atoms and six Mn(II) atoms with the former exhibiting Jahn–Teller axial elongations. The bridging ligands were found to bind in a variety of modes and four μ_4-oxo ligands are present at the core of the cluster. Magnetic susceptibility studies were carried out in the polycrystalline state. Values between 12 and 14 for the ground states were obtained. A theoretical simulation of the magnetic data was made and the model successfully explains the high spin ground states of the magnetic exchange coupling between the 10 metal spin sites, which is fully consistent with the experimental data.

Two new high-nuclearity molecular Mn_x species with $x=8$ or 9 have been synthesized and their structural and magnetic characterizations have been carried out [16]. The complexes $(N^nBu_4)[Mn_8O_6Cl_6)(O_2CPh)_7(H_2O)_2]$ and $[Mn_9Na_2O_7(O_2CPh)_{15}$-$(MeCN)_2]$ were obtained. The former complex comprises an $[Mn_8O_6Cl_6]^{8+}$ core which may be described as resulting from the fusion of two $[Mn_4O_2]$ butterfly units sharing one "body" or "hinge" Mn atom. An eighth Mn^{III} ion is connected to the resultant $[Mn_7O_4]$ unit by two additional bridging O^{2-} ions. The latter complex possesses a mixed-metal undecanuclear $[Mn_9Na_2O_7]$ in which an $\{Mn_7O_4]$ unit is formed in the same manner as in the former complex. Both complexes were characterized by CV in CH_2Cl_2; in the former, an oxidation and a reduction were observed at 0.91 and 0.12 V respectively versus ferrocene, while the latter complex reveals no reversible processes. Magnetic susceptibility studies indicate an $S=11$ ground state for $(N^nBu_4)[Mn_8O_6Cl_6)(O_2CPh)_7(H_2O)_2]$ and an $S=4$ ground state for $[Mn_9Na_2O_7)(O_2CPh)_{15}(MeCN)_2]$.

A remarkable octadecanuclear Mn carboxylate has been synthesized and its structure and magnetic properties have been studied [17]. A dark-brown MeCN solution of $(NaBu_4)[Mn_4O_2(O_2CPh)_9(H_2O)]$ which was stirred for five days with one equivalent of potassium hydrogen phthalate, gave a similarly coloured solution and an off-white precipitate of KO_2CPh. The solution was filtered and the filtrate was concentrated at ambient temperature over 10 days giving black crystals of $K_4[Mn_{18}O_{16}(O_2CPh)_{22}(phth)_2(H_2O)_4]\cdot 10MeCN$ in about 30% yield. Its structure has been obtained: all Mn centres are in the +3 oxidation state. There is a central Mn_4 unit with seven Mn atoms above and below this unit, respectively, all of which are held together by 16 μ_3-O^{2-} ions. Peripheral ligation is provided by 22 $PhCO_2$ groups (in the familiar *syn-syn* bridging mode), two terminal H_2O groups on each of two Mn atoms and two μ_4-$phth^{2-}$ groups whose O atoms coordinate to different Mn atoms. This latter mode is a novel one for this binding group and both $phth^{2-}$ groups ligate to a total of six Mn atoms. Variable temperature solid-state magnetic susceptibility studies were carried out on powdered samples in the range 2.00–320 K. Appreciable magnetic exchange interactions are present in the title compound. Interestingly this compound has an $S=0$ ground state which is the exception rather than the rule.

The crystal structures of $[Mn_6O_2\{O_2C\text{-}3,5\text{-}(NO_2)_2\text{-}C_6H_3\}_{10}(C_5H_5N)_2$-$\{(CH_3)_2CO\}_2]\cdot 2(CH_3)CO\cdot 2(C_2H_5)_2O$ and $[Mn_6O_2(O_2CC_6H_5)_{10}(NCCH_3)_4]$ have been obtained [18]. Both compounds contain the $Mn_6O_2(O_2CR)_{10}(L)_x$ $(x=4)$ structural motif. The six octahedrally coordinated Mn centres are arranged as two $Mn^{II}_2Mn^{III}_2(\mu_4\text{-}O)$ tetrahedra sharing the Mn^{III}–Mn^{III} edge.

The manganese(III) and (II) complexes of 3,4-dihydroxy-2-benzoic acid have been characterized by cyclic voltammetry, UV–VIS spectroscopy and magnetic susceptibility studies [19]. The neutral or monoanionic forms of the ligand do not form metal complexes. Electrochemical oxidation of the dianion form of the ligand gives rise to the corresponding semiquinone and quinone forms. The dianion and semiquinone forms of the ligand form Mn(III) and Mn(II) complexes with 1:2 stoichiometry.

4.2. *Complexes with oxygen and nitrogen donor ligands*

The synthesis of the novel hydroxo-bridged complex $\{[Mn(OEP)]_2(OH)\}ClO_4$ from the mononuclear precursor $\{[Mn(OEP)(H_2O)]ClO_4$, or dinuclear Mn(II) complexes has been achieved [20]. It may be prepared by the protonation of an oxo-bridged manganese complex or more reliably by the hydrolysis of Mn(III)OEP precursors. The crystal structure of $\{[Mn(OEP)]_2(OH)\}ClO_4$ reveals two Mn(III) ions which are five-coordinate and bridged by a single hydroxo ligand with an average Mn–O distance of 2.011 Å and an Mn–O(H)–Mn bridge angle of 152.73° while the average $Mn–N_p$ distance is 2.006 Å. The two porphyrins are nearly eclipsed. The bridging hydroxo ligand was found to mediate a relatively strong antiferromagnetic interaction ($2J = -71.0 \pm 0.4\ cm^{-1}$) between the two Mn(III) centres. The mononuclear precursor was characterized by X-ray crystallography and magnetic studies. It contains a five-coordinate Mn(III) atom and is a simple paramagnet.

The synthesis and magnetic exchange properties of linear trinuclear oxo-bridged $M^{III}ORu^{IV}OM^{III}$ complexes, (M = Fe, Cr, Mn) by two-electron redox reactions has been reported [21]. In particular, the two-electron reductions of the porphyrin complexes $Ru^{VI}(O)_2(P)$ by Fe(II), Cr(II) and Mn(II) compounds of porphyrins and salicylaldimines resulted in the formation of the heterometallic oxo-bridged complexes $(L)M^{III}ORu^{IV}(P)OM^{III}(L)$, where P is the dianion of 5,10,15,20-tetraarylporphyrins such as TPP or OEP, L = TPP, OEP or TMP or the dianions of *N,N'*-(4-methyl-4-azaheptane-1,7-diyl)bis(salicylaldimine) or salen. A detailed study of temperature- and field-dependent magnetic properties of these novel compounds has been carried out.

The reaction between 5,10,15,20-tetrakis(2-hydroxyphenyl)porphyrin and several ditosylthreitol derivatives has resulted in nine new chiral porphyrins [22]. Within these porphyrins, the chiral frameworks are constructed from threitol straps which may be easily varied by changing the protecting group used at the 2,3-diol positions of the threitol unit. The manganese derivatives of six of these porphyrins were tested for use as asymmetric catalysts in the epoxidation of unfunctionalized olefins. In one case up to 88% ee was obtained in the epoxidation of 1,2-dihydronaphthalene when a bulky imidazole ligand was used to block the unhindered face of the porphyrin catalyst.

For the first time, the experimental density distribution of tetrafluoroborate salt of the mixed-valence compound bis(μ-oxo)tetrakis(bpy)dimanganese(III,IV) has been obtained from 9 K X-ray diffraction data along with a calculation of the valence shift in the electrostatic potential of the two manganese nuclei [23]. The most salient feature of the density deformation maps is the large accumulation of density at the μ-oxygen atoms inside the planar 4-membered Mn(III)-O-Mn(IV)-O ring. The results from two calculations of electrostatic potential at each Mn atom are 4.0 and 2.9 eV which are comparable to that of 3.7 eV measured experimentally. A ^{55}Mn ESE–ENDOR study of the mixed-valence dinuclear species [di-μ-oxotetrakis(bpy)dimanganese(III)/(IV)] has been carried out [24]. This gave the hyperfine and nuclear quadrupolar parameters for the spin $I=5/2$ of ^{55}Mn nuclei of manganese. The data obtained on the $g=2$ Mn multi-line EPR signal of the S_2 state of the photosystem PSII oxygen-evolving complex demonstrate that this EPR signal cannot come from a dinuclear Mn(III)–Mn(IV) centre. The ENDOR spectra are consistent with a tetranuclear Mn cluster origin for the photosystem II multi-line EPR signal.

The reaction of [MnL(H$_2$O)]ClO$_4$, L = salen analogues and K$_3$[Fe(CN)$_6$] has been examined [25]. One of the products of this reaction, namely K[Mn(3-MeOsalen)]$_2$[Fe(CN)$_6$], has been characterized, and has a unique two-dimensional structure and displays three-dimensional magnetic ordering. The unit cell contains two trinuclear molecular units with the unsymmetrical unit being one half of the trinuclear molecular unit. The Fe ion is surrounded octahedrally by six CN$^-$ groups, two of which bridge to the Mn ions to give a linear bridging unit (3-MeOsalen)Mn-NC-Fe-CN-Mn(3-MeOsalen) in which the Mn–N bond length is 2.290(5) Å. Another two CN-groups are bound to the Mn atoms of the adjacent chains with a distance of 2.415(5) Å thereby creating a two-dimensional network in which the net unit is composed of a cyclic octanuclear structure and internally bridged by a sandwich structure. This results in a six-coordinate square bipyramidal geometry for the Mn ion in which two apical sites are occupied by nitrogen atoms of the chain and another nitrogen atom of the adjacent chain, and the equatorial sites are occupied by a N$_2$O$_2$ donor set. The average Mn–O distances are 1.873(4) Å and Mn–N distances are 1.970(5) Å. Magnetic susceptibility measurements were made using a SQUID magnetometer and the effective magnetic moment at room temperature was 7.33 BM per trinuclear unit. Field cooled magnetization curves were obtained. Overall the magnetic studies indicate ferromagnetic coupling within each layer but antiferromagnetic coupling between layers.

A bioinorganic approach to functional models of Mn catalase using dinucleating ligands providing stable dinuclear Mn complexes with structures relating to the μ-oxo-bis-(μ-carboxylato)dimanganese core has been described [26]. Complexes with C_s symmetry were studied owing to their high catalytic activity to disproportionate hydrogen peroxide. A dinuclear *cis*-{Mn^{IV}(=O)}$_2$ intermediate was detected in the disproportionation reaction and a mechanistic scheme to catalyse the reaction through the interconversion of *cis*-{Mn^{IV}(=O)}$_2$/*cis*{Mn^{III}(OH)}$_2$ is proposed. The electronic equivalence of two Mn ions was demonstrated to be necessary for CAT-like activity.

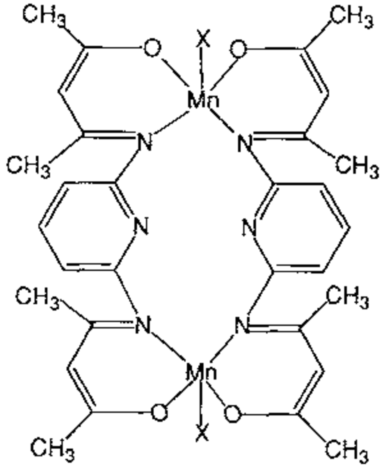
The preparation and characterization of Mn(III) complexes containing optically active Schiff base ligands with phenyl substituents have been achieved [27]. In particular the orientation of the phenyl substituents and their effects on properties such as redox potentials has been studied. The crystal structure of the complex [Mn{7-Phsal-(*SS*)-stien}Cl]·CH$_2$Cl$_2$ where 7-Phsal-(*SS*)-stien is the dianion of the product formed as a result of the condensation of 2 mol of 2-hydroxybenzophenone and 1 mol of (*SS*)-1,2-diphenylethylenediamine has been obtained. It shows two independent molecules in the unit cell in which the coordination geometry about each Mn atom is distorted square pyramidal, the tetradentate Schiff base ligand lies in the equatorial plane while the chloro ligand occupies the apical position. The Mn–Cl bond length is 2.391(3) Å in molecule A whereas it is 2.313(3) Å in molecule B. The CD and absorption spectra were measured in dichloromethane, acetonitrile and methanol solutions and bands have been assigned to d–d, d π^*, and π–π^* transitions. All complexes exhibit a quasi-reversible redox process assignable to the Mn(III)/Mn(II) redox couple in a fairly small range (−0.60 to −0.47 V versus Ag/Ag$^+$). Those complexes with axial phenyl groups offer most resistance to oxidation.

The first example of a manganese polymer possessing a trimeric mixed-valence repeating unit has been synthesized [28]. In the compound [Mn$_3$-(Hsaladhp)$_2$(acetato)$_2$(5-Cl-salicylato)$_2$]$_2$. H$_3$saladhp = 2-(salicylideneaminato)-1,3-dihydroxy-2-methylpropane, the saladhp ligand acts as a tridentate chelating ligand using an imine nitrogen, phenolate and alkoxide oxygen atoms to coordinate to Mn(III). The central Mn and two terminal Mn ions are bridged by an alkoxide oxygen from the saladhp ligand, an acetato ligand and a carboxylato oxygen yielding an Mn–Mn separation of 3.482(1) Å. A phenolate oxygen atom forms a bridge between the trimers. The cluster is valence trapped as evidenced by the long central Mn(II) to heteroatom bond lengths and by the Jahn–Teller distortion of the high spin terminal Mn(III) ions. Variable temperature magnetic susceptibility measurements indicate the presence of weak antiferromagnetic interactions with intratrimer exchange coupling dominant over intertrimer exchange coupling.

The preparation and structure of a mononuclear manganese(III) complex containing a salicylate ligand in which the phenoxide and carboxylate functionalities mimic the side groups in the amino acids tyrosine, aspartic and glutamic acid has been reported [29]. Specifically, the complex [Mn(C$_7$H$_4$O$_3$)(bpy)(H$_2$O)]ClO$_4$ · H$_2$O exhibits elongated octahedral coordination with mutually *trans* water molecules in the axial positions. The equatorial plane is occupied by two oxygen and nitrogen atoms of the requisite ligands and almost coincides with the salicylate and bpy ligand planes. Equatorial Mn–O bond lengths are 1.830(2) and 1.871(4) Å while the axial Mn–O distances are longer 2.225 Å and 2.240(4) Å typical of axial elongation in d^4 systems. The Mn–N distances range from 1.863 to 1.911 Å.

The structure of tris(8-quinolinolato-*N*,*O*)manganese(III) ethanol solvate has been reported [30]. The Mn atom displays a meridonal arrangement of nitrogen and oxygen atoms; the ethanol molecules do not take part in the coordination but are trapped in a cage-like cavity. The Mn-O bond lengths are 1.912(4), 1.916(5) and 1.897(5) Å while the Mn-N bond lengths are 2.038(6), 2.209(6) and 2.243(5) Å.

A mononuclear Mn(III) Schiff base complex containing a coordinated methanol molecule has been synthesized and its crystal structure elucidated [31]. The complex [Mn(C$_{14}$H$_{10}$N$_2$O$_5$)(C$_8$H$_7$O$_3$)(CH$_4$O)] contains an Mn atom with an O$_5$N coordination sphere. Significant tetragonal elongation is observed and Mn-O(amide) = 1.931(2) Å, Mn-O(methanol) = 2.269(3) Å and Mn-O(salicylato) = 2.234(3) Å. The structure of the complex [(5,5′-Cl-salen)Mn$^{\mathrm{III}}$(H$_2$O)Cl] has been reported [32]. It was isolated while attempting to grow crystals of $[(5,5'\text{-Cl-salen})\text{Mn}^{(IV)}(\text{M-O})]_2$ from CH_2Cl_2. The chloride ion is assumed to come from the reaction of the solvent with the dimer while the water molecule is presumed to come from water present in the CH_2Cl_2 since no precautions were taken to exclude air or water during the reaction. The Mn atom is in a pseudo-octahedral environment with the four donor atoms of the Schiff base defining the equatorial plane with Mn-O distances of 1.874(3) and 1.883(2) and Mn-N distances of 1.973(3) and 1.986(2) Å. The Mn-O(H_2O) distance is 2.319(3) and Mn-Cl is 2.572(1) Å.



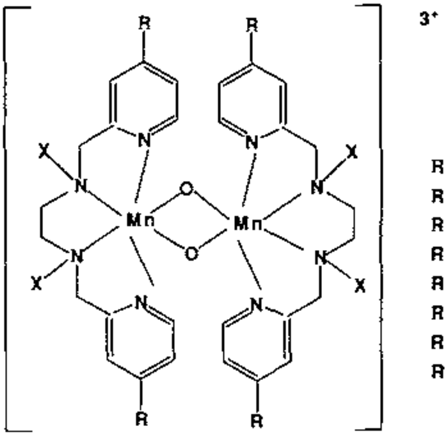
X = Cl, Br, OAc or NCS

(4)

Dinuclear complexes including those of Mn(III) bridged by diaminopyridine have been synthesized [33]. Trivalent manganese salts were reacted with 2,6-diaminopyridine and acetylacetone to give complexes of the type $[\text{Mn}(C_{15}H_{17}N_3O_2)X]$, (**4**) where X=Cl, Br, OAC or NCS. Conductance studies show the complexes to be non electrolytes while cryoscopic molecular weight determination are indicative of a dimeric form being five coordinate square pyramidal with 2,6-diaminopyridine residues acting as bridges. These complexes were characterized by electronic spectroscopy.

The preparation of various di-μ-oxo manganese(III/IV) complexes (**5**) which serve as functional models of *L plantarum* pseudo-catalase has been described [34]. The influence of electronic and steric factors in the catalysis of hydrogen disproportionation in neutral aqueous medium has been studied. Catalytic activity was found to correlate with electron density present on the metal and accessibility to the catalytic site.

The coordination chemistry of mixed pyridine-phenol ligands has been explored [35]. It has culminated in the syntheses and crystal structures of Mn(III) and Ni(II) complexes of 2-(2-hydroxyphenyl)pyridine in which the ligand displays a different binding mode in each case. The Mn complex comprises neutral tris-chelate Mn(III)



R = X = H
R = H; X = Me
R = OEt; X = Me
R = Me; X = Me
R = Cl; X = Me
R = NO_2 X = Me
R = H; X = Et
R = H; X = ^{i}Pr

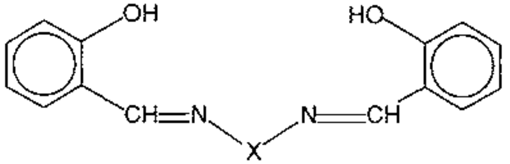
(5)

units with a *mer*-N_3O_3 donor set and exhibits Jahn–Teller distortion. It undergoes a quasi-reversible one-electron oxidation at $E_{1/2} = +0.03$ V versus Fe/Fe^+, while a completely irreversible reduction from Mn(III) to Mn(II) is also present at −1.57 V and an irreversible ligand-based oxidation at 0.76 V versus Fe/Fe^+.

The solution equilibria and redox reactivities of a dioxo-bridged manganese complex have been studied [36]. Specifically, the kinetics of the reactions of the dinuclear complex $[(bpy)_2Mn^{III}O_2Mn^{IV}(bpy)_2]^{3+}/NO_2^-$ in aqueous acidic media buffered with bpy-$Hbpy^+$ have been studied. This complex was stabilized in buffer where it co-exists with the diaqua derivative $[(H_2O)_2Mn^{III}O_2Mn^{IV}(bpy)]^{3+}$. The reduction of the former complex was found to be kinetically insignificant but that of the latter is rapid following the sequence $Mn^{III}Mn^{IV} \rightarrow (Mn^{III})_2 \rightarrow Mn^{II}Mn^{III} \rightarrow 2Mn^{II}$. When NO_2^- was in excess, first order kinetics were observed at 830 nm whereas the profile was biphasic at 525 nm. At 30 °C and $I = 1.0\ mol\ dm^{-3}$ k_1K_1H and k_2K_2H are 34.0 ± 0.8 and $3.3 \pm 0.2\ dm^3\ mol^{-1}\ s^{-1}$ respectively. Addition of bpy retards, while Mn^{2+} accelerates, the reaction.

Using a biomimetic synthetic approach the dinuclear complex $[Mn_2(\mu\text{-}O(\mu\text{-}OAc)_2(bpea)_2](ClO_4)_2$, bpea = *N*,*N*-bis(2-pyridylmethyl)ethylamine, was prepared in good yield; its crystal structure has been determined [37]. The reaction of $Mn(O_2CCH_3)_3 \cdot 2H_2O$ with bpea in a 1:1 ratio in methanol followed by the addition of $NaClO_4$ gave the title compound in 75% yield. Its crystal structure reveals two independent equivalents in the asymmetric unit with a single unique water molecule in the crystal lattice. In each of the independent units the Mn atoms are bridged by one oxo ligand and two acetate groups. Each Mn atom is bound to one facially-coordinating tridentate bpea ligand where the aliphatic nitrogen donor is *trans* to an acetate oxygen atom. The Mn···Mn separation is 3.11 Å while Mn–O distances are in the range 2.00(2)–2.07(2) Å. The pyridine ligands in each bpea ligand are divided into two groups; those in which the nitrogen atoms are *trans* to the bridging oxo group while in the other group the nitrogen atoms are *cis* to the bridging oxo group and *trans* to one of the bridging acetate oxygen atoms. The average Mn–N distance for the former is 2.04 Å while it is 2.21 Å in the latter. The complex was further characterized by EPR and electronic spectroscopies and CV.

The kinetics of the reaction between Mn(III)–Schiff base complexes (**6**) and hydrogen peroxide in aqueous solution and in micellar SDS solution was studied [38]. The rate was found to be first order in hydrogen peroxide and complex, and inversely proportional to the proton concentration. The second-order rate constants increase in the sequence $[Mn(salophen)(OAc)] > [Mn(salen)(OH_2)]ClO_4 > [Mn(salen)(OAc)] \cdot H_2O$. At SDS concentrations below the critical micellar concentration there is almost no effect on the reaction rate while at higher concentrations a slight increase in the rate was observed. A mechanism involving Mn^{II} and a peroxo intermediate has been proposed.



X = $(CH_2)_2$, salen;
o-C_6H_4, salophen

(6)

The synthesis and characterization of a conjugate compound where a reactive tricationic metalloporphyrin moiety (endowed with nuclease activity within the minor groove) is attached to a bisbenzimidazole dye, namely Hoechst 33258 (2′-[4-hydroxyphenyl]-5-[4-methyl-1-piperazinyl]-2,5′-bi- 1H-benzimidazole) which has a strong preference for adenine–thymine rich regions, have been reported [39]. This conjugate is a potential sequence-selective DNA cleaver.

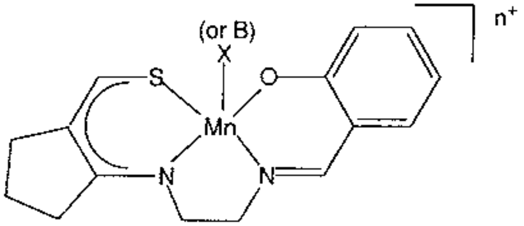
Single-crystal absorption spectroscopy at variable temperature has been used to determine the exchange couplings between the metal centres in the electronic ground and excited states in homodinuclear complexes of Mn(II) and Fe(III) containing the (μ-O)bis(μ-acetato)dimetal core [40]. The complexes are $[LM(\mu\text{-}O)(\mu\text{-}CH_3CO_2)ML'](ClO_4)_2$ where L and L′ denote 1,4,7-triazacyclononane and 1,4,7-triamethyl-1,4,7-triazacyclononane respectively. The ground state coupling constant for the Mn complex is $J = +10\ cm^{-1}$; exchange interactions in the excited state have been qualitatively analysed.

Using the pentadentate ligand 2,6-bis(salicylideneaminomethyl)-4-methylphenol, L, tetranuclear Mn(III) complexes have been successfully isolated [41]. The complexes $[Mn_4(L)_2(O)_2(CH_3COO)_2)] \cdot 2CH_3CN$ and $[Mn_4(L)_2(O)_2(C_6H_5COO)_2)] \cdot 2CH_3OH$ have been characterized by IR and electronic spectroscopies, CV and magnetic susceptibility. The X-ray crystal structure of the former has been obtained; it shows a tetranuclear structure in which two incomplete cubanes share faces via oxo-bridges. The Mn–O distances are in the range 1.880(4)–1.957(3) for in-plane bonds and 2.105(3)–2.286(3) Å for bonds along the elongated axes. The Mn–N bond distances are 1.989(4) and 2.039(4) Å.

The crystal structure and magnetic properties of TCNQ compounds with Mn(III) and Fe(II) have been reported [42]. Specifically, the complex $[Mn^{II}(salen)(TCNQ)_{0.5}][Mn^{III}(salen)(TCNQ)_{0.5}(CH_3OH)]\cdot CH_3OH\cdot H_2O$ has been synthesized and its crystal structure shows it to comprise two distinct $[Mn^{III}(salen)]^+$ chromophores which are bridged by two kinds of $TCNQ^{2-}$ anions in μ_4 and μ_2 modes generating a one-dimensional structure. Temperature dependent magnetic susceptibility measurements show that the magnetic interaction between the metal centres is small.

4.3. Complexes with oxygen, nitrogen and sulphur donor ligands

Complexes which may be realistic models for the proposed Mn(III) biosite in purple phosphatase have been synthesized [43]. In particular, two series of five-coordinate high spin complexes of general formula [MnL(X)], (7), X = Cl, Br, NCS or N_3 and $[MnL(B)]ClO_4]$, B = py, 3-methylpyridine or 4-methylpyridine have been synthesized using methyl-2-[2-(salicylideneamino)ethylamino]cyclopent-1-ene-1-carbodithiolate, H_3L, as a tetradentate ligand with an $(N_2OS)^{2-}$ donor set. These complexes have been characterized by IR and UV–VIS spectroscopies, magnetic measurements and electrochemical studies. The crystal structure of Mn(L)Br has been solved by Patterson and Fourier methods. The manganese atom is in a distorted square-pyramidal geometry in which the basal positions are occupied by an S, two N and the O atoms of the ligand L. The axial position is occupied by the bromine atom. The Mn–S bond of 2.271(2) and C–S bond distance of 1.717(9) Å is evidence that the sulphur atom functions as a thiolate ligand. The UV–VIS spectra show two transitions at 685 and 570 nm in addition to a strong charge-transfer band at 440 nm which was assigned to a phenolate $O\rightarrow Mn(d_\pi{}^*)$ ligand-to-metal charge transfer. For the Cl, Br and NCS [Mn(L)X] derivatives, a one-electron quasi-reversible Mn^{III}–Mn^{II} reduction with $E_{1/2}$ close to -0.12 V (versus SCE) as well as an irreversible Mn^{III}–Mn^{IV} oxidation.



n = 0; X = Cl, Br, NCS or N_3
1; B = py, 3Me-py or 4-Me-py

(7)

4.4. Complexes with nitrogen donor ligands

The first example of a membrane-bound cytochrome P-450 enzyme-mimic which exhibits oscillating behaviour in the reduction of manganese(III) porphyrin has been obtained [44]. Manganese(III) porphyrin and a rhodium complex were incorporated into Zwitterionic L-adipalmitoylphosphatidylcholine. In air at 48 °C and at formate concentrations of 0.25 M, the reduction of the Mn(II) porphyrin was not observed at [Rh]:[Mn] $<$ 10:1. Under aerobic conditions reoxidation of the Mn(II) species is much faster than its reduction. At ratios [Rh]:[Mn] $>$ 10:1 net reduction of the Mn(III) species took place Oscillations in the concentration of Mn(II) porphyrin were detected at [Rh]:[Mn] $=$ 10:1. Using UV–VIS spectroscopy to monitor the Mn(III) species a complementary regression curve was obtained indicating that the porphyrin shuttles between the $+2$ and $+3$ oxidation state. By means of an oxygen-selective electrode the concentration of oxygen at the start of the experiment was measured to be 5.2 mg L^{-1} which dropped to almost zero when the Mn(II) species was formed. It was tentatively proposed that the Mn(III) species upon reduction moves towards the middle of the bilayer, these alterations may lead to changes in bilayer packing which in turn change the local oxygen concentration. This mechanism may account for the onset of oscillations.

The results of a visible wavelength spectroelectrochemical investigation of Mn(TPP)Cl reduction in various non-aqueous solvents have been reported [45]. The results show that the donor number rather than dielectric constant is the solvent property which controls axial ligand dissociation. Solvents with a donor number of approximately 17 promote partial or complete dissociation of axial chloride while those with a lesser number do not possess this ability. The crystal structure of [Mn(OEPH$_2$)(OClO$_3$)] has been determined [46]. The molecules in the lattice form weak dimers with interplanar distances of 3.49 Å and are laterally shifted by 3.27 Å. The Mn atom is thought to have a pseudo six-coordinate environment with the pair of porphyrin rings having overlapping π orbitals. The axial Mn–O bond length is 2.183(2) Å and the equatorial Mn–N bond lengths average 2.000(5) Å. The compound is isomorphous with [Fe(OEP)(OClO$_3$)] and the two structures are compared. A manganese porphyrin-spermine-oligonucleotide molecule, Mn(trisMPyP-spermine-5′-TFO) which forms a stable helical structure and cleaves a double-stranded DNA sequence of HIV-1, has been synthesized [47].

Interest in the redox behaviour of manganese in the presence of nitrogen–sulphur compounds formed in flue-gas desulphurization systems has resulted in the systematic kinetic analysis of the possible oxidation of Mn^{II} by -ON(NO)SO$_3$- in basic and acidic solutions [48]. The redox cycling of Mn$^{II/III}$ in the presence of $^-$ON(NO)SO$_3^-$ in the absence and presence of oxygen was studied by spectral monitoring of Mn^{III} as a function of [-ON(NO)SO$_3$-], [Mn^{II}] and pH. Typical autocatalytic behaviour was observed for the auto-oxidation reaction and the induction period is dependent on the concentrations of Mn^{III} and $^-$ON(NO)SO$_3^-$. In acidic conditions the reaction does not take place unless Mn^{III} or O$_2$ are present. The concentrations of O$_2$, Mn^{III} and -ON(NO)SO$_3$- determine whether oxidation of Mn^{II} to Mn^{III} or reduction of Mn^{III} to Mn^{II} in one or two redox cycles is observed.

The kinetics and mechanism of the oxidation of the sulphite ion by $[Mn(cydta)(OH_2)]^-$ have been reinvestigated [49]. This study confirmed the presence of two parallel pathways in which S(IV) is oxidized with orders of one and two for [S(IV)], respectively. The rate dependence on $[H^+]$ was also confirmed. In contrast to previous thinking, an outer-sphere mechanism has been suggested based on spectroscopic studies.

The complexes $(TPP)Mn[N_4C(R)]$, $R = CH_2CH_3$, C_6H_5, $CH = CH_2$ and $CH = CHCN$, have been synthesized [50]. Each complex was characterized by IR, UV–VIS and ^1H NMR spectroscopy and mass spectrometry. The redox properties of each complex were studied in dichloromethane, benzonitrile, THF and pyridine. The electron-withdrawing effect of the tetrazolato ligand is found to be greater than that of the azido ligand. The synthesis of halogenated porphyrin dimers covalently linked by an ethylene moiety has been achieved [51]. The dimers MnPFPP-C_2MNCFPP, MnPFPP-C_2-MnDCPP and MnDCPP-C_2-MnDCPP where $H_2PFPP =$ 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin, $H_2CFPP =$ 5,10,15,20-tetrakis-(2,6-dichlorophenyl)porphyrin were characterized by UV–VIS spectroscopy, fluorescence spectroscopy and CV. The interactions of these porphyrins with lipid bilayers of liposomal membranes were studied. The redox potential of the halogenated porphyrins increased with increasing extent of halogenation. These complexes catalysed transmembrane electron transfer with the activity being dependent on the steric effects of the halogen portions of the porphyrin ring.

5. Manganese(II)

5.1. Complexes with halide ligands

A new dimetallic compound of Mn(II) and Cu(II), $Cu(en)_2MnCl_4$ has been synthesized [52]. The structure consists of alternating Mn(II) and Cu(II) ions bridged by chlorine ligands. The Mn(II) coordination environment closely approximates tetrahedral symmetry with the average Cl–Mn–Cl bond angle being 109.3° and Mn–Cl bond lengths in the range 2.347(2)–2.391(2) Å. In the crystal, the chains lie in magnetically equivalent layers separated by about 7 Å. The magnetic susceptibility of the compound was measured over the range 2–300 K. At room temperature, the χT product (per MnCu) was found to be 4.80 emu mol^{-1} K. Upon lowering the temperature χT remains quite constant until 20–10 K and decreases to 1.54 emu mol^{-1} K at 1.6 K. This decrease has been rationalized by either a dominant Mn(III)···Mn(II) antiferromagnetic interaction within the chain or cooperative intrachain and interchain Mn(II)···Cu(II) interactions of opposite signs.

5.2. Complexes with oxygen donor ligands

The preparation of an unusual trapped-valence manganese complex has been reported [53]. In particular, the preparation and characterization of $[Mn_{12}O_{12}(O_2CEt)_{16}(H_2O)_3]$ and a salt of its singly reduced form

$(PPh_4)[Mn_{12}O_{12}(O_2CEt)_{16}(H_2O)_4]$ and analogue complexes have been achieved. The structure of the latter complex indicates that the added electron is localized in an outer (originally Mn^{III}) ion rather than an inner (cubane) Mn^{IV} producing a trapped-valence $Mn^{II}Mn_7^{III}Mn_4^{IV}$ anion. Both complexes exhibit magnetic susceptibility relaxation phenomena at low temperatures.

A calorimetric and X-ray crystallographic investigation of Mn(II) selectivity by cyclohexano-15-crown-5 with nitrate or triflate as the counterion in propylene carbonate to which water was added (up to 134 mM) has been carried out [54]. The reaction was found to proceed with a strong driving force, log $K = 4.7$–5.0; it is enthalpically driven but the enthalpy decreases as the water concentration increases for the case of the Mn(II) nitrate salt. For the triflate ion, more negative values of enthalpy and $T\Delta S$ were observed. In the crystal structure, the Mn(II) ion is coordinated by a pentagonal bipyramid of oxygen atoms supplied by the equatorial crown ether and apical monodentate triflate ions. The Mn–O distances are in the range 2.149(3)–2.278(4) Å.

The synthesis and structure of the first characterized compound containing a chain of Keggin polyoxoanions $(ET)_8[PMnW_{11}O_{39}]\cdot 2H_2O$ where ET is the organic donor bis(ethylenedithio)tetrathiafulvalene has been described [55]. A salient feature of this compound is the fact that the undecatungsto complex of Mn^{2+} ions is connected by a common oxygen atom forming chains, this oxygen atom connects two opposite positions of the Keggin unit occupied by the Mn ions. Site-selective XANES and EXAFS using high resolution fluorescence detection have been demonstrated for a physical mixture of MnF_2, $BaMn_8O_{16}\cdot 2H_2O$ and the mixed-valence complex $Mn_3O(O_2CPh)_6(PY)_2(H_2O)$ [56].

The preparation and structural characterization of a manganese antimony μ_5-oxo ethoxide have been reported [57]. The title compound $Mn_8Sb_4(\mu_5\text{-}O)_4(\mu_3\text{-}OEt_4)_4(\mu\text{-}OEt)_{16}$ is a newly characterized intermediate in the hydrolysis series of the Mn(II)–Sb(III) ethoxide system and is the result of a study concerning the synthesis, structural characterization and study of the sol-gel process of dimetallic antimony(III) ethoxides containing divalent transition metal and alkaline earth ions. Four of the Mn(II) atoms are approximately octahedrally coordinated while the remaining four are five-coordinate with a distorted square pyramidal coordination.

The crystal structure and magnetic properties of a manganese(II) mellitate complex have been reported [58]. A manganese(II) chloride tetrahydrate aqueous solution was added to an aqueous solution of mellitic acid, the mixture was stirred while the pH was adjusted to 6.0 by a 0.05 N NaOH and subsequently filtered. The filtrate was sealed and allowed to stand in a water bath at 50 °C for a week, after which time colourless brick crystals were obtained. The crystal structure of $[Mn_2(C_6(COO)_6](H_2O)_6\}[Mn(H_2O)_6]\cdot 2H_2O$ reveals two independent types of manganese ions in the structure. The structure is comprised of multilayered $[Mn_2\{C_6(COO)_6(H_2O)_6]_n^{2n-}$ units perpendicular to the *b*-axis, where one Mn ion is coordinated in an octahedral geometry with three water molecules and three oxygen atoms of different mellitate anions. The other Mn ion is situated on a crystallographic centre of symmetry and bound to six water molecules in an octahedral fashion and acts as a counter cation intercalated between neighbouring layers. The Mn–O bond distances range from 2.160 to 2.246 Å.

The synthesis and characterization of Mn(II), Co(II) and Ni(II) complexes of 2-, 3- and 4-cyanobenzoates has been reported [59]. Based on IR spectra, a bridging didentate coordination mode to the metal is suggested and the magnetic data indicate that metal–metal interactions via bridging ligand atoms may exist.

Complexes of Mn, Co, Ni and Cd with 2-, 3- and 4-nitrobenzoic acids in the solid state with a metal:ligand ratio of 1:2 have been obtained as mono-, bis- or tris-hydrates [60]. The carboxylate ligand appears to be a didentate chelating ligand or in a symmetrically or asymmetrically bridging mode. The NO_2 group does not coordinate with the metal ions. These compounds are unstable, melting above 573 K, and decompose explosively.

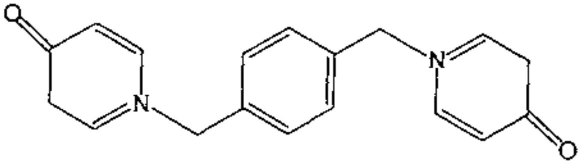
Single crystals of the novel phase MnCu(pbaOH)(H_2O), pbaOH = 2-hydroxy-1,3-propylenebis(oxamato), have been obtained and characterized [61]. The structure comprises oxamato-bridged Mn(II)Cu(II) dimetallic chains running along the direction of the *a*-axis. Antiferromagnetic ordering occurs at 2.4 K while a magnetic field of 0.9 Oe is sufficient to overcome weak interactions such that the compound may be described as a metamagnet built from ferrimagnetic chains.

5.3. *Complexes with oxygen and nitrogen donor ligands*

The facile synthesis of a bis(μ-carboxylato)dimanganese complex with labile solvent molecules and a nitrate ion in the terminal positions has been described [62]. The complex $[Mn_2(XDK)(NO_3)(H_2O)_2(CH_3OH)_4](NO_3)$, H_2XDK = *m*-xylenediamine bis(Kemps triacid imide) was characterized by X-ray crystallography and contains two octahedral Mn(II) ions bridged by two carboxylate groups of XDK. This compound is a precursor in the preparation of bis(μ-carboxylato)dimanganese(II) complexes with N-donor didentate terminal ligands. Its reaction with L = 2,2′-bpy, 4,4′-Me_2bpy or phen, gave $[Mn_2(XDK)L_2(NO_3)_2(H_2O)]$ in high yields. The structure of the 2,2′-bpy derivative was obtained and it comprises an asymmetric dinuclear Mn core with an Mn···Mn distance of 4.557(2) Å.

The effects of replacing Fe(III) with Mn(II) in a dinuclear BPMP, where BPMP is the anion of 2,6-bis[bis(2-pyridylmethyl)-amino)methyl]-4-methylphenol to afford the isoelectronic $Fe^{II}Mn^{II}$ complex have been explored [63]. In connection with this, the synthesis and properties of the heterodimetallic complexes $[Fe^{III}Mn^{II}BPMP(O_2CCH_2CH_3)_2]^+$, $[Fe^{III}Mn^{II}BPMP(O_2CCH_3)_2]^+$ and $[Fe^{II}Mn^{II}BPMP(O_2CCH_2CH_3)_2]^+$ have been reported. In the $Fe^{III}Mn^{II}$ complexes the high spin $Fe(^{III})$ is antiferromagnetically coupled to the $Mn(^{II})$ ion resulting in an $S=0$ ground state accounting for its featureless ^1H NMR spectrum and EPR silence. The $Fe^{II}Mn^{II}$ complex on the other hand displays a plethora of spectroscopic features, since the metal ions are antiferromagnetically coupled the NMR spectrum displays a number of well resolved resonances in spite of the presence of Mn(II) which typically exhibits broad NMR features. This is a good illustration of the ability of the Fe(II) ion to affect the relaxation properties of the Mn(II) ion. The crystal structure of the latter complex has an Fe–Mn distance of 3.360(4) Å with a (μ-phenoxo)(μ-carboxylato)dimetal cluster.

A polymeric 34- and 68-membered metallacyclic network forming a novel woven polycatenated structure $[Mn(C_{18}H_{16}N_2O_2)_3](ClO_4)_2$ has been recently synthesized [64]. Exploration of the effect of changing the position of the exocyclic donor on the heterocyclic unit from ortho to the para position relative to the ring nitrogen in *N*,*N*″-*p*-phenylenedimethylenebis(pyrid-4-one), *p*-XBP4, (**8**), has yielded the polymer $\{[Mn(p\text{-XBP4})](ClO_4)_2\}_n$. The polymer has been characterized by X-ray crystallography and is composed of a network of octahedrally coordinated Mn centres linked by *p*-XBP4 ligands with two distinct geometries, A and B, which are present in a 2:1 ratio. In A, one of the pyridone rings is essentially orthogonal to the central *p*-xylyl unit while the other is in an "open book" conformation with respect to it. These bridges link Mn atoms creating open 34-membered rings in which hydrogen bonding is apparent. In the B arrangement, the pyridone rings are centrosymmetrically disposed but are skewed to a position which is intermediate between an orthogonal orientation and an open-book conformation with respect to the *p*-xylyl unit. These bridges link pairs of the 34-membered rings creating a set of 68-membered rings. These interpenetrating networks are stabilized by π–π interactions. FAB–MS studies indicate that in solutions of the polymer in water and methanol, the polymer breaks up.



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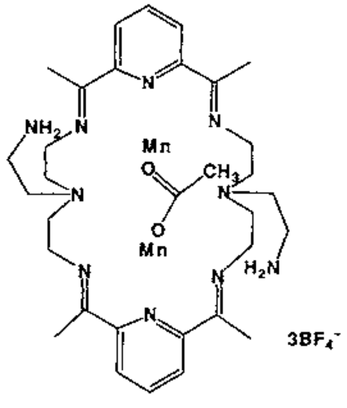
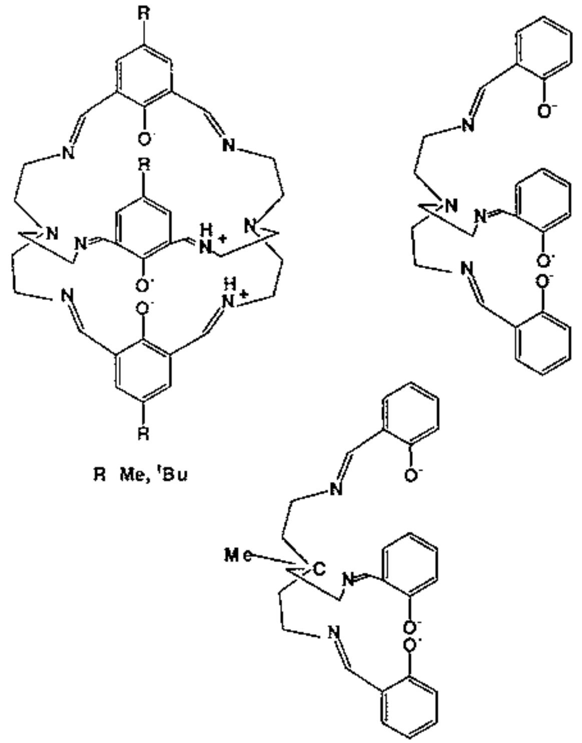


(9)

A communication has appeared detailing the synthesis of a structural model with a novel single carboxylato bridge for the metal-containing active site in the D-xylose isomerase [65]. The dinuclear (μ-carboxylato)Mn(II) complex (**9**), derived from a macrocyclic ligand has been studied by X-ray crystallography. The macrocyclic trication accommodates two Mn ions each being coordinated by five nitrogen atoms, the two metal atoms are thus located at the opposite ends of the 2,4-membered macrocycle which has a semi-open concertina-like conformation. The metal atoms are bridged in an unusual *syn–anti* manner by an acetato ligand. Magnetic susceptibility studies were carried out, a plot of magnetic susceptibility versus the reciprocal of temperature indicates linear Curie behaviour only at temperatures above 10 K indicating the presence of a small exchange interaction. The complex was further characterized by EPR spectroscopy.

The geometric control of the redox state of manganese cations has been explored [66]. A comparison of the structures of four monomanganese complexes containing ligands with the same $[N_3(O^-)_3]$ donor set has been made. The cryptands (**10**) can act as mononucleating ligands and were obtained as Mn(II), Mn(III) and Mn(IV) complexes. In the Mn(II) complexes the Mn–N distances are considerably longer than the Mn–O bonds. The Mn(III) complex exhibits tetragonal distortion while the Mn(IV) complex has a regular octahedral geometry.

The facile synthesis of two manganese salicylate complexes $[Mn_2(Hsal)_2(H_2O)_4]$



(10)

and polymeric $[\{Mn_2(sal)_2(Hsal)(H_2O)(H_3O)(PY)_4 \cdot 2PY\}_n]$ each containing asymmetrically bridging salicylate ligands has been reported [67]. The crystal structure of the dimer shows it to comprise two associated and symmetry-related pseudo seven-coordinate metal centres with an Mn–Mn distance of 3.719 Å. Each Mn atom is symmetrically chelated by two $Hsal^-$ ligands with two coordinated water molecules perpendicular to the central plane. The two metal atoms are associated with one another via the carboxylate oxygen atoms from a second pair of chelating Hsal ligands, thereby creating two asymmetric bridges with Mn–O distances of 2.213(3) and 2.576(3) Å. The ability of these two complexes to catalyse the disproportionation of hydrogen peroxide was investigated. The dimer alone was found not to decompose hydrogen peroxide; however, the presence of added pyridine generated considerable activity. During the first 60 s, each molecule of the dimer disproportionated 1552 molecules of H_2O_2. Similarly with the polymeric complex when dissolved in pyridine considerable enhancement of the catalytic activity was observed; during the first 150 s each molecule disproportionated 2924 molecules of H_2O_2. This observation may aid in our understanding of the role of nitrogen-containing heterocyclic bases which are known to be proximate to the active sites of manganocatalases.

The reaction mixture consisting of the dioxygen molecule, aliphatic aldehyde and a Mn complex with a pentadentate ligand derived from 2,6-diacetylpyridine and triethylenetetramine was investigated [68]. Based on electrochemical data under a dioxygen atmosphere it is proposed that an intermediate is formed in which dioxygen is assumed to coordinate to the Mn(II) complex through hydrogen bonding with the hydrogen atom of the chelate group, the dioxygen molecule accepts an electron from the aldehyde through the formation of the intermediate to yield an organic peracid with no increase in the oxidation state of the metal ion.

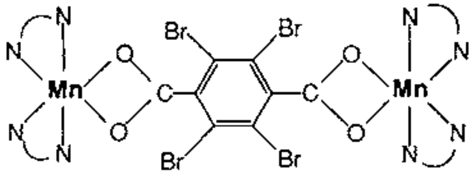
The synthesis and catalase activity of manganese(II) complexes of *cis*-5-norbornene-*endo*-2,3-dicarboxylic acid, $ndaH_2$, has been reported [69]. Manganese(II) chloride tetrahydrate reacts at room temperature with $ndaH_2$ in the presence of aqueous sodium hydroxide (1:1:2 molar ratio) yielding $[Mn(nda)H_2O]$ in 75% yield. This complex reacts with phen yielding the mononuclear adduct $[Mn(\eta^1\eta^1\text{-nda})(phen)2] \cdot EtOH \cdot H_2O$. The latter complex has been characterized by X-ray crystallography. The nda^{2-} ligand is didentate, the Mn atom is ligated by four nitrogen atoms from each of the phen ligands and two oxygen atoms from each of the carboxylate moieties of the nda^{2-} ligand. The Mn–N distances are in the range 2.241(3) to 2.331(4) Å while the Mn–O distances are 2.117 and 2.093 Å. Both complexes were characterized by IR spectroscopy and magnetic susceptibility data. Their catalytic activity towards disproportionation of H_2O_2 was studied. A ternary Mn(II) complex exhibiting a dinuclear arrangement with a rather unusual one-oxygen bridging mode of the carboxylate ligand has been synthesized [70]. The reaction of Mn(II) 2,6-dimethoxybenzoic acid and bpy or 2-methylpyrazine generated adducts which were characterized by X-ray diffraction. IR and EPR spectroscopy and thermogravimetry. In the bpy adduct, the two Mn atoms share two carboxylate groups in a single-atom bridging mode. Coordination about each metal is completed by a monodentate carboxylate, a water molecule and a chelating didentate bpy molecule. The monatomic bridging carboxylate reveals C–O bond lengths of 1.282 and 1.228 Å and the Mn–O distances are 2.177 and 2.297 Å indicative of an asymmetric mode. Other Mn–O distances are normal for a high spin octahedral Mn(II) while Mn–N distances are 2.256 and 2.262 Å.

A note has appeared describing an X-ray diffraction study of Mn(II) complexes containing DMF [71]. The structures of the solvated Mn(II) ion and Mn(II) complexes with py, 3-methylpyridine, and 4-methylpyridine were obtained at 23 °C. The Mn(II) ion binds six DMF molecules and has an octahedral structure and has Mn–O bond length of 2.21(1) Å. The structures of $[Mn(L)]^{2+}$ (L = py, 3-methylpyridine and 4-methylpyridine) were also found to be octahedral in DMF with Mn–O and Mn–N bond lengths 2.21(1) Å for py, 2.23(1) Å for 3-methylpyridine and 2.21(1) Å for 4-methylpyridine. In DMF, the steric interaction between DMF molecules and the first coordination sphere of the Mn ion is large.

A manganese analogue of the active site in methane monooxygenase has been obtained [72]. The complex $Mn_2L(OH)(ClO_4)$, L = the macrocyclic ligand 1,4,10,13-tetraza-7,16-dioxacyclooctadecane with 2-pyridylmethyl pendant arms was synthesized by mixing hydrated metal acetate and the ligand L (1:1) in MeOH and the addition of a small excess of sodium perchlorate gave a white solid in 75% yield. In the solid state, the two manganese atoms are bonded to four nitrogen atoms (two from pyridine and two from the macrocycle) and two oxygen atoms, one from a bridging hydroxo ligand and one from an ether group. The complex is highly symmetrical but the geometry about each metal centre is highly distorted. Attempts to oxidize the dimer with hydrogen peroxide in slightly alkaline aqueous solution were unsuccessful. The hydroxylation of cyclohexane by this complex was achieved in the presence of *tert*-butyl hydroperoxide, and cyclohexanol and cyclohexanone were obtained as products. The yield of the different oxidation products was the same when the reaction was performed with the dimer or a 1:2 mixture of the ligand and $MnCl_2$-$4H_2O$. The reaction was found to be more rapid when it was performed with the latter and is completed in 6 h versus 24 h for the dimer. The catalyst was not altered in the reaction, a second addition of TBHP after 24 h doubled the amount of cyclohexanol and cyclohexanone. Further experiments will be conducted to determine the nature of the active oxidizing species in particular its oxidation level.

Novel dinuclear Mn(II) complexes, (11), containing the tetrabromophthalate dianion (TBPHTA), have been synthesized and the effect of the halogen substituent in TBPHTA on the magnetic exchange interaction between the two manganese ions has been studied [73,74]. In particular, the complexes $[Mn_2(TBPHTA)(L)_4](ClO_4)_2$, L = bpy, phen, Me_2bpy, NO_2-phen were obtained and characterized by IR spectroscopy, elemental analysis and conductivity measurements. A weak antiferromagnetic interaction between the two metal ions is indicated from the magnetic susceptibility studies.

A study of the redox chemistry of the Mn complexes of 3-aminopyrazine-2-carboxylate, has been carried out [75]. An Mn(II) mononuclear complex having 1:2 stoichiometry shows an oxidation at +0.78 V verses SCE. Controlled-potential electrolysis at +0.80 V verses SCE gave a dinuclear Mn(III) species possessing a 1:2 metal:ligand stoichiometry. Addition of $Mn^{III}(urea)_6(ClO_4)_3$ to a solution of the ligand yielded a mononuclear Mn^{III} complex when the concentration of the metal



(11)

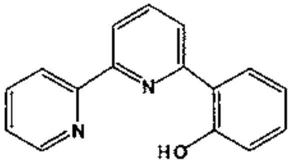
ion was less than 1 mM while a dinuclear species was obtained at higher metal concentrations. The dinuclear complex was reduced in two steps at +0.24 and −0.58 V versus SCE.

The dinuclear complexes Mn_2(II, II) $[Mn_2(L^{m,n})(RCOO)_2$, ($m,n = 2,3, 2,4$, or 3,3; R = Me, Ph) were prepared where ($L^{m,n}$) are dinucleating macrocycles with two 2,6-bis(iminomethyl)-4-methyl-phenolate moieties which are combined through two lateral chains -$(CH_2)_m$- and -$(CH_2)_n$- at the imino nitrogens [76]. The crystal structure of $[Mn_2(L^{3,3})(RCOO)_2]$ was obtained and shows it to comprise a pair of Mn(II) ions which are bridged by two phenolic oxygens with an Mn·Mn separation of 3.367(1) Å. In addition the acetate group coordinates in a didentate manner to each Mn ion giving a six coordinate environment about the metal ion. This complex is oxidized with Br_2 to give a mixed-valence complex. The ability of these complexes to decompose hydrogen peroxide in DMF and DMSO has been studied.

The use of a slow replacement reaction has facilitated the growth of $[Mn(4,4'\text{-bpy})_2(NCS)_2(H_2O)_2]_n$ for the first time [77]. The complex has been characterized by elemental analysis, IR spectra and thermal analysis. The X-ray crystal structure shows that the coordination environment about the Mn(II) ion is distorted octahedral; the $Mn(NCS)_2(H_2O)_2$ coordination planes are bridged by 4,4′-bipyridine ligands forming an infinite chain structure. A second bpy exists in the lattice linked by hydrogen bonds to coordinated water molecules. Magnetic studies infer the absence of any magnetic interaction between the metal ions.

The preparation and crystal structure determinations of complexes of mixed pyridine-phenol ligands which are dinuclear by virtue of phenolate bridges between the metal centres have been achieved [78]. The complexes $[Mn_4L^1_6][BPh_4]$ and $[Mn_4L^1_5(MeCN)][PF_4]$ containing the terdentate ligand L^1, (**12**), were characterized by X-ray crystallography. The former complex consists of a linear chain with a $Mn^{II}(\mu\text{-}O)_2Mn^{II}(\mu\text{-}O)_2Mn^{II}(\mu\text{-}O)_2Mn^{II}$ core with highly distorted Mn^{II} centres. Sections of the aromatic ligands overlap resulting in π-stacking interactions which may provide additional stabilization. In the latter complex, which is a mixed-valence one, there is an Mn^{III} centre which is coordinated by two L^1 ligands and an Mn^{III} centre which shares two phenolates with the Mn^{II} centre; a terdentate L^1 with an MECN ligand completes the coordination sphere. The contributions made by metal oxidation state, coordination modes available to the ligand and non-covalent interactions to the structure are evaluated.

The preparation, crystal structure and magnetic behaviour of the first mixed-valence $Mn^{II/III}$ complex polymer in a one-dimensional infinite chain bridged by



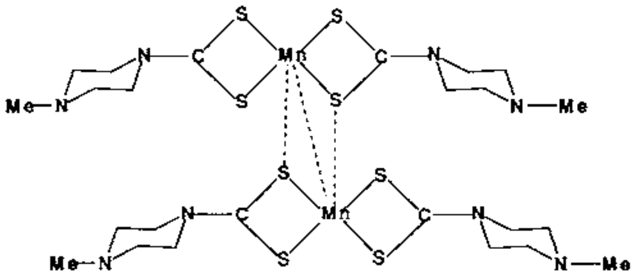
(12)

salicylate in a *syn-anti* configuration has been reported [79]. The complex $[Mn_4(sal)_4(H_2O)(Py)_8]_n[salH]_{[illegible]} \cdot 4n$py contains a tetranuclear repeat unit together with 2*n*salH$^-$ and 4*n*py. In the chain all Mn atoms are bridged by salicylate carboxylate groups in a *syn-anti* fashion, are arranged alternately and are six-coordinate. Magnetic studies have been carried out; the carboxylate group can mediate a very weak antiferromagnetic exchange interaction. The X-band EPR spectrum of the complex exhibits a sixline manganese hyperfine pattern centred at $g = 1.998$, $A = 97$ G.

5.4. *Complexes with sulfur donor ligands*

The electronic band structure and magnetic coupling in the chain compounds Ba_2MnX_3, X = S, Se and Te, has been studied using EH tight-binding band calculations [80]. This study was undertaken in order to assess the geometric and electronic factors responsible for the observed small changes in the values of the antiferromagnetic coupling between the Mn(II) ions as the chalcogenides become heavier. An analysis of the influence of the bridging atom electronegativity and size and bridging angle on the bandwidth of the *d*-block bands of the Mn(II) ions.

Carbodithioate complexes of Mn(II) and Mn(III) have been prepared and studied by IR and electronic spectroscopy and magnetic susceptibility measurements [81]. The complexes exhibit abnormal room temperature magnetic moments and variable temperature magnetic studies suggest antiferromagnetic coupling in the complexes. The carbodithioate ligands used were 4-methylpiperazine-1-carbodithioate and 4-phenylpiperazine-1-carbodithioate, and the complex structure is shown in scheme (13).



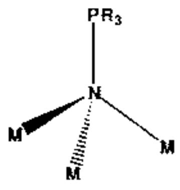
(13)

5.5. Complexes with selenium donor ligands

The synthesis and characterization of Mn(II) chalcogenolato complexes has been described [82]. Protolysis of $[\{Mn(N(SiMe_3)_2\}_2(thf)]$ with 2,4,6-$R'_3C_6H_2EH$, E = Se, R′ = Me or ᵗBu; E = Te, R′ = Me, in non-coordinating solvents (preferably light petroleum) provided a convenient route to the complexes $[\{Mn(EC_6H_2R'_3\text{-}2,4,6)_2\}]$. For R′ = Me, coordination polymers which are soluble only in strongly coordinating solvents were obtained. Those complexes with R′ = ᵗBu were found to be dimeric and readily dissolved in less polar solvents such as toluene. In the presence of excess bpy, a 1:2 adduct $[Mn(SeC_6H_2Me_3\text{-}2,4,6)_2(bpy)_2]$ was formed indicating that Mn(II) is able to increase its coordination sphere to give octahedral adducts. The crystal structure of $[\{Mn(\mu\text{-}SeC_6H_2Me_3\text{-}2,4,6)_2\}_\infty]$ was determined, it exists in the solid state as a one-dimensional infinite chain with symmetrically bridging selonate ligands which surround the metal giving a flattened tetrahedral geometry. The Mn–Se bond distances of 2.590(3) Å and the mesityl groups are oriented around the chain so as to minimize steric interactions.

5.6. Complexes with nitrogen donor ligands

The first phosphorane iminato complexes of Mn(II) and Co(II) with a heterocubane structure in which the μ_3-N type bridging mode (**14**) is found have been synthesized recently [83]. The manganese complex was obtained by the reaction of MnI_2 with the silylated phosphorane imine $Me_3SiNPEt_3$ gives $[MnI_2(Me_3SiNPEt_3)_2]$ which on heating to above 200 °C causes the cleavage of trimethylsilyl halide concomitant with the formation of the heterocubane $[\{MnI(NPEt_3)\}_4]$. Extraction of the solidified melt with dichloromethane gave a shiny red complex. It was characterized by EI–MS, magnetic susceptibility, IR spectroscopy and X-ray crystallography. The magnetic susceptibility at 20 °C was 3.1 BM per Mn atom indicating the presence of a spin–spin interaction between the Mn atoms. The Mn–N distances are 2.137(5) Å and Mn–Mn distances are 2.961(1) Å.



(**14**)

The self-assembly of a ferromagnetically coupled Mn(II) tetramer has been reported [84]. The reaction of $Mn(CH_3CO_2)_2 \cdot 4H_2O$ with KL, L⁻ = tris[3-(2′-pyridyl)pyrazol-1-yl]hydroborate in methanol followed by treatment with KPF_6 gave a yellow solid. Characterization of this solid by elemental analysis and

FAB–MS indicated the formulation $[MnL]PF_6$, while ES–MS results were consistent with the formation of a tetrameric species $[Mn_4L4]^{4+}$. X-ray crystallography confirmed this; the tetrameric unit contains four crystallographically independent Mn^{II} ions arranged approximately in a tetrahedron with Mn–Mn separations between 6.218 and 6.293 Å. Each ligand L^- sits above one triangular face of this tetrahedron donating one didentate arm to each of three metal ions on the face. The Mn–N distances are in the range 2.17–2.38 Å typical of Mn^{II}-(pyridyl) and Mn^{II}-N(pyrazolyl) distances in high-spin complexes. The coordination geometry about the Mn atoms is highly distorted octahedral. Aromatic π-stacking interactions between the pyrazolyl rings are present which may help stabilize this structure. The tetramer was further characterized by EPR spectroscopic and magnetic susceptibility studies. Low-temperature magnetic measurements (5–300 K) confirmed the presence of a weak ferromagnetic interaction. It is thought that this exchange is facilitated by π–π interactions.

The synthesis and reactivity of Mn(II) complexes of tertiary amines and their reactivity towards the dioxygen molecule has been reported [85]. The complexes $MnI_2(NR_3)$, $R_3 = Et_3$, $MeEt_2$ or $^nPr_3$ were prepared by the reaction of the tertiary amine with anhydrous Mn(II) iodide in dry diethyl ether with rigorously anaerobic and anhydrous conditions employed during the course of the synthesis. For $R_3 = Et_3$ and $^nPr_3$ recrystallization in diethyl ether under dry argon conditions yielded orange-pink crystals for both complexes which were suitable for crystallography. Both complexes are dinuclear with pseudo-tetrahedral manganese centres which are bridged by two iodine atoms. The bridged $Mn^{II}I_2$ moiety is planar in both cases; a slight elongation of the Mn–I bridge bonds is apparent in the $^nPr_3$ complex presumably due to the greater steric demands by the ^nPr groups. The Mn–N distance is 2.18(3) Å (R = Et), and 2.17(4) Å (R = ^nPr) while the Mn–I distances are in the ranges 2.634(6)–2.765(5) Å and 2.632(6)–2.804(8) Å respectively. The reaction of the complexes with oxygen has been studied, for R = Et, 2 mol of oxygen was absorbed per mole of complex while for the R = ^nPr only one mole is absorbed. These complexes do not reversibly bind dioxygen.

A communication has appeared which describes the synthesis, structure and magnetic behaviour of the two-dimensional compound $[Mn(4acpy)_2(N_3)_2]_n$ in which the coordination mode of the azido ligand is "end-to-end" [86]. This compound was prepared by the addition of an aqueous solution of sodium azide to an ethanol/water solution of 4-acetylpyridine and $MnCl_2 \cdot H_2O$; the final clear solution was kept in the dark for several days after which light yellow crystals of the complex were obtained. In this compound, each Mn atom is octahedrally coordinated to four azido ligands and two 4-acetylpyridine ligands in a *trans* fashion. Each azido ligand bridges two manganese atoms in an end-to-end fashion with the Mn atom lying on a crystallographic centre of inversion. Repetition of this basic unit generates a 2D polymer in which Mn–N distances are 2.192(3) and 2.214(3) Å and Mn–Mn distances are 5.997(2) Å. As a consequence of the long Mn–Mn distances in neighbouring layers the interactions between these atoms are expected to be negligible at high temperature giving an $S = 5/2$ two-dimensional magnetic system. Variable temperature solid-state magnetic susceptibility and EPR spectroscopic studies were performed on powdered samples from 290 to 4 K and are indicative of a moderate antiferromagnetic coupling.

The crystal structure of $[Mn(bpy)_2Cl(H_2O)_2]ClO_4$ has been obtained [87]. It consists of discrete $[Mn(bpy)_2Cl(H_2O)_2]^+$ cations and perchlorate anions. The Mn atom is in a distorted octahedral enviromnent surrounded by a pair of *cis* related chelating bpy ligands, an aqua and a chloro ligand. The Mn–N bonds range from 2.235(3) to 2.291(3) Å while the Mn–O bond length is 2.167(3) Å and the Mn–Cl bond is 2.447(1) Å. Adjacent cations are linked into dimers by pairs of Cl···O hydrogen bonds.

The synthesis of an Mn(II) complex of the "tripod" ligand tris(2-benzimidazolylmethyl)amine, L, which contains both five- and six-coordinate manganese atoms in the unit cell has been reported [88]. The reaction of $MnCl_2$ with tris(2-benzimidazolylmethyl)amine in ethanol gave golden yellow crystals of a neutral *cis*-$[Mn(L)Cl_2]$, a $[MnLCl]^+$ cation, a chloride anion, ethanol and water molecules. In the neutral molecule the Mn atom is in an octahedral environment being ligated by two chlorine atoms and four nitrogen atoms. One Mn–Cl bond length of 2.378(3) Å is unremarkable whereas the other length of 2.538(2) Å is unusual and significantly longer than observed in related structures and may be a consequence of the steric constraint imposed by the tripodal benzimidazolyl ligand. The Mn–N distances fall into two distinct groups, namely, those with three ligating nitrogen atoms from the imidazole functions range from 2.217(6) to 2.229(5) while the fourth ligating nitrogen forms a longer bond of 2.515(7). In the cation the geometry about the metal is distorted trigonal bipyramidal and presumably manganese adopts this configuration to alleviate steric crowding. The Mn–N bond lengths in the trigonal plane range from 2.135(8) to 2.147(4) Å. The axial Mn–Cl distance is 2.316(2) while a fourth nitrogen occupies the other axial position at a distance of 2.514(6) Å which is unusually long and indicative of the steric requirements of the ligand. The complexes were also characterized with elemental analysis and FAB MS. Attempts to oxidize the compound with hydrogen peroxide were unsuccessful imparting interesting properties as a precursor to heteronuclear or homonuclear complexes.

The ferromagnetic behaviour of Mn(II) complexes with pyridine-substituted nitronyl nitroxide radicals has been investigated [89]. In particular, compounds of the formula $Mn(dtbz)_2(NITpPy)_2(H_2O)_2$ and $Mn(tnp)_2(NITpPy)_2(H_2O)_2$, dtbz = 3,5-dinitrobenzoate, tnp = 2,4,6-trinitrophenolate, NITpPy = 2-(4-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl 3-oxide have been synthesized. The crystal structure of the dtbz derivative has been obtained; it is mononuclear with the Mn centre in an octahedral environment and bound to two nitronyl nitroxide radicals via the nitrogen atom of the pyridine ring and four oxygen atoms from water molecules and dinitrobenzoate. The Mn–N axial bonds are 2.263(3) Å while the Mn–O equatorial bonds are 2.177(3) and 2.149(2) Å. Variable temperature magnetic susceptibility measurements for both compounds suggest ferromagnetic coupling between the Mn atoms and the radicals with $J = 2.08$ and $1.03\ cm^{-1}$ for the dtbz and tnp derivatives, respectively. This is thought to be due to the orbital orthogonality between the π^* molecular orbital of the NITpPy radical and the d_{xy}, d_{yz} and d_{xz} orbitals of the metal.

5.7. Complexes with nitrogen and sulphur donor ligands

The electrochemical synthesis of manganese complexes containing pyrimidine-2-thiones has been achieved [90]. In a procedure where manganese metal is the anode of a cell containing the ligand (pyrimidine-2-thione, pymth or 4,6-dimethylpyrimidine-2-thione, 4,6-$Me_2(pymt)_2$) and nitrogen donor didentate ligand such as phen or bpy in an acetonitrile solution the complexes [$Mn(pymt)_2phen$], [Mn-4,6-$Me_2(pymt)_2phen$] and [Mn 4,6-$Me_2(pymt)_2bpy$] were obtained. When the thione ligand is the only one present in solution the manganese complex is not produced, rather, oxidation of the ligand to disulphide occurs. The X-ray crystal structures of bis-4,6-dimethylpyrimidyl-2,2′-disulphide and 1,10-phenanthroline-bis-(4,6-dimethylpyrimidine-2-thiolato)Mn(II) were determined. In the Mn complex the metal has a distorted octahedral *trans* MnS_2N_4 geometry with one nitrogen atom of each pyramidine ligand uncoordinated. The Mn–N distances fall in the range 2.241(6) to 2.277(7) Å while the Mn–S distances are 2.594(3) and 2.591(3) Å.

6. Manganese(I)

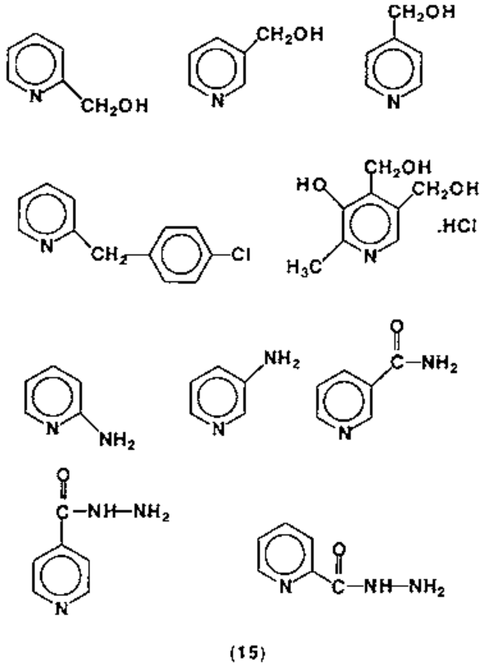
6.1. Complexes with oxygen donor ligands

Spectroelectrochemistry with a novel low-temperature optically transparent thin-layer electrochemical cell has been used to obtain IR and UV–VIS spectra: of some unstable *ortho*-semiquinone and *ortho*-quinone complexes of Mn(I) [91]. The $[Mn(CO)_3(L)(DBQ)]^+$, L = H_2O, PPh_3, DBQ = 3,5-di-*tert*-butyl-1,2-benzoquinone cations are the first spectroscopically characterized tricarbonyl *o*-quinone complexes of Mn(I) reported in the literature.

6.2. Complexes with oxygen and nitrogen donor ligands

One-dimensional manganese polymers containing pyridone ligands have been synthesized, structurally characterized and their magnetic properties have been studied [92]. The complex $[\{Mn_2(chp)_2(O_2CMe)_2(MeOH)_2\}_n]$, Hchp = 6-chloro-2-pyridone was synthesized by the reaction of Mn(II) acetate with Na(chp) in ethanol yielding a pale precipitate which was crystallized by diffusion of diethyl ether vapour into a methanol solution. X-ray crystallography reveals two unique Mn sites within the asymmetric unit; Mn(1) lies on a two-fold rotation axis and is bound to oxygen and nitrogen donors of two chelating chp ligands and to two oxygen atoms from two acetate ligands. It is bridging to the second Mn atom via the chp oxygen atom in a μ-bridging fashion and by a 1,3-bridging acetate ligand. The second Mn atom lies on an inversion centre and its coordination sphere is completed by two methanol molecules. Thus the coordination geometry of each Mn atom is distinct; Mn(1) has two N- and four O- donors with a very distorted geometry while Mn(2) has an octahedral array of oxygen atoms. The closest Mn···Mn distance within the polymer is 3.7599(14) Å. Results from magnetic studies are indicative of antiferromagnetic exchange.

The interaction of the pentacyanonitrosylmanganate(I) anion, $[Mn(NO)(CN)_5]^{3-}$ with potentially mono-, di- and tridentate pyridine derivatives (**15**) has generated mixed-ligand complexes which have been characterized by IR spectroscopy, electrical conductance and magnetic measurements [93]. The complexes have the general formula $[Mn(NO)(CN)_2(L)_2(H_2O)]$ and $[Mn(NO)(CN)_2(LL)_2(H_2O)]$ and octahedral structures have been proposed for them.

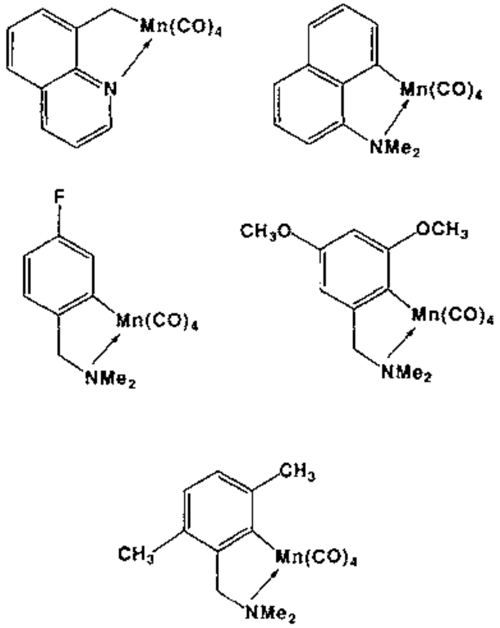


(**15**)

6.3. *Complexes with nitrogen donor ligands*

The influence of the halide ligand on electronic transitions in *fac*-$XMn(CO)_3(bpy)$ and *mer*-$ClMn(CO)_3(bpy)$, X = Cl, I, has been studied using MO calculations [94]. Self-consistent calculations using the Amsterdam density-functional program were carried out; they show that for the *fac*-isomer the two highest orbitals have metal-halide antibonding character with the LUMO being a π^* (bpy) orbital. The first absorption band was assigned to electronic transitions having mixed metal-halide to bpy CT character. In the second absorption the band was assigned to CT transitions from the corresponding metal-halide bonding orbitals to bpy. In the case of *fac*- and *mer*-ClMn(CO)$_3$(bpy) the energy of the highest filled orbitals is higher for the latter which is in accord with their spectroscopic data and may explain their differing photochemistries.

The synthesis of a series of cyclomanganated compounds derived from several nitrogen-containing ligands (**16**), has been described [95]. The compounds have been characterized by IR, ^{1}H and ^{13}C{^{1}H} NMR spectroscopy showing the *N*,*N*-dimethylbenzylamine derivative to be coordinated as a chelating ligand. The orientation in the cyclometalation of benzylamine derivatives tends to avoid the steric interaction between the R groups ortho to the Mn–C bond and a CO unit. When the R group is OMe the latter compound isomerizes in order that the interaction between the O atom of the methoxy unit and the carbon atom of the carbonyl group may take place.



(16)

The characterization of isocyanurate metal complexes including those of manganese which form molecular ribbons in the solid state has been achieved [96]. The complex [M(cyan-N)(H$_2$O)$_5$](cyan-N)·2H$_2$O, M = Ni, Co, Cu, were prepared by the reaction of LiC$_3$H$_2$N$_3$O$_3$ and MnCl$_2$·6H$_2$O in water. The bond lengths to the transition metal centre show the expected monotonic decrease on going from manganese to cobalt to nickel. In the solid state, these complexes form an extended aggregate of cross-linked molecular ribbons which are stacked perpendicular to the crystallographic direction-[010]. The crystals were found to grow preferentially in the direction of propagation of the molecular ribbons and in the direction of stacking.

6.4. Complexes with nitrogen and phosphorus donor ligands

A cationic manganese–carbonyl complex with a phosphazenylphosphine ligand has been synthesized and structurally characterized [97]. The structure of *cis-trans*[$\{N_3P_3Cl_4(C_6H_5)(PPh_2)\}$ $Mn(CO)_2(bpy)\{P(OOPh_3\}]PF_6$ consists of discrete complex cations and PF_6- anions linked by several weak C–H · · · O and C–H · · · F interactions. The cation displays approximately distorted octahedral coordination with the manganese bonded to two mutually *cis* carbonyl ligands, two nitrogen atoms of the bpy ligand and two phosphorus atoms of the phosphite and phosphazenylphosphine ligand, respectively. Analysis of the bond lengths reveals that coordination of the phosphazenylphosphine ligand induces minor structural changes in the phosphazene ring. The Mn–N distances are 2.050(5) and 2.053(5) Å while Mn–P distances are 2.210(2) and 2.362(2) Å.

6.5. Complexes with phosphorus donor ligands

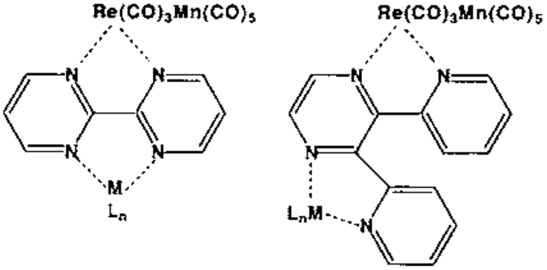
The results of efforts to achieve a successive hydrogen substitution in the bifunctional $Mn_2(\mu\text{-}H)(\mu\text{-}PCyH)(CO)_2$ have been reported [98]. In THF solution, this complex was deprotonated by excess DBU to an anionic species which upon addition of two equiv. of $ClAuPPh_3$ at 20 °C in 1 h gave the isomers $Mn_2(AuPPh_3)_2(\mu_4\text{-}PCy)(CO)_8$ and $Mn_2(\mu\text{-}AuPPh_3)(\mu_3\text{-}PCy(AuPPh3)(CO)_8$. The former complex, which is the thermodynamically preferred isomer, was crystallized and identified by single crystal X-ray analysis while the latter was characterized by ^{31}P NMR spectroscopy. A solution of $Mn_2(AuPPh_3)(\mu_4\text{-}PCy)(CO)_8$ gave rise to an equilibrium mixture of $Mn_2(AuPPh_3)_2(\mu_4\text{-}PCy)(CO)_8$ and $Mn_2(\mu\text{-}AuPPh_3)$-$(\mu_3\text{-}PCy(AuPPh_3)(CO)_8$ in several solvents. The factors influencing the isomerization process between μ_3-P and μ_4-P-bridged pairs have been studied and found to depend on the kind of phosphine attached to gold(I) which may be controlled by electronic or steric factors and by the polarity of the solvents used. In a related paper [99], further efforts to obtain the missing monoaurated dimanganese isomers by selective synthetic routes as well as the structural characterization and mutual conversion of these isomers has been reported. The complexes $Mn_2(\mu\text{-}AuPR_3)(\mu_4\text{-}PCyH)(CO)_8$ and $Mn_2(\mu\text{-}H)(\mu_3\text{-}PCy(AuPR_3))(CO)_8$, R = Cy, Ph, $p\text{-}C_6H_2O_4Me$, $p\text{-}C_6H_4F$, were separated by fractional crystallization procedures and identified by means of ^1H, ^{31}P NMR, UV–VIS and IR spectroscopies. For R = Ph derivatives the X-ray crystal structures have been obtained.

7. Manganese(O)

7.1. Complexes with nitrogen donor ligands

An article describing the synthesis and spectroscopic properties (^1H NMR, UV VIS and Raman) of complexes $(CO)_5MnRe(CO)_3L$, $(CO)_5MnRe$-$(CO)_3(L)Re(Br)(CO)_3$, L = 2,2′-bipyrimidine (BPYM), 2,3-bis(2-pyridyl)pyrazine

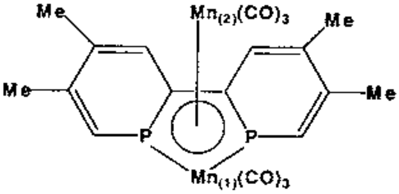
(DPP) and $(CO)_5MnRe(CO)_3(L)Re(BPYM)W(CO)_4$, (**17**), has appeared [100]. These represent the first examples of polynuclear species in which two metal atoms are linked by a direct Mn–Re covalent bond and the other metal moiety is separated from the dinuclear entity by a bridging diimine ligand. As such these complexes offer a chance to study ligand-mediated mutual influence of the metal-containing fragments on spectroscopic and photochemical properties. The crystal structure of $(CO)_5MnRe(CO)_3(BPYM)Re(Br)(CO)_3$ and asymmetric bonding within the bridging bonding ligand has been found. This asymmetry is reflected in the ^1H NMR spectrum and is also reflected in the presence of two absorption bands in the visible region belonging to separate transitions from the two metal fragments to BPYM. This asymmetry was not observed for the DPP-bridged complex.



(17)

7.2. Complexes with phosphorus donor ligands

A novel 8-electron coordination mode for both 2,2′-biphosphinines and 1,4-diphosphadienes has been described [101]. The reaction of 4,4′,5,5′-tetramethyl-2,2′-biphosphinine (tmbp) with $Mn_2(CO)_{10}$ gave the red-orange dinuclear complex $[Mn_2(tmbp)(CO)_6]$ in which the tmbp ligand acts as an 8-electron donor through its central 1,4-diphosphadiene unit. The tricyclic system is essentially planar (**18**) and the central C_2P_2-Mn(1) ring is η^5-bound to the second manganese atom which lies at 1.8550(6) Å from the C_2P_2Mn(1) nucleus. From X-ray crystallography, the 5-membered C_2MnP_2 unit is delocalized with intracyclic Mn–P distances being 2.1903(6) Å in comparison to the P–Mn(2) bonds at 2.4062(6) Å. This delocalization occurs at the expense of aromaticity in the phosphinine rings.



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