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3. Manganese

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CONTENTS

INTRODUCTION

This review article profiles the advances in manganese chemistry as reported in the literature for 1991. It is based on a search of Volumes 114, 115 and 116 of *Chemical Abstracts*. In addition major inorganic chemistry journals have been searched separately for the calender year 1991. A review of the involvement of manganese, through its coordination chemistry, in photosynthetic water oxidation has appeared [1]. It describes how the recent identification of a multi-nuclear manganese-containing active site in Photosystem II has spawned further research in the coordination chemistry of high-valent manganese which may lead to useful catalysts for the redox process involving water.

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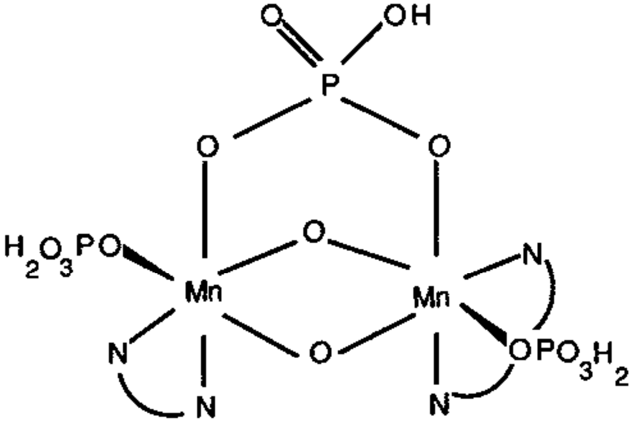
3.1 MANGANESE(V)

3.1.1 Complexes with oxygen donor ligands

The high-resolution near-infrared photoluminescences of manganese(V) doped crystals of $Ba_5(PO_4)_3Cl$ (apatite structure) and Ca_2VO_4Cl (spodiosite structure) have been reported [2]. They are assigned to intraconfigurational ^1E-$^3A_2$ transitions and the vibrational sideband structure was interpreted in terms of the bending and stretching vibrations of the $[MnO_4]^{3-}$ entity.

The oxidation of tartronate and mesoxalate ions by permanganate ion has been studied in 0.1 M to 2.0 M aqueous NaOH solution [3]. The proposed mechanism involves an outer-sphere electron transfer to $[MnO_4]^-$ ion which generates an organic radical anion and manganate(VI). The latter reacts with both substrates in a second, slower step, giving manganate(V) as a relatively stable product in a strong alkaline medium. The radical anion radical is rapidly oxidized by $[MnO_4]^-$ to give carbonate, carboxylate and oxalate.



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3.2 MANGANESE(IV)

3.2.1 Complexes with oxygen donor ligands

The first bis-(μ-oxo)-manganese dimer containing a bridging inorganic phosphate ion has recently been synthesized [4]. This dimer may be of utility as a structural model for the dinuclear metal centre in the purple acid phosphatase (PAP) enzyme. Treatment of $[(bpy)_2Mn(O)_2Mn(bpy)_2)]^{3+}$ with H_3PO_4 (pH = 2.3) gave a stable green solution. Slow crystallization from a 0.5 M H_3PO_4 aqueous solution yielded thin red-brown plate crystals of

$[(bpy)(H_2PO_4)Mn(\mu\text{-}HPO_4)(\mu\text{-}O)_2Mn(H_2PO_4)(bpy)]\cdot H_2O$ (1). The structure of the dimer, which was obtained from X-ray diffraction, possesses two Mn(IV) centres bridged by two μ_2-oxo groups and one μ_2-phosphate; Mn-O and Mn-N bond lengths are similar to literature values for other $Mn^{IV}{}_2(\mu\text{-}O)_2$ complexes. The Mn-O bonds in the bridging and terminal phosphate groups differ, the latter being longer. The location of protons on the phosphate oxygens was explored by studying the relative P-O bond lengths; when protonated, the P-O bond length was found to be longer by 0.05 to 0.09 Å in comparison to that of other non-coordinated oxygen atoms in the same phosphate moiety. A possible mechanism for formation of (1) by a disproportionation reaction has been postulated.

Evidence for a weak manganese-oxygen double bond in compound I of manganese horseradish peroxidase has been presented [5]. The generation, isolation and characterization of this species has been described. Resonance Raman and EPR spectroscopies support an oxo-manganese(IV) protein free radical configuration with an unusually weak, but exchange-resistant, Mn=O for this species.

Several manganese complexes of α-hydroxy acids have been studied recently [6]. The X-ray structure of $Na_3[NaMn^{IV}{}_2(HIB)_6].4MeOH$ (where H_2HIB = 2-hydroxyisobutyric acid) has been determined. It was prepared by the reaction of $MnCl_2$, H_2HIB, and $NaOCH_3$ in methanol, and its structure comprises a mixed-metal trinuclear cluster composed of two Mn(IV) octahedra which are bridged by a sodium ion giving rise to a very short Mn-Na bond, 2.98 Å. This complex is unique in possessing all oxygen ligation. An *O,O'*-coordination shell is trigonally compressed along a face containing three alkoxide ligands. The X-band EPR spectrum at 100K indicates an isolated $S = {}^3/_2$ system.

3.2.2 *Complexes with oxygen and nitrogen donor ligands*

Several manganese(IV) complexes with tridentate *S*-alkylisothiosemicarbazones have recently been prepared and characterized by IR, ESR, electronic spectroscopy and magnetic susceptibilities [7].

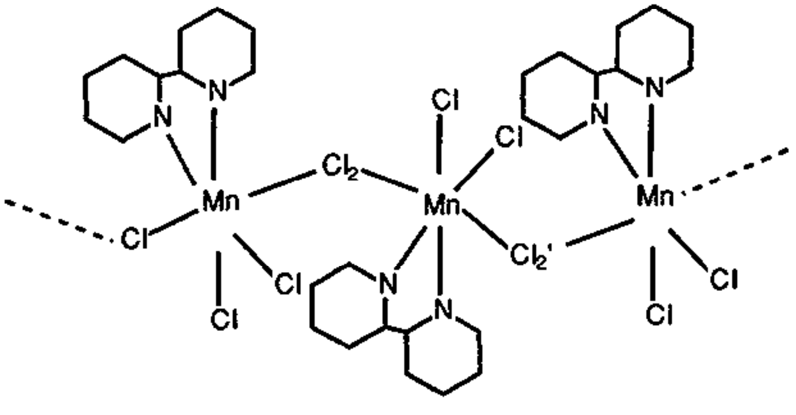
The synthesis and characterization of several new bis(μ-oxo)dimanganese-(III,IV) and -(IV,IV) complexes containing the tetradentate ligand *N,N'*-bis(2-pyridylmethyl)-1,2-ethanediamine has been documented [8]. In particular, the crystal structure of a manganese(IV) complex, bis(μ-oxo)bis[*N,N*-(2-pyridylmethyl)-1,3-propanediamine]dimanganese perchlorate trihydrate has been described. The geometry about each manganese atom is roughly octahedral, with two *cis* oxo bridges and four nitrogen atoms from the pyridyl and amino groups. The Mn·····Mn separation is 2.719 (3) Å. The magnetic properties of the (III,IV) complexes are consistent with a doublet ground state whereas the (IV,IV) complexes have singlet ground states. EPR and cyclic voltammetry studies have been reported for these complexes.

A group of complexes of coordination type $Mn^{IV}O_4N_2$ which exhibit a strong EPR signal near $g = 4$ has been described [9]. The X-ray structures of $Mn^{IV}(amp)_2$ where amp = the dianion of *N*-(2-hydroxyphenyl)salicylaldimine, and $Mn^{IV}(azp)_2$ (where azp = the dianion of 2,2'-dihydroxyazobenzene) have been obtained. In both complexes, the ligands are acting as meridional tridentate *O,N,O*-donors and the coordination spheres exhibit large deviations from octahedral geometries; this is reflected in their EPR spectra. The Mn-O distances are in the range 1.861(4) - 1.893 (6) Å with a value of Mn-N(azomethine) = 1.968 (8) Å being shorter than the average Mn-N(azo) length of 2.007 (10) Å. The Mn(IV)–Mn(III) reduction potentials in DMSO have been measured and are correlated with the p*K* of the oxygen donor functions.

3.3 MANGANESE(III)

3.3.1 Complexes with halide ligands

It has recently been discovered that excess Me_3SiCl provides a convenient and high-yield synthesis of both $(NEt_4)MnCl_5$ and $[MnCl_3(bpy)]_n$, (**2**), starting from $Mn_{12}O_{12}(OAc)_{16}(H_2O)_4 \cdot 2HOAc \cdot 4H_2O$ [10]. The X-ray crystal structures of (**2**) determined at both room and low-temperatures show this compound to be polymeric. It consists of infinite chains of $MnCl_2(bpy)$ units which are joined by asymmetrically bridging Cl^- ions. The Mn atoms are in distorted octahedral environments. Terminal Mn-Cl (low temperature form) bond lengths are approximately 2.24 Å while the bridging Mn-Cl2 and Mn-Cl2' are 2.51 and 2.71 Å respectively. The structures of the low temperature and room temperature forms are similar with only a few small differences in bond lengths and angles. The Mn-Cl bond at low temperature (2.710 (2) Å) is elongated with respect to that at room temperature (2.762 (2) Å).



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3.3.2 *Complexes with oxygen donor ligands*

The aqueous electrochemistry of binuclear mixed-valence oxo-bridged manganese clusters, $[Mn^{III}Mn^{IV}(O)_2(bpy)_4]^{3+}$, $[Mn^{III}Mn^{IV}(O)_2(edda)_2]^-$, and $[Mn^{III}Mn^{IV}(O)_2(bispicen)_2]^{3+}$, where bpy = 2,2'-bipyridyl, edda = ethylenediamine-*N,N'*-diacetate, bispicen = *N,N'*-bis(2-methylpyridyl)ethane-1,2-diamine, has been explored and it has been demonstrated that ancillary ligands play a significant role in regulating proton-coupled electron transfer in these oxo-bridged systems [11].

The physical properties of a manganese tetramer with all-oxygen coordination have been studied recently [12]. Magnetic susceptibility measurements and EPR spectroscopy on $Mn_4(\mu_3\text{-}O)_2(O_2CCPh_3)_6(OEt)_2$, consisting of a central planar core of metal atoms (two Mn(II), two Mn(III)) bridged by two μ_3-oxo ligands, show that the molecule contains a unique type of Mn(II) centre that is relatively electron-poor. The effects of these unique centres are evident in the Mn 2*p* binding energies and redox chemistry.

Treatment of $Mn_3O(O_2CPh)_6(py)_2(H_2O)$ with 2,2'-biphenol (biphenH$_2$) and NEt_3 in MeCN results in fragmentation to give $(NEt_3H)_2[Mn(biphen)_2(biphenH)]$ which is the first example of an Mn(III) atom ligated to only phenoxide-like oxygen atoms [13]. It possesses a five-coordinate trigonal bipyramidal Mn(III) centre ligated by two chelating biphen^{2-} groups and a monodentate biphenH$^-$, in the latter the second phenoxide oxygen is protonated and not ligated to the manganese atom. It has been used as a precursor to other complexes one of which is a mixed-valence $Mn^{II}Mn^{III}$ dinuclear complex $Mn_2(biphen)_2(biphenH)(bpy)_2$, which displays a large Mn·····Mn separation of 3.182 (6) Å. The latter, although not a model for the photosynthetic water oxidation site, does show that Mn(III) can be stabilized in a predominantly phenoxide environment.

Complexes with the formulation $[Mn^{III}{}_4O_2(O_4CR)_x(L\text{-}L)_2]^z$ (x = 6 or 7; L–L = a chelating ligand; z = –1, 0, 1) and possessing the $[Mn_4(\mu_3\text{-}O)_2]^{8+}$ core with a "butterfly" disposition of manganese atoms have been prepared [14]. An Mn_4O_2 complex has been obtained which contains an H_2O ligand and represents important progress in modelling the water oxidation centre. In addition, this complex was used as a precursor to higher nuclearity manganese aggregates

The reaction of $[Mn_4O_2(OAc)_7(bpy)_2](ClO_4).3H_2O$ with Me_3SiCl resulted in the formation of a remarkable high nuclearity product $[Mn_{11}O_{10}Cl(OAc)_{11}(bpy)_2(MeCN)_2(H_2O)_2](ClO_4)_2.8MeCN$, a mixed-valence manganese (III/IV) aggregate with an unprecedented structure [15]. X-ray crystallography shows the core of this aggregate comprises two $\{Mn_4O_3Cl\}^{6+}$ cubane units which are "bridged" by a nearly linear $[Mn_3O_4]^+$ moiety. The cubane units contain three Mn(III) and one Mn(IV) species with each Mn(III)Mn(IV) pair bridged by an AcO$^-$ group and three Mn(III) centres are bridged by a μ_3-Cl$^-$ ion with long Mn-Cl bonds (2.534(7) - 2.688(7) Å). The two remaining coordination sites on Mn(2) are occupied by a bpy group; the remaining two sites on Mn(1) and Mn(3) are occupied by bridging groups to the central Mn_3 unit. The Mn^{III} - Mn^{III} distances are in the range 3.173(5) - 3.239(5) Å and the Mn^{III}-Mn^{IV} are in the range 2.737(5) - 2.835(5) Å. The two cubane units are held together by the central Mn_3O_4 unit via linkages to two oxygen atoms and two acetate groups. The three Mn atoms are slightly V-shaped with an angle of 162.91° and the Mn–Mn distances are

2.864(5) and 2.873(5) Å. The axial sites for the manganese atoms are occupied by AcO^-, MeCN and H_2O groups.

Manganese superoxide dismutase from *Escherischia coli* was prepared in homogeneous Mn^{3+} and Mn^{2+} forms and has been characterized recently by a combination of optical absorption, circular and magnetic circular dichroism, and EPR spectroscopies [16].

The characterization of $H_2MnP_3O_{10}{\cdot}2H_2O$ has been carried out using TGA-DTA analyses, EXAFS, IR and UV-VIS spectroscopies [17]. The manganese atom is in a distorted octahedral environment with four equatorial Mn-O bonds (1.86Å); the axial Mn-O bonds are of lengths 2.24 and 2.09 Å.

The kinetics of the reaction of $[S_2O_3]^{2-}$ with $[Mn(acac)_3]$ and the derivatives $[Mn(acac)_2(H_2O)_2]^+$ and $[Mn(acac)(H_2O)(OH)]$ have been investigated in aqueous perchlorate media containing varying total quantities of acac over the pH range 4.2 - 8.5 [18]. The reaction rate is first order in $[S_2O_3]^{2-}$ but consumes no $[S_2O_3]^{2-}$; 1 mole of acetylacetone is consumed per mole of Mn(III) reduced. EPR and kinetic data suggest a $[S_2O_3]^{2-}/[S_2O_3]^-$ catalytic cycle which provides a low-energy path for acac to Mn(III) electron transfer. Rate constants for the reduction of the species have been determined and inner- and outer-sphere mechanisms have been proposed.

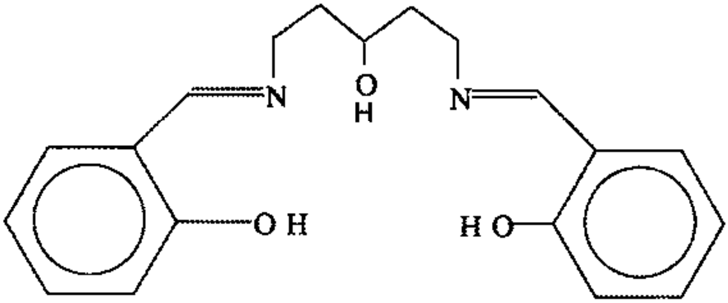
The reaction of $MnAsO_4.H_2O$ with $LiNO_3$ at 200°C gave $LiMnAsO_4(OH)$ and was accompanied by a large change in the framework geometry [19]. This was due to an unusual switch in the Jahn-Teller distortion of the $Mn^{III}O_6$ octahedra from four short Mn-O(As) and two long Mn-OH_2 bonds, to two short and two long Mn-O(As) bonds plus two intermediate Mn-OH bonds. This is suggestive of the fact that microporous materials containing Jahn-Teller ions may act as more flexible hosts for intercalation and catalytic reactions in comparison to those based solely on rigid polyhedra.

The reaction of tetramethylammonium permanganate ($(TMA)MnO_4$), lactic acid (H_2Lc), and tetramethylammonium hydroxide (TMA-OH), in methanol gave rise to the manganese(III) dimer, $(TMA)_3[Mn^{III}_2(Lc)_4HLc].H_2O$ [6]. The X-ray structure shows this to be the first example of an Mn(III) dimer with axial compression. Two $Mn^{III}Lc$ units, which possess a propellar configuration, are bridged by the carboxylate of an HLc, having a protonated hydroxyl oxygen atom and weak bridges from coordinated alkoxides of the adjacent $Mn^{III}Lc_2$ unit. The Mn–Mn distance is 3.09 Å. In addition a compound of composition $(cat)_2[Mn^{III}(L)_2HL]$, (where cat^+ = tetra-n-butyl ammonium(1+) or Na^+ ion), was prepared and is most likely to possess an infinite chain structure that has a *trans*-$Mn^{III}L_2$ plane, is linked by the anti-coordination of the carboxylate oxygens of HL^-. The relevance of these compexes as models for the oxygen-evolving complex and diffusible intermediates of the manganese lignin peroxidase has been discussed.

The electronic structure and magnetism in manganese(III) chain compounds have been reported [20]. In particular, the linear chain series $(cat)_2[Mn^{III}(sal)_2(CH_3OH)_2][Mn^{III}(sal)_2]$, where cat = Na^+, K^+, NH_4^+, and sal = salicylate, have been prepared by the reaction of $MnCl_2$ with salicyclic acid and the appropriate base; molecular structures have been determined. Variable-temperature magnetic susceptibilities were measured to determine the magnitude of magnetic exchange in these chains. The exchange interaction was found to be weakly antiferromagnetic with all three salts behaving as one-dimensional magnets and the sodium salt exhibiting three-dimensional exchange. A spin exchange model is used to support the findings.

The preparation and properties of a nonanuclear complex, $[Mn_9O_7(O_2CC_6H_5)_{13}(py)_2]$ have been reported [21]. The crystal structure of this species shows that there are five distinct manganese coordination environments with all Mn atoms in the +3 oxidation state. The base of the nonanuclear core may be viewed as two "butterfly" type Mn_4O_2-units which share a central five-coordinate manganese atom. FAB, EPR and IR spectroscopy have been employed to further characterize this species. Antiferromagnetic coupling between all manganese atoms has been established.

A binucleating ligand, 1,5-bis(salicylideneamino)-3-pentanol (H_3L), (3), has been used to synthesize the complex $[Mn_2L(CH_3O)Cl_2(CH_3OH)]$ [22]. The complex has been characterized by X-ray crystallography, electronic spectroscopy, magnetic susceptibility and electrochemical studies. The two manganese atoms are bridged by the alkoxide oxygen atom of L and the methoxy oxygen atom, with an Mn-Mn separation of 3.006(2) Å. The coordination geometry about each metal atom is an elongated octahedron due to weak coordination by the chloride ion and the methanol molecule in the apical positions. An antiferromagnetic interaction between the two manganese atoms has been demonstrated.



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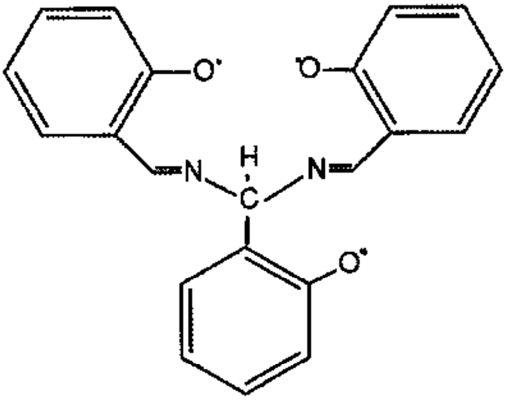
3.3.3 *Complexes with oxygen and nitrogen donor ligands*

The molecular structure of $Mn(NO_3)_2.3L$ where L = 2,4 dichlorophenoxyacetic hydrazide has been obtained [23]. The manganese atom has a coordination number of 7, the NO_3^- ligands are mono and bidentate, one L ligand is bidentate and the remaining two are monodentate.

The use of a diamagnetic metal complex as a "spacer" for paramagnetic centres in order to effect a change in distance between interacting metal centres has been used to synthesize two novel series of heterotrinuclear complexes with the structural units $[LMn^{III}\text{-}\{\mu\text{-}(dmg)_3Mn^{II}\}Mn^{III}L]^{2+}$ and $[LMn^{IV}\text{-}\{\mu\text{-}(dmg)_3Mn^{II}\}Mn^{IV}L]^{4+}$ where L = 1,4,7-trimethyl-1,4,7-triazacyclononane, dmg = dianion of dimethylglyoxime, and M^{II} = Zn, Cu, Ni, or high-spin Mn [24]. The X-ray structure of $Mn^{III}Zn^{II}Mn^{III}$ has been obtained and shows a $[Zn(dmg)_3]^{4-}$ anion bridging two Mn(III) ions through its deprotonated oxime oxygens with an Mn·····Zn separation of 3.565 (2) Å. Oxidation of this complex in MeCN using NO^+ as an oxidant gave rise to an $Mn^{IV}Zn^{II}Mn^{IV}$ complex whose structure could not be determined. The two Mn^{IV} are separated by about 7 Å and have a moderately strong ferromagnetic interaction.

An investigation of the scope of manganese-salmp chemistry where salmp is the pentadentate ligand 2-(bis(salicylideneamino)methyl)phenolate(3–), (4), has been described [25]. The complexes $[Mn_2(salmp)_2]^{0—(2-)}$ were prepared and their structures obtained. The *trans*- C_{2h} conformation is shown in (5), each has a planar $Mn_2(\mu\text{-}O)_2$ bridge unit which is rhomboidal in the neutral and dianionic species, and an irregular quadrilateral in the monoanionic species. The terminal bond distances and Mn·····Mn separations tend to decrease with increasing oxidation level. $Mn_2(salmp)_2$ exhibits a Jahn-Teller distortion which results in a very large difference (0.34 Å) in bridging Mn-O distances. These complexes comprise the only series in which the oxidation states $Mn^{III}Mn^{III}$, $Mn^{III}Mn^{II}$, $Mn^{II}Mn^{II}$ have been structurally characterized.



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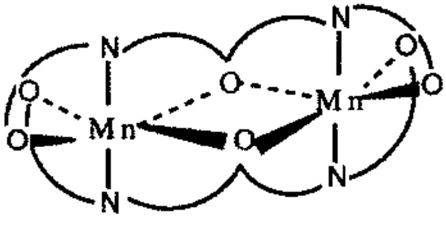

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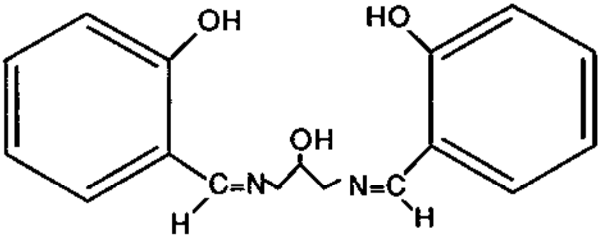
Several manganese(III) complexes formed with the potentially binucleating ligand 2-OH-SALPN (6), have been reported [26]. In particular an Na^+-linked polymeric species $[Mn(2\text{-}OH\text{-}SALPN)(OAc)(NaClO_4)(MeCN)]_x$ containing chains of six-coordinate Mn(III) centres bridged by seven-coordinate Na^+ ions via bridging acetate linkages has been described. Weak antiferromagnetic coupling exchange interactions between Mn(III) atoms has been demonstrated.



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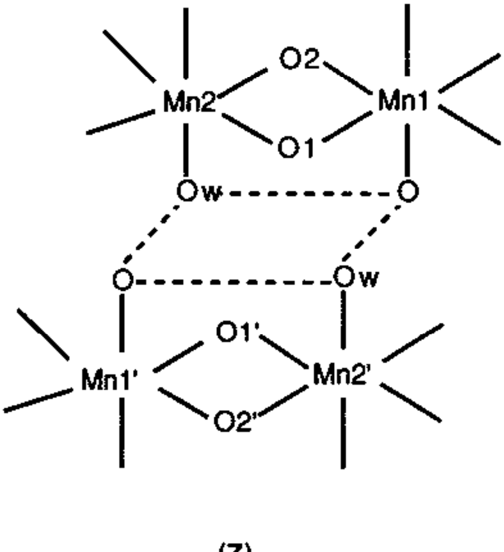
The results from spectroscopic, including ESR studies, have shown the existence of a redox interaction between the binuclear Mn_2(III/IV), $[Mn_2O_2(bpy)_4]^{3+}$, and the binuclear Mn_2(II/II) complexes, $[Mn_2(L\text{-}py)(CH_3COO)_2]^+$ and $[Mn_2(L\text{-}py)Cl_2]^+$ in dilute acetronitrile solution [27]. Electrochemical data suggest an important role for chloride in these reactions.

The oxidation of polyamine ligands has been demonstrated recently in polynuclear manganese complexes [28]. The reaction of triethylenetetramine, trien, with manganese(III) acetate and sodium acetate in methanol solution, followed by addition of NH_4PF_6 gave red needles of a septanuclear manganese salt, $[Mn_7(trien)_2(dien)_2O_4(OAc)_8](PF_6)_4.2H_2O$. The crystal structure of the cation shows it comprises two $[Mn_4(\mu_3\text{-}O)_2]$ units in a familiar butterfly arrangement in which one manganese atom is shared at the wingtip. Charge requirements are consistent with the presence of six Mn^{III} ions and one Mn^{II} ion. An unexpected feature of this complex is the presence of the dien ligand. It has been proposed that under "acidic" conditions due to NH_4PF_6, oxidation of trien to an imine intermediate followed by hydrolysis to give dien occurs. A ^{13}C NMR spectrum of a CH_2Cl_2 extract of the mother liquor showed resonances due to dien and trien. It has not been established whether oxidation proceeds before or after complexation to manganese.

The ability of chloride ion to induce structural change in a model complex for the photosynthetic water oxidation centre has recently been described [29]. Treatment of $[(Mn_3O(OAc)_6(py)_3](ClO_4)$ with acetronitrile and 1.5 equivalents of dibenzoylmethane, dbm, gave an Mn_4^{III} complex, $[(Mn_4O_2(OAc)_6(py)_2(dbm)_2]$. When 1 equivalent of $^nBu_2NCl$ was added to the hot MeCN recrystallization medium, an $Mn_3^{III}Mn^{IV}$ complex, $[(Mn_4O_3Cl(OAc)_3(dbm)_3]$, was obtained. The crystal structures of both these complexes have been obtained and the structural changes induced by the addition of chloride ligand are discussed in the light of chloride dependence of water oxidation in the native system.

In an attempt to model as closely as possible the ligation environment around the Mn_4 unit of the photosynthetic water oxidation centre efforts to replace the bpy ligand with the picolinate ligand, pic^-, such that an $[Mn_4O_2]^{8+}$ complex in which the number of nitrogen-based ligands is halved with a concomitant increase in carboxylate ligation has been reported [30]. Two complexes, $(N^nBu_4)[[Mn_4O_2(O_2CMe)_7(pic)_2]$ and $(N^nBu_4)[[Mn_4O_2(O_2CPh)_7(pic)_2]$ have been obtained. The crystal structure of the anion in the former reveals an $[Mn_4(\mu_3\text{-}O)_2]^{8+}$ core with the four manganese atoms in a "butterfly" arrangement and the oxygen atoms triply bridging each wing. The peripheral ligation is via seven μ-AcO^- and two chelating pic^- groups. This anion is very similar to the previously reported complex, $[Mn_4O_2(O_2CMe)_7(bpy)_2]^+$, demonstrating little structural consequence in substition of a pic^- with a bpy ligand. Treatment of this complex with PhCOOH in acetonitrile afforded the complex $(N^nBu_4)[[Mn_4O_2(O_2CPh)_7(pic)_2]$ demonstrating facile carboxylate exchange with more acidic acids. The results of ^1H NMR and electrochemical studies have been presented. Variable temperature magnetic susceptibility studies have been performed in the range 5 to 300K and spin frustration present in these complexes has been examined in detail.

In an attempt to obtain an accurate model for the "dimer-of-dimers" structural type in the oxygen evolving complex of photosystem II the synthesis of the complex $[(Mn_2O_2)_2(tphpn)_2]^{4+}$, has been achieved [31]. The solid-state structure of this cation indicates a mixed-valence species which consists of a linked pair of $[Mn^{III}Mn^{IV}O_2]^{3+}$ cores. The results from EPR spectroscopy are discussed.



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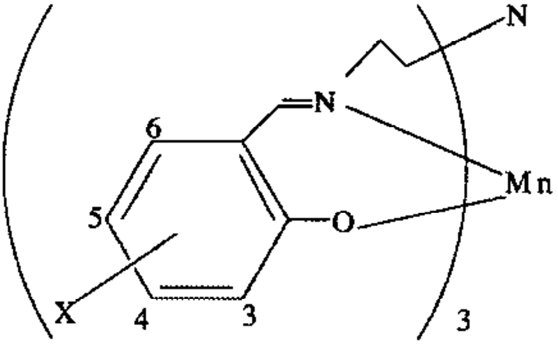
The synthesis and structural characterization of a novel dimer of di(μ-oxo)-dimanganese(III,IV) dimers, $[\{Mn_2(tmdp)(O)_2(H_2O)\}_2](CF_3SO_3)_4.6H_2O$, (7), Htmdp = 1,5-

bis[bis(2-pyridylmethyl)amino]3-pentanol, which contains two coordinated water molecules has been reported [32]. The cation consists of two di(μ-oxo)Mn_2 dimers which are linked by two tmdp bridges to form a dimer of dimers with a bilayered structure. The Mn_2O_2 planes are not faced directly but slid with respect to each other. The manganese atoms are in a distorted octahedral geometry. The two water molecules are separated by 3.3 Å. The measured magnetic moments are indicative of an antiferromagnetic interaction between the manganese atoms.

The effect of axial anions on the thermal stability of square pyramidal Mn(III) complexes has been documented [33]. In particular, complexes of the type [Mn(SB)X] where SB is a tetradentate Schiff base; X = OAc^-, SCN^-, Cl^-, Br^-, or I^- have been studied. A correlation between the thermal stabilities of these complexes and the electronegativities of their axial donor atoms has been found.

The syntheses, spectra and electrochemistry of Mn(III) complexes with $Mn^{III}N_3O_3$ coordination by sexidentate Schiff-base ligands, (**8**) formed by the condensation of tris(2-aminoethyl)amine with salicylaldehydes, have been reported [34]. The complexes were prepared readily, as highly crystalline brown to green solids and are soluble in dmf, and moderately soluble in chloroform and dimethyl sulfoxide. Their magnetic moments, in dmf solution, as determined by NMR gave μ_{eff} in the range 4.79 - 5.30 at 298K, being consistent with the presence of monomeric high-spin d^4 ($S = 2$) manganese (III) systems. ^1H NMR spectroscopy indicated that in solution the symmetry of these complexes is very low (C_1). Cyclic voltammetric studies in dmf solution reveal an irreversible Mn^{III}-Mn^{II} couple, with E_{pc} in the range –0.62 to –0,05 V *vs*. SCE, and a quasi-reversible Mn^{IV}-Mn^{III} with E_f in the range +0.42 to +0.86 V *vs*. SCE.



X = H, 3-Me, 4-Me, 5-Me, 3,4-Me_2, 3,5-Cl_2

(**8**)

An Mn^{III}-porphyrin in which an axial imidazole ligand and a carboxylic acid group are juxtaposed on opposite sides of the porphyrin plane and are both covalently linked to the plane has recently been synthesized [35]. This porphyrin which is a biomimetic model of cytochrome P-450, has been shown to be an extremely efficient catalyst for the activation of 30% H_2O_2 in hydrocarbon oxygenations carried out in CH_2Cl_2-H_2O; initial rates at 1 minute of up to 500 turnovers per minute were obtained at O°C for the epoxidation of cyclooctene.

Irradiation of $[\{Mn(L)(H_2O)\}_2](ClO_4)_2{\cdot}4H_2O$ with visible light, where L is a tetradendate unsymmetric Schiff's anionic ligand 4-{2-(2-hydroxyphenylmethyleneamino)ethylamino]pent-3-en-2-one, gave rise to a dimeric $[\{Mn(salen)(H_2O)\}_2](ClO_4)_2{\cdot}H_2O$ containing the symmetrical dianionic Schiff's base ligand *N,N"*-bis(salicylidene)ethylenediaminato [36]. The X-ray crystal structure of the dimer has been reported and reveals that each $[Mn(salen)H_2O]^+$ moiety is linked to its neighbour across a crystallographic inversion centre by two oxygen atoms. The bridging Mn-O bonds are long 2.390(3) Å and complete a distorted octahedral geometry about each manganese atom. The manganese atom separation is 3.361(2) Å.

The preparation and characterization of $[Mn_2(O_2CMe)_2(bpy)_2(H_2O)(S_2O_8)]$ via the oxidation of $Mn(O_2CMe)_2{\cdot}4H_2O$ with $(NH_4)_2S_2O_8$ in aqueous solution has been reported [37]. Elemental analysis, IR spectroscopy and X-ray crystallography point to the the first example of an asymmetric Mn_2^{III} complex containing the $(\mu\text{-}O)(\mu\text{-}O_2CMe)_2$ core. Other Mn_2^{III} complexes containing this core have been advanced as possible models for Mn-catalase. In addition one bpy ligand is coordinated to each metal atom. Ligation at each metal centre is completed by a terminal water molecule at Mn(1) or a terminal peroxydisulfate anion at Mn(2). The O-O bond in S_2O_8 is exceptionally long, 1.604(20) Å, having been activated as a result of binding to an Mn atom.

3.3.4 Complexes with sulfur donor ligands

The structure of benzyltriphenylphosphonium imidazole(*O*-mercaptophenol) manganese(III) acetonitrile solvate has been reported [38]. The Mn^{III} ion is in a distorted square-pyramidal S_2O_2N environment. The average Mn-S length is 2.28Å, while the Mn-N is 2.157Å and Mn-O(average) = 1.905Å.

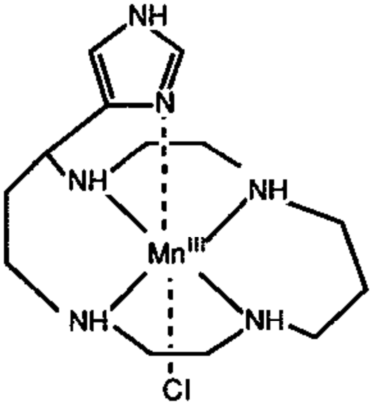
3.3.5 Complexes with nitrogen donor ligands

The preparation and characterization by thermal decomposition and X-ray crystallography of a manganese complex $Mn_3(HL)_2.10H_2O$, H_4L = edta, with ethylenediaminetriacetoacetate ligand has been described [39].

The stoichiometry, stability constants and structure of manganese(II) complexes with *p*-hydroxybenzylidene- and vanillylidene-2-4-methylpyrimidine were studied using elemental analysis, conductance measurements, UVvis and IR spectroscopy [40].

The synthesis and reactivity of adducts of tetrakis(4-nitrophenyl)porphyrinmanganese(III) chloride, MnLCl, L = *meso*-tetra(4-nitrophenyl)porphyrin) has been reported [41]. In particular, adducts of MnLCl with diatomic molecules such as CO, NO and some organic bases were studied and stability constants were obtained. Electron-attracting substituents e.g,. NO_2^- on the porphyrin cycle can facillitate the reduction of Mn(III) to Mn(II).

The synthesis, X-ray structure and chemical properties of a five-coordinate Mn(III) complex with an imidazole-pendant cyclam (9), [42]. The Mn(III) atom sits in the cyclam N_4 plane with an imidazole nitrogen and a chloride ion in the axial positions. The Mn-N distances are 2.039(4), 2.039(4), 2.044(4), and 2.029(4) Å. The axial Mn-N distance is 2.277(4) and Mn-Cl is 2.463(2) Å respectively, reflecting a *Jahn-Teller* distortion for a high-spin d^4 ion. This complex has been found to be an efficient catalyst for alkene epoxidation.



(9)

The structural and magnetic characterization of Mn(III) complexes of 11,4,8,11-Tetraazacyclotetradecane (Cyclam) has been documented recently [43]. The complexes adopt a *trans* geometry and exhibit axial elongation typified by d^4 complexes; their magnetic properties are consistent with their formulation as monomeric high-spin d^4 systems.

The synthesis, characterization and novel photochemical reduction of Mn(TPP)(NO_3) and Mn(TPP)(NO_2) where TPP = 5,10,15,20-tetraphenylporphyrinate(2-), to produce O=Mn^{IV}(TPP) has been reported [44]. Irradiation of the nitrate and nitrite complexes produced the metal-oxo species with quantum yields of 1.58×10^{-4} and 5.30×10^{-4} respectively. The X-ray crystal structure of the nitrate complex shows the NO_3^- to be coordinated in a monodentate fashion via an oxygen atom (in contrast to Co(porph)(NO_3) and Fe(TPP)(NO_3) which are bidentate) with an Mn-O bond of 2.101 (3) Å. The average Mn-N porphyrin bond is 2.007 Å and the manganese core displacement is 0.21 Å. The crystal structure of the nitrite complex reveals a unique monodentate O-bound coordination mode with an Mn-O bond of 2.059 (4) Å. The average Mn-N porphyrin distance is 2.012 Å and the manganese core displacement is 0.22 Å. Previously characterized Co and Fe nitrite porphyrin complexes are bound through the nitrogen atom of the nitrite moiety.

The synthesis, characterization, single-crystal X-ray structures, and photochemistry of (μ-sulfato)bis[(5,10,15,20-tetraphenylporphyrinato)manganese(III)], $[Mn(TPP)]_2(SO_4)$, and hydrogen sulfato(5,10,15,20-tetraphenylporphyrinato)manganese(III), $Mn(TPP)(OSO_3H)$ have been documented [45]. In the former, the sulfate anion is in a monodentate bridging coordination, Mn-O distances 2.019 (5) and 2.008 (5) Å are in the short end of the range observed for other O-bound ligands; the stereochemistry is similar to that found in the analogous iron system. The average Mn-pyrrole N distance in both rings is 2.008 Å with the metal displaced above the mean plane of the nitrogen atoms by 0.19 and 0.22 Å In the latter, coordination by the hydrogen sulfate ligand through one of the oxygen atoms is observed. The Mn-O bond distance of 2.078(5) Å is similar to that observed in nitrate and nitrite complexes. The average $Mn\text{-}N_{pyrrole}$ distance is 1.991 Å with the metal 0.23 Å above the mean plane of the nitrogen atoms. Irradiation between 350 and 420 nm cleanly produced Mn^{II}(TPP) identified by its electronic and EPR spectra, but, in contrast with other manganese oxoanion complexes, metal-oxo species were not formed and oxidation of hydrocarbons did not occur.

The reactions of $(Ph)_2(MeOCO)COOH$ with two water-soluble non μ-oxo dimer-forming manganese(III) porphyrins, [*meso*-tetrakis(2,6-dimethyl-3-sulfonatophenyl)porphinato]manganese(III) hydrate and [*meso*-tetrakis(2,6-dichloro-3-sulfonatophenyl)porphinato]manganese(III) hydrate, have been studied in aqueous solutions at 30°C, $\mu = 0.2$ (with $NaNO_3$), and in the pH range from 5.3 to 12.6 [46]. These reactions have been compared with those for Iron(III) porphyrins.

The kinetics of the redox interaction of $[Mn(cdta)]^-$, where cdta is *trans*-cyclohexane-1,2-*N,N,N',N'*-tetra-acetatomanganate(III), with a series of amine-*N*-polycarboxylates, namely iminodiacetate (ida), nitriloacetate (nta), and ethylenediaminetetraacetate (edta) was studied in the pH range 3.0 to 10.0, with variable reductant concentrations at constant ionic strength, 0.05 mol dm^{-3} $NaClO_4$, at 30°C [47]. All reactions were found to be first order both in complex and reductant concentration. Oxidation of (ida) is thought to proceed by an inner-sphere mechanism whereas an outer-sphere mechanism has been proposed for (nta) and (edta).

The kinetics and mechanism of the reaction of *trans*-cyclohexane-1,2-diamine-*N,N,N',N'*-tetra-acetatomanganate(III) with substituted thioureas reductants in aqueous solution has been studied using stopped-flow techniques in the pH ranges 2.5–4.5 and 9.2–10.2 [48]. The reactions are first order in both oxidant and reductant. An initial increase in absorbance followed by a steady decrease in absorbance indicated the formation of a precursor complex prior to the electron transfer step.

The kinetics of the $Mn(CN)_6{}^{3-}$ disproportionation reaction in an acidic medium has been studied recently [49]. The fast disproportionation gave $Mn(CN)_6{}^{2-}$ and $Mn(H_2O)_6{}^{2+}$. This reaction was studied by amperometry, using a rotating platinum-disk electrode, at a 1.0 V (vs. SCE) constant potential, in the acidity range 0.01 to 2.0 M and at temperatures between –5 and 15°C. The reaction kinetics were found to be pseudo-firtst order in $[Mn(CN)_6{}^3]$ and the rate constant dependent on acidity according to the equation, $k_{obs} = k_a + k_b[H_3O^+] + k_c[H_3O^+]^2$.

The re-examination of a binuclear [Mn-Cu] metalloporphyrin complex has established the presence of an $[Mn^{III}(imid)\ Cu^{II}]^{2+}$ [50]. This compound possesses antiferromagnetic coupling between the Mn^{III} and Cu^{II} and across an imidazolate bridge.

The reaction of a manganese(II) salt with 5,14-dihydro-7,16-diethyl-(*E*)-or-(*Z*)-dipyrido[*b*,*i*][1,4,8,11]tetraazacyclotetradecine gave a 1:1 complex with an anion in the axial position as the fifth ligand [51]. The spectral properties and redox characteristics of these complexes were reported.

3.4 MANGANESE(II)

3.4.1. Complexes with oxygen donor atoms

The thermodynamics and kinetics of complexation of manganese(II) complexes with carboxy-containing ligands has been reported [52].

Several mixed valence manganese carboxylates of various nuclearities have been prepared and their crystal , molecular structures and magnetic properties studied [53]. For all compounds trapped valency was observed in addition to antiferro and ferromagnetic intramolecular exchange interactions.

The coordination compounds formed between Mn(II) and thiophene-2-carboxylic acid and 4,5-imidazoledicarboxylic acid in aprotic solvents, such as DMSO, acetonitrile and DMF, have been studied using cyclic voltammetry, polarography and UV-visible spectroscopy [54]. In all cases the complexes are formed under anhydrous conditions, with their ligands deprotonated.

The thermal and solution stabilities of metal(II) chelates, including Mn(II) with peonolphenylhydrazone have been determined [55]. Among these metal chelates, manganese has the lowest solution stability whereas its thermal stability is the highest.

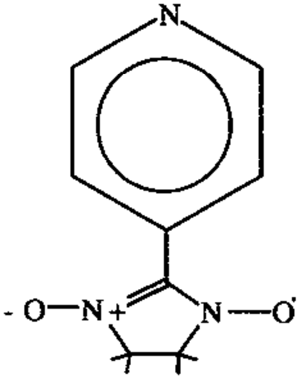
The oxidation kinetics of Mn^{II} in aqueous solution by atmospheric ozone was studied at various temperatures, pH-s and pressures of ozone [56]. Below a pH of 4.5 the reaction product was MnO_2 whereas Mn_2O_3 was formed above a pH of 5.

The thermodynamics of Mn(II) benzoate complex formation was studied and stability constants were measured potentiometrically at temperatures within the range 25 to 40°C [57]. The change in entropy was evaluated based on enthalpy measurements and the free energy change was calculated from the stability constant.

The thermodynamic stability constant for the complex formed between Mn(II) with 2,4 pentanedione-1(2-chlorophenylhydrazone) [58] and 2,4 pentanedione-1(3-chlorophenylhydrazone) [59] has been determined potentiometrically at different temperatures and ionic strengths.

The synthesis, crystal structure and magnetic properties of a linear trinuclear complex $Mn^{II}_3(CH_3COO)_6(bpy)_2$ has been reported [60]. This complex is interesting because of the duality of bridging modes exhibited by the acetate groups. The structure consists of linear trinuclear units of manganese atoms in which each Mn atom is μ-linked by three acetate ligands. Two of the acetate groups are bidentate bridging ligands whereas the third one is bridging through one oxygen atom only to the central Mn atom, notably it also chelates the terminal Mn atom. The central Mn atom has an octahedral coordination sphere composed of oxygen atoms from six acetate ligands while the terminal Mn atoms show distorted environments of four oxygen atoms and two nitrogens from a bipyridine molecule. The *J* electron exchange parameter has been determined for this complex via magnetic susceptibility and high-field magnetization measurements.

The structure and magnetic properties of $[Mn(hfac)_2NITpPy]_2$, hfac = hexafluoroacetylacetonato, where both the pyridine and an NO group of the radical are coordinated to metal ions has been reported [61]. The crystal structure consists of centrosymmetric dimers and shows each Mn(II) atom to be coordinated by four oxygen atoms belonging to the hfac fragments one oxygen atom of the NITpPy radical (**10**), and the nitrogen atom from the pyridine ring of the second NITpPy molecule. The pyridine rings in this dimeric unit may be considered to be stacked; the shortest contact between two atoms belonging to the rings being 3.56 Å. Magnetic data suggests that for this four-spin system, an antiferromagnetic interaction between the manganese and radical through the NO group is dominant while a weak ferromagnetic interaction through pyridine might be responsible for the diamagnetic ground state. In a related paper [62], the synthesis and magnetic properties of a compound of formula $Mn(hfac)_2NITPhOMe$, where NITPhOMe = 2-(4-methoxyphenyl)-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide, a molecular based ferromagnet possessing a unique helical structure and high potential interest for magneto-optical investigations has been described.



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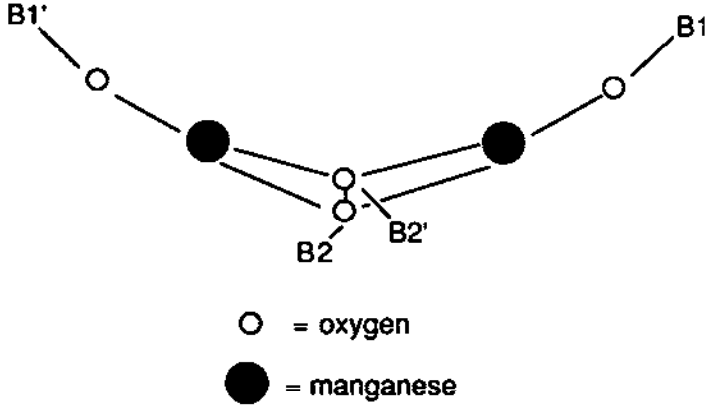
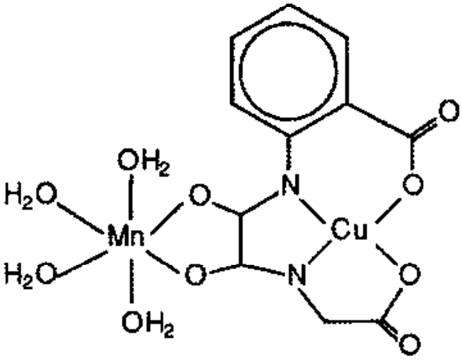
The characterization of the neutral homoleptic compound $[Mn(OMes^*)_2]_2$ Mes* = 2,4,6 $^tBuC_6H_2$, and the synthesis of the base adduct $Mn(OCPh_3)_2(py)_2$ have been reported [63]. The former consists of well-separated, aryloxide-bridged dimers with no crystallographically imposed symmetry. The manganese and oxygen atoms of the Mn_2O_4 core displays a trigonal planar geometry for both the metal and bridging oxygen atoms. The Mn-Mn separation is 3.156(2) Å, with the bridging M-O distances averaging 2.050(8) Å and the terminal M-O distances 1.873(4) Å. The latter complex consists of well separated monomers with a very irregular four-coordinate arrangement of ligands about the manganese. The Mn-O and Mn-N distances are 1.956(4) and 2.202 (8) Å respectively. The O-Mn-O angle involving the alkoxide substituents is very wide 140.4 (2)° whereas the N-Mn-N angle is 95.6 (2)°. The M-O bonding in these complexes is thought to be primarily ionic in sharp contrast to higher oxidation state early transition-metal complexes.

The first homoleptic transition-metal derivative $[Mn(OBR_2)(\mu\text{-}OBR_2)]_2$, (**11**), of the quasi-alkoxide ligand $[OBR_2]^-$, (where R is $2,4,6\text{-}{}^{i}Pr_3C_6H_2$) has recently been synthesized and structurally characterized [64]. The boryl ligand was used in place of OR^- an attempt to obtain mononuclear complexes, the rationale being that although the $[OBR_2]^-$ ligand possesses two lone pairs of electrons, one of these pairs might be used by the empty *p* orbital on the boron atom implying that the other could still be utilized for bridging to the metal centre. It was hoped that the reduction in electron density at oxygen coupled with the large bulky substituents on the boron atom would be sufficient to prevent bridging through oxygen, thereby generating a mononuclear species. A dimer was obtained; this consisted of a slightly folded Mn_2O_2-core with a dihedral angle of 155.8°, the metal atoms have pyramidal coordination with very irregular angles (e.g. M-O-M = 96.1(3)° and O-M-O = 81.0(3)°). Average terminal Mn-O and bridging Mn-O distances are 1.890(7) and 2.080(7) Å respectively, while the O-B terminal distance is 1.318(16) Å; the O-B bridging distance is 1.358(14) Å with all the boron centres having trigonal planar geometries. The Mn·····Mn distance is 3.094(5) Å. These structural features indicate that the metal-ligand interaction is predominantly ionic. Attempts to obtain an estimate of the bridge strength by ^1H NMR spectroscopy were unsuccessful.



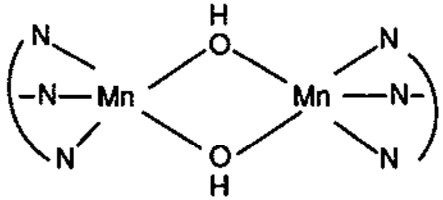
(11)

The compound $MnCu(obze)(H_2O)_4{\cdot}2H_2O$ (where obze is oxamido-*N*-benzoato-*N*-ethanoato) was obtained by the slow diffusion of equimolar aqueous solutions of $Na_2[Co(obze)]{\cdot}2H_2O$ and manganese(II) perchlorate [65]. Results of X-ray crystallography show the structure to be composed of $Mn^{II}Cu^{II}$ heterobinuclear molecules, (**12**), with the manganese and copper centres being bridged by an oxamido group. The manganese atom possesses a distorted octahedral geometry surrounded by four water molecules and two oxamido oxygen atoms. The dihedral angle between the equatorial planes of the two metal ions is 7.8°. This compound behaves as antiferromagnetically coupled Mn^{II}Cu^{II} isolated pairs with a quintet-septet energy gap, $3J = -100.8$ cm^{-1}, and can be viewed as an assembly of molecules with a large positive spin density on the manganese side and a small negative density on the copper side. Using very mild experimental conditions these molecules polymerize giving a molecular-based material of formula MnCu(obze)(H$_2$O)$_2$ which shows a ferromagnetic transition at $T_c = 4.6$K. In a related paper [66], thermal treatment (warming at 100°C under vacuum for 48 hours) of a compound of formula, MnCu(pbaOH)(H$_2$O)$_3$, (where pbaOH is 2-hydroxy-1,3-propanediylbis(oximato)) gave a new compound of formula MnCu(pbaOH)(H$_2$O)$_2$ by removal of a water molecule from the copper(II) coordination sphere. Magnetic measurements show that the latter compound orders magnetically at $T_c = 30$K, whereas in the former complex, spontaneous magnetization occurs below $T_c = 4.6$K.



(12)

The first example of a dinuclear complex in which both manganese atoms are bridged solely by hydroxo groups has been reported [67]. The reaction of MnCl$_2$ with 1 equivalent of K[HB(3,5-^{i}Pr$_2$pz)$_3$], where HB(^{i}Pr$_2$pz)$_3$ = hydrotris(3,5-diisopropyl-1-pyrazolyl)borate, in the presence of excess 3,5-^{i}Pr$_2$pz in a CH$_2$Cl$_2$/CH$_3$OH mixture gave Mn(Cl)(3,5-^{i}Pr$_2$pz)(HB3,5-^{i}Pr$_2$pz)$_3$ as an air-stable white solid. The latter was then reacted with 1 M aqueous NaOH giving [MnHB(3,5-^{i}Pr$_2$pz)$_3$]$_2$(OH)$_2$ (**13**). Two hydroxo groups lie between two manganese(II) atoms with identical bond lengths, viz 2.094 (4) and 2.089 (5) Å. The Mn–Mn separation of 3.31 Å is close to a known Mn–Mn separation for the oxygen evolving complex in photosystem II. The magnetic susceptibility of a powdered sample measured 6.88 μ_B is indicative of a weak interaction between the two high-spin manganese(II) ions. Anaerobic oxidation with KMnO$_4$ gave a bis(μ–oxo)manganese(III,III) complex where the Mn-O bonds are in the range 1.79 – 1.81 Å, typical for manganese-oxo bonds. The Mn–Mn separation is 2.70 Å with the manganese atoms being five-coordinate; this is probably attributable to the steric hindrance of the ligand. It is EPR silent and this, coupled with its low magnetic susceptibility of 2.81 μ_B/mol, is suggestive of a strong antiferromagnetic interaction between the two manganese atoms. This complex may also be generated from (13) by the oxidation under a dioxygen atmosphere, although the yield was not very high. In a related paper [68], the aerobic oxidation of (13) has been discussed. In addition to the bis(μ–oxo) complex previously obtained, a deep blue complex was obtained, the crystal structure of which was determined. The complex is a dinuclear manganese one in which each manganese(IIII) centre is bridged solely by an oxo ligand. The complex has an unusual structural feature in that the central carbon atom of one isopropyl group in each tris(pyrazoyl)borate ligand is oxygenated and it coordinates to each manganese atom as an alkoxo ligand. Labelling experiments indicate that the μ–oxo atom originated from the hydroxo groups in (13) and both the alkoxo oxygen atoms arise from the same dioxygen molecule. A reaction mechanism for this aerobic oxidation has been proposed and is discussed.



(13)

The structure of $Mn_3(CH_3COO)_6(H_2O)_4 \cdot 2H_2O$ has been determined from a single-crystal X-ray diffraction study [69]. It consists of MnO_6 octahedra which are linked by acetate bridges to form $Mn_3(CH_3COO)_6(H_2O)_4$ units in the *bc* plane. Mn-O distances are in the range 2.170(5) to 2.231(6) Å.

The characterization of a new anhydrous polymeric manganese(II) complex, *catena*-tris(betaine)manganese(II) tetrachloromanganate(II), $[Mn(Me_3NCH_2COO)_3]_n.nMnCl_4$, has been reported [70]. The crystal structure comprises discrete tetrachloromanganate anions and linear cationic chains. The manganese atoms adopt axially distorted (C_{3i}) coordination geometries. The Mn-O bond lengths are comparable to those found for common manganese(II) carboxylates in which there is octahedral coordination This cationic polymeric chain constitutes a new structural variety exhibiting not only a unique tris(carboxylato-*O,O'*) bridging geometry, but also an unusual skew-skew coordination mode of the carboxylato group.

3.4.2 Complexes with oxygen and nitrogen donor ligands

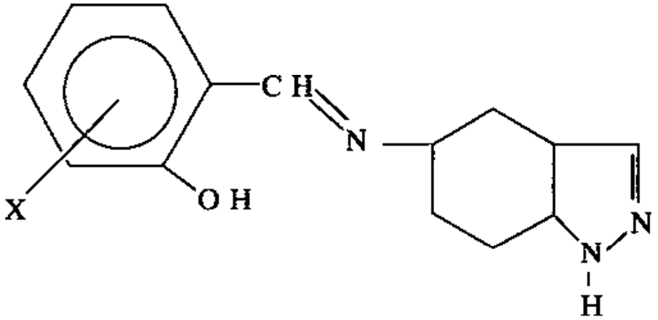
Using flexible polydentate ligation a novel Mn_4 moiety with phenolato bridging, has been assembled from a mononuclear precursor [71]. The crystal structure of $[Mn_4O_2L_2]^{2+}$, H_3L =

$N(CH_2CH_2N{=}NCHC_6H_4OH)_3$ has been determined and shows two types of Mn coordination spheres namely, MnN_3O_3 and $MnNO_3$ both of which are axially elongated. The shortest Mn·····Mn separation is 2.906(3) Å.

The synthesis and properties of several μ-oxamido heterobinuclear copper(II)-manganese(II) complexes have been reported [72]. Elemental analysis, IR and electronic spectroscopy, and conductance measurements suggest an oxamido bridged structure with copper(II) in a planar environment and manganese(II) in a distorted octahedral one.

The crystal structure of a seven-coordinate tripodal manganese(II) complex, $[Mn(pyo)_3tren](PF_6)_2.EtOH$ (where pyo = 2-pyridinecarboxyaldehyde *N*-oxide and tren = $N(CH_2CH_2NH)_3$) has been obtained [73]. The manganese atom possesses a monocapped antitrigonal prism coordination environment.

Several manganese(II) complexes with an indazole Schiff base have been synthesized and characterized [74]. The bonding in these complexes is depicted in (**14**).

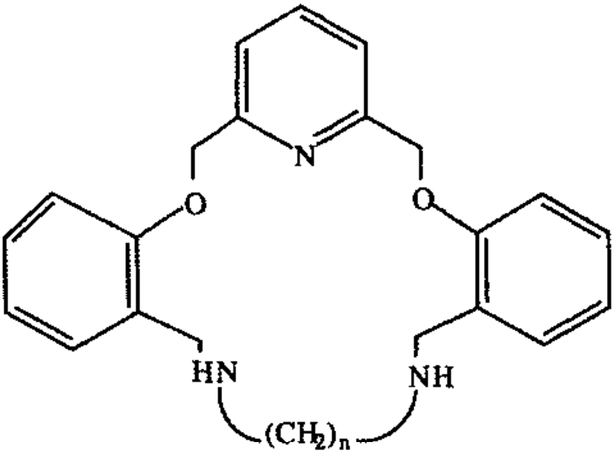


X = C_4H_4, *p*-OH, H

(14)

The reaction of *N,N',N''*-tris(2*S*)-2-hydroxypropyl-1,4,7-triazacyclononane (H_3L) with $MnCl_2$ in neutral or slightly basic conditions gave $[Mn^{II}(H_3L)(L)Mn^{IV}][PF_6]_3$ [75]. The crystal structure shows that the molecule is a hydrogen-bridged dimer in which the two halves of the molecule have different geometries. One half, $[Mn(H_3L)]^+$, exhibits a trigonal prismatic geometry, and has bond lengths typical of Mn^{II}–O and Mn^{II}–N bonds; thus it is an manganese(II) species. The other half of the molecule possesses shorter bond lengths and is an Mn^{IV} species with a pseudo-octahedral geometry. The two manganese centres are weakly antiferromagnetically coupled. In a related paper [76], absorption and CD spectroscopic studies, in addition to temperature-dependent paramagnetism studies, have been performed on this dimer. A third complex is produced by addition of a strong base such as Et_3N to a solution of the dimer. This results in further oxidation to give an Mn^{II} species $[MnL]^+$. Using the analogous unmethylated ligand, *N,N',N''*-tris(2-hydroxyethyl)-1,4,7-triazacyclononane, $L'H_3$, gave a monomeric complex, $[MnL'][ClO_4]$, the crystal structure of which has also been determined. The complex has pseudo-octahedral geometry and its cations are arranged in pairs with weak contacts between the alkoxy groups of one molecule and the methylene hydrogens of the other.

The interaction of manganese(II) with the macrocyclic ligands L^1 and L^2, **(15)**, each possessing an N_3O_2-donor set, has been investigated [77]. The X-ray crystal structure of the endomacrocyclic complex, $[MnL^1Br(EtOH)][ClO_4]$, has been reported. The manganese atom is seven-coordinate, with a distorted pentagonal bipyramidal environment. The macrocyclic donor atoms occupy the equatorial plane while the axial sites are filled by a bromide anion and an ethanol molecule. The stability constants for this complex have been determined in 95% methanol. Conductometric titration of the 1:1 complex with chloride indicated the formation of a 2:1 complex presumably through bridging of a chloride ion.

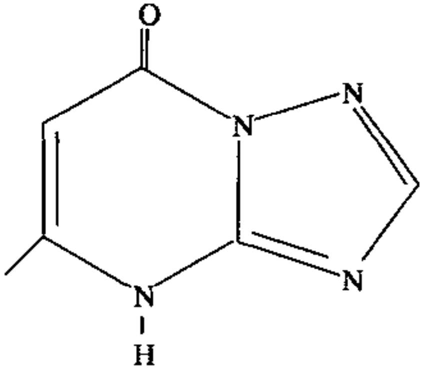


L^1 n = 2
L^2 n = 3

(15)

A series of tetranuclear heteronuclear complex ions with the general formula $[M\{(OH)_2CrA_4\}_3]^{5+}$ and $[M\{(OH)_2CoA_4\}_3]^{5+}$, where M is a divalent metal ion, and A_4 is a single tetradentate amino ligand, two bidentate amines, or four monodentate amines, have been synthesized and characterized [78]. The magnetic properties of these complexes have been studied. General energy diagrams illustrating relationships between energy, spin and degeneracy for tetranuclear systems are given. In all cases irrespective of S_1 and the sign of *J* the ground state has a higher spin than the nearest excited states.

The synthesis, spectroscopic and magnetic properties of a series of polynuclear metal coordination compounds of the general formula $MX_2(mtpH)_2$, where mtpH = 5-methyl[1,2,4]triazolo[1,5-*a*]pyrimidin-7-ol), **(16)** and X = Cl, Br, has been described [79]. IR spectroscopy and X-ray powder diffraction patterns for $MnBr_2(mtpH)_2$ indicate the possibility of a five-coordinate structure in which both nitrogen and oxygen atoms of mtpH interact with the manganese centre and are involved in hydrogen bonding.



(16)

The X-ray crystal structure of $[Mn_2(\mu\text{-}LL)_4(NCS)_2](NCS)_2$ [LL = $Ph_2P(O)(CH_2)P(O)Ph_2$], a cage containing four chains linking two pentacoordinate manganese(II) atoms and containing 16-membered rings has been reported [80]. Its structure is highly symmetrical and has a central mirror plane. It consists of two five-coordinate manganese centres bridged by four LL ligands with the fifth coordination site on each manganese atom occupied by an isothiocyanate group; the two remaining isothiocyanate counter-ions are disordered in the crystal lattice. Magnetic susceptibility measurements show that there is no interaction between the manganese atoms. Reaction with SO_2 has been studied, with a total of five moles absorbed per mole of complex; results of IR spectroscopy suggest that the SO_2 molecule is not strongly bound but is simply sitting inside the cage-like structure.

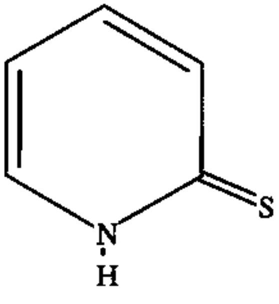
The X-ray crystal structure of $[Mn(thiamine)Cl_2(H_2O)]_2[thiamine]_2Cl_4.2H_2O$, the first example of a metal ion bridging two thiamine molecules, has been reported [81]. The compound which could be a possible model for the metal-bridged enzyme-coenzyme complex in thiamine catalysis, consists of a cyclic dimer of a complex cation with two thiamine molecules bridged by two Mn(II) ions across a crystallographic centre of symmetry. Each manganese atom is coordinated by two chloride atoms, a water molecule, a nitrogen atom of the pyrimidine from a thiamine and an oxygen atom from the hydroxyethyl side chain of another thiamine. Two free-base thiamine molecules, related by a centre of symmetry in the unit cell, form a base-pair through hydrogen bonds.

The use of different nitrogen-containing bases to influence aggregation in manganese complexes has been demonstrated recently [82]. The quantitative reaction of manganese powder with trifluoroacetic acid gave $Mn(O_2CF_3)_2$. Recrystallization from pyridine gave the mononuclear complex $[Mn(O_2CF_3)_2(py)_4]$ in which the manganese atom is in an octahedral environment and the trifluoroacetate ligands occupy axial positions. The use of benzonitrile, (benz), gave rise to the trinuclear complex $[Mn_3(O_2CF_3)_6(benz)_6]$, in which the three manganese atoms possess octahedral environments; the six trifluoroacetate ligands are bridging and the benz ligands show terminal ligation.

3.4.3 Complexes with sulfur donor ligands

The thermal behaviour of a complex of manganese(II) with 1-hydroxypryridine-2-thione has been studied using TG and DSC methods [83]. The intermediate and end-products from the decomposition in air have been investigated by X-ray powder diffractometry and IR spectroscopy.

The formation of manganese(II) complexes with monodentate sulfur donor ligands has recently been demonstrated [84]. The reaction of manganese(II) chloride with 2(1*H*)-pyridinethione, HL, (17), in ethanol gave a pale yellow solution which, upon concentration, yielded pale yellow crystals of composition $\{MnCl_2(HL)_4\}$. IR spectroscopy for this complex exhibited NH absorptions at 3172 cm^{-1} and C=S absorptions at 1140 cm^{-1}; FAB MS showed peaks at *m/z* 569 and 418 a.m.u. The complex is paramagnetic with a magnetic moment $\mu_{eff} = 5.97$ BM. The crystal structure shows the manganese atom in an octahedral environment with the two chloride ligands occupying axial sites and the four thione ligands are *S*-bonded to the manganese in equatorial positions.



(17)

The synthesis and characterization of the first well-characterized neutral homoleptic thiolate complex of Mn has recently been documented [85]. Treatment of $[Mn\{N(SiMe_3)_2\}_2]$ with two equivalents of HSAr, Ar = 2,4,6-^{t}Bu$_3$C$_6$H$_2$, gave the complex [Mn(SAr)$_2$]$_2$, an isomorphous, well separated dimer with a crystallographically imposed inversion centre. The [Mn$_2$S$_2$] unit is planar, with planar or nearly planar, coordination about the metal centre; the sulfur atoms of the thiolato bridges are pyramidal. The angles about the metal centre are very irregular; the Mn·····Mn separation is 3.554 Å. The M-S terminal bonds (2.317(3) Å) are shorter than the Mn-S bridging bonds (2.440(3), 2.446(3) Å). In addition, this is the first three-coordinate open-shell transition metal thiolate to be strucutrally characterized. The low-coordination of the metal atoms and the low degree of association are due to the steric crowding by the bulky aryl groups. Preliminary magnetic data indicate the presence of two high-spin, antiferromagnetically coupled metal centres.

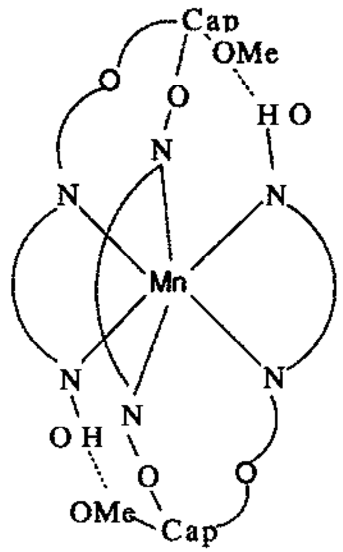
The synthesis and characterization of manganese(II) complexes of *N*-phenyl-*N*'-(6-substituted)benzothiazoylthiocarbamides have been described [86]. These complexes are thought to be distorted octahedral ones containing M-N and M-S binding sites.

A novel polynuclear manganese(II) complex, [Mn(L)Cl(CH$_3$OH)]$_n$ has been isolated using a thiolic ligand L = 2-[2-(pyridyl)ethylamino]ethanethiol [87]. The X-ray crystal structure reveals a complex that may best be described as a polynuclear helical chain. In essence, the complex consists of a mononuclear [Mn(L)Cl(CH$_3$OH)] unit. The thiolic ligand forms a meridional chelate with thiolate sulfur, amino nitrogen and pyridyl nitrogen atoms coordinated to the manganese atom. The manganese atom is further coordinated by the methanol oxygen atom and chloride ion. In addition, a thiolate sulfur atom of a neighbouring mononuclear unit approaches the manganese atom (Mn-S = 2.642(3), Mn-Mn 4.669(2) Å) forming a distorted octahedron; thus, mononuclear units are linked in a helical chain parallel to the *c* axis throughout the crystal.

3.4.4 *Complexes with nitrogen donor ligands*

Stability constants for the complexation of 5-(4'-amino-2'-azabutane)-5-methyl-3,7-diazanonane-1,9-diamine with metal(II) ions including Mn(II) have been determined [88]. The complexes formed are strong as evidenced by their stability constants and this has been ascribed to the almost ideal "cage-like" geometry of the complexes.

The synthesis and characterization of an unusual manganese(II) dioxime complex, Mn^{II}(CDO)(CDOH)$_2$(BPh(OCH$_3$))$_2$, (**18**), (CDOH$_2$ = 1,2-cyclohexanedione dioxime) having a pseudo-clathrochelate structure has been reported [89]. The manganese atom is six-coordinate in a trigonal environment and the structure is unusual in the fact that the complex is only partially capped at each end. Only one of the three CDO ligands is covalently bonded to both boron atoms in the two caps while the two remaining ones are directly involved in only one of the two caps. Each boron atom forms covalent bonds with only two of the three proximate dioxime oxygens. The third "free" hydroxyl is intramolecularly hydrogen bonded to a methoxyl substituent of the tetrahedral boron cap. The average Mn-N distance is 2.285 (3) Å.

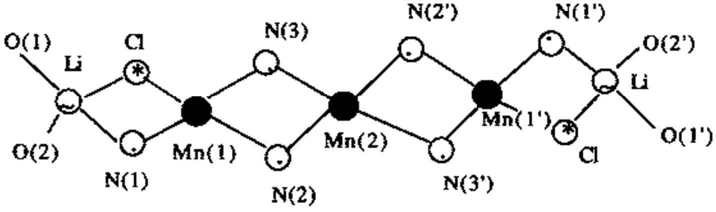


(18)

The preparation and characterization of a tris-manganese(II) complex with 2-pyridylcarbaldehyde-*N,N*-dimethylhydrazone (pch) has been reported [90]. The ligand was found to be bidentate, binding through the pyridine and azomethyne nitrogen atoms. The manganese atom is in a distorted octahedral geometry.

The preparation and spectroscopic properties of a manganese complex with hemiporphyrazine, namely 5,26:13,18-diimino-7,11:20,24-dinitrilodibenzo[*c,n*]-1,6,12,17-tetraazacyclodocosine, has been described [91]. This complex is square planar and ESCA spectral data indicate the presence of two types of nitrogen atoms in the metal-free macrocycle which become chemically equivalent upon complexation.

The reaction of $MnCl_2$ with $LiNR_2$, (R = Me, Et, ^iPr), resulted in the formation of the corresponding dialkylamido complexes [92]. The compounds $[Mn_3(\mu\text{-}NEt_2)_6(\mu\text{-}Cl)_2\{Li(thf)_2\}_2]$, **(19)**, $[Mn_2(\mu\text{-}N^iPr_2)_2(N^iPr_2)_2]$, and $[Mn_2(NMe_2)_4(LiCl)]$, were isolated. The molecular and crystal structures of **(19)** and $[Mn_2(\mu\text{-}N^iPr_2)_2(N^iPr_2)_2]$ were determined. Crystallization of $[Mn_2(NMe_2)_4(LiCl)]$ was not possible owing to its low solubility in common organic solvents and the presence of manganese-bonded dimethylamido groups was established by IR spectroscopy. Compound **(19)** consists of a trinuclear core $Mn_3(NEt_2)_6Cl_2$, which results from edge sharing by three tetrahedra through four bridging diethyl-amido groups. In addition, two bridging diethylamido groups and two bridging chloride ions coordinate two manganese atoms to terminal $Li(thf)_2$ moieties. Each manganese centre is in a distorted tetrahedral environment with N-Mn-N angles ranging from 91.5(2) to 129.5(3)°. The chain is completed by two tetrahedrally coordinated lithium atoms. The Mn(1)-Mn(2) distance is 2.917(2) Å, while the Mn-N distances are in the range 2.06(1) to 2.220(1) Å. $[Mn_2(\mu\text{-}N^iPr_2)_2(N^iPr_2)_2]$ is a dimer with a nearly planar arrangement of the Mn_2N_4 backbone, with virtual D_{2h} molecular symmetry. The manganese atoms, related through a crystallographic inversion centre, possess two bridging and two terminal diisopropylamido groups. Each manganese atom possesses a distorted trigonal-planar geometry (angles are 96.2(2), 126.5(2), and 136.2(2)°, respectively) while the nitrogen atoms of the terminal N^iPr_2 groups have a regular trigonal-planar geometry(angles of 117.1(4), 130.2(6) and 112.6(7)°, respectively). Each bridging nitrogen atom has a highly distorted tetrahedral geometry (with angles of 109.7(5) C-N-C, 114.5(5) and 116.2(4) Mn-N-C, and 83.4(2)° Mn-N-Mn, respectively. The $Mn–N^iPr_2$ distances are similar to those of compound (**19**), $Mn–N_t$ =1.925(6) and $Mn–N_b$ = 2.140(5) and 2.138(5). The Mn–Mn distance is 2.844(1) Å; this distance and that in (**19**) are indicative of a direct metal-metal interaction. The reactivity of all three compounds with carbon monoxide and carbon dioxide was studied and is discussed.



(19)

The reaction of $Mn\{N(SiMe_3)_2\}_2$ with dimesitylphosphane, $HPMes_2$, or dimesitylarsane, $HAsMes_2$, (Mes = 2,4,6-$Me_3C_6H_2$), have been investigated [93]. For those reactions involving 1 or 2 equiv. of $HPMes_2$, a dimer $\{Mn\{N(SiMe_3)_2\}(\mu\text{-}PMes_2)\}_2$, featuring a three-coordinate manganese atom with terminal amide and bridging phosphide groups, was obtained. In those reactions where 1 or 2 equiv. of $HAsMes_2$ was used, the dimer $\{Mn\{N(SiMe_3)_2\}(\mu\text{-}AsMes_2)\}_2$ was obtained. The crystal structures of both complexes have been described; average Mn-P and Mn-N distances of 2.524(3) and 1.973 (5) Å respectively, are noted in the former. The average Mn-As and Mn-N distances are 2.610(2) and 1.960(8) Å in the latter. The results of magnetic studies and NMR spectroscopy are presented.

The results of efforts to synthesize low-coordinate metal complexes using sterically demanding bis-(amido) ligands have been described [94]. The reaction of $Me_2Si(NHMes)_2$, with $Mn\{N(SiMe_3)_2\}_2$ in the presence of $LiN(SiMe_3)_2$ gave $[Li(Mn\{NMes\}_2SiMe_2)_2N(SiMe_3)_2]$ which features a dimeric manganese salt of the dianion of $Me_2Si(NHMes)_2$ and a Li^+ ion sandwiched between two mesityl rings. The Mn·····Mn separation is 2.848(3) Å and both manganese atoms are three-coordinate. The use of the bulky amine $Dipp(H)NCH_2CH_2N(H)Dipp$, (where Dipp = 2,6-$^iPr_2C_6H_3$), gave a monomeric manganese(II) amide,

$Mn[N(Dipp)CH_2CH_2N(H)Dipp]_2$, consisting of a four-coordinate manganese atom, the angles about which indicate planar rather than a tetrahedral geometry.

The stability of Mn(II)/Mn(III) in azide medium and its reaction with Co(II)/Co(III) has been investigated [95]. Co(III)/Co(II) azide complexes have been used as a quantitative method for the determination of S(IV) oxides in rain water. The autoxidation of Co(II) to Co(III) was found to be accelerated by the presence of Mn(II). The interaction of Mn(II)/Mn(III) with Co(II)/Co(III) according to the overall reaction:

$$\mathrm{Co(III)} + \mathrm{Mn(II)} \longrightarrow \mathrm{Co(II)} + \mathrm{Mn(III)} \qquad \text{equ. (1)}$$

was studied as a function of azide concentration. The equilibrium constant for this reaction increased from 0.0239 at 2 M azide concentration to 0.0289 at 0.1 M azide concentration. Kinetic measurements on the forward and reverse reactions gave an equilibrium constant of 0.0175 at 1 M azide concentration. In a related paper, a study of the sulfite-induced autooxidation of manganese(II) in aqueous medium as a function of the Mn(II), Mn(III), S(IV) and O_2 concentrations has been documented [96]. The data reported clearly demonstrate that this reaction is autocatalysed by manganese(III). The use of azide as a ligand promotes the stabilization of reactive intermediates and the elucidation of the reaction mechanism. The concentrations of O_2, Mn(II) and S(IV) determine whether oxidation of Mn(II) to Mn(III) alone, or, reduction of Mn(III) to Mn(II), or both processes occur in one or two redox cycles.

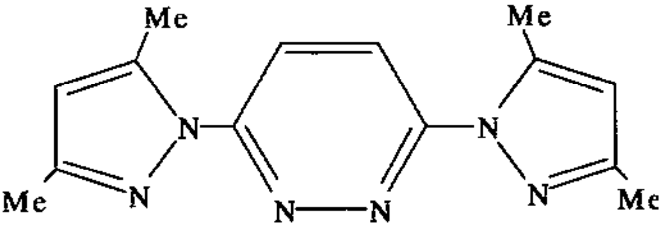
3.5 MANGANESE(I)

3.5.1 Complexes with oxygen donor ligands

The results of an electrochemical and spectroelectrochemical study on $[Mn(CO)_3(DBCat)]^-$, where DBCat = 3,5-Di-*tert*-butylcatecholate, have been reported [97]. This complex was found to undergo a metal-localized one-electron reduction and two successive one-electron oxidations that are ligand localized. All redox steps were found to be electrochemically reversible or quasi-reversible. The oxidations were followed by rapid coordination of a sixth ligand, i.e. THF, PPh_3, or CO in CO-saturated CH_2Cl_2 solution. In argon -saturated CH_2Cl_2, a CO ligand disproportionation of the oxidation products takes place. The existence of a four-membered redox series was established. EPR, IR and UV-VIS spectroscopies were used to study the various species.

3.5.2 Complexes with nitrogen donor ligands

Treatment of $MnBr(CO)_5$ with 3,6-bis(3,5-dimethylpyrazol-1-yl)pyridazine, L, **(20)** in refluxing tetrahydrofuran or toluene gave orange, air stable crystals of $[MnBr(CO)_3L]$ [98]. Results of infrared and ^1H NMR spectroscopy indicated that the tetradentate heterocycle acts as a monochelating ligand giving rise to a mononuclear complex.



(20)

The reaction of $[\mathrm{Mn(CN)(CO)_2L(L\text{-}L)}]$ with $[\mathrm{MnBr(CO)_2L'(L'\text{-}L')}]$ in the presence of $\mathrm{Tl[PF_6]}$ gave $[\mathrm{(L\text{-}L)L(OC)_2Mn(\mu\text{-}CN)Mn(CO)_2L(L\text{-}L)}][\mathrm{PF_6}]$, ($\mathrm{L = L' = P(OPh)_3}$, and L-L = L'- L' = dppm) which may have *trans,trans*, *cis,trans*, *trans,cis*, or *cis,cis* geometry depending on the structures of the mononuclear precursors [99]. Cyclic voltammetry and IR spectroscopic studies have been performed on these complexes and details of the oxidative isomerisation process provides insight into the intermetallic interactions within the $\mathrm{Mn(\mu\text{-}CN)Mn}$ framework are reported.

3.5.3 Complexes with phosphorus donor ligands

The reaction of *trans*-$[\mathrm{Mn(CN)(CO)(dppm)_2}]$ with $[\mathrm{Fe\{P(OMe)_3\}(NO)}]_2(\eta\text{-}\ \mathrm{C_3H_4R})[\mathrm{PF_6}]$ (R = H, 1-Me, or 2-Me) in THF resulted in allylic alkylation of the cyanide ligand giving the allyl isocyanide complexes *trans*-$[\mathrm{Mn(CO)(CNCH_2CMe{=}CH_2)(dppm)_2}][\mathrm{PF_6}]$.thf and *trans*-$[\mathrm{Mn(CO)(CNCH_2CH{=}CHR)(dppm)_2}][\mathrm{PF_6}]$.thf (R = H or Me) [100]. An X-ray crystal structure for the former shows the manganese(I) atom possesses approximately octahedral coordination where the carbonyl and 2-methylallyl isocyanide ligands are mutually *trans* and the dppm ligands occupying the equatorial positions.

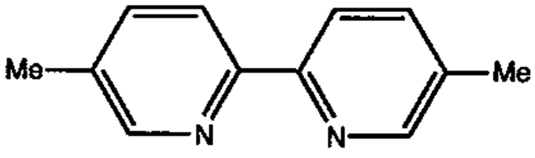
3.5.4 Complexes with boron donor ligands

The synthesis and X-ray crystal structure of a zwitter-ionic manganese sandwich complex $\{[\mathrm{Li^+\text{-}(THF)}][\mathrm{Li^+(TMEDA)}]_2\}\{$*commo*-$\mathrm{Mn_3[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]_4}\}^{3-}$ has been reported [101]. This complex has a "butterfly" structure due to the bonding of the terminal manganese atoms to two adjacent boron atoms of each of the central carborane ligands as well as to the planar pentagonal faces of the terminal carborane ligands. The Mn(2)-Mn(1)-Mn(2a) angle is 75.5(1)° and the Mn(2)-Mn(2a) distance is 3.283(2) Å indicating no bonding between the terminal manganese atoms. Magnetic measurements on a powdered sample were obtained and strongly support the assignment that this complex as a high-spin Mn(I)-Mn(III)-Mn(I) trimer with significant antiferromagnetic coupling between the central manganese atom and the two terminal manganese atoms.

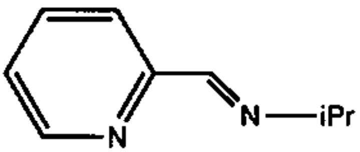
3.6 MANGANESE(0)

3.6.1 Complexes with nitrogen donor ligands

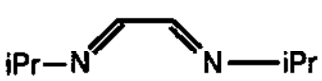
The photochemistry, over a range 133 and 298 K, of five metal-metal bonded carbonyls $(CO)_5MnMn(CO)_5(\alpha\text{-diimine})$ where α-diimine = 4,4'-dimethyl-2,2'bipyridine, (bpy'), pyridine-2-carbaldehyde *N*-isopropylimine, (^{i}Pr-pyca), 1,4-diisopropyl-1,4,diaza-1,3-butadiene, (^{i}Pr-DAB), 1,2-di-*p*-tolyl-1,4-diaza-1,3-butadiene. (pTol-DAB), 1,4-di-*p*-anisyl-1,4-diaza-1,3-butadiene, (pAn-DAB) (**21**), by irradiation into their metal to α-diimine charge-transfer band has been studied [102]. The radicals produced by homolysis of the metal-metal bond and release of CO couple to form various products. The crystal structure of $(CO)_4Mn(\sigma\text{-}N,\sigma\text{-}N',\eta^2\text{-}CN\text{-}^i\text{Pr-pyca})Mn(CO)_3$ has been obtained and shows both Mn atoms to be in a distorted octahedral enviromment with an Mn-Mn distance of 2.758 Å. The mechanistic aspects of these reactions are discussed.



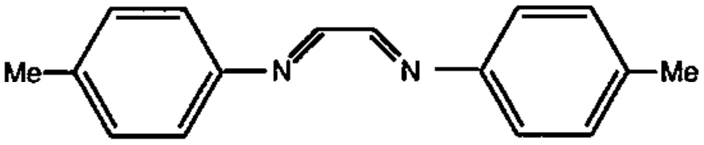
bpy'



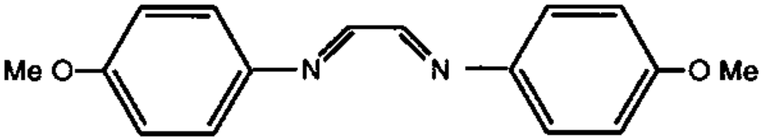
^{i}Pr-pyca



^{i}Pr-DAB



pTol-DAB



pAn-DAB

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