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Manganese 1994

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Contents

1. Introduction

This review illustrates the progress in manganese coordination chemistry for 1994. Its underlying focus is on coordination chemistry with meagre attention to organometallic complexes. It is based on a literature search of volumes 120-122 of *Chemical Abstracts* in addition to a separate search of major inorganic chemistry journals. A review concerning the coordination chemistry of Mn(II)/Mn(III) complexes with the ligand 2,2′-bipyridine with special emphasis on redox and structural transformations of the μ-oxo bridged dimeric unit in different oxidation states has appeared [1].

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2. Manganese(VII)

Mononuclear *tert*-butylimido compounds of Mn(VII) and Mn(VI) have recently been synthesized [2]. The syntheses of $Mn(NR)_3Cl$, which have been obtained as air-stable green crystals, were achieved by the reaction of Mn(III) chloride in acetonitrile with $NHR(SiMe_3)$, $R = {}^tBu$, CMe_2CH_2Me. The chlorine atom in the title compound has been substituted by Br, OC(O)R ($R = Me$ or CF_3), OC_6X_5 ($X = F$ or Cl), $OCH(CF_3)_2$, SC_6F_5, C_6F_5 or NH^tBu by use of $SiMe_3Br$ and silver, thallium and lithium salts of other reagents. The mechanism of formation of the compounds is discussed and a mechanism which accounts for the instability of compounds possessing an X-group with β-H atoms. It was found that β-H transfer to an N^tBu group gives the Mn(V) dimer $[Mn(N^tBu)_2(NH^tBu)]_2$ which occurs with the formation of ketones from alkoxides while for alkyls decomposition appears to involve homolysis of the Mn-C bond and a radical pathway. The crystal structures for the compounds $Mn(N^tBu)_3X$, $X = OC(O)Me$, OC_6F_5, SC_6F_5, $[Mn(N^tBu)_2(NH_2^tBu)]Y$, $Y = CF_3SO_3$ or PF_3 and $[Li(dme)]_2[Mn(N^tBu)_4]$ have been determined. For all these compounds the manganese centre has a distorted tetrahedral geometry; in the first three Mn-N(imido) bond lengths are 1.664(3)-1.673(9) Å while Mn-X distances are 1.91(3), 1.896(2) and 2.289(1) Å indicative of single bonds. For the cationic species, the Mn-N(imido) distances are in the range 1.531(8)-1.655(8) Å.

3. Manganese(V)

The photo-oxidation of $[Mn(\eta^5\text{-}C_5H_5)(CO)_3]$ in low temperature matrices containing 25% oxygen has led to the formation of an oxide $[Mn(\eta^5\text{-}C_5H_5)O_2]$ where the Mn atom is in an unusual oxidation state of V [3]. The $^{16}O\text{-}^{18}O$ isotopic shift of $\nu_{asym}(MnO_2)$ gives an upper limit for the O-Mn-O bond angle in the range 110-120°.

4. Manganese(IV)

4.1. Complexes with oxygen donor ligands

The synthesis and X-ray structure of $[Mn_8Fe_4O_{12}(O_2CMe)_{16}(H_2O)_4] \cdot 2MeCO_2H \cdot 4H_2O$ have been described [4]. The structure comprises a central $[Mn_4^{IV}O_4]^{8+}$ cubane core held within a non-planar ring of four Mn^{III} and four Fe^{III} ions by eight $\mu_3\text{-}O^{2-}$ ions with the Mn^{III} and Fe^{III} ions in alternating positions. The replacement of four Mn^{III} ions in the isostructural $[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4] \cdot 2MeCO_2H \cdot 4H_2O$ by four Fe^{III} ions causes a change in the spin of the ground state of the complex from $S_T = 10$ for $Mn_4^{IV}Mn_8^{III}$ to $S_T = 2$ for $Mn_4^{IV}Mn_4^{III}Fe_4^{III}$ and its origin is discussed.

The tetranuclear species $[Mn_4^{IV}O_6(bpy)_6]^{4+}(ClO_4) \cdot H_2O$ was isolated from an aqueous nitric acid solution of $Mn^{III}(bpy)Cl_3(H_2O)$ upon addition of $NaClO_4$ [5]. The cation has a non-rectilinear chain structure $[(bpy)_2Mn_a^{IV}O_2Mn_b^{IV}(bpy)\text{-}O_2Mn_c^{IV}(bpy)O_2Mn_d^{IV}(bpy)_2]^{4+}$ with metal-metal distances Mn_a-Mn_b = 2.746(5) Å, Mn_b-Mn_c = 2.760(5) Å, Mn_c-Mn_d = 2.735(4) Å. The complex was studied by electronic and EPR spectroscopy, cyclic voltammetry and magnetic susceptibility.

The structural and magnetic effects of successive protonations of oxo bridges in high-valent manganese dimers has been investigated [6]. The preparation and characterization of $[Mn^{IV}(salpn)]_2(\mu\text{-}O)(\mu\text{-}OH)(CF_3SO_3)_2$, the first bis-(hydroxo)-bridged Mn(IV) dimer has been achieved. This complex, along with $([Mn^{IV}(salpn)(\mu\text{-}O)]_2$ and $[Mn^{IV}(salpn)]_2(\mu\text{-}O)(\mu\text{-}OH)(CF_3SO_3)$ completes the series of Mn complexes isolated in three different protonation states of the bridges without a change in oxidation states of the Mn atom or a change in other ligands. The effects of oxo bridge protonation on the structure and magnetism of this series of complexes was studied. Each successive protonation of the bridge results in a 2200 cm^{-1} decrease in the energy of the lowest energy charge transfer transition, a lengthening of the Mn-Mn distance and a dramatic decrease in the antiferromagnetic coupling without a significant change in the manganese X-ray absorption energies. The EXAFS spectra show an increase in the Mn-Mn distance from 2.73 to 2.83 to 2.93 Å for successive protonations. Temperature-dependent magnetic susceptibility measurements show that antiferromagnetic coupling decreases from $J = -92$ cm^{-1} to -48 cm^{-1} upon the first protonation to -6 cm^{-1} upon the second protonation.

The first dimanganese(IV) compound to include simultaneously a bridging acetato ligand, a bis(μ-oxo) bridge and a molecule of water of crystallization has recently been synthesized [7]. Bipyridine (600 mg) was added to a solution of $Mn(CH_3COO)_2 \cdot 4H_2O$ (500 mg) in 20 ml of water and 3 ml of acetic acid. After dissolution of the ligand, a solution of ceric perchlorate (10 ml) was added. The resulting light brown solution was filtered and left aside for a week to obtain 280 mg of well-formed crystals of $[Mn_2(\mu\text{-}O)_2(\mu\text{-}OAc)(H_2O)_2(bpy)_2](ClO_4] \cdot H_2O$. It has been studied by optical and EPR spectroscopy. Analysis of the thermal variation of its magnetic susceptibility gives one of the weakest antiferromagnetic interactions $J = -43.7$ cm^{-1}, determined for a bis-(μ-oxo)-bridged Mn_2^{IV} species.

The oxidation of α,β-unsaturated alcohols with soluble Mn(IV) phosphate dissolved in 3M phosphoric acid has been studied [8]. Simple non-autocatalytic kinetics were observed with the reaction being first order with respect to Mn^{IV} and a rate constant of 970 M^{-1} s^{-1} for the reaction between Mn^{IV} and Mn^{II}.

4.2. Complexes with sulfur donor ligands

Two new thiotellurites $Cs_2Mn(TeS_3)_2$ and $Rb_2Mn(TeS_3)_2$ which feature a layered structure based on the pyramidal TeS_3^{2-} have been synthesized [9]. The X-ray powder diffraction data for $Cs_2Mn(TeS_3)_2$ indicate that $Mn(TeS_3)_2^{2-}$ are relatively flat and lie perpendicular to the c axis. The layers are separated by a bilayer of Cs^+ ions. Each Mn ion is octahedrally coordinated with the MnS_6 octahedra sharing all the corners with neighbouring TeS_3^{2-} pyramids and vice versa. The Mn-S distances are equivalent 2.624(3) Å and S-Mn-S angles indicate a distorted coordination sphere of Mn from an ideal octahedron to elongated trigonal antiprism.

5. Manganese(III)

5.1. Complexes with halide ligands

Single crystals of the fluoride hydrate Mn_3F_8 were prepared and characterized by X-ray methods [10]. The structure contains Jahn-Teller distorted $[Mn(H_2O)_2F_4]^-$ anions in addition to crystal water molecules. A hydrogen bonding network between anions and cations, i.e. $[Mn(H_2O)_6]^{2+}$, was observed.

5.2. Complexes with oxygen donor ligands

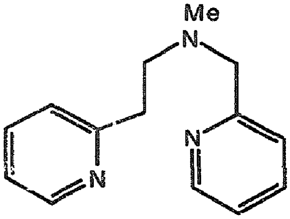
Several examples of the highly anisotropic EPR spectra from mixed-valence dimanganese complexes and the catalase enzyme from *Thermus thermophilus* have been simulated using a non-linear least squares fitting procedure [11]. From these simulated spectra the intrinsic ^{55}Mn hyperfine tensor of each manganese ion has been obtained which enabled the oxidation state and electronic orbital configuration of Mn(III) to be assigned.

A topotactic ion-exchange reaction of $MnAsO_4 \cdot H_2O$ to give $LiMnAsO_4(OH)$ gave rise to a switch in magnetic properties [12]. The formation of $LiMnAsO_4(OH)$ results in the deprotonation of water molecules bridging adjacent Mn^{3+} cations. This increased negative charge on the hydroxide groups results in a switch of local Jahn-Teller modes which gives rise to a switch from antiferromagnetic to ferromagnetic order within infinite Mn-O-Mn chains in the framework, overall in both materials the order is antiferromagnetic.

The synthesis, characterization and novel redox properties of a new triply bridged dimanganese(III) complex with a $\{Mn_2^{III}(\mu-O)(\mu-O_2CCH_3)_2\}^{2+}$ core has been reported [13]. When glacial acetic acid was added to a medium conducive to the synthesis of $[Mn^{III}Mn^{IV}(\mu\text{-}O)_2(\mu\text{-}O_2CMe)(MeL)_2](ClO_4)_2 \cdot H_2O$, MeL = (**1**), the formation of a dimanganese(III) complex $[Mn_2^{III}(\mu-O)(\mu-O_2CCH_3)_2(MeL)_2]$-$(PF_6)_2 \cdot H_2O$ (**2**), was observed. The novel oxidative transformation of $\{Mn_2^{III}(\mu-O)(\mu-Ac)_2\}^{2+}$ to a lower potential species $\{Mn_2^{IV}(\mu-O)(\mu-Ac)_2\}^{2+}$ via electrochemically generated $\{Mn^{III}Mn^{IV}(\mu\text{-}O)(\mu\text{-}Ac)_2\}^{3+}$ is presented.

The complex formation and redox reactions of manganese ions with tungstaphosphates in solution has been investigated [14]. Alkaline hydrolysis of a mixture containing Mn(II) and $P_2W_{18}O_{62}^{2-}$ in the presence of oxygen led to the formation of a 2:17 complex between Mn(III) and the heteropolyanion with a 1:1 ratio. In the absence of oxygen, Mn(II) stabilizes in the form of a complex with $[P_2W_{17}O_{61}]^{10-}$.

A new method for the synthesis of manganese(III) acetate dihydrate from manganese(II) acetate tetrahydrate, lead(IV) oxide and acetic acid as solvent has been described [15]. In comparison to existing methods, increased purity and yields



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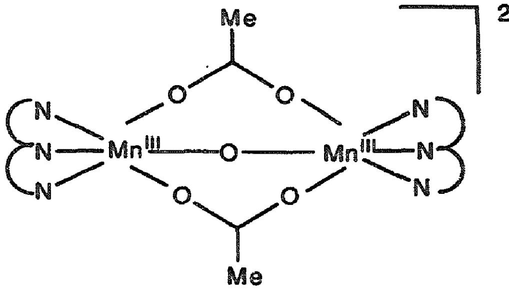


(2)

have been obtained and the starting materials are inexpensive and readily available. The complex has been characterized by melting point, elemental analysis and potentiometric titration.

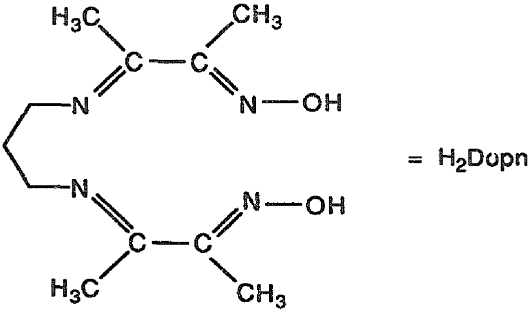
The application of electrospray mass spectrometry, ESMS, to highly oxidizing transition-metal oxo species including manganese was investigated [16]. The spectral data reported were obtained from solutions in acetonitrile but other solvents such as acetone and dichloromethane were found to work equally well. The mass spectrum of $KMnO_4$ displayed little or no fragmentation and showed an intense $[MnO_4]^-$ ion. The less abundant but highly solvated $[MnO_4(MeCN)]^-$ and $[MnO_4(MeCN)_2]^-$ as well as the dimeric $[MnO_4\text{-}K\text{-}MnO_4]^-$ were also observed.

The kinetics of the oxidation of pyridoxine by Mn(III) in aqueous acetic acid medium was investigated [17]. The reaction is first order with respect to Mn^{III}. The effects of varying concentrations of Mn^{III}, pyridoxine, added Mn^{II}, and various anions have been studied. A mechanism has been proposed.

Suitable procedures to covalently link Mn_x aggregates into aggregates-of-aggregates and polymers-of-aggregates under mild conditions have been successfully obtained recently [18]. The covalent linkage of $[Mn_4O_2(O_2CPh)_6(dbm)_2]$, dbm = dibenzoylmethane, to give the dimeric $[Mn_4O_2(O_2CPh)_6(dbm)_2(bpe)]_2 \cdot 2CH_2Cl_2 \cdot 2MeCN$, bpe = *trans*-1,2-bis(4-pyridyl)ethene was obtained. Its crystal structure has been determined and it reveals that the Mn_4 units are in a butterfly arrangement. When the starting complex was treated with 4,4′-bpy the complex $[Mn_4O_2(O_2CPh)_6(dbm)_2(4,4'\text{-bpy})]_n$ was obtained. Its structure reveals it to be a "staircase" or "zig-zag" polymer. Solid state magnetic studies are being carried out.

5.3. Complexes with oxygen and nitrogen donor ligands

A series of heterodinuclear $Cu^{II}M$ complexes where M = Cr(III), Mn(III), Fe(III), Co(II), Co(III), Ni(II) Cu(II) and Zn(II) containing the oximato dianion $Dopn^{2-}$ (3), as a bridging ligand and 1,4,7-trimethyl-1,4,7-triazacyclononane as one of two capping ligands has been synthesized by means of the $[Cu(DopnH)]^+$ cation as a ligand for the different ML^{n+} centres [19]. These complexes were characterized by IR, electronic, EPR spectroscopy and by temperature dependent magnetic susceptibility measurements.



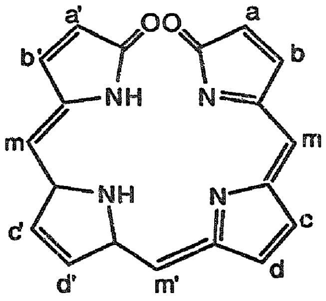
(3)

The impact of substitution in the bispicen ligand, (bispicen = *N,N'*-bis(2-pyridylmethyl)ethane-1,2-diamine), on the electrochemical and other properties of bis(μ-oxo)dimanganese(III,III), -(III,IV) and -(IV,IV) complexes has been investigated [20]. The synthesis and characterization and isolation of these complexes was accomplished using the following ligands, *N,N'*-bis(2-pyridylmethyl)-*N,N'*-dimethyl-1,2-ethanediamine(bispicMe$_2$en) and *N,N'*-bis(2-pyridylmethyl)-*N,N'*-dimethyl-(-)$_D$1,2-cyclohexanediamine(bispicMe$_2$(-)chxn). The X-ray structures of $[(\text{bispicenMe}_2\text{en})\text{Mn(O)}]_2(\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$, $[(\text{bispicenMe}_2\text{en})\text{Mn(O)}]_2(\text{ClO}_4)_2.5\text{H}_2\text{O}$ and $[(\text{bispicMe}_2(\text{-})\text{chxn})\text{MnO}_2\text{Mn}(\text{bispicMe}_2(\text{-})\text{chxn})](\text{ClO}_4)_3$ have been obtained.

The reductions of $[(\text{bpy})_2\text{Mn}^{\text{IV}}(\text{O})_2\text{Mn}^{\text{III}}(\text{bpy})_2]^{3+}$ with ascorbate, hydroquinone and bisulfite have been studied [21]. The complex was found to undergo rapid reductions by all three agents to 2Mn^{2+}(aq) in aqueous media buffered by bpy-bpyH$^+$ with net changes of 3 electrons occurring in each case. The ascorbate system involves a Mn$^{\text{III}}$Mn$^{\text{IV}}$-ascorbate complex. For the hydroquinone and HSO_3^- complex decay profiles suggest a multistep process in which intermediate Mn states and radicals derived from the reductants participate. The patterns are autocatalytic in nature with the active catalytic species appearing to be the $(\text{Mn}^{\text{III}})_2$ intermediate. Solvent kinetic isotope effects were studied and are close to 4.0 for ascorbate reduction and the initial step of the hydroquinone reduction but approach unity for the bisulfite reduction indicating proton transfer coupled to electron transfer for the organic reductants.

A detailed EPR spectroscopic analysis of the Mn(III)/Mn(IV) form of the *Lactobacillus plantarum* Mn catalase has been reported [22]. It reveals features relevant to the chemical nature of the dimer. The spectral simulation method employed calculated the hyperfine shifts by perturbation theory to third order on the basis of a direct numerical approach.

Coordination patterns for biliverdin-type ligands with manganese have been studied [23]. The bilindione ligand has up until now received little or no attention but due to the presence of two keto groups at opposite ends this tetrapyrrole ligand adopts a helical arrangement which minimizes contacts between its terminal keto groups. A monomeric [{(OEB)Mn^{III}(py)}] and dimeric $\{(OEB)Mn^{III}(py)\}_2$ complex of octaethylbilindione, OEB, (4) have been characterized by X-ray crystallography and spectroscopic techniques. The dimer comprises two helical (OEB)Mn units of like chirality joined by O-Mn bonds giving C_2 symmetry. Each Mn atom is five-coordinate and the magnetic susceptibility indicate high-spin ($S=2$) d^4 Mn^{III}. This dimer cleaves in pyridine solution generating a monomeric species, {(OEB)Mn^{III}(py)}. This complex also contains a five-coordinate Mn atom with coordination to four pyrrole nitrogen atoms of the bilindione ligand and to one pyridine ligand.



a-d' ethyl, m,m' = H; H_3OEB

(4)

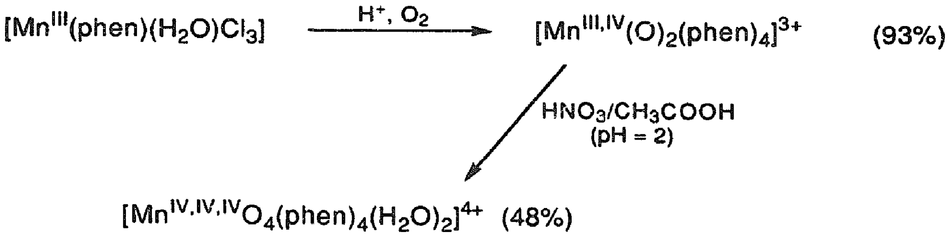
The cluster expansion of a high-valent oxomanganese dimer in aqueous solution has been studied [24]. The acidification of the dimer $[Mn_2^{III,IV}(O)_2(bpy)_4]^{3+}$ gave rise to an intermediate on a msec time scale which generated the product $[Mn_3^{IV}(O)_4(bpy)_4(H_2O)_2]^{4+}$ and Mn^{2+} on a considerably slower time scale. The kinetics of these changes were studied using stopped-flow UV-VIS spectrophotometry. The rate of formation of the intermediate was found to be independent of added Mn^{2+} instead showing a marked dependence on changes in the concentration of $[Mn_2^{III,IV}(O)_2(bpy)_4]^{3+}$, bpy or H^+. The kinetics suggest that the rate determining step involves the loss of a bpy ligand.

A communication has appeared detailing the synthesis of complexes containing the (μ-oxo)(μ-acetato)dimanganese(III/III) core [25]. Specifically, the complexes $\{[(bispicen)Mn]_2(\mu\text{-}O)(\mu\text{-}OAc)\}(ClO_2)_3$, where bispicen = *N*,*N'*-bis(2-pyridylmethyl)ethane-1,2-diamine and $\{[(bispicMe_2en)Mn]_2(\mu\text{-}O)(\mu\text{-}OAc)\}(ClO_2)_3$ where $bispicMe_2en$ = *N*,*N'*-bis(2-pyridylmethyl)-*N*,*N'*-dimethylethane-1,2-diamine were synthesized. In the former, the isomer isolated was the *cis*-α species, the Mn-Mn distance is 3.276(3) Å, the Mn-O-Mn bridging angle is 130.8(4)° and $Mn\text{-}O_{oxo}$ and $Mn\text{-}O_{acetato}$ bond lengths are 1.801(3) and 2.031(5) Å respectively. The Mn-N bond *trans* to the acetate group is longer than other Mn-N bonds. In the latter, the Mn-Mn distance is 3.292(14) Å, the Mn-O-Mn bridging angle is 133(3)° and $Mn\text{-}O_{oxo}$ and $Mn\text{-}O_{acetato}$ bond lengths of 1.79(2) and 1.90(3) Å; the axial

$Mn\text{-}N_{py}$ bond distances are 2.19(3) and 2.17(3) Å and equatorial $Mn\text{-}N_{amine}$ distances are 2.01(4) and 2.24(5) Å. These complexes were further characterized by electronic spectroscopy and magnetic measurements.

The ligand (2-pyridyl)bis(2-pyridylamino)methane was found to undergo metal-assisted deamination/oxidation in the presence of the oxophilic Mn^{III} and Fe^{III} ions forming novel mononuclear complexes but forms the expected bis-ligand complex with the Ni^{II} ion [26]. For the Mn case, the X-ray structure shows $[Mn(L)_2]^+$ cations and well-separated perchlorate anions, the Mn is coordinated via the pyridyl nitrogen and methanolato oxygen atoms of the ligand. The axial Mn-O distances of 1.856(3) Å are relatively short while the equatorial bond distances of 2.152(3) and 2.174(3) Å are long in comparison to those of other Mn^{III} complexes. The axial compression observed in this complex is unusual in that most other Mn^{III} complexes exhibit axial elongation. This complex exhibits a quasi-reversible one-electron oxidation and its magnetic moment is 4.95 μ_B.

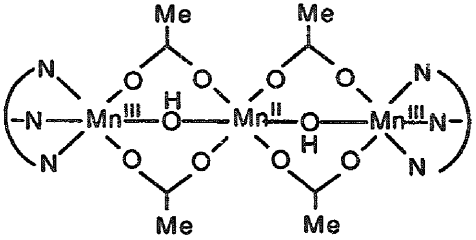
An improved synthesis for the complex $[Mn^{III}Mn^{IV}(O)_2(phen)_4](ClO_4)_3 \cdot 2CH_3COOH \cdot 2H_2O$ has been obtained [27]. Its crystal structure has also been obtained and in contrast to the previously published structure it shows crystallographically distinct Mn^{III} and Mn^{IV} ions typical of electron localized species. Conditions for the generation of the trimeric species $[Mn_3^{IV}O_4(phen)_4(H_2O)]^{4+}$ by the acidification of an aqueous solution of the former have been described (5).



(5)

A rare example of a linear trinuclear manganese complex possessing a (μ-hydroxo)bis(μ-carboxylato) bridging unit which can mediate a weak antiferromagnetic interaction between Mn(II) and Mn(III) ions has been discovered [28]. The complex formulated as $[Mn(HB(3,5\text{-}^iPr_2pz)_3)](OH)(OAc)_2Mn(OH)(OAc)_2[Mn(HB(3,5\text{-}^iPr_2pz)_3)] \cdot 3,5\text{-}^iPr_2pzH \cdot 3MeCN$, $HB(3,5\text{-}^iPr_2pz)_3)$ = hydridotris(3,5-diisopropyl-1-pyrazolyl)borate and $3,5\text{-}^iPr_2pzH$ = 3,5 diisopropyl borate (**6**), was subjected to X-ray crystallography. The oxygen atoms that bridge the two manganese atoms are identified as hydroxide like based on their distances (av. 2.01 Å), the average $Mn\text{-}C_{carbox}$. is 2.13 Å for Mn(2) while the distances are distinctly shorter for Mn(1) and Mn(3), 2.05 Å implying Mn(1) and Mn(3) are in the +3 state whereas Mn(2) is in the +2 state. Magnetic studies have been carried out.

In a related paper [29] a novel monomeric side-on peroxo complex which exhibits two isomeric forms depending on the temperature and solvent has been obtained. The complex $Mn(O_2)(3,5\text{-}^iPr_2H)(HB(3,5\text{-}^iPr_2pz)_3)$ has been characterized by X-ray



(6)

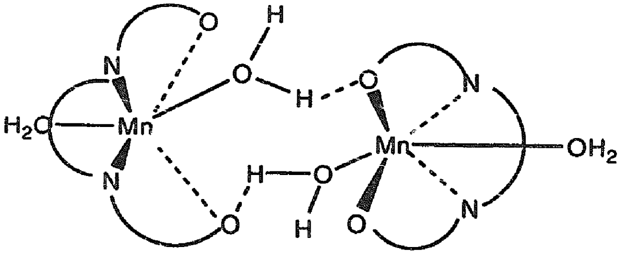
crystallography. It exhibits thermochromic behaviour e.g. a solution of this complex in diethyl ether or toluene changed its colour reversibly in the range from -78 to -20°C, the higher temperature resulting in a browner colour whereas it is a dark blue colour at -78°C. X-Ray crystallography establishes it as being a monomeric 6-coordinate side-on peroxo Mn(III) complex. The O-O distance in both isomers is 1.43 Å typical for a peroxide bound to a transition metal ion. The presence of hydrogen bonding in the blue form between a hydrogen atom of the pyrazole ligand and the peroxide which occurs at predominantly low temperatures ($<$-50°C) was seen in the crystal data.

The template reaction of salicylaldehyde and 2-[(3-aminopropyl)amino]ethanol yielded an Mn(III) complex of 1-[(2-hydroxylethyl)amino]-2-(salicylideneamino)-ethane ($H_2L_{6\text{-}5\text{-}5}$) [30]. An X-ray crystal structure of the complex [Mn($H_2L_{6\text{-}5\text{-}5}$)$_2$]Br shows the Mn atom to be in an octahedral environment with coordination to two phenolic oxygen atoms, two imine nitrogen atoms and two amine nitrogen atoms of the Schiff-base ligands. Both of the 2-hydroxylethyl groups of the ligands are uncoordinated and are *cis* to each other thereby forming hydrogen bonds with the bromide ion. The equatorial Mn-O distance is 1.895(5) Å while the Mn-N distances are 1.996(5), 2.114(6) and 2.027(5) Å. The axial Mn-O distance of 2.034(5) and the Mn-N(amine) of 2.341(6) Å are considerably longer than the in plane distances. The effective magnetic moment of 5.00 BM is close to the spin only value for a high spin d^4 system. The complex was characterized by electronic spectroscopy.

Water soluble Mn(III) and Mn(IV) complexes of tridentate ONO ligands have been synthesized [31]. Specifically, complexes of sulfonated azophenol and salicyaldimine ligands were isolated. The coordination sphere of the complexes is of the type $Mn(ONO)_2$ where the O and N atoms are of the phenolic and azo/azomethine type. They were characterized by cyclic voltammetry and EPR spectroscopy.

The synthesis, structural characterization and physico-chemical properties of a novel dimer-of-di(μ-oxo)manganese(III)manganese(IV)-dimers containing two coordinated water molecules has been described [32]. The complex [{Mn_2(tmdp)$(O)_2(H_2O)$}$_2$]$(CF_3SO_3)_4 \cdot 6H_2O$, Hdmtp = 1,5-bis[bis(2-pyridylmethyl)amino]-3-pentanol, comprises two di(μ-oxo)manganese(III)manganese(IV) dimers which are linked by two tmdp ligands and a hydrogen bonding network between the two coordinated water molecules and two alkoxo groups giving rise to a dimer-of-dimers possessing a bilayered structure with a dimer-dimer separation of 5.9 Å. ESR spectroscopic and magnetic susceptibility studies were carried out.

The synthesis and characterization of $[Mn(3,5,Cl\text{-salen})(H_2O)_2]_2(ClO_4)_2$, 3,5,Cl-salen = *N*,*N'*-3,5-dichloro(salicylidene)-1,2-diaminoethane, which may be a possible model for Photosystem II has been achieved [33]. The complex was obtained by reacting 0.55 mmol of the disodium salt of the ligand with and equimolar amount of the Mn(II) perchlorate in ethanol. After stirring for 5 days in the presence of air, the solution was filtered and the filtrate evaporated to dryness. Slow evaporation of an isopropyl alcohol solution of the solid gave crystals suitable for crystallography. The complex displays a planar tetradentate Schiff base tightly bound to the Mn(III) centre by Mn-N (1.963(4) and 1.973(4) Å) and Mn-O (1.889(3) and 1.871(3) Å) bonds. An array of hydrogen bonding links the two Mn centres. This H bonding in combination with bulky ligands gives rise to a coordination cleft in which the bridging aqua groups are located (7). An aqueous solution of this compound in the presence of *p*-benzoquinone evolves dioxygen upon irradiation with a tungsten bulb. It is believed that the coordination cleft enables the photo-excited *p*-benzoquinone to enter the cleft and abstract a hydrogen radical.

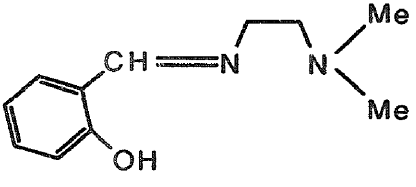


(7)

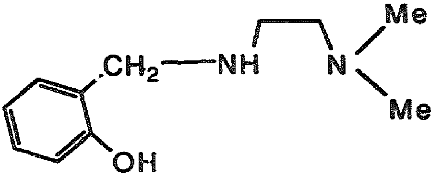
The compound $[Mn(salphen)(EtOH)_2](BPh_4)$ has been prepared [34]. It consists of a planar tetradentate Schiff base tightly bound to an Mn^{III} atom with Mn-N bonds of 1.97(1) and 1.99(2) Å, two Mn-O bonds of 1.85(1) Å and two capping ethanol groups in a distorted octahedral arrangement. Pairs of molecules are linked across inversion centres by hydrogen bonds from ethanol to phenoxy oxygen atoms and π-bond formation due to the overlap of phenyl rings is observed. This compound represents a further example of a photosynthetic model compound linked by hydrogen and π bonds.

The dinuclear Mn(III/IV) complex $[Mn_2O_2(dpa)_2]^+$ Hdpa = *N*, N-bis(2-pyridylmethyl)glycine was found to exhibit much higher activity for decomposition of hydrogen peroxide when compared to analogous compounds with tris(2-pyridylmethyl)amine or 1,4,8,11-tetraazacyclotetradecane [35]. Dioxygen evolution was measured in the presence of pyridinium bromide as a proton donor and showed a decrease in rate compared to evolution in the absence of a proton donor. It is thought that the oxygen atom of the carbonyl group in the dpa ligand may act as a proton acceptor which may explain why this complex has a greater activity compared to analogous compounds.

Manganese(III) complexes containing the ligands (**8**) and (**9**) have been synthesized and characterized [36]. In each complex the Mn atom is in a distorted octahedral environment consistent with a d^4 ion exhibiting a strong Jahn-Teller distortion. Solid state magnetic susceptibility measurements and cyclic voltammetric studies were also carried out.

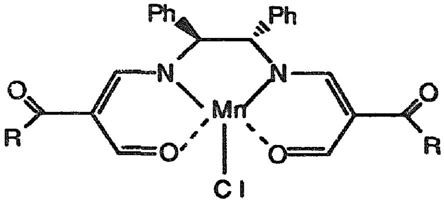


(8)



(9)

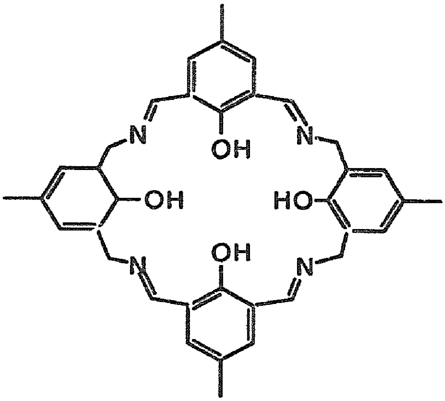
Several Mn(III) complexes containing an optically active *N*, *N'*-ethylenebis-β-ketoimine ligand have been prepared and a crystal structure for one of these complexes was obtained (**10**) [37]. Their catalytic ability in the enantioselective epoxidation of non-functionalized olefins has been tested. Dihydronapthalene derivatives were converted into the corresponding optically active epoxides with good to high enantioselectivities.



(10)

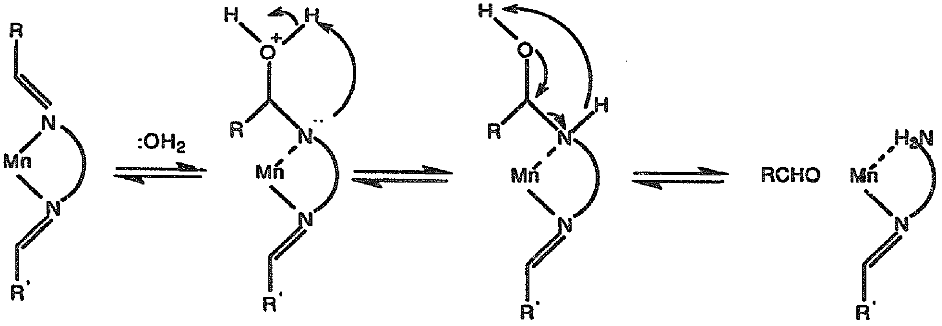
A tetranucleating macrocycle and its dimanganese derivative have recently been synthesized and characterized [38]. The condensation of 2,6-bis(aminomethyl)-4-methylphenol with 2,6-diformyl-4-methylphenol resulted in the tetra-Schiff base containing two of each component as the dihydrochloride salt $H_4L \cdot 2HCl$ (**11**). X-Ray crystallography indicates that its salient feature is the presence of dialdehyde-derived oxygens as phenoxide anions despite the fact that there is an overall dipositive charge from protonation. Condensation of the dialdehyde and diamine in the presence of Mn^{2+} and dioxygen gave crystals of $[Mn_2(H_2L)(\mu\text{-}O_2CMe)(\mu\text{-}OH)(MeOH)_2][ClO_4]_2 \cdot 2MeOH$ which were analysed by X-ray crystallography. The two manganese atoms have tetragonally distorted octahedral environments. Magnetic studies were carried out.

The rearrangement of an unsymmetrical ligand H_2L^1 which was obtained by the condensation of 8-amino-4-methyl-5-azaoct-3-en-2-one with 3-ethoxysalicylaldehyde



H_4L (11)

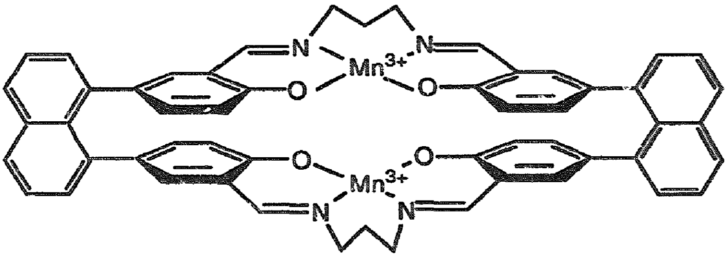
in the presence of Mn(III) to form a symmetrical ligand *N,N′*-bis(3-ethoxysalicylidene)-propane-1,3 diamine H_2L^2 has been reported [39]. The Mn(III) complexes of both symmetrical and unsymmetrical ligands have been obtained and their characterization by elemental analysis, IR spectroscopy, magnetic susceptibility, FAB MS has been achieved. In addition, the X-ray crystal structure for the complex containing the unsymmetrical ligand had provided further insight into the mechanism by which Schiff bases rearrange about the Mn atom. A mechanism has been proposed in which rearrangement occurs via a series of reversible hydrolysis steps (**12**) and most combinations of the rearrangement process have now been characterized.



(12)

The origin of the high reactivity of a peroxide adduct of [Mn(salen)Cl] towards organic acid anhydrides has been studied [40]. In an electrochemical study, the CVs of systems containing the Mn(III) complex, dioxygen and an organic base have been obtained. In addition, MNDO/PM3 calculations were carried out on model systems. It is thought that the peroxide adduct of the Mn(III) Schiff base may act as an electrophile towards the organic acid anhydride. The high reactivity of the latter was ascribed electron distribution in its frontier orbitals.

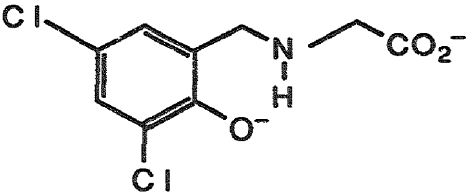
The synthesis of the first example of a custom-designed bis-manganese water splitting complex has been achieved [41]. In this complex (**13**), the two manganese centres are held in close proximity by a single macrocyclic ligand. It was prepared through the use of a highly efficient Mn(II) assisted condensation/macrocyclization. When the complex was suspended in water in the presence of *p*-benzoquinone at 25°C and irradiated with a 300 W tungsten lamp for 18 hours oxygen evolution was detected.



(13)

A rare pseudo-Jahn-Teller compression, the first of its kind, for a mononuclear Mn(III) complex containing polydentate ligands has recently been demonstrated [42]. Treatment of the deprotonated ligand, L^{2-}, (**14**), (H_2L = *N*-(3,5-dichloro-2-hydroxybenzyl)glycine) with manganese(II) in a (2:1) molar ratio under aerobic conditions produced a purple-tinged dark brown complex $[M^{III}L_2]^-$. The complex was characterized by IR, mass spectrometry and X-ray crystallography. The effective magnetic moment was found to be 4.87 μ_B at 300 K. The crystal structure reveals that the Mn atom is coordinated to two tridentate ligands in a distorted octahedral arrangement with the donor atoms of each ligand being facially oriented. Notable is the axial compression of the rhombically distorted octahedron. The Mn-O axial bond distance of 1.880(4) Å is significantly shorter than the equatorial Mn-O and Mn-N bond distances of 2.137(4) and 2.118(4) Å.

Exploration of alternative preparative methods for the synthesis of Mn(III) aqua



(14)

complexes has led to the facile synthesis of two new complexes [43]. Oxidation of Mn(II) by nitric acid in the presence of phen resulted in [Mn(phen)(OH_2)Cl_3] while the reaction of MnO(OH) with acac in glacial acetic acid yielded [Mn(acac)$_2$(OH_2)$_2$]$ClO_4 \cdot 2H_2O$ in crystalline form. X-Ray crystallography has been carried out and both complexes exhibit distortions in the axial bonds of the octahedron.

5.4. *Complexes with sulfur donor ligands*

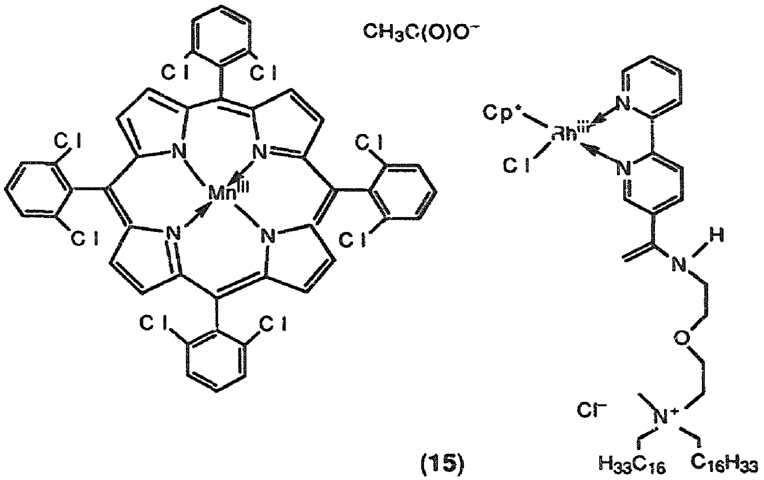
Mass spectral studies on dithiocarbamato metal complexes derived from heterocyclic secondary amines having the MS_6 and MS_4 chromophores have been carried out [44]. Complexes of Mn(III), Fe(III), and Co(III) exhibited similar fragmentation behaviour. For all cases the base peak was found to be $[ML_2]^+$

5.5. *Complexes with nitrogen donor ligands*

The reduction of the manganese porphyrins [MnTCPP] and [MnTMPyP] by dithionate and Co(II) sepulchrate were studied in order to provide evidence for electron transfer via the periphery of a porphyrin ring [45]. The reduction of [MnTMPyP] by both reducing agents was found to be strongly dependent on the ionic strength of the medium and reduction with the cobalt agent was catalysed by the chloride ion. Kinetic data are consistent with attack of the reducing agent at the periphery of the ring. In the case of [MnTCPP], reduction by cobalt is biphasic and is indicative of two parallel pathways, namely, attack of the $[Co(sep)]^{2+}$ at the periphery of the ring and the axial waters. The kinetic data for the reaction with dithionate are consistent with rate-determining formation of a radical anion followed by rapid intramolecular reduction of Mn(III) to Mn(II).

A dimetallic membrane-bound cytochrome P_{450} mimic catalysing the epoxidation of alkenes with good turnover numbers (5-360 nmole epoxide product/nmole P_{450}/minute) has been developed [46]. A manganese porphyrin and a rhodium complex (**15**), were incorporated into positively-charged dimethyl-dioctadecylammonium (DODAC) chloride and negatively charged dihexadecylphosphate (DHP) by an ethanol injection method. Gel permeation chromatography and electron microscopy were used to show that the porphyrin and the rhodium complex were bound to the bilayers of the vesicle and that the vesicle structure was not destroyed by the incorporation procedure.

The catalytic oxidation of water to molecular oxygen with rigidly linked manganese porphyrin dimers has been reported [47]. In particular, dimanganese complexes consisted of dimers of TPP, Ar=4-$^tBuC_6H_4$, 2,4,6-$Me_3C_6H_2$, and C_6F_5 linked by an *o*-phenylene bridge. The latter exhibited the highest activity and its maximum turnover was 9.2 mol O_2 per mol catalyst in the presence of $^nBu_4NOH$. The number of electrons *n* involved in the reaction was determined by a rotating disk electrode to be 3.7 which was exactly twice that found for the corresponding monomer [MnPEPP]. It was concluded that oxygen evolution in the present case was based on a four electron oxidation. Clarification of the detailed mechanism is underway.



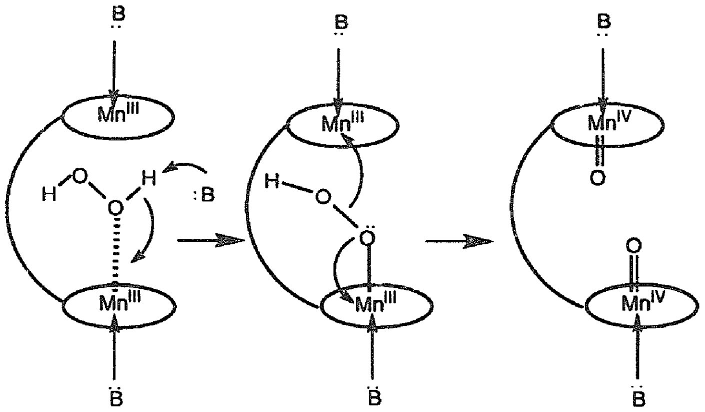
(15)

The catalase activity of manganese porphyrin dimers linked by various spacer molecules was explored [48]. A series of dimers was synthesized and their oxygen evolution was determined. When the two manganese atoms were approximately 4 Å apart, the dimer exhibited the highest catalase activity indicating that the Mn atoms cooperatively function in the rate-determining step of the disproportionation of H_2O_2. High catalase activity in this model system is thought to develop when each oxygen atom of the hydrogen peroxide molecule interacts with each Mn atom in the dimer. The homolytic cleavage of the O-O bond could be facilitated by the coordination of each oxygen in the peroxy ion to the Mn atoms. This reaction also requires a base, and studies (using 4-Me_2N-py, 1-methyl-imidazole and 3,4 dimethylpyridine) revealed a correlation between catalytic activity and basicity. It is thought that the base assists in the deprotonation of hydrogen peroxide and in the donation of electrons to the metal thereby enhancing the cleavage of the O-O bond of the coordinated hydroperoxide group (**16**).

The kinetics of the electron-transfer reactions of a manganese(III) complex of *trans*-cyclohexane-1,2-diamine-*N*, *N*, *N*′, *N*″,-tetraacetate ($cdta^{4-}$) with thioglycolic acid and gluthathione were studied at 30°C in aqueous media over a pH range of 2.0-10.33 using various reductant concentrations at constant ionic strength, $I = 0.20$ mol dm^3 ($NaClO_4$) [49]. The reactions were found to be first order in complex and reductants and are thought to proceed by an inner-sphere mechanism.

The magnetization in single monoclinic crystals of $Cs_2K[Mn(CN)_6]$ has been measured from 2 to 300 K and from 0.5 to 5.0 T along the [100], [010] and [011] crystal directions [50]. The data may be fit by the same general ligand-field model that was used for $Cs_2K[Fe(CN)_6]$. The transferability of this ligand-field model between $3d^4$ and $3d^5$ low-spin systems indicates the potential utility of ligand-field modelling.

The synthesis of chloro Mn^{III} *meso*-5,10,15,20-tetrakis[2-chloro-



(16)

6-(2,3,4,6-tetraacetyl-*O*-β-glucosyl)-phenyl] porphyrins has been reported [51]. They are robust catalysts for the asymmetric epoxidation of 4-chlorostyrene with dilute hydrogen peroxide.

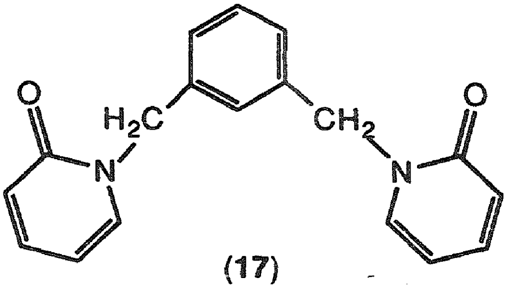
6. Manganese(II)

6.1. Complexes with oxygen donor ligands

Two new members of the family $[M_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$ have been synthesized [52]. In particular the Mn and Zn derivatives have been obtained and X-ray crystallography has been carried out. For the Mn case the complex $Na_{16}[Mn_4(H_2O)_2(P_2W_{15}O_{56})_2] \cdot 53H_2O$ was found to comprise a rhomb-like Mn_4O_{16} group encapsulated between two fragments of the $[(P_2W_{15}O_{56})]^{12-}$ polyanion. It exhibits antiferromagnetic exchange interactions and an $S=0$ ground state.

A report has appeared illustrating an approach which may be employed to link dinuclear units to form extended polymeric large-ring arrays [53]. The dimer $[Mn_2(m\text{-XBP})_2Cl_4(H_2O)]_n$ where *m*-XBP is *N*,*N*′-*m*-phenylenedimethylenebis(pyridin-2-one), (17), has been characterized by X-ray crystallography and its structure reveals it to consist of pairs of manganese atoms linked by two Cl bridges. The geometry at each Mn atom is distorted trigonal bipyramidal with coordination being completed by an oxygen atom from each *m*-XBP ligand and a chloride ion. The non-bridging chlorides are *trans*-disposed in the dimeric unit. The Mn···Mn and Cl···Cl distances are 3.85 and 3.41 Å respectively while the Mn-O distances are 2.096(3) and 2.163(3) Å. A novel feature of the structure is the way in which the *m*-XBP ligands link sets of dinuclear units thereby producing 52-membered rings.

The synthesis of oxo-bridged manganese dimers incorporating alkali and alkaline earth cations has been reported [54]. Oxygenation of the mononuclear complex in



(17)

CH_3CN generated the dimer $[(L)Mn^{III}]_2(\mu\text{-}O)$, where L = 3,3′-17-crown-6-SAL-3-CH_3-OPHEN. This dimer when reacted with KPF_6 and $Ba(SO_3CF_3)_2$ in dmf formed $[(L)Mn^{III}]_2(\mu\text{-}O)\cdot 2KPF_6$ and $[(L)Mn^{III}]_2(\mu\text{-}O)\cdot 2Ba(SO_3CF_3)_2$ respectively which were isolated and characterized by spectroscopic and electrochemical means. These dimers exhibited two-electron transfer processes generating the corresponding $Mn^{II}Mn^{II}$ (μ-oxo)dimer. Inclusion of cations in the crown ether portion of the dimer revealed that the formal reduction potential of the dimer shifted to more positive values e.g. $E^\circ = -120$ mV, CH_2Cl_2 for $[(L)Mn^{III}]_2(\mu\text{-}O)$, 0 mV CH_3CN for the potassium derivative and 180 mV CH_3CN for the barium derivative vs. SSCE. The results of UV-VIS spectroscopy suggest that the observed shift in the reduction potential may be due to an electrostatic effect rather than perturbation of the Mn(II) d orbitals.

The coordination behaviour of *N*-substituted amino acids with Mn(II) complexes has been investigated [55]. In particular, a series of complexes of Ar-SO_2-*N*-amino acids (Ar-SO_2- = 4-toluensulfonyl-, benzenesulfonyl, amino acid = glycine, DL-α- and β-alanine, asparagine, and glutamine) with Mn(II) were synthesized and characterized spectroscopically and by thermal means. The crystal structures for the α-alanine and glutamine complexes have been reported. In both the Mn atom is octahedrally coordinated by six oxygen atoms. In the case of α-alanine, the amino acid monoanion bridges two Mn atoms through the carboxyl group giving rise to a 1D polymer with coordination to Mn being completed by two water molecules. For the glutamine derivative, each amino acid monoanion bridges two Mn atoms via the carbonyl group binding a third Mn atom using the carbonyl oxygen of the terminal amide group generating a 2D polymer. The mean Mn-O distances for the former are 2.178A whereas in the latter the average is 2.183 Å.

The decomposition of peroxomonosulfate induced by Mn(II) in acid solution has been studied [56]. The rate constants for this process were found to be $5.1 \pm 0.3 \times 10^{-3}$ and $9.7 \pm 0.2 \times 10^{-3}$ $M^{-1/2}$ s^{-1} at 50°C in H_2SO_4 and $HClO_4$ media respectively. The presence of Mn(III) as an intermediate and as a minor product was confirmed.

The synthesis of the molecular sieve, Mn-APO-20, at higher substitution levels than previously reported using the tetrahedral species $[Me_4N]_2[MnCl_4]$ has been achieved [57]. Fully crystalline products were obtained at all substitution levels except the 1.0 mol. fraction substitution. Products using the 0.2 and 0.4 mol fractions were pale green whereas those for 0.6 and 0.8 mol were pale-green and pale-pink the latter indicating the presence of octahedral Mn^{2+} ions.

The coordination behaviour of the ligand N,N′-1,2-xylene-α,α′-diylbis(pyridin-2-one), several metals including Mn^{II} has been explored [58]. Spectroscopic data are presented.

Single crystals of Mn_3WO_6 were generated using a CO_2-LASER technique in a hydrogen atmosphere and their X-ray crystal structure was obtained [59]. It consists of WO_6 octahedra which are surrounded by six inner-sphere and six outer-sphere MnO_6 polyhedra.

The synthesis of a new dinuclear manganese complex of a pyridoxal derivative and its use as an oxidation catalyst has been reported [60]. The complex $[Mn_2L(OAc)_2]$ where $H_3L =$ N,N′-[4(3-hydroxy-5-hydroxymethyl-2-methyl)-pyridylmethylene]-1,3-diaminopropane-2-ol was characterized by IR and UV spectroscopy and magnetic measurements. Based on these, the proposed structure is a mixed-valence Mn(II)/Mn(III) complex comprising an endogenous μ-oxo and exogenous μ-carboxylato bridges. Experiments were conducted to test its ability as a catalyst for olefin oxidation and results are presented.

A solid state ESR study of manganese(II) halide-triphenylphosphine oxide complexes has been carried out [61]. The complexes $MnX_2(OPPh_3)_2$, $X = Cl$ or Br were heated for 1 hour and their ESR spectra recorded at room temperature. The chloride adduct was transformed to $[Mn(OPPh_3)_4][MnCl_4]$ at 175 and 225°C. The bromide adduct $MnBr_2(OPPh_3)_2$ exhibited hyperfine coupling in the $g = 2.029$ region.

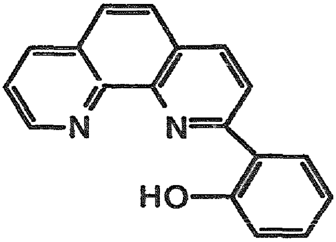
6.2. Complexes with oxygen and nitrogen donor ligands

The optical properties of and spin interactions in the trinuclear compound $[Mn(Me_6\text{-}[14]ane\text{-}N_4)]_2Cu(pba)\}(CF_3SO_3)_2 \cdot 2H_2O$, ($Me_6$-[14]ane-$N_4$ = (±)-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane and pba = 1,3-propylenebis(oxamato)) have been investigated [62]. In this complex, a central Cu(II) ion is bridged by oxamato groups to two peripheral Mn(II) ions. The absorption spectra have been recorded in pyridine at room temperature and in KBr pellets in the 10-290 K range. In addition to a transition at 613 nm due to Cu(II), narrow and rather intense Mn(II) spin-forbidden transitions in the 360-424 nm range were observed. These transitions are activated by an exchange mechanism. The temperature dependence of this transition was investigated and a theoretical expression for it has been derived. Least -squares fitting of experimental data has enabled the J interaction parameter with Mn(II) and Cu(II) in their local ground states to be calculated as $-28.2\ cm^{-1}$.

Exchange interactions in metal radical systems have been studied recently [63]. The ligands 3- and 4-(N-oxy-N-butylamino)pyridines (3NOPy and 4NOPy) bearing unpaired electrons have been prepared and reacted with Cr(TPP)Cl and hexafluoroacetylacetonato manganese(II). For the case of manganese, the complexes Mn(3 and $4NOPy)_2(hfac)_2$ and $[Mn(4NOPy)]_n$ were obtained. The complex $Mn(4NOPy)_2(hfac)_2$ has the two 4NOPy ligands coordinated via the pyridine nitrogens in a *trans* configuration rather than the nitroxide radical whereas the dimer $[Mn(4NOPy)]_n$ has each Mn coordinated with the pyridine nitrogen of one ligand and the oxygen of the nitroxide of another ligand in a *cis* configuration. These complexes were further characterized by EPR spectroscopy, SQUID susceptibily measurements and Faraday-balance magnetometry.

The synthesis and structural characterization of the neutral complex $[Mn_2(Cr_2O_7)_2(bpy)_4]$ involving an unprecedented bridging coordination of the dichromate ion via the terminal oxo atoms has been documented [64]. The structure contains a centre of inversion with two $\mu_{1,5}$-dichromato bridges between the two Mn(II) atoms forming a twelve-membered "polymetalloether" ring with an Mn···Mn separation of 7.880 Å and two terminal bpy ligands which complete the ligation. Coordination about the Mn atom is distorted octahedral with Mn-O bonds averaging 2.090 Å, two distinctive Mn···Cr distances 3.686 and 3.440 Å were found. The average Mn-N bond is 2.232(9) Å with one longer Mn-N bond length of 2.322(10) Å which is trans to an Mn-O bond. This complex is notable because of the great disparity in valence namely, Mn(II) and Cr(VI), the strongly valence-trapped nature of this core is evident from the Cr-O bond lengths, 1.631(8) Å.

The X-ray structure and variable-temperature magnetic susceptibility of $[Mn_4L_6][ClO_4]_2$, HL = (**18**), an unusual tetranuclear complex with a chain-like structure containing two phenolate bridges between each adjacent pair of Mn(II) ions has been reported [65]. Specifically, the complex comprises four crystallographically independent Mn(II) ions with two phenolate groups bridging each adjacent pair of ions. All Mn(II) ions are 6-coordinate, with the terminal metal centres being coordinated by two tridentate ligands L giving *cis*-N_4O_2 donor sets. The two inner metal centres have one associated tridentate ligand with the other three sites being occupied by bridging phenolate groups from the ligands attached to the metals on either side giving *cis*-N_4O_2 donor sets. The structure appears to be stabilized by aromatic π-stacking interactions. Selected bond distances range from 2.084(8) to 2.157(8) for Mn-O Å and 2.139(9) to 2.307(10) Å for Mn-N while Mn-Mn distances range from 3.333 to 3.372 Å. The magnetic moment is 5.80 μ_B at 300 K.



(18)

The effect of a ligating anion on the catalase activity of dinuclear Mn(II) complexes of Schiff-base macrocycles has been investigated [66]. Specifically, the complexes $[Mn_2(X\text{-}L^n)(Y)](ClO_4)$ where $H_2(X\text{-}L^n)$ is a Schiff-base formed by a 2:2

condensation of 4-X-2,6 and bis(ω-aminoalkyl)methylamine. The crystal structure for the derivative X = Me, Y = Cl and n = 2 has been obtained. It comprises dinuclear cations $[Mn_2(Me\text{-}L^2)(m\text{-}Cl)]^+$, perchlorate anions and dmf molecules. The two Mn ions are bridged by two phenolic oxygens from Me-L^2 and the chloride. The Mn-Mn distance is 3.086 Å. The catalase activity of the complexes was examined and it was found to be dependent on the nature of the ligating anion Y^-. It is proposed that the dissociation of Y^- is involved in the rate determining step.

The synthesis and structure of an $Mn^{II,II}$ complex salt $[Mn_2(\eta^1\eta^1\mu_2\text{-oda})(phen)_4(H_2O)_2][Mn_2(\eta^1\eta^1\mu_2\text{-oda})(phen)_4(\eta^1\text{-do})_2]\cdot 4H_2O$, do = acid and its catalytic ability towards the disproportionation of H_2O_2 have been reported [67]. X-Ray crystallographic data show "concertina shaped" dianion and dication components. In the dianion, $[Mn_2(\eta^1\eta^1\mu_2\text{-oda})(phen)_4(\eta^1\text{-do})_2]^{2-}$, each of the two symmetry related Mn(II) atoms are lighted by the nitrogen atoms of two phen groups. An oda^{2-} ligand bridges the two metals by using one carboxylate oxygen atom from each end of the dialled while a monodentate oda^{2-} ligand is strongly bonded to each metal by a single carboxylate oxygen giving an overall N_4O_2 octahedral coordination geometry. The structure of the dication $[Mn_2(\eta^1\eta^1\mu_2\text{-oda})(phen)_4(H_2O)_2]^{2+}$ is similar to the dianion with N_4O_2 coordination geometry. The mean Mn-N distance in the dication is 2.287 Å while it is shorter in the dianion 2.351 Å. The complex was found to catalytically disproportionate H_2O_2 at 25°C, during the first five minutes of the reaction *ca.* 6×10^3 molecules of H_2O_2 were decomposed making it apparently superior to that of most dinuclear manganese catalase mimetic complexes reported so far.

A remarkably stable hydrogen bonded dimeric Mn(II) complex, $[Mn(L)(OH_2)]_2(Me_2SO)_2$, L = the dianion of *N*, *N'*-bis(3-bromo-5-)-1,2-diamino-(2-methyl)ethane] has been obtained as a result of the recrystallization of a Mn(III) Schiff base acetate complex from dimethyl sulfoxide [68]. It comprises an N_2O_2 coordination sphere about each Mn atom with a capping water and a capping dimethyl sulfoxide in the axial positions. The close proximity of the water molecules between the Mn(II) moieties leads to very strong hydrogen bonding and a short Mn·····Mn separation of 4.6 Å. A strong π-π interaction between overlapping ligands also facilitates the dimerization.

The isolation of $[Mn_2(salen)_2(O_2CPr)(EtOH)(H_2O)][O_2CPr]$ and $[Mn(salpn)(O_2CBu)]$ from the direct reaction of the appropriate manganese(II) carboxylate and the appropriate Schiff base in ethanol has been described [69]. The isolation of these complexes demonstrates the great diversity of structural possibilities available for Schiff base complexes containing carboxylate ligands. The dinuclear complex comprises two Mn atoms residing in the equatorial plane of two phenolic oxygen atoms and two imine nitrogen atoms of the salen ligand are bridged by a single butyrate group. Coordination of an ethanol molecule for Mn(1) and a H_2O molecule for Mn(2) completes the octahedral environment. The molecule exhibits Jahn-Teller distortion in the axial direction. This is the first example of non-charged donors such as water and ethanol coordinating manganese in preference to strongly coordinating carboxylate groups. The monomeric complex is only the second such Mn complex with nitrogen and carboxylate ligands to be crystallographically characterized. The complexes were further characterized by cyclic voltammetry, IR spectroscopy and magnetic susceptibility measurements.

A communication has appeared describing the syntheses, X-ray crystal structures and magnetic studies of two dinuclear Mn(II) complexes $[Mn(OC_6X_3H_2)_2(bpy)]_2$, X = Cl, Br, which exhibit intra- and intermolecular ferromagnetic interactions [70]. In each complex two identical Mn(II) ions are symmetrically bridged by two phenoxy ligands in addition to a terminal phenoxy and a bpy ligand leading to highly distorted trigonal bipyramidal coordination. In the chloro derivative each terminal phenoxy ligand is involved in a stacking interaction with one of the bridging phenoxy groups such that the dihedral angles formed between the aromatic planes are 7.3(8) and 12.7(5)° and neighbouring C-C separations vary from 3.27 to 3.51 Å. In the bromo derivative the two terminal phenoxy ligands and one of the bridging phenoxy ligands form an intramolecular triple stack of phenyl units on one side of the dimer generating dihedral angles of 0.6 and 6.9° and C-C separations varying from 3.27 to 3.51 Å. Both derivatives in the crystal form chains in which the bipyridine ligands of each dimer are involved in intermolecular π-π interactions with the neighbouring dimers in the chain. Magnetic measurement were carried out, the effective magnetic moment for the chloro derivative at 300 K is 5.93μ_B per manganese atom and 5.93 μ_B per manganese atom for the bromo derivative.

The complex $[Mn_3(CH_3CO_2)_2(bpc)_2(py)_4(H_2O)_2]\cdot 0.5H_2O$, bpc = 2,2′-bipyridyl-3,3′-dicarboxylate, has been prepared and characterized [71]. X-Ray crystallography shows the complex to be comprised of a trinuclear Mn(II) unit in which the three metal atoms are joined linearly by two acetate groups and two bpc groups. Each pair of Mn atoms is bridged by an acetate group in a didentate fashion while the carboxylate groups from two different bpc ions bridge in a unidentate fashion. The Mn-O distances are in the range 2.094-2.247 Å while the Mn-N distances are in the range 2.252-2.261 Å. The magnetic properties of the complex were also investigated.

The isolation, characterization and structure of a novel dinuclear Mn(II) complex, $[Mn(phen)(bet)(NO_3)(H_2O)_2](NO_3)\cdot H_2O$, bet = $Me_3N^+CH_2CO_2^-$ has been reported [72]. In this complex the metal atom is in a highly distorted tetrahedral environment being coordinated by a didentate phen, a unidentate carboxylato group of the bet ligand, a unidentate nitrato ligand and two aqua ligands.

Mononuclear and dinuclear Mn(II) complexes of tridentate *bis*-benzimidazolyl ligands have been prepared and characterized [73].

Complex compounds of Mn(II) of composition $Mn(H_2L)_2\cdot nH_2O$ where H_3L are oximes of pyruvylamino acids $CH_3C(=NOH)$-C(O)-NH-CHR-COOH have been synthesized and characterized spectroscopically and by thermoanalytical means [74]. A X-ray crystal structure for Mn(II) bis-catena[-μ-{nopropyonyl)-L-alaninato(1-)-*O*,*N*:*O′*}] was obtained. The crystal structure exhibits flat networks perpendicular to the direction *c* and are the result of polymerization in two crystallographically independent directions. The Mn atoms are octahedrally coordinated with coordination via nitrogen atoms of the oximato group and oxygen atoms of the amido group giving a five-membered chelate and via a mondentate bridging carboxy group.

The coordinating ability of the chlorosulfate ion in complexes of transition metal bis(chlorosulfates) derived from diamines has been investigated [75]. The reaction of the transition metal bis(chlorosulfates) with 1,3-propylenediamine and *o* -phenylenediamine gave complexes of the form $[M(SO_3Cl)_2(L)_2]$ where L is the diamine ligand and M = Cr, Mn, Fe, Co, Ni, and Cu. These complexes were characterized by IR and electronic spectroscopy and magnetic susceptibility measurements.

The synthesis and characterization of biologically active semicarbazone complexes of oxovanadium and manganese has been reported [76]. Based on elemental analysis, magnetic moments, IR, ^1H NMR and electronic spectroscopy a tetracoordinate tetrahedral geometry for the manganese complexes is proposed. Some of the complexes exhibited antifungal and antibacterial activity.

Four novel dinuclear Mn(II) complexes containing extended isophthalato-bridged structures have been synthesized [77]. The complex $[Mn_2(1PHTA)(L)_4](ClO_4)_2$, L = bpy, phen, 5-nitro-1,10-phenanthroline, Me_2bpy and 1PHTA = isophthalate dianion, were characterized and each Mn atom is thought to be penta-coordinated in a square pyramidal environment with a quartet ground state.

6.3. *Complexes with sulfur donor ligands*

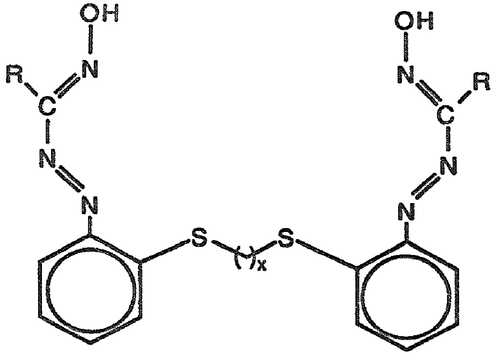
Two novel heterocubane clusters with divalent Mn ions have recently been synthesized and characterized [78]. The reaction in a 3:1 molar ratio of $^iC_3H_7XNa$, (X = S, Se) and $MnBr_2$ with $(SiMe_3)_2Te$ in acetonitrile gave $(Et_4N_4)[Mn_4Te_4(Si^iC_3H_7)_4] \cdot 2MeCN$ and $(Et_4N_4)[Mn_4Te_4(Se^iC_3H_7)_4] \cdot 1.5MeCN$. Both are discrete complex ions whose frameworks comprise Mn_4 and Te_4 tetrahedra which are intertwined such that the corners of one tetrahedron lie above the centres of the faces of the other. The terminally coordinated ligands are at a distance of 2.413 Å for S and 2.537 for Se. There is no significant Mn-Mn bonding. Cyclic voltammetric measurements show that these anions do not undergo reversible or quasi-reversible electronic transitions.

The synthesis, crystal structure and vibrational spectrum of $K_2Mn[P_2S_6]$ have been reported [79]. The crystal structure is composed of columns of face-sharing S_6 polyhedra which are centred alternately by Mn octahedra with Mn-S bond distances of 2.647 Å and P_2 pairs.

6.4. *Complexes with sulfur and nitrogen donor ligands*

Low spin complexes of Mn(II), Fe(II) and Fe(III) bound to the thioether function have been obtained through designing a new family of acyclic hexadentate N,S ligands [80]. The manganese derivative Mn^{II}Ph3L (**19**), has been characterized by X-ray crystallography and reveals a distorted MnS_2N_4 core with Mn-N bonds 1.900(12) A and 1.923(10) Å and Mn-S (2.350(5) Å all of which are much shorter than those in comparable thioether ligated high-spin Mn(II) species. This is proposed to be due to metal-ligand backbonding in this complex. Magnetic measurements have been obtained for all species (1.84-1.88 μ_B for Mn complex).

The syntheses and characterization of thiolate-bridged Mn(II) complexes with *NNS*-tridentate thiolic ligands has been reported [81]. In particular, the complexes



R	x	H_2R_xL
Ph	2	H_2Ph2L
α-Naphthyl	2	H_2Np2L
Ph	3	H_2Ph3L
α-Naphthyl	3	H_2Np3L

(19)

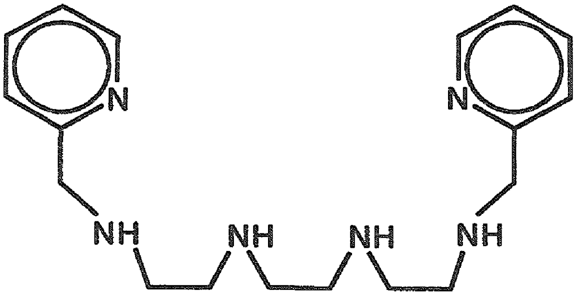
$[Mn(L_a)Cl]_n$, $[Mn\{Mn(L_b)_2\}_2]Cl_2 \cdot 2CH_3OH$, $[Mn(L_c)Cl]_n$, and $[Mn(L_d)Cl(CH_3OH)]_n$, HL_a = 2-[(2-aminoethyl)amino]ethanethiol, HL_b = 2-[(3-aminopropyl)amino]ethanethiol, HL_c = 2-[(2-aminoethyl)amino]ethanethiol, and HL_d = 2-[[2-(2-pyridyl)ethylamino]ethanethiol were characterized by elemental analysis and IR and electronic spectroscopies.

The preparation, characterization and biological activities of manganese(II) complexes possessing nitrogen-sulfur donor ligands have been reported [82]. Reaction of $MnCl_2$ with thiosemicarbazone resulted in the formation of 1:1 and 1:2 complexes which are proposed to have tetrahedral geometries.

6.5. Complexes with nitrogen donor ligands

A new hexadentate N_6-ligand, 1,10-bis-(2-pyridylmethyl)-1,4,7,10-tetrazadecane (**20**), has been synthesized as its hydrochloride salt, and its coordination properties to various transition metals have been studied [83]. Its Mn(II) complex has been synthesized and characterized by X-ray crystallography. This mononuclear complex comprises a trigonal prismatic arrangement of nitrogen atoms about the central metal, and Mn-N bond distances range from 2.240(5) to 2.334(6) Å. All complexes were studied using electronic spectroscopy and cyclic voltammetry. All exhibit quasi-reversible redox couples corresponding to M(II)↔M(III) couple, for Mn this was +1.100 V vs Ag/AgCl in acetonitrile.

The crystal structure and the spectroscopic and magnetic properties of bis(μ-end-on-azido)bis(2,2′:6′,2″-terpyridine)dimanganese(II) dihydrate, $[Mn(terpy)(N_3)_2]_2 \cdot 2H_2O$ have been reported [84]. It was prepared by adding 0.395 g $Mn(terpy)(Cl)_2 \cdot H_2O$ to a saturated aqueous solution of sodium azide. The structure comprises a dimer formed by the union of two $Mn(terpy)(N_3)_2 \cdot H_2O$ fragments and the Mn ions in the dimer are linked by two end-on bridging azide groups. The two other azides are present as terminal ligands. The coordination about each Mn ion is distorted octahedral with Mn-N distances for the terpy ligand being 2.275(3), 2.233(3) and 2.268(3) Å, while Mn-Azide distances were 2.182(3) and 2.272(2) Å. The complex has been further characterized by ESR spectroscopy and magnetic

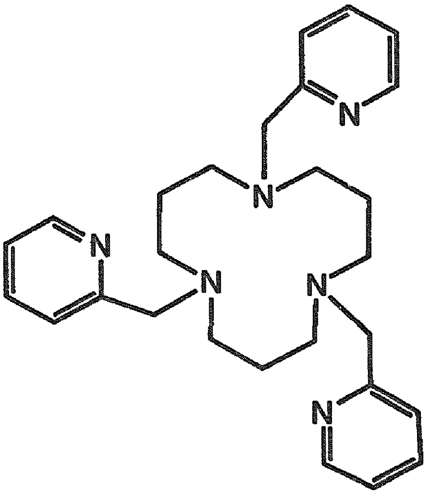


(20)

measurements. It was found to exhibit an intradimer ferromagnetic exchange interaction.

A reliable procedure has been developed to prepare 1,5,9-tris(2-pyridylmethyl)-1,5,9-triazacyclododecane, (**21**), and its Mn(II) complexes were also synthesized [85]. For the Mn(II) case, its effective magnetic moment at room temperature was found to be 6.00 μ_B, cyclic voltammetry gave a value of 1.48 V vs NHE. These new complexes are more resistant to oxidation in comparison to the analogous 1,4,7-tris(2-pyridylmethyl)-1,4,7-triazacyclononane. Results from molecular mechanics calculations were used to rationalize this behaviour and show that the minimum strain energy M-N(sp^3) distances to be 2.37 Å for the 1,5,9 derivative and 2.12 Å for the 1,4,7 complex.

The syntheses of three new ferromagnetic materials based on hexacyanomanganate

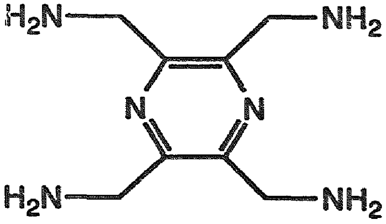


(21)

"building blocks" that have magnetic ordering temperatures near 40 K has been reported [86]. The Mn-based Prussian blue analogues $K_2Mn^{II}[Mn^{II}(CN)_6]$, $Mn_3[Mn(CN)_6]\cdot 12H_2O$ and $CsMn[Mn(CN)_6]\cdot {}^1/_2H_2O$ were characterized by X-ray powder diffraction and by variable temperature magnetic studies.

The *ab initio* structure determination from X-ray powder diffraction of pyridazine (pydz) adducts of MX_2, (M = Mn, Fe, Co, Ni, Cu or Zn; X = Cl or Br) has been described [87]. The complexes were prepared using a reagent molar ratio of 1:1. The crystal structures of $[NiCl_2(pydz)]$ and $[NiBr_2(pydz)]$ show the compounds to comprise infinite polymeric chains of nickel atoms bridged by Cl or Br and pyridazine ligands in an octahedral arrangement. The analogues of Mn, Fe and Co are isomorphous with the nickel compounds while those of Cu and Zn display different diffraction patterns.

The synthesis of the new bis(tridentate) chelate 2,3,5,6-tetrakis(aminomethyl)pyrazine, (tampyz), (**22**) and the synthesis and characterization of its $Mn^{(II)}$, $Cu^{(II)}$, and $Zn^{(II)}$ complexes have been reported [88]. This chelate was found to form a quasi-linear one-dimensional polymeric complex with $MnCl_2$ in water. The complex $[\{Mn(tampyz)Cl_2\cdot 2H_2O\}_\infty]$ was analysed by X-ray crystallography and found to be columnar and is an extended quasi-linear chain polymer with the bis(tridentate) ligands and metal atoms arranged alternately. The coordination about the Mn atom is a very distorted octahedral one with $Mn\text{-}N_{pyz}$ being 2.216(2) Å and $Mn\text{-}N_{amine}$ being 2.314(3) and 2.253(3) Å. The chelate rings are highly strained. The copper complex may be considered to have a square-planar or octahedral coordination about the copper while in the zinc complex the zinc atoms are five coordinate in a trigonal-bipyramidal arrangement.



(22)

The synthesis and characterization of Mn(II) and Ni(II) complexes of substituted 1,10-phenanthroline ligands has been accomplished [89]. The substituted ligands include 2,9-di(*o*-tolyl)-1,10-phen (i), 2,9-di(2-methoxyphenyl)-1,10-phen (ii), 2,9-di(2-ethoxyphenyl)-1,10-phen (iii), 2-(*o*-tolyl)-1,10-phen (iv), 2-(2-ethoxyphenyl)-1,10-phen (v) and 2,9-bis(*N*-pyrazolylmethyl)1,10-phen (vi). 1:1 metal-to-ligand complexes were isolated with (ii) and (vi) and 1:2 metal-to-ligand complexes were isolated with all except (vi). Electrochemical studies on the latter type complexes suggest that M(II)↔M(I) electron transfer is metal localized whereas M(I)↔M(0) electron transfer is ligand localized.

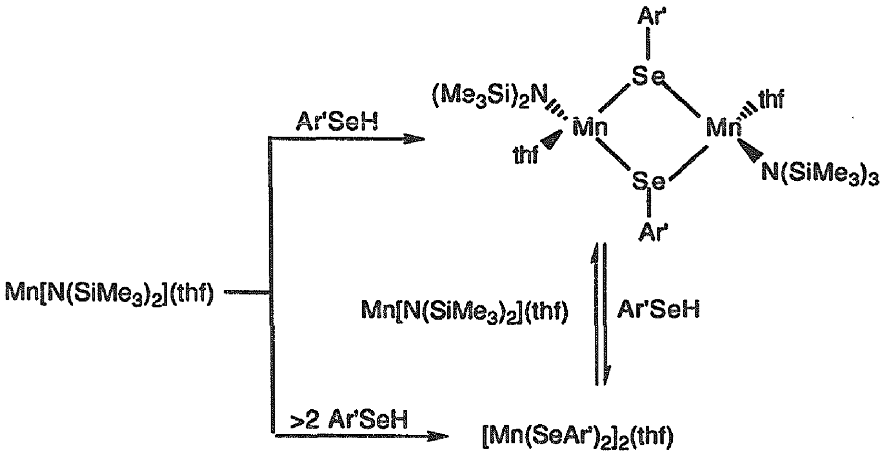
The reduction of acidophthalocyaninatomaganese(III) by boronate, thioacetate or hydrogen sulfide gave acidophthalocyaninatomaganese(II), [Mn(X)Pc^{2-}]$^-$; X= Cl, Br, NCO NCS which was isolated as the tetra^{n}butylammonium salt [90]. These complexes have been characterized by CV, UV-VIS-nIR spectroscopies and their magnetic properties have been studied.

The crystal structure of the yellow cis-[Mn(phen)$_2$(NCS)$_2$] has been described [91]. The MnN_6 core is a distorted octahedral one with Mn-N(phen) distances of 2.294(2)and 2.301(3) Å while the Mn-NCS distances are 2.139(3) Å.

Complexes of Mn(II), Cr(III) and Ni(II) with methylhydrazinecarboxylate and 1,1-dimethylhydrazinecarboxylate ligands have been prepared [92]. These complexes are thought to be formed in trace amounts during long term storage of CO_2-contaminated hydrazine propellants and may serve as homogeneous catalysts for the decomposition of the propellants. They were prepared by reacting salts of the metals with CO_2 saturated solutions of the hydrazines in EtOH. They were characterized by DTA, TGA, electronic and IR spectroscopy and magnetic susceptibility measurements.

6.6. Complexes with selenium donor ligands

The isolation and structural characterization of a reaction intermediate [Mn{N(SiMe$_3$)$_2$}(μ-SeC$_6$H$_2$-^{i}Pr$_3$-2,4,6)(thf)]$_2$ has been described (23) [93]. The Mn_2Se_2 ring forms a planar parallelogram with Mn-Se distances of 2.582(2) and 2.645(2) Å. The steric requirement of the bulky amido and selenolato ligands are reflected in the wide N(1)-Mn-Se(1) angle of 136.4(2)° while the O-Mn-Se and Se-Mn-Se angles are reduced to 100.7(1) and 82.0(1) respectively.



(23)

7. Manganese(I)

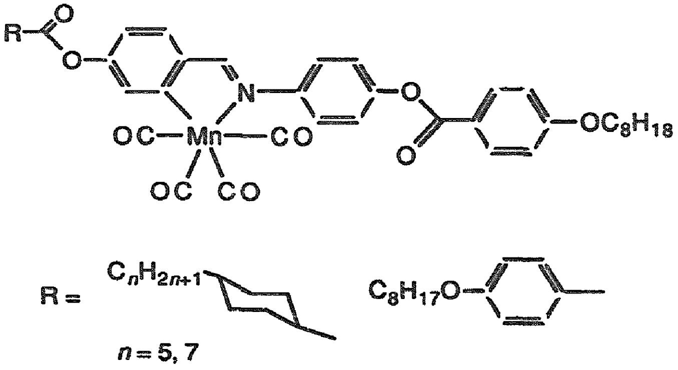
7.1. Complexes with halide ligands

The crystal structures of *fac*-[bis(dimethylphosphino)methane]bromotricarbonylmanganese(I) and rhenium(I) have been reported [94]. The metal atom is in an octahedral environment with the primary distortion due to the short bite of the dmpm ligand. The Mn-Br distance is 2.528(1) Å while the Mn-P distances are 2.317(2) and 2.322(2) Å.

7.2. Complexes with nitrogen donor ligands

The unusually stable radical anionic complexes $[(CO)_5MnRe(CO)_3(bpy)]^{\cdot-}$ and $[(CO)_5MnRe(CO)_2(bpy)Re(CO)_3Br]^{\cdot-}$ have been studied by cyclic voltammetry and IR spectroelectrochemistry at variable temperatures [95].

The first example of liquid crystalline metal complexes exhibiting simple octahedral coordination and the first examples of calamitic liquid crystalline complexes containing manganese have recently been synthesized [96]. The complex (**24**) consists of an aromatic imine bound to an $Mn(CO)_4$ moiety in an orthometallated mode.



(**24**)

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