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5. Manganese 1993

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CONTENTS

INTRODUCTION

This review describes the developments in manganese chemistry as reported in the literature for 1993. It is based on a search of Volumes 118, 119 and 120 of *Chemical Abstracts*. As in previous reviews, it focuses on mainly on coordination chemistry. In addition, major inorganic chemistry journals have been searched separately for the calendar year 1993. A review which profiles metalloenzymes including manganese has appeared [1].

5.1 MANGANESE(IV)

5.1.1 Complexes with oxygen donor ligands

Oxygenation reactions of the symmetrical (X-SALPRN)Mn^{II} complexes, ($H_2SALPRN$ = 1,3-bis(salicylideneamino)propane, X = H, 5-Cl, 5-CH_3O) have been studied in CH_3CN and CH_2Cl_2 [2]. The choice of solvent and rate of oxygenation were found to play important roles in

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determining isolable products. The bis(μ-oxo) dimer [(X-SALPRN)Mn^{IV}(μ-O)]$_2$ was isolated from CH_3CN whereas in CH_2Cl_2, in addition to the dimer, a green compound formulated as {[X-SALPRN)Mn^{III}]$_2$}$_x$ where x = 1 or 2, was obtained. In a related paper [3], chemical and electrochemical investigations were carried out. These studies have shown that the bis(μ-oxo) dimers most likely form by the reaction of [LMn-O_2] and [LMn^{II}], not [LMn-O_2]$^-$ and [LMn^{III}]$^+$. An interesting result was that oxygenated intermediates were sensitive to the type of Lewis acid in solution. Complete decomposition was observed when H^+ or [LMn^{III}]$^+$ was present.

Colloidal Mn(IV) has been identified in permanganate oscillating reactions [4]. Several electrolytes were tested for their ability to suppress oscillation in MnO_2^--Mn^{2+}-$H_2PO_4^-$ and MnO_4^--H_2O_2-$H_2PO_4^-$ systems. The strength of the effect was found to be dependent on the concentration, charge and radius of the cation. A hydrophilic colloid, gum arabic, protected the oscillator from the influence of electrolytes.

The oxidation reactions of soluble Mn(IV) phosphate in 3M phosphoric acid have been studied [5]. Using ultra-centrifugation and electron microscopy it was determined that manganese was not present as a colloid. It was found to oxidize oxygen-containing bifunctional substrates in an autocatalytic way.

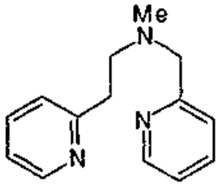
5.1.2 *Complexes with oxygen and nitrogen donor ligands*

Direct evidence for the presence of {Mn^{IV}(=O)}$_2$ and {$Mn^{II}Mn^{IV}$(=O)} intermediates in the HO_2 disproportionation reaction using a μ-phenoxo-bis(μ-carboxylato)dimanganese(II) complex has been reported [6]. The dinuclear complex [Mn_2(L)($PhCO_2$)$_2$(NCS)], [L = 2,6-bis{*N*-{2-(dimethylamino)ethyl]iminomethyl}-4-methylphenolate(1–)] has been synthesised and its X-ray crystal structure obtained. This complex behaves as a 1:1 electrolyte in dmf solution and FAB spectral studies indicate that the complex dissociates into [Mn_2(L)($PhCO_2$)$_2$]$^+$ and the NCS^- ion. When H_2O_2 was added to a dmf solution of the complex, catalytic decomposition of H_2O_2 occurred with more than 1000 turnovers based on volumetric measurement of evolved dioxygen.

The facile synthesis and structure of the Mn^{IV}-Mn^{IV} dinuclear complex [Mn(salpn)O]$_2$(DMSO)$_2$, (salpnH_2 = *N,N'*-bis(salicylidene)-1,3-diaminopropane) has been documented [7]. Both Mn atoms were found to be in octahedral environments made up from the tetradentate Schiff base and two μ-oxo O atoms which are both *cis*.

A series of Mn(IV) complexes [Mn(R, R'-L)$_2$]·nS, [R = H, Cl, Br, CH_3O; n = $^1/_2$, 1, $^3/_2$, 2; S = H_2O, thf where H_2(R, R'-L) denotes *o*-salicylideneaminomethyl)phenol and its substituted derivatives] has been prepared [8]. They have been characterised by IR and electronic spectroscopy, magnetic studies, cyclic voltammetry and spectroelectrochemical methods. An X-ray crystal structure has been obtained for [Mn(5-Cl'-L)$_2$]·2thf and it has an MnO_4N_2 coordination sphere.

A new mixed-valence dinuclear complex containing the [Mn^{IV}(μ-O)$_2$(μ-O_2CMe)Mn^{III}]$^{2+}$ core has been synthesised and isolated in the solid state [9]. The complex [Mn_2(μ-O)$_2$(μ-O_2CMe)L_2][ClO_4]$_2$·H_2O, L = methyl[2-(2-pyridyl)ethyl](2-pyridylmethyl)amine, (**1**) has been characterised by EPR spectroscopy, magnetic and redox studies.



(1)

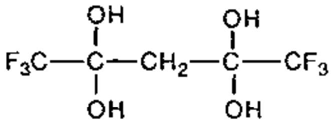
5.2 MANGANESE(III)

5.2.1 Complexes with oxygen donor ligands

The successful development of synthetic procedures to prepare distorted cubane $[Mn_4O_3Cl]^{6+}$ complexes with arenecarboxylate ligation and their characterization by crystallographic, magnetochemical and spectroscopic means has been documented [10]. These species possess the same structure and are isolated at the same oxidation level as the corresponding alkanecarboxylate derivatives. Improved solubility in solvents such as toluene has facilitated the accumulation of good EPR and NMR spectroscopic data.

Structural and magnetic characterization of a series of Mn^{III} chains containing malonate ligands which are isostructural to previously characterized Mn^{III}-salicylate chains have been achieved [11]. The results from both the salicylate and malonate series were combined in order to evaluate spin Hamiltonian parameters for one-dimensional $S = 2$ systems.

A straightforward route to good yields of the doubly-hydrated form of hexafluoroacetylacetone (2), and its employment as a ligand has been reported [12]. Its crystal structure confirms a bis(*gem*-diol) structure with an extended-chain conformation. The preparation of the complex $(pyH)_2[Mn_2(hfpt)(hfac)_4]$, hfac = hexafluoroacetylacetone, hfpt = 1,1,1,5,5,5-hexafluoropentane-2,2,4,4-tetrol, has been achieved. Its crystal structure shows the anion to be comprised of two $Mn(hfac)_2$ fragments bridged by the $hftp^{4-}$ group which functions as a didentate chelate ligand to each Mn^{III} ion. Variable temperature magnetic susceptibility studies have been conducted to establish the sign and magnitude of the magnetic exchange interactions between the Mn^{III} ions as mediated by this ligand.

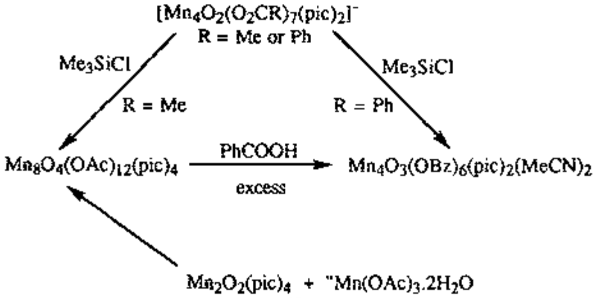


$$F_3C-\overset{OH}{\underset{OH}{C}}-CH_2-\overset{OH}{\underset{OH}{C}}-CF_3$$

(2)

The preparation and X-ray structure of a new $Mn^{IV}{}_4Mn^{III}{}_8$ complex $[Mn_{12}O_{12}(O_2CPh)_{16}(H_2O)_4]$ have been described [13]. The complex consists of a central $[Mn^{IV}{}_4O_4]^{8+}$ cubane held within a non-polar ring of eight Mn^{III} centres which are held together by eight μ_3-O^{2-} ions. An analogous complex $[Mn_{12}O_{12}(O_2CPh)_{16}(H_2O)_4]\cdot MeCOOH\cdot 4H_2O$ was also prepared; detailed magnetic susceptibility and EPR spectroscopic data are presented for these complexes. The former has an $S = 9$ ground state in zero applied field, but with the introduction of a magnetic field the ground state has the $M_S = -10$ component of an $S = 10$ state. The latter complex has an $S = 10$ ground state in both zero applied fields as well as in large magnetic fields. High-field EPR spectroscopic experiments with a CO_2 laser spectrometer show that there are appreciable zero-field interactions for both of the complexes and high magnetic anisotropy is present.

A new program aimed at controlled covalent linkage of Mn_x complexes leading to aggregates-of-aggregates and polymers-of-aggregates has been successful [14]. The reversible aggregation of a tetranuclear complex to an octanuclear product has been described. The direction of nuclearity change is controlled by carboxylate abstraction and steric bulk. The various transformations are summarized in (3).



(3)

Studies on the thermophilic cyanobacterium *Synechococcus elongatus* suggest a great difference in atomic structure between cyanobacterial enzymes and spinach enzymes [15]. In particular, hyperfine constants as measured by ENDOR for ^1H and ^{15}N nuclei located within magnetic contact to the tetranuclear manganese cluster of the photosynthetic water oxidizing site have been obtained. The data suggest there may be no un-ionized water or hydroxo ligands directly bound to the Mn cluster but rather a "dry" environment with long (weak) H-bonds from solvent exchangeable protons to μ-oxo bridges or to terminally coordinated ligands.

The first crystallographically characterized dinuclear manganese model which approaches some of the structural, spectroscopic and functional properties of the Mn catalases has been reported [16]. The complex $Na_2[Mn(II)(2\text{-}OHsalpn)]_2{\cdot}2CH_3OH$ was prepared and isolated as a yellow powder by the reaction of the ligand 2-OHsalpn with 3 equivalents of NaOMe and 1 equivalent of $Mn(ClO_4)_2{\cdot}6H_2O$ in methanol. Upon oxidation by O_2 in acetonitrile the corresponding $Mn(III)_2$ dimer, $[Mn(III)(2\text{-}OHsalpn)]_2$ was obtained. An X-ray crystal structure of a ring-substituted derivative of the latter complex, namely, $[Mn(III)(2\text{-}OH(5\text{-}NO_2\text{-}sal)pn)]_2$ has been obtained. The reaction of these two complexes with H_2O_2 has been studied in acetonitrile and the system was found to cycle between $Mn(II)_2$ and $Mn(III)_2$ oxidation levels maintaining its dinuclear integrity during the process. The complex $[Mn(III)(2\text{-}OHsalpn)]_2$ was found to have reasonable turnover rates, saturation kinetics were exhibited with H_2O_2. Similar $^{18}O_2$ labelling as the enzyme was exhibited and azide insensitivity under conditions where Mn catalase is not inhibited by azide was found. In addition it forms a catalytically inactive Mn(III, IV) form which may be reduced to a catalytically active state by NH_2OH.

Electron microscopy, density, thermal and analytical powder diffraction analyses have been used to study the phases of $MnXO_4{\cdot}nH_2O$ (X = P, As) and a simple new salt $MnAsO_4$ has been synthesised [17]. Samples with $n > 1$ behave as intergrowths of stoichiometric, crystalline $MnXO_4{\cdot}H_2O$ and amorphous $MnXO_4{\cdot}mH_2O$ with $m \sim 4$. Detailed thermal analyses of these materials show that arsenate alone can be dehydrated without loss of oxygen, leading to the synthesis of a simple new solid $MnAsO_2$. Its structure has been determined by X-ray powder diffraction and it constitutes an example of a monoclinically -distorted $CuSO_4$ type structure. Chains of edge-sharing MnO_6 octahedra containing two different Mn^{3+} sites which display cooperative [4+2] and [2+2+2] Jahn-Teller distortions are linked through distorted AsO_4 groups.

The stoichiometry and kinetics of oxidation of S^{IV} to S^{VI} by acetylacetanato complexes of Mn(III) were determined in aqueous perchlorate media containing excess acetylacetone in the 4.0 - 8.6 pH range [18]. The complex $[Mn(acac)_3]$ is kinetically inactive but the hydrolytic derivatives $[Mn(acac)_2(H_2O)_2]^+$ and $[Mn(acac)_2(H_2O)(OH)]$ were found to oxidize S^{IV} to S^{VI} quantitatively. In a related paper [19], the kinetics and mechanism of oxidation of the oxalate ion by $[Mn(acac)_3]$ in the pH range 6.6 - 8.6 was studied. The species $[Mn(acac)_2(H_2O)_2]^+$ and $[Mn(acac)_2(H_2O)(OH)]$ oxidised oxalate through inner-sphere intermediates.

The outer-sphere oxidation of 4-oxopentanoic (4-OPA) acid to acetic acid by aquomanganese(III) ions was found to exhibit a first-order dependence on (4-OPA) and [Mn(III)](aq) [20]. The kinetics and mechanism of α, β–unsaturated alcohols by Mn(III) acetate in aqueous sulphuric acid media has been studied [21]. The reaction was found to proceed through an outer sphere mechanism. The data suggest that disproportionation of the manganese-alcohol complex into free radicals was the rate determining step in the presence of $[Mn^{II}]$. The kinetics and mechanism of the reduction of bis(pentane-2,4-dionato)diaquo manganese(III) by hydroxylamine and L-ascorbic acid has been investigated in aqueous solution at 25°C and ionic strength 0.5 mol dm^{-3} [22]. Inner sphere mechanisms have been implicated for both reductants.

The involvement of Mn(III) in the $[MnO_4]^-$-SO_4 redox process has been studied [23]. Evidence for an Mn(III) intermediate has been obtained by conducting the reaction in the presence of F^-. The reaction was monitored by *in situ* EPR and electronic absorption spectroscopy and physico-chemical techniques were used to ascertain the identity of the isolated Mn(III) products. The evidence suggests that in the presence of fluoride ions, manganese(VII) ions are reduced to Mn(III) and then to Mn(II).

The kinetics of the reaction of Mn(III) with oxalic acid has been studied in sulfuric acid solutions [24]. Pseudo-first order rate constants have been estimated by a non-linear least squares method.

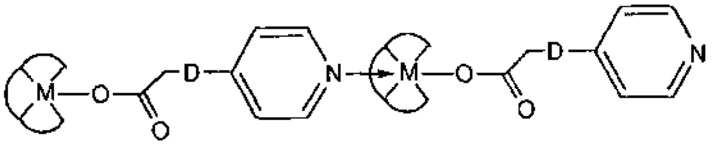
5.2.2 *Complexes with oxygen and nitrogen donor ligands*

The stabilization of high-valent manganese in aqueous media through binding of the oxidant resistant ligand $PO_2{}^{3-}$ has been investigated [25]. The mixed-valent dimer $[Mn^{III}\ Mn^{IV}(\mu$-

$O)_2(bpy))_4]^{3+}$ has been shown to disproportionate in aqueous H_3PO_4. An Mn(III) product has been characterised as $[Mn^{III}(bpy)(HPO_4)(H_2PO_4)]_x$ which is a polymeric material. The Mn^{III} ions bridged by two μ_2-phosphate ligands are 4.93 Å apart with each Mn(III) atom bridged in this manner to two other $[Mn^{III}(bpy)(HPO_4)(H_2PO_4)]$ formula units thus generating a polymeric array. The complex shows weak antiferromagnetic coupling of the Mn(III) ions consistent with the long Mn....Mn separation and the high temperature magnetic moment of $6.68\mu_B$ confirms the Mn(III) oxidation state.

Dinuclear Mn complexes containing the $[Mn_2(\mu\text{-}O)(\mu\text{-}O_2CR)_2]^{2+}$ core and employing the bpy ligand have recently been synthesised [26]. These complexes have the general formulation $[Mn_2O(O_2CR)_2X_2(bpy)_2]$, $X = Cl^-$, N_3^-, H_2O and are potential models for the Mn catalase enzymes. The complexes were characterised by cyclic voltammetry and solid-state magnetic susceptibilities. These complexes were found to be invaluable in permitting the influence of X on a variety of properties such as structural and magnetochemical parameters to be assessed.

The synthesis and structures of polar coordination polymers $[(salen)MnO_2CCH_2D\text{-}B:]_n$, (D = NH, S; -B: = 4-pyridyl, 4-cyanophenyl) has been reported [27]. The reaction between Mn(salen)Br and *N*-4-pyridylglycine gave Mn(salen)(*N*-4-pyridylglycinate) which crystallizes as an infinite-chain coordination polymer. The polymer chains consist of metal centres bridged by 4-pyridylglycinate ligands. The Mn atoms are octahedrally coordinated with the salen ligand occupying four equatorial sites, a carboxylate oxygen occupying one axial site and a pyridyl nitrogen of an adjacent molecule occupying a *trans* axial site. This pattern is repeated generating a polymer with a head-to-tail alignment of the backbone (4). The reaction of Mn(salen)Br with (4-pyridylthio)acetic acid gave Mn(salen)(4-pyridylthio)acetate), which has a similar structure to the former. In contrast, reaction of Mn(salen)Br with *N*-(4-cyanophenyl)glycinate gave a compound whose crystal structure consists of a mixture of the monomeric $(H_2O)Mn(salen)(N\text{-}(4\text{-}$cyanophenyl)glycinate) and an Mn(salen){*N*-(4-cyanophenyl)glycinate} polymer. The polymer consists of adjacent Mn(salen) moieties bridged by a single carboxylate unit in a *syn-anti* conformation.

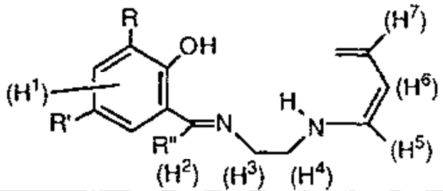


(4)

A new dinuclear dimanganese(III) polyimidazole complex which contains a (μ-oxo) and a (μ-carboxylato)-bridged structure has been prepared [28]. The core observed in this study has only been previously been seen as part of a more complex cluster structure. The crystal structure of $[Mn_2O(TMIMA)_2(OAc)](ClO_4)_3{\cdot}2CH_3CN$, TMIMA = tris(1-methylimidazol-2-yl)methyl)amine has been obtained and the coordination about each Mn atom is distorted octahedral as expected for Jahn-Teller d^4 ions. The Mn-O(oxo) distances are 1.784(3) and 1.789(3)Å while Mn-O(acetate) are 2.029(3) and 2.042(4)Å. The Mn-N(imidazole) distances range from 2.063(3) to 2.124(4) Å while the Mn-N (amine) distances are significantly longer at 2.352(4) and 2.373(4) Å. The structure is reminiscent of those reported for other diiron(III) complexes of N_4-tripodal ligands thus lending credence to the proposal that Mn proteins have dinuclear active site structures similar to those of non-heme oxo-iron proteins.

New mixed-metal complexes $[Cr^{III}_2M^{II}O(O_2CCH_3)_6(C_5H_5N)_3]\cdot$solv and $[Mn^{III}_2M^{II}O(O_2CCH_3)_6(C_5H_5N)_3]\cdot$solv, (M = Co, Ni, or Mn; solv = solvent) were prepared and characterised by X-ray diffraction and IR spectroscopy [29]. The IR spectroscopic data indicate that all six compounds possess the same oxo-centred triangular molecular unit. In each molecule four carboxylate ions form bridges between different metal atoms and two form bridges between like atoms.

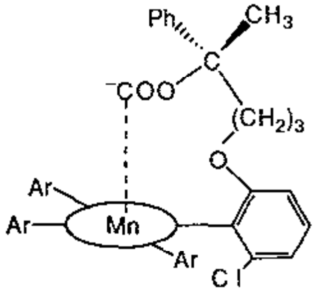
The synthesis and characterisation of several manganese(II) complexes with unsymmetrical Schiff bases (**5**) have been described [30]. X-ray crystal structures have been obtained for $[MnL^3(H_2O)_2]ClO_4\cdot EtOH$ and $[MnL^1(H_2O)_2]ClO_4$ which are both monomeric and have MnN_2O_4 coordination spheres.



	R	R'	R''
H_2L^1	H	H	H
H_2L^2	H	H	Me
H_2L^3	EtO	H	H
H_2L^4	H	MeO	H
H_2L^5	H	Cl	H
H_2L^6	Br	Br	H

(5)

The structure of monomeric hydrated Mn(III) tetra(4-*N*-methylpyridyl)-porphyrin pentachloride has been obtained [31]. It provides a second example of a planar diaqua-ligated metalloporphyrin with an extensive anion-water network which interdigitates between successive layers of porphyrins.



(6)

The synthesis and activity of a tailed chiral Mn(III)-tetraaryl-porphyrin (6) bearing a covalently bonded carboxylic group has been reported [32]. Its catalytic activity for alkene epoxidation by hydrogen peroxide has been explored and it was found to be an effective catalyst. Its salient feature is the presence of a stereogenic centre which is adjacent to a carboxylic group covalently bonded to the porphyrin ring through a single flexible chain.

A communication has appeared which outlines the first synthesis of a salicylhydroximato complex of Mn(III) [33]. It has been characterized by UV-VIS spectroscopy, elemental analysis and cyclic voltammetry.

The crystal structure of chlorobis(*N*-phenylsalicylideneaminato-*O*,*N*)manganese(III), a Schiff-base complex derived by an electrochemical route, has been reported [34]. The molecule possesses a trigonal bipyramidal configuration with Mn-O bond lengths of 1.866(2) and 1.858(2) Å while the Mn-N bonds are 2.193(2) and 2.158(2)Å.

Mono- and tetra-nuclear manganese(III) complexes of the tripodal tris[2-(salicylideamino)ethyl]amines have been reported [35]. X-ray crystallography indicates that the symmetry of the MnN_3O_3 coordination sphere in the two solvates $[MnL^2]\cdot 3H_2O$ and $[MnL^2]\cdot MeOH$ varies considerably with the former exhibiting C_3 symmetry while the latter possesses C_1 symmetry. These complexes have been characterised by electronic spectroscopy, magnetic studies, X-ray crystallography and cyclic voltammetry.

5.2.3 Complexes with oxygen and phosphorus donor ligands

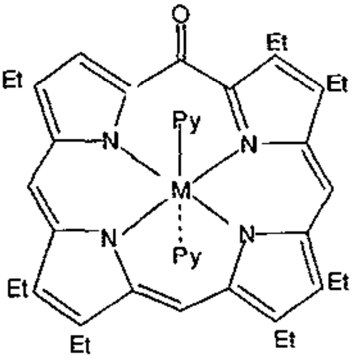
The kinetics of the oxidation of thiocyanate by Mn(III) in pyrophosphate medium has been established over the pH range 2-3. [36]. Manganese(III) was found to be stabilized by pyrophosphate in weakly acidic solutions and the nature of this complex was elucidated spectrophotometrically. It was found to be first order in Mn^{III} whereas the order in $[NCS^-]$ was unity, an increase in $[H^+]$ increased the rate.

5.2.4 Complexes with nitrogen donor ligands

The extensive electrochemistry of $[(TMPyP)Mn^{III}Cl]^{4+}(Cl^-)_4$ in dmf has been studied [37]. Conductometry, cyclic voltammetry, rotating disk electrode voltammetry, coulometry, thin-layer UV-VIS spectroelectrochemistry and ESR spectroscopy in dmf have been carried out. Three sequential electroreduction processes which involve a total transfer of five electrons have been observed. The first which occurs at $E_{1/2} = +0.11V$ involves a quasi-reversible metal-centred one-electron transfer, while the second at $E_{1/2} = -0.69V$, involves two electrons which are transferred to the conjugated porphyrin macrocycle. Finally, three subsequent two-electroreductions between −0.90 and −1.12 V are centred at the 1-methyl-4-pyridyl groups of the macrocycle.

The coordination patterns for oxophlorin ligands have been explored [38]. A dimeric Mn(III) complex of octaethyloxophlorin, $OEPOH_3$ $\{Mn^{III}(OEPO)\}_2$ has been identified and its cleavage into monomers in pyridine solution has been demonstrated. The structure of the monomer $\{(py)_2Mn^{III}(OEPO)\}$, (7), has been determined and shows manganese to be six-coordinate. The

Mn-N(porphyrin) distances of 2.022(4) and 2.018(3) Å are significantly shorter than the Mn-N(pyridine) of 2.376(4) Å consistent with the presence of high-spin Mn(III).



(7)

The efficient cleavage, in vitro, of a 35-mer corresponding to the (+) strand DNA sequence containing the first eight codons of HIV-1 TAT gene by a tailored cationic manganese porphyrin has been achieved [39]. Breaks have been observed at low concentrations (10nM) and with only 2.6 molecules of the metalloporphyrin conjugate per molecule of target.

The preparation, properties and electronic Raman spectra of di(cyano)phthalocyaninatomanganate(III) and -(II) has been described [40]. In particular, iodophthalocyaninatomanganese(III) reacts with cyanide in acetone to yield di(cyano)phthalocyaninatomanganate(II), whereas in dichloromethane, di(cyano)phthalocyaninatomanganate(III) is formed.

It has recently been demonstrated that the photochemistry of metallophthalocyanines in the presence of azaferrocene provides a new route to ring-reduced species [41]. The electronic absorption spectra show that Mn(II)-phthalocyanine (Mn(II)-Pc) coordinates azaferrocene in dmso solution yielding a 1:1 adduct. It is thought that a two-electron reduction takes place in which both the Mn centre and the macrocycle are reduced giving an Mn(I) species namely, $[Mn^{I}(Pc\text{-}3)]^{2-}$, Pc-3 = phthalocyanine trianion. In dmf solution a two electron reduction of the macrocyclic ligand is thought to have occurred generating the species $[Mn^{II}(Pc\text{-}4)]^{2-}$.

Studies on membrane-bound cytochrome P-450 mimics have led to the discovery of a two-phase system consisting of an aqueous sodium formate solution and a trichloroethane solution of Mn(III) (tpp) together with $[Rh^{(III)}(\eta^5\text{-}C_5Me_5)(bpy)Cl_2$ as a redox-active phase transfer catalyst [42]. This system was found to be capable of catalysing the epoxidation of alkene under an atmospheric pressure of oxygen.

5.2.5 Clusters

The second example of a high nuclearity Mn-oxo cluster which does not contain carboxylate ligands and a unique example of an anionic low-valent high-nuclearity cluster has been synthesised recently [43]. The reaction of $(Et_4N)_2MnCl_4$ with $MeC(CH_2OH)_3$ in acetonitrile in the presence of atmospheric oxygen gave the oxoalkoxomanganese cluster $(Et_4N)_2[Mn_{10}O_2Cl_8\{(OCH_2)_3CMe\}_6]\cdot 4MeOH\cdot 2H_2O$. Its crystal structure has been obtained and shows it to possess a decametallate core with fourteen doubly bridging and four triply bridging alkoxo groups. The cluster charge is consistent with the presence of eight Mn^{III} and two Mn^{II} centres. The room-temperature magnetism, 11.9 BM/Mn_{10}, is substantially smaller than the expected value of 16.2 BM for high spin manganese and is indicative of the existence of an antiferromagnetic interaction between the Mn sites.

5.3 MANGANESE(II)

5.3.1 Complexes with halide ligands

A reaction which may be viewed as the inorganic analogue of the Grignard reaction has been studied [44]. Specifically, the insertion of a metal into a phosphorus-halogen bond has been studied using crude manganese metal powder and dibromo- and diiodo-phosphoranes. The subtle nature of these reactions is evidenced by the fact that reaction of the phosphoranes R_3PI_2, (R = phenyl or substituted aryl) with manganese proceeds with insertion by the metal into P-X bonds yielding monomeric tetrahedral complexes whereas the reaction of R_3PX_2, (R_3 = mixed aryl/alkyl, trialkyl; X = Br or I) with manganese does not involve insertion into the P-X bond but leads to quantitative isolation of polymeric complexes $[\{MnX_2(PR_3)\}_n]$. The crystal structure of the monomeric complex $[MnI_2(PPh_3)_2]$ has been obtained. In a related paper [45], the reaction of a course-grain unactivated manganese powder with $PI_2(NMe_2)_3$ and $PI_2(C_6H_4SMe\text{-}o)_3$ has given rise to two unusual complexes. The complex $[\{MnI_2(P(NMe_2)_3]\}_2]$ possesses a dimeric structure in complete contrast to previously characterised complexes with this stoichiometry. This is thought to be a result of the high basicity and large steric requirements of the ligand. The complex $[MnI_2\{P(C_6H_4SMe\text{-}o)_3\}]$ is a simple monomeric complex with a didentate chelating moiety in which phosphorus and one sulfur atom coordinate to manganese.

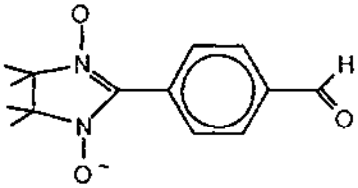
Rare examples of five-coordinate Mn(II) complexes possessing monodentate ligands have been synthesised recently [46]. The complexes $[MnBr_2(PEt_3)]$ and $[MnI_2(PMeEt_2)]$ were prepared by the mixing of stoichiometric quantities of the appropriate manganese(II) salt with the phosphine in dry diethyl ether/argon. X-ray crystal structures have been obtained for both complexes and show them to comprise polymeric chains with a single phosphine coordinated at each trigonal-bipyramidal centre. They were found to absorb one mole of O_2 per mole of complex in diethylether solution at –30°C.

The first example of a mixed phosphine-phosphine oxide manganese complex has been described [47]. It was obtained when a preformed solution of $[MnI_2(PPh_2Me)_2(O_2)]$ in pentane at –40°C under argon was allowed to warm to room temperature the complex $[MnI_2(OPPh_2Me)(PPh_2Me)]$ was obtained. When the same reaction was carried out under dry dioxygen both phosphines were oxidised yielding $[MnI_2(OPPh_2Me)_2]$. X-ray crystallography was performed and both these complexes were found to be pseudo-tetrahedral monomers.

5.3.2 *Complexes with oxygen donor ligands*

A new compound in the Mn(II)/$[Cu(opba)]^{6-}$, opba = *o*-phenylenebis(oxamato) system has been reported [48]. Specifically, the compound $MnCu(opba)(H_2O)_2 \cdot DMSO$ whose crystal structure has been obtained consists of oxamato-bridged $Mn^{II}Cu^{II}$ chains running along the *b* axis with an Mn---Cu intrachain separation of 5.387(1) Å. The Mn(II) ion is in a distorted octahedral coordination environment with four oxygen atoms coming from two oxamato groups in the equatorial plane and two water molecules in the apical positions. The compound is a metamagnet with a critical field of ca. 5 kOe.

The structure and magnetic properties of a layered molecular material which comprises manganese hexafluoroacetylacetonate and nitronyl nitroxide radicals have been described [49]. The reaction of $Mn(hfac)_2$, hfac = hexafluoroacetylacetonate, with 2-(4-benzaldehyde)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide, the NITBzald nitronyl nitroxide radical, (**8**), yielded the compound $[Mn(hfac)_2]_3(NITBzald)_2$ whose crystal structure was obtained. It consists of chains in which the $Mn(hfac)_2$ units are bridged by the nitronyl nitroxide radicals through the two oxygen atoms of the NO groups. The chains are connected by another $Mn(hfac)_2$ unit which is coordinated by the aldehyde oxygens of two NITBzald radicals belonging to different chains in such a way that planes parallel to the [201] crystallographic plane are formed.



(**8**)

Voltammetric and spectroscopic studies on the behaviour of Mn(II) and Mn(III) complexes with isoquinolinecarboxylic acid in aprotic media have been carried out [50]. These studies have concluded that this ligand behaves differently in comparison to other previously reported carboxylate ligands, no dinuclear complexes were obtained in solution presumably because a steric effect precludes a bridging interaction.

The reaction kinetics and mechanism of formation of $[MnMo_9O_{32}]^{6-}$ by hypochlorous acid oxidation of Mn^{2+} in the presence of molybdate has been studied [51]. The kinetics was found to exhibit autocatalytic behaviour. A mechanism involving sequential one-electron oxidation steps of Mn^{2+} through to Mn^{4+} via Mn^{3+} together with the equilibrium $Mn^{2+} + Mn^{4+} \rightarrow 2\,Mn^{3+}$ which favours Mn^{2+} and Mn^{4+} is able to account for the observed autocatalysis.

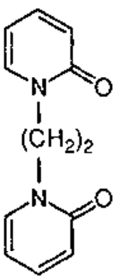
The molecular structure and magnetic properties of a series of compounds of general formula $M^{II}\,C_5O_5 \cdot 3H_2O$ including manganese has been documented [52]. The structures for Cu, Mn and Fe consist of chains in which the croconate anions bridge two metal ions by using three oxygen atoms in a monodentate and didentate fashion.

The coordination behaviour of *N*-substituted amino acids toward the Mn(II) ion has recently been investigated [53]. In particular, a series of complexes with $Ar\text{-}SO_2\text{-}N\text{-}$ amino acids of general formula Mn(Ar-SO_2-*N*-aminoacidate)$_2$·x solvent, where Ar-SO_2 = tosyl or benzenesulfonyl group. The crystal and molecular structures of the α-alanine and glutamine complexes has been reported. For both compounds the Mn(II) atom is in an octahedral environment surrounded by six oxygen atoms.

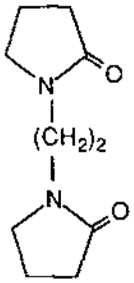
The EPR and optical absorption spectra of Mn^{2+} ions in lead acetate glasses have been investigated [54]. The EPR spectra indicate that there is a rapid fall in the intensity near the glass transition temperature T_g and that the site symmetry around the transition metal ion is octahedral.

An unsymmetrical dimanganese(II) complex with a structurally unique (μ-carboxylato)$_3$ unit has been synthesised and characterised [55]. The complex $[Mn\{HB(3,5\text{-}^iPr_2pz)_3\}(\mu\text{-}OBz)_3Mn(3,5\text{-}^iPr_2pzH)_2]$, $\{HB(3,5\text{-}^iPr_2pz)_3$ = hydrotris(3,5-diisopropyl-1-pyrazolyl)borate, $(3,5\text{-}^iPr_2pzH)_2$ = 3,5-diisopropylpyrazole, OBz = benzoate, was synthesised from a mixture of $[Mn(Cl)\{HB(3,5\text{-}^iPr_2pz)_3\}]$, $(3,5\text{-}^iPr_2pzH)_2$, $MnCl_2{\cdot}4H_2O$ and NaOBz. An X-ray crystal structure has been obtained for this complex.

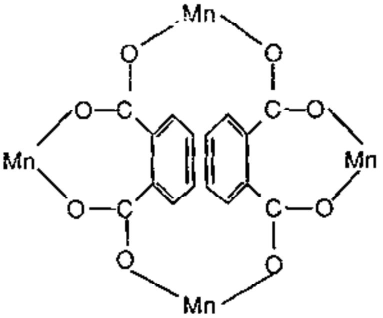
The potential and versatility of *N,N'*-ethylenebis(2-pyridone)], (ebpy), (**9**) and *N,N'*-ethylenebis(2-pyrrolidone), (ebpyrr), (**10**) as ligands in the formation of unusual framework coordination compounds has been demonstrated recently [56]. The complex $[Mn_2(ebpy)_3(NO_3)_4]_n$ was formed by treating manganese(II) nitrate with (**9**) while the reaction of hydrated erbium(III) nitrate with (**10**) gave $[Er_2(ebpyrr)_3(NO_3)_6]_n$. An X-ray analysis for the manganese complex shows the stoichiometry to be $[Mn(ebpy)_{1.5}(NO_3)_2]$ with Mn being six-coordinate. Adjacent manganese centres are linked *via* ebpy ligands in two orthogonal directions: in one case the -CH_2-CH_2- bridge geometry is *anti-* whereas in the other it is *gauche-* giving rise to 36-membered macrocyclic rings each containing four manganese atoms linked by one edge to form a chain of macrocycles extending along the crystallographic *b* direction.



(**9**)



(**10**)

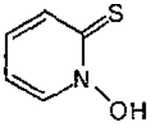


(**11**)

A novel cyclic tetranuclear manganese(II) complex which contains two phthalato bridging ligands, the first example of a sixteen-membered macrocyclic complex containing four manganese atoms has been synthesised [57]. The complex $[Mn_4(\mu\text{-}phth)(bpy)_8](ClO_4){\cdot}3H_2O$ was prepared by the addition of a methanolic solution of the phthalate piperidinium salt to a methanolic solution of manganese(II) perchlorate and bpy which was refluxed for 4 hours. A yellow powder was filtered off after cooling. An X-ray crystal structure has been obtained. The four manganese atoms are bridged by phth dianions, coordinated in didentate modes, through the oxygen atoms of their carboxylate groups as indicated in structure (**11**).

5.3.3 *Complexes with oxygen and sulfur donor ligands*

An example of the MnO_3S_3 system in the form of the redox triad MnL_3^z ($z = 0, \pm 1$) which incorporates the fungitoxic *O,S*-ligand 1-hydroxy-2-pyridinethione (**12**) has recently been synthesised [58]. The metal redox properties and EPR spectra have been analysed. Since single crystals of MnL_3 could not be grown, its facial nature was established via isomorphism with CoL_3 the structural characterization of which is reported.



(**12**)

5.3.4 *Complexes with oxygen and nitrogen donor ligands*

A heterodinuclear compound of formula $[Mn(Me_6\text{-}[14]ane\text{-}N_4)Cu(oxpn)](CF_3SO_3)_2$ where $(Me_6\text{-}[14]ane\text{-}N_4)$ = (±)-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane and oxpn = *N,N'*-bis(3-aminopropyl)oxamide has been synthesised [59]. Its crystal structure has been obtained and found to be composed of oxamido-bridged $Mn^{II}Cu^{II}$ dications and noncoordinated triflate anions. The Mn atom is in a distorted octahedral environment while the copper(II) ion is in square-planar surroundings. The intramolecular Mn---Cu separation is 5.436 Å. Magnetic susceptibility, and EPR and NMR spectroscopic studies have been conducted.

The synthesis of Mn(II) complexes with TCNQ (tetracyanoquinodimethane) radical ions has been achieved and their crystal structures and magnetic properties have been studied in order to explore the nature of the magnetic interaction between metal centres and TCNQ radicals [60]. In $[Mn_2(tpa)(\mu\text{-}O_2CCH_3)_2](TCNQ)_2\cdot 2CH_3CN$, tpa = tris(2-pyridylmethyl)-amine, the manganese ions were bridged by acetate ions with no room remaining for TCNQ coordination. Thus no magnetic interactions between the Mn ion and TCQN anion were observed due to a lack of coordination of TCNQ to the manganese ion. In $[Mn(tpa)(TCNQ)(CH_3OH)](TCNQ)\cdot 2CH_3CN$, one of the TCNQ ions which forms a column structure directly coordinates to the metal ion, and the Mn complex is successfully assembled into the organic radical network. Magnetic susceptibility measurements for the latter and $[Mn(tpa)(NCS)_2](CH_3CN)$ lead to the conclusion that the Mn ions are antiferromagnetically coupled through the TCNQ column where the Mn-Mn separation is 15.397(2) Å. A superexchange mechanism operates through the σ- and π- orbitals of the TCNQ column in $[Mn(tpa)(TCNQ)(CH_3OH)](TCNQ)\cdot 2CH_3CN$.

A series of hydroxo complexes of first -row divalent metal ions including Mn was synthesised with the aid of the hindered tris(pyrazolyl)borate ligand $HB(3,5\text{-}{}^iPr_2pz)_3$, hydrotris(3,5-diisopropyl-1-pyrazolyl)borate [61]. Using X-ray crystallography it was established that they comprise a dinuclear structure solely bridged with a bis(hydroxo) unit. It was of interest to study the fixation of CO_2 by these complexes. When reacted with CO_2 μ-carbonato species with a variety of coordination modes were obtained. The order of the coordination distortions of the carbonate groups for this series of complexes is: Zn>Mn~Fe~Co>Ni~Cu. On the other hand the reactivities of the hydroxo complexes toward CO_2 fixation was Zn>Cu>Ni~Co>Mn>Fe.

Manganese complexes which bear structural similarities to the active site of Mn-SOD and which are effective for superoxide dismutation have been synthesised [62]. The anaerobic reactions of $Mn(Cl)\{HB(3,5\text{-}^iPr_2pz)_3\}$ and $Mn(Cl)\{3,5\text{-}^iPr_2pzH\}\{HB(3,5\text{-}^iPr_2pz)_3\}$ [$HB(3,5\text{-}^iPr_2pz)_3$ = hydridotris(3,5-diisopropyl-1-pyrazolyl)borate; $3,5\text{-}^iPr_2pzH$ = 3,5-diisopropylpyrazole] with NaOBz gave the Mn(II) complexes $Mn(OBz)\{HB(3,5\text{-}^iPr_2pz)_3\}$ and $Mn(OBz)\{3,5\text{-}^iPr_2pzH)\}\{HB(3,5\text{-}^iPr_2pz)_3\}$. X-ray crystallography on the latter complex shows its structural features to be very similar to the active site of Mn-SOD namely a monomeric structure with an N_4O ligand set. The benzoate group is coordinated to the manganese atom unidentately while the non-ligating oxygen atom of the benzoate forms a hydrogen bond with the proton of the $3,5\text{-}^iPr_2pzH$ group. The mean H-O distance is 1.67(4)Å and H-N distance is 1.04(4)Å. The former complex possesses a N_3O_2 donor set. Both complexes were examined with respect to SOD activity and were found to be potent SOD mimics.

The electronic interactions in mixed-valence and mixed-metal ion clusters has been studied by inelastic neutron scattering [63]. The series of complexes $[Fe^{III}_2M^{II}O(OOCMe)_6(py)_3](py)$, (M = Mn, Fe, Co) was examined and significant differences in behaviour between the mixed-valence and mixed-metal systems were demonstrated. Energy transfers of magnetic origin were observed consistent with transitions between low-lying energy levels of the exchange-coupled metal ion clusters and excellent agreement was obtained with the Heisenberg spin-only formulation for both energies and transition intensities.

A new series of tripodal complexes with the condensation product of 2,2',2"-triaminoethylamine (tren) and 2-pyridinecarboxylaldehyde *N*-oxide (pyo) as the ligand have been obtained [64]. The crystal structures of $[Mn(pyo_3tren)](PF_6)_2{\cdot}C_2H_5OH$ and $[Co(pyo_3tren)](PF_6)_2{\cdot}CH_3CN$ have been determined. Both possess a heptacoordinate metal centre (MN_4O_3) with coordination polyhedra which are monocapped anti-trigonal prisms exhibiting C_3 symmetry.

Modelling studies have been carried out on Mn(II) Schiff base complexes in an effort to find (i) new modes for storing and releasing electrons and (ii) precursors for manganese aggregates [65]. In a preliminary report, the reduction and subsequent oxidation of [Mn(salophen)] and [Mn(salen)] have been described. The reduction of the former leads to an Mn(II) dimer from a twofold reductive coupling of imino groups on adjacent [Mn(salophen)] units as in equation 1.

$$2[Mn(salophen)(thf)] + 4Na \xrightarrow{thf,\ dme} [Mn_2(salophen)_2Na_4(dme)_6] \qquad (1)$$

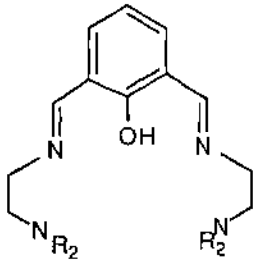
The Mn(II)....Mn(II) distance in the product is exceptionally short 2.699(2)Å. The conformation of the ligand gives rise to cavities which accommodate four centrosymmetric sodium cations completing the coordination with dme molecules. Magnetic susceptibility measurements between 1.9

and 300K were obtained. The data indicate an antiferromagnetic coupling for the μ-amido-Mn(II) dimer. The complex undergoes 4e⁻ oxidations by cleaving two C-C bonds across the dimer thereby restoring the original imino functionalities. In addition, two further electrons come from the oxidation of Mn(II) to Mn(III). For the [Mn(salen)] case, reduction gives a reactive compound which was subsequently oxidised as shown in equation 2. The complex obtained contains a tetrahedral arrangement of four unbridged Mn(III) atoms around a central oxo group. The magnetic susceptibility at 300K was 4.6μ_B.

$$4[\mathrm{Mn(salen)}] \xrightarrow{\text{Na, thf, diglyme}} \xrightarrow{\text{diglyme Et}_2\text{O, O}_2} [\{\mathrm{Mn_2(salen_2)}\}(\mu_4\text{-O})(\mathrm{NaDiglyme})_2] \quad (2)$$

The template reaction of 2,6-diformyl-4-methylphenol, 1,8-diamino-3,6-dialkyl-3,6-diazaoctane (alkyl = methyl or ethyl) and manganese(II) benzoate tetrahydrate in 1:1:2 molar ratio gave a macrocyclic tetranuclear Mn(II) complex, $[Mn_4(L^n)(PhCO_2)_6]$ where H_2L^n is a [2+2] macrocycle obtained from the condensation of 2,6-diformyl-4-methylphenol and 1,8-diamino-3,6-dialkyl-3,6-diazaoctane [66]. An adduct of the methyl complex $[Mn_4(L^n)(PhCO_2)_6(Me_2CHOH)_2 \cdot CH_2Cl_2$ has been characterised crystallographically and shows two pairs of Mn atoms to be bridged by a phenolic oxygen and two benzoate groups. The manganese ions in each pair are inequivalent. Magnetic susceptibility measurements were made in the temperature range 4.2-300K and are indicative of a weak antiferromagnetic interaction between the Mn(II) ions in each pair.

The synthesis of manganese complexes using 2,6-bis[2-(dialkylamino)ethyliminomethyl]-4-methylphenol, [alkyl = methyl (HL^1) or ethyl (HL^2)] has been achieved [67]. Two types of dinuclear complexes, $[Mn_2L(RCO_2)_2(NCS)]$, L = L^1 or L^2 (**13**) ; R = CH_3 or C_6H_5 and $[Mn_2LCl_3]$ (L= L^1 or L^2) have been obtained. The X-ray crystal structure for $[Mn_2L^1(CH_3CO_2)_2(NCS)] \cdot H_2O \cdot CH_3OH$ confirms the presence of a μ–phenoxo-bis(μ–carboxylato) bridging system. Magnetic susceptibility measurements over the range 4.2-300K indicate a weak antiferromagnetic interaction for the NCS complexes and no appreciable interaction for the chloride complexes.

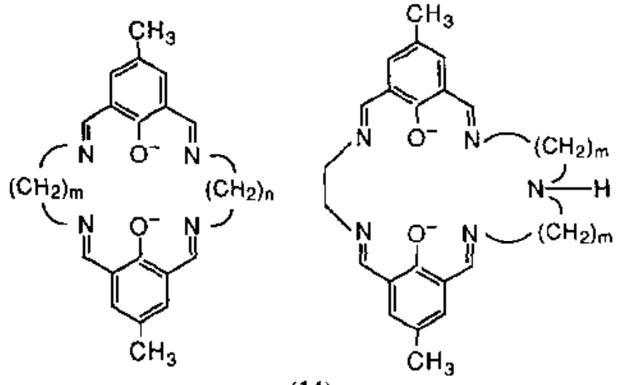


HL^1 R = CH_3
HL^2 R = C_2H_5

(**13**)

A communication has appeared which details a study of the geometrical significance of a μ-phenoxo-bis(μ–carboxylato)dimanganese core for catalase-like activity in dinuclear manganese(II) complexes [68]. The complexes $[Mn_2L^1(PhCO_2)_2(NCS)]$, {L^1 = 2,6-bis[*N*-(dimethylaminoethyl)iminomethyl]-4-methyl-phenolate(1–)}, $[Mn_2L^2(MeCO_2)_2(NCS)]$, {L^2 = 4-methyl-2,6-bis[*N*-(2-pyridylethyl)iminomethyl]-phenolate(1–)}, and $[Mn_2L^3(PhCO_2)_2(NCS)]$, {L^3 = 2,6-bis[bis(2-pyridylmethyl)aminomethyl]-4-methyl-phenolate(1–)} were characterised by X-ray crystallography. All were found to disproportionate H_2O_2 catalytically but vary significantly in their relative catalase-like activity.

Heterodinuclear $Cu^{II}Pb^{II}$ and $Cu^{II}M^{II}$ (M = Mn, Fe, Co, Ni, Cu and Zn) complexes containing macrocycles having dissimilar 4- and 5-coordination sites have been synthesised [69]. The heterodinucleating macrocycles with two 2,6-bis(iminomethyl)-4-methylphenolate entities combined through two lateral chains $-(CH_2)_2-$ and $-(CH_2)_mNH(CH_2)_m-$ (m = 2, 3) at the imino nitrogens (**14**) have been prepared as dinuclear $Cu^{II}Pb^{II}$ complexes which were then used as precursors to obtain the complex [CuM(L1)]XY, [XY = $(ClO_4)_2$, $(NO_3)(PF_6)$, $(AcO)(BPh_4)$] where L1 is a macrocycle with an N_2O_2 or N_3O_2 donor set. These complexes have been characterised and the crystal structure for $[CuMn(L1)](AcO)(BPh_4)$ has been obtained. The Cu(II) and Mn(II) atoms lie at the 4- and 5- coordination sites of the macrocycle with the acetate group bridging the two metal ions giving rise to a nearly square-pyramidal geometry for the Cu and a highly distorted six-coordinate environment for the Mn atom. The Cu-Mn separation is 3.122(2) Å. Results from cryomagnetic studies indicate an antiferromagnetic spin-exchange interaction within each molecule. Cyclic voltammetry studies have also been conducted.



(**14**)

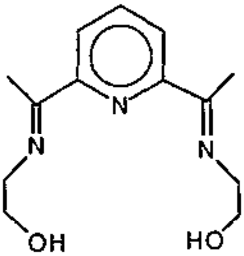
The structural characterisation and magnetic properties of the Ni(II) and Mn(II) chloride derivatives of 2-(2-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxy-3-oxide (NIT2-Py), have been reported [70]. Metal-nitroxide interactions of $-80\ cm^{-1}$ ($H = -2JS_iS_j$) were observed. This coupling constant is weak and is thought to be due to a reduced overlap of the magnetic orbitals owing to a peculiar geometric arrangement in the chelate. These chloride adducts illustrate the coordination of this free radical to weak electrophilic metal centres.

The first structurally characterised bridging unit with a monatomic carboxylate bridge in an Mn or Fe model complex has recently been demonstrated [71]. The complex $Mn_3(5\text{-}NO_2\text{-}salimH)_2(OAc)_4$ where $5\text{-}NO_2\text{-}salimH_2$ = 4-[2-(5-NO_2-salicylideneimine)ethyl]imidazole is the first μ-phenolato, μ-carboxylato-*O*, μ-carboxylato-*O,O'* type model for the 'carboxylate shift' in polymanganese and polyiron enzymes. The Mn-Mn distance is 3.270Å which is shorter that any previously seen Mn or Fe complex containing a monatomic carboxylate bridge.

Picolinic acid was employed in the preparation of the complex $[Mn(C_5H_4NCO_2H)(C_5H_4NCO_2)Cl]_2$ [72]. It was prepared by dissolving $MnCl_2{\cdot}4H_2O$ in ethanol with stirring at 298K, and picolinic acid dissolved in warm ethanol was then added dropwise. The room-temperature magnetic moment was found to be 5.8 BM. A crystal structure was obtained, each Mn atom is octahedral and is surrounded by two nitrogen atoms (Mn-N =2.268(6) Å), two carboxylic oxygen atoms (Mn-O = 2.191(4) Å), and two Cl^- ions which function as bridging ligands linking edge-sharing dimeric units. The complex was further characterised by IR and Raman spectroscopies. In related papers, the preparation, structure and spectroscopic details of a study on the reaction between Mn(II) ion and quinaldic acid [73] in the presence of azide and thiocyanate ions and quinolinic acid [74] has been described.

The coordination chemistry of quaterpyridine with transition metal ions has been explored [75]. The reaction of $Mn(ClO_4)_2{\cdot}xH_2O$ and $Mn(CH_3CO_2)_3{\cdot}xH_2O$ with 2,2':6',2":6"2"'-quaterpyridine, qtpy, in acetonitrile or methanol yielded the complexes $[Mn(qtpy)(H_2O)_2](ClO_4)_2$ and $[Mn(qtpy)(CH_3CO_2)(H_2O)](ClO_4)$ respectively. X-ray crystallography revealed that the latter complex is a distorted pentagonal-bipyramid with equatorial sites occupied by four nitrogen atoms of the quaterpyridine and one of the oxygen atoms of the chelating acetate ligand. The former complex may be described as a skew-trapezoidal-bipyramid. It was found to catalyse alkene epoxidation by PhIO. Cyclic voltammetry studies were carried out and a reduction was observed at −1.7V which is believed to be a ligand-centred reduction.

Seven coordinate manganese complexes of 2,6-bis[1-(2-hydroxyethylimino)ethyl]pyridine, L, (**15**), have been structurally characterised [76]. The complexes $[Mn(L)(H_2O)_2](ClO_4)$, $[Mn(L)(H_2O)_2](NCS)_2$, and $[Mn(L)(H_2O)_2](N_3)_2$, are approximately pentagonal bipyramidal with the five donor atoms from the ligand occupying the pentagonal plane and extensive hydrogen bonding is in evidence for all structures.



(**15**)

An unusual anion dependence on the product formed between Mn(II) and permanganate in acetate buffer has been observed [77]. Specifically, $[(bpy)_2Mn^{III}(\mu{-}O)_2Mn^{IV}(bpy)_2]^{3+}$ was isolated from solutions containing $Mn(II)/MnO_4^-/AcO^-$ and bipyridine when ClO_4^- was the counterion, whereas when NO_3^- was used $[(bpy)(H_2O)Mn^{III}(\mu{-}O)(\mu{-}OAc)_2Mn^{III}(bpy)(H_2O)]^{2+}$

was obtained. It has been postulated that in the buildup of the former complex, the acetate appears to bring the dimer unit together. The acetate subsequently departs and is replaced by the $(\mu\text{–O})_2$ group; $1e^-/2H^+$ or $1e^-/1H^+$ proton-coupled electron transfer has been found for the latter complex.

The preparation and characterization of binuclear complexes of manganese, cobalt nickel, copper and zinc with kanamycin (O-(3-amino-3-deoxy-α-D-glucopyranosyl)-)1→4)-2-deoxy-D-streptamine) sulphate have been described [78]. The spectral results indicate an octahedral coordination environment for the metal atoms.

The manganese(II) complex of a hydrazone ligand derived from pyruvic acid and semicarbazide has been prepared [79]. It has been characterized by IR spectroscopy, TGA, and X-ray diffraction analysis. The manganese atom is in a distorted octahedral environment with ONO donor ligands. The crystal structure contains one molecule of water of crystallisation and a tight hydrogen-bonding network in the crystal imparts high thermal stabiltiy to the complex.

The reaction of manganese(II) with antipyrine-4-azo-β-ethylcyanoacetate and antipyrine-4-azo-β-acetylacetone gave rise to complexes of the type ML_2 [80]. The electronic spectral and magnetic data indicate that the complexes are octahedral high-spin ones.

The synthesis and characterisation of mono and dinuclear complexes of manganese with 2,6-bis[*N*-(2-pyridylethyl)iminomethyl]-4-methylphenol have been described [81]. Methods of characterisation include infrared, electronic and ESR spectroscopies and magnetic suceptibility measurements.

5.3.5 Complexes with sulfur donor ligands

The reaction system $MnCl_2/2Na_2S_2/2.2CS_2/Et_4NSH/2Et_4NCl$ in acetonitrile gave $(Et_4N)_3[Mn(CS_4)_2Cl]$ in high yield [82]. A by-product, $(Et_4N)_2[MnS_{12}]$, was also isolated from the reaction mixture filtrate. X-ray crystallography determinations were made for these complexes. The complex $[Mn(CS_4)_2Cl]^{3-}$ has a square pyramidal geometry with the nearly planar five-membered chelate rings of the perthiocarbonate ligand in the *trans* orientation and the chloride in the apical position. The Mn-Cl distance is 2.400(2) Å and the Mn-S distance range form 2.35 - 2.56Å. In the $[Mn(S_6)_2]^{2-}$ complex the Mn atom is in a distorted tetrahedral environment in which the MnS_6 rings adopt a chair-type conformation.

An isomorphous and isostructural set of metal tetrathiolate complexes $[Et_4]_2[M(S\text{-}2\text{-}Ph\text{-}C_6H_4)_4]\cdot 2CH_3CN$, (M = Mn, Fe, Co, Ni, Zn, Cd, Hg) has been discovered recently [83]. The X-ray structural determinations have been carried out and show the complexes to possess high crystallographic symmetry. The salts crystallize in a space group which requires the anions $[M^{II}(SAr)_4]^{2-}$ to have rigorous S_4 point symmetry. Each of the anions has a tetragonally compressed $[MS_4]$ core. The Mn-S distances are 2.430(2)Å.

5.3.6 Complexes with nitrogen donor ligands

The synthesis and characterisation of compounds having the general formula *trans*-$M^{II}(py)_4(X_2)$, (M^{II} = V, Mn, Fe, Co, Ni, Ru; X = NCS, Cl, Br, I) have been achieved [84]. In particular the Mn(II) and V(II) compounds have been characterised by ESR spectroscopy using the iron, cobalt, nickel and ruthenium compounds as solid solvents. The g values of the manganese and vanadium compounds were 2 and 1.98 respectively.

An investigation of complex formation between Mn(II) and ethylenediamine-N,N'-disuccinic acid H_4L and its cyclized form H_3L has been carried out at 25°C and 0.1(KNO_3) ionic strength [85].

Complex formation between Mn(II) and bis(2-oxy-5-amylbenzyl)amine in a two phase system has been studied [86].

The complexation of Mn(II) and Zn(II) with py, 3Me-py and 4Me-py in dmf containing 0.1 mol dm^{-3} NEt_4ClO_4 as ionic medium at 25°C has been investigated [87]. For the manganese case, the formation of $[MnL]^{2+}$ was in evidence and a formation constant, reaction enthalpy and entropy were determined. The stability of $[MnL]^{2+}$ (M = Mn or Zn) complexes in dmf linearly increases with increasing basicity of the pyridine ligands. A plot of formation enthalpies and entropies versus ligand basicity was not linear. For both metal ions in dmf, formation of the 3-Me-py complexes is enthalpically less favourable and entropically more favourable than those of py or 4-Me-py.

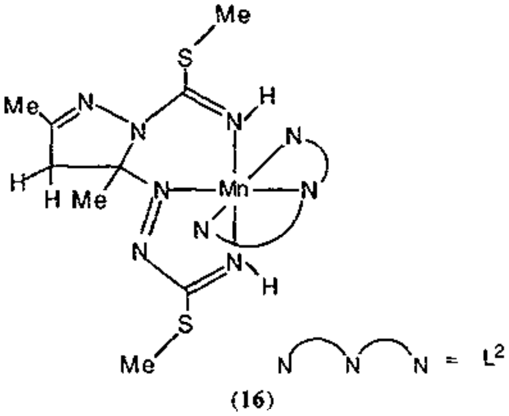
A molecular orbital study has been carried out in order to ascertain the nature of the interaction between metal centres in CN-bridged dinuclear Mn and Fe complexes [88]. Using the cyano-bridged cationic model complex, $\{[Mn]\text{-}CN\text{-}[Mn]\}^+$, where [Mn] = *cis* or *trans-mer*-$Mn(CO)_2(PH_3)_3$, extended Hückel MO calculations indicate that a weak Mn---Mn interaction exists which is mediated by the CN bridge. The energy and composition of the HOMO's was found to be determined by stereochemistry as is the Mn atom at which the HOMO is localized. The stereochemical control of the oxidation of dinuclear CN-bridged manganese cationic carbonyl compounds in terms of their electronic structure is discussed.

An investigation of the chemistry of complexes of the cage amine ligand sarcophagine (3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane) with manganese in both di- and tripositive states has been carried out [89]. In a related paper [90], the synthesis and structures of Mn(II) and Mn(III) diaminosarcophagine (1,8,-diamino-3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane) have been reported. Both complexes show that the six secondary nitrogen atoms of the ligand are bound to the manganese in a configuration which is approximately half way between a trigonal prism and an octahedron. For the Mn(II) complex Mn-N distances range from 2.228(3) to 2.253(3)Å with a mean of 2.238 Å while in the Mn(III) case they range from 2.115(4) to 2.127(4) with a mean of 2.122 Å.

The first stable eight-coordinate Mn(II) complex containing all donor atoms from chelating nitrogen ligands has been structurally characterized [91]. The reaction of $Mn(ClO_4)_2{\cdot}6H_2O$ with the tripodal amine ligand tris(2-methylpyridyl)amine yielded an eight-coordinate complex in which Mn(II) is surrounded by six pyridyl and two amine nitrogens to form a bicapped trigonal antiprism geometry. Oxidation of this complex with H_2O_2 produced a dimeric dioxo-bridged Mn(III, IV) complex $[Mn_2(\mu\text{-}O)_2(TMPA)_2](ClO_4)_3$ which exhibits antiferromagnetic coupling between two valence trapped Mn ions giving an $S = {}^1/_2$ ground state in its EPR spectrum and similar to that exhibited by the S_2 state of PSII. The Mn(II) complex is oxidized by oxygen in the presence of catechol in methanol solution.

A new tetradentate ligand, 1,3-pyrimidinyl(2,4,6-pyrimidinetrione) and its M(II) complexes including manganese have been prepared and characterised by elemental analysis, magnetic susceptibility measurements and electronic and IR spectroscopy [92]. The divalent metal complexes are tetrahedral and the 10 D_q values suggest that the ligand has a strength similar to ethylenediamine.

The synthesis of low spin $[Mn^{II}(L^2)_2]I_2 \cdot 2MeOH$ (**16**) has been described [93]. The ligand was prepared *in situ* by a condensation reaction of *S*-methylisothiosemicarbazide and pentane-2,4-dione with $MnCl_2$ in MeOH by air oxidation. An X-ray structure indicates that two tridentate ligands are coordinated meridionally with the polyhedron about the metal ion being best described as a Jahn-Teller compressed octahedron with two short Mn-N distances (1.89Å) in *trans* positions and four longer equatorial bonds (av. 1.985Å). The compression may also be ascribed to the restricted bite of the tridentate chelate.



(**16**)

5.3.7 *Clusters*

The reaction of divalent metal ions with the trivacant tungstophosphate ligands B-$\alpha\{PW_9O_{34}\}^{9-}$ and $\{P_2W_{15}O_{56}\}^{12-}$ which are derived from the well-known Keggin and Dawson-Wells polyoxoanions has been studied [94]. For the case of manganese a tetranuclear cluster, $K_{10}[Mn_4(H_2O)_2(PWH_9O_{34})_2] \cdot 20H_2O$ has been obtained. Its crystal structure and magnetic properties have been reported.

A facile synthetic route to discrete tetranuclear iron and manganese complexes which are significant additions to the class of polynuclear complexes has been obtained [95]. The manganese cluster, $[Mn_4(OEt)_4(EtOH)_2(DPM)_4]$, HDPM = dipivaloylmethane, contains an $\{Mn_4(OEt)_4\}^{4+}$ core in which the Mn atoms are in two distinct coordination environments. Two of the Mn atoms are in octahedral environments while the other two possess distorted square pyramidal geometry. These complexs has been characterised by electronic, Mossbauer and ^1H NMR spectroscopies. The data indicate that the cubes remain intact in solvent mixtures containing the appropriate alcohol.

5.4 MANGANESE(I)

5.4.1 Complexes with oxygen and nitrogen donor ligands

The preparation and characterisation of an unusual mixed-valence complex dianion $[Mn_3(CO)_6(\mu_2\text{-}NO_2)_4(\mu_2ONO)_2O]^{2-}$ has been achieved [96]. The complex formally contains two $[Mn^I(CO)_3(NO_2)_3]^{2-}$ units which coordinate through both $\mu_2\text{-}NO_2$ and μ_2ONO linkages to a central Mn^{II} ion. The PPN^+ salt has been fully characterised and shows the central Mn atom to lie at the centre of an inversion and is bound to six oxygen atoms and displays a trigonal elongation from octahedral geometry. The second Mn atom in the asymmetric unit is bound to three carbonyl groups, two nitrogen atoms and an oxygen atom with a slightly distorted octahedral geometry.

5.4.2 Complexes with oxygen and phosphorus donor ligands

The preparation and structural determination of the complex $[\{Mn(CO)_3(dppe)\}_2(\mu\text{-}acac)]ClO_4$ which constitutes the first example in which a κ(O), κ(O'), *β*-diketonato ligand holds two metals together and is the only bridge between them [97]. The disposition of the ligand may be described as W-shaped and coordination about the Mn atoms may be described as octahedral. The Mn-O distances are 2.03(1) and 2.016(9) Å while Mn-P distances range from 2.328(5)-2.349(5) Å.

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