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DIOXYGEN REACTIVITY-STRUCTURE CORRELATIONS IN MANGANESE(II) COMPLEXES

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CONTENTS

A. INTRODUCTION

The utilization of dioxygen in biological systems and organic syntheses is of the utmost importance. A feature shared by almost all biological dioxygen reactions, including the transport of O_2, is the involvement of metal ions via complexation and activation [1]. Some examples are cytochromes, superoxide dismutase, hemoglobin and myoglobin. The metals involved usually are manganese, iron and copper. Manganese, for example, has been implicated as a possible dioxygen evolving agent in photosynthesis. Calvin postulated [2] that a $Mn^{III}—O—O—Mn^{III}$ linkage could be important in the final dioxygen evolution step. Another aspect of dioxygen manganese reactivity is the well documented advantage of using manganese in some form as a catalyst to effect various organic oxidations. Manganese(III) is known [3] to oxidize alkylbenzenes, alcohols, carboxylic acids, phenols and ethers. MnO_2 has proved [4] to be a highly selective heterogeneous oxidant for amines, hydrazines, hydrocarbons, heterocyclic compounds and other natural products. Evidence has been presented in certain cases that an oxygen atom can be directly transferred from the oxidant to the substrate.

An intimate involvement of manganese and dioxygen can therefore be anticipated in numerous areas of research. The literature dealing with transition metal dioxygen complexes is vast and has been reviewed several times [5,6]. The reader is referred to these manuscripts in order to gain a fundamental understanding of the interactions between metal complexes and dioxygen. While these reviews were at the time rather comprehensive they, for the most part, dealt primarily with cobalt and iridium because these were the two metal systems which had received the most attention. More recently the synthetic iron models for the dioxygen-binding hemoproteins have been reviewed [7]. The renewed interest in the oxygenation of manganese complexes during the last decade prompts this review. While the higher oxidation state chemistry of manganese was reviewed in this journal in 1972 [8] little mention was made of manganese dioxygen reactions.

The nomenclature employed in this review will follow that set forth by Vaska [6]. The coordination of dioxygen is usually thought of in terms of an oxidative addition reaction. All known dioxygen complexes can be essentially divided into two types, superoxo and peroxo, with the valences of dioxygen being negative one and two, respectively. These two major types can in turn be further divided into smaller classes depending on the monomeric or dimeric nature of the species. It will be evident shortly that other terms must be involved to describe the manganese—oxygen linkage.

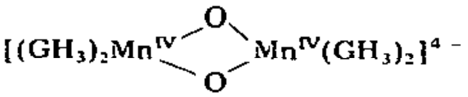
The scope of this review will span the areas of dioxygen reactivity with somewhat classical coordination compounds and selected biomolecules. Reports of reversible and irreversible dioxygen coordination as well as nonreactivity with dioxygen will be discussed. Reports dealing with the interaction of manganese complexes with dioxygen species other than molecular oxygen (e.g., O_2^- and O_2^{2-}) will also be mentioned. The discussion regarding inorganic systems will be subdivided according to the type of "manganese-complexed" polydentate ligand employed while the biological systems discussion will revolve around superoxide dismutase and manganese substituted heme proteins.

B. INORGANIC SYSTEMS

(i) Bidentate ligands

Manganese(II) complexes of a number of bidentate ligands wherein the donor set is O_2 have been recently studied by Sawyer and coworkers as models for photosynthetic dioxygen evolution. Chemical or electrochemical

($E^\circ = 0.3$ V) oxidation in basic medium of a dimeric manganese(II) gluconate complex [9,10], I, is reported to yield a species in solution probably formulated as



$$[(GH_3)_2Mn^{IV}(\mu\text{-}O)_2Mn^{IV}(GH_3)_2]^{4-}$$

where GH_3^{2-} represents the dianion of gluconic acid which results from the removal of the carboxylate proton and one of the secondary alcoholic protons. Under low dioxygen partial pressures the di-μ-oxo species is reported to evolve O_2 with regeneration of the manganese(II) precursor. This conclusion is based on electrochemical data alone and measurements of Ar-purged solutions of the di-μ-oxo material with an oxygen electrode gave no measureable O_2 partial pressure.

The complexes of manganese with a series of aliphatic and aromatic polyhydroxy ligands in basic media have been studied [11] by electrochemical, spectrophotometric and magnetic methods. The results indicate that glucarate, glycerate, L-tartrate and meso-tartrate stabilize the +2, +3 and +4 oxidation states of manganese in much the same manner as gluconate ion. The reactivity of these materials with O_2, however, was not noted. Contained in this report, nevertheless, was the observation that $[Mn^{III}(\text{catechol})_3]^{3-}$ was oxidized by dioxygen to a short-lived intensely blue complex which appeared to be a semiquinone. The complex, however, decomposed to give a green-yellow solution.

More recently sorbitol, a straight-chain hexitol, has been reported [12] in a corresponding study to complex and stabilize the +2, +3 and +4 oxidation states of manganese in aqueous alkaline solution. As in previous studies, the oxidation state assignments have been deduced from magnetic and visible spectral measurements on these species in solution. Molecular oxygen oxidizes the Mn(II) and Mn(III) complexes to the Mn(III) and Mn(IV) complexes respectively and in turn is reduced to the peroxide anion in each case. Electrochemical studies suggested peroxide as the reduced dioxygen species. Additional documentation for the tetravalent state has appeared [13] with the synthesis of bis(tetramethylammonium) tris(sorbitolato) manganese(IV) and the report that it is an ESR-active monomeric high spin complex of manganese(IV).

In another related study [14] the oxidation product of tris(3,5-di-tert-butylcatecholato)manganate(III), II, is reported to reversibly bind O_2 in DMSO solutions. The results of a series of UV-visible spectrophotometric, ESR and electrochemical experiments served as a basis for this conclusion. For low metal-to-oxygen ratios a 1 : 1 O_2 adduct is formed, whereas when the ratio is increased irreversible chemical oxidation of coordinated catechol by O_2 is the predominant reaction. Additional ESR data indicated to these workers that the primary step in the oxygenation of the complex is the irreversible formation of a mixed catechol-semiquinone complex and that it is this species that reversibly binds dioxygen. The formulation in solution of the oxygenated species was suggested to be $[(O_2)Mn^{III}(Cat)(semiquinone)_2(OH)_3]^-$. The mode of O_2 binding was not postulated.

With these bidentate O_2-ligands, we believe that the question of Mn oxidation state is still very much open to question. The isolation and characterization of a solid state material would certainly help to confirm or deny the conclusions inferred from solution chemistry. Manganese promoted oxidation of the O_2-ligand in solution must always be considered a distinct possibility. Solid state materials would enable more direct measurements to be made such as O_2 uptake, O_2-release, X-ray diffraction, etc.

In discussing the bidentate ligands with an O_2 donor set it should be noted that the rather common bis(salicylaldehydo)manganese(II) does not show any reactivity with O_2 [15].

Three studies employing bidentate ligands with an ON donor set have appeared. In 1968 Lewis et al. [16] reported on the properties of a series of manganese(II) complexes of the $Mn^{II}(SAL\text{-}NR)_2$ type where SAL-NR, III, is an acronym for the Schiff base formed between salicylaldehyde and a selected primary amine. The ON ligand field rendered the manganese(II) susceptible to oxidation by O_2 but the products of the reaction with O_2 were not characterized.

In conjunction with an investigation of the redox behavior of complexes of manganese 8-quinolinol(HQ), IV, reactivity of these materials with O_2 was also explored [17,18]. $Mn^{II}Q_2 \cdot 2\ H_2O$ was shown to react with O_2 or H_2O_2 in 50% CH_3OH/H_2O to yield $Mn_2^{III}OQ_4(HQ)_2 \cdot 2\ CH_3OH$ and $[MnQ]^+$. The oxygenated black crystalline material was reported to be high spin in the solid state and dissolved in acetonitrile and pyridine; whereas, in DMSO the proposed μ-oxo bridged species was found to be diamagnetic and was stated to arise from strong antiferromagnetic coupling of the type observed for other μ-oxo bridged binuclear Mn(III) and Mn(IV) complexes. The molecular form of the complex in DMSO was stated to be $[(HQ)Mn^{III}Q_2{-}O{-}Mn^{III}Q_2(HQ)]$. No rationale was given for this solvent dependent magnetic behavior. The interaction of several related 8-quinolinol manganese complexes with O_2^- was also explored electrochemically. $Mn^{II}Q_2 \cdot 2\ H_2O$ and $[MnQ_3]^-$ are stated to possess the ability to disproportionate O_2^- according to the following reaction

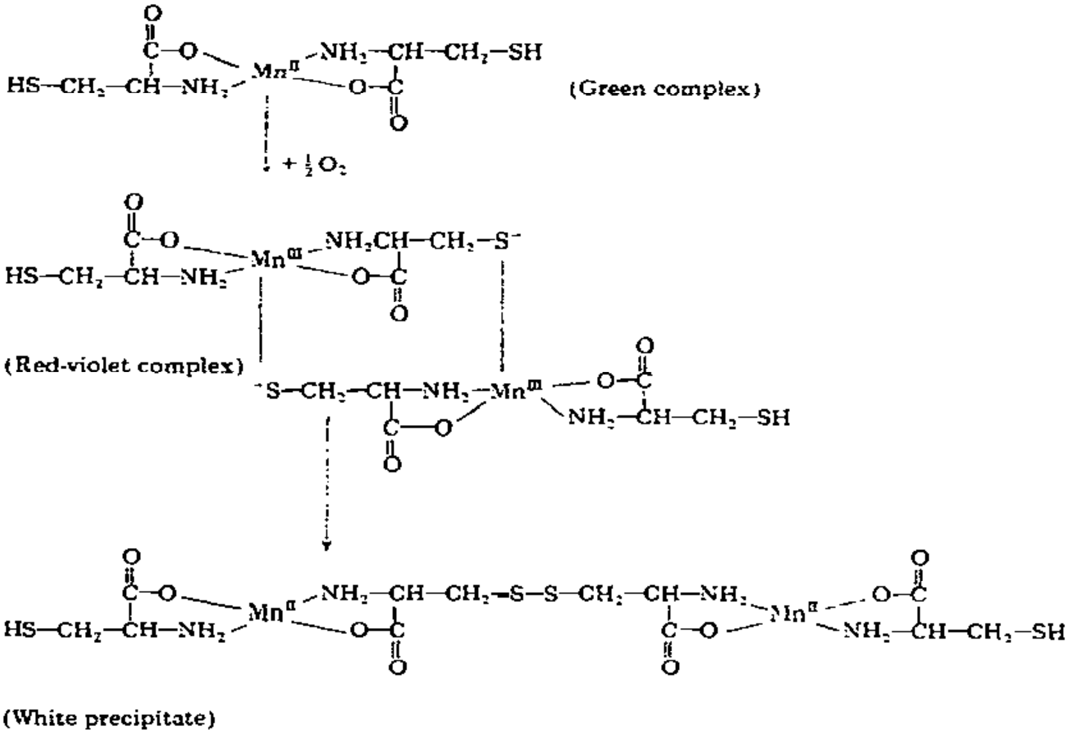
$$Mn^{II}Q_2 \cdot 2\ H_2O + O_2^- \rightarrow Mn^{III}Q_2(O_2H)(H_2O) + OH^-$$

The reaction is postulated to be favored as a result of the strong interaction of the product species, Mn^{III} and HO_2^-. A cyclic catalytic process modelled after superoxide dismutase was proposed based on the independently observed companion reaction

$$[Mn^{III}Q_3(O_2H)]^- + O_2^- \rightarrow [Mn^{II}Q_3]^- + O_2 + HO_2^-$$

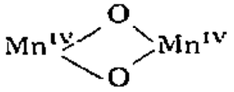
Further characterization of the oxygenated materials has not appeared.

Complexes formed between manganese(II) and cystine as well as several dipeptides have been prepared and their subsequent oxidation reactions have been discussed [19]. The green Mn^{II}(cystine)$_2$ complex in the presence of O_2 is oxidized to a red-violet complex in methanol solution. The red-violet complex rapidly decomposes to form a white precipitate, which was concluded to be a dinuclear complex with a disulfide bridge. The authors proposed the following mechanism



It should be noted that the existence of the peptide dimer, the nature of the Mn(III) complex and the fate of any dioxygen reactant are open to question. The dipeptide complexes were reported to yield Mn(III) products upon oxygenation; however, again no compound characterization was reported.

A study [20] conducted on the peroxydisulfate oxidation of Mn^{III}(pic)$_3$ · H_2O (pic = pyridine-2-carboxylate, V) seems pertinent here. In aqueous solution under reflux, $[S_2O_8]^{2-}$ oxidation yielded a green complex formulated as $Mn_2(pic)_4O_2$. Magnetic susceptibility and X-ray photoelectron spectroscopic data led the authors to conclude that each manganese exhibited the tetravalent state with two oxide ions bridging the metal centers (see below). In the experimental section of ref. 20 the authors state that the $Mn_2(pic)_4O_2$ complex was isolated as green crystals. It seems worthwhile to submit these crystals to an X-ray spectroscopist for possible structural information. The lability of the coordinated oxygen species was not described.



In 1967 Goodwin and Sylva [21] reported on an oxidized manganese complex of 1,10-phenanthroline (N_2 donor set), VI. The complex $[Mn_2(phen)_4O_2](ClO_4)_4$ was formulated to contain two oxide bridges between manganese(IV) centers. Nyholm and Turco [22] had earlier reported the synthesis of a similar compound with 2,2'-bipyridyl substituting for phen, except that mixed valence states (III, IV) for the manganese atoms contained within the molecular unit were postulated. In 1972 an X-ray crystal structure determination [23] of the bipyridyl complex revealed the complex indeed to have discrete Mn(III) and Mn(IV) ions from the inequivalence of bond lengths about the manganese ions. The corresponding (IV, IV) and (III, IV) complexes of 1,10-phenanthroline have recently been prepared [24,25] and partially characterized. Electrochemical experiments on these materials have yielded Mn_2(IV, IV), Mn_2(IV, III) and Mn_2(III, III) species. Yellow monomeric tris(1,10-phenanthroline) and tris(2,2-bipyridyl)manganese(II) complexes were not sensitive to dioxygen [26]. For both classes of complexes an irreversible electrochemical oxidation [25] of Mn(II) to Mn(III) was observed followed by decomposition of the Mn(III) product to form the previously mentioned dimeric Mn_2(III, IV) complex.

The dipyridyl Mn_2(III, IV) complex has been discussed [28] as a possible dioxygen-generating catalyst in the photochemical oxidation of water. Its use, however, in a cyclic system to mimic plant photosynthesis has been seriously questioned [27,29]. Nevertheless, kinetic and isotope studies [30,31] have indicated that a dimeric Mn(IV) group does produce dioxygen in 6—15 M sulfuric acid at 60—100°C.

Cooper and Calvin [32] have examined the electronic and IR spectra of these dimeric mixed valence state complexes. Broad bands, observed in the near IR region, were assigned to an inter-valence transition. No comparable bands were observed for the Mn_2(IV, IV) complex of phenanthroline. Lowering the pH of the solution reversibly cleaves the Mn_2(III,IV) dimers. Isotope labeling experiments with ^{18}O aided the assignment of the manganese—oxygen stretching frequency at 688 cm^{-1}. The authors concluded that these Mn_2(III, IV) complexes were compatible with those of other class II systems [33] in that there existed weak but non-negligible interactions between Mn centers. Cyclic voltammetry of the dipyridyl and phenanthroline Mn_2(III, IV) dimers yielded respectively reversible anodic waves at 1.25 V and 1.37 V vs. S.C.E. corresponding to oxidation of Mn_2(III, IV) to Mn_2(IV, IV). Photochemical experiments [34] on these interesting materials have shown that acidic solutions of Mn_2(IV, IV) are reduced to Mn_2(III, IV) in the dark. The Mn_2(III, IV) complex of dipyridyl was observed to reduce to the Mn(II) state via the Mn_2(III,III) state by photoexcitation.

Nyholm and Sutton [35] have examined the chemistry of Mn(II) and Mn(III) complexes employing the bidentate ligand, *o*-phenylenebis(dimethylarsine), VII, (As_2 donor set). All attempts to oxidize the bivalent manganese complex to the Mn(III) state were unsuccessful.

(ii) Tridentate ligands

A large amount of the data concerning manganese complexes of tridentate ligands involves Schiff-base type materials. Mukherjee and Ray [36] have studied the magnetic moments of some Mn(II) derivatives with ligands formed from selected aldehydes and amino acids, VIII, (O_2N donor set). The complexes synthesized were sensitive to dioxygen but the oxygenated species were not isolated nor characterized. West and co-workers [37] have described the magnetic properties of a series of manganese(II) complexes which incorporate dibasic ligands derived from substituted salicylaldehydes and variously substituted β-hydroxyanilines, IX, or anthranilic acid (O_2N donor set). The extreme sensitivity of the complexes to dioxygen was noted. The only data given on the oxygenated species were their black/brown color (probably MnO(OH)) compared with the yellow color of their manganese(II) precursor.

The complex chemistry of manganese(II) with the tridentate ligands 2,2′,2″-terpyridine and 2,2′,2″-terpyridine 1,1′,1″-trioxide has been studied [27,28,38] X and XI (N_3 and O_3 donor sets respectively). In contrast to the Mn(II)-dipy and -phen complexes, the electrochemical oxidation of the Mn(II)-terpy complex is not accompanied by a single straightforward rearrangement to a dinuclear manganese(III,IV) complex as occurred in the bidentate case. Mn(II)-terpyO_3 (O_3 donor set) exhibits discrete one-electron reversible oxidation-reduction processes that are consistent with the formation of stable mononuclear Mn(III) and Mn(IV) species. Again in contrast to their bidentate analogs dimerization of Mn(III) and (IV) was not observed. The manganese(IV) complex of 2,2′,2″-terpyridine 1,1′,1″-trioxide did react with water, a fact which was rationalized to the high positive Mn(IV)/Mn-(III) redox couple.

(iii) Tetradentate ligands

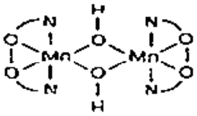
The most thoroughly studied category to date regarding manganese complexes and their reactions with oxygen species concerns tetradentate ligands. First to be dealt with will be N_2O_2 donor sets derived primarily from substituted salicylaldehydes and selected diamines. The initial report of an oxygenated manganese complex was that by Pfeiffer et al. [39] wherein the air oxidation of Mn($SALC_2$), XII, was investigated. The product of the reaction was postulated to be Mn($SALC_2$)OH with trivalent manganese in a high spin electron configuration. Air oxidation of the same precursor in a variety of organic solvents was reported [16] later to afford dark brown materials whose magnetic properties and composition were shown to be solvent dependent. Magnetic susceptibilities of most of these materials were temperature dependent which served as evidence for antiferromagnetic coupling between manganese centers. A dimer, $Mn_2(SALC_2)_2O_2$, was suggested in the latter case in contrast to the previously assigned mononuclear hydroxy compound. Little evidence for these assignments was provided.

Still further work has been performed [40,41] on $Mn(SALC_2)$ with respect to its reaction with dioxygen. A variety of structural proposals were presented for the different oxygenated products obtained in DMSO under different conditions. Various dark red-brown materials were proposed to exhibit one of the following manganese-oxygen links: $Mn^{III}—O_2—Mn^{III}$, $Mn^{IV}{=}O$ and $(Mn^{IV}—O)_n$. No X-ray data have appeared to support any of these bonding suggestions. Unfortunately most conventional physicochemical measurements cannot distinguish these three linkages. Further the manganese oxygen ratio in the former two cases provides no assistance in this matter. X-ray photoelectron spectroscopic data [42] on several of these complexes have been collected. Significant positive chemical shifts were observed in going from Mn(II) precursor to select oxygenated manganese. In certain cases, however, a surprisingly near zero shift was observed. These results suggested that either (1) an increase in coordination number accompanies oxygenation, (2) a significant spin—spin interaction exists between oxidized manganese centers, (3) the manganese(II) state has been retained, or (4) the higher valence state manganese complexes are significantly more covalently bound. Expansion of this study to numerous other manganese systems suggests that a poor correlation exists between electron binding energy and formal manganese oxidation state.

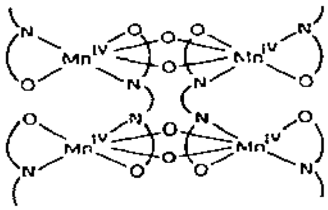
More recently pyridine solutions of $Mn(SALC_2)$ have again been reacted [43] with O_2. In this case the ethylene backbone has been substituted with methyl and/or phenyl groups. In boiling pyridine or pyridine at −15°C, the major product was reported to be $Mn(SALC_2)(OH)$ together with an appreciable quantity of MnO_2. Dioxygen uptake experiments performed at −15°C indicated that each Mn atom reacted with approximately 0.6 oxygen atom. These results forced the authors to conclude that a mixture of products was obtained. Reversibility of the oxygenation reaction that produced $Mn(SALC_2)(OH)$ was not possible in any case examined. Again the $Mn^{III}—OH$ formulation must be viewed with considerable caution since elemental analysis cannot distinguish a water of hydration from a bound hydroxide.

A related complex, $Mn(SALC_3)$, has received much study and a number of contradictory results have also been obtained on this system. Johnson and Beveridge [44] reported that $Mn(SALC_3)(H_2O)$ reacted reversibly with O_2, N_2 and CO forming 1 : 1 gas adducts as evidenced by gas uptake experiments and IR band assignments. The N_2 and CO uptake experiments have since been shown [45] to be inconclusive. On the other hand, these workers confirmed that $Mn(SALC_3)$ did absorb one mole of O_2 per mole of Mn. The product of this reaction was not characterized. Several years later in a separate study [46] $Mn(SALC_3)$ was suspended in benzene and exposed to air. The formulae postulated for the two products obtained via this method were

$[Mn(SALC_3)(O_2)(H_2O)]$ and $[Mn(SALC_3)(O)(C_6H_6)_{0.5}]$. If the parent complex were suspended in pyridine, $[Mn(SALC_3)(O)(Py)]$ was the suggested product. No definitive evidence in any of these three cases was presented regarding the bonding state of manganese or oxygen. A re-examination [47] of this latter product via X-ray structural analysis revealed it to be dimeric with each manganese atom octahedrally coordinated to the non-planar $SALC_3$ ligand and to two bridging hydroxy groups. Four molecules of pyridine were associated with each dimeric unit; however, they were not directly bonded to the manganese atoms. The authors pointed out that the *cis* hydroxy groups imply a reaction proceeding through an initial dioxygen adduct. The close Mn—Mn distance of 2.72 Å was employed to explain the antiferromagnetic nature of the complex. While the authors prefer two formally Mn(III) centers which are hydroxy bridged, the X-ray and magnetic data could have been interpreted as two Mn(IV) centers bridged by two oxide ions.

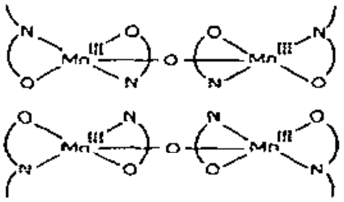


A somewhat more extensive study [48,49] involving $Mn(SALC_n)$, where $n = 2—10$, and dioxygen has now been carried out. Reactivity with O_2 has been demonstrated to be a function of the methylene carbon chain length which joins azomethine donors. All manganese(II) materials rapidly reacted with O_2 when moist or dissolved in pyridine, but only $C_6—C_{10}$ derivatives reacted in the solid state. Regardless of the manner of oxygenation the uptake of O_2 corresponded to $n_{O_2}/n_{Mn} = 0.5$. The C_6, C_7 and C_{10} analogs appeared to react fastest while electron withdrawing groups on the aromatic ring retarded any reaction with O_2. Although possessing quite different solubility properties all oxygenated products exhibited the same empirical formula, $Mn(SALC_n)(O)$. Each compound was ESR active and exhibited an IR spectrum identical to its precursor except for two new intense sharp bands ca. 615 cm^{-1} assignable to Mn—O vibrational modes. Upon heating the oxygenated materials to approximately 150°C in vacuo weight loss, equivalent to one oxygen atom per manganese, was observed albeit with some sample decomposition. The above data along with low temperature magnetic susceptibility data suggested to these workers that all fully oxygenated complexes in this series have a di-μ-oxo manganese(IV) linkage. The great insolubility of the solid state and DMSO oxygenated products indicated that the di-μ-oxo linkage is part of a polymeric array (see below). In the light of this study earlier oxygenation products (e.g., $[Mn_2(SALC_2)_2O_2]$ and $[Mn(SALC_3)(O)]$)



have been proposed to be di-μ-oxomanganese(IV) materials rather than μ-peroxo or di-μ-hydroxomanganese(III) species.

Oxygen uptake measurements as a function of time have revealed additional interesting facets to this study. Oxygenations are two-step processes. An initial O_2 uptake to $n_{O_2}/n_{Mn} = 0.25$ occurred followed by uptake to 0.5. This was observed with each ligand (C_2—C_{10}) in (1) the solid state where applicable, (2) suspended in DMSO and (3) dissolved in pyridine. In the $SALC_8$ case an intermediate oxidized product, $[Mn(SALC_8)(O)]$, has been isolated and characterized. Based on $\mu_{eff} = 4.8$ B.M. at room temperature, ESR inactivity and dioxygen reversibility, a μ-oxomanganese(III) material was proposed.



A related yet different approach to the study of manganese complexes of $SALC_n$ has been reported by Boucher and co-workers [50,51]. Employing a sec-butyl group in the five position of the SAL moiety in order to enhance complex solubility, these workers synthesized two manganese(III) chelates wherein $n = 2$ and 3. Mild base hydrolysis of chloroform solutions of the Mn(III) complex, $[Mn(BuSALC_n)(H_2O)]\ (ClO_4)$, in air yielded red-brown materials of general formula $[Mn_2(BuSALC_n)_2(O)_2] \cdot x\ H_2O$. The complexes were dimeric in $CHCl_3$ and showed a reduced room temperature magnetic moment, $\mu_{eff} = 2.5$ B.M. IR and visible spectral properties were reported to be consistent with a di-μ-oxomanganese(IV) ring. Electrochemical and deoxygenation studies were performed on these materials for comparison with the analogous dipyridine and 1,10-phenanthroline species.

A re-examination [52] of these complexes using low temperature magnetic susceptibility techniques has revealed that the previously formulated $Mn_2^{IV}O_2$ complexes would be better described as μ-oxohydroxomanganese(III, IV) species. In this same report circular dichroism measurements were made on several new manganese(III, IV) dimers of $BuSALC_2$ where the diamine is now optically active and previously resolved. The results on $[Mn_2(BuSALC_2)(OH)(O)] \cdot x\ H_2O$ implied that a mixture of various geometrical and optical isomers must be present in solution. The mixed valence dimers exhibited electronic transitions in the ligand field and charge-transfer regions arising from both Mn(III) and Mn(IV) sites.

Manganese(II) complexes of another tetradentate system possessing an O_2N_2 donor set, bis(salicylidene)-*o*-phenylenediamine, XIII, have been subjected [53] to oxygenation studies. The complex that was isolated upon exposure to atmospheric oxygen was formulated as Mn^{III}(SALOPHEN)(OH). The complex failed to obey the Curie-Weiss law and its temperature dependence was ascribed to a weak antiferromagnetic interaction. It seems conceivable that this material may also be dimeric and analogous to the previously described oxygenated $SALC_n$ complexes.

Tetradentate ligands with a N_4 donor set have received considerable attention lately. The first ligand system in this regard was phthalocyanine, XIV. Elvidge and Lever [54] first noted the behavior of $Mn^{II}(Pc)$ when the complex was dissolved in pyridine and allowed to stand in the air. Purple crystals of the oxygenated complex were isolated and initially formulated as $(Pc)Mn^{IV}{=}O$. Subsequent to this result an X-ray structural study [55], however, revealed the complex to be a μ-oxodimanganese(III) species. Each manganese(III) was pseudo-octahedral with pyridine and bridging oxide occupying axial sites with the four nitrogen atoms of Pc serving as the in-plane field. An oxygen adduct intermediate was proposed in this study. Calvin and coworkers [56] later proposed that the intermediate was $(HO)Mn^{III}(Pc)$. This apparently is not the case since $(HO)Mn^{III}(Pc)$ has been shown [57] to have a different spectrum and different chemistry from that of the intermediate. In a later report [58] other nitrogenous bases besides pyridine were also shown to be effective in producing $[(B)(Pc)Mn{-}O{-}Mn(Pc)(B)]$.

The formation of a dioxygen complex of $Mn^{II}(Pc)$ in poly(2-methyl-1-vinylimidazole)-N,N-dimethylformamide solution has recently been communicated [59]. This conclusion was demonstrated based solely on comparison of electronic absorption spectra and ESR measurements of $Mn^{II}(Pc)$ and its oxygenated partner. Changes observed in the ESR spectra were the disappearance of manganese(II) complex absorption features and the appearance of a strong peak centered at $g = 2.0015$. These changes were attributed to the formation of O_2^- following transfer of one electron from Mn(II) to O_2 resulting in the formation of undetectable Mn(III). It should be noted that under close examination the ESR data discussed in the text of this paper do not match the ESR data which may be calculated from the figures available in the paper. Presumably this is a typographical error but none the less such an irregularity should be noted. Because of the absence of any effect of poly-(2-methyl-1-vinylimidazole) on the electronic spectrum of the complex the authors concluded that the composition in solution was $(DMF)Mn^{III}(Pc)(O_2)$. No oxygenated materials were isolated.

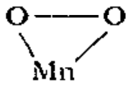
A re-examination [60] of $Mn^{II}(Pc)$ and its reactivity with dioxygen in purified dimethylacetamide (DMA) is reported to generate an exceptionally thermally stable, sparingly soluble 1 : 1 adduct. This species was characterized by elemental analysis, magnetic measurements, IR, electronic, ESR and mass spectroscopy. In the presence of certain nitrogenous ligands or in sunlight, in vacuo, the adduct is converted back to $Mn^{II}(Pc)$. Addition of imidazole to the oxygen adduct dissolved in aerated DMA generated the familiar μ-oxodimanganese(III) material. The 1 : 1 adduct was formulated as $PcMn^{III}(O_2^-)$ with a moderately ionic bond. This conclusion was based on the similarity of the solution spectra of typical $Mn^{III}(Pc)X$ complexes and the oxygen adduct and the appearance of a band in the ^{16}O and ^{18}O IR spectra at 1154 cm^{-1} and 1094 cm^{-1} respectively which was assigned to a coordinated terminal superoxide ion. It should be noted that the employment of IR evidence to deduce the nature of coordinated reduced oxygen has been seriously criticized [61].

A limited investigation [62] of the ESR and visible spectra of manganese(II) 4,4′,4″,4‴-tetrasulfophthalocyanine, [Mn^{II}(TSPC)], has revealed that in the presence of axial ligands such as azide, cyanide or imidazole, oxidation of the manganese(II) chelate occurs in aqueous solution. The rate of the oxidation process increased with increasing concentration of axial ligand. There was no evidence for the presence of a dioxygen complex. Oxidation to a manganese(III) complex was suggested and by analogy with Mn^{II}(Pc) the general formula Mn^{III}(TSPC)(OH)L was proposed. Some additional information, however, has been provided that shows the ESR of Cookson et al. [62] (their Fig. 5) is apparently identical to the ESR spectrum of the dioxygen adduct of Lever et al. [60]. As a result the original identification of the species in Fig. 5 of ref. 62 as a Mn(II) derivative appears to be in error.

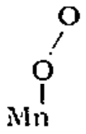
Meso-tetraphenylporphyrin(TPP), XV, provides a second N_4 donor set which has received considerable study in the last few years. Basolo and co-workers [63,64] have examined the reaction of Mn^{II}(TPP)(Py) with dioxygen in toluene at −79° C. Dioxygen is reported to reversibly bind to manganese with replacement of pyridine to form a five coordinate complex as suggested by optical and ESR measurements in solution. Under these conditions after 14 h exposure to one atmosphere O_2, 70% of the initial manganous complex could be regenerated. In contrast, oxygenation of Mn(TPP)-(Py) in toluene at higher temperature (i.e. room temperature or even at −45° C) led to irreversible oxidation. In methylene chloride the manganese(II) complex was even more prone to oxidation. Further study [65] of this system by Reed and co-workers supported the hypothesis that pyridine must be removed before dioxygen can react. As further support, solutions of Mn^{II}(TPP)(Py) which contained a small molar excess of pyridine were reported to be essentially unaffected by dioxygen. It should be noted, however, that in this experiment slow irreversible oxidation to manganese(III) occurred over several hours.

Four coordinate Mn^{II}(TPP) on the other hand, rapidly and irreversibly oxidized in dioxygen to an undescribed manganese(III) product. The high preference for five coordination on the part of high spin manganese(II) in Mn^{II}(TPP) has been advanced to explain this lack of dioxygen reactivity. The preference for five coordination could be traced [66] to the inability of the ligands to cause adoption of a low spin state which would permit manganese to move to an in-plane position. This same argument has been employed to account for the fact that manganese hemoglobin and Mn($\alpha,\alpha,\alpha,\alpha$-$T_{piv}$PP)L (e.g., "picket-fence" porphyrin) do not carry O_2. Oxygenation of a toluene-THF solution of Mn^{II}(TPP) at −90° C was stated in this study to be reversible and formation of a five-coordinate complex, Mn(TPP)(O_2), was postulated. No characterization of this product, however, has been communicated.

A $Mn^{IV}(O_2^{2-})$ valence formalism in which the Mn(IV) is in a $^4(t_2^3)$ ground state has been suggested from the Basolo et al. [63,64] investigation. Based primarily on ESR evidence an "edge-on" structure (A) has been advanced for the manganese-dioxygen linkage rather than a bent structure (B) [65]. Ab initio calculations [67] have been carried out for the edge-on and bent structures of the $Mn(TPP)O_2$ system in addition to twelve other probable manganese-dioxygen configurations. A stable configuration was predicted for both edge-on and bent arrangements but the calculations suggested a $Mn^{III}(O_2^-)$ rather than $Mn^{IV}(O_2^{2-})$ formalism.



A



B

A detailed ESR study of the reversible dioxygen adducts of Mn^{II}(TPP) and manganese octaethylporphyrin has recently been reported [68]. Solely on the basis of the magnetic resonance parameters obtained, it was possible to rule out most possible combinations of an odd-electron configuration and manganese—dioxygen binding geometry. These results coupled with qualitative bonding considerations again supported the description in terms of a Mn^{IV}–O_2^{2-} valency formalism with a symmetric, edge-on dioxygen (A).

Equilibrium constants incorporating derivatives of this system have been measured [69] for the reaction

$$Mn[T(para\text{-}X)PP](L) + O_2 \rightleftharpoons Mn[T(para\text{-}X)PP](O_2) + L$$

where X=Cl, F, H, CH_3 and OCH_3 and L = pyridine. Spectrophotometric titrations of toluene solutions at −78°C with molecular oxygen confirmed the 1 : 1 stoichiometry of the porphyrinatomanganese—dioxygen complex. Log K_{eq} exhibited some dependence on the para-substituent (e.g. −5.75 for X=OCH_3 and −6.53 for X=Cl). The experimentally determined equilibrium constants were fitted to the Hammett equation ($-\log K_{eq}$ vs. 4σ) to give a Hammett P value of -0.41 ± 0.08. An equilibrium constant for the oxygenation (−75°C) of four coordinate Mn^{II}(TPP) was estimated as K_{O_2} ca. $10^{2.1}$ mm^{-1}.

The synthesis of polystyrene-covalently bonded metalloporphyrin complexes and their reaction with dioxygen have been published [70]. Although only the cobalt(II) complex with O_2 was studied, both manganese(II) and (III) were prepared. Since the latter was prepared by air oxidation of Mn(II) it is entirely conceivable that a manganese—dioxygen complex mediated the reaction.

It is also interesting to note that the tendency for oxygenation is considerably reduced [71] for Mn(II) complexes of N-methylporphyrin relative to porphyrin. This change was attributed to the fact that the manganese is not able to lie in the plane of the four nitrogen atoms of the deformed porphyrin ligand.

Several neutral N_4 tetradentate ligands have been studied with manganese, such as the 14-membered macrocyclic ligand, meso-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane ([14]-ane N_4), XVI. Mn([14]-ane N_4)X_2 complexes [72] were found to be sensitive to dioxygen in solution but when dry in the solid state these materials could be handled for short periods of time in the laboratory atmosphere. Nitromethane and acetonitrile solutions of these complexes are oxidized to manganese(III) products; however, the properties and characteristics of the oxygenated materials were not reported. Extended exposure to O_2 (days) produced dark insoluble materials which appeared to be hydrous oxides of manganese.

In a related study [73] these same workers synthesized a series of Mn(II) and Mn(III) complexes of the dianionic conjugated cyclic Schiff-base ([14]-12eneN_4), XVII. The isolated Mn(II) complexes, Mn([14]12eneN_4)(L), were observed to be five-coordinate with the fifth ligand being triethyl- or tri-n-propylamine which had been part of the original reaction mixture. The proposed geometry of the neutral complex was square pyramidal with the metal ion displaced from the N_4 plane toward the amine adduct. Purging toluene or benzene solutions of the Mn(II) complex with dry oxygen gas yielded a dark amorphous solid which was again postulated to be an oxide of manganese. The Mn(III) compounds, Mn([14]12eneN_4)X, are stable in the solid state under dry N_2 gas. Exposure to the atmosphere over a period of weeks results in slow discoloration, which is accompanied by an odor characteristic of ligand decomposition. This observation is no doubt more attributable to hydrolysis than to oxygenation.

Linear tetradentate ligands with a N_4 donor set have been considered [74] in the literature. Air stable solid Mn(II) complexes employing Schiff bases formed from pyridine-2-carboxaldehyde and selected diamines, XVIII, have been synthesized. None of these high spin complexes, Mn($PYC_{2(3)}$)$(X)_2$, regardless of the anion (X) employed were found to be sensitive to dioxygen even in a variety of solutions. At this point it might be as well to indicate that while Mn^{II}($SALC_n$) is extremely dioxygen sensitive, Mn^{II}(PYC_n) is unreactive with dioxygen under mild conditions. A summary discussion of relationships of this type will be presented later.

Chiswell [75] has described the reactivity of dioxygen with a series of neutral Mn(II) complexes containing the tetradentate ligand (N_4 donor set) derived from α-diketones and 2-pyridylhydrazones, XIX. Reactions in cold pyridine were studied. Each oxygenation complex had a Mn/O ratio of 1.0/1.3. The odd manganese to oxygen atom ratio was explained by the isolation of four products via fractional crystallization and column chromatography. The data led the author to postulate a di-μ-hydroxomanganese(III) species similar to that previously suggested for Mn($SALC_3$)(OH). The three remaining products were empirically formulated as (i) MnO_2, (ii) Mn(N_4ligand)(Py)-(O_2), and (iii) Mn(N_4ligand)(Py)(O). The latter two materials may, in fact, be dimeric. Assignment of these stoichiometries was based essentially on elemental analysis data. No reversible oxygenation was noted.

In concluding this section we should note, derived from salicylaldehyde and 1,2,4,5-tetraaminobenzene(TSAB), XX, a unique ligand which binds two metal ions. The synthesis of the ligand, which incorporates two N_2O_2 donor sets, and its manganese(II) complex have been reported [76]. The isolated complex has the empirical formula $Mn_2(TSAB)(L)$ where L = H_2O and $N(C_2H_5)_3$. Surprisingly, no mention was made of dioxygen reactivity.

(iv) Pentadentate ligands

The dioxygen reactivity of manganese complexes employing linear and macrocylic pentadentate ligands have been actively studied over the last few years. Five coordinate high spin, yellow, manganese(II) complexes of ZSALRDPT, XXI, have been prepared and characterized [77]. Each complex reacted rapidly with dioxygen in solution, and one derivative (Z=3-OCH_3, R=CH_3) reacted in the solid state. The extent and rate of O_2 uptake was observed to be a function of the aromatic (Z) and amine (R) substituents. Electron donating groups promoted more extensive oxygenation for a specific time frame than did electron withdrawing groups. Detailed oxygenation studies revealed at least two different operating oxygenation processes. Initial O_2 uptake was rapid (0.5 h) for all but two derivatives (R=n-C_3H_7 and C_6H_5) corresponding to $n_{O_2}/n_{Mn} = 0.5$. Additional O_2 consumption occurred thereafter at a very different rate which depended on Z and appeared to continue indefinitely regardless of the solvent. The two-step oxygenation was attributed to first irreversible oxidation of Mn(II) → Mn(III) followed by oxidation of the ligand. The secondary oxidation was inhibited sufficiently in two cases (Z=5-NO_2, R=H, CH_3) such that products Mn(5-NO_2SALDPT)(OH) and Mn(5-NO_2SALMeDPT)(OH), were isolated and characterized. Physical measurements on these two materials suggested them to be normal high spin manganese(III) species.

A re-investigation [78] of these reactions under rigorously anhydrous conditions yielded similar results except that the isolated compounds were formulated as $[Mn(5\text{-}NO_2SALRDPT)]_2O_2$. Extension to the 3-nitro derivative gave an analogous material. Heating the materials in vacuo (110°C) liberated weight equivalent to 32 a.m.u. In addition to recovering the manganese(II) precursor, thermal gravimetry coupled with chemical ionization mass spectrometry verified that the material being removed (150°C) was O_2. A μ-peroxo-manganese(III) structure was postulated for the nitro-derivatives. A mechanistic scheme was suggested by analogy to the oxygenation of cobalt(II) chelates [79].

$$Mn^{II}L + O_2 \rightleftharpoons LMn^{III}(O_2^-)$$

$$LMn^{III}(O_2^-) + LMn^{II} \rightleftharpoons LMn^{III}\text{—}(O_2^{2-})\text{—}Mn^{III}L$$

Production of the Mn^{III}—(OH^-) species was postulated to arise via (1) deoxygenation of μ-peroxomanganese(III), (2) outer sphere oxidation of hydrated manganese(II) followed by (3) hydrolysis to yield $LMn^{III}(OH)$.

$$LMn^{III}\text{—}O_2\text{—}Mn^{III}L + 2\ H_2O \rightarrow 2\ LMn^{II}(H_2O) + O_2$$

$$LMn^{II}(H_2O) \rightarrow [LMn^{III}(H_2O)]^+ + e$$

$$[LMn^{III}(H_2O)]^+ \rightarrow LMn^{III}(OH) + H^+$$

Formation of hydroxomanganese(III) through μ-peroxomanganese(III) via the following reaction was ruled out based in part on a negative test for H_2O_2.

$$LMn^{III}\text{—}(O_2^{2-})\text{—}Mn^{III}L + H_2O \rightarrow 2\ LMn^{III}(OH) + H_2O_2$$

A substantial nitrogen substituent effect on the rate and extent of oxygenation has been noted [77]. When $R=CH_3$ secondary oxidation is very slow. When $R=n\text{-}C_3H_7$ initial O_2 uptake is also slow. These results suggested that dioxygen attack was proceeding *cis* to N—R. A similar effect was observed for $R=C_6H_5$ where the weaker aromatic nitrogen donor may also prove critical. These steric effects have been found to be just as pronounced in comparable oxygenation studies of cobalt(II) chelates [80] and in reactions of nitric oxide with identical manganese(II) chelates [81]. Analogous manganese(II) complexes incorporating neutral linear pentadentate N_5 ligands derived from pyridine-2-aldehyde and triamines demonstrated no reactivity with dioxygen [82].

The synthesis and X-ray crystal structure characterization of a manganese(II) complex of the neutral ligand 2,6-diacetylpyridinebis-(picolinoylhydrazone), XII, has been reported [83]. The manganese(II) was found to be heptacoordinate with the N_3O_2 donor set of the ligand occupying in-plane positions with two anion donors completing the pentagonal bipyramidal structure. Since the complex was prepared in the atmosphere it was concluded that no dioxygen sensitivity was observed. Similar observations [84] have been noted with a second neutral N_3O_2 ligand, 2,6-diacetylpyridinebis(semicarbazone). The pentagonal-bipyramid complex apparently was air stable since no special precautions were given for excluding dioxygen while performing the X-ray structure determination. Further studies [85—87] of this type have been carried out with other neutral pentadentate ligands derived from pyridine-2,6-dicarboxaldehyde and a series of polyfunctional α,ω-aromatic diamines. The ligands fields, XXIII, produced included O_2N_3, S_2N_3 and N_5 donor sets. In a few cases, X-ray diffraction data confirmed pentagonal bipyramidal geometry. No reactivity with dioxygen was noted.

The employment of neutral macrocyclic pentadentate ligands with manganese(II) has produced analogous results [88]. The template reaction of 2,6-diacetylpyridine and 1,4,7,10-tetraazadecane in the presence of $MnCl_2 \cdot 4\ H_2O$ has been demonstrated to yield Mn(DIACPY-1,4,7,10)Cl_2, XXIV. The high spin seven-coordinate manganese(II) complex was unaffected by dioxygen. Extension of this work [89] to include manganese(II) complexes of other tetraaza derivatives (1,4,8,11 and 1,5,8,12) provided the same results. The pentagonal bipyramidal nature of several of these manganese(II) complexes has been verified by X-ray structural analysis [90,91]. With the same results regarding dioxygen reactivity, yet another unique set of neutral ligand systems (N_5 donor set) has been communicated [92], XXV and XXVI. No structural data for manganese(II) complexed with XXIX was given; however, a pentagonal pyramid structure was suggested from X-ray crystal data for the manganese derivative of XXVIII wherein one of the anions occupied the apical position. Both orange-yellow compounds were air stable.

Surprisingly no dioxygen-reactivity was detected [93] with the high spin manganese(II) complex of a dianionic acyclic pentadentate ligand, XXVII, (S_2N_3 donor set). All attempts to prepare the corresponding manganese(III) complex by oxidation of Mn(II) were unsuccessful. On the other hand, a somewhat similar hexadentate ligand ($S_2N_2O_2$ donor set), XXVIII, was stated not to form a Mn(II) complex but instead stabilized a Mn(III) state. In the former case, the lower oxidation state was predicted to be stabilized by the presence of sulfur donors; whereas, in the latter case Mn(II) was stated not to be favored because of the absence of ligand field stabilization energy which would otherwise accrue to Mn(III).

(v) Hexadentate ligands

Investigations dealing with manganese(II) complexes which incorporate a hexadentate ligand are indeed sparse. Manganese(II) complexes possessing ligands derived from substituted salicylaldehydes or pyridine-2-carboxaldehyde and selected tetraamines have been synthesized [94] (O_2N_4 and N_6 donor sets, respectively, XXIX, XXX). As in the pentadentate case, the cationic N_6 materials possess no dioxygen reactivity in solution or in the solid state. On the other hand the O_2N_4 derivatives provide another set of dioxygen sensitive compounds, both in solution and in the solid state. The nature of the oxygenated products has not been established.

C. BIOLOGICAL SYSTEMS

(i) Manganese porphyrin-containing proteins

Manganese is widely distributed in nature but occurs only in trace amounts in biological materials [95]. In spite of these very small amounts, it is clear that manganese plays several important roles in the maintenance of life and regulation of biological functions. A discussion of the biological systems that are specific in their requirement for manganese has recently appeared [96]. It is not the intent of this review to cover these subjects again but in the interest of manganese—dioxygen chemistry it is necessary that a few biologically related studies be mentioned.

Manganese-substituted hemoglobin (Hb) and myoglobin (Mb) have been prepared in order to explore the function of the heme iron in hemoglobin. Mn^{II}(Hb) was observed not to bind molecular oxygen reversibly both in complexes of manganese mesoporphyrin IX and globin [97] and manganese protoporphyrin IX and globin [98]. Hybrid hemoglobins have been prepared [99] containing manganese protoporphyrin IX in one type of hemoglobin subunit and iron protoporphyrin IX in the other type of subunit. These molecules are found to be tetrameric. While the iron-containing subunits have oxygen affinity, the manganese-containing subunits bound neither O_2 nor CO. It has also been shown [100] that manganese porphyrin-containing myoglobins and their dithionite-reduced compounds do not form complexes with O_2 and CO. Despite the fact that MnHb could not reversibly bind molecular oxygen, equilibrium allosteric properties of Hb were shown [101] to be retained when manganese is substituted for iron. In other words, MnHb underwent conformational changes upon binding of ligands such as nitric oxide equivalent to those of Hb.

In a related study [100] apoproteins of cytochrome *c* peroxidase, horseradish peroxidase and sperm whale myoglobin were recombined with manganese complexes of proto-, hemato-, meso- and deutero-porphyrins to form manganese porphyrin—protein complexes. The manganese containing peroxidases reacted with hydroperoxides to form peroxide compounds. The peroxide compounds of manganese porphyrin-containing horseradish peroxidases were highly stable and appeared based on visible spectra to be a manganese(IV) derivative. Because of the slow rate of formation of the peroxide compound, the molar stoichiometry between Mn—porphyrin—HR—peroxidase and H_2O_2 was not accurately determined. The peroxide compounds of manganese porphyrin-containing cytochrome *c* peroxidase were less stable. Spectrophotometric titration of Mn—meso-CCP with H_2O_2 suggested a molar stoichiometry of 1 : 1 to form the peroxide compound. Two reducing equivalents of ferrocyanide were required to convert the peroxide compound to the original Mn—meso-CCP. Thus the oxidation state of manganese in this compound was formally equivalent to manganese(V). None of the manganese porphyrin-containing myoglobins reacted with hydroperoxides even in a 10—20-fold excess.

Manganese has been shown [102,103] to affect the oxygen affinity of hemoglobin and hemocyanin. Each HbCO tetramer has been found to bind two manganese(II) ions while oxyhemocyanin bound approximately six Mn(II) ions. In the Hb case manganese increased the oxygen affinity only slightly below 25% oxygen saturation and caused a decrease in oxygen affinity above 25% saturation. It is not clear whether manganese is directly involved with dioxygen in this study or only with the protein.

(ii) Superoxide dismutase

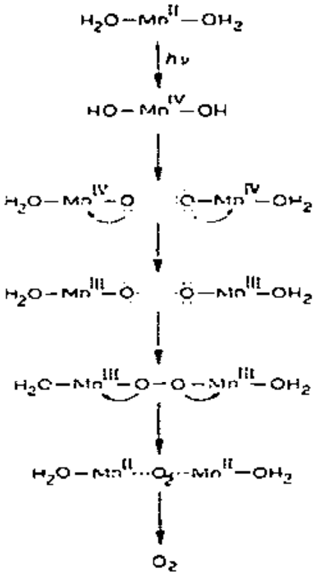
Superoxide dismutase (SD) from the matrix of *Escherichia coli* has been observed [104] to contain tightly bound manganese. One of the functions of this enzyme is to catalytically scavenge the dioxygen one electron reduction product, superoxide anion free radical, in aerobic species by way of the reaction:

$$O_2^- + O_2^- \xrightarrow{2H^+} H_2O_2 + O_2$$

Isolation and characterization of a manganese-containing SD from yeast which is cyanide insensitive has also been reported [105]. The properties of yeast SD indicated a close relationship to the chicken liver mitochondrial enzyme. Yeast SD contains four subunits with each subunit having one manganese ion. The absorption spectra in the visible region suggested Mn(III) in the resting enzyme. SD from *E. coli* has been observed [106] to lose metal and activity when dialyzed against a chelating agent. Reconstitution of the apoenzyme with $MnCl_2$ restored activity suggesting the essentiality of manganese. A high spin Mn(III) complex of highly distorted octahedral symmetry with one Mn atom per *E. coli* SD enzyme dimer is postulated. Preliminary X-ray crystallographic studies of SD from *E. coli* and SD from yeast mitochondria have been published [107]. Molecular parameters are not available as yet. The purification and characterization of a manganese containing SD from bovine heart mitochondria has recently been reported [108]. The enzyme appears to contain two manganese atoms per mole of enzyme. It was observed to have a molecular weight of 86,000 and to contain four noncovalently bound subunits of equal size. The catalytic mechanism of manganese-containing SD from *E. coli* has been studied [109] by pulse radiolysis. The results were interpreted in terms of four oxidation and reduction reactions. Four forms of the enzyme were postulated in which Mn(IV), Mn(III), Mn(II) and Mn(I) are respectively present. It is conceivable that these electron transfer processes may proceed through manganese—oxygen bound intermediates.

(iii) Photosystem II

The necessity of manganese in photosynthetic oxygen evolution has been known for some time. Recent estimation [110] of the content of Mn in chloroplasts of various higher plants was of one Mn for 50—100 chlorophyll molecules. Two different functions were ascribed [111] to Mn. Two-thirds of the Mn was found within photosystem II activity where it was directly involved at the oxidant site. The remaining 1/3 was very tightly bound and was recognized to have a structural role. The fragility of the O_2 evolving system in vitro has severely restricted the approaches whereby this process can be adequately studied. Some time ago Calvin and co-workers indicated that a manganese porphyrin may be involved, but currently this idea is not well accepted [112]. Several mechanisms have been proposed to account for the role of manganese. Photo-oxidation of manganese to a higher valence state is a characteristic of many of these. Calvin [113] and Wang [114] have proposed mechanisms for the O_2 evolving systems involving manganese. Calvin's mechanism incorporates two manganese atoms and is outlined below.



Wang proposed for the oxidation of coordinated water the following scheme starting with a photochemically generated Mn(IV) species.

More recent investigations [115—117] concluded that there are three manganese atoms per water-oxidizing unit and that all three are equivalent. A concerted reaction sequence that involves hydroperoxo and peroxo intermediates has been proposed for a three-manganese model system.

A connection between chloroplast manganese and superoxide dismutase activity has recently been suggested [118]. Particles prepared for spinach chloroplast membranes have been shown to have SD-like activity of two kinds, one inactivated by heating and inhibited by H_2O_2 and the other insensitive to both of these treatments. The possibility that the photosynthetic water-splitting system and SD have evolved from a single precursor was advanced.

D. PERTINENT STRUCTURE-REACTIVITY CORRELATIONS WITH Fe AND Co ANALOGUES

In certain instances we have been able to relate the chemistry of Fe and Co dioxygen systems to the comparable Mn systems. In particular, depending on the solvent system $Co^{II}SALC_2$ yields both monomeric end-on superoxo and dimeric μ-peroxo-dioxygen complexes [119], with coordinated pyridine in the superoxo case. With the comparable $Mn^{II}SALC_3$ system in pyridine, the oxygenated complex has been shown to be a dimer by X-ray techniques composed of either di-μ-hydroxo or di-μ-oxo groups. The pyridine moieties are not coordinated in the Mn case. The very obvious difference in the dioxygen binding of these complexes is not conveniently explained. Presumably the difference lies in the ability of Mn to accommodate the higher oxidation states. It has been suggested that an intermediate μ-peroxo complex is formed in the Mn case prior to isolation of the di-μ-oxo species but no substantial evidence has been offered.

The structure of $(CoSALDPT)_2O_2$, a reversible O_2 carrier, has been determined [120]. The Co—O linkage was shown to be μ-peroxo in nature. As discussed previously, the comparable O_2 plus MnSALDPT system has been studied. Very similar reactivity patterns were found to exist between the two systems. Hence, it seems reasonable to conclude that the oxygenated complexes of Mn with the empirical formula (MnSALDPT)O may be μ-peroxo in nature.

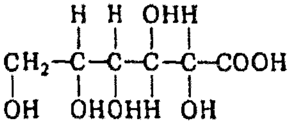
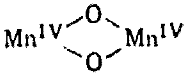
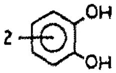
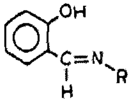
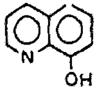
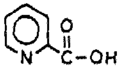
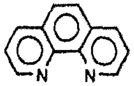
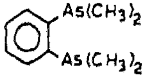
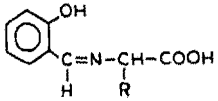
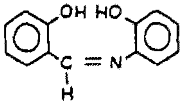
X-ray crystallographic results [121] on $Fe(T_{piv}PP)$ (1-MeIm)O_2 show the dioxygen bonding to be end-on. Recent work on the comparable Mn system shows that $Mn(T_{piv}PP)L$ does not react with O_2. The preference for five coordination in Mn^{II} has been advanced to explain this lack of O_2 reactivity. It must be pointed out, however, that other MnTPP type systems do react with O_2 and both end-on and edge-on bonding schemes have been developed to explain the O_2—Mn interaction.

E. CONCLUSIONS

Table 1 compiles most of the data which has been discussed in a form that allows some conclusions to be drawn concerning dioxygen reactivity patterns with manganese complexes. First, those complexes composed of neutral uncharged ligands (PHEN, BIPY, TERPY, PYC_n, DIACPY-1,4,7,10 and PY-1,4,7,10, etc.) are not sensitive to dioxygen. Therefore, regardless of the number and type of donor atoms and subsequent complex geometry, manganese(II) appears not to be susceptible to reaction with dioxygen. The sole exception to this hypothesis seems to be $Mn([14]aneN_4)X_2$. Unfortunately, the nature and extent of the reactivity is not reported. It should be noted that stabilization of higher manganese oxidation states with several of these ligands is not precluded via reaction with a suitable oxidant. Several of these situations have been discussed (e.g., PHEN and BIPY).

The situation regarding negatively charged ligands is quite different. For example, dianionic N_4 donors such as Pc, TPP, $[14]12eneN_4$ and the Schiff base derived from diketones and 2-pyridylhydrazine sensitize manganese(II) to dioxygen. This result might be expected if we consider the reaction with O_2 to be an oxidative addition. In other words, the better donating dianionic N_4

TABLE 1

No.	Ligand	Mn—O linkage	Ligand abbreviation	Dioxygen reactivity	Ref.
I	 $\underset{\mathrm{OH}}{\mathrm{CH_2}}-\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}-\overset{\mathrm{OH}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}-\mathrm{COOH}$		GH	Yes	9, 10
II		Not reported	CAT	Yes	14
III		Not reported	SALN·R	Yes	16
IV		$\mathrm{Mn^{III}}$—O—$\mathrm{Mn^{III}}$	QH	Yes	17, 18
V			PIC	Not reported	20
VI			PHEN	No	21—25
VII			DIARS	No	35
VIII		Not reported		Yes	36
IX		Not reported		Yes	37

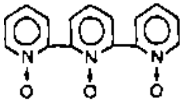
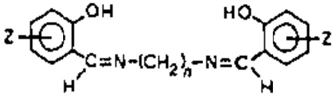
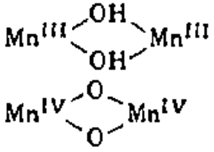
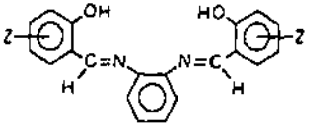
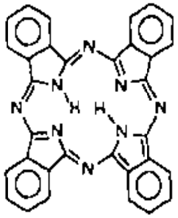
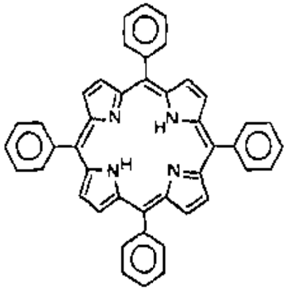
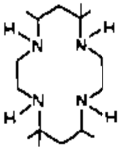
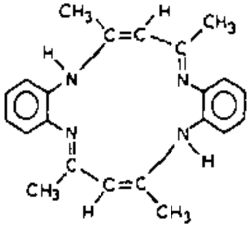
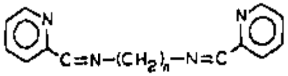
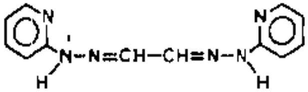
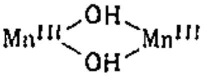
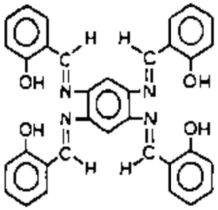
X			TERPY	No	27
XI			TERPY O_3	No	28
XII		Mn^{III}—OH  $Mn^{III}(OH)_2Mn^{III}$ $Mn^{IV}(O)_2Mn^{IV}$	SALC$_n$	Yes	40–52
XIII		Mn^{III}—OH	SALOPHEN	Yes	53
XIV		Mn^{III}—O—Mn^{III} Mn^{III}—(O_2^-)	Pc	Yes	54–60
XV		Mn^{IV}—(O_2^{2-}) Mn^{III}—(O_2^-)	TPP	Yes	63–71

TABLE 1 (continued)

No.	Ligand	Mn—O linkage	Ligand abbreviation	Dioxygen reactivity	Ref.
XVI		Not reported	[14]ane N_4	Yes	72
XVII		Not reported	[14]12rene N_4	Yes	73
XVIII			PYC_n	No	74
XIX			N_4 ligand	Yes	75
XX			TSAB	No	76

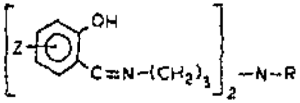
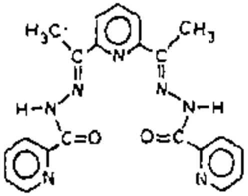
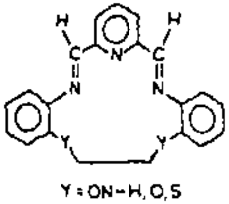
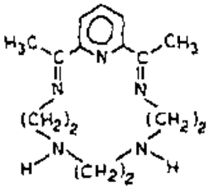
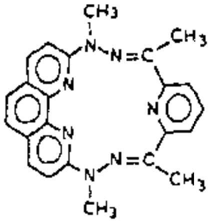
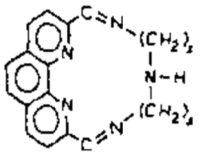
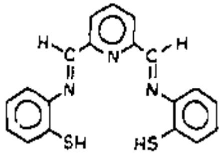
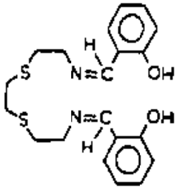
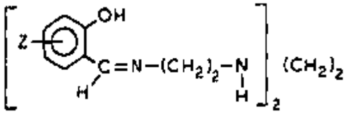
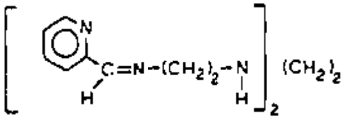
XXI		$Mn^{III}—OH$ $Mn^{III}—O_2^{2-}—Mn^{III}$	ZSALRDPT	Yes	77, 78
XXII			DiP	No	83
XXIII				No	85—87
XXIV			DIACPY- 1, 4, 7, 10	No	88, 89
XXV				No	92
XXVI				No	92

TABLE 1 (continued)

No.	Ligand	Mn—O linkage	Ligand abbreviation	Dioxygen reactivity	Ref.
XXVII				No	93
XXVIII					93
XXIX			ZSAL-1, 4, 7, 10	Yes	82
XXX			PY-1, 4, 7, 10	No	82

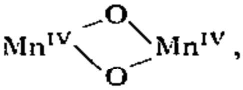
ligands should be more effective in stabilization of a higher oxidation state. This idea seems to have validity in that those dianionic ligands even with a mix of nitrogen and oxygen donor render the manganese(II) dioxygen reactive (e.g., $SALC_n$). The trend is followed not only with tetradentate ligands but also higher polydentate ligands. Uncharged PYDPT(N_5) complexes display no reactivity whereas SALDPT(O_2N_3) complexes are extremely oxygen sensitive, even in the solid state. Likewise PY-1,4,7,10, etc. (N_6) complexes are unreactive whereas SAL-1,4,7,10, etc. (O_2N_4) complexes are reactive. That the situation is probably more complicated than we have suggested is supported by the fact that both dianionic DIP and DAPSC ligands (O_2N_3) do not provoke dioxygen reactivity. The oxygen donors in this case are carbonyl in nature while in the SAL-related ligands the oxygen is phenolic. The very poor coordinating affinity of carbonyl oxygen relative to a deprotonated phenolic oxygen may account for this observation.

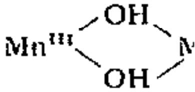
Some discrepancies appear in the literature regarding all oxygen donor ligands. The "charged-ligand-requirement" does not universally promote reactivity with O_2. Salicylaldehyde and acetylacetonato complexes are insensitive whereas gluconate and catecholato complexes have been suggested to possess some reversible coordinating ability for dioxygen at low temperature. It should be noted, however, that the ligand may be the site of O_2 attack in the catechol case and in the gluconate case the process is quite sensitive to pH. In this situation even $Mn(H_2O)_6^{2+}$ is sensitive to O_2.

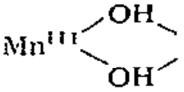
That steric effects are important is supported by the observation that various substituents attached to the ligand can alter the degree of dioxygen reactivity. This has been dramatically demonstrated with manganese(II) complexes of SALDPT and $SALC_n$.

Structural effects have been shown to be critical in both degree of reactivity and the type of manganese-oxygen linkage produced. The pronounced tendency for five-coordination by Mn^{II}(TPP)(PY) and its reluctance to spin-pair dictates loss of pyridine prior to dioxygen attack. The failure of peroxo-oxygen to bridge manganese in TPP complexes and in Pc complexes may be structurally related. The O_2 reactivity dependence on the amine substituent in SALRDPT clearly shows the necessity for an accessible site. On the other hand, SAL-1,4,7,10 and SAL-1,5,9,13 complexes are potentially octahedral yet these materials are extremely sensitive to dioxygen. Dibridged versus mono-bridged oxygen species may be structure oriented. For example, $SALC_n$ complexes appear to be di-μ-oxo bridged (2 vacant *cis* positions) while SALDPT complexes (1 vacant position) may be μ-peroxo bridged.

In conclusion, it seems that regardless of geometry the controlling factor that determines the reactivity of a certain manganese complex with dioxygen rests mainly with the strength of the donor atoms and the subsequent ligand environment. No good correlation presently exists between ligand environment, structure, mode of dioxygen coordination and extent of electron transfer between manganese and oxygen. The proposed linkages to date include

$Mn^{III}—(O_2^-)$, $Mn^{IV}—(O_2^{2-})$, $Mn^{III}—(O_2^{2-})—Mn^{III}$, 
$Mn^{IV}\begin{matrix} O \\ \quad \\ O \end{matrix}Mn^{IV}$,


$Mn^{III}\begin{matrix} OH \\ \quad \\ OH \end{matrix}Mn^{III}$ and $Mn^{III}—O—Mn^{III}$

It is surprising that only one superoxo containing linkage has been put forward. It should further be pointed out that no isolable, highly O_2 reversible manganese system has come forward. In addition, X-ray structural data are very limited and at this time are supportive of only $Mn^{III}—O—Mn^{III}$ and  $Mn^{III}\begin{matrix} OH \\ \quad \\ OH \end{matrix}Mn^{III}$. Clearly with additional study manganese may be shown to exhibit more varied dioxygen reactivity than any of the other first row transition metals.

ACKNOWLEDGEMENT

The financial support from NIH Research Grant 21844 from the National Institute of General Medical Sciences is gratefully appreciated.

NOTE ADDED IN PROOF

McAuliffe et al. [122] have recently reported in a preliminary fashion that a series of over 200 compounds of formula $MnLX_2$, where L = tertiary phosphine but not PPh_3 and X = anion, react reversibly with dioxygen in the solid state and when dissolved in non-hydroxylic solvents. The high spin $MnLX_2$ complexes are postulated to be dimers or tetramers in the solid state. The complexes can undergo repeated oxygenation—deoxygenation cycles both in the solid state and in THF solution. The $MnLX_2 \cdot O_2$ complexes exhibit a magnetic moment of ca. 6.9 BM which the authors rationalize as arising from a 50:50 mixture of $Mn^{II}LX_2(^3O_2)$ and $Mn^{II}LX_2(^1O_2)$. Infrared spectral bands at 1402—1430 cm^{-1} are assigned to neutral coordinated O_2. Reappearance of an ESR spectrum characteristic of high spin Mn^{II} after 50% of the dioxygen is added is interpreted as evidence for two species in the solid state. The mode of dioxygen binding is not suggested. Even though the authors claim Mn^{II} for the oxygenated species, a new band in the visible region (τ_{max} = 569 nm) is observed which could have been interpreted as evidence for Mn^{III}. The authors also do not rule out the possibility that the phosphine ligand maybe undergoing oxygenation. Regardless of the precise formulation, this class of reversible O_2 carriers appears to have great practical potential.

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