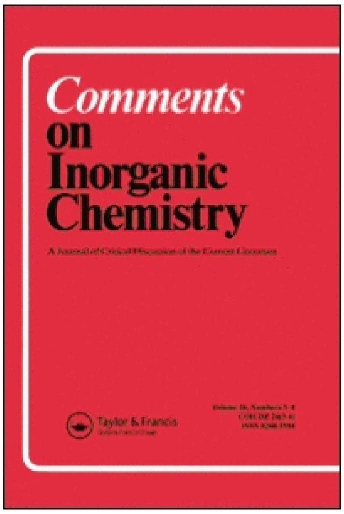

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New Insights into the Reactivity of Mn(II) Coordination Complexes with Dioxygen

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New Insights into the Reactivity of Mn(II) Coordination Complexes with Dioxygen

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As a clearer picture of the oxygen activation processes by manganese(II) coordination complexes begins to emerge, we are more likely to understand the biological significance of the Mn$-$O$_2$ interaction in various enzymes and to use the activated oxygen molecule for the catalytic oxidation of organic substrates. This Comment describes some of the recent advancements in the area of dioxygen activation by manganese(II) complexes. Details regarding the binding of the O$_2$ moiety to the metal center and the reaction pathway that is taken during the four electron reduction of the O$-$O double bond are presented. Particular attention is given to new information on Mn(II) Schiff-base complexes as these results provide strong evidence for a more straightforward and simpler oxygen activation process than previously thought. Also described in this article are examples of unique intermetal oxygen atom transfer reactions that the oxo bridged dimers of Mn Schiff-base complexes undergo with electrophilic metal compounds. This recently discovered reactivity pattern for the oxo bridged complexes likely provides the opportunity to resolve the long-standing controversy regarding the multiple oxidation products that are reported to form upon oxidation of Mn(II) compounds by O$_2$.

Key Words: *oxygen activation, manganese Schiff-base complex, oxo bridged dimer, dimerization, oxo transfer reaction, electrochemistry*

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Abbreviations

DMF—N,N-dimethylformamide
DMSO—dimethysulfoxide
1-MeIM—CH_3-imidazole
E°—formal reduction potential
PhIO—iodosylbenzene
ESR—electron spin resonance
OEC—oxygen evolving complex
PSII—photosystem II
DMA—N,N-dimethylacetamide
CV—cyclic voltammetry or cyclic voltammogram
RDE—rotating disk electrode
CA—chronoamperometry
ECE—E = electrochemical and C = chemical step
SSCE—sodium chloride saturated calomel electrode

I. INTRODUCTION

An understanding of the reactivity of metal complexes toward O_2 is pertinent to such diverse topics as biological oxygen transport and homogeneous catalysis.[1,2] Thus, the reversible and irreversible binding of dioxygen to transition metal compounds has received considerable attention for many years. Among the middle transition metals, Mn, Fe, and Co, the reactivity of manganese complexes toward O_2 is the least well understood despite the fact that it was 60 years ago that Pfeiffer and his research collaborators published the first paper describing the reactivity of the compound (SALEN)Mn^{II}, Figure I.1, toward O_2.[3] However, over the past dozen or so years, there has been renewed attention paid to manganese-O_2 chemistry primarily because of the relevance of manganese redox enzymes that catalyze O_2 evolution from H_2O, O_2^-, and H_2O_2.[4] Complexes of Mn(II) with porphyrin and Schiff-base ligands are the most thoroughly studied systems with regard to O_2 activation processes, and their chemistry is the focus of this Comment.

Pfeiffer and co-workers found that oxygenation of the yellow (SALEN)Mn^{II} complex in $CHCl_3$ produced a rather intractable red-brown solid. They postulated that the majority of the solid was comprised of [(SALEN)Mn^{III}-OH],[3,5] but that other compounds might also be present. This result and its interpretation have lead to the long-standing notion that reaction of Mn(II) com-

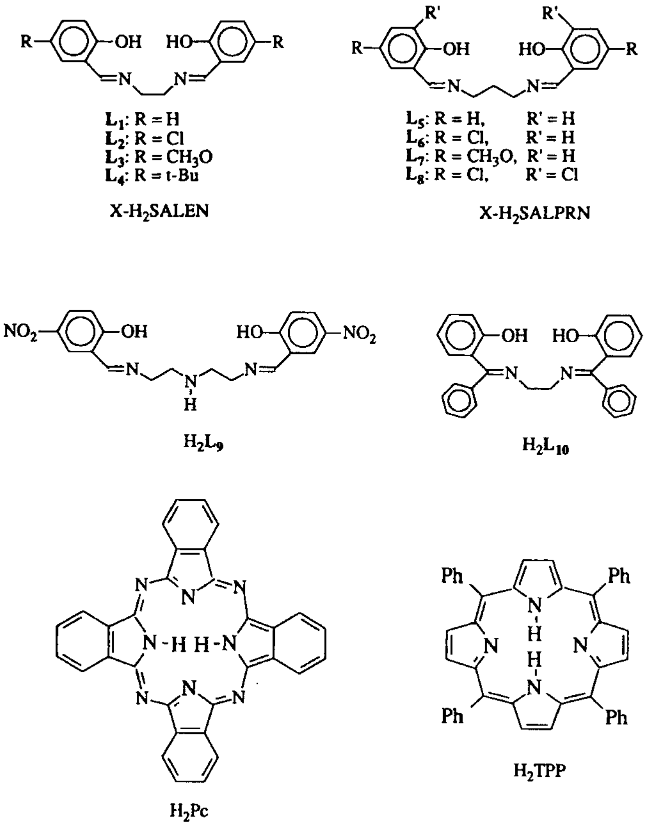


FIGURE I.1 Ligand structures discussed in this Comment.

pounds with O_2 produces a complex mixture of products, and that homolysis of the O–O bond, which we refer to as O_2 activation, occurs as a consequence of the oxygen binding process.

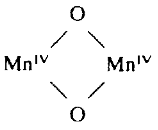
Illustrated below are some of the simpler oxygenated compounds that have been proposed to form for manganese complexes, and all have been claimed to occur for the Schiff-bases.[6] However, in no single ligand system have all of the oxygenated complexes been unambiguously identified. There are also many higher nuclearity oxo bridged manganese compounds containing either **1** or **3** as a subunit, for which excellent reviews are available,[7] but they are generally not formed by reaction with O_2 and so they will not be discussed explicitly in this Comment.

$Mn^{III}\text{-}O\text{-}Mn^{III}$

1
μ-oxo dimer

$Mn^{III}\text{-}O\text{-}O\text{-}Mn^{III}$

2
η¹, η¹-peroxo



$Mn^{IV}(\mu\text{-}O)_2Mn^{IV}$

3
bis(μ-oxo) dimer

$-(Mn^{III}\text{-}O\text{-}Mn^{III})_x\text{-}O$

4
poly-catena-oxo

Owing to the multi-component product mixtures thought to occur especially in Schiff-base chemistry, multi-step O_2 activation pathways have been proposed[8,9] and Scheme 1 is an example. A similar set of reactions is often used to explain reactivity of the porphyrins even though oxygenated products are not isolated; one typically isolates $[\text{porphyrin}Mn^{III}]^+$ and decomposition products. This scheme contains intermediates and products that are closely related to those found during the reaction of O_2 with Fe(II) and Co(II).[1]

We are aware of only two examples of $Mn^{III}-Mn^{III}$ μ-oxo dimers without additional bridging groups spanning the metal centers that have been isolated and unambiguously characterized[10-12] despite the suggestion that this type of dimer plays a prominent role in the O_2 activation process. In contrast, the bis(μ-oxo) dimer is much more common and can be synthesized from Mn(II) using O_2 or from Mn(III) using other oxidants.[13-34]

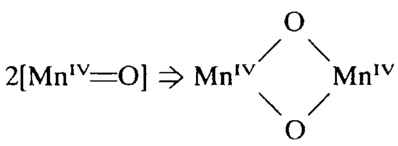
A particularly exciting recent development in the O_2 activation

$$Mn^{II} + O_2 \Rightarrow Mn^{III}\text{-}O_2$$

$$Mn^{III}\text{-}O_2 + Mn^{II} \Rightarrow Mn^{III}\text{-}O\text{-}O\text{-}Mn^{III}$$

$$Mn^{III}\text{-}O\text{-}O\text{-}Mn^{III} \Rightarrow 2[Mn^{IV}{=}O]$$

$$[Mn^{IV}{=}O] + Mn^{II} \Rightarrow Mn^{III}\text{-}O\text{-}Mn^{III}$$



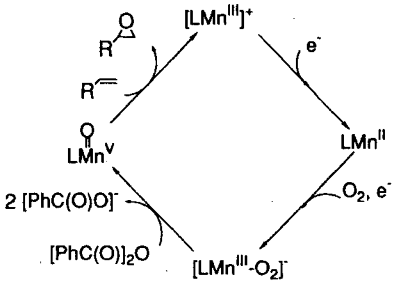
$$2[Mn^{IV}{=}O] \Rightarrow Mn^{IV}(\mu\text{-}O)_2Mn^{IV}$$

SCHEME 1

area is the isolation and crystallographic characterization of two manganese compounds with O_2 bound in the η^1, η^1-peroxo fashion.[35,36] In at least one instance[35] the O_2 could be released by irreversibly decomposing the compound with acid. An η^1, η^1-peroxo complex is thought to form for a Schiff-base ligand complex,[37] and apparently the bound O_2 can be released by thermal means, but both these claims need further investigation in order to be fully substantiated.

Our interest in the reactivity of tetradentate Mn(II) Schiff-base complexes toward O_2 was stimulated by reports that the porphyrin analogues are good catalysts for epoxidizing olefins using O_2. The reaction could be driven starting with the Mn(III) complex via chemical reducing agents[38,39] or more efficiently by electrochemical means.[40–43] Scheme 2 was proposed by Murray and co-workers[40] to explain the electrochemical results. We, and others, reasoned that the Schiff-base ligands would allow for greater control over electronic, steric, and stereochemical properties of the catalyst than the porphyrins, thereby affording tunability of the catalyst to the desired substrate. Electronic properties of the catalyst have been addressed by Kochi and co-workers[44,45] while various aspects of stereochemical control currently are being examined by others[46–49] (in both kinds of studies PhIO is used as the source of the oxygen).

The Schiff-base compounds are moderately good electrocatalysts,[50] likely operating by Scheme 2, but their activity is reduced after a relatively short period of time. From CV results, Section II.5, it seemed likely that a catalytically inactive dimer formed during the reaction. Any one of the dimers shown above could



SCHEME 2

have accounted for loss of the catalytic activity. We were interested in ascertaining the nature of the dimer, which we now know to be a bis(μ-oxo) dimer, how it is formed, and ultimately how to control its formation.

We will show in this Comment that analysis of recently obtained data from our lab and others reveals a simpler process than the one in Scheme 1. From our studies thus far,[51-54] it is possible to demonstrate that **3** is the kinetic product of oxygenation and that intermetal oxygen atom transfer reactions between **3** and the Mn(II) starting material account in part for the multitude of products that have been suggested from prior studies. The Comment is divided into two parts: The first provides a limited overview of studies detailing intermediates involved in the oxygenation process while the second describes primarily the chemistry of Schiff-base complexes.

II. REACTIVITY OF LMn(II) WITH O_2

II.1. Coordination Requirements

In the mid 1960's it was reported that manganoglobin did not bind O_2.[55] This unexpected result led to the conclusion that a five coordinate Mn(II) center could not be oxygenated. Subsequent O_2 binding studies using $TPPMn^{II}$, Figure I.1, with various axial bases supported this idea.[56] X-ray crystal structures have since been reported for Mn(II) porphyrin complexes[57,58] with zero or one axial ligand but *no six coordinate compounds* have been isolated. Thus much of what was learned about using physical attributes of the axial ligand, e.g., π donor and acceptor capabilities, to manipulate reactivity of O_2 toward Co(II) compounds[1] may not be applicable to the Mn porphyrin complexes.

Four coordination appears to be a less stringent requirement for the Schiff-base complexes. For example, the oxygenation can be performed in solvents like DMSO or DMF[59-65] where one or possibly even two axial ligands may be present. The X-ray crystal structure of $L_{10}Mn^{II}(py)_2$ shows that both pyridines ligate the metal center.[44] Furthermore, in our electrochemical experiments,[52,54] we observe that inclusion of a 5–10 fold molar excess of 1-MeIM, relative to the metal complex in CH_3CN, does not inhibit or enhance O_2 binding even though we can observe that the 1-MeIM coordinates to the metal center. At higher 1-MeIM concentrations, 50-fold excess, some inhibition occurs but it is not large. From the limited data set of the Schiff-bases and the porphyrins, their appears not to be a strong correlation between reactivity of the metal complex toward O_2 and coordination number.

II.2. Griffith vs. Pauling Type Coordination of O_2 to LMn(II)

The reaction of Mn(II) complexes with O_2 has been probed by ESR, IR, and UV-vis spectroscopy. While O_2 is commonly bound to Fe and Co centers in the Pauling fashion,[66] the coordination mode of O_2 to Mn(II) still remains an unresolved issue except in a few instances. As the following discussion shows, ligand type and reaction conditions influence whether Griffith or Pauling type bonding is adopted, but the Griffith type appears to be the more common.

The most thorough studies in this area are those of Basolo and Hoffman.[67-69] Their primary observation was that reaction of $TPPMn^{II}$ with O_2 in toluene at −78°C gives rise to a six line ESR spectrum at $g = 5.4$. The formula assigned to the adduct was $[TPPMn^{IV}(\eta^2\text{-}O_2)]$. One expects Mn(III) species to be ESR silent while Mn(IV) complexes are ESR active. The η^2 coordination mode was controversial at the time because Fe and Co analogues had been assigned as η^1-superoxo species,[1,66] and changes in the UV-vis spectrum upon oxygenation were most consistent with formation of a Mn(III) species.

During the debate, MO calculations were used either to support the structure proposed by Basolo and Hoffman[70] or to show[71] that $[TPPMn^{III}(\eta^1\text{-}O_2)]$ was a better description. Eventually, rigorous Hartree–Fock MO calculations[72] were interpreted as showing that the η^2-peroxo formulation is strongly favored but that an η^1-superoxo form cannot be completely excluded. Interestingly, rotation of the bound O_2 in $[TPPTi^{IV}(\eta^2\text{-}O_2)]$ proceeds through an η^1-superoxo intermediate.[73,74] There may be a similar small energy barrier between the two forms in manganese compounds.

The coordination geometry issue was settled for $[TPPMn\text{–}O_2]$ through low temperature IR studies with $^{16}O^{18}O$.[75] Griffith type coordination was substantiated by the appearance of a single band in the IR spectrum assignable to ν_{O-O} for the $^{16}O^{18}O$ molecule. Previous studies of TPPCo^{II} with a similar gas mixture had given rise to two O–O stretches (O_2 bound in an η^1-superoxo geometry) for the assymmetrically labeled O_2 molecule.[76,77] Thus there is now little doubt that oxygenation of TPPMn^{II} in toluene produces [TPPMn^{IV}(η^2-O_2)]. Nakamoto and co-workers have also shown that [OEPMn–O_2] has the oxygen bound in the η^2 manner.[78]

We recently found[79] that the product from reaction of L_7Mn^{II} with O_2 in DMF has an ESR spectrum, Figure II.2.1, similar to the one for the porphyrins, so it, and probably other Schiff-base complexes, adopt the Griffith type bonding. It is likely that O_2 adducts of $Mn^{II}X_2PR_3$ (X = Cl, Br, or I and R = alkyl and/or aryl groups), initially claimed to have η^1 bonding,[80,81] also bind O_2 in an η^2 fashion based on the six line ESR spectra observed for some of the compounds upon oxygenation. In retrospect, Griffith type bonding of O_2 should not have been controversial as it is commonly found in O_2 adducts of early and late transition metals,

$$\boxed{L_7Mn^{II} + O_2 \xrightarrow{\text{DMF, -30°C}} [L_7Mn^{IV}(\eta^2\text{-}O_2)]}$$

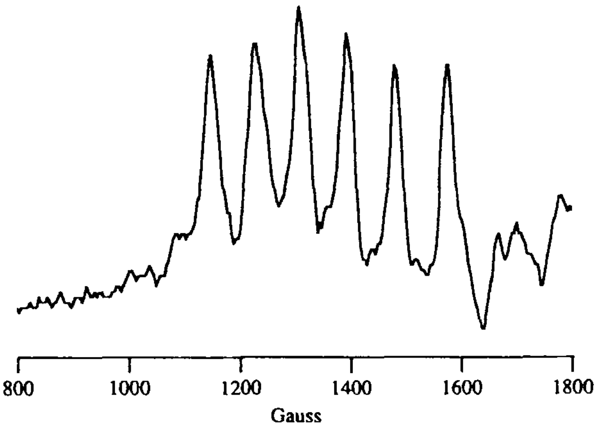
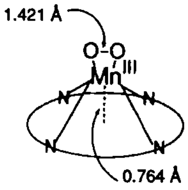


FIGURE II.2.1 ESR spectrum taken at 6 K of L_7Mn^{II} oxygenated at −30°C in DMF. The product appears to be [$L_7Mn^{IV}(\eta^2$-$O_2)$].

especially for those metals that can undergo two electron oxidations. It is now known that under certain conditions even iron(II) complexes can bind the O_2 in a side-on fashion.[77]

The X-ray crystal structure of $[TPPMn^{III}(\eta^2\text{-}O_2)]^-$, **5**, recently has been determined[82] and the structure is shown schematically below. The Mn center in **5** lies 0.764 Å out of the plane of the macrocycle. Basolo and Hoffman earlier had suggested that if the O_2 was side-on bound to the manganese center in $[TPPMn^{IV}(\eta^2\text{-}O_2)]$, the rigidity of the porphyrin macrocycle would prevent the metal from adopting an octahedral bonding mode because of steric repulsion between the O_2 and the porphyrin ligand. Clearly this is borne out in the structure of $[TPPMn^{III}(\eta^2\text{-}O_2)]^-$.

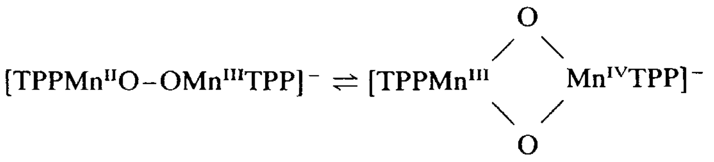


5

Spectroscopic data obtained for the oxygenation of $PcMn^{II}$, Figure I.1, shows that the mode of O_2 binding is strongly dependent on the solvent used during the reaction. In DMF, a species having an ESR signal at $g = 2$ with no hyperfine structure attributable to the metal center is observed.[83] The signal could be that of $[PcMn^{III}(\eta^1\text{-}O_2)]$ but unbound O_2^- is a second possibility (see below). Nakamoto and co-workers found by IR spectroscopy[78] that in an Ar matrix the O_2 is bound side-on like $[TPPMn^{IV}(\eta^2\text{-}O_2)]$. Perhaps the most interesting results are those of Lever and coworkers who recorded an 18-line ESR spectrum for the O_2 adduct prepared in DMA.[84,85] It seems probable, from recent ESR data on polynuclear manganese compounds,[86] that the multi-line signal arises from a dinuclear mixed-valent compound rather than $[PcMn^{III}(\eta^1\text{-}O_2)]$ as originally thought. If the compound is indeed a mixed-valent dimer, the 18-line spectrum is an unprecedented one as 16-line spectra are commonly observed for the dimers. This rather exceptional ESR result gains further importance in that it appears to more closely resemble the 19-line ESR spectrum observed for the S_2 state in the OEC of PSII[87,88] than any of the other model compounds for the OEC that have been prepared to date.

II.3. Additional Reaction Intermediates

Basolo and Hoffman also observed in their studies[67–69] that some oxygenated samples exhibited an ill-defined multi-line spectrum (greater than 6 lines) at $g \sim 2$. No attempt was made to assign a structure to the compound other than to suggest that it was a dimer, most likely with an oxygen bridge. The oxygenation of $\mathrm{TPPMn^{II}}$ has been reinvestigated by Perrée-Fauvet and co-workers.[89] They detected a complex having a 16-line pattern at $g \sim 2$ with a spectral width of 1220 G, which they proposed to arise from the unstable complex **6**, Eq. (1). The important suggestion made by these workers was that **6** forms in a fashion that is concerted with respect to O–O bond cleavage, a pathway we also favor, and not through species like those in Scheme 1.



$$[\mathrm{TPPMn^{II}O{-}OMn^{III}TPP}]^- \rightleftharpoons [\mathrm{TPPMn^{III}} \overset{\mathrm{O}}{\underset{\mathrm{O}}{\diamond}} \mathrm{Mn^{IV}TPP}]^-$$

6

(1)

There are also two ESR studies regarding the reaction of $\mathrm{TPPMn^{II}}$ with O_2 in C_6H_5Cl.[89,90] The results differ from those for reaction in toluene. Dismukes and co-workers[90] reported that the addition of O_2 to a C_6H_5Cl solution of the complex generated O_2^- as an initial product[91] along with $[\mathrm{TPPMn^{III}}]^+$. Either species **7** or **8** in Scheme 3 was proposed to account for the 16-line spectrum observed at $g \sim 2$ that appeared following initial formation of O_2^-. The spectral width recorded for **7** or **8**, 1410 G, is substantially larger than the one for the mixed-valent dimer produced in toluene, 1220 G, Eq. (1). This information was used to assign the oxidation states for the metal centers at the +2 and +3 levels in **7** or **8** and +3 and +4 for the dimer in Eq. (1). The reasons for the solvent

$$\mathrm{TPPMn^{II}} + \mathrm{O_2} \rightarrow [\mathrm{TPPMn^{III}}]^+ + \mathrm{O_2^-}$$

$$\mathrm{TPPMn^{II}} + \mathrm{O_2^-} \rightarrow [\mathrm{TPPMn^{III}O_2}]^-$$

$$[\mathrm{TPPMn^{III}O_2}]^- + \mathrm{TPPMn^{II}} \Leftrightarrow \underset{\mathbf{7}}{[\mathrm{TPPMn^{II}O{-}OMn^{III}TPP}]^-}$$

$$[\mathrm{TPPMn^{II}O{-}OMn^{III}TPP}]^- \Leftrightarrow \mathrm{TPPMn^{IV}O} + [\mathrm{TPPMn^{III}O}]^-$$

$$\mathrm{TPPMn^{IV}O} + \mathrm{TPPMn^{II}} \Leftrightarrow \mathrm{TPPMn^{III}OMn^{III}TPP}$$

$$[\mathrm{TPPMn^{III}O}]^- + \mathrm{TPPMn^{II}} \Leftrightarrow \underset{\mathbf{8}}{[\mathrm{TPPMn^{II}OMn^{III}TPP}]^-}$$

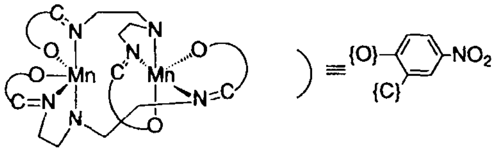
SCHEME 3

dependence of the reaction are not obvious, but it illustrates the difficulty of proposing a general O_2 activation pathway for Mn(II) complexes.

ESR studies for the Schiff-bases are less extensive than for the porphyrins but there is a particularly noteworthy and controversial one regarding oxygenation of $\mathbf{L_9}\mathrm{Mn^{II}}$.[92] A 16-line spectrum was observed for the oxygenation product. Hendrickson and co-workers assigned to the compound the formula $[(\mathbf{L_9})_2\mathrm{Mn^{II}{-}Mn^{III}}(\eta^1\eta^1\text{-}\mathrm{O_2})]^-$, an analogue of **7** in Scheme 3. However, Dismukes and co-workers showed, based on theoretical arguments[86] and from the oxygenation of $\mathrm{TPPMn^{II}}$ in chlorobenzene,[90] that the data were more consistent with a $\mathrm{Mn^{III}{-}Mn^{IV}}$ dimer and not a $\mathrm{Mn^{II}{-}Mn^{III}}$ dimer. This reinterpretation of the data by Dismukes has gained common acceptance.

However, in neither **7** nor **8** nor in the oxidized form of $\mathbf{L_9}\mathrm{Mn^{II}}$ is the coordination mode of the oxygen ligand(s) accurately known. It seems likely that the nature of the bridging ligand (oxo, $\eta^1\eta^1$-peroxo, or $\eta^1\eta^1$-superoxo) and the coordination geometry about the metal center (five or six coordinate) will influence the ESR parameters, maybe not in a predictable way. Support for this contention comes from the wide range in spectral widths recorded for mixed-valent $\mathrm{Mn^{III}{-}Mn^{IV}}$ bis(μ-oxo) dimers, 980 G to 1250 G, which have metal cores that structurally are all quite similar. The ligands on these dimers include chelating amines, macrocyles, and the Schiff-bases. Until more ESR spectral data on a variety of mixed-valent dimers becomes available, some caution seems in order when using ESR spectral widths alone to assign manganese oxidation states.

Armstrong and co-workers also examined the reaction of L_9Mn^{II} with O_2.[93] They isolated and crystallographically characterized $[L_9Mn^{III}]_2(\mu\text{-}O)$. No attempts to oxidize the complex to the Mn^{III}–Mn^{IV} form or to reduce it to the Mn^{II}–Mn^{III} state have been reported. Obviously this information could be used for comparison with the ESR results reported by Hendrickson and co-workers.[92] Perhaps the more important observation Armstrong made regarding L_9Mn^{II} itself was that it is a dinuclear compound, **9**, and that the manganese is five coordinate. This compound, or one of its close analogues, seems to be ideal for probing for the existence of the $\eta^1\eta^1$-peroxo and $Mn^{IV}{=}O$ intermediates, Scheme I. Furthermore, if the ligand remains pentadentate during the oxygenation, it would show that a five coordinate Mn(II) complex can react with O_2, Section II.1. Thus reinvestigating the oxygenation process for $[L_9Mn^{II}]_2$ or structural analogues may provide substantial insights into the overall O_2 activation process.



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II.4. Formation of Isolable Oxygenated Complexes—Background

It is clear from the discussion above that the Mn(II) porphyrin complexes have provided the bulk of the information regarding intermediates in the oxygen activation process. In contrast, since Schiff-base compounds generally form isolable oxygen containing products, they permit the study of the chemistry of the oxygenated products themselves. This portion of the Comment therefore focuses primarily on the chemistry of compounds with ligands L_1–L_8, Figure I.1. First we briefly describe earlier work reported by Taylor and co-workers[6] which laid much of the groundwork for our investigations. The second part presents newly acquired information that we and others have gained relating to the oxygenated products. Unfortunately we must speculate to some extent on the nature of some of the products because we have been unable to obtain crystals suitable for X-ray analysis. Hopefully this situation will change soon.

Taylor and co-workers investigated the stoichiometry of the oxygenation reaction using three, four, and potentially five coordinate Schiff-base ligand complexes (complexes with ligands analogous to **L₉** were assumed to be mononuclear). The emphasis was placed on the latter two types. Virtually all of the experiments were performed in DMSO or similar solvents where both products and reactants were soluble. As discussed in Sections II.6 and II.8, this solubility condition can lead to complicating side reactions.

Oxygen uptake measurements revealed a 1:2 O_2:Mn(II) ratio in many instances, implicating production of dinuclear complexes, but the dimers were not isolated though it was generally felt that these were Mn^{III}, Mn^{III} $\eta^1\eta^1$-peroxo dimers. Both greater and lesser values of the O_2:Mn(II) ratio were also recorded. It is likely that ligand decomposition occurred when large quantities of O_2 were involved as the imine linkage ($R_2C{=}NR'$) is susceptible to oxidation itself. Ratios less than 1:2, which at the time were difficult to explain, can now be accounted for by our observations that the kinetic oxidation product, $[LMn^{IV}(\mu\text{-}O)]_2$, reacts with LMn^{II}. For example, oxidation of L_5Mn^{II} under some conditions leads to formation of the bis(μ-oxo) dimer and a higher nuclearity species, but as discussed in Section II.8 the cluster arises from the reaction in Eq. (2).[53]

$$[L_5Mn^{IV}(\mu\text{-}O)]_2 + 2L_5Mn^{II} \rightarrow [\{L_5Mn^{III}\}_2(O)]_2 \qquad (2)$$

II.5. Electrochemical Studies on the Schiff-Base Complexes

We first approached the O_2 activation process using electrochemical methods since the design of robust electrocatalysts was our goal. All of our electrochemical experiments are performed in nonaqueous solvents starting with the O_2 insensitive Mn(III) complex which is then reduced to the O_2 sensitive Mn(II) form.

Whereas one electron reversible electrochemical behavior is typical for the Mn(III/II) couple under N_2, we found the voltammetry

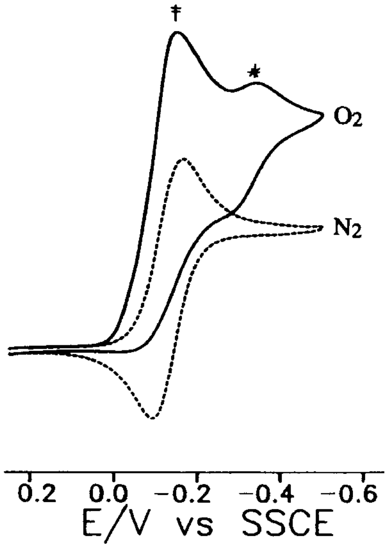


FIGURE II.5.1 CVs of $[L_2Mn^{III}]^+$ under N_2 and O_2 in 0.1 M $TBAClO_4/CH_3CN$. The peak marked with a ‡ corresponds to the ECE process in Scheme 4 and the one denoted with a * is from $[L_2Mn^{IV}(\mu\text{-}O)]_2$.

$[LMn^{III}]^+ + e^- \rightarrow LMn^{II}$ E

$LMn^{II} + O_2 \rightarrow [LMn^{IV}(\eta^2\text{-}O_2)]$ C
10

$[LMn^{IV}(\eta^2\text{-}O_2)] + e^- \rightarrow [LMn^{III}(\eta^2\text{-}O_2)]^-$ E
11

SCHEME 4

under O_2 to be much richer. Compounds with ligands of the type L_1–L_8 exhibit an electrochemical response under O_2 that indicates oxygen binding for the Mn(II) form with subsequent formation of a new species reducible at more negative potentials than the starting material. CVs for $[L_2Mn^{III}]^+$ under N_2 and O_2 atmospheres are representative, in the broadest sense, of these electrochemical features, Figure II.5.1.[52]

The redox processes occurring under the potential-current envelope in Figure II.5.1 which are marked with a ‡ are interpreted in terms of the ECE reaction sequence,[94] Scheme 4, while the one denoted by the * arises from reduction of $[\mathbf{L}_2\mathrm{Mn}^{IV}(\mu\text{-O})]_2$ to $[(\mathbf{L}_2)_2\text{-}\mathrm{Mn}^{III}\mathrm{Mn}^{IV}(\mu\text{-O})_2]^-$. Assignment of the latter process as being due the dimer was made by electrochemically, synthesizing bulk quantities of the *homovalent* compound $[\mathbf{L}_2\mathrm{Mn}^{IV}(\mu\text{-O})]_2$ from reduction of $[\mathbf{L}_2\mathrm{Mn}^{III}]^+$ under O_2 and comparing its $E°$ to the one in the CV shown in Figure II.5.1. The potentials matched exactly.[52] It was extremely fortunate for us that the redox process for the dimer appears at a potential more negative than the one for the starting material (see Section II.7), as this permitted us to easily monitor its formation.

The current increase at ‡ is a clear indication that the oxygen adduct **10** is more easily reduced than the starting material. The amount that the current increases under O_2 is related to the oxygen binding ability of the Mn(II) complex, but because of the dimerization reaction the analysis is often qualitative at best (see Sections II.6 and II.8). It is not surprising that **10** is easily reduced as the manganese is in a relatively high oxidation state. Creager and Murray[95] also reported that $[\mathrm{TPPMn}^{III}(\eta^2\text{-}O_2)]^-$ was formed via an analogous ECE reaction scheme while Sawyer and co-workers[96,97] confirmed that $[\mathrm{Cl}_8\text{–}\mathrm{TPPMn}^{IV}(\eta^2\text{-}O_2)]$ is more easily reduced, $E°(\mathrm{Mn}^{IV/III}) = -0.13$ V vs. SSCE, than $[\mathrm{Cl}_8\text{–}\mathrm{TPPMn}^{III}]$, $E°(\mathrm{Mn}^{III/II}) = -0.16$ V vs. SSCE. The difference in reduction potentials between $[\mathrm{LMn}^{III}]^+$ and **10** is likely to be distinct for each compound examined, and at this time we have no estimate as to what the range in potentials will be.

Once Scheme 4 and the nature of the dimer had been established, our main challenge has been to determine which species are responsible for $[\mathrm{LMn}^{IV}(\mu\text{-O})]_2$ formation. The diffusion layer around the electrode surface in the CV experiment is composed of at least $[\mathrm{LMn}^{III}]^+$, $[\mathrm{LMn}^{II}]$, $[\mathrm{LMn}^{IV}(\eta^2\text{-}O_2)]$, and $[\mathrm{LMn}^{III}(\eta^2\text{-}O_2)]$. It seemed most natural to propose that the dimer formed by the reaction in Eq. (3), $[\mathrm{LMn}^{III}(\eta^2\text{-}O_2)]^-$, should be a strong Lewis base that is being generated in the presence of a strong Lewis acid, $[\mathrm{LMn}^{III}]^+$. This view was consistent with the suggestion by Dismukes and co-workers[90] that **5** is reactive toward Lewis acids, Scheme 3. However, we did not expect step 3 in Scheme 3 to apply here because *neutral homovalent* compounds were isolated from electrochemical syntheses. Alternatively, the reaction could have been the one in Eq. (4), thus making $[\mathrm{LMn^{III}(\eta^2\text{-}O_2)}]^-$ a deadend species with regard to $[\mathrm{LMn^{IV}(\mu\text{-}O_2)}]_2$ formation.

$$[\mathrm{LMn^{III}(\eta^2\text{-}O_2)}]^- + [\mathrm{LMn^{III}}]^+ \rightarrow [\mathrm{LMn^{IV}(\mu\text{-}O)}]_2 \qquad (3)$$

$$[\mathrm{LMn^{IV}(\eta^2\text{-}O_2)}] + [\mathrm{LMn^{II}}] \rightarrow [\mathrm{LMn^{IV}(\mu\text{-}O)}]_2 \qquad (4)$$

The conclusion we have arrived at from analysis of all the electrochemical data is that $[\mathrm{LMn^{IV}(\mu\text{-}O)}]_2$ forms by the set of reactions in Scheme 5, Eqs. (5)–(7).[54] The implication of this view of the data is that the oxygen binding–dimerization reactions, Eqs. (6) and (7), are highly competitive kinetically with the oxygen binding–reduction steps in Scheme 4. We have used CA, CV, RDE, and bulk electrolysis experiments to support this proposition. The following discussion presents a few of the interesting observations that we made during our electrochemical studies that have lead to our invoking Scheme 5.

Among the first interesting results we obtained using CV were that at low $[\mathrm{LMn^{III}}]^+$ concentrations (~0.1 mM) the O_2 binding affinity was not strongly influenced by the $E°$ of the metal complex and that the stoichiometry of the reaction was often nearly 1:1 O_2:Mn. Low metal complex concentrations are necessary to avoid formation of substantial amounts of the bis(μ-oxo) dimer. The first observation is unusual because one expects metal centers having more negative $E°$'s to possess higher O_2 affinities than ones that are less powerful reducing agents. However, Basolo and co-workers[56] had previously shown for the $\mathrm{TPPMn^{II}}$ complexes that O_2 affinity was not very sensitive to the $E°$ for the metal. The significance of the stoichiometry being nearly 1:1, at least from our perspective, is that most of the compounds that we have examined could be

$$[\mathrm{LMn^{III}}]^+ + e^- \rightarrow \mathrm{LMn^{II}} \qquad (5)$$

$$\mathrm{LMn^{II}} + O_2 \rightarrow [\mathrm{LMn^{IV}(\eta^2\text{-}O_2)}] \qquad (6)$$

$$[\mathrm{LMn^{IV}(\eta^2\text{-}O_2)}] + [\mathrm{LMn^{II}}] \rightarrow [\mathrm{LMn^{IV}(\mu\text{-}O)}]_2 \qquad (7)$$

SCHEME 5

used as epoxidation catalysts as they all efficiently form $[LMn^{III}(\eta^2\text{-}O_2)]^-$, Scheme 2. We have no reason not to believe that it is $[LMn^{III}(\eta^2\text{-}O_2)]^-$ that reacts with the anhydride in Scheme 2 to form the active epoxidation catalyst.

The CV experiments also allowed us to determine that the bis(μ-oxo) dimer forms extremely rapidly and that it can be generated in high yield. Using L_2Mn as an example, the dimer in Figure II.5.1 is forming in 60–80% yield based on $[L_2Mn^{III}]^+$, and the redox process for $[L_2Mn^{IV}(\mu\text{-}O)]_2$ is detectable up to scan rates of 2 V/s; this places a lower limit of 75 ms on its formation.[52] This is an impressively fast reaction when one considers the number of events occurring within this short time period; binding of O_2 to Mn(II), dimerization with a second Mn(II) complex, reduction of the O–O bond by four electrons, and reorganization of the ligand from square planar to the *cis*-β configuration[98] (see Section II.6 and Figure II.6.1[24–27]). Thus there must be a large driving force for bis(μ-oxo) dimer formation in order to justify having this complex set of reactions occur so rapidly. The facility of the dimer forming reaction throws doubt on the applicability of Scheme 1.

Of all the complexes that we have investigated, the compound L_6Mn^{II} exhibits the greatest propensity to form its bis(μ-oxo) dimer.[54] This turned out to be an important factor in allowing us to support Eq. (4) to account for dimer formation. Apparently the O_2 binding rate for L_6Mn^{II} is inefficient enough that all of the L_6Mn^{II} in the vicinity of the electrode surface is not drained away in the form of $[L_6Mn^{IV}(\eta^2\text{-}O_2)]$ or $[L_6Mn^{III}(\eta^2\text{-}O_2)]^-$. The dimerization reaction is so facile that we can observe a substantial amount of $[L_6Mn^{IV}(\mu\text{-}O)]_2$ in an RDE experiment, a result we have not seen for any other Schiff-base complex. In the RDE experiment the concentration of the Mn(II) starting material near the electrode surface is extremely small while that for Mn(II) is high under the reaction conditions.[94] Thus detecting the bis(μ-oxo) dimer in the RDE voltammogram provided very strong evidence for dimerization by Eq. (4).

We were also able to determine from CV data that dimer formation is first order in metal complex.[54] By combining this information with the results described above, it seems most likely that the rate determining step in the overall reaction is Eq. (6) in Scheme 5. (Pseudo first order reaction conditions in O_2 are unavoidable in these experiments since the flux of O_2 to the electrode surface is so much greater than for the metal complex). Frederick and Taylor[9] also report that oxygenation of some other Schiff-base complexes is first order in Mn(II), is first order in O_2 as well, and that the reaction proceeds in two stages. They postulated the first oxygenation product to be a μ-oxo dimer and the second to be a bis(μ-oxo) dimer. However, we can show that the reaction most likely occurs in the opposite order (Sections II.6 and II.8).

The electrochemical experiments described above, and some others that were not discussed,[51–54] provided us with strong evidence for dimerization by Scheme 5 but we needed to electrochemically synthesize and characterize compounds that would provide more definitive proof for this pathway. This was accomplished by performing a bulk electrolysis experiment using a mixture of $[L_8Mn^{III}]^+$ and $[L_7Mn^{III}]^+$. These particular compounds were chosen because they have a large separation in the formal potentials for their Mn(III/II) couples (0.2 V; see Table I in Section II.7).

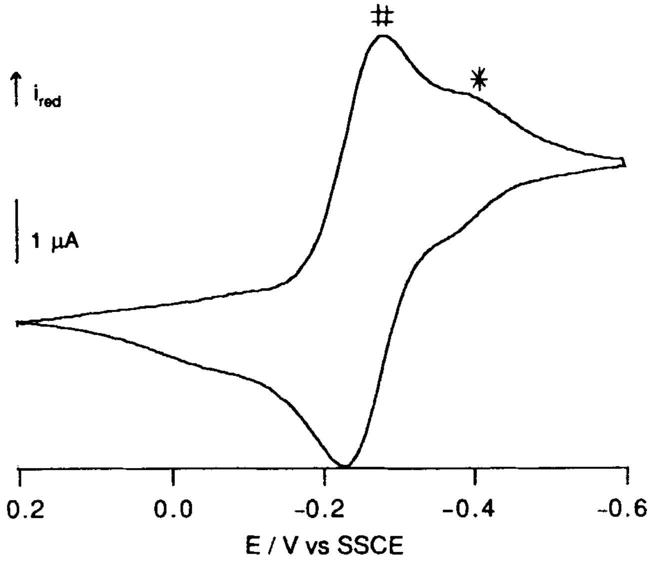


FIGURE II.5.2 CV of the product from the bulk electrolysis of a nearly 1:1 mixture of $[L_7Mn^{III}]^+$ and $[L_8Mn^{III}]^+$ produced under conditions where only 5% of $[L_7Mn^{III}]^+$ was reduced and 100% of $[L_8Mn^{III}]^+$ was reduced. The # indicates the $[L_8Mn^{IV}(\mu\text{-}O)]_2$ dimer and * indicates the $[L_7L_8Mn^{IV}(\mu\text{-}O)]_2$ dimer.

This condition allows for the application of a potential where the ECE process for $[\mathbf{L_8}\mathrm{Mn^{III}}]^+$ occurs while simultaneously reducing only a trace amount of $[\mathbf{L_7}\mathrm{Mn^{III}}]^+$. Thus we would have a high concentration of $[\mathbf{L_8}\mathrm{Mn^{III}}(\eta^2\text{-}\mathrm{O_2})]^-$ in the presence of a large quantity of $[\mathbf{L_7}\mathrm{Mn^{III}}]^+$. Clearly if the dimerization were to proceed via Eq. (3), $[\mathbf{L_7L_8}\mathrm{Mn_2^{IV}}(\mu\text{-O})_2]$ would be the dominant product.

The solid isolated from the experiment is comprised almost exclusively of the homoligand complex $[\mathbf{L_8}\mathrm{Mn^{IV}}(\mu\text{-O})]_2$ as determined by CV, Figure II.5.2.[94] The trace amount of $[\mathbf{L_7L_8}\mathrm{Mn_2^{IV}}(\mu\text{-O})_2]$ that is detected likely arises from the $[\mathbf{L_7}\mathrm{Mn^{III}}]^+$ that is unavoidably reduced during the electrolysis. We also found that high concentrations of Mn(III) cause decomposition of $[\mathrm{LMn^{IV}}(\eta^2\text{-}\mathrm{O_2})]$ and/or $[\mathrm{LMn^{III}}(\eta^2\text{-}\mathrm{O_2})]^-$ as the yield of the dimer from this experiment is relatively low. Thus by combining all the information from the various electrochemical techniques, with particular emphasis being placed on the bulk electrolysis experiment just described, we feel confident about using the reactions in Scheme 5 to describe formation of $[\mathrm{LMn^{IV}}(\mu\text{-O})]_2$.

II.6. Reaction of LMn(II) with O_2

After establishing that $[\mathrm{LMn^{IV}}(\mu\text{-O})]_2$ forms in the electrochemically driven reaction by Eqs. (5)–(7), we sought to determine if the dimers could be synthesized in a pure state by reaction of $\mathrm{LMn^{II}}$ in the absence of electrochemical influence. Syntheses of the bis(μ-oxo) dimers with SALPRN type ligands were reported, Eqs. (8) and (9), as was the structure of $[\mathbf{L_5}\mathrm{Mn^{IV}}(\eta^2\text{-}\mathrm{O_2})]$, Figure II.6.1, while our studies were in progress.[24–27] The most significant structural feature is the ligand adopting the *cis*-β geometry in this dimer whereas it is planar in the starting material. This result illustrates the conformational mobility of the Schiff-base ligand and probably accounts to some degree for the ability to isolate oxygenated compounds while only [porphyrin $\mathrm{Mn^{III}}]^+$ and decomposition products are isolated for the porphyrins upon oxygenation.

$$[\mathbf{L_5}\mathrm{Mn^{III}}\cdot\mathrm{H_2O}]^+ + \mathrm{NaOH} \rightarrow [\mathbf{L_5}\mathrm{Mn^{IV}}(\mu\text{-O})]_2 \qquad (8)$$

$$[\mathbf{L_5}\mathrm{Mn^{III}AcAc}] + \mathrm{H_2O_2} \rightarrow [\mathbf{L_5}\mathrm{Mn^{IV}}(\mu\text{-O})]_2 \qquad (9)$$

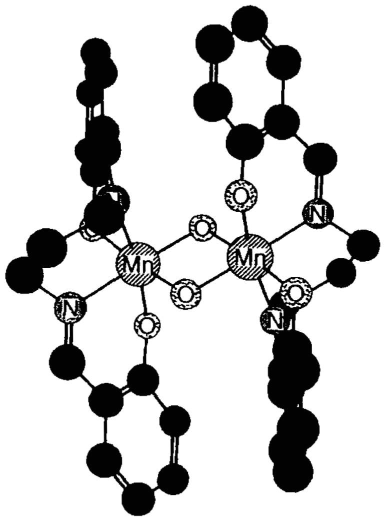
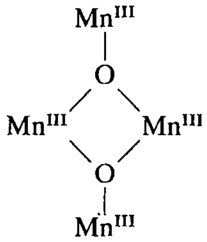


FIGURE II.6.1 Schematic representation of $[L_5Mn^{IV}(\mu\text{-}O)]_2$. Cell parameters and fractional coordinate data were taken from Ref. 27.

An interesting sidelight to our discussion about the O_2 activation process is that the synthetic method in Eq. (8) was originally reported for $[L_4Mn^{III}\cdot H_2O]^+$ and the product was assigned as $[L_4Mn^{IV}(\mu\text{-}O)]_2$.[99] This was subsequently reformulated by the same researchers to be $[(L_4)_2Mn^{III}Mn^{IV}(\mu\text{-}O)(\mu\text{-}OH)]$.[100] Other investigators[101] repeated this work with some modifications of the synthetic procedures and suggested that it was possible to selectively form either type of complex. We repeated the conditions originally reported using $[L_2Mn^{III}\cdot H_2O]^+$ and found by CV that a mixture of at least two compounds forms which varies in the relative ratio of the components[79]; one product is probably $[L_2Mn^{IV}(\mu\text{-}O)]_2$ and the other appears to be $[L_2Mn^{III}]_2(\mu\text{-}O)$. Our observation provides some insight into why multiple products have been claimed, all of which may be correct, using this synthetic methodology (see also Section II.7).

We quickly found that analytically pure samples of the bis(μ-oxo) dimers could be synthesized by the simple oxygenation process. However, we also found that reaction conditions play a critical role in determining the purity of the product. If the oxidation is performed in a solvent where both LMn^{II} and $[LMn^{IV}(\mu\text{-}O)]_2$ are sparingly soluble (CH_3CN generally seems to work best), $[LMn^{IV}(\mu\text{-}O)]_2$ forms in nearly 100% yield in some cases—an observation different from that of Pfeiffer and others and one that called into question the pathway in Scheme 1. However, when carrying out a reaction where LMn^{II} and $[LMn^{IV}(\mu\text{-}O)]_2$ are both soluble, at least one other species is isolated in addition to the bis(μ-oxo) dimer—a result more in keeping with the conclusions of others. For the X-SALPRN complexes the second product is most likely $[\{LMn^{III}\}_2(O)]_2$, **12**, while it is $[LMn^{III}]_2(\mu\text{-}O)$, **13**, for X-SALEN, Eq. (10). Although we do not have structural information yet, we suspect that the metal core in **12** is as shown schematically below.

$$\underset{\text{X-SALEN}}{[LMn^{IV}(\mu\text{-}O)]_2 + [LMn^{III}]_2(\mu\text{-}O)} \overset{O_2}{\Leftarrow} LMn^{II} \overset{O_2}{\Rightarrow} \underset{\text{X-SALPRN}}{[LMn^{IV}(\mu\text{-}O)]_2 + [\{LMn^{III}\}_2(O)]_2} \quad (10)$$



12

An important observation we made during the experiments with X-SALPRN complexes in particular was that the rate of oxygenation could be used to control which products formed.[53] For example, bubbling O_2 through a CH_2Cl_2 solution of the (X-SALPRN)Mn^{II} compound produces a much higher yield of the bis(μ-oxo) dimer relative to $[\{LMn^{III}\}_2(O)]_2$ than if air is allowed to slowly diffuse into a solution (12–24 hrs) of the Mn(II) complex. If we are careful and allow the diffusion process to proceed extremely slowly, it is possible to isolate $[\{LMn^{III}\}_2(O)]_2$ with none of the bis(μ-oxo) dimer present. This ability to control product formation was important as it suggested to us that it was the reaction of $[LMn^{IV}(\mu\text{-}O)]_2$ with Mn(II) that lead to isolation of the second species—a concept that had not been considered in prior investigations. We show in Section II.8 that indeed this is the case.

Controlling the chemistry of the X-SALEN type complexes proved to be quite challenging. We have focused our studies primarily on the L_2Mn complex because it provides us with the most reproducible results.[52] The other complexes have reactivities that are similar (bis(μ-oxo)dimers are formed) but not necessarily identical to that for L_2Mn. These results are somewhat frustrating, but at the same time enlightening, as they show that subtle changes to the ligand affect the oxygenation chemistry even within the same class of ligands.

$[L_2Mn^{IV}(\mu\text{-}O)]_2$ can be isolated in pure form upon slow oxygenation (24–48 hrs) of L_2Mn^{II} in CH_3CN, but fast oxidation in CH_3CN or oxidation in DMF leads to a product that is contaminated with variable amounts of the μ-oxo dimer. Figure II.6.2

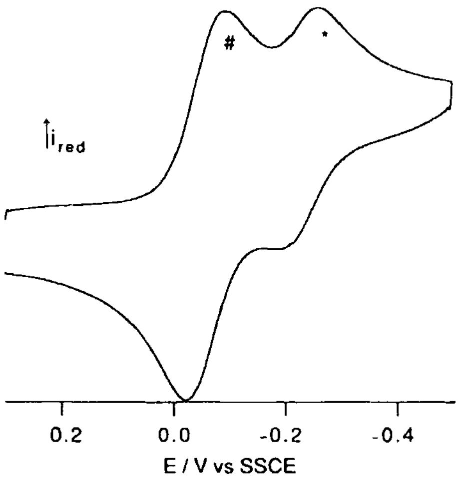


FIGURE II.6.2 CV of the product from oxidation of L_2Mn^{II} in DMF taken in 0.1 M $TBAClO_4$/DMF. The # denotes the $[L_2Mn^{III}]_2(\mu\text{-}O)$ and the * is $[L_2Mn^{IV}(\mu\text{-}O)]_2$. The amount of $[L_2Mn^{III}]_2(\mu\text{-}O)$ varies between preparations as discussed in the text.

shows one example where the μ-oxo dimer predominates. The redox potential for $[\mathbf{L}_2\mathrm{Mn}^{\mathrm{III}}]_2(\mu\text{-O})$ is nearly coincident with the one for $[\mathbf{L}_2\mathrm{Mn}^{\mathrm{III}}]^+$ itself and initially we thought that our samples were contaminated with $[\mathbf{L}_2\mathrm{Mn}^{\mathrm{III}}]^+$. Unfortunately we still do not have a good method for separating the bis(μ-oxo) and μ-oxo dimers, but the bis(μ-oxo) dimer can be converted to its μ-oxo form (see Section II.8).

II.7. Physical Characterization of the Oxygenated Complexes

Figure II.7.1 shows IR and CV data for the red-brown $[\mathbf{L}_6\mathrm{Mn}^{\mathrm{IV}}(\mu\text{-O})]_2$ and the green-black $[\{\mathbf{L}_6\mathrm{Mn}^{\mathrm{III}}\}_2(\mathrm{O})]_2$ complexes. The 650 cm^{-1} band in the IR spectrum of $[\mathbf{L}_6\mathrm{Mn}^{\mathrm{IV}}(\mu\text{-O})]_2$ is characteristic of the $\mathrm{Mn}_2\mathrm{O}_2$ core and it is readily seen that this band is absent in the spectrum of $[\{\mathbf{L}_6\mathrm{Mn}^{\mathrm{III}}\}_2(\mathrm{O})]_2$. A more striking difference is in the CV's. First, the oxidation process at positive potentials recorded for $[\{\mathbf{L}_6\mathrm{Mn}^{\mathrm{III}}\}_2(\mathrm{O})]_2$ is absent in $[\mathbf{L}_6\mathrm{Mn}^{\mathrm{IV}}(\mu\text{-O})]_2$. Second, the oxidation and reduction processes for $[\{\mathrm{LMn}^{\mathrm{III}}\}_2(\mathrm{O})]_2$ are multi-electron events,[53] Eq. (11), hence the asymmetrically shaped peaks in the CV, whereas the bis(μ-oxo) dimers undergo sequential one electron reductions at widely separated potentials, Eq. (12). The mixed-valent nature of the one electron reduced complex $[(\mathrm{L}_5)_2\mathrm{Mn}^{\mathrm{III}}\mathrm{Mn}^{\mathrm{IV}}(\mu\text{-O})_2]^-$ is demonstrated by its ESR spectrum, Figure II.7.2. This spectrum is typical of mixed-valent antiferromagnetically coupled manganese dimers with lightly trapped valences.[102]

$$[[\{\mathrm{LMn}^{\mathrm{IV}}\}_2(\mathrm{O})]_2]^{4+} \overset{-4\,e^-}{\leftrightharpoons} [\{\mathrm{LMn}^{\mathrm{III}}\}_2(\mathrm{O})]_2 \overset{+4\,e^-}{\rightleftharpoons} [[\{\mathrm{LMn}^{\mathrm{II}}\}_2(\mathrm{O})]_2]^{4-} \tag{11}$$

$$[\mathrm{LMn}^{\mathrm{IV}}(\mu\text{-O})]_2 + e^- \rightleftharpoons [(\mathrm{L})_2\mathrm{Mn}^{\mathrm{III}}\mathrm{Mn}^{\mathrm{IV}}(\mu\text{-O})_2]^- + e^- \rightarrow \begin{array}{l}\text{dimer}\\ \text{dissociation}\end{array} \tag{12}$$

The electrochemical properties of the bis(μ-oxo) dimers themselves turned out to be quite interesting and unusual. Apparently as a result of the ligand adopting the cis-β configuration, Figure II.6.1, and the presence of the oxo ligands, the Mn(IV) state in

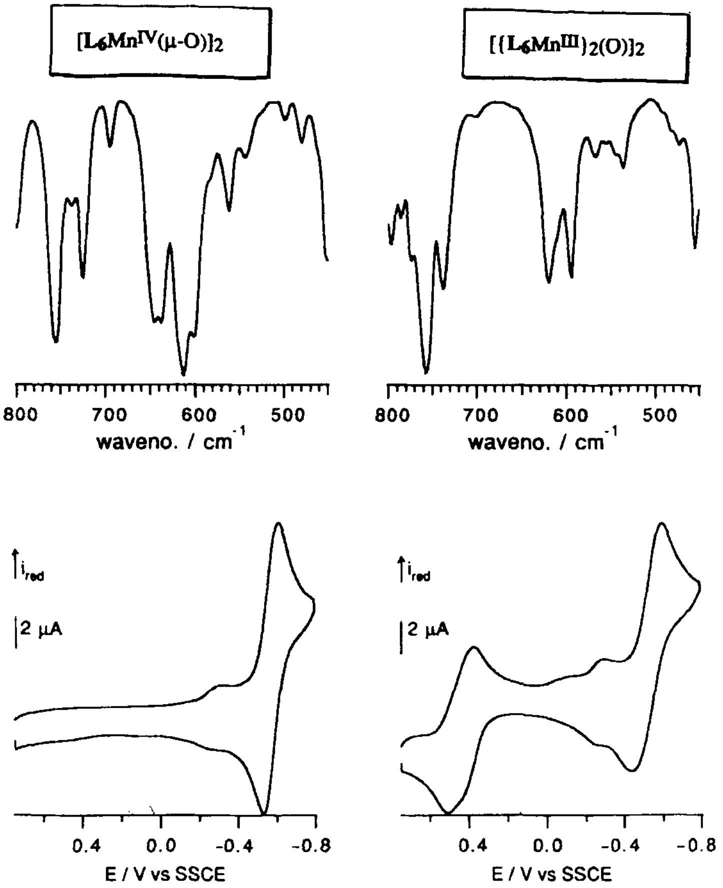
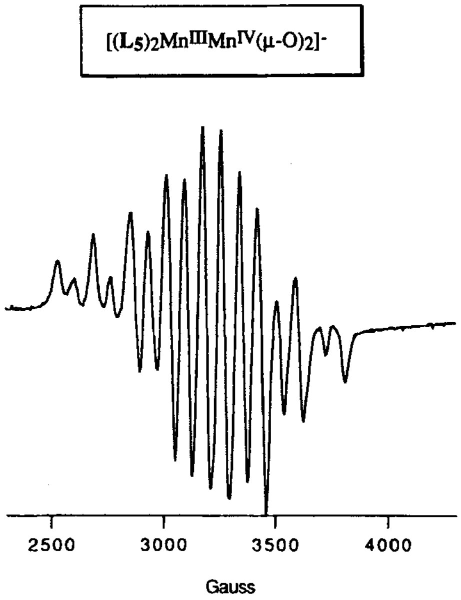


FIGURE II.7.1 FTIR spectra of $[L_5Mn^{IV}(\mu\text{-}O)]_2$ and $[\{L_5Mn^{III}\}_2(O)]_2$ as KBr disks. CV's of $[L_5Mn^{IV}(\mu\text{-}O)]_2$ and $[\{L_5Mn^{III}\}_2(O)]_2$ in 0.1 M $TBAPF_6/CH_2Cl_2$.

the dimer is more stable than the Mn(III) in the starting material, Table I. With regard to the change of the ligand geometry, the oxidation of $[L_5Mn^{III}]^+$ occurs at a potential > 1 V while the E° for the $Mn^{III/IV}$ couple in $L_5Mn^{III}AcAc$ is at +518 mV vs. SSCE.[24] The significant role that the oxo ligands play in the stabilization process is demonstrable by comparing E°'s for the one electron $Mn^{III/IV}$ couples in $L_5Mn^{III}AcAc$ ($E^0 = +518$ mV vs. SSCE) and $[L_5Mn^{IV}(\mu\text{-}O)]_2$, $E^\circ = -480$ mV vs. SSCE. As noted above, the



$g_x = 2.0092$	$A_{1x} = 492$ MHz	$A_{2x} = 231$ MHz
$g_y = 2.0061$	$A_{1y} = 448$ MHz	$A_{2y} = 227$ MHz
$g_z = 1.9925$	$A_{1z} = 385$ MHz	$A_{2z} = 209$ MHz

FIGURE II.7.2 ESR spectrum of $[(L_5)_2Mn^{III}Mn^{IV}(\mu\text{-}O)_2]^-$ at 6 K in CH_2Cl_2. The best fit parameters listed on the figure were determined for a $S = 1/2$ system having rhombic symmetry.

TABLE I

E° vs. SSCE for $[LMn^{IV}(\mu\text{-}O)]_2$ and $[LMn^{III}]PF_6$ complexes.

Ligand	E° vs. SSCE/mV $Mn^{IV/III}\text{-}Mn^{IV}$	E° vs. SSCE/mV $Mn^{III/II}$
L_2	-270^a	-128^c
L_6	-340^b	$+60^d$
L_7	-590^b	-25^d
L_8	-260^b	-175^d

0.1 M Bu_4NClO_4 or Bu_4NPF_6 in ^{a}DMF, $^bCH_2Cl_2$, $^cCH_3CN$ and 5 mM 1-MeIM, $^dCH_3CN$.

very negative reduction potential of the dimer turned out to be quite fortunate for our studies as this allowed us to easily observe its formation by the various electrochemical techniques.

The $[L_2Mn^{IV}(\mu\text{-}O)]_2$ complex has additional interesting chemical and electrochemical attributes besides the stabilization of its Mn(IV) state. By the normal criteria applied to CV, the first reduction is *electrochemically* reversible, Eq. (12).[94] However, by using the longer time scale bulk electrolysis experiment we were able to show that the reduction is *chemically* irreversible.[52] This irreversibility is also evident in UV-vis spectrophotometric titrations using chemical reductants. One electron is consumed per mole of bis(μ-oxo) dimer using either method and the "decomposition" product is $[[(L_2)_2Mn^{II}Mn^{III}]_2(\mu\text{-}O)]^-$, Eq. (13). This is confirmed by comparing the ESR spectrum of the product from Eq. (13) with an

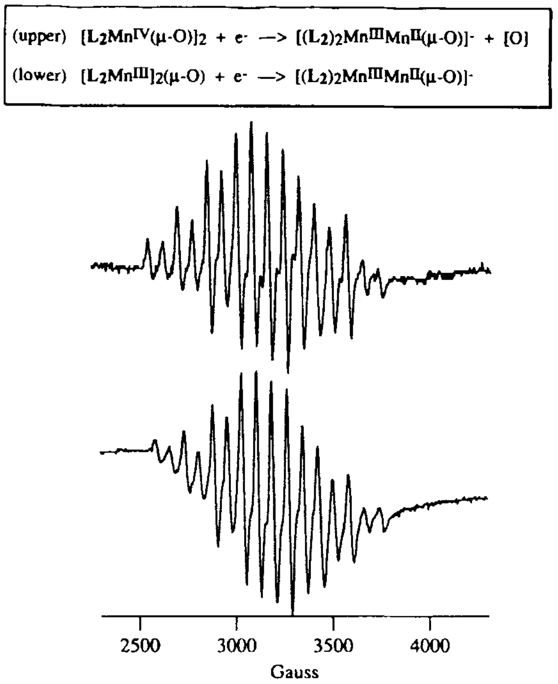


FIGURE II.7.3 ESR spectra at 6 K of the product from the electrochemical reduction of $[L_2Mn^{IV}(\mu\text{-}O)]_2$ (upper) and $[L_2Mn^{III}]_2(\mu\text{-}O)$ in 0.1 M $TBAClO_4$/DMF.

authentic sample of the mixed-valent μ-oxo dimer and finding that they are identical, Figure II.7.3. We do not know the fate of the ejected oxo ligand in Eq.(13).

$$[L_2Mn^{IV}(\mu\text{-}O)]_2 + e^- \rightarrow [[(L_2)_2Mn^{II}Mn^{III}]_2(\mu\text{-}O)]^- + [O] \tag{13}$$

Subsequently we found that the reduction was simply accelerating the rate of conversion of $[L_2Mn^{IV}(\mu\text{-}O)]_2$ to the μ-oxo dimer as a DMF solution of $[L_2Mn^{IV}(\mu\text{-}O)]_2$ spontaneously decomposes to $[L_2Mn^{III}]_2(\mu\text{-}O)$ over a 24–48 hr period. The likely cause for the instability of $[L_2Mn^{IV}(\mu\text{-}O)]_2$ is strain induced by the relatively short ethylenediamine derived backbone. Apparently the strain is relieved as the ligand returns to the square planar geometry from the *cis*-β configuration. Nevertheless, it is clear that the kinetic product of oxygenation is the bis(μ-oxo) dimer but thermodynamically it is unstable toward formation of the μ-oxo dimer. This result further exposes the difficulties in understanding and controlling the oxygenation process.

II.8. Reactivity of the Oxygenated Products

Perhaps the most intriguing discovery we made since beginning our studies of $Mn(II)-O_2$ chemistry is that bridging oxo ligands can participate in both complete and incomplete intermetal oxygen atom transfer reactions[51–54, 103, 104] (the term oxo transfer is often used for brevity). We are unaware of any examples of bridging oxo ligands undergoing these types of reactions prior to our reports. Oxo bridged dimers have been used for intermetal oxo transfer reactions in a few instances[105–107] but mononuclear fragments with terminal oxo ligands are the active agents. Homolysis of the Schiff-base dimers does not occur.

Among the first reactions we investigated was the one in Eq. (14).[53] We felt that this reaction would be the origin of $[\{LMn^{III}\}_2(O)]_2$ in the X-SALPRN complexes. The easiest way to monitor the reaction was by CV where we expected the oxidation process for $[\{LMn^{III}\}_2(O)]_2$ to appear upon addition of LMn^{II}. Fortunately the result is unambiguous in its interpretation as illustrated by Figure

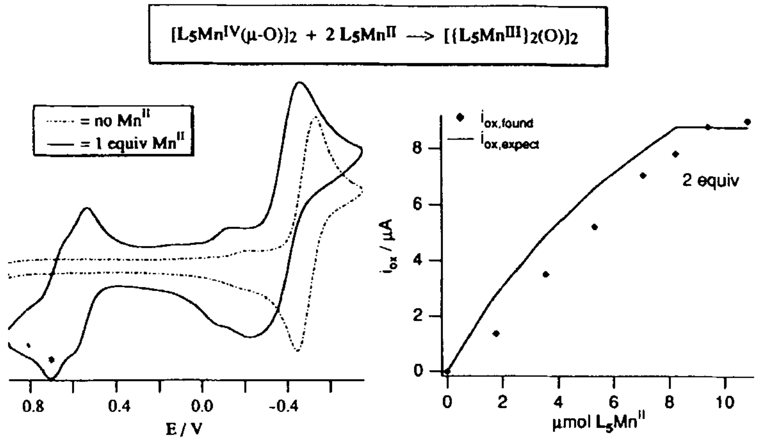


FIGURE II.8.1 (a) CV's of $[L_5Mn^{IV}(\mu\text{-}O)]_2$ before (-·-·-) and after (——) addition of 1 equiv of L_5Mn^{II}. (b) The graph represents the increase in current for the process marked with a # on (a) as a function of the amount of L_7Mn^{II} added to the electrolysis solution.

II.8.1. It can be seen from the graph on the figure that two equivalents of Mn(II) are required for complete reaction to occur. Actually we used this experiment to establish the nuclearity of $[\{LMn^{III}\}_2(O)]_2$ as no crystals suitable for an X-ray analysis are available yet.

$$[(X\text{-SALPRN})Mn^{IV}(\mu\text{-}O)]_2 + 2\ (X\text{-SALPRN})Mn^{II} \rightarrow [\{(X\text{-SALPRN})Mn^{III}\}_2(O)]_2 \qquad (14)$$

Clearly, uncovering the incomplete oxo transfer reaction in Eq. (14) is significant as it allows us to establish that the bis(μ-oxo) dimer is the kinetic product of oxygenation while the tetrametallic compound is a secondary reaction product. Furthermore, it gives us the first piece of evidence that the multitude of oxygenation products that had been claimed by other workers in this area probably arise from similar types of reactions. As noted, many of those studies were carried out in solvents where both $[LMn^{IV}(\mu\text{-}O)]_2$ and LMn^{II} were soluble. The chemistry in Eq. (14) also makes it possible to explain why the oxygenation rate controls which products form. Slow oxygenation keeps the concentration of $[\mathrm{LMn}^{\mathrm{IV}}(\mu\text{-O})]_2$ low relative to the Mn(II), thus favoring cluster building, but fast oxidations rapidly remove the Mn(II) in the form of the bis(μ-oxo) dimer.

We also examined the reaction of $[\mathrm{L_2Mn}^{\mathrm{IV}}(\mu\text{-O})]_2$ with $\mathrm{L_2Mn}^{\mathrm{II}}$ and again found that an oxo transfer reaction occurs in a 1:2 bis(μ-oxo):Mn(II) ratio, Eq. (15).[108] Initially we expected that a tetrametallic compound would be produced as is seen for the X-SALPRN compounds, but this proved not to be the case as no oxidation processes at positive potentials (see Figure II.7.1) are observed in the voltammogram. We now know that the product is the μ-oxo dimer and Figure II.8.2 shows the evolution of $[\mathrm{L_2Mn}^{\mathrm{IV}}(\mu\text{-O})]_2$ to

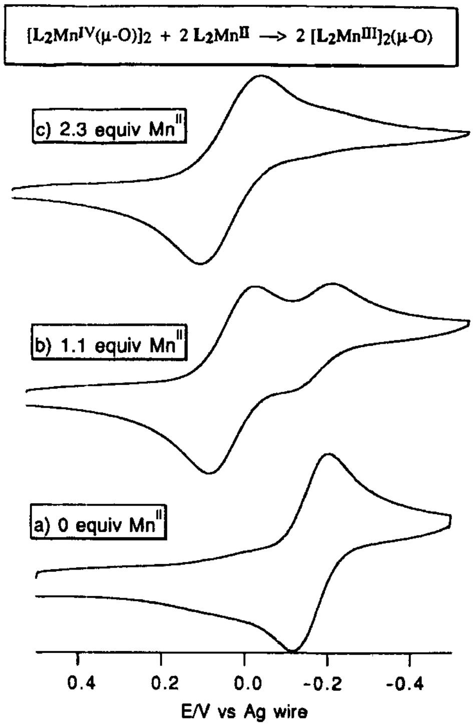


FIGURE II.8.2 CV's of $[\mathrm{L_2Mn}^{\mathrm{IV}}(\mu\text{-O})]_2$ with (a) 0 equiv (b) 1.1 equiv and (c) 2.3 equiv of $\mathrm{L_2Mn}^{\mathrm{II}}$.

$[L_2Mn^{III}]_2(\mu\text{-}O)$. Presumably the reaction pathway includes a tetrametallic intermediate but it is not stable for steric reasons.

$$[L_2Mn^{IV}(\mu\text{-}O)]_2 + 2\ L_2Mn^{II} \rightarrow 2[L_2Mn^{III}]_2(\mu\text{-}O) \qquad (15)$$

II.9. Additional Oxo Transfer Reactions

All of the oxygenated complexes react stoichiometrically and irreversibly with L_1Fe^{II}, Eqs. (16)–(18).[51-53] Figure II.9.1 shows CV's for the reaction of $[LMn^{IV}(\mu\text{-}O)]_2$ with L_1Fe^{II}. As μ-oxo iron compounds generally are quite stable, we anticipated that complete oxo transfer reactions of LFe^{II} with compounds having terminal oxo ligands, $L'M^n{=}O$, would be routinely cited. However, in almost all instances a heterobimetallic complex forms, Eq. (19),[103,104] so the chemistry of the oxygenated manganese complexes we are studying is rather unique.

$$[LMn^{IV}(\mu\text{-}O)]_2 + 4L_1Fe^{II} \rightarrow 2[L_1Fe^{III}]_2(\mu\text{-}O) + 2LMn^{II} \qquad (16)$$

$$[LMn^{III}]_2(\mu\text{-}O) + 2L_1Fe^{II} + \rightarrow [L_1Fe^{III}]_2(\mu\text{-}O) + 2LMn^{II} \qquad (17)$$

$$[\{LMn^{III}\}_2(O)]_2 + 4L_1Fe^{II} \rightarrow 2[L_1Fe^{III}]_2(\mu\text{-}O) + 4LMn^{II} \qquad (18)$$

$$L'M^n{=}O + LFe^{II} \rightarrow L'M^{n-1}\text{-}O\text{-}Fe^{III}L \qquad (19)$$

$$[L_7Mn^{IV}(\mu\text{-}O)]_2 + 4\ L_1Fe^{II} \longrightarrow 2\ [L_1Fe^{III}]_2(\mu\text{-}O) + 2\ L_7Mn^{II}$$

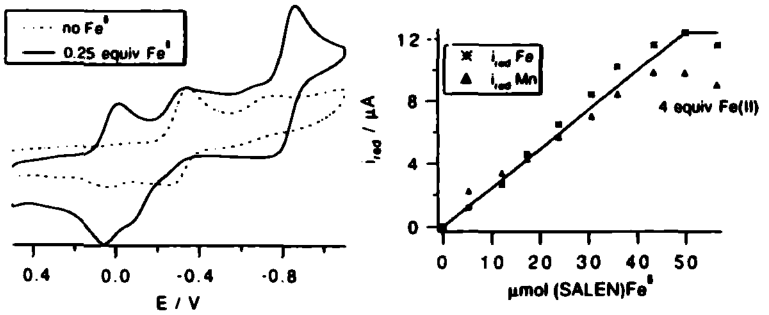
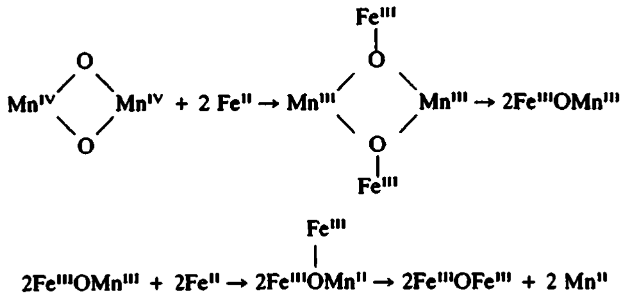


FIGURE II.9.1 CV's of $[L_7Mn^{IV}(\mu\text{-}O)]_2$ before (- - - - -) and after (——) addition of 0.25 equiv of L_1Fe^{II}. The graph represents the increase in current for the process marked with a * on (a) as a function of the amount of L_1Fe^{II} added to the electrolysis solution.



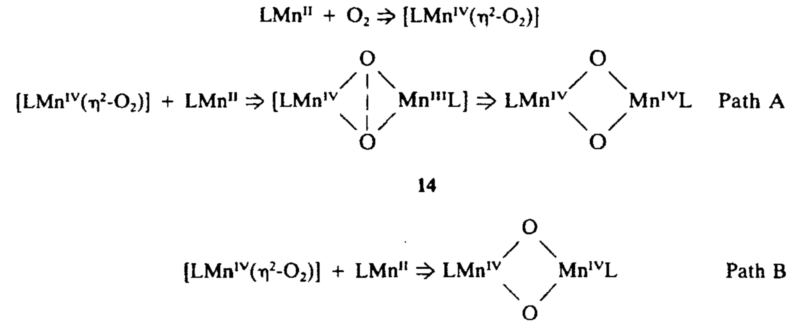
SCHEME 6

The extreme rapidity of the oxo transfer makes these reactions even more unusual. Preliminary kinetic measurements suggest that the $t_{1/2}$ at 0°C is 5 s or less for Eq. (16). The impressive feature of the reaction occurring so rapidly is that formally two oxygen atoms and four electrons are being exchanged. Kinetically, oxo transfer reactions involving terminal oxo groups appear to be relatively slow. Thus, the oxo ligands in the Schiff-base compounds are highly unusual compared to other types of oxo ligands. Bridging oxo ligands in other compounds may exhibit similar reactivity and are worthy of further investigation. Interestingly, protonation of $[\mathrm{L_5Mn^{IV}}(\mu\text{-O})]_2$ appears to be slower, $k = 1920\ \mathrm{M^{-1}s^{-1}}$ at 0°C, than the intermetal oxygen atom transfer we are observing.[109,110]

We postulate that the chemistry observed in Eq. (16) proceeds through a pathway that is described by Scheme 6. If this proposition is close to being correct, then the tetranuclear complexes, $[\{\mathrm{LMn^{III}}\}_2(\mathrm{O})]_2$ that we have been isolating from the oxygenation reactions actually provide a snapshot of what is one of the key intermediates in the scheme. This provides some commonality between the various kinds of reactions that can be observed for the oxygenated manganese compounds.

III. CONCLUSIONS

Our understanding of $\mathrm{Mn(II)-O_2}$ chemistry has expanded greatly during the past decade as researchers have focussed on modeling biological oxygen evolution processes and on finding new homogeneous catalysts. From the evidence that has been gathered thus far it appears that the $\mathrm{O_2}$ activation process for manganese, taken



SCHEME 7

as a whole, is relatively simple. We propose in Scheme 7 that the dimer forms in either a stepwise reduction of the O–O bond, Path A, or a single step, Path B, following generation of the initial oxygen adduct. Either path accounts for the high yield and the selective formation of the bis(μ-oxo) dimer, and both paths combine the information obtained thus far from ESR, electrochemical, and chemical experiments. While we currently favor the more straightforward process in Path B, experiments are ongoing to ascertain if **14**, the dashed line is meant to indicate a non-integral bond order for the bound O_2, in Path A is an intermediate.

The obvious questions that still need attention are (a) do mononuclear intermediates form prior to formation of the oxo bridged dimers (preliminary evidence suggests not), (b) are compounds identified as final oxygenation products actually formed by oxo transfer reactions with the kinetic oxygenation product, (c) can the oxygenation process be controlled so that new catalysts can be developed, and (d) will a single oxygen activation pathway apply to all the various types of manganese compounds that are capable of reducing oxygen by four electrons? Clearly Mn(II)–O_2 chemistry still needs extensive attention to resolve these issues. The intent of this Comment was to demonstrate that considerable progress has been made in addressing some of these questions and, with the rapid pace of identifying and characterizing oxygenated products and intermediates, we can hope the overall picture for O_2 activation will be settled in the near future.

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References

1. R. D. Jones, D. A. Summerville and F. Basolo, Chem. Rev. **79**, 139 (1979).
2. (a) T. G. Spiro (Ed.), *Metal Ion Activation of Dioxygen* (Wiley, New York, 1980). (b) A. E. Martell and D. T. Sawyer (Eds.), *Oxygen Complexes and Oxygen Activation by Transition Metals* (Plenum Press, New York, 1988). (c) R. A. Sheldon and J. K. Kochi, *Metal Catalyzed Oxidations of Organic Compounds* (Academic Press, New York, 1981). (d) W. J. Mijs and C. R. H. I. DeJonge, *Organic Syntheses by Oxidation with Metal Compounds* (Plenum Press, New York, 1986). (e) L. I. Simándi, Int. Rev. Phys. Chem. **8**, 21 (1989).
3. P. Pfeiffer, E. Breith, E. Lubbe and T. Tsumaki, Annalen **503**, 84 (1933).
4. V. L. Pecoraro, *Manganese Redox Enzymes* (VCH, New York, 1992).
5. T. Tsumaki, Nippon Kagaku Zasshi **55**, 1245 (1934).
6. (a) W. M. Coleman and L. T. Taylor, Coord. Chem. Rev. **32**, 1 (1980). (b) G. L. Johnson and W. D. Beveridge, Inorg. Nucl. Chem. Lett. **3**, 323 (1967). (c) J. Lewis, F. E. Mabbs and H. Weigold, J. Chem. Soc. A 1699 (1968). (d) R. K. Boggess, J. W. Hughes, W. M. Coleman and L. T. Taylor, Inorg. Chim. Acta **38**, 183 (1980). (e) M. Tamaki, I. Masuda and K. Shinra, Chem. Lett. 165 (1972).
7. (a) G. Christou, Acc. Chem. Res. **22**, 328 (1989). (b) G. Christou and J. B. Vincent, in *Metal Clusters in Proteins*, ed. L. Que, Jr., ACS Symp. Ser. 372, 1988. (c) H. H. Thorp and G. W. Brudvig, New. J. Chem. **15**, 479 (1991). (d) L. Que, Jr. and A. E. True, Prog. Inorg. Chem. **38**, 97 (1990).
8. E.-I. Ochiai, Inorg. Nucl. Chem. Lett. **10**, 453 (1974).
9. F. C. Frederick and L. T. Taylor, Polyhedron **5**, 887 (1986).
10. R. F. Ziolo, R. H. Stanford, G. R. Rossman and H. B. Gray, J. Am. Chem. Soc. **96**, 7910 (1974).
11. L. H. Vogt, A. Zalkin and D. H. Templeton, Inorg. Chem. **6**, 1725 (1967).
12. (a) The unsupported oxo bridged compound $[XTPPMn^{IV}]_2(\mu\text{-}O)$ has been prepared by reaction of $[XTPPMn^{III}]$ and PhIO (X is N_3^- or OCN^-). See B. C. Schardt, F. J. Hollander and C. L. Hill, J. Am. Chem. Soc. **104**, 3964 (1982). (b) J. A. Smegal, B. C. Schardt and C. L. Hill, J. Am. Chem. Soc. **105**, 3510 (1983). (c) M. J. Camenzid, B. C. Schardt and C. L. Hill, Inorg. Chem. **23**, 1984 (1984).
13. H. S. Maslen and T. N. Waters, J. Chem. Soc., Chem. Commun. 760 (1973).
14. M. Suzuki, H. Senda, M. Suenaga, T. Sugisawa and A. Uehara, Chem. Lett. 923 (1990).
15. M. Suzuki, S. Tokura, M. Suhara and A. Uehara, Chem. Lett. 477 (1988).
16. M. Suzuki, H. Senda, Y. Kobayashi, H. Oshio and A. Uehara, Chem. Lett. 1763 (1988).

17. K. J. Brewer, A. Leigeois, J. W. Otvos, M. Calvin and L. O. Spreer, J. Chem. Soc., Chem. Commun. 1219 (1988).
18. K. J. Brewer, M. Calvin, R. S. Lumpkin, J. W. Otvos and L. O. Spreer, Inorg. Chem. **28**, 4446 (1989).
19. A. R. Oki, J. Glerup and D. J. Hodgson, Inorg. Chem. **29**, 2435 (1990).
20. M. A. Collins, D. J. Hodgson, K. Michelsen and E. Pedersen, J. Chem. Soc., Chem. Commun. 1659 (1987).
21. D. K. Towle, C. A. Botsford and D. J. Hodgson, Inorg. Chim. Acta **141**, 167 (1988).
22. P. A. Goodson, J. Glerup, D. J. Hodgson, K. Michelsen and H. Weihe, Inorg. Chem. **30**, 4909 (1991).
23. K. S. Hagen, W. H. Armstrong and H. Hope, Inorg. Chem. **27**, 967 (1988).
24. E. J. Larson and V. L. Pecoraro, J. Am. Chem. Soc. **113**, 7809 (1991).
25. E. J. Larson and V. L. Pecoraro, J. Am. Chem. Soc. **113**, 3810 (1991).
26. E. J. Larson, M. S. Lah, X. Li, J. A. Bonadies and V. L. Pecoraro, Inorg. Chem. **31**, 373 (1992).
27. J. W. Gohdes and W. H. Armstrong, Inorg. Chem. **31**, 368 (1992).
28. N. Katajima, U. P. Singh, H. Amagai, M. Osawa and Y. Moro-oka, J. Am. Chem. Soc. **113**, 7757 (1991).
29. P. M. Plaskin, R. C. Stoufer, M. Mathew and G. J. Palenik, J. Am. Chem. Soc. **94**, 2121 (1972).
30. S. R. Cooper and M. Calvin, J. Am. Chem. Soc. **99**, 6623 (1977).
31. S. R. Cooper, G. C. Dismukes, M. P. Klein and M. Calvin, J. Am. Chem. Soc. **100**, 7248 (1978).
32. M. Stebler, A. Ludi and H.-B. Bürgi, Inorg. Chem. **25**, 4743 (1986).
33. C. A. McAuliffe, R. V. Parish, F. M. Ashmawy, R. M. Issa and S. A. Amer, J. Chem. Soc., Dalton Trans. 2009 (1987).
34. S. Pal, J. W. Gohdes, W. C. A. Wilisch and W. H. Armstrong, Inorg. Chem. **31**, 713 (1992).
35. U. Bossek, T. Weyhermüller, K. Wieghardt, B. Nuber and J. Weiss, J. Am. Chem. Soc. **112**, 6387 (1990).
36. R. Bhula, G. J. Gainsford and D. Weatherburn, J. Am. Chem. Soc. **110**, 7550 (1988).
37. W. M. Coleman and L. T. Taylor, Inorg. Chim. Acta **30**, L291 (1978).
38. I. Tabushi, Coord. Chem. Rev. **86**, 1 (1988).
39. W. Y. Lu, J. F. Bartoli, P. Battioni and D. Mansuy, New J. Chem. **16**, 621 (1992) and references therein.
40. S. E. Creager, S. A. Raybuck and R. W. Murray, J. Am. Chem. Soc. **108**, 4225 (1986).
41. F. Ojima, N. Kobayashi and T. Osa, Bull. Chem. Soc. Jpn. **63**, 1374 (1990).
42. C.-Y. Lin and Y. O. Su, J. Electroanal. Chem. **265**, 305 (1989).
43. B. Meunier, Chem. Rev. **92**, 1411 (1992) and references therein.
44. K. Srinivasan, P. Michaud and J. K. Kochi, J. Am. Chem. Soc. **108**, 2309 (1986).
45. K. Srinivasan, S. Perrier and J. K. Kochi, J. Mol. Catal. **36**, 297 (1986).
46. R. Irie, K. Noda, Y. Ito and T. Katsuki, Tetrahedron. Lett. **32**, 1055 (1991).
47. R. Irie, K. Noda, Y. Ito, N. Matsumoto and T. Katsuki, Tetrahedron. Lett. **31**, 7345 (1990).
48. E. N. Jacobsen, W. Zhang, A. R. Muci, J. R. Ecker and L. Deng, J. Am. Chem. Soc. **113**, 7063 (1991).
49. E. N. Jacobsen, W. Zhang and M. L. Guler, J. Am. Chem. Soc. **113**, 6703 (1991).

50. C. P. Horwitz, S. E. Creager and R. W. Murray, Inorg. Chem. **29**, 1006 (1990).
51. G. C. Dailey and C. P. Horwitz, Inorg. Chem. **31**, 3693 (1992).
52. G. C. Dailey, C. P. Horwitz and C. A. Lisek, Inorg. Chem. **31**, 5325 (1992).
53. C. P. Horwitz, P. J. Winslow, J. T. Warden and C. A. Lisek, Inorg. Chem., **32**, 82 (1993).
54. C. P. Horwitz, Y. Ciringh, C. Liu and S. Park, submitted to Inorg. Chem.
55. C. Bull, R. G. Fisher and B. M. Hoffman, Biochem. Biophys. Res. Commun. **59**, 140 (1974).
56. R. D. Jones, D. A. Summerville and F. Basolo, J. Am. Chem. Soc. **100**, 4416 (1978).
57. C. A. Reed, J. K. Kouba, C. J. Grimes and S. K. Cheung, Inorg. Chem. **17**, 2666 (1978).
58. B. Gonzales, J. Kouba, S. Yee, C. A. Reed, J. F. Kirner and W. R. Scheidt, J. Am. Chem. Soc. **97**, 3247 (1975).
59. T. Yarino, T. Matsushita, I. Masuda and K. Shinra, Chem. Commun. 1317 (1970).
60. J. D. Miller and F. D. Oliver, J. Inorg. Nucl. Chem. **34**, 1873 (1972).
61. T. Matsushita, T. Yarino, I. Masuda, T. Shono and K. Shinra, Bull. Chem. Soc. Jpn. **46**, 1712 (1973).
62. S. J. Ebbs and L. T. Taylor, Inorg. Nucl. Chem. Lett. **10**, 1137 (1974).
63. C. J. Boreham and B. Chiswell, Inorg. Chim. Acta **24**, 77 (1977).
64. S. J. E. Titus, W. M. Barr and L. T. Taylor, Inorg. Chim. Acta **32**, 103 (1979).
65. F. C. Frederick, W. M. Coleman and L. T. Taylor, Inorg. Chem. **22**, 792 (1983).
66. M. H. Gubelmann and A. F. Williams, Structure and Bonding **55**, 1 (1983).
67. C. J. Weschler, B. M. Hoffman and F. Basolo, J. Am. Chem. Soc. **97**, 5278 (1975).
68. B. M. Hoffman, C. J. Weschler and F. Basolo, J. Am. Chem. Soc. **98**, 5473 (1976).
69. B. M. Hoffman, T. Szymanski, T. G. Brown and F. Basolo, J. Am. Chem. Soc. **100**, 7253 (1978).
70. L. K. Hanson and B. M. Hoffman, J. Am. Chem. Soc. **102**, 4602 (1980).
71. A. Dedieu, M.-M. Rohmer, H. Veillard and A. Veillard, Nouv. J. Chim. **3**, 653 (1979).
72. J. E. Newton and M. B. Hall, Inorg. Chem. **24**, 2573 (1985).
73. R. Guilard, J.-M. Latour, C. Lecomte, J.-C. Marchon, J. Protas and D. Ripoll, Inorg. Chem. **17**, 1228 (1978).
74. M. B. Hall, in *Oxygen Complexes and Oxygen Activation by Transition Metals*, eds. A. E. Martell and D. T. Sawyer (Plenum Press, New York, 1988).
75. M. W. Urban, K. Nakamoto and F. Basolo, Inorg. Chem. **21**, 3406 (1982).
76. M. Kozuka and K. Nakamoto, J. Am. Chem. Soc. **103**, 2162 (1981).
77. K. Nakamoto, Coord. Chem. Rev. **100**, 363 (1990).
78. T. Watanabe, T. Ama and K. Nakamoto, Inorg. Chem. **22**, 2470 (1983).
79. G. C. Dailey and C. P. Horwitz, unpublished results.
80. C. A. McAuliffe, H. F. Al-Khateeb, D. S. Barratt, J. C. Briggs, A. Challita, A. Hosseiny, M. G. Little, A. G. Mackie and K. Minten, J. Chem. Soc., Dalton Trans. 2147 (1983).
81. C. A. McAuliffe, M. G. Little and J. B. Raynor, J. Chem. Soc., Chem. Commun. 68 (1982).

82. R. B. VanAtta, C. E. Strouse, L. K. Hanson and J. S. Valentine, J. Am. Chem. Soc. **109**, 1425 (1987).
83. K. Uchida, S. Naito, M. Soma, T. Onishi and K. Tamaru, J. Chem. Soc., Chem. Commun. 217 (1978).
84. A. B. P. Lever, J. P. Wilshire and S. K. Quan, J. Am. Chem. Soc. **101**, 3668 (1979).
85. Addition of nitrogen bases to the solution results in formation of the μ-oxo bridged product, the structure of which is described in Ref. 11.
86. G. C. Dismukes, in *Mixed Valency Systems: Applications in Chemistry, Physics, and Biology*, ed. K. Prassides (Kluwer, 1990).
87. G. W. Brudvig and R. H. Crabtree, Prog. Inorg. Chem. **37**, 99 (1989).
88. K. Wieghardt, Angew. Chem. Int. Ed. Engl. **28**, 1153 (1989).
89. M. Perrée-Fauvet, A. Gaudemer, J. Bonvoisin, J. J. Girerd, C. Boucly-Goester and P. Boucly, Inorg. Chem. **28**, 3533 (1989).
90. G. C. Dismukes, J. E. Sheats and J. A. Smegal, J. Am. Chem. Soc. **109**, 7202 (1987).
91. (a) Superoxide and other reduced forms of oxygen often act as reducing agents toward Mn(III) complexes making the suggestion of free O_2^- unique. See J. S. Valentine and A. E. Quinn, Inorg. Chem. **15**, 1997 (1976). (b) T. Matsushita and T. Shono, Bull. Chem. Soc. Jpn. **54**, 3743 (1981). (c) W. M. Coleman and L. T. Taylor, Inorg. Chem. Acta **61**, 13 (1982).
92. B. Mabad, J.-P. Tuchagues, Y. T. Hwang and D. H. Hendrickson, J. Am. Chem. Soc. **107**, 2801 (1985).
93. C. A. Kipke, M. J. Scott, J. W. Gohdes and W. H. Armstrong, Inorg. Chem. **29**, 2193 (1990).
94. A. J. Bard and L. R. Faulkner, *Electrochemical Methods* (Wiley, New York, 1980).
95. S. E. Creager and R. W. Murray, Inorg. Chem. **26**, 2612 (1987).
96. P. K. S. Tsang and D. T. Sawyer, Inorg. Chem. **29**, 2848 (1990).
97. S. A. Richert, P. K. S. Tsang and D. T. Sawyer, Inorg. Chem. **27**, 1814 (1988).
98. In order for the oxo ligands to adopt a cis orientation about each metal center, the ligand must distort from its square planar geometry to the *cis*-β configuration. A number of examples of Schiff-base complexes with this ligand geometry are known when an additional bidentate ligand chelates to the metal center. See for example R. B. Lauffer, R. H. Heistand and L. Que, Jr., Inorg. Chem. **22**, 50 (1983).
99. L. J. Boucher and C. G. Coe, Inorg. Chem. **15**, 1334 (1976).
100. L. J. Boucher and C. G. Coe, Inorg. Chem. **14**, 1289 (1975).
101. C. A. McAuliffe, R. V. Parish, S. M. Abu-El-Wafa and R. M. Issa, Inorg. Chim. Acta **115**, 91 (1986).
102. M. B. Robin and P. Day, Adv. Inorg. Chem. Radiochem. **10**, 248 (1967).
103. R. H. Holm, Chem. Rev. **87**, 1401 (1987).
104. B. O. West, Polyhedron **8**, 219 (1989).
105. J. L. Templeton, B. C. Ward, G. J.-J. Chen, J. W. McDonald and W. E. Newton, Inorg. Chem. **20**, 1248 (1981).
106. G. J.-J. Chen, J. W. McDonald and W. E. Newton, Inorg. Chim. Acta **35**, 93 (1979).
107. G. J.-J. Chen, J. W. McDonald and W. E. Newton, Inorg. Chim. Acta **19**, L67 (1976).

108. Taken from the PhD thesis of G. C. Dailey, Rensselaer Polytechnic Institute (1992).
109. E. J. Larson, P. J. Riggs, J. E. Penner-Han and V. L. Pecoraro, J. Chem. Soc. Chem. Commun. 102 (1992).
110. J. M. Carroll and J. R. Norton, J. Am. Chem. Soc. **114**, 8744 (1992). 1170 (1980).