

Reactivity of Dioxygen with Manganese Schiff-Base Complexes: A Chemical and Electrochemical Investigation

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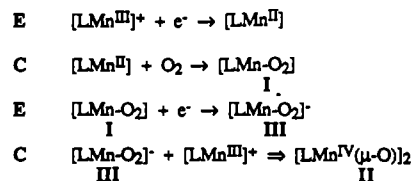
The bis(μ -oxo) dimers [(X-SALPRN)Mn^{IV}(μ -O)]₂, where X = 5-Cl, **1c**, 3,5-Cl₂, **2c**, and 5-CH₃O, **3c**, and SALPRN is 1,3-bis(salicylideneamino)propane, were prepared by two routes: oxidation of (X-SALPRN)Mn^{II}, X = 5-Cl, **1b**, 3,5-Cl₂, **2b**, and 5-CH₃O, **3b**, with O₂ in acetonitrile or bulk electrochemical reduction of the Mn(III) salt, [(X-SALPRN)Mn^{III}]PF₆, X = 5-Cl, **1a**, 3,5-Cl₂, **2a**, and 5-CH₃O, **3a**, in the presence of dioxygen in 0.2 M TBAPF₆/CH₃CN. Reaction of a mixture of **2b** and **3b** with oxygen produced **2c**, **3c**, and the mixed-ligand complex [(3,5-Cl₂-SALPRN)Mn^{IV}(5-CH₃O-SALPRN)Mn^{IV}(μ -O)]₂, **4**. The ternary mixture also formed when a CH₃CN solution of **2a** and **3a** was electrolyzed at a potential sufficient to produce the Mn(II) form of both complexes. Electrolysis of the same mixture at a potential where essentially only **2b** was reduced produced **2c**, a trace of **4**, and an insoluble green solid that appeared to be polymeric. The data from cyclic voltammetry, rotating disk electrode voltammetry, and bulk electrochemistry experiments suggested an ECC reaction pathway leading to formation of the bis(μ -oxo) dimers. The chemical steps in the ECC pathway were the same as those when **1b**, **2b**, or **3b** was oxidized in the absence of external reducing equivalents. Bulk electrolysis with H₂O present completely inhibited bis(μ -oxo) dimer formation and resulted in the precipitation of a green solid insoluble in common organic solvents.

Introduction

The reactivity of molecular oxygen toward manganese(II) complexes is still poorly understood when compared to the well-developed chemistry of iron¹ and cobalt² with dioxygen. Complicated reaction pathways are postulated³ to account for the variety of oxygenated products isolable from the reaction of O₂ with manganese(II) porphyrin⁴ and Schiff-base complexes.⁵ The products isolated using the porphyrin complexes, in general, are the Mn(III) porphyrin and decomposition products. In contrast, a wide array of oxygenated dimers such as μ -oxo, bis(μ -oxo), and $\eta^1\eta^1$ -peroxo species have been claimed for the Schiff-base complexes.

We are investigating oxygenation reactions of tetradentate Mn(II) Schiff-base complexes⁶⁻⁸ in part because these compounds are moderately efficient electrocatalytic olefin epoxidation catalysts when O₂ is used as the oxygen source.^{9a} In order to better understand the catalytic chemistry, and to design new catalysts,

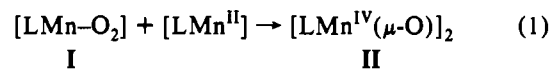
Scheme I



it is important to study the overall oxygen activation process. Thus far we have found that a Mn^{IV}-Mn^{IV} bis(μ -oxo) dimer is the kinetic oxygenation product but the dimer is reactive toward the Mn(II) starting material⁶ or it decomposes.⁸

Mn^{IV}-Mn^{IV} bis(μ -oxo) dimers with Schiff-base ligands, L, are synthesized by at least five different routes: oxidation of [LMn^{II}] with O₂,^{6-8,10} electrochemical reduction of [LMn^{III}]⁺ in the presence of molecular oxygen,⁸ oxidation of [LMn^{III}L'] (L' is either OCH₃ or acetylacetonate) with H₂O₂ or Na₂O₂,^{11a} and reaction of [LMn^{III}]⁺ with NaOH in the presence of O₂. Given these diverse methods for preparing the bis(μ -oxo) dimer, there must be a large driving force for its formation. We present here new chemical and electrochemical evidence which indicates that the first two synthetic routes probably follow a common reaction pathway. In addition, the synthesis using Na₂O₂ may involve intermediates analogous to those in the first two preparative methods.

The oxygenation of [LMn^{II}] compounds has been suggested³ to proceed via the reaction shown in eq 1. The data from prior



electrochemical studies regarding O₂ activation by Mn(II) Schiff-base complexes was interpreted in terms of Scheme I, an ECEC reaction pathway (E = electrochemical, C = chemical step), leading to isolation of the dimer.^{9a} Finally, the reaction sequence in Scheme II was used^{11a} to explain formation of the bis(μ -oxo) dimer using H₂O₂.

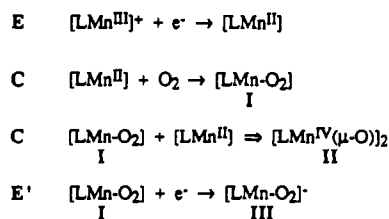
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Scheme III



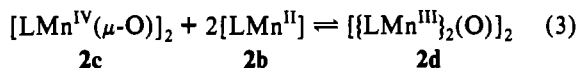
sequence leading to the bis(μ -oxo) dimer, Scheme III, and a competing electron transfer step removing I¹⁴ from the dimer-forming route, E'. A key observation that led to these conclusions was that formation of II was strongly suppressed rather than enhanced by high concentrations of [LMn^{III}]⁺ suggesting that step 4 of Scheme I did not occur. Porphyrin^{13,15} analogues of III, [TPPMn^{III}(η^2 -O₂)]⁻, and [Cl₈TPPMn^{III}(η^2 -O₂)]⁻ also are unreactive toward their corresponding Mn(II) and possibly Mn(III) forms.^{9b}

Deliberate addition of an excess of water to an electrolysis solution effectively extinguished bis(μ -oxo) dimer formation. This experiment served to show that if adventitious water were present in the electrolysis solution, it was unlikely to be the oxygen source in the bis(μ -oxo) dimer. More significantly, it reveals that if a species like IV, Scheme II, were produced during the electrolysis without the presence of a base like [AcAc]⁻, decomposition of II or III would occur. It is known that [TPPMn^{III}(η^2 -O₂)]⁻ is decomposed by proton sources.¹⁵ These data provide the background for the interpretation of the experimental results discussed below.

Oxygenation of [LMn^{II}]. Oxygenation of [(X-SALPRN)Mn^{II}] complexes in acetonitrile generally leads to isolation of the corresponding Mn^{IV}Mn^{IV} bis(μ -oxo) dimer in high yield.⁶ Electrochemical properties for compounds 1c, E°_{1c} = -0.34 V, and 3c, E°_{3c} = -0.59 V, have been discussed,⁶ and compound 2c exhibited analogous behavior, E°_{2c} = -0.26 V, eq 2.



Interestingly, oxygenation of 2b was accompanied by the incomplete intermetal oxygen atom transfer reaction,¹⁶ eq 3, that



produced a species that, from our studies of other X-SALPRN complexes, appeared to be a tetranuclear cluster, 2d.⁶ We have sought to verify the nuclearity of these complexes by mass spectrometry but without success, but combustion analytical data support this formulation. Compound 2d exhibited the two multi-electron redox processes, E_{red} = -0.145 V and E_{ox} = +0.75 V vs SSCE, which are characteristic of the clusters.⁶ The cluster-building reaction occurred in this particular instance because both 2b and 2c have some solubility in CH₃CN whereas all the other bis(μ -oxo) dimers investigated previously were highly insoluble in this solvent. Electrochemical experiments were not affected by the chemistry in eq 3, unlike kinetic measurements¹⁷

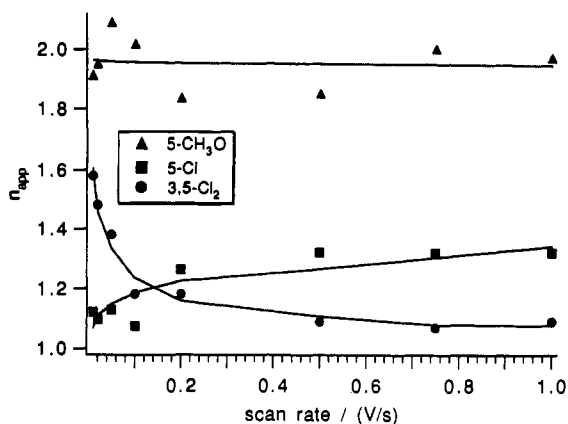


Figure 1. n_{app} vs scan rate for an approximately 1 mM solutions of 1a, 2a, and 3a.

and O₂ uptake experiments,¹⁸ because the quantity of [LMn^{II}] always remained low relative to the concentration of the bis(μ -oxo) dimer. Attempted recrystallization of 2d in air afforded only 2c. Presumably the 2b that was released was oxidized to II.

Oxygenation of a mixture of 2b and 3b in CH₃CN yielded a red-brown precipitate which contained 2c, 3c, and [(3,5-Cl₂-SALPRN)Mn^{IV}(5-CH₃O-SALPRN)Mn^{IV}(μ -O)₂], 4, E° = -0.335 V, as determined by cyclic voltammetry. There was no evidence in the voltammogram for higher nuclearity species like 2d. A cyclic voltammogram (CV) of a 1:1 mixture of 2c and 3c did not show the redox process for 4, indicating that ligand exchange did not occur. Owing to the close proximity of the formal potentials for 2c and 4, it was not possible to determine accurately their relative concentrations, and no attempts were made to isolate 4 in pure form.

Cyclic Voltammetry. The results obtained from the cyclic voltammetric experiments for the three [LMn^{III}]⁺ compounds studied here are comparable to those discussed previously.^{8,9} In summary, the presence of O₂ resulted in an enhancement of the cathodic current and a shift to positive potentials for the [LMn^{III/II}]^{+/0} process and a diminution in the anodic current for the [LMn^{II/III}]^{0/+} process compared to the N₂ data, Figure 2a. These types of changes are expected for an ECE reaction sequence where the reduction potential of the second electrochemical step is positive of that for the first.¹⁹ Note that the positive potential shift under O₂ has not been observed previously.⁹ A shift to negative potentials for reductions and a general broadening of the current-potential envelope occurred in these experiments from electrode fouling under O₂. Frequent refreshing of the electrode surface was necessary to obtain reproducible results.

Both compounds 1 and 2 exhibited kinetically limited O₂ binding, as an anodic current assignable to [LMn^{II}] with no bound O₂ was observed in the CV. This process was detected for compound 2 at the lowest scan rate examined, 0.01 V/s. A comparison of the data obtained for our three compounds showed that the O₂ binding efficiency increased according to the reducing power of the metal center, 2 << 1 < 3.^{20,21} This order was arrived at by determining the scan rate at which an anodic current for

(14) ESR results, unpublished and ref 3, suggest that I is best formulated as [LMn^{IV}(η^2 -O₂)] like the porphyrin analogues reported by Basolo, Hoffman, and co-worker: Weschler, C. J.; Hoffman, B. M.; Basolo, F. *J. Am. Chem. Soc.* 1975, 97, 5278. A description of the intermediates involved in the oxygenation of the Schiff-base complexes will be forthcoming.

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(20) 1-MeIM has no effect on the overall electrochemistry that is recorded, but it does decrease the rate of electrode fouling. It also shifts the formal potentials for all the [LMn^{III}]⁺ complexes to more negative values: E°₁ = 0.060 V, E°₂ = 0.175 V, and E°₃ = -0.025 V without 1-MeIM and E°₁ = -0.025 V, E°₂ = 0.095 V, and E°₃ = -0.060 V with 1-MeIM, all vs SSCE in CH₃CN.

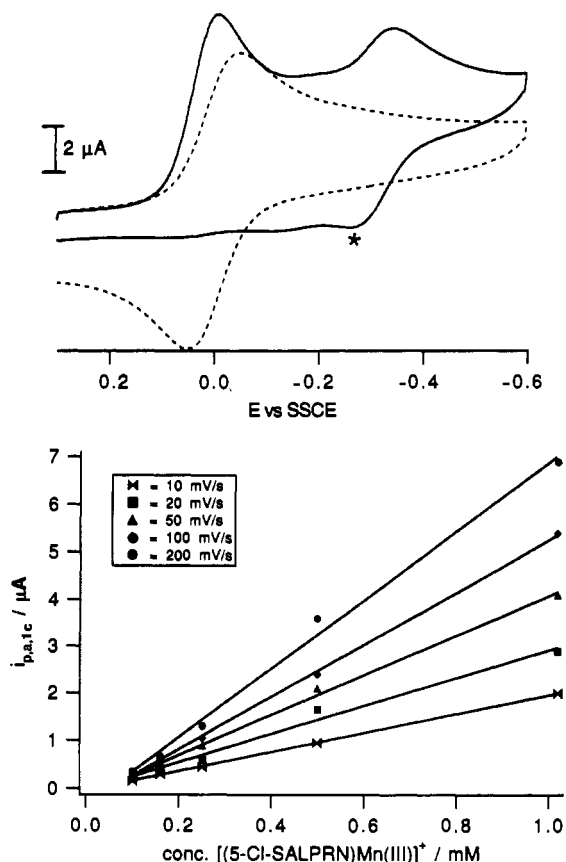


Figure 2. (a) Top: CVs for complex **1a**, 0.5 mM, under N_2 (---) and O_2 (—). The asterisk on the figure denotes redox processes for compound **1c**; $v = 0.050$ V/s. (b) Bottom: $i_{p,a,1c}$ vs concentration of $[(5\text{-Cl-SALPRN})\text{Mn}^{\text{III}}]^+$ in mM at the scan rates indicated on the figure. The lines on the figure were determined from a linear least-squares fit to the data.

unoxxygenated $[\text{LMn}^{\text{II}}]$ was detectable. It is also consistent with the known oxygenation chemistry of $\text{Co}(\text{II})$ complexes.²

Even though in complex **2** not all of the $[\text{LMn}^{\text{II}}]$ reacted with O_2 at 0.01 V/s, substantial O_2 binding and reduction did occur as $n_{\text{app}} = 1.6$ ($n_{\text{app}} = i_{p,c,O_2}/i_{p,c,N_2}$ at the same scan rate).⁹ For an ideal two-electron process n_{app} should be 2.8.¹⁹ Figure 1 illustrates the rapid decrease in the oxygen binding/reduction reactions with increasing scan rate for **2** as compared to the relatively constant values observed for the other compounds. The lines are drawn for purposes of clarity; they are not fits to the data. Interestingly, the n_{app} value for **2** at 0.01 V/s was only slightly less than the one for **3** ($n_{\text{app},3} = 1.95$), the complex that overall reacted most efficiently with oxygen. The large n_{app} for **2** at slow scan rates was an important result because it showed that under the bulk electrolysis conditions described below, a significant portion of the $[\text{LMn-O}_2]$ that formed would be reduced to $[\text{LMn-O}_2]^-$. This condition made it possible to test whether **III** and $[\text{LMn}^{\text{III}}]^+$ were responsible for bis(μ -oxo) dimer formation.

The quantity of bis(μ -oxo) dimer produced during the potential sweep was the more significant difference in the CVs of the three complexes. For complex **1**, the redox process for **1c** was observed at all scan rates investigated (0.01–1 V/s), and illustrated in Figure 2a is a CV for **1** in an oxygen-saturated solution at 0.05 V/s. A plot of the anodic peak current for **1c** (the asterisk on Figure 2a), $i_{p,a,1c}$, was proportional to $v^{1/2}$ up to 0.2 V/s. The diffusion-controlled response recorded for dimer formation demonstrated that it was produced rapidly on the CV time scale.

(21) The **a** and **b** designations are not used in the sections describing the electrochemistry of these compounds unless it is necessary for purposes of clarity. It is implicit that the starting material for all electrochemical studies is **1a**, **2a**, or **3a** and the species that reacts with O_2 is **1b**, **2b**, or **3b**.

Previous experiments on $(5\text{-Cl-SALEN})\text{Mn}^{\text{II}}$ allowed us to place a lower limit of 75 ms for the formation of its bis(μ -oxo) dimer.⁸ Owing to slow heterogeneous charge-transfer kinetics for **1a**, the oxygen binding step could not be "outrun" so a full kinetic analysis is precluded at this time.

A graphical presentation of the data described above in terms of $i_{p,a,1c}$ at constant scan rate as a function of the concentration of **1** is shown in Figure 2b. These data reveal that bis(μ -oxo) dimer formation was first order in the starting manganese complex. The dependence of $i_{p,a,1c}$ on the O_2 concentration could not be assessed because the flux of O_2 to the electrode surface was so much greater than for the manganese complex that pseudo-first-order conditions were maintained at readily attained Mn and O_2 concentrations.²²

While the bis(μ -oxo) dimer was barely detectable in a CV for **2** under O_2 at 0.01 V/s, it formed in reasonable yield in a bulk electro-synthesis experiment. Slow dimerization is attributed to steric inhibition caused by the chloro group. This could arise by limiting a close approach of two Schiff-base complexes or by slowing the rate of interconversion of the square planar ligand in **2a** to its *cis*- β configuration in **2c**.^{11c,23,24} Regardless of why dimer formation was slow, the consequence was a larger n_{app} for **2**, $n_{\text{app},2} = 1.6$, than for **1**, $n_{\text{app},1} = 1.3$, at slow scan rates. Compound **3** also showed minimal formation of its bis(μ -oxo) dimer because its highly efficient oxygen binding/reduction reactions produce a high concentration of $[\text{LMn-O}_2]^-$ while simultaneously removing the $[\text{LMn}^{\text{II}}]$ that, as discussed below, was necessary for dimerization. Compound **3c** was isolable from a bulk electro-synthesis, but its yield was low.

Rotating Disk Electrode Voltammetry. The cyclic voltammetry experiments did not provide sufficient information to distinguish between the various species that could produce **II**. However, RDE voltammetry experiments allow us to demonstrate that bis(μ -oxo) dimer formation most likely proceeds by reaction of $[\text{LMn-O}_2]$ and $[\text{LMn}^{\text{II}}]$. This is possible because, on the limiting current plateau for the $[\text{LMn}^{\text{III/II}}]^{+/0}$ reduction process, the vast majority (>95%) of the manganese at the electrode surface is in the +2 oxidation state,¹⁹ and so the reactions that are being probed in this regime of the applied potential are those that involve Mn^{II} species. Therefore if a reduction event assignable to a bis(μ -oxo) dimer was observed, this would be strong evidence that its formation was a consequence of a reaction according to eq 1.

The results of previous RDE voltammograms using Schiff-base complexes^{9a} were interpreted as following the ECE portion of Scheme 1. Only a single two-electron redox process was observed, and this was assigned to the formation of **III**. No reduction processes were detected at potentials characteristic of the bis(μ -oxo) dimers. These results indicated that the Mn^{II} Schiff-base complexes were efficiently bound O_2 and were readily reduced to **III** but that they were inefficient at producing the corresponding bis(μ -oxo) dimer. This same behavior was observed for the $[(5\text{-CH}_3\text{O-SALPRN})\text{Mn}^{\text{II}}]^+$ complex.

The 5-Cl-SALPRN complex exhibited unique behavior compared to that of the other Schiff-base compounds, and Figure 3 shows RDE voltammograms for **1a** under O_2 and N_2 . The appearance of two distinct and well-separated redox processes was clearly different from prior results. As the E° of a sample of the isolated dimer **1c** was the same as that observed for the

(22) The relative oxygen content of the electrolysis solution was determined by comparing the cathodic currents for the direct reduction of O_2 at the GC electrode, $E_{p,\text{red}} = -1.2$ V vs SSCE, in a solution saturated with O_2 to those containing various N_2/O_2 mixtures. The maximum O_2 concentration in CH_3CN is 8.1 mM; see: Sawyer, D. T.; Chlericato, G., Jr.; Angelis, C. T.; Nanni, E. J., Jr.; Tsuchiya, T. *Anal. Chem.* **1982**, *54*, 1720.

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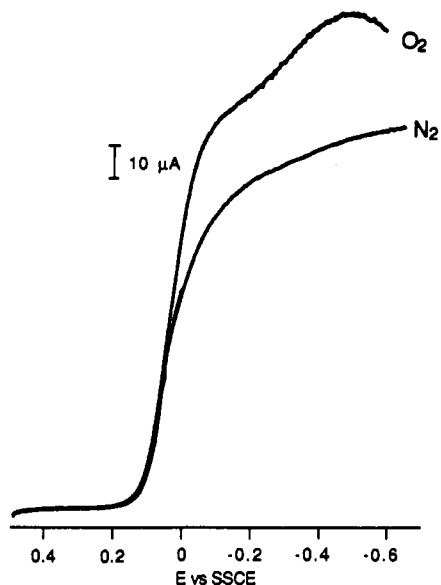


Figure 3. RDE voltammogram for **1a**, 1.1 mM, under N₂ and O₂: $\omega = 225$ rpm; $\nu = 0.005$ V/s.

product seen at the more negative potentials on the figure, we assign this to the same bis(μ -oxo) dimer complex. Dimer formation was observed up to at least $\omega = 900$ rpm, which was consistent with the rapid reaction observed in the cyclic voltammetry experiments for this complex. The small current increase in the potential region for the [(5-Cl-SALPRN)Mn^{III/II}]⁺⁰ couple under O₂ also was consistent with the CV result for this compound, Figure 2a, and demonstrated that reduction of the oxygen adduct I to III occurred only to a minor degree. Unfortunately electrode fouling was a significant problem which precluded determining kinetic parameters. Nevertheless, this experiment was the first strong evidence that bis(μ -oxo) dimer production followed eq 1.

Bulk Electrolysis of Bis(μ -oxo) Dimers. The bulk electrolysis experiments described below provide persuasive evidence that II was produced according to eq 1. The combination of **2a** and **3a** was used to demonstrate this because these complexes have the large separation in formal reduction potentials required to make the bulk electrolysis experiments readily interpretable. A bis(μ -oxo) dimer was isolated for each of the Schiff-base complexes by reduction of the appropriate [LMn^{III}]⁺ salt in the presence of O₂. Electrolysis of a mixture of **2a** and **3a** at $E_{app} = -0.3$ V vs SSCE produced the dark red-brown powder characteristic of the bis(μ -oxo) dimers. An electrochemical analysis of the sample showed that it contained the same mixture of bis(μ -oxo) dimers, **2c**, **3c**, and **4**, formed by oxygenation of **2b** and **3b**, but again we have not determined the relative proportions. Despite these limitations, this experiment showed that **4** formed under our standard reaction conditions.

Reduction of a mixture of **2a** and **3a** also was performed at $E_{app} = 0.05$ V. This potential was chosen because essentially 100% of the **2a** at the electrode surface would be reduced to its Mn^{II} form and its oxygenated form could also be reduced to III, but only 5% of **3a** would be reduced to the [LMn^{II}] state. By performance of the electrolysis at 0.05 V, a nearly ideal test for ascertaining the importance of step 4 in Scheme I was achieved. Reduction of a solution that contained a 1:1.2 molar ratio of **2a**:**3a** under these conditions produced a smaller quantity of solid material than was recovered when **2a** alone was reduced. Much of the solid was a light green material insoluble in common organic solvents. A CV taken of the soluble portion of the material is shown in Figure 4 along with the CV for a sample of pure **2c**. Only a trace of **4** (the asterisk on the figure) was observed, and no **3c** was detected (its concentration may have been too low to detect). The fact that only a trace of the mixed-ligand bis(μ -oxo) dimer was formed revealed that a [LMn^{III}]⁺ species was not

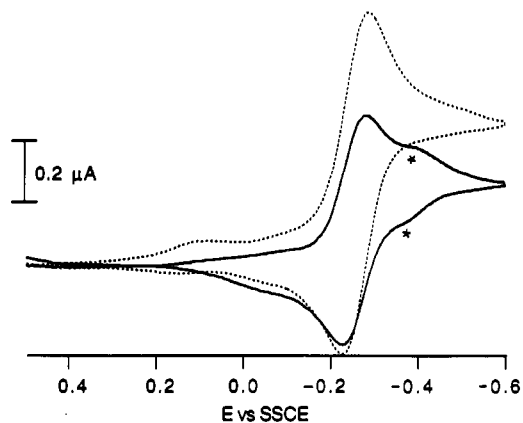


Figure 4. CV of the soluble portion of the product isolated from the bulk electrolysis (see text for experimental details) of a mixture of **2a**, 2.85 mM, and **3a**, 3.37 mM (—), and CV of a sample of pure **2c** (---). The asterisk on the figure denotes the mixed-ligand bis(μ -oxo) dimer. The current-potential envelope for the supporting electrolyte alone has been digitally subtracted from both curves; $\nu = 0.02$ V/s.

crucial to formation of this dimer but rather its presence appeared to be deleterious to general formation of bis(μ -oxo) dimers. These observations provide a strong case for proposing that [LMn^{II}] and [LMn-O₂] couple to form the bis(μ -oxo) dimer.

The green solid from above was assumed to be a decomposition product from reaction of [LMn-O₂] or [LMn-O₂]⁻ with [(5-CH₃O-SALPRN)Mn^{III}]⁺. Alternatively, it may have been that the [(5-CH₃O-SALPRN)Mn^{III}]⁺ complex just did not couple with [(3,5-Cl₂-SALPRN)Mn-O₂]⁻. In order to distinguish between these processes, electrolyses were performed on single metal complex component solutions at a potential insufficient to reduce all of the [LMn^{III}]⁺ complex at the electrode surface to its LMn^{II} form. Under these conditions, the green insoluble solid was again isolated. An FTIR spectrum of the solid isolated from reduction of **2a**, $E_{app} = 0.075$ V vs SSCE, showed it to be similar to **2a**, but there was no evidence for the PF₆ counterion (supplementary material Figure S2), and it was not grossly different from **2d**, Figure S1. The spectra are consistent with a ligand structure that remained essentially planar as in the starting material, but overall the compound appeared to be polymeric, possibly through formation of μ -oxo bridges. Thus the presence in general of [LMn^{III}]⁺ species caused the oxygenation reaction to follow a reaction pathway which did not produce the bis(μ -oxo) dimer.²⁵ The results from these bulk electrolysis experiments, and the supporting evidence from RDE voltammetry, are the factors for proposing Scheme III as the most likely reaction pathway leading to isolation of the bis(μ -oxo) dimer starting from [LMn^{III}]⁺.

The role that H₂O played in the formation of II was examined by adding it in a 10-fold excess to a mixture of **2a** and **3a** and then electrolyzing the solution at $E_{app} = 0.05$ V. It was anticipated, on the basis of the reaction of other M-O₂ complexes with electrophiles,²⁶ that the bound O₂ in intermediates I and III would be electron rich and could be protonated by water; [(TPP)Mn^{III}-(η^2 -O₂)]⁻ is reactive toward proton sources.¹⁵ Exchange of oxo ligands with water during dimer formation was an additional complicating factor in the overall O₂ activation chemistry that needed to be considered.²⁷ The only product isolated from the experiment was an insoluble powder whose FTIR spectrum was

(25) Oxygenation of a solution containing a 1:1 mixture of [LMn^{III}]⁺: [LMn^{II}] in the absence of external reducing equivalents leads to nearly complete inhibition of bis(μ -oxo) dimer formation: Dailey, G. C.; Horwitz, C. P. Unpublished results.

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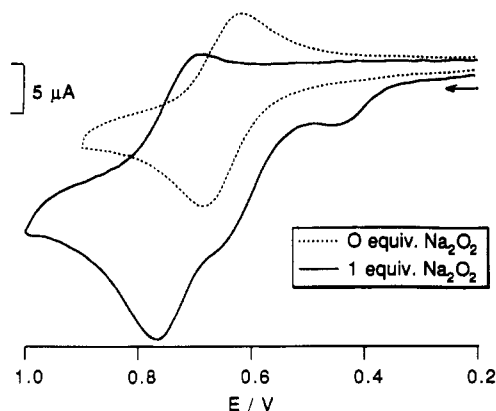
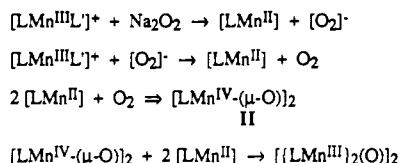


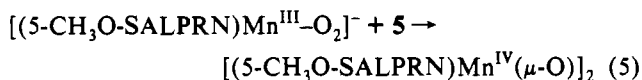
Figure 5. CV of a solution of $[(5\text{-CH}_3\text{O-SALPRN})\text{Mn}^{\text{III}}(\text{AcAc})]$ (32.1 μmol) in DMF taken before (---) and after (—), 24 h, addition of Na_2O_2 (16.7 μmol). $v = 100$ mV/s.

Scheme IV



essentially identical to the one described above, Figure S2. It appears that water intercepts the oxygenated intermediate(s) in a fashion analogous to that for a Mn(III) Lewis acid.

Reaction of Na_2O_2 with $[(5\text{-CH}_3\text{O-SALPRN})\text{Mn}^{\text{III}}(\text{AcAc})]$. As a further test for the hypothesis that the $[\text{LMn}^{\text{III}}\text{O}_2]^-$ intermediate was unsuitable to act as a source for the bis(μ -oxo) dimer, we examined the reaction of Na_2O_2 with $[(5\text{-CH}_3\text{O-SALPRN})\text{Mn}^{\text{III}}(\text{AcAc})]$, **5**, in DMF as the bis(μ -oxo) dimer presumably would be formed by the reactions in eqs 4 and 5.



Reaction of $[(\text{SALPRN})\text{Mn}^{\text{III}}(\text{AcAc})]$ with Na_2O_2 in DMF resulted in precipitation of the bis(μ -oxo) dimer in high yield.^{11b} We chose to try to synthesize **3c** because it is soluble in DMF, making the reaction more easily monitored by spectroscopic and electrochemical means. Reaction of the green compound **5** with Na_2O_2 proceeded slowly, taking *ca.* 24 h, and produced a dark green black solution and not the red-brown solution characteristic of bis(μ -oxo) dimers. The sluggishness of the reaction may be due in part to the low solubility of Na_2O_2 in DMF. Analysis of the solution by cyclic voltammetry showed a new oxidation process at positive potentials, Figure 5, reminiscent of the higher nuclearity clusters reported here and earlier.⁶ Results of our previous investigations demonstrated that the higher nuclearity compounds formed via reaction of the bis(μ -oxo) dimer with $[\text{LMn}^{\text{II}}]$. A reduction process at negative potentials also was detected which could arise from both the bis(μ -oxo) dimer and the cluster as these species have similar reduction potentials.⁶

Scheme IV is proposed to account for cluster formation; see eq 3.⁶ The Mn(II) species likely was generated by reduction processes nominally involving peroxide and superoxide species. Superoxide is known to reduce Mn(III) porphyrins²⁸ and Schiff-

base complexes.^{29–31} The cluster may not have been observed for the SALPRN complex^{11b} because its bis(μ -oxo) dimer is highly insoluble in DMF at room temperature which effectively precludes reaction with its Mn(II) form.

The reactions of **3b** with approximately 0.5 molar equiv of Na_2O_2 or KO_2 in DMF also were examined. Both reactions were allowed to proceed over a 48-h period (the reaction with KO_2 appeared complete in less than 1 h) and resulted in pale green (Na_2O_2) and red-brown (KO_2) solutions being formed.³² These solutions were analyzed by cyclic voltammetry. In the case of Na_2O_2 , three electrochemically irreversible oxidation events were detected, one of which was near, but not identical, to the oxidation potential for the $\{[(5\text{-CH}_3\text{O-SALPRN})\text{Mn}^{\text{III}}]_2(\text{O})_2\}$ complex, and a poorly defined reduction process also was present. For the KO_2 reaction, multiple (at least three) broad, electrochemically irreversible oxidation waves but no reduction processes were observed. Since the oxidation wave was both clearly discernible and appeared electrochemically reversible in Figure 5, we favor a reaction between $[(5\text{-CH}_3\text{O-SALPRN})\text{Mn}^{\text{II}}]$ generated *in situ* and O_2 to produce the bis(μ -oxo) dimer following which the dimer reacted with additional $[(5\text{-CH}_3\text{O-SALPRN})\text{Mn}^{\text{II}}]$ present in solution.⁶ The key point to make about the reaction between **5** and Na_2O_2 is that bis(μ -oxo) dimer formation appears to depend on intermediates generated from $[\text{LMn}^{\text{II}}]$. This interpretation provides supporting evidence for our conclusions from the electrochemical data.

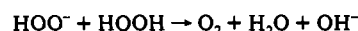
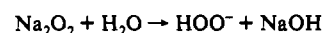
Conclusions. Our electrochemical and chemical studies on these Schiff-base complexes show that the bis(μ -oxo) dimers most likely form by reaction of $[\text{LMn-O}_2]$ and $[\text{LMn}^{\text{II}}]$, not $[\text{LMn-O}_2]^-$ and $[\text{LMn}^{\text{III}}]^+$. A particularly interesting result was that the oxygenated intermediates were sensitive to the type of Lewis acid in solution. Complete decomposition occurred when H^+ or $[\text{LMn}^{\text{III}}]^+$ was present, but benzoic anhydride activates similar Schiff-base complexes for the olefin epoxidation reaction.⁹ Thus there appears to be a balance in choosing conditions that permit useful chemistry to be derived from an oxygenation reaction as opposed to decomposition.

Whereas intermediate **III** is deleterious to production of the bis(μ -oxo) dimer, it is the species one desires to generate in order to exploit the electrocatalytic olefin epoxidation reaction.⁹ Intermediate **III** can be produced in high yield by using complexes that either efficiently bind O_2 or that dimerize slowly. Conversely, for the synthesis of the bis(μ -oxo) dimer, the ideal reagent is one in which the $[\text{LMn}^{\text{II}}]$ complex reacts at a moderate rate with oxygen but then rapidly with a nearby unoxxygenated $[\text{LMn}^{\text{II}}]$ complex. The 5-Cl-SALPRN complex studied in this investigation approximates these ideal attributes.

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Supplementary Material Available: FTIR spectra of **2c,d** Figure S1, and **2a**, the electrolysis product in the presence of H_2O , and the electrolysis product formed at $E_{\text{app}} = 0.075$ V vs SSCE, Figure S2 (3 pages). Ordering information is given on any current masthead page.

- (29) The Schiff-base ligands studied here most likely oxidize at potentials much greater than 1 V so H_2O_2 is not a strong enough oxidizing agent to oxidize the ligand.
 (30) (a) Coleman, W. M., III; Taylor, L. T. *Inorg. Chem. Acta* **1982**, *61*, 13.
 (b) Matsushita, T.; Shono, T. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3743.
 (31) As noted by one of the reviewers, in DMF the reactions shown below may occur and HOO^- may be the reducing agent for Mn(III):



- (32) We thank a reviewer for the suggestion that $[\text{LMn}^{\text{II}}]$ complexes react with O_2^{2-} and O_2^- and these species might also participate in formation of the cluster.

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