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Synthesis, Spectroscopic Characterization, and Electrochemical Properties of [(5-Cl-SALEN)Mn^{IV}(μ-O)]$_2$ (5-Cl-SALEN = 1,2-Bis(5-chlorosalicylideneamino)ethane)

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Reaction of the complex (5-Cl-SALEN)Mn^{II} (5-Cl-SALEN = 1,2-bis(5-chlorosalicylideneamino)ethane), formed by electrochemical reduction of [(5-Cl-SALEN)Mn^{III}]$^+$ or initially synthesized in the Mn(II) form, with dioxygen in CH_3CN produces the bis(μ-oxo) dimer [(5-Cl-SALEN)Mn^{IV}(μ-O)]$_2$. Cyclic voltammetry experiments reveal that the dimer forms in less than 75 ms and that oxygen binding by (5-Cl-SALEN)Mn^{II} is most likely the rate-determining step in the dimerization process. The dimer has a moderately intense vibrational band in its FTIR spectrum at 652 cm^{-1}, the region characteristic of the bis(μ-oxo)manganese core, and a moderately intense absorption band in the UV–vis spectrum at λ_{max} = 482 nm (ϵ = 9300 M^{-1} cm^{-1} in DMF) arising from an oxo ligand to metal dπ* charge-transfer transition. A cyclic voltammogram of the dimer in 0.1 M Bu_4NPF_6/DMF shows what appears to be a reversible redox couple at $E°$ = –270 mV vs SSCE, but a bulk electrochemical reduction of a solution of the dimer and a spectrophotometric titration with Cp_2Co as an outer-sphere reductant reveal that the dimer is unstable. The ESR spectrum of this decomposition product taken as a frozen DMF solution at 6 K displays a 16-line pattern typical of an antiferromagnetically coupled $S = {}^1/_2$ mixed-valent manganese species, consistent with the presence of a bridging oxo ligand.

Introduction

The overall oxygen activation pathway for Mn(II) coordination complexes remains somewhat uncertain,[3] but progress is being made in characterizing both oxygenated intermediates[4] and reaction products.[5–7] Manganese complexes with porphyrin and Schiff-base type ligands have been the most widely studied systems to date. In the case of the porphyrin compounds, the oxygenation process generally leads to isolation of the Mn(III) porphyrin along with some unidentified decomposition products.[8] Schiff-base complexes are reported to have a complicated oxygenation chemistry, and many different types of oxygenated products have been claimed.[9] We recently demonstrated that Mn(II) complexes with SALPRN type ligands (SALPRN = 1,3-bis(salicylideneamino)propane) exhibit reactions with O_2 that are dependent on both the solvent and the rate of oxygenation.[7] Two solids were isolated in that study: a Mn(IV)–Mn(IV) bis(μ-oxo) dimer and a higher nuclearity cluster. However, it was possible to show that the higher nuclearity cluster formed as the result of an incomplete inter-metal oxygen atom transfer process[10] between the bis(μ-oxo) dimer and the Mn(II) starting material.

The present study is concerned with examining the oxygenation chemistry of the complex (5-Cl-SALEN)Mn^{II} (5-Cl-SALEN = 1,2-bis(5-chlorosalicylideneamino)ethane). This compound was chosen because analogous manganese SALEN ligand complexes can be used in an electrocatalytic olefin epoxidation scheme and it was of interest to determine how the oxygen was activated by the manganese complex. It was suggested in that study that a dinuclear manganese complex containing oxo ligands was formed from reaction of the electrochemically generated intermediate [(SALEN)MnO$_2$]$^-$ with [(SALEN)Mn^{III}]$^+$.[11] Formation of the dimer was proposed to account for instability of the catalyst, but the nature of the product was unknown. We have sought to isolate the oxygenated manganese product, as its identification will help unravel portions of the oxygen activation process and, in addition, will aid in the design of new catalysts[12] that circumvent the deactivation process.

Determination of the oxygenated compounds that form for the SALEN class of ligands is also of interest because there are some suggestions that these compounds will not form bis(μ-oxo) dimers. It has been postulated that the ethylenediamine-derived backbone

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will not be sufficiently flexible to adopt the cis-β ligand configuration that allows the oxo ligands to be disposed in a cis orientation at both metal centers. There are a number of iron,[13] cobalt,[14] and chromium[15] complexes having SALEN ligands that do adopt the cis-β ligand configuration when chelated with bidentate oxygen donor ligands. We have found that a bis(μ-oxo) dimer readily forms when the 5-Cl-SALEN ligand complex is used, and this report describes the facile synthesis, spectroscopic characterization, and electrochemical properties of the complex [(5-Cl-SALEN)Mn^{IV}(μ-O)]$_2$ (**2**).

Experimental Section

Physical Measurements. IR spectra of solids (KBr disks) were taken on a Perkin-Elmer 1800 FT-IR spectrometer, while UV–vis spectra were obtained using a Hewlett-Packard HP8452A diode array spectrophotometer controlled with a Zenith computer. Mass spectrometric data were measured at the Monsanto Co. with a Sciex API-III triple-quadrupole mass spectrometer using an electrospray interface operated in the positive-ion mode. The orifice potential was 35 or 50 V. Sample solutions (0.1–1 mg/mL in 50:50 CH_2Cl_2/DMSO) were infused continuously into the electrospray interface at a flow rate of 5 μL/min. Elemental analyses were done by Quantitative Technologies, Inc., Whitehouse, NJ.

Electrochemistry. Electrochemical measurements were made using an EG&G Princeton Applied Research Model 273 potentiostat/galvanostat and recorded on a Graphtec WX-1200 X-Y recorder or the Zenith computer. Cyclic voltammograms (CVs) were obtained in a one- or three-compartment cell with a glassy carbon disk working electrode [$A \sim 0.071$ cm^2 (polished with 1-μm diamond paste (Buehler)], a Pt wire counter electrode, and a SSCE (sodium chloride saturated calomel electrode) reference electrode or, for glovebox experiments, a Ag wire quasi-reference electrode. Rotating disk electrode voltammetry was performed using a Pine Instruments AFASR Analytical Rotator with a glass carbon disk electrode ($A \sim 0.46$ cm^2). Bulk electrolyses were performed using a carbon crucible (Atomergic) as the working electrode, a Pt mesh counter electrode separated from the working electrode compartment by a medium-porosity frit, and a reference electrode inserted directly into the electrolysis solution. The supporting electrolytes were Bu_4NClO_4 (TBAP) (Baker analyzed) and Bu_4NPF_6 ((TBA)PF_6) (Fluka puriss).

Materials. 5-Chlorosalicylaldehyde, salicylaldehyde (Aldrich), and ethylenediamine (Fisher) were used as received. The solvents DMF (stored under N_2), CH_3CN, and CH_3OH were purified by standard methods.[16] The (SALEN)Fe^{II} complex was prepared under N_2 using standard Schlenk techniques according to methods detailed in the literature.[17] All air-sensitive solids were stored and manipulated in a N_2-filled glovebox (Vacuum Atmospheres).

(5-Cl-SALEN)Mn^{II} (1) and [(5-Cl-SALEN)Mn^{III}]PF$_6$ (1$^+$PF$_6$). The bis(aldehydo)manganese(II) complex was synthesized in deoxygenated CH_3OH (10 mL) by reaction of $Mn(C_2H_3O_2)_2{\cdot}4H_2O$ (1 mmol) with the 5-chlorosalicylaldehyde (2 mmol). The yellow slurry was refluxed for approximately 30 min to ensure complete complex formation and cooled to only slightly above room temperature; then a solution of ethylenediamine in deoxygenated CH_3OH (1 mmol in 10 mL) was added. The mixture was refluxed for an additional 1 h, during which time condensation was evidenced by formation of the orange-yellow manganese Schiff-base complex. After the solution had cooled to room temperature, compound **1** was recovered by filtration through a medium-porosity frit, washed with CH_3OH (2 × 10 mL), and then dried in vacuo at room temperature overnight. **1**$^+$PF$_6$ was prepared by adding a 4-fold molar excess of NH_4PF_6 as a solid to the cooled slurry of **1** and then bubbling O_2 through the CH_3OH until all of the orange-yellow **1** was consumed and a dark brown homogeneous solution remained. The volatiles were removed in vacuo, and the solid product was washed with copious quantities of H_2O to remove residual salts and then dried in vacuo at room temperature overnight.

Electrochemical Synthesis of [(5-Cl-SALEN)Mn^{IV}(μ-O)]$_2$ (2). A 3 mM CH_3CN solution (10 mL) of **1**$^+$PF$_6$ containing 0.2 M (TBA)PF$_6$ was placed along with a stir bar in the carbon crucible working electrode. The cell potential was maintained at −190 mV vs SSCE with continuous stirring and bubbling of O_2 through the electrolysis solution until the current decayed to about 10% of its original value. The red-brown solid present in the electrolysis medium was recovered by filtration through a medium-porosity glass frit, washed with CH_3CN followed by petroleum ether, and then dried in vacuo at room temperature. The isolated yield of **2** was as high as 31% based on starting **1**$^+$PF$_6$ but varied with individual electrolyses. Anal. Calcd (found) for $C_{32}H_{24}Cl_4Mn_2N_4O_6$ (MW = 812; MS m/z = 813 (MH$^+$), electrospray): C, 47.32 (46.14); H, 2.98 (2.95); N, 6.90 (6.31).

Synthesis of [(5-Cl-SALEN)Mn^{IV}(μ-O)]$_2$ by Air Oxidation of 1. A single-neck round-bottom flask was charged with **1**, an orange-yellow powder, in the nitrogen atmosphere glovebox. Deoxygenated CH_3CN (10 mL) was added to the solid, and the flask was sealed with a rubber septum. The slurry was sonicated for 1 min, following which an 18- or 20-gauge syringe needle was placed through the rubber septum such that the tip of the needle was well above the liquid level. This apparatus was allowed to stand undisturbed for 24–48 h. Darkening of the solution above the solid was noticed within 10 min of the needle insertion. A red-brown solid was recovered from the light brown solution, washed with CH_3CN followed by petroleum ether, and then dried in vacuo at room temperature. Yields up to 80% based on starting mass of (5-Cl-SALEN)Mn^{II} were achieved with this method. Anal. Calcd (found) for $C_{32}H_{24}Cl_4Mn_2N_4O_6$: C, 47.32 (47.22); H, 2.98 (2.90); N, 6.90 (6.64). UV–vis in DMF [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 324 (19 700), 412 (10 900), 482 (9300).

Bulk Electrochemical Reduction of 2. A solution of **2** (16.3 μmol) in DMF (10 mL) containing 0.2 M (TBA)PF$_6$ was reduced at E_{appl} = 150 mV negative of its peak reduction potential, $E_{p,red}$ in the carbon crucible working electrode in the glovebox. The potential was maintained until 1.605 C (1.02 equiv) was consumed, at which point the current had decayed to less than 10% of the starting value, indicating that the electrolysis was complete. The solution color changed during the course of the electrolysis from very dark red-brown to light brown. An ESR spectrum of the electrolysis solution was obtained at 6 K. In a separate, but analogously conducted experiment, a second working electrode was inserted into the electrochemical solution at predetermined intervals during the electrolysis to record the CV, v = 100 mV s^{-1}, of the working solution of **2**, 0.71 mM in 0.1 M (TBA)PF$_6$/DMF. These intermediate CVs were recorded after passing Q_{tot} = 0, 172, 343, 514, 685 (1 electron equiv), and 756 C (110% electrolysis).

Spectrophotometric Titration of 2. Gastight syringes were used for this experiment. A 790-μL aliquot of a 0.26 mM solution of **2** in DMF (0.21 μmol) was placed in a quartz cuvette containing a magnetic stir bar, DMF was added to bring the total solution volume to 3.0 mL, and the cuvette was fitted with a rubber septum. A 39.1 mM solution of Cp_2Co and a 21.0 mM solution of [Cp_2Fe][PF_6], both in CH_3CN (10 mL), were prepared, and these solutions were taken up in 10-μL gastight syringes. The cuvette was placed in the UV–vis spectrophotometer, stirring was initiated by an air-driven magnetic stirrer, and then the syringe containing the Cp_2Co was admitted through the septum with the needle tip situated near the stir bar. The titration required 5 μL (0.196 μmol) of the cobaltocene solution, which was added in 1-μL aliquots, with a spectrum recorded about 15–30 s after each addition. Further additions of Cp_2Co produced a spectrum that exhibited changes consistent with the presence of unoxidized Cp_2Co. After the final portion of reductant was added, 10 μL of the [Cp_2Fe][PF_6] solution was added in 2-μL aliquots with spectra recorded 15–30 s after each addition.

Results

Synthesis of [(5-Cl-SALEN)Mn^{IV}(μ-O)]$_2$ (2). Two synthetic methods were used to prepare the bis(μ-oxo) dimer with the 5-Cl-

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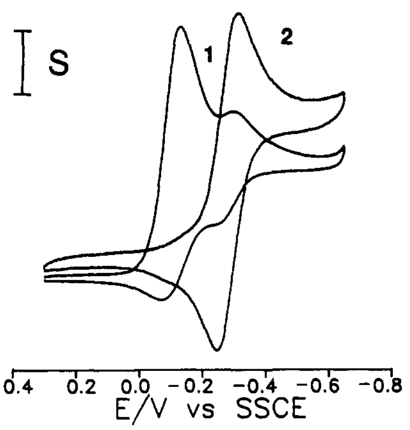

Figure 1. Cyclic voltammograms of (1) 2.0 mM $[(5\text{-Cl-SALEN})Mn^{III}]PF_6$ (O_2 atmosphere; S = 2.3 μA) and (2) 1.1 mM $[(5\text{-Cl-SALEN})Mn^{IV}(\mu\text{-O})]_2$ (N_2 atmosphere; S = 0.7 μA). Experimental conditions: v = 10 mV s^{-1}, GC electrode, and 0.1 M $(TBA)ClO_4$/DMF.

SALEN ligand. One involved electrochemical reduction of the Mn(III) complex to its Mn(II) form under an O_2 atmosphere, while the second was simply slow oxygenation of the Mn(II) compound in CH_3CN (eqs 1 and 2). The dimer was produced

$$[(5\text{-Cl-SALEN})Mn^{III}]^+ + O_2 + ne^- \xrightarrow{CH_3CN} [(5\text{-Cl-SALEN})Mn^{IV}(\mu\text{-O})]_2 \quad (1)$$

$$(5\text{-Cl-SALEN})Mn^{II} + O_2 \xrightarrow{CH_3CN} [(5\text{-Cl-SALEN})Mn^{IV}(\mu\text{-O})]_2 \quad (2)$$

in 30% yield by the bulk electrolysis method and in greater than 80% by the alternate synthesis. Electrolyses were performed at a potential that reduced greater than 90% of 1^+PF_6 at the electrode surface and less than 5% of the product. No other parameters were optimized in the bulk electrosynthesis experiments. We found that slow oxygenation of the Mn(II) complex was the best way to synthesize the dimer, as the yields were high and reproducible. Support for the bis(μ-oxo) formulation comes from the analytical results discussed below. Once precipitated, the dimer was soluble in DMF and DMSO. Repeated attempts to grow crystals of **2** for X-ray structural analysis were thwarted by its decomposition. The nature of the decomposition product is described below.

A goal of this research project was to identify the species responsible for the new redox process reported to appear when the cyclic voltammograms of various $[(X\text{-SALEN})Mn^{III}]^+$ complexes were recorded under an oxygen atmosphere.[11] The CV of a sample of **2** isolated from an electrosynthesis experiment is superimposed onto the voltammogram for 1^+PF_6 in DMF under O_2 (Figure 1). Clearly, the compound isolated from the bulk electrolysis is the same one formed during the reduction of 1^+PF_6 under O_2. Isolation of the bis(μ-oxo) dimer was somewhat unexpected on the basis of previous suggestions that it would be unstable. Details regarding the electrochemical and chemical properties of **2** and a possible reaction pathway by which it is formed are discussed below.

Spectroscopic Characterization of 2. The mass spectrum of a sample of **2** synthesized by the bulk electrolysis method showed a molecular ion at 813 amu using the electrospray technique in the positive-ion detection mode. This mass corresponds to the formulation $[(5\text{-Cl-SALEN})_2Mn_2O_2H]^+$, which suggests that **2** is $[(5\text{-Cl-SALEN})Mn(O)]_2$, MW = 812. Combustion analytical data, particularly for the compound prepared by slow oxygenation, are also consistent with the dimer formulation. The ESR spectrum of a frozen solution of **2** that was synthesized by either oxygenation route was silent, so the product is assigned as a homovalent antiferromagnetically coupled dimer.

The FTIR spectrum of **2** as a KBr disk exhibits a moderately intense vibrational band at 652 cm^{-1}. This band is in a region of the spectrum characteristic of the bis(μ-oxo) core,[18] and it appeared at virtually the same position in the SALPRN complexes we recently reported.[7] An η^1-η^1 peroxo complex, a plausible alternative structure with the same formulation, would be expected to show a vibrational band in the 750–900 cm^{-1} region for the O–O bond.[19] All bands in this region of the spectrum in the present case can be assigned to ligand vibrations. No bands indicative of either of the supporting electrolyte ions were detected in the spectrum of the bulk electrolysis product. There are no other outstanding features in the IR spectrum.

The UV–vis spectrum of **2** is characterized by ill-defined absorption bands between 300 and 550 nm. A broad absorption band with moderate intensity appearing at low energy, λ_{max} = 482 (ϵ = 9300 M^{-1} cm^{-1}), for **2** is a spectral feature that is not observed for complex **1** or 1^+PF_6 or for other unoxygenated manganese compounds that we have investigated. The compound $[(SALPRN)Mn^{III}(AcAc)]$ (AcAc = 2,4-pentanedionato),[5b] a structural analogue of compound **2**, has only a very weak absorption band in this region of the spectrum, so the ligand structure does not cause a new charge-transfer type transition to occur. The low-energy absorption band of **2** most likely arises from an oxo ligand to metal $d\pi^*$ charge-transfer transition as has been suggested for the complex $Mn^{IV}{}_2(tmpa)_2(\mu\text{-O})_2$, λ_{max} = 641 nm (ϵ = 1100 M^{-1} cm^{-1}) (tmpa = tris(2-pyridylmethyl)amine),[20a] and other Mn(IV)–Mn(IV) bis(μ-oxo) dimers.[18c,20b]

Electrochemistry of 2. The CV of **2** in 0.1 M TBAP/DMF is characterized by what appears to be a nearly reversible one-electron redox couple (Figure 1) with $E°_2$ = −270 mV vs SSCE (eq 3). A plot of the anodic peak current, $i_{p,a,2}$ vs the square root

$$[(5\text{-Cl-SALEN})Mn^{IV}(\mu\text{-O})]_2 + e^- \rightleftharpoons [(5\text{-Cl-SALEN})_2Mn^{III}Mn^{IV}(\mu\text{-O})_2]^- \quad (3)$$

of the scan rate, $v^{1/2}$, was linear over the range of potential sweep rates investigated, 20–200 mV s^{-1}, and the $i_{p,c,2}/i_{p,a,2}$ ratio was nearly unity at those same potential sweep rates. Data from faster scan rates were of limited value because these compounds have slow heterogeneous electron-transfer kinetics. The diffusion coefficient, D_2,[21] using n = 1 (the n = 1 value was confirmed by rotating disk electrode voltammetric experiments) is 2.5 × 10^{-6} cm^2 s^{-1}. The complex has a second irreversible reduction at more negative potentials that caused the dimer to dissociate, forming **1** and other unidentified products. An irreversible oxidation process was also observed at potentials near the solvent limit, 1 V, but it is not known if this corresponded to a ligand- or metal-centered oxidation process.

As was the case with all of the SALPRN bis(μ-oxo) dimer complexes,[5b,6a,7] the Mn(IV) centers in **2** are stabilized relative to the Mn(III) state in the starting material. In this instance, the difference in the formal potentials between **1** and **2** is not as

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dramatic as it is in the SALPRN analogues, and this presumably is caused by the backbone strain in **2**. The Mn(IV) centers in these complexes are also reduced at potentials more negative than have been reported for other Mn(IV)–Mn(IV) bis(μ-oxo) dimers. Stabilization of the Mn(IV) state in **2** is consistent with the results from the visible spectrum where the oxo ligand to metal dπ^* transition appears at 0.5–0.6 eV higher in energy for **2** than for the other dimers.[18c,20]

Formation of the bis(μ-oxo) dimer according to eq 1 is facile, and it is produced in high yield according to the cyclic voltammogram. For example, an analysis of the electrochemical data obtained using the experimental conditions shown in Figure 1 revealed that 60–80% of the starting material was converted to **2**. This analysis was performed in the following manner: If we assume that all $\mathbf{1}^+PF_6$ was transformed into the bis(μ-oxo) dimer in the vicinity of the electrode surface, the concentration of electroactive manganese in the dimer would be half the concentration of the starting material. Consequently, $i_{p,a,2}$ should be $(i_{p,a,1})/2$ (under N_2), as the diffusion coefficients for **2** and **1**, $D_1 = 2.1 \times 10^{-6}$ cm^2 s^{-1}, in DMF are comparable. The measured $i_{p,a,2}$ in Figure 1 is 30–40% $i_{p,a,1}$ in an N_2 atmosphere.

Cyclic voltammograms that were recorded using $\mathbf{1}^+PF_6$ in a CH_3CN solution, as was employed in the bulk electrosynthesis experiments, showed a greater quantity of **2** than those recorded using DMF. The O_2 must compete with the solvent for coordination to the manganese(II) center, and this appears to be a more efficient process in CH_3CN than in DMF. Estimating the yield of the dimer in acetonitrile is precluded by the insolubility of isolated **2** in this solvent; D_2 cannot be assessed. Nevertheless, it was possible to detect dimer formation at scan rates as high as 2 V/s for a 1.7 mM solution of $\mathbf{1}^+PF_6$. This places a lower limit of 75 ms for the formation of **2** at room temperature. At scan rates greater than 2 V/s, there was not substantial oxygen binding by the Mn(II) complex, as the anodic current was nearly as large as the cathodic current for the $[Mn(III/II)]^{+/0}$ couple so the dimerization reaction could be even faster. Even though precise assessment of the O_2-binding kinetics could not be made for this system, it does appear as though the O_2-binding step is the rate-determining step in the overall dimerization process. The reaction was always pseudo first order in oxygen owing to its high concentration and high flux rate in CH_3CN.

Bulk Electrochemical Reduction of 2. Bulk electrolysis is a longer time scale technique than cyclic voltammetry and provides a better measure of the chemical stability of a compound than does cyclic voltammetry. Bulk electrochemical reduction of **2** under N_2 in $(TBA)PF_6$/DMF solution revealed that one electron was consumed per molecule of dimer complex but the dimer was not stable under these conditions. The results obtained from intermittent monitoring of the electrolysis solution by cyclic voltammetry are illustrated in Figure 2. These voltammograms were recorded after 0, 50, 75, and 110% of the required number of coulombs were consumed for $n = 1$ (0, 343, 514, and 756 C). The shift in potential between the 0 and 50% curves arises from the use of the Ag wire quasi-reference electrode.[21] It is evident that **2** does not remain intact during the electrolysis, as its redox couple diminishes and concomitantly a new redox process appears at slightly more positive potentials. This experiment reveals that while **2** shows electrochemically reversible behavior according to cyclic voltammetric data, even at scan rates as slow as 20 mV/s, reduction is in fact a chemically irreversible process at longer times.

An ESR spectrum of the electrolysis solution taken at 6 K after 1 electron equiv was consumed revealed that the product of the reduction was not (5-Cl-SALEN)Mn^{II}, despite the fact that the formal potentials for the decomposition product and **1** are nearly coincident.[22] Compound **1** displayed a broad ill-defined ESR spectrum centered around $g = 2$ in a frozen DMF solution, 6 K. The electrolysis product, DMF at 6 K, exhibited the 16-line spectrum characteristic of a lightly valence-trapped Robin and Day class II dinuclear species[23] with antiferromagnetically coupled manganese centers. Experiments are in progress to identify the species giving rise to the 16-line ESR spectrum. Preliminary mass spectral evidence, combustion analytical data, and an intermetal oxygen atom transfer reaction with (SALEN)-Fe^{II} [7,10,24] that produced a quantitative yield of the iron oxo dimer (eq 4)[24] suggest the likelihood that the product is a μ-oxo dimer. Chemical investigations are proceeding to firmly establish the nature of the decomposition product.

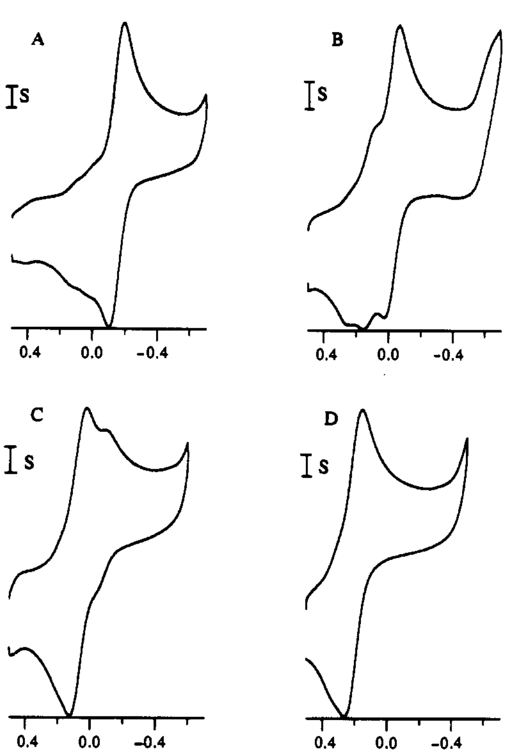

Figure 2. Cyclic voltammograms of a 0.71 mM solution of $[(5\text{-Cl-SALEN})Mn^{IV}(\mu\text{-O})]_2$ taken after (A) 0, (B) 343, (C) 514, and (D) 756 C were consumed during a bulk electrochemical reduction of **2** at E_{appl} = 150 mV negative of $E_{p,red}$. Experimental conditions: E vs Ag wire, v = 100 mV s^{-1}, GC electrode, S = 10 μA, 0.2 M $(TBA)PF_6$/DMF.

$$[(5\text{-Cl-SALEN})Mn]_2(O) + 2(SALEN)Fe^{II} \rightarrow [(SALEN)Fe]_2(O) + 2(5\text{-Cl-SALEN})Mn^{II} \quad (4)$$

The decomposition of **2** under reducing conditions was further demonstrated by a UV–vis spectrophotometric titration in which the dimer was reduced with a stoichiometric quantity of Cp_2Co and then reoxidized with $[Cp_2Fe][PF_6]$. Two isosbestic points were observed at 356 and 400 nm, the broad absorption bands at 482 and 412 nm decreased markedly, a new absorption feature appeared at 370 nm, and the red-brown solution lightened to a pale yellow-brown during the reduction process (Figure 3). No new absorption bands were evident up to 820 nm that were assignable to an intervalence-charge-transfer (IT) band for the mixed-valent species. Oxidation of the reduced dimer with

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[22] The bulk electrolysis decomposition reaction sometimes consumes 2 electron equiv, producing [(5-Cl-SALEN)Mn^{II}] (**1**). This alternate decomposition product may depend on the purity of the DMF, but we have not performed a detailed investigation of this aspect of the chemistry. Nevertheless, for all bulk electrolyses in DMF, the bis(μ-oxo) dimer is unstable.

[23] Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 248.

[24] Dailey, G. C.; Horwitz, C. P. *Inorg. Chem.* **1992**, *31*, 3693.

[25] Dailey, G. C.; Horwitz, C. P. Unpublished results.

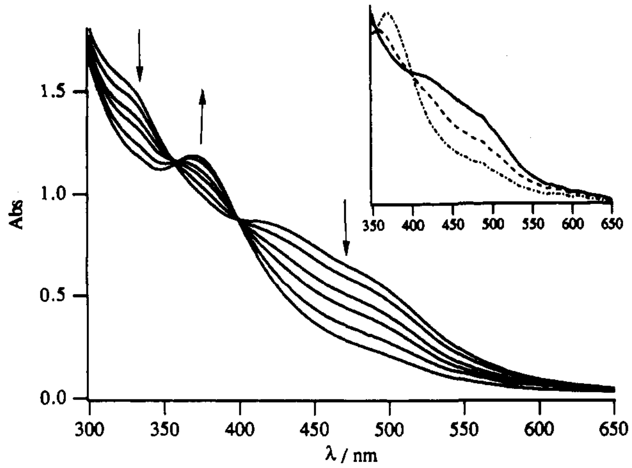

Figure 3. Spectrophotometric titration of 0.21 μmol of $[(5\text{-Cl-SALEN})\mathrm{Mn^{IV}}(\mu\text{-O})]_2$ in DMF with five 1-μL aliquots of a 39.1 mM $\mathrm{Cp_2Co}$ solution. Inset: (—) before reduction; (– • –) after reduction; and (- - -) after reoxidation.

$[\mathrm{Cp_2Fe}][\mathrm{PF_6}]$ allowed comparing spectra for the starting material and the reoxidized complex, and they were not identical. This reoxidized product exhibits an absorption band in the 500-nm region like **2**, but with a lower molar absorptivity (inset, Figure 3).

Discussion

Even though an X-ray structure has not been obtained for **2**, all the analytical and spectroscopic data obtained in this study provide a strong indication that the bis(μ-oxo) dimer $[(5\text{-Cl-SALEN})\mathrm{Mn^{IV}}(\mu\text{-O})]_2$ is the product of oxygenation of the $[(5\text{-Cl-SALEN})\mathrm{Mn^{II}}]$ complex. This dimer can be formed in good yield and in pure form by two synthetic routes. The conclusions from previous studies using analogues of the (5-Cl-SALEN)Mn complex were that multiple oxygenated products could be formed. Among the postulated structures for these compounds were bis(μ-oxo) dimers,[9a,d] mixed-valent μ-oxo μ-hydroxo dimers,[9a,c] μ-oxo dimers,[9e,h,i] η^1-η^1-peroxo dimers,[9f,h,j] and polycatena oxo polymers.[9g-j] The key to our successful isolation of the dimer in pure form is related to the fact that the compound precipitates from solution once it is produced. Precipitation obviously removes the possibility for further reactions with the Mn(II) starting material and limits occurrence of other decomposition reactions.

As noted in the Introduction, it has been suggested that the cis-β ligand configuration would not form using SALEN type ligands. However, as there are crystallographically characterized complexes with the SALEN ligand in the cis-β ligand geometry,[13-15] we assume an analogous structure for **2**. The rapidity of the reaction that forms the dimer is quite remarkable, given the structural changes that occur for the ligands and the fact that a total of four electrons are involved in the O-O bond cleavage reaction. Thus not only is there a small barrier to the ligand deformation process for these complexes, but there is also a high driving force to formation of the corresponding bis(μ-oxo) dimer. Interestingly, transient formation of a bis(μ-oxo) dimer has recently been postulated to occur in the reaction of $[(\mathrm{TPP})\mathrm{Mn^{III}}]^+$ (TPP = tetraphenylporphyrinato) with the superoxide anion,[4a] so this dimer appears to play a general role in the overall oxygen activation process by manganese complexes.

The results from the present study reveal that while the bis(μ-oxo) dimer **2** is the isolable oxygenation product, it is not a stable molecule. This is an important finding because it demonstrates that **2** is the kinetic oxygenation product but another oxygenated species in the thermodynamic product. It also provides further evidence that oxygen activation by the Schiff-base complexes that we have been investigating must proceed through formation of the bis(μ-oxo) dimer before other isolable products form. If this is the case, then the commonly postulated oxygen activation pathways are unnecessarily complicated and a new oxygen activation pathway will need to be proposed. The ease of formation of **2** is likely to limit the utility of the very simple SALEN type Schiff-base complexes in catalytic reactions unless ligand modifications are introduced to prevent the dimerization.[26]

The instability of **2** is in stark contrast to the properties of the analogous SALPRN bis(μ-oxo) dimer complexes.[7] The decomposition of **2**, which was not obvious from cyclic voltammetric experiments, probably accounts for the difficulties that have been encountered in isolating and characterizing pure oxygenated SALEN ligand complexes. Despite numerous attempts, we have not been successful in obtaining X-ray-quality crystals of **2**, so we cannot assess whether there is strain in the complex arising from the ethylenediamine backbone that is not present in the complexes with the 1,3-diaminopropane-derived backbone.[6] It seems likely that if strain were present in **2**, it would be relieved by allowing the ligand to adopt a square planar configuration like the one found for $[(\mathrm{SALEN})\mathrm{Fe^{III}}]_2(\mu\text{-O})$.[17b]

The ability to selectively synthesize **2** in the presence or absence of external reducing equivalents suggests that the previously postulated electrochemical reaction pathway shown in Scheme I[11] needs modification. As a result of the experiments performed in this study, it is probable that the ECEC pathway presented in Scheme I is unnecessarily complicated. A more straightforward reaction scenario accounting for the formation of **2** is dimerization of I with unoxygenated Mn(II) (eq 5). This is of course consistent with the oxygenation chemistry observed in eq 1. Dimerization that proceeds according to eq 5 also accounts for the less than 100% yield of **2** in the cyclic voltammograms, as some of the intermediate I is consumed in step 3 of Scheme I; the fate of the reduced oxygenated manganese complex II is uncertain. The unreactive nature of II is analogous to the chemistry reported for $[(\mathrm{TPP})\mathrm{MnO_2}]^-$ [8b] and $[(\mathrm{Cl_8TPP})\mathrm{MnO_2}]^-$ [8c] ($\mathrm{Cl_8TPP}$ = tetrakis(2,6-dichlorophenyl)porphinato), likely structural models for intermediate II in Scheme I. Our studies with the Schiff-base complexes and those of others[8] with the manganese porphyrins lead us to conclude that $[\mathrm{LMnO_2}]^-$ complexes are surprisingly unreactive toward electrophiles but $\mathrm{LMnO_2}$ intermediates are reactive. Further speculation regarding the reactivity of the $[\mathrm{LMnO_2}]^-$ intermediate is unwarranted at this time.

Scheme I

$$\underset{\mathbf{1^+}}{[(5\text{-Cl-SALEN})\mathrm{Mn^{III}}]^+} + e^- \rightarrow \underset{\mathbf{1}}{(5\text{-Cl-SALEN})\mathrm{Mn^{II}}}$$

$$(5\text{-Cl-SALEN})\mathrm{Mn^{II}} + \mathrm{O_2} \rightarrow \underset{\mathrm{I}}{[(5\text{-Cl-SALEN})\mathrm{MnO_2}]}$$

$$[(5\text{-Cl-SALEN})\mathrm{MnO_2}] + e^- \rightarrow \underset{\mathrm{II}}{[(5\text{-Cl-SALEN})\mathrm{MnO_2}]^-}$$

$$[(5\text{-Cl-SALEN})\mathrm{MnO_2}]^- + [(5\text{-Cl-SALEN})\mathrm{Mn^{III}}]^+ \rightarrow \underset{\mathbf{2}}{[(5\text{-Cl-SALEN})\mathrm{Mn(O)}]_2}$$

$$\underset{\mathrm{I}}{[(5\text{-Cl-SALEN})\mathrm{MnO_2}]} + (5\text{-Cl-SALEN})\mathrm{Mn^{II}} \rightarrow \underset{\mathbf{2}}{[(5\text{-Cl-SALEN})\mathrm{Mn^{IV}}(\mu\text{-O})]_2} \quad (5)$$

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[26] See: Jacobsen, E. N.; Zhang, W.; Guler, M. L. *J. Am. Chem. Soc.* **1991**, *113*, 6703 and references therein.

Concluding Remarks. The oxygen activation process for manganese Schiff-base complexes appears to be less complicated than previously thought. Our studies clearly show that reaction conditions will play a significant role in the products that are isolated from an oxygenation reaction. The instability and reactivity of the oxygenated products were unanticipated aspects of the oxygenation process but seem to be a common occurrence among at least the Schiff-base complexes. Studies are continuing to further refine our understanding of the oxygen activation process and to utilize the oxygen atom transfer properties of these Schiff-base complexes.

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