

# Reaction of the Schiff-Base Complexes (X-SALPRN)Mn<sup>II</sup> [X = H, 5-Cl, 5-CH<sub>3</sub>O; SALPRN = 1,3-Bis(salicylideneamino)propane] with Dioxygen and Reactivity of the Oxygenated Products

Colin P. Horwitz,<sup>1</sup> Patrick J. Winslow,<sup>2</sup> Joseph T. Warden,<sup>1</sup> and Carol A. Lisek<sup>3</sup>

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12180-3590, and Monsanto Company, St. Louis, Missouri 83198

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The Schiff-base complexes (X-SALPRN)Mn<sup>II</sup> [X = H, 5-Cl, 5-CH<sub>3</sub>O; SALPRN = 1,3-bis(salicylideneamino)propane] were reacted with dioxygen in CH<sub>3</sub>CN and CH<sub>2</sub>Cl<sub>2</sub>. Mn(IV), Mn(IV) bis(μ-oxo) dimers [(X-SALPRN)Mn<sup>IV</sup>(μ-O)]<sub>2</sub> [X = H (1), 5-Cl (2), 5-CH<sub>3</sub>O (3)] were isolated in high yields and as the sole products from oxygenation in CH<sub>3</sub>CN, but two products were isolated when the oxygenation was performed in CH<sub>2</sub>Cl<sub>2</sub>. One product was the bis(μ-oxo) dimer, while the second was a green compound formulated as {(X-SALPRN)Mn<sup>III</sup>]<sub>2</sub>O<sub>x</sub>}<sub>x</sub>, where x = 1 or 2 [X = H (4), 5-Cl (5), 5-CH<sub>3</sub>O (6)]. These green compounds formed by reaction of 1-3 with its appropriate Mn(II) complex in a 1:2 ratio. The bis(μ-oxo) dimers each exhibited a single, reversible one-electron couple E°<sub>1</sub> = -480 mV, E°<sub>2</sub> = -340 mV, and E°<sub>3</sub> = -590 mV all vs SSCE. All of the green compounds exhibited two redox processes, both of which were multielectron transfer reactions. The ESR spectrum of a frozen solution of the mixed-valence form of 1 observed at 6 K showed the presence of an antiferromagnetically coupled S = 1/2 system with the following best fit parameters: g<sub>x</sub> = 2.0092, g<sub>y</sub> = 2.0061, g<sub>z</sub> = 1.9925; A<sub>1x</sub> = 492 MHz, A<sub>1y</sub> = 448 MHz, A<sub>1z</sub> = 385 MHz, A<sub>2x</sub> = 231 MHz, A<sub>2y</sub> = 227 MHz, A<sub>2z</sub> = 209 MHz. A complete intermetal oxygen atom transfer reaction for compound 4 was observed to occur with (SALEN)Fe<sup>II</sup> [SALEN = 1,2-bis(salicylideneamino)ethane] resulting in formation of the (SALPRN)Mn<sup>II</sup> and [(SALEN)Fe<sup>III</sup>]<sub>2</sub>(μ-O) (7), both in quantitative yield.

## Introduction

The control and understanding of the reactions of transition metal complexes with dioxygen is relevant to oxygen transport in biological systems,<sup>4</sup> oxygenase enzymes,<sup>5</sup> and homogeneous oxygenation catalysts.<sup>6</sup> Reactivity patterns for some Fe(II) and Co(II) coordination compounds toward dioxygen<sup>4</sup> are well established, and the chemistry of dinuclear Cu(I) compounds and O<sub>2</sub> is rapidly moving forward.<sup>7</sup> There has been less emphasis placed on understanding the reaction chemistry of Mn(II) complexes toward O<sub>2</sub> because a complicated set of reactions is thought to accompany the oxidation process<sup>8</sup> and there are conflicting reports as to the products that form.<sup>9-11</sup> Only recently have some of the purported intermediates in postulated reaction

schemes been isolated and spectroscopically characterized,<sup>12,13</sup> but only some of these compounds have been prepared using oxygen.<sup>13</sup> We are studying the oxygenation reaction of manganese Schiff-base complexes to determine the catalytically active oxygen components in a recently reported electrocatalytic olefin epoxidation reaction.<sup>14</sup> Firmly establishing the oxygen activation pathway will be an important step forward to exploiting this important reaction.

Oxygenation reactions of the symmetrical (X-SALPRN)Mn<sup>II</sup> complexes (I) [X = H (Ia), 5-Cl (Ib), 5-CH<sub>3</sub>O (Ic); H<sub>2</sub>SALPRN = 1,3-bis(salicylideneamino)propane] are the focus of this report. These complexes were chosen because they are among the simplest Schiff-base compounds that react with O<sub>2</sub> and form solid compounds that could be isolated and characterized from the oxygenation reactions, and while this work was in progress, the bis(μ-oxo) dimer [(SALPRN)Mn<sup>IV</sup>(μ-O)]<sub>2</sub> (I)<sup>15</sup> was characterized by single-crystal X-ray crystallography.<sup>15a-c</sup> Two different syntheses are reported for compound 1, one of which involves an oxidation of an appropriate precursor with molecular oxygen<sup>10a,15a,b</sup> while the other uses H<sub>2</sub>O<sub>2</sub><sup>15c,d</sup> as the oxidant. Our studies reveal that the choice of solvent and the rate of oxygenation both play

- (1) Rensselaer Polytechnic Institute.
- (2) NSF-REU participant Summer 1991 at Rensselaer Polytechnic Institute.
- (3) Monsanto Co.
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important roles in determining the isolable products. We demonstrate here that the bis( $\mu$ -oxo) dimer like **1** is the primary oxygenation product from reaction of Mn(II) with O<sub>2</sub> but under some reaction conditions it undergoes an intermetal oxygen atom transfer reaction<sup>16</sup> with Mn(II) as a complicating side reaction.

## Experimental Section

**Physical Measurements.** IR spectra of solids (KBr disks) were taken on a Perkin-Elmer 1800 FT-IR spectrometer. UV-vis spectra were measured using a Hewlett-Packard HP8452A diode array spectrophotometer controlled with a Zenith computer. Electron paramagnetic resonance studies were performed with a Varian E-9 spectrometer interfaced to either a PDP-11/23A minicomputer operating under Berkeley Software Distribution Unix (BSD 2.9) compiled with real-time process extensions<sup>17</sup> or a MacIntosh IICI with LabVIEW 2 (National Instruments). Cryogenic temperatures were obtained with an Air Products LTD-3-100 Heli-Tran cryostat. Sample temperatures were monitored by a calibrated thermocouple situated beneath the 3-mm i.d. quartz sample tube. Mass spectrometric data were measured at Monsanto 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<sub>2</sub>Cl<sub>2</sub>/DMSO) were infused continuously into the electrospray interface at a flow rate of 5  $\mu$ L/min. Elemental analyses were done by Quantitative Technologies, Inc., Whitehouse, NJ.

**Electrochemistry.** Electrochemical measurements were made using an EG&G PAR Model 273 potentiostat/galvanostat controlled with the Zenith computer and recorded on a Graphtec WX-1200 XY recorder. Cyclic voltammograms, CVs, were obtained in a one or three compartment cell with a glassy-carbon disk [ $A \sim 0.071$  cm<sup>2</sup> (polished with 1- $\mu$ m diamond paste (Buehler)] working electrode, 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 was used. The supporting electrolytes were Bu<sub>4</sub>NClO<sub>4</sub> (TBAP) (Baker analyzed) and Bu<sub>4</sub>NPF<sub>6</sub> (TBAPF<sub>6</sub>) (Fluka puriss), while CH<sub>2</sub>Cl<sub>2</sub>, distilled from P<sub>4</sub>O<sub>10</sub>, and DMF, distilled in vacuo from P<sub>4</sub>O<sub>10</sub>, were used as solvents.

**Materials.** The following reagent grade chemicals were used as received: Salicylaldehyde (Fluka), 5-Cl-salicylaldehyde and 5-CH<sub>3</sub>O-salicylaldehyde (Aldrich), ethylenediamine (Fisher), and 1,3-diaminopropane (Aldrich). The solvents CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>CN, CH<sub>3</sub>OH, and THF were distilled under N<sub>2</sub> from appropriate drying agents.<sup>18</sup> The (SALEN)-Fe<sup>II</sup> complex was prepared under a N<sub>2</sub> atmosphere using standard Schlenk techniques and a procedure detailed in the literature.<sup>19</sup> All air-sensitive solids were stored in a N<sub>2</sub>-filled glovebox (Vacuum Atmospheres).

**Synthesis of (X-SALPRN)Mn<sup>II</sup> [X = H (Ia), 5-Cl (Ib), 5-CH<sub>3</sub>O (Ic)].** Syntheses for the three Schiff-base complexes are essentially identical so only the one for X = H is detailed. The methodology is a modification of well-developed procedures detailed in the literature.<sup>19a</sup> Salicylaldehyde (0.5 mL, 4.7 mmol) and 1,3-diaminopropane (195  $\mu$ L, 2.4 mmol) were combined in reagent grade methanol (15 mL), and the yellow solution was refluxed for approximately 30 min. The solution was cooled to room temperature, and a yellow solid precipitated. KOH (265 mg, 4.7 mmol) in deaerated H<sub>2</sub>O (15 mL) was added to the methanol solution forming a homogenous solution. The solution was stirred for 15 min, and then Mn(CH<sub>3</sub>C(O)O)<sub>2</sub>·4H<sub>2</sub>O (575 mg, 2.4 mmol) dissolved in deaerated water was added resulting in precipitation of an off-yellow solid. The slurry was stirred for 1 h to ensure complete reaction, filtered through a medium-porosity frit, washed with 2  $\times$  20 mL of deaerated water, and then dried at room temperature in vacuo for 24 h. The solid was then washed with hot acetonitrile and dried in vacuo. Data for **Ia** are as follows. Yield: 91%. Anal. Calcd (found) for C<sub>17</sub>H<sub>16</sub>MnN<sub>2</sub>O<sub>2</sub>: C, 60.89 (60.64); H, 4.78 (4.71); N, 8.36 (8.35); Mn, 16.42 (15.66). UV-vis in DMF [ $\lambda$ , nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 360 (6900)]. Data for **Ib** are as follows. Yield: 54%. Anal. Calcd (found) for C<sub>17</sub>H<sub>14</sub>Cl<sub>2</sub>MnN<sub>2</sub>O<sub>2</sub>: C, 50.49 (49.68); H, 3.46 (3.35); N, 6.93 (7.17); Mn, 13.61 (13.45). UV-vis in DMF [ $\lambda$ , nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 374 (10 400)]. Data for **Ic** are as follows. Yield: 83%. Anal. Calcd (found) for C<sub>19</sub>H<sub>20</sub>MnN<sub>2</sub>O<sub>4</sub>: C, 57.72 (54.95); H, 5.06

(5.13); N, 7.09 (6.73); Mn, 13.92 (12.87). UV-vis in DMF [ $\lambda$ , nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 382 (8700)].

**Oxidation of (X-SALPRN)Mn<sup>II</sup> Complexes. Procedure A.** The syntheses for the three bis( $\mu$ -oxo) dimer complexes were essentially identical so only the one for X = H is detailed. The (SALPRN)Mn<sup>II</sup> complex was loaded in a flask in the glovebox and suspended in deaerated CH<sub>3</sub>CN (15 mL), and a rubber septum was placed in the neck of the flask. After removal of the flask from the glovebox, a syringe needle was admitted into the flask and O<sub>2</sub> was bubbled at a moderate rate into the solution. Admission of the O<sub>2</sub> immediately caused a darkening of the solution to red-brown, and the solid changed from yellow to red-brown. Reaction was complete after approximately 15 min, and the red-brown solid was recovered by filtration in air, washed with CH<sub>3</sub>CN, and dried in vacuo yielding a red-brown powder. All compounds were recrystallized from a CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether mixture in air: [(SALPRN)Mn<sup>IV</sup>( $\mu$ -O)]<sub>2</sub> (**1**), 64% yield (MW = 702; MS  $m/z$  = 703, MH<sup>+</sup>); [(5-Cl-SALPRN)Mn<sup>IV</sup>( $\mu$ -O)]<sub>2</sub> (**2**), 83% yield; [(5-CH<sub>3</sub>O-SALPRN)Mn<sup>IV</sup>( $\mu$ -O)]<sub>2</sub> (**3**), 69% yield (MW = 822; MS  $m/z$  = 823, MH<sup>+</sup>) (yields all based on the amount of starting (X-SALPRN)Mn<sup>II</sup>). Anal. Calcd (found) for C<sub>34</sub>H<sub>32</sub>N<sub>4</sub>O<sub>6</sub>Mn<sub>2</sub>·2CH<sub>2</sub>Cl<sub>2</sub> (**1**): C, 49.54 (50.23); H, 4.12 (4.59); N, 6.42 (6.78). Calcd (found) for C<sub>34</sub>H<sub>28</sub>N<sub>4</sub>O<sub>6</sub>Cl<sub>4</sub>Mn<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub> (**2**): C, 45.40 (44.87); H, 3.24 (3.50); N, 6.05 (5.92). Calcd (found) for C<sub>38</sub>H<sub>40</sub>N<sub>4</sub>O<sub>10</sub>·Mn<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub> (**3**): C, 51.59 (53.72); H, 4.63 (5.20); N, 6.17 (6.05).

**Procedure B.** The initial sample preparation was similar to that described in procedure A, but CH<sub>2</sub>Cl<sub>2</sub> was used in place of acetonitrile. After approximately 15 min of reaction with O<sub>2</sub> a homogeneous deep red-brown solution formed and oxygen bubbling was stopped. Petroleum ether was added in air to the solution causing precipitation of a red-brown powder. In the case of the compound with X = 5-CH<sub>3</sub>O, a red-brown solid precipitated without addition of petroleum ether. These solids were recovered by filtration, washed with petroleum ether, and then dried in vacuo. The filtrate was green-black, and further addition of petroleum ether caused precipitation of a green powder that was subsequently recovered by filtration, washed with petroleum ether, and dried in vacuo. The ratio of the isolated solids varied between preparations for reasons presented in the Discussion. The green compounds are denoted as {(SALPRN)Mn<sup>III</sup>]<sub>2</sub>O<sub>x</sub>} (**4**), {(5-Cl-SALPRN)Mn<sup>III</sup>]<sub>2</sub>O<sub>x</sub>} (**5**), and {(5-CH<sub>3</sub>O-SALPRN)Mn<sup>III</sup>]<sub>2</sub>O<sub>x</sub>} (**6**) ( $x = 1$  or 2).

**Procedure C.** The initial sample preparation procedure was analogous to the one described in procedure B. After the flask was removed from the glovebox, a syringe needle was inserted through the rubber septum but was placed well above the surface of the solution. Air was allowed to diffuse through the needle for 12–24 h during which time the solution darkened to a green-black color and all of the yellow starting material was consumed. The flask was occasionally agitated to resuspend the unreacted starting material. The solution was filtered in air when no starting material was observed, petroleum ether was added to the filtrate causing precipitation of any bis( $\mu$ -oxo) dimer that formed the solution was filtered, and then additional petroleum ether was added to precipitate the green powder, which was recovered by filtration, washed with petroleum ether and dried in vacuo: {(SALPRN)Mn<sup>III</sup>]<sub>2</sub>O<sub>x</sub>} (**4**), 45% yield; {(5-Cl-SALPRN)Mn<sup>III</sup>]<sub>2</sub>O<sub>x</sub>} (**5**), 49% yield; {(5-CH<sub>3</sub>O-SALPRN)Mn<sup>III</sup>]<sub>2</sub>O<sub>x</sub>} (**6**), 43% yield based on starting (X-SALPRN)Mn<sup>II</sup>. Anal. Calcd (found) for C<sub>34</sub>H<sub>32</sub>N<sub>4</sub>O<sub>5</sub>Mn<sub>2</sub> (**4**): C, 59.48 (60.73); H, 4.66 (4.70); N, 8.16 (8.08). Calcd (found) for C<sub>34</sub>H<sub>28</sub>N<sub>4</sub>O<sub>5</sub>Cl<sub>4</sub>Mn<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub> (**5**): C, 46.20 (45.90); H, 3.30 (3.27); N, 6.18 (6.00). Calcd (found) for C<sub>38</sub>H<sub>40</sub>N<sub>4</sub>O<sub>9</sub>Mn<sub>2</sub> (**6**): C, 56.57 (55.65); H, 4.96 (5.18); N, 6.95 (6.73).

**Spectrophotometric Titration of [(SALPRN)Mn<sup>IV</sup>( $\mu$ -O)]<sub>2</sub> (**1**) and {(SALPRN)Mn<sup>III</sup>]<sub>2</sub>O<sub>x</sub>} (**4**) with Cp<sub>2</sub>Co.** The procedures for these titrations were identical so only the one for reaction of **1** with Cp<sub>2</sub>Co is described in detail. A 3.0-mL aliquot of a 0.071 mM solution (0.21  $\mu$ mol) of [(SALPRN)Mn<sup>IV</sup>( $\mu$ -O)]<sub>2</sub> dissolved in CH<sub>2</sub>Cl<sub>2</sub> was placed in a quartz cuvette containing a magnetic stir bar and fitted with a rubber septum in the glovebox. A 40 mM solution of Cp<sub>2</sub>Co and a 39.5 mM solution of [Cp<sub>2</sub>Fe][PF<sub>6</sub>] both in CH<sub>3</sub>CN (10 mL) were prepared in the glovebox, and these solutions were taken up in 10- $\mu$ L gastight syringes. The cuvette was placed in the UV-vis spectrophotometer, stirring was initiated by an air-driven magnetic stirrer, and then the reductant was added in 1.0- $\mu$ L aliquots with the spectrum recorded 15–30 s after addition of the cobaltocene. These additions were continued until no further spectral changes were observed (6.0  $\mu$ L, 0.24  $\mu$ mol). Following addition of the requisite amount of Cp<sub>2</sub>Co, the [Cp<sub>2</sub>Fe][PF<sub>6</sub>] oxidant was added in 1.0- $\mu$ L aliquots and the spectrum recorded 30 s after its addition; 6.0  $\mu$ L of the oxidant was added. For titration of **4**, 0.29  $\mu$ mol of **4** (assuming

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a [(SALPRN)Mn<sup>III</sup>]<sub>2</sub>O formulation) required 0.59 μmol of Cp<sub>2</sub>Co and 0.59 μmol of [Cp<sub>2</sub>Fe][PF<sub>6</sub>] for complete reduction and oxidation, respectively.

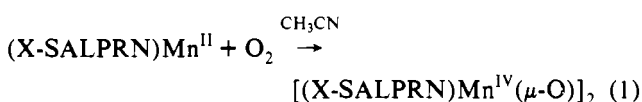
**Reaction of [(SALPRN)Mn<sup>IV</sup>(μ-O)]<sub>2</sub> (1) with (SALPRN)Mn<sup>II</sup>.** Stock solutions of [(SALPRN)Mn<sup>IV</sup>(μ-O)]<sub>2</sub>, 0.82 mM (25.0 mL), and (SALPRN)Mn<sup>II</sup>, 2.35 mM (10.0 mL), in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M TBAPF<sub>6</sub> were prepared in the glovebox. An aliquot, typically 1–2 mL, of the (SALPRN)Mn<sup>II</sup> solution was added to the solution of the bis(μ-oxo) dimer, reaction was allowed to proceed for approximately 10 min, and then the CV was recorded. Additions of the (SALPRN)Mn<sup>II</sup> complex were continued until no further changes in the peak current were observed for the oxidation process centered near 0.8 V.

**Reaction of [(SALPRN)Mn<sup>III</sup>]<sub>2</sub>O<sub>x</sub> (4) with (SALEN)Fe<sup>II</sup>.** A solution of 4, 0.81 mM (25.0 mL) assuming a [(SALPRN)Mn<sup>III</sup>]<sub>2</sub>O formulation, in CH<sub>2</sub>Cl<sub>2</sub> with 0.1 M TBAPF<sub>6</sub> was prepared. (SALEN)Fe<sup>II</sup> was added to this solution in approximately 2-mg quantities, and the CV was recorded approximately 10 min after each addition of the iron complex. Additions of the iron complex were continued until no further increase in the peak height for the Fe(III), Fe(III) → Fe(II), Fe(III) couple was detected; 14.1 mg (43.9 μmol) of (SALEN)Fe<sup>II</sup> was required.

**Spectrophotometric Titration of [(SALPRN)Mn<sup>III</sup>]<sub>2</sub>O<sub>x</sub> (4) with (SALEN)Fe<sup>II</sup>.** A 0.50-mL aliquot of a 0.16 mM solution of 4 in DMF (0.08 μmol), assuming a [(SALPRN)Mn<sup>III</sup>]<sub>2</sub>O formula unit, was placed in a quartz cuvette containing a magnetic stir bar, the solution volume was brought up to 3.0 mL with DMF, and the cuvette was fitted with a rubber septum in the glovebox. A 9.95 mM solution of (SALEN)Fe<sup>II</sup> in DMF (10.0 mL) was prepared in the glovebox and taken up in a 50-μL gastight syringe. The cuvette was placed in the spectrophotometer, stirring was initiated by an air-driven magnetic stirrer, and then the syringe containing the (SALEN)Fe<sup>II</sup> was admitted through the septum and the tip of the needle placed near the stir bar. The iron reagent was added in 2.0-μL aliquots and the spectrum recorded 15–30 s after each addition; 16.0 μL (0.16 μmol) was required for complete reaction.

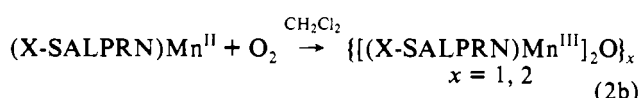
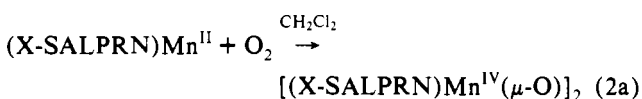
## Results

**Oxidation in CH<sub>3</sub>CN.** Admission of O<sub>2</sub> or air to a slurry of the (X-SALPRN)Mn<sup>II</sup> starting materials in CH<sub>3</sub>CN caused rapid darkening of the solution and deposition of a red-brown powder. Typical isolated yields were 60–80% yield based on the quantity of starting Ia–c. FT-IR, UV-vis, and mass spectrometric data, combustion analyses, and electrochemical measurements obtained on these red-brown compounds reveal that they are bis(μ-oxo) dimers like the ones previously reported<sup>15a–c</sup> having the formulation [(X-SALPRN)Mn<sup>IV</sup>(μ-O)]<sub>2</sub> [X = H (1), 5-Cl (2), 5-CH<sub>3</sub>O (3)], eq 1. The straightforward oxygenation method employed here



to synthesize these dimers contrasts with the more elaborate preparative methods reported by others.<sup>10a,15a–c</sup> An important point to make is that a cyclic voltammogram of the filtrate from oxidation of [(SALPRN)Mn<sup>II</sup>] in CH<sub>3</sub>CN showed 1 as the only electroactive species, so selectivity toward 1 is high under the reaction conditions.

**Oxidation in CH<sub>2</sub>Cl<sub>2</sub>.** Oxidation of the slightly soluble Mn<sup>II</sup> Schiff-base complexes in CH<sub>2</sub>Cl<sub>2</sub> using methods similar to those in CH<sub>3</sub>CN resulted in formation of a homogenous red-brown solution from which two products were isolated, a bis(μ-oxo) dimer (1–3) and a green compound (4–6) which is best formulated as [(X-SALPRN)Mn<sup>III</sup>]<sub>2</sub>O<sub>x</sub>, where x = 1 or 2 but most probably 2 [X = H (4), 5-Cl (5), 5-CH<sub>3</sub>O (6)], eqs 2a,b. The yield of the



**Table I.** Electrochemical and UV-Vis Data

| compd | electrochemistry data <sup>a</sup>                                  |   | UV-vis data <sup>b</sup><br>λ <sub>max</sub> /nm (10 <sup>3</sup> ε/M <sup>-1</sup> cm <sup>-1</sup> ) |
|-------|---|---|--|
|       | E <sub>ox</sub> <sup>c</sup><br>(ΔE <sub>p</sub> ) <sup>d</sup> /mV | E <sub>red</sub><br>(ΔE <sub>p</sub> ) <sup>d</sup> /mV |  |
| 1     |   | –480 (90)   | 320 (15.2), 460 (5.7)  |
| 2     |   | –340 (65),<br>–255 (60) <sup>e</sup>                    | 324 (20.9), 420 sh, 476 (9.8)  |
| 3     |   | –590 (75),<br>–495 (80) <sup>e</sup>                    | 330 sh, 368 (15.2), 440 sh, 500 (7.5)  |
| 4     | 445 (140)   | –520 (150)  | 320 (15.7), 368 sh, 460 (3.2)  |
| 5     | 590 (125)   | –370 (115)  | 324 (15.3), 368 sh, 476 (2.7)  |
| 6     | 310 (135)   | –615 (170)  | 348 (14.3), 400 sh, 500 (2.9)  |

<sup>a</sup> E vs SSCE in 0.1 M TBAClO<sub>4</sub> or TBAPF<sub>6</sub>/CH<sub>2</sub>Cl<sub>2</sub> at a GC electrode and v = 50 mV/s. <sup>b</sup> DMF solution. <sup>c</sup> E<sub>ox</sub> is the average of the more anodic oxidation and the more cathodic reduction. <sup>d</sup> ΔE<sub>p</sub> is the potential difference between the more anodic oxidation and the more cathodic reduction. <sup>e</sup> E vs SSCE in 0.1 M TBAClO<sub>4</sub>/DMF at a GC electrode and v = 50 mV/s.

green compound was substantially improved if the oxidation was performed by the slow diffusion of air into the CH<sub>2</sub>Cl<sub>2</sub> over a 12–24-h period; a green-black solution formed using this oxygenation method. These green species have not been identified previously, but we will show that they are formed from the bis(μ-oxo) dimers. It is likely that they were prepared but not detected in other studies on the oxygenation of manganese Schiff-base complexes.<sup>20,21</sup>

The green solids are generally more soluble than their corresponding bis(μ-oxo) dimers. Compounds 4–6 are soluble in CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>CN, and DMF, while the only common solvent for 1–3 was CH<sub>2</sub>Cl<sub>2</sub>. Numerous attempts have been made to produce X-ray-quality crystals of these products but thus far these have met without success. Recrystallization of the solids often led to isolation of the corresponding bis(μ-oxo) dimer. Mass spectra have also been unobtainable using fast atom bombardment, field desorption, or electrospray techniques so the exact identification of 4–6 is still ambiguous.

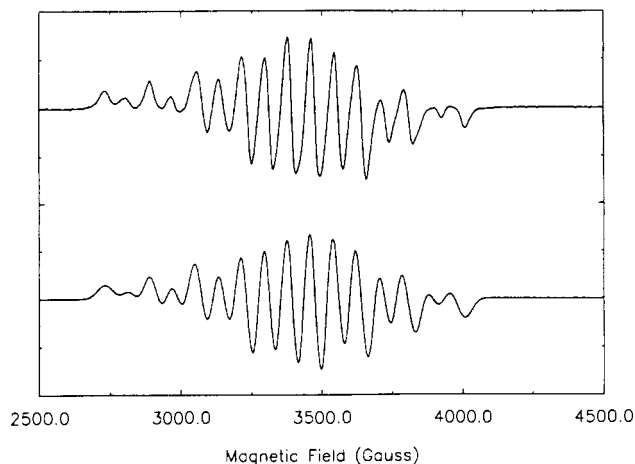
**Spectroscopic Characterization of 1–6.** The FT-IR spectrum for each bis(μ-oxo) dimer exhibits a strong absorption band at approximately 650 cm<sup>-1</sup> that is a characteristic of the Mn<sub>2</sub>O<sub>2</sub> portion of the dimer.<sup>22</sup> (Tentative assignments are as follows: 1, 646 cm<sup>-1</sup>; 2, 644 cm<sup>-1</sup>; 3, 644 cm<sup>-1</sup>). The FT-IR spectra of complexes 4–6 are devoid of the 650-cm<sup>-1</sup> vibrational band, but we have not identified a characteristic Mn–oxygen stretch in these compounds. Isotopic labeling studies are planned to ascertain the Mn–oxygen vibrational modes in these molecules.

The UV-vis spectra of the Mn(IV), Mn(IV) bis(μ-oxo) dimers in CH<sub>2</sub>Cl<sub>2</sub> are reported in Table I. These compounds show broad ill-defined features between 300 and 600 nm, but the broad absorption centered in the 480–500-nm region is a feature not observed in either Ia–c or its oxidized form, [(X-SALPRN)Mn<sup>III</sup>]<sup>+</sup>. Absorption maxima for compounds 4–6 are also given in Table I and like the bis(μ-oxo) dimers the bands are broad and ill-defined. The broad absorption band detected in the 480–500-nm region for these compounds has an absorption coefficient about half the value for its corresponding bis(μ-oxo) dimer assuming a [(X-SALPRN)Mn<sup>III</sup>]<sub>2</sub>O formula unit. This low-energy band appears to be a feature common to oxygenated Schiff-

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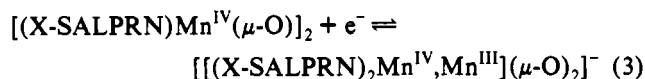
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**Figure 1.** ESR spectrum of a frozen solution, 6 K, of the mixed-valence form of compound **1** produced by bulk electrochemical reduction in 0.2 M TBAPF<sub>6</sub>/CH<sub>2</sub>Cl<sub>2</sub> solution, upper trace, and the simulation of the spectrum using the parameters discussed in the text, lower trace.

base complexes, but owing to the broadness of the absorption band no band assignments are made.

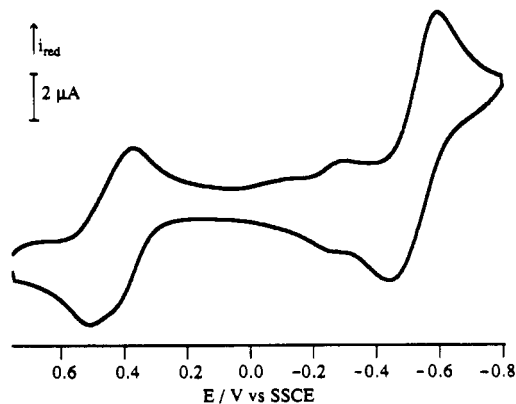
**Electrochemistry of Compounds 1–3.** All of the bis( $\mu$ -oxo) dimers exhibit basically the same electrochemical properties, a reversible redox couple in the  $-340$  to  $-590$  mV range (vs SSCE), eq 3 and Table I.<sup>15a</sup> The shifts in formal potentials,  $E^\circ$ , for the



three compounds are consistent with the electron-donating or -withdrawing properties of the substituent group.<sup>23</sup> A broad electrochemically irreversible reduction for the dimers is observed at more negative potentials that is assigned to the [Mn(III), Mn(IV)]<sup>-</sup>  $\rightarrow$  [Mn(III), Mn(III)]<sup>2-</sup> process. This reduction caused decomposition of the dimer back to the Mn(II) starting material. The redox properties of the dimers are strongly solvent dependent as the  $E^\circ$  for compounds **2** and **3** shift to more positive values by nearly 100 mV in DMF, Table I, and  $E^\circ_1 = -390$  mV vs SSCE in DMSO.<sup>15a</sup>

A bulk electrolysis experiment performed on **1** confirmed that one electron equivalent was consumed per dimer, and the ESR spectrum taken at 6 K of the solution showed it to be a mixed-valence product **1<sup>-</sup>**, Figure 1, upper trace. The 16-line pattern in the ESR spectrum is evidence for an antiferromagnetically coupled mixed-valence dimer having an overall spin of  $S = 1/2$ .<sup>24</sup> The starting material shows no signals in the ESR spectrum at 6 K. Further details regarding the spectrum of **1<sup>-</sup>** are discussed below.

A spectrophotometric titration of **1** (0.21  $\mu$ mol) with cobaltocene as an outer-sphere reductant supported the coulometric measurements (0.24  $\mu$ mol of Cp<sub>2</sub>Co was consumed). The color of the solution changed from red-brown for the starting complex to yellow-brown by the end of the titration. The notable spectral features accompanying the titration were the three isosbestic points observed at  $\lambda = 282, 358,$  and  $402$  nm, the new weak absorption that appeared at  $\lambda_{max} = 374$  nm, and the marked decrease in the broad absorption band of **1** at  $460$  nm. No new absorption bands were observed that could be assigned to an intervalence charge-transfer band for **1<sup>-</sup>**. Reoxidation of **1<sup>-</sup>** with the ferrocenium



**Figure 2.** Cyclic voltammogram of compound **4** (0.61 mM). Conditions:  $v = 20$  mV s<sup>-1</sup>, 0.1 M TBAPF<sub>6</sub>/CH<sub>2</sub>Cl<sub>2</sub>, and GC electrode.

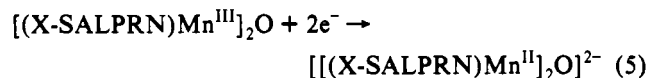
cation essentially regenerated the original spectrum for **1**, and electrochemical measurements confirmed the chemical stability of the reduced dimer.<sup>25</sup>

**Electrochemistry of Compounds 4–6.** The formulation of these compounds is not unambiguous. However, as described below, the best formulation is  $\{[(X-SALPRN)Mn^{III}]_2O\}_x$ , where  $x = 1$  or 2. For the sake of simplicity, the formula with  $x = 1$  is used throughout this section. The electrochemical characteristics of **4–6**, Figure 2, are similar with the shifts expected as a result of the electron-donating or -withdrawing properties of the groups on the aromatic rings.<sup>23</sup> The redox process at positive potentials, at least in methylene chloride, shows evidence for two closely spaced oxidations at approximately 440 and 530 mV and two less well resolved reductions. Coulometric measurements revealed the oxidation to be a two-electron process, eq 4. Cyclic



voltammograms in DMF and CH<sub>3</sub>CN show a less pronounced separation between the two oxidation and corresponding reduction processes. Taken as a whole, these observations are consistent with weakly interacting metal sites with a comproportionation constant,  $K_{comp}$ , of 33.<sup>26</sup> Alternatively, the complexes may have noninteracting metal centers that are in very similar, but not identical, environments making their redox processes occur in close proximity. The different solvating abilities of the three solvents could cause merging of the current-potential envelopes accounting for the overlap of the redox processes.

The redox process at  $E_{red} = -520$  mV is broad and has a large peak splitting. Coulometric measurements, as well as a spectrophotometric titration with cobaltocene as an outer-sphere reductant, showed that two electron equivalents were consumed per [(SALPRN)Mn<sup>III</sup>]<sub>2</sub>O formula unit, eq 5. The small, poorly



shaped waves positive of the main cathodic and anodic currents most likely arise from adsorption of the complex onto the electrode surface, and we have observed similar phenomena with other metal Schiff-base complexes.<sup>27</sup>

A spectrophotometric titration using Cp<sub>2</sub>Co as a reductant was performed on complex **4**, and this is illustrated in Figure 3.

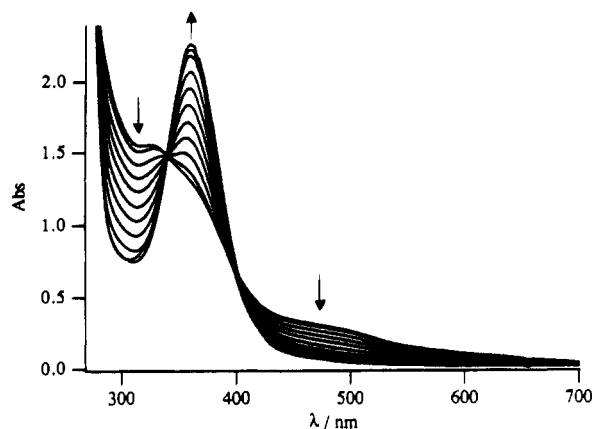
(23) Boggess, R. K.; Hughes, J. W.; Coleman, W. M.; Taylor, L. T. *Inorg. Chim. Acta* **1980**, *38*, 183.

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(25) We have evidence that the one electron reduced product of [(5-Cl-SALEN)Mn<sup>IV</sup>( $\mu$ -O)]<sub>2</sub>, a bis( $\mu$ -oxo) dimer (5-Cl-SALEN is 1,2-bis((5-chlorosalicylidene)amino)ethane), is unstable but produces a 16-line ESR spectrum at 6 K similar to the one in Figure 2: Dailey, G. C.; Horwitz, C. P. *Inorg. Chem.*, in press.

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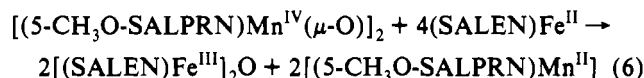
**Figure 3.** Spectrophotometric titration of compound **4** with  $\text{Cp}_2\text{Co}$ . Reaction conditions: 0.29  $\mu\text{mol}$  of **4** in  $\text{CH}_2\text{Cl}_2$ , using a formulation of  $[(\text{SALPRN})\text{Mn}^{\text{III}}]_2\text{O}$ , and 1- $\mu\text{L}$  additions of a 59 mM solution of  $\text{Cp}_2\text{Co}$  in  $\text{CH}_3\text{CN}$ . All additions starting at 0  $\mu\text{L}$  are shown.

Like the electrochemical measurements, 2 equiv of  $\text{Cp}_2\text{Co}$  was consumed before reaction was complete. The color of the solution changed from green-black to yellow-green after 1 molar equiv of  $\text{Cp}_2\text{Co}$  was added and then to pale yellow upon addition of the second equivalent. The two isosbestic points are at  $\lambda = 338$  and 402 nm, while the intense new absorption is at  $\lambda_{\text{max}} = 360$  nm. The absorption at 360 nm appears at a position identical to one for **1a** and provides some, although not compelling, evidence for a Mn(III) center in **4**. The reduction was also monitored by cyclic voltammetry in order to probe for decomposition products. No redox process for **1a** was observed in the voltammogram, and the peak current for the oxidation process at 530 mV changed by less than 10% strongly suggesting that **1** did not form. This experiment reveals that the doubly reduced complex is stable and, more importantly, the absorption at 360 nm does not arise from  $(\text{SALPRN})\text{Mn}^{\text{II}}$ .

**ESR Spectroscopy.** The ESR spectrum of **1<sup>-</sup>** is illustrated as the upper trace in Figure 1, and it is consistent with the assignment of this species to an antiferromagnetically coupled, valence-trapped binuclear manganese complex. Simulation of the ESR spectrum of **1<sup>-</sup>** is presented in Figure 1 (lower trace) and was performed using a protocol based on a second-order perturbation solution of the spin Hamiltonian for an anisotropic,  $S = 1/2$  system possessing rhombic symmetry ( $g_x \neq g_y \neq g_z$ ,  $A_x \neq A_y \neq A_z$ ).<sup>28</sup> The Gaussian line shape function was used for all simulations. An iterative least-squares routine based on the Monte Carlo method was utilized for extracting the spectroscopic parameters from the experimental ESR spectrum of **1<sup>-</sup>**. The optimal fit for the spectrum in Figure 1 was obtained with the parameters  $g_x = 2.0092$ ,  $g_y = 2.0061$ ,  $g_z = 1.9925$ ;  $A_{1x} = 492$  MHz,  $A_{1y} = 448$  MHz,  $A_{1z} = 385$  MHz; and  $A_{2x} = 231$  MHz,  $A_{2y} = 227$  MHz,  $A_{2z} = 209$  MHz. Expressing these dimer hfs (hyperfine splitting constant) parameters in terms of the isotropic monomer equivalents yields 221 MHz for Mn(III) and 222 MHz for Mn(IV). These values are consistent with previously published data for mixed-valence Mn(III)/Mn(IV) complexes.<sup>29</sup> Similarly the spectral width of 1230 G is within the range 980–1250 G generally found for mixed-valence bis( $\mu$ -oxo) dimers of manganese.<sup>24,29</sup> As noted earlier by Diril et al.,<sup>30</sup> most simulations of ESR spectra of mixed-valence dimers have employed either isotropic or axial

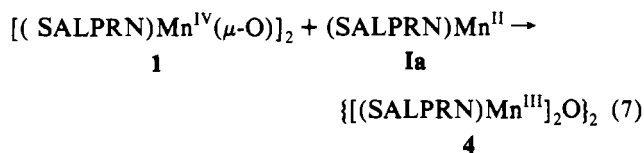
models for the  $g$  and  $A$  tensors. These simulations in general have not reproduced the reported experimental spectra with a reasonable degree of fidelity. Indeed, our initial attempts to simulate the spectrum of **1** assuming axial symmetry for both the  $g$  and  $A$  tensors were unsuccessful in that we could not reproduce simultaneously the splitting pattern (peak positions) and peak intensities. Our experience suggests that interpretation of the ESR spectra of these valence-trapped dimers necessitates the imposition of rhombic character to the coupled representation of the  $g$  and  $A$  tensors.

**Reactivity of the Bis( $\mu$ -oxo) Dimer.** Large manganese oxo clusters can be prepared by redox condensation reactions like those employed in metal carbonyl cluster chemistry.<sup>31,32</sup> One of us recently reported<sup>33</sup> that in an attempt to prepare a mixed iron–manganese oxo cluster using **3** and  $(\text{SALEN})\text{Fe}^{\text{II}}$  by a methodology analogous to the redox condensation reaction, a complete oxygen atom transfer reaction resulted. The products of the reaction were the Mn(II) complex, **1c**, and the iron oxo dimer  $[(\text{SALEN})\text{Fe}(\text{III})]_2(\mu\text{-O})$  (**7**), and these complexes were formed in quantitative yields, eq 6. This was the first report of a four electron two oxygen atom transfer reaction and a unique example of the transfer of  $\mu_2$ -bridging oxo ligands.<sup>16,34</sup>



We now show that  $[(\text{SALPRN})\text{Mn}^{\text{IV}}(\mu\text{-O})]_2$  reacts with  $(\text{SALPRN})\text{Mn}^{\text{II}}$  in  $\text{CH}_2\text{Cl}_2$  producing compound **4** and that the reaction is most likely of the incomplete oxygen atom transfer type.<sup>16</sup> Illustrated in Figure 4a are CVs recorded for **1** (6.12  $\mu\text{mol}$ ) with no  $(\text{SALPRN})\text{Mn}^{\text{II}}$  added (---) and one with 8.95  $\mu\text{mol}$  of  $(\text{SALPRN})\text{Mn}^{\text{II}}$  added (—). Formation of compound **4** is obvious. This reaction clearly shows that the bis( $\mu$ -oxo) products can be reactive toward the Mn(II) starting material and presumably other electrophiles.

The quantity of **4** produced was determined by monitoring the growth of the current for the oxidation process marked with an asterisk on the figure,  $i_{\text{ox},4}$ , and this is illustrated in Figure 4b. The monotonic growth in  $i_{\text{ox},4}$  stopped after the addition of slightly more than 2 molar equiv of **1a**, and the measured currents closely matched those predicted for reaction according to eq 7. An error



of 10–15% in the current measurements was assumed in this experiment primarily from weighing and transferring solids in the glovebox. The predicted currents were calculated by determining the diffusion coefficient for a pure sample of **4** from the Randles–Sevcik equation<sup>35,36</sup> assuming a one electron oxidation process,  $D_4 = 4.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ , and then using the reactant and product stoichiometries in eq 7. While this approach is simplified and  $n = 2$  for each  $[(\text{SALPRN})\text{Mn}^{\text{III}}]_2\text{O}$  unit, eq 4, the errors

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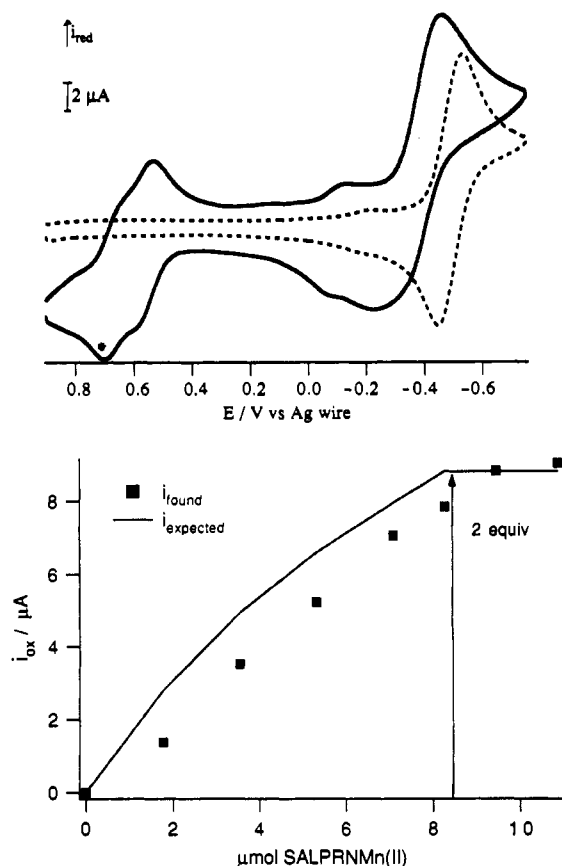
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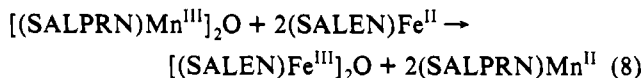
(36)  $i_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} \nu^{1/2} C^*$ , where  $n$  is the number of electrons,  $A$  is the electrode area,  $D$  is the diffusion coefficient,  $\nu$  is the scan rate, and  $C^*$  is the bulk concentration.



**Figure 4.** (a) Top: Cyclic voltammograms of compound **1** (0.61 mM, 6.12  $\mu\text{mol}$ ) before (---) and after (—) addition of 8.95  $\mu\text{mol}$  of (SALPRN)Mn<sup>II</sup>. Conditions:  $v = 50 \text{ mV s}^{-1}$ , 0.1 M TBAPF<sub>6</sub>/CH<sub>2</sub>Cl<sub>2</sub>, and GC electrode. (b) Bottom: Dependence of  $i_{\text{ox},4}$  (asterisk on the figure) on the quantity of (SALPRN)Mn<sup>II</sup> added to an electrolysis solution containing 4.1  $\mu\text{mol}$  of compound **1** in 0.1 M TBAPF<sub>6</sub>/CH<sub>2</sub>Cl<sub>2</sub>.

in  $D_4$  and  $n$  were applied in a consistent manner. The match of the observed and predicted currents is good, especially toward the end of the (SALPRN)Mn<sup>II</sup> addition. The rationale for assigning **4** a tetranuclear metal core is provided in the Discussion.

**Reactivity of Compound 4.** Compound **4** also undergoes a complete intermetal oxygen atom transfer reaction with (SALEN)-Fe<sup>II</sup> producing [(SALEN)Fe<sup>III</sup>]<sub>2</sub>( $\mu$ -O) and (SALPRN)Mn<sup>II</sup>. The significance of this experiment is that it clearly shows that **4**, and presumably **5** and **6**, contains oxo type ligands. The reaction was monitored by cyclic voltammetry, and the data revealed that 2 equiv of the iron complex was required for complete reaction with **4** (this assumes a [(SALPRN)Mn<sup>III</sup>]<sub>2</sub>O formula, eq 8. Overall the reaction corresponds to a net two electron one oxygen atom transfer reaction.

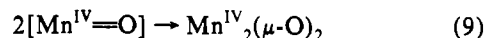


The spectrophotometric titration of a DMF solution of **4** with (SALEN)Fe<sup>II</sup> is complicated, unlike the titration reported for the reaction given in eq 7.<sup>33</sup> Nevertheless, the broad absorption band for **4** at 460 nm, Table I, does decrease monotonically with addition of the iron reagent and concomitantly a strong absorption band grows in at 378 nm from both the Mn(II) and the iron  $\mu$ -oxo dimer produced during the titration. Further additions of (SALEN)Fe<sup>II</sup> beyond 2 molar equiv produces a spectrum that is consistent with the presence of unreacted (SALEN)Fe<sup>II</sup> in solution.

## Discussion

**Oxygenation Reactions.** The reaction of manganese(II) compounds, including Schiff-base complexes, with dioxygen is a rich

and complicated chemistry. The oxygen activation pathways commonly invoked<sup>8</sup> to account for the isolation of more than one reaction product often suggest the existence of the oxo intermediate [Mn<sup>IV</sup>=O] (**II**).<sup>12</sup> It is this species that is thought to dimerize or react with Mn(II) in an incomplete oxygen atom transfer reaction forming the bis( $\mu$ -oxo) or  $\mu$ -oxo dimer, respectively, eqs 9 and 10. Recently it has been suggested that the bis( $\mu$ -oxo) dimer may be generated without going through an intermediate like **II**.<sup>15c,37</sup>



Our results clearly demonstrate that reaction conditions markedly influence the products isolated from the oxygenation of Mn(II) Schiff-base complexes. While this may not be an unexpected observation based on studies of manganese porphyrins,<sup>37-39</sup> it complicates proposing a unique reaction pathway to account for the isolated products. This is particularly true if the oxygenated product reacts with the starting material. However, the highly selective formation of the bis( $\mu$ -oxo) dimer for the Schiff-base complexes in CH<sub>3</sub>CN, it being the only species detected in the isolated solid and the filtrate from an oxygenation reaction, suggests that the postulated reaction schemes are unnecessarily complicated. Furthermore, it is improbable that the dimer would be formed so selectively if an intermediate like **II** played a role in the activation process.<sup>15c</sup>

We believe that the ability to isolate the bis( $\mu$ -oxo) dimer for the Schiff-base complexes studied here is in large part related to the ligand flexibility;<sup>17,25,40</sup> indeed all of the other bis( $\mu$ -oxo) dimers that are structurally characterized have highly flexible ligands.<sup>41</sup> In the case of manganese porphyrins, another well-studied system, the metal-ligand bonding would need to distort significantly in order to have the oxo ligands in a cis orientation and the Mn centers in the +4 oxidation state in a bis( $\mu$ -oxo) dimer. A close analogue to the bis( $\mu$ -oxo) dimer in the porphyrin ligand system is [TPPMn<sup>III</sup>]-O<sub>2</sub><sup>-</sup> (TPP is tetraphenylporphinato)<sup>42</sup> for which an X-ray crystal structure is available. The compound shows the Mn(III) center lying well out of the least-squares plane of the pyrrole nitrogens, 0.764 Å, and long Mn-N bonds are present. Recently, it has been concluded from ESR data that an unstable bis( $\mu$ -oxo) dimer forms upon reaction of [TPPMn(III)]<sup>+</sup> with superoxide,<sup>37</sup> and it is possible that a similar dimer results when Mn(II) porphyrins react with O<sub>2</sub>. If this structural assignment is correct, the bis( $\mu$ -oxo) dimer may be involved in O<sub>2</sub> activation by manganese porphyrins under some reaction conditions.

**Compounds 4-6.** The variable yields of **4-6** that are observed when oxidizing a CH<sub>2</sub>Cl<sub>2</sub> slurry of **Ia-c** arise because the ratio

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of bis( $\mu$ -oxo) dimer to unoxoxygenated **1a-c** in solution will depend on experimental parameters like stirring rate, oxygen addition rate, solvent volume, and others. Oxygenation by the slow-diffusion technique maintains a low quantity of bis( $\mu$ -oxo) dimer in solution, which can then react with the sparingly soluble (X-SALPRN)Mn<sup>II</sup>. Greater control over the quantity and addition rate of O<sub>2</sub> should result in higher yields of compounds **4-6**. The simpler oxygenation chemistry found in acetonitrile arises because both the products and reactants are poorly soluble in the reaction medium so no follow up chemistry like eq 7 occurs. We have recently found<sup>43</sup> that reaction of (3,5-Cl<sub>2</sub>-SALPRN)Mn<sup>II</sup> with O<sub>2</sub> in CH<sub>3</sub>CN leads to isolation of the same two types of products described here because the bis( $\mu$ -oxo) dimer and the Mn(II) complex are soluble in acetonitrile.

Formulation of compounds **4-6** as tetranuclear clusters,  $\{[(X-SALPRN)Mn^{III}]_2O\}_2$ , is based primarily on the electrochemical results discussed below. However with the information currently available, it is not possible to exclude the possibility that these compounds are simple  $\mu$ -oxo dimers. The electrochemistry of a tetranuclear oxo-bridged manganese cluster with a Schiff-base ligand<sup>44</sup> exhibits four one-electron redox processes some of which have potentials that are closely spaced,<sup>44</sup> behavior that is reminiscent of the CV for compound **4**, Figure 4. In contrast, the [PcMn<sup>III</sup>]<sub>2</sub>( $\mu$ -O) complex (Pc is the phthalocyaninato ligand)<sup>45</sup> exhibits strikingly different electrochemical properties. No electrochemical measurements are reported for [(5-NO<sub>2</sub>-SALDIEN)Mn]<sub>2</sub>( $\mu$ -O) (**8**), 5-NO<sub>2</sub>-SALDIEN is *N,N'*-bis(5-nitrosalicylidene)-1,7-diamino-3-azapentane, the only well-established  $\mu$ -oxo Schiff-base complex,<sup>9a</sup> so comparisons of its electrochemical properties to those for **4-6** are not possible. However, compound **8** is much more unstable than **4-6** as it spontaneously decomposes back to the Mn(II) starting complex upon standing in solution. Finally, although somewhat peripheral to the manganese complexes, compound **7** shows only a single one-electron reduction.<sup>46</sup> Thus it is the combination of these observations that lead to the proposal that compounds **4-6** have the  $\{[(X-SALPRN)Mn^{III}]_2O\}_2$  formulation.

We suggest a Mn<sub>4</sub>( $\mu_3$ -O)<sub>2</sub> core for compounds **4-6**. The tetranuclear manganese Schiff-base complex mentioned above contains this arrangement of metal centers.<sup>44</sup> In addition, the Mn<sub>4</sub>( $\mu_3$ -O)<sub>2</sub> core is a firmly established structural motif using other ligand types.<sup>31,47</sup> It is not obvious why the higher nuclearity cluster forms in preference to the simpler  $\mu$ -oxo dimer. Only four examples of  $\mu$ -oxo-bridged manganese complexes are reported that do not have additional bridging ligands,<sup>9a,48-50</sup> and two of these compounds are unstable to loss of the oxo ligand. Reports of stable heterobimetallic  $\mu$ -oxo complexes containing Mn(III) centers are available,<sup>51</sup> but few detailed physical properties for these complexes are provided. The inability to obtain single crystals of compounds **4-6** makes existence of the Mn<sub>4</sub>( $\mu_3$ -O)<sub>2</sub>

core a tentative assignment, and further speculations as to the structure of these compounds are unwarranted.

**Reaction with (SALEN)Fe<sup>II</sup>.** Inner-sphere electron-transfer reactions involving exchange of single atoms and single electrons are not unusual. However those involving multiple atoms and multiple electrons are rare,<sup>52</sup> and as we have noted,<sup>33</sup> the reaction of **3** with (SALEN)Fe<sup>II</sup> is unique in that it is extremely rapid.<sup>16</sup> Outer-sphere electron transfer in eqs 6 and 8 can be effectively discounted in the present case because the iron complex is not capable thermodynamically of reducing either type of oxygenated manganese complex. Therefore it is likely that a Mn<sub>2</sub>Fe<sub>2</sub>O<sub>2</sub> species is an intermediate in the reaction involving the bis( $\mu$ -oxo) dimer but a more complicated process must occur for the reaction with **4**. Interestingly, the model compound for this Mn<sub>2</sub>Fe<sub>2</sub>O<sub>2</sub> intermediate is the tetranuclear manganese species formed by eq 7.

The complete intermetallic oxygen atom transfer reactions observed for **3** and **4** are novel because they involve bridging oxo ligands. Furthermore, iron complexes usually undergo incomplete oxygen atom transfer reactions forming heterobimetallic complexes.<sup>16</sup> The unique behavior observed for (SALEN)Fe<sup>II</sup> here and previously<sup>33</sup> is most likely related to formation of the thermodynamically stable iron oxo dimer.<sup>19b</sup> The important feature of the atom transfer chemistry described in this report is that it may be possible to use the manganese complexes as oxygenation catalysts with other electrophilic or oxophilic species.

**Concluding Remarks.** While the reactivity of manganese Schiff-base complexes toward O<sub>2</sub> remains complicated, individual components of the overall reaction are beginning to be defined. The bis( $\mu$ -oxo) dimer is the first stable compound recoverable from the oxygenation process for the Schiff-base complexes investigated here, and this species holds the key to the formation of the other oxygenated complexes. The reactivity studies we have undertaken for compounds **1-3** with the manganese and iron reagents and those for compounds **4-6** with (SALEN)Fe<sup>II</sup> appear to be the first attempts, other than protonation reactions,<sup>53</sup> to investigate the chemical properties of oxygenated manganese Schiff-base complexes. In part, it is the lack of reactivity studies that has hindered understanding how the various oxygenated compounds form. As the bis( $\mu$ -oxo) dimer has the pivotal role in the oxygenation chemistry, we are currently investigating a reaction pathway that accounts for the selective formation of the dimer from Mn(II) starting materials.

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