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Facile and Complete Four Electron Two Oxygen Atom Transfer Reactions Involving Manganese Bis(μ-oxo) Dimers

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Inner-sphere electron-transfer reactions typically involve exchange of one electron and one atom between metal centers. Multielectron atom transfer reactions occur less frequently,[1] and as a subset of this class of reaction, the complete intermetallic oxygen atom transfer reaction is still uncommon.[2]

All intermetallic oxygen atom transfer reactions reported in the literature thus far involve transfer of a single terminal oxo group.[2,3] This contribution describes an unprecedented four electron two oxygen atom transfer reaction where the oxo ligands are of the μ_2 bridging type and the reaction is extremely rapid, which makes it particularly noteworthy. Interestingly, other than Bronsted acid/base chemistry,[4] the reactivity of bridging oxo ligands toward electrophiles has received little attention despite the possibility that they may play a role in the assembly of large oxo-containing clusters.[5] We have used cyclic voltammetry and UV–vis spectroscopy to quantitatively monitor the chemical transformations, and the results are presented herein.

When either of the bis(μ-oxo) dimers [(5-Cl-SALEN)Mn^{IV}(μ-O)]$_2$ (**1a**)[6,7] or [(5-CH_3O-SALPRN)Mn^{IV}(μ-O)]$_2$ (**2a**)[7–9] reacts with (SALEN)Fe^{II} (**3b**)[7] in DMF[10] under N_2, the solution changes color from red for **1a** or **2a** to deep red orange for [(SALEN)Fe^{III}]$_2$(μ-O) (**3a**) (eq 1; L and L′ are appropriate

$$[\text{LMn}^{\text{IV}}(\mu\text{-O})]_2 + 4\text{L}'\text{Fe}^{\text{II}} \rightarrow 2\text{LMn}^{\text{II}} + 2[\text{L}'\text{Fe}^{\text{III}}]_2(\mu\text{-O}) \quad (1)$$

Schiff-base ligands). The Mn(II) complexes (5-Cl-SALEN)Mn (**1b**) and (5-CH_3O-SALPRN)Mn (**2b**) are pale yellow. The iron dimer has been isolated from a reaction performed in CH_2Cl_2, and the spectroscopic and electrochemical data for this material are identical to that of a sample of **3a** prepared by methods described in the literature.[11]

The formal potential for **3a**, $E°_{3a} = -1.02$ V vs SSCE, is well separated from those for the Mn(II) complexes, $E°_{1b} = -125$ mV and $E°_{2b} = -120$ mV both vs SSCE in 0.1 M Bu_4NPF_6/DMF, making its detection straightforward.[12] A pseudotitration experiment was performed in an inert-atmosphere glovebox by recording the simultaneous growth of redox couples for **3a** and **1b** or **2b** upon addition of the iron complex. After solid **3b** was added to a solution of **1a** or **2a** the reaction was allowed to proceed for 10 min and then the cyclic voltammogram, CV, was recorded. Shown in Figure 1a are CVs for a solution of **2a** (0.78 mM, 3.9 μmol) before (- - -) and after (—) addition of **3b** (1.4 mg, 4.4 μmol). The irreversible reduction seen in Figure 1a (- - -) at −750 mV causes some manganese dimer decomposition, but by restriction of the potential excursion to values positive of this process, the CV for **2a** is reversible by standard electrochemical criteria[13] and no dimer breakup is observed. The irreversible reduction *does not* affect analyzing the data, particularly the Mn(III/II) reduction, as the potential sweeps are initiated at positions far positive of this process.

The result of a titration experiment using 12.9 μmol of **2a** is shown graphically in Figure 1b where the reduction currents for **3a**, $i_{\text{red,Fe}}$ (■), and [(5-CH_3O-SALPRN)Mn^{III}]$^+$ $i_{\text{red,Mn}}$ (▲), are plotted as a function of the quantity of (SALEN)Fe^{II} added to the electrolysis solution. The currents for both species increase monotonically until 4 molar equiv of (SALEN)Fe^{II} is added/mol of **2a**. The line on the figure is the predicted current values for formation of **3a** calculated using the diffusion coefficient for a pure sample of the dimer, $D_{3a} = 4.2 \times 10^{-6}$ cm^2 s^{-1}, and the Randles–Sevcik equation[11] and then using eq 1 as a guide to its concentration on the basis of the stoichiometry in eq 1. Currents were calculated for the Mn(II) using a similar procedure, but since $D_{2b} = 4.5 \times 10^{-6}$ cm^2 s^{-1}, they are omitted from the figure

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(6) Dailey, G. C.; Horwitz, C. P.; Lisek, C. A. Submitted for publication in *Inorg. Chem.* Data for **1a**: UV–vis in DMF [λ, nm (ϵ, M^{-1} cm^{-1})] 324 (19 700), 412 (10 900), 482 (9300); $E°_{1a} = -278$ mV vs SSCE. Anal. Calcd (found) for $C_{32}H_{24}Cl_4Mn_2N_4O_6$ (MW = 812; MS m/z = 813, MH^+ electrospray): C, 47.32 (46.62); H, 2.98 (2.85); N, 6.90 (6.55).

(7) Ligand abbreviations: **1**, 5-Cl-SALEN is 1,2-bis((5-chlorosalicylidene)amino)ethane; **2**, 5-CH_3O-SALPRN is 1,3-bis((5-methoxysalicylidene)amino)propane; **3**, SALEN is 1,2-bis(salicylideneamino)ethane.

(8) Horwitz, C. P.; Winslow, P. J.; Warden, J. T.; Lisek, C. A. Submitted for publication in *Inorg. Chem.* Data for **2a**: UV–vis in DMF [λ, nm (ϵ, M^{-1} cm^{-1})] 330 (sh), 368 (15 200), 440 (sh), 500 (7500); $E°_{2a} = -495$ mV vs SSCE. Anal. Calcd (found) for $C_{38}H_{40}N_4O_{10}Mn_2 \cdot CH_2Cl_2$ (MW = 822; MS m/z = 823, MH^+ electrospray): C, 51.59 (53.72); H, 4.63 (5.20); N, 6.17 (6.05).

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(11) Data for **3a**: UV–vis in CH_3CN [λ, nm (ϵ, M^{-1} cm^{-1})]: 222 (67 650), 234 (69 750), 286 (sh), 330 (18 750); $E° = -1.04$ V vs SSCE.

(12) A Ag wire quasi-reference electrode was used for glovebox experiments. A mixture of **3a** and **1b** or **2b** was prepared to determine the formal potentials, $E_{3a} = -820$, $E_{1b} = +110$, and $E_{2b} = +20$ mV, but shifts in potential are expected owing to changes in the solution composition.

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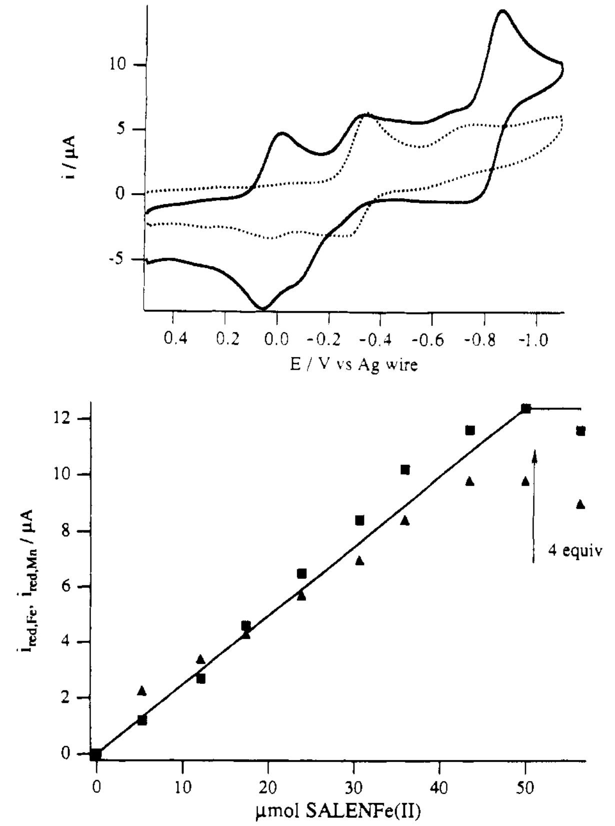

Figure 1. (a) Top: Cyclic voltammograms of **2a** (0.79 mM, 3.89 μmol) before (- - -) and after (—) addition of (SALEN)Fe^{II} (4.4 μmol) in 0.1 M Bu$_4$NPF$_6$/DMF (v = 100 mV/s). (b) Bottom: Dependence of $i_{red,Fe}$ (■) and $i_{red,Mn}$ (▲) on the quantity of (SALEN)Fe^{II} added to a solution containing 12.9 μmol of **2a** in 0.1 M TBAPF$_6$/DMF (v = 100 mV/s).

for purposes of clarity. The measured currents for $i_{red,Mn}$ are suppressed toward the end of the titration owing to an as yet undetermined interaction of Mn(II) with (SALEN)Fe^{II}. Similar titration results are obtained using the bis(μ-oxo) compound **1a**. An experimental error of 10–15% is expected in the measured current values from weighing and transferring solids in the glovebox.

The spectrophotometric titration of a DMF solution of **2a** (16.2 μM, 0.05 μmol) with (SALEN)Fe^{II} (19.9 mM in DMF), added in 1-μL aliquots via a gastight syringe, is illustrated in Figure 2. The broad absorption band for **2a** at 525 nm decreases monotonically, and the well-defined isosbestic point at 444 nm demonstrates that the reaction has no long-lived intermediates. The strong absorption band growing at 378 nm is a combination of **2a** released from the reaction and **3a**. A spectrum of a mixture of **2a** and **3a** yields a spectrum similar to the one at the end of the titration shown in Figure 2. Further additions of (SALEN)Fe^{II} beyond 4 molar equiv produce changes in the spectrum that are consistent with unreacted (SALEN)Fe^{II} in solution.

An intriguing aspect of this oxygen atom transfer reaction is its rapidity. For example, when (SALEN)Fe^{II} (0.2 μmol) was added rapidly via syringe to a stirred solution of **2a** (16.4 μM, 0.05 μmol) at 0 °C, the reaction was complete in less than 20 s as measured by UV–vis spectroscopy, but it is beyond our current instrumental capabilities to assess the kinetic parameters precisely. The data are consistent with a second-order reaction having a half-life less than 5 s, but overlap of absorption bands for both reactants complicates the analysis. Experiments are being designed to overcome these difficulties so that a kinetic investigation can be undertaken.

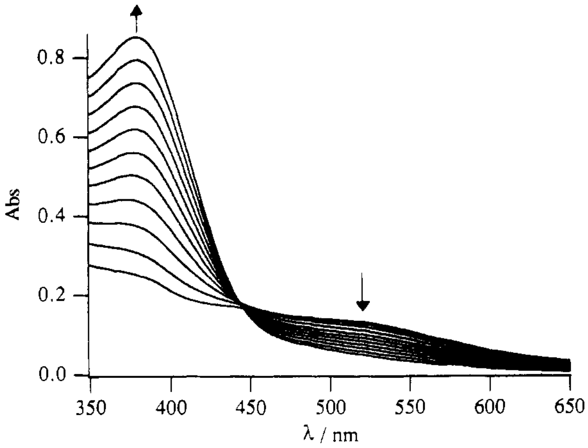

Figure 2. Spectrophotometric titration of **2a** (16.4 μM, 0.05 μmol) with (SALEN)Fe^{II} (19.9 mM) in DMF. The iron compound was added in 1-μL aliquots; all additions starting at 0 μL through 10 μL are shown.

It might be suggested that the oxygen atom transfer agents here are mononuclear complexes, but all of the electrochemical data for **1a** and **2a** provide no evidence for appreciable quantities of monomers in equilibrium with the dimers. Recent reports of protonation reactions on analogues of **2a** also give no indication that mononuclear species are present.[4a] We believe that the Mn$_2$(μ_2-O)$_2$ core is sufficiently flexible to undergo a cluster-building reaction forming a Mn$_2$Fe$_2$(μ_3-O)$_2$ species as a short-lived intermediate. There are examples of complexes with the Mn$_4$(μ_3-O)$_2$ core.[14,15] We have prepared one from reaction of analogues of **2a** with (SALPRN)Mn^{II};[6] thus, it is reasonable to suggest the transient formation of the tetranuclear species.

The assembly of the tetranuclear core and its decomposition to the final products both undoubtedly follow complicated reaction sequences, and investigations are ongoing to determine a plausible reaction pathway. Ultimately it is the stability of the Fe–O–Fe unit that must drive the chemistry depicted by eq 1 and also the ability of each manganese center to act as a two electron acceptor. Interestingly, (SALEN)Fe^{II} participates in *incomplete* oxygen atom transfer reactions with metal complexes having terminal oxo ligands, the only reaction type investigated thus far,[2,16,17] while other oxygen sources react with **3b** to form **3a**.[18] Regardless of the mechanistic details of the oxygen atom transfer reaction, our observations clearly show that bridging oxo ligands are reactive toward electrophilic metal complexes.

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