tibility measurements of **3–5** indicate that the antiferromagnetic exchange coupling constant, *J*, is not significantly altered by substituting chloride for a terminal nitrogen donor. Mössbauer spectra of **2–5** have isomer shifts (0.51–0.54 mm s^{-1}) similar to those observed in previous compounds.[2] The quadrupole splittings are more variable (1.66–1.94 mm s^{-1}), however. The values for compounds **2**, **3**, and **5** fall within the range reported for other (μ-oxo)bis(μ-carboxylato)diiron(III) complexes (1.27–1.80 mm s^{-1}).[2,8] The 1.94 mm s^{-1} splitting found for **4** is somewhat larger, approaching the 2.12 mm s^{-1} value found for metClHr.[22] On the basis of similar solubility, infrared spectroscopic, and optical properties of **4** and **5**, we conclude that only two of the three imidazole rings of the potentially tridentate ligand TMICMe are coordinated in **5**.

In conclusion, use of the dicarboxylate ligand $MPDP^{2-}$ has enabled the assembly of a new class of $\{Fe_2O(O_2CR)_2\}^{2+}$ model complexes having terminal monodentate ligands. Preliminary experiments have revealed facile exchange of the labile chloride ligand; for example $[Fe_2O(MPDP)(4,4'\text{-}Me_2bpy)_2(NO_3)_2]$ has been isolated from the reaction of **3** with $AgNO_3$.[23] This class of compounds will be good precursors for preparing functionally more relevant $\{Fe_2O(O_2CR)_2\}^{2+}$ complexes in which reactions that mimic the chemistry of diiron oxo proteins can be investigated.

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Supplementary Material Available: A text section presenting the synthesis and spectroscopic and analytical data for Na_2MPDP and analytical and IR data for **2–5** and tables of atomic positional and thermal parameters for **2–4** (17 pages). Ordering information is given on any current masthead page.

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Fluoride Ion Promoted Oxidative Cleavage of (μ-Oxo)iron(III) Tetraarylporphyrins

The (μ-oxo)iron(III) porphyrin derivative PFe–O–FeP is the ubiquitous product of iron(III) prophyrin base hydrolysis or iron(II) porphyrin oxidation by dioxygen. The (μ-oxo)iron(III) porphyrin dimers are known to undergo sequential porphyrin-ring-centered electrochemical oxidation[1] with generation of iron porphyrin π cation radicals.[2,3]

$$PFe^{III}\text{–}O\text{–}Fe^{III}P \xrightarrow{-e} \xrightarrow{-e} {}^{\bullet}PFe^{III}\text{–}O\text{–}Fe^{III}P^{\bullet}$$

Even though ligand binding is not detected for the neutral (μ-oxo)iron(III) porphyrin, we have previously shown that the doubly oxidized dication radical is cleaved by fluoride ion in a heterolytic manner and a reactive high-valent iron porphyrin monomeric product is identified at low temperature.[4]

$${}^{\bullet}PFe^{III}\text{–}O\text{–}Fe^{III}P^{\bullet} + \text{excess } F^- \rightarrow {}^{\bullet}PFe^{IV}(F){=}O + PFe^{III}F_2^-$$

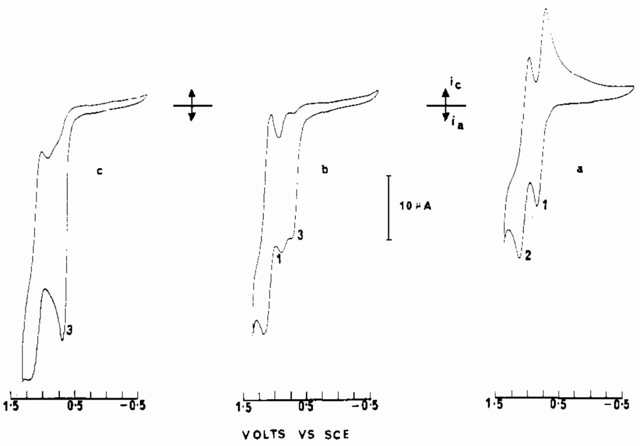

Figure 1. Effect of fluoride ion addition on the voltammogram for the oxidation of $[(TPP)Fe]_2O$ (dichloromethane solvent, 0.1 M Pr_4NClO_4, 2.4 mM $[(TPP)Fe]_2O$): (a) absence of F^-; (b) 2.6 mM $Bu_4NF\cdot 3H_2O$; (c) 4.3 mM $Bu_4NF\cdot 3H_2O$. Potentials are adjusted to the SCE reference.[7] The scan rate is 50 mV/s.

Additional redox reactions known for (μ-oxo)iron(III) tetraphenylporphyrin (TPP) include photodisproportionation[5] and oxygen transfer from *p*-cyano-*N*,*N*-dimethylaniline *N*-oxide to give high-valent monomeric iron porphyrins.[6] Here we investigate the unique electrochemical reactivity of (μ-oxo)iron(III) tetraphenylporphyrin with fluoride ion.

Figure 1 demonstrates the changes in voltammograms for the oxidation of the dimeric complex as the concentration of fluoride ion is varied.[7] Cleanly reversible anodic waves are seen for $[(TPP)Fe]_2O$ in Figure 1a (waves 1 and 2). Addition of fluoride ion ($[(TPP)Fe]_2O{:}F^-$ = 1:1) results in the appearance of a new anodic wave (wave 3 of Figure 1b; $E_{p,a}$ = 0.75 V) that is cathodically shifted from wave 1 of $[(TPP)Fe]_2O$ ($E_{p,a}$ = 0.90 V). Addition of approximately a 2-fold molar excess of fluoride ion results in the disappearance of wave 1 and conversion to the newly formed redox species (wave 3, Figure 1c). Addition of tetrakis((2,6-difluorophenyl)porphyrin)iron(III) fluoride, $[(F8\text{-}TPP)Fe^{III}F]$, which has a high affinity for fluoride binding, results in the reappearance of wave 1 of $[(TPP)Fe]_2O$ and loss of peak current due to wave 3.

Figure 2 demonstrates the effect of potential scan rate on the reversibility of wave 3 in the voltammograms for the oxidation of the dimeric complex in the presence of excess fluoride ion. The oxidation wave appears irreversible at a scan rate of 20 mV/s. At higher scan rates the reduction current is enhanced (Figure 2c). This behavior is apparent for even the first CV scan. Subsequent scans showed only a slight reduction in the oxidation current but remained constant after three to four scans. The anodic current response is considerably enhanced, as if a catalytic electrode process was present. The catalytic nature of the wave is presumably due to a fast regeneration of the starting material or a product that is also electroactive in the same potential region. These observations are consistent with an EC or ECE type mechanism characteristic of an unstable or highly reactive oxidation product. Similar voltammetric behavior is observed for

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(7) The reference electrode was a Ag wire immersed in a 0.1 M $AgNO_3$/acetonitrile solution separated from the bulk solution by porous Vycor glass. Potentials were adjusted to the conventional aqueous SCE reference by a factor of 0.38 V as described in ref 4. The ferrocenium/ferrocene potential ($E_{1/2} = (E_{p,a} + E_{p,c})/2$) was +0.15 V in CH_2Cl_2 with Ag/Ag^+ (0.1 M), CH_3CN reference, and a Pt working electrode.

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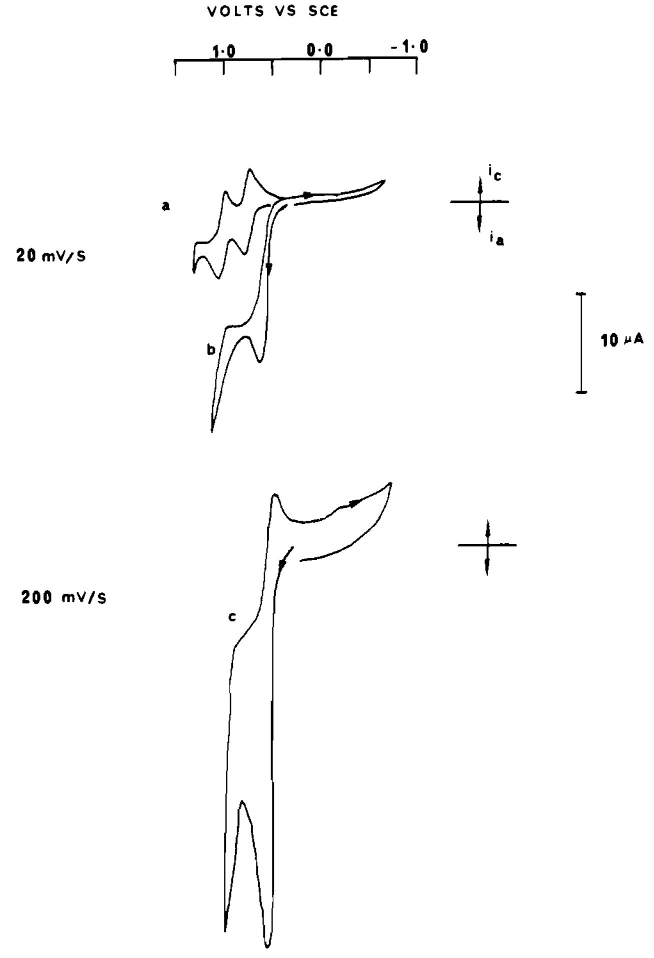

Figure 2. Effect of potential scan rate on the voltammogram for the oxidation of $[(TPP)Fe]_2O$ in the presence of fluoride ion (dichloromethane solvent, 0.1 M Pr_4NClO_4, 1.0 mM $[(TPP)Fe]_2O$): (a) absence of F^-, 20 mV/s; (b) 3 mM $Bu_4NF \cdot 3H_2O$, 20 mV/s; (c) 3 mM $Bu_4NF \cdot 3H_2O$, 200 mV/s. Potentials are adjusted to the SCE reference.[7]

p-methoxyaryl- and *p*-fluoroaryl-substituted (μ-oxo)iron(III) tetraarylporphyrins with respective first oxidation potentials at 0.60 and 0.90 V in the presence of fluoride ion.

Bulk electrolysis of a CH_2Cl_2 solution of 1 mM $[(TPP)Fe]_2O$, 10 mM tetrabutylammonium fluoride trihydrate ($Bu_4NF \cdot 3H_2O$), 0.1 M tetrapropylammonium perchlorate (supporting electrolyte), and 5–10% cyclohexene at +1.0 V (vs SCE) using a platinum-basket working electrode showed the generation of cyclohexene oxide, cyclohexenol, and cyclohexenone. Substrate oxidation is expected, as the bulk electrolysis product of $[(TPP)Fe]_2O$ in the presence of fluoride ion is the $(TPP)FeF_2^-$ species, which was shown to cause electrocatalytic oxidation of alkenes when subjected to similar electrolytic conditions.[4]

The $[(TPP)Fe]_2O$ complex was examined by NMR and optical spectroscopy in an attempt to detect any specific interaction with fluoride ion. Figure 3 shows proton NMR spectra of $[(TPP)Fe]_2O$ in the presence of increasing equivalents of fluoride ion. As is evident from the figure, the pyrrole proton signal at 13.5 ppm and the phenyl proton signal at 7.6 ppm are unaffected by the addition of fluoride ion. Pyrrole proton signals at lower fields and a split meta proton signal would have been observed if the porphyrin dimer was cleaved to generate the monomeric high-spin iron(III) complex. Coordination of fluoride ion to the (μ-oxo)iron(III) dimer would likely affect the pyrrole proton chemical shift due to an expected change in the antiferromagnetic coupling.

The visible spectral bands at 570 and 612 nm for $[(TPP)Fe]_2O$ also remained unchanged upon addition of excess fluoride ion. The intensities of the visible bands at 570 nm and 632 nm (diagnostic band for the $(TPP)Fe^{III}F_2^-$ complex) were monitored in the presence and absence of iodine. The intensities remained constant in the absence of the iodine oxidant. However, a steady decrease in the intensity at 570 nm was accompanied by a corresponding increase in the intensity at 632 nm when iodine was added. This indicates that the cleavage of the dimer occurs only under oxidative conditions and in the process generates the difluoroiron(III) porphyrin anion, $(TPP)FeF_2^-$.

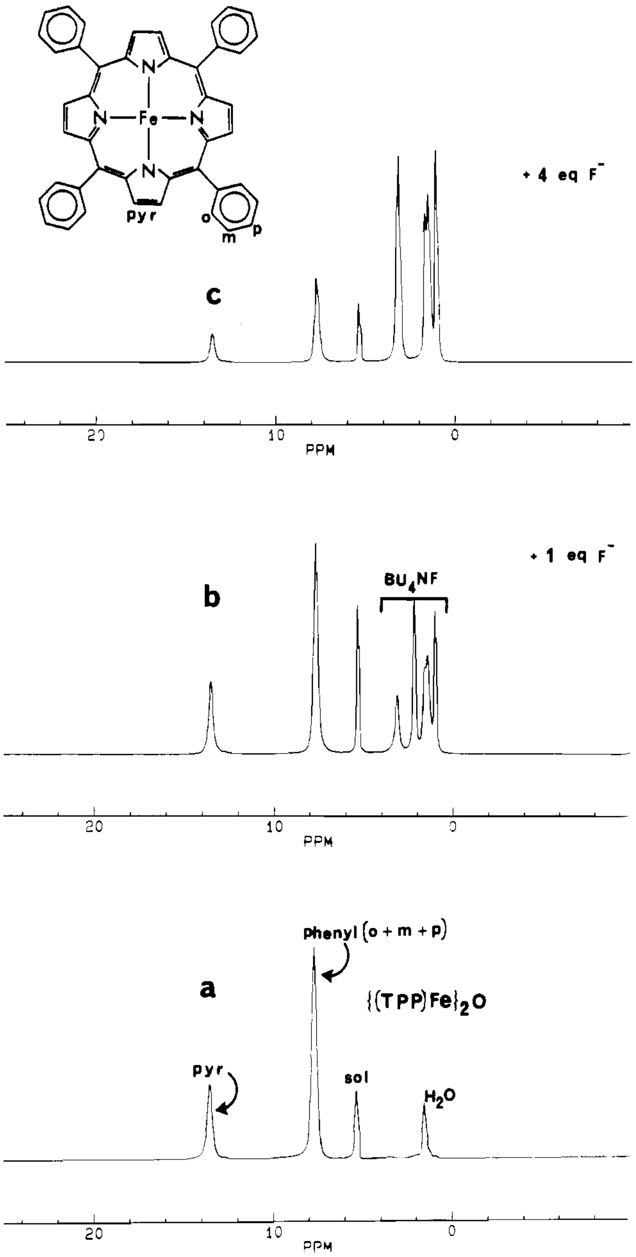

Figure 3. Proton NMR spectra at 300 MHz (TMS reference, CD_2Cl_2 solvent, 25 °C): (a) $[(TPP)Fe]_2O$ in CD_2Cl_2; (b) solution in (a) plus 1 equiv of F^-; (c) solution in (a) plus 4 equiv of F^-. A solution of $Bu_4NF \cdot 3H_2O$ in CD_2Cl_2 was used for fluoride ion addition.

The voltammogram for the oxidation of the (μ-oxo)iron(III) porphyrin derivative in the presence of excess fluoride ion is similar to that reported for the oxidation of the monomeric $(TPP)FeF_2^-$ complex.[4,8] Detection of the oxidation wave at 0.75 V (Figure 2b,c) even during the first potential scan (initiated at 0.40 V) implies that this wave is due to an oxidative electrochemical process that involves $[(TPP)Fe]_2O$ and fluoride ion. However, both optical and NMR spectral data give no indication of any specific interaction with the fluoride salt. Experiments performed with water-saturated dichloromethane and in the absence of the fluoride salt did not show any changes in the voltammetric behavior of $[(TPP)Fe]_2O$. This observation confirms that water from the fluoride salt alone is not involved in the oxidative cleavage process.

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The appearance of voltammetric waves due to both $[(TPP)Fe]_2O$ and the fluoride-bound species at low fluoride ion concentrations (less than 2 equiv) implies the change in potential is not due to removal of oxidized $[(TPP)Fe]_2O$ by fluoride ion cleavage but instead is probably due to a concerted electron-transfer–fluoride ion coordination by a weakly associated fluoride ion. The irreversibility and the cathodic shift in the oxidation wave for the new species relative to $[(TPP)Fe]_2O$ indicate the possibility that the initial oxidation is metal centered with generation of a transient iron(IV)–iron(III) mixed-valent dimeric species.

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Oxygen Atom Transfer Catalyzed by an Oxo-Bridged Molybdenum(V) Compound

We would like to report the catalysis of an oxygen atom transfer reaction by a μ-oxo Mo(V) dimer. The potential use of these dimers as catalysts in such reactions has largely been ignored because of the emphasis in oxo–molybdenum chemistry on the modeling of active sites in oxo-transfer enzymes such as xanthine oxidase and nitrate reductase.[1] These enzymes are believed to catalyze oxygen atom transfer using MoO_2^{2+} and MoO^{2+} as the oxidized and reduced forms of the active sites.[2] Early attempts to model these enzymes were hindered by the formation of μ-oxo Mo(V) dimers through reaction of freshly made MoO^{2+} with unreacted MoO_2^{2+} according to reaction 1.[3] Reaction 1 is usually

$$MoO_2^{2+} + MoO^{2+} \rightarrow Mo_2O_3^{4+} \qquad (1)$$

considered to be capable of breaking any catalytic cycle if the oxo-bridged dimer is formed irreversibly.[3] Catalysis is still possible if reaction 1 is in equilibrium provided that sufficient quantities of MoO_2^{2+} and MoO^{2+} are available to the substrate.[4] However, the oxo-bridged dimer itself has been considered to be unreactive to oxygen atom transfer.

We have previously reported the structure of $Mo_2O_3(dtc)_2I_2(THF)_2$ (I) (Figure 1).[5] Two features make I a viable candidate for oxygen atom transfer catalysis. First, its THF ligands are weakly associated with the metal atoms, as indicated by the long Mo–O(THF) bond lengths (2.448 (4) Å), the equivalence of the THF ^{1}H NMR lines from the complex with those of free THF, and the facile loss of THF from the complex upon dissolution in acetonitrile and acetone solvents. In fact a detailed ^{1}H NMR study indicates that the solvent molecules from $Mo_2O_3(dtc)_2I_2(solv)_2$ species, where solv = THF, tetrahydrothiophene and dioxane, are completely dissociated in solutions of noncoordinating solvents such as the dichloromethane used in this study.[6] Second, I does not exist in equilibrium with its MoO_2^{2+} and MoO^{2+} counterparts, as indicated by obedience to the Beer–Lambert law over a wide concentration range (2.68×10^{-5} to 5.3×10^{-4} M) in methylene chloride and THF. These points indicate that the THF molecules in I are largely, if not completely, dissociated from the complex in solution. As a result each molybdenum atom should have an empty coordination site available where reduction by oxygen atom transfer could take place.

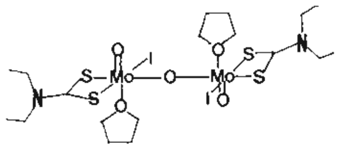

Figure 1. Structure of $Mo_2O_3(dtc)_2I_2(THF)_2$ (I).

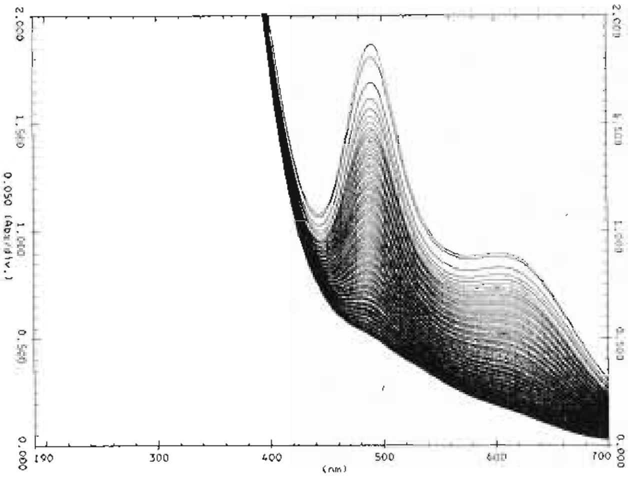

Figure 2. Changes in the electronic spectrum of $Mo_2O_3(dtc)_2I_2(THF)_2$ (I) during reaction with biotin *S*-oxide.

We have now shown that $Mo_2O_3(dtc)_2I_2(THF)_2$ can be used to reduce a variety of oxygen atom donating heterocyclic amine oxides and sulfoxides, including pyridine *N*-oxide, nicotinamide *N*-oxide, dimethyl sulfoxide, diphenyl sulfoxide, and biotin *S*-oxide, in either CH_2Cl_2 or THF. In these reactions oxygen atom transfer to I results in the appropriate heterocyclic amine or sulfide and an MoO_2^{2+} compound. This process can be followed spectrophotometrically by observing the disappearance of the bands characteristic of I at 614 and 490 nm (Figure 2). Upon completion of the reaction, a spectrum characteristic of an MoO_2^{2+} compound is observed with no apparent bands in the visible region.[7] The molybdenum product of this reaction can be further characterized as an MoO_2^{2+} compound by infrared spectroscopy. The complex can be formed by reaction of I with excess pyridine *N*-oxide in methylene chloride. Its isolation is then accomplished by evaporating the solvent and subliming the excess pyridine *N*-oxide. The infrared spectrum of the MoO_2^{2+} compound exhibits a band characteristic of the Mo═O stretching frequency which is shifted to 939 cm^{-1} as compared to 975 cm^{-1} in I. This is consistent with the trend usually observed for series of homologous oxo-molybdenum species in which the Mo═O stretching frequency varies in the order $MoO^{2+} > Mo_2O_3^{4+} > MoO_2^{2+}$.[8]

Samples of the MoO_2^{2+} compound that have been isolated in the manner described above can be used to oxidize triphenylphosphine to triphenylphosphine oxide, TPPO, in CH_2Cl_2 or THF with concomitant reformation of I. This reaction is evidenced by the reappearance of the electronic spectrum of I. The reformation of I is apparently the result of the rapid and irreversible reaction, according to reaction 1, of the immediate product of oxo transfer to TPP, probably an MoO^{2+} complex, with the MoO_2^{2+} remaining in solution. We have not observed any spectroscopic evidence of the existence of MoO^{2+} in our reaction systems.

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