coordinate, and labile in both Fe(II) and Fe(III) complexes. Hemes are found with a variety of spin states and coordination numbers of 5 or 6 depending upon the field strength of the axial ligands.[36]

A second important factor in the FeN_4 system is its high reduction potential in comparison with that of the heme, Fe(salen), or bleomycin systems. Generally, the $dmgBF_2$ system is 500 mV more oxidizing than its heme or Fe(salen) analogue. In fact the $FeN_4(CH_3CN)_2^+$ species lies at a potential comparable to that of compound I of horse radish peroxidase.[37]

An unfortunate consequence of the strong oxidizing character of this system is that a number of axial ligated derivatives are too unstable toward spontaneous reduction to be easily detected. This includes all bis(amine) complexes as well as complexes containing CN^- or SR^-. In the less oxidizing Fe(salen), heme, or other systems slow spontaneous reduction by CN^-,[38] piperidine,[39] and SR^-[35] of Fe(III) to Fe(II) is reported. As a general rule, species with potentials above 0.7 V vs SCE containing oxidizable ligands were difficult to detect in visible or EPR spectroscopy. Lever[40] has described an empirical set of parameters which are an excellent guide to the redox potential of metal complexes in CH_3CN solution, and the relative stabilities of the ferric systems described here are consistent with these.

The low-spin character of FeN_4 is also manifested in the chemistry of the oxo-bridged diiron species. Heme, Fe(salen), and a variety of other oxo-bridged diiron complexes are 5-coordinate and display oxo to Fe charge-transfer bands in the 300–400-nm region. The $[FeN_4(L)]_2O$ systems are 6-coordinate and undergo ligand substitution trans to the oxo bridge in solution. From the reactions outlined in eqs 4 and 7, π-donor ligands lead to oxo-bridge cleavage, while π-acceptor ligands and good σ-donors tend to stabilize the oxo bridge. Detailed investigations of the effects of trans ligands on the reactions of the oxo-bridged complexes are in progress.

Acknowledgment. Support of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

Registry No. $[FeN_4(CH_3CN)]_2O$, 136676-32-9; $[FeN_4(py)]_2O$, 136676-33-0; $[FeN_4(MeIm)]_2O$, 136676-34-1; $[FeN_4(TMIC)]_2O$, 136676-35-2; $Et_4N[FeN_4Cl_2]$, 136676-37-4; $Et_4N[FeN_4Br_2]$, 136676-39-6; $FeN_4(CH_3CN)_2^+$, 136676-40-9; $FeN_4(CH_3CN)_2^+PF_6^-$, 136676-41-0; $FeN_4(CH_3CN)_2^+ClO_4^-$, 136676-42-1; $[FeN_4(CH_3CN)_2^+]_2SO_4^{2-}$, 136676-43-2; $[FeN_4]_2O$, 136676-45-4; $FeN_4(SCN)_2^-$, 136676-44-3.

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Kinetics of the Reduction of Oxo-Bridged Diiron Complexes of Bis(difluoro(dimethylglyoximato)borate) with Hydroxy Aromatics, Amines, and Phosphines

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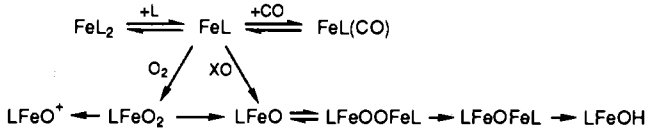
We present the first detailed study of rates of reduction of an oxo-bridged diiron complex with a variety of reducing agents including hydroquinones, catechols, substituted phenols, anilines, and phosphines. Overall results are consistent with coordination of the reductant trans to the oxo bridge via replacement of a labile CH_3CN followed by electron transfer and oxo-bridge cleavage. *N,N,N',N'*-tetramethyl-1,4-phenylenediamine (Wurster's reagent) reacts in a two-step reaction in which Wurster's blue is produced and then destroyed. The reactivity of the oxo-bridged complex is compared with that of the heme and Fe(salen) systems, and relationships to more active oxidants are discussed. The importance of the ligand environment in controlling activation of dioxygen by iron(II) in the catalyzed autoxidation of hydroquinone and peracid oxidation of 2,4,6-tri-*tert*-butylphenol is described.

Introduction

Oxo-bridged diiron complexes are well-known[1] and have been widely studied as models for a variety of non-heme iron proteins[2] known to possess this structural unit. Spectroscopic, magnetic, and structural investigations of the oxo-bridged diiron unit are extensive. However, few chemical reactions associated with Fe–O–Fe have been described, and no detailed studies of its redox reactions are reported. The "oxo dimer" is usually considered a chemical dead end in heme and Fe(salen) systems.

In a broader context the oxo-bridged diiron species is one of several potentially active oxidants accessible via dioxygen binding/O–O bond fission or via the so called "peroxide shunt" route[3] using peracids or iodosylbenzene as the oxidant in place of dioxygen. Scheme I summarizes the entry into these oxidants via dissociative substitution in Fe(II) complexes with two functional coordination sites. (L is a neutral monodentate ligand, and charges assume a dianionic N_4 ligand not shown.) The exact relationships among the several active oxidants listed in Scheme I are largely unknown,[5] and no information about the kinetics of substrate oxidations by them is available, even in widely studied heme models for P450 chemistry.[3] In a catalytic process where the active oxidant is only a transient intermediate, the task is elucidating the "active oxidant" is a formidable problem. In the few cases where kinetic data are available,[6,7] formation of the active oxidant

Scheme I. Dissociative Entry into Active Oxidants Using O_2 or XO (XO = Peracids, Amine Oxides, Iodosylbenzene, etc.)[4] and Inhibition by CO



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is rate determining and no information about the redox step is obtained. Kinetic data for the redox step have been reported with more stable oxo complexes[8] especially those of Cr,[9] Mo,[10] and Ru.[11]

We have recently described the novel low-spin oxo-bridged complex[12] $[AFe^{III}(dmgBF_2)_2]_2O$ (**1**) (axially bound CH_3CN denoted by A), which shows a distinct oxo to Fe charge-transfer band at 672 nm and undergoes clean reduction to well-characterized Fe(II)[13,14] products. The $(dmgBF_2)_2$ ligand (abbreviated as N_4 hereafter) confers a low-spin hexacoordinate geometry on the iron, making ligand-substitution reactions more sluggish, and electronically stabilizes the Fe(II) oxidation state, making Fe(III) derivatives much stronger oxidizing agents than heme[15] or iron Schiff base analogues.[16,17] Here we present a survey of the kinetics and mechanism of reduction of this unique oxo-bridged complex with a variety of substrates and discuss other active oxidants relevant to the role of iron in living systems.

Experimental Section

The oxo-bridged complex **1** and FeN_4A_2 were prepared as previously described.[12,13] All other reagents were of the highest purity available and used as received or after recrystallization (2,4,6-tri-*tert*-butylphenol, *p*-tosylmethyl isocyanide).

Kinetic Measurements. Reagents were injected as CH_3CN solutions via syringe into a thermostated (25 °C) CH_3CN solution of **1** (1×10^{-4} M), and the reaction was followed by visible spectroscopy. Spectra were typically scanned between 350 and 750 nm (displaying clean isosbestic points) or monitored at wavelengths of maximum absorbance change. Pseudo-first-order rate constants were obtained using a least-squares analysis by microcomputer and were independent of the wavelength monitored (typically λ_{max} of **1** as well as MLCT bands of the Fe(II) products were analyzed). Kinetic results were found to be generally unaffected by air, the drying of the CH_3CN, or use of different synthetic samples of **1**. Stock solutions of **1** undergo a very slow spontaneous reduction over days and were therefore made up fresh.

Product Characterization. The Fe(II) reduction product was identified in all cases by visible spectroscopy as FeN_4A_2 or as axial ligated species on the basis of comparison with spectra obtained in independent spectrophotometric titration experiments. In the cases listed in the following table, the organic products were identified and quantified directly under the conditions of the kinetic measurements on the basis of their UV–visible characteristics:

product	λ_{max}, nm	ϵ, M^{-1} cm^{-1}
2,4,6-tri-*tert*-butylphenoxyl radical	390	1400
N,N,N',N'-tetramethylphenylene diamine radical	565	13000
3,3',5,5'-tetramethyldiphenoquinone	416	50000
diazomesitylene	331	12600
1,2-benzoquinone	385	1600
3,5-di-*tert*-butyl-1,2-benzoquinone	400	2000

Difference techniques were used to subtract the absorbance of FeN_4A_2 [λ_{max} = 444 nm (ϵ = 7700 M^{-1} cm^{-1})].

Table I. Kinetic Data[a] for Reduction of **1** at 25 °C

substrate	CH_3CN soln k, M^{-1} s^{-1}	CH_2Cl_2 soln[f] k, s^{-1}
Hydroquinones		
hydroquinone	4.3	33
tetrafluorohydroquinone	2.4	68
Catechols		
catechol	1.7	140
4-nitrocatechol	2.8	
tetrachlorocatechol	1.0	48
3,5-di-*tert*-butylcatechol	8.3	
pyrogallol (3-OHcat)	4.7	
Phenols		
picric acid	0.4	
4-nitrophenol	0.2	0.3
2,4,6-tri-*tert*-butylphenol	0.1	0.022
2,6-dimethylphenol	0.06	0.045
Anilines		
1,4-phenylenediamine	>30[b]	
tmpd	>30[b]	
4-methoxyaniline	1.7[c]	
2,4,6-trimethylaniline	0.007	
4-nitroaniline	<0.0001[e]	
Phosphines		
PPh_3	0.02	0.10
$P(OEt)_3$	0.03	
PMe_2Ph	*d*	
PBu_3	*d*	
PEt_3	*d*	

[a] Error typically ±10%. [b] Reaction complete on mixing at [S] = 0.001 M. [c] The product Kk_{et} is given (see text). [d] Kinetics complicated by ligation to **1** (see text). [e] At [S] = 0.05 M less than 10% change within 30 min. [f] Data in CH_2Cl_2 solution from plots of k_{obs} vs 1/[A] in the region [A] = 0.05 – 1.0 M at fixed [S] = 0.01 M except for hydroquinones and catechols where [S] = 0.001 M.

In other cases, an indirect method was used where, typically, stoichiometric amounts of substrate were stirred with 50–100 mg of **1** suspended in CH_3CN. (Owing to the limited solubility of **1**, these reactions, for the most part, also involve conditions of excess dissolved substrate.) In a typical experiment, a suspension of 100 mg of **1** in 10 mL of CH_3CN (containing 1 equiv of substrate) was stirred until the green color of **1** disappeared. The solvent was evaporated in vacuo and the organic reaction product extracted with ether, leaving a quantitative yield of yellow FeN_4A_2 behind. The inorganic and organic products were then identified by spectroscopic methods, for example, triphenylphosphine oxide ($\nu_{P=O}$ = 1200 cm^{-1}) and 1,4-benzoquinone ($\nu_{C=O}$ = 1600 cm^{-1}). 1,4-Benzoquinone and 3,3',5,5'-tetramethyldiphenoquinone were also confirmed by NMR spectroscopy.

Catalyzed Autoxidation of Hydroquinone (H_2Q). A sample of FeN_4A_2 (0.003 g) was added to 100 mL of 0.0085 M H_2Q in CH_2Cl_2, and the mixture was stirred rapidly in air. Oxidation of H_2Q was monitored from the decrease in absorbance at 285 nm measured by diluting 0.14 mL of the reaction solution in 3 mL of CH_2Cl_2 in a 1-cm quartz cuvette. No appreciable oxidation is observed in the absence of catalyst.

Catalyzed Oxidation of Tri-*tert*-butylphenol by *m*-Chloroperoxybenzoic Acid (MCPBA). Visible spectra of nitrogen-purged (the phenoxy radical is oxygen sensitive) CH_3CN solutions of FeN_4A_2 (10^{-4} M) containing 0.01–0.1 M tri-*tert*-butylphenol were recorded with time following addition of .001 M MCPBA. Increases in absorbance due to the blue phenoxy radical at 600 and/or 390 nm with time were monitored. Negligible reaction is observed under these conditions in the absence of catalyst.

Results and Discussion

The reactions of **1** were studied in CH_3CN solution, in which it exists as a hexacoordinate complex with CH_3CN coordinated trans to the oxo bridge. Reactions were studied by visible spectroscopy, monitoring the decay of the characteristic low-energy oxo to Fe CT band (672 nm for **1**) or growth of MLCT bands due to the well-characterized[13] Fe(II) products. Substrates (reducing agents) which are poor ligands (phenols, hindered amines, triphenylphosphine) do not observably bind to FeN_4A_2 or **1** in CH_3CN solution and simply reduce **1** to FeN_4A_2. Substrates which are also effective ligands may bind to **1** or the Fe(II) product

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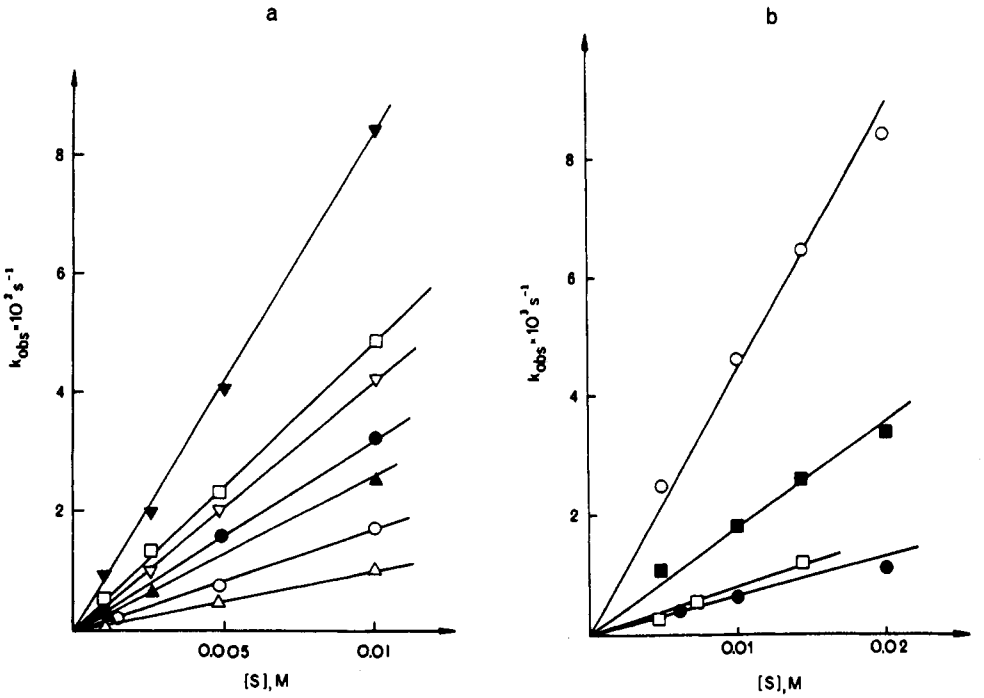

Figure 1. Pseudo-first-order rate constant for reduction of **1** in CH_3CN solution vs substrate concentration [S]: (*a*) S = 3,5-di-*tert*-butylcatechol (▼), pyrogallol (□), 4-nitrocatechol (●), hydroquinone (▽), tetrafluorohydroquinone (▲), catechol (○), tetrachlorocatechol (△); (b) S = picric acid (○), *p*-nitrophenol (■), 2,4,6-tri-*tert*-butylphenol (□), 2,6-dimethylphenol (●).

or both. Characteristic shifts in the MLCT (Fe to oxime) band for Fe(II) and LMCT (oxo to Fe) band for the oxo-bridged Fe(III) complexes are diagnostic of ligation. The ligation of redox-inactive 1-methylimidazole, pyridine, and tosylmethyl isocyanide trans to the oxo bridge in **1** has been described elsewhere.[12]

A variety of substrates were selected to probe oxo transfer, electron transfer, and H atom transfer activities including some whose reaction with peroxidases[18] or oxo–metal complexes[8-11] have been investigated. A remarkably similar pattern of reactivity was found consistent with a mechanism involving axial coordination of substrate followed by the rate-determining redox step.

Several reactions of **1** were also investigated in dichloromethane solution (containing CH_3CN) and found to proceed much more rapidly than in CH_3CN as expected for a mechanism requiring ligation via replacement of coordinated CH_3CN. An inverse first-order dependence on $[CH_3CN]$ was established for the reduction of **1** in dichloromethane solution in these cases.

The kinetic data are summarized in Table I, and the results are discussed in detail below. In CH_3CN, the slopes of plots of the pseudo-first-order rate constants vs substrate concentration, [S], are tabulated. A reference state of unit activity for the solvent is implicit. For data in dichloromethane solution, the tabulated rate constants are obtained from the slopes of plots of k_{obs} vs $1/[A]$ at a fixed substrate concentration, [S]. These different units should be noted and the factor of 19.1 ($[CH_3CN]$, neat) introduced when cross-solvent comparisons are made.

Polyhydroxybenzenes. Two-electron reductants including hydroquinone (H_2Q) and catechols give clean reductions to FeN_4A_2 (eq 1) with a pseudo-first-order rate constant linearly dependent

$$AFeN_4\text{–}O\text{–}FeN_4A + H_2Q + 2A \rightarrow 2FeN_4A_2 + H_2O + Q \quad (1)$$

upon the concentration of the reductant, as seen in Figure 1. The stoichiometry in eq 1 was established by spectrophotometric titration. For H_2Q, an inverse dependence of the rate on $[CH_3CN]$ is found in CH_2Cl_2 solution, indicating a preequilibrium involving axial binding. The relative rates for different polyhydroxybenzenes change only slightly for large differences in the redox potential of the reductant.[19] These results are most consistent with a mechanism involving rapid axial binding through a hydroxy group followed by electron transfer/proton loss. The insensitivity of the rate to the redox potential of the substrate is inconsistent with an outer-sphere process such as is reported for the hydroquinone reduction of a $[Rh_2(CH_3COO)_4]^+$ complex.[20]

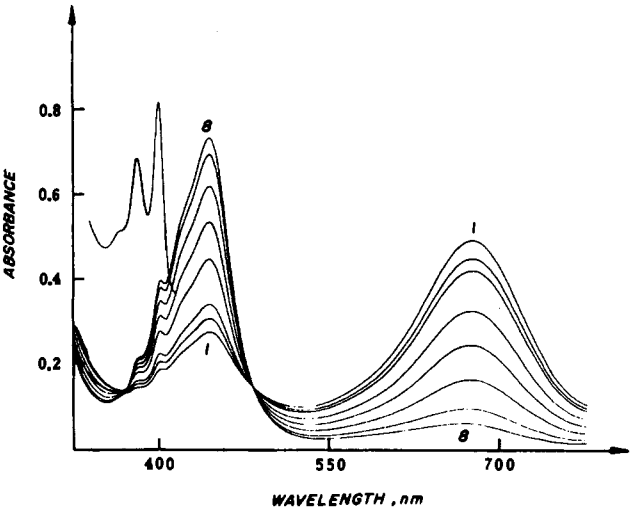

Figure 2. Spectral data for the reaction of **1** with 8 mM 2,4,6-tri-*tert*-butylphenol vs time. Times are 0, 3, 15, 28, 41, 72, 97, and 160 min for 1–8, respectively. The inset displays the difference spectrum with the FeN_4A_2 spectrum subtracted and the absorbance scale expanded × 2, showing the phenoxyl radical spectrum. (Weaker features observed for the radical at 600 nm are not shown.)

Phenols. Phenols also give clean reductions to FeN_4A_2 at rates about 1 order of magnitude less than hydroquinones. The tri-*tert*-butylphenol reagent is unique in giving a stable phenoxyl radical, which definitively establishes the stoichiometry and products shown in eq 2 on the basis of characteristic visible (Figure 2) and EPR spectra.[21] The same products are observed in di-

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$$AFeN_4\text{–}O\text{–}FeN_4A + 2t\text{-}Bu_3PhOH + 2A \rightarrow 2FeN_4A_2 + 2t\text{-}Bu_3PhO^{\bullet} + H_2O \quad (2)$$

chloromethane solution at significantly faster rates which show an inverse dependence on $[CH_3CN]$. These observations provide strong evidence for a mechanism involving axial ligation of the phenol followed by intramolecular electron transfer/proton loss generating the phenoxyl radical.

It is not the purpose of this work to explore the fate of the unstable phenoxyl radicals which would be produced in the reactions of the other phenols studied with **1**. However, products expected from the coupling of phenoxyl radicals were detected. In the case of 2,6-dimethylphenol a yellow product identified as 3,3′,5,5′-tetramethyldiphenoquinone, from its visible spectrum, is produced in greater than 70% yield under conditions of excess substrate and 10^{-4} M **1** in CH_3CN and also on a preparative scale at stoichiometric levels of substrate.

The rather small differences in rates among these vastly different reducing agents is explicable primarily in terms of moderate differences in the preequilibrium step involving replacement of CH_3CN by a weak ROH ligand. The net differences in rate then reflect the number of OH groups, steric considerations, and factors associated with the redox step. The absence of any correlation with phenol activity (note picric acid) argues against mechanisms requiring proton dissociation from the phenol prior to the rate-determining step.

The ability of even nitro-substituted phenols to reduce is remarkable, since 4-nitrophenol is reported not to react with either horse radish peroxidase/H_2O_2 or with heme/MCPBA systems.[6,22] We attribute the greater reactivity of **1** with these poor reductants to mechanistic differences. These other systems do not involve coordination of the phenol to iron but rather are proposed[6] to react by attack of the phenol on a ligated oxo group via H atom abstraction. Coordination of the hydroxy group to the labile axial sites in **1** may stabilize the radical produced via 1-electron transfer, and the cleavage of the Fe–O–Fe unit coupled to the reduction provides a significant driving force for the reaction. Specifically, the oxo-bridge cleavage may prevent favorable back-electron-transfer and subsequent ligand binding to the Fe(II) products makes the net reaction thermodynamically downhill. While it is also possible for **1** to transfer two electrons in a single step, we have no explicit evidence for or against this mechanistic possibility at this time.

Anilines. Reduction with 4-methoxyaniline (MA) differs from the above examples in three ways. A spectral shift of the band assigned to oxo to metal CT to 682 nm is observed at the higher concentrations of MA indicative of ligation of MA trans to the oxo group. This ligation is well established with good donors such as pyridine or methylimidazole, which are not easily oxidized.[12] The Fe(II) product is observed to be an equilibrium mixture of FeN_4A_2 (444 nm), $FeN_4A(MA)$ (485 nm), and $FeN_4(MA)_2$ (532 nm) depending on [MA]. Curvature in plots of k_{obs} vs [MA] is found (Figure 3) at high [MA] reaching a limiting value when the oxo-bridged species is fully ligated. The results are interpreted in terms of the mechanism shown in eq 3 involving rapid MA

$$\tfrac{1}{2}[AFeN_4]_2O + L \overset{K}{\rightleftharpoons} \tfrac{1}{2}[LFeN_4]_2O \xrightarrow{k_{et}} Fe^{II}N_4 + L_{ox} \quad (3)$$

binding to the dimer, followed by a slow electron-transfer step involving the bound aniline ligand. As the experiments give no information about stepwise ligation of MA to **1**, we have treated the problem in terms of a single equilibrium constant (K) and rate-determining redox step (k_{et}). This approximation is equivalent to treating the ligation as noncooperative binding to equivalent sites. Linear least-squares analysis of $1/k_{obs}$ vs $1/[L]$ gives an excellent fit of the data, and the values $K = 960 \pm 40$ M^{-1} (in good agreement with qualitative estimates of K from spectrophotometric data) and $k_{et} = 1.8 \times 10^{-3}$ s^{-1}.

$$1/k_{obs} = 1/(Kk_{et}[L]) + 1/k_{et} \quad (4)$$

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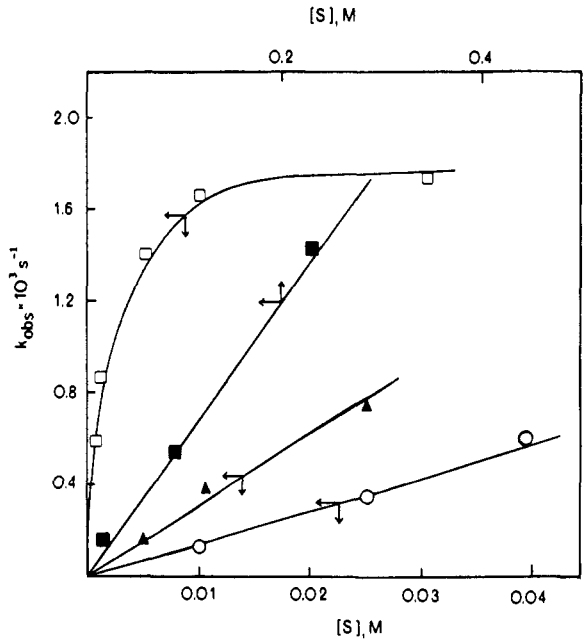

Figure 3. Pseudo-first-order rate constants for reduction of **1** vs [S]: S = 4-methoxyaniline (□), mesidine (■), PPh_3 (○), and $P(OEt)_3$ (▲).

The organic products of the methoxyaniline oxidation were not identified but are presumed to arise from competing reactions of the intermediate N-centered radical.[20] The speciation of rapidly equilibrating Fe(II) products at each [MA] (isosbestic points are found) is fully consistent with expectations based upon an independent determination of the stepwise equilibria ($K_1 = 100$ M^{-1} and $K_2 = 20$ M^{-1}) for MA binding to FeN_4A_2 in CH_3CN. We note that the ligation of MA to FeN_4A_2 is 1 order of magnitude weaker than ligation to **1** ($K = 960$ M^{-1}).

The more weakly basic anilines such as 4-nitroaniline do not bind to the oxo-bridged species and are poor reducing agents. The sterically hindered mesidine (2,4,6-trimethylaniline) gives a strictly linear dependence on [S] shown in Figure 3 and is not observed to bind to either **1** or the FeN_4A_2 product up to 0.5 M. The coupled product diazomesitylene is identified as the major organic product in this case. Electron-donating substituents on the aniline result in rapid reductions which for *N,N,N′,N′*-tetramethyl-1,4-phenylenediamine (commonly known as Wurster's reagent and abbreviated here as tmpd) can be shown to involve a simple one-electron transfer.

Wurster's reagent undergoes a rapid reaction with **1** assigned to an outer-sphere electron-transfer process giving at most 1 $tmpd^{\bullet+}$ blue radical (identified by its visible and EPR spectrum[23]) per dimer. A subsequent slower step results in the decay of the $tmpd^{\bullet+}$ absorbance with additional formation of FeN_4A_2 observed at 444 nm. This complex behavior is unique to the oxo-bridged species. Monomeric $FeN_4Cl_2^-$ and $FeN_4A_2^+$ (formed via chloride or acid cleavage of **1**) react rapidly and cleanly to give 1 $tmpd^{\bullet+}$ per Fe, and the radical spectrum persists long after the reaction is completed.[12] The more complex behavior with **1** is proposed to arise from an unusual reactivity[24] of the one-electron-reduced $[Fe\text{–}O\text{–}Fe]^-$ (eq 5) perhaps involving subsequent cleavage (eq 6)

$$AFeN_4\text{–}O\text{–}FeN_4A + tmpd \rightarrow AFeN_4\text{–}O\text{–}FeN_4A^- + tmpd^{\bullet+} \quad (5)$$

$$AFeN_4\text{–}O\text{–}FeN_4A^- \rightarrow FeN_4A_2 + AFeN_4O^- \quad (6)$$

$$AFeN_4O^- + tmpd^{\bullet+} \rightarrow tmpdO + FeN_4A_2 \quad (7)$$

(23) (a) Michaelis, L.; Schubert, M. P.; Granick, S. *J. Am. Chem. Soc.* **1939**, *61*, 1981. (b) Nickel, U.; Jaenicke, W. *Ber. Buns.-Ges Phys. Chem.* **1982**, *86*, 695.
(24) Cyclic voltammetry studies of **1**[12] and other oxo-bridged species produce a one-electron reduction product which is unstable with respect to oxo-bridge cleavage: Bottomley, L. A.; Ercolani, C.; Gorce, J. N.; Pennesi, G.; Rossi, G. *Inorg. Chem.* **1986**, *25*, 2339.

to give a stronger oxidant which destroys tmpd$^{\bullet+}$ (eq 7). The monomeric oxo intermediate shown in eq 6 is probably more realistically formulated as a hydroxy iron(III) species, as even in dry CH_3CN, water is in large excess over **1**.

If tmpd and Cl^- are added simultaneously to **1** (chloride cleavage of **1** is slow compared to the redox reaction), then a clean formation of two Wurster's blue radicals per dimer is observed. Chloride ion must efficiently trap the partially reduced dimer or cleavage products thereof,[24] preventing its reaction with tmpd$^{\bullet+}$.

Phosphines. Reduction by PPh_3 proceeds cleanly with isosbestic points giving FeN_4A_2 (triphenylphosphine is too hindered to bind to Fe(II)) and triphenylphosphine oxide identified by IR spectroscopy. A linear plot of the pseudo-first-order rate constant vs $[PPh_3]$ is shown in Figure 3. Reduction with $P(OEt)_3$ also shows a simple first-order dependence on $[P(OEt)_3]$. In this case the iron product is identified from its visible spectrum[13] as FeN_4A-$(P(OEt)_3)$ (λ_{max} = 454 nm). No spectral shift is detected associated with ligation to **1**.

Trialkylphosphines (triethyl-, tributyl-, and dimethylphenylphosphine) show evidence of ligation to **1** as well as to the Fe(II) product giving a more complex rate dependence on $[PR_3]$. These results will be described elsewhere. The rapid reaction of PEt_3 with **1** contrasts with the drastic conditions reportedly required to reduce $[FeTPP]_2O$ with Et_3P.[25]

Cyanide Ion. Addition of cyanide ion causes rapid reduction of monomeric[12] $Fe^{III}N_4A_2^+$ to Fe(II) in a reaction analogous to that reported for hemes[26] but much more rapidly owing to the greater oxidizing strength of these systems. However, reaction of the oxo-bridged complex **1** with CN^- titrates cleanly with isosbestic points (except at very low added CN^- where FeN_4A_2 is the Fe(II) product) according to eq 8, affording a mixture of

$$2AFeN_4\text{–}O\text{–}FeN_4A + 6CN^- \rightarrow 2AFeN_4CN^- + [NCFeN_4\text{–}O\text{–}FeN_4CN]^{2-} + 2\text{“}CN\text{”} \quad (8)$$

two distinct products, one absorbing at 760 nm (ϵ = 8850 M^{-1} cm^{-1} per Fe) assigned to $[(CN)FeN_4]_2O^{2-}$ and the other a previously characterized[27] Fe(II) complex $AFeN_4CN^-$, which has an MLCT band at 490 nm and ϵ = 9000 M^{-1} cm^{-1}. The species absorbing at 760 nm is not an Fe(III) monomeric cyano complex as it has no EPR spectrum but undergoes clean reduction with hydroquinone to give a quantitive yield of $AFeN_4CN^-$ based on the 490-nm absorbance. The low-energy band at 760 nm is consistent with an oxo to iron CT band.

The detailed mechanism of the reaction with CN^- has not been fully elucidated but likely involves rapid cleavage of a mixed ligated dimer $(AFeN_4\text{–}O\text{–}FeN_4CN)^-$, where one Fe is reduced to Fe(II) and the other (most likely the one retaining the Fe–O bond) ends up as a rather inert CN^--ligated oxo-bridged species.[28] An alternative would invoke CN^- trapping of oxo-bridge cleavage products of **1** in which $FeN_4A_2^+$ is reduced by CN^- in a known reaction[12] while $AFeN_4O^-$ merely undergoes ligation because of its much lower predicted reduction potential (too low to oxidize CN^-).

Ligation Effects. The axial CH_3CN ligand in **1** is replaced in CH_3CN solution by MeIM, py, or TMIC producing spectrally distinct oxo-bridged species. Preliminary investigations of these species show that they undergo reduction by hydroquinone much more slowly than **1**. Ligation effects where the ligand is also redox active have already been described above for anilines and phosphines. These results show that the ligand trans to the oxo bridge plays an important role in its reactivity. Additional studies are required to elucidate these effects.

Catalyzed Oxidation. While the oxo-bridged complex studied in this work is clearly a much better oxidant than oxo-bridged heme or iron Schiff base complexes, it is clearly a "slowpoke" compared to some of the more active oxidative intermediates created using peracids or iodosylbenzene summarized in the Introduction. More active oxidants, as well as **1**, are accessible from reaction of FeN_4A_2 with *m*-chloroperoxybenzoic acid (MCPBA) in CH_3CN.

Reaction of FeN_4A_2 with MCPBA in CH_3CN produces **1** in reasonably good yield, as evidenced by the disappearance of the 444-nm absorbance of FeN_4A_2 and the growth of the 672-nm band of **1**. A large excess of MCPBA must be avoided or complete bleaching of the spectrum occurs. In the presence of an excess of tri-*tert*-butylphenol rapid catalytic formation of the blue phenoxyl radical is observed (much more rapid than the reaction of the phenol with **1**) and no evidence for the 672-nm absorbance of the oxo-bridged species or destruction of FeN_4A_2 is found. These results parallel observations using Fe(III) porphyrin catalysts[6] in which the phenol traps the active oxidant prior to oxo-bridge formation or catalyst destruction. It is important to note that the generation of these active oxidants by this route does not constitute dioxygen activation.

The more difficult problem of activating dioxygen requires attention to the ligation environment of the iron. No activation of dioxygen in CH_3CN solution by FeN_4A_2 is found. Dioxygen binding is neither competitive with solvent trapping of the pentacoordinate intermediate, FeN_4L, nor thermodynamically favorable under these conditions. The advantage of the peroxide shunt pathway is in the facile O–O bond fission in MCPBA leading directly to a more active oxidant.

Catalyzed activation of dioxygen by FeN_4A_2 is possible if the ligation environment[29,30] is adjusted to allow O_2 to compete more efficiently for the FeN_4L intermediate. Solutions of FeN_4A_2 is CH_2Cl_2 containing 0.01 M CH_3CN are air sensitive, slowly producing **1**. (The rate of oxidation increases as $[CH_3CN]$ decreases.) In the presence of hydroquinone, a clean catalyzed oxidation to quinone is observed in CH_2Cl_2 solution.

The rapid turnover in these catalytic examples requires that a more active oxidant than **1** is involved, and work is in progress to better characterize these. In systems where the active oxidants are well established (for example, $pyRu(bpy)_2O$ ($k = 5 \times 10^5$ M^{-1} s^{-1} with H_2Q)) species much more reactive than oxo-bridged analogues are found.[11a] However, the oxo-bridged $[AFe^{III}N_4]_2O$ is more reactive than $[LRu^{IV}(TMP)]_2O$ reported not to react with phosphites.[11f] These examples underscore the need to take mechanistic differences and conditions into account when apparently analogous systems are compared.

Summary. Results presented here for the redox reactions of **1** provide a quantitative data base which may be useful in comparison with other active oxidative species. This simple oxo-bridged iron complex is the first to display the variety of reactivities (ligation, one- or two-electron transfer, and Bronsted basicity) that have led to the claim[2] that "the Fe_2O unit constitutes the most versatile iron center yet encountered in biology".

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Registry No. **1**, 136676-32-9; tmpd, 100-22-1; PPh_3, 603-35-0; $P(OEt)_3$, 122-52-1; hydroquinone, 123-31-9; tetrafluorohydroquinone, 771-63-1; catechol, 120-80-9; 4-nitrocatechol, 3316-09-4; tetrachlorocatechol, 1198-55-6; 3,5-di-*tert*-butylcatechol, 1020-31-1; pyrogallol, 87-66-1; picric acid, 88-89-1; 4-nitrophenol, 100-02-7; 2,4,6-tri-*tert*-butylphenol, 732-26-3; 2,6-dimethylphenol, 576-26-1; 1,4-phenylenediamine, 106-50-3; 4-methoxyaniline, 104-94-9; 2,4,6-trimethylaniline, 88-05-1; 4-nitroaniline, 100-01-6.

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(26) Del Gaudio, J.; La Mar, G. N. *J. Am. Chem. Soc.* **1976**, *98*, 3014.
(27) de Silva, D. G. A. H.; Thompson, D. W.; Stynes, D. V. *Inorg. Chem.*, in press.
(28) Alternative formulations of the 760-nm product as $Fe^{IV}N_4O(CN)^-$ or peroxo-bridged species cannot be ruled out at this time but are deemed less likely.
(29) Axial ligand control of dioxygen binding may be exerted via either the concentration or nature of the axial ligand, since the rate of substitution as well as the position of the equilibrium depends on both factors. The nature of the N_4 ligand will influence the lability of axial ligands[13] as well as the dioxygen affinity and reactivity.
(30) The widely studied dioxygen binding to pentacoordinate Co(II) complexes makes use of the more favorable ligation characteristics with this metal: Basolo, F.; Hoffman, B. M.; Ibers, J. A. *Acc. Chem. Res.* **1975**, *8*, 384.