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First Diferric Complex with an $Fe_2(\mu\text{-}O)(\mu\text{-}OH)$ Core. Structure and Reactivity of $[Fe_2(\mu\text{-}O)(\mu\text{-}OH)(6TLA)_2](ClO_4)_3$

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The thermodynamic stability of the (μ-oxo)diferric unit has led to the synthesis and characterization of a large number of complexes.[1] The complexes exhibit Fe–O–Fe angles that range from 180° to 113.8°, usually determined by the bites of additional bridging ligands. In many instances, the (μ-oxo)diferric unit forms as a result of autoxidation reactions of high-spin ferrous complexes. Indeed nature may have taken advantage of the stability of this structural motif for use in the active sites of diiron proteins[1c] such as hemerythrin,[2] rubrerythrin,[3] ribonucleotide reductase,[4] and fatty acid desaturase.[5] In the course of our efforts to model such protein active sites, we have found the first complex with a (μ-oxo)(μ-hydroxo)diferric core by suitable manipulation of the terminal ligands. Furthermore this complex has mild oxidative properties.

The reaction of 1 equiv of FeX_2 (X = ClO_4 or CF_3SO_3) and 6TLA[6] with 5 equiv of ^tBuOOH in methanol/H_2O at −40 °C affords a red powder, **1**. It is EPR silent at 2 K and exhibits UV–vis bands at 396 nm (ϵ = 4150 M^{-1} cm^{-1}) and 550 nm (ϵ = 670 M^{-1} cm^{-1}), features distinct from those of the transient $[Fe(6TLA)OOR]^{2+}$ species reported earlier.[7] The Mössbauer spectrum of **1** at 4.2 K consists of a single quadrupole doublet withn ΔE_Q = 1.66 mm/s and δ = 0.51 mm/s; the spectrum recorded in the presence of a 6.0-T applied field shows that the ground state is diamagnetic. Taken together, the data indicate an antiferromagnetically coupled (μ-oxo)diferric unit.[1]

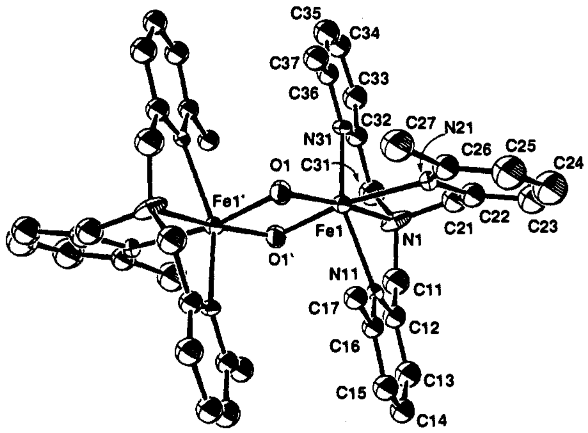

Figure 1. ORTEP drawing of the cation of **1** with atom-labeling scheme. Selected bond lengths (Å) and bond angles (deg) are as follows. Molecule A: Fe1A–O1A, 1.906(8); Fe1A–O1A′, 1.981(8); Fe1A–N1A, 2.174(9); Fe1A–N11A, 2.239(9); Fe1A–N21A, 2.194(9); Fe1A–N31A, 2.188(9); Fe1A–Fe1A′, 2.95(1); O1A–O1A′, 2.53(1); Fe1A–O1A–Fe1A′, 98.7(4); N21A–Fe1A–O1A, 168.2(3); N21A–Fe1A–O1A′, 108.2(3). Molecule B: Fe1B–O1B, 1.960(9); Fe1B–O1B′, 1.91(1); Fe1B–N1B, 2.18(8); Fe1B–N11B, 2.28(1); Fe1B–N21B, 2.196(9); Fe1B–N31B, 2.18(1); Fe1B–Fe1B′, 2.94(1); O1B–O1B′, 2.52(1); Fe1B–O1B–Fe1B′, 98.7(6); N21B–Fe1B–O1B, 168.9(4); N21B–Fe1B–O1B′, 109.4(4). No evidence for hydrogen bonding to the bridging oxygens can be found in the unit cell.

X-ray crystallography shows **1** (ClO_4) to be best formulated as $[Fe_2O(OH)(6TLA)_2](ClO_4)_3$,[8] the first diferric complex with an oxo and a hydroxo bridge (Figure 1).[9] There are two unique molecules in the unit cell, each with an inversion center at the center of the Fe_2O_2 core. Each iron atom is in a distorted octahedral environment consisting of the four nitrogens from 6TLA and two bridging oxygen atoms. The average Fe–N_{py} bond length is 2.21 Å, which is 0.06 Å longer than those found in (μ-oxo)diferric TPA complexes.[10] The longer Fe–N_{py} bonds probably arise from the presence of the 6-methyl groups on the pyridine rings, whose steric interactions prevent the pyridine nitrogens from coordinating to the iron(III) center at the optimum bond length.[7] As partial compensation, the Fe–N_{amine} distance is 0.05 Å shorter than those in TPA complexes,[10] resulting in Fe–N bonds of comparable length for **1**.

The Fe–μ-O bonds have lengths of 1.906(8)–1.981(8) Å, averaging 1.94 Å for the two molecules of the unit cell. Such bond lengths border on the short end of the range found for bis(μ-hydroxo)diiron(III) complexes (1.96–2.06 Å).[11] However, the presence of three ClO_4 ions associated with each dinuclear unit, the Mössbauer evidence for a (μ-oxo)diferric center, and electrospray ionization mass spectral data[8b] require that one of the bridging oxygen atoms is an oxide and the other a hydroxide. The observed Fe–μ-O bond lengths must then result from a disorder imposed by the inversion symmetry in the unit cell, with the average Fe–O bond distance observed being a compromise between Fe–μ-O and Fe–μ-OH distances. In corroboration, we

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[6] Abbreviations: TPA = tris(2-pyridylmethyl)amine; 6TLA = tris[(6-methyl-2-pyridyl)methyl]amine; OBz = benzoate; Pc = phthalocyaninato dianion.

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[8] (a) IR: ν(OH) = 3386 cm^{-1}. Anal. for $\mathbf{1}\cdot ClO_4\cdot THF\cdot 2H_2O$. Calcd for $C_{46}H_{61}Cl_3Fe_2N_8O_{16}$: C, 45.43; H, 5.02; N, 9.22; Cl, 8.75. Found: C, 45.60; H, 5.08; N, 9.23; Cl, 9.05. **CAUTION!** Metal complexes with organic ligands and perchlorate anions are potentially explosive. (b) The electrospray ionization mass spectra of **1** exhibit peaks at 1205, 1105, and 1007 with isotope patterns consistent with $[\{Fe_2O(OH)(6TLA)_2](ClO_4)_4\}^-$, $\{[Fe_2O(O)(6TLA)_2](ClO_4)_3\}^-$, and $\{[Fe_2O(OH)(6TLA)_2](ClO_4)_2\}^+$, respectively.

[9] Crystal data for $\mathbf{1}\cdot ClO_4\cdot THF$ ($C_{46}H_{57}Cl_3Fe_2N_8O_{15}$, fw. 1179.05) at 176 K: black prisms, monoclinic, space group $P2_1/a$ (No. 14), a = 12.421(4) Å, b = 18.98(1) Å, c = 21.55(1) Å, β = 93.55(3)°, V = 5072(3) $Å^3$, Z = 4. For 3517 unique, observed reflections with $I > 2\sigma(I)$ and 432 parameters, the current discrepancy indices are R = 0.081, R_w = 0.075.

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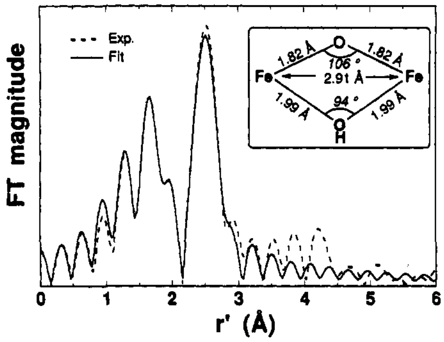

Figure 2. Fourier transformed EXAFS data ($k = 2$–14 Å^{-1}) of **1**. The experimental data (Fourier filtered from $r' = 1.0$–3.0 Å) were fitted by using one N/O at 1.82 Å ($\sigma^2 = -0.000\,24$), 1 N/O at 1.99 Å ($\sigma^2 = 0.0012$), four N/O at 2.20 Å ($\sigma^2 = 0.0084$), and one Fe at 2.91 Å ($\sigma^2 = 0.0036$) (residual, 13%). Omission of any one of these shells from the fit more than doubled the residual.

note that the Fe–Fe distance for **1** is 2.94(1) Å, which is 0.1–0.2 Å shorter than those observed for $Fe_2(\mu\text{-}OH)_2$[11] and $Fe_2(\mu\text{-}OR)_2$[12] complexes.

To obtain further support for the proposed structure, we have analyzed EXAFS data for **1**.[13] Since this technique provides a radial distribution of scatterers about the metal center,[14] the metal–ligand distances obtained would be unaffected by the disorder imposed by the unit cell. Figure 2 shows the Fourier transformed EXAFS spectrum of **1**; the features at $r' < 2.2$ Å correspond to the first coordination sphere, and that at $r' = 2.5$ Å corresponds to the Fe–Fe component. The best fit of this spectrum gives one N/O at 1.82 Å, one N/O at 1.99 Å, four N/O at 2.20 Å, and one Fe at 2.91 Å. There is good agreement between the EXAFS and crystallographic results for the average Fe–N distance and the Fe–Fe separation. The 1.82-Å scatterer would then correspond to the μ-oxo bridge, and the 1.99-Å scatterer to the μ-hydroxo bridge (Figure 2 inset). While the length of the Fe–μ-OH bond falls within the expected range for such bridges,[11] the Fe–μ-O bond is on the long end relative to most other Fe–μ-O bonds.[1] The longer bond may result from the steric strains imposed by the $Fe_2(\mu\text{-}O)(\mu\text{-}OH)$ core, as the Fe–O–Fe angle is the smallest of any (μ-oxo)diferric unit in the literature.[1] This structure is also maintained in solution as indicated by its NMR spectrum (supplementary material); seven pyridine β protons are found in the 15–30 ppm region, consistent with the presence of the μ-oxo bridge and inequivalent 6TLA ligands.

When **1** is incubated with 1-methyl-1,4-cyclohexadiene or PPh_3 in CH_3CN under Ar, a slow loss of its characteristic visible spectrum is observed. The reaction is complete in 2–3 h at 80 °C, and its NMR reveals sharp paramagnetically shifted signals typical of high-spin [Fe^{II}6TLA] complexes.[15] Thus **1** appears to be reduced to an Fe(II) species, and 1-methyl-1,4-cyclohexadiene and PPh_3 are oxidized to toluene and $OPPh_3$, respectively. From GC measurements, the yields of the oxidation products are found to be (1.1 ± 0.1)/2Fe.

While there are a large number of diferric complexes with $Fe_2(OR)_2$ (R = H, alkyl, or aryl) cores, **1** represents the first example of a diferric complex with an oxo and a hydroxo bridge.[16] We believe this to be a result of the 6TLA ligand, whose methyl groups sterically prevent the ferric center from making strong Fe–N bonds. This situation engenders an Fe(III) ion with strong Lewis acidity, and, in the absence of other potential ligands, only the deprotonated forms of water can mitigate the high effective charge on the Fe(III). The same considerations also provide the driving force for the reduction of **1**, as the longer Fe–N bond lengths required by the steric interactions would be more easily accommodated by the larger ionic radius of Fe(II).[7] Similarly, the coordination of pyridine to the FePc unit serves to drive the reduction of $[FePc]_2O$ concomitant with the oxidation of Ph_3P.[17] These examples demonstrate that the manipulation of the coordination environment to stabilize Fe(II) can activate the usually "inert" (μ-oxo)diiron(III) unit to carry out oxidation chemistry.

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Supplementary Material Available: NMR spectrum of **1** and tables of the fractional atomic coordinates, thermal parameters, bond lengths, and bond angles for $[Fe_2O(OH)(6TLA)_2](ClO_4)_3\cdot$THF (23 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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