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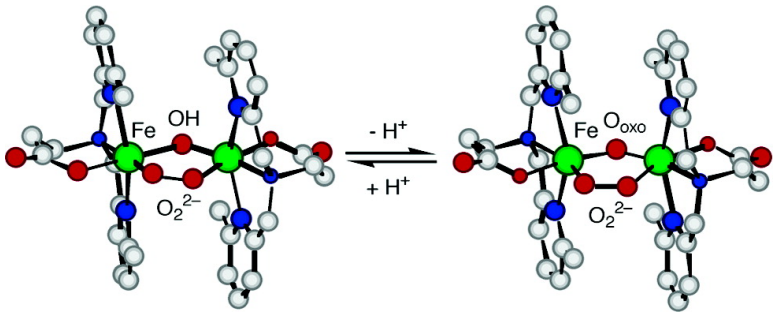
J. Am. Chem. Soc., **2005**, 127 (3), 826-827• DOI: 10.1021/ja045594a • Publication Date (Web): 29 December 2004



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Structural and Spectroscopic Characterization of (μ-Hydroxo or μ-Oxo)(μ-peroxo)diiron(III) Complexes: Models for Peroxo Intermediates of Non-Heme Diiron Proteins

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μ-1,2-Peroxodiiron(III) species have been spectroscopically identified as reaction intermediates for the dioxygen activating diiron proteins or some variants such as methane monooxygenase (MMO), ribonucleotide reductase (RNR), stearoyl-acyl carrier protein Δ^9-desaturase (Δ^9D), and ferritin.[1,2] Some of them are further activated to bis(μ-oxo)diiron(IV) or bis(μ-oxo)diiron(III,IV) species, which are responsible for oxidation of substrates. Diiron centers of those proteins have a common carboxylate-rich environment (four carboxylate and two N donors for MMO, RNR, and Δ^9D). Various synthetic (peroxo)diiron(III) complexes including three structurally characterized complexes have been developed, and they provided a chemical basis for understanding of structural and various spectroscopic properties of the (peroxo)diiron complexes.[3−6] To obtain further fundamental insights into structural and spectroscopic properties and reactivities of the (peroxo)diiron(III) species, further model (peroxo)diiron(III) complexes are needed, which have a biologically relevant ligand environment such as terminal carboxylate(s) and bridging hydroxide or oxide commonly found in diiron(III) forms.[1] Here, we report the first structurally characterized (μ-hydroxo)(μ-peroxo)diiron(III) complex $[Fe_2(6Me_2\text{-}BPP)_2(OH)(O_2)]X$ (**2**·X: X = CF_3SO_3 (**2**·OTf), $B(3\text{-}ClPh)_4$ (**2**·$B(3\text{-}ClPh)_4$)) and (μ-oxo)(μ-peroxo)diiron(III) complex $[Fe_2(6Me_2\text{-}BPP)_2(O)(O_2)]$ (**3**) with a tripodal ligand ($6Me_2$-BPP)[7] having a terminal carboxylate and the relationship among ligand environmental effects, spectroscopic properties, and reactivity.

Reaction of $[Fe_2(6Me_2\text{-}BPP)_2(O)(OH)](OTf)\cdot 3.5H_2O$ (**1**)[8] with ~100 equiv of H_2O_2 in methanol at −80 °C gave a blue complex **2**, which can be further converted to a purple complex **3** by addition of Et_3N. Crystal structure of **2**·$B(3\text{-}ClPh)_4$ showed that the complex has an $Fe_2(\mu\text{-}OH)(\mu\text{-}1,2\text{-}O_2)$ core and each iron has a six-coordinate structure with N_3O_3 donors (Figure 1A). Two iron centers are inequivalent; the peroxo oxygen in the Fe1 site is trans to a tertiary amine nitrogen, while that in the Fe2 site is trans to a carboxylate oxygen. The structure of **3** is similar to **2**·$B(3\text{-}ClPh)_4$, but unfortunately, μ-oxo and μ-1,2-peroxo groups are disordered over two positions with 0.5 occupancy (Figure 1B). Detailed discussion about metric parameters of **3** may not be warranted, but comparison of the structural features with **2** is useful. The O1−O2 bond length of **2**·$B(3\text{-}ClPh)_4$ is 1.396(5) Å (cf. 1.41(1) Å for **3**), which is slightly shorter than those of the (peroxo)diiron(III) complexes (1.406(8)−1.426(6) Å).[4] The Fe···Fe distance (3.396(1) Å) of **2** is comparable to those of the complexes with a bridging phenolate or alkoxide

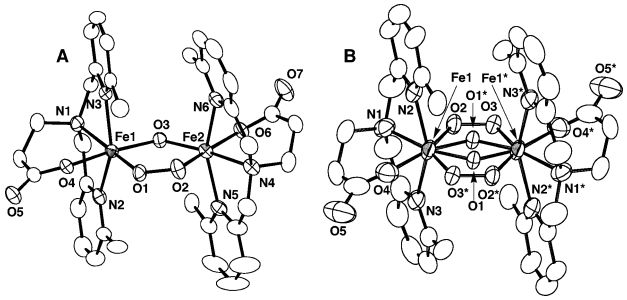

Figure 1. ORTEP views (50% probability) of **2**·$B(3\text{-}ClPh)_4$ (A) and **3** (B). Selected bond distances (Å) and angles (deg) for **2**·$B(3\text{-}ClPh)_4$: Fe1−O1, 1.867(4); Fe1−O3, 2.006(4); Fe1−O4, 1.986(4); Fe1−N1, 2.208(4); Fe1−N2, 2.232(5); Fe1−N3, 2.204(4); Fe2−O2, 1.887(4); Fe2−O3, 1.943(4); Fe2−O6, 1.999(4); Fe2−N4, 2.183(5); Fe2−N5, 2.193(5); Fe2−N6, 2.221-(5); O1−O2, 1.396(5); Fe1···Fe2, 3.396(1); Fe1−O3−Fe2, 118.6(2); Fe1−O1−O2, 123.1(3); Fe2−O2−O1, 120.4(3); Fe1−O1−O2−Fe2, −14.5(4).

(3.327(2)−3.462(3) Å)[4a,b] whereas longer than that of **3** (3.171(1) Å). Mössbauer spectra of **2**·$B(3\text{-}ClPh)_4$ and **3** at 80 K showed single quadrupole doublets with δ (ΔE_Q) = 0.50 (1.31) and 0.50 (1.46) mm/s, respectively. The ΔE_Q values are comparable to that of **1** (δ (ΔE_Q) = 0.44 (1.56) mm/s) but larger than that of $[Fe_2(6Me_2\text{-}BPP)_2(OH)_2]^{2+}$ (**4**) (δ (ΔE_Q) = 0.42 (1.16) mm/s), suggesting that the peroxide also acts as a stronger π-donor and causes a larger electric field gradient around the Fe(III) centers as the oxo bridge.

It is noted that the bridging hydroxide and oxide significantly influence the spectroscopic properties. The electronic spectrum of **2**·OTf showed an intense peroxide (π_v* orbital)-to-Fe(III) (d_π orbital) LMCT band[5] at 644 nm (ϵ = 3000 M^{-1} cm^{-1}), whereas that of **3** showed a CT band at 577 nm (ϵ = 1500 M^{-1} cm^{-1}) (Figure 2). Such a significant blue shift and low intensity of the CT band of **3** can be partly ascribed to a stronger π-donation of the bridging oxide, which increases the d_π orbital energy of Fe(III) centers (diminishing the Lewis acidity of Fe(III) centers), increases the energy gap between d_π orbitals and π_v* orbital of the peroxide, and decreases an overlap between them, leading to a blue shift and low intensity of the CT band.[2] The terminal carboxylate also influences the CT energy and reactivity. A closely related (μ-oxo)-(μ-peroxo)diiron(III) complex $[Fe_2(6Me_3\text{-}tpa)_2(O)(O_2)]^{2+}$ (**5**) having N_4 donors exhibits a CT band at 648 nm (ϵ = 1200 M^{-1} cm^{-1}),[6,9] which is red-shifted relative to that of **3**, indicating that the terminal carboxylate also functions as a stronger donor. In addition, **5** can be converted into a bis(μ-oxo)diiron(III,IV) species by O−O bond cleavage, which is accelerated by treatment of $HClO_4$. In contrast, no such conversion was detected for **3** and the reaction with $HClO_4$

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10.1021/ja045594a CCC: $30.25

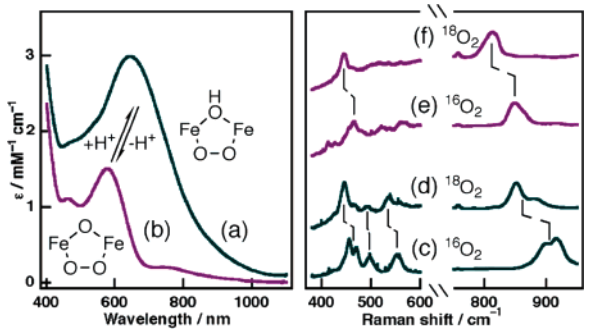

Figure 2. Electronic spectra of **2**·OTf (a) and **3** (b) in CH_3OH at −80 °C and resonance Raman spectra of **2** (prepared from $H_2{}^{16}O_2$ (c) and $H_2{}^{18}O_2$ (d)) and **3** (prepared from $H_2{}^{16}O_2$ (e) and $H_2{}^{18}O_2$ (f)) in CH_3OH at −80 °C.

caused the conversion to **2**,[10] suggesting an increase of basicity of the bridging oxide by stronger donation of the carboxylate in **3**.

The resonance Raman spectra of **2** and **3** (Figure 2c−f) showed several features which shifted downward by ^{18}O-substitution. For complex **2**, we assigned two bands at 919 and 896 cm^{-1} to the ν(O−O) as a Fermi doublet (the intrinsic $\nu_{O-O}{}^0 = 908$ cm^{-1}; 881 and 850 cm^{-1} for an $^{18}O_2$ sample, $\nu_{O-O}{}^0 = 861$ cm^{-1}).[11] The bands at 548 ($^{18}O_2$: 536 cm^{-1}) and 498 ($^{18}O_2$: 493 cm^{-1}) can be assigned to the ν_{as}(Fe−O_{OH}) + ν_{as}(Fe−O_{O-O}) and ν_s(Fe−O_{OH}), respectively, based on normal coordinate analysis (NCA).[12] The analysis also indicated that the bands at 473 and 456 cm^{-1} can be assigned to ν_s(Fe−O_{O-O}) as a Fermi doublet ($\nu_{Fe-O}{}^0 = 460$ cm^{-1}; 447 cm^{-1} for a $^{18}O_2$ sample). For complex **3**, a band at 847 cm^{-1} ($^{18}O_2$: 814 cm^{-1}) can be assigned to the ν(O−O) and a band at 465 cm^{-1} ($^{18}O_2$: 446 cm^{-1}) to the ν_s(Fe−O_{O-O}). The ν(O−O) of **2** is similar to those of (peroxo)diiron(III) complexes (880−900 cm^{-1}),[3,5] whereas it is significantly higher than that of **3** (847 cm^{-1}) and **5** (848 cm^{-1}).[6] It has been shown that the ν(O−O) and ν_s(Fe−O_{O-O}) depend on the Fe−O−O angle; as the Fe−O−O angle becomes larger, the ν(O−O) becomes higher and the ν_s(Fe−O_{O-O}) becomes lower by mechanical coupling.[5] This is also the case for **2** (Fe−$O-O_{av}$ = 121.8°) and **3** (Fe−O−O = ∼115°): the ν(O−O) of **2** (908 cm^{-1}) is higher than that of **3** (847 cm^{-1}), and the ν_s(Fe−O_{O-O}) of **2** (460 cm^{-1}) is lower than that of **3** (465 cm^{-1}). However, a large change in the ν(O−O) (Δ = 61 cm^{-1}) and a small change in the ν_s(Fe−O_{O-O}) (Δ = 5 cm^{-1}) between **2** and **3** also suggest the presence of some other contributions such as the bonding nature of the peroxide as observed for CT energies and intensities; the stronger donation of the peroxide in **2** increases the ν(O−O) and ν_s(Fe−O_{O-O}), leading to an increase of change in the ν(O−O) and a decrease of change in the ν_s(Fe−O_{O-O}) by an offset effect.[13]

It has been proposed that the changes in the ν(O−O) and ν_s(Fe−O_{O-O}) frequencies for RNR-W48F/D84E (868 and 457 cm^{-1}),[2,14] Δ^9D (898 and 442 cm^{-1}),[15] and ferritin (851 and 485 cm^{-1})[16] depend on the Fe−O−O angles. Very short Fe···Fe distances (∼2.5 Å) have been reported for the peroxo-intermediates of ferritin[17] and RNR-W48A/D84E.[18] Such a short Fe···Fe distance requires a small Fe−O−O angle as observed for $[Mn_2(L)_2(O)_2(O_2)]^{2+}$ (Mn···Mn = 2.531(7) Å and Mn−O−O = 106.9°).[19] However, for the relatively high ν(O−O) frequency (868 cm^{-1}) of RNR-W48F/D84E, Solomon et al. pointed out that a short (2.5 Å) Fe···Fe distance reported for RNR-W48A/D84E which is proposed to be analogous to RNR-W48F/D84E is not supported from spectroscopic analyses for RNR-W48F/D84E.[2] A lower CT energy of RNR-W48F/D84E (∼700 nm) compared to those of the model complexes suggests the high Lewis acidity of Fe(III) centers in RNR-W48F/D84E relative to the model complexes except for $[Fe_2\{HB(3,5\text{-}^{iPr2}pz)_3\}_2(O_2)(PhCO_2)_2]$.[2,5]

In summary, structures and spectroscopic properties of both (μ-hydroxo)(μ-peroxo) and (μ-oxo)(μ-peroxo)diiron(III) complexes provide fundamental chemical insights into the nature of (μ-1,2-peroxo)diiron(III) complexes, although further comprehensive structural and spectroscopic data of model complexes and proteins are needed.

Acknowledgment. Financial support of this research by the Ministry of Education, Science, and Culture Grant-in-Aid for Scientific Research to H. F., M. S., T. K., and Y. W. is gratefully acknowledged.

Supporting Information Available: Synthesis, X-ray crystallography, spectroscopic characterization, analyses of Fermi resonance, and NCA results. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Abbreviations used: $6Me_2$-BPP = *N*,*N*-bis(6-methyl-2-pyridylmethyl)-3-aminopropionate; $6Me_3$-tpa = tris(6-methyl-2-pyridylmethyl)amine; L = 1,4,7-trimethyl-1,4,7-triazacyclononane; $HB(3,5\text{-}^{iPr2}pz)_3$ = hydrotris(3,5-isopropyl-1-pyrazolyl)borate.

(8) Synthesis, X-ray crystallography, and spectroscopic characterization of the complexes are given in the Supporting Information.

(9) Lower intensity of CT band of **5** relative to that of **3** suggests some other contributions together with the Lewis acidity of Fe(III) centers.

(10) Complexes **2** and **3** can be reversibly converted by treatment of $HClO_4$ or Et_3N at −80 °C (see Figures S5 and S6).

(11) Quantitative analyses of Fermi resonance are given in the Supporting Information.

(12) NCA was performed by the Wilson GF matrix method with Urey−Bradley force field using ring models ($Fe_2(\mu$-OH or O)(μ-O_2)) obtained by X-ray analyses. Reasonable fittings were obtained (see Supporting Information).

(13) This is in line with larger force constants (K(O−O) = 3.55 and K(Fe−O_{O-O}) = 2.18 mdyn/Å) for **2** relative to those of **3** (K(O−O) = 3.25 and K(Fe−O_{O-O}) = 1.84 mdyn/Å).

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JA045594A