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The Flexible $\mathrm{Fe_2(\mu\text{-}O)_2}$ Diamond Core: A Terminal Iron(IV)−Oxo Species Generated from the Oxidation of a Bis(μ-oxo)diiron(III) Complex

Hui Zheng,[†] Sun Jae Yoo,[‡] Eckard Münck,[‡] and
Lawrence Que, Jr.*[,†]

Department of Chemistry and
Center for Metals in Biocatalysis
University of Minnesota
Minneapolis, Minnesota, 55455
Department of Chemistry
Carnegie Mellon University
Pittsburgh, Pennsylvania 15213

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Iron(IV)−oxo species are proposed to be the key reactive species in many nonheme iron enzymes.[1−3] Spectroscopic studies implicate high-valent (μ-oxo)diiron species as intermediates in the oxidation chemistry of the diiron centers in methane monooxygenase (MMO)[4] and ribonucleotide reductase (RNR),[5] while mononuclear $\mathrm{Fe^{IV}{=}O}$ units have been proposed as the oxidant for several mononuclear nonheme iron enzymes.[2,3] Our synthetic efforts to obtain models for such high-valent intermediates have yielded a series of $\mathrm{[Fe_2(O)_2(L)_2](ClO_4)_3}$ complexes, where L is tris(2-pyridylmethyl)amine (TPA) or its ring-alkylated derivatives.[6] Of these, only $\mathrm{[Fe_2(\mu\text{-}O)_2(5\text{-}Et_3\text{-}TPA)_2](ClO_4)_3}$ (**1**) has been structurally characterized and found to have an $\mathrm{Fe_2(\mu\text{-}O)_2}$ core.[7] Such complexes with L = TPA or 5-alkylated TPA are valence-delocalized $\mathrm{Fe^{III}Fe^{IV}}$ species with an $S = {}^3/_2$ ground-state arising from double exchange interactions between low spin $\mathrm{Fe^{III}}$ ($S_1 = {}^1/_2$) and low spin $\mathrm{Fe^{IV}}$ ($S_2 = 1$) centers.[8] In contrast, complexes with L = 6-Me-TPA or 6-$\mathrm{Me_3}$-TPA (**2**) are valence localized $S = {}^1/_2$ species derived from the antiferromagnetic coupling between a high spin $\mathrm{Fe^{III}}$ ($S_1 = {}^5/_2$) and a high spin $\mathrm{Fe^{IV}}$ ($S_2 = 2$) ion.[9,10] These latter complexes have electronic properties resembling those of high-valent intermediate **X** of RNR (RNR−**X**), the species responsible for the oxidation of the Tyr122 residue to its catalytically essential radical form.[11] In this contribution, we report the synthesis of **2** (L = 6-$\mathrm{Me_3}$-TPA) by one-electron oxidation of its diiron(III) precursor $\mathrm{[Fe^{III}_2(\mu\text{-}O)_2(6\text{-}Me_3\text{-}TPA)_2](ClO_4)_2}$ (**3**), and provide resonance Raman evidence for an $\mathrm{Fe^{III}{-}O{-}Fe^{IV}{=}O}$ structure derived from the isomerization of the $\mathrm{Fe_2(\mu\text{-}O)_2}$ diamond core, demonstrating the accessibility of a terminal $\mathrm{Fe^{IV}{=}O}$ unit in a nonheme environment.[12]

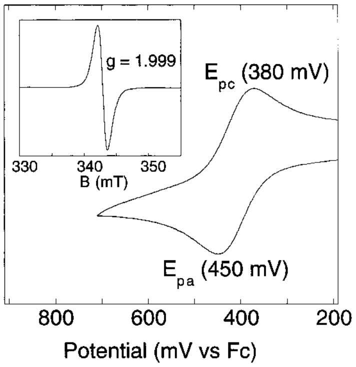

Figure 1. Cyclic voltammogram of **3** in $\mathrm{CH_3CN}$ (1 mM) with 0.1 M $\mathrm{N(C_4H_9)_4BF_4}$ at −40 °C (scan rate = 100 mV/s). The potential was calibrated with ferrocene as the internal standard. The inset is an X-band EPR spectrum of **2** (T = 20 K, power = 0.1008 mW).

Complex **3** can be reversibly oxidized to **2** by cyclic voltammetry ($E_{1/2} = 0.41$ V vs Fc, $\Delta E = 70$ mV) at −40 °C in $\mathrm{CH_3CN}$ (Figure 1). This observation suggests that **2** may also be accessed by treatment of **3** with suitable one-electron oxidants, instead of the earlier reported reactions with $\mathrm{H_2O_2}$.[8−10] Indeed addition of one equiv of $\mathrm{(NBu_4)_2Ce(NO_3)_6}$[13] ($E_{1/2} = 0.62$ V vs Fc, $\Delta E = 75$ mV, −40 °C) to a 0.1 mM solution of **3** in $\mathrm{CH_3CN}$ at −40 °C affords a species with a nearly isotropic EPR signal at $g = 1.999$ (Figure 1 inset), previously observed for related $\mathrm{Fe^{III}Fe^{IV}}$ complexes;[9,10] quantification of the signal shows that **2** is produced in 85 ± 5% yield. At higher concentrations, **2** precipitates as a brown solid. A Mössbauer study of solid **2** (for details, see Supporting Information) reveals that about 84% of the Fe present belongs to an $\mathrm{Fe^{III}Fe^{IV}}$ complex with parameters similar to those previously reported for $\mathrm{[Fe_2(O)_2(6\text{-}Me\text{-}TPA)_2]^{3+}}$.[9]

The elemental analysis of solid **2** (stored in dry ice prior to the analysis) fits very well to its formulation as $\mathrm{[Fe_2(O)_2(6\text{-}Me_3\text{-}TPA)_2][Ce(NO_3)_6]{\cdot}H_2O}$ (calcd (obs): C, 37.67 (37.82); H, 3.74 (3.76); Cl, 0 (0), N, 14.65 (14.46)). Further support derives from the positive ion electrospray mass spectrum of the above reaction solution (Figure 2), which reveals ion clusters with $m/z \geq 969$ corresponding to $\mathrm{\{[Fe_2(O)_2(6\text{-}Me_3\text{-}TPA)_2](NO_3)(ClO_4)\}^+}$ and $m/z \geq 1006$ corresponding to $\mathrm{\{[Fe_2(O)_2(6\text{-}Me_3\text{-}TPA)_2](ClO_4)_2\}^+}$, based on their masses and isotopic distribution patterns. We also observe clusters of positive ions with $m/z \geq 987$ and 1024 corresponding to the above ions plus a water molecule (presumably from trace amounts in the solvent). These observations suggest that water is a ligand and that the cation of **2** is best formulated as $\mathrm{[Fe_2(O)_2(H_2O)(L)_2]^{3+}}$.

Resonance Raman spectroscopy provides the key insight into the structure of **2**. The resonance Raman spectrum of **2** obtained with 457.9 nm excitation shows a strong feature at 840 cm^{-1} (Figure 3, panel A), that disappears with the decay of **2** upon warming. While neither the addition of 300 equiv of $\mathrm{H_2{}^{16}O}$ or $\mathrm{D_2O}$ affects the Raman spectrum, the addition of 300 equiv of $\mathrm{H_2{}^{18}O}$ results in the downshift of the 840 cm^{-1} peak by 5 cm^{-1}

[†] University of Minnesota.

[‡] Carnegie Mellon University.

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(13) $\mathrm{(NBu_4)_2Ce(NO_3)_6}$ was synthesized from the ion-exchange reaction of $\mathrm{(NH_4)_2Ce(NO_3)_6}$ with $\mathrm{NBu_4Cl}$ in aqueous solution and precipitated as a yellow solid (calcd (obs): C, 38.54 (38.39); H, 7.28 (7.36); N, 11.23 (10.95)).

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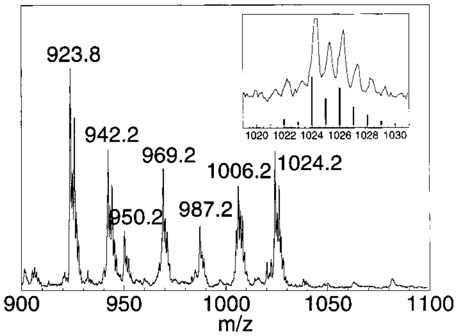


Figure 2. Positive ion electrospray ionization mass spectrum of **2**. The inset shows the experimental data, while the bars below represent the isotopic distributions calculated for $\{[Fe_2(O)_2(H_2O)(6\text{-}Me_3\text{-}TPA)_2](NO_3)(ClO_4)\}^+$. The ions at *m/z* of 923.8, 942.2, and 950.2 belong to diiron(III) impurities.

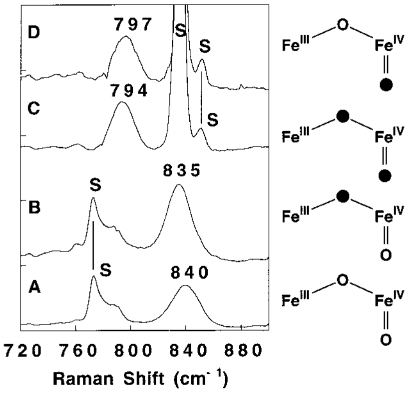
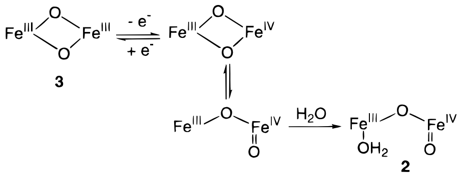


Figure 3. Resonance Raman spectra of (A) **2** in CH_3CN, (B) sample A with addition of 300 equiv of $H_2{}^{18}O$, (C) ^{18}O-labeled **2** in CD_3CN, (D) sample C with addition of 300 equiv of H_2O. Spectra obtained with 457.9 nm excitation at 77 K. Experimental frequencies are referenced to internal solvent vibrations.

(panel B). In contrast, the 840 cm^{-1} band downshifts by 46 cm^{-1} in a sample derived from ^{18}O-labeled precursor **3** (panel C).[14] Addition of 300 equiv of $H_2{}^{16}O$ to this latter sample effects a 3-cm^{-1} upshift of the 794 cm^{-1} band (panel D). It thus appears that **2** is a species with two distinct oxygen atoms: one that contributes significantly to the vibration and does not exchange with solvent water and another that is a minor component of the vibration but does readily exchange with solvent water.

The simplest way to make the two oxygen atoms of the $[Fe_2(\mu\text{-}O)_2]^{3+}$ core distinct is for the core to isomerize to an $Fe^{III}-\mu\text{-}O-Fe^{IV}{=}O$ unit as shown in Scheme 1; the proposed structure is consistent with the Raman data. The 840 cm^{-1} frequency observed for **2** is much higher than those found for the $Fe_2(\mu\text{-}O)_2$ cores of **1** and **3** (660−690 cm^{-1})[15,18] but matches that expected for either the ν_{asym} of an Fe−O−Fe unit with an angle of ∼160° [16,17] or the ν_{Fe-O} of a terminal $Fe^{IV}{=}O$ unit.[18] Either may be assigned as the major component of the 840 cm^{-1} mode, as both should downshift by ∼40 cm^{-1} upon ^{18}O substitution. However all Fe−O−Fe units studied thus far exchange readily with solvent.[16,19] On the other hand, terminal $Fe^{IV}{=}O$ moieties, thus far found only in heme complexes, can be inert to solvent exchange when the sixth coordination site is inaccessible to solvent water.[20] Taken together, the data are most consistent with the labeling scheme shown for **2** in Figure 3. The vibration at 840 cm^{-1} is proposed to arise principally from the ν_{Fe-O} of an exchange-inert terminal $Fe^{IV}{=}O$ moiety with a small contribution from the ν_{asym} of an Fe−O−Fe unit that is susceptible to solvent exchange.

Scheme 1



Our results demonstrate that the $Fe^{III}(O)_2Fe^{IV}$ diamond core structure can be quite flexible. The oxidation of **3** appears likely to afford a transient high-valent $Fe_2(\mu\text{-}O)_2$ complex, as suggested by its reversible electrochemical behavior, which in turn isomerizes to give a complex with a terminal $Fe^{IV}{=}O$ moiety (Scheme 1). Computational studies propose a similar isomerization for the putative $Fe^{IV}{}_2(\mu\text{-}O)_2$ core of MMO intermediate **Q** in the course of its reaction with methane.[21] Complex **2** thus serves as an experimental precedent for this proposed isomerization and a demonstration that a terminal $Fe^{IV}{=}O$ moiety can be isolated in a nonheme ligand environment.

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Supporting Information Available: Mössbauer spectra and analysis for solid **2** (PDF). This material is available free of charge on the Internet via http://pubs.acs.org.

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[14] $[Fe_2(\mu\text{-}O)(\mu\text{-}OH)(6\text{-}Me_3\text{-}TPA)_2](ClO_4)_3$ (**4**) was dissolved in dry CH_3CN and allowed to exchange with 1000 equiv of $H_2{}^{18}O$ at −20 °C. The ^{18}O-incorporated **4** was then precipitated by the addition of THF. This solid was then dissolved in dry CH_3CN, followed by the addition of 1 equiv of NEt_3. The ^{18}O-incorporated **3** was then recrystallized from dry THF. The incorporation of ^{18}O into **3** was confirmed by its characteristic $Fe-{}^{18}O-Fe$ vibration at 662 cm^{-1}.

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