

Raman Evidence for a Trapped-Valence Fe^{II}–O–Fe^{III} Complex Formed from an Outer-Sphere Reaction of Diiron(II) with Dioxxygen

Jonathan D. Cohen,^{1a} Sonha Payne,^{1b} Karl S. Hagen,^{*,1b} and Joann Sanders-Loehr^{*,1a}

Department of Chemistry, Biochemistry and Molecular Biology, Oregon Graduate Institute of Science and Technology, Portland, Oregon 97291-1000
Department of Chemistry, Emory University Atlanta, Georgia 30322

Received November 11, 1996

Dinuclear iron clusters bridged by an oxo or hydroxo ligand have been identified as cofactors in the metalloproteins hemerythrin, methane monooxygenase, and ribonucleotide reductase where they catalyze the reversible binding or activation of O₂.² Each of these proteins has been trapped in a mixed-valence state, ascribed to an Fe^{II}–OH–Fe^{III} intermediate from the appearance of a rhombic EPR signal with all three *g* values below 2.0.³ Although crystal structures have been determined for several of these enzymes² and numerous model compounds⁴ in both diiron(II) and diiron(III) states, the mixed-valence species proposed as reaction intermediates are mainly amenable to spectroscopic detection. Recently, a crystal structure was reported for a hydroxo-bridged complex, [Fe₂OH(μ-piv)₂L₂]²⁺, L = 1,4,7-trimethyl-1,4,7-triazacyclononane, in a trapped-valence Fe^{II}Fe^{III} state.³ Using the same L terminal ligand, but replacing the two pivalate bridges with bulkier triphenylacetates, we have obtained the first stable oxo-bridged Fe^{II}Fe^{III} complex and determined its crystal structure. The unusual domination of its resonance Raman (RR) spectrum by an asymmetric Fe–O–Fe stretch at 711 cm⁻¹ provides strong evidence for a class II trapped-valence condition.

The hydroxo-bridged diiron(II) compound [Fe₂OH(O₂-CCPh₃)₂L₂](BPh₄) (**1-BPh₄**) was isolated under anaerobic conditions from an acetonitrile solution of the triflate salt (**1-CF₃SO₃**)⁵ by metathesis with NaBPh₄.⁶ The reaction of **1** with O₂ in dry CH₃CN yields the green mixed-valence compound [Fe₂O(O₂CCPh₃)₂L₂]⁺ (**2**). The BPh₄ salts of **1** and **2** are considerably less soluble in acetonitrile than the triflate salts; exposure of **1-BPh₄** to O₂ affords crystalline **2-BPh₄**⁶ within minutes at room temperature (Figure 1). Further oxidation by the H₂O₂ byproduct from the formation of **2** affords the orange diiron(III) complex, [Fe₂O(O₂CCPh₃)₂L₂]²⁺ (**3**).⁶ The second step is prevented by using stoichiometric amounts of H₂O₂ or a trialkylamine *N*-oxide as the oxidant for **1**.

The crystal structures of **1-BPh₄** and **2-BPh₄** are isomorphous with no imposed symmetry (Figures 1 and S1). In the former, the metrical parameters are similar to the analogous hydroxo-bridged diiron(II) acetate and trifluoroacetate complexes.⁷ The monocation of **2-BPh₄** is nearly isostructural to the dication of **3-BPh₄**. However, the core distances of **2-BPh₄**, including Fe–

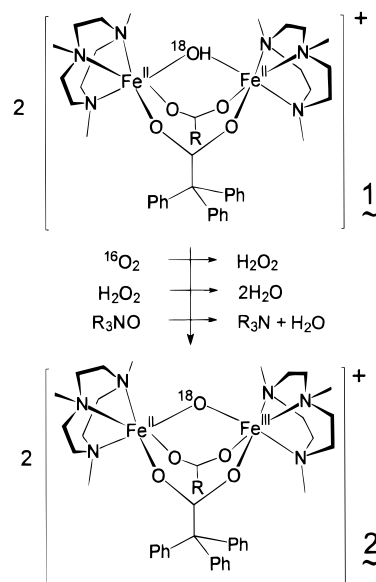


Figure 1. Conversion of **1** to **2** (R = CPh₃, R₃NO = 4-methylmorpholine *N*-oxide) showing isotope distribution. A second equivalent of each oxidant converts **2** to **3**. Selected interatomic distances (Å) and angles (deg):⁶ **1-BPh₄**, Fe^{II}–Fe 3.424(2) Å, Fe(1)–OH 2.007(8), Fe(2)–OH 2.002(7), Fe(1)–O₂CR 2.115(6), 2.127(6), Fe(2)–O₂CR 2.112(6), 2.141(6), and Fe–OH–Fe 117.3(4)°. **2-BPh₄**, Fe^{II}–Fe 3.155(1), Fe(1)–O 1.818(4), Fe(2)–O 1.844(4), Fe(1)–O₂CR 2.089(4), 2.111(4), Fe(2)–O₂CR 2.154(4), 2.109(4), and Fe–O–Fe 119.0(2)°. **3-BPh₄**, Fe^{III}–Fe 3.160(1), Fe(1)–O 1.796(3), Fe(2)–O 1.792(3), Fe(1)–O₂CR 2.032(4), 2.069(4), Fe(2)–O₂CR 2.028(3), 2.053(3), and Fe–O–Fe 123.4(2)°.

μ-oxo, are at least four standard deviations longer than the corresponding distances in **3-BPh₄**. Magnetic susceptibility measurements and EPR spectra indicate that **2** has an *S* = 1/2 spin state,⁵ but the similar Fe–*μ*-oxo bond lengths of 1.818(4) and 1.844(4) Å cannot distinguish between a delocalized or a trapped-valence classification.

The Raman spectrum of **2** provides more definitive evidence for a trapped-valence species on the vibrational time scale. It exhibits a strong band at 711 cm⁻¹ that undergoes a 36-cm⁻¹ downshift with *μ*-¹⁸O (Figure 2). This peak is assigned to the asymmetric stretch of an Fe–O–Fe moiety on the basis of its frequency being close to the value of 720 cm⁻¹ predicted for a diiron(III) complex⁸ and its ¹⁸O-shift being close to the value of –34 cm⁻¹ calculated⁹ for a complex with an Fe–O–Fe angle of 119°. An additional band at 1416 cm⁻¹ shifts –71 cm⁻¹ with *μ*-¹⁸O and is assigned to 2*ν*_{as}(Fe–O–Fe). Since overtone progressions are frequently observed in Fe–O–Fe complexes,¹⁰ this provides further support for the *ν*_{as}(Fe–O–Fe) assignment. Finally, the RR spectrum of **2** has no ¹⁸O-sensitive vibrational mode in the 400–550-cm⁻¹ range that could correspond to the Fe–O–Fe symmetric stretch (Figure 2). This behavior is reminiscent of the diiron(III) [N₅FeOFex₃]⁺ complexes (X = Cl⁻ or Br⁻) where ligand asymmetry results in *ν*_{as}(Fe–O–Fe) being ~3× more intense than *ν*_s(Fe–O–Fe).¹¹ In contrast, the symmetric Fe–O–Fe structure in compound **3** results in an intense *ν*_s(Fe–O–Fe) at 519 cm⁻¹ that shifts –20 cm⁻¹ with *μ*-¹⁸O, similar to other tribridged diiron(III) complexes.

(1) (a) Oregon Graduate Institute. (b) Emory University.

(2) (a) Feig, A. L.; Lippard, S. J. *Chem. Rev.* **1994**, *94*, 759–805. (b) Nordlund, P.; Eklund, H. *Curr. Opin. Struct. Biol.* **1995**, *5*, 758–766.

(3) Bossek, U.; Hummel, H.; Weyhermüller, T.; Bill, E.; Wieghardt, K. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2642–2644 and references therein.

(4) (a) Chaudhuri, P.; Wieghardt, K. *Prog. Inorg. Chem.* **1987**, *35*, 329–436. (b) Kurtz, D. M., Jr. *Chem. Rev.* **1990**, *90*, 585–606.

(5) Payne, S. C.; Day, E. P.; Wang, D.; Chen, S.; Orsz, R.; Hagen, K. S., Manuscript in preparation.

(6) X-ray analysis of **1-BPh₄**: colorless crystals, orthorhombic, *Pbca*, *a* = 20.418(2) Å, *b* = 19.279(1) Å, *c* = 37.606(2) Å, *V* = 14 803(2) Å³, *Z* = 8, *R* = 8.2%, and GOF = 1.02. **2-BPh₄**: dark green crystals, orthorhombic, *Pbca*, with *a* = 20.5573(9) Å, *b* = 19.3176(8) Å, *c* = 37.744(1) Å, *V* = 14 989(1) Å³, *Z* = 8, *R* = 7.2%, and GOF = 1.02. **3-BPh₄**: yellow/orange dichroic crystals, triclinic, *P1*, with *a* = 12.937(2) Å, *b* = 14.977(3) Å, *c* = 25.627(5) Å, *α* = 93.84(1)°, *β* = 91.12(1)°, *γ* = 96.26(1)°, *V* = 4923(2) Å³, *Z* = 2, *R* = 6.6%, and GOF = 1.02.

(7) (a) Hartman, J. R.; Rardin, R. L.; Chaudhuri, P.; Pohl, K.; Wieghardt, K.; Nuber, B.; Weiss, J.; Papaefthymiou, G. C.; Frankel, R. B.; Lippard, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 7387–7396. (b) Lachicotte, R.; Kitaygorodskiy, A.; Hagen, K. S. *J. Am. Chem. Soc.* **1993**, *115*, 8883–8884.

(8) Sanders-Loehr, J.; Wheeler, W. D.; Shiemke, A. K.; Averill, B. A.; Loehr, T. M. *J. Am. Chem. Soc.* **1989**, *111*, 8084–8093.

(9) Wing, R. M.; Callahan, K. P. *Inorg. Chem.* **1969**, *4*, 871–874.

(10) Czernuszewicz, R. S.; Sheats, J. E.; Spiro, T. G. *Inorg. Chem.* **1987**, *26*, 2063–2067.

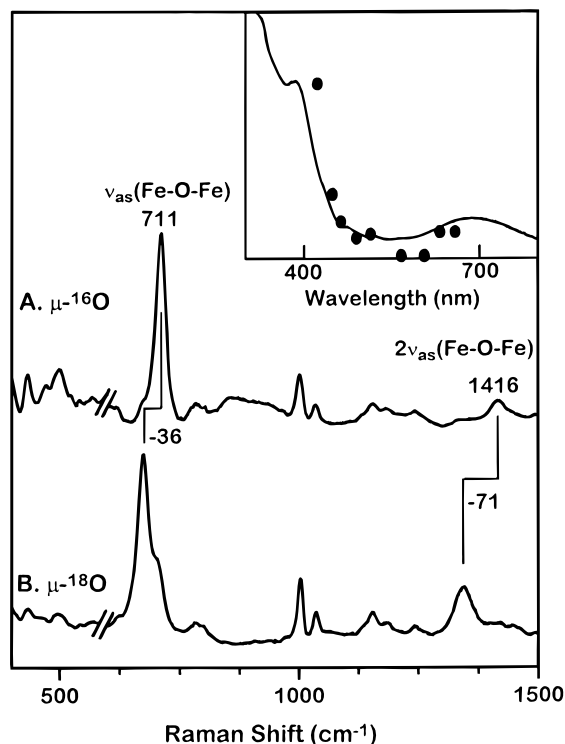


Figure 2. Raman spectra of solid **2-BPh₄** with a (A) ¹⁶O or (B) ¹⁸O bridge. Compound **1** was synthesized in CH₃CN with stoichiometric H₂¹⁶O or H₂¹⁸O and then oxidized with ¹⁶O₂ under anhydrous conditions to form **2**. Each spectrum was obtained with 413.1-nm (25 mW) excitation on a 0.67-m spectrograph equipped with a cooled CCD detector on two separate samples (above and below 600 cm⁻¹) in sealed capillaries at 298 K. Inset: Absorption spectrum in CH₂Cl₂ (—) and RR enhancement profile of solid (●) for intensity of 711-cm⁻¹ ν_{as} (Fe—O—Fe) relative to 1003-cm⁻¹ phenyl mode.

Compound **2** exhibits major absorption bands at 325 (ϵ 2650), 385 (ϵ 1930), and 685 nm (ϵ 435 M⁻¹ cm⁻¹). The Raman enhancement profile for ν_{as} (Fe—O—Fe) shows greatest intensity upon excitation within the 385-nm absorption band (Figure 2, inset), in agreement with its assignment as oxo \rightarrow Fe CT. The selective enhancement of the ν_{as} mode is explained by asymmetry in the oxo \rightarrow Fe^{III} transition, with the structural change in the electronic excited state corresponding to the atomic displacements of the asymmetric stretch. The 685-nm band is likely to have metal-to-metal CT character based on its additional enhancement of the Fe—O—Fe stretch, its large half-width (fwhm) of 3500 cm⁻¹, and its ϵ of 435 M⁻¹ cm⁻¹. A similar assignment has been made for the 740-nm electronic transition in the mixed-valence complex, [Fe₂(OH)₃(L)₂]²⁺.¹²

(11) Gómez-Romero, P.; Witten, E. H.; Reiff, W. M.; Backes, G.; Sanders-Loehr, J.; Jameson, G. B. *J. Am. Chem. Soc.* **1989**, *111*, 9039-9047.

The nature of the bridging carboxylate ligands appears to play a major role in determining whether oxidants such as O₂ react with the diiron site via an inner-sphere or an outer-sphere mechanism. The enzyme ribonucleotide reductase quantitatively incorporates an atom from O₂ into the μ -oxo group, indicating that the conversion from diiron(II) to diiron(III) involves an inner-sphere reaction with O₂,¹³ and the diiron site has been shown to undergo carboxylate shifts upon change in oxidation state.^{2b} The acetate analogue of coordinatively saturated **1**, [Fe₂(OH)(OAc)₂L₂]⁺, has been proposed to undergo an inner-sphere reaction with O₂, where dissociation of a bridging carboxylate provides an open coordination site for O₂ binding.¹⁴ In contrast, the bridging oxygen of **1** itself is conserved during oxidation with ¹⁶O₂, H₂¹⁶O₂, or R₃N¹⁶O as demonstrated by the near quantitative recovery of Fe—¹⁸O—Fe in both **2-BPh₄** (Figure 2B) and **2-CF₃SO₃**. It is possible that the bulkier triphenylacetate of **1** may prevent the carboxylate shift, thereby directing the reaction to adopt a slower outer-sphere path with respect to the iron. This pathway could involve a hydrogen-bonded complex between the μ -OH of **1** and an oxygen atom of the oxidant. The unusual stability of mixed-valence **2** is most likely due to steric effects from the bulkier bridging ligands which constrain it to an outer-sphere oxidation.

The tendency of asymmetric diiron complexes to produce a strongly enhanced ν_{as} (Fe—O—Fe) mode at 700–850 cm⁻¹ has implications for the identification of reaction intermediates by RR spectroscopy. The lower end of the range overlaps with vibrations of di- μ -oxo diiron complexes which have been proposed as models for compound X of ribonucleotide reductase and compound Q of methane monooxygenase,¹⁵ whereas the upper end of the range overlaps with the ν (O—O) vibration of coordinated peroxide and the ν (Fe=O) vibration of high-valent iron intermediates.¹⁶ Thus, careful analyses and isotopic substitutions are required to achieve conclusive vibrational assignments for dinuclear iron species.

Acknowledgment. This work was supported by grants from the National Institutes of Health (GM 18865 to J.S.-L. and GM 46506 to K.S.H.). This paper is dedicated to Professor Ralph G. Wilkins, who first discovered the mixed-valence intermediate in hemerythrin,¹⁷ on the occasion of his 70th birthday.

Supporting Information Available: Synthetic details, elemental analyses, thermal ellipsoid plots, and tables of atomic positional and thermal parameters for compounds **1**, **2**, and **3** (42 pages). See any current masthead page for ordering and Internet access information.

JA9638871

(12) Gamelin, D. R.; Bommar, E. L.; Mathonière, C.; Kirk, M. L.; Wieghardt, K.; Girerd, J.-J.; Solomon, E. I. *Inorg. Chem.* **1996**, *35*, 4323-4335.

(13) Ling, J.; Sahlin, M.; Sjöberg, B.-M.; Loehr, T. M.; Sanders-Loehr, J. *J. Biol. Chem.* **1994**, *269*, 5595-5601.

(14) Feig, A. L.; Masschelein, A.; Bakac, A.; Lippard, S. J. *J. Am. Chem. Soc.* **1997**, *119*, 334-342.

(15) Que, L., Jr.; Dong, Y. *Acc. Chem. Res.* **1996**, *29*, 190-196.

(16) Oertling, W. A.; Kean, R. T.; Wever, R.; Babcock, G. T. *Inorg. Chem.* **1990**, *29*, 2633-2645.

(17) Wilkins, R. G.; Harrington, P. C. *Adv. Inorg. Biochem.* **1983**, *5*, 51-85.