Valence Detrapping in $Fe^{II}Fe^{III}$ Models of Iron-Oxo Proteins

Mark S. Mashuta,[1] Robert J. Webb,[2]
Kenneth J. Oberhausen,[1] John F. Richardson,[1]
Robert M. Buchanan,*,[1] and David N. Hendrickson*,[3]

Department of Chemistry, University of Louisville
Louisville, Kentucky 40292
School of Chemical Sciences
University of Illinois, Urbana, Illinois 61801
Department of Chemistry, D-006
University of California at San Diego
La Jolla, California 92093-0506

Received October 24, 1988

A binuclear oxo-bridged iron site is believed to be present in methane monooxygenase,[4] ribonucleotide reductase,[5] and purple acid phosphatase[6] and known for hemerythrin.[7] A few crystallographically characterized (μ-oxo)bis(μ-carboxylate)Fe_2^{III} model complexes have been reported[8-13] as well as two Fe_2^{II} complexes[14,15a] modeling deoxyhemerythrin. The synthesis and physical properties of two $Fe^{II}Fe^{III}$ complexes have been reported.[15,16] The crystal structure, however, of only one of these $Fe^{II}Fe^{III}$ complexes has been communicated.[15a] Two additional $Fe^{II}Fe^{III}$ complexes have been prepared by electrochemical[17] or chemical reduction[15b] of diiron(III) complexes. In this communication we show that an analogous $Fe^{II}Fe^{III}$ complex with imidazolyl instead of pyridine ligand arms valence detraps above ~100 K. Histidine ligation is known[18] to be present in the Fe_2^{III} methemerythrin site.

Several new $Fe^{II}Fe^{III}$ complexes of the composition $[Fe^{II}Fe^{III}(bimp)(\mu\text{-}O_2CR)_2]X_2$ have been prepared and characterized, where R is CH_3, CH_2CH_3, or Ph, X^- is ClO_4^-, BF_4^- or BPh_4^-, and H-bimp is pictured below:

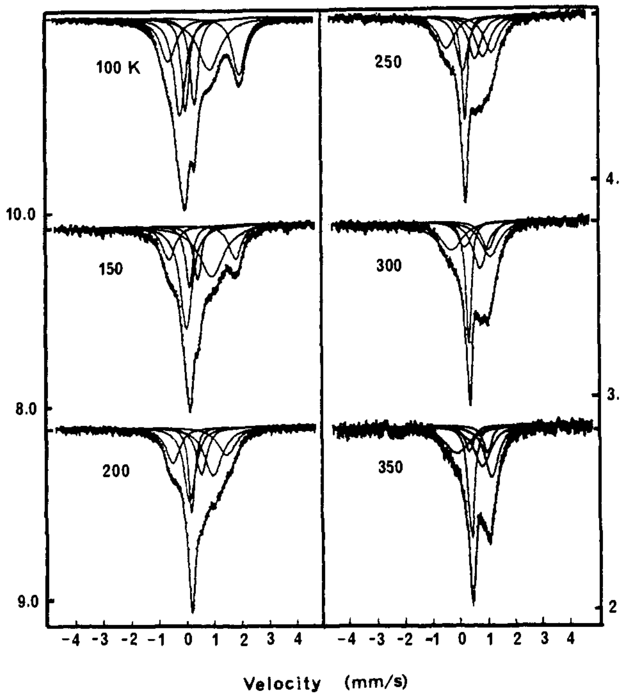
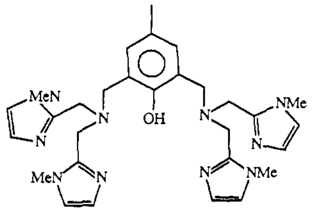


Figure 1. ^{57}Fe Mössbauer spectra at various temperatures for a polycrystalline sample of $[Fe^{II}Fe^{III}(bimp)(\mu\text{-}O_2CCH_3)_2](ClO_4)_2\cdot 2H_2O$ (**3**).

These new $Fe^{II}Fe^{III}$ complexes were prepared in a manner similar to that[19] used to prepare $[Mn^{II}Mn^{III}(bimp)(\mu\text{-}O_2CCH_3)_2](ClO_4)_2$.



The X-ray structure[20] was determined for $[Fe^{II}Fe^{III}(bimp)(\mu\text{-}O_2CPh)_2](BPh_4)_2\cdot 2CH_2CN$ (**1**) at 298 K. As with the 182 K structure[15a] of $[Fe^{II}Fe^{III}(bpmp)(\mu\text{-}O_2CCH_2CH_2CH_3)_2](BPh_4)_2\cdot 2CH_3COCH_3$ (**2**), the X-ray structure of **1** indicates a trapped-valence complex.

The electrochemistry of the Fe_2 bimp complexes differs from that reported[15a,16] for the Fe_2 bpmp complex. Two reversible one-electron waves[21] are observed at 435 and -245 mV vs SCE for the Fe_2 bimp complex. These waves correspond to $Fe_2^{III}/Fe^{II}Fe^{III}$ and $Fe^{II}Fe^{III}/Fe_2^{II}$ couples, respectively, which are reported[15a,16] to occur at 690 and -10 mV vs SCE for the Fe_2 bpmp complex. The bimp complex is easier to oxidize than the bpmp complex; however, it is interesting that the separation between the two waves is the same for both complexes. Complex **1** exhibits an intervalence charge-transfer transition at 7500 cm^{-1} (ϵ = 100 $M^{-1}\ cm^{-1}$).

It was most interesting to find that the EPR and ^{57}Fe Mössbauer properties of $[Fe^{II}Fe^{III}(bimp)(\mu\text{-}O_2CR)_2]X_2$ depends on R, X^-, and which solvate molecule is present. For example, even though

---

[1] University of Louisville.

[2] University of Illinois.

[3] University of California, San Diego.

[4] (a) Woodland, M. P.; Patil, D. S.; Cammack, R.; Dalton, H. *Biochim. Biophys. Acta* **1986**, *873*, 237-242. (b) Fox, B. G.; Surerus, K. K.; Münck, E.; Lipscomb, J. D. *J. Biol. Chem.* **1988**, *263*, 10553-10556.

[5] (a) Sjöberg, B.-M.; Gräsland, A. *Adv. Inorg. Biochem.* **1983**, *5*, 87-110. (b) Lammers, M.; Follman, H. *Struct. Bonding* **1983**, *54*, 27-91.

[6] Antanaitis, B. C.; Aisen, P. *Adv. Inorg. Biochem.* **1983**, *5*, 111-136.

[7] (a) Wilkins, P. C.; Wilkins, R. G. *Coord. Chem. Rev.* **1985**, *79*, 195-214, and references therein. (b) Lippard, S. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 344-361.

[8] Armstrong, W. H.; Spool, A.; Papaefthymiou, G. C.; Frankel, R. B.; Lippard, S. J. *J. Am. Chem. Soc.* **1984**, *106*, 3653-3667.

[9] Wieghardt, K.; Pohl, K.; Gebert, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 727-728.

[10] Toftlund, H.; Murray, K. S.; Zwack, P. R.; Taylor, L. F.; Anderson, O. P. *J. Chem. Soc., Chem. Commun.* **1986**, 191-193.

[11] Vincent, J. B.; Huffman, J. C.; Christou, G.; Li, Q.; Nanny, M. A.; Hendrickson, D. N.; Fong, R. H.; Fish, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 6898-6900.

[12] Gomez-Romero, P.; Casan-Pastor, N.; Ben-Hussein, A.; Jameson, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 1988.

[13] Oberhausen, K. J.; Richardson, J. F.; Webb, R. J.; Hendrickson, D. N.; Buchanan, R. M., manuscript in preparation.

[14] Chaudhuri, P.; Wieghardt, K.; Nuber, B.; Weiss, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 778-779.

[15] (a) Borovik, A. S.; Que, L., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 2345-2347. (b) Borovik, A. S.; Murch, B. P.; Que, L., Jr.; Papaefthymiou, V.; Münck, E. *J. Am. Chem. Soc.* **1987**, *109*, 7190-7191.

[16] (a) Suzuki, M.; Uehara, A.; Endo, K. *Inorg. Chim. Acta* **1986**, *123*, L9-L10. (b) Suzuki, M.; Uehara, A.; Oshio, H.; Endo, K.; Yanaga, M.; Kida, S.; Saito, K. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3547-3555.

[17] Hartman, J. A.; Raidin, R. L.; Chaudhuri, P.; Pohl, K.; Wieghardt, K.; Nuber, B.; Weiss, J.; Papaefthymiou, C.; Frankel, R. B.; Lippard, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 7387-7396.

[18] (a) Stenkamp, R. E.; Sieker, L. C.; Jensen, L. H. *J. Am. Chem. Soc.* **1984**, *106*, 618-622. (b) Sheriff, S.; Hendrickson, W. A.; Stenkamp, R. E.; Sieker, L. C.; Jensen, L. H. *Proc. Natl. Acad. Sci. U.S.A.* **1985**, *82*, 1104. (c) Stenkamp, R. E.; Sieker, L. C.; Jensen, L. H.; McCallum, J. D.; Sanders-Loehr, J. *Proc. Natl. Acad. Sci. U.S.A.* **1985**, *82*, 713.

[19] Buchanan, R. M.; Oberhausen, J. J.; Richardson, J. F. *Inorg. Chem.* **1988**, *27*, 971.

[20] Crystal data: $C_{95}H_{93}N_{12}O_5B_2Fe_2$, triclinic, $P\bar{1}$, a = 15.995 (3) Å, b = 23.475 (4) Å, c = 11.464 (3) Å, α = 97.57 (2)°, β = 101.74 (2)°, γ = 85.22 (1)°, V = 41.708 $Å^3$, Z = 2, D_c = 1.287 g/cm^3, μ = 4.055 cm^{-1}, R = 8.5% for 12082 observed reflections $I \geq 3\sigma(I)$ on an Enraf-Nonius diffractometer (Mo Kα radiation, 295 K). This is a preliminary structural report as final details concerning the disordered CH_3CN atoms and final cycles are yet to be completed. The phenoxo bridge Fe-O lengths are 1.951 (5) and 2.126 (5) Å for the Fe^{III} and Fe^{II} ions, respectively. The Fe^{III}-O-Fe^{II} angle is 115.1° and Fe---Fe separation is 3.426 (2) Å.

[21] Buchanan, R. M.; Mashuta, M. S.; Richardson, J. F.; Oberhausen, K. J.; Webb, R. J.; Nanny, M. A.; Hendrickson, D. N., submitted for publication.

0002-7863/89/1511-2745$01.50/0 © 1989 American Chemical Society

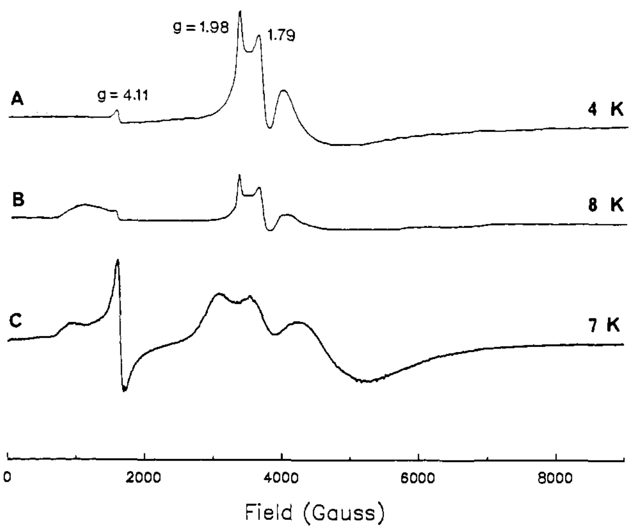


Figure 2. X-band EPR spectra of complex **3**. Traces A and B correspond to a 8000-G scan of a frozen acetonitrile solution at 4 and 8 K, respectively. Trace C is a spectrum of a ground polycrystalline sample at 7 K.

complex **1** is valence trapped, we have found that a microcrystalline sample of $[Fe^{II}Fe^{III}(bimp)(\mu\text{-}O_2CCH_3)_2](ClO_4)_2\cdot 2H_2O$ (**3**)[22] converts from valence trapped at temperatures below ~100 K to valence detrapped at temperatures above ~350 K, as indicated by Mössbauer spectra (Figure 1). In addition to equal-area high-spin Fe^{II} ($\delta = 0.881$ (4) and $\Delta E_Q = 2.537$ (8) mm/s) and Fe^{III} ($\delta = 0.3997$ (14) and $\Delta E_Q = 0.314$ (3) mm/s) doublets there is at 100 K a valence-detrapped doublet with $\Delta E_Q = 1.065$ (8) mm/s and $\delta = 0.567$ (4) mm/s vs iron foil at room temperature. At 350 K the valence-detrapped doublet dominates and has $\Delta E_Q = 0.59$ (5) mm/s and $\delta = 0.74$ (3) mm/s (all parameters are given in Supplementary Material). It is well known[23] that mixed-valence complexes can convert from valence trapped to valence detrapped over a large temperature range.

It is somewhat surprising that $Fe^{II}Fe^{III}$ complex **3** becomes detrapped in view of the very weak magnetic exchange interaction which is present. The value of μ_{eff} per molecule for **3** varies gradually from 7.21 μ_B at 298.3 K to 6.60 μ_B at 100 K, below which it drops more rapidly to 2.69 μ_B at 5.0 K. Fitting the data to the theoretical susceptibility equation resulting from an isotropic interaction characterized by $\hat{H} = -2J\hat{S}_1\cdot\hat{S}_2$, where $S_1 = {}^5/_2$ and $S_2 = 2$, gives $J = -2.5$ cm^{-1} and $g = 1.9$. The J value obtained with this simple model may be changed by employing a more complicated model incorporating the effects of double exchange[24] or Fe^{II} zero-field interactions. However, double exchange is not likely important for most of the change in the μ_{eff} vs T data for **1** occurs below ~100 K where this complex is largely valence trapped.

The weakness of the exchange interaction in **3** is reflected in the 7 K X-band EPR spectrum observed for a polycrystalline sample (Figure 2). Features are seen at $g = 6.95$, 4.05, 2.18, 1.90, and 1.44. Since J is small for **3** and the single-ion, zero-field interaction for the Fe^{II} ion is probably appreciable ($|D| \cong |J|$), the $\pm{}^1/_2$ and $\pm{}^3/_2$ Kramers doublets of the $S = {}^3/_2$ lowest energy excited state are close in energy to the $S = {}^1/_2$ ground state, as we found[25] for $Mn^{II}Mn^{III}$ complexes which also have $S_1 = {}^5/_2$ and $S_2 = 2$ ions. At 7 K there are appreciable populations in the $S = {}^1/_2$ and $S = {}^3/_2$ states. In low symmetry each of the three Kramers doublets could give three EPR signals, and there could even be transitions between them. Strain effects could also be important. In a later paper, considerably more EPR data and a detailed explanation will be given. The appearance of the EPR spectrum for these $Fe^{II}Fe^{III}$ complexes changes dramatically not only when the carboxylate substituent R or anion X^- are changed but also when the state of the complex is changed, for example, from polycrystalline solids to frozen solutions (Figure 2). Such a sensitivity is found for the EPR signal for the $Fe^{II}Fe^{III}$ protein site, which changes from one protein species to another[26] and even when the semi-met $Fe^{II}Fe^{III}$ form is prepared either by oxidizing the $Fe_2{}^{II}$ protein or by reducing the $Fe_2{}^{III}$ protein.[27]

Acknowledgment. We are thankful for support from National Institutes of Health Grant HL13652 (D.N.H.), National Science Foundation Grant RII-8610671 (R.M.B.), and the Commonwealth of Kentucky EPSCOR program.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond distances and angles for $[Fe^{II}Fe^{III}(bimp)(\mu\text{-}O_2CPh)_2](BPh_4)_2\cdot 2CH_2CN$ and variable temperature ^{57}Fe Mössbauer fitting parameters for $[Fe^{II}Fe^{III}(bimp)(\mu\text{-}O_2CCH_3)_2]\cdot(ClO_4)_2\cdot 2H_2O$, figures showing plots of μ_{eff} vs temperature for $Fe^{II}Fe^{III}$ complex **3**, and an ORTEP drawing of the $[Fe^{II}Fe^{III}(bimp)(\mu\text{-}O_2CPh)_2]^{2+}$ cation (20 pages). Ordering information is given on any current masthead page.

---

[22] Anal. $C_{33}H_{47}N_{10}O_{15}Cl_2Fe_2$ (**3**) Found (Calcd): C, 38.81 (39.36); H, 4.65 (4.67); N, 14.11 (13.92); Fe, 11.07 (11.13), Cl, 7.65 (7.05).

[23] (a) Dong, T.-Y.; Hendrickson, D. N.; Iwai, K.; Cohn, M. J.; Geib, S. J.; Rheingold, A. L.; Sano, H.; Motoyama, I.; Nakashima, S. *J. Am. Chem. Soc.* **1985**, *107*, 7996–8008. (b) Dong, T.-Y.; Kambara, T.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1986**, *108*, 5857–5865. (c) Sorai, M.; Nishimori, A.; Hendrickson, D. N.; Dong, T.-Y.; Cohn, M. J. *J. Am. Chem. Soc.* **1987**, *109*, 4266–4275.

[24] Papaefthymiou, V.; Girerd, J.-J.; Moura, I.; Moura, J. J. G.; Münck, E. *J. Am. Chem. Soc.* **1987**, *109*, 4703–4710.

[25] (a) Chang, H.-R.; Larsen, S. K.; Boyd, P. D. W.; Pierpont, C. G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1988**, *110*, 4565–4576. (b) Diril, H.; Chang, H.-R.; Nilges, M. J.; Zhang, X.; Potenza, J. A.; Schugar, H. J.; Isied, S. S.; Hendrickson, D. N. *J. Am. Chem. Soc.*, in press.

[26] (a) Kurtz, D. M.; Sage, J. T.; Hendrich, M.; Debrunner, P.; Lukat, G. S. *J. Biol. Chem.* **1983**, *258*, 2115. (b) Bertrand, P.; Guigliarelli, B.; Gayda, J. P. *Arch. Biochem. Biophys.* **1986**, *245*, 305. (c) Harrington, P. C.; Muhoberac, B. B.; Wharton, D. C.; Wilkins, R. G. *Biochemistry* **1981**, *20*, 6135. (d) Debrunner, P. C.; Hendrich, M. P.; DeJersey, J.; Keough, D. T.; Sage, J. T.; Zerner, B. *Biochim. Biophys. Acta* **1983**, *745*, 103. (e) Davis, J. C.; Averill, B. A. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 4623–4627. (f) Woodland, M. P.; Dalton, H. *J. Biol. Chem.* **1984**, *259*, 53. (g) Chasteen, N. D.; Antannaitis, B. C.; Aisen, P. *J. Biol. Chem.* **1985**, *260*, 2926.

[27] Muhoberac, B. B.; Wharton, D. C.; Babcock, L. M.; Harrington, P. C.; Wilkins, R. G. *Biochim. Biophys. Acta* **1980**, *626*, 337–345.