for the catalytic asymmetric construction of C–C bonds.

In conclusion, we have found that rare earth alkoxides exhibit basic character, which can be utilized in aldol, cyanosilylation, and nitroaldol reactions. Furthermore, we have succeeded in preparing the optically active lanthanum alkoxide for the first time and demonstrating that it is a useful catalyst for a catalytic asymmetric nitroaldol reaction. Many applications of this new catalytic methodology in synthesis are under investigation.

Acknowledgment. This study was financially supported by a Grant-in-Aid for Scientific Research on Priority Areas (Multiplex Organic Systems) from the Ministry of Education, Science and Culture, Japan.

Supplementary Material Available: Experimental procedures and spectral data for **2b**, **5a**, (*R*)-**5d**, and **7a**, and the ^{1}H and ^{13}C NMR spectra of **8** and **ii** (7 pages). Ordering information is given on any current masthead page.

New Class of Bridged Diiron(III) Complexes with a Single Hydroxo Bridge. The Preparation and Structure of (μ-Hydroxo)bis((octaethylporphinato)iron(III)) Perchlorate

W. Robert Scheidt,*[1a] Beisong Cheng,[1a] Martin K. Safo,[1a] Fabio Cukiernik,[1b] Jean-Claude Marchon,*[1b] and Peter G. Debrunner*[1c]

Department of Chemistry and Biochemistry
University of Notre Dame
Notre Dame, Indiana 46556
Laboratoire de Chimie de Coordination
Unité de Recherche Associée au CNRS No. 1194
Département de Recherche Fondamentale
Centre d'Études Nucléaires de Grenoble
38041 Grenoble Cedex, France
Department of Physics, University of Illinois
Urbana, Illinois 61801

Received December 20, 1991

We report that the μ-oxo-bridged iron(III) octaethylporphyrinate, $[Fe(OEP)]_2O$, can be protonated to yield the μ-hydroxo species, $\{[Fe(OEP)]_2(OH)\}^+$, via a mixed-phase reaction.[2] The formulation of this complex has been confirmed by an X-ray diffraction study[3] which reveals a single bridging group and a single counterion per two iron(III) porphyrinate units as shown in Figure 1. The lack of any other "supporting" bridging ligands for a (μ-hydroxo)diiron(III) complex is unprecedented[4] as all such previously characterized complexes have either one or two additional bridging ligands, typically either carboxylate or hydroxide groups. Thus this compound represents the first example of a new class of bridged diiron(III) complexes with a single hydroxo bridge. Moreover, model hydroxoiron porphyrinate species are of biological interest, as they have been suggested as possible intermediates[5] in the reduction of dioxygen to water by the hemoprotein cytochrome *c* oxidase, and the biophysical properties of well-defined model species are required in defining these intermediates.

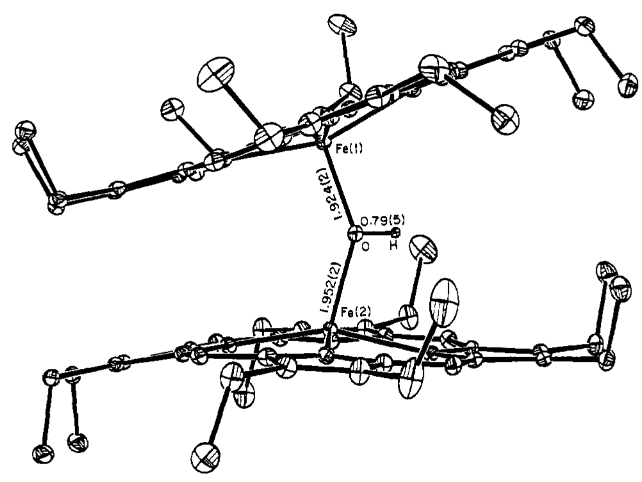

Figure 1. ORTEP diagram of the structure of the cation of $\{[Fe(OEP)]_2(OH)\}ClO_4$. Thermal ellipsoids are drawn at the 25% probability level. Porphyrin hydrogen atoms are omitted for clarity, while the refined H atom position of the bridging hydroxide ligand is shown. The Fe–O(H)–Fe bridge is in the plane of the paper.

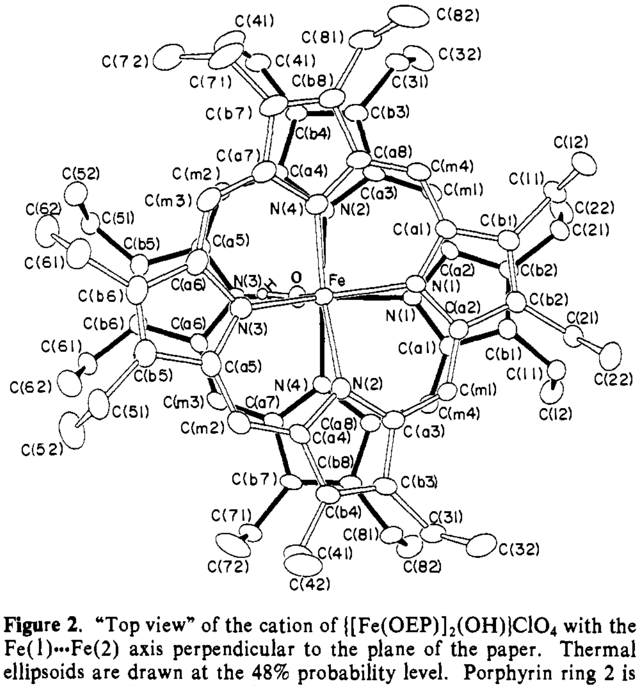

Figure 2. "Top view" of the cation of $\{[Fe(OEP)]_2(OH)\}ClO_4$ with the Fe(1)···Fe(2) axis perpendicular to the plane of the paper. Thermal ellipsoids are drawn at the 48% probability level. Porphyrin ring 2 is drawn with solid bonds while ring 1 is drawn with open bonds.

The structure of this new molecule exhibits several interesting features, many that are distinct from previously characterized (μ-hydroxo)diiron(III) complexes. The two Fe–O(OH) distances of 1.924 (3) and 1.952 (3) Å are similar to or slightly shorter than those observed in previously characterized multibridged (μ-hydroxo)diiron(III) complexes, whose values range from 1.96 to 2.06 Å,[4,6,7] but are significantly longer than those of any μ-oxo

---

[1] (a) University of Notre Dame. (b) Centre d'Études Nucléaires de Grenoble. (c) University of Illinois at Urbana—Champaign.

[2] To $[Fe(OEP)]_2O$ (350 mg, 0.293 mmol) in CH_2Cl_2 (15 mL) was slowly added 20 mL of dilute aqueous $HClO_4$ (0.220 mmol) with magnetic stirring. After stirring for an additional 3 min, the two phases were separated and the CH_2Cl_2 phase was dried with $MgSO_4$, filtered, and washed with CH_2Cl_2. The filtrate was taken to dryness, redissolved in 15 mL of CH_2Cl_2, and crystallized by allowing hexane to diffuse into the solution. After 10 days, crystalline $\{[Fe(OEP)]_2(OH)\}ClO_4$ was isolated.

[3] The complex crystallizes in the triclinic space group $P\bar{1}$, with a = 14.813 (3) Å, b = 14.838 (5) Å, c = 18.389 (5) Å, α = 80.75 (3)°, β = 70.40 (2)°, and γ = 89.65 (2)°, V = 3753.0 Å^3, Z = 2($\{[Fe(OEP)]_2(OH)\}ClO_4\cdot 3CH_2Cl_2$), 14983 observed data, all observations at 124 K. Low-temperature data collection is necessary to avoid loss of CH_2Cl_2 solvate molecules. The structure was solved by direct methods (MULTAN) and difference Fourier techniques. Most porphyrin hydrogen atoms, including the hydroxo hydrogen atom, were located from difference Fourier syntheses. All hydrogen atoms were idealized except the hydroxo hydrogen atom, whose coordinates and temperature factor were refined by full-matrix least-squares methods. Final refinements with anisotropic thermal parameters for all non-hydrogen atoms and an isotropic thermal parameter for the μ-hydroxo H atom led to R_1 = 0.076, R_2 = 0.084.

[4] Kurtz, D. M., Jr. *Chem. Rev.* **1990**, *90*, 585.

[5] Han, S.; Ching, Y.-C.; Rousseau, D. L. *Nature* **1990**, *348*, 89 and references therein.

complex, whose values range from 1.73 to 1.82 Å.[4,8,9] The resulting Fe···Fe distance is 3.707 (1) Å. The Fe–O(H)–Fe angle of 146.2 (2)° is significantly larger than the analogous angles in the previously known multibridged μ-hydroxo systems, whose values range from 103.2 to 123.1°.[4,6,7] This relatively large Fe–O–Fe angle is a consequence, at least in part, of the steric requirements of bringing two porphyrin rings close together (Figure 1). It is important to note that all μ-oxo porphyrin derivatives have much larger Fe–O–Fe angles because of these steric requirements; the smallest such angle is 161.1°, found in a covalently linked biporphyrin,[9] while all others are much closer to linearity (>170°).[8] The displacement of each iron(III) from its respective 24-atom porphyrin plane is 0.44 or 0.41 Å; the average Fe–N_p bond distance is 2.037 (10) Å. The values of both parameters are those expected for five-coordinate high-spin iron(III) derivatives.[10] The average O–Fe–N_p bond angle is 101°.[11]

A perhaps unexpected feature of the interaction between the two porphyrin rings is seen in Figure 2. All pyrrole rings nearly overlap; the $1N_1$–Fe(1)–Fe(2)–$2N_1$ torsion angle is 8.6°. The close approach of the two porphyrin rings leads to a core deformation in which the two closest pyrrole groups are more nearly coplanar than the complete porphyrin ring systems;[12] a curious feature is that porphyrin ring 2 is much more distorted than ring 1. The bridging hydroxo ligand is in an extremely hydrophobic environment; the closest *intermolecular or interionic* distance to the hydroxide oxygen atom is 6.755 Å to a perchlorate oxygen atom; the hydroxide hydrogen atom to oxygen distance is *larger* still (H···O = 7.433 Å). However, the hydrogen atom is close to one porphinato nitrogen atom (H···2N(3) = 2.49 Å); the distance to the next closest nitrogen is longer at H···1N(3) = 2.89 Å. We can speculate that this highly unusual hydroxide ion environment is quite stabilizing for this monobridged complex, with the porphyrin macrocycles inhibiting substantial rearrangement of the entire ligand set while the hydrophobic character of the bridge binding site inhibits formation of a di(μ-hydroxo) bridge.[13]

The UV–vis spectrum of $\{[Fe(OEP)]_2(OH)\}^+$ has a strongly blue-shifted Soret band with λ_{max} (CH_2Cl_2) at 361.7 nm ($\epsilon = 1.76 \times 10^5$ cm^{-1} M^{-1}). To our knowledge, this blue shift is the largest observed for any iron(III) porphyrinate derivative and presumably reflects the extremely close interporphyrin ring separation[14] caused by the hydroxide bridge. For comparison, the Soret band of dimeric $[Fe(OEP)]_2O$ is observed at 385 nm while that of monomeric $[Fe(OEP)(OClO_3)]$ is at 389 nm. Finally, it should be noted that the complex has substantial stability even in dilute solution; the spectrum of an 8.0×10^{-5} M CH_2Cl_2 solution is unchanged for at least 2 days.

Mössbauer spectra of $\{[Fe(OEP)]_2(OH)\}^+$ show a quadrupole split doublet with $\Delta E_q = 1.13$ mm/s and an isomer shift of 0.40 mm/s, consistent with high-spin iron(III). The Mössbauer spectra also show that bulk samples of the complex contain small amounts of a second species with $\Delta E_q = 2.76$ mm/s and an isomer shift of 0.36 mm/s. Our best bulk sample to date has this impurity present at ~8–10%. Magnetic susceptibility measurements are, of course, complicated by the presence of this impurity,[15] thus far preventing an accurate estimate of the Fe–Fe coupling mediated by the hydroxide bridge. Our preliminary measurements indicate that relatively large J values ($J = -50$ to -160 cm^{-1}) lead to acceptable fits of the magnetic susceptibility versus temperature curves of the impure bulk samples.[17] The difference in magnetic coupling between $\{[Fe(OEP)]_2(OH)\}^+$ and $[Fe(OEP)]_2O$,[21] both of which are devoid of additional bridging ligands, may well be smaller than that observed earlier for the protonated and unprotonated forms of (μ-oxo)bis(μ-acetato)diiron(III) complexes.[7] Finally, it is to be noted that samples of $\{[Fe(OEP)]_2(OH)\}^+$ do not show an EPR signal either in the solid state or in CH_2Cl_2 solution (77 K), consistent with coupling between the two iron centers.

Work in progress on this novel chemical system includes the preparation of μ-hydroxo species in anhydrous media, the preparation of μ-hydroxo-bridged diiron species with other porphyrinate ligands, the study of the kinetics of the protonation and possible ligand-exchange reactions, the preparation of purer samples for temperature-dependent magnetic susceptibility study to better define the magnetic interactions between the diiron(III) center, a detailed assignment of the (porphyrinate)Fe–(OH) vibrational spectrum, and the preparation of related metalloporphyrin derivatives (especially manganese) and mixed-valence species (especially Fe(II)–Fe(III)).

Acknowledgment. We thank the National Institutes of Health for support of this research under GM-38401 (W.R.S.) and GM-16406 (P.G.D.). W.R.S. acknowledges the kind hospitality of Professor Irene Morgenstern-Badarau (University of Paris, Orsay) during the time when this manuscript was first written.

Supplementary Material Available: Table SI containing atomic coordinates and Tables SII and SIII containing complete listings of bond distances and angles for $\{[Fe(OEP)]_2(OH)\}ClO_4$ (12 pages); listing of observed and calculated structure factor amplitudes (×10) for $\{[Fe(OEP)]_2(OH)\}ClO_4$ (62 pages). Ordering information is given on any current masthead page.

---

(6) (a) Murch, B. P.; Bradley, F. C.; Boyle, P. D.; Papaefthymiou, V.; Que, L., Jr. *J. Am. Chem. Soc.* **1987**, *109*, 7993. (b) Murch, B. P.; Boyle, P. D.; Que, L., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 6728. (c) Chiari, B.; Piovesana, O.; Tarantelli, T.; Zanazzi, P. F. *Inorg. Chem.* **1983**, *22*, 2781. (d) Bailey, N. A.; McKenzie, E. D.; Worthington, J. M.; McPartlin, M.; Tasker, P. A. *Inorg. Chim. Acta* **1977**, *25*, L137. (e) Borer, L.; Thalken, L.; Ceccarelli, C.; Glick, M.; Zhang, J. H.; Reiff, W. M. *Inorg. Chem.* **1983**, *22*, 1719. (f) Thich, J. A.; Ou, C.-C.; Powers, D.; Vasilious, B.; Mastropaolo, D.; Potenza, J. A.; Schugar, H. J. *J. Am. Chem. Soc.* **1976**, *98*, 1425. (g) Treichel, P. M.; Dean, W. K.; Calabrese, J. C. *Inorg. Chem.* **1973**, *12*, 2908. (h) Ou, C.-C.; Lalancette, R. A.; Potenza, J. A.; Schugar, H. J. *J. Am. Chem. Soc.* **1978**, *100*, 2053.

(7) (a) Armstrong, W. H.; Lippard, S. J. *J. Am. Chem. Soc.* **1984**, *106*, 4632. (b) Chaudhuri, P.; Wieghardt, K.; Nuber, B.; Weiss, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 778.

(8) (a) Strauss, S. H.; Pawlik, M. J.; Skowyra, J.; Kennedy, J. R.; Anderson, O. P.; Spartalian, K.; Dye, J. L. *Inorg. Chem.* **1987**, *26*, 724. (b) Hoffman, A. B.; Collins, D. M.; Day, V. W.; Fleischer, E. B.; Srivastava, T. S.; Hoard, J. L. *J. Am. Chem. Soc.* **1972**, *94*, 3620. (c) Lay, K. L.; Buchler, J. W.; Kenny, J. E.; Scheidt, W. R. *Inorg. Chim. Acta* **1986**, *123*, 91. (d) Swepston, P. N.; Ibers, J. A. *Acta Crystallogr., Sect. C* **1985**, *C41*, 671. (e) Bartczak, T. J.; Latos-Grazynski, L.; Wyslouch, A. *Inorg. Chim. Acta* **1990**, *171*, 205. (f) Ivanca, M. A.; Lappin, A. G.; Scheidt, W. R. *Inorg. Chem.* **1991**, *30*, 711. (g) Our unpublished X-ray structure determination of $[Fe(OEP)]_2O$ shows two equivalent Fe–O bond lengths (1.754 and 1.760 Å) and an Fe–O–Fe angle of 171.84°.

(9) Landrum, J. T.; Grimmett, D.; Haller, K. J.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1981**, *103*, 2640.

(10) Scheidt, W. R.; Reed, C. A. *Chem. Rev.* **1981**, *81*, 543.

(11) Even though the average values of the O–Fe–N_p angles at the two iron atoms are the same, the environments at the two irons are very different. Fe(1) has four nearly equivalent O–Fe–N_p angles (98.77 (11), 99.20 (12), 102.51 (12), and 101.94 (12)°), while Fe(2) has very nonequivalent O–Fe–N_p angles (98.30 (11), 101.95 (11), 113.92 (11), and 89.12 (11)°).

(12) The dihedral angle between the two close pyrrole rings is 6.6° while the dihedral angle between the two porphyrin mean planes is 19.9°.

(13) Boersma, A. D., and Goff, H. M. (*Inorg. Chim. Acta* **1984**, *89*, L49–L52) have reported the solution characterization of dimeric iron(III) species that they formulated as dihydroxo-bridged species.

(14) Buchler, J. W.; De Cian, A.; Fischer, J.; Kihn-Botulinski, M.; Paulus, H.; Weiss, R. *J. Am. Chem. Soc.* **1986**, *108*, 3652–3659.

(15) We have corrected the experimental data using the susceptibility data observed for intermediate-spin $[Fe(OEP)(OH_2)]ClO_4$, which we have prepared[16] in pure form by the reaction of $[Fe(OEP)]_2O$ with somewhat larger quantities of protons.

(16) Cheng, B.; Debrunner, P. G.; Scheidt, W. R. Work in progress.

(17) Further evidence for relatively strong coupling between the two iron(III) ions comes from the paramagnetic NMR line shifts[18-20] of the methyl and methylene protons. Over the temperature range 20 to −55 °C, the methylene proton peaks of $\{[Fe(OEP)]_2(OH)\}ClO_4$ shift by less than 0.9 ppm and the methyl peak shifts by even less, which is consistent with relatively large (negative) values of the coupling constant J. We thank a reviewer for suggesting this experiment.

(18) Maroney, M. J.; Kurtz, D. M., Jr.; Nocek, J. M.; Pearce, L. L.; Que, L., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 6871.

(19) La Mar, G. N.; Eaton, G. R.; Holm, R. H.; Walker, F. A. *J. Am. Chem. Soc.* **1973**, *95*, 63.

(20) Balch, A. L.; Hart, R. L.; Latos-Grażyński, L. *Inorg. Chem.* **1990**, *29*, 3253.

(21) Lueken, H.; Buchler, J. W.; Lay, K. L. *Z. Naturforsch.* **1976**, *31b*, 1596.