Mixed-Valent Heptairon Chloride Cluster Supported by the Porphyrin-Linked Dicarboxylate Ligand PDK

Xiao-Xiang Zhang and Stephen J. Lippard*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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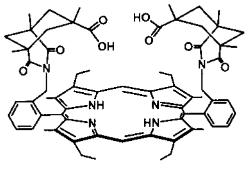
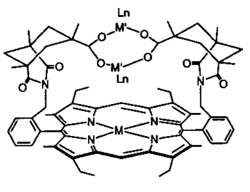
Significant advances have been achieved in the design and synthesis of metalloporphyrins and dinuclear metal complexes for mimicking the structures and functions of the active sites of cytochrome P-450[1] and non-heme diiron enzymes.[2] These synthetic model studies provide useful information about the metalloenzymes that otherwise would be difficult to obtain. Our laboratory has a longstanding interest in obtaining functional models of soluble methane monooxygenase (sMMO).[3] Efforts to prepare such compounds have on occasion led to polyiron clusters having unprecedented structural and electronic properties. Examples include the molecular 18-wheeler[4] and ferric wheel,[5] mixed-valent polyiron oxo complexes that model the biomineralization of the ferritin core[6] and complexes containing $\{Fe_4O_2\}^{8+}$ centers.[7]

Recently, we designed and synthesized[8] a porphyrin-linked dicarboxylate ligand PDK, where H_4(α,α-PDK) is α,α-5,15-bis-(α-*N*-(Kemp's triacid imido)-*o*-tolyl)-2,8,12,18-tetraethyl-3,7,13,-17-tetramethylporphyrin, that incorporates features of both the hydroxylase (MMOH) and reductase (MMOR) proteins in the sMMO system.[2a,9] Assembling both heme iron and carboxylate-bridged non-heme diiron units in a single molecule, this ligand can supply a redox-active metalloporphyrin to deliver electrons, like MMOR, as well as the bis(carboxylato)diiron core of MMOH to activate substrates. We previously reported[10] that reaction of H_4(α,α-PDK) with $FeBr_2$ in the presence of 2,6-lutidine afforded a novel triiron(II) complex $[Fe_3(\alpha,\alpha\text{-PDK})(Lut)(Br)_2(\eta^2\text{-}\mu_3\text{-HBr})]$ (**1**), in which a neutral HBr molecule bound to the three ferrous ions in an unprecedented manner. A similar triiron(II) complex $[Fe_3(\alpha,\alpha\text{-PDK})(Lut)(I)_2(\eta^2\text{-}\mu_3\text{-HI})]$ (**2**), with basically the identical geometrical arrangement to **1**, was isolated when FeI_2 was used to replace $FeBr_2$.[10] Here we report that reaction of H_4(α,α-PDK) with $FeCl_2$ under the same conditions gives a mixed-valent heptairon chloride cluster $[Fe_7(\alpha,\alpha\text{-PDK})_2(\mu_4\text{-Cl})(\mu_3\text{-Cl})_4(\mu\text{-Cl})_2\text{-}(Cl)(H_2O)_2]$ (**3**), the nature of which is described.



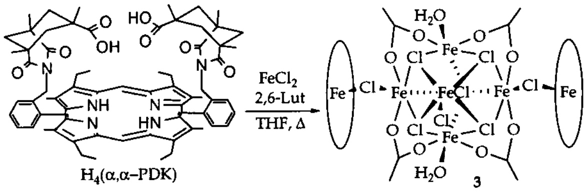
H_4(α,α-PDK)



$[MM'_2L_n(\alpha,\alpha\text{-PDK})]$

Compound **3** was obtained in 65% yield by reacting H_4(α,α-PDK) with excess $FeCl_2$ in the presence of 2,6-lutidine in THF at reflux under an inert atmosphere (Scheme 1). An X-ray crystal structure determination revealed the formation of a compound having an unprecedented structure of C_2 symmetry containing a central open cage Fe_5Cl_5 cluster supported by four bridging carboxylate groups from two PDK ligands (Figure 1, Scheme 1). In order to supply bridging carboxylate ligands to the central cluster, the two Kemp's triacid moieties in each PDK ligand of **3** have rotated toward one side of the porphyrin ring, away from the convergent orientation adopted in **1** and **2**.[10] The two porphyrin units both have bound iron and are arranged in a V-shape, the dihedral angle between the rings being 117°. The individual rings are relatively planar (rmsd ± 0.146 Å), compared to the nonplanar, distorted conformation found in **1** (rmsd ± 0.288 Å) and **2** (rmsd ± 0.212 Å).[10] The coordination sphere of each 5-coordinate heme iron Fe(1) is completed by chloride ion Cl(1) that forms a bridge to non-heme iron Fe(2) in the central cluster. Four of the five non-heme iron atoms in the cluster (Figure 1), Fe(2), Fe(2A), Fe(3), and Fe(3A), form an approximately planar quadrilateral, the edges of which are bridged by carboxylates from the PDK ligands. All have six-coordinate octahedral geometries. The fifth iron atom, Fe(4), in the cluster is coordinated only by chloride ions and has five-coordinate, square-pyramidal geometry. In addition to the two bridging chloride ions, Cl(1) and Cl(1A), linking the heme and non-heme iron atoms, there are three other chloride ion binding modes in the molecule including one μ_4-Cl ion, Cl(5), four μ_3-Cl ions, Cl(2), Cl(2A), Cl(3), and Cl(3A), and one terminal Cl ion, Cl(4). The average Fe−Cl bond lengths decrease, as expected, with coordination number. The distances are 2.20 Å to the terminal chloride ion, 2.34 Å to μ_2-Cl, 2.48 Å to μ_3-Cl, and 2.69 Å to μ_4-Cl. The significantly longer distances between the chloride ion with the unusual μ_4-face-bridging coordination mode and the iron atoms indicate very weak Fe−Cl bonding.

Scheme 1



Based on charge balance, the heptairon complex **3** can be formulated as a mixed-valent species, $[Fe^{III}_2Fe^{II}_5(\alpha,\alpha\text{-PDK})_2(\mu_4\text{-}$

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(1) (a) Mansuy, D. *Coord. Chem. Rev.* **1993**, *125*, 129−142. (b) Meunier, B. *Chem. Rev.* **1992**, *92*, 1411−1456.

(2) (a) Feig, A. L.; Lippard, S. J. *Chem. Rev.* **1994**, *94*, 759−805. (b) Que, L., Jr.; True, A. E. *Prog. Inorg. Chem.* **1990**, *38*, 97−200. (c) Que, L., Jr.; Dong, Y. *Acc. Chem. Res.* **1996**, *29*, 190−196.

(3) (a) Watton, S. P.; Masschelein, A.; Rebek, J., Jr.; Lippard, S. J. *J. Am. Chem. Soc.* **1994**, *116*, 5196−5205. (b) Herold, S.; Lippard, S. J. *J. Am. Chem. Soc.* **1997**, *119*, 145−156. (c) LeCloux, D. D.; Barrios, A. M.; Mizoguchi, T. J.; Lippard, S. J. *J. Am. Chem. Soc.* **1998**, *120*, 9001−9014. (d) Lee, D.; Lippard, S. J. *J. Am. Chem. Soc.* **1998**, *120*, 12153−12154. (e) LeCloux, D. D.; Barrios, A. M.; Lippard., S. J. *Bioorg. Med. Chem.* **1999**, *7*, 763−772.

(4) Watton, S. P.; Fuhrmann, P.; Pence, L. E.; Caneschi, A.; Cornia, A.; Abbati, G. L.; Lippard, S. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2774−2776.

(5) Taft, K. L.; Delfs, C. D.; Papaefthymiou, G. C.; Foner, S.; Gatteschi, D.; Lippard, S. J. *J. Am. Chem. Soc.* **1994**, *116*, 823−832.

(6) Taft, K. L.; Papaefthymiou, G. F.; Lippard, S. J. *Science* **1993**, *259*, 1302−1305.

(7) (a) Gorun, S. M.; Lippard, S. J. *Inorg. Chem.* **1988**, *27*, 149−156. (b) Armstrong, W. H.; Roth, M. E.; Lippard, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 6318−6326.

(8) Zhang, X.-X.; Lippard, S. J. *J. Org. Chem.* **2000**, *65*, 5298−5305.

(9) Gassner, G. T.; Lippard, S. J. *Biochemistry* **1999**, *38*, 12768−12785.

(10) Zhang, X.-X.; Fuhrmann, P.; Lippard, S. J. *J. Am. Chem. Soc.* **1998**, *120*, 10260−10261.

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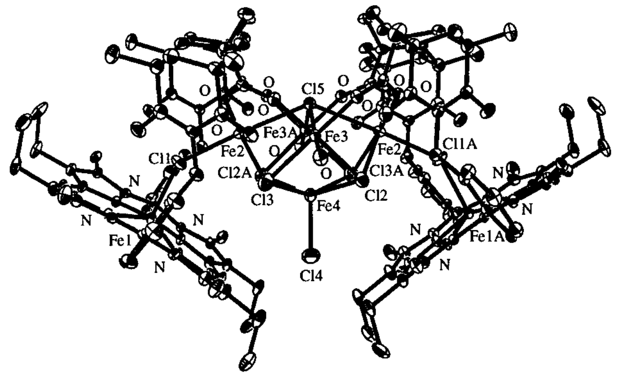


Figure 1. ORTEP plot of **3**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn to enclose 30% probability. Selected interatomic distances (Å) and angles (deg): Fe(1)···Fe(2), 4.432(2); Fe(2)···Fe(3), 3.475(2); Fe(2)···Fe(4), 3.423(2); Fe(3)···Fe(4), 3.299(2); Fe(1)−N(301), 2.058(6); Fe(1)−N(302), 2.057(6); Fe(1)−N(303), 2.051(6); Fe(1)−N(304), 2.051(5); Fe(1)−Cl(1), 2.254(3); Fe(2)−O(102), 2.033(5); Fe(2)−O(202), 2.055(5); Fe(2)−Cl(1), 2.432(3); Fe(2)−Cl(3), 2.498(3); Fe(2)−Cl(2A), 2.539(3); Fe(2)−Cl(5), 2.749(2); Fe(3)−O(101), 2.016(5); Fe(3)−O(201), 2.024(6); Fe(3)−O(401), 2.162(6); Fe(3)−Cl(2), 2.449(3); Fe(3)−Cl(3), 2.461(3); Fe(3)−Cl(5), 2.638(2); Fe(4)−Cl(2), 2.476(2); Fe(4)−Cl(2A), 2.476(2); Fe(4)−Cl(3), 2.456(3); Fe(4)−Cl(3A), 2.456(3); Fe(4)−Cl(4), 2.197(5); Fe(1)−Cl(1)-Fe(2), 142.1(1); Fe(3)−Cl(2)-Fe(4), 84.11(9); Fe(3)−Cl(2)−Fe(2A), 90.11(10); Fe(4)−Cl(2)−Fe(2A), 86.08(9); Fe(4)−Cl(3)−Fe(3), 84.27(11); Fe(2)−Cl(3)−Fe(4), 87.39(11); Fe(2)−Cl(3)−Fe(3), 88.95(11); Fe(3)−Cl(5)−Fe(3A), 131.77(13).

Cl)(μ_3-Cl)$_4$(μ-Cl)$_2$Cl(H$_2$O)$_2$]. The mixed-valent nature of the compound was confirmed by a Mössbauer study. The Mössbauer spectrum (Figure 2) of solid **3** at 77 K displays two overlapping quadrupole doublets. Doublet A has $\delta = 0.92$ mm/s and $\Delta E_Q =$ 2.47 mm/s; doublet B has $\delta = 0.47$ mm/s and $\Delta E_Q = 1.10$ mm/s. The isomer shifts are characteristic of high-spin Fe(II) and high-spin Fe(III), respectively. The approximate area ratio between doublet A and doublet B suggests that the two heme iron atoms are in the +3 oxidation state and that the five non-heme irons have +2 oxidation. The assignment of doublet B to the Fe(III) heme units is in agreement with Mössbauer parameters typical of high-spin iron(III) porphyrin complexes.[11] The short Fe(1)−Cl(1) distance of 2.254(3) Å further supports the assignment.

The formation of the mixed-valent iron chloride cluster **3** rather than the chloride analogue of **1** and **2** was unexpected in view of the generally similar reactivities of FeCl$_2$, FeBr$_2$, and FeI$_2$. The failure to isolate [Fe$_3$(α,α-PDK)(Lut)(Cl)$_2$(η^2-μ_3-HCl)] is presumably due to its instability. We propose (Scheme 2) that this complex forms initially upon reaction of FeCl$_2$ with H$_4$(α,α-PDK), as occurs for FeBr$_2$ and FeI$_2$. Because of the smaller radius of the chloride (1.81 Å) compared to bromide (1.96 Å) and iodide (2.20 Å) ion, the anticipated product is unstable and converts to an Fe$^{II}_2$Fe^{III} intermediate (Scheme 2). This conversion requires formal oxidation of heme iron(II) to iron(III), a reaction that occurs when HCl is added to iron(II) porphyrin complexes in the synthesis of iron(III) porphyrins.[12] A similar oxidation occurred when **1** was treated with excess propionitrile.[10,13] In the presence of a trace amount of water, presumably from FeCl$_2$, lutidine bound to the non-heme iron atoms in the putative Fe$^{II}_2$Fe^{III} intermediate will be displaced to afford a species having low coordinate non-heme iron(II) centers, which dimerizes to generate a new, Fe$^{II}_4$-Fe$^{III}_2$ intermediate. Reaction with additional FeCl$_2$ produces the final isolated complex **3**.

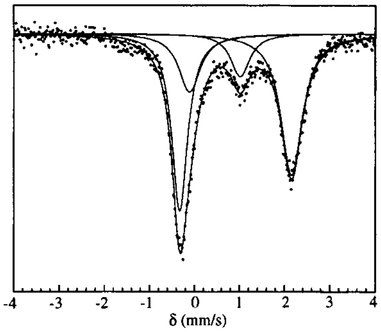
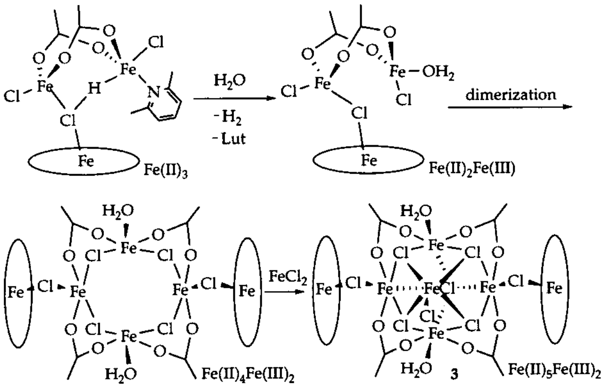


Figure 2. Mössbauer spectrum of **3** at 77 K. The solid lines are the theoretical fits corresponding to the superposition of two inequivalent iron sites. See text for derived Mössbauer parameters.

Scheme 2



Complex **3** represents a very rare example[14] of a molecule containing four different halide coordination modes, terminal, μ_2, μ_3, and μ_4, in a single molecule, the μ_4-Cl having unusual tetragonal pyramidal geometry. The proposed mechanism for formation of **3** provides a rationale for the reaction difference of FeCl$_2$ with H$_4$(α,α-PDK) compared to FeBr$_2$ and FeI$_2$ and is consistent with the proposed binding mode of the HX molecules in **1** and **2**.[10] Preliminary results show that the PDK ligand can support the formation of a variety of metal clusters having interesting structural features.[13] Once again, our attempts to assemble carboxylate−diiron centers[3−7] to mimic that in sMMO and related proteins have afforded a novel polyiron cluster.

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Supporting Information Available: Synthetic and X-ray structural details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Sams, J. R.; Tsin, T. B. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. IV.; pp 425−477.

(12) (a) Adler, A. D.; Longo, F. R.; Kampas, F.; Kim, J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443−2445. (b) Kobayashi, H.; Higuchi, T.; Kaizu, Y.; Osada, H.; Aoki, M. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3137−3141.

(13) Zhang, X.-X.; Lippard, S. J. Unpublished results.

(14) Tsai, H.-L.; Wang, S.; Folting, K.; Streib, W. E.; Hendrickson, D. N.; Christou, G. *J. Am. Chem. Soc.* **1995**, *117*, 2503−2514.