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Air-Stable, Electron-Deficient Fe(II) Catalytic Porphyrins. Characterization and Molecular Structures of Rare High Spin Fe(II) Hexacoordinated Porphyrins

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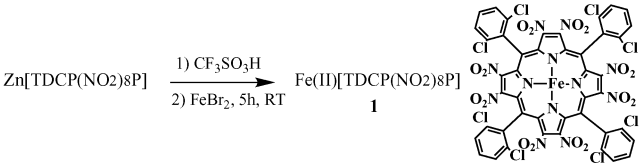
The synthesis, characterization, and molecular structures of the first air-stable, hexacoordinated high spin Fe(II) porphyrins (**1**) with axial alcohols are reported (**1** = Fe(II) *meso*-tetrakis(*o*-dichlorophenyl)-β-octanitroporphyrin). The structure of **1** with two axial waters is also presented. The very different conformations and metrics observed with the two types of ligands illustrate the acute interplay between ligands, conformations, and spin states in Fe porphyrins.

Cytochromes P450 are a class of monooxygenase enzymes that catalyze hydroxylations and epoxidations in vivo and mediate drug metabolism, steroid synthesis, and both activation and detoxification of chemical carcinogens.[1a,b] Multiple redox stages of the iron porphyrin prosthetic group have been identified or invoked in the catalytic cycle of cytochrome P450 including high and low spin Fe(II) and Fe(III), as well as higher oxidation states involving Fe(IV) and Fe(IV) π cation radicals.[1a−h] The crucial catalytic roles of cytochrome P450 have naturally led to intense efforts that seek to duplicate the biological processes in vitro, and several classes of synthetic porphyrins have been developed that mimic the enzymatic catalysis.[1c,d,f,2] In particular, we have recently synthesized a series of electron-deficient porphyrins bearing one to eight β-nitro substituents with a remarkably wide range of redox potentials,[3] whose Mn and Fe complexes catalyze the epoxidation of alkenes and hydroxylations of aromatic compounds by H_2O_2.[4]

We describe here the synthesis and characterization of the air-stable Fe(II) complex of the β-pernitro derivative of this series and report the first molecular structures of Fe(II) porphyrins ligated by two axial alcohols that provide evidence of the rare hexacoordinated, high spin Fe(II) porphyrin state.[1i]

Complex **1**, Fe(II) [5,10,15,20-tetrakis-(2,6-dichlorophenyl)-2,3,7,8,12,13,17,18-octanitro-porphyrin] was prepared by demetalation of the recently reported Zn derivative[3b] with CF_3SO_3H followed by treatment with $FeBr_2$ in absolute ethanol.



$$\mathrm{Zn[TDCP(NO_2)_8P]} \xrightarrow[\text{2) FeBr}_2\text{, 5h, RT}]{\text{1) CF}_3\text{SO}_3\text{H}} \mathrm{Fe(II)[TDCP(NO_2)_8P]}$$

1

The Fe(II) complex was purified by chromatography on silica gel (elution with 80/20 CH_2Cl_2/EtOH) (yield 65%) and crystallized from EtOH without any attempts to exclude dioxygen. Its MALDI mass spectrum exhibits molecular peaks centered at 1303.69 in good agreement with a calculated mass of 1303.8 for unligated **1**. In EtOH, **1** displays a Soret absorption band at 463 nm and three additional peaks at 553,

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(1) Extensive reviews relevant to the ensuing discussion can be found in *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: New York, 2000. (a) Mansuy, D.; Battioni, P. Vol. 4; p 1; (b) Poulos, T. L. Vol. 4; p 189; (c) Groves, J. T.; Shalyaev, K.; Lee, J. Vol. 4; p 17; (d) Suslick, K. S. Vol. 4; p 41; (e) Weiss, R.; Gold, A.; Trautwein, A. X.; Terner, J. Vol. 4; p 65; (f) Meunier, B.; Robert, A.; Pratviel, G.; Bernardou, J. Vol. 4; p 119; (g) Walker, F. A. Vol. 5; p 81; (h) La Mar, G. N.; Satterlee, J. D.; De Ropp, J. S. Vol. 5; p 185; (i) Scheidt, W. R. Vol. 3; p 49; (j) Kadish, K. M.; Van Caemelbecke, E.; Royal, G. Vol. 8; p 1; (k) Lecomte, C.; Rohmer, M. M.; Bernard, M. Vol. 7; p 39; (l) Senge, M. O. Vol. 1; p 239; (m) Raman, C. S.; Martásek, P.; Masters, B. S. S. Vol. 4; p 293; (n) Shelnutt, J. A. Vol. 7; p 167.

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600, and 640 nm with respective ϵ values of 149, 16.1, 17.6, and 12.2 mM^{-1} cm^{-1}. Cyclic voltammetry in CH_2Cl_2/0.1 M Bu_4NPF_6 showed that **1** is remarkably difficult to oxidize because of the multiple electron-withdrawing substituents: $E_{1/2}$ for the reversible one-electron oxidation of Fe(II) to Fe(III) occurs at +1030 mV versus SCE, an unprecedentedly high potential[1j] which readily explains why the Fe(II) complex is air-stable.

Evidence for a high spin Fe(II) assignment for **1**$(EtOH)_2$ derives from both Mössbauer and magnetic susceptibility data for powdered samples of **1**$(EtOH)_2$. At 77 K, the Mössbauer spectrum consists of a quadrupole doublet with quadrupole splitting of 2.136(2) mm/s and an isomer shift of 0.921(1) mm/s relative to metallic iron, values which decrease to $\Delta E = 2.064(4)$ mm/s and $\delta = 0.844(2)$ mm/s at ambient temperature. These parameters parallel those observed for the fully characterized[5] (vide infra) hexacoordinated, high spin Fe(II)-$(TPP)(THF)_2$ (TPP = 5,10,15,20- tetraphenylporphyrin, THF = tetrahydrofuran) for which $\Delta E = 2.65$ and $\delta = 0.95$ mm/s at 77 K and $\Delta E = 2.42$ and $\delta = 0.89$ mm/s at 195 K.[5a] Magnetic measurements on **1**$(EtOH)_2$ in the temperature range 4.2−295 K and field range 0−5000 Oe yield an effective paramagnetic moment of 5.41 μ_B, also consistent with an $S = 2$ high spin Fe(II). (A diamagnetic correction was applied using the Zn analogue.[3b])

Although pentacoordinated high spin Fe(II) porphyrins with the Fe displaced out-of-plane are common in vivo and in vitro,[1b,g−i] hexacoordinated high spin Fe(II) complexes with the Fe in plane are extremely rare.[1i,k] Indeed, only two such species have been characterized crystallographically. One is a bis(*N*-alkyl)porphyrin with two axial metallocycles which displays a substantially expanded core.[6] The other is $Fe(II)(TPP)(THF)_2$, originally described by Reed et al.[5a] with long Fe−N bonds of 2.057(3) Å at room temperature (RT), consistent with $d_{x^2-y^2}$ orbital occupancy, and Fe−O bonds of 2.351(3) Å, consistent with d_{z^2} occupancy and the weak nature of the axial ligands. The complex was reexamined by Lecomte et al.[5b] who found that the Fe−N distances increase to 2.067(1) Å upon cooling to 100 K, and that the Fe−O bonds contract to 2.2922(7) Å with no magnetic transition associated with Fe−O contraction. Electron density maps supported a $^5E_{2g}$ ground state[1k,5b] $[(d_{x^2-y^2})^1\ (d_{z^2})^1\ (d_{xz,yz})^3\ (d_{xy})^1]$. The molecular structure of **1**$(EtOH)_2$, determined at RT,[7] is shown in Figure 1. The unique Fe−N distances are 2.069(6) and 2.078(6) Å, metrics clearly comparable to those reported[5] for $Fe(II)(TPP)(THF)_2$. The Fe−O distances are 2.153(11) Å, values shorter than those for the THF complex but which likely reflect the fact that the ethanols are better ligands than THF, and also the effect of the multiple electron-withdrawing substituents of **1**. The Fe sits strictly in the plane of the porphyrin. Despite the 12 peripheral substituents, which generally result in severe skeletal distortions,[1i,l,8] the macrocycle of **1** is essentially planar with an average deviation from the 24-atom porphyrin plane of only 0.08 Å, and maximum displacements of 0.13 and 0.10 Å at any one β or meso carbon, respectively. (It is instructive to compare the bond distances in **1**$(EtOH)_2$ with those in the corresponding high spin $Ni(II)(MeOH)_2$,[9] in which the $d_{x^2-y^2}$ orbital is singly occupied. Indeed, at 200 K, the Ni−N distances, 2.060(3) and 2.066(3) Å, are only slightly shorter than those in the high spin Fe(II).)

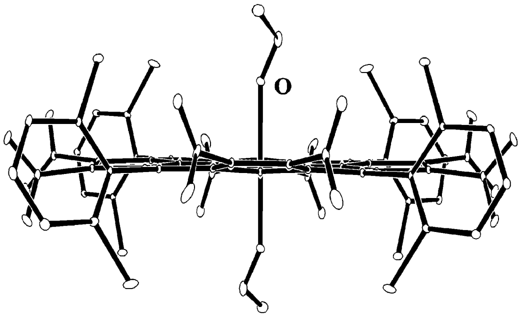

Figure 1. Edge-on view of **1**$(EtOH)_2$, illustrating the planar conformation of the macrocycle. Thermal ellipoids have been reduced to 1% probability, and hydrogen atoms have been omitted for clarity.

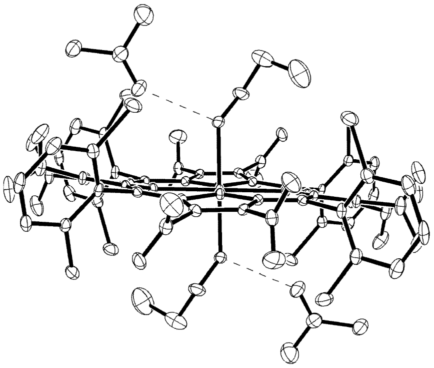

Figure 2. Edge-on view of **1**$(PrOH)_2$, showing the planar macrocycle and the hydrogen-bonding of the propanol ligands to acetones of crystallization. Thermal ellipsoids enclose 50% probability.

An additional complex of **1** was investigated at 100 K using synchrotron radiation. Compound **1** was crystallized from *n*-propanol/acetone to yield **1**$(PrOH)_2$ in which each hydroxyl group of the axial propanols is hydrogen-bonded to the keto group of an acetone,[10] Figure 2. At 100 K, the Fe−N distances are 2.088(2) and 2.095(2) Å, and the Fe−O distances to the alcohol ligands are 2.151(2) Å, again diagnostic of high spin Fe(II). The O−O distances from the alcohols to the ketones are 2.70 Å, clearly indicative of hydrogen-

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(7) Crystals of **1**$(EtOH)_2$ were grown from mixtures of EtOH, pentane, and methylene chloride. Crystal data include the following: triclinic, space group $P\bar{1}$ (No. 2), $Z = 1$, $a = 12.001(2)$ Å, $b = 12.110(4)$ Å, $c = 12.258(3)$ Å, $\alpha = 70.51(2)°$, $\beta = 88.85(2)°$, $\gamma = 73.60(2)°$, $V = 1605.7(7)$ Å^3, $\rho_{calcd} = 1.532$ g cm^{-3}, $F(000) = 744$, $\mu = 6.376$ mm^{-1}, crystal size 0.20 × 0.10 × 0.072 mm^3. A total of 4709 reflections were measured on an Enraf-Nonius CAD4 diffractometer with graphite monochromated Cu Kα radiation ($\lambda = 1.54178$ Å) at room temperature with 4456 unique ($R_{int} = 0.068$). The data were corrected for Lorentz and polarization effects (XCAD4VAX) and absorption (Gaussian method). The structure was solved with SIR92 and refined on F^2 (SHELXTL Version 5). Final R1 ($I > 2\sigma(I) = 0.109$); wR2 = 0.286 (4454 data) based on 420 parameters. Hydrogen atoms were included using a riding model.

(8) Fajer, J. *J. Porphyrins Phthalocyanines* **2000**, *4*, 382−386.

(9) Unpublished results.

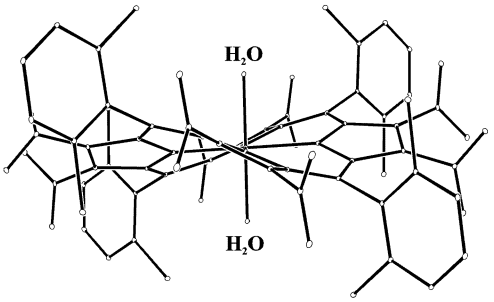

Figure 3. Edge-on view of highly distorted **1**(H_2O)$_2$. Thermal ellipsoids are drawn at the 1% probability level. The acetones hydrogen-bonded to the water ligands are not shown.

bonds. At 100 K, the porphyrin remains again essentially planar with average displacements from the 24 atom porphyrin plane of 0.09 Å.

In all the hexacoordinated structures with long M−N bonds and expanded cores that we have described so far, that is, the high spin Fe(II) and Ni(II) complexes discussed above, as well as the Zn analogue of **1** and the high spin Ni(II) derivative with 7 instead of 8 nitro groups reported previously,[3] the porphyrin macrocycle remained planar. However, when **1** was crystallized from wet acetone, the product **1**(H_2O)$_2$, also hydrogen-bonded to acetone, exhibits a nonplanar, ruffled[1i,l] structure at 100 K,[11] in which the unique meso carbons are displaced up and down, out-of-plane by 0.75 and −0.80 Å, and the β carbons in any one pyrrole ring by ±0.30−0.34 Å, with an average displacement of 0.39 Å from the 24 atom plane; that is, the molecule is severely distorted as shown in Figure 3. Particularly surprising are the short Fe−N distances which average 1.945(7) Å, and the equally short Fe−O bonds to the waters of 1.976(6) Å, distances that are incompatible with a high spin Fe(II) assignment.[1i] To our knowledge, there are no reported hexacoordinated, intermediate spin Fe(II) porphyrins,[1i] but two structures of low spin Fe(II) halogenated porphyrins, which are also nonplanar, reveal Fe−N distances ranging between 1.958(6)[12a] and 1.963(7) Å.[12b] Consistent with the general bathochromic optical trends observed for nonplanar porphyrins,[1l,8] the Soret absorption band has red-shifted to 476 nm in acetone/water relative to the Soret band at 463 nm for **1** in EtOH.

Several different quintet ground state configurations for high spin Fe(II) porphyrins are theoretically possible with different distributions of the 6 d electrons (in D_{4h} symmetry)[1k]: $^5B_{2g}$, $^5A_{1g}$, $^5B_{1g}$, and $^5E_{2g}$. Which of these is favored in the present electron-deficient porphyrins, and the actual electron distribution in the lower spin state of the aquated species, should be amenable to electron density mappings at low temperature using synchrotron radiation, and such studies are presently underway.

The very different planar and nonplanar macrocycle conformations described here further illustrate the considerable plasticity of the porphyrin skeleton and the acute sensitivity and interplay between axial ligands, spin states, and conformations of Fe porphyrins recently reported.[1i,l,13] This interplay and its concomitant consequences on electron distribution, and thus on physical and chemical properties, may well fulfill a significant biological role in the many heme proteins, including some cytochromes P450, which have recently been shown to incorporate distorted porphyrins.[1b,m,n]

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Supporting Information Available: Crystallographic data in CIF format; ORTEP diagrams (Figures S1−S3) for **1**(EtOH)$_2$, **1**(PrOH)$_2$, and **1**(H_2O)$_2$; and Mössbauer spectrum of **1**(EtOH)$_2$, Figure S4. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Crystals of **1**(PrOH)$_2$·(acetone)$_2$ were grown from mixtures of acetone and propanol. Crystal data include the following: triclinic, space group $P\bar{1}$ (No. 2), $Z = 1$, $a = 11.346(1)$ Å, $b = 11.655(1)$ Å, $c = 12.766(1)$ Å, $\alpha = 105.36(1)°$, $\beta = 91.51(1)°$, $\gamma = 104.58(1)°$, $V = 1567.6(2)$ Å^3, $\rho_{calcd} = 1.632$ g cm^{-3}, $F(000) = 782$, $\mu = 0.668$ (Mo Kα) mm^{-1}, crystal size 0.15 × 0.05 × 0.025 mm^3. A total of 36733 reflections were measured at 100 K on a MAR345 image plate detector at beamline X7B ($\lambda = 0.9035$ Å) at the National Synchrotron Light Source at Brookhaven with 3826 unique ($R_{int} = 0.036$). The data were scaled and merged using Denzo/Scalepack. The structure was solved with SHELXS-86 and refined on F^2 (SHELXTL Version 5). Final R1 ($I > 2\sigma(I) = 0.029$); wR2 = 0.086 (3822 data) based on 439 parameters.

(11) Crystals of **1**(H_2O)$_2$·(acetone)$_2$ were grown from mixtures of acetone and hexanes. Crystal data include the following: monoclinic, space group $C2/c$ (No. 15), $Z = 4$, $a = 17.244(2)$ Å, $b = 27.055(4)$ Å, $c = 13.712(1)$ Å, $\beta = 112.21(1)°$, $V = 5922.5(12)$ Å^3, $\rho_{calcd} = 1.633$ g cm^{-3}, $F(000) = 2936$, $\mu = 0.702$ (Mo Kα) mm^{-1}, crystal size 0.10 × 0.10 × 0.025 mm^3. A total of 36561 reflections were measured at 100 K on a MAR345 image plate detector at beamline X7B ($\lambda = 0.9385$ Å) with 3168 unique ($R_{int} = 0.069$) and processed with Denzo/Scalepack. The structure was solved with SHELXS-86 and refined on F^2 (SHELXTL Version 5). Final R1 ($I > 2\sigma(I) = 0.061$); wR2 = 0.165 (all data) based on 418 parameters.

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