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Notes

X-ray Crystallographic Structure of (*meso*-Tetraphenylporphinato)bis(phenylphosphinic methyl ester)iron(III) Perchlorate: A New High-Spin Six-Coordinate Ferric Porphyrin

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Introduction

In contrast to the wide range of six-coordinate low-spin ferric porphyrin complexes[1] with nitrogen and phosphorus donor ligands, few examples of pure six-coordinate high-spin ferric porphyrins with oxygen donor ligands such as sulfoxide,[2] phosphine oxide,[2] and water[3,4] are known. This is principally due to the presence of an expanded porphinato core and the necessity to find moderate field strength neutral axial ligands. Weak field anionic ligands such as chloride and iodide lead to five-coordinated high-spin derivatives.[1]

The chemistry of phosphorus donor ligands has remained an area of extensive interest in metalloporphyrin chemistry due to the ability of these ligands to stabilize both ferrous and ferric states in metalloporphyrins[5] and hemoproteins.[6] Thus trimethylphosphine complexation to myoglobin and hemoglobin allowed the possibility to determine experimentally the rate of self-exchange electron transfer reactions.[7] The use of this ligand to record iron NMR via spin polarization transfer has also been recently demonstrated.[8] We have been pursuing the reaction of ferric porphyrin with various low basicity phosphorus derivatives to determine the influence of this factor on the electronic state of low-spin ferric porphyrins.[9] We now show that ferric porphyrin complexation is not limited to the phosphonous diester but that the phenylphosphinic methyl ester also forms an hexacoordinated complex which is sufficiently stable to allow solution and solid-state characterization. We report the preparation and X-ray structure of the complex Fe(TPP)-[OP(H)(OMe)(Ph)]$_2$ClO$_4$.

Table 1. Crystal Data for Fe(TPP)[OP(H)(OMe)(Phe)]$_2$ClO$_4$, **1**

formula	FeP$_2$O$_4$N$_4$C$_{58}$H$_{46}$·ClO$_4$·CH$_2$Cl$_2$	Z	4
mol wt	1163.5	D_x, g cm^{-3}	1.337
cryst syst	monoclinic	T, K	294
space group	$C2/c$	μ(Mo Kα), cm^{-1}	5.119
a, Å	25.867(6)	R	0.079
b, Å	14.781(4)	R_w	0.072
c, Å	16.096(3)	Δ/ρ, e Å^{-3}	0.28
β, deg	111.41(2)		
V, Å^3	5730(2)		

Experimental Section

EPR spectra were recorded on a Varian spectrometer equipped with a temperature controller at 90 K as solids. Visible spectra were measured on a Uvikon 941 spectrometer in chloroform.

Synthesis of Fe[OP(H)(OMe)(Ph)]$_2$ClO$_4$, 1. To a solution of 0.2 g (0.26 mmol) of Fe(TPP)ClO$_4$[10] in 20 mL of CH$_2$Cl$_2$ was added 8 equiv of OP(H)(OMe)(Ph)[11] by a syringe at room temperature in a Schlenk tube under an Ar atmosphere. The solution was stirred for 10 min. After addition of 40 mL of pentane, fine crystals were collected by filtration and washed with pentane. The yield was (87%). Anal. Calcd for C$_{58}$H$_{46}$N$_4$O$_8$P$_2$ClFe: C, 64.47; H, 4.26; N, 5.19; P, 5.74. Found: C, 63.87; H, 4.32; N, 5.26; P, 5.84. UV−vis (λ, nm CHCl$_3$): 401, 523, 667. ESR: $g = 5.29$, $g = 1.85$ (solid).

Single Crystal Structure Determination on Fe[OP(H)(OMe)-(Ph)]$_2$ClO$_4$. Crystallographic data are collected in Table 1. Crystals of the compound were obtained as reported in results. The X-ray study was carried out on an ENRAF-Nonius CAD4 diffractometer using graphite monochromatized Mo Kα radiation. The cell parameters are obtained by fitting a set of 25 high-θ reflections. The data collection ($2\theta_{max} = 54°$, scan $\omega/2\theta = 1$, $t_{max} = 60$ s, range h,k,l: h −30 to +30, k 0 to 17, l 0 to 19, intensity controls without appreciable decay (1.5%)) gives 5448 reflections from which 2832 reflections satisfied $I > 2\sigma(I)$. After Lorenz and polarization corrections the structure was solved with direct methods[12] which reveal the Fe, Cl, and P atoms and some C atoms. The remaining non-hydrogen atoms of the structure were found after successive scale for factor refinements and Fourier difference. The perchlorate anion was found in two different sites. After isotropic ($R = 0.115$) and then anisotropic refinement ($R = 0.095$), some hydrogen atoms were found with a Fourier difference (in particular P−H), and the remaining ones were set in geometrical positions and then refined. The whole structure was refined by the full-matrix least-square techniques (use of F magnitude; $x, y, z, \beta_{i,j}$ for Fe, P, Cl, O, N, and C atoms; x, y, z for perchlorate anion and x, y, z for hydrogen atoms; 405 variables and 2832 observations; $w = 1/\sigma(F_o)^2 = [\sigma^2(I) + (0.04F_o{}^2)^2]^{-1/2}$) with the resulting $R = 0.079$, $R_w = 0.072$ and $S_w = 1.98$ (residual $\Delta\rho < 0.28$ e Å^{-3}). Atomic scattering factors were taken from ref 19. The calculations were performed on a Hewlett Packard 9000-710 for stucture determination and on a digital MicroVaX 3100 with the Molen package[13] for refinement and Ortep calculations.

Results and Discussion

The synthesis of Fe[OP(H)(OMe)(Ph)]$_2$ClO$_4$ compound is achieved by displacement of coordinate perchlorate from Fe-(TPP)ClO$_4$[10] according to the equation

$$\text{Fe(TPP)ClO}_4 + \text{OP(H)(OMe)(Ph) (excess)} \rightarrow \text{Fe[OP(H)(OMe)(Ph)]}_2\text{ClO}_4$$

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

(2) Mashiko, T.; Kastner, M. E.; Spartalian, K.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1978**, *100*, 6354.

(3) (a) Kastner, M. E.; Scheidt, W. R.; Mashiko, T.; Reed, C. A. *J. Am. Chem. Soc.* **1978**, *100*, 666. (b) Scheidt, W. R.; Cohen, I. A.; Kastner, M. E. *Biochemistry* **1979**, *18*, 3546.

(4) A high-spin six-coordinate iron(III) porphyrinate having the mixed-axial ligation of pyridine and isocyanate has been also reported, see: Scheidt, W. R.; Lee, Y. J.; Geiger, D. K.; Taylor, K.; Hatano, K. *J. Am. Chem. Soc.* **1982**, *104*, 3367.

(5) Simonneaux, G.; Sodano, P. *Inorg. Chem.* **1988**, *27*, 3956.

(6) Brunel, C.; Bondon, A.; Simonneaux, G. *J. Am. Chem. Soc.* **1994**, *116*, 11827.

(7) Brunel, C.; Bondon, A.; Simonneaux, G. *Biochim. Biophys. Acta* **1992**, *1101*, 73.

(8) Mink, L. M.; Polam, J. R.; Christensen, K. A.; Bruck, M. A.; Walker F. A. *J. Am. Chem. Soc.* **1995**, *117*, 9329.

(9) Guillemot, M.; Simonneaux, G. *J. Chem. Soc., Chem. Commun.* **1995**, *2093.*

(10) Reed, C. A.; Mashiko, T.; Bentley, S. P.; Kastner, M. E.; Scheidt, W. R.; Spartalian, K.; Lang, G. *J. Am. Chem. Soc.* **1979**, *101*, 2948.

(11) Sander, M. *Chem. Ber.* **1960**, *93*, 1220.

S0020-1669(96)00338-2 CCC: $12.00

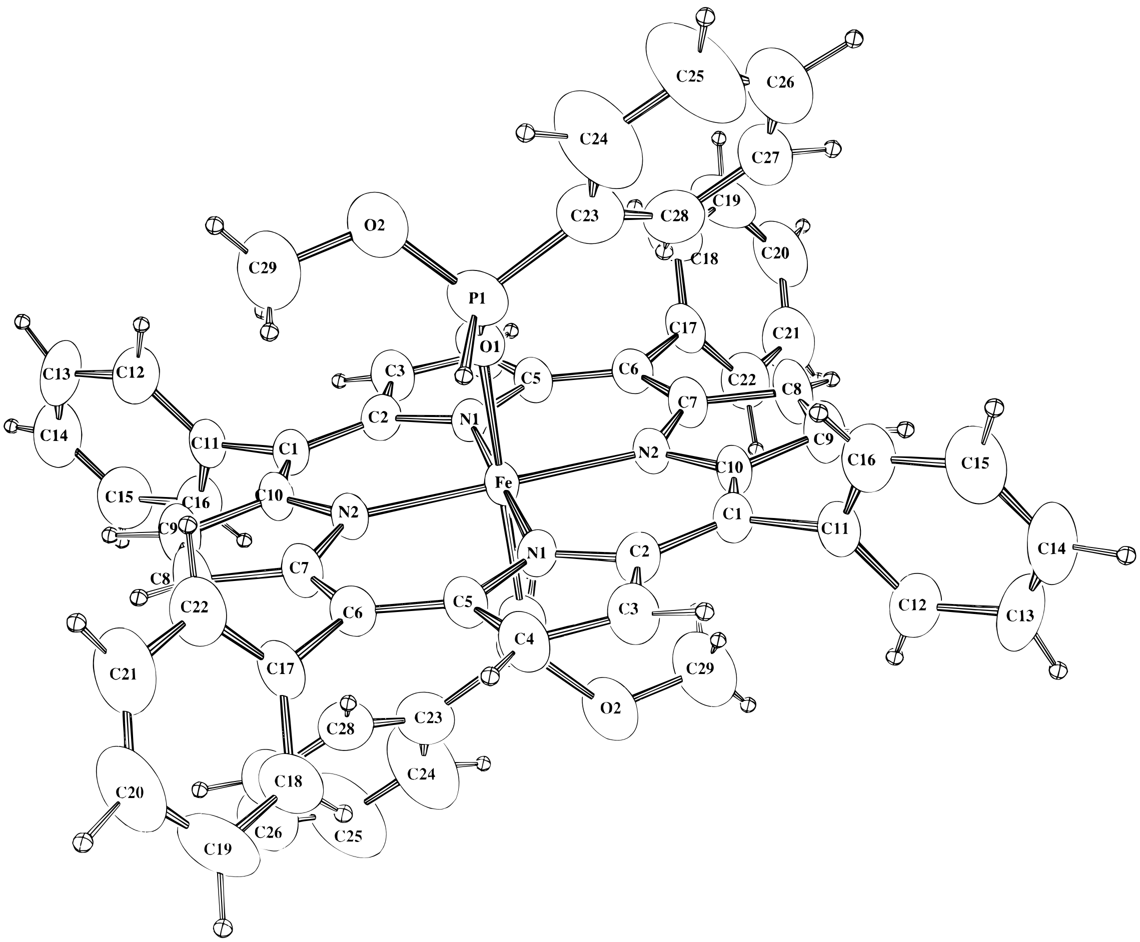

Figure 1. Molecular structure for Fe(TPP)[OP(H)(OMe)(Ph)]$_2$ClO$_4$, **1**.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1**

Fe−O1	2.102(5)	P1−H1	1.41(8)
Fe−N1	2.034(6)	O2−C29	1.44(1)
Fe−N2	2.038(5)	N1−C2	1.376(9)
P1−O1	1.467(6)	N1−C5	1.380(8)
P1−O2	1.541(7)	N2−C7	1.378(9)
P1−C23	1.75(1)	N2−C1O	1.368(9)
		C1−C2	1.41(1)
O1−Fe−O1	180(0)	O1−P1−H1	114(3)
O1−Fe−N1	90.3(2)	O2−P1−C23	103.9(4)
O1−Fe−N1	89.7(2)	O2−P1−H1	99(3)
O1−Fe−N2	90.0(2)	C23−P1−H1	111(3)
O1−Fe−N2	90.0(2)	P1−O1−P1	137.6(3)
N1−Fe−N1	180(0)	Fe−O2−C29	119.9(7)
O1−P1−O2	114.8(4)	Fe−N1−C2	126.7(5)
O1−P1−C23	112.4(4)	Fe−N1−C5	127.1(5)

In solution, the complex has a red-brown color, as previously reported by Reed and co-workers[2] for the bis(triphenylphosphine oxide) adduct, and shows a visible spectrum with λ_{max} at 401, 523, and 667 nm. In fact, the single crystals of Fe[OP(H)(OMe)(Ph)]$_2$ClO$_4$ used in the structural study discussed below arose from an initially unsuccessful attempt to recrystallize Fe[TPP][P(OMe)$_2$(Ph)]$_2$ClO$_4$.[9] Presumably some traces of acidic water catalyze a partial hydrolysis of the phosphonous diester, yielding the phosphinic ester. It is well-known that the partial hydrolysis of phosphonous diesters takes place slowly in neutral medium, but with a trace of acid, the partial esters are instantly produced in almost quantitavely yield.[14]

The ESR spectrum of a polycrystalline sample presents a tetragonal features with $g = 5.28$ and $g = 1.89$, according with a high-spin ferric porphyrin.

The X-ray structure of **1** is shown in Figure 1; selected bond distances and angles are given in Table 2. The iron(III) atom is centered in the plane of the porphinato ligand in spite of its high-spin character, as it has been demonstrated previously for the other high-spin six-coordinate derivatives. As a consequence of the in-plane high-spin iron(III) atom there is a large radial expansion of the porphinato core. The average Fe−N bond distance of 2.036(6) Å is much longer than the typical values of low-spin hexacoordinate derivatives (1.970(14)−2.000(4) Å)[1]. A similar pattern of bond length differences are also noted for two high-spin six-coordinate iron(III) derivatives, [Fe(TPP)(H$_2$O)$_2$]ClO$_4$[3] and [Fe(TPP)(TMSO)$_2$]ClO$_4$ (TMSO is tetramethylene sulfoxide).[2] The average Fe−N bond distance of 2.036(6) Å is slightly shorter than the 2.045(8) Å mean value previously reported for three high-spin derivatives.[1] However this distance is slightly longer than the Fe−N distances found in [Fe(TP$_{piv}$P)(OSO$_2$CF$_3$)(H$_2$O)] recently reported by Weiss and Trautwein (mean value 2.021(16) Å).[15] This compound was described as an high-spin/intermediate admixed species with the high-spin component predominating.

The axial Fe−O bond distance of 2.102 (5) Å is much longer than the metal−oxygen distance (1.791 (6) Å) found in a tetrahedral phosphine complex such as FeCl$_3$(O=TMPP),[16] where TMPP is tris(2,4,6-trimethoxyphenyl)phosphine. This is

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(12) Sheldrick, G. M. In *Crystallographic Computing 3: Data Collection, Structure Determination, Protteins and Databases*; Sheldrick, G. M., Krüger, C., Goddard, R., Eds.; Clarendron Press: Oxford, U.K., 1985.

(13) ENRAF-NONIUS Molecular Determination Package. Delft University, The Netherlands. Current version: 1990.

(14) Frank, A. W. *Chem. Rev.* **1961**, *61*, 389.

(15) Gismelseed, E. L.; Bominaar, E. L.; Bill, E.; Trautwein, A. X.; Winkler, H.; Nasri, H.; Doppelt, P.; Mandon, D.; Fisher, J.; Weiss, R. *Inorg. Chem.* **1990**, *29*, 2741.

consistent with a weak field ligand and the population of the $3d_{z^2}$ orbital as required by the high-spin state. As previously reported,[1] it appears that axial coordination of two weak field ligands with two longer than normal bond distances can lead to the high-spin state. The axial Fe−O bond distance is quite comparable to those observed in $[Fe(TPP)(TMSO)_2]ClO_4$ (2.069 (3) and 2.087 (3) Å) which is another example of six-coordinate high-spin ferric porphyrin[2]. This Fe−O distance is also quite similar to the Fe−O separations found in a bidentate diphosphine dioxide complex [2.122(6) Å] of iron(II).[17] However, such complex differs from the oxidation state and the presence of the bidentate ligand. Moreover these structural data cannot be interpreted strictly since there is a major steric influence of the porphyrin. Actually the ligand forms a bent interaction with the metal (Fe−O−P = 137.6 (3)°) whereas, for example, in $FeCl_3$(O═TMPP) the Fe−O−P angle is 163.6 (5)°.

Among the limited data on phosphorus oxo acids with a P−H bond, the distances and the angles found in the phenylphosphinic methyl ester ligand are typical of this class of compound. The average P═O distance of 1.5008 (7) Å in 1 is comparable to the P═O distance found in methylenebis(phosphinic acid)[18a] where P═O distances are 1.488(1) and 1.492 (1) Å and in (2-amino-2-carboxyethyl)phosphinic acid where the P═O distance is 1.501(1) Å).[18b] As far as we are aware, the present study of **1** represents the first example of a structurally characterized phosphinic derivative of metalloporphyrins.

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Supporting Information Available: Tables of parameters, positional and thermal parameters for all atoms, anisotropic displacement parameters for non-hydrogen atoms, and bond distances and bond angles (12 pages). Ordering information is given on any current masthead page.

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(16) Dunbar, K. R.; Haefner, S. C.; Quillevéré, A. *Polyhedron* **1990**, *9*, 1695.

(17) Barclay, J. E.; Evans, D. J.; Hughes, D. L.; Leigh, G. F. *J. Chem. Soc., Dalton Trans.* **1993**, 69.

(18) (a) King, C.; Roundhill, D. M.; Fronczek, F. R. *Inorg. Chem.* **1986**, *25*, 1290. (b) Schwalbe, C. H.; Freeman, S.; DasGupta, M. *Acta Crystallogr.* **1993**, *C49*, 1826.

(19) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974.