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Molecular Structure of Diaquo- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinatoiron(III) Perchlorate and Perchlorato- $\alpha,\beta,\gamma,\delta$ -tetraphenyl- porphinatoiron(III). Two New Structural Types for Iron(III) Porphyrins

Sir:

The stereochemistry of heme centers is justly deemed significant in understanding the function and mechanism of heme proteins.¹ We wish to report the molecular structures of two new iron(III) porphyrins with weak-field axial ligands which demonstrate that iron(III) porphyrins display greater structural diversity than has generally been recognized and point out that there are potential difficulties in assigning stereochemistry from magnetic properties. The two iron(III) porphyrins are a five-coordinate derivative, perchlorato- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinatoiron(III), FeTPP(OClO₃), and a six-coordinate derivative, diaquo- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinatoiron(III) perchlorate, [FeTPP(OH₂)₂]⁺ClO₄⁻.

FeTPP(OClO₃) is conveniently prepared by the reaction of FeTPP(Cl) with AgClO₄ in dry THF.^{2,3} [FeTPP(OH₂)₂]⁺ was obtained by recrystallization of FeTPP(OClO₃) from THF in the presence of aqueous perchloric acid.

FeTPP(OClO₃) has an unusual effective magnetic moment of 5.0 μ_B at room temperature, decreasing linearly with temperature (to 4.1 μ_B at 40 K). Its Curie-Weiss behavior to 4.2 K (Weiss constant = -5 K), together with the Mössbauer observation⁴ of a single compound over the range of 4.2-298 K, rules out the existence of a spin state equilibrium. The similarity of the Mössbauer spectrum⁴ to its reported OEP analogue^{5,6} suggests that FeTPP(OClO₃) has either an $S = 3/2$ ground state with a large orbital contribution to its magnetic moment⁷ or a quantum mechanically mixed spin state arising from $S = 3/2$ and $S = 5/2$ spin states.⁹ [FeTPP(OH₂)₂]⁺ has a magnetic susceptibility of 5.5 μ_B which is independent of temperature over the range of 77-297 K.¹⁰ Although the magnetic moment is apparently too low for a high-spin complex, electron spin resonance measurements (powder sample from crushed single crystals, 77 K) show an axial spectrum with a strong feature at $g = 6$, which is typical of high-spin iron(III) porphyrins. Remaining ambiguities in the spin state assignment of these complexes are expected to be resolved by detailed Mössbauer, ESR, and magnetic susceptibility measurements in progress.

Crystal data and refinement results are as follows: Fe(N₄C₄₄H₂₈)(ClO₄)·1/2C₈H₁₀; monoclinic, $a = 14.705$ (2), $b = 15.487$ (3), $c = 17.470$ (3) Å; $\beta = 95.17$ (1)°; space group

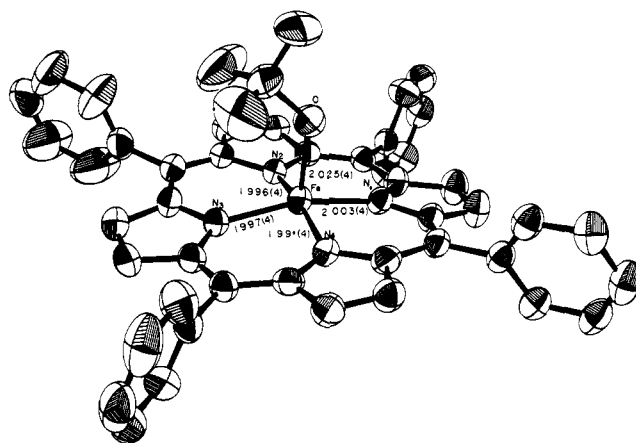


Figure 1. A perspective view of the FeTPP(OClO₃) molecule. The individual values of the bond distances in the coordination group are displayed.

$P2_1/n$; $Z = 4$; $\rho_{\text{calcd}} = 1.37$, $\rho_{\text{obsd}} = 1.37$ g/cm³; $R_1 = 0.074$, $R_2 = 0.077$;¹¹ 5124 unique observed data ($F_o > 3\sigma(F_o)$, $2\theta < 55^\circ$). Fe(N₄C₄₄H₂₈)(OH₂)₂ClO₄·2C₄H₈O: orthorhombic, $a = 16.772$ (2), $b = 12.823$ (2), and $c = 21.301$ (2) Å; space group $Pbcn$; $Z = 4$; $\rho_{\text{calcd}} = 1.38$, $\rho_{\text{obsd}} = 1.39$ g/cm³; $R_1 = 0.063$, $R_2 = 0.062$; 3730 unique observed data ($F_o > 3\sigma(F_o)$, $2\theta < 63.7^\circ$). Intensity data were collected on a Syntex P1 diffractometer with graphite-monochromated Mo K α radiation using θ - 2θ scanning.

The molecular stereochemistry and bond parameters of the coordination group of FeTPP(OClO₃) are displayed in Figure 1. Although the complex is clearly five coordinate, the parameters of the coordination group do not conform to those expected^{12,13} for high-spin five-coordinate iron(III) porphyrins. Thus the average Fe-N bond distance (1.997 (5) Å) is considerably shorter than the 2.065-Å value typical of high-spin derivatives, such as chlorohemin¹⁴ and the methoxyiron(III) derivative of mesoporphyrin IX dimethyl ester.¹⁵ Rather, the Fe-N bond distance is only slightly longer than the 1.990-Å value typical of *low-spin* six-coordinate iron(III) porphyrins.¹⁶ A second important distinction is found in the displacement of the iron(III) atom. In FeTPP(OClO₃), the iron(III) atom is displaced by only 0.27 Å out of the plane defined by the four porphyrinato nitrogen atoms and 0.30 Å out of the mean plane of the 24-atom core. The usual displacement is ~0.5 Å in the five-coordinate high-spin iron(III) derivatives.^{12,13} Since the large displacement of the iron(III) atom and the long Fe-N bonds in the high-spin iron(III) porphyrins are generally associated with the occupancy of the 3d_{x²-y²} orbital, the structural parameters of FeTPP(OClO₃) are consistent with an iron(III) atom in which the 3d_{x²-y²} orbital is either unoccupied or partially occupied; namely an intermediate spin ($S = 3/2$) or a quantum mechanically mixed ($S = 3/2, 5/2$) spin state. Indeed, the similarity of the porphyrinato coordination parameters with those of five-coordinate high-spin d⁴ manganese(III) porphyrins,¹⁷ in which the 3d_{x²-y²} orbital is safely presumed to be unoccupied,¹⁸ is noteworthy. The short Fe-N bond distances in FeTPP(OClO₃) are achieved by a quasi-D_{2d} ruffling of the porphyrinato core. The axial Fe-O distance of 2.025 (4) Å is the shortest known metal to perchlorate oxygen distance,¹⁹ but short axial bond distances appear to be a usual feature of five-coordinate iron(III) porphyrins.^{12,13}

An overall view of the [FeTPP(OH₂)₂]⁺ClO₄·2THF molecule is given in Figure 2. The iron(III) atom is located at a crystallographic inversion center and thus the [FeTPP(OH₂)₂]⁺ ion has required C_i- $\bar{1}$ symmetry with the iron(III) atom precisely centered in the plane of the porphyrinato ligand. An in-plane position of the iron(III) atom in porphyrinato complexes has been demonstrated previously only for *low-spin*

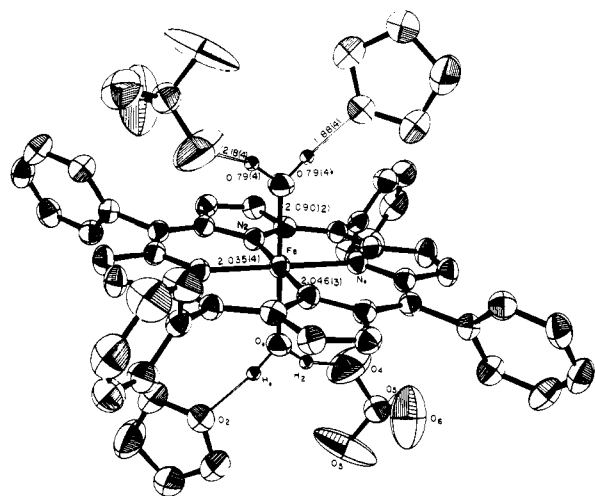


Figure 2. A view of the $[\text{FeTPP}(\text{OH}_2)_2]^+$ ion. Bond distances in the coordination group and the hydrogen bonding of the aquo ligands and the perchlorate anion and the THF solvates are shown.

six-coordinate derivatives. There is, however, one significant difference in the structure of $[\text{FeTPP}(\text{OH}_2)_2]^+$ and the structures of the low-spin six-coordinate complexes. The average Fe-N bond distance of 2.041 (8) Å $[\text{FeTPP}(\text{OH}_2)_2]^+$ is substantially longer than the 1.990-Å value typical of the low-spin derivatives.¹⁶ Such an increase in the Fe-N bond distance with the concomitant expansion of the porphyrin core suggests¹³ significant population of the $3d_{x^2-y^2}$ orbital, with either a high-spin ($S = 5/2$) or a quantum mechanically mixed ($S = 3/2, 5/2$) ground state. The only first-row six-coordinate transition metal porphyrin complex in which the $3d_{x^2-y^2}$ orbital is unequivocally populated is the paramagnetic d^8 bis(imidazole)- $\alpha,\beta,\gamma,\delta$ -tetra(4-*N*-methylpyridyl)porphyrinatonicckel(II) cation.²⁰ The average Ni-N bond distance in this high-spin complex is 2.038 Å. In the nickel complex and probably $[\text{FeTPP}(\text{OH}_2)_2]^+$ as well, the resistance of the porphyrin core to radial expansion leads to shortened M-N bonds relative to the values observed with monodentate ligands. We also note that the structural parameters of $[\text{FeTPP}(\text{OH}_2)_2]^+$ are mirrored by the structure of $[\text{FeTPP}(\text{tetramethylene sulfoxide})_2]^+$ currently under investigation in these laboratories.²¹

The axial Fe-O(aquo) bond distance of 2.090 (2) Å is at the upper end of distances observed for high-spin iron(III) aquo complexes.²² As is shown in Figure 2, the aquo ligand protons are hydrogen bonded to the THF solvent molecules and to the perchlorate anion. The perchlorate anion bridges, via hydrogen bonds, adjacent $[\text{FeTPP}(\text{OH}_2)_2]^+$ ions.

The structures reported herein demonstrate two new structural types for iron(III) porphyrins. These are (1) a five-coordinate type which differs from the previously known type by having short Fe-N bonds and a moderate out-of-plane metal atom displacement and (2) a six-coordinate type characterized by an in-plane iron(III) atom and long Fe-N bond distances. Examples of both types have relatively high magnetic moments. Using a variety of physical probes, we are currently investigating how these types of complexes relate to hemoproteins having weak-field ligands, particularly cyto-

chrome c' and aquo methemoglobin. They may also be useful in shedding light on the question of core expansion²³ vs. doming²⁴ in the interpretation of resonance Raman structure sensitive bands in metalloporphyrins and hemoproteins.

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References and Notes

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- Single crystals of a $1/2$ *m*-xylene solvate were obtained by recrystallization from *m*-xylene-heptane: $\nu(\text{ClO}_4^-)$ 1170 (s), 845 (br), 610 (m) cm^{-1} (KBr).
- G. Lang, personal communication, $\Delta E_0 = 3.4$ and $\delta = 0.39$ mm/s at 4.2 K in the absence of an applied magnetic field.
- While our work with the tetraphenylporphyrin derivatives was in progress, a reinvestigation⁶ of $\text{FeOEP}(\text{OCIO}_3)$ was published. Mossbauer spectroscopy has led⁶ to the assignment of an $S = 3/2$ spin state. However, the extent of quantum mechanical mixing with a higher spin state, if any, remains uncertain.
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- $R_1 = \sum \|F_o\| - \|F_c\| / \sum F_o$; $R_2 = [\sum w(F_o - F_c)^2 / \sum w(F_o)^2]^{1/2}$.
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