

values of pH, which lie somewhat below the straight line corresponding to our Figure 2, and using the same value of K_{OH} as above, we get the result reported in the table. Although the values of k_4 are seen to be all of the same order of magnitude, they vary somewhat more strongly than might be expected for a series of very similar ligands. Taking K_{out} the formation constant of the outer-sphere complex, from the Fuoss equation,¹⁶ we calculated the rate constants for the exchange between the ligand and a coordinated water molecule; these constants are designated by k^*_{AlOH} in the table. No data on the rate of water exchange on $AlOH^{2+}$ are available for comparison; our results do confirm, however, the stabilizing influence of OH.

Owing to the proton ambiguity of reactions 1 and 2, we cannot evaluate k_1 and k_2 separately. We calculated the value to be assigned to k_1 if pathway 2 were nonexistent, and vice versa for k_2 . These values obviously constitute upper limits for the corresponding rate constants. They are also given in Table I, with values for salicylic acid recalculated as explained above. If we want to proceed further, we must make some assumption about either k_1 or k_2 . Assuming k^*_{AlOH} to be the same for reaction 2 as for reaction 4, and again taking K_{out} from the Fuoss equation,¹⁶ we estimated the contribution of reaction 2 to the intercept of Figure 2. From the difference, we calculated the values of k_1 given in the table.

From the rate of water exchange³ on Al^{3+} we should predict⁵ a value of $\sim 0.6 M^{-1} s^{-1}$ for k_1 . The somewhat higher value found for sulfosalicylic acid had previously⁵ been discussed in terms of internal hydrolysis.¹⁷ An alternative explanation would be the assumption of a concerted mechanism. This assumption would be compatible with the slight increase of the rate constant with increasing basicity of the ligand which can be discerned from our table. It can also explain the existence of more specific effects which become apparent when we compare the rate constants reported for water-ligand exchange between the inner and outer coordination spheres when¹⁸ $Co(CN)_6^{3-}$,¹⁹ SO_4^{2-} , and²⁰ $Fe(CN)_6^{3-}$ serve as ligands. This alternative assumption is further strengthened by the fact that an associative interchange mechanism has recently been assigned to the formation of Fe^{3+} complexes on the basis of the negative²¹ or zero²² values found for the volume of activation. If this is correct, then the fact that complex formation is accelerated by the presence of OH^- in the inner coordination sphere can no longer serve as a criterion for the dissociative mechanism of the unhydrolyzed species, and it would be reasonable to assume an associative mechanism for all trivalent cations in their unhydrolyzed form.^{23,24}

Registry No. AlL^+ , 68813-17-2; H_2L , 96-97-9; Al^{3+} , 22537-23-1.

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Molecular Stereochemistry of Iodo(meso-tetraphenylporphinato)iron(III)

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The molecular stereochemistry of iodo(meso-tetraphenylporphinato)iron(III), FeTPPI, was examined to determine if the axial ligand has any substantial influence on the coordination geometry of the iron(III) atom in this high-spin porphinato derivative. After completion of this work, the structure of the related bromide complex, FeTPPBr, was reported.¹ We are thus able to compare the structures of the chloro,² bromo, and iodo derivatives of $[FeTPP]^+$.

Experimental Section

FeTPPI was prepared by the reaction of a $CHCl_3$ solution of $(FeTPP)_2O^{3,4}$ with a 100-fold excess of aqueous KI/H_2SO_4 . The aqueous layer was removed, the $CHCl_3$ solution was filtered and concentrated, and crystals were grown by allowing pentane to diffuse into the solution.

Preliminary examination of a crystal of FeTPPI with dimensions of $0.27 \times 0.20 \times 0.53$ mm established that the Laue symmetry and systematic absences were consistent with the monoclinic space group $P2_1/n$. Lattice constants $a = 10.118$ (3) Å, $b = 16.352$ (4) Å, $c = 21.211$ (7) Å, and $\beta = 89.56$ (2)° came from a least-squares refinement that utilized the setting angles of 60 reflections. These constants led to a calculated density of 1.51 g/cm³ for a cell content of four FeTPPI molecules; the experimental density was 1.49 g/cm³. All measurements were made at the ambient laboratory temperature of 20 ± 1 °C.

Diffracted intensities were measured by θ - 2θ scanning using graphite-monochromated Mo $K\alpha$ radiation. The scan range used was 1.0° below $K\alpha_1$ to 1.0° above $K\alpha_2$. Backgrounds were collected at the extremes of the scan for 0.5 times the time required for the scan itself. All independent data to $(\sin \theta)/\lambda \leq 0.648$ Å⁻¹ were measured. Four standard reflections, measured periodically, showed no trend with time. Variable 2θ scan rates were used as described previously;⁵ the slowest was $2.0^\circ/\text{min}$ and the fastest was $12.0^\circ/\text{min}$. Net intensities were reduced to relative squared amplitudes, $|F_o|^2$, with correction for the absorption of x-radiation ($\mu = 1.34$ mm⁻¹). Reflections having $F_o > 3\sigma(F_o)$ were taken to be observed. A total of 6175 unique data, 77% of the theoretical number possible, were used in the subsequent solution and refinement of the structure.

The structure was solved by the usual heavy-atom method.⁶ Isotropic block-diagonal least-squares refinement smoothly converged.⁷ A difference Fourier synthesis gave the approximate positions of all hydrogen atoms in the asymmetric unit of the structure; these atoms were then assigned to theoretically calculated positions ($C-H = 0.95$ Å, $B(H) = B(C) + 1.0$ Å²), and their contributions to the calculated structure amplitudes were included in subsequent cycles of refinement. Anisotropic temperature factors and the imaginary component of anomalous scattering were now included, and the structure was refined to convergence. This led to a conventional residual (R_1) of 0.049, a weighted residual (R_2) of 0.059, and an error of fit of 1.90. A final difference Fourier synthesis had one peak of ~ 1.1 e/Å³ near the iodide and several peaks of 0.5 - 0.7 e/Å³ near the iron and iodide, but it was otherwise featureless. Final atomic coordinates and associated thermal parameters are reported in Table I. A listing of the final observed

Table I. Structural Parameters of the Atoms in Crystalline FeTPPI^a

atom type	coordinates			anisotropic parameters, Å ²					
	10 ⁴ x	10 ⁴ y	10 ⁴ z	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
Fe ^b	3695 (0)	3272 (0)	3488 (0)	3.72 (2)	3.09 (2)	2.18 (2)	0.28 (2)	0.15 (2)	0.22 (2)
I ^b	1402 (0)	2673 (0)	3296 (0)	4.58 (1)	4.87 (1)	4.39 (1)	-0.50 (1)	-0.08 (1)	-0.41 (1)
N ₁	3600 (3)	3622 (2)	4418 (1)	4.3 (1)	3.3 (1)	2.3 (1)	0.3 (1)	0.0 (1)	0.0 (1)
N ₂	4787 (3)	2269 (2)	3782 (1)	3.9 (1)	3.4 (1)	2.4 (1)	0.6 (1)	0.0 (1)	0.3 (1)
N ₃	4625 (3)	3146 (2)	2626 (1)	3.9 (1)	3.7 (1)	2.7 (1)	0.5 (1)	0.3 (1)	0.4 (1)
N ₄	3412 (3)	4493 (2)	3263 (1)	4.0 (1)	3.4 (1)	2.4 (1)	0.1 (1)	0.3 (1)	0.3 (1)
C _{a1}	3053 (4)	4324 (2)	4650 (2)	4.1 (2)	3.8 (2)	2.6 (1)	0.0 (1)	-0.1 (1)	-0.2 (1)
C _{a2}	3802 (4)	3123 (2)	4936 (2)	4.1 (2)	4.0 (2)	2.5 (1)	-0.2 (1)	-0.2 (1)	0.2 (1)
C _{a3}	4855 (4)	1962 (2)	4387 (2)	3.9 (2)	3.8 (2)	3.0 (2)	0.2 (1)	-0.3 (1)	0.5 (1)
C _{a4}	5411 (4)	1706 (2)	3404 (2)	3.9 (2)	3.8 (2)	2.9 (2)	0.8 (1)	0.1 (1)	0.4 (1)
C _{a5}	5218 (4)	2443 (2)	2397 (2)	3.8 (2)	4.0 (2)	2.8 (1)	0.5 (1)	0.6 (1)	0.3 (1)
C _{a6}	4479 (4)	3664 (2)	2111 (2)	3.9 (2)	4.1 (2)	2.4 (1)	0.5 (1)	0.5 (1)	0.7 (1)
C _{a7}	3467 (4)	4835 (2)	2668 (2)	3.9 (2)	3.1 (2)	3.4 (2)	0.0 (1)	0.2 (1)	0.2 (1)
C _{a8}	2922 (4)	5092 (2)	3653 (2)	4.1 (2)	3.2 (2)	3.5 (2)	0.2 (1)	0.2 (1)	0.2 (1)
C _{b1}	2893 (4)	4260 (3)	5323 (2)	5.7 (2)	4.3 (2)	2.7 (2)	0.0 (2)	0.2 (1)	-0.6 (1)
C _{b2}	3358 (4)	3520 (3)	5494 (2)	6.0 (2)	4.4 (2)	2.4 (2)	0.3 (2)	-0.2 (1)	-0.1 (1)
C _{b3}	5514 (4)	1190 (3)	4375 (2)	5.6 (2)	4.2 (2)	3.2 (2)	1.2 (2)	0.2 (2)	1.0 (1)
C _{b4}	5854 (4)	1031 (3)	3776 (2)	5.6 (2)	4.0 (2)	3.6 (2)	1.6 (2)	0.5 (2)	0.6 (1)
C _{b5}	5415 (5)	2521 (3)	1730 (2)	5.6 (2)	4.8 (2)	2.8 (2)	1.3 (2)	0.8 (1)	0.2 (1)
C _{b6}	4958 (4)	3263 (3)	1553 (2)	5.7 (2)	4.8 (2)	2.7 (2)	0.9 (2)	0.5 (1)	0.7 (1)
C _{b7}	3015 (4)	5656 (3)	2695 (2)	5.8 (2)	3.8 (2)	3.9 (2)	0.5 (2)	0.9 (2)	0.9 (1)
C _{b8}	2682 (4)	5818 (3)	3298 (2)	5.8 (2)	3.5 (2)	3.8 (2)	0.7 (2)	0.6 (2)	0.4 (1)
C _{m1}	4385 (4)	2346 (2)	4926 (2)	4.2 (2)	4.0 (2)	2.5 (1)	0.0 (1)	-0.2 (1)	0.4 (1)
C _{m2}	5600 (4)	1775 (2)	2755 (2)	4.2 (2)	3.9 (2)	2.9 (2)	0.9 (1)	0.4 (1)	0.3 (1)
C _{m3}	3969 (4)	4454 (2)	2131 (2)	4.3 (2)	3.7 (2)	2.7 (1)	0.1 (1)	0.2 (1)	0.8 (1)
C _{m4}	2720 (4)	5023 (2)	4301 (2)	4.3 (2)	3.5 (2)	2.9 (2)	0.0 (1)	0.1 (1)	-0.4 (1)
C ₁	4591 (4)	1956 (2)	5557 (2)	5.0 (2)	3.8 (2)	2.4 (1)	0.6 (1)	-0.3 (1)	0.4 (1)
C ₂	5801 (5)	2033 (3)	5848 (2)	5.7 (2)	6.6 (3)	3.7 (2)	0.2 (2)	-0.6 (2)	1.7 (2)
C ₃	5964 (5)	1741 (4)	6453 (2)	7.1 (3)	7.5 (3)	4.3 (2)	0.4 (2)	-2.2 (2)	1.4 (2)
C ₄	4939 (6)	1378 (3)	6766 (2)	8.9 (3)	5.4 (2)	3.2 (2)	-0.1 (2)	-1.1 (2)	1.3 (2)
C ₅	3769 (5)	1291 (3)	6483 (2)	7.9 (3)	5.1 (2)	3.8 (2)	-1.3 (2)	0.4 (2)	1.1 (2)
C ₆	3575 (5)	1588 (3)	5875 (2)	6.1 (2)	5.4 (2)	3.1 (2)	-0.6 (2)	-0.4 (2)	0.4 (2)
C ₇	6343 (4)	1100 (3)	2421 (2)	5.3 (2)	4.6 (2)	2.7 (2)	1.9 (2)	0.4 (1)	0.7 (1)
C ₈	5728 (5)	402 (3)	2225 (2)	7.2 (3)	4.9 (2)	4.8 (2)	0.9 (2)	1.4 (2)	0.3 (2)
C ₉	6454 (7)	-214 (3)	1925 (2)	12.5 (4)	4.2 (2)	4.5 (2)	1.4 (3)	1.6 (3)	0.0 (2)
C ₁₀	7775 (6)	-130 (4)	1839 (2)	10.6 (4)	7.8 (3)	3.7 (2)	5.0 (3)	1.7 (2)	1.5 (2)
C ₁₁	8389 (5)	567 (4)	2023 (2)	6.5 (3)	10.7 (4)	4.3 (2)	4.3 (3)	0.7 (2)	0.6 (2)
C ₁₂	7695 (5)	1193 (3)	2313 (2)	5.4 (2)	7.6 (3)	4.4 (2)	2.3 (2)	0.0 (2)	0.0 (2)
C ₁₃	4045 (4)	4942 (2)	1531 (2)	5.3 (2)	3.4 (2)	2.8 (2)	0.7 (2)	0.5 (1)	0.5 (1)
C ₁₄	2918 (4)	5118 (3)	1182 (2)	5.4 (2)	5.6 (2)	4.1 (2)	0.4 (2)	-0.1 (2)	1.2 (2)
C ₁₅	3023 (5)	5568 (3)	637 (2)	7.3 (3)	6.0 (3)	4.1 (2)	1.5 (2)	-1.4 (2)	1.2 (2)
C ₁₆	4242 (5)	5847 (3)	431 (2)	8.5 (3)	4.7 (2)	3.6 (2)	1.2 (2)	0.7 (2)	1.4 (2)
C ₁₇	5333 (5)	5688 (3)	774 (2)	6.7 (3)	5.0 (2)	4.3 (2)	0.1 (2)	1.4 (2)	0.9 (2)
C ₁₈	5244 (4)	5231 (3)	1321 (2)	5.4 (2)	4.6 (2)	3.6 (2)	0.2 (2)	0.4 (2)	0.7 (2)
C ₁₉	2150 (4)	5729 (2)	4656 (2)	4.5 (2)	3.2 (2)	3.1 (2)	0.0 (1)	0.4 (1)	0.0 (1)
C ₂₀	2908 (4)	6150 (3)	5097 (2)	4.9 (2)	3.9 (2)	5.1 (2)	-0.6 (2)	0.4 (2)	-0.4 (2)
C ₂₁	2386 (5)	6777 (3)	5453 (2)	7.2 (3)	4.4 (2)	4.7 (2)	-1.6 (2)	0.9 (2)	-1.2 (2)
C ₂₂	1103 (5)	7016 (3)	5350 (2)	7.4 (3)	4.3 (2)	5.8 (3)	-0.4 (2)	2.4 (2)	-1.4 (2)
C ₂₃	346 (5)	6621 (3)	4914 (3)	5.8 (3)	6.3 (3)	6.7 (3)	1.8 (2)	0.6 (2)	-0.8 (2)
C ₂₄	869 (5)	5960 (3)	4579 (2)	5.4 (2)	5.6 (2)	4.7 (2)	0.7 (2)	-0.3 (2)	-1.3 (2)

^a The numbers in parentheses are the estimated standard deviations. For I 10⁵x = 14 020 (3), 10⁵y = 26 734 (2), and 10⁵z = 32 964 (1).

^b For Fe 10⁵x = 36 952 (5), 10⁵y = 32 719 (3), 10⁵z = 34 884 (2).

and calculated structure amplitudes (×10) is available as supplementary material.

Results and Discussion

Figure 1 presents a perspective view of the FeTPPI molecule. The figure also illustrates the numbering scheme employed for the atoms and all bond distances in the porphinato core. Individual bond distances and angles are given in Tables II and III (supplementary material). There is no required crystallographic symmetry for the monomeric FeTPPI molecule; however, the molecule displays approximate fourfold symmetry. Chemically equivalent bond parameters are thus appropriately averaged, and averaged values of bond parameters in the core are summarized in Table IV; the averaged values are unremarkable.

Figure 2 is a formal diagram of the porphinato core displaying the perpendicular displacements of the atoms, in units of 0.01 Å, from the mean plane of the core. The displacement of the iron atom from this mean plane is 0.53 Å and is 0.46

Table IV. Values of Averaged Bond Parameters in FeTPPI^{a, b}

A. Bond Lengths, Å			
Fe-N	2.066 (11)	C _m -C _p	1.501 (7)
N-C _a	1.379 (9)	C _a -C _b	1.429 (6)
C _a -C _m	1.393 (7)	C _b -C _b	1.347 (6)
B. Bond Angles, Deg			
C _a -N-C _a	105.9 (2)	C _a -C _m -C _a	124.4 (6)
N-C _a -C _b	109.7 (3)	C _a -C _b -C _b	107.4 (3)
N-C _a -C _m	125.8 (3)	C _b -C _a -C _m	124.5 (5)
N-Fe-N	87.2 (2)	I-Fe-N	102.8 (7)

^a C_a and C_b represent the respective α- and β-pyrrole carbon atoms, C_m stands for the methine carbon, and C_p is a phenyl carbon atom bonded to the core. ^b The numbers in parentheses are the estimated standard deviations.

Å from the mean plane of the four nitrogen atoms. Thus, the porphinato core displays a small net doming (~0.07 Å) away from the iron atom. Note (Figure 2) that all atoms of the porphinato core are below the plane defined by the four

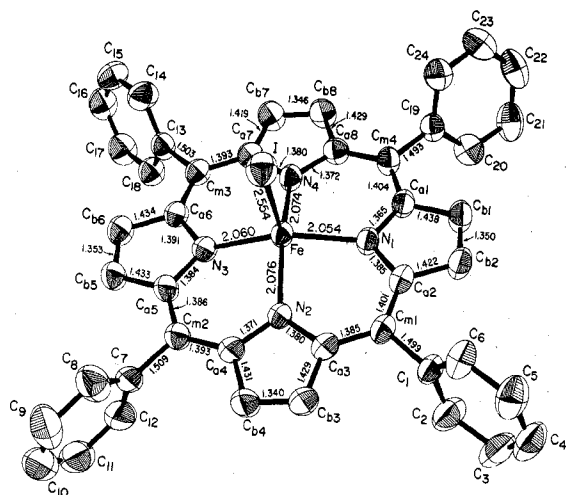


Figure 1. Computer-drawn perspective view of the FeTPPI molecule. The numbering scheme used for the atoms is displayed. The individual bond distances in the coordination group and the porphyrinato core are shown. Esd's are 0.003 for the distance involving iron and 0.005 Å otherwise.

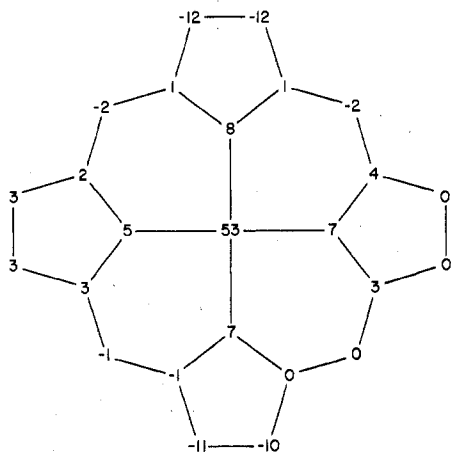


Figure 2. Formal diagram of the porphyrinato skeleton in FeTPPI illustrating the perpendicular displacements, in units of 0.01 Å, from the mean plane of the core. The orientation of the core is approximately the same as shown in Figure 1.

porphyrinato nitrogen atoms and away from the iron(III) atom.

Table V summarizes three coordination group parameters for the nine high-spin iron(III) porphyrins of known structure. The parameters are the average Fe-N bond distance and the displacement of the iron(III) atom from the mean plane of the four nitrogen atoms and the mean plane of the core. It is seen that, save for [FeTPP]₂O, the average Fe-N bond distance of 2.068 (8) Å agrees to within one esd. Parameters in the coordination groups of the bromo and iodo derivatives of [FeTPP]⁺ are quite similar; however, the chloro derivative has a substantially smaller displacement of the iron(III) atom (0.39 Å). These differences, however, appear to be related to the conformation of the porphyrinato core rather than to the anionic axial ligand.

The porphyrinato core in FeTPP₂O has crystallographically required planarity,^{2a} and a redetermination of structure^{2b} shows that no substantial nonplanarity is obscured by the known disorder. Both Fe(MesoP)(OCH₃) and Fe(Proto IX)SPhNO₂ have nearly planar porphyrinato cores; the average displacement of the iron(III) atom is 0.47 (3) Å. The remaining high-spin complexes have substantially less planar cores than the above three complexes; the average value of the iron displacement from the mean plane of the core is 0.54 (1) Å. These conformational differences most probably result from environ-

Table V. Coordination Group Parameters of Five-Coordinate High-Spin Iron(III) Porphyrins

complex ^a	Fe-N	Δ(N ₄)	Δ(core)	ref
Fe(MesoP)(OCH ₃)	2.073 (6)	0.46	0.49	8
Fe(Proto IX)Cl	2.062 (10)	0.48	0.55	9
FeTPP ₂ O	2.060 (3)	0.39	0.39	2b
FeTPPBr	2.069 (9)	0.49	0.56	1
FeTPPI	2.066 (11)	0.46	0.53	this work
FeTPP(NCS)	2.065 (10)	0.49	0.55	10
[FeTPP] ₂ O	2.087 (8)	0.50	0.54	4
Fe(Proto IX)SPhNO ₂	2.064 (18)	0.43	0.45	11
[Fe(ODM)] ₂ O	2.065 (8)	0.51	0.53	12
av	2.068 (8)	0.47 (4)	0.51 (6)	

^a Abbreviations: MesoP, mesoporphyrin dianion; Proto IX, protoporphyrin IX dianion; ODM, 5,15-dimethyl-2,3,7,8,12,13,17,18-octaethylporphyrin dianion.

mental influences rather than the identity of the axial ligand (note the differences between FeTPP₂O and Fe(Proto IX)Cl).

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Registry No. FeTPPI, 25482-28-4.

Supplementary Material Available: Tables II and III, bond distances and angles in FeTPPI, and a listing of structure factor amplitudes (×10) (31 pages). Ordering information is given on any current masthead page.

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Synthesis and Structure of Di-*n*-propylammonium Ethoxybis(di-*n*-propylmonothiocarbamate)dioxouranate-(VI), a Mixed-Chelate Alkoxide of Uranium

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Although many reports involving the uranyl ion UO₂²⁺ have appeared in the chemical literature, most concern the chemistry of the simple salts (and adducts of these compounds)² and complexes which exhibit uranyl-oxygen and uranyl-nitrogen linkages.³ The chemistry of the common organic chelating species such as tropolonates,⁴ β-diketonates,⁵ and Schiff bases⁶