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Molecular Stereochemistry of Low-Spin Five-Coordinate Phenyl(*meso*-tetraphenylporphyrinato)iron(III)

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Single crystals of the low-spin phenyliron(III)–*meso*-tetraphenylporphyrin complex $Fe(C_6H_5)TPP\cdot C_5H_{12}$ (**1**) of composition $C_{55}H_{45}N_4Fe$ were obtained by recrystallization of the known complex $Fe(C_6H_5)TPP\cdot THF$. The effective magnetic moment (2.3–2.7 μ_B in the range of temperature 4.2–297 K) shows that **1** is a low-spin five-coordinate compound. The crystals belong to the triclinic system, space group $P\bar{1}$, with $a = 12.556$ (4) Å, $b = 16.866$ (6) Å, $c = 12.216$ (4) Å, $\alpha = 109.79$ (2)°, $\beta = 114.91$ (2), $\gamma = 72.30$ (2)°, $V = 2167$ Å^3, $Z = 2$, and $d_{calcd} = 1.25$ g cm^{-3}. Discrepancy indices are $R(F) = 0.060$ and $R_w(F) = 0.088$ for 4968 reflections having $I > 3\sigma(I)$. **1** is a five-coordinate compound in which the average Fe–N_p bond distance is 1.962 Å and the Fe–C bond length is 1.955 (3) Å. The iron(III) atom is displaced by 0.17 Å from the mean plane of the porphyrin core; this displacement is very short. In evidence $C_6H_5^-$ is a very strong field ligand, and this property is at the origin of the low-spin character of **1**.

The presence of organometallic iron porphyrin species in hemoproteins has been reported recently;[1] σ-phenylprotohemins have been indeed obtained by the action of phenylhydrazine with myoglobin or hemoglobin. Alkyl- and aryliron(III)–porphyrin complexes have been synthesized and studied.[2-13] Their spectroscopic and magnetic properties[10] indicate the presence of five-coordinate low-spin ($S = {}^1/_2$) compounds. However, so far, no structural studies have confirmed the presence of this stereochemistry, which is highly unusual with this spin state.[14] We have obtained crystals of the phenyliron(III)–meso-tetraphenylporphyrin complex, $Fe(C_6H_5)TPP\cdot C_5H_{12}$, and present here its crystal structure.

Experimental Section

General Procedures. All experiments were done under inert atmosphere by Schlenk techniques. Solvents were rigorously purified and dried under argon. The free tetraphenylporphyrin $TPPH_2$ and its iron(III) chloro complex were prepared from published methods.[15,16]

UV–visible spectra were obtained on a Cary 210 spectrometer. The magnetic susceptibility measurements were carried out with a Faraday-type magnetometer equipped with a continuous-flow cryostat in the temperature range 4.2–297 K. The polycrystalline powder samples weighed about 45 mg. The applied magnetic field was 0.7 T. Mercury tetrakis(thiocyanato)cobaltate(II) was used as a susceptibility standard.

Synthesis of $Fe(C_6H_5)TPP\cdot C_5H_{12}$ (1). $Fe(C_6H_5)TPP\cdot THF$ was synthesized by using the method described by Reed et al.[4] Black single crystals suitable for X-ray studies were obtained by slow diffusion of a pentane layer (60 mL) into a benzene solution (10 mL) of $Fe(C_6H_5)TPP\cdot THF$ (10 mg) in the dark at 6 °C. UV (λ_{max}): solution in toluene (25 °C) 545 nm (e), 520, 424 (e), 410, 398 (e); solution in THF (25 °C) 522 nm (e), 428 (e), 417, 398 (e).

X-ray Methods. A systematic search in reciprocal space using a Philips PW1100/16 automatic diffractometer showed that crystals of **1** belong to the triclinic system.

The unit-cell dimensions and their standard deviations were obtained and refined at room temperature with Cu K$\bar{\alpha}$ radiation ($\lambda = 1.5418$ Å) by using 25 carefully selected reflections and the standard Phillips software. Final results: $C_{55}H_{45}N_4Fe$, mol wt 817.8, $a = 12.556$ (4) Å, $b = 16.866$ (6) Å, $c = 12.216$ (4) Å, $\alpha = 109.79$ (2)°, $\beta = 114.91$ (2)°, $\gamma = 72.30$ (2)°, $V = 2167$ Å^3, $Z = 2$, $d_{calcd} = 1.25$ g cm^{-3}, $d_{obsd} = 1.23 \pm 0.02$ g cm^{-3}, $\mu = 30.95$ cm^{-1}, $F_{000} = 858$, space group $P\bar{1}$.

A parallelepipedic crystal of 0.60 × 0.30 × 0.20 mm was sealed in a Lindemann glass capillary and mounted on a rotation-free goniometer head. All quantitative data were obtained from a Philips PW 1100/16 four-circle automatic diffractometer, controlled by a P852 computer, using graphite-monochromated radiation and standard software (in bisecting mode). The vertical and horizontal apertures in front of the scintillation counter were adjusted so as to minimize the background counts without loss of net peak intensity at the 2σ level. The total scan width in the $\theta/2\theta$ flying step scan used was $\Delta\theta = 1.00 +$ (Cu $K\alpha_1\alpha_2$ splitting) with a step width of 0.05° and a scan speed of 0.020° s^{-1}. A total of 6015 reflections were recorded (5° $< \theta <$ 57° ($h,\pm k,\pm l$)). The resulting data set was transferred to a PDP 11/60 computer, and for all subsequent computations, the Enraf-Nonius SDP/V18 package was used[17] with the exception of a local data reduction program.

Three standard reflections measured every hour during the entire data collection period showed no significant trend.

The raw step scan data were converted to intensities by using the Lehmann–Larson method[18] and then corrected for Lorentz, polarization, and absorption factors, the latter computed by the numerical integration method of Busing and Levy[19] (transmission factors between 0.30 and 0.59). No extinction correction was applied. A unique data set of 4968 reflections having $I > 3\sigma(I)$ was used for determining and refining the structure.

The structure was solved with the heavy-atom method. After refinement of the heavy atoms, a difference-Fourier map revealed maxima of residual electronic density close to the positions expected

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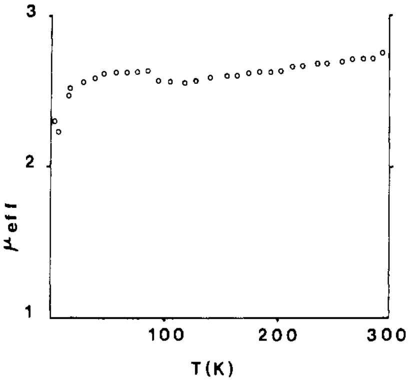

Figure 1. Effective magnetic moment of $Fe(C_6H_5)TPP{\cdot}C_5H_{12}$ vs. temperature.

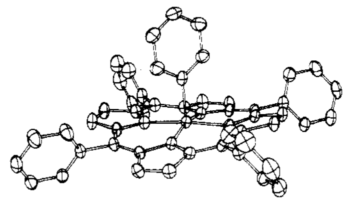

Figure 2. ORTEP plot of $Fe(C_6H_5)TPP$. Ellipsoids are scaled to enclose 40% of the electronic density. Hydrogen atoms are omitted.

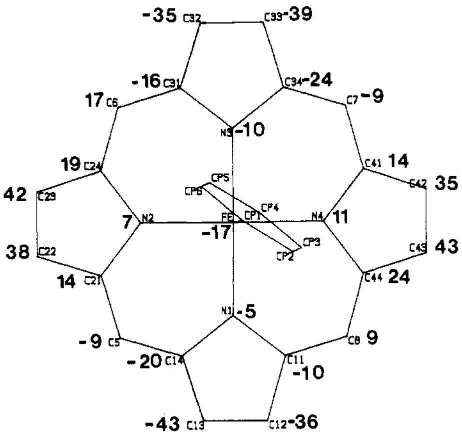

Figure 3. Stick model of the porphyrin core with the labeling scheme used. The dark numbers are the deviations in 0.01-Å units of the atoms from the porphyrin core mean plane.

for hydrogen atoms; they were introduced in structure factor calculations by their computed coordinates (C–H = 0.95 Å) and isotropic temperature factors of 6 $Å^2$ (10 $Å^2$ for pentane hydrogens) but not refined. Full-matrix least-squares refinement converged to $R(F) = 0.060$ and $R_w(F) = 0.088$ ($w = (1/\sigma_{count}^2 + (pI)^2)^{1/2}$). The unit weight observation was 1.98 for $p = 0.08$. A final difference map revealed no significant maxima.

Table I lists the atomic positional parameters for all non-hydrogen atoms with the estimated standard deviations.

Results and Discussion

Figure 1 shows the variation of the effective magnetic moment with temperature (4.2-297 K). The effective magnetic moment of 2.3–2.7 μ_B provides evidence for a low-spin ferric complex ($S = 1/2$). These rather high values are consistent with those given for $(OEP)Fe^{III}(4\text{-}OCH_3C_6H_4)$.[10]

The UV–vis spectra of **1** in toluene or in THF are consistent with those reported in the literature.

Figure 2 shows the structure of the $Fe^{III}(C_6H_5)TPP$ molecule. Figure 3 is a formal diagram of the porphyrinato core, which displays the perpendicular displacements (in units of 0.01 Å) of each atom from the mean plane of the 24-atom core. Table II gives selected bond distances and angles in $Fe(C_6H_5)TPP$ (the other values are given in Tables VI and VII (supplementary material)). Figure 3 clearly shows the five-coordinate nature of the complex. The $(Fe–N_p)_{av}$ distance is 1.962 (2) Å. This is clearly shorter than the average 1.994 (1) Å distance found in the low-spin five-coordinate $[Fe(NO)OEP]ClO_4$[20] and also slightly shorter than the $(Fe–N_p)_{av}$ distance of 1.990 Å found for a number of low-spin six-coordinate iron(III) species.[14] It is also slightly shorter than the $(Fe–N_p)_{av}$ values of 2.001 (3) and 1.982 (5) Å found respectively in the low-spin five-coordinate ferrous species Fe(NO)TPP[21] and Fe(CS)TPP.[22] The corresponding $C_t{\cdots}N_p$[14]

Table I. Positional Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	B, $Å^2$
Fe	0.39714 (4)	0.16675 (3)	0.08553 (4)	2.46 (1)
N1	0.5456 (2)	0.1345 (2)	0.2185 (2)	2.62 (6)
C11	0.6348 (3)	0.1828 (2)	0.2928 (3)	2.84 (8)
C12	0.7120 (3)	0.1505 (2)	0.4089 (3)	3.30 (9)
C13	0.6733 (3)	0.0810 (2)	0.3920 (3)	3.11 (8)
C14	0.5723 (3)	0.0698 (2)	0.2777 (3)	2.69 (8)
C5	0.5136 (3)	0.0019 (2)	0.2307 (3)	2.67 (8)
N2	0.3562 (2)	0.0555 (2)	0.0524 (2)	2.72 (7)
C21	0.4175 (3)	−0.0071 (2)	0.1197 (3)	2.69 (8)
C22	0.3624 (3)	−0.0807 (2)	0.0626 (3)	3.27 (9)
C23	0.2643 (3)	−0.0627 (2)	−0.0365 (3)	3.27 (9)
C24	0.2587 (3)	0.0224 (2)	−0.0411 (3)	2.76 (8)
C6	0.1642 (3)	0.0665 (2)	−0.1215 (3)	2.82 (8)
N3	0.2552 (2)	0.1920 (2)	−0.0593 (2)	2.93 (7)
C31	0.1623 (3)	0.1475 (2)	−0.1269 (3)	2.93 (8)
C32	0.0653 (3)	0.1952 (2)	−0.2087 (3)	3.70 (9)
C33	0.0981 (3)	0.2673 (2)	−0.1939 (3)	4.0 (1)
C34	0.2162 (3)	0.2662 (2)	−0.1016 (3)	3.23 (9)
C7	0.2860 (3)	0.3258 (2)	−0.0695 (3)	3.30 (9)
N4	0.4593 (2)	0.2608 (2)	0.0872 (2)	2.84 (7)
C41	0.4029 (3)	0.3205 (2)	0.0153 (3)	3.21 (8)
C42	0.4792 (3)	0.3790 (2)	0.0465 (3)	4.2 (1)
C43	0.5813 (3)	0.3572 (2)	0.1383 (3)	3.93 (9)
C44	0.5683 (3)	0.2854 (2)	0.1659 (3)	2.96 (8)
C8	0.6489 (3)	0.2522 (2)	0.2662 (3)	2.74 (8)
C51	0.5544 (3)	−0.0657 (2)	0.3017 (3)	2.95 (8)
C52	0.6628 (3)	−0.1206 (2)	0.3133 (3)	3.48 (9)
C53	0.6973 (4)	−0.1845 (2)	0.3746 (4)	4.5 (1)
C54	0.6257 (4)	−0.1922 (3)	0.4278 (4)	5.3 (1)
C55	0.5184 (4)	−0.1368 (3)	0.4184 (4)	5.5 (1)
C56	0.4825 (3)	−0.0743 (2)	0.3551 (3)	4.5 (1)
C61	0.0553 (3)	0.0268 (2)	−0.2012 (3)	2.89 (8)
C62	−0.0197 (3)	0.0232 (3)	−0.1488 (3)	4.6 (1)
C63	−0.1184 (3)	−0.0152 (3)	−0.2185 (4)	5.4 (1)
C64	−0.1441 (3)	−0.0504 (3)	−0.3433 (4)	4.5 (1)
C65	−0.0700 (3)	−0.0472 (3)	−0.3966 (3)	4.1 (1)
C66	0.0289 (3)	−0.0088 (2)	−0.3269 (3)	3.55 (9)
C71	0.2331 (3)	0.4000 (2)	−0.1299 (3)	3.73 (9)
C72	0.1399 (4)	0.4615 (3)	−0.1059 (4)	5.2 (1)
C73	0.0896 (5)	0.5297 (3)	−0.1660 (5)	6.5 (2)
C74	0.1342 (5)	0.5354 (3)	−0.2451 (4)	6.3 (1)
C75	0.2262 (4)	0.4749 (3)	−0.2703 (4)	5.3 (1)
C76	0.2762 (4)	0.4068 (2)	−0.2129 (3)	4.4 (1)
C81	0.7551 (3)	0.2927 (2)	0.3526 (3)	3.18 (8)
C82	0.7426 (4)	0.3720 (2)	0.4343 (4)	4.5 (1)
C83	0.8421 (4)	0.4064 (3)	0.5183 (4)	5.2 (1)
C84	0.9545 (3)	0.3624 (2)	0.5222 (4)	4.7 (1)
C85	0.9679 (3)	0.2843 (3)	0.4416 (4)	4.4 (1)
C86	0.8696 (3)	0.2500 (2)	0.3575 (3)	3.8 (1)
CP1	0.3128 (3)	0.2344 (2)	0.2003 (3)	3.07 (8)
CP2	0.3589 (3)	0.3011 (2)	0.2979 (3)	4.0 (1)
CP3	0.2949 (4)	0.3522 (3)	0.3749 (4)	4.8 (1)
CP4	0.1862 (3)	0.3363 (3)	0.3554 (4)	4.6 (1)
CP5	0.1419 (3)	0.2703 (3)	0.2608 (4)	5.0 (1)
CP6	0.2048 (3)	0.2190 (3)	0.1820 (3)	4.4 (1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $\frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\alpha)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

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Table II. Selected Bond Lengths (Å), Angles (deg) and Averages with Their Estimated Standard Deviations

	Metal Atoms		
Fe-N1	1.952 (2)	N1FeN2	89.18 (8)
Fe-N2	1.961 (2)	N1FeN4	90.37 (8)
Fe-N3	1.969 (2)	N2FeN3	89.54 (9)
Fe-N4	1.961 (2)	N3FeN4	89.50 (9)
Fe-C_{p_1}	1.955 (3)	N1FeCP1	93.61 (9)
		N2FeCP2	98.51 (9)
		N3FeCP1	91.77 (9)
		N4FeCP1	96.61 (10)
	Pyrrole Rings		
N-C_α	1.389 (1)	$C_\alpha NC_{\alpha'}$	104.4 (1)
C_α-C_β	1.434 (1)	$C_\alpha C_\beta C_{\beta'}$	107.2 (1)
C_β-$C_{\beta'}$	1.348 (2)	$NC_\alpha C_\beta$	110.6 (1)
C_α-C_m	1.384 (1)	$NC_\alpha C_m$	125.1 (1)
		$C_\alpha C_m C_\alpha$	123.0 (1)
		$C_\alpha C_m C_p$	118.6 (1)
	Phenyl Rings		
C_m-C_p	1.501 (2)	C-C-C	120.5 (1)
C-C	1.374 (1)		
	Phenyl Group		
C_P-C_P	1.382 (2)	Fe-C_P-C_P	120.4 (1)
		C_P-C_P-C_P	120.0 (1)

separation of 1.953 (1) Å clearly indicates a distinct contraction of the porphyrinato core when the coordination number of low-spin ferric porphyrin derivatives changes from 6 to 5. This contraction does not seem to be present in the nitrosyl complexes, but these complexes have electronic structures that are unusual for iron(III) and iron(II) species. Fe(NO)TPP[21] and $[Fe(NO)TPP]^+$[20] have respectively $S = {}^1/_2$ and $S = 0$ spin states owing to the odd electron originally on the NO ligand.

The Fe–C bond distance of 1.955 (3) Å is slightly longer than that present in the iron(III) derivative, FeTTP(Cl) ($C = C(p\text{-}ClC_6H_4)_2$),[23] in which a vinylidene moiety is inserted into a Fe–N_p bond (1.914 (7) Å). Compared to all the non-porphyrin–iron complexes presenting a σ Fe–C(sp^2) bond, it is longer than the corresponding distance in the low-spin iron(III) complexes $Fe(C_{22}H_{22}N_4)(C_6H_5)$[24] (1.933 (3) Å) and shorter in all other cases.[25]

The Fe–C bond is tilted with respect to the normal to the porphyrin mean plane by an angle of 1.85 (4)° and does not lie exactly in the mean plane of the phenyl ring, the Fe$\cdots C_{P_1}\cdots C_{P_4}$ angle is 176.0 (1)°. The angular distorsions are due to the crystal packing. The porphyrinato skeleton is not domed as in most of the five-coordinate iron porphyrins but ruffled[26] (see Figure 3). The ruffling allows shorter Fe–N_p bond and a larger contraction of the core. Thus, it is most probably a consequence of the crystal packing. As usual, the individual pyrrole rings are planar but the dihedral angles between the pyrroles and the porphyrin mean plane are 9.4 (N_1), −8.8 (N_2), 7.3 (N_3), −7.9 (N_4)°.

With C_α and C_β to denote the respective α- and β-carbons in a pyrrole ring, C_m for a methine carbon, and C_p for a phenyl carbon that is bonded to the core, average bond lengths for the chemically analogous types of bonds are N–C_α = 1.389 (1), C_α–C_β = 1.434 (1), C_β–C_β = 1.348 (2), C_α–C_m = 1.384 (1), and C_m–C_p = 1.501 (2) Å.

The porphinato phenyl rings have normal geometries with a $(C–C)_{av}$ bond distance of 1.374 (1) Å and a $(C–C–C)_{av}$ bond angle of 120.5 (1)°. Their dihedral angles with the porphyrin core mean plane are 60.3, 113.8, 75.9, and 62.7°.

The phenyl ring bound to the iron atom has also a normal geometry with a $(C–C)_{av}$ bond distance of 1.382 (2) Å and a $(C–C–C)_{av}$ bond angle of 120.0 (1)°. Its dihedral acute angles with the mean plane formed by N_i, Fe, and CP_1 atoms (with i = 1–4) are respectively 55.0, 35.5, 54.5, and 36.0°; with the porphyrin core mean plane, its dihedral angle is 86.1°. The Fe atom is 0.1 Å out of the pheny-ring mean plane.

The displacement of the iron(III) atom with respect to the porphyrinato nitrogen mean plane is 0.17 Å. This displacement is shorter than reported values observed in other low-spin five-coordinate iron(II) and iron(III) porphyrinates: 0.22 Å in Fe^{II}(CS)OEP,[22] 0.21 Å in Fe^{II}NO(TPP),[21] and 0.29 Å in $[Fe(NO)(OEP)]ClO_4$.[20] In evidence, $C_6H_5^-$ is a very strong field ligand; this property is at the origin of the low-spin character of $Fe(C_6H_5)TPP$. One should also note that the small out-of-plane displacement of the metal atom results in tight contacts (range: 2.966 (2)–2.817 (2) Å).

The $(C–C)_{av}$ bond distance in the C_5H_{12} molecule of recrystallization is 1.35 (1) Å and the $(C–C–C)_{av}$ bond angle is 140.0 (2)°. No unusual intermolecular contacts have been found.

Acknowledgment. P.D. thanks Prof. Raymond Weiss and Prof. Jean Fischer (Université Louis Pasteur, Strasbourg, France) for useful discussions.

Registry No. **1**, 92284-31-6; $Fe(C_6H_5)TPP$, 70936-44-6.

Supplementary Material Available: Listings of hydrogen atom parameters (Table III), temperature factors of all anisotropic atoms (Table IV), observed and calculated structure factors (×10) for all observed reflections (Table V), individual bond distances in $Fe(C_6H_5)TPP$ (Table VI), and individual bond angles in $Fe(C_6H_5)TPP$ (Table VII) (30 pages). Ordering information is given on any current masthead page.

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