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Preparation and Physical and Stereochemical Characterization of the Tricyanomethanide Salt of 5,10,15,20-Tetraphenylporphinatoiron(III). A Six-Coordinate Intermediate-Spin Complex

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The preparation of the tricyanomethanide ($C(CN)_3^-$) salt of 5,10,15,20-tetraphenylporphinatoiron(III) is described. The magnetic moment, Mössbauer, and molecular structure are consistent with the assignment of an intermediate-spin ($S = {}^3/_2$) ground state. The magnetic moment is 5.4 μ_B and independent of temperature over the range 78–298 K. The isomer shift is 0.30 mm/s and the quadrupole splitting is 3.18 mm/s at 298 K. Crystals of FeTPP($C(CN)_3$) crystallize as the chloroform solvate in the monoclinic system, space group $P2_1/m$. The unit cell has a = 17.547 (3) Å, b = 9.260 (2) Å, c = 13.250 (2) Å, β = 102.50 (1)°, and Z = 2. Measurement of diffracted intensities employed a four-circle diffractometer with Mo Kα radiation. The FeTPP$^+$ moiety has required C_s symmetry and the tricyanomethanide ion serves as a bridging ligand with two of the three nitrogen atoms bonding to different iron(III) atoms. The structure is thus an infinite column of alternating FeTPP$^+$ and $C(CN)_3^-$ units. The tetragonal coordination group has an average iron–porphinato nitrogen bond distance of 1.995 (3) Å; the equivalent axial Fe–N bond distances are 2.317 (3) Å.

The magnetic properties of iron(III) porphyrins command much current interest. Iron(III) porphyrins are generally found to be either high spin ($S = {}^5/_2$) or low spin ($S = {}^1/_2$). In some heme protein derivatives, a thermal equilibrium of high- and low-spin states is observed,[2] but no such behavior has been reported for iron(III) porphyrin complexes in the solid state. Maltempo and co-workers[3] have suggested the possibility of a quantum-mechanically mixed spin state to account for the anomalous magnetic properties of oxidized cytochrome *c′*. Recently, the existence of intermediate-spin ($S = {}^3/_2$) iron(III) porphyrins has been recognized.[4,5] Dolphin and co-workers[4] have characterized perchloratooctaethylporphinatoiron(III), FeOEP($OClO_3$),[6] and its diethanol solvate as intermediate-spin complexes. The infrared data for FeOEP($OClO_3$) are consistent with the axial coordination of perchlorate while that for [FeOEP$(C_2H_5OH)_2$]ClO_4 is consistent with six-coordination. The magnetic behavior and Mössbauer parameters for the two complexes are quite similar and the assignment of the same spin state to both appears reasonable.

Kastner et al.[5] also find that the magnetic and Mössbauer parameters of FeTPP($OClO_3$) are consistent with an intermediate-spin complex and have determined its molecular structure. However, they[5] find that the six-coordinate diaquo derivative, [FeTPP$(OH_2)_2$]ClO_4, has magnetic, Mössbauer, and structural parameters consistent with a high-spin complex. Several other six-coordinate iron(III) porphyrins[7] utilizing weak field ligands such as dimethyl sulfoxide, tetramethylene sulfoxide (TMSO), and pyridine *N*-oxide are also high-spin complexes. There thus is some question concerning the nature of axial ligation in iron(III) porphyrins which can give rise to intermediate-spin complexes.

The preparation of the tricyanomethanide ($C(CN)_3^-$) salt of 5,10,15,20-tetraphenylporphinatoiron(III) has been described.[8] The infrared spectrum of FeTPP($C(CN)_3$) shows[8] a single band (2190 cm^{-1}, Nujol mull) in the CN stretching region. This suggests that the $C(CN)_3^-$ ion retains its planar structure and that the interaction between the $C(CN)_3^-$ and the tetraphenylporphinatoiron(III) moiety is weak. We were sufficiently intrigued by this unusual behavior to characterize the compound further. We report herein the magnetic characterization of this complex and its molecular structure, both of which are consistent with an intermediate-spin ($S = {}^3/_2$) species.

Experimental Section

FeTPP($C(CN)_3$) was prepared by the cleavage of the oxo bridge of $(FeTPP)_2O$ by two slightly different procedures. The first followed the literature method[8] (cyanoform in benzene) with the following modifications: (1) No excess of perchloric acid was used in the preparation of cyanoform from $KC(CN)_3$.[9] (2) Only the minimum of amount of cyanoform needed to cleave $(FeTPP)_2O$ was used. Both of these steps were taken to minimize perchlorate contamination of the final product.[10] The second utilized the treatment of a chloroform solution of $(FeTPP)_2O$ with an aqueous solution of $KC(CN)_3$ and H_2SO_4 in tenfold molar excess. After separation of the aqueous layer, a solid powder product was obtained by evaporation. Single crystals were best obtained by concentrating the original chloroform solutions and allowing pentane to diffuse into the solution.[11] Samples prepared by both methods appear to be identical with the exception of the chloroform solvate molecule incorporated in samples prepared by the second method.

Mössbauer data were collected on a Ridl 400 channel analyzer, Model 34-12B, using an Elscint Mössbauer drive, Model MFD-4. Pulse height discrimination was performed with a high count rate amplifier (Elscint, Model CAV-N-1) and single-channel analyzer (Elscint, Model SCA-N-2A). All spectra were observed using powders and isomer shifts are reported relative to iron metal. Magnetic susceptibilities were measured on powdered samples by the Faraday method using an Ainsworth electronic balance and an Alpha cryostat. $HgCo(SCN)_4$ was used as a standard, and susceptibilities were corrected for diamagnetism using the value -386×10^{-6} cgs units/mol for tetraphenylporphine and standard values for other elements present.[12] The moment was 5.4 μ_B and independent of temperature between 78 and 298 K. A room temperature determination of the magnetic moment in chloroform solution (5 mg/mL) by the Evans method[13] gave μ = 5.1 μ_B.

Preliminary examination of a crystal of FeTPP($C(CN)_3$) on a Syntex $P\bar{1}$ automated diffractometer established a two-molecule monoclinic unit cell. The systematic absences were consistent with either $P2_1$ or $P2_1/m$ as the space group. Least-squares refinement of the setting angles of 60 reflections, collected at $\pm 2\theta$, led to the following cell constants ($\bar{\lambda}$ 0.71069 Å): a = 17.547 (3) Å, b = 9.260 (2) Å, c = 13.250 (2) Å, and β = 102.50 (1)°. For a cell content of $2[Fe(N_4C_{44}H_{28})(C_4N_3)\cdot CHCl_3]$, the calculated density is 1.387 g/cm^3 and the experimental density was 1.376 g/cm^3.

Intensity data were measured on the Syntex diffractometer using graphite-monochromated Mo Kα radiation and θ–2θ scanning. Data were collected in shells of increasing 2θ. For $2\theta \leq 39.7°$, scan rates of 1–8°/min were used with background counts collected at the extremes of the scan for the same time as the scan itself. For $39.7° < 2\theta \leq 57.0°$, scan rates of 2°/min were used and background counts were collected for half the scan time. The base scan width was 2.3° at 2θ = 0° and included an allowance for spectral dispersion. Four standard reflections were measured every 50 reflections during data collection; no significant fluctuations were noted. Intensity data were reduced and standard deviations calculated as described previously.[14] A total of 3872 unique reflections having $F_o \geq 3\sigma(F_o)$ were retained as observed (73% of the theoretical number possible) and were used in the solution and refinement of the structure.

The structure was solved by the heavy-atom method[15] and refined by a combination of full-matrix and block-diagonal least-squares

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methods.[16] The Patterson map suggested placement of the iron atom and the porphinato core at $y = {}^1/_4$, which is a mirror plane in the space group $P2_1/m$. This space group was then assumed; all subsequent developments of structure solution and refinement were consistent with this choice of space group. The chloroform solvate molecule was also found to have required mirror symmetry and to be disordered over two different orientations. Occupancy factors of the major (0.83) and minor orientations (0.17) were derived from least-squares refinement. The $C(CN)_3^-$ ion also has mirror symmetry with the plane of the group perpendicular to the mirror plane at $y = {}^3/_4$. After isotropic refinement, a difference Fourier synthesis revealed approximate hydrogen atom positions for the porphinato ligand; these were idealized (C–H = 0.95 Å, $B(\mathrm{H}) = B(\mathrm{C}) + 1.0$ Å^2) and included in subsequent refinement cycles as fixed contributors. The refinement was carried to convergence using anisotropic temperature factors for all heavy atoms except those of the minor portion of the chloroform solvate molecule. The final values of the discrepancy indices were $R_1 = \sum|F_o| - |F_c|/\sum|F_o| = 0.063$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o^2)]^{1/2} = 0.076$. The final data/parameter ratio was 13.4; the estimated standard deviation in an observation of unit weight was 2.25. A final difference Fourier synthesis showed several peaks ≤ 0.6 e/Å^3 in the region of the disordered chloroform molecule and was otherwise featureless.

A listing of the final observed and calculated structure amplitudes (×10) is available (supplementary material). Atomic coordinates and the associated temperature factors in the asymmetric unit of structure are given in Tables I and II.

Results and Discussion

A major point of our interest in FeTPP(C(CN)$_3$) was the question of how the physical properties of the iron(III) porphyrin moiety are effected by the presence of an apparently very weak ligand. As noted previously,[8] the infrared spectrum of FeTPP(C(CN)$_3$) in the CN stretching region shows essentially the same spectrum as KC(CN)$_3$. This result was interpreted as suggesting weak coordination of $C(CN)_3^-$ which retains its planar delocalized structure. The molecular structure of FeTPP(C(CN)$_3$) (vide infra) appears to confirm these expectations.

The effective magnetic moment of FeTPP(C(CN)$_3$), determined in the solid state, is 5.4 μ_B and is independent of temperature between 298 and 78 K. The moment in $CHCl_3$ solution is slightly lower at 5.1 μ_B. The observed moment lies between the spin-only moment of 5.9 μ_B observed to low temperature for five-coordinate high-spin ($S = {}^5/_2$) iron(III) porphyrins[17] and the spin-only value of 3.9 μ_B observed for the intermediate-spin ($S = {}^3/_2$) five-coordinate bis(*N*,*N*-dialkyldithiocarbamato)iron(III) halides.[18] The effective magnetic moments of intermediate-spin FeOEP(OClO$_3$) and FeOEP(C_2H_5OH)$_2$ClO$_4$ are reported[4] as 4.8 and 4.5 μ_B, respectively, at room temperature. The magnetic moment[5] of FeTPP(OClO$_3$) is 5.0 μ_B at room temperature. Unlike FeTPP(C(CN)$_3$), both perchlorato complexes show some temperature dependence for the magnetic moments.

The ESR powder spectrum of FeTPP(C(CN)$_3$) shows an axial pattern with $g_\| = 2.00$ and $g_\perp = 5.26$ at 78 K. In frozen toluene solution, the ESR spectrum shows a broad weak signal at $g = 5.6$. Treatment of the toluene solution with a drop of HCl and refreezing lead to the ESR spectrum of FeTPPCl.[19] Comparison of the intensities (using DPPH in a sealed capillary) suggests that the $g = 5.6$ signal is due to the presence of a small amount of a high-spin impurity. Whether the powder sample signal is also due to a high-spin impurity is to be clarified by examination of single-crystal ESR.

Although the magnetic moment data for FeTPP(C(CN)$_3$) are suggestive of an intermediate-spin ground state, the Mössbauer evidence is more compelling. From the Mössbauer data (Table III), we can eliminate the possibility that FeTPP(C(CN)$_3$) is a high-spin complex having an unusually low magnetic moment. The quadrupole splitting of FeTPP(C(CN)$_3$) is seen to be much larger than that observed for either five- or six-coordinate high-spin iron(III) porphyrins.

Table I. Atomic Coordinates in the Unit Cell[a]

	coordinates ×10^4		
atom type	*x*	*y*	*z*
Fe[b]	2086 (0)	$^1/_4$	3162 (0)
N_1	2364 (2)	$^1/_4$	4704 (2)
N_2	3217 (2)	$^1/_4$	3126 (2)
N_3	1804 (2)	$^1/_4$	1617 (2)
N_4	957 (2)	$^1/_4$	3196 (2)
C_{a1}	1858 (2)	$^1/_4$	5362 (3)
C_{a2}	3105 (2)	$^1/_4$	5335 (3)
C_{a3}	3843 (2)	$^1/_4$	3965 (3)
C_{a4}	3537 (2)	$^1/_4$	2264 (3)
C_{a5}	2313 (2)	$^1/_4$	955 (3)
C_{a6}	1063 (2)	$^1/_4$	990 (3)
C_{a7}	324 (2)	$^1/_4$	2358 (3)
C_{a8}	635 (2)	$^1/_4$	4056 (3)
C_{b1}	2295 (3)	$^1/_4$	6410 (3)
C_{b2}	3046 (3)	$^1/_4$	6382 (3)
C_{b3}	4555 (2)	$^1/_4$	3605 (3)
C_{b4}	4368 (2)	$^1/_4$	2567 (3)
C_{b5}	1881 (2)	$^1/_4$	−92 (3)
C_{b6}	1121 (2)	$^1/_4$	−66 (3)
C_{b7}	−380 (2)	$^1/_4$	2721 (3)
C_{b8}	−193 (2)	$^1/_4$	3759 (3)
C_{m1}	3794 (2)	$^1/_4$	4992 (3)
C_{m2}	3126 (2)	$^1/_4$	1246 (3)
C_{m3}	367 (2)	$^1/_4$	1330 (3)
C_{m4}	1053 (2)	$^1/_4$	5083 (3)
C_1	4548 (2)	$^1/_4$	5803 (3)
C_2	4901 (2)	1258 (4)	6167 (3)
C_3	5601 (2)	1258 (5)	6890 (3)
C_4	5940 (3)	$^1/_4$	7248 (4)
C_5	3589 (2)	$^1/_4$	421 (3)
C_6	3807 (3)	1269 (6)	45 (4)
C_7	4263 (4)	1284 (8)	−699 (4)
C_8	4470 (3)	$^1/_4$	−1058 (4)
C_9	−392 (2)	$^1/_4$	549 (3)
C_{10}	−753 (2)	1249 (4)	193 (3)
C_{11}	−1457 (2)	1248 (4)	−521 (3)
C_{12}	−1809 (2)	$^1/_4$	−863 (3)
C_{13}	559 (2)	$^1/_4$	5904 (3)
C_{14}	367 (3)	1263 (4)	6292 (3)
C_{15}	−93 (3)	1261 (4)	7022 (4)
C_{16}	−319 (3)	$^1/_4$	7381 (3)
C_{17}	2266 (2)	−1151 (3)	3534 (2)
C_{18}	2486 (2)	$-^1/_4$	3985 (3)
C_{19}	3048 (3)	$-^1/_4$	4937 (4)
N_5	2133 (1)	2 (3)	3237 (2)
N_6	3495 (3)	$-^1/_4$	5714 (4)
C_{20}[c]	7003 (6)	$^1/_4$	2062 (8)
Cl_1[c]	6233 (2)	$^1/_4$	1011 (3)
Cl_2[c]	7577 (1)	996 (3)	2056 (3)
C_{21}[d]	7274	$^1/_4$	2613
Cl_3[d]	7279 (13)	$^1/_4$	1306 (18)
Cl_4[d]	7804 (7)	1128 (12)	3211 (10)

[a] Numbers in parentheses are the estimated standard deviations. [b] For iron $10^5x = 20\,857$ (3) and $10^5z = 31\,621$ (4). [c] Occupancy = 0.83. [d] Occupancy = 0.17.

High-spin iron(III) porphinato complexes also show asymmetric line broadening at temperatures above ~15 K due to dipole interactions between thermally populated Kramers' doublets.[20] This is not observed for FeTPP(C(CN)$_3$), which has a well-resolved quadrupole doublet at room temperature. However, ^{57}Fe Mössbauer spectra exhibiting unusually large quadrupole splittings are characteristic of intermediate-spin complex. Values of ΔE_Q for the known $S = {}^3/_2$ bis(*N*,*N*-dialkyldithiocarbamato)iron(III)[18,21] and tetraazoiron(III)[22] complexes are in the range of 2.3–3.0 mm/s. The two perchloratoiron(III) porphyrin species characterized as intermediate spin[4,5] and FeTPP(C(CN)$_3$) all show ΔE_Q values greater than 3.0 mm/s.

The molecular stereochemistry of FeTPP(C(CN)$_3$) also supports the assignment of an intermediate-spin ground state. An $S = {}^3/_2$ ground state for a d^5 ion requires that the highest

Table II. Thermal Parameters[a]

atom type	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	2.51 (2)	3.34 (2)	2.25 (2)	0	0.02 (2)	0
N_1	2.7 (1)	3.2 (1)	2.5 (1)	0	0.3 (1)	0
N_2	2.5 (1)	2.9 (1)	2.6 (1)	0	0.0 (1)	0
N_3	3.0 (1)	2.7 (1)	2.6 (1)	0	−0.1 (1)	0
N_4	2.9 (1)	2.9 (1)	2.3 (1)	0	0.2 (1)	0
C_{a1}	3.2 (2)	3.5 (2)	2.7 (2)	0	0.2 (1)	0
C_{a2}	3.1 (2)	3.6 (2)	2.6 (2)	0	−0.1 (1)	0
C_{a3}	2.9 (2)	3.2 (2)	2.7 (2)	0	−0.1 (1)	0
C_{a4}	2.6 (2)	3.8 (2)	2.6 (2)	0	0.3 (1)	0
C_{a5}	3.3 (2)	3.3 (2)	2.3 (2)	0	0.4 (1)	0
C_{a6}	3.0 (2)	2.6 (2)	2.7 (2)	0	−0.2 (1)	0
C_{a7}	2.6 (2)	3.1 (2)	3.0 (2)	0	−0.0 (1)	0
C_{a8}	2.9 (2)	2.9 (2)	3.0 (2)	0	0.5 (1)	0
C_{b1}	3.9 (2)	6.5 (3)	2.4 (2)	0	0.5 (1)	0
C_{b2}	3.8 (2)	6.9 (3)	2.5 (2)	0	0.1 (2)	0
C_{b3}	2.5 (2)	5.2 (2)	3.7 (2)	0	0.2 (1)	0
C_{b4}	2.7 (2)	6.0 (3)	3.2 (2)	0	0.4 (1)	0
C_{b5}	3.6 (2)	4.7 (2)	2.5 (2)	0	0.2 (1)	0
C_{b6}	3.4 (2)	3.8 (2)	2.4 (2)	0	−0.2 (1)	0
C_{b7}	2.5 (2)	4.2 (2)	3.5 (2)	0	0.0 (1)	0
C_{b8}	2.8 (2)	3.8 (2)	3.6 (2)	0	0.5 (1)	0
C_{m1}	2.8 (2)	3.3 (2)	2.7 (2)	0	−0.2 (1)	0
C_{m2}	3.4 (2)	3.8 (2)	2.6 (2)	0	0.5 (1)	0
C_{m3}	2.6 (2)	2.6 (2)	3.1 (2)	0	−0.1 (1)	0
C_{m4}	3.4 (2)	2.7 (2)	2.9 (2)	0	0.6 (1)	0
C_1	2.7 (2)	4.3 (2)	2.6 (2)	0	−0.3 (1)	0
C_2	5.7 (2)	4.6 (2)	6.8 (2)	1.2 (2)	−3.0 (2)	−1.3 (2)
C_3	6.2 (2)	5.9 (2)	7.2 (2)	2.3 (2)	−3.1 (2)	−0.7 (2)
C_4	3.2 (2)	7.8 (3)	3.6 (2)	0	−0.4 (2)	0
C_5	3.0 (2)	7.7 (3)	2.9 (2)	0	0.5 (1)	0
C_6	11.7 (4)	8.7 (3)	8.7 (3)	1.8 (3)	6.3 (3)	−0.6 (2)
C_7	12.9 (4)	16.0 (5)	8.8 (3)	3.6 (4)	7.2 (3)	−1.3 (3)
C_8	4.3 (3)	21.4 (8)	3.5 (3)	0	1.2 (2)	0
C_9	2.7 (2)	3.4 (2)	2.6 (2)	0	−0.1 (1)	0
C_{10}	5.3 (2)	3.1 (1)	6.5 (2)	0.1 (1)	−2.4 (1)	0.0 (1)
C_{11}	5.1 (2)	4.1 (2)	6.8 (2)	−0.8 (1)	−2.4 (2)	−0.3 (2)
C_{12}	3.2 (2)	5.2 (2)	3.9 (2)	0	−0.5 (2)	0
C_{13}	3.2 (2)	3.3 (2)	2.6 (2)	0	0.5 (1)	0
C_{14}	10.9 (3)	3.6 (2)	8.6 (3)	−0.4 (2)	6.9 (3)	−0.5 (2)
C_{15}	10.2 (3)	4.7 (2)	8.3 (3)	−0.7 (2)	6.0 (2)	0.9 (2)
C_{16}	4.0 (2)	5.8 (3)	3.5 (2)	0	1.6 (2)	0
C_{17}	3.1 (1)	3.3 (1)	3.3 (1)	−0.3 (1)	0.5 (1)	−0.7 (1)
C_{18}	3.5 (2)	3.6 (2)	3.6 (2)	0	−0.1 (2)	0
C_{19}	5.0 (3)	5.5 (3)	5.6 (3)	0	−0.3 (2)	0
N_5	3.9 (1)	3.4 (1)	3.6 (1)	−0.2 (1)	0.3 (1)	−0.2 (1)
N_6	7.5 (3)	12.0 (5)	6.0 (3)	0	−2.2 (2)	0
C_{20}	7.5 (5)	17.5 (10)	7.3 (5)	0	2.3 (4)	0
Cl_1	11.0 (2)	13.3 (2)	13.0 (2)	0	−1.9 (2)	0
Cl_2	8.6 (1)	11.0 (2)	29.8 (3)	−0.1 (1)	−1.2 (2)	2.6 (2)
C_{21}	7.7 (10)					
Cl_3	15.4 (6)					
Cl_4	12.4 (3)					

[a] The numbers in parentheses are the estimated standard deviations.

energy d orbital be unoccupied, which, for the usual choice of coordinate systems in porphinato complexes,[23] is the $3d_{x^2-y^2}$ orbital. Population of this orbital in iron(III) porphyrin species, i.e., high-spin derivatives, leads to Fe–N bond distances ≥2.065 Å for the five-coordinate derivatives[24,25] and Fe–N distances of ≥2.040 Å in the six-coordinate derivatives.[5,7] With the $3d_{x^2-y^2}$ orbital unoccupied, as in the six-coordinate low-spin derivatives, the Fe–N distances are 1.990 Å.[24,25] The average porphinato nitrogen–iron bond distance in FeTPP(C(CN)$_3$) of 1.995 (3) Å[26] is thus seen to be consistent[25] with an unoccupied $3d_{x^2-y^2}$ orbital as required by an intermediate-spin ground state. This average Fe–N bond distance is comparable to the 1.997 (5) Å value observed in intermediate-spin FeTPP(OClO$_3$).[5]

An overall view of the stereochemistry of FeTPP(C(CN)$_3$) is provided in Figure 1. The prophinato plane of FeTPP(C(CN)$_3$) lies on a crystallographically required mirror plane (at $y = {}^1/_4$) and hence the iron(III) atom is required to be centered in the plane of the ligand. The tricyanomethanide ion also has required mirror symmetry with the plane of the ion perpendicular to the crystallographic mirror plane (at $y = -{}^1/_4$ and ${}^3/_4$ in Figure 1). N_5 and N_5' are mirror related atoms in Figure 1. N_5 interacts with the iron(III) atom of the porphyrin moiety shown in Figure 1 and N_5' with the iron(III) atom translated by the *b* unit cell vector. Thus, the tricyanomethanide ion functions as a bridging ligand.

The Fe–N_5 distance of 2.317 (3) Å appears to be a rather long bonding distance[27] and is consistent with the assignment of $C(CN)_3^-$ as a weakly binding ligand. However, the observed deviations of the tricyanomethanide ion from D_{3h} symmetry suggests a real interaction between the iron(III) atom and the $C(CN)_3^-$ ion. The angles at the central carbon atom are 116.9 (2)° ($C_{17}C_{18}C_{19}$) and 125.9 (4)° ($C_{17}C_{18}C_{17}'$). The opening of the second angle from the ideal value of 120° serves to bring N_5 closer to the iron atom. The 174.0 (3)° angle formed by $N_5C_{17}C_{18}$ also serves this end. These distortions also allow

Table III. Mössbauer Parameters for Selected Iron(III) Porphyrins

compound	S	T, K	δ,[a] mm/s	ΔE_Q, mm/s	comments[h]	ref
$FeTPP(C(CN)_3)$	$^3/_2$	298	0.30	3.18	$\Gamma = 0.44, 0.35$	b
		78	0.30	3.03	$\Gamma = 0.35, 0.35$	
FeTPP(Cl)[c]	$^5/_2$	4.2	0.42	0.46	severely broadened at room temp	d
FeTPP(I)[c]	$^5/_2$	6	0.46	0.75	severely broadened at room temp	d
$FeOEP(OClO_3)$	$^3/_2$	295	0.29	3.16	$\Gamma = 0.27, 0.26$	e
		115	0.37	3.52	$\Gamma = 0.30, 0.31$	
		4.2	0.37	3.57	$\Gamma = 0.29, 0.31$	
$[FeOEP(C_2H_5OH)_2]ClO_4$	$^3/_2$	295	0.29	2.97	$\Gamma = 0.31, 0.31$	e
		115	0.36	3.32	$\Gamma = 0.33, 0.31$	
		4.2	0.38	3.47	$\Gamma = 0.31, 0.30$	
$FeTPP(OClO_3)$	$^3/_2$	4.2	0.39	3.4		f
$[FeTPP(OH_2)_2]ClO_4$	$^5/_2$	298	0.33	1.69	$\Gamma_+ = 1.3, \Gamma_- = 0.46$	g
		78	0.41	1.53	$\Gamma_+ = 1.7, \Gamma_- = 0.63$	

[a] Relative to Fe metal. [b] This work. [c] These compounds represent the maximum and minimum quadrupole splitting observed for monomeric FeTPP(X) complexes. [d] C. Maricondi, D. K. Straub, and L. M. Epstein, *J. Am. Chem. Soc.*, 94, 4157 (1972). [e] Reference 4. [f] Reference 5. [g] I. A. Cohen and W. R. Scheidt, unpublished. [h] Full width at half maximum.

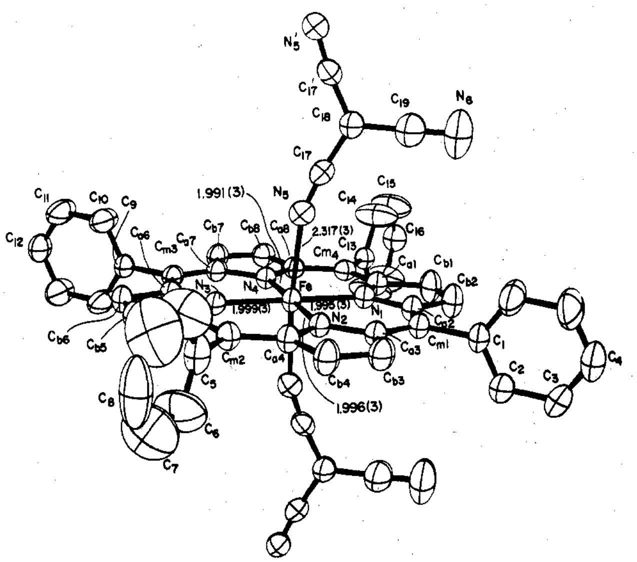

Figure 1. A computer-drawn model of the $FeTPP(C(CN)_3)$ system. The labeling scheme used for the crystallographically unique atoms is shown. Also displayed in the figure are the bond distances in the coordination group. The porphinato plane lies on a mirror plane as do atoms C_{18}, C_{19}, and N_6 of both $C(CN)_3^-$ ions shown.

Table IV. Bond Lengths (Å) in the Porphinato Skeleton and and $C(CN)_3^-$ Ligand[a]

$Fe-N_1$	1.995 (3)	$C_{a1}-C_{m4}$	1.380 (5)
$Fe-N_2$	1.996 (3)	$C_{a2}-C_{m1}$	1.380 (5)
$Fe-N_3$	1.999 (3)	$C_{a3}-C_{m1}$	1.383 (5)
$Fe-N_4$	1.991 (3)	$C_{a4}-C_{m2}$	1.385 (5)
$Fe-N_5$	2.317 (3)	$C_{a5}-C_{m2}$	1.394 (5)
N_1-C_{a1}	1.373 (5)	$C_{a6}-C_{m3}$	1.391 (5)
N_1-C_{a2}	1.385 (5)	$C_{a7}-C_{m3}$	1.380 (5)
N_2-C_{a3}	1.383 (4)	$C_{a8}-C_{m4}$	1.398 (5)
N_2-C_{a4}	1.377 (5)	$C_{b1}-C_{b2}$	1.328 (6)
N_3-C_{a5}	1.381 (5)	$C_{b3}-C_{b4}$	1.348 (6)
N_3-C_{a6}	1.383 (4)	$C_{b5}-C_{b6}$	1.343 (6)
N_4-C_{a7}	1.389 (4)	$C_{b7}-C_{b8}$	1.345 (6)
N_4-C_{a8}	1.377 (5)	$C_{m1}-C_1$	1.513 (5)
$C_{a1}-C_{b1}$	1.434 (5)	$C_{m2}-C_5$	1.497 (6)
$C_{a2}-C_{b2}$	1.413 (6)	$C_{m3}-C_9$	1.500 (5)
$C_{a3}-C_{b3}$	1.430 (6)	$C_{m4}-C_{13}$	1.494 (5)
$C_{a4}-C_{b4}$	1.426 (5)	N_5-C_{17}	1.144 (4)
$C_{a5}-C_{b5}$	1.430 (5)	N_6-C_{19}	1.152 (6)
$C_{a6}-C_{b6}$	1.425 (5)	$C_{18}-C_{17}$	1.403 (3)
$C_{a7}-C_{b7}$	1.419 (5)	$C_{18}-C_{19}$	1.423 (6)
$C_{a8}-C_{b8}$	1.421 (5)		

[a] The numbers in parentheses are the estimated standard deviations.

for a more nearly linear FeN_5C_{17} bond angle (161.7 (2)°), although the crystalline arrangement precludes a linear FeN_5C_{17} group.[29] These observations suggest an alternate interpretation of the bonding parameters between the iron(III) atom and the axial ligand, namely, that the observed $Fe-N_5$ distance is a manifestation of the electron configuration of the iron(III) atom. The $S = {}^3/_2$ spin state requires population of the $3d_{z^2}$ orbital. Six-coordinate metalloporphyrins in which this orbital is populated have quite long axial bond distances;[25] the axial M–N bond distances of the low-spin d^7 cobalt(II)[32] and high-spin d^4 manganese(III)[33] derivatives are observed to be ≥0.3 Å longer than in analogous derivatives in which the $3d_{z^2}$ orbital is unoccupied. Thus both the equatorial and axial bond parameters of $FeTPP(C(CN)_3)$ are seen to be consonant with an intermediate-spin ground state.

A major difference between the high-spin $[FeTPP(OH_2)_2]^+$[5] and $[FeTPP(TMSO)_2]^+$[7] ions and the intermediate-spin six-coordinate $FeTPP(C(CN)_3)$ system is the apparent strength of the axial ligand interaction with the central metal atom. Although the axial ligands in these complexes are all weak field ligands, the Fe–O distances in the two high-spin complexes are ≈2.09 Å,[5,7] whereas the axial Fe–N distances in $FeTPP(C(CN)_3)$ are 2.32 Å. The increased tetragonal distortion in $FeTPP(C(CN)_3)$ must lead to a stabilization of the d_{z^2} orbital (and d_{xy}, d_{yz}, d_{xz} as well) relative to the $d_{x^2-y^2}$ level. In other words, $FeTPP(C(CN)_3)$ can be regarded as a pseudo-square-planar complex. We expect that if the axial Fe–O bond distances in $[FeTPP(OH_2)_2]^+$ could be increased, at some distance greater than 2.09 Å the complex would become an intermediate-spin complex. This hypothetical situation may be approximated by the diethanol solvate of the $FeOEP^+$ cation, whose structure is under investigation.[34] We anticipate that this complex will show relatively long axial bonds to the ethanol ligands.

The bond lengths of the $C(CN)_3^-$ ion are comparable to those observed previously[28,35,36] and are consistent with a delocalized structure. The tricyanomethanide ion in $FeTPP(C(CN)_3)$ is slightly nonplanar. The central carbon atom is displaced by 0.091 Å from the mean plane of the three nitrogen atoms; C_{17} and C_{19} are displaced by 0.046 and 0.030 Å, respectively, from this plane. Similar deviations from planarity are observed for $NH_4(C(CN)_3)$[35] but not for other salts;[28,36] the nonpolarity of the ammonium salt is considered a consequence of packing effects.

The agreement between chemically analogous bond parameters of the porphinato core is satisfactory and the estimated standard deviation for the averaged values suggests that the esd's for individual values are reasonable. Using C_a and C_b to denote the respective α- and β-pyrrole carbon atoms and

Table V. Bond Angles (deg)

N_1FeN_2	90.0 (1)	$C_{b4}C_{a4}C_{m2}$	124.1 (4)
N_2FeN_3	90.1 (1)	$C_{b5}C_{a5}C_{m2}$	124.3 (4)
N_3FeN_4	89.8 (1)	$C_{b6}C_{a6}C_{m3}$	124.9 (3)
N_4FeN_1	90.1 (1)	$C_{b7}C_{a7}C_{m3}$	124.8 (3)
$N_1C_{a1}C_{b1}$	109.3 (3)	$C_{b8}C_{a8}C_{m4}$	124.0 (4)
$N_1C_{a2}C_{b2}$	109.5 (3)	$C_{a2}C_{m1}C_{a3}$	124.7 (3)
$N_2C_{a3}C_{b3}$	109.3 (3)	$C_{a4}C_{m2}C_{a5}$	123.4 (4)
$N_2C_{a4}C_{b4}$	110.0 (3)	$C_{a6}C_{m3}C_{a7}$	123.9 (3)
$N_3C_{a5}C_{b5}$	109.7 (3)	$C_{a8}C_{m4}C_{a1}$	123.5 (4)
$N_3C_{a6}C_{b6}$	109.4 (3)	$C_{a2}C_{m1}C_1$	117.4 (3)
$N_4C_{a7}C_{b7}$	109.5 (3)	$C_{a3}C_{m1}C_1$	117.9 (3)
$N_4C_{a8}C_{b8}$	110.4 (3)	$C_{a4}C_{m2}C_5$	117.4 (4)
$C_{a1}N_1C_{a2}$	105.6 (3)	$C_{a5}C_{m2}C_5$	118.9 (3)
$C_{a3}N_2C_{a4}$	105.7 (3)	$C_{a6}C_{m3}C_9$	119.2 (3)
$C_{a5}N_3C_{a6}$	105.8 (3)	$C_{a7}C_{m3}C_9$	116.9 (3)
$C_{a7}N_4C_{a8}$	105.2 (3)	$C_{a8}C_{m4}C_{13}$	117.1 (3)
$C_{a1}C_{b1}C_{b2}$	107.4 (4)	$C_{a1}C_{m4}C_{13}$	119.5 (3)
$C_{a2}C_{b2}C_{b1}$	108.2 (4)	$N_5C_{17}C_{18}$	174.0 (3)
$C_{a3}C_{b3}C_{b4}$	107.7 (3)	$N_6C_{19}C_{18}$	179.1 (4)
$C_{a4}C_{b4}C_{b3}$	107.3 (4)	$C_{17}C_{18}C_{19}$	116.9 (2)
$C_{a5}C_{b5}C_{b6}$	107.2 (4)	$C_{17}C_{18}C_{17}'$	125.9 (4)
$C_{a6}C_{b6}C_{b5}$	107.9 (3)	N_5FeN_1	87.6 (1)
$C_{a7}C_{b7}C_{b8}$	108.0 (3)	N_5FeN_2	88.6 (1)
$C_{a8}C_{b8}C_{b7}$	107.0 (4)	N_5FeN_3	92.4 (1)
$N_1C_{a1}C_{m4}$	126.5 (3)	N_5FeN_4	91.5 (1)
$N_1C_{a2}C_{m1}$	125.2 (3)	N_5FeN_5'	174.3 (1)
$N_2C_{a3}C_{m1}$	125.7 (4)	FeN_5C_{17}	161.7 (2)
$N_2C_{a4}C_{m2}$	126.0 (3)	FeN_1C_{a1}	127.0 (2)
$N_3C_{a5}C_{m2}$	126.0 (3)	FeN_1C_{a2}	127.4 (3)
$N_3C_{a6}C_{m3}$	125.7 (3)	FeN_2C_{a3}	127.0 (3)
$N_4C_{a7}C_{m3}$	125.8 (3)	FeN_2C_{a4}	127.3 (2)
$N_4C_{a8}C_{m4}$	125.6 (3)	FeN_3C_{a5}	126.8 (2)
$C_{b1}C_{a1}C_{m4}$	124.2 (4)	FeN_3C_{a6}	127.4 (3)
$C_{b2}C_{a2}C_{m1}$	125.3 (4)	FeN_4C_{a7}	127.5 (3)
$C_{b3}C_{a3}C_{m1}$	125.0 (3)	FeN_4C_{a8}	127.4 (2)

C_m for methine carbon, averaged bond distances are $N-C_a$ = 1.381 (5) Å, C_a-C_b = 1.425 (7) Å, C_a-C_m = 1.386 (7) Å, and C_b-C_b = 1.341 (9) Å. Averaged values for bond angles are NC_aC_b = 109.6 (4)°, C_aNC_a = 105.6 (3)°, $C_aC_bC_b$ = 107.6 (4)°, NC_aC_m = 125.8 (4)°, $C_bC_aC_m$ = 124.6 (5)°, and $C_aC_mC_a$ = 123.9 (6)°. The averaged value of an individually determined C–C bond distance in the peripheral phenyl group is 1.35 (3) Å; the average value of the internal angle is 120.0°. The thermal parameters of the phenyl ring attached to C_{m2} suggest the possibility of minor disorder in this group; thermal parameters of the three remaining phenyl groups are unremarkable. The required symmetry leads to 90° dihedral angles between the peripheral phenyl groups and the porphinato plane.

The molecular packing arrangement of $FeTPP(C(CN)_3)$ in the crystal is elegant. The $FeTPP^+$ and $C(CN)_3^-$ groups form an infinite column of alternating units parallel to the *b* axis. A second such parallel column is related to the first by the twofold screw axis. Chloroform molecules are located in voids between the chains. Contacts between atoms of the porphinato groups of the two chains range from 3.5 Å upward. The N_6 atom of $C(CN)_3^-$ makes moderately close contacts to the $CHCl_3$ solvate (3.25 Å) and the porphyrin (3.35 Å) in the other column.

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Supplementary Material Available: A list of the structure factor amplitudes (×10) (18 pages). Ordering information is given on any current masthead page.

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