Table III. Mean Planes for the Peptide Groups and Deviations Therefrom

plane 1: $0.2193X + 0.5854Y + 0.7805Z + 3.2632 = 0$
plane 2: $0.8106X - 0.3764Y + 0.4487Z + 3.8327 = 0$

Atoms Used to Defined Plane 1 and Their Deviations (Å), with esd's

C(24)	−0.054(5)	N(21)	0.047(4)
C(23)	0.021(5)	O(21)	0.007(4)
C(22)	−0.064(5)	H(1)	0.05(4)

Atoms Used to Define Plane 2 and Their Deviations (Å), with esd's

C(14)	0.015(6)	N(11)	−0.017(5)
C(13)	0.004(6)	O(11)	−0.005(5)
C(12)	0.019(6)	H(2)	−0.06(4)

teristic of a peptide linkage. As shown in Figure 2, the two independent sets of angles and distances agree well with each other and with the commonly accepted "standard" dimensions for a peptide unit.[10] The two peptide units examined here are also essentially planar as shown by the figures in Table III. No atom in the second one deviates from the mean plane by more than 3σ. In the first peptide unit there are larger deviations, three of which are as high as $10-12\sigma$. However, these are still quite small in absolute value (ca. 0.05 Å).

In summary, the complex we have studied appears to give, as expected, a convenient specimen (actually two independent ones) of the dipeptide unit, in a form that is unperturbed by coordination while retaining the considerable advantage of having two heavy atoms present to assist in the structure solution. We hope to extend this approach next to other di- and higher polypeptides, including those with chiral centers, in order to obtain accurate structural information on such peptides in a reasonably rapid and convenient way.

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Supplementary Material Available: A table of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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Preparation and Characterization of the Anionic Complex Potassium Dicyano(*meso*-tetraphenylporphinato)iron(III) Bis(acetone)

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Abstract: The synthesis and structural characterization of potassium dicyano(*meso*-tetraphenylporphinato)iron(III) bis(acetone) are reported. The material crystallizes with two formula units in space group $P2_1/n$ of the monoclinic system with cell dimensions of $a = 9.601$ (2) Å, $b = 11.439$ (2) Å, $c = 20.283$ (3) Å, and $\beta = 100.78$ (1)° at 20 °C. Measurement of diffracted intensities employed θ–2θ scans with graphite-monochromated Mo Kα radiation on a Syntex $P\bar{1}$ diffractometer. All independent data for $(\sin\theta)/\lambda < 0.67$ Å^{-1} were measured; 3873 reflections were retained as observed. These data were employed in the determination of structure and least-squares refinement. The final conventional and weighted discrepancy factors are 0.050 and 0.056, respectively. The $[\mathrm{Fe(TPP)(CN)_2}]^-$ ion has crystallographically required C_i—$\bar{1}$ symmetry with an average Fe–N bond distance of 2.000 (6) Å. The Fe–C–N group is essentially linear with Fe–C = 1.975 (2) Å, in distinct contrast to the "bent" geometry found in cyano heme proteins.

Iron porphyrins serve as the prosthetic group for the biologically important class of proteins known as the hemoproteins. Our understanding of the variety of functions and reactions of the hemoproteins has been aided by ligand binding studies. These studies have been carried out on the hemoproteins[3] as well as model compounds, porphinatoiron complexes.[4] The strong binding of cyanide ion to ferric hemoproteins and porphinatoiron(III) species has been long recognized. Binding of the strong field cyano ligand leads to low-spin ferric derivatives and this feature has been utilized in a number of NMR studies of the hemoproteins[5,6] and porphinatoiron(III) derivatives.[7-11] Further, equilibrium studies have demonstrated[11,12] the stepwise binding of cyanide ion. These studies have been undertaken on dissolved species and surprisingly there are, to our knowledge, no published reports of the preparation of solid cyanoporphinatoiron(III) derivatives.[13] We report herein the preparation of the anionic complex dicyano-*meso*-tetraphenylporphinatoiron(III), $[\mathrm{Fe(TPP)(CN)_2}]^-$, isolated as the K$^+$ salt, and its structural characterization.

Experimental Section

Synthesis of K[Fe(TPP)(CN)$_2$]·2(CH$_3$)$_2$C=O. [Fe(TPP)(H$_2$O)$_2$]-

0002-7863/80/1502-3017$01.00/0

Table I. Fractional Monoclinic Coordinates and Isotropic Temperature Factors for $K[Fe(TPP)(CN)_2]\cdot 2(CH_3)_2CO$[a]

atom	x	y	z	B_{iso}[b]
Fe	0.0	0.0	0.0	2.7
K	0.466 25(16)	0.039 32(17)	0.004 72(8)	6.6
N_1	0.021 28(19)	0.074 63(15)	−0.086 97(8)	2.9
N_2	0.118 68(19)	0.125 81(15)	0.050 40(8)	3.0
C_{a1}	−0.034 42(25)	0.035 52(19)	−0.150 77(10)	3.0
C_{a2}	0.095 28(24)	0.174 89(18)	−0.095 29(10)	3.1
C_{a3}	0.181 15(25)	0.218 09(19)	0.023 51(11)	3.3
C_{a4}	0.159 56(25)	0.135 26(19)	0.118 74(10)	3.2
C_{b1}	0.008 59(27)	0.112 89(20)	−0.199 50(11)	3.6
C_{b2}	0.085 45(28)	0.198 24(21)	−0.165 84(11)	3.6
C_{b3}	0.2653(3)	0.284 50(23)	0.076 37(12)	3.9
C_{b4}	0.2532(3)	0.233 58(23)	0.134 59(12)	4.0
C_{m1}	0.169 63(24)	0.244 07(19)	−0.044 30(10)	3.2
C_{m2}	0.119 04(25)	0.062 28(19)	0.166 81(10)	3.2
C_1	0.238 42(25)	0.354 59(19)	−0.061 64(11)	3.3
C_2	0.1821(3)	0.461 06(23)	−0.048 17(13)	4.2
C_3	0.2462(4)	0.565 45(23)	−0.060 45(15)	4.9
C_4	0.3690(3)	0.562 82(26)	−0.086 40(16)	5.1
C_5	0.4245(3)	0.459 00(28)	−0.100 34(18)	5.2
C_6	0.3613(3)	0.354 50(24)	−0.088 25(14)	4.5
C_7	0.170 99(26)	0.092 54(20)	0.238 93(10)	3.4
C_8	0.1278(3)	0.195 05(23)	0.266 02(12)	4.2
C_9	0.1804(4)	0.226 35(26)	0.331 94(13)	4.6
C_{10}	0.2770(4)	0.155 73(28)	0.371 24(13)	4.9
C_{11}	0.3189(4)	0.0539(3)	0.345 85(15)	5.3
C_{12}	0.2667(3)	0.021 91(24)	0.279 68(13)	4.5
C_{13}	0.173 69(26)	−0.092 17(19)	−0.000 69(10)	3.3
N_3	0.276 81(25)	−0.142 45(20)	−0.001 41(12)	5.0
O	0.5719(4)	−0.0276(3)	0.132 31(15)	10.3
C_{14}	0.6297(4)	0.0230(3)	0.181 25(17)	6.4
C_{15}	0.6412(5)	−0.0317(4)	0.247 01(20)	8.2
C_{16}	0.7047(7)	0.1339(4)	0.178 07(23)	9.5
H_{b1}	−0.0174(23)	0.1014(19)	−0.2469(11)	3.8(5)
H_{b2}	0.1254(23)	0.2617(20)	−0.1829(10)	3.7(5)
H_{b3}	0.3177(26)	0.3521(23)	0.0688(12)	5.1(6)
H_{b4}	0.2964(27)	0.2573(22)	0.1765(13)	5.2(6)
H_2	0.1028(25)	0.4661(20)	−0.0295(11)	3.9(6)
H_3	0.2043(26)	0.6305(24)	−0.0506(12)	5.3(7)
H_4	0.417(3)	0.6322(29)	−0.0934(15)	8.3(9)
H_5	0.499(3)	0.4583(25)	−0.1209(14)	6.3(3)
H_6	0.4038(27)	0.2826(24)	−0.0993(13)	5.8(7)
H_8	0.0637(27)	0.2446(23)	0.2379(12)	5.3(6)
H_9	0.1505(27)	0.2917(23)	0.3477(13)	5.5(7)
H_{10}	0.317(3)	0.1863(26)	0.4158(14)	7.0(8)
H_{11}	0.392(3)	0.0036(23)	0.3679(15)	6.2(8)
H_{12}	0.2961(25)	−0.0527(23)	0.2608(12)	4.8(6)

[a] The estimated standard deviations of the least significant digits are given in parentheses. [b] The isotropic equivalents are given for the atoms that were refined anisotropically.

Table II. Selected Interatomic Distances (Å) and Angles (deg) for $K[Fe(TPP)(CN)_2]\cdot 2(CH_3)_2CO$[a]

	Distances		
Fe-N_1	2.004(2)	C_2-C_3	1.387(4)
Fe-N_2	1.995(2)	C_3-C_4	1.379(4)
Fe-C_{13}	1.975(2)	C_4-C_5	1.353(4)
C_{13}-N_3	1.147(3)	C_5-C_6	1.383(4)
N_1-C_{a1}	1.379(3)	C_7-C_8	1.391(3)
N_1-C_{a2}	1.376(3)	C_7-C_{12}	1.377(3)
N_2-C_{a3}	1.376(3)	C_8-C_9	1.385(3)
N_2-C_{a4}	1.372(3)	C_9-C_{10}	1.368(4)
C_{a1}-C_{b1}	1.443(3)	C_{10}-C_{11}	1.365(4)
C_{a1}-C_{m2}'	1.385(3)	C_{11}-C_{12}	1.391(4)
C_{a2}-C_{b2}	1.441(3)	K-K″	1.146(4)
C_{a2}-C_{m1}	1.389(3)	K-N_3	2.750(3)
C_{a3}-C_b3	1.433(3)	K-N_3''	2.746(3)
C_{a3}-C_{m1}	1.391(3)	K-O	2.707(3)
C_{a4}-C_{b4}	1.438(3)	K-O″	2.738(3)
C_{a4}-C_{m2}	1.393(3)	O-C_{14}	1.192(4)
C_{b1}-C_{b2}	1.332(3)	C_{14}-C_{15}	1.458(5)
C_{b3}-C_{b4}	1.341(3)	C_{14}-C_{16}	1.466(5)
C_{m1}-C_1	1.498(3)	C_{b1}-H_{b1}	.957(21)
C_{m2}-C_7	1.495(3)	C_{b2}-H_{b2}	.918(22)
C_1-C_2	1.380(3)	C_{b3}-H_{b3}	.951(25)
C_1-C_6	1.386(4)	C_{b4}-H_{b4}	.915(26)
	Angles		
N_1-Fe-N_2	90.07(7)	C_{a2}-C_{b2}-H_{b2}	124.5(14)
N_1-Fe-C_{13}	89.77(8)	C_{a3}-C_{b3}-H_{b3}	123.4(15)
N_2-Fe-C_{13}	89.23(8)	C_{a4}-C_{b4}-H_{b4}	126.5(16)
Fe-C_{13}-N_3	177.8(3)	C_{b2}-C_{b1}-H_{b1}	129.2(13)
Fe-N_1-C_{a1}	127.03(14)	C_{b1}-C_{b2}-H_{b2}	128.1(13)
Fe-N_1-C_{a2}	127.07(13)	C_{b4}-C_{b3}-H_{b3}	129.2(15)
Fe-N_2-C_{a3}	126.86(14)	C_{b3}-C_{b4}-H_{b4}	126.2(16)
Fe-N_2-C_{a4}	127.05(14)	C_{m1}-C_1-C_2	122.37(22)
C_{a1}-N_1-C_{a2}	105.90(16)	C_{m1}-C_1-C_6	119.46(22)
C_{a3}-N_2-C_{a4}	106.04(17)	C_6-C_1-C_2	118.11(23)
N_1-C_{a1}-C_{m2}'	126.15(18)	C_1-C_2-C_3	121.37(26)
N_1-C_{a1}-C_{b1}	109.47(19)	C_2-C_3-C_4	119.32(27)
C_{m2}'-C_{a1}-C_{b1}	124.38(20)	C_3-C_4-C_5	119.83(26)
N_1-C_{a2}-C_{m1}	126.08(19)	C_4-C_5-C_6	121.21(29)
N_1-C_{a2}-C_{b2}	109.67(18)	C_5-C_6-C_1	120.15(27)
C_{m1}-C_{a2}-C_{b2}	124.25(20)	C_{m2}-C_7-C_8	120.81(22)
N_2-C_{a3}-C_{m1}	126.56(19)	C_{m2}-C_7-C_{12}	120.96(22)
N_2-C_{a3}-C_{b3}	109.67(19)	C_{12}-C_7-C_8	118.18(21)
C_{m1}-C_{a3}-C_{b3}	123.75(20)	C_7-C_8-C_9	121.17(27)
N_2-C_{a4}-C_{m2}	126.52(19)	C_8-C_9-C_{10}	119.66(27)
N_2-C_{a4}-C_{b4}	109.64(19)	C_9-C_{10}-C_{11}	119.99(25)
C_{m2}-C_{a4}-C_{b4}	123.84(21)	C_{10}-C_{11}-C_{12}	120.68(29)
C_{a1}-C_{b1}-C_{b2}	107.47(20)	C_{11}-C_{12}-C_7	120.29(27)
C_{a2}-C_{b2}-C_{b1}	107.47(20)	C_{13}-N_3-K	100.68(18)
C_{a3}-C_{b3}-C_{b4}	107.40(21)	C_{13}-N_3-K′	124.48(19)
C_{a4}-C_{b4}-C_{b3}	107.22(21)	N_3-K-O	87.47(10)
C_{a2}-C_{m1}-C_{a3}	123.31(19)	N_3''-K-O″	86.94(10)
C_{a1}'-C_{m2}-C_{a4}	123.22(19)	K-O-C_{14}	133.76(29)
C_{a1}'-C_{m2}-C_7	119.38(19)	K-O″-C_{14}''	145.29(28)
C_{a2}-C_{m1}-C_1	119.58(19)	O-C_{14}-C_{15}	119.8(4)
C_{a3}-C_{m1}-C_1	117.08(18)	O-C_{14}-C_{16}	122.6(4)
C_{a4}-C_{m2}-C_7	117.40(19)	C_{15}-C_{14}-C_{16}	117.2(4)
C_{a1}-C_{b1}-H_{b1}	123.4(13)		

[a] Primed atoms are related to unprimed atoms by the transformation $(-x, -y, -z)$. Double-primed atoms are related to unprimed atoms by the transformation $(1 - x, -y, -z)$. The estimated standard deviations of the least significant digits are given in parentheses.

ClO_4[15] was prepared by cleavage of the μ-oxo bridge of $[Fe(TPP)]_2O$ with aqueous perchloric acid in $CHCl_3$ and crystallized by addition of pentane. $[Fe(TPP)(H_2O)_2]ClO_4$ (0.2 g) was dissolved in 25 mL of methanol containing 0.2 g of KCN. The solution was stirred for 10 min at room temperature. The methanol was removed by rotary evaporation and the resulting solid was extracted with acetone saturated with KCN. Single crystals of $K[Fe(TPP)(CN)_2]\cdot 2(CH_3)_2C{=}O$ were obtained by concentrating the acetone solution and allowing pentane-heptane to diffuse slowly into the solution. The resulting crystals appear to easily lose the acetone molecule of solvation; hence freshly prepared crystals were sealed into thin-walled glass capillaries.

The infrared spectrum was obtained as a KBr pellet on a JASCO IRA-2 spectrometer. A very weak cyanide band is observed at 2120 cm^{-1}, and the C=O stretch of acetone at 1708 cm^{-1}. UV-visible spectra were obtained in methanol (dried over Mg turnings) on a Shimazu Model 200S spectrophotometer: λ_{max}(MeOH), ϵ ($M^{-1}\ cm^{-1}$) 424, 1.22×10^5; 539, 7.9×10^3; 560, 8.2×10^3; 596 nm, 7.6×10^3. $\mu = 2.26\ \mu_B$ at 21 °C.

X-ray Structure Determination. A crystal of $K[Fe(TPP)(CN)_2]\cdot 2(CH_3)_2C{=}O$ with dimensions of 0.3 × 0.5 × 0.6 mm was mounted in a thin-walled glass capillary. Preliminary examination of the crystal on a Syntex $P\bar{1}$ four-circle diffractometer established a two-molecule monoclinic unit cell. The systematic absences observed were consistent with the space group $P2_1/n$ (no. 14). The unit cell parameters, at 20 ± 1 °C, were obtained from a least-squares refinement of the setting angles of 30 reflections ($28 \leq 2\theta \leq 37°$), each collected at $\pm 2\theta$: a = 9.601 (2) Å, b = 11.439 (2) Å, c = 20.283 (3) Å, β = 100.78 (1)° (λ 0.710 73 Å). The unit cell volume of 2188 $Å^3$ and a cell content of two $K[Fe(TPP)(CN)_2]\cdot 2(CH_3)_2C{=}O$ led to a calculated density of 1.329 g/cm^3; the experimentally determined density was 1.33 g/cm^3. With

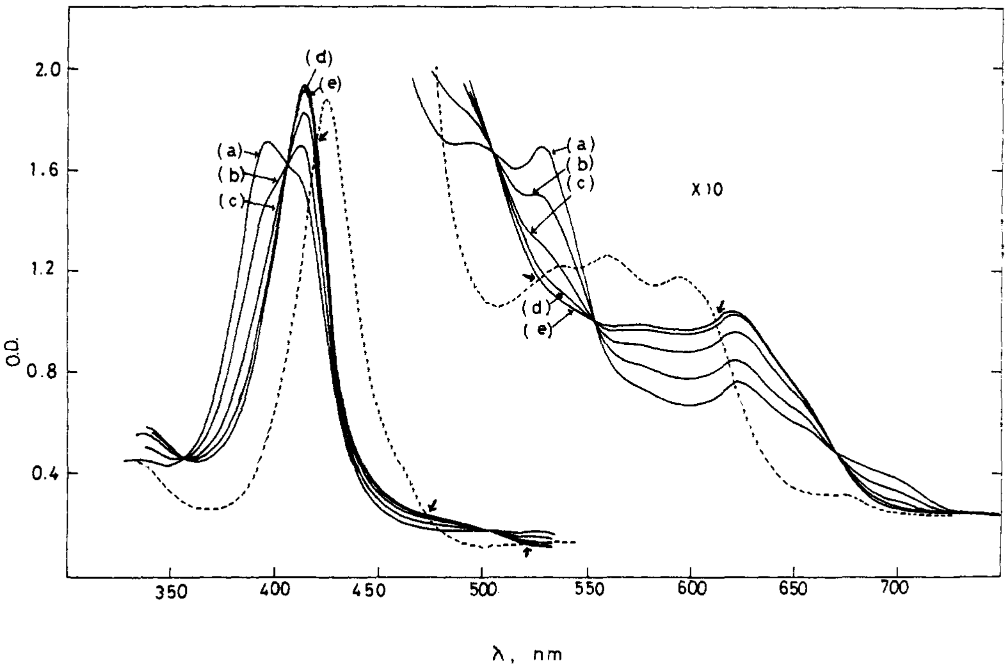

Figure 1. Spectral changes for the titration of $[Fe(TPP)(H_2O)_2]ClO_4$ (1.55×10^{-5} M) with KCN in methanol. KCN concentration: (a) none, (b) 2.7×10^{-6}, (c) 6.8×10^{-6}, (d) 1.4×10^{-5}, (e) 5.4×10^{-5}, (broken line) 3.5×10^{-3} M. High KCN concentration isosbestic points are marked with arrows.

two $[Fe(TPP)(CN)_2]^-$ ions per cell and space group $P2_1/n$, a center of symmetry is imposed on that ion (and on the K^+ ion as well).

X-ray intensity data were collected with graphite-monochromated Mo $K\alpha$ X-radiation and θ-2θ scanning. Variable scan rates (2-24°/min) with scans of 0.6° below $K\alpha_1$ to 0.6° above $K\alpha_2$ and backgrounds collected at the extremes of the scan for a total of 0.5 times the time required for the scan were employed. Throughout the data collection four standard reflections from diverse regions of reciprocal space were monitored every 50 reflections. The intensities of the standard reflections showed no systematic variations during the time required to collect the data. The intensity data were reduced and standard deviations calculated as described previously.[16] With a linear absorption coefficient of 0.485 mm^{-1} for Mo $K\alpha$ radiation and several ψ scans showing less than ±5% variation in intensities, an absorption correction was not deemed necessary. A total of 3873 unique reflections having $(\sin\theta)/\lambda \leq 0.67$ Å^{-1} and $F_o > 3\sigma(F_o)$ were retained as observed (70% of the theoretical number possible) and used in the solution and refinement of structure.

The structure was solved by the heavy-atom method and refined by block-diagonal and full-matrix least-squares techniques. A Patterson map revealed the positions of the iron, potassium, nitrogen, and α carbon atoms of the ligand; the remainder of the atoms were found in a difference Fourier. Atomic form factors were taken from Cromer and Mann[17] and that for hydrogen from Stewart, Davidson, and Simpson.[18] The effects of anomalous scattering of the iron and potassium atoms were included in the calculated structure amplitudes.[19] After four cycles of block-diagonal refinement the potassium atom was removed and relocated from a difference electron density map. From this map it was apparent that the potassium atom was disordered across the center at $\frac{1}{2}, 0, 0$. Refinement on the isotropic model converged after five cycles of block-diagonal refinement. The thermal parameters were converted to anisotropic and refinement converged after three additional cycles with $R_1 = \Sigma[|F_o| - |F_c|]/\Sigma|F_o| = 0.072$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o^2)]^{1/2} = 0.094$. All 20 hydrogen atoms were then located from a difference electron density map. The porphinato hydrogen atoms were allowed to vibrate isotropically and their position and thermal parameters included with the parameters being refined. The hydrogen atoms on the acetone of solvation were included as fixed contributors with d(C-H) = 0.95 Å[20] and with isotropic thermal parameters 1 Å^2 larger than the isotropic thermal parameter of the carbon atom to which the hydrogen atom is attached. Refinement of this model utilized a full-matrix least-squares refinement program. Each cycle of refinement contained two blocks. One block contained the scale factor and the thermal parameters and the other block contained the scale factor and the atom coordinates. Three cycles of refinement resulted in convergence with $R_1 = 0.050$ and $R_2 = 0.056$. The highest residual in the final electron density difference map was 0.42 e/Å^3. The error in an observation of unit weight was 1.74 and the final data/parameter ratio was 11.3 (*includes* refined hydrogen atoms in the parameter count). A listing of the final observed and calculated structure amplitudes (×10) is available as supplementary material. Atomic coordinates and the associated isotropic or isotropic equivalent temperature factor are listed in Table I. Tables III and IV give anisotropic temperature factors and root-mean-square displacements of the atoms refined anisotropically and are available as supplementary material. Table II presents selected interatomic distances and angles for the contents of the unit cell.

Results and Discussion

A major difficulty that we and others[21] have encountered in preparing solid cyanoporphinatoiron(III) derivatives has been the production of unwanted μ-oxo derivatives (FeOFe). In preparing $[Fe(TPP)(CN)_2]^-$ derivatives, this difficulty has been circumvented by saturating all solutions with CN^-. This procedure presents obvious difficulties in preparing monocyano species. The weak cyano infrared stretch at 2120 cm^{-1} (solid state) compares reasonably well with 2112- and 2125-cm^{-1} stretches (aqueous pyridine solution) reported by Caughey[4,21] for the dicyano and monocyano complexes, respectively, of the iron(III) derivative of protoporphyrin IX. It is possible that the cyano frequency in $K[Fe(TPP)(CN)_2]$ is somewhat affected by the interaction of the cyano nitrogen atom with the potassium ion (vide infra).

The reaction of cyanide with $[Fe(TPP)(H_2O)_2]^+$ appears to proceed in two steps. Figure 1 shows the spectral changes observed upon addition of cyanide ion to a solution of $[Fe(TPP)(H_2O)_2]^+$. The solid lines are the spectral variations at low concentrations of cyanide ion ($[CN^-]$ range 0.0-5.4×10^{-5} M); the broken line shows the ultimate spectrum observed at high cyanide ion concentrations. Different isosbestic points are observed at low and high cyanide ion concentrations. The high concentration isosbestic points ($[CN^-]$ range 8.1×10^{-5} to $>5 \times 10^{-3}$ M) at 419, 473, 530, and 613 nm are marked by arrows on Figure 1. These data, as well as the optical density changes observed as a function of cyanide ion concentration (Figure 2), are consistent with the stepwise equilibria

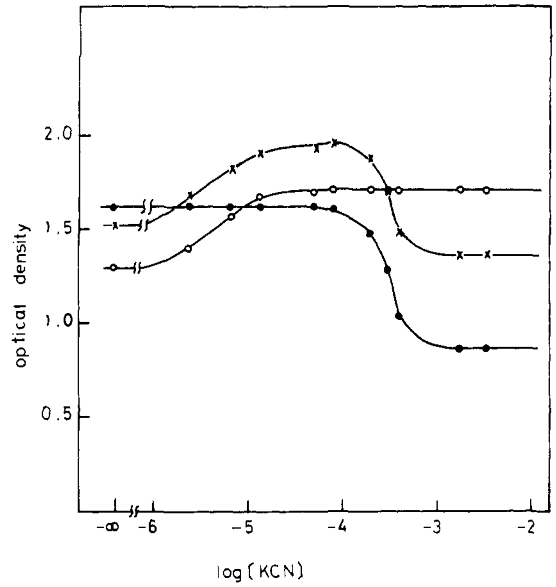

Figure 2. Optical density vs. log [KCN]: (- ● -) at 405 nm; (- X -) at 414 nm; (- O -) at 419 nm.

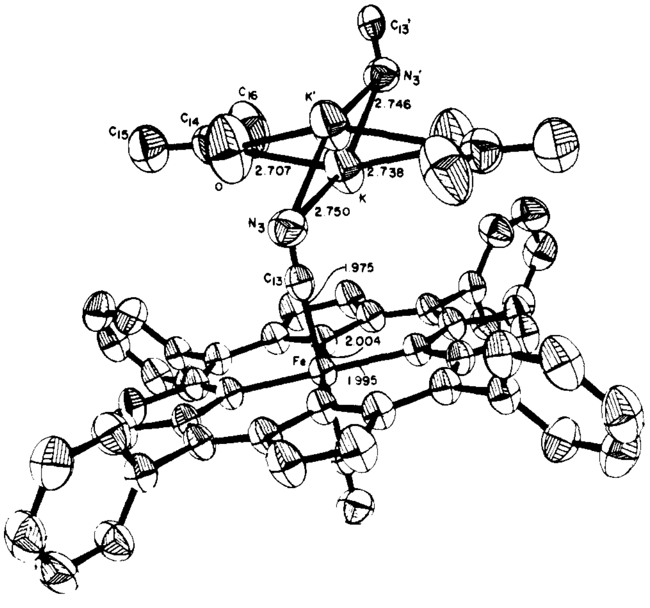

Figure 3. An ORTEP plot of the [Fe(TPP)(CN)$_2$]$^-$ ion and the potassium ion.

$$[\mathrm{Fe(TPP)(H_2O)_2}]^+ \xrightleftharpoons{\mathrm{CN^-}} [\mathrm{Fe(TPP)(CN)(H_2O)}] \xrightleftharpoons{\mathrm{CN^-}} [\mathrm{Fe(TPP)(CN)_2}]^-$$

Such stepwise additions of CN$^-$ to porphinatoiron(III) species have been observed previously.[11,12,22] All such reactions have been performed in coordinating solvents and it is probable that the monocyano species is a six-coordinate complex. The spectrum of [Fe(TPP)(H$_2$O)$_2$]ClO$_4$ in neutral methanol solution displays a distinct shoulder (410 nm) in the Soret region. The exact peak shape is dependent on solvent, concentration, temperature, etc., and suggests that various (probably high-spin six-coordinate) states of [Fe(TPP)]$^+$ exist in solution. However, despite the small differences in initial spectral shapes of [Fe(TPP)(H$_2$O)$_2$]$^+$, the isosbestic points corresponding to the monoligation of cyanide ion are the same.

The final spectrum of low-spin [Fe(TPP)(CN)$_2$]$^-$ (Figure 1) compared to the spectrum of a typical low-spin hemichrome, [Fe(TPP)(HIm)$_2$]ClO$_4$, shows red shifts in both the Soret and visible bands of the spectrum. Such red-shifted spectra, caused by axial anionic ligands, were originally noted by Valentine[23] and have been observed by others.[24,25]

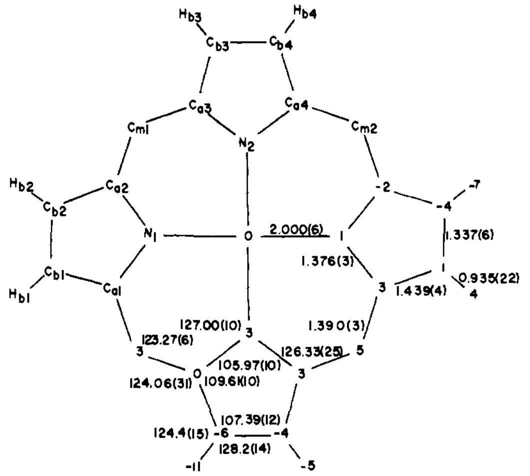

Figure 4. A formal diagram of the porphinato core in [Fe(TPP)(CN)$_2$]$^-$. The upper left portion of the diagram illustrates the labeling scheme of the core atoms. On the lower right-hand portion of the diagram the perpendicular displacements (in units of 0.01 Å) of each atom from the mean plane of the core are displayed. Also shown are averaged values of bond parameters for chemically equivalent types. The estimated standard deviations (in parentheses) are calculated on the assumption that all values are drawn from the same population.

Figure 3 gives a perspective view of the [Fe(TPP)(CN)$_2$]$^-$ ion and the environment of the disordered potassium ion. The half-atoms of potassium are well resolved with a K···K separation of 1.146 (4) Å. Also shown in Figure 3 are the interatomic distances involving the potassium. The observed K–N and K–O (carbonyl) separations are normal. The K–O distances observed in a number of K$^+$ antibiotic complexes[26-28] range from 2.67 to 2.83 Å but cluster around 2.75 Å, close to the sum of the ionic radius of K$^+$ and the van der Waals radius of oxygen (2.73 Å). Observed K–N (cyano) separations range from 2.75 Å upwards[29-31] or slightly less than the sum of the ionic radius of K$^+$ and the van der Waals radius of nitrogen (2.83 Å). It would thus appear that the K$^+$ ion in K[Fe(TPP)(CN)$_2$] is disordered about the inversion center to avoid too close an approach to the cyano nitrogen and carboxyl oxygen atoms; if the K$^+$ were located precisely at the inversion center at ½, 0, 0, the K–O and K–N distances would be 2.66 and 2.69 Å, respectively.[32]

An adjacent pair of [Fe(TPP)(CN)$_2$]$^-$ anions, related by the lattice translation along *a*, are linked by the K$^+$ cationic group. This can be seen with the aid of Figure 3; C$_{13}$' is bonded to Fe' (not pictured) of the next porphyrin unit which is generated by the *a* lattice translation. Thus the crystal structure consists of quasi-linear [K((CH$_3$)$_2$C=O)$_2$]$^+$[Fe(TPP)(CN)$_2$]$^-$ chains parallel to the *a* axis; the two parallel chains within a unit cell are related to each other by a twofold screw axis.

Figure 4 is a formal diagram of the porphinato core illustrating the numbering scheme used for the crystallographically unique atoms. Figure 4 also displays the displacement of the unique atoms from the mean plane of the core. The porphinato core is seen to be essentially planar with no remarkable displacement of any individual atom. The dihedral angles between the phenyl groups and the core are 71.7 and 65.6°. Individual bond distances and angles are tabulated in Table II. An inspection of Table II shows that chemically equivalent bond distances and angles of the core display high internal precision. Averaged values (with estimated standard deviations) for the various chemical types are displayed in Figure 4.

Table V. Comparison of Selected Bond Lengths (Å)

compd	Fe-C	C-N	ref
$Na_2[Fe(CN)_5(NO)]$	1.91(2)	1.16(3)	37
$[Fe_2(CN)_{10}(NH_3)]^{4-}$	1.91(4)	1.18(6)	38
$Na_2[Fe(CN)_5(NH_3)]$	1.92(3)	1.151(15)	39
$Cs_2Li[Fe(CN)_6]$	1.926(3)	1.148(5)	40
$Sr[Fe(CN)_5(NO)]$	1.94(2)	1.13(2)	41
$K_3[Fe(CN)_6]$	1.95(2)	1.14(2)	30
$K[Fe(TPP)(CN)_2]$	1.975(2)	1.147(3)	this work

An interesting feature of the geometric structure of the porphinato core involves the positions of the hydrogen atoms attached to the β-pyrrole carbon atoms. The C_b–H_b vectors (Figure 4) do not bisect the appropriate C_a–C_b–C_b angles. Rather the average H_b–C_b–C_b angle is 3.8° larger than the average H_b–C_b–C_a angle, presumably to increase the $H_b\cdots H_b$ separations on any given pyrrole ring; this angle deformation leads to a calculated increase in adjacent $H_b\cdots H_b$ separations of ~0.06 Å. It is presumed that such deformations occur in all *meso*-tetraphenylporphyrin derivatives; however, this derivative is only the second *meso*-TPP derivative in which hydrogen atom positions were refined. Similar angle inequivalences (2.5–4.0°) have been observed for the β-pyrrole alkyl substituents of a number of octaethylporphyrin derivatives.[33] The refined atoms of the phenyl rings of $[Fe(TPP)(CN)_2]^-$ were well behaved with $(C\text{-}H)_{av} = 0.94\ (4)$ Å. The average C–C bond distance in the phenyl groups is 1.379 (11) Å.

The average Fe–N bond distance of 2.000 (6) Å in $K[Fe(TPP)(CN)_2]$ is slightly longer than the 1.990-Å value observed in low-spin six-coordinate neutral[34] or cationic[35,36] iron(III) porphyrinate complexes and is consistent with a low-spin state for the iron(III) atom. The axial Fe–C distance is 1.975 (2) Å. Table V lists the observed Fe–C distances in a number of simple cyanoiron(III) complexes. Although the standard deviations for the Fe–C distances are frequently rather large, it nonetheless appears that the Fe–C distance in $K[Fe(TPP)(CN)_2]$ is significantly longer. A similarly longer Fe–C distance was observed in the porphinatoiron(II) derivative of *tert*-butyl isocyanide.[42] The apparent stronger bonding of cyanide by Fe(III) in the penta- and hexacyano complexes compared to the axial bonding of CN^- in the Fe(III) porphyrinate presumably reflects diminished π bonding of the axial CN^- ligands as a result of the competition between the porphinato ligand and the CN^- for metal π density.

The Fe–C–N angle is essentially linear at 177.8 (3)° and the Fe–C vector is just slightly tipped (1.6°) from the normal to the mean porphinato plane. This (expected) geometry is in distinct contrast to the structures of a number of cyanohemoprotein derivatives.[43-47] All hemoprotein derivatives have apparent Fe–C–N angles that are distinctly nonlinear. This curious nonlinear Fe–X–Y grouping is also observed in carbon monoxide hemoprotein complexes. These nonideal geometries of the coordinated axial ligand are presumed to result from constraints of the size of the ligand-binding pocket. Detherage et al.[45] have suggested that the true structure of these hemoprotein derivatives is not a bent three-atom grouping but a linear Fe–X–Y group tilted off the heme normal, a suggestion supported by the calculations of Case and Karplus.[48] These stereochemically more reasonable structures are certainly consistent with the results of this investigation.

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Supplementary Material Available: Listing of observed and calculated structure amplitudes (×10) and Tables III and IV, observed anisotropic temperature factors and root-mean-square displacements (21 pages). Ordering information is given on any current masthead page.

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