Stereochemistry of Carbonylmetalloporphyrins. The Structure of (Pyridine)(carbonyl)(5,10,15,20-tetraphenylporphinato)iron(II)

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Abstract: The six-coordinate carbon monoxide complex of an iron(II) porphyrin, Fe(TPP)(CO)(Py) (TPP = 5,10,15,20-tetraphenylporphyrin dianion, Py = pyridine), has been prepared and its structure determined from three-dimensional x-ray diffraction data. The linear (179 (2)°) Fe–C–O arrangement found here is to be contrasted with the bent Fe–C–O arrangements reported for three carbon monoxide hemoproteins. The Fe–C and C–O distances are 1.77 (2) and 1.12 (2) Å, respectively. The average Fe–N(porphyrin) distance is 2.02 (3) Å, somewhat shorter than the Fe–N(Py) distance of 2.10 (1) Å trans to the CO group in this octahedral complex. The Fe atom is displaced only 0.02 Å from the porphyrin N_4 plane toward the CO group. The porphyrin core is nearly planar and all bond parameters in the core agree well with those found in other porphyrins. The complex crystallizes with four formula units and eight benzene molecules in the monoclinic space group $C_{2h}{}^5$-$P2_1/c$ with a = 13.246 (17), b = 19.555 (26), c = 19.822 (25) Å, and β = 105.49 (3)°. The final agreement indices on $F_o{}^2$, based on the least-squares refinement of 205 variables for 3161 observations (including $F_o{}^2 \leq 0$), are R = 0.18 and R_w = 0.23. The conventional R index on F_o for reflections with $F_o{}^2 \geq 3\sigma(F_o{}^2)$ is 0.090.

Crystallographic studies of several carbon monoxide hemoproteins, for example erythrocruorin,[1] the bloodworm *Glycera dibranchiata*,[2] and myoglobin[3] have been interpreted in favor of bent Fe–C–O bonds of approximately 135–145°. Insofar as we are aware there are no precedents for this angular arrangement in any transition metal complexes containing terminal CO groups. In view of the utility of model compounds for understanding the bonding of small molecules to hemoproteins[4] and because of the surprising absence of structural studies on model carbon monoxide complexes of iron(II) porphyrins,[5] the present study of Fe(TPP)(CO)(Py) was undertaken.

Experimental Section

Preparation of Fe(TPP)(CO)(Py). All reactions were carried out under dinitrogen using modified Schlenk tubes. All solvents were thoroughly saturated with dry N_2. Tetraphenylporphyrin free base (500 mg) was dissolved in a mixed solvent of 20 ml of pyridine and 50 ml of chloroform. To the solution was quickly added about 130 ml of a saturated solution of iron(II) acetate in acetic acid, prepared by refluxing iron powder in acetic acid. The mixture was stirred for 2 h at 50–60 °C. Then carbon monoxide was bubbled into the solution for 20 min and the solution was kept at 5 °C overnight under a CO atmosphere to yield lustrous purple crystals of Fe(TPP)(CO)(Py). Anal. Calcd for $C_{50}H_{33}FeN_5O$: C, 77.42; H, 4.26; N, 9.03. Found: C, 78.04; H, 4.26; N, 8.87.

Crystallographic Data. Crystals of Fe(TPP)(CO)(Py) more suitable for x-ray study were grown by slow cooling of a saturated benzene solution of Fe(TPP)(CO)(Py) under a CO atmosphere. This procedure yields material of formula Fe(TPP)(CO)(Py)·$2C_6H_6$.

Preliminary precession photographs of the crystals displayed monoclinic symmetry and systematic absences consistent with the centrosymmetric space group $C_{2h}{}^5$-$P2_1/c$. These photographs also indicated that the crystals are highly mosaic. This mosaicity does not result from loss of solvent of crystallization, as all crystals examined had been sealed under dry nitrogen in capillaries. On the basis of an examination of a number of crystals one was selected as being least mosaic. This crystal, which was mounted with the [100] direction approximately along the spindle axis, displayed faces of the forms {0 21} and {1 10} and had a calculated volume of 0.033 mm^3.

The lattice parameters, obtained as previously described[7] by hand centering 20 reflections in the range 16° < 2θ < 25° on a FACS-I diffractometer using Mo Kα_1 radiation (λ 0.709 30 Å), are a = 13.246 (17) Å, b = 19.555 (26) Å, and c = 19.822 (25) Å, and β = 105.49 (3)°. The calculated density, based on four Fe(TPP)(CO)(Py) and eight benzene molecules per unit cell is 1.25 g/cm^3 and agrees well with an observed value of 1.24 (2) g/cm^3, as measured by flotation in aqueous zinc chloride solution.

Based on ω scans using a narrow source and open counter the width at half height of trial reflections was found to be 0.5 to 1°. Accordingly, data were collected in shells of 2θ by the ω-scan method, using graphite monochromatized Mo Kα radiation. The scan range in ω was 2.0°. The takeoff angle was 3.2°. A fully open aperture (6 × 6 mm) was positioned 24 cm from the crystal. In order to minimize x-ray exposure of the crystal a step-scan mode was employed, with the 2.0° scan broken up into 40 steps of 1-s counting duration each. Background counts of 20-s duration were taken at each end of the scan range. If a reflection failed to obey the condition $I > 3\sigma(I)$, the peak was rescanned and the background counting time was increased from 20 to 40 s.[7] The results of the two peak scans and separate background counts were summed. In the processing of the data these rescanned reflections were brought to the same scale as singly scanned reflections by division by 2.

Data were collected in the range $2 < 2\theta \leq 35°$. Beyond 35° there appeared to be less than 10% of the measured reflections statistically observable. During the course of data collection six standards were measured every 100 reflections. The deviations of these standards were all within counting statistics. Thus our initial expectation that the crystals might be x-ray sensitive, based on the known photosensitivity of iron porphyrin carbon monoxide complexes, was unfounded.

The data were processed in the usual manner,[7] using a value of p of 0.05. Of the 3519 reflections measured, 3161 are unique after exclusion of equivalent reflections and systematically absent reflections and these were used in subsequent calculations. Based on trial calculations employing a linear absorption coefficient of 3.48 cm^{-1} no absorption correction was deemed necessary.

Solution and Refinement of Structure. The Fe atom and the atoms of the porphyrin core were located in an origin-removed, sharpened Patterson synthesis. Subsequent refinements and difference Fourier syntheses led to the location of all non-hydrogen atoms. The structure was refined by full-matrix, least-squares techniques. The usual procedures, computer programs, atomic scattering factors, and anomalous terms were employed.[8] The quantity minimized was $\Sigma w(F_o{}^2 - F_c{}^2)^2$ with $w = 1/\sigma^2(F_o{}^2)$. All the data (including $F_o{}^2 < 0$) were used. The agreement indices for the refinement on $F_o{}^2$ are

$$R = \Sigma|F_o{}^2 - F_c{}^2|/\Sigma F_o{}^2$$

$$R_w = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w F_o{}^4]^{1/2}$$

In all of the refinements, the four phenyl rings of the TPP moiety and the two benzene rings were treated as rigid groups.[9] All other individual, non-hydrogen atoms were refined isotropically. The hydrogen atoms were included as a fixed contribution before the last cycle, their positions being idealized assuming a trigonal, planar geometry and using a C–H distance of 0.95 Å. Each hydrogen atom was assigned a thermal parameter of 1.0 Å^2 greater than the isotropic thermal parameter of the carbon atom to which it is attached. The

Table I. Positional and Thermal Parameters for the Nongroup Atoms of Fe(TPP)(CO)(Py)·$2C_6H_6$

ATOM	X[a]	Y	Z	B,A^2	ATOM	X	Y	Z	B,A^2
FE	0.23792(21)	0.12643(13)	0.32007(13)	2.64(7)	C5	0.3074(13)	0.13314(94)	0.16574(80)	2.77(40)
O	0.2301(12)	0.27476(75)	0.32455(73)	6.55(37)	C6	0.2019(13)	0.13003(92)	0.16241(80)	2.41(38)
N1	0.3774(10)	0.13161(77)	0.29351(68)	1.82(33)	C7	0.1211(13)	0.13219(96)	0.09879(84)	3.14(42)
N2	0.16245(96)	0.12968(72)	0.21870(61)	2.49(31)	C8	0.0289(12)	0.13334(87)	0.11483(77)	3.01(38)
N3	0.10243(96)	0.12056(71)	0.34649(63)	2.90(30)	C9	0.0533(12)	0.13048(90)	0.19031(77)	2.58(38)
N4	0.31690(97)	0.12067(71)	0.42228(61)	2.52(31)	C10	-0.0195(12)	0.12992(93)	0.22827(78)	2.57(40)
N5	0.2424(13)	0.01943(72)	0.31178(77)	3.37(37)	C11	0.0021(12)	0.12646(98)	0.30068(77)	2.37(37)
C	0.2334(17)	0.2171(10)	0.3231(10)	5.00(50)	C12	-0.0729(13)	0.1258(10)	0.34125(84)	2.78(42)
CPY1	0.1540(14)	-0.01337(96)	0.28192(88)	3.61(45)	C13	-0.0215(14)	0.1220(10)	0.40820(85)	3.72(44)
CPY2	0.1560(18)	-0.0853(12)	0.2670(11)	4.49(63)	C14	0.0894(12)	0.12041(88)	0.41272(77)	2.30(36)
CPY3	0.2502(17)	-0.1180(11)	0.28216(97)	5.56(54)	C15	0.1674(13)	0.11729(89)	0.47417(77)	2.47(39)
CPY4	0.3394(18)	-0.0832(13)	0.3131(12)	4.78(70)	C16	0.2739(14)	0.11779(94)	0.47848(85)	3.16(42)
CPY5	0.3331(18)	-0.0141(12)	0.3291(10)	3.97(57)	C17	0.3563(14)	0.11560(98)	0.54132(88)	3.59(47)
C1	0.4741(14)	0.1329(10)	0.34178(89)	2.82(44)	C18	0.4471(12)	0.11802(89)	0.52434(78)	2.54(40)
C2	0.5516(13)	0.13544(98)	0.29977(85)	3.75(43)	C19	0.4245(13)	0.12307(97)	0.44983(82)	3.04(41)
C3	0.4980(13)	0.13593(93)	0.23213(78)	2.43(41)	C20	0.5014(12)	0.12898(90)	0.41366(78)	2.74(37)
C4	0.3892(12)	0.13299(88)	0.22680(79)	2.20(38)					

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables.

Table II. Derived Parameters for the Rigid Group Atoms of Fe(TPP)(CO)(Py)·$2C_6H_6$

ATOM	X	Y	Z	B,A^2	ATOM	X	Y	Z	B,A^2
CP11	0.33656(81)	0.13402(84)	0.09690(45)	4.27(47)	CP41	0.61159(66)	0.13008(83)	0.45259(51)	2.79(43)
CP12	0.35970(95)	0.19608(59)	0.07008(70)	5.00(53)	CP42	0.6602(11)	0.07087(56)	0.48443(69)	5.08(55)
CP13	0.38675(96)	0.19775(57)	0.00690(74)	6.70(59)	CP43	0.7633(11)	0.07331(58)	0.52562(63)	5.04(52)
CP14	0.39067(84)	0.13737(85)	-0.02946(45)	5.64(51)	CP44	0.81774(66)	0.13495(84)	0.53497(53)	4.66(48)
CP15	0.36753(96)	0.07531(59)	-0.00264(70)	5.95(53)	CP45	0.7691(11)	0.19416(56)	0.50313(71)	5.85(56)
CP16	0.34048(94)	0.07363(57)	0.06054(74)	5.88(56)	CP46	0.6660(11)	0.19172(59)	0.46194(63)	4.66(56)
CP21	-0.13491(69)	0.12976(95)	0.18833(52)	4.20(44)	CB1	0.07506(81)	0.3796(12)	0.39631(64)	6.26(62)
CP22	-0.1923(13)	0.06946(61)	0.17327(69)	6.50(62)	CB2	0.0291(16)	0.43980(76)	0.41113(73)	8.61(74)
CP23	-0.2960(12)	0.07129(67)	0.13316(74)	7.15(59)	CB3	-0.0693(16)	0.43801(82)	0.42381(70)	9.27(73)
CP24	-0.34235(69)	0.13342(99)	0.10812(55)	7.65(57)	CB4	-0.12172(82)	0.3761(13)	0.42166(68)	9.44(69)
CP25	-0.2850(13)	0.19373(65)	0.12319(73)	9.36(67)	CB5	-0.0758(16)	0.31589(78)	0.40683(77)	7.91(76)
CP26	-0.1812(13)	0.19189(64)	0.16329(75)	7.16(60)	CB6	0.0226(16)	0.31768(80)	0.39415(72)	8.12(68)
CP31	0.13498(76)	0.11981(78)	0.54144(40)	3.24(39)	CB'1	0.56640(99)	0.4018(11)	0.33597(64)	10.98(74)
CP32	0.12927(91)	0.18219(55)	0.57401(67)	3.90(49)	CB'2	0.4941(16)	0.45198(61)	0.30548(95)	10.97(79)
CP33	0.10616(92)	0.18395(57)	0.63849(67)	4.35(49)	CB'3	0.4012(13)	0.43388(93)	0.25675(88)	8.53(79)
CP34	0.08876(79)	0.12333(84)	0.67041(41)	4.78(45)	CB'4	0.38061(98)	0.3656(11)	0.23851(63)	9.08(69)
CP35	0.09447(96)	0.06095(59)	0.63785(70)	5.55(57)	CB'5	0.4529(16)	0.31538(64)	0.26900(93)	8.83(72)
CP36	0.11758(95)	0.05919(53)	0.57336(70)	5.25(54)	CB'6	0.5458(13)	0.33348(87)	0.31773(86)	9.95(75)

RIGID GROUP PARAMETERS

GROUP	X_C[a]	Y_C	Z_C	DELTA[b]	EPSILON	ETA
CP1	0.36362(47)	0.13569(45)	0.03372(38)	3.0395(80)	3.091(10)	1.3239(64)
CP2	-0.23863(65)	0.13159(48)	0.14823(35)	-0.059(12)	3.0431(90)	0.3142(68)
CP3	0.11187(45)	0.12157(45)	0.60593(35)	-3.2035(80)	-3.1297(95)	-1.7855(59)
CP4	0.71466(62)	0.13252(44)	0.49378(34)	-0.032(10)	-3.3364(82)	-2.8043(66)
CB	-0.02333(73)	0.37785(55)	0.40898(35)	-3.176(15)	-3.272(11)	-2.6925(78)
CB'	0.47350(79)	0.38368(57)	0.28724(45)	-2.864(13)	3.167(11)	2.6658(82)

[a] x_C, y_C, and z_C are the fractional coordinates of the origin of the rigid group. [b] The rigid group orientation angles delta, epsilon, and eta (radians) have been defined previously: S. J. La Placa and J. A. Ibers, *Acta Crystallogr.*, 18, 511 (1965).

final agreement indices on F_o^2 for the 3161 reflections and 205 variables are $R = 0.18$ and $R_w = 0.23$. The conventional agreement indices on F_o for the 1223 reflections with $F_o^2 \geq 3\sigma(F_o^2)$ are $R = 0.090$ and $R_w = 0.094$.

An analysis of $\Sigma w(F_o^2 - F_c^2)^2$ as a function of F_o^2, setting angles, and Miller indices shows no unusual trends. The standard deviation of an observation of unit weight is 1.37 e^2. A final difference Fourier map is essentially featureless with the highest peak equal to 0.75 (12) e/Å^3 around the N(5) atom. Remaining peaks have electron densities less than 0.6 (1) e/Å^3. The featureless difference Fourier map and especially the limited number of observations discouraged us from carrying out refinements based on anisotropic vibrations of the atoms. There is no reason to believe that the metrical details obtained are significantly affected by the absence of an anisotropic model.

The final positional and thermal parameters for the nongroup atoms appear in Table I. Derived positional parameters and thermal parameters for the rigid group atoms are given in Table II. The calculated positions and estimated thermal parameters for the hydrogen atoms are given in Table III.[10] A listing of the observed and calculated structure amplitudes appears in Table IV.[10] Entries with $F_o < 0$ are for those reflections having $F_o^2 < 0$.

Description of the Structure and Discussion

The crystal structure consists of four discrete molecules of Fe(TPP)(CO)(Py) and eight molecules of benzene. The contents of a unit cell are shown in Figure 1, and a view of the Fe(TPP)(CO)(Py) molecule with the numbering scheme used is shown in Figure 2. In Table V the bond distances and angles in the Fe(TPP)(CO)(Py) molecule are presented.

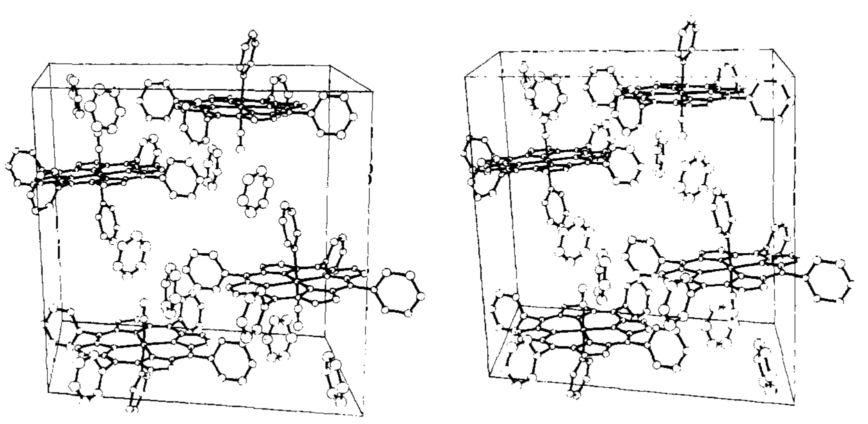


Figure 1. Stereoscopic view of the contents of one unit cell of Fe(TPP)(CO)(Py)·$2C_6H_6$. The *z* axis is horizontal to right; the *y* axis is almost vertical, and the *x* axis is about perpendicular to the paper going away from the reader. Vibrational ellipsoids are drawn at the 20% level. Hydrogen atoms have been omitted.

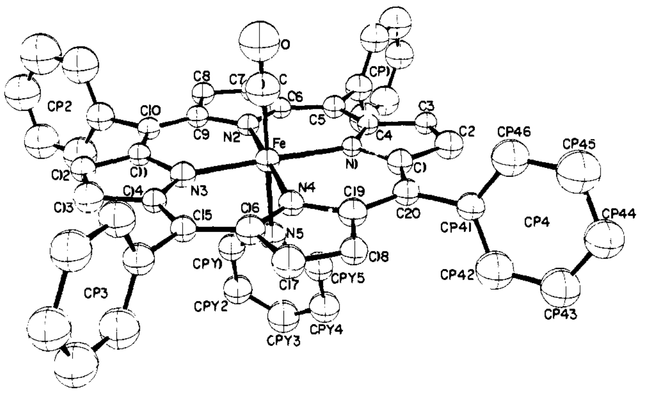


Figure 2. A drawing of the Fe(TPP)(CO)(Py) molecule with the numbering sequence. Hydrogen atoms have been omitted.

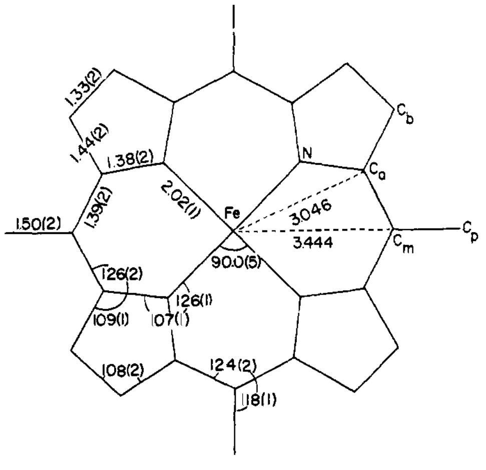


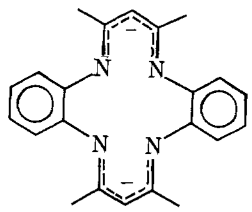
Figure 3. Diagram giving the averaged (D_{4h}) bond distances (Å) and angles (deg) in the porphyrin skeleton of the Fe(TPP)(CO)(Py) molecule.

In this porphyrin complex the geometry of the TPP moiety is very similar to that found in other metalloporphyrins.[6,11,12] The averaged bond distances and angles for the four crystallographically nonequivalent pyrrole rings are presented in Figure 3. They agree within experimental error with those found for other low spin iron(II) porphyrin structures.[6]

The deviations from planarity of the porphyrin skeleton are given in Table VI. They are significant, but comparable with those found in other metalloporphyrins.[6,11,12]

The inner coordination sphere of the complex, with selected bond parameters, is shown in Figure 4. The environment of the central iron atom is that of an axially distorted octahedron. The four equivalent Fe-N(pyrrole) distances average 2.02 (3) Å, comparing well with those in low spin iron porphyrin structures: 2.004 (4) Å for Fe(TPP)(piperidine)$_2$,[13] 2.001 (3) Å for Fe(NO)(TPP),[14] and 2.008 (4) Å for Fe(NO)(TPP)(N-MeIm).[15]

The axial Fe-N(pyridine) bond distance is 2.10 (1) Å. This bond length may be compared with the Fe-N(axial) distances of 2.088 (3) Å found in Fe(I)(CO)(Py),[16] 2.122 (5) Å in Fe(I)(CO)(NH_2NH_2),[16,17] 2.180 (4) Å in Fe(NO)(TPP)(N-MeIm),[15] and 2.127 (3) Å in Fe(TPP)(piperidine)$_2$.[13] All these bond lengths exceed that of 2.00 Å expected for a low-spin Fe-N distance. The long Fe-N distances in the first two structures have been attributed to the strong trans effect of the CO ligand.[16] A similar trans effect has been observed in the ruthenium(II) carbonyl porphyrin complexes, Ru(TPP)(CO)(Py)·$1.5C_7H_8$[18] and Ru(TPP)(CO)(EtOH).[19] The Ru-N(Py) and Ru-O(EtOH) distances are 2.193 (4) and 2.21 (2) Å, respectively, as compared with the Ru-N(porphyrin) distance of 2.052 (9) Å, but in the last two iron structures, the long Fe-N bond lengths are attributed to the steric interactions between nitrogen atoms of the porphinato core and the hydrogen atoms of the imidazole or piperidine ligands.[13,15]



I

The pyridine ring is not exactly perpendicular to the plane of the porphyrin (interplanar angle = 100.4°). It is oriented such that the normal to the ring bisects the N(1)-Fe-N(2) and N(3)-Fe-N(4) angles, thereby minimizing the steric interactions between porphyrin nitrogen atoms and pyridine hydrogen atoms. The nonbonded contacts between the ortho H atoms and the porphyrin ring are HCPY(5)-N(1), 2.59 Å; HCPY(1)-N(3), 2.55 Å.

The Fe-C(carbonyl) distance is 1.77 (2) Å and is slightly longer than the bond distances observed in Fe(I)(CO), 1.694 (4) Å,[16] in Fe(I)(CO)(NH_2NH_2), 1.751 (6) Å,[16,17] and in Fe(I)(CO)(Py), 1.730 (3) Å.[16] This observation may represent a stronger binding of CO to iron(II) complexes of ligand I than to iron(II) porphyrin complexes, consistent with the lower CO stretching frequencies in these complexes: 1921-1940 cm^{-1} in Fe(I)(CO)X[16] vs. 1980 cm^{-1} in Fe(TPP)(CO)(Py).

Table V. Bond Distances (Å) and Angles (deg) for Fe(TPP)(CO)(Py)·$2C_6H_6$

Fe-C	1.77 (2)			Fe-N(1)-C(1)	124 (1)	Fe-N_4-C_a	126 (1)
Fe-N(1)	2.05 (1)	Fe-N(pyrrole)	2.02 (3)[a]	Fe-N(1)-C(4)	126 (1)		
Fe-N(2)	1.99 (1)			Fe-N(2)-C(6)	129 (1)		
Fe-N(3)	2.00 (1)			Fe-N(2)-C(9)	126 (1)		
Fe-N(4)	2.02 (1)			Fe-N(3)-C(11)	126 (1)		
Fe-N(5)	2.10 (1)			Fe-N(3)-C(14)	127 (1)		
C-O	1.12 (2)			Fe-N(4)-C(16)	127 (1)		
N(1)-C(1)	1.38 (2)	N-C_a	1.38 (2)	Fe-N(4)-C(19)	127 (1)		
N(1)-C(4)	1.37 (2)			C(1)-N(1)-C(4)	110 (1)	C_a-N_4-C_a	107 (2)
N(2)-C(6)	1.35 (2)			C(6)-N(2)-C(9)	105 (1)		
N(2)-C(9)	1.40 (2)			C(11)-N(3)-C(14)	106 (1)		
N(3)-C(11)	1.40 (2)			C(16)-N(4)-C(19)	107 (1)		
N(3)-C(14)	1.37 (2)			N(1)-C(1)-C(2)	105 (1)	N_4-C_a-C_b	109 (2)
N(4)-C(16)	1.38 (2)			N(1)-C(4)-C(3)	108 (1)		
N(4)-C(19)	1.38 (2)			N(2)-C(6)-C(7)	111 (1)		
C(1)-C(2)	1.48 (2)	C_a-C_b	1.44 (2)	N(2)-C(9)-C(8)	110 (1)		
C(3)-C(4)	1.42 (2)			N(3)-C(11)-C(12)	108 (1)		
C(6)-C(7)	1.42 (2)			N(3)-C(14)-C(13)	109 (1)		
C(8)-C(9)	1.45 (2)			N(4)-C(16)-C(17)	109 (2)		
C(11)-C(12)	1.44 (2)			N(4)-C(19)-C(18)	108 (1)		
C(13)-C(14)	1.45 (2)			C(1)-C(2)-C(3)	108 (1)	C_a-C_b-C_b	108 (2)
C(16)-C(17)	1.42 (2)			C(2)-C(3)-C(4)	109 (2)		
C(18)-C(19)	1.43 (2)			C(6)-C(7)-C(8)	108 (2)		
C(2)-C(3)	1.34 (2)	C_b-C_b	1.33 (2)	C(7)-C(8)-C(9)	106 (1)		
C(7)-C(8)	1.34 (2)			C(11)-C(12)-C(13)	108 (1)		
C(12)-C(13)	1.32 (2)			C(12)-C(13)-C(14)	108 (2)		
C(17)-C(18)	1.33 (2)			C(16)-C(17)-C(18)	108 (2)		
C(1)-C(20)	1.38 (2)	C_a-C_m	1.39 (2)	C(17)-C(18)-C(19)	108 (1)		
C(4)-C(5)	1.39 (2)			N(1)-C(1)-C(20)	131 (2)	N_4-C_a-C_m	126 (2)
C(5)-C(6)	1.38 (2)			N(1)-C(4)-C(5)	125 (2)		
C(9)-C(10)	1.37 (2)			N(2)-C(6)-C(5)	125 (1)		
C(10)-C(11)	1.39 (2)			N(2)-C(9)-C(10)	125 (1)		
C(14)-C(15)	1.37 (2)			N(3)-C(11)-C(10)	125 (2)		
C(15)-C(16)	1.39 (2)			N(3)-C(14)-C(15)	126 (2)		
C(19)-C(20)	1.40 (2)			N(4)-C(16)-C(15)	126 (1)		
C(5)-CP(11)	1.51 (2)	C_m-C_p	1.50 (3)	N(4)-C(19)-C(20)	128 (1)		
C(10)-CP(21)	1.52 (2)			C(4)-C(5)-C(6)	126 (2)	C_a-C_m-C_a	124 (2)
C(15)-CP(31)	1.51 (2)			C(9)-C(10)-C(11)	126 (1)		
C(20)-CP(41)	1.46 (2)			C(14)-C(15)-C(16)	124 (2)		
N(5)-CPY(1)	1.33 (2)			C(19)-C(20)-C(1)	121 (1)		
N(5)-CPY(5)	1.33 (2)			C(4)-C(5)-CP(11)	117 (1)	C_a-C_m-C_p	118 (1)
CPY(1)-CPY(2)	1.43 (3)			C(6)-C(5)-CP(11)	117 (1)		
CPY(2)-CPY(3)	1.37 (3)			C(9)-C(10)-CP(21)	118 (1)		
CPY(3)-CPY(4)	1.36 (3)			C(11)-C(10)-CP(21)	116 (1)		
CPY(4)-CPY(5)	1.40 (3)			C(14)-C(15)-CP(31)	117 (1)		
O-C-Fe	179 (2)			C(16)-C(15)-CP(31)	118 (1)		
C-Fe-N(1)	90.0 (8)	C-Fe-N_4	90.5 (11)	C(19)-C(20)-CP(41)	120 (1)		
C-Fe-N(2)	89.4 (7)			C(1)-C(20)-CP(41)	120 (1)		
C-Fe-N(3)	90.5 (9)			C(20)-C(1)-C(2)	124 (1)	C_b-C_a-C_m	125 (2)
C-Fe-N(4)	92.0 (7)			C(3)-C(4)-C(5)	127 (2)		
C-Fe-N(5)	177.5 (8)			C(5)-C(6)-C(7)	124 (2)		
N(1)-Fe-N(2)	89.1 (5)	N_4-Fe-N_4	90.0 (9)	C(8)-C(9)-C(10)	125 (1)		
N(2)-Fe-N(3)	91.3 (5)			C(10)-C(11)-C(12)	127 (1)		
N(3)-Fe-N(4)	89.7 (5)			C(13)-C(14)-C(15)	125 (2)		
N(4)-Fe-N(1)	90.0 (5)			C(15)-C(16)-C(17)	126 (2)		
N(1)-Fe-N(3)	179.4 (6)			C(18)-C(19)-C(20)	124 (1)		
N(2)-Fe-N(4)	178.3 (6)			CPY(5)-N(5)-CPY(1)	120 (2)		
N(1)-Fe-N(5)	89.0 (7)	N_4-Fe-N(5)	89.5 (11)	N(5)-CPY(1)-CPY(2)	120 (2)		
N(2)-Fe-N(5)	88.3 (6)			CPY(1)-CPY(2)-CPY(3)	119 (2)		
N(3)-Fe-N(5)	90.5 (7)			CPY(2)-CPY(3)-CPY(4)	120 (2)		
N(4)-Fe-N(5)	90.3 (6)			CPY(3)-CPY(4)-CPY(5)	119 (2)		
				CPY(4)-CPY(5)-N(5)	121 (2)		

[a] The value in parentheses is the standard deviation of a single observation, taken to be the larger of that estimated from the inverse matrix or that obtained from the values averaged on the assumption that they are from the same population.

The displacement of the iron atom in the complex Fe(TPP)(CO)(Py) toward the CO group is small and not significant (0.02 Å for the N_4 plane and 0.00 Å for the porphyrin plane). The comparable displacements are 0.11 Å in Fe(I)(CO)(NH_2NH_2) (0.00 Å after correction for the displacement of the Fe in the four-coordinate complex Fe(I)),[20] 0.07 Å in Fe(NO)(TPP)(N-MeIm),[15] and 0.08 Å in Ru(TPP)(CO)(Py).[18]

The most significant feature of the present structure is the linear Fe-C-O bond (179 (2)°). While such a linear bond is to be expected on the basis of the extensive literature on transition metal carbonyl complexes, the result is nonetheless highly significant since bent Fe-C-O bonds with bond angles of 135-145° appear to be the rule in various carbon monoxide complexes of hemoproteins.[1-3] The fact that in the present structure, a close analogue of the carbon monoxide complexes of the hemoproteins, the Fe-C-O linkage is linear strongly suggests that another interpretation of the results of the protein studies is in order. The allegedly bent Fe-C-O linkage in these proteins is derived from Fourier maps on which the C and O

Table VI. Deviations (Å, × 10^2) from Weighted Least-Squares Planes and Angles between Planes[a]

Atom	Plane 1	Plane 2	Plane 3
Fe	−2	0	31
O	−292	−290	84
C		−177	63
N(5)		211	1 (2)
CPY(1)			1 (2)
CPY (2)			−2 (2)
CPY(3)			1 (2)
CPY(4)			1 (2)
CPY(5)			−2 (2)
N(1)	−1 (2)	−3 (2)	
C(1)		−7 (2)	
C(2)		−6 (2)	
C(3)		−3 (2)	
C(4)		1 (2)	
C(5)		4 (2)	
N(2)	1 (2)	2 (2)	
C(6)		7 (2)	
C(7)		7 (2)	
C(8)		0 (2)	
C(9)		0 (2)	
C(10)		−5 (2)	
N(3)	−1 (2)	6 (2)	
C(11)		−4 (2)	
C(12)		−8 (2)	
C(13)		−6 (2)	
C(14)		0 (2)	
C(15)		3 (2)	
N(4)	1 (2)	5 (2)	
C(16)		4 (2)	
C(17)		5 (2)	
C(18)		4 (2)	
C(19)		1 (2)	
C(20)		−6 (2)	
CP(11)		9	
CP(21)		−4	
CP(31)		−9	
CP(41)		−9	

Angles between Normals to the Planes

Plane A	Plane B	Angle, deg
2 (porphyrin)	1 (four N atoms)	1.39
2	3 (pyridine)	100.4
2	CP1 (phenyl 1)	83.8
2	CP2 (phenyl 2)	80.9
2	CP3 (phenyl 3)	86.8
2	CP4 (phenyl 4)	76.2
2	CB (benzene)	84.6
2	CB′ (benzene)	93.4
3	CP1	98.5
3	CP2	22.3
3	CP3	96.0
3	CP4	27.2
3	CB	147.5
3	CB′	20.8
CB	CB′	128.0

Coefficients of the Plane Equation $A + By + Cz = D$[b]

Plane	A	B	C	D
1	0.539	−19.509	−1.273	−2.729
2	0.271	−19.534	−0.912	−2.705
3	4.916	4.441	−19.164	−4.710
CP1	11.434	−2.172	4.838	4.026
CP2	7.215	−2.181	−18.760	−4.789
CP3	11.697	−1.133	4.223	3.729
CP4	7.423	−3.774	−18.351	−4.257
CB	2.328	−2.585	17.705	6.210
CB′	8.844	2.034	−17.615	−0.091

[a] The entries for which an error is not indicated are for atoms which were not included in the calculation of the plane. [b] The plane is in crystal coordinates as defined by W. C. Hamilton, *Acta Crystallogr.*, 18, 502 (1965).

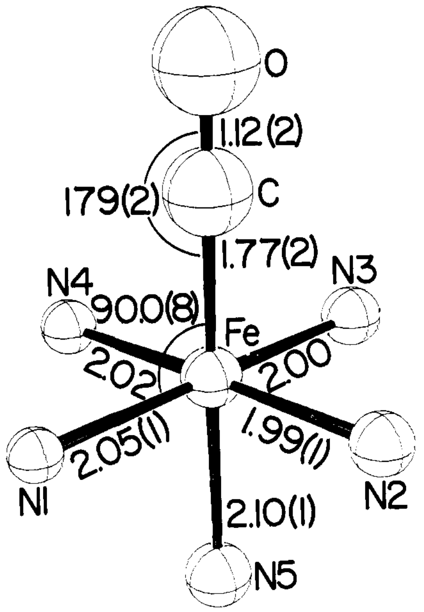


Figure 4. Drawing illustrating the inner coordination sphere of the carbonyl complexes with selected metrical details. The 50% ellipsoids are displayed.

atoms remain unresolved. These maps have apparently been interpreted on the assumption that the Fe–C vector is perpendicular to the porphyrin plane. It is much more reasonable, in our opinion, to expect that owing to the fixed nature of the globin pocket bending will occur at the Fe atom, leading to a linear Fe–C–O bond which is not perpendicular to the porphyrin plane. The resolution of the Fourier maps of the carbon monoxide complexes of hemoproteins is not sufficient to eliminate this chemically more reasonable possibility.

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Supplementary Material Available: Table III, hydrogen atom coordinates, and Table IV, structure amplitudes (24 pages). Ordering information is given on any current masthead page.

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