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Structure of the Iron(III)-"Capped" Porphyrin, FeCl(C_2-Cap), [5,10,15,20-[Pyrromellitoyltetrakis(*o*-(oxyethoxy)phenyl)]porphyrinato]chloroiron(III)

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Abstract: The structure of the iron(III) "capped" porphyrin, [5,10,15,20-[pyrromellitoyltetrakis(*o*-(oxyethoxy)phenyl)]porphyrinato]chloroiron(III), FeCl(C_2-Cap), has been determined from single-crystal, X-ray diffraction data collected at −150 °C. The material crystallizes as the trichloroform solvate, FeCl(C_2-Cap)·3CHCl$_3$, in space group C_{2h}^5-$P2_1/c$ of the monoclinic system with four formula units in a cell of dimensions a = 14.473 (5) Å, b = 19.514 (9) Å, c = 22.830 (11) Å, β = 101.61 (2)°, V = 6316 Å^3. The structure was described by 396 variables, and at convergence of the full-matrix, least-squares refinement the values of R and R_w (on F, 9897 data having $F_0^2 > 3\sigma(F_0^2)$) are 0.065 and 0.078. The chloro ligand is outside the "cap" and the iron atom is above the mean plane of the porphyrin core away from the "cap". The geometry about the iron atom is typical for FeCl(porphyrin) systems, with Fe–Cl = 2.242 (1) Å and with Fe 0.46 Å above the mean N$_4$ plane and 0.47 Å above the mean 24-atom porphyrin plane. The porphyrin itself is slightly nonplanar, with the mean displacement from the least-squares plane being 0.076 Å and the maximum displacement being 0.208 Å. Although the conformations of the side chains that link porphyrin to "cap" are distinctly different from those found in the related free-base porphyrin, H$_2$(C_2-Cap), the "cap" to porphyrin distances are very similar in the two structures. The separations between the centroids of the phenyl "cap" and respectively those of the four pyrrole nitrogen atoms and the 24-atom porphyrin skeleton are 4.03 and 4.01 Å in FeCl(C_2-Cap) and 3.86 and 3.96 Å in H$_2$(C_2-Cap). These separations are too small to accommodate O$_2$ or CO within the cap and imply considerable flexibility of these "capped" porphyrins in solution where binding of O$_2$ or CO to Fe$^{\text{II}}$(C_2-Cap) systems occurs.

To elucidate structure–function relationships in hemoproteins requires knowledge of the intrinsic properties of the heme group—its affinities for bases and for axial ligands—together with a precise sterochemical knowledge of the structures involved. Owing to the size and complexity of protein crystal structure analyses, it is presently only through the use of model compounds that we can obtain at least in part such information.[1,2] Among the well-characterized model systems the "chelated-heme",[3] "picket-fence",[4] and "capped"[5] porphyrins are of particular interest owing to their ability to bind dioxygen reversibly. The ligation of small molecules, including O$_2$ and CO, to these modified porphyrins has been studied extensively.[6-10] But structural studies on these molecules have not kept pace with the ligation studies, owing in large measure to the difficulty of growing suitable crystals. In particular, there are no structural results on the "chelated-heme" systems and only one structural result on a "capped" system, namely the structure of the free-base "capped" porphyrin, 5,10,15,20-[pyrromellitoyltetrakis(*o*-(oxyethoxy)phenyl)]porphyrin, H$_2$(C_2-Cap).[11] In this paper we present structural results for FeCl(C_2-Cap). As we shall see, the "cap"-to-porphyrin separation in this molecule is very close to that in H$_2$(C_2-Cap) and is far too small to accommodate a CO or O$_2$ molecule.

Table I. Crystal Data and Data Collection Procedures for FeCl(C_2-Cap)·3CHCl$_3$

formula	$C_{65}H_{45}Cl_{10}FeN_4O_{12}$
formula weight, amu	1484.5
space group	C_{2h}^5-$P2_1/c$
a, Å	14.473 (5)
b, Å	19.514 (9)
c, Å	22.830 (11)
β, deg	101.61 (2)
V, Å^3	6316
Z	4
temp, °C	−150^a
crystal volume, mm^3	0.0896
radiation	graphite-monochromated Mo Kα (λ(Mo Kα_1) = 0.7093 Å)
linear absorption coefficient, cm^{-1}	7.29
transmission factors	0.696–0.872
detector aperture	4.5 mm wide, 6 mm high, 32 cm from crystal
takeoff angle, deg	3.4
scan speed	2.0° in 2θ per min
λ^{-1} sin θ limits, Å^{-1}	0.0431–0.6291 (3.5° < 2θ(Mo Kα_1) < 53.0°)
background	10 s at each end of scan with rescan option^b
scan range	0.8° below Kα_1 to 0.9° above Kα_2
data collected	±h,k,l
p	0.04
all data, including systematic absences	13835
unique data, with $F_0^2 > 3\sigma(F_0^2)$	9897

^{a} Reference 13. ^{b} Lenhert, P. G. *J. Appl. Crystallogr.* 1975, *8*, 568–570.

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[1] Ibers, J. A.; Holm, R. H. *Science* (Washington, D.C.) **1980**, *209*, 223–235.

[2] Jameson, G. B.; Robinson, W. T.; Ibers, J. A. In "Hemoglobin and Oxygen Binding"; Ho, C. Ed., Elsevier North Holland, Amsterdam, 1982; pp 25–35.

[3] Traylor, T. G. *Acc. Chem. Res.* **1981**, *14*, 102–109 and references therein.

[4] Collman, J. P.; Gagne, R. R.; Halbert, T. R.; Marchon, J.-C.; Reed, C. A. *J. Am. Chem. Soc.* **1973**, *95*, 7868–7870.

[5] Almog, J.; Baldwin, J. E.; Huff, J. *J. Am. Chem. Soc.* **1975**, *97*, 227–228.

[6] Traylor, T. G.; Berzinis, A. P. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 3171–3175.

[7] Collman, J. P.; Brauman, J. I.; Collins, T. J.; Iverson, B.; Sessler, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 2450–2452.

[8] Collman, J. P.; Brauman, J. I.; Doxsee, K. M.; Halbert, T. R.; Suslick, K. S. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *75*, 564–568.

[9] (a) Ellis, P. E., Jr.; Linard, J. E.; Szymanski, T.; Jones, R. D.; Budge, J. R.; Basolo, F. *J. Am. Chem. Soc.* **1980**, *102*, 1889–1896. (b) Hashimoto, T.; Dyer, R. L.; Crossley, M. J.; Baldwin, J. E.; Basolo, F. *Ibid.* **1982**, *104*, 2101–2109.

[10] Linard, J. E.; Ellis, P. E., Jr.; Budge, J. R.; Jones, R. D.; Basolo, F. *J. Am. Chem. Soc.* **1980**, *102*, 1896–1904.

[11] Jameson, G. B.; Ibers, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 2823–2831.

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Table II. Positional and Thermal Parameters for $FeCl(C_2\text{-}Cap)\cdot 3CHCl_3$

ATOM	X[A]	Y	Z	B11[B] OR B, A^2	B22	B33	B12	B13	B23
FE	-0.331597(37)	0.257582(26)	0.175618(22)	15.28(26)	7.16(13)	4.03(10)	-0.32(15)	1.69(12)	-0.48(9)
CL1	-0.283567(72)	0.177960(49)	0.245926(42)	31.57(54)	10.71(25)	6.87(18)	-0.10(29)	1.40(25)	2.25(17)
CL11	0.20547(11)	0.215473(71)	0.267349(65)	70.66(96)	21.37(38)	20.74(33)	-9.05(48)	13.23(45)	-3.13(28)
CL12	0.16274(12)	0.119694(75)	0.168137(63)	86.3(10)	25.95(42)	18.15(31)	-8.91(53)	20.04(46)	-3.48(29)
CL13	0.01897(10)	0.156809(66)	0.234043(61)	54.46(81)	20.47(35)	18.52(30)	7.45(42)	4.48(39)	6.23(26)
CL21	0.06313(11)	0.239091(76)	0.487373(83)	63.72(93)	23.92(42)	43.37(50)	8.96(50)	33.13(56)	8.98(37)
CL22	-0.06826(10)	0.129227(86)	0.491178(66)	43.78(78)	43.15(54)	18.94(32)	-9.78(52)	6.47(40)	0.79(34)
CL23	-0.03525(18)	0.174470(90)	0.378243(69)	238.3(21)	37.09(55)	17.44(32)	59.06(89)	39.31(68)	9.51(34)
CL31A	0.16501(44)	0.37316(41)	0.09198(29)	35.0(15)	56.7(17)	16.24(75)	-1.7(15)	6.08(81)	-10.93(97)
CL32A	0.2140(11)	0.43184(63)	0.20979(72)	37.7(24)	48.2(25)	10.59(66)	20.2(23)	7.25(91)	-1.0(15)
CL33A	0.2426(12)	0.50950(20)	0.11053(21)	239.(11)	35.4(11)	27.89(86)	11.4(22)	34.0(22)	10.58(76)
CL31B	0.1528(10)	0.4017(12)	0.08411(66)	38.8(42)	83.4(52)	18.3(18)	-5.4(43)	4.9(20)	-10.9(27)
CL32B	0.2131(24)	0.4395(14)	0.2053(16)	66.5(55)	66.9(56)	12.2(20)	18.0(50)	-1.8(22)	-6.7(33)
CL33B	0.28336(70)	0.51317(36)	0.11108(29)	55.3(47)	31.8(16)	27.0(13)	10.1(17)	14.4(15)	11.1(10)
O1	-0.08201(20)	0.49795(14)	0.22179(12)	1.87(5)					
O2	-0.14558(19)	0.44662(14)	0.10262(12)	1.76(5)					
O3	-0.18387(20)	0.54059(15)	0.04585(13)	2.17(5)					
O4	-0.25402(20)	0.21469(15)	-0.05358(13)	2.20(5)					
O5	-0.37832(19)	0.32279(14)	-0.08698(12)	1.87(5)					
O6	-0.47073(21)	0.26352(15)	-0.03542(13)	2.37(5)					
O7	-0.67151(23)	0.22549(17)	0.01017(15)	3.02(6)					
O8	-0.61822(19)	0.35451(14)	-0.03705(12)	1.77(5)					
O9	-0.62231(21)	0.36552(16)	0.06067(14)	2.47(6)					
O10	-0.50371(20)	0.50636(15)	0.23147(13)	2.23(5)					
O11	-0.43467(19)	0.55871(14)	0.14208(12)	1.92(5)					
O12	-0.27589(20)	0.55343(15)	0.15355(13)	2.12(5)					
N1	-0.31176(21)	0.34857(15)	0.22268(14)	1.22(5)					
N2	-0.20552(21)	0.27671(15)	0.15001(13)	1.19(5)					
N3	-0.36897(21)	0.20021(15)	0.09862(14)	1.24(5)					
N4	-0.47371(22)	0.27049(16)	0.17361(14)	1.34(5)					
C1	-0.37469(27)	0.38143(19)	0.25140(17)	1.44(6)					
C2	-0.32535(28)	0.43260(21)	0.29150(18)	1.71(7)					
C3	-0.23355(27)	0.42955(19)	0.28823(17)	1.51(6)					
C4	-0.22425(26)	0.37745(19)	0.24577(16)	1.30(6)					
C5	-0.13945(26)	0.35902(19)	0.22955(17)	1.36(6)					
C6	-0.13221(26)	0.31368(19)	0.18356(17)	1.35(6)					
C7	-0.04761(28)	0.30193(20)	0.16109(17)	1.59(7)					
C8	-0.06950(28)	0.25922(20)	0.11425(17)	1.61(7)					
C9	-0.16789(27)	0.24160(19)	0.10807(17)	1.35(6)					
C10	-0.21530(26)	0.19306(19)	0.06779(17)	1.33(6)					
C11	-0.30933(26)	0.17392(19)	0.06440(17)	1.37(6)					
C12	-0.35686(28)	0.12194(20)	0.02489(18)	1.64(7)					

ATOM	X	Y	Z	B, A^2
C13	-0.44508(27)	0.11700(20)	0.03488(17)	1.56(6)
C14	-0.45355(26)	0.16581(19)	0.08063(17)	1.30(6)
C15	-0.53589(26)	0.17773(19)	0.10227(16)	1.31(6)
C16	-0.54522(27)	0.22716(19)	0.14479(17)	1.36(6)
C17	-0.63151(28)	0.24250(21)	0.16365(18)	1.72(7)
C18	-0.61377(28)	0.29498(20)	0.20310(18)	1.78(7)
C19	-0.51625(27)	0.31270(19)	0.20946(17)	1.43(6)
C20	-0.47019(26)	0.36561(19)	0.24606(16)	1.36(6)
C27	-0.04585(31)	0.52409(22)	0.17165(20)	2.19(8)
C28	-0.05018(30)	0.47221(21)	0.12272(19)	2.03(7)
C29	-0.20514(28)	0.48784(20)	0.06698(18)	1.60(7)
C36	-0.27627(30)	0.23547(22)	-0.11509(19)	2.08(7)
C37	-0.37447(31)	0.26373(22)	-0.12577(19)	2.17(8)
C38	-0.42552(28)	0.31361(21)	-0.04249(18)	1.74(7)
C45	-0.70646(31)	0.24771(22)	-0.04928(20)	2.21(8)
C46	-0.71146(29)	0.32417(21)	-0.04903(18)	1.94(7)
C47	-0.58095(28)	0.36917(20)	0.02020(17)	1.71(7)
C54	-0.50937(30)	0.57896(22)	0.22328(19)	2.13(7)
C55	-0.42736(32)	0.59896(23)	0.19624(20)	2.40(8)
C56	-0.35415(27)	0.53474(20)	0.12955(17)	1.61(7)
C63	0.14146(36)	0.14182(26)	0.23894(23)	3.15(9)
C64	0.01720(42)	0.16274(30)	0.45371(27)	4.19(11)
C65A	0.24375(81)	0.42361(64)	0.13775(52)	3.37(26)
C65B	0.2486(13)	0.4406(11)	0.13805(82)	1.73(37)

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. [b] The form of the anisotropic thermal ellipsoid is: $\exp[-(B11h^2 + B22k^2 + B33l^2 + 2B12hk + 2B13hl + 2B23kl)]$. The quantities given in the table are the thermal coefficients × 10^4.

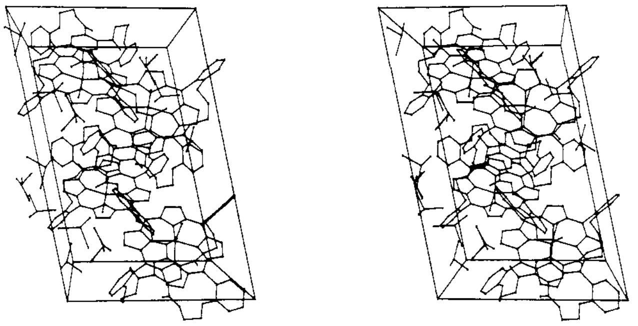

Figure 1. Crystal packing diagram for $FeCl(C_2\text{-}Cap)\cdot 3CHCl_3$. The view is down the *b* axis.

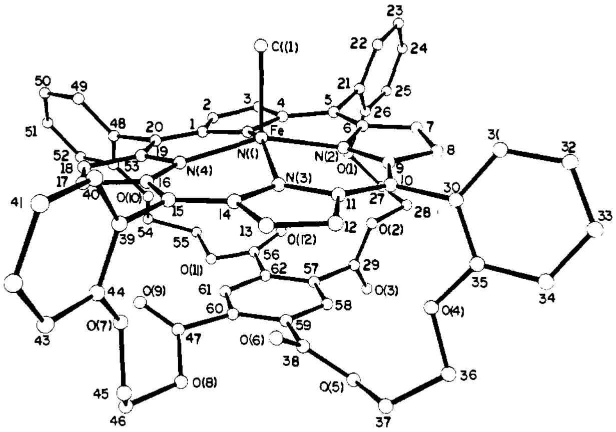

Figure 2. Molecular geometry and atomic numbering scheme for $FeCl(C_2\text{-}Cap)$. Hydrogen atoms are omitted for clarity.

Experimental Section

A powder sample of $FeCl(C_2\text{-}Cap)$, prepared by the reaction of $FeCl_2$ with $H_2(C_2\text{-}Cap)$ in THF, was kindly supplied by Dr. John R. Budge and Professor Fred Basolo. The $H_2(C_2\text{-}Cap)$ had been prepared by Dr. T. Szymanski from the literature method of Baldwin and co-workers.[5,12] Hexane was diffused into a chloroform solution of $FeCl(C_2\text{-}Cap)$ at 5 °C over a period of 18 months. On the basis of the crystal structure determination, the material formed is $FeCl(C_2\text{-}Cap)\cdot 3CHCl_3$.

Preliminary film photographs showed symmetry and systematic absences consistent with the monoclinic space group C_{2h}^5-$P2_1/c$ and also provided evidence for rapid solvent loss from the crystals. The crystals

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(12) Almog, J.; Baldwin, J. E.; Dyer, R. L.; Peters, M. *J. Am. Chem. Soc.* **1975**, *97*, 226–227.

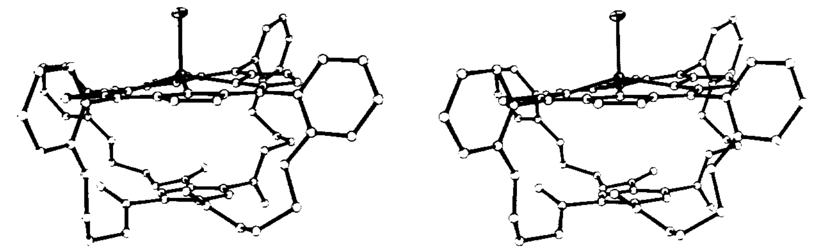

Figure 3. Stereodiagram of FeCl(C_2-Cap). Probability ellipsoids are drawn at the 50% level. Hydrogen atoms are omitted for clarify.

Table III. Derived Parameters for the Rigid Group Atoms for FeCl(C_2-Cap)·3CHCl$_3$

ATOM	X	Y	Z	B,A^2	ATOM	X	Y	Z	B,A^2
C21	-0.04812(15)	0.38752(12)	0.26486(11)	1.48(6)	C43	-0.75972(17)	0.11824(13)	-0.00207(11)	2.31(8)
C22	0.01083(19)	0.343607(98)	0.30354(12)	1.91(7)	C44	-0.68508(19)	0.15934(10)	0.02577(12)	1.85(7)
C23	0.09521(17)	0.36798(13)	0.33750(12)	2.41(8)	H1C40	-0.58777(23)	0.05215(17)	0.13019(14)	2.8
C24	0.12063(16)	0.43627(14)	0.33278(12)	2.44(8)	H1C41	-0.71334(27)	-0.01699(12)	0.08334(17)	3.2
C25	0.06168(19)	0.48019(10)	0.29410(13)	2.29(8)	H1C42	-0.82119(22)	0.02446(17)	0.00038(17)	3.0
C26	-0.02269(17)	0.45581(12)	0.26014(11)	1.67(7)	H1C43	-0.80347(24)	0.13506(18)	-0.03573(14)	3.3
H1C22	-0.00653(26)	0.29700(11)	0.30675(18)	2.9	C48	-0.52710(19)	0.40606(12)	0.28352(11)	1.52(6)
H1C23	0.13544(24)	0.33802(17)	0.36390(16)	3.3	C49	-0.56080(20)	0.372415(95)	0.32877(12)	1.98(7)
H1C24	0.17822(20)	0.45291(19)	0.35596(17)	3.4	C50	-0.61055(20)	0.40868(13)	0.36488(11)	2.26(8)
H1C25	0.07904(26)	0.52679(11)	0.29088(18)	3.2	C51	-0.62660(19)	0.47858(12)	0.35574(11)	2.22(8)
C30	-0.15968(17)	0.15881(13)	0.02688(10)	1.44(6)	C52	-0.59290(20)	0.512228(94)	0.31050(12)	2.02(7)
C31	-0.08541(18)	0.11546(14)	0.051179(82)	1.77(7)	C53	-0.54315(19)	0.47597(12)	0.27438(10)	1.72(7)
C32	-0.03046(16)	0.08596(13)	0.01440(11)	2.05(7)	H1C49	-0.54985(30)	0.32471(10)	0.33500(17)	3.0
C33	-0.04977(18)	0.09983(14)	-0.04668(10)	2.05(7)	H1C50	-0.63355(29)	0.38572(17)	0.39576(15)	3.1
C34	-0.12403(19)	0.14318(14)	-0.070976(82)	2.02(7)	H1C51	-0.66055(28)	0.50333(17)	0.38039(16)	3.3
C35	-0.17899(16)	0.17268(13)	-0.03420(11)	1.75(7)	H1C52	-0.60385(30)	0.55993(10)	0.30426(18)	3.0
M1C31	-0.07223(26)	0.10599(20)	0.092860(86)	2.8	C59	-0.41133(17)	0.37427(12)	-0.00052(11)	1.60(7)
H1C32	0.02023(22)	0.05637(18)	0.03098(15)	3.0	C60	-0.48166(13)	0.39723(13)	0.02829(12)	1.62(7)
H1C33	-0.01226(24)	0.07970(20)	-0.07178(14)	3.0	C61	-0.46289(15)	0.45017(13)	0.06985(11)	1.63(7)
H1C34	-0.13721(27)	0.15264(20)	-0.112657(86)	3.0	C62	-0.37379(17)	0.48015(12)	0.08261(11)	1.58(7)
C39	-0.62098(16)	0.13470(12)	0.07508(11)	1.37(6)	C57	-0.30346(13)	0.45719(13)	0.05380(12)	1.61(7)
C40	-0.63151(17)	0.06896(13)	0.09654(10)	1.98(7)	C58	-0.32223(15)	0.40425(13)	0.01223(11)	1.76(7)
C41	-0.70615(19)	0.02787(10)	0.06870(12)	2.22(8)	H1C61	-0.51089(19)	0.46584(19)	0.08951(16)	2.6
C42	-0.77025(17)	0.05251(13)	0.01939(12)	2.02(7)	H1C58	-0.27424(19)	0.38858(19)	-0.00743(16)	2.7

RIGID GROUP PARAMETERS

GROUP	X_C^A	Y_C	Z_C	DELTA^B	EPSILON	ETA
R1	0.03626(12)	0.411898(90)	0.298819(75)	0.2137(14)	2.7623(16)	0.4220(18)
R2	-0.10472(12)	0.129319(83)	-0.009898(77)	0.8711(23)	2.3730(12)	-1.5267(23)
R3	-0.69562(12)	0.093602(88)	0.047234(77)	0.4066(17)	2.4916(16)	-2.7544(19)
R4	-0.57685(12)	0.442321(87)	0.319631(74)	-0.1232(18)	2.5758(14)	2.1715(19)
R5	-0.39256(12)	0.427207(83)	0.041043(72)	-1.5103(15)	2.7899(14)	2.3880(17)

[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: La Placa, S. J.; Ibers, J. A. *Acta Crystallogr.* 1965, *18*, 511–519.

Table VI. Geometry of the Coordination Sphere in High-Spin Fe(III)-Porphyrin Complexes, FeX(porphyrin)

	Fe-N, Å	Fe-X, Å	N-Fe-N, deg	ΔN_4, Å^a	Δ_{porph}, Å^b	ref
FeF(TPP)^c	2.072 (1)^d	1.792 (3)	86.99 (1)	0.47	0.47	16
FeCl(TPP)	2.049 (9)	2.192 (12)		0.38	0.38	17
FeBr(TPP)	2.069 (9)	2.348 (2)	86.8	0.49	0.56	18
FeI(TPP)	2.066 (11)	2.554 (2)	87.2 (2)	0.46	0.53	19
FeCl(Proto IX)^e	2.062 (10)	2.218 (6)	87.0	0.48	0.55	20
Fe(SPhNO$_2$)(Proto-IX)	2.064 (18)	2.324 (2)	87.5 (6)	0.43	0.45	21
Fe(OCH$_3$)(MesoP)^f	2.073 (6)	1.842 (4)	86.7 (2)	0.46	0.43	22
FeCl(C_2-Cap)^g	2.063 (3)	2.242 (1)	87.2 (4)	0.46	0.47	this work

[a] Distance of the Fe atom from the least-squares plane through the 4 N atoms of the porphyrin core. [b] Distance of the Fe atom from the least-squares plane through the 24-atom porphyrin in core. [c] TPP = 5,10,15,20-tetraphenylporphyrinato. [d] Estimated standard deviation of a single observation is given in parentheses. [e] Proto-IX = protoporphyrin IX dimethyl ester dianion. [f] MesoP = mesoporphyrin IX dimethyl ester dianion. [g] Structure determined at –150 °C; all other structures were determined at room temperature.

used for the collection of intensity data was cut from a larger crystal contained in a glovebag saturated with CHCl$_3$ vapor. The crystal was quickly transferred to the cold stream[13] of a Picker diffractometer. The cold stream ($t \approx -150$ °C at the crystal) provided complete protection of the crystal from desolvation during the period of data collection. Intensity data were collected by methods standard in this laboratory.[14] Crystal data and details of data collection are given in Table I.

The structure was solved by direct methods (MULTAN80). Refinement of the structure proceeded along lines standard in this laboratory.[14] In

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(13) Huffman, J. C. Ph.D. Thesis, Indiana University, 1974.

(14) See, for example: Waters, J. M.; Ibers, J. A. *Inorg. Chem.* **1977**, *16*, 3273–3277.

Table VII. Bond Distances (Å) for FeCl(C_2-Cap)·3CHCl$_3$

Fe-Cl(1)	2.242 (1)	
Fe-N(1)	2.065 (3)	Fe-N 2.063 (3)[a]
Fe-N(2)	2.059 (3)	
Fe-N(3)	2.062 (3)	
Fe-N(4)	2.064 (3)	
N(1)-C(1)	1.382 (5)	N-C_a[b] 1.384 (7)
N(1)-C(4)	1.390 (5)	
N(2)-C(6)	1.381 (5)	
N(2)-C(9)	1.376 (5)	
N(3)-C(11)	1.375 (5)	
N(3)-C(14)	1.384 (5)	
N(4)-C(16)	1.395 (5)	
N(4)-C(19)	1.389 (5)	
C(1)-C(2)	1.443 (6)	C_a-C_b 1.437 (6)
C(4)-C(3)	1.430 (5)	
C(6)-C(7)	1.438 (6)	
C(9)-C(8)	1.444 (6)	
C(11)-C(12)	1.437 (6)	
C(14)-C(13)	1.437 (5)	
C(16)-C(17)	1.432 (6)	
C(19)-C(18)	1.432 (6)	
C(2)-C(3)	1.347 (6)	C_b-C_b 1.347 (6)
C(7)-C(8)	1.342 (6)	
C(12)-C(13)	1.345 (6)	
C(17)-C(18)	1.354 (6)	
C(5)-C(4)	1.398 (5)	C_a-C_m 1.398 (5)
C(5)-C(6)	1.393 (5)	
C(10)-C(9)	1.400 (5)	
C(10)-C(11)	1.398 (5)	
C(15)-C(14)	1.398 (5)	
C(15)-C(16)	1.394 (5)	
C(20)-C(19)	1.409 (5)	
C(20)-C(1)	1.397 (5)	
C(5)-C(21)	1.509 (4)	C_m-C_α 1.514 (7)
C(10)-C(30)	1.507 (5)	
C(15)-C(39)	1.516 (4)	
C(20)-C(48)	1.522 (5)	
C(26)-O(1)	1.370 (4)	1.365 (4)
C(35)-O(4)	1.362 (4)	
C(44)-O(7)	1.364 (4)	
C(53)-O(10)	1.365 (4)	
O(1)-C(27)	1.444 (5)	1.431 (11)
O(4)-C(36)	1.435 (5)	
O(7)-C(45)	1.418 (6)	
O(10)-C(54)	1.429 (5)	
C(27)-C(28)	1.500 (6)	1.497 (6)
C(36)-C(37)	1.498 (6)	
C(45)-C(46)	1.494 (6)	
C(54)-C(55)	1.496 (6)	
C(28)-O(2)	1.453 (5)	1.453 (6)
C(37)-O(5)	1.461 (5)	
C(46)-O(8)	1.448 (5)	
C(55)-O(11)	1.451 (5)	
O(2)-C(29)	1.330 (5)	1.339 (6)
O(5)-C(28)	1.345 (5)	
O(8)-C(47)	1.341 (5)	
O(11)-C(56)	1.339 (5)	
C(29)-O(3)	1.203 (5)	1.205 (5)
C(38)-O(6)	1.205 (5)	
C(47)-O(9)	1.200 (5)	
C(56)-O(12)	1.211 (5)	
C(29)-C(57)	1.517 (5)	1.510 (9)
C(38)-C(59)	1.511 (5)	
C(47)-C(60)	1.514 (5)	
C(56)-C(62)	1.497 (5)	
C(63)-Cl(11)	1.762 (5)	1.760 (11)
C(63)-Cl(12)	1.759 (6)	
C(63)-Cl(13)	1.778 (6)	
C(64)-Cl(21)	1.746 (6)	
C(64)-Cl(22)	1.765 (6)	
C(64)-Cl(23)	1.752 (7)	
C(65A)[c]-Cl(31A)	1.70 (1)	
C(65A)-Cl(32A)	1.79 (2)	
C(65A)-Cl(33A)	1.79 (1)	
C(65B)-Cl(31B)	1.83 (2)	
C(65B)-Cl(32B)	1.71 (4)	
C(65B)-Cl(33B)	1.66 (2)	

[a] Here, and elsewhere, the estimated standard deviation given in parentheses following a mean value is the larger of that calculated for an individual observation on the assumption that the values averaged are from the same population or of that calculated for an individual parameter from the inverse of the least-squares matrix. [b] The nomenclature is that of: Hoard, J. L. *Science* (Washington, D.C.) 1971, *174*, 1295–1302. [c] The chloroform solvate composed of atoms C(65), Cl(31), Cl(32), and Cl(33) is disordered over sites A and B with a distribution of 0.75:0.25.

the refinement only the Fe and Cl atoms were refined anisotropically; all other nonhydrogen atoms were refined isotropically, with the phenyl groups restricted to their idealized geometry (D_{6h}). The only complication in the refinement was the disorder of one of the three chloroform groups. Refinement of both alternative positions with a variable occupancy factor was carried out. Prior to the final cycle of refinement on F, all hydrogen atoms, except those for the disordered chloroform molecule, were idealized and included as fixed contributions. The final cycle, involving 396 variables and 9897 observations, converged to values of the usual R and R_w indices of 0.065 and 0.078 and to an error in an observation of unit weight of 2.47 e. Elaboration of the model, e.g., anisotropic refinement of the carbon atoms, was not attempted owing to the expense involved with minimal expectation of dramatic changes in porphyrin parameters derived from these low-temperature data. Moreover, an analysis of $\sum w(|F_o| - |F_c|)^2$ as a function of $|F_o|$, setting angles, and Miller indices revealed no unusual trends. In the final difference electron density map, the three highest peaks (0.9–1.2 e/Å^3) were in the vicinity of the disordered solvent molecule. Neither in this map nor throughout the refinement process was there any indication of disorder in the side chains. The final parameters of the atoms are listed in Tables II and III. Table IV[15] lists the idealized positions of the H atoms, while Table V[15] presents the values of $10|F_o|$ vs. $10|F_c|$ for those reflections used in the refinement.

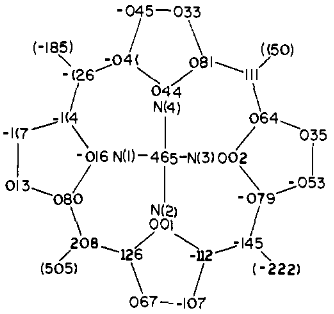

Figure 4. Displacements (×10^3) of atoms from the least-squares plane of the 24-atom porphyrin skeleton. The estimated standard deviations are 0.003 Å for nitrogen atoms and 0.004 Å for carbon atoms. Displacements in parentheses were not included in the calculation of the least-squares plane.

Results

The crystal structure of FeCl(C_2-Cap)·3CHCl$_3$ consists of the packing of discrete monomeric molecules of FeCl(C_2-Cap) and

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(15) Supplementary material.

Table VIII. Bond Angles (deg) for FeCl(C_2-Cap)·$3CHCl_3$

Cl(1)-Fe-N(1)	103.5 (1)	
Cl(1)-Fe-N(2)	99.4 (1)	
Cl(1)-Fe-N(3)	103.0 (1)	
Cl(1)-Fe-N(4)	105.3 (1)	
N(1)-Fe-N(2)	87.3 (1)	N-Fe-N 87.2 (4)
N(1)-Fe-N(4)	86.6 (1)	
N(2)-Fe-N(3)	87.2 (1)	
N(3)-Fe-N(4)	87.6 (1)	
N(1)-Fe-N(3)	153.5 (1)	
N(2)-Fe-N(4)	155.2 (1)	
C(1)-N(1)-C(4)	105.6 (3)	C_a-N-C_a 105.7 (4)
C(6)-N(2)-C(9)	106.2 (3)	
C(11)-N(3)-C(14)	105.6 (3)	
C(16)-N(4)-C(19)	105.2 (3)	
N(1)-C(1)-C(2)	109.4 (3)	N-C_a-C_b 109.8 (3)
N(1)-C(4)-C(3)	110.0 (3)	
N(2)-C(6)-C(7)	109.5 (3)	
N(2)-C(9)-C(8)	109.5 (3)	
N(3)-C(11)-C(12)	110.1 (3)	
N(3)-C(14)-C(13)	109.7 (3)	
N(4)-C(16)-C(17)	109.9 (3)	
N(4)-C(19)-C(18)	110.0 (3)	
C(1)-C(2)-C(3)	107.6 (4)	C_a-C_b-C_b 107.4 (4)
C(2)-C(3)-C(4)	107.3 (4)	
C(6)-C(7)-C(8)	107.6 (4)	
C(7)-C(8)-C(9)	107.2 (4)	
C(11)-C(12)-C(13)	107.1 (4)	
C(12)-C(13)-C(14)	107.4 (4)	
C(16)-C(17)-C(18)	107.3 (4)	
C(17)-C(18)-C(19)	107.5 (4)	
N(1)-C(1)-C(20)	126.2 (4)	N-C_a-C_m 125.5 (4)
N(1)-C(4)-C(5)	125.2 (4)	
N(2)-C(6)-C(5)	125.7 (4)	
N(2)-C(9)-C(10)	125.7 (4)	
N(3)-C(11)-C(10)	125.7 (4)	
N(3)-C(14)-C(15)	125.5 (4)	
N(4)-C(16)-C(15)	125.5 (4)	
N(4)-C(19)-C(20)	124.8 (4)	
C(2)-C(1)-C(20)	124.2 (4)	C_b-C_a-C_m 124.6 (4)
C(3)-C(4)-C(5)	124.7 (4)	
C(7)-C(6)-C(5)	124.7 (4)	
C(8)-C(9)-C(10)	124.7 (4)	
C(12)-C(11)-C(10)	124.1 (4)	
C(13)-C(14)-C(15)	124.8 (4)	
C(17)-C(16)-C(15)	124.5 (4)	
C(18)-C(19)-C(20)	125.2 (4)	
C(4)-C(5)-C(6)	124.5 (4)	C_a-C_m-C_a 124.3 (4)
C(9)-C(10)-C(11)	124.1 (4)	
C(14)-C(15)-C(16)	124.7 (4)	
C(19)-C(20)-C(1)	123.7 (4)	
C(4)-C(5)-C(21)	119.0 (3)	C_a-C_m-C_α 117.9 (11)
C(6)-C(5)-C(21)	116.5 (3)	
C(9)-C(10)-C(30)	117.1 (3)	
C(11)-C(10)-C(30)	118.9 (3)	
C(14)-C(15)-C(39)	116.3 (3)	
C(16)-C(15)-C(39)	118.9 (3)	
C(19)-C(20)-C(48)	117.9 (3)	
C(1)-C(20)-C(48)	118.3 (3)	
C(5)-C(21)-C(22)	118.1 (2)	120.0 (13)
C(5)-C(21)-C(26)	121.9 (2)	
C(10)-C(30)-C(31)	119.2 (2)	
C(10)-C(30)-C(35)	120.7 (2)	
C(15)-C(39)-C(40)	120.2 (2)	
C(15)-C(39)-C(44)	119.6 (2)	
C(20)-C(48)-C(49)	118.8 (2)	
C(20)-C(48)-C(53)	121.1 (3)	
C(25)-C(26)-O(1)	121.2 (2)	123.3 (16)
C(34)-C(35)-O(4)	124.6 (2)	
C(43)-C(44)-O(7)	124.4 (2)	
C(52)-C(53)-O(10)	123.0 (2)	
C(21)-C(26)-O(1)	118.8 (2)	116.7 (16)
C(30)-C(35)-O(4)	115.4 (3)	
C(39)-C(44)-O(7)	115.5 (2)	
C(48)-C(53)-O(10)	116.9 (3)	
C(26)-O(1)-C(27)	116.0 (3)	118.9 (20)
C(35)-O(4)-C(36)	119.7 (3)	
C(44)-O(7)-C(45)	119.8 (3)	
C(53)-O(10)-C(54)	120.2 (3)	
O(1)-C(27)-C(28)	112.6 (4)	108.4 (29)
O(4)-C(36)-C(37)	106.4 (4)	
O(7)-C(45)-C(46)	108.1 (4)	
O(10)-C(54)-C(55)	106.5 (4)	
C(27)-C(28)-O(2)	111.2 (4)	109.8 (23)
C(36)-C(37)-O(5)	110.0 (4)	
C(45)-C(46)-O(8)	111.4 (4)	
C(54)-C(55)-O(11)	106.4 (4)	
C(28)-O(2)-C(29)	116.3 (3)	116.5 (4)
C(37)-O(5)-C(38)	116.1 (3)	
C(46)-O(8)-C(47)	116.6 (3)	
C(55)-O(11)-C(56)	117.0 (3)	
O(2)-C(29)-O(3)	125.2 (4)	125.2 (4)
O(5)-C(38)-O(6)	125.5 (4)	
O(8)-C(47)-O(9)	124.9 (4)	
O(11)-C(56)-O(12)	125.0 (4)	
O(2)-C(29)-C(57)	110.5 (3)	111.1 (10)
O(5)-C(38)-C(59)	110.5 (3)	
O(8)-C(47)-C(60)	112.5 (3)	
O(11)-C(56)-C(62)	110.7 (3)	
O(3)-C(29)-C(57)	124.3 (3)	123.8 (9)
O(6)-C(38)-C(59)	124.0 (4)	
O(9)-C(47)-C(60)	122.4 (3)	
O(12)-C(56)-C(62)	124.3 (4)	
C(29)-C(57)-C(58)	118.3 (3)	120.0 (37)
C(29)-C(57)-C(62)	121.7 (3)	
C(38)-C(59)-C(60)	122.2 (3)	
C(38)-C(59)-C(58)	117.6 (3)	
C(47)-C(60)-C(59)	126.3 (3)	
C(47)-C(60)-C(61)	113.7 (3)	
C(56)-C(62)-C(61)	118.9 (3)	
C(56)-C(62)-C(57)	121.0 (3)	
Cl(11)-C(63)-Cl(12)	111.2 (3)	110.2 (12)
Cl(11)-C(63)-Cl(13)	109.4 (3)	
Cl(12)-C(63)-Cl(13)	109.8 (3)	
Cl(21)-C(64)-Cl(22)	110.2 (3)	
Cl(21)-C(64)-Cl(23)	111.9 (3)	
Cl(22)-C(64)-Cl(23)	108.5 (3)	
Cl(31A)-C(65A)-Cl(32A)	111.2 (8)	
Cl(31A)-C(65A)-Cl(33A)	111.8 (7)	
Cl(32A)-C(65A)-Cl(33A)	104.4 (7)	
Cl(31B)-C(65B)-Cl(32B)	106 (2)	
Cl(31B)-C(65B)-Cl(33B)	111 (1)	
Cl(32B)-C(65B)-Cl(33B)	121 (1)	

$CHCl_3$ solvent (Figure 1). There are no unusual intermolecular contacts.

The FeCl(C_2-Cap) molecule has its expected connectivity. The molecular geometry and numbering scheme are shown in Figure 2. Figure 3 presents a stereoview of the molecule. As can be seen from these figures, the chloro ligand is outside the cap rather than in it. The resultant coordination geometry about the Fe atom is very similar to that found in other five-coordinate Fe(III) porphyrin systems[16-22] (Table VI). It is difficult to understand the metrical trends in the series FeX(TPP), X = F, Cl, Br, I,[16-19]

Table IX. Least-Squares Planes for $FeCl(C_2\text{-}Cap)\cdot 3CHCl_3$

name	coefficients $Ax + By + Cz - D = 0$[a] A	B	C	D	atoms defining the plane displacement[b]				
I	1.664	−13.516	15.397	−1.786	N(1) −015 (3)	N(2) 014 (3)	N(3) −015 (3)	N(4) 016 (3)	
II	1.382	−13.741	15.297	−1.763	C(5) 148 (4)	C(10) −150 (4)	C(15) 145 (4)	C(20) −147 (4)	
py-1	0.225	−13.311	16.278	−1.079	N(1) −006 (3)	C(1) 010 (4)	C(2) −007 (4)	C(3) 001 (4)	C(4) 005 (4)
py-2	1.554	−15.079	13.497	−2.460	N(2) −007 (3)	C(6) 002 (4)	C(7) 008 (4)	C(8) −015 (4)	C(9) 015 (4)
py 3	2.435	−13.582	14.837	−2.157	N(3) 003 (3)	C(11) −003 (4)	C(12) 001 (4)	C(13) 002 (4)	C(14) −003 (4)
py-4	1.233	−12.791	16.390	−1.201	N(4) 003 (3)	C(16) −004 (4)	C(17) 003 (4)	C(18) 000 (4)	C(19) −002 (4)
ph-1	9.159	−4.747	−19.347	−7.404	C(21)-C(26) 0				
ph-2	8.696	15.300	0.724	1.061	C(30)-C(35) 0				
ph-3	10.205	−7.130	−16.830	−8.561	C(39)-C(44) 0				
ph-4	10.744	3.890	10.894	−0.995	C(48)-C(53) 0				
ph-5 (cap)	2.147	−13.032	15.629	−5.769	C(57)-C(62) 0				
ester-1	5.362	−9.513	−19.383	−7.021	O(2) 003 (3)	C(29) −018 (4)	O(3) 004 (3)	C(57) 002 (3)	
ester-2	10.379	−8.404	8.959	−7.420	O(5) 002 (3)	C(38) −012 (4)	O(6) 003 (3)	C(59) 001 (2)	
ester-3	4.641	−18.201	2.220	−9.399	O(8) −004 (3)	C(47) 029 (4)	O(9) −007 (3)	C(60) −003 (2)	
ester-4	−1.630	−13.621	16.333	−4.582	O(11) 001 (3)	C(56) −008 (4)	O(12) 002 (3)	C(62) 001 (2)	
porph	1.509	−13.581	15.409	−1.758	see Figure 4				

Dihedral Angles, deg

	porph	I	cap	py-1	py-2	py-3	py-4	ph-1	ph-2	ph-3	ph-4
porph		0.7	3.2	5.3	6.6	3.7	3.4	106.7	111.9	95.9	66.9
I			2.6	5.8	6.8	3.2	3.5	ester-1	ester-2	ester-3	ester-4
cap				7.7	8.8	2.7	3.9	101.3	37.5	37.7	15.2
py-1					9.6	9.0	4.4				
py-2						7.0	9.9				
py-3							6.1				

[a] Plane is in crystal coordinates as defined by Hamilton, W. C. *Acta Crystallogr.* 1961, *14*, 185–189. [b] The displacement (Å) is generated by placing a decimal point prior to the first digit.

Table X. Torsional Angles (Deg) in the Linkages for $FeCl(C_2\text{-}Cap)\cdot 3CHCl_3$

atoms[a]	chain 1	chain 2	chain 3	chain 4
C(25)-C(26)-O(1)-C(27)	65.2 (4)	−4.9 (4)	−27.2 (5)	2.3 (4)
C(26)-O(1)-C(27)-C(28)	78.1 (4)	164.6 (3)	161.1 (3)	154.6 (3)
O(1)-C(27)-C(28)-O(2)	55.8 (5)	60.9 (4)	69.6 (4)	56.1 (4)
C(27)-C(28)-O(2)-C(29)	77.0 (4)	−109.9 (4)	−93.0 (4)	−141.2 (4)
C(28)-O(2)-C(29)-O(3)	7.7 (6)	−6.7 (6)	−7.9 (6)	−13.5 (6)
C(28)-O(2)-C(29)-C(57)	−175.4 (3)	171.3 (3)	177.1 (3)	165.2 (3)
O(3)-C(29)-C(57)-C(58)	99.9 (4)	−35.9 (5)	−34.5 (5)	−14.2 (5)
O(2)-C(29)-C(57)-C(58)	−77.1 (4)	146.1 (3)	140.7 (3)	167.1 (3)

[a] Only the atoms of chain 1 are listed here; atoms in chains 2, 3, and 4 are defined analogously as shown in Figure 2.

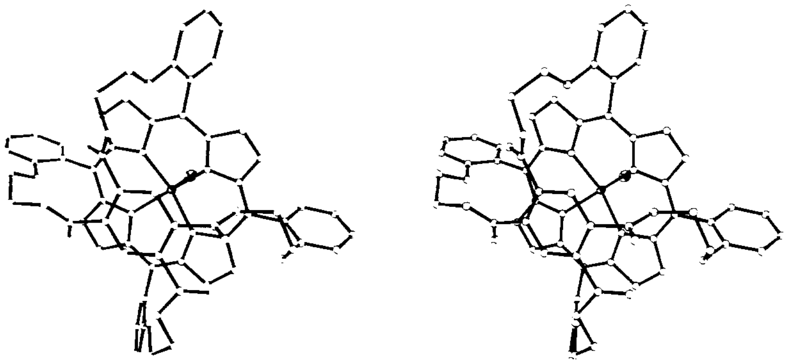

Figure 5. Stereodiagram of $FeCl(C_2\text{-}Cap)$ perpendicular to the porphyrin plane. Chain 1 is in the lower right, and the chains are numbered in a counterclockwise direction.

at least with respect to the ΔN_4 and Δ_{porph} distances. Hence it is sufficient to note that these distances in the present structure fall within the range generated by the FeX(TPP) series. Consequently, the presence of the cap has placed no apparent steric restraints on the coordination geometry of the Fe atom.

Bond distances and angles are presented for FeCl(C_2-Cap) in Tables VII and VIII, respectively. The porphyrin portion of the molecule appears to be normal in all respects, with good internal consistency among chemically equivalent bond parameters. Figure 4 displays the deviations of the atoms of the porphyrin core from the best least-squares plane through the 24-atom segment. The mean deviation is 0.076 Å and the maximum is 0.208 Å. The porphyrin core is thus more nearly planar than in H_2(C_2-Cap), where the mean deviation from the plane is 0.135 Å and the maximum derivation is 0.354 Å.[11]

In the description of the structure of H_2(C_2-Cap), we noted that the cap was centered over the porphyrin and that the two planes were essentially parallel (dihedral angle, 0.03°).[11] In FeCl(C_2-Cap), the analogous dihedral angle is 3.0° (Table IX). In H_2(C_2-Cap) the steric strain engendered by the cap was apparent in the presence of two types of C_a–C_m–C_α angles that resulted from buckling of the *meso*-tetraphenylporphyrin moiety. This is not apparent in the present structure. Whereas in the free base two of the ester groups were approximately coplanar with the cap plane and the other two were almost perpendicular, in FeCl(C_2-Cap) there are three ester groups approximately parallel to the cap plane (Table IX and Figure 5). Here again the C_{phenyl}–C_{ester} bond of ester group 4 (the one most nearly coplanar with the cap) is significantly shorter, indicating the possibility of resonance interaction with the cap.

In H_2(C_2-Cap), the conformations of side chains 2 and 4, which have ester groups nearly perpendicular to the cap, are very nearly the same, while chains 1 and 3, though very different in the ether–ethyl portions, are similar in the ester–phenyl cap portions. In the present structure there is only a general similarity in the conformations of chains 2 and 3 (Table X). Of course, the torsion angles of side chains with similar conformations in the two structures are approximately equal. Thus, in two structures of the cap four very different conformations for the chains have been observed, evidence for considerable conformational flexibility.

In H_2(C_2-Cap) the separation between centroids of the cap and the 24-atom porphyrin core is 3.96 Å; in FeCl(C_2-Cap) it is 4.01 Å. In H_2(C_2-Cap) the separation of the cap from the N_4 plane of the porphyrin is 3.86 Å; in FeCl(C_2-Cap) it is 4.03 Å. It is remarkable that the separation of cap from porphyrin is so similar in these two very different structures. This suggests that a separation of about 4 Å between cap and porphyrin is a comfortable one in the solid state where a balance between intramolecular strain and intermolecular contacts exists. Clearly, this separation must expand in solution by a minimum of 1–1.5 Å in the analogous Fe(II) systems, Fe(base)(C_2-Cap); these systems bind CO as well as the more open porphyrins while they bind O_2 less well.[9,10] Whether these relative differences in CO and O_2 binding can be ascribed to steric interactions between modified porphyrin and liganded molecule remains mere speculation until the structure of a CO or O_2 complex in the "capped" series can be determined.

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Supplementary Material Available: Table IV, the idealized positions of the hydrogen atoms, and Table V, a listing of $10|F_o|$ and $10|F_c|$ (35 pages). Ordering information is given on any current masthead page.

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(16) Anzai, K.; Hatano, K.; Lee, Y. J.; Scheidt, W. R. *Inorg. Chem.* **1981**, *20*, 2337–2339.

(17) Hoard, J. L.; Cohen, G. H.; Glick, M. D. *J. Am. Chem. Soc.* **1967**, *89*, 1992–1996.

(18) Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1977**, *30*, 2655–2660.

(19) Hatano, K.; Scheidt, W. R. *Inorg. Chem.* **1979**, *18*, 877–879.

(20) Koenig, D. F. *Acta Crystallogr.* **1965**, *18*, 663–673.

(21) Tang, S. C.; Koch, S.; Papaefthymiou, G. C.; Foner, S.; Frankel, R. B.; Ibers, J. A.; Holm, R. H. *J. Am. Chem. Soc.* **1976**, *98*, 2414–2434.

(22) Hoard, J. L.; Hamor, M. J.; Hamor, T. A.; Caughey, W. S. *J. Am. Chem. Soc.* **1965**, *87*, 2312–2319.