

- (30) F. W. S. Benfield and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1324 (1974).
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- (32) Weak but fairly sharp infrared peaks in the 1550–1650-cm⁻¹ region are helpful for identifying the described compounds but provide no unambiguous structural information. Compounds of the M(C₈H₈)(C₈H₈)(dmpe)

type show a weak peak at 1650–60 cm⁻¹ which we ascribe to a mode involving one or both C₈ ligands. The 1550–60-cm⁻¹ peak for compounds of the M(C₈H₈)₂(C₈H₅) type is probably a phenyl mode since it is absent in the spectrum of M(C₈H₈)₂(CH₃). The 1590–1600-cm⁻¹ peak for the M(C₈H₈)[C₈H₈(C₈H₅)](L-L) species might suggest that they are unique yet that this peak is a C₈-phenyl combination mode seems quite probable.

Crystal and Molecular Structure of an N-Substituted Porphyrin, Chloro(2,3,7,8,12,13,17,18-octaethyl-N-ethylacetatoporphine)cobalt(II)

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Abstract: The crystal and molecular structure of the title compound were determined from three-dimensional x-ray crystallographic data, and refined to $R = 0.041$ for 2417 reflections by least-squares methods. The monoclinic unit cell, space group $P2_1/n$, has dimensions $a = 15.214$ (4) Å, $b = 17.020$ (7) Å, $c = 14.760$ (2) Å, and $\beta = 93.59$ (1)° for $Z = 4$. The cobalt(II) atom is 5-coordinate, even though one of the bonds is much weaker than the other four, with the substituted nitrogen atom 0.4 Å farther from the cobalt atom than are the other nitrogen atoms. The deviation of the porphyrin ring from planarity is increased markedly by the coordination; the ring of the substituted nitrogen atom is deviated 44° from the mean plane of the other three nitrogen atoms. The chlorine atom leans decidedly toward the substituted nitrogen atom. The side chain is essentially planar, and no inter- or intramolecular oxygen coordination is found.

A great deal of interest has been shown recently in the porphyrins,²⁻¹⁷ in great part because of their biological importance in such compounds as vitamin B₁₂. In addition to normal porphyrins⁵⁻⁸ and their metal complexes,⁹⁻¹¹ a wide variety of nonplanar porphyrins has been studied, including N-substituted examples,¹²⁻¹⁴ protonated cations,¹⁵ partially saturated derivatives,¹⁶ and nonplanar forms of the normal varieties.¹⁷

This investigation deals with octaethylporphyrin which has an ethyl acetate group substituted on one of the nitrogen atoms. (See Figure 1.) The effect of N-substitution on nonmetallo octaethylporphyrin (OEP) has been shown to have a significant effect on the normal planarity of the macrocycle.¹² The effect of coordination of a great variety of metal ions on such macrocycles is of great interest, because the normal square planar or octahedral geometries cannot be expected due to steric interference of the carbon atom substituted on the nitrogen of the macrocycle. It was of interest to determine if the carboxylate group of the substituted side chain could coordinate to the central metal intra- or intermolecularly. Cobalt(II) complexes of porphyrins which are not N-substituted are normally found to be pyramidal or octahedral;⁹ the substitution on the nitrogen atom causes the present complex to be different in a variety of ways.

Experimental Section

The compound was prepared by Mr. D. Ward and Professor A. W. Johnson,¹⁸ University of Sussex, by standard methods. Crystal data:¹⁹ C₄₀H₅₁ClCoN₄O₂; $M = 714.24$; monoclinic; $a = 15.214$ (4), $b = 17.020$ (7), $c = 14.760$ (2) Å; $\beta = 93.59$ (1)°; $U = 3814.5$ Å³; $Z = 4$; $F(000) = 1516$; $d_{\text{calcd}} = 1.24$, $d_{\text{obsd}} = 1.24$ (1) g cm⁻³; space group $P2_1/n$ (nonstandard); Mo $K\alpha_1$ (λ 0.70926 Å) radiation for cell dimension and intensity measurements, $\mu(\text{Mo } K\alpha) = 5.76$ cm⁻¹.

Systematic absences on Weissenberg and precession photographs lead to the conclusion that the space group is $P2_1/n$, a nonstandard setting of $P2_1/c$. Preliminary cell dimensions were measured from precession photographs using Mo $K\alpha$ radiation and

were subsequently adjusted by least-squares refinement of the setting angles of 12 reflections measured on a Hilger and Watts Y 290 four-circle diffractometer using Mo $K\alpha_1$ radiation (λ 0.70926 Å) with a graphite crystal monochromator. A crystal measuring 0.70 × 0.18 × 0.17 mm was mounted with the c axis almost coincident with the ϕ axis of the diffractometer. Intensity measurements were made by the θ - 2θ step-scan procedure, each reflection being scanned in 72 1-sec steps of 0.01° about $2\theta_{\text{calcd}}$. The peak profiles were somewhat broad, with a slight shoulder to one side of the peak maximum. Stationary background counts were measured for 36 sec at each end of the scan range. The intensities of the (020), (110), and (101) reflections were checked every 100 reflections to monitor crystal and electronic stability. No deviations greater than statistical were observed. Intensities were collected for reflections with θ (Mo $K\alpha$) $\leq 20^\circ$. Out of a total of 4081 reflections, there were 2625 with $I \geq 3\sigma(I)$, of which 2417 were used as unique. These were corrected for Lorentz and polarization effects, but correction for absorption was not necessary.

Structure Analysis. The position of the cobalt atom was determined from a three-dimensional Patterson synthesis. A structure factor calculation based on this position yielded $R = 0.507$. The coordinates of the other nonhydrogen atoms were obtained from three subsequent difference Fourier and least-squares cycles. Least-squares refinement of positional and isotropic thermal parameters, with the program CRYLSQ²⁰ in the blocked mode gave $R = 0.094$. The function minimized was $\sum w(|F_d| - |F_c|)^2$, where $w = 1/\sigma^2(F^2)$. Scattering factors for hydrogen²¹ and for other atoms²² were taken from standard sources. Anomalous dispersion factors $\Delta f'$ and $\Delta f''$ for Co and Cl were taken from ref 23. Anisotropic refinement of Co and Cl caused the decrease of R to 0.086. The locations of the 24 nonmethyl hydrogen atoms were calculated; the 27 methyl hydrogen atoms could not be located on a difference map at this point, and so were not included. With the 24 hydrogen atoms included, a structure factor calculation yielded an R factor of 0.077. Because the difference map showed residual effect consistent with anisotropic behavior of the ethylacetato chain (C(37)-C(40), O(1), and O(2)), anisotropic refinement was performed, causing R to decrease to 0.068. A peak search routine at this point yielded positions of at least one or two hydrogen atoms on each terminal carbon of the eight ethyl groups on the macrocycle. Peak heights for the hydrogen atoms ranged from 0.4 to 0.7

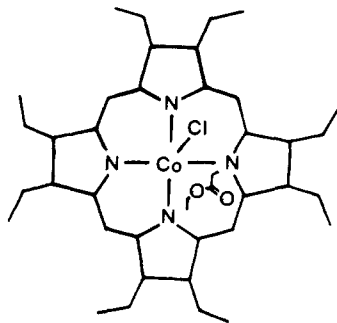


Figure 1. Schematic drawing of the title compound.

$e/\text{\AA}^3$. Calculation of the other hydrogen atom positions allowed inclusion of 24 more hydrogen atoms in a subsequent least-squares routine, which yielded an R factor of 0.058. An attempt to refine all the hydrogen atom parameters so far located, holding the parameters of all nonhydrogen atoms invariant, yielded six chemically unrealistic hydrogen atom positions. These atoms were deleted. The difference Fourier showed evidence of slight anisotropic ef-

fects, hence the ethyl group carbon atoms were refined anisotropically, yielding an R factor of 0.049. Addition of the six deleted hydrogen atoms at calculated positions, with C-H bond lengths²⁴ 0.95 Å and H-C-H bond angles 109.5° and with B values equal to those of the carbon atom to which they were attached yielded an R value of 0.049. Input of three hydrogen atoms on the terminal carbon atom of the side chain, from a further peak search and calculation, followed by refinement of all the hydrogen atom parameters and separately of those of the nonhydrogen atoms lead to an R factor of 0.041 and to the final positional and thermal parameters given in Table I. The final least-squares refinement leads to no change in the positional parameters of the nonhydrogen atoms greater than 0.001 Å, and no change in hydrogen atom positions greater than 0.01 Å. The maximum electron density unaccounted for is 0.34 $e/\text{\AA}^3$, associated with the cobalt atom. The error for an observation of unit weight is 1.23 e .

Results

Figure 2 shows the molecule,¹⁹ with the atom numbering system used. The final positional and thermal parameters are listed in Table I, and bond distances are given in Table II along with analogous data for the free base cation.¹²

Table I. Positional and Thermal Parameters^a

	$10^4 X$	$10^4 Y$	$10^4 Z$	(a) Nonhydrogen Atoms					
				$10^4 (U \text{ or } U_{11})$	$10^4 U_{22}$	$10^4 U_{33}$	$10^4 U_{12}$	$10^4 U_{13}$	$10^4 U_{23}$
Co	1200.8 (.6)	208.2 (.5)	2301.7 (.5)	504 (6)	377 (5)	281 (5)	-23 (5)	17 (4)	12 (4)
Cl	652 (1)	1448 (1)	2193 (1)	674 (13)	486 (11)	562 (12)	59 (10)	48 (10)	17 (9)
N(1)	1299 (3)	-125 (3)	3654 (3)	410 (13)					
N(2)	399 (3)	-696 (3)	2020 (3)	405 (13)					
N(3)	1743 (3)	56 (3)	1067 (3)	400 (13)					
N(4)	2685 (3)	712 (3)	2713 (3)	421 (14)					
C(1)	1802 (4)	197 (4)	4376 (4)	452 (17)					
C(2)	1549 (4)	-165 (4)	5213 (4)	488 (18)					
C(3)	876 (4)	-645 (4)	5004 (4)	488 (18)					
C(4)	708 (4)	-617 (4)	4022 (4)	419 (17)					
C(5)	44 (4)	-1027 (4)	3559 (4)	448 (18)					
C(6)	-96 (4)	-1091 (4)	2622 (4)	426 (17)					
C(7)	-699 (4)	-1627 (4)	2147 (4)	463 (18)					
C(8)	-544 (4)	-1563 (4)	1250 (4)	476 (18)					
C(9)	152 (4)	-994 (3)	1176 (4)	408 (17)					
C(10)	575 (4)	-790 (4)	411 (4)	421 (18)					
C(11)	1310 (4)	-341 (3)	360 (4)	360 (16)					
C(12)	1746 (4)	-181 (4)	-474 (4)	437 (17)					
C(13)	2408 (4)	313 (4)	-274 (4)	469 (18)					
C(14)	2408 (4)	474 (3)	700 (4)	390 (17)					
C(15)	2921 (4)	1044 (4)	1136 (4)	471 (18)					
C(16)	2934 (4)	1246 (4)	2044 (4)	440 (17)					
C(17)	3072 (4)	1989 (4)	2447 (4)	463 (18)					
C(18)	2900 (4)	1930 (4)	3356 (4)	495 (18)					
C(19)	2670 (4)	1149 (4)	3537 (4)	469 (18)					
C(20)	2378 (5)	809 (4)	4315 (4)	523 (19)					
C(21)	2025 (5)	-21 (4)	6132 (4)	831 (60)	818 (59)	352 (43)	-40 (50)	-21 (41)	47 (38)
C(22)	2785 (6)	-569 (6)	6312 (5)	906 (70)	1216 (74)	678 (58)	-63 (63)	-159 (52)	111 (52)
C(23)	394 (5)	-1168 (4)	5630 (4)	783 (58)	604 (52)	448 (45)	-5 (45)	155 (41)	121 (39)
C(24)	702 (6)	-2011 (5)	5637 (5)	1056 (69)	713 (59)	781 (62)	-14 (54)	127 (53)	225 (49)
C(25)	-1290 (5)	-2189 (5)	2594 (5)	698 (55)	740 (59)	756 (55)	-194 (49)	109 (45)	11 (47)
C(26)	-808 (6)	-2920 (5)	2955 (6)	1052 (74)	790 (64)	1060 (69)	-209 (57)	135 (57)	344 (54)
C(27)	-946 (5)	-2035 (4)	473 (4)	619 (51)	595 (52)	582 (49)	-117 (44)	-94 (41)	-60 (40)
C(28)	-432 (6)	-2760 (5)	271 (6)	989 (71)	779 (63)	944 (65)	12 (56)	-206 (55)	-362 (51)
C(29)	1465 (4)	-532 (4)	-1380 (4)	610 (50)	615 (52)	369 (41)	8 (41)	-7 (36)	-58 (35)
C(30)	1760 (5)	-1365 (5)	-1497 (5)	801 (59)	888 (60)	587 (57)	108 (48)	-3 (47)	-246 (46)
C(31)	3085 (5)	629 (5)	-879 (5)	740 (64)	790 (56)	556 (49)	-217 (51)	217 (44)	10 (42)
C(32)	3954 (6)	233 (7)	-769 (6)	787 (61)	1629 (92)	1061 (78)	21 (66)	465 (56)	116 (71)
C(33)	3234 (5)	2720 (4)	1926 (5)	628 (54)	484 (47)	637 (52)	-122 (41)	56 (44)	-61 (38)
C(34)	2447 (5)	2988 (4)	1335 (5)	835 (62)	484 (50)	710 (53)	-47 (46)	36 (49)	57 (42)
C(35)	2851 (5)	2586 (4)	4030 (5)	784 (62)	574 (51)	550 (50)	-109 (47)	34 (44)	-202 (40)
C(36)	1958 (7)	2936 (5)	4056 (6)	1086 (82)	920 (68)	916 (67)	94 (64)	87 (59)	-293 (55)
C(37)	3107 (4)	-57 (4)	2748 (4)	509 (47)	465 (46)	425 (41)	-13 (36)	-52 (35)	-7 (32)
C(38)	4070 (5)	-37 (5)	3035 (5)	662 (65)	496 (62)	839 (61)	-71 (53)	-26 (47)	-56 (44)
C(39)	5342 (6)	-845 (6)	3344 (7)	671 (52)	924 (59)	1696 (79)	90 (44)	71 (52)	84 (55)
C(40)	5646 (7)	-1584 (5)	3035 (8)	1168 (72)	882 (63)	1806 (88)	166 (54)	34 (63)	268 (58)
O(1)	4492 (4)	526 (4)	3226 (5)	723 (47)	666 (44)	2208 (83)	-32 (38)	-357 (48)	-90 (47)
O(2)	4406 (4)	-750 (3)	3025 (5)	600 (42)	591 (40)	1732 (66)	13 (33)	-95 (41)	44 (39)

Table I. (Continued)

	(b) Hydrogen Atoms					(b) Hydrogen Atoms			
	10 ⁴ X	10 ⁴ Y	10 ⁴ Z	10 ³ U		10 ⁴ X	10 ⁴ Y	10 ⁴ Z	10 ³ U
H(5)	-365 (30)	-1302 (26)	-3889 (30)	59 (15)	H(292)	785 (24)	-510 (21)	-1444 (24)	23 (11)
H(10)	353 (31)	-1039 (28)	-111 (32)	77 (16)	H(301)	1529 (29)	-1714 (25)	-1072 (29)	63 (14)
H(15)	3285 (29)	1387 (25)	769 (29)	55 (14)	H(302)	2388 (32)	-1384 (27)	-1427 (32)	63 (15)
H(20)	2548 (34)	1114 (30)	4932 (35)	89 (17)	H(303)	1531 (35)	-1579 (30)	-2090 (36)	72 (18)
H(211)	1534 (26)	-95 (23)	6514 (27)	46 (12)	H(311)	3175 (29)	1194 (26)	-801 (30)	61 (14)
H(212)	2223 (32)	556 (27)	6172 (33)	67 (15)	H(312)	2830 (39)	665 (34)	-1484 (40)	97 (20)
H(221)	3202 (37)	-486 (32)	5797 (38)	96 (19)	H(321)	4152 (56)	200 (50)	-118 (62)	155 (33)
H(222)	2564 (39)	-1096 (34)	6276 (41)	98 (21)	H(322)	4416 (46)	555 (41)	-1045 (47)	136 (26)
H(223)	3055 (53)	-464 (44)	6949 (54)	140 (31)	H(323)	3881 (58)	-291 (50)	-1030 (60)	166 (35)
H(231)	-277 (30)	-1178 (26)	5428 (30)	59 (15)	H(331)	3736 (28)	2611 (25)	1551 (29)	45 (14)
H(232)	523 (33)	-918 (28)	6243 (33)	71 (17)	H(332)	3418 (31)	3133 (28)	2319 (32)	58 (15)
H(241)	569 (20)	-2316 (17)	5075 (21)	77 (8)	H(341)	1958 (29)	3057 (26)	1660 (30)	49 (14)
H(242)	461 (40)	-2281 (33)	6063 (39)	99 (20)	H(342)	2242 (39)	2565 (34)	883 (39)	106 (21)
H(243)	1292 (35)	-2034 (29)	5819 (33)	50 (16)	H(343)	2556 (31)	3518 (28)	1016 (32)	66 (16)
H(251)	-1714 (33)	-2347 (28)	2198 (33)	61 (16)	H(351)	3257 (31)	2972 (28)	3849 (32)	73 (15)
H(252)	-1564 (35)	-1962 (32)	3079 (36)	89 (19)	H(352)	3052 (33)	2392 (28)	4652 (33)	67 (16)
H(261)	-426 (48)	-2725 (41)	3509 (49)	135 (26)	H(361)	1681 (35)	3146 (32)	3496 (38)	91 (18)
H(262)	-408 (50)	-3145 (44)	2570 (52)	146 (28)	H(362)	1948 (37)	3415 (32)	4522 (37)	157 (18)
H(263)	-1203 (52)	-3256 (43)	3137 (49)	143 (28)	H(363)	1609 (33)	2602 (30)	4297 (34)	91 (17)
H(271)	-980 (30)	-1723 (27)	-63 (31)	57 (15)	H(371)	3091 (28)	-390 (23)	2160 (28)	51 (13)
H(272)	-1560 (32)	-2137 (28)	584 (33)	72 (16)	H(372)	2849 (31)	-429 (26)	3134 (32)	58 (15)
H(281)	-265 (39)	-3045 (35)	765 (41)	109 (21)	H(391)	5229 (27)	-698 (24)	4070 (27)	35 (13)
H(282)	178 (40)	-2584 (35)	44 (39)	99 (21)	H(392)	5594 (44)	-456 (38)	3069 (45)	119 (24)
H(283)	-724 (43)	-3084 (38)	-248 (44)	115 (23)	H(401)	6364 (42)	-1660 (34)	3125 (40)	127 (22)
H(291)	1731 (31)	-217 (28)	-1863 (32)	68 (15)	H(402)	5431 (47)	-1614 (40)	2420 (50)	163 (26)
					H(403)	5348 (46)	-2042 (40)	3345 (46)	158 (25)

^aThe units of U are Å^2 . The anisotropic temperature factor is in the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hlc^*a^* + 2U_{23}kcb^*c^*)]$.

Table II. Bond Distances (Å)

	Co complex	Nonmetallo complex ^a		Co Complex	Nonmetallo complex ^a
Co—Cl	2.271 (2)		C(11)—C(12)	1.460 (8)	1.41 (2)
Co—N(1)	2.072 (5)		C(12)—C(13)	1.332 (8)	1.36 (2)
Co—N(2)	1.992 (5)		C(12)—C(29)	1.503 (8)	1.54 (2)
Co—N(3)	2.063 (5)		C(13)—C(14)	1.463 (8)	1.45 (2)
Co—N(4)	2.455 (5)		C(13)—C(31)	1.505 (10)	1.51 (2)
N(1)—C(1)	1.385 (7)	1.40 (2)	C(14)—C(15)	1.379 (8)	1.43 (2)
N(1)—C(4)	1.365 (7)	1.37 (1)	C(15)—C(16)	1.383 (9)	1.37 (2)
N(2)—C(6)	1.376 (8)	1.37 (2)	C(16)—C(17)	1.409 (9)	1.42 (2)
N(2)—C(9)	1.375 (7)	1.38 (2)	C(17)—C(18)	1.386 (8)	1.38 (2)
N(3)—C(11)	1.375 (7)	1.36 (2)	C(17)—C(33)	1.491 (9)	1.52 (2)
N(3)—C(14)	1.376 (7)	1.36 (1)	C(18)—C(19)	1.404 (9)	1.40 (2)
N(4)—C(16)	1.411 (8)	1.40 (2)	C(18)—C(35)	1.501 (9)	1.52 (2)
N(4)—C(19)	1.427 (8)	1.41 (2)	C(19)—C(20)	1.383 (9)	1.36 (2)
N(4)—C(37)	1.456 (8)	1.51 (2)	C(21)—C(22)	1.497 (12)	1.49 (3)
C(1)—C(2)	1.455 (8)	1.44 (2)	C(23)—C(24)	1.509 (11)	1.58 (2)
C(1)—C(20)	1.368 (9)	1.40 (2)	C(25)—C(26)	1.523 (11)	1.52 (2)
C(2)—C(3)	1.330 (9)	1.34 (2)	C(27)—C(28)	1.500 (11)	1.56 (2)
C(2)—C(21)	1.516 (9)	1.52 (2)	C(29)—C(30)	1.500 (10)	1.53 (2)
C(3)—C(4)	1.458 (9)	1.44 (2)	C(31)—C(32)	1.484 (12)	1.49 (2)
C(3)—C(23)	1.507 (9)	1.51 (2)	C(33)—C(34)	1.507 (10)	1.57 (2)
C(4)—C(5)	1.373 (8)	1.39 (2)	C(35)—C(36)	1.486 (12)	1.55 (2)
C(5)—C(6)	1.391 (9)	1.40 (2)	C(37)—C(38)	1.499 (10)	1.49 (2)
C(6)—C(7)	1.443 (8)	1.47 (2)	C(38)—O(1)	1.177 (10)	1.19 (2)
C(7)—C(8)	1.363 (9)	1.31 (2)	C(38)—O(2)	1.317 (10)	1.31 (2)
C(7)—C(25)	1.496 (10)	1.47 (2)	C(39)—C(40)	1.423 (14)	1.45 (4)
C(8)—C(9)	1.445 (8)	1.47 (2)	C(39)—O(2)	1.480 (10)	1.49 (2)
C(8)—C(27)	1.499 (9)	1.52 (2)	Average C—H dist 0.98 (6)		
C(9)—C(10)	1.378 (8)	1.40 (2)	Maximum C—H dist 1.13		
C(10)—C(11)	1.360 (8)	1.38 (2)	Minimum C—H dist 0.87		

^aReference 12.

Bond angles are shown in Table III, and important torsion angles are listed in Table IV. Table V contains data on several mean planes of interest, along with analogous data for the free base cation.¹²

Coordination has caused the porphyrin ring to lose its ef-

fective mirror plane¹² through N(2) and N(4); the chlorine atom leans slightly nearer N(3) than N(1); the N(1) ring deviates more than does the N(3) ring from the mean plane of N(1), N(2), and N(3); and several of the bond distances and angles which were equivalent in the free base¹² within

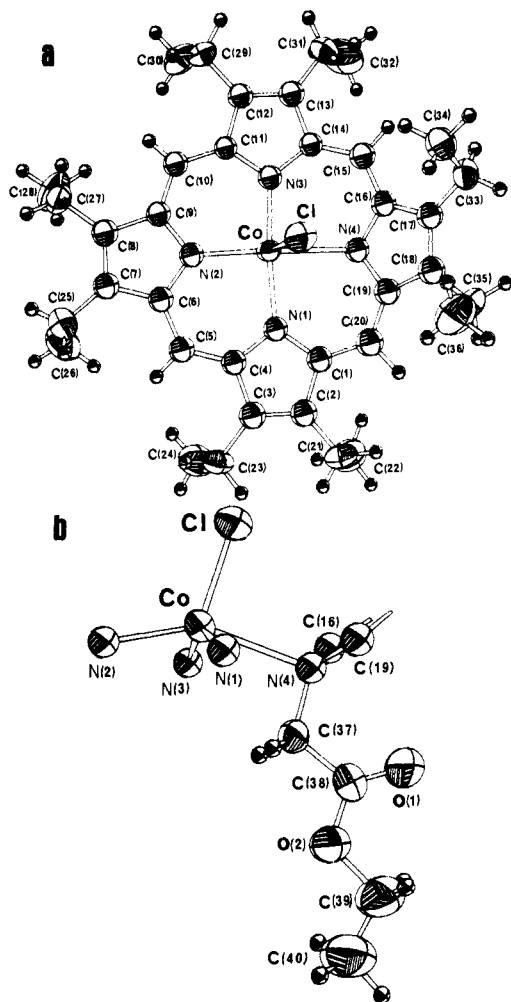


Figure 2. A perspective drawing of the molecule, with atom numbering: (a) the macrocyclic portion of the molecule; (b) the coordination sphere and side chain, with the carbon atoms bonded to N(4). This portion of the molecule is viewed from 90° about the x axis and, to avoid eclipsing the N(1) and N(3) atoms, 10° about the (original) y axis of figure (a). Thermal ellipsoids are drawn to include 50% probability. The hydrogen atoms are drawn arbitrarily small. Except for H(5), which is bonded to C(5), the first two digits of each hydrogen atom number represent the carbon atom to which it is attached. The third digit, if any, is merely to distinguish the hydrogen atoms from each other.

statistical limits are no longer so in the complex. Stereoprojections of the free base cation¹² and the cobalt(II) complex are given in Figure 3.

The N(4) atom is about 0.4 \AA farther from the cobalt atom than are the other three nitrogen atoms. The distance between the N(2) and N(4) atoms in the coordinated molecule (4.30 \AA), however, is no different from that of these two atoms in the free base. The cobalt atom lies slightly closer to N(2) than to N(1) or N(3). The chlorine atom leans decidedly in the direction of N(4). Contact distances less than 4.0 \AA of the chlorine atom with nonhydrogen atoms, resulting from this tilt of the chlorine atom, are as follows: N(4) $3.381(5)$; C(14) 3.934 ; C(15) $3.937(7)$; C(16) $3.509(7)$; C(17) $3.791(6)$; C(18) $3.818(6)$; C(19) $3.585(6)$.

The distortion of the N(4) ring from the plane of the other three nitrogen atoms is markedly increased in the cobalt complex over its out-of-plane position in the free base (Figure 3). However, the N(4) ring itself retains its essential planarity (Table V), unlike the N-substituted ring in an analogous corrole.¹³

The side chain oxygen atoms do not approach the cobalt atom of the same or of any symmetry related molecule. The side chain seems fortuitously to lie in a plane with N(2), Co, and N(4) (Table V). In the free base,¹² the last carbon atom in the side chain is twisted from this orientation, probably by packing forces. It is perhaps somewhat surprising that the side chain has almost the same conformation in the complex as in the free base, considering the different packing forces expected and the effect of metal coordination on the macroring.

The packing of the complex is shown in Figure 4. In the free base cation¹² the terminal carbon atoms of all eight ethyl groups point in the same direction as the N-substituted side chain (Figure 3). In the complex, the two terminal carbon atoms of the ethyl groups of the N(4) ring are oriented in the opposite direction. The probable cause of this effect is more efficient packing. The N(4) ring is severely tilted in the complex, so much so that upon free rotation the ethyl groups might point upward or outward, but not downward. Since the cobalt and chlorine atoms already occupy the volume above the macrocycle, no extra volume is required for the terminal carbon atoms to point upward. In the free base cation, with a much more planar structure and with no chlorine atom above the macrocycle, the preferred

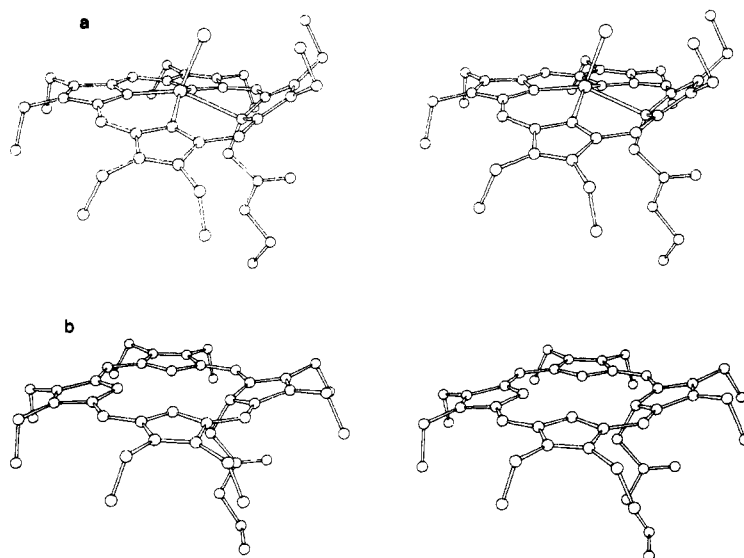


Figure 3. Stereoscopic pairs representing (a) the metal complex, and (b) the nonmetallo free base cation, drawn from the data of ref 12.

Table III. Bond Angles (deg)

	Co complex	Nonmetallo complex ^a		Co complex	Nonmetallo complex ^a
N(1)—Co—Cl	109.1 (1)		C(23)—C(3)—C(2)	128.1 (5)	128.9 (13)
N(2)—Co—Cl	119.0 (1)		C(22)—C(21)—C(2)	112.2 (5)	112.7 (13)
N(3)—Co—Cl	102.7 (1)		C(23)—C(3)—C(4)	124.6 (4)	122.7 (11)
N(4)—Co—Cl	91.2 (1)		C(5)—C(4)—C(3)	123.8 (4)	128.3 (11)
N(2)—Co—N(1)	89.8 (2)		C(24)—C(23)—C(3)	113.8 (5)	111.0 (11)
N(3)—Co—N(1)	143.9 (2)		C(6)—C(5)—C(4)	126.6 (4)	126.9 (10)
N(4)—Co—N(1)	81.2 (2)		C(7)—C(6)—C(5)	125.9 (4)	121.8 (10)
C(1)—N(1)—Co	129.4 (3)		C(8)—C(7)—C(6)	106.2 (4)	105.7 (10)
C(4)—N(1)—Co	122.8 (2)		C(25)—C(7)—C(6)	124.8 (4)	124.2 (12)
N(3)—Co—N(2)	89.5 (2)		C(25)—C(7)—C(8)	128.6 (5)	129.8 (12)
N(4)—Co—N(2)	149.7 (2)		C(9)—C(8)—C(7)	107.4 (4)	108.2 (11)
C(6)—N(2)—Co	126.5 (3)		C(27)—C(8)—C(7)	127.9 (4)	127.3 (10)
C(9)—N(2)—Co	127.1 (2)		C(26)—C(25)—C(7)	112.7 (5)	115.9 (11)
N(4)—Co—N(3)	81.4 (2)		C(27)—C(8)—C(9)	124.6 (5)	124.3 (11)
C(11)—N(3)—Co	122.2 (2)		C(10)—C(9)—C(8)	127.8 (4)	125.5 (12)
C(14)—N(3)—Co	128.8 (2)		C(28)—C(27)—C(8)	113.5 (5)	112.8 (12)
C(16)—N(4)—Co	109.5 (2)		C(11)—C(10)—C(9)	127.9 (4)	127.2 (13)
C(19)—N(4)—Co	109.2 (2)		C(12)—C(11)—C(10)	124.7 (4)	128.2 (12)
C(37)—N(4)—Co	95.3 (2)		C(13)—C(12)—C(11)	107.9 (4)	108.3 (12)
C(4)—N(1)—C(1)	106.5 (4)	110.7 (11)	C(29)—C(12)—C(11)	123.9 (4)	125.3 (10)
C(2)—C(1)—N(1)	108.8 (4)	104.9 (9)	C(29)—C(12)—C(13)	128.2 (5)	126.4 (11)
C(20)—C(1)—N(1)	125.2 (4)	125.6 (12)	C(14)—C(13)—C(12)	106.8 (5)	106.4 (11)
C(3)—C(4)—N(1)	109.6 (4)	106.6 (10)	C(31)—C(13)—C(12)	129.1 (5)	130.4 (14)
C(5)—C(4)—N(1)	126.6 (4)	125.1 (13)	C(30)—C(29)—C(12)	114.1 (5)	110.5 (13)
C(9)—N(2)—C(6)	106.1 (4)	104.2 (9)	C(31)—C(13)—C(14)	124.0 (4)	123.2 (11)
C(5)—C(6)—N(2)	123.3 (4)	126.5 (4)	C(15)—C(14)—C(13)	123.7 (4)	125.2 (11)
C(7)—C(6)—N(2)	110.5 (4)	111.8 (12)	C(32)—C(31)—C(13)	114.2 (5)	114.0 (13)
C(8)—C(9)—N(2)	109.8 (4)	110.2 (11)	C(16)—C(15)—C(14)	126.8 (4)	127.8 (11)
C(10)—C(9)—N(2)	122.3 (4)	124.1 (10)	C(17)—C(16)—C(15)	128.7 (4)	126.5 (11)
C(14)—N(3)—C(11)	106.5 (4)	109.1 (11)	C(18)—C(17)—C(16)	108.1 (4)	108.3 (10)
C(10)—C(11)—N(3)	126.2 (3)	123.1 (12)	C(33)—C(17)—C(16)	123.8 (4)	122.8 (12)
C(12)—C(11)—N(3)	109.1 (4)	108.6 (9)	C(33)—C(17)—C(18)	127.4 (5)	128.8 (11)
C(13)—C(14)—N(3)	109.6 (4)	107.5 (11)	C(19)—C(18)—C(17)	108.5 (5)	108.2 (11)
C(15)—C(14)—N(3)	126.2 (4)	127.3 (13)	C(35)—C(18)—C(17)	127.4 (5)	125.4 (10)
C(19)—N(4)—C(16)	106.3 (4)	107.4 (9)	C(34)—C(33)—C(17)	113.6 (5)	112.5 (12)
C(37)—N(4)—C(16)	117.8 (4)	115.7 (9)	C(35)—C(18)—C(19)	123.7 (5)	126.4 (12)
C(37)—N(4)—C(19)	117.9 (4)	114.8 (10)	C(20)—C(19)—C(18)	130.6 (4)	125.9 (12)
C(15)—C(16)—N(4)	122.1 (4)	125.9 (10)	C(36)—C(35)—C(18)	113.5 (6)	110.8 (12)
C(17)—C(16)—N(4)	108.8 (4)	107.6 (11)	O(1)—C(38)—C(37)	126.4 (5)	126.8 (13)
C(18)—C(19)—N(4)	108.3 (4)	108.3 (11)	C(35)—C(38)—C(37)	110.5 (5)	111.0 (10)
C(20)—C(19)—N(4)	120.8 (4)	125.5 (10)	O(2)—C(38)—O(1)	123.1 (5)	122.0 (13)
C(38)—C(37)—N(4)	114.3 (4)	112.0 (9)	C(39)—O(2)—C(38)	117.6 (6)	117.8 (12)
C(20)—C(1)—C(2)	125.7 (4)	129.4 (13)	O(2)—C(39)—C(40)	108.7 (6)	108.0 (19)
C(3)—C(2)—C(1)	107.7 (4)	109.4 (12)			
C(21)—C(2)—C(1)	123.7 (4)	123.0 (10)			
C(19)—C(20)—C(1)	127.8 (5)	128.0 (13)			
C(21)—C(2)—C(3)	128.6 (5)	127.4 (12)			
C(4)—C(3)—C(2)	107.2 (5)	108.4 (11)			

^a Reference 12.

orientation is downward, in the same direction as the side chain and all the other ethyl groups.

Discussion

Normal porphyrin rings, as opposed to N-substituted porphyrin rings, are generally almost exactly planar. For example, the atoms of one form of octaethylporphyrin (OEP) are within 0.05 Å of the mean plane.⁵ However, a form of tetraphenylporphyrin (H₂TPP)⁶ as well as the triclinic (planar)¹⁰ and tetragonal (buckled)¹⁷ forms of NiOEP clearly illustrate that relatively small energies are required to cause distortion of porphyrin macrocycles to nonplanarity. Cobalt(II) complexes of normal porphyrins retain the planarity of the ligand. For example, square pyramidal⁹ and octahedral¹⁹ geometries around the cobalt atom contain almost precisely planar macrocycles. In contrast, the N-substituted porphyrin molecule¹² deviates significantly from planarity, the largest effect being the bending of the N(4) ring upward from the mean plane of the rest of macrocycle (Figure 3). A comparison of the atomic distances from the mean plane of N(1), N(2), and N(3) in the free base cation and the cobalt complex is given in Table V.

In the N-substituted OEP, the cobalt atom cannot be expected to be coplanar with the four nitrogen atoms of the macrocycle. In the free base cation¹² the midpoint between N(1) and N(3) is only 2.27 Å from C(37); in the cobalt complex, the corresponding distance is 2.44 Å. Thus in the complex, the cobalt atom may be expected to lie above the mean plane of the nitrogen atoms for purely steric reasons. Even in the position above the macrocycle in which the cobalt atom is found, it is still in close contact with C(37) and the hydrogen atoms attached to it (contact distances (Å): Co—C(37), 2.96; Co—H(371), 3.10; Co—H(372), 2.87). In order to attain Co—N bonds approximately equal to 2.0 Å, a normal bond length in cobalt(II) porphyrins,⁹ the macrocycle folds slightly, with the N(4) ring tilting upward at a severe angle with respect to the rest of the macrocycle (see Table V and Figure 3), bringing the N(4) atom lone pair toward the direction of the Co atom. The cobalt atom can then form strong bonds with three of the nitrogen atoms and the chlorine atom. The bond to N(4), 2.45 Å in length, must be regarded as weak at best.

The geometry around the cobalt atom cannot be regarded as approximating a square pyramid, a trigonal bipyra-

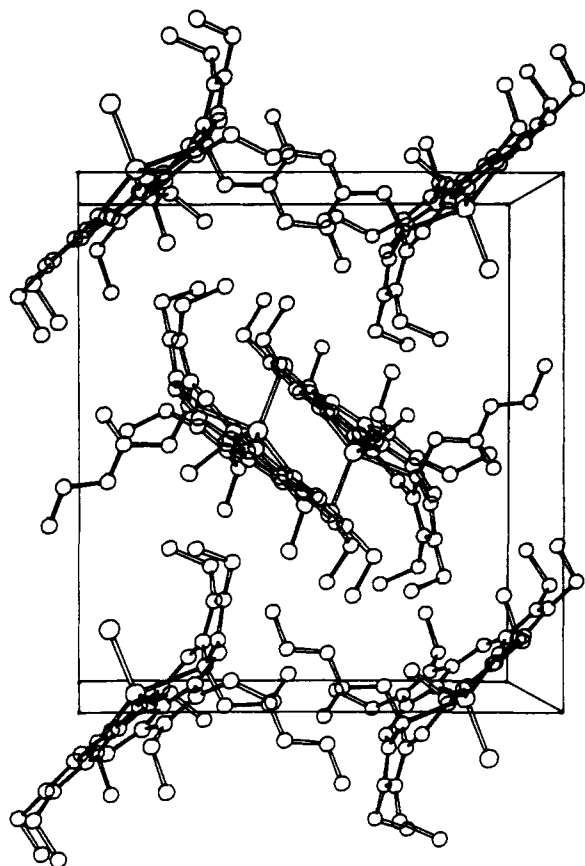


Figure 4. Packing diagram. A view of the unit cell from above its center at a distance of 40 Å. The *c* axis runs almost directly away from the viewer, with the *b* axis upward and *a* axis to the right.

Table IV. Important Torsion Angles^a

	Complex	Free base cation ¹²
Cl-Co-N(1)-C(1)	-62.5	
Cl-Co-N(1)-C(4)	102.5	
Cl-Co-N(2)-C(6)	-89.8	
Cl-Co-N(2)-C(9)	82.4	
Cl-Co-N(3)-C(11)	-99.0	
Cl-Co-N(3)-C(14)	60.9	
Cl-Co-N(4)-C(16)	-55.0	
Cl-Co-N(4)-C(19)	61.6	
Cl-Co-N(4)-C(37)	-176.9	
Co-N(4)-C(37)-C(38)	-177.1	
C(16)-N(4)-C(37)-C(38)	67.5	-52
C(19)-N(4)-C(37)-C(38)	-62.1	73
N(4)-C(37)-C(38)-O(1)	0.1	-28
N(4)-C(37)-C(38)-O(2)	-178.3	157
C(37)-C(38)-O(2)-C(39)	-176.4	178
O(1)-C(38)-O(2)-C(39)	5.2	3
C(38)-O(2)-C(39)-C(40)	-162.9	111

^a The angle (deg) given is the angle through which the plane of the first three atoms listed must be turned to achieve the plane of the last three atoms listed. A positive value indicates clockwise rotation, looking down the bond from the second atom to the third, until the first atom eclipses the fourth.

mid, or even an intermediate configuration between these two. The coordination about the cobalt atom is perhaps best described as arising from partial tetrahedral hybridization involving Co, N(1), N(2), N(3), and Cl, constrained by the steric requirements of the macrocyclic ring and modified by introduction of a weak bond to N(4). Partial tetrahedral hybridization explains the fact that the Co-Cl bond deviates so markedly from perpendicular to the mean plane of N(1), N(2), and N(3).

The magnetic susceptibility of the compound was found¹⁸

Table V. Mean Planes of the Cobalt(II) Complex and the Free Base Cation^a

A. Planes (values for free base cation in italics)	
Plane 1	Co, N(1), N(3), Cl $\sigma = 0.042002$ Co 0.1759, N(1) -0.0707, N(3) -0.0687, Cl -0.0365
Plane 2	N(2), Co, N(4), C(37), C(38), O(1), O(2), C(39), C(40) $\sigma = 0.094271$ N(2) -0.0637, Co 0.0326, N(4) 0.1001, C(37) 0.0278 C(38) -0.0273, O(1) -0.0180, O(2) -0.0539, C(39) -0.1916, C(40) 0.1941
Plane 3	N(1), N(2), N(3) $\sigma = 0$ N(1) 0, 0, N(2) 0, 0, N(3) 0, 0, N(4) 0.0854, 0.284, Co 0.6129, C(1) 0.0122, 0.010, C(2) -0.3294, 0.064, C(3) -0.4471, 0.086, C(4) -0.2265, 0.039, C(5) -0.2423, 0.085, C(6) -0.1796, 0.156, C(7) -0.4233, 0.457, C(8) -0.4232, 0.442, C(9) -0.1844, 0.156, C(10) -0.2127, 0.138, C(11) -0.1778, 0.086, C(12) -0.2751, 0.168, C(13) -0.1284, 0.201, C(14) 0.0608, 0.068, C(15) 0.4304, -0.014, C(16) 0.6684, -0.053, C(17) 1.5964, -0.467, C(18) 1.6154, -0.417, C(19) 0.6860, -0.014, C(20) 0.4099, -0.024, C(21) -0.5561, 0.186, C(23) -0.8208, 0.103, C(25) -0.7541, 0.840, C(27) -0.7303, 0.779, C(29) -0.5056, 0.249, C(31) -0.2125, 0.371, C(33) 2.5251, -0.784, C(35) 2.5619, -0.754.
Plane 4	N(1), C(1), C(2), C(3), C(4) $\sigma = 0.0017$ N(1) 0.0242, 0.002, C(1) -0.0253, 0.000, C(2) 0.0175, -0.001, C(3) -0.0031, 0.002, C(4) -0.0132, -0.002, C(21) 0.1278, 0.091, C(23) 0.0586, -0.037, C(20) -0.2170, 0.001, C(5) -0.0629, 0.042, Co -0.2313
Plane 5	N(2), C(6), C(7), C(8), C(9) $\sigma = 0.0006$ N(2) 0.0157, -0.008, C(6) -0.0120, 0.009, C(7) 0.0038, -0.007, C(8) 0.0056, 0.002, C(9) -0.0130, 0.004, C(5) -0.1667, 0.009, C(10) -0.1317, -0.071, C(25) -0.1131, -0.162, C(27), -0.0816, -0.099, Co 0.2639
Plane 6	N(3), C(11), C(12), C(13), C(14) $\sigma = 0.000295$ N(3) -0.0109, -0.006, C(11) 0.0094, -0.014, C(12) -0.0044, -0.017, C(13) -0.0020, 0.013, C(14), 0.0080, -0.004, C(10) 0.0787, 0.108, C(15) 0.1997, -0.051, C(29) -0.0218, -0.039, C(31) -0.0786, 0.084, Co 0.4292
Plane 7	N(4), C(16), C(17), C(18), C(19) $\sigma = 0.000094$ N(4) 0.0001, -0.027, C(16) 0.0035, 0.017, C(17) -0.0058, 0.000, C(18) 0.0059, -0.017, C(19) -0.0037, 0.027, C(15) 0.1581, 0.090, C(20) 0.1032, 0.212, C(33) 0.1638, -0.097, C(35) 0.1693, -0.065, Co 2.0469, Cl 3.3411

B. Equations of Planes in the form $Px + Qy + Rz = S$, where *X*, *Y*, *Z* are units in Angstroms with respect to *a*, *b**, and *c**

	<i>P</i>	<i>Q</i>	<i>R</i>	<i>S</i>
1	-0.8571	-0.4543	-0.2430	-10.2767
2	0.2407	0.1352	-0.9611	-0.5536
3	-0.5436	0.8370	-0.0627	12.8391
4	0.6568	-0.7483	-0.0928	-12.0246
5	-0.6843	0.7213	-0.1073	10.7994
6	-0.6034	0.7769	-0.1800	11.4844
7	-0.9492	0.2255	-0.2193	-0.4038

C. Angles between Planes

1-2	91.96	2-3	87.56	3-5	10.76	5-6	7.01
1-3	84.21	2-4	81.60	3-6	8.30	5-7	33.30
1-4	101.56	2-5	87.94	3-7	44.06	6-7	38.05
1-5	73.45	2-6	82.37	4-5	168.31		
1-6	78.00	2-7	89.27	4-6	163.94		
1-7	40.15	3-4	167.84	4-7	140.53		

^a Data for the free base cation are from ref 12. The numbers after each atom represent the perpendicular distance from the plane in Angstrom units. The value of σ is the sum of the squares of the distances of the atoms defining the plane from the plane.

to be 5.1 μ_B , as measured by the Faraday method. This value is higher than normal²⁵ for either regular tetrahedral complexes of cobalt(II), which range from 3.9 to 4.4 μ_B or for 5-coordinate cobalt(II) complexes, which have moments 4.5 to 4.7 μ_B .²⁶ The value is more in the range of octahedral complexes,²⁶ despite the fact that there is no x-ray evidence for a sixth donor atom. The Co-N bond lengths are in the range of pseudo-tetrahedral cobalt(II) complexes.

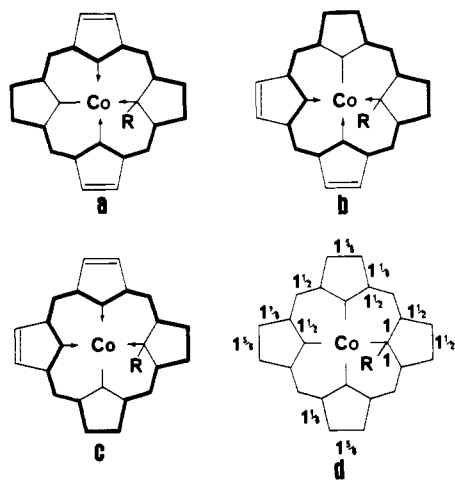


Figure 5. Principal resonance forms of the macrocycle. Broad lines represent the electron delocalization in the macrocycle. Part d shows the net bond order of representative bonds.

The bond distances in the macrocycle allow the following deductions to be made about the predominant resonance forms of the coordinated molecule. (1) Ring delocalization through the bonds of N(4), the substituted nitrogen atom, is minimal. (2) Eighteen π electron delocalization involves the carbon skeleton of the N(4) ring and of any one of the other pyrrole rings plus the nitrogen atoms of the other two pyrrole rings (see Figure 5). Thus the bond distances of the carbon skeleton in the N(4) ring reflect bond orders of $1\frac{1}{2}$ each, whereas the β - β bonds of the other rings are $1\frac{5}{6}$ order. The α - β bonds are then $1\frac{1}{6}$ order, in reasonable agreement with the bond distances found (Table II). Perhaps the delocalization of the carbon skeleton of the N(2) ring is slightly more extensive than that of the N(1) or N(3) rings, since the β - β bond distance in the N(2) ring is 0.02 Å shorter. (3) Surprisingly, the nonplanarity of the macrocycle does not seem to block the extensive delocalization of the π bonding. Similar observations for somewhat similar systems have been reported previously.^{16,27,28}

Changes in the macroring bond lengths upon coordination may result from π bonding between the unsubstituted nitrogen atoms and the metal. Notable in the bond lengths of the β - β bonds is the lack of change in that of the C(17)-C(18) bond, in the substituted pyrrole ring. The β - β bond of the opposite ring has lengthened on coordination; those of the other two rings have shortened slightly. The α - β bonds of the three nonsubstituted rings have changed in the opposite manner. The relative importance of the various resonance forms (Figure 5a compared to 5b and c) must change on coordination. Through the changes are small in some cases, each is in accord with the relatively more important contribution of resonance forms b and c upon coordination.

This result may stem from the relatively greater dative π bonding ability of N(2), than N(1) and N(3) in the geometry of the molecule.

In conclusion, the stereochemistry of the N-substituted metal porphyrin complexes is determined by (a) the steric requirements of the ligand, (b) the flexibility of the ligand to fold, and (c) the possible coordination geometries of the metal. Metals of different coordination geometry are presently under investigation.

Acknowledgments. The authors thank Mr. D. Ward and Professor A. W. Johnson for the gift of the crystal and Dr. F. March for many helpful discussions. We are indebted to Professor R. Mason for his hospitality and for the use of his facilities during this investigation. One of us (K.M.T.) was supported by the Science Research Council, U.K.

Supplementary Materials Available: structure factor amplitudes (20 pages). Ordering information is given on any current masthead page.

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