N-Methylporphyrin Complexes. Crystal and Molecular Structure of Chloro-*N*- methyl-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatocobalt(II)[1]

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Abstract: The crystal and molecular structure of chloro-*N*-methyl-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatocobalt(II), $[Co(N_4C_{45}H_{31})Cl]$, has been determined from three-dimensional single-crystal x-ray diffraction data, collected by counter techniques. The dark purple crystals are triclinic, space group $P\bar{1}$ (No. 2), with two formula units in a unit cell of dimensions: a = 7.484 (2), b = 14.972 (4), c = 17.398 (5) Å; α = 102.93 (1)°, β = 97.03 (1)°, and γ = 94.13 (1)°. The structure has been refined by least-squares methods to $R = 0.064$ ($R_w = 0.087$) for 3703 unique reflections with $F^2 > 3\sigma(F^2)$. The coordination geometry about the cobalt(II) ion in the monomeric neutral complex is based on a distorted square pyramid. Three of the four basal coordination sites are occupied by normal pyrrole nitrogens of the porphyrin ligand (Co–N 2.063 (5), 2.063 (5), and 2.016 (4) Å), while the alkylated nitrogen occupying the fourth position forms a much longer bond to cobalt (Co–N 2.381 (5) Å). The apical position is occupied by the chloride ion (Co–Cl 2.242 (3) Å). The *N*-methyl group exerts a profound influence on the overall structure, causing the N-alkylated pyrrole ring to deviate strongly from the mean plane of the remainder of the porphyrin ligand, and blocking access to the sixth coordination site on the cobalt(II) ion. The cobalt ion is displaced considerably out of the mean porphyrin plane toward the apical position, and remains high spin in this novel coordination environment.

Metalloporphyrin chemistry continues to be a very active area of research, at least in part because of successes in relating the properties of simple synthetic metalloporphyrin systems[2–9] to the properties of more complex porphyrin-containing biological compounds. In particular, studies of porphyrin complexes of cobalt(II) have been of interest due to the oxygen binding properties of synthetic cobalt(II) porphyrin complexes[10] and cobaltohemoglobin.[11]

We have recently undertaken systematic synthetic, mechanistic, and structural studies of transition metal complexes of N-methylated porphyrin ligands.[1,12–15] The geometric and electronic constraints associated with alkylation at one of the pyrrole nitrogen atoms may allow these complexes to serve as models for the "sitting-atop" complexes which have been discussed as possible intermediates in metalation reactions of normal porphyrins.[16] One of the primary stereochemical effects of N-alkylation is associated with blockage of the coordination site by the alkyl group,[1,17] and the resultant strong tendency toward five-coordination will allow systematic exploration of the chemical properties associated with similar five-coordinate geometry at a wide variety of metal ions.

The detailed structure of chloro-*N*-methyl-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatocobalt(II) has been determined by single-crystal x-ray diffraction methods, and is the subject of this report.[1] As the first in a series of structures of *N*-methylporphyrin transition metal complexes, the coordination geometry found for this novel species is of interest relative to the suitability of these species as models for biological intermediates and their value as probes of five-coordinate properties. The structure of a closely related complex, chloro-(2,3,7,8,12,13,17,18-octaethyl-*N*-ethylacetatoporphine)cobalt(II), has been recently determined,[17] and will be compared in detail with the present structure.

Experimental Section

The synthesis and analytical characterization of chloro-*N*-methyl-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatocobalt(II) has been previously reported.[1] The magnetic moment, μ_{eff}, of the title complex was determined to be 4.9 ± 0.1 μ_B over the range 150–295 K (Faraday method, $Hg[Co(NCS)_4]$ calibrant, Cahn Research magnetic susceptibility system).

Crystal Data. For $Co(N_4C_{45}H_{31})Cl$ (mol wt 722.1, triclinic); a = 7.484 (2), b = 14.972 (4), c = 17.398 (5) Å; α = 102.93 (1)°, β = 97.03 (1)°, γ = 94.13 (1)°; V = 1875.7 Å^3; ρ_{obsd} = 1.27, ρ_{calcd} = 1.28 g cm^{-3}; Z = 2; and $F(000)$ = 746; space group $P\bar{1}$; Mo Kα radiation, λ_1 0.709 30 Å, λ_2 0.713 59 Å, μ(Mo Kα) = 5.86 cm^{-1}.

Data Collection and Reduction. Preliminary Weissenberg and precession photographs revealed only Laue symmetry $\bar{1}$, consistent with the space groups $P1$ and $P\bar{1}$.[18] The centric space group $P\bar{1}$ was chosen arbitrarily for all further structural work with this compound. The correctness of this choice is attested to only by the ultimate solution and refinement of this structure, as reported below.

The large, dark purple crystal chosen for data collection was mounted on the Enraf-Nonius CAD-3 diffractometer, with the a axis approximately coincident with the diffractometer ϕ axis. After accurate centering, the orientation matrix for data collection and the unit cell parameters reported above were obtained from least-squares calculations on the automatically determined[19] 2θ, χ, and ϕ settings of 27 reflections (at ambient temperature, 20 (±1) °C) with 2θ values in the range 16–25°. The measured density reported was obtained by neutral buoyancy in aqueous zinc chloride solution.

The intensities of 6630 unique reflections with $3.00° < \theta < 25.00°$ were measured by θ–2θ scans, employing Zr-filtered Mo Kα radiation. These data were collected in two shells. Intensity data from the shell with $3° < \theta < 20°$ have been the basis for a preliminary report of this structure.[1] At θ values less than 3°, reflections were cutoff on the low θ side by the beam stop. The shell of data for which $20° < \theta < 25°$ was collected subsequently and merged with the data from the first shell, thus forming the data base of 6630 unique reflections for the present report. The scan range employed was 1.2° (in 2θ) to either side of the calculated K$\bar{\alpha}$ peak position, at a constant scan rate of 10° min^{-1}. The number of times a given reflection was scanned varied according to the intensity, with weak reflections being scanned a maximum of six times. Background was counted at both ends of the scan, for a total time equal to the scan time. The takeoff angle was 3.5°, and zirconium foil attenuators were inserted automatically (to avoid coincidence losses) if the peak count rate exceeded 2500 counts s^{-1}. The intensity of one of three reference reflections ($0\,0\,\bar{5}$, $0\,\bar{6}\,0$, and $2\,0\,\bar{2}$) was measured every 25 reflections. None of these control reflections showed any significant or systematic changes in intensity during the course of data collection.

Lorentz and polarization corrections were applied to the observed data. The uncertainty parameter, g, in the formula used for the standard deviation in the intensity,[20,21] was taken as 0.04. Reflections for which $F^2 > 3\sigma(F^2)$ were judged to be observed, and the 3703 reflections which met this criterion were employed in the solution and refinement of the structure. Due to the very low absorption coefficient (μ = 5.86 cm^{-1} for Mo Kα radiation), no absorption correction was judged to be necessary. The data collection crystal was columnar in shape, with approximate dimensions 0.20 × 0.22 × 0.40 mm (long dimension along a).

Solution and Refinement of the Structure. The position of the co-

Table I. Atomic Coordinates (Fractional)[a]

Atom	x	y	z
Co(II)	0.20083 (12)	0.17596 (6)	0.25463 (5)
N1	0.5148 (6)	0.1943 (3)	0.3056 (3)
N2	0.2657 (6)	0.3033 (3)	0.2326 (3)
N3	0.2439 (7)	0.0387 (3)	0.2351 (3)
N4	0.0119 (6)	0.1462 (3)	0.1571 (3)
Cl$^-$	0.0997 (3)	0.2108 (1)	0.3728 (1)
C5	0.5807 (9)	0.1743 (5)	0.2258 (4)
C11	0.5641 (8)	0.1322 (4)	0.3532 (4)
C12	0.6522 (9)	0.1832 (4)	0.4277 (4)
C13	0.6574 (8)	0.2759 (4)	0.4284 (4)
C14	0.5740 (8)	0.2837 (4)	0.3530 (4)
C21	0.4033 (8)	0.3718 (4)	0.2705 (4)
C22	0.3802 (10)	0.4552 (5)	0.2434 (4)
C23	0.2338 (10)	0.4382 (5)	0.1913 (4)
C24	0.1527 (9)	0.3437 (4)	0.1851 (4)
C31	0.1203 (8)	−0.0316 (4)	0.1883 (4)
C32	0.1793 (9)	−0.1197 (5)	0.1921 (4)
C33	0.3368 (10)	−0.1046 (5)	0.2426 (4)
C34	0.3760 (8)	−0.0053 (4)	0.2709 (4)
C41	−0.0689 (8)	0.2087 (4)	0.1206 (4)
C42	−0.2246 (9)	0.1635 (5)	0.0645 (4)
C43	−0.2359 (9)	0.0734 (5)	0.0669 (4)
C44	−0.0847 (8)	0.0620 (4)	0.1241 (4)
C1	0.5204 (8)	0.0372 (4)	0.3284 (4)
C2	−0.0393 (8)	−0.0211 (4)	0.1401 (3)
C3	−0.0043 (8)	0.3012 (4)	0.1344 (4)
C4	0.5427 (8)	0.3644 (4)	0.3290 (4)
H12	0.7002	0.1582	0.4704
H13	0.7080	0.3255	0.4718
H22	0.4587	0.5109	0.2588
H23	0.1710	0.4803	0.1640
H32	0.1189	−0.1781	0.1642
H33	0.4218	−0.1352	0.2697
H42	−0.3039	0.1915	0.0322
H43	−0.3258	0.0264	0.0368
H1C5	0.5230	0.1167	0.1947
H2C5	0.5522	0.2216	0.1994
H3C5	0.7080	0.1720	0.2333

[a] Estimated standard deviations in parentheses.

balt(II) ion was initially assigned from the highest nonorigin peak appearing in the Patterson map. Starting positions for all non-hydrogen atoms were then obtained from a series of Fourier syntheses phased by the atoms in known positions. Scattering factors for cobalt(II), chloride ion, carbon, and nitrogen were taken from ref 22. Scattering factors for spherical bonded hydrogen atoms[23] were also taken from ref 22, as were correction terms $\Delta f'$ and $\Delta f''$ for anomalous dispersion due to cobalt and chlorine.

Due to computer limitations, least-squares refinement[24] of the structure was carried out in alternate cycles on two separate blocks of parameters. On cycle A, the scale factor was refined, together with the positional and anisotropic thermal parameters of all non-hydrogen atoms except the meso carbons (C1-C4) and the carbon atoms of the phenyl ring. In a subsequent cycle B, refinement was carried out on the scale factor, together with positional and anisotropic thermal parameters for the meso carbons (C1-C4) and group positional and individual isotropic thermal parameters for the carbon atoms of the phenyl rings. In all B cycles, the phenyl groups were refined as rigid, planar bodies of D_{6h} symmetry, with fixed C-C distances of 1.397 Å.[25] Hydrogen atoms were included in fixed idealized positions 0.95 Å away from carbon, with isotropic thermal parameters 1 Å^2 larger than the carbon atom to which they were attached. The positions of the hydrogen atoms on C5 (the methyl group on N1 of the porphyrin ligand) represent the results of a least-squares fit (idealized tetrahedral geometry) to the hydrogen atom positions observed about C5 in a difference Fourier synthesis.

Several repetitions of the cycle A–B sequence of least-squares refinement (on F) lowered R ($= [\sum \| F_o| - |F_c\|]/\sum |F_o|$) to its final value of 0.067 (unobserveds not included) and R_w ($= [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$) to 0.087. The error in an observation of unit weight was 1.54. On the final pair of cycles of refinement, no shift in any parameter was greater than 10% of the estimated standard deviation in that parameter. The NUCLS refinement program minimizes $\sum w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure amplitudes, respectively, and w is the weight ($= 4F_o{}^2/\sigma^2(F_o{}^2)$). Correction for extinction was not deemed necessary. A final difference Fourier electron density map showed no peak higher than 0.32 e Å^{-3} and no depression lower than −0.39 e Å^{-3}.

Table II. Anisotropic Thermal Parameters[a]

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Co(II)	109 (2)	29 (1)	23 (1)	0 (1)	−6 (1)	7 (1)
N1	116 (10)	30 (3)	24 (2)	−2 (4)	−6 (4)	−6 (2)
N2	102 (10)	34 (3)	24 (2)	−5 (4)	−7 (4)	11 (2)
N3	107 (10)	32 (3)	25 (2)	6 (4)	−10 (4)	2 (2)
N4	94 (8)	32 (3)	23 (2)	−5 (4)	−12 (4)	6 (2)
Cl$^-$	234 (4)	56 (1)	31 (1)	−4 (2)	27 (1)	6 (1)
C5	155 (14)	51 (4)	23 (2)	12 (6)	18 (5)	8 (3)
C11	103 (12)	35 (3)	28 (3)	13 (5)	0 (4)	10 (2)
C12	133 (13)	41 (4)	28 (3)	0 (6)	−4 (5)	7 (2)
C13	105 (12)	41 (4)	30 (3)	−1 (5)	−7 (5)	13 (3)
C14	80 (11)	37 (3)	28 (3)	−2 (5)	−3 (4)	9 (2)
C21	116 (12)	30 (3)	29 (3)	−7 (5)	−3 (5)	8 (2)
C22	214 (17)	43 (4)	36 (3)	6 (7)	−8 (6)	18 (3)
C23	190 (16)	39 (4)	38 (3)	−16 (6)	−13 (6)	17 (3)
C24	136 (13)	36 (3)	28 (3)	4 (6)	−3 (5)	13 (2)
C31	137 (13)	26 (3)	26 (2)	−3 (5)	0 (5)	3 (2)
C32	156 (15)	36 (4)	37 (3)	15 (6)	−16 (5)	2 (3)
C33	187 (16)	33 (3)	41 (3)	22 (6)	−9 (6)	10 (3)
C34	109 (12)	32 (3)	32 (3)	8 (5)	1 (5)	7 (2)
C41	105 (12)	36 (3)	26 (2)	4 (5)	−10 (4)	9 (2)
C42	130 (14)	44 (4)	29 (3)	4 (6)	1 (5)	10 (3)
C43	141 (14)	44 (4)	30 (3)	16 (6)	0 (5)	10 (3)
C44	90 (12)	39 (3)	25 (2)	0 (5)	−8 (4)	8 (2)
C1	130 (13)	35 (3)	29 (3)	8 (5)	−2 (5)	9 (2)
C2	116 (12)	34 (3)	24 (2)	−9 (5)	−4 (4)	5 (2)
C3	117 (12)	35 (3)	28 (2)	8 (5)	1 (4)	13 (2)
C4	112 (12)	30 (3)	29 (2)	−7 (5)	−8 (4)	6 (2)

[a] Estimated standard deviations in parentheses. The form of the anisotropic thermal ellipsoid is given by: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Final atomic positional parameters for the nongroup atoms are listed in Table I. Table II lists the anisotropic thermal parameters obtained for the nongroup atoms. Table III contains the positional parameters for the rigid phenyl groups obtained directly from the refinement, while Table IV lists the positional parameters for the atoms of the rigid phenyl rings derived from the group orientations and geometries.

Results and Discussion

The calculated bond lengths and angles involving Co(II) in the chloro-*N*-methyl-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatocobalt(II) complex (hereafter abbreviated as Co(N-CH$_3$TPP)Cl) are reported in Table V, while the bond lengths and angles within the *N*-methyltetraphenylporphyrin ligand (hereafter N-CH$_3$TPP) are found in Table VI. In all cases, standard deviations reported include contributions from the errors in the unit cell parameters.

The general layout of the complex, and the numbering scheme used in the following discussion, is shown in Figure 1. Numbers were assigned to the phenyl carbon atoms as Ph*mn*, where *m* was the number of the meso carbon to which the phenyl group was attached, and *n* depended on the position of the atom in the ring relative to the meso carbon (Ph11, for example, would be the phenyl carbon atom attached directly to C1, Ph12 the next, and so on).

Figure 2 shows a detailed view of the coordination geometry immediately about the Co(II) ion. These first two figures corroborate the expected features of the structure, namely, the five-coordinate nature of the cobalt(II) coordination and the

Table III. Group Parameters for the Rigid Phenyl Rings[a]

Group	x_g[b]	y_g	z_g	δ[c]	ϵ	η
Ph1	0.7528 (4)	−0.0720 (2)	0.4050 (2)	−2.978 (3)	−2.582 (3)	−2.886 (4)
Ph2	−0.2783 (4)	−0.1860 (2)	0.0654 (2)	−0.657 (3)	2.972 (2)	1.469 (3)
Ph3	−0.1855 (4)	0.4171 (2)	0.0439 (2)	−2.429 (6)	2.065 (2)	1.390 (6)
Ph4	0.7792 (5)	0.5269 (2)	0.4115 (2)	2.968 (3)	2.545 (3)	−2.895 (4)

[a] Estimated standard deviations in parentheses. [b] x_g, y_g, z_g are the fractional coordinates of the group centers. [c] The angles which describe the group orientations have been defined previously.[26]

Table IV. Derived Positional and Thermal Parameters[a] for Phenyl Carbon and Hydrogen Atoms

Atom	Carbon x	Carbon y	Carbon z	B (Å^2)	Hydrogen[b]		
Ph11	0.6378 (5)	−0.0192 (3)	0.3688 (3)	3.0 (1)			
Ph12	0.5681 (5)	−0.0795 (3)	0.4111 (3)	4.5 (2)	0.4360	−0.0848	0.4155
Ph13	0.6831 (7)	−0.1322 (3)	0.4474 (3)	5.5 (2)	0.6332	−0.1753	0.4777
Ph14	0.8677 (6)	−0.1248 (3)	0.4413 (3)	5.4 (2)	0.9500	−0.1626	0.4673
Ph15	0.9374 (4)	−0.0646 (4)	0.3990 (3)	5.1 (2)	1.0696	−0.0592	0.3946
Ph16	0.8224 (6)	−0.0118 (3)	0.3627 (3)	3.9 (1)	0.8723	0.0313	0.3324
Ph21	−0.1625 (6)	−0.1062 (2)	0.1011 (2)	2.8 (1)			
Ph22	−0.2438 (7)	−0.1566 (3)	0.1484 (2)	4.1 (1)	−0.2190	−0.1355	0.2078
Ph23	−0.3596 (7)	−0.2364 (3)	0.1127 (3)	5.1 (2)	−0.4177	−0.2725	0.1466
Ph24	−0.3941 (6)	−0.2658 (3)	0.0298 (3)	4.2 (1)	−0.4770	−0.3230	0.0042
Ph25	−0.3128 (6)	−0.2154 (3)	−0.0175 (2)	4.2 (1)	−0.3376	−0.2365	−0.0769
Ph26	−0.1970 (6)	−0.1356 (3)	0.0181 (2)	3.2 (1)	−0.1389	−0.0995	−0.0158
Ph31	−0.1042 (6)	0.3592 (3)	0.0875 (2)	3.0 (1)			
Ph32	−0.0941 (6)	0.3454 (3)	0.0061 (2)	3.7 (1)	−0.0286	0.2942	−0.0210
Ph33	−0.1753 (7)	0.4033 (3)	−0.0375 (2)	4.4 (2)	−0.1680	0.3934	−0.0957
Ph34	−0.2667 (7)	0.4749 (3)	0.0004 (3)	5.1 (2)	−0.3249	0.5163	−0.0308
Ph35	−0.2769 (7)	0.4887 (3)	0.0818 (3)	5.1 (2)	−0.3423	0.5400	0.1089
Ph36	−0.1956 (7)	0.4308 (3)	0.1253 (2)	4.4 (2)	−0.2029	0.4407	0.1836
Ph41	0.6633 (6)	0.4482 (3)	0.3724 (3)	3.1 (1)			
Ph42	0.8484 (6)	0.4506 (3)	0.3674 (3)	4.4 (2)	0.8979	0.3959	0.3359
Ph43	0.9643 (5)	0.5292 (4)	0.4065 (3)	6.2 (2)	1.0968	0.5309	0.4029
Ph44	0.8952 (7)	0.6055 (3)	0.4505 (3)	5.9 (2)	0.9782	0.6618	0.4785
Ph45	0.7101 (7)	0.6032 (3)	0.4555 (3)	5.5 (2)	0.6606	0.6578	0.4871
Ph46	0.5941 (5)	0.5245 (3)	0.4165 (3)	4.2 (1)	0.4616	0.5229	0.4200

[a] Estimated standard deviations in parentheses. [b] Fixed calculated positions, as described in the text. Each set of coordinates is that of a hydrogen atom attached to the phenyl carbon atom on the same line.

Table V. Bond Lengths (Å) and Angles (deg) Involving Co(II)[a]

(a) Bond Lengths			
Co(II)-N1	2.381 (5)	Co(II)-N4	2.016 (4)
Co(II)-N2	2.063 (5)	Co(II)-Cl$^-$	2.243 (2)
Co(II)-N3	2.063 (5)		
(b) Bond Angles			
N1-Co-Cl$^-$	96.7 (1)	Co-N1-C11	113.6 (4)
N2-Co-Cl$^-$	103.3 (1)	Co-N1-C14	112.7 (4)
N3-Co-Cl$^-$	105.9 (2)	Co-N1-C5	96.1 (3)
N4-Co-Cl$^-$	116.6 (2)	Co-N2-C21	130.0 (4)
N1-Co-N2	81.9 (2)	Co-N2-C24	123.6 (4)
N1-Co-N3	81.5 (2)	Co-N3-C31	123.3 (4)
N1-Co-N4	146.7 (2)	Co-N3-C34	130.9 (3)
N2-Co-N3	147.8 (2)	Co-N4-C41	126.4 (4)
N2-Co-N4	89.4 (2)	Co-N4-C44	125.8 (4)
N3-Co-N4	89.6 (2)		

[a] Estimated standard deviations in parentheses.

stereochemical blockage of the sixth coordination site by the methyl group on pyrrole nitrogen N1. Due to the novelty of this complex, few species are available in the literature for comparison with the present structure. In the detailed discussion of the Co(N-CH$_3$TPP)Cl structure which follows, the principal comparison to be drawn will be to the structure of the closely related *N*-ethylacetatoporphyrin derivative, chloro(2,3,7,8,12,13,17,18-octaethyl-*N*-ethylacetatoporphine)cobalt(II) (hereafter abbreviated as Co(N-EtAOEP)Cl).[17] A related structure which will also be valuable for comparison is the N-methylated copper 8,12-diethyl-2,3,7,13,17,18,21-heptamethylcorrole.[27] Although direct comparisons of this high spin cobalt(II) *N*-methylporphyrin species to normal porphyrin structures are made difficult by the marked geometric and electronic distortions introduced by the N-methylation, comparison with the structures of a series of low spin Co(II) porphyrin complexes[28-33] will allow important conclusions to be drawn concerning the degree of distortion of the porphyrin core relative to these nonmethylated complexes.

The coordination geometry about the cobalt(II) ion is essentially that of an extremely distorted square pyramid. Three of the four basal positions are occupied by the nonalkylated pyrrole nitrogens of the porphyrin ligand. As in the related Co(N-EtAOEP)Cl complex,[17] the Co-N bond trans to the alkylated position is markedly shorter than the other two Co-N distances (here 2.016 (4) Å for Co-N4 vs. 2.063 (5) Å for the two equivalent Co-N2 and Co-N3 distances). These Co-N distances are significantly longer than the equatorial bond lengths observed in other known five-[28-31] and six-coordinate[32,33] cobalt(II) porphyrin complexes, where typical Co-N distances range from 1.96 to 2.00 Å. The fourth basal position in the primary Co(II) coordination sphere is occupied by the alkylated pyrrole nitrogen (N1), which makes a very long bond to the cobalt ion (Co-N1 2.381 (5) Å). This bond is, however, significantly shorter than the comparable Co-N bond length

Table VI. Bond Lengths (Å) and Angles (deg) for the *N*-Methylporphyrin Ligand[a]

(a) Bond Lengths			
N1-C5	1.504 (8)	N3-C31	1.385 (7)
N1-C11	1.416 (9)	N3-C34	1.387 (8)
N1-C14	1.415 (7)	C31-C32	1.434 (10)
C11-C12	1.405 (8)	C32-C33	1.353 (9)
C12-C13	1.382 (9)	C33-C34	1.454 (9)
C13-C14	1.415 (9)	C31-C2	1.413 (9)
C11-C1	1.393 (8)	C34-C1	1.387 (8)
C14-C4	1.389 (9)	N4-C41	1.377 (9)
N2-C21	1.388 (7)	N4-C44	1.373 (7)
N2-C24	1.374 (8)	C41-C42	1.443 (8)
C21-C22	1.444 (10)	C42-C43	1.355 (10)
C22-C23	1.360 (10)	C43-C44	1.459 (9)
C23-C24	1.452 (9)	C41-C3	1.392 (8)
C21-C4	1.395 (9)	C44-C2	1.391 (9)
C24-C3	1.397 (8)	C1-Ph11	1.483 (8)
		C2-Ph21	1.491 (6)
		C3-Ph31	1.497 (8)
		C4-Ph41	1.485 (6)
(b) Bond Angles			
C11-N1-C14	106.3 (5)	C24-C3-C41	125.4 (6)
C11-N1-C5	114.1 (5)	C41-N4-C44	106.7 (5)
C14-N1-C5	114.1 (5)	N4-C41-C3	124.3 (5)
N1-C11-C1	123.5 (5)	N4-C41-C42	110.2 (5)
N1-C11-C12	108.6 (5)	C3-C41-C42	125.4 (6)
C12-C11-C1	127.9 (6)	C41-C42-C43	106.7 (6)
C11-C12-C13	108.7 (6)	C42-C43-C44	107.4 (5)
C12-C13-C14	107.8 (5)	C43-C44-N4	109.0 (6)
C13-C14-N1	108.6 (6)	C43-C44-C2	125.9 (5)
C13-C14-C4	127.2 (5)	N4-C44-C2	125.1 (5)
N1-C14-C4	124.1 (5)	C44-C2-Ph21	118.2 (5)
C14-C4-Ph41	116.3 (5)	C31-C2-Ph21	117.2 (5)
C21-C4-Ph41	119.1 (5)	C44-C2-C31	124.5 (5)
C14-C4-C21	124.6 (5)	C31-N3-C34	105.2 (5)
C21-N2-C24	105.3 (5)	N3-C31-C2	126.4 (6)
N2-C21-C4	125.8 (6)	N3-C31-C32	110.6 (5)
N2-C21-C22	110.7 (5)	C2-C31-C32	123.0 (5)
C4-C21-C22	123.4 (5)	C31-C32-C33	107.5 (5)
C21-C22-C23	106.4 (6)	C32-C33-C34	106.7 (6)
C22-C23-C24	107.2 (7)	C33-C34-C1	123.8 (6)
C23-C24-N2	110.3 (5)	N3-C34-C33	110.0 (5)
C23-C24-C3	123.1 (6)	N3-C34-C1	126.1 (5)
N2-C24-C3	126.5 (6)	C34-C1-Ph11	120.0 (5)
C24-C3-Ph31	116.8 (5)	C11-C1-Ph11	115.8 (5)
C41-C3-Ph31	117.7 (5)	C34-C1-C11	120.0 (5)

[a] Estimated standard deviations in parentheses.

of 2.455 (4) Å in the structure of the *N*-ethylacetatoporphyrincobalt(II) derivative.[17] The Co-Cl bond length of 2.243 (2) Å is only slightly shorter than the corresponding bond length in the *N*-ethylacetato derivative. The near proximity of the methyl group to the cobalt(II) ion is indicated by the Co-C5 distance of 2.947 (7) Å.

Other five-coordinate high spin cobalt(II) complexes are known in which the coordination geometry is highly irregular, although none of these species closely approximates the coordination environment found in the present study. For example, dichloro-1,1,7,7-tetraethyldiethylenetriaminecobalt(II)[34] (Co(Et$_4$dien)Cl$_2$) exhibited a structure intermediate between the idealized trigonal bipyramidal and square pyramidal forms, best described as a very distorted square pyramid. In this compound, Co-N bond lengths ranged from 2.16 (2) to 2.21 (1) Å, with Co-Cl bond lengths of 2.357 (7) Å (apical Cl) and 2.319 (6) Å. A similar intermediate structure was found for dichlorobis(2-dimethylaminoethyl)methylaminecobalt(II) (Co(Me$_5$dien)Cl$_2$).[35] In this case, Co-N bond lengths ranged from 2.089 (15) to 2.317 (14) Å, while Co-Cl bond lengths were in the range 2.282 (6)-2.358 (6) Å. While the structure of bromotris(3-aminopropyl)aminecobalt(II) bromide ([Co(trpn)Br]Br)[36] was found to be basically trigonal bipyramidal, an unusually long Co-Br bond indicated distortion toward a four-coordinate, "pseudo-tetrahedral" geometry. In this case, Co-N bond lengths were 2.055 (10) Å (equatorial) and 2.194 (9) Å (axial). Thus, the present high spin Co(N-CH$_3$TPP)Cl complex involves stronger Co-N and Co-Cl bonding than in the above examples of severely distorted five-coordinate geometries, with the exception of the very long Co-N1 bond. Although this bond is obviously rather weak, the structure does not seem to be directly comparable to the type of "pseudotetrahedral" five-coordinate structure exemplified by [Co(trpn)Br]Br above, although others[17] have suggested that it may be regarded in this way. It must be admitted, at the same time, that the very weak Co-N1 bond does imply a tendency toward four-coordination at cobalt(II) in this complex. Studies already in progress[37] on complexes of N-CH$_3$TPP with the larger Mn(II) and Hg(II) metal ions will show comparatively stronger bonding to the alkylated pyrrole nitrogen than is the case for the Co(N-CH$_3$TPP)Cl complex presented here.

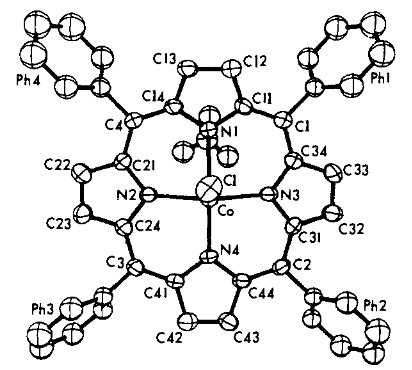

Figure 1. A view of the Co(N-CH$_3$TPP)Cl complex from directly above the complex plane. The apical chloride ion partly obscures the Co(II) ion, and the methyl group is seen partly obscured in its position below the alkylated nitrogen (N1).

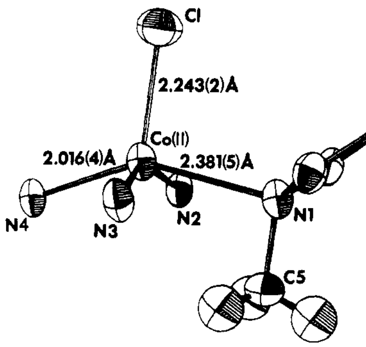

Figure 2. A view of the coordination geometry about the Co(II) ion, showing the distorted square pyramidal coordination geometry and the proximity of the *N*-methyl group (C5) to the metal ion. The carbon atoms of the N1 pyrrole ring are included to show the extreme deviation of this ring from the plane of the coordinating atoms.

One of the principal structural effects of N-methylation of the porphyrin ligand is in the position of the cobalt(II) ion relative to the plane of the coordinating nitrogen atoms. As is seen in Table VII, the cobalt ion is 0.555 Å out of the plane of the three strongly coordinating pyrrole nitrogen atoms (N2-4) in the direction of the apical chloride ion. This is an extremely large displacement, as may be seen by comparison with the position of the cobalt(II) ion in normal cobalt(II) porphyrin derivatives (for example, 0.144 Å above the plane of the four coordinating nitrogen atoms in the 3,5-dimethylpyridine-Co(TPP) complex[28]). Even if the best planes through the individual pyrrole rings are taken, the cobalt ion is considerably

Table VII. Deviations from Least-Squares Planes[a]

(a) Plane 1

Atoms determining plane: N1 (0.066), N2 (−0.089), N3 (−0.129), N4 (−0.129), C11 (−0.368), C12 (−1.051), C13 (−1.072), C14 (−0.376), C21 (−0.016), C22 (0.237), C23 (0.262), C24 (0.052), C31 (−0.006), C32 (0.250), C33 (0.253), C34 (−0.010), C41 (−0.005), C42 (0.092), C43 (0.038), C44 (−0.074), C1 (−0.180), C2 (−0.061), C3 (0.065), C4 (−0.205)

Other atoms: Co^{2+} (−0.665)

Plane 2

Atoms determining plane: N2 (−0.036), N3 (−0.089), N4 (−0.073), C21 (0.034), C22 (0.294), C23 (0.325), C24 (0.113), C31 (0.037), C32 (0.287), C33 (0.284), C34 (0.023), C41 (0.058), C42 (0.160), C43 (0.103), C44 (−0.018), C1 (−0.152), C2 (−0.011), C3 (0.130), C4 (−0.162)

other atoms: Co^{2+} (−0.618), N1 (0.103), C11 (−0.338), C12 (−1.025), C13 (−1.042), C14 (−0.339)

Plane 3

Atoms determining plane: N2, N3, N4.

Other atoms: Co^{2+} (0.555), N1 (−0.154)

Plane 4

Atoms determining plane: N1 (0.000), C11 (−0.006), C12 (0.002), C13 (−0.004), C14 (0.004).

Other atoms: Co^{2+} (−1.794), C1 (−0.080), C4 (−0.056)

Plane 5

Atoms determining plane: N2 (0.006), C21 (−0.016), C22 (0.018), C23 (0.004), C24 (−0.011)

Other atoms: Co^{2+} (−0.272), C3 (0.020), C4 (−0.106)

Plane 6

Atoms determining plane: N3 (0.004), C31 (−0.014), C34 (−0.025), C32 (0.006), C33 (0.002)

Other atoms: Co^{2+} (−0.184), C1 (−0.134), C2 (0.002)

Plane 7

Atoms determining plane: N4 (−0.001), C41 (0.014), C42 (0.000), C43 (−0.009), C44 (0.017)

Other atoms: Co^{2+} (−0.360), C2 (0.113), C3 (0.081)

Plane 8

Atoms determining plane: Ph11-Ph16

Other atoms: C1 (−0.018)

Plane 9

Atoms determining plane: Ph21-Ph26

Other atoms: C2 (0.000)

Plane 10

Atoms determining plane: Ph31-Ph36

Other atoms: C3 (0.107)

Plane 11

Atoms determining plane: Ph41-Ph46

Other atoms: C4 (−0.026)

(b) Equations of the Planes[b]

Plane no.	*A*	*B*	*C*	*D*	Plane no.	*A*	*B*	*C*	*D*
1	4.700	−0.374	−14.476	−2.143	7	5.208	−0.901	−13.493	−2.188
2	4.672	−0.325	−14.529	−2.201	8	0.056	8.210	11.764	4.216
3	−4.645	0.523	14.521	2.302	9	6.186	−9.296	0.720	0.055
4	7.023	−0.393	−7.925	1.117	10	5.893	7.831	−0.590	2.147
5	4.856	−2.622	−13.447	−2.638	11	0.537	−8.668	15.857	2.376
6	4.569	2.194	−14.976	−2.326					

(c) Selected Dihedral Angles between Planes (degrees)

3-1	0.81	3-5	8.34	3-7	5.85	2-10	69.83
3-2	0.82	3-6	10.45	2-8	50.60	2-11	52.78
3-4	31.59			2-9	60.42		

[a] In section (a), numbers in parentheses refer to the distance (in Å) of the given atom from the calculated plane. [b] In the form $Ax + By + Cz = D$.

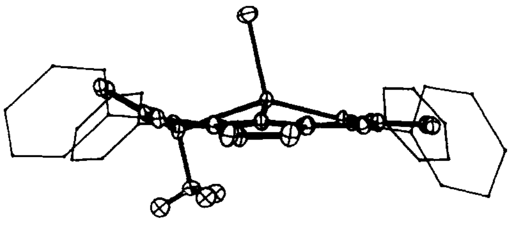

Figure 3. A side-on view of the Co(N-CH$_3$TPP)Cl complex, showing the large out-of-plane displacement of the metal ion and the deviation of the N-methylated pyrrole ring from the plane of the remainder of the porphyrin core.

above these planes in every case (from 0.18 Å for the N3 ring to 0.36 Å for the N4 ring). This very large out-of-plane axial displacement of the cobalt(II) ion is consistent with the high spin nature of the complex, and is a very dramatic feature of this structure as compared to the normal porphyrins. The large out-of-plane displacement is reflected in the angles at the cobalt ion, with the N_2-Co-N_3 angle of 147.8 (2) and the N-Co-Cl angles (from 7 to 16° greater than 90°) testifying to the extent of this axial displacement. Due to the methylation at N1, the angles N-Co-Cl are not uniform. The chloride group is not directly over the cobalt(II) ion, but is tilted slightly toward the methylated nitrogen (N1-Co-Cl 96.7 (1)° vs. N4-Co-Cl 116.6 (2)°). This unusual tilt of the chloride ion toward the N-substituted pyrrole ring was also seen in the *N*-ethylacetato-OEP derivative,[17] but occurs to a significantly smaller extent in the present structure.

The configuration of the porphyrin itself is dramatically altered by the N-methylation. Figure 3 makes clear the dramatic tilt in the orientation of the alkylated N1 pyrrole ring with respect to the roughly planar remainder of the porphyrin ligand. With respect to the plane of the strongly coordinating atoms N2-N4, for example, the least-squares plane through the N1 pyrrole ring lies at an angle of 31.6° (cf. dihedral angles of 8.3°, 10.4°, and 5.9° for the non-methylated pyrrole rings with respect to this same plane). This change of orientation is the expected accompaniment to the change in hybridization at N1 on methylation. The bond distances N1-C11 (1.416 (9) Å) and N1-C14 (1.415 (7) Å) are significantly longer than the corresponding N-C distances in the non-methylated pyrrole rings (average value 1.381 (3) Å), reflecting the decreased electron delocalization through N1 in the methylated pyrrole ring. The tilt in the plane of the N1 pyrrole ring also is such as to allow coordination of N1 to the cobalt(II) ion through the remaining lone pair.

Extensive delocalization still exists through the entire porphyrin ring, including the N1 ring, despite the large deviation

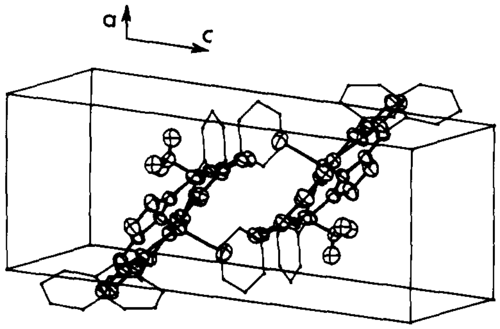

Figure 4. A view (in parallel projection) of the contents of one unit cell, to illustrate the packing arrangement of the Co(N-CH_3TPP)Cl complex units.

from planarity discussed above. This is made clear by a detailed comparison of the ligand bond lengths in a complex such as the 3,5-dimethylpyridine-Co(TPP) species studied by Scheidt and Ramanuja[28] with those in the *N*-methyl-TPP ligand of the present structure. The notation to be employed during the course of this comparison will be the standard one, in which the meso carbon is designated C_m, carbon adjacent to the pyrrole nitrogen is C_α, and the other type of carbon in the pyrrole ring is designated C_β. Thus, in the study by Scheidt and Ramanuja average bond lengths in the porphyrin ligand for the various types of bonds are quoted as: N-C_α 1.376 (7) Å, C_α-C_m 1.384 (8) Å, C_α-C_β 1.44 (1) Å, C_β-C_β 1.34 (1) Å, and C_m-C_p 1.497 (4) Å.

In the present structure, the average of the four C_β-C_β bond lengths is 1.362 Å, which clearly indicates the presence of electron delocalization through these bonds. It may be noted, however, that the difference between the C_β-C_β bond length of the N-alkylated pyrrole ring (C12-C13 1.382 (9) Å) and the three C_β-C_β bond lengths in the non-methylated pyrrole rings (average C_β-C_β for N2, N3, N4 rings 1.356 (5) Å) is possibly significant. The C_α-C_m bond lengths in the present study are all equal within experimental error, and, with an average value of 1.395 Å, compare closely to the corresponding value quoted above from the study by Scheidt and Ramanuja.[28] An appreciable difference is seen, however, for the length of the C_α-C_β bond in the methylated N1 ring (C11-C12 1.405 (8) Å, C14-C13 1.415 (9) Å) as compared to the non-methylated rings ($\overline{C_\alpha\text{-}C_\beta}$ 1.448 Å for the N2, N3, and N4 rings). Thus, bond length changes in the N-methylated pyrrole ring indicate that the electron delocalization through the N1 ring seems to be strongly altered according to the following pattern: lower delocalization through the N-C_α bond compared with the normal pyrrole rings (as noted above), higher delocalization through the C_α-C_β bond, and possibly lower delocalization through the C_β-C_β bond. This same pattern was also observed in the structure of the related free base form of 21-ethoxycarbonylmethyl-2,3,7,8,12,13,17,18-octaethylporphyrin, where N-alkylation of one of the pyrrole rings by the ethylacetato group resulted in bond distances for that ring of N-C_α 1.41 Å, C_α-C_β 1.41 Å, and C_β-C_β 1.38 Å.[38] Thus, it appears clear that the changes seen in the pattern of electron delocalization through the N-methylated pyrrole ring are a direct consequence of the change in hybridization at N1 on methylation. As expected, these changes in the pattern of electron delocalization for the N-methylated porphyrin are significantly different from the types of alterations seen in system such as the homoporphyrins[39] and porphodimethenes,[40] where the perturbations to the electronic π system of the porphyrin arise from very different sources.

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Supplementary Material Available: Table VIII, a listing of observed and calculated structure factor amplitudes (46 pages). Ordering information is given on any current masthead page.

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