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Structures of *N*-Methylporphyrin Complexes. 3.[1] Chloro-*N*-methyl-α,β,γ,δ-tetraphenylporphinatomanganese(II)

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The crystal and molecular structure of chloro-*N*-methyl-α,β,γ,δ-tetraphenylporphinatomanganese(II), $Mn(N_4C_{45}H_{31})Cl$, 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 $a = 7.558$ (6) Å, $b = 14.993$ (12) Å, $c = 17.476$ (13) Å, $\alpha = 103.13$ (2)°, $\beta = 97.09$ (3)°, and $\gamma = 94.00$ (2)°. The structure has been refined by least-squares methods to $R = 0.072$ ($R_w = 0.094$) for 3815 unique reflections with $F^2 > 3\sigma(F^2)$. The coordination geometry about the manganese(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 nitrogen atoms of the porphyrin ligand (Mn–N = 2.118 (5), 2.156 (5), and 2.155 (6) Å), while the alkylated nitrogen occupying the fourth position forms a much longer bond to manganese (Mn–N = 2.368 (5) Å). The apical position is occupied by the chloride ion (Mn–Cl = 2.295 (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 manganese(II) ion. The manganese(II) ion is displaced far out of the mean porphyrin plane toward the apical position and is high spin in this novel coordination environment.

Introduction

Recent definitive structural characterizations[2] of manganese(II)–porphyrin systems have demonstrated that the manganese(II) ions in these systems prefer to be high-spin, highly displaced out of the mean plane of the macrocycle, and five-coordinate. Interest in the study of manganese(II) porphyrins arises from the recent observation[3] of reversible binding of dioxygen by a synthetic manganese(II) porphyrin complex, *meso*-tetraphenylporphyrin(pyridine)manganese(II). Earlier studies on manganese(II)–porphyrin systems have included studies on incorporation of manganese porphyrins into protein systems.[4,5]

We have recently undertaken systematic synthetic, mechanistic, and structural studies of transition metal complexes of *N*-methylated porphyrin ligands.[1,6–9] In comparison with normal porphyrin systems, metal complexes of *N*-methylporphyrins show strong tendencies toward five-coordination, with large out-of-plane displacements of the metal ion, due to the strong stereochemical influence of the *N*-methyl group.[1,10] The geometric and electronic constraints attendant upon *N*-alkylation may allow these complexes to serve as models for the possible "sitting-atop" complexes which have been discussed as intermediates in metalation reactions of normal porphyrins.[11]

As one of the members of this series of complexes, the detailed structure of chloro-*N*-methyl-α,β,γ,δ-tetraphenylporphinatomanganese(II) has been determined by single-crystal x-ray diffraction methods. Manganese(II) in this complex is high-spin ($\mu_{\text{eff}} = 5.9 \pm 0.1\ \mu_B$ at 23 °C),[9] as is also the case with the manganese(II) complexes of nonmethylated *meso*-tetraphenylporphyrin.[2] In the complexes of the "planar"[12] porphyrins with manganese(II), the manganese ion is found out of the plane of the macrocycle to a large extent,[2] as a consequence of the high-spin electronic configuration. The degree of this out-of-plane displacement of the manganese(II) ion due to the electronic configuration about manganese will be compared in the present study with the large out-of-plane displacement required by the steric presence of the *N*-methyl group.

Experimental Section

The synthesis and analytical characterization of chloro-*N*-methyl-α,β,γ,δ-tetraphenylporphinatomanganese(II) has been previously reported.[9] The magnetic moment, μ_{eff}, of the title compound was determined to be 5.9 ± 0.1 μ_B at 23 °C (Faraday method, $Hg[Co(NCS)_4]$ calibrant, Cahn Research magnetic susceptibility system). A single crystal of the compound was characterized by x-ray fluorescence using a scanning electron microscope, and peaks characteristic of manganese and chlorine were observed.[13]

Crystal Data. For $Mn(N_4C_{45}H_{31})Cl$ (mol wt 718.12, triclinic), $a = 7.558$ (6) Å, $b = 14.993$ (12) Å, $c = 17.476$ (13) Å, $\alpha = 103.13$ (2)°, $\beta = 97.09$ (3)°, $\gamma = 94.00$ (2)°, $V = 1903.9$ Å^3, $\rho_{\text{calcd}} = 1.25$ g cm^{-3}, $Z = 2$, and $F(000) = 742$; space group $P\bar{1}$, Mo Kα radiation, λ_1 0.709 30 Å, λ_2 0.713 59 Å, and μ(Mo Kα) = 4.72 cm^{-1}.

Data Collection and Reduction. Preliminary Weissenberg and precession photographs revealed only Laue symmetry $\bar{1}$, consistent with the space groups $P1$ and $P\bar{1}$.[14] The photographs also showed that the crystal structure of the manganese(II) *N*-methyl-α,β,γ,δ-tetraphenylporphyrin complex was isomorphous with that of the corresponding cobalt(II) complex (see cell parameters reported above and ref 1). Due to this strong similarity in lattice spacings and symmetry, the centric space group $P\bar{1}$ was chosen for all further structural work with this compound.

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[15] 2θ, χ, and ϕ settings of 27 reflections (at ambient temperature, 20 (±1) °C) with 2θ values in the range 16–25°.

The intensities of 6616 unique reflections with $3.00° < \theta < 25.00°$ were measured by θ–2θ scans, employing Zr-filtered Mo Kα radiation. At θ values less than 3°, reflections were cut off on the low-θ side by the beam stop. The scan range employed was 1.2° (in 2θ) to either side of the calculated Kα 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

Table I. Atomic Coordinates (Fractional)[a]

Atom	x	y	z
Mn(II)	0.190 34 (12)	0.177 76 (6)	0.264 15 (6)
N1	0.504 5 (6)	0.191 8 (3)	0.302 7 (3)
N2	0.260 1 (6)	0.306 4 (3)	0.234 5 (3)
N3	0.233 0 (6)	0.033 9 (3)	0.236 2 (3)
N4	0.009 7 (6)	0.145 2 (3)	0.156 7 (3)
Cl^-	0.076 7 (3)	0.214 1 (1)	0.382 0 (1)
C5	0.564 1 (8)	0.171 3 (5)	0.222 7 (4)
C11	0.553 8 (8)	0.129 9 (4)	0.350 5 (4)
C12	0.644 9 (8)	0.180 2 (4)	0.424 3 (4)
C13	0.652 2 (8)	0.273 6 (4)	0.424 4 (4)
C14	0.566 9 (8)	0.281 7 (4)	0.350 3 (4)
C21	0.397 2 (8)	0.372 3 (4)	0.269 8 (4)
C22	0.376 6 (9)	0.455 1 (5)	0.241 5 (4)
C23	0.221 5 (9)	0.439 0 (4)	0.190 0 (4)
C24	0.149 7 (8)	0.345 3 (4)	0.185 8 (4)
C31	0.113 6 (8)	−0.034 4 (4)	0.188 1 (4)
C32	0.172 1 (9)	−0.123 5 (4)	0.190 6 (4)
C33	0.327 8 (9)	−0.107 9 (4)	0.241 3 (4)
C34	0.367 3 (8)	−0.009 3 (4)	0.270 6 (4)
C41	−0.068 9 (8)	0.208 6 (4)	0.121 0 (3)
C42	−0.225 0 (8)	0.163 0 (4)	0.065 1 (4)
C43	−0.235 8 (8)	0.073 1 (4)	0.067 7 (4)
C44	−0.086 4 (8)	0.061 3 (4)	0.123 6 (3)
C1	0.510 2 (8)	0.033 7 (4)	0.326 3 (4)
C2	−0.042 9 (8)	−0.022 1 (4)	0.139 2 (3)
C3	−0.006 9 (8)	0.302 0 (4)	0.134 8 (3)
C4	0.539 1 (8)	0.362 9 (4)	0.326 7 (4)
H12	0.693 2	0.155 1	0.466 7
H13	0.705 5	0.323 2	0.467 1
H22	0.456 2	0.510 0	0.256 1
H23	0.170 2	0.480 7	0.162 2
H32	0.112 8	−0.181 7	0.162 3
H33	0.411 9	−0.138 4	0.268 4
H42	−0.304 0	0.190 8	0.033 0
H43	−0.325 5	0.026 3	0.038 1
H1C5	0.504 4	0.114 1	0.192 1
H2C5	0.535 3	0.218 9	0.196 9
H3C5	0.690 0	0.168 0	0.228 7

[a] Estimated standard deviations in parentheses.

maximum of five 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 (00$\bar{5}$, 0$\bar{6}$0, and 20$\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[16,17] was taken as 0.04. Reflections for which $F^2 > 3\sigma(F^2)$ were judged to be observed and the 3815 reflections which met this criterion were employed in the solution and refinement of the structure. Due to the very low absorption coefficient ($\mu = 4.72$ 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 0.25 × 0.22 × 0.35 mm (long dimension along a).

Solution and Refinement of the Structure. Due to the noted similarities between lattice parameters, the final refined atomic coordinates from the chloro-*N*-methyl-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatocobalt(II) structure[1] were used to assign the initial coordinates of all nonhydrogen atoms. Scattering factors for manganese(II), chloride ion, carbon, and nitrogen were taken from ref 18. Scattering factors for spherically bonded hydrogen atoms[19] were also taken from ref 18, as were correction terms $\Delta f'$ and $\Delta f''$ for anomalous dispersion due to manganese and chlorine.

Due to computer limitations, least-squares refinement[20] of the structure was carried out in the same manner as for the corresponding cobalt(II) complex.[1] As before, the phenyl groups were refined as rigid, planar bodies of D_{6h} symmetry, with fixed C–C distances of 1.397 Å.[21] Hydrogen atoms were included in fixed, idealized positions 0.95 Å away from carbon, with isotropic thermal parameters 1 Å^2 larger than those of the carbon atoms to which they were attached.

Table II. Anisotropic Thermal Parameters[a]

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Mn(II)	123 (2)	30 (1)	24 (1)	5 (1)	−7 (1)	7 (1)
N1	132 (10)	32 (2)	24 (2)	7 (4)	0 (3)	9 (2)
N2	125 (10)	32 (3)	25 (2)	0 (4)	−11 (4)	10 (2)
N3	134 (10)	28 (2)	26 (2)	6 (4)	−12 (4)	3 (2)
N4	132 (10)	33 (3)	22 (2)	6 (4)	−7 (3)	7 (2)
Cl^-	262 (5)	65 (1)	37 (1)	6 (2)	35 (2)	7 (1)
C5	161 (14)	56 (4)	25 (2)	19 (6)	16 (5)	12 (3)
C11	100 (11)	40 (3)	30 (3)	12 (5)	−3 (4)	12 (2)
C12	144 (13)	40 (4)	32 (3)	6 (5)	−14 (5)	5 (2)
C13	142 (13)	44 (4)	31 (3)	9 (5)	−8 (5)	12 (2)
C14	105 (11)	37 (3)	28 (2)	−4 (5)	−7 (4)	7 (2)
C21	136 (12)	31 (3)	26 (2)	−1 (5)	−2 (4)	8 (2)
C22	187 (15)	40 (4)	41 (3)	9 (6)	−14 (6)	19 (3)
C23	187 (15)	37 (3)	37 (3)	−8 (6)	−10 (5)	14 (3)
C24	137 (12)	33 (3)	29 (2)	6 (5)	−5 (4)	10 (2)
C31	146 (13)	30 (3)	30 (3)	3 (5)	2 (5)	6 (2)
C32	178 (15)	36 (3)	44 (3)	9 (6)	−15 (6)	7 (3)
C33	203 (16)	35 (3)	41 (3)	14 (6)	−14 (6)	6 (3)
C34	140 (13)	35 (3)	31 (3)	11 (5)	1 (5)	9 (2)
C41	118 (12)	42 (3)	22 (2)	8 (5)	−2 (4)	9 (2)
C42	123 (12)	44 (4)	30 (3)	−6 (5)	−3 (4)	8 (2)
C43	128 (12)	44 (4)	28 (3)	14 (5)	−3 (4)	6 (2)
C44	106 (11)	35 (3)	24 (2)	5 (5)	−2 (4)	4 (2)
C1	132 (13)	34 (3)	28 (2)	11 (5)	1 (4)	8 (2)
C2	133 (12)	35 (3)	22 (2)	−2 (5)	−3 (4)	2 (2)
C3	140 (12)	34 (3)	28 (2)	6 (5)	−2 (4)	11 (2)
C4	124 (12)	32 (3)	33 (3)	−6 (5)	−5 (4)	8 (2)

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

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.

The least-squares refinement (on F) ultimately lowered R $(=[\sum||F_o| - |F_c||/\sum|F_o|])$ to its final value of 0.072 (unobserved reflections not included) and R_w $(=[\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2})$ to 0.094. The error in an observation of unit weight was 1.68. On the final pair of refinement cycles, 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 secondary extinction was not deemed necessary. A final difference Fourier electron density map showed no peak higher than 0.31 e Å^{-3} and no depression lower than −0.36 e Å^{-3}.

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 Mn(II) in the chloro-*N*-methyl-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatomanganese(II) complex (hereafter abbreviated as Mn(*N*-CH_3TPP)Cl) are reported in Table V, while the bond lengths and angles within the *N*-methyltetraphenylporphyrin ligand (hereafter *N*-CH_3TPP) 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 numbering scheme used in the following discussion are shown in Figure 1. Numbering of all atoms was carried out in exactly the same manner as for the corresponding cobalt(II) complex, Co(*N*-CH_3TPP)Cl.[1] Figure 2 shows the coordination geometry in detail.

These first two figures make clear the great similarity between the Mn(*N*-CH_3TPP)Cl and Co(*N*-CH_3TPP)Cl complexes. The manganese(II) ion is five-coordinate, with the

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

Group	x_g[b]	y_g	z_g	δ[c]	ϵ	η
Ph1	0.7459 (4)	−0.0723 (2)	0.4029 (2)	−2.959 (3)	−2.580 (3)	−2.887 (3)
Ph2	−0.2799 (4)	−0.1859 (2)	0.0635 (2)	−0.669 (3)	2.984 (2)	1.484 (3)
Ph3	−0.1866 (4)	0.4166 (2)	0.0446 (2)	−2.435 (6)	2.064 (2)	1.398 (6)
Ph4	0.7798 (4)	0.5223 (2)	0.4077 (2)	2.934 (3)	2.557 (3)	−2.878 (4)

[a] Estimated standard deviations in parentheses. [b] x_g, y_g, and z_g are the fractional coordinates of the group centers. [c] The angles which describe the groups orientations have been defined previously.[22]

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

	Carbon				Hydrogen[b]		
Atom	x	y	z	B, Å^2	x_H	y_H	z_H
Ph11	0.6295 (5)	−0.0210 (3)	0.3664 (3)	3.1 (1)			
Ph12	0.5630 (5)	−0.0813 (3)	0.4088 (3)	4.7 (2)	0.4321	−0.0878	0.4130
Ph13	0.6794 (7)	−0.1327 (3)	0.4453 (3)	5.9 (2)	0.6318	−0.1759	0.4756
Ph14	0.8623 (6)	−0.1237 (3)	0.4394 (3)	5.7 (2)	0.9456	−0.1604	0.4656
Ph15	0.9288 (4)	−0.0633 (3)	0.3970 (3)	5.1 (2)	1.0597	−0.0569	0.3928
Ph16	0.8123 (5)	−0.0120 (3)	0.3605 (3)	3.9 (1)	0.8599	0.0312	0.3301
Ph21	−0.1651 (5)	−0.1064 (2)	0.1000 (2)	2.9 (1)			
Ph22	−0.2490 (6)	−0.1565 (3)	0.1462 (2)	4.4 (1)	−0.2270	−0.1355	0.2054
Ph23	−0.3638 (6)	−0.2360 (3)	0.1097 (2)	5.2 (2)	−0.4238	−0.2718	0.1428
Ph24	−0.3946 (6)	−0.2654 (2)	0.0270 (3)	4.5 (1)	−0.4767	−0.3222	0.0008
Ph25	−0.3107 (6)	−0.2153 (3)	−0.0192 (2)	4.2 (1)	−0.3328	−0.2363	−0.0785
Ph26	−0.1960 (6)	−0.1358 (3)	0.0173 (2)	3.4 (1)	−0.1359	−0.1000	−0.0158
Ph31	−0.1055 (6)	0.3590 (3)	0.0880 (2)	3.3 (1)			
Ph32	−0.9616 (6)	0.3448 (3)	0.0068 (2)	3.9 (1)	−0.0314	0.2934	−0.0201
Ph33	−0.1773 (7)	0.4023 (3)	−0.0366 (2)	4.8 (2)	−0.1706	0.3922	−0.0947
Ph34	−0.2677 (7)	0.4741 (3)	0.0011 (3)	5.0 (2)	−0.3258	0.5154	−0.0300
Ph35	−0.2771 (7)	0.4884 (3)	0.0823 (3)	5.4 (2)	−0.3418	0.5398	0.1093
Ph36	−0.1960 (7)	0.4308 (3)	0.1257 (2)	4.6 (1)	−0.2027	0.4410	0.1838
Ph41	0.6607 (5)	0.4450 (3)	0.3698 (3)	3.5 (1)			
Ph42	0.8432 (6)	0.4443 (3)	0.3636 (3)	4.6 (1)	0.8886	0.3885	0.3320
Ph43	0.9624 (4)	0.5217 (4)	0.4015 (3)	6.4 (2)	1.0931	0.5212	0.3970
Ph44	0.8990 (6)	0.5997 (3)	0.4456 (3)	6.4 (2)	0.9843	0.6551	0.4727
Ph45	0.7164 (7)	0.6004 (3)	0.4518 (3)	6.0 (2)	0.6711	0.6562	0.4834
Ph46	0.5973 (5)	0.5230 (3)	0.4139 (3)	4.7 (2)	0.4666	0.5235	0.4184

[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 Mn(II)[a]

(a) Bond Lengths			
Mn(II)-N1	2.368 (5)	Mn(II)-N4	2.118 (5)
Mn(II)-N2	2.155 (6)	Mn(II)-Cl$^-$	2.295 (3)
Mn(II)-N3	2.156 (5)		
(b) Bond Angles			
N1-Mn-Cl$^-$	104.2 (1)	Mn-N1-C11	111.4 (4)
N2-Mn-Cl$^-$	106.4 (1)	Mn-N1-C14	110.9 (4)
N3-Mn-Cl$^-$	109.6 (2)	Mn-N1-C5	99.7 (3)
N4-Mn-Cl$^-$	118.6 (2)	Mn-N2-C21	128.6 (4)
N1-Mn-N2	80.8 (2)	Mn-N2-C24	124.2 (4)
N1-Mn-N3	80.9 (2)	Mn-N3-C31	124.6 (4)
N1-Mn-N4	137.2 (2)	Mn-N3-C34	128.4 (3)
N2-Mn-N3	142.5 (2)	Mn-N4-C41	125.1 (3)
N2-Mn-N4	86.1 (2)	Mn-N4-C44	125.4 (4)
N3-Mn-N4	85.6 (2)		

[a] Estimated standard deviations in parentheses.

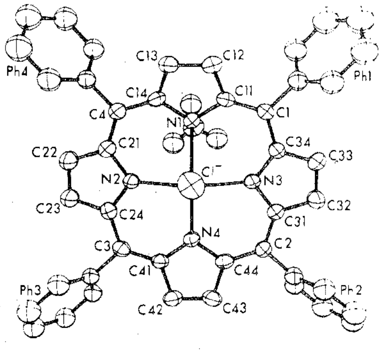

Figure 1. A view of the Mn(N-CH$_3$TPP)Cl complex from directly above the complex plane. The Mn(II) ion is obscured by the apical chloride ion in this top view, and the N-methyl group is seen partly obscured in its position below the alkylated nitrogen (N1).

methyl group on pyrrole nitrogen N1 providing effective stereochemical blockage against coordination of a sixth ligand species. The coordination geometry seen here is clearly based on the square pyramid, although it is seen to be considerably distorted, as was the case in the Co(N-CH$_3$TPP)Cl complex[1] and in the related N-ethylacetatoporphine derivative, chloro(2,3,7,8,12,13,17,18-octaethyl-N-ethylacetatoporphine)cobalt(II).[10]

Examination of the detailed coordination geometry of the manganese(II) ion in this complex reveals important differences from the related cobalt(II) complex.[1] As in the cobalt(II) complex, the Mn–N bond trans to the alkylated position is markedly shorter than the other two Mn–N distances (Mn–N4 2.118 (5) Å vs. 2.155 (6) and 2.156 (5) Å for Mn–N2 and Mn–N3, respectively). These bonds between manganese(II) and the nonalkylated pyrrole nitrogens are all approximately 0.1 Å longer than the corresponding Co–N bonds in Co(N-CH$_3$TPP)Cl (cf. Co–N4 = 2.016 (4), Co–N2 = 2.063 (5), Co–N3 = 2.063 (5) Å), which is expected on the grounds that the ionic radius of the high-spin manganese(II) ion is 0.08 Å greater (for the six-coordinate case) than for the high-spin cobalt(II) ion.[23] The fourth basal position in the primary coordination sphere of the manganese(II) ion is occupied by the alkylated pyrrole nitrogen atom (N1), which makes a long bond to manganese (Mn–N1 = 2.368 (5) Å). Interestingly, this bond, instead of being 0.1 Å longer than

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

(a) Bond Lengths

N1-C5	1.493 (8)	C12-C13	1.398 (10)
N1-C11	1.422 (9)	C13-C14	1.408 (9)
N1-C14	1.427 (7)	C11-C1	1.410 (8)
C11-C12	1.404 (8)	C14-C4	1.392 (9)
N3-C31	1.366 (7)	C33-C34	1.446 (9)
N3-C34	1.389 (8)	C31-C2	1.420 (8)
C31-C32	1.443 (10)	C34-C1	1.374 (8)
C32-C33	1.354 (10)		
N2-C21	1.362 (7)	C23-C24	1.452 (9)
N2-C24	1.371 (8)	C21-C4	1.408 (8)
C21-C22	1.448 (10)	C24-C3	1.410 (8)
C22-C23	1.452 (9)		
N4-C41	1.379 (8)	C43-C44	1.447 (8)
N4-C44	1.372 (7)	C41-C3	1.402 (8)
C41-C42	1.454 (8)	C44-C2	1.392 (9)
C42-C43	1.356 (10)		
C1-Ph11	1.478 (8)	C3-Ph31	1.486 (8)
C2-Ph21	1.486 (6)	C4-Ph41	1.476 (6)

(b) Bond Angles

C11-N1-C14	105.8 (5)	C24-C3-C41	125.1 (6)
C11-N1-C5	114.9 (5)	C41-N4-C44	107.2 (5)
C14-N1-C5	114.3 (5)	N4-C41-C3	125.8 (5)
N1-C11-C1	123.8 (5)	N4-C41-C42	109.3 (5)
N1-C11-C12	109.2 (5)	C3-C41-C42	125.0 (6)
C12-C11-C1	126.9 (6)	C41-C42-C43	106.6 (6)
C11-C12-C13	108.1 (6)	C42-C43-C44	107.8 (5)
C12-C13-C14	108.2 (5)	C43-C44-N4	109.1 (5)
C13-C14-N1	108.8 (6)	C43-C44-C2	125.6 (5)
C13-C14-C4	126.8 (5)	N4-C44-C2	125.3 (5)
N1-C14-C4	124.3 (5)	C44-C2-Ph21	118.4 (5)
C14-C4-Ph41	116.3 (5)	C31-C2-Ph21	116.4 (5)
C21-C4-Ph41	119.1 (1)	C44-C2-C31	125.2 (5)
C14-C4-C21	124.5 (5)	C31-N3-C34	106.4 (5)
C21-N2-C24	106.0 (5)	N3-C31-C2	126.1 (6)
N2-C21-C4	125.3 (6)	N3-C31-C32	110.4 (5)
N2-C21-C22	110.6 (5)	C2-C31-C32	123.5 (5)
C4-C21-C22	124.0 (5)	C31-C32-C33	106.7 (5)
C21-C22-C23	106.7 (6)	C32-C33-C34	107.6 (6)
C22-C23-C24	106.4 (6)	C33-C34-C1	125.2 (6)
C23-C24-N2	110.3 (5)	N3-C34-C33	108.9 (5)
C23-C24-C3	123.0 (6)	N3-C34-C1	125.8 (5)
N2-C24-C3	126.7 (6)	C34-C1-Ph11	120.3 (5)
C24-C3-Ph31	116.8 (5)	C11-C1-Ph11	115.2 (4)
C41-C3-Ph31	118.0 (6)	C34-C1-C11	124.5 (6)

[a] Estimated standard deviations in parentheses.

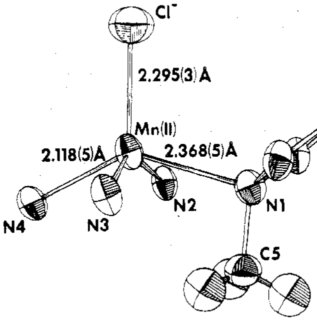

Figure 2. A view of the coordination geometry about the Mn(II) ion, showing the distorted square-pyramidal coordination geometry and the proximity of the *N*-methyl group (C5) to the metal ion. The carbon atoms of the N1 pyrrole ring are included to show the extreme deviation of this ring from the plane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

the corresponding bond in the Co(N-CH_3TPP)Cl complex, is, if anything, slightly shorter (cf. Co–N1 = 2.381 (5) Å in Co(N-CH_3TPP)Cl). Thus, it appears that the larger size of the manganese(II) ion is compensated by stronger bonding to the alkylated pyrrole nitrogen position than is seen in the cobalt(II) derivative. Strong stereochemical blockage on the base of the complex is implicit in the Mn–C5(methyl) distance of 3.004 (7) Å.

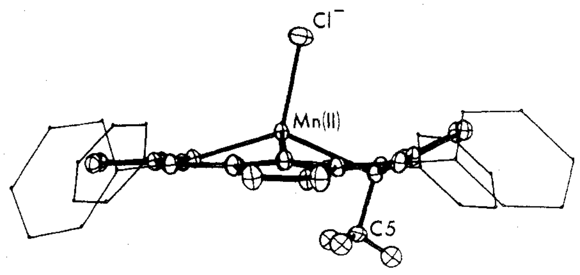

Figure 3. A side-on view of the Mn(N-CH_3TPP)Cl complex, showing the large out-of-plane displacement of the metal ion and the deviation of the *N*-methylated pyrrole ring from the plane of the remainder of the porphyrin core.

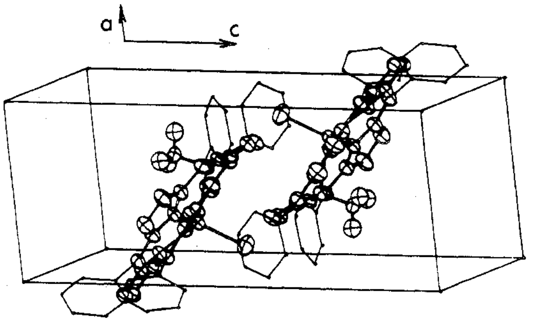

Figure 4. A view of the contents of one unit cell, illustrating the packing arrangement of the Mn(N-CH_3TPP)Cl complex units.

The position of the apical chloride ion relative to the manganese(II) ion and to the porphyrin ligand also provides some interesting differences when compared with its position in the Co(N-CH_3TPP)Cl structure. The larger size of the manganese(II) ion makes the Mn–Cl bond (Mn–Cl = 2.295 (3) Å) significantly longer than the Co–Cl bond (Co–Cl = 2.243 (2) Å) in the cobalt(II) complex. At the same time, the manganese(II) ion is displaced very considerably out of the plane of the coordinating nitrogen atoms (see Figure 3 and detailed comments below) toward the apical chloride ion. The chloride ion is not directly over the manganese(II) ion but is tilted slightly in the direction of the alkylated nitrogen atom, N1. This tilt is superimposed on the apical displacement of the manganese(II) ion and is reflected in the angles N4–Mn–Cl = 118.6 (2)° and N1–Mn–Cl = 104.2 (1)°. This tilt of the chloride ion in the manganese(II) complex is much less dramatic than in the Co(N-CH_3TPP)Cl complex, where angles N4–Co–Cl = 116.6 (2)° and N1–Co–Cl = 96.7 (1)° were seen.

As mentioned above, the manganese(II) ion is far above the mean plane of the porphyrin ligand (see Table VII). This displacement is presumably due to the combined effects of alkylation at pyrrole nitrogen N1 and to the high-spin electronic configuration about manganese(II). The manganese(II) ion in Mn(N-CH_3TPP)Cl is 0.69 Å above the plane of the three strongly coordinating pyrrole nitrogens (N2–N4) in the direction of the apical chloride ligand. Even if the best planes through the individual pyrrole rings are taken, the manganese ion is considerably above these planes in every case (0.33 Å above the plane of N2 pyrrole ring, 0.25 Å above the N3 pyrrole ring, and 0.54 Å above the N4 pyrrole ring). All of these displacements are considerably larger than the corresponding distances in the Co(N-CH_3TPP)Cl complex.

In contrast to the situation for cobalt(II), where *N*-methylporphyrin complexes[1,10] are high spin and the complexes of "planar" porphyrins[12] are low spin,[24-29] both the manganese(II) *N*-methylporphyrin complex reported herein and

Table VII

(a) Deviations from Least-Squares Planes[a]

Plane 1

Atoms determining plane: N1 (0.079), N2 (−0.138), N3 (−0.184), N4 (−0.134), C11 (−0.397), C12 (−1.015), C13 (−1.019), C14 (−0.351), C21 (−0.024), C22 (0.257), C23 (0.274), C24 (0.030), C31 (−0.026), C32 (0.250), C33 (0.248), C34 (−0.028), C41 (−0.014), C42 (0.074), C43 (0.020), C44 (−0.077), C1 (−0.175), C2 (−0.064), C3 (0.045), C4 (−0.172)
Other atoms: Mn^{2+} (−0.849)

Plane 2

Atoms determining plane: N2 (−0.074), N3 (−0.134), N4 (−0.071), C21 (0.039), C22 (0.325), C23 (0.347), C24 (0.099), C31 (0.024), C32 (0.294), C33 (0.288), C34 (0.015), C41 (0.055), C42 (0.147), C43 (0.088), C44 (−0.015), C1 (−0.134), C2 (−0.008), C3 (0.117), C4 (−0.116)
Other atoms: Mn^{2+} (−0.792), N1 (0.129), C11 (−0.313), C12 (−0.974), C13 (−0.973), C14 (−0.300)

Plane 3

Atoms determining plane: N2, N3, N4
Other atoms: Mn^{2+} (0.689), N1 (−0.267)

Plane 4

Atoms determining plane: N1 (0.000), C11 (−0.008), C12 (0.002), C13 (−0.002), C14 (−0.001)
Other atoms: Mn^{2+} (−1.891), C1 (−0.062), C4 (−0.050)

Plane 5

Atoms determining plane: N2 (0.003), C21 (−0.008), C22 (0.012), C23 (−0.003), C24 (−0.004)
Other atoms: Mn^{2+} (−0.330), C3 (0.053), C4 (−0.050)

Plane 6

Atoms determining plane: N3 (0.001), C31 (−0.003), C34 (−0.006), C32 (0.002), C33 (0.000)
Other atoms: Mn^{2+} (−0.249), C1 (−0.072), C2 (0.040)

Plane 7

Atoms determining plane: N4 (−0.001), C41 (0.016), C42 (0.001), C43 (−0.012), C44 (0.021)
Other atoms: Mn^{2+} (−0.545), C2 (0.111), C3 (0.072)

Plane 8

Atoms determining plane: Ph11–Ph16
Other atoms: C1 (−0.011)

Plane 9

Atoms determining plane: Ph21–Ph26
Other atoms: C2 (0.003)

Plane 10

Atoms determining plane: Ph31–Ph36
Other atoms: C3 (0.106)

Plane 11

Atoms determining plane: Ph41–Ph46
Other atoms: C4 (−0.043)

(b) Equations of Planes[b]

Plane no.	*A*	*B*	*C*	*D*
1	4.752	−0.389	−14.525	−2.153
2	4.733	−0.339	−14.566	−2.215
3	−4.829	0.567	14.363	2.286
4	7.049	−0.572	−8.184	0.969
5	4.847	−3.112	−13.337	−2.824
6	4.624	2.557	−15.030	−2.387
7	5.235	−0.887	−13.598	−2.208
8	−0.038	8.289	11.748	4.104
9	6.193	−9.420	1.038	0.084
10	5.957	7.869	−0.694	2.136
11	0.513	−8.620	15.987	2.415

(c) Selected Dihedral Angles between Planes (deg)

3–1	1.0	3–6	12.0	2–9	61.3
3–2	1.2	3–7	4.2	2–10	69.6
3–4	29.2	2–8	50.2	2–11	52.6
3–5	9.8				

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

manganese(II) complexes with "planar" porphyrins[2] are high-spin complexes. Thus, comparisons between the present structure and the structures of the "planar" manganese(II) porphyrins are much more meaningful in terms of deciphering the structural effects of *N*-methylation of the N1 pyrrole ring.

In the structure of the 1-methylimidazole adduct of Mn(TPP) (TPP is the dianion of α,β,γ,δ-tetraphenylporphyrin), the Mn–N (pyrrole) bond lengths average 2.128 Å, only slightly shorter than the Mn–N2 and Mn–N3 bond lengths reported above for the Mn(*N*-CH_3TPP)Cl structure.

Thus, the bonding to the nonmethylated pyrrole nitrogen atoms seems to be as strong in the *N*-methylporphyrin complex as in the normal five-coordinate Mn^{II}–TPP complex. It may be noted that the Mn^{II}–N bond length in the four-coordinate high-spin Mn(TPP) complex is significantly shorter in length at 2.090 Å,[2] reflecting a slight increase in Mn–N bond strength in the absence of an apical ligand. In the Mn(TPP)(1-MeIm) (1-MeIm = 1-methylimidazole) complex, the manganese(II) ion was found to be displaced 0.56 Å out of the mean porphyrin plane. Comparison is difficult due to the lack of planarity of the *N*-CH_3TPP ligand in the present structure, but the displacement of the Mn(II) ion seems even larger in the Mn(*N*-CH_3TPP)Cl complex. For example, the Mn(II) ion is 0.79 Å above the best plane calculated through pyrrole rings 2, 3, and 4 and the meso carbon atoms and 0.69 Å above the plane through nitrogen atoms N2, N3, and N4. In the four-coordinate Mn(TPP) complex,[2] the displacement of manganese(II) out of the ligand plane is much less dramatic, being estimated as at least 0.19 Å. Thus, it appears that the "out-of-plane" displacement of the manganese(II) ion is much more pronounced than in the nonmethylated porphyrin complexes. A very large displacement of this type is consistent with the high-spin d^5 electronic configuration about the metal ion, since in this configuration the $d_{x^2-y^2}$ orbital must be populated.[2,30,31]

The configuration of the porphyrin ligand itself in Mn(*N*-CH_3TPP)Cl is very similar to that found in the Co(*N*-CH_3TPP)Cl structure. 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. If the N2–N3–N4 plane is adopted as a reference plane, the least-squares plane through the N1 pyrrole ring makes an angle of −29.2° with this reference plane. This may be compared to the dihedral angles of 9.8, 12.0, and 4.2° between the planes through the N2, N3, and N4 pyrrole rings and the reference plane. This change in orientation of the N1 pyrrole ring is a result of the altered hybridization at pyrrole nitrogen atom N1 on methylation at this position. The increased p-orbital character at N1 after methylation is reflected in the bond lengths to the adjacent carbon atoms (N1–C11 = 1.422 (9) Å, N1–C14 = 1.427 (7) Å). These distances are essentially equal to the corresponding distances in the Co(*N*-CH_3TPP)Cl structure, and are significantly longer than the corresponding N–C distances in the nonalkylated pyrrole rings (average N–C_α distance 1.373 Å in Mn(*N*-CH_3TPP)Cl), where the nitrogen atoms are still essentially sp^2 hybridized.

As in the Co^{II}-*N*-CH_3TPP complex, extensive delocalization still exists through the entire porphyrin macrocycle, including the N1 ring. Adopting the standard notation, in which the meso carbons are designated C_m, carbon adjacent to pyrrole nitrogen is C_α, and the other pyrrole ring carbons are C_β, the average bond lengths for various types of bonds in a typical "planar" porphyrin structure[24] are as follows: 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, C_m–C_p = 1.497 (4) Å. Beginning with the C_β–C_β bonds in the Mn(*N*-CH_3TPP)Cl complex, the magnitudes of all four bond lengths indicate significant delocalization of electrons still present across these bonds (C12–C13 = 1.398 (10) Å, C22–C23 = 1.357 (9) Å, C32–C33 = 1.354 (10) Å, C42–C43 = 1.356 (10) Å). The C12–C13 bond is seen to be significantly longer than the average of the other three C_β–C_β bonds (1.356 (6) Å), in agreement with the trend suggested for the corresponding bonds by the results for the Co(*N*-CH_3TPP)Cl complex.[1] The C_α–C_m bonds of the Mn(*N*-CH_3TPP)Cl complex are all equivalent, with an average length of 1.401 Å (cf. 1.395 Å for $\overline{C_\alpha-C_m}$ in Co(*N*-CH_3TPP)Cl). Finally, the C_α–C_β bond lengths do exhibit considerable differences on comparing the alkylated pyrrole ring with the nonmethylated rings. In the *N*-methylated N1 ring, the bond lengths C11–C12 (1.404 (8) Å) and C13–C14 (1.408 (9) Å) clearly indicate a larger amount of delocalization through these bonds than for the corresponding bonds in the nonmethylated pyrrole rings ($\overline{C_\alpha-C_\beta}$ = 1.448 Å), as well as being significantly shorter than the average C_α–C_β bond distance of 1.44 (1) Å quoted earlier as being typical for the planar porphyrin systems.

The general structural similarity of the Mn(II) and Co(II) complexes of *N*-methyltetraphenylporphyrin gives some insight into the electrochemical behavior of these complexes, which has recently been reported.[8] Mn(*N*-CH_3TPP)Cl and Co(*N*-CH_3TPP)Cl both undergo a metal-center oxidation at 0.77 V vs. Ag/AgCl in acetonitrile solution. The complexes in the reduced state are both high spin, and the electron removed should have substantial $d_{x^2-y^2}$ orbital character in each case. The similar structures of the reduced forms and essentially identical oxidation potentials lead to the prediction that the structures and spin states of the oxidized complexes are very similar also, barring fortuitous compensation effects. This result is in marked contrast to the electrochemical behavior of the MnTPP and CoTPP complexes. The reduction of Mn(TPP)(Cl)H_2O occurs at −0.21 V[32] vs. Ag/AgCl while that of Co(TPP)Cl occurs at 0.52 V.[33] The structures of Co(II)[24–29] and Co(III)[34–36] porphyrins show coordination number changes as well as bond length alterations. The spin states of CoTPP and Co(TPP)Cl are both low spin. MnTPP and Mn(TPP)(Cl)H_2O are both high spin.[32] The structure of MnTPP has recently been reported,[2] and structural comparison of this complex with the six-coordinate Mn(TPP)(Cl)H_2O again shows a difference in coordination number. It appears, therefore, that the structural similarity of *N*-alkylated porphyrin complexes may well make interpretation of electrochemical behavior as a function of d-orbital population a more straightforward matter than in the case of nonalkylated porphyrin complexes. The similarities make a study of the electron-transfer rates of metal complexes in this novel coordination geometry an intriguing prospect.

Thus, it appears that the larger size of the manganese(II) ion, as compared to cobalt(II), has resulted in a much more regular coordination geometry in Mn(*N*-CH_3TPP)Cl than was seen in the Co(*N*-CH_3TPP)Cl complex[1] or in the very similar *N*-ethylacetatoporphyrin derivative of cobalt(II).[10] In particular, a stronger bond to the alkylated pyrrole nitrogen atom and increased out-of-plane displacement of the metal ion toward the apical chloride ion are prominent features of this structure. Studies employing even larger metal ions (including Ag(I) and Hg(II)) to form complexes with *N*-CH_3TPP are under way in these laboratories.

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Registry No. Mn(*N*-CH_3TPP)Cl, 59765-80-9.

Supplementary Material Available: Listing of observed and calculated structure factor amplitudes (45 pages). Ordering information is given on any current masthead page.

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Preparation, Properties, and Crystal and Molecular Structure of Ethylenediammonium Tetrachlorocobaltate(II) Chloride, $(NH_3CH_2CH_2NH_3)_2(CoCl_4)Cl_2$

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The compound ethylenediammonium tetrachlorocobaltate(II) chloride, $(NH_3CH_2CH_2NH_3)_2(CoCl_4)Cl_2$, has been prepared and its structure determined crystallographically. This substance crystallizes in the centrosymmetric orthorhombic space group *Pnam* [$D_{2h}{}^{16}$; No. 62] with $a = 12.884$ (9), $b = 6.151$ (5), $c = 19.291$ (7) Å; $Z = 4$. X-ray diffraction data complete to $2\theta = 50°$ (Mo Kα radiation) were collected with a Picker FACS-I diffractometer, and the structure was solved by means of Patterson and Fourier syntheses. All atoms, including hydrogens, have been located; convergence of the least-squares refinement process occurred with $R_F = 4.4\%$ and $R_{wF} = 3.7\%$ for 1477 independent reflections. The crystal is formed from distorted tetrahedral $CoCl_4{}^{2-}$ ions: the largest difference in Co–Cl bond lengths is 0.041 Å and the largest difference in the Cl–Co–Cl angles is 23.0°; it also contains diprotonated ethylenediamine ions and chloride ions. An extensive hydrogen-bonding network connects these species and probably accounts for the $CoCl_4{}^{2-}$ ion distortions. Visible and infrared spectra are consistent with the structural data.

Introduction

Several years ago while attempting to prepare the well-known green *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride following a published procedure,[2] we obtained varying mixtures of the desired compound with an unexpected blue product. The blue product, which had been reported by earlier workers,[3,4] was found to have the composition $CoCl_2{\cdot}2en{\cdot}4HCl$ (en = ethylenediamine). In agreement with earlier work, we found that the controlling factor in the synthesis of these two compounds is the concentration of hydrochloric acid. A curious additional feature of our study was the discovery that two different crystalline forms of the blue compound could be isolated, only one of which had been reported previously, and this suggested the possibility of isomerism or some other structural difference.

A limited investigation of the electronic spectrum had led Schultz[5] to the speculation that the blue compound was a salt of the formula $(enH_2)_2(CoCl_6)$. This would be consistent with the empirical formula, but the blue color strongly suggests the presence of the tetrahedral $CoCl_4{}^{2-}$ chromophore. Since no other examples of a hexachlorocobaltate(II) ion are known, we undertook a more complete characterization of the compound, including determination of the x-ray crystal structure, in order to establish unambiguously the structure of the negative ion present. We also investigated possible structural differences in the two crystal modifications of the compound.

Experimental Section

Preparation and Properties. (a) Plate Crystals. Cobalt(II) chloride hexahydrate (10 g, 44 mmol) was dissolved in 30 mL of concentrated hydrochloric acid (350 mmol). To this mixture a solution of ethylenediamine (2.7 g, 45 mmol) in 10 mL of water was added dropwise with stirring, producing a highly exothermic reaction. The mixture was heated briefly to produce a clear solution and then allowed to cool slowly to 0 °C. Blue thin tabular crystals were deposited in high yield. These were washed with ethanol and ether and dried at 100 °C. Anal. Calcd for $(C_2H_{10}N_2)_2CoCl_6$: C, 12.1; H, 5.1; N, 14.1; Cl, 53.7. Found: C, 11.9; H, 5.1; N, 14.0; Cl, 53.5 ± 0.1. (Cl was determined gravimetrically as AgCl; C, H, and N analyses were performed by Midwest Microlab.)

(b) Needle Crystals. The same quantities of reagents were used as above, but the cobalt chloride was first dissolved in water along with the ethylenediamine, followed by slow addition of the concentrated HCl. After brief heating and slow cooling of the mixture to 0 °C, blue long prismatic crystals were deposited in high yield. These were