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Stereochemistry of Manganese Porphyrins. I. Molecular Stereochemistry of Chloro- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinato(pyridine)manganese(III)

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Chloro- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinato(pyridine)manganese(III) crystallizes in the monoclinic system, space group $P2_1/n$, as the benzene solvate. The unit cell has $a = 13.149$ (3) Å, $b = 23.380$ (6) Å, $c = 14.786$ (4) Å, and $\beta = 100.50$ (1)° and contains four molecules. The calculated and experimental densities are 1.277 and 1.292 g/cm³, respectively, at $20 \pm 1^\circ$. Measurement of diffracted intensities employed θ - 2θ scans with graphite-monochromated Mo K α radiation on a Syntex four-circle diffractometer. All independent reflections for $(\sin \theta)/\lambda \leq 0.626 \text{ \AA}^{-1}$ were measured; 4980 reflections were retained as observed. These data were employed for the determination of structure using the heavy-atom method and least-squares refinement. The final conventional and weighted discrepancy factors were 0.055 and 0.075, respectively. The octahedral MnN₅Cl coordination group has an average equatorial Mn-N bond length of 2.009 Å. The axial Mn-Cl bond length is 2.467 (1) Å and the axial Mn-N bond length is 2.444 (4) Å; the elongation of the axial bonds is attributable to the unpaired electron in the d_{z^2} orbital of the high-spin manganese(III) ion.

Six-coordinate high-spin manganese(III) complexes should have a distorted coordination group resulting from the removal of the degeneracy between the d_{z^2} and the $d_{x^2-y^2}$ orbitals. With six equivalent ligands, the degeneracy is removed by a Jahn-Teller distortion. Nonequivalent ligands should also remove the degeneracy (without the necessity of invoking the Jahn-Teller theorem); the distorted octahedral complex will have (for either case) two long and four short bonds or four long and two short bonds. With nonequivalent bidentate ligands, bond length differences (two long, four short) of 0.13-0.17 Å have been observed.^{1,2}

Consequently, six-coordinate high-spin manganese(III) porphyrins might be expected to have a coordination group in which the axial bonds were 0.15-0.20 Å longer than normal. However, earlier studies of low-spin six-coordinate cobalt(II) macrocycles³⁻⁵ have shown that the tetragonal elongation resulting from the population of d_{z^2} orbital is substantially larger than 0.2 Å. For the cobalt(II) porphyrin derivatives studied,^{3,4} the axial bond elongation amounted to 0.4-0.5 Å. Thus it seemed likely that the axial bonds in the six-coordinate manganese(III) porphyrins might display larger elongations than those previously observed for manganese(III) complexes utilizing bidentate ligands.^{1,2}

All attempts to prepare manganese(III) porphyrin derivatives with two Lewis bases as the axial ligands failed⁶ and

only derivatives with an anion and a neutral Lewis base as the axial ligands could be obtained as crystalline solids. We report herein the quantitative molecular stereochemistry of one such derivative, chloro- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinato(pyridine)-manganese(III), to be written as Cl(py)MnTPP.⁹ While this study was in progress, the structure of N₃(CH₃OH)MnTPP was reported¹⁰ and we compare herein the pertinent stereochemical features of the two complexes.

Experimental Section

Chloro- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinato(pyridine)manganese(III). Crystals of Cl(py)MnTPP were obtained as the benzene solvate by slow evaporation of 1:1 benzene-pyridine solutions of ClMnTPP. Crystals were mounted in thin-walled capillaries to prevent loss of the solvate molecules. Preliminary X-ray photographic study established a four-molecule monoclinic unit cell. Systematic extinctions suggested $P2_1/n$ as the uniquely probable space group.¹¹ Precise lattice constants and diffracted intensities were derived from measurements carried out on a Syntex P1 diffractometer using a crystal of dimensions $0.2 \times 0.3 \times 0.5$ mm. The setting angles of 30 reflections, each collected at $\pm 2\theta$, were determined ($\lambda 0.71069$ Å) using the automatic centering program supplied with the computer-controlled diffractometer. All measurements were made at the ambient laboratory temperature of $20 \pm 1^\circ$. Least-squares refinement of these 30 reflections led to the lattice constants $a = 13.149$ (3) Å, $b = 23.380$ (6) Å, $c = 14.786$ (4) Å, and $\beta = 100.50$ (1)°. For a cell containing four molecules (MnClN₅C₄₉H₃₃C₆H₆) the density was calculated

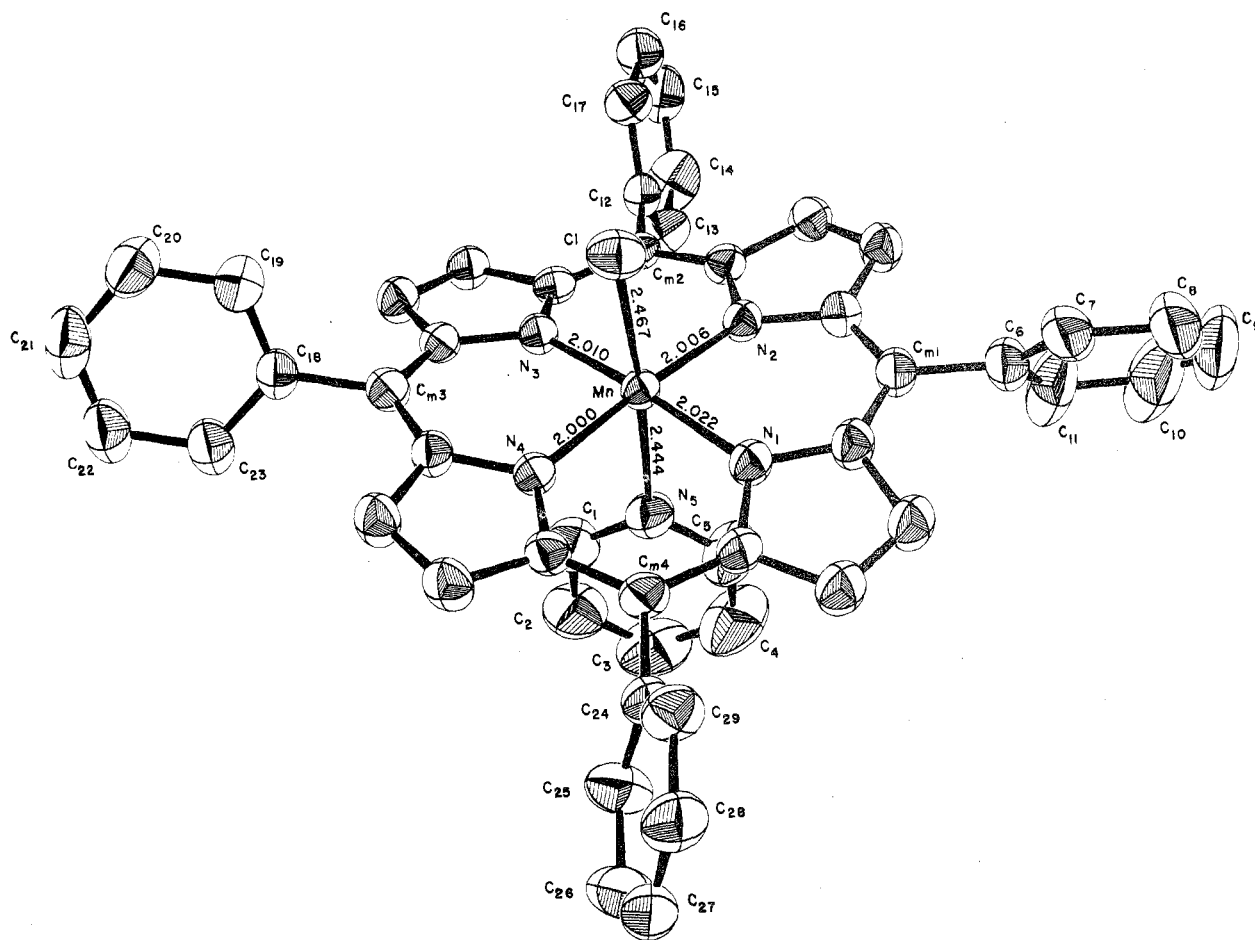


Figure 1. Computer-drawn model in perspective of the Cl(py)MnTPP molecule. Each atom is represented by an ellipsoid having the orientation and relative size concomitant with the thermal parameters listed in Table II. The bond distances of the coordination group are also shown.

to be 1.277 g/cm³; the experimental density of freshly prepared crystals was found to be 1.292 (5) g/cm³.

Intensity data were collected on a Syntex *P* $\bar{1}$ diffractometer using graphite-monochromated Mo K α radiation at a takeoff angle of $\sim 4^\circ$. The θ - 2θ scanning technique was employed with a scan range of 1.0° at $2\theta = 0^\circ$ and an increment to allow for spectral dispersion; background counts were taken at the extremes of the scan for a duration of 0.5 times the time required for the scan itself. Other data collection techniques were the same as previously described.³ Four standard reflections that were well distributed in reciprocal space were used for periodic checking (every 50 reflections) on the alignment and possible deterioration of the crystal; a small monotonic decrease ($\sim 3\%$) was observed during the course of measurements. All independent data having $(\sin \theta)/\lambda \leq 0.626 \text{ \AA}^{-1}$ were thus measured.

The net intensities were reduced to a set of relative squared amplitudes as described previously³ and all data having $F_o > 3\sigma(F_o)$ were considered observed. With a linear absorption coefficient of 0.27 mm^{-1} and the cited dimensions of the crystal, an absorption correction was deemed unnecessary. A total of 4980 independent data were taken to be observed (54% of the theoretical number possible) and were used for the determination of structure by the usual heavy-atom method¹² and for the refinement of structure by block-diagonal¹³ and full-matrix least-squares¹⁴ techniques. The four benzene molecules in the unit cell were located at centers of symmetry (0, 0, 0; $1/2, 0, 0$; and the symmetry related positions) but were poorly defined. Consequently, they were refined as two three-atom rigid groups with individual isotropic temperature factors. Refinement employing isotropic temperature factors for all atoms was followed by a difference Fourier synthesis which revealed electron density concentrations appropriately located for all hydrogen atom positions. The coordinates of the hydrogen atoms of the porphyrin and pyridine ring were idealized (C-H = 1.0 \AA , $B(\text{H}) = B(\text{C}) + 1.0 \text{ \AA}^2$) and included in the refinement as fixed contributions. The refinement was then carried to convergence using anisotropic temperature factors for all heavy atoms (see

paragraph at end of paper regarding supplementary material available). The largest shift per error in the final cycle of refinement was 0.50, with most being less than 0.10. The final value of $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$ was 0.055; that of $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$ was 0.075. The largest peak in the final difference Fourier map was 0.77 e/\AA^3 and was in the region of a solvent molecule. Except for the area around the solvent molecules, the map was essentially featureless. Atomic coordinates and the associated anisotropic thermal parameters in the asymmetric unit of structure are listed in Tables I and II, respectively.

Chloro- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinato(4-picoline)manganese(III). Crystals of Cl(4-pic)MnTPP were obtained as the 4-picoline solvate by slow evaporation of a benzene-4-picoline solution of ClMnTPP. Crystal data: monoclinic; $a = 13.24$, $b = 19.97$, $c = 17.03 \text{ \AA}$; $\beta = 94.47^\circ$; $Z = 4$; space group $P2_1/c$. Intensity data were measured in a manner similar to that just described; however, considerable crystal decomposition was noted during the course of the measurements. Preliminary structure analysis by the heavy-atom method revealed an MnN₅Cl coordination group, with dimensions similar to those found for Cl(py)MnTPP. Owing to the crystal decomposition, structure analysis was terminated.

Discussion

Figure 1 is a computer-drawn¹⁵ model in perspective of the Cl(py)MnTPP molecule as it exists in the crystal. Also displayed in Figure 1 are the bond distances of the coordination group and the special symbols used to identify the atoms of the axial ligands and the peripheral phenyl groups. Figure 2 is a formal diagram of the porphinato core displaying values of all structurally independent bond lengths of the core and the special symbols used to identify the atoms of the core.

Figure 3, a formal diagram of the porphinato core with the same relative orientation as Figure 2, shows the perpendicular

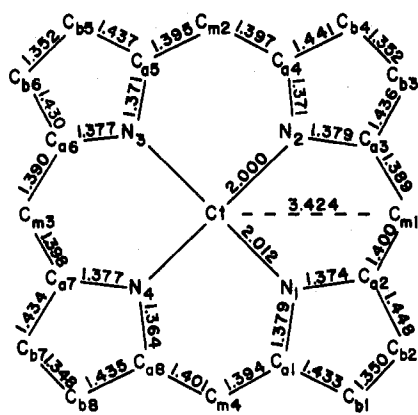


Figure 2. Formal diagram of the porphinato core displaying values of all structurally independent bond distances of the core. Also displayed are the special symbols used to identify the atoms of the core. Two important radii of the core are shown; C_t represents the center of the porphinato core.

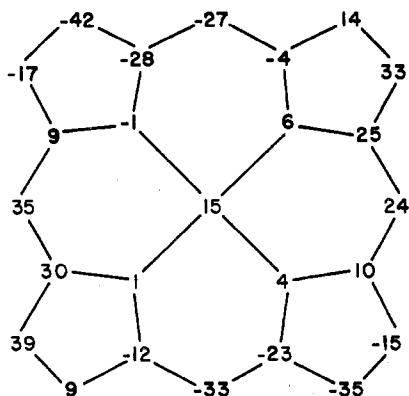


Figure 3. Diagram to illustrate the displacements of the atoms of the porphinato core from the mean plane. The perpendicular displacements of the atoms from the mean plane, in units of $\text{Å} \times 10^{-2}$, replace the symbols of these atoms that are carried on the identically oriented diagram of Figure 2.

displacement of each atom from the mean plane of the core. In Figure 3, each numbered atom in Figure 2 has been replaced by the value of the displacement (in units of 0.01 Å) of this atom from the mean plane. The skeletal configuration is seen to be best described by an S_4 ruffling. The departures from planarity are not remarkable for porphyrins; for example, similarly ruffled cores are found for two crystalline forms of ClMnTPP .^{16,17} Despite the deviations from exact planarity exhibited by the core, local flatness is maintained (to within 0.02 Å) for all pyrrole rings.

Although no crystallographic symmetry is imposed on the core, the dimensional variations in bond lengths and angles of chemically analogous bond types differ immaterially from fourfold geometry. Using C_α and C_β to denote the respective α - and β -carbon atoms of a pyrrole ring, C_m for methine carbon, and C_p for a phenyl carbon atom that is bonded to the core, the averaged bond lengths (Table III) in the porphine skeleton are $\text{N}-C_\alpha = 1.374$ (4, 6), $C_\alpha-C_m = 1.396$ (4, 6), $C_\alpha-C_\beta = 1.437$ (4, 7), $C_\beta-C_\beta = 1.350$ (2, 7), and $C_m-C_p = 1.501$ (4, 6) Å , wherein the first number in parentheses following each averaged length is the mean deviation in units of $\text{Å} \times 10^{-3}$ and the second is the value of the estimated standard deviation for an individually determined length.¹⁸ The agreement in the bond angles of a given chemical type in the core is equally close (Table IV). The averaged values are $C_\alpha\text{N}C_\alpha = 106.6$ (2, 3), $\text{N}C_\alpha C_\beta = 109.4$ (3, 4), $\text{N}C_\alpha C_m = 125.7$ (3, 4), $C_\alpha C_\beta C_\beta = 107.3$ (4, 4), $C_\alpha C_m C_\alpha = 123.6$ (2, 4), and $C_\alpha C_m C_p = 118.1$ (4, 4)°.

The dihedral angles between the plane of the porphinato

Table I. Atomic Coordinates in the Unit Cell^a

Atom type ^b	Coordinates		
	10^4x	10^4y	10^4z
Mn ^c	1580 (0)	3018 (0)	-1181 (0)
Cl	931 (1)	3643 (1)	-2505 (1)
N ₁	726 (3)	2330 (2)	-1680 (3)
N ₂	495 (3)	3224 (1)	-444 (2)
N ₃	2502 (3)	3639 (1)	-549 (2)
N ₄	2733 (3)	2757 (1)	-1797 (2)
N ₅	2359 (3)	2409 (2)	103 (3)
C _{a1}	1068 (3)	1872 (2)	-2131 (3)
C _{a2}	-259 (3)	2200 (2)	-1555 (3)
C _{a3}	-498 (3)	3010 (2)	-559 (3)
C _{a4}	557 (3)	3656 (2)	191 (3)
C _{a5}	2349 (3)	3962 (2)	189 (3)
C _{a6}	3440 (3)	3806 (2)	-749 (3)
C _{a7}	3560 (3)	3086 (2)	-1936 (3)
C _{a8}	2756 (3)	2273 (2)	-2308 (3)
C _{b1}	271 (4)	1447 (2)	-2292 (4)
C _{b2}	-544 (4)	1642 (2)	-1945 (4)
C _{b3}	-1077 (4)	3337 (2)	-6 (3)
C _{b4}	-431 (4)	3728 (2)	466 (3)
C _{b5}	3234 (3)	4321 (2)	486 (3)
C _{b6}	3890 (3)	4234 (2)	-107 (3)
C _{b7}	4088 (4)	2803 (2)	-2576 (4)
C _{b8}	3612 (4)	2297 (2)	-2785 (3)
C _{m1}	-860 (3)	2524 (2)	-1054 (3)
C _{m2}	1430 (3)	3984 (2)	534 (3)
C _{m3}	3893 (3)	3587 (2)	-1455 (3)
C _{m4}	2018 (4)	1835 (2)	-2417 (3)
C ₁	3359 (4)	2458 (3)	467 (4)
C ₂	3842 (5)	2115 (3)	1181 (5)
C ₃	3298 (6)	1717 (3)	1525 (5)
C ₄	2255 (7)	1662 (3)	1165 (5)
C ₅	1818 (5)	2021 (3)	447 (4)
C ₆	-1915 (4)	2310 (2)	-984 (4)
C ₇	-2685 (4)	2280 (3)	-1766 (5)
C ₈	-3661 (5)	2082 (3)	-1697 (8)
C ₉	-3866 (6)	1926 (4)	-861 (9)
C ₁₀	-3122 (7)	1947 (4)	-82 (8)
C ₁₁	-2131 (6)	2139 (3)	-139 (6)
C ₁₂	1334 (3)	4410 (2)	1277 (3)
C ₁₃	1492 (5)	4242 (2)	2184 (4)
C ₁₄	1294 (5)	4627 (3)	2865 (4)
C ₁₅	941 (5)	5162 (2)	2608 (5)
C ₁₆	804 (4)	5335 (2)	1714 (4)
C ₁₇	1008 (4)	4963 (2)	1043 (4)
C ₁₈	4796 (3)	3904 (2)	-1703 (3)
C ₁₉	4618 (4)	4412 (3)	-2172 (4)
C ₂₀	5436 (5)	4706 (3)	-2452 (5)
C ₂₁	6424 (5)	4494 (3)	2222 (4)
C ₂₂	6611 (4)	3993 (3)	-1739 (4)
C ₂₃	5799 (4)	3697 (2)	-1477 (4)
C ₂₄	2274 (4)	1287 (2)	-2863 (3)
C ₂₅	2995 (4)	922 (2)	-2373 (4)
C ₂₆	3230 (5)	405 (3)	-2746 (5)
C ₂₇	2762 (4)	260 (2)	-3634 (4)
C ₂₈	2071 (5)	625 (2)	-4136 (4)
C ₂₉	1815 (4)	1141 (2)	-3750 (4)
C ₃₀ ^d	5805	346	443
C ₃₁ ^d	6006	-216	209
C ₃₂ ^d	5201	-562	-234
C ₃₃ ^d	709	434	-79
C ₃₄ ^d	1028	-137	-28
C ₃₅ ^d	318	-571	51

^a The figure in parentheses following each datum is the estimated standard deviation in the last significant figure. ^b Atoms are identified in agreement with Figures 1-3. ^c For Mn $10^4x = 15,803$ (5), $10^4y = 30,177$ (3), $10^4z = -11,811$ (4). ^d Parameters derived from group refinement.

core and the planes of the phenyl groups are 59.8 , 79.7 , 69.1 , and 72.0° . The averaged value of the internal angles in the phenyl groups is 120.0 (5, 5)°. The individual C-C bond distances in the four structurally independent phenyl rings are foreshortened from the standard 1.397-Å distance to 1.381 Å owing to the complex thermal motion of these peripheral

Table II. Anisotropic Thermal Parameters^a

Atom type	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mn	2.41 (2)	2.46 (2)	2.87 (2)	-0.19 (2)	0.57 (2)	-0.43 (2)
Cl	4.32 (6)	4.23 (6)	3.73 (5)	0.59 (5)	0.01 (5)	0.50 (5)
N ₁	2.9 (2)	2.8 (2)	3.6 (2)	-0.4 (1)	0.6 (1)	-0.6 (1)
N ₂	2.7 (1)	2.6 (1)	3.1 (2)	-0.2 (1)	0.7 (1)	-0.3 (1)
N ₃	2.6 (1)	2.7 (2)	2.8 (1)	-0.2 (1)	0.6 (1)	-0.4 (1)
N ₄	2.7 (1)	2.6 (1)	3.2 (2)	-0.2 (1)	0.6 (1)	-0.5 (1)
N ₅	4.0 (2)	3.7 (2)	4.3 (2)	0.0 (2)	0.5 (2)	0.6 (2)
C _{a1}	3.3 (2)	2.7 (2)	4.0 (2)	-0.3 (1)	0.9 (2)	-0.8 (2)
C _{a2}	2.9 (2)	3.5 (2)	3.8 (2)	-0.7 (2)	0.4 (2)	-0.5 (2)
C _{a3}	2.8 (2)	3.3 (2)	3.4 (2)	-0.1 (2)	0.8 (1)	0.1 (2)
C _{a4}	3.2 (2)	2.6 (2)	3.1 (2)	0.0 (1)	0.9 (2)	-0.2 (1)
C _{a5}	3.1 (2)	2.5 (2)	2.4 (2)	0.2 (1)	0.3 (1)	0.1 (1)
C _{a6}	2.6 (2)	2.6 (2)	3.3 (2)	-0.1 (1)	0.5 (1)	-0.3 (1)
C _{a7}	2.6 (2)	3.2 (2)	3.2 (2)	-0.2 (1)	0.6 (1)	-0.2 (2)
C _{a8}	2.7 (2)	2.9 (2)	3.6 (2)	0.0 (1)	0.5 (2)	-0.7 (2)
C _{b1}	4.2 (2)	3.6 (2)	6.1 (3)	-0.9 (2)	1.6 (2)	-1.4 (2)
C _{b2}	3.7 (2)	3.8 (2)	5.2 (3)	-1.1 (2)	1.0 (2)	-1.3 (2)
C _{b3}	3.4 (2)	3.9 (2)	4.3 (2)	-0.4 (2)	1.5 (2)	-0.5 (2)
C _{b4}	3.6 (2)	3.5 (2)	3.6 (2)	0.0 (2)	1.4 (2)	-0.1 (2)
C _{b5}	3.4 (2)	3.0 (2)	3.4 (2)	-0.4 (2)	0.8 (2)	-0.8 (2)
C _{b6}	3.1 (2)	3.2 (2)	4.0 (2)	-0.6 (2)	0.7 (2)	-0.8 (2)
C _{b7}	3.5 (2)	4.0 (2)	4.5 (2)	-0.5 (2)	1.6 (2)	-1.2 (2)
C _{b8}	3.6 (2)	4.1 (2)	4.2 (2)	-0.1 (2)	1.4 (2)	-1.4 (2)
C _{m1}	2.7 (2)	3.5 (2)	4.0 (2)	-0.5 (2)	0.9 (2)	-0.5 (2)
C _{m2}	3.1 (2)	2.4 (2)	2.6 (2)	0.0 (1)	0.6 (1)	-0.3 (1)
C _{m3}	2.8 (2)	3.1 (2)	3.6 (2)	0.0 (2)	0.7 (2)	-0.4 (2)
C _{m4}	3.5 (2)	2.9 (2)	3.7 (2)	-0.1 (2)	0.4 (2)	-0.8 (2)
C ₁	4.3 (3)	5.6 (3)	5.7 (3)	0.4 (2)	-0.2 (2)	1.4 (2)
C ₂	6.1 (3)	6.6 (4)	6.1 (3)	1.1 (3)	-0.7 (3)	1.6 (3)
C ₃	9.5 (5)	6.3 (4)	5.6 (3)	1.0 (3)	-1.2 (3)	2.4 (3)
C ₄	10.4 (5)	7.3 (4)	6.9 (4)	-1.4 (4)	0.6 (4)	3.6 (4)
C ₅	5.8 (3)	6.6 (3)	5.3 (3)	-1.2 (3)	-0.3 (2)	2.4 (3)
C ₆	3.1 (2)	4.0 (2)	7.2 (3)	-0.6 (2)	1.6 (2)	-2.1 (2)
C ₇	3.4 (2)	4.3 (3)	10.9 (5)	0.0 (2)	0.4 (3)	-2.3 (3)
C ₈	3.2 (3)	5.9 (4)	19.2 (9)	-0.5 (3)	1.0 (4)	-3.7 (5)
C ₉	5.7 (4)	7.8 (5)	24.8 (12)	-3.5 (4)	7.6 (6)	-6.0 (6)
C ₁₀	9.8 (6)	8.7 (5)	15.4 (8)	-4.3 (5)	8.2 (6)	-3.3 (5)
C ₁₁	7.4 (4)	7.6 (4)	8.8 (5)	-3.6 (3)	4.8 (4)	-1.9 (3)
C ₁₂	2.8 (2)	3.2 (2)	2.9 (2)	-0.4 (1)	0.8 (1)	-0.7 (2)
C ₁₃	6.7 (3)	3.9 (2)	3.5 (2)	-0.3 (2)	1.3 (2)	-0.3 (2)
C ₁₄	7.6 (4)	6.4 (3)	3.7 (3)	-1.0 (3)	2.6 (2)	-1.0 (2)
C ₁₅	5.3 (3)	4.6 (3)	7.0 (3)	-1.3 (2)	3.2 (3)	-2.5 (2)
C ₁₆	4.4 (2)	4.1 (2)	5.6 (3)	-0.2 (2)	1.4 (2)	-1.3 (2)
C ₁₇	4.1 (2)	3.4 (2)	4.1 (2)	-0.1 (2)	0.6 (2)	-0.8 (2)
C ₁₈	3.2 (2)	3.3 (2)	3.6 (2)	-0.7 (2)	1.3 (2)	-1.1 (2)
C ₁₉	4.6 (3)	4.4 (3)	6.8 (3)	-0.4 (2)	2.1 (2)	0.5 (2)
C ₂₀	6.2 (3)	4.2 (3)	7.6 (4)	-1.2 (2)	2.6 (3)	0.0 (3)
C ₂₁	5.1 (3)	5.8 (3)	6.5 (3)	-2.6 (2)	3.0 (3)	-2.4 (3)
C ₂₂	3.5 (2)	5.8 (3)	6.3 (3)	-1.1 (2)	1.5 (2)	-1.2 (3)
C ₂₃	3.4 (2)	4.8 (3)	4.9 (3)	-0.5 (2)	1.2 (2)	-0.6 (2)
C ₂₄	3.5 (2)	2.9 (2)	4.7 (2)	-0.5 (2)	1.3 (2)	-1.0 (2)
C ₂₅	5.1 (3)	4.5 (3)	5.1 (3)	1.2 (2)	0.4 (2)	-1.0 (2)
C ₂₆	5.4 (3)	4.5 (3)	7.0 (4)	1.5 (2)	1.0 (3)	-0.6 (3)
C ₂₇	4.6 (3)	3.7 (2)	6.6 (3)	-0.5 (2)	2.4 (2)	-1.6 (2)
C ₂₈	5.8 (3)	3.9 (2)	5.2 (3)	-0.6 (2)	1.2 (2)	-1.7 (2)
C ₂₉ ^b	5.0 (3)	3.7 (2)	4.2 (2)	-0.2 (2)	0.7 (2)	-1.1 (2)
C ₃₀ ^b	13.6 (5)					
C ₃₁ ^b	15.7 (6)					
C ₃₂ ^b	13.5 (5)					
C ₃₃ ^b	20.3 (8)					
C ₃₄ ^b	25.8 (11)					
C ₃₅ ^b	20.9 (8)					

^a The number in parentheses following each datum is the estimated standard deviation in the least significant figure. B_{ij} is related to the dimensionless β_{ij} employed during refinement as $B_{ij} = 4\beta_{ij}/a_i^2 a_j^2$. ^b Isotropic thermal parameters derived from group refinement.

groups. This pattern of foreshortening has been noted and discussed previously.^{19,20}

The pyridine ligand is planar; the dihedral angle between the plane of the pyridine and the mean plane of the core is 88.6°. The dihedral angles between the pyridine plane and the planes defined by N₅MnC_{m1} and N₅MnC_{m3} are 8.1 and 7.7°, respectively. The orientation of the pyridine ring with respect to rotation around the complexing Mn-N₅ bond is thus quite favorable for minimizing the steric interactions between the pair of hydrogen atoms of the pyridine (the hydrogen atoms

bonded to C₁ and C₅; see Figure 1) and the porphinato core. The nonbonded contacts of the type H... (porphinato core atom) range from 2.74 Å upward.

The equatorial Mn-N bond distances in the MnN₅Cl coordination group average to 2.009 (7, 4) Å. This Mn-N distance is quite comparable to those observed for high-spin five-coordinate manganese(III) porphyrins, wherein Mn-N = 2.008 Å in ClMnTPP (acetone solvate),¹⁶ 2.01 Å in ClMnTPP (chloroform solvate),¹⁷ and 2.005 Å in N₃MnTPP.²¹ This bond distance is slightly shorter than the 2.031-Å distance

Table III. Bond Lengths in the Coordination Group, Porphinato Skeleton, and Pyridine Ligand^a

Type	Length, Å	Type	Length, Å	Type	Length, Å
Mn-N ₁	2.022 (4)	C _{a1} -C _{b1}	1.433 (7)	C _{m1} -C ₆	1.495 (6)
Mn-N ₂	2.006 (4)	C _{a2} -C _{m1}	1.400 (7)	C _{m2} -C ₁₂	1.505 (6)
Mn-N ₃	2.010 (3)	C _{a2} -C _{b2}	1.448 (7)	C _{m3} -C ₁₈	1.500 (6)
Mn-N ₄	2.000 (4)	C _{a3} -C _{m1}	1.389 (6)	C _{m4} -C ₂₄	1.506 (6)
Mn-N ₅	2.444 (4)	C _{a3} -C _{b3}	1.436 (6)	C _{b1} -C _{b2}	1.350 (7)
Mn-Cl	2.467 (1)	C _{a4} -C _{m2}	1.397 (6)	C _{b3} -C _{b4}	1.352 (7)
N ₁ -C _{a1}	1.379 (6)	C _{a4} -C _{b4}	1.441 (6)	C _{b5} -C _{b6}	1.352 (6)
N ₁ -C _{a2}	1.374 (6)	C _{a5} -C _{m2}	1.395 (6)	C _{b7} -C _{b8}	1.348 (7)
N ₂ -C _{a3}	1.379 (5)	C _{a5} -C _{b5}	1.437 (6)	N ₅ -C ₁	1.332 (7)
N ₂ -C _{a4}	1.371 (6)	C _{a6} -C _{m3}	1.390 (6)	N ₅ -C ₅	1.311 (7)
N ₃ -C _{a5}	1.371 (5)	C _{a6} -C _{b6}	1.430 (6)	C ₁ -C ₂	1.385 (8)
N ₃ -C _{a6}	1.377 (5)	C _{a7} -C _{m3}	1.398 (6)	C ₂ -C ₃	1.330 (11)
N ₄ -C _{a7}	1.377 (5)	C _{a7} -C _{b7}	1.434 (6)	C ₃ -C ₄	1.383 (12)
N ₄ -C _{a8}	1.364 (5)	C _{a8} -C _{m4}	1.401 (6)	C ₄ -C ₅	1.392 (9)
C _{a1} -C _{m4}	1.394 (6)	C _{a8} -C _{b8}	1.435 (6)		

^a The numbers in parentheses are the estimated standard deviations.

observed in six-coordinate high-spin N₃(CH₃OH)MnTPP¹⁰ and the 2.028 Å found for the *low-spin* manganese(II) derivative ON(4-Me(pip))MnTPP.²² All of the above manganese porphyrins have an unoccupied d_{x₂-y₂} orbital concomitant with the relatively short manganese-porphyrin nitrogen bonds. By contrast, high-spin manganese(II) porphyrins, with an occupied d_{x₂-y₂} orbital, should have substantially longer manganese-porphyrin nitrogen bond distances. The >2.08-Å Mn-N distance observed in four-coordinate MnTPP²³ and the 2.13-Å distance observed in five-coordinate (*N*-MeIm)MnTPP²³ are in agreement with this expectation.

The equatorial Mn-N distances are longer than the 1.97-Å value observed²⁴ in the binuclear manganese(III) phthalocyanine (pyMnPc)₂O; the difference is the consequence of the slightly smaller hole size of phthalocyanines compared to that of porphyrins. The Mn-N bond distance is also comparable to the Fe-N distances in low-spin iron(II) porphyrins: 2.004 Å in (pip)₂FeTPP²⁰ and 2.008 Å in ON(*N*-MeIm)FeTPP²² and slightly longer than the Fe-N distances in low-spin Im₂FeTPP²⁵ (1.989 Å) and 1.990 Å in N₃(py)FeTPP.²⁶

The two axial complexing bonds are both rather long with Mn-Cl = 2.467 (1) Å and Mn-N_{py} = 2.444 (4) Å. The

Mn-Cl bond length can be compared to the 2.363-¹⁶ and 2.38-Å¹⁷ Mn-Cl bond lengths in the two forms of five-coordinate CIMnTPP. Thus, an ~0.1-Å lengthening of the Mn-Cl bond occurs in the six-coordinate manganese(III) complex compared to the "normal" Mn-Cl length in the five-coordinate complexes. A similar ~0.1-Å increase in the axial anionic bond length is observed in N₃(CH₃OH)MnTPP¹⁰ (Mn-N_{N₃} = 2.176 Å) and N₃MnTPP²¹ (2.045 Å). However, the Mn-Cl bond is shorter than the 2.551-Å Mn-Cl bond distance observed in [Mn^{III}(*ms*-[14]aneN₄)Cl₂]Cl·3H₂O;²⁷ in this centrosymmetric complex, the Mn-Cl bonds must share equally the repulsive effect of the singly populated d_{z₂} orbital. The Mn-N_{py} bond (2.444 Å) would appear to be subject to an even greater elongation than the Mn-Cl bond. This bond length is comparable to the axial bond lengths observed in the six-coordinate low-spin cobalt(II) porphyrins for which a bond elongation of ~0.4 Å was noted. (The Co-N bond in (pip)₂CoTPP³ is 2.436 Å, and it is 2.386 Å in (3-pic)₂CoOEP.⁴) Evidence that the Mn-N_{py} bond extension is >0.2 Å comes from consideration of the Mn-N bond distances in simpler manganese(III) complexes and in the (pyMnPc)₂O oligomer. The Mn-N_{py} bond distance in (pyMnPc)₂O is 2.15 Å.²⁴ The extended Mn-N bond distances in acetylacetonatobis(*N*-phenylaminotroponiminato)manganese(III)¹ and di-μ-oxo-tetrakis(2,2'-bipyridine)dimanganese(III,IV)² are 2.153 and 2.21 Å, respectively; the respective short Mn-N distances are 2.02 and 2.13 Å. The Mn-N_{py} distance appears especially long compared to the Mn-O bond distance of 2.329 Å to coordinated methanol in N₃(CH₃OH)MnTPP;¹⁰ methanol is a ligand that is certainly not noted for its strong complexing power. Hence, the axial bonding system in Cl-(py)MnTPP appears to be decidedly asymmetric and composed of a normal or slightly weaker than normal bond to the anion and a very weak bond to the Lewis base. The large differences in the Mn-O bond length (in N₃(CH₃OH)MnTPP) and the Mn-N_{py} bond length (in Cl(py)MnTPP) further suggest that considerable variation in the bond lengths to neutral axial ligands in six-coordinate manganese(III) porphyrins could be anticipated.

The manganese(III) ion is displaced 0.145 Å out of the mean porphyrin plane and 0.12 Å out of the mean plane of the four

Table IV. Bond Angles in the Coordination Group, Porphinato Skeleton, and Pyridine Ring^a

Angle	Value, deg	Angle	Value, deg	Angle	Value, deg
N ₁ MnN ₂	89.2 (1)	C _{m1} C _{a3} C _{b3}	124.7 (4)	C _{a1} C _{m4} C ₂₄	118.1 (4)
N ₁ MnN ₃	172.8 (2)	N ₂ C _{a4} C _{m2}	126.6 (4)	C _{a8} C _{m4} C ₂₄	117.9 (4)
N ₁ MnN ₄	90.5 (1)	N ₂ C _{a4} C _{b4}	109.7 (4)	C _{a1} C _{b1} C _{b2}	108.0 (4)
N ₁ MnN ₅	87.0 (1)	C _{m2} C _{a4} C _{b4}	123.8 (4)	C _{a2} C _{b2} C _{b1}	106.9 (4)
N ₁ MnCl	95.3 (1)	N ₃ C _{a5} C _{m2}	125.0 (4)	C _{a3} C _{b3} C _{b4}	107.8 (4)
N ₂ MnN ₃	90.1 (1)	N ₃ C _{a5} C _{b5}	109.7 (4)	C _{a4} C _{b4} C _{b3}	106.7 (4)
N ₂ MnN ₄	173.6 (2)	C _{m2} C _{a5} C _{b5}	125.0 (4)	C _{a5} C _{b5} C _{b6}	106.9 (4)
N ₂ MnN ₅	87.5 (1)	N ₃ C _{a6} C _{m3}	125.4 (4)	C _{a6} C _{b6} C _{b5}	107.5 (4)
N ₂ MnCl	96.4 (1)	N ₃ C _{a6} C _{b6}	109.5 (4)	C _{a7} C _{b7} C _{b8}	107.2 (4)
N ₃ MnN ₄	89.4 (1)	C _{m3} C _{a6} C _{b6}	125.1 (4)	C _{a8} C _{b8} C _{b7}	107.1 (4)
N ₃ MnN ₅	85.8 (1)	N ₄ C _{a7} C _{m3}	125.1 (4)	C ₁ N ₅ C ₅	117.9 (5)
N ₃ MnCl	91.9 (1)	N ₄ C _{a7} C _{b7}	109.3 (4)	N ₅ C ₁ C ₂	122.7 (6)
N ₄ MnN ₅	86.1 (1)	C _{m3} C _{a7} C _{b7}	125.3 (4)	C ₁ C ₂ C ₃	119.6 (6)
N ₄ MnCl	90.0 (1)	N ₄ C _{a8} C _{m4}	125.9 (4)	C ₂ C ₃ C ₄	118.8 (6)
N ₅ MnCl	175.5 (1)	N ₄ C _{a8} C _{b8}	109.8 (4)	C ₃ C ₄ C ₅	118.7 (6)
C _{a1} N ₁ C _{a2}	106.9 (4)	C _{m4} C _{a8} C _{b8}	124.1 (4)	C ₄ C ₅ N ₅	122.4 (6)
C _{a3} N ₂ C _{a4}	106.7 (3)	C _{a2} C _{m1} C _{a3}	123.2 (4)	MnN ₁ C _{a1}	125.8 (3)
C _{a5} N ₃ C _{a6}	106.3 (3)	C _{a2} C _{m1} C ₆	118.5 (4)	MnN ₁ C _{a2}	127.0 (3)
C _{a7} N ₄ C _{a8}	106.5 (3)	C _{a3} C _{m1} C ₆	118.1 (4)	MnN ₂ C _{a3}	126.6 (3)
N ₁ C _{a1} C _{m4}	125.8 (4)	C _{a4} C _{m2} C _{a5}	123.7 (4)	MnN ₂ C _{a4}	126.1 (3)
N ₁ C _{a1} C _{b1}	109.1 (4)	C _{a4} C _{m2} C ₁₂	117.1 (4)	MnN ₃ C _{a5}	127.2 (3)
C _{m4} C _{a1} C _{b1}	125.0 (4)	C _{a5} C _{m2} C ₁₂	119.0 (4)	MnN ₃ C _{a6}	126.4 (3)
N ₁ C _{a2} C _{m1}	126.0 (4)	C _{a6} C _{m3} C _{a7}	123.6 (4)	MnN ₄ C _{a7}	125.6 (3)
N ₁ C _{a2} C _{b2}	109.2 (4)	C _{a6} C _{m3} C ₁₈	117.9 (4)	MnN ₄ C _{a8}	126.8 (3)
C _{m1} C _{a2} C _{b2}	124.5 (4)	C _{a7} C _{m3} C ₁₈	118.5 (4)	MnN ₅ C ₁	120.4 (4)
N ₂ C _{a3} C _{m1}	126.0 (4)	C _{a1} C _{m4} C _{a8}	124.0 (4)	MnN ₅ C ₅	121.6 (4)
N ₂ C _{a3} C _{b3}	109.0 (4)				

^a The numbers in parentheses are the estimated standard deviations.

porphyrato nitrogens in the direction of the axial chloride ligand. This displacement is about half that observed in the five-coordinate manganese(III) porphyrins.^{16,17,21} The displacement of the manganese(III) ion further suggests that the Mn-Cl bond is stronger than the Mn-N_{py} bond. The Cl...N_{porphyrin} contacts are 3.18, 3.23, 3.33, and 3.35 Å; the sum of the van der Waals radii of Cl and N is 3.30 Å.²⁸ A survey of the intermolecular contacts less than 4.0 Å reveals no unusual nonbonded contacts.

There has been considerable interest in studying the role of iron in hemoglobin by examining the effects on structure and function resulting from the replacement of the iron by other metal ions. Recently, manganese(III) hemoglobin (Mn^{III}Hb), in which the iron has been replaced by manganese, has been shown to have the same quaternary structure as methemoglobin (Fe^{III}Hb).²⁹ Mn^{III}Hb also displays allosteric effects in its redox properties, changes in proton affinity on binding NO, and kinetics of ligand binding.³⁰ Our stereochemical results for Cl(py)MnTPP suggest another experiment with manganese-substituted hemoglobins.

It has been shown that inositol hexaphosphate (IHP) can switch the quaternary structure of some high-spin ferric hemoglobins from the oxy (R or normal) quaternary structure to the deoxy (T) quaternary structure.^{31,32} The stereochemical interpretation of the R → T transition of Fe^{III}Hb, in the presence of IHP, is a lengthening of the Fe-N bonds, a larger displacement of the iron(III) ion out of plane, and a concomitant increase in the displacement of the heme-linked histidine from the plane of the porphyrin ring. Given the long Mn-N axial bond distance in Cl(py)MnTPP and the additional possibility of variability, it would appear likely that IHP could induce R → T transitions in Mn^{III}Hb as easily as in Fe^{III}Hb.³³

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Registry No. Cl(py)MnTPP-C₆H₆, 55669-26-6; Cl(4-pic)MnTPP, 55669-27-7.

Supplementary Material Available. A listing of structure factor amplitudes (×10) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.50 for photocopy or \$2.50 for microfiche, referring to code number AIC50285I-9-75.

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