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Stereochemistry of Manganese Porphyrins. 3. Molecular Stereochemistry of α,β,γ,δ-Tetraphenylporphinato(1-methylimidazole)manganese(II)[1,2]

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Abstract: α,β,γ,δ-Tetraphenylporphinato(1-methylimidazole)manganese(II) crystallizes as the tetrahydrofuran solvate in the monoclinic system, space group $P2_1/n$. The unit cell has a = 27.405 (7) Å, b = 9.645 (5) Å, and c = 17.768 (9) Å, and β = 112.45 (2)°, and contains four molecules. The calculated and experimental densities are 1.258 and 1.27 g/cm^3, respectively, at 20 ± 1 °C. Measurement of diffracted intensities employed ω scans with graphite-monochromated Mo Kα radiation on a Syntex four-circle diffractometer. All independent reflections for $(\sin\theta)/\lambda \leq 0.626$ Å^{-1} were measured; 5276 reflections were retained as observed. These data were employed in the determination of structure using the heavy-atom method and block-diagonal least-squares refinement of the 540 structural parameters. The final conventional and weighted discrepancy factors are 0.052 and 0.061, respectively. The structural parameters of the square-pyramidal MnN_5 coordination group reflects the large size of the high-spin manganese(II) atom; the average equatorial Mn–N distance is 2.128 Å and the axial Mn–N bond distance is 2.192 Å. The manganese atom is displaced 0.56 Å from the mean skeletal plane. The relevance of this structure to deoxyhemoglobin and manganese-substituted deoxyhemoglobin is discussed.

The stereochemistry of high-spin manganese(II) porphyrins, the isoelectronic high-spin iron(III) and the high-spin iron(II) porphyrins are expected to be dominated by the large size of the metal atom. This large size should yield derivatives in which the metal atom is substantially out of the porphyrin plane. We report herein the molecular stereochemistry of a five-coordinate high-spin manganese(II) derivative, α,β,γ,δ-tetraphenylporphinato(1-methylimidazole)manganese(II), to be written as Mn(1-MeIm)(TPP).[4] We compare the molecular stereochemistry of Mn(1-MeIm)(TPP) with other five-coordinate metalloporphyrin derivatives including those which, like the high-spin manganese(II) derivative, contain spherically symmetric metal ions. We also compare the results for Mn(1-MeIm)(TPP) with those obtained for high-spin four-coordinate MnTPP[5] in which the out-of-plane displacement is considerably smaller.

The structure of Mn(1-MeIm)(TPP) is of considerable interest as a model for the coordination group in manganese-substituted heme proteins, and in particular for manganese-substituted hemoglobin, MnHb. MnHb has been shown to exhibit allosteric properties in its axial ligation and oxidation-reduction reactions.[6] In addition, x-ray studies have

Table I. Atomic Coordinates in the Unit Cell[a]

Atom type[b]	Coordinates		
	10^4x	10^4y	10^4z
Mn[c]	777 (0)	1691 (1)	2879 (0)
N_1	833 (1)	2121 (3)	1741 (2)
N_2	1614 (1)	1832 (3)	3398 (2)
N_3	795 (1)	2299 (3)	4047 (2)
N_4	14 (1)	2597 (3)	2376 (2)
N_5	562 (1)	−482 (3)	2943 (2)
N_6	300 (2)	−2634 (4)	2669 (3)
C_{a1}	413 (1)	2315 (4)	1017 (2)
C_{a2}	1277 (1)	2023 (3)	1562 (2)
C_{a3}	1952 (1)	1843 (3)	2988 (2)
C_{a4}	1921 (1)	1802 (4)	4215 (2)
C_{a5}	1204 (1)	1994 (3)	4765 (2)
C_{a6}	349 (1)	2421 (4)	4216 (2)
C_{a7}	−310 (1)	2834 (4)	2792 (2)
C_{a8}	−288 (1)	2762 (4)	1564 (2)
C_{b1}	601 (1)	2274 (4)	358 (2)
C_{b2}	1127 (1)	2110 (4)	693 (2)
C_{b3}	2487 (1)	1831 (4)	3574 (2)
C_{b4}	2474 (1)	1807 (4)	4318 (2)
C_{b5}	1005 (1)	1893 (4)	5410 (2)
C_{b6}	483 (1)	2164 (4)	5070 (2)
C_{b7}	−831 (1)	3181 (4)	2221 (2)
C_{b8}	−820 (1)	3137 (4)	1467 (2)
C_{m1}	−111 (1)	2588 (3)	927 (2)
C_{m2}	1797 (1)	1890 (3)	2137 (2)
C_{m3}	1735 (1)	1798 (4)	4855 (2)
C_{m4}	−161 (1)	2712 (4)	3639 (2)
C_1	373 (2)	−1399 (5)	2373 (3)
C_2	447 (2)	−2486 (5)	3468 (3)
C_3	611 (2)	−1177 (5)	3646 (3)
C_4	88 (4)	−3909 (8)	2177 (6)
C_5	−507 (1)	2744 (4)	74 (2)
C_6	−735 (2)	1587(4)	−391 (3)
C_7	−1091 (2)	1725 (5)	−1186 (3)
C_8	−1224 (1)	3006 (5)	−1525 (2)
C_9	−1015 (2)	4161 (5)	−1071 (2)
C_{10}	−659 (2)	4039 (4)	−274 (2)
C_{11}	2230 (1)	1855 (4)	1810 (2)
C_{12}	2424 (2)	3062 (4)	1622 (2)
C_{13}	2831 (2)	3042 (5)	1338 (3)
C_{14}	3039 (2)	1790 (5)	1227 (2)
C_{15}	2843 (2)	585 (5)	1402 (3)
C_{16}	2439 (2)	610 (4)	1696 (3)
C_{17}	2134 (1)	1541 (4)	5696 (2)
C_{18}	2214 (2)	2498 (5)	6324 (2)
C_{19}	2578 (2)	2223 (6)	7102 (3)
C_{20}	2861 (2)	1008 (6)	7260 (2)
C_{21}	2793 (2)	66 (5)	6653 (3)
C_{22}	2432 (1)	335 (4)	5869 (2)
C_{23}	−595 (1)	2883 (4)	3955 (2)
C_{24}	−679 (2)	4114 (4)	4271 (2)
C_{25}	−1091 (2)	4271 (5)	4533 (3)
C_{26}	−1422 (2)	3168 (6)	4478 (2)
C_{27}	−1344 (2)	1927 (5)	4164 (3)
C_{28}	−931 (2)	1787 (5)	3906 (3)
C_{29}	1521 (5)	1046 (20)	7798 (7)
C_{30}	1898 (6)	717 (24)	8587 (9)
C_{31}	1706 (6)	840 (30)	9104 (6)
C_{32}	1134 (5)	1365 (22)	8661 (6)
C_{33}	1069 (6)	1344 (25)	7934 (10)

[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, 2, and 3. [c] For Mn $10^5x = 7768$ (2), $10^5y = 16\,909$ (5), $10^5z = 28\,792$ (3).

shown that $Fe^{III}Hb$ and $Mn^{III}Hb$ have the same quaternary structure.[7] That the manganese(II) atom can serve as a qualitatively acceptable substitute for the iron(II) atom in hemoglobin in some reactions appears quite reasonable from the structure of Mn(1-MeIm)(TPP).

Experimental Section

Single crystals of the tetrahydrofuran solvate of Mn(1-MeIm)(TPP) were obtained from THF-1-MeIm solutions of MnTPP (under nitrogen). Crystals were mounted in thin-walled glass capillaries in a nitrogen-filled drybox. A large number of crystals were examined before one, with approximate dimensions of 0.33 × 0.33 × 0.37 mm, was found that was acceptable for data collection. Preliminary work on the diffractometer established a monoclinic unit cell; the systematic absences suggested $P2_1/n$[8] as the uniquely probable space group. Precise lattice constants and diffracted intensities were derived from measurements carried out on a Syntex P$\bar{1}$ diffractometer at the ambient laboratory temperature of 20 ± 1°. Lattice constants, $a = 27.405$ (7) Å, $b = 9.645$ (5) Å, $c = 17.768$ (9) Å, and $\beta = 112.45$ (2)° (λ 0.710 69 Å), came from a least-squares refinement of the setting angles of 30 reflections, each collected at $\pm 2\theta$. For a cell content of $4[MnN_6C_{48}H_{34}\cdot(C_4H_8O)]$, the calculated density is 1.258 g/cm^3; the experimental density of the crystals, determined immediately after removal from the inert atmosphere, was 1.27 g/cm^3.

Intensity data were collected using graphite-monochromated Mo Kα radiation with "wandering" ω-scan techniques using programs and conditions as described previously.[9] A variable scan rate was used; for reflections with $2\theta < 31.3°$ the rate ranged from 1.0 to 6.0 deg ω/min and for reflections with $2\theta \leqslant 52.9°$ the rate was 0.5–6.0 deg/min. 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 decrease of less than 1% was observed during the measurements. With a linear absorption coefficient of 0.37 mm^{-1} and the cited crystal dimensions, an absorption correction was deemed unnecessary. The net intensities were reduced to a set of relative squared amplitudes as described previously,[10] and a total of 5276 independent data having $F_o > 3\sigma(F_o)$ were considered observed (59% of the theoretical number possible).

These data were used for determination of structure by the heavy-atom method[11] and refinement by block-diagonal least-squares techniques.[12] The structure was initially refined to convergence using isotropic temperature factors for all atoms bonded to hydrogen and anisotropic temperature factors for all other atoms. A difference Fourier synthesis revealed the positions of all hydrogen atoms; the coordinates of the hydrogen atoms were idealized (C–H = 0.95 Å, $B(H) = B(C) + 1.0$ Å^2) and included in subsequent refinements as fixed contributors; this change in the model was significant at the 99% confidence level. The THF molecule was refined as a five-carbon ring with no hydrogen atoms. The high temperature factors of the atoms of the THF ring suggest either some positional disorder or partial occupancy of the ring or both. The refinement was carried to convergence using anisotropic temperature factors for all heavy atoms. The final value of $R_1 = \Sigma|F_o| - |F_c|/\Sigma|F_o|$ was 0.052; that of $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$ was 0.061. The data to parameter ratio was 9.8. The largest shift/error in the final cycle was 0.41, excluding the solvent molecule, the largest was 0.17. The largest peak in the final difference Fourier map was 0.59 e/Å^3 and was in the region of the solvent molecule. A listing of final observed and calculated structure factors is available (see paragraph at end of paper regarding supplementary data).

Atomic coordinates and the associated anisotropic thermal parameters in the asymmetric unit of structure are listed in Tables I and II, respectively.

Discussion

Figure 1 is a computer-drawn model[13] in perspective of the Mn(1-MeIm)(TPP) 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. This numbering scheme is maintained in all tables. Individual bond lengths and angles are given in Tables III and IV.

Although no crystallographic symmetry is imposed on the Mn(1-MeIm)(TPP) molecule, bond lengths and angles of the porphinato core retain effective fourfold geometry. Using C_a and C_b to denote the respective α- and β-carbon atoms of a pyrrole ring, C_m for methine carbon, and C_p for a phenyl car-

Table II. Anisotropic Thermal Parameters[a]

Atom type	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mn	3.10 (2)	3.45 (2)	3.65 (2)	0.06 (2)	1.43 (1)	0.15 (2)
N_1	3.4 (1)	3.7 (1)	3.8 (1)	0.3 (1)	1.4 (1)	0.3 (1)
N_2	3.4 (1)	3.8 (1)	3.7 (1)	0.0 (1)	1.5 (1)	0.0 (1)
N_3	3.2 (1)	4.2 (1)	3.8 (1)	0.1 (1)	1.4 (1)	−0.3 (1)
N_4	3.3 (1)	3.9 (1)	4.0 (1)	0.2 (1)	1.4 (1)	0.2 (1)
N_5	4.7 (1)	4.0 (1)	5.0 (1)	−0.4 (1)	2.1 (1)	0.0 (1)
N_6	9.9 (3)	4.1 (2)	9.7 (3)	−2.2 (2)	6.5 (2)	−1.3 (2)
C_{a1}	4.1 (2)	3.5 (1)	3.9 (2)	0.1 (1)	1.6 (1)	0.3 (1)
C_{a2}	3.9 (1)	3.1 (1)	4.3 (2)	0.3 (1)	2.0 (1)	0.2 (1)
C_{a3}	3.5 (1)	3.3 (1)	4.3 (1)	0.0 (1)	1.9 (1)	0.0 (1)
C_{a4}	3.2 (1)	3.7 (1)	4.0 (1)	−0.2 (1)	1.5 (1)	0.0 (1)
C_{a5}	3.8 (1)	3.8 (2)	4.0 (1)	−0.1 (1)	1.6 (1)	−0.3 (1)
C_{a6}	3.5 (1)	4.0 (2)	4.3 (2)	0.1 (1)	1.9 (1)	−0.1 (1)
C_{a7}	3.3 (1)	3.8 (2)	4.5 (2)	0.2 (1)	1.6 (1)	0.3 (1)
C_{a8}	3.6 (1)	3.8 (2)	4.4 (2)	0.1 (1)	1.5 (1)	0.1 (1)
C_{b1}	4.6 (2)	4.0 (2)	3.7 (2)	0.1 (1)	1.8 (1)	−0.1 (1)
C_{b2}	4.5 (2)	4.3 (2)	4.1 (2)	0.1 (1)	2.0 (1)	0.0 (1)
C_{b3}	3.3 (1)	4.2 (2)	4.7 (2)	−0.1 (1)	1.6 (1)	0.2 (1)
C_{b4}	3.4 (1)	4.5 (2)	4.4 (2)	−0.2 (1)	1.5 (1)	0.1 (1)
C_{b5}	4.1 (2)	5.5 (2)	3.9 (2)	0.1 (1)	1.7 (1)	−0.1 (1)
C_{b6}	4.1 (2)	5.7 (2)	4.2 (2)	0.1 (1)	2.2 (1)	0.0 (1)
C_{b7}	3.6 (1)	5.8 (2)	5.0 (2)	0.5 (2)	1.8 (1)	0.2 (2)
C_{b8}	3.6 (1)	5.6 (2)	4.9 (2)	0.6 (1)	1.3 (1)	0.8 (2)
C_{m1}	3.7 (1)	3.2 (1)	3.9 (1)	0.1 (1)	1.1 (1)	0.2 (1)
C_{m2}	3.7 (1)	3.0 (1)	4.4 (1)	0.0 (1)	2.0 (1)	0.0 (1)
C_{m3}	3.4 (1)	3.9 (2)	3.6 (1)	−0.2 (1)	1.2 (1)	−0.1 (1)
C_{m4}	3.3 (1)	4.0 (2)	4.7 (2)	0.0 (1)	2.0 (1)	−0.2 (1)
C_1	10.5 (3)	5.8 (2)	6.9 (2)	−2.7 (2)	5.3 (2)	−1.0 (2)
C_2	9.6 (3)	5.6 (3)	8.0 (3)	−1.0 (2)	2.8 (3)	2.1 (2)
C_3	9.4 (3)	6.0 (2)	5.6 (2)	−1.6 (2)	1.4 (2)	1.4 (2)
C_4	23.7 (9)	7.2 (4)	16.8 (7)	−7.6 (5)	13.0 (7)	−5.6 (4)
C_5	3.5 (1)	3.7 (1)	4.2 (2)	−0.1 (1)	1.5 (1)	0.0 (1)
C_6	5.4 (2)	4.1 (2)	5.7 (2)	−0.6 (2)	1.4 (2)	−0.2 (2)
C_7	5.2 (2)	5.7 (2)	5.4 (2)	−1.2 (2)	0.9 (2)	−1.3 (2)
C_8	3.9 (2)	6.9 (2)	4.3 (2)	0.1 (2)	0.9 (1)	−0.2 (2)
C_9	5.3 (2)	5.5 (2)	4.9 (2)	0.6 (2)	0.8 (2)	0.8 (2)
C_{10}	5.4 (2)	4.3 (2)	4.5 (2)	0.0 (2)	0.6 (1)	0.3 (1)
C_{11}	3.8 (1)	3.8 (2)	3.9 (1)	0.2 (1)	1.8 (1)	0.1 (1)
C_{12}	5.2 (2)	4.1 (2)	5.8 (2)	0.1 (1)	3.2 (2)	0.6 (1)
C_{13}	5.7 (2)	5.9 (2)	6.1 (2)	−0.4 (2)	3.2 (2)	1.2 (2)
C_{14}	4.9 (2)	7.1 (2)	4.9 (2)	−0.1 (2)	3.0 (2)	0.0 (2)
C_{15}	6.1 (2)	5.6 (2)	7.5 (2)	0.2 (2)	4.3 (2)	−1.1 (2)
C_{16}	5.5 (2)	4.2 (2)	6.7 (2)	0.0 (1)	3.6 (2)	−0.5 (2)
C_{17}	3.4 (1)	5.4 (2)	3.7 (1)	−0.6 (1)	1.5 (1)	0.0 (1)
C_{18}	4.7 (2)	7.5 (3)	4.4 (2)	−0.1 (2)	1.4 (2)	−1.0 (2)
C_{19}	5.1 (2)	10.2 (3)	4.7 (2)	−0.6 (2)	1.6 (2)	−1.5 (2)
C_{20}	4.0 (2)	11.4 (3)	4.4 (2)	−0.6 (2)	1.2 (1)	1.1 (2)
C_{21}	4.2 (2)	7.6 (3)	5.7 (2)	0.1 (2)	1.5 (2)	1.6 (2)
C_{22}	3.6 (2)	5.6 (2)	4.8 (2)	−0.3 (1)	1.4 (1)	0.5 (2)
C_{23}	3.5 (1)	4.6 (2)	4.3 (2)	0.3 (1)	1.8 (1)	0.3 (1)
C_{24}	4.7 (2)	5.4 (2)	5.7 (2)	0.2 (2)	2.5 (2)	−0.8 (2)
C_{25}	5.4 (2)	7.6 (3)	5.9 (2)	1.5 (2)	3.0 (2)	−0.3 (2)
C_{26}	4.6 (2)	10.0 (3)	4.6 (2)	1.5 (2)	2.5 (2)	1.5 (2)
C_{27}	5.2 (2)	8.0 (3)	7.3 (2)	−1.1 (2)	3.5 (2)	0.8 (2)
C_{28}	5.3 (2)	5.3 (2)	7.2 (2)	−0.5 (2)	3.6 (2)	0.1 (2)
C_{29}	18.6 (9)	39 (2)	14.5 (7)	−10 (1)	10.9 (7)	−11 (1)
C_{30}	24 (1)	41 (3)	21 (1)	11 (2)	14 (1)	3 (1)
C_{31}	23 (1)	61 (4)	9.1 (6)	10 (2)	7.0 (7)	3 (1)
C_{32}	21 (1)	48 (3)	9.4 (6)	10 (1)	8.0 (7)	1 (1)
C_{33}	16 (1)	48 (3)	22 (1)	9 (1)	10.2 (9)	1 (1)

[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 $B_{ij} = 4\beta_{ij}/a_i^*a_j^*$.

bon atom that is bonded to the core, the average bond lengths of a given chemical type in the core are N–C_a = 1.373 (4) Å, C_a–C_m = 1.408 (4) Å, C_a–C_b = 1.445 (6) Å, C_b–C_b = 1.345 (7) Å, and C_m–C_p = 1.502 (6) Å. The number in parentheses following each averaged length is the estimated standard deviation calculated on the basis that the values are all drawn from the same population. Average bond angles of a chemical type are C_aNC_a = 107.1 (1)°, NC_aC_b = 109.0 (2)°, NC_aC_m = 125.5 (3)°, $C_aC_bC_b$ = 107.4 (4)°, $C_aC_mC_a$ = 126.0 (6)°, and $C_aC_mC_p$ = 117.0 (5)°. Except for the C_b–C_b bond lengths,[14] the bond parameters of the core in Mn(1-MeIM)(TPP) are those which are compatible with an expanded por-

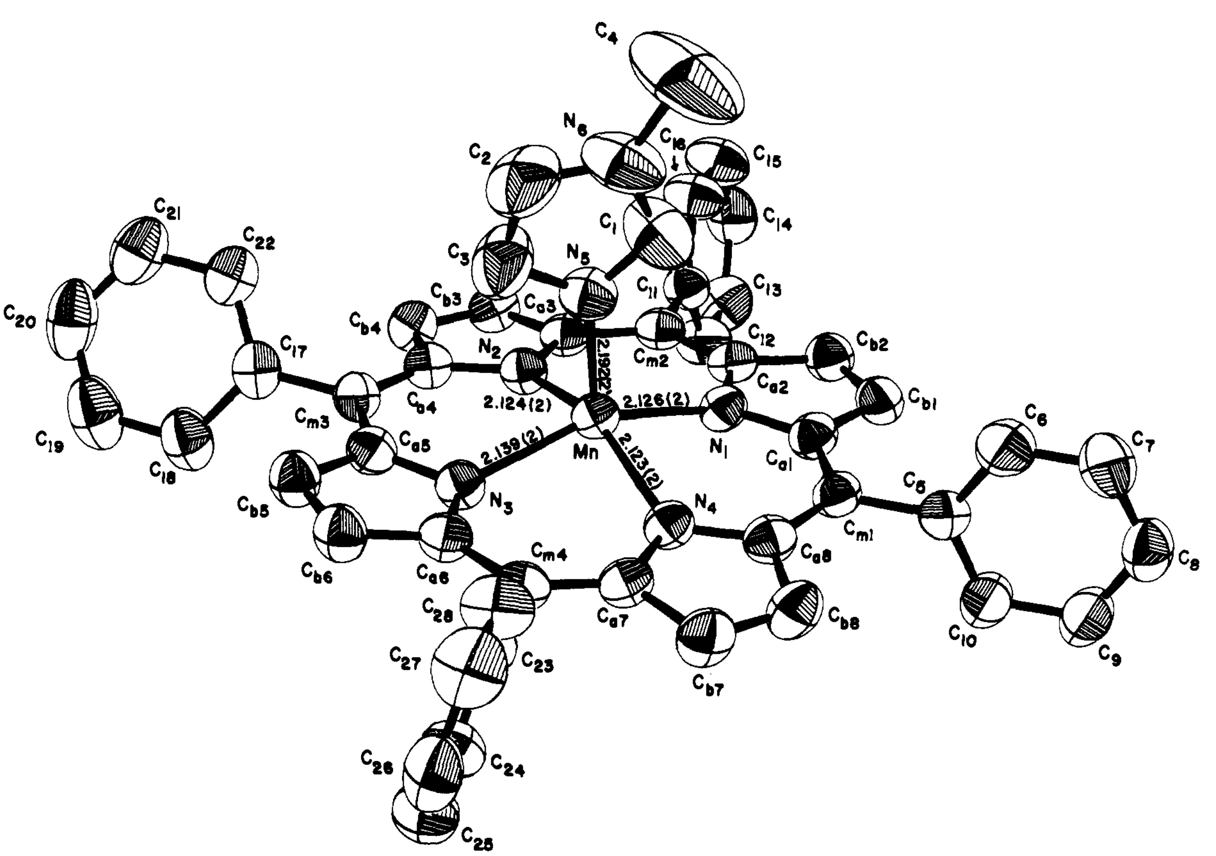

Figure 1. A computer-drawn model of the Mn(1-MeIm)(TPP) molecule. The label assigned to each atom is displayed. Also shown are the bond distances of the coordination group.

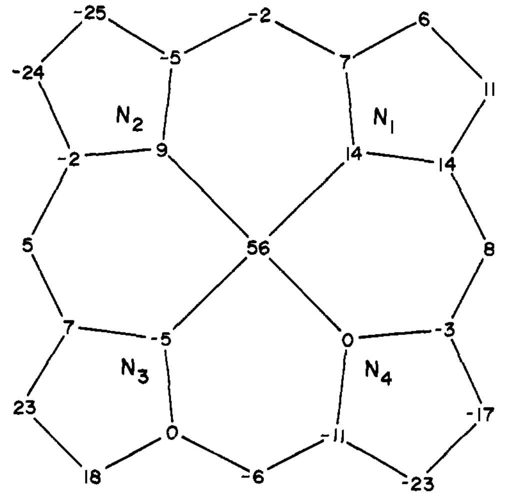

Figure 2. A formal diagram of the porphinato core showing the perpendicular displacement of each atom, in units of 0.01 Å, from the mean plane of the 24-atom core. The diagram has the same general orientation as that given in Figure 1; in addition, each pyrrole ring is identified by the label assigned to its nitrogen atom.

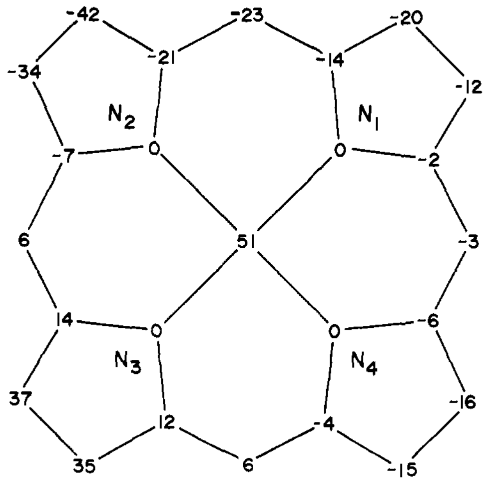

Figure 3. A formal diagram of the porphinato core showing the perpendicular displacement of each atom, in units of 0.01 Å, from the mean plane of the four porphinato nitrogen atoms. The diagram has the same orientation as Figure 2.

phinato core.[15,16] The 2.065 Å radius of the central hole, Ct···N, while not as large as the 2.098 Å value in Cl_2SnTPP,[15] still corresponds to a substantially expanded core.

Figures 2 and 3 display some aspects of the porphinato core conformation of the molecule. These figures are drawn with the same general orientation (N_1 at upper right, N_2 at upper left, etc.) as Figure 1. Each labeled atom of Figure 1 has been replaced by the value of its perpendicular displacement, in units of 0.01 Å, from the mean plane of the 24-atom core in Figure 2. Figure 3 displays the perpendicular displacements of each atom from the mean plane of the coplanar (±0.002 Å) nitrogen atoms. The dihedral angle between these two mean planes is 3.0°. The manganese(II) atom is displaced out of the porphyrin nitrogen atom plane by 0.512 Å and by 0.557 Å out of the mean plane of the 24-atom core. Thus the entire core, to a very crude approximation, "domes" away from the nitrogen atom plane. From Figures 2 and 3 it is seen that three pyrrole rings (N_1, N_2, and N_4) tilt upwards, out of the mean plane, toward (or following) the manganese(II) atom while the fourth (N_3) pyrrole ring tilts downward. The tilting of the pyrrole rings can be specified by noting the displacement of the manganese(II) atom from the mean plane of each pyrrole ring. For pyrrole rings N_1, N_2, and N_4, the Mn atom is displaced by 0.38, 0.14, and 0.36 Å, respectively, and by 0.85 Å from the mean plane

Table III. Bond Lengths in the Coordination Group, Porphinato Skeleton, and *N*-Methylimidazole Ligand[a]

Type	Length, Å	Type	Length, Å	Type	Length, Å
$\mathrm{Mn{-}N_1}$	2.126 (2)	$\mathrm{C_{a2}{-}C_{m2}}$	1.405 (3)	$\mathrm{C_{m1}{-}C_5}$	1.497 (3)
$\mathrm{Mn{-}N_2}$	2.124 (2)	$\mathrm{C_{a2}{-}C_{b2}}$	1.441 (3)	$\mathrm{C_{m2}{-}C_{11}}$	1.510 (3)
$\mathrm{Mn{-}N_3}$	2.139 (2)	$\mathrm{C_{a3}{-}C_{m2}}$	1.407 (3)	$\mathrm{C_{m3}{-}C_{17}}$	1.497 (3)
$\mathrm{Mn{-}N_4}$	2.123 (2)	$\mathrm{C_{a3}{-}C_{b3}}$	1.438 (3)	$\mathrm{C_{m4}{-}C_{23}}$	1.505 (3)
$\mathrm{Mn{-}N_5}$	2.192 (2)	$\mathrm{C_{a4}{-}C_{m3}}$	1.413 (3)	$\mathrm{C_{b1}{-}C_{b2}}$	1.344 (3)
$\mathrm{N_1{-}C_{a1}}$	1.372 (3)	$\mathrm{C_{a4}{-}C_{b4}}$	1.457 (3)	$\mathrm{C_{b3}{-}C_{b4}}$	1.336 (3)
$\mathrm{N_1{-}C_{a2}}$	1.376 (3)	$\mathrm{C_{a5}{-}C_{m3}}$	1.413 (3)	$\mathrm{C_{b5}{-}C_{b6}}$	1.347 (3)
$\mathrm{N_2{-}C_{a3}}$	1.380 (2)	$\mathrm{C_{a5}{-}C_{b5}}$	1.449 (3)	$\mathrm{C_{b7}{-}C_{b8}}$	1.352 (3)
$\mathrm{N_2{-}C_{a4}}$	1.372 (3)	$\mathrm{C_{a6}{-}C_{m4}}$	1.410 (3)	$\mathrm{N_5{-}C_1}$	1.295 (4)
$\mathrm{N_3{-}C_{a5}}$	1.371 (3)	$\mathrm{C_{a6}{-}C_{b6}}$	1.439 (3)	$\mathrm{N_5{-}C_3}$	1.378 (4)
$\mathrm{N_3{-}C_{a6}}$	1.370 (3)	$\mathrm{C_{a7}{-}C_{m4}}$	1.405 (3)	$\mathrm{N_6{-}C_1}$	1.348 (4)
$\mathrm{N_4{-}C_{a7}}$	1.376 (3)	$\mathrm{C_{a7}{-}C_{b7}}$	1.440 (3)	$\mathrm{N_6{-}C_2}$	1.326 (4)
$\mathrm{N_4{-}C_{a8}}$	1.370 (3)	$\mathrm{C_{a8}{-}C_{m1}}$	1.401 (3)	$\mathrm{N_6{-}C_4}$	1.492 (5)
$\mathrm{C_{a1}{-}C_{m1}}$	1.409 (3)	$\mathrm{C_{a8}{-}C_{b8}}$	1.447 (3)	$\mathrm{C_2{-}C_3}$	1.338 (5)
$\mathrm{C_{a1}{-}C_{b1}}$	1.448 (3)				

[a] The numbers in parentheses are the estimated standard deviations.

Table IV. Bond Angles in the Coordination Group, Porphinato Skeleton, and *N*-Methylimidazole Ring[a]

Angle	Value, deg	Angle	Value, deg	Angle	Value, deg
$\mathrm{N_1MnN_2}$	86.71 (6)	$\mathrm{C_{m3}C_{a4}C_{b4}}$	125.3 (2)	$\mathrm{C_{a1}C_{b1}C_{b2}}$	107.3 (2)
$\mathrm{N_1MnN_3}$	152.33 (7)	$\mathrm{N_3C_{a5}C_{m3}}$	125.1 (2)	$\mathrm{C_{a2}C_{b2}C_{b1}}$	107.5 (2)
$\mathrm{N_1MnN_4}$	86.32 (6)	$\mathrm{N_3C_{a5}C_{b5}}$	109.2 (2)	$\mathrm{C_{a3}C_{b3}C_{b4}}$	108.1 (2)
$\mathrm{N_1MnN_5}$	110.76 (7)	$\mathrm{C_{m3}C_{a5}C_{b5}}$	125.7 (2)	$\mathrm{C_{a4}C_{b4}C_{b3}}$	107.2 (2)
$\mathrm{N_2MnN_3}$	86.54 (6)	$\mathrm{N_3C_{a6}C_{m4}}$	125.3 (2)	$\mathrm{C_{a5}C_{b5}C_{b6}}$	106.8 (2)
$\mathrm{N_2MnN_4}$	151.96 (8)	$\mathrm{N_3C_{a6}C_{b6}}$	109.0 (2)	$\mathrm{C_{a6}C_{b6}C_{b5}}$	107.9 (2)
$\mathrm{N_2MnN_5}$	107.83 (7)	$\mathrm{C_{m4}C_{a6}C_{b6}}$	125.7 (2)	$\mathrm{C_{a7}C_{b7}C_{b8}}$	107.4 (2)
$\mathrm{N_3MnN_4}$	87.15 (6)	$\mathrm{N_4C_{a7}C_{m4}}$	125.4 (2)	$\mathrm{C_{a8}C_{b8}C_{b7}}$	107.1 (2)
$\mathrm{N_3MnN_5}$	96.85 (7)	$\mathrm{N_4C_{a7}C_{b7}}$	109.2 (2)	$\mathrm{C_1N_5C_3}$	104.4 (2)
$\mathrm{N_4MnN_5}$	100.04 (7)	$\mathrm{C_{m4}C_{a7}C_{b7}}$	125.4 (2)	$\mathrm{N_5C_1N_6}$	111.8 (3)
$\mathrm{C_{a1}N_1C_{a2}}$	106.9 (2)	$\mathrm{N_4C_{a8}C_{m1}}$	125.5 (2)	$\mathrm{C_1N_6C_2}$	107.1 (2)
$\mathrm{C_{a3}N_2C_{a4}}$	107.1 (2)	$\mathrm{N_4C_{a8}C_{b8}}$	109.2 (2)	$\mathrm{C_1N_6C_4}$	125.5 (3)
$\mathrm{C_{a5}N_3C_{a6}}$	107.2 (2)	$\mathrm{C_{m1}C_{a8}C_{b8}}$	125.3 (2)	$\mathrm{C_2N_6C_4}$	127.4 (3)
$\mathrm{C_{a7}N_4C_{a8}}$	107.1 (2)	$\mathrm{C_{a1}C_{m1}C_{a8}}$	125.7 (2)	$\mathrm{N_6C_2C_3}$	107.0 (3)
$\mathrm{N_1C_{a1}C_{m1}}$	125.8 (2)	$\mathrm{C_{a1}C_{m1}C_5}$	116.5 (2)	$\mathrm{C_2C_3N_5}$	109.7 (3)
$\mathrm{N_1C_{a1}C_{b1}}$	109.0 (2)	$\mathrm{C_{a8}C_{m1}C_5}$	117.7 (2)	$\mathrm{MnN_1C_{a1}}$	125.4 (1)
$\mathrm{C_{m1}C_{a1}C_{b1}}$	125.1 (2)	$\mathrm{C_{a2}C_{m2}C_{a3}}$	126.2 (2)	$\mathrm{MnN_1C_{a2}}$	126.8 (1)
$\mathrm{N_1C_{a2}C_{m2}}$	125.4 (2)	$\mathrm{C_{a2}C_{m2}C_{11}}$	116.7 (2)	$\mathrm{MnN_2C_{a3}}$	127.0 (1)
$\mathrm{N_1C_{a2}C_{b2}}$	109.2 (2)	$\mathrm{C_{a3}C_{m2}C_{11}}$	117.0(2)	$\mathrm{MnN_2C_{a4}}$	125.6 (1)
$\mathrm{C_{m2}C_{a2}C_{b2}}$	125.4 (2)	$\mathrm{C_{a4}C_{m3}C_{a5}}$	125.4 (2)	$\mathrm{MnN_3C_{a5}}$	123.5 (1)
$\mathrm{N_2C_{a3}C_{m2}}$	125.4 (2)	$\mathrm{C_{a4}C_{m3}C_{17}}$	116.9 (2)	$\mathrm{MnN_3C_{a6}}$	122.9 (1)
$\mathrm{N_2C_{a3}C_{b3}}$	108.9 (2)	$\mathrm{C_{a5}C_{m3}C_{17}}$	117.7 (2)	$\mathrm{MnN_4C_{a7}}$	125.2 (1)
$\mathrm{C_{m2}C_{a3}C_{b3}}$	125.7 (2)	$\mathrm{C_{a6}C_{m4}C_{a7}}$	126.7 (2)	$\mathrm{MnN_4C_{a8}}$	126.3 (1)
$\mathrm{N_2C_{a4}C_{m3}}$	126.0 (2)	$\mathrm{C_{a6}C_{m4}C_{23}}$	117.1 (2)	$\mathrm{MnN_5C_1}$	130.4 (2)
$\mathrm{N_2C_{a4}C_{b4}}$	108.7 (2)	$\mathrm{C_{a7}C_{m4}C_{23}}$	116.2 (2)	$\mathrm{MnN_5C_3}$	125.2 (2)

[a] The numbers in parentheses are the estimated standard deviations.

of pyrrole ring N_3. The conformation of the core can be most simply described by noting its similarity to the three sides and raised flap of an umbrella tent. Similar deformations of the porphyrin core, although not as extreme, have been found in Tl(Cl)(OEP)[17] and $Nb_2(O)_3(TPP)_2$.[18] Each of these derivatives, along with Mn(1-MeIm)(TPP), has a large metal atom which is displaced substantially out-of-plane.

The dihedral angles between the mean plane of the porphyrin skeleton and the mean planes of the four phenyl groups are 85.1, 81.0, 56.4, and 78.9°. The average value of the internal angles of the peripheral phenyl groups is 120.0°. The individual C-C bond distances (average = 1.380 Å) in the four phenyl groups are foreshortened from the standard aromatic separation of 1.397 Å because of the complex thermal motion of these groups. This pattern of foreshortening has been noted and discussed previously;[5,15] this effect largely disappears at low temperature.[5]

The 1-methylimidazole ligand is planar (±0.004 Å); the manganese(II) atom is 0.018 Å out of this plane. The angle between the normal to the ligand plane and the normal to the mean plane of the core is 82.8°. The Mn-N(1-MeIm) vector is tipped 10.9° from the normal to the core and 8.0° from the normal to the mean porphinato nitrogen plane. A nonbonded contact of 3.40 Å between the *N*-methyl group and a neighboring porphyrin core is a possible reason for the tilt of the ligand. Similar off-axis distortions have been found in other imidazole adducts of metalloporphyrins[19] and may well occur in the coordination group of heme proteins. Moffat et al.[20] have suggested that the apparent nonlinear binding of cyanide and carbon monoxide in cyanomethemoglobin and carbonmonoxyhemoglobin results from a tilting of these ligands off the heme axis. In these cases, the proximal histidine ligand may also bind off axis in a way that minimizes the overall distortion of the heme coordination group.

Table V. Stereochemical Parameters of Five-Coordinate Metalloporphyrins[a]

Metalloporphyrin	Distances in Å					Ref
	$M-N_p$	Ct···N	$M\cdots P_N$	$M\cdots P_c$	$M-L_{ax}$	
$Mg(H_2O)(TPP)$	2.072	2.054	0.27	0.27	2.099	27
Mn(Cl)(TPP)[b]	2.088	1.990	0.27	0.27	2.373	28
Fe(X)(porphyrin)[c]	2.067	2.015	0.45	0.45	2.218, 1.842[c]	30
Mn(1-MeIm)(TPP)	2.128	2.065	0.52	0.56	2.192	This work
Fe(2-MeIm)(TPP)	2.086	2.04	0.42	0.55	2.161	31
Co(1-MeIm)(TPP)	1.977	1.973	0.13	0.14	2.157	19a
Zn(py)(TPyP)	2.073	2.047	0.33	0.33	2.143	32
Tl(Cl)(OEP)	2.212	2.10	0.69	0.75	2.449	17

[a] N_p is porphinato nitrogen; Ct denotes the center of the porphinato core; P_N, the mean plane of the four porphinato nitrogen atoms; P_c, the mean plane of the 24-atom core. [b] Average of the two determinations. The results for $Mn(N_3)(TPP)$[29] are similar. [c] Average values from the structure of chlorohemin and the methoxyiron(III) derivative of mesoporphyrin IX dimethyl ester, M–L are the Fe–Cl and Fe–O distances, respectively.

The dihedral angles between the 1-methylimidazole plane and the planes defined by N_5MnC_{m1} and N_5MnN_1 are 29.7 and 15.4°, respectively. Thus the orientation of the axial ligand is somewhat between the most favorable and least favorable for minimizing steric interactions of the ligand hydrogen atoms with porphyrin core atoms.[16] With the large displacement of the Mn atom out of the porphyrin plane, there are, however, no significant contacts between the ligand and atoms of the core ($H_{Im}\cdots$core atoms > 2.94 Å).

The coordination group geometry of Mn(1-MeIm)(TPP) reflects the large size of the high-spin d^5 Mn atom. The average Mn–porphyrin nitrogen ($Mn-N_p$) bond distance is 2.128 (7) Å. A careful examination of Figures 1 and 2 reveals, however, that the $Mn-N_p$ bond distances fall into two classes. The first class is to the nitrogen atoms of the three pyrrole rings which "follow" the Mn atom; their average value is 2.124 (2) Å. The second is to the pyrrole ring which tilts away; its value (2.139 (2) Å)[21] is significantly different than those of the first class. The axial Mn–N(1-MeIm) bond distance is 2.192 (2) Å. All Mn–N bond distances in Mn(1-MeIm)(TPP) are shorter than the few $Mn^{II}-N$ bond distances available for comparison.[22] These structures encompass a variety of coordination geometries; $Mn^{II}-N$ bond distances range from 2.19 to 2.4 Å. The most pertinent structural comparison can be made with the trigonal bipyramidal complex $MnCl_2(2\text{-MeIm})_3$.[22i] The equatorial Mn–N bond distances in this complex are 2.195 Å; the axial Mn–N distance is longer at 2.249 Å. The structures of two four-coordinate manganese(II) macrocycles, MnTPP[5] and MnPc,[4,23] are also known. Both complexes have shorter Mn–N complexing bond lengths than does Mn(1-MeIm)-(TPP), In MnPc,[23] the short Mn–N bond distance of 1.938 (3) Å is attributable to the combination of the small hole size of the phthalocyanato ligand and the intermediate-spin ($S = 3/2$) state of the metal ion. In the toluene solvate of MnTPP,[5] the distance from the porphinato nitrogen atoms to the high spin manganese(II) ion is in the range of 2.082–2.092 Å. The range of values results from the uncertainty in the exact out-of-plane displacement of the metal atom. The suggested upper limit of 2,092 Å is quite comparable to the Mn–Np distances in Mn(1-MeIm)(TPP); a small shortening of the complexing bonds is usually observed with a decrease in coordination number.

The observed preference[2] of the isolable manganese(II) porphyrins to form five-coordinate but not six-coordinate complexes, in contrast to its near neighbors Cr(II),[24] Mn(III), Fe(II), and Fe(III),[16] appears to result from the inability of axial ligands to effect a change from a high-spin to a low-spin manganese(II) configuration. The structure of Mn(1-MeIm)(TPP) clearly shows that when the $d_{x^2-y^2}$ orbital is populated, the metal atom is too far out of the porphyrin plane to permit effective interaction with a sixth (axial) ligand. It should be noted that the apparent inability to form low-spin manganese(II) porphyrins is not precluded by the geometrical requirements of the porphinato ligand; a comparison of structure for a series of four-coordinate porphyrin and phthalocyanine complexes[23] suggests that an intermediate-spin Mn(II) porphyrin would have $Mn-N_p \approx 1.985-2.015$ Å. Low-spin Mn(II) porphyrins would have comparable $Mn-N_p$ distances. Nitric oxide appears to be the only ligand which, when reacted with Mn(II) porphyrins, effects the transition to a low-spin species.[25,26] The molecular stereochemistry of one such nitrosyl derivative has been determined.[26] The average $Mn-N_p$ bond distance in low-spin nitrosyl (4-methylpiperidine)-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatomanganese is 2.028 Å and the Mn atom is nearly centered in the porphyrin plane.

The stereochemical parameters of five-coordinate metalloporphyrins are compared in Table V. The large size of the d^5 manganese(II) atom is quite clear from these data; all structural parameters sensitive to the size of the metal atom (metal atom displacement, Ct···N, $M-N_p$, and M–L (axial) bond lengths) are larger in Mn(1-MeIm)(TPP) than any of the other first-row transition metal complexes entered in Table V. Indeed, only the parameters of the thallium(III) derivative[17] are larger.

A comparison of the structural parameters of Fe(2-MeIm)(TPP)[31] with those of Mn(1-MeIM)(TPP) is particularly enlightening. The type of imidazole ligand required to synthesize the two high-spin five-coordinate derivatives are quite different. As has already been noted, manganese(II) derivatives have a distinct preference for five-coordination irrespective of the choice of axial ligand. With iron(II) derivatives, however, low-spin six-coordinate complexes are readily formed and an imidazole which is sterically inhibitory to six-coordination must be employed to form the five-coordinate complex.[33] The stereochemistry of the five-coordinate iron(II) complex might be thought to be distorted by the (necessary) use of the 2-methylimidazole ligand. However, the differences in the structural parameters of the Mn(II) and Fe(II) derivatives are seen to closely approach the differences in their ionic radii (0.05 Å).[34] Thus the structural results for Mn(1-MeIm)(TPP) strongly support the belief that the coordination group geometry of Fe(2-MeIm)(TPP) is unaffected by the use of the 2-methylimidazole ligand and is therefore typical of that of high-spin five-coordinate iron(II) porphyrin derivatives.

Recent work[6] has indicated close similarities between the functional properties of hemoglobin and myoglobin and the manganese-substituted proteins and that manganese-substituted hemoglobins display the same T → R conformational changes as hemoglobin. Manganese(III)-substituted hemoglobin has been shown to have a very similar structure to that of methemoglobin.[7] As noted previously, the stereochemistry of the five-coordinate iron(II) and manganese(II) porphyrins, which are presumed to be appropriate models of metalloporphyrin stereochemistry in the proteins, are also quite similar. Thus, to the extent that the allosteric properties of MnHb and Hb are determined by the stereochemistry of the metalloporphyrin, their close similarity is not unexpected.

Other than the previously noted short contacts between the 1-methylimidazole ligand and a neighboring porphinato core, the molecules are well separated in the crystal. Intermolecular contacts range from 3.60 Å upwards.

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Supplementary Material Available: Listings of structure factor amplitudes (× 10) (24 pages). Ordering information is given on any current masthead page.

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