

Stereochemistry of Low-Spin Cobalt Porphyrins. VI.
Molecular Stereochemistry of
(1,2-Dimethylimidazole)- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinatocobalt(II)

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Abstract: 1,2-Dimethylimidazole- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinatocobalt(II) crystallizes in the triclinic system as the dibenzene solvate, space group $P\bar{1}$. The unit cell has $a = 13.610$ (3) Å, $b = 15.014$ (4) Å, $c = 12.267$ (3) Å, $\alpha = 92.87$ (1)°, $\beta = 91.33$ (1)°, and $\gamma = 104.77$ (1)° and contains two molecules. The calculated and experimental densities are 1.268 and 1.26 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 four-circle diffractometer. All independent reflections for $(\sin \theta)/\lambda \leq 0.648$ Å⁻¹ were measured; 8986 reflections were retained as observed. These data were used for the determination of structure using the heavy-atom technique. The final conventional and weighted discrepancy factors were 0.048 and 0.072, respectively. The square-pyramidal CoN₅ coordination group has equatorial bond lengths of 1.985 (2) Å; the axial Co-N₆ bond is 2.216 (2) Å. The cobalt is displaced 0.18 Å from the mean porphinato plane and 0.15 Å from the plane of the porphinato nitrogens.

Earlier structural studies of amine complexes of low-spin ($S = 1/2$) cobalt(II) porphyrins have demonstrated that the presence of the odd electron in the 3d_{z²} orbital of the cobalt atom has an important effect in modulating the geometry of the axial Co-N bond(s).^{1,2} Thus for the five-coordinate 1-methylimidazolecobalt(II) derivative of tetraphenylporphyrin, in which the electron density associated with the odd electron in the 3d_{z²} orbital of the cobalt atom is concentrated in the sixth coordination position as a "phantom" ligand, the axial Co-N bond is 2.157 Å. However, for six-coordinate bis(piperidine)tetraphenylporphinatocobalt(III), in which the full effect of the unpaired electron in the 3d_{z²} orbital is along the two axial Co-N bonds, the axial bonds are elongated to 2.436 Å.

Hoard and Scheidt have suggested that the axial Co-N bond in the five-coordinate porphinato complexes should be readily stretched.³ They suggest that substantial increases in this axial bond distance are possible before the enthalpy of formation becomes too unfavorable for bond formation. Therefore, the coordination of a somewhat sterically hindered ligand to a cobalt(II) porphyrin should yield a complex with an increased axial bond distance relative to the distances found for complexes utilizing sterically unhindered ligands.

The quantitative stereochemical parameters reported herein for 1,2-dimethylimidazole- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinatocobalt(II), DMImCOTPP, demonstrate a readily extensible axial Co-N bond. The data reported herein have also been utilized elsewhere for a discussion³ of how the low-spin cobalt atom can serve as a qualitatively acceptable substitute for the iron atom both in the high-spin five-coordinate hemes of deoxyhemoglobin and in the low-spin oxygenated hemes of oxyhemoglobin.

Experimental Section

Crystals of DMImCoTPP were obtained as the benzene solvate by the slow evaporation of benzene solutions of the complex. Preliminary X-ray photographic studies of the crystals suggested a two-molecule triclinic unit cell, space group $P1$ or $P\bar{1}$.⁴ Lattice constants, $a = 13.610$ (3) Å, $b = 15.014$ (4) Å, $c = 12.267$ (3) Å, $\alpha = 92.87$ (1)°, $\beta = 91.33$ (1)°, and $\gamma = 104.77$ (1)° (λ 0.71069 Å), came from a least-squares refinement that utilized the setting angles of 27 reflections, each collected at $\pm 2\theta$, given by the automatic centering routine supplied with the Syntex P $\bar{1}$ diffractometer. A Delauney reduction using these cell parameters confirmed the triclinic description of the unit cell. These constants led to a calculated density at $20 \pm 1^\circ$ of 1.268 g/cm³ for a cell content of 2(CoN₅C₁₉H₃₆·2C₆H₆). The experimental density, measured by flotation, was 1.26 g/cm³.

Intensity data were measured on a Syntex P $\bar{1}$ diffractometer using the θ - 2θ scanning technique with graphite-monochromated Mo K α radiation. The base width of each scan was 1.2° plus an increment to allow for spectral dispersion; background counts were taken at the extremes of scan for a duration of one-half the time required for the scan itself. A variable 2θ scan rate was used as described previously;² the slowest was 1.0°/min and the fastest was 12.0°/min. Four standard reflections that were well distributed in reciprocal space were used for periodic (every 50 reflections) checking on the alignment and possible deterioration of the crystal; only random variations were noted. All independent data having $(\sin \theta)/\lambda \leq 0.648$ Å⁻¹ were measured.

The specimen crystal had dimensions of 0.4 × 0.4 × 0.6 mm. With a linear absorption coefficient of 0.42 mm⁻¹ for Mo K α radiation, the maximum error in any structure amplitude resulting from neglect of absorption corrections was seen to be $\leq 2.5\%$. The net intensities were reduced directly to a set of relative squared amplitudes, $|F_o|^2$, by application of the standard Lorentz and polarization factors. Standard deviations were calculated as described previously.² All data having $F_o < 3\sigma(F_o)$ were taken to be unobserved, leaving 8986 independent observed data from ~ 11000 independent observations. Only the observed data were used for the determination and refinement of structure.

The initial choice of centrosymmetric $P\bar{1}$ as the space group was fully confirmed by all subsequent developments during the determination of structure. The structure was solved by standard heavy-atom methods.⁵ Block-diagonal least-squares refinement⁶

(4) N. F. M. Henry and K. Lonsdale, Ed., "International Tables for X-Ray Crystallography," Vol. I, 2nd ed, The Kynoch Press, Birmingham, England, 1965, p 75.

(5) The Fourier program ALFF was used. C. R. Hubbard, C. O. Quicksall, and R. A. Jacobson, "The Fast Fourier Algorithm and the Programs ALFF, ALFFDP, ALFFPROJ, ALFFT, and FRIEDEL," IS-2625, Ames Laboratory, Iowa State University, Ames, Iowa, 1971.

(1) W. R. Scheidt, *J. Amer. Chem. Soc.*, **96**, 90 (1974).

(2) W. R. Scheidt, *J. Amer. Chem. Soc.*, **96**, 84 (1974).

(3) (a) J. L. Hoard and W. R. Scheidt, *Proc. Nat. Acad. Sci. U. S.*, **70**, 3919 (1973). (b) A quantitative emendation has been made: *ibid.*, **71**, 1578 (1974).

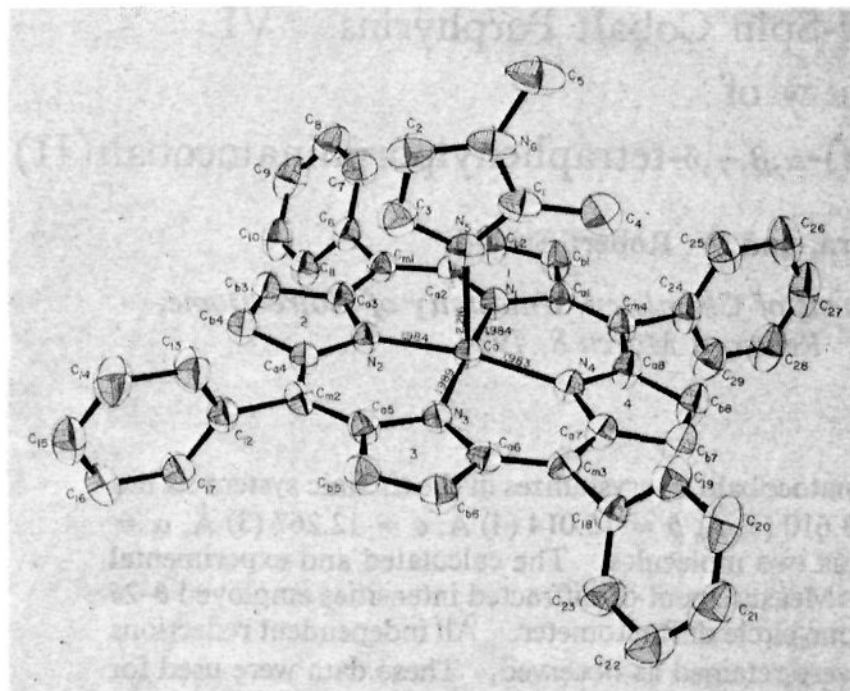


Figure 1. Computer-drawn model in perspective of the DMIm-CoTPP molecule. Each atom is represented by an ellipsoid having the orientation and relative size required by the thermal parameters listed in Table II. Each atom is identified with the symbol used throughout the paper.

was followed by a difference synthesis which revealed electron density concentrations appropriately located for all hydrogen atom positions except those of the two methyl groups of the imidazole and the benzene solvates. Refinement was continued with fixed coordinates and isotropic thermal parameters (fixed one unit higher than that of the associated atom) for the hydrogen atoms; this refinement was then carried to convergence using anisotropic thermal parameters for all other atoms. The final value of

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

was 0.048, that of

$$R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}$$

was 0.072, with a final data/parameter ratio of 14.7. The estimated standard deviation of an observation of unit weight was 2.2. The final parameters shifts were less than 50% of the estimated standard deviations during the final cycle,⁷ with most being less than 15%. A final difference Fourier was judged to be significantly free of features with the largest peak having a density of 0.5 e/Å³.

Atomic coordinates and the associated anisotropic thermal parameters in the asymmetric unit of structure are listed in Tables I and II, respectively; bond parameters⁸ are listed in Tables III and IV. The numbering scheme used for the atoms is displayed in Figure 1.

Discussion

Figure 1 is a model⁹ in perspective of the DMIm-CoTPP molecule as it exists in the crystal. Also displayed in Figure 1 are the identifying labels assigned to the atoms, and the bond distances in the coordination group.

The departures of the atoms of the porphine core

(6) The program REFINE, written by J. J. Park at Cornell University was used. The function minimized was $\sum w(|F_o| - S|F_c|)^2$ where w is the weight ($= 1/\sigma^2$) and S is the scale factor. Atomic form factors were from D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968), with real and imaginary corrections for anomalous dispersion in the form factor of the cobalt atom from D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).

(7) See paragraph at end of paper regarding supplementary material.

(8) Estimated standard deviations in bond lengths and angles were calculated following W. R. Busing, K. O. Martin, and H. A. Levy "ORFFE, a Fortran Crystallographic Function and Error Program," ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

(9) C. K. Johnson, "ORTEP, a Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations," ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

Table I. Atomic Coordinates in the Unit Cell

Atom type	Coordinates ^a		
	10 ⁴ x	10 ⁴ y	10 ⁴ z
Co ^b	1444 (0)	2618 (0)	2887 (0)
N ₁	1653 (1)	2235 (1)	1356 (1)
N ₂	2927 (1)	2853 (1)	3203 (1)
N ₃	1268 (1)	3144 (1)	4367 (1)
N ₄	30 (1)	2638 (1)	2485 (1)
C _{a1}	938 (2)	2033 (2)	500 (2)
C _{a2}	2534 (2)	2125 (2)	906 (2)
C _{a3}	3648 (2)	2642 (1)	2534 (2)
C _{a4}	3437 (2)	3140 (1)	4200 (2)
C _{a5}	1988 (2)	3369 (1)	5218 (2)
C _{a6}	388 (2)	3263 (1)	4815 (2)
C _{a7}	-686 (2)	2868 (2)	3150 (2)
C _{a8}	-462 (2)	2413 (2)	1471 (2)
C _{m1}	3483 (2)	2304 (2)	1439 (2)
C _{m2}	3007 (2)	3380 (2)	5153 (2)
C _{m3}	-547 (2)	3134 (2)	4256 (2)
C _{m4}	-56 (2)	2101 (2)	546 (2)
N ₅	1225 (1)	1211 (1)	3470 (2)
N ₆	656 (2)	-237 (1)	3900 (2)
C _{b1}	1372 (2)	1780 (2)	-483 (2)
C _{b2}	2360 (2)	1839 (2)	-236 (2)
C _{b3}	4608 (2)	2787 (2)	3125 (2)
C _{b4}	4476 (2)	3098 (2)	4148 (2)
C _{b5}	1542 (2)	3608 (2)	6208 (2)
C _{b6}	553 (2)	3541 (2)	5959 (2)
C _{b7}	-1620 (2)	2799 (2)	2536 (2)
C _{b8}	-1483 (2)	2513 (2)	1508 (2)
C ₁	476 (2)	458 (2)	3331 (2)
C ₂	1602 (2)	97 (2)	4423 (2)
C ₃	1939 (2)	974 (2)	4163 (2)
C ₄	-465 (3)	351 (2)	2658 (3)
C ₅	25 (3)	-1190 (2)	3920 (3)
C ₆	4371 (2)	2186 (2)	805 (2)
C ₇	4373 (2)	1335 (2)	295 (2)
C ₈	5185 (2)	1246 (2)	-332 (2)
C ₉	6000 (2)	1993 (2)	-435 (2)
C ₁₀	6017 (2)	2837 (2)	78 (2)
C ₁₁	5200 (2)	2927 (2)	681 (2)
C ₁₂	3680 (2)	3645 (2)	6155 (2)
C ₁₃	3698 (2)	3002 (2)	6926 (2)
C ₁₄	4366 (2)	3230 (2)	7834 (2)
C ₁₅	5005 (2)	4099 (2)	7983 (2)
C ₁₆	4988 (2)	4749 (2)	7242 (2)
C ₁₇	4330 (2)	4522 (2)	6326 (2)
C ₁₈	-1440 (2)	3278 (2)	4865 (2)
C ₁₉	-2277 (2)	2547 (2)	4988 (2)
C ₂₀	-3111 (2)	2671 (2)	5543 (3)
C ₂₁	-3122 (2)	3531 (3)	5983 (2)
C ₂₂	-2294 (2)	4272 (2)	5864 (3)
C ₂₃	-1460 (2)	4144 (2)	5302 (2)
C ₂₄	-744 (2)	1817 (2)	-457 (2)
C ₂₅	-1237 (2)	896 (2)	-691 (2)
C ₂₆	-1913 (2)	633 (3)	-1610 (2)
C ₂₇	-2074 (2)	1311 (3)	-2269 (2)
C ₂₈	-1573 (2)	2230 (3)	-2055 (2)
C ₂₉	-900 (2)	2476 (2)	-1147 (2)
C ₃₀	5048 (4)	259 (3)	6406 (5)
C ₃₁	4298 (4)	745 (3)	6393 (5)
C ₃₂	3412 (3)	416 (3)	6952 (5)
C ₃₃	3277 (3)	-367 (3)	7518 (4)
C ₃₄	4025 (3)	-839 (3)	7525 (4)
C ₃₅	4906 (3)	-513 (3)	6999 (4)
C ₃₆	2868 (3)	4376 (3)	93 (4)
C ₃₇	2325 (4)	4564 (3)	988 (4)
C ₃₈	1544 (4)	5021 (3)	822 (4)
C ₃₉	1349 (3)	5261 (3)	-234 (4)
C ₄₀	1891 (3)	5067 (3)	-1095 (3)
C ₄₁	2657 (3)	4629 (3)	-934 (3)

^a Numbers in parentheses are the estimated standard deviations.

^b For Co 10⁵x = 14,444 (2), 10⁵y = 26,179 (2), 10⁵z = 28,868 (2).

from the mean plane of the core are displayed in Figure 2, which is drawn in the same orientation as Figure 1.

Table II. Anisotropic Thermal Parameters^a

Atom type	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	2.17 (1)	2.88 (1)	2.29 (1)	0.67 (1)	-0.02 (1)	-0.05 (1)
N ₁	2.4 (1)	3.4 (1)	2.5 (1)	0.7 (1)	0.0 (1)	-0.1 (1)
N ₂	2.4 (1)	3.0 (1)	2.4 (1)	0.7 (1)	0.0 (1)	-0.1 (1)
N ₃	2.4 (1)	2.9 (1)	2.6 (1)	0.6 (1)	0.0 (1)	-0.1 (1)
N ₄	2.5 (1)	3.5 (1)	2.6 (1)	0.9 (1)	0.0 (1)	0.0 (1)
C _{a1}	2.8 (1)	3.9 (1)	2.6 (1)	0.7 (1)	-0.1 (1)	-0.4 (1)
C _{a2}	2.8 (1)	3.5 (1)	2.7 (1)	0.7 (1)	0.2 (1)	-0.3 (1)
C _{a3}	2.5 (1)	3.1 (1)	2.9 (1)	0.8 (1)	0.1 (1)	0.1 (1)
C _{a4}	2.5 (1)	3.1 (1)	2.8 (1)	0.7 (1)	-0.2 (1)	0.1 (1)
C _{a5}	2.9 (1)	3.1 (1)	2.6 (1)	0.6 (1)	-0.0 (1)	-0.2 (1)
C _{a6}	3.0 (1)	2.7 (1)	2.7 (1)	0.7 (1)	0.3 (1)	0.0 (1)
C _{a7}	2.7 (1)	3.5 (1)	3.0 (1)	1.1 (1)	0.1 (1)	0.3 (1)
C _{a8}	2.6 (1)	4.4 (1)	2.8 (1)	1.1 (1)	-0.3 (1)	0.1 (1)
C _{m1}	2.6 (1)	3.3 (1)	2.9 (1)	0.9 (1)	0.2 (1)	0.1 (1)
C _{m2}	2.8 (1)	3.0 (1)	2.6 (1)	0.5 (1)	-0.3 (1)	-0.1 (1)
C _{m3}	2.7 (1)	3.1 (1)	3.0 (1)	1.0 (1)	0.4 (1)	0.2 (1)
C _{m4}	2.7 (1)	4.3 (1)	2.6 (1)	0.8 (1)	-0.3 (1)	-0.3 (1)
N ₅	3.7 (1)	3.1 (1)	3.2 (1)	0.9 (1)	0.4 (1)	0.2 (1)
N ₆	5.2 (1)	2.8 (1)	3.9 (1)	1.0 (1)	1.5 (1)	0.5 (1)
C _{b1}	3.1 (1)	5.8 (1)	2.9 (1)	1.0 (1)	-0.1 (1)	-0.8 (1)
C _{b2}	3.3 (1)	5.7 (1)	2.7 (1)	1.1 (1)	0.2 (1)	-0.9 (1)
C _{b3}	2.7 (1)	4.5 (1)	3.1 (1)	1.3 (1)	-0.1 (1)	-0.0 (1)
C _{b4}	2.7 (1)	4.2 (1)	3.1 (1)	1.1 (1)	-0.4 (1)	-0.0 (1)
C _{b5}	3.4 (1)	4.4 (1)	2.9 (1)	1.0 (1)	0.0 (1)	-0.8 (1)
C _{b6}	3.2 (1)	4.3 (1)	2.8 (1)	0.9 (1)	0.3 (1)	-0.5 (1)
C _{b7}	3.0 (1)	6.2 (1)	3.4 (1)	2.1 (1)	-0.1 (1)	0.2 (1)
C _{b8}	3.1 (1)	6.5 (1)	3.1 (1)	2.0 (1)	-0.3 (1)	0.1 (1)
C ₁	4.2 (1)	3.2 (1)	3.6 (1)	0.9 (1)	1.0 (1)	0.1 (1)
C ₂	6.1 (2)	4.1 (1)	4.2 (1)	2.0 (1)	0.4 (1)	0.9 (1)
C ₃	4.7 (1)	3.9 (1)	4.1 (1)	1.3 (1)	0.1 (1)	0.3 (1)
C ₄	5.0 (1)	4.7 (1)	6.0 (2)	0.6 (1)	-0.7 (1)	0.0 (1)
C ₅	6.9 (2)	3.0 (1)	6.8 (2)	0.5 (1)	2.7 (1)	0.9 (1)
C ₆	2.7 (1)	4.3 (1)	2.7 (1)	1.3 (1)	0.1 (1)	0.0 (1)
C ₇	4.0 (1)	4.4 (1)	4.0 (1)	1.5 (1)	0.5 (1)	-0.4 (1)
C ₈	4.8 (1)	6.0 (2)	4.5 (1)	2.7 (1)	0.5 (1)	-0.4 (1)
C ₉	3.9 (1)	7.9 (2)	4.2 (1)	2.8 (1)	1.0 (1)	0.3 (1)
C ₁₀	3.0 (1)	6.5 (1)	3.9 (1)	1.1 (1)	0.3 (1)	0.4 (1)
C ₁₁	2.9 (1)	4.6 (1)	3.3 (1)	1.0 (1)	0.1 (1)	0.1 (1)
C ₁₂	2.7 (1)	3.6 (1)	2.6 (1)	0.8 (1)	-0.2 (1)	-0.3 (1)
C ₁₃	4.0 (1)	4.2 (1)	3.7 (1)	0.2 (1)	-0.9 (1)	0.7 (1)
C ₁₄	4.6 (1)	5.6 (1)	3.8 (1)	1.0 (1)	-0.8 (1)	1.1 (1)
C ₁₅	3.7 (1)	5.8 (1)	3.2 (1)	1.1 (1)	-0.8 (1)	-0.3 (1)
C ₁₆	4.1 (1)	4.3 (1)	3.8 (1)	0.5 (1)	-1.0 (1)	-0.7 (1)
C ₁₇	4.1 (1)	3.6 (1)	3.5 (1)	0.6 (1)	-0.7 (1)	-0.2 (1)
C ₁₈	2.7 (1)	3.9 (1)	3.0 (1)	1.3 (1)	0.3 (1)	0.3 (1)
C ₁₉	3.2 (1)	4.7 (1)	4.6 (1)	1.1 (1)	0.4 (1)	0.6 (1)
C ₂₀	3.0 (1)	7.1 (2)	5.6 (1)	1.1 (1)	0.8 (1)	1.6 (1)
C ₂₁	4.4 (1)	9.0 (2)	4.4 (1)	3.6 (1)	1.1 (1)	0.3 (1)
C ₂₂	5.3 (1)	6.6 (2)	6.0 (2)	3.2 (1)	0.9 (1)	-0.9 (1)
C ₂₃	4.2 (1)	4.4 (1)	5.5 (1)	1.6 (1)	1.1 (1)	-0.2 (1)
C ₂₄	2.7 (1)	5.8 (1)	2.6 (1)	1.2 (1)	-0.2 (1)	-0.4 (1)
C ₂₅	3.9 (1)	5.7 (1)	4.3 (1)	0.4 (1)	-0.2 (1)	-1.0 (1)
C ₂₆	3.8 (1)	8.1 (2)	4.5 (1)	0.4 (1)	-0.3 (1)	-1.7 (1)
C ₂₇	3.3 (1)	11.3 (2)	3.5 (1)	2.0 (1)	-0.2 (1)	-1.6 (1)
C ₂₈	4.6 (1)	9.1 (2)	3.1 (1)	2.5 (1)	-0.5 (1)	-0.4 (1)
C ₂₉	4.6 (1)	6.4 (2)	3.4 (1)	2.1 (1)	-0.4 (1)	0.2 (1)
C ₃₀	7.8 (3)	7.5 (2)	12.5 (4)	2.4 (2)	1.0 (2)	1.6 (2)
C ₃₁	7.7 (3)	7.5 (2)	13.7 (4)	1.9 (2)	0.9 (2)	3.6 (2)
C ₃₂	6.2 (2)	6.0 (2)	14.9 (4)	1.5 (2)	-0.6 (2)	1.6 (2)
C ₃₃	6.1 (2)	6.2 (2)	10.2 (3)	1.0 (1)	-0.8 (2)	1.1 (2)
C ₃₄	7.0 (2)	6.7 (2)	9.4 (3)	1.5 (2)	-1.4 (2)	1.1 (2)
C ₃₅	7.6 (2)	6.1 (2)	11.0 (3)	2.4 (2)	-0.3 (2)	0.7 (2)
C ₃₆	8.2 (2)	5.4 (2)	10.8 (3)	2.4 (2)	-2.4 (2)	-1.3 (2)
C ₃₇	10.8 (3)	6.0 (2)	8.9 (3)	-0.5 (2)	-1.1 (2)	1.6 (2)
C ₃₈	8.0 (3)	9.1 (3)	9.0 (3)	0.6 (2)	2.3 (2)	0.4 (2)
C ₃₉	5.6 (2)	7.9 (3)	11.3 (3)	1.7 (2)	-0.2 (2)	-0.6 (2)
C ₄₀	7.3 (2)	7.4 (2)	8.2 (2)	2.4 (2)	-1.4 (2)	-2.0 (2)
C ₄₁	7.9 (2)	7.3 (2)	8.1 (2)	3.4 (2)	-1.4 (2)	-2.2 (2)

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

Each labeled atom of Figure 1 has been replaced in Figure 2 by the value of the out-of-plane displacement in units of 0.01 Å. The departures from planarity of

the porphinato core of this derivative are small relative to those in a number of other porphyrins. Local flatness is preserved in the trigonal carbon atoms of the

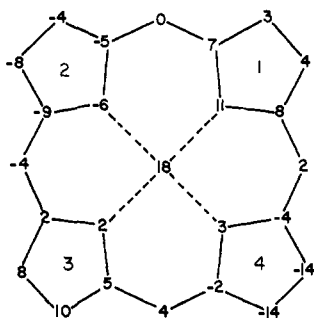


Figure 2. Formal diagram of the porphinato core with the same relative orientation as Figure 1. Each atom symbol has been replaced by its perpendicular displacement, in units of 0.01 Å, from the mean plane of the porphinato core.

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

Type	Length (Å)	Type	Length (Å)	Type	Length (Å)
Co-N ₁	1.984 (2)	C _{a1} -C _{b1}	1.432 (3)	C _{m1} -C ₆	1.498 (3)
Co-N ₂	1.984 (2)	C _{a2} -C _{m1}	1.391 (3)	C _{m2} -C ₁₂	1.495 (3)
Co-N ₃	1.989 (2)	C _{a2} -C _{b2}	1.441 (3)	C _{m3} -C ₁₈	1.497 (3)
Co-N ₄	1.983 (2)	C _{a3} -C _{m1}	1.404 (3)	C _{m4} -C ₂₄	1.505 (3)
Co-N ₅	2.216 (2)	C _{a3} -C _{b3}	1.441 (3)	C _{b1} -C _{b2}	1.351 (4)
N ₁ -C _{a1}	1.383 (3)	C _{a4} -C _{m2}	1.390 (3)	C _{b3} -C _{b4}	1.346 (3)
N ₁ -C _{a2}	1.375 (3)	C _{a4} -C _{b4}	1.433 (3)	C _{b5} -C _{b6}	1.347 (4)
N ₂ -C _{a3}	1.381 (3)	C _{a5} -C _{m2}	1.388 (3)	C _{b7} -C _{b8}	1.345 (4)
N ₂ -C _{a4}	1.383 (3)	C _{a5} -C _{b5}	1.440 (3)	N ₅ -C ₁	1.319 (3)
N ₃ -C _{a5}	1.380 (3)	C _{a6} -C _{m3}	1.397 (3)	N ₅ -C ₃	1.401 (4)
N ₃ -C _{a6}	1.378 (3)	C _{a6} -C _{b6}	1.439 (3)	N ₆ -C ₂	1.390 (4)
N ₄ -C _{a7}	1.384 (3)	C _{a7} -C _{m3}	1.391 (3)	N ₆ -C ₁	1.353 (3)
N ₄ -C _{a8}	1.385 (3)	C _{a7} -C _{b7}	1.441 (3)	N ₆ -C ₅	1.467 (4)
C _{a1} -C _{m4}	1.385 (3)	C _{a8} -C _{m4}	1.385 (3)	C ₂ -C ₃	1.335 (4)
		C _{a8} -C _{b8}	1.437 (4)	C ₁ -C ₄	1.482 (4)

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

inner 16-membered ring and, of course, in the pyrrole rings.

Bond lengths in the porphinato skeleton depart immaterially from 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 carbon atom that is bonded to the core, the averaged values for bond lengths of a given chemical type in the porphine skeleton are N-C_a, 1.381 (3, 3); C_a-C_m, 1.391 (4, 3); C_a-C_b, 1.438 (3, 3); C_b-C_b, 1.347 (2, 4); C_m-C_p, 1.499 (3, 3) Å, wherein the first number in parentheses following each averaged length is the mean deviation in units of 0.001 Å and the second is the value of the estimated standard deviation for an individually determined length.¹⁰ Similar trivial departures from dimensional equivalence are observed for bond angles of a given chemical type: C_aNC_a, 104.7 (1, 2); C_aC_mC_a, 123.0 (6, 2); NC_aC_b, 110.7 (1, 2); NC_aC_m, 125.9 (1, 2); C_aC_bC_b, 107.0 (2, 2); and C_aC_mC_p, 118.5° (4, 2).

The dihedral angles between the mean plane of the porphine skeleton and the planes of the four phenyl groups are 61.3, 83.5, 63.3, and 85.45°. The averaged value of the internal angles in the phenyl rings is 120.0° (7, 3)°. The sum of the angles subtended at C_p is 360.0°, corresponding to a planar trigonal carbon atom. The individually determined C-C bond distances of the four structurally independent phenyl rings

(10) This notation for reporting averaged values for both bond lengths and angles is used throughout the discussion.

show the typical values found for tetraphenylporphyrin derivatives.¹¹

The equatorial Co-N bonds of the square-pyramidal CoN₅ coordination group average to 1.985 (2, 2) Å. The "radius of the central hole," Ct···N, is 1.979 Å. These equatorial structural radii are quite comparable to the Co-N and Ct···N distances, 1.977 and 1.973 Å, respectively, found for MImCoTPP¹ and the 1.987 Å Co-N (\equiv Ct···N) distance that characterizes Pip₂-CoTPP.²

The cobalt atom is displaced from the mean plane (P_N) of the porphinato nitrogen atoms and mean plane (P_O) of the porphinato core toward the axial ligand. The value of the Co···P_N displacement is 0.15 Å; Co···P_O is 0.18 Å. The difference in the two displacements is the consequence of a small (<0.05 Å) doming of the core toward the metal atom, which is a general feature of five-coordinate metalloporphyrins. The axial Co-N_e bond to the 1,2-dimethylimidazole ligand is 2.216 (2) Å, N_e···P_O is 2.37 Å, and N_e···P_N is 2.35 Å; all distances, but notably Co-N_e, are significantly longer than the corresponding distances in related cobalt(II) porphyrin derivatives utilizing sterically unhindered ligands. This can be seen from the structural parameters of the 1-methylimidazolecobalt(II) derivatives of *meso*-tetraphenylporphine¹ and octaethylporphine¹² and the 3,5-lutidinecobalt(II) derivative of tetraphenylporphine¹³ which are, respectively, as follows: Co-N_e, 2.157, 2.15, and 2.161; Co···P_N, 0.13, 0.14, and 0.14; N_e···P_O, 2.30, 2.33, and 2.33 Å. The 2.216-Å Co-N_e bond distance is still substantially shorter than the 2.436-Å distance in low-spin six-coordinate Pip₂CoTPP.

That this 0.06 Å increase in the Co-N_e distance, relative to the sterically unhindered derivatives, corresponds to a readily extensible Co-N_e bond in the five-coordinate complexes can be understood from an examination of the nonbonded interactions of the axial ligand with the porphinato core. The plane of the imidazole ring is rotated 20° from coincidence with a coordinate plane (Figure 1); a rotation of 45° would correspond to the most favorable orientation of the ligand plane. The 5.2° tilt of the Co-N_e bond from the normal to the equatorial porphinato plane requires the hydrogen atom of carbon C₃ of the ligand to approach rather closely two atoms of the core: H···N₂ = 2.65 and H···C_{a4} = 2.57 Å (Figure 1). The most favorable orientation of the 2-methyl substituent, which represents the equilibrium configuration of the librating methyl group, corresponds to intramolecular contacts of H···N₄ \approx H···C_{m4} \approx 2.83 Å. The axial bonding in the molecule is not sufficiently assertive to require a commonly observed ruffling of the core that would eliminate the need for the short H···C_{a4} contact of 2.57 Å. Thus although some stretch in the N_e···P_O distance is required by the steric interactions, we judge that the magnitude of the observed stretch is in accord with expectation of a readily extended Co-N_e bond.

In addition to the stretch in the Co-N_e bond, other evidence that the interaction of 1,2-dimethylimidazole with cobalt(II) porphyrins is weaker than that of the sterically unhindered imidazoles comes from a thermo-

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

Angle	Value, deg	Angle	Value, deg	Angle	Value, deg
N ₁ CoN ₂	89.4 (1)	C _{a8} C _{m4} C ₂₄	117.5 (2)	C _{a2} C _{b2} C _{b1}	107.0 (2)
N ₁ CoN ₃	173.6 (1)	N ₁ C _{a1} C _{m4}	125.9 (2)	C _{a3} C _{b3} C _{b4}	106.9 (2)
N ₁ CoN ₄	90.2 (1)	N ₁ C _{a1} C _{b1}	110.9 (2)	C _{a4} C _{b4} C _{b3}	107.3 (2)
N ₁ CoN ₅	94.0 (1)	C _{m4} C _{a1} C _{b1}	123.2 (2)	C _{a5} C _{b5} C _{b6}	106.8 (2)
N ₂ CoN ₃	90.2 (1)	N ₁ C _{a2} C _{m1}	126.0 (2)	C _{a6} C _{b6} C _{b5}	107.0 (2)
N ₂ CoN ₄	168.6 (1)	N ₁ C _{a2} C _{b2}	110.6 (2)	C _{a7} C _{b7} C _{b8}	107.0 (2)
N ₂ CoN ₅	89.5 (1)	C _{m1} C _{a2} C _{b2}	123.3 (2)	C _{a8} C _{b8} C _{b7}	107.2 (2)
N ₃ CoN ₄	89.0 (1)	N ₂ C _{a3} C _{m1}	125.9 (2)	C ₁ N ₅ C ₃	104.9 (2)
N ₃ CoN ₅	92.4 (1)	N ₂ C _{a3} C _{b3}	110.5 (1)	N ₃ C ₁ N ₆	111.6 (2)
N ₄ CoN ₅	101.9 (1)	C _{m1} C _{a3} C _{b3}	123.6 (2)	N ₅ C ₁ C ₄	125.8 (2)
C _{a1} N ₁ C _{a2}	104.8 (2)	N ₂ C _{a4} C _{m2}	125.8 (2)	N ₆ C ₁ C ₄	122.6 (2)
C _{a3} N ₂ C _{a4}	104.8 (2)	N ₂ C _{a4} C _{b4}	110.5 (2)	C ₁ N ₆ C ₂	107.0 (2)
C _{a5} N ₃ C _{a6}	104.7 (2)	C _{m2} C _{a4} C _{b4}	123.5 (2)	C ₁ N ₆ C ₅	127.7 (3)
C _{a7} N ₄ C _{a8}	104.6 (2)	N ₃ C _{a5} C _{m2}	125.9 (2)	C ₂ N ₆ C ₅	125.2 (3)
C _{a2} C _{m1} C _{a3}	122.4 (2)	N ₃ C _{a5} C _{b5}	110.7 (2)	N ₅ C ₂ C ₂	110.3 (3)
C _{a4} C _{m2} C _{a5}	123.5 (2)	C _{m2} C _{a5} C _{b5}	123.4 (2)	C ₃ C ₂ N ₆	106.2 (2)
C _{a6} C _{m3} C _{a7}	122.4 (2)	N ₃ C _{a6} C _{m3}	125.7 (2)	CoN ₆ C ₁	132.6 (2)
C _{a1} C _{m4} C _{a8}	123.7 (2)	N ₃ C _{a6} C _{b6}	110.7 (2)	CoN ₆ C ₃	122.5 (2)
C _{a2} C _{m1} C ₆	118.8 (2)	C _{m3} C _{a6} C _{b6}	123.6 (2)	CoN ₁ C _{a1}	127.1 (2)
C _{a3} C _{m1} C ₆	118.7 (2)	N ₄ C _{a7} C _{m3}	126.0 (2)	CoN ₁ C _{a2}	128.1 (1)
C _{a4} C _{m2} C ₁₂	117.8 (2)	N ₄ C _{a7} C _{b7}	110.6 (2)	CoN ₂ C _{a3}	127.6 (1)
C _{a5} C _{m2} C ₁₂	118.7 (2)	C _{m3} C _{a7} C _{b7}	123.4 (2)	CoN ₂ C _{a4}	127.0 (1)
C _{a6} C _{m3} C ₁₅	119.2 (2)	N ₄ C _{a8} C _{m4}	125.6 (2)	CoN ₃ C _{a5}	126.7 (1)
C _{a7} C _{m3} C ₁₈	118.4 (2)	N ₄ C _{a8} C _{b8}	110.7 (2)	CoN ₃ C _{a6}	128.1 (1)
C _{a1} C _{m4} C ₂₄	118.7 (2)	C _{m4} C _{a8} C _{b8}	123.7 (2)	CoN ₄ C _{a7}	128.1 (1)
		C _{a1} C _{b1} C _{b2}	106.7 (2)	CoN ₄ C _{a8}	127.3 (2)

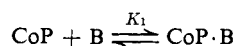
^a The numbers in parentheses are the estimated standard deviations.

dynamic study by Walker¹⁴ of the relationship between amine basicity (pK_a) and log K₁.¹⁵ For a series of sterically unhindered imidazoles, the relationship is approximately linear. However, for 1,2-dimethylimidazole, log K₁ is ~2.8 rather than the ~3.6 that would be expected for an imidazole of similar basicity but no steric hindrance.

There has been much recent interest concerning the tension of the axial linkage in deoxyhemoglobin and related molecules.^{3,16-20} The magnetic spin-state equilibrium of iron(III) that frequently occurs in the hemoproteins is thought to result from changes in the axial tension and the concomitant changes in the iron(III)-histidine bond distances.²⁰ Smith and Williams have suggested²⁰ that the esr investigation of cobalt-substituted hemoproteins would be a convenient probe for changes in the axial tension. They suggest that the ¹⁴N superhyperfine splitting constants may be correlated with the Co-N_ε bond distances and changes thereof. However, esr data of Walker²¹ for a series of five-coordinate imidazole complexes of Co(*p*-OCH₃)TPP, including sterically hindered derivatives, show only random differences in the ¹⁴N superhyperfine splitting constants A_N. These data, together with the structural data reported herein, suggest restraint in interpreting esr data in support of differences (or lack of differences) in Co-N_ε distances of model systems and cobalt-substituted hemoproteins.

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Hoard and Scheidt³ have suggested that the axial connection in deoxycobaltohemoglobin²² is capable of supporting enhanced tension with a somewhat smaller value of N_ε···P_μ (of perhaps 2.70–2.75 Å) compared to deoxyhemoglobin. (P_μ is the mean plane of the porphyrin core including a contribution from the peripheral substituents.³) Compared to deoxyHb, the additive components of N_ε···P_μ in deoxyCoHb are an increased Co–N_ε distance, as demonstrated herein, an increased doming of the porphinato core (P_N···P_μ) and a decreased displacement of the metal from the mean plane of the porphinato nitrogens. This description leads to an axial connection in deoxyCoHb which can be compatible with Perutz's postulated trigger^{23,24} for the initiation of cooperative interaction of the subunits during the reversible oxygenation of hemoglobin.

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Supplementary Material Available. A listing of structure factor amplitudes 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 \$5.00 for photocopy or \$3.00 for microfiche, referring to code number JACS-74-4815.

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