structure (X) toward a square pyramidal structure with SnCl₃ axial (*i.e.*, IX) simply means that the forward reaction in Scheme II commences at some stage intermediate between X and XI and terminates at some (symmetrically related) stage intermediate between XII and XIII; *i.e.*, the observed structure lies on the reaction coordinate of the idealized Berry pseudorotation process X → XI.

In contrast to the case of (cycloocta-1,5-diene)(phosphine)₂Ir(CH₃) species (see Scheme I, in the introduction), the rate-limiting step in the present equilibration of vinylic protons clearly occurs during the second pseudorotation (about P(1)), during which the strong π-acceptor ligand, SnCl₃, is moved into the energetically unfavorable axial position. The energy required for this step clearly will decrease with increasing P(1)–Ir–P(2) angle, since it involves, *inter alia*, the transformation of phosphine ligands from an axial–equatorial pair (for which the idealized angle is 90°) to a diequatorial pair (for which the ideal interligand angle is 120°).

Our previous studies on (cycloocta-1,5-diene)(phosphine)₂Ir(CH₃) species[1-3] have shown the P–Ir–P angle to be 84.9 (2)° for P(1)⌒P(2) = Ph₂P(CH₂)₂PPh₂, 93.4 (1)° for P(1)⌒P(2) = Ph₂P(CH₂)₃PPh₂, and 101.5 (2)°

for P(1) = P(2) = PMe₂Ph. It follows, therefore, that the energy required for equilibration of the vinylic diene protons in the trichlorostannatoiridium(I) species will vary as a function of phosphine ligand in the order (PMe₂Ph)₂ < Ph₂P(CH₂)₃PPh₂ < Ph₂P(CH₂)₂PPh₂; *i.e.*, the effect of chelation and of chelate ring size is predicted (*as observed*[4b]) to be precisely the opposite to that found in the *methyl*iridium(I) systems.

Stereochemistry of Low-Spin Cobalt Porphyrins. III. The Crystal Structure and Molecular Stereochemistry of Bis(piperidine)-α,β,γ,δ-tetraphenylporphinatocobalt(II)

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Abstract: Bis(piperidine)-α,β,γ,δ-tetraphenylporphinatocobalt(II) crystallizes in the triclinic system, space group $P\bar{1}$. The unit cell has $a = 11.503\ (3)$ Å, $b = 11.830\ (4)$ Å, $c = 9.934\ (4)$ Å, $\alpha = 101.99\ (2)°$, $\beta = 115.64\ (2)°$, $\gamma = 101.49\ (2)°$ and contains one molecule. The calculated and experimental densities are 1.271 and 1.265 g/cm³, respectively, at $20 \pm 1°$. Measurement of diffracted intensities employed θ–2θ scans with graphite-monochromated Mo Kα radiation on a Syntex four-circle diffractometer. All independent reflections for $(\sin \theta/\lambda) \leqslant 0.648$ Å^{-1} were scanned; 4360 reflections were retained as observed. These data were employed for the determination of structure using the heavy-atom technique and anisotropic least-squares refinement of the 277 structural parameters. The final conventional and weighted discrepancy factors were 0.043 and 0.059, respectively. The octahedral CoN₆ coordination group in the centrosymmetric (C_i–$\bar{1}$) molecule approximates to full tetragonal symmetry. Equatorial bond lengths are 1.987 Å with an esd for an individual determination of 0.002 Å. The axial Co–N bond is extended to 2.436 (2) Å and is attributable to the unpaired electron located principally in the d_{z^2} orbital. Bond distances and angles of any specified chemical class in the porphinato core display trivial departures from D_{4h} symmetry.

Our interest in the structural characterization of low-spin cobalt(II) porphyrins was prompted by Walker's[1] electron spin resonance (esr) studies of low-spin cobalt(II) porphyrins. She observed three distinctive classes of compounds in toluene glasses at 77°K. These involve the coordination by the cobalt(II) atom of (a) a single molecule of a nitrogen base, (b) two molecules of base, or (c) one molecule of base and one molecule of reversibly bound oxygen. A particu-

larly notable feature is the invariance of the esr parameters, within each class, with respect to large differences in the basicity, chemical constitution, and the steric requirements of the nitrogen base. Equally pertinent are the studies of Hoffman, *et al.*,[2,3] on co-

(1) F. A. Walker, *J. Amer. Chem. Soc.*, **92**, 4235 (1970).

(2) B. M. Hoffman and D. H. Petering, *Proc. Nat. Acad. Sci. U. S.*, **67**, 637 (1970).

(3) (a) B. M. Hoffman, C. A. Spilburg, and D. H. Petering, *Cold Spring Harbor Symp. Quant. Biol.*, **36**, 343 (1971); (b) C. A. Spilburg, C. Bull, and B. M. Hoffman, *Fed. Proc., Fed. Amer. Soc. Exp. Biol.*, **31**, 484 (1972); (c) G. C. Hsu, C. A. Spilburg, C. Bull, and B. M. Hoffman, *Proc. Nat. Acad. Sci. U. S.*, **69**, 2122 (1972).

baltohemoglobin, CoHb, the product obtained upon replacement of the protoheme in hemoglobin by cobalt(II) protoporphyrin IX. Their preparations of CoHb combine reversibly and cooperatively with molecular oxygen.

The quantitative stereochemical parameters reported herein for the bis(piperidine)-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatocobalt(II) molecule, Pip$_2$CoTPP, and those reported[4] in paper IV of this series for the 1-methylimidazole-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatocobalt(II) molecule, MImCoTPP, display the role played by the odd electron in modulating the geometry of the axial bond systems. They lead, indeed to a qualitatively satisfying correlation of the thermodynamic data[5] with structure. Furthermore, they provide a substantial part of the data which are utilized elsewhere[6] for discussion of an especially interesting question: namely, whether the parameters of the axial connection between the cobalt(II) protoporphyrin and the globin in deoxycobaltohemoglobin[3] are compatible with a stereochemical trigger for cooperative oxygenation of the type postulated by Perutz[7] in his stereochemical mechanism for the reversible oxygenation of hemoglobin. (That the cobalt atom serves as a qualitatively acceptable substitute for the iron atom in the oxygenated species is apparently attributable to the transfer, in the cobalt porphyrin, of an estimated 80% of the electron density associated with the odd electron to the antibonding $2p\pi^*$ orbital of the dioxygen ligand.[3])

Experimental Section

Pip$_2$CoTPP was prepared in crystalline form by slow evaporation of a 1:1 (by volume) CHCl$_3$–piperidine solution nearly saturated with CoTPP. Preliminary X-ray photographic study established a one-molecule unit cell with $P1$ or $P\bar{1}$ as the space group. A freshly prepared crystal with approximate dimensions of $0.3 \times 0.4 \times 0.4$ mm was mounted in a thin-walled glass capillary. Lattice constants, $a = 11.503 (3)$ Å, $b = 11.803 (4)$ Å, $c = 9.934 (4)$ Å, $\alpha = 101.99 (2)°$, $\beta = 115.64 (2)°$, and $\gamma = 101.49 (2)°$ (λ 0.71069 Å), came from a least-squares refinement that utilized the setting angles of 24 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 $20 \pm 1°$ of 1.271 g/cm^3 for the crystal. The experimental density of freshly prepared crystals, measured by flotation, was 1.265 g/cm.^{3}

Intensity data were measured on the Syntex P$\bar{1}$ diffractometer using the θ–2θ scanning technique with graphite-monochromated Mo Kα radiation at a takeoff angle of $\sim 4°$. The range of each scan consisted of the base width of 1.7° at $2\theta = 0$ and an increment $\Delta(2\theta) = (0.692) \tan \theta°$, to allow for spectral dispersion; background counts were taken at the extremes of the scan for a duration of 0.4 times the time required for the scan itself. A variable 2θ scan rate was used; the slowest was 1.0°/min, the fastest was 4.0°/min. The slowest scan rate was used for reflections with intensities less than 25 Hz accumulated over a 2-sec θ–2θ scan of $\pm 0.4°$ from the Kα peak center; the fastest scan rate was used for reflections having intensities greater than 375 Hz over the same scan range. Intermediate scan rates were selected automatically by the control program based on a linear interpolation of the above limits. Three 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; a

small monotonic decrease ($\sim 5\%$) was observed during the course of measurements. All independent data having $(\sin \theta)/\lambda \lesssim 0.648$ Å^{-1} were thus measured.

With the cited dimensions of the crystal and a linear absorption coefficient of only 0.46 mm^{-1} for Mo Kα radiation, the maximum error in any structure amplitude resulting from the neglect of absorption corrections was seen to be $\leqslant 3\%$. The net intensities were reduced directly to a set of relative squared amplitudes, $|F_o|^2$, by application of the standard Lorentz and polarization factor (Lp) and a linear correction for decomposition. Standard deviations were calculated from

$$\sigma^2(F_o) = (Ct + k^2B + p^2(Ct - kB)^2/4|F_o|^2(Lp)^2$$

where Ct is the count of the scan, k is the ratio of scanning time to background counting time, B is the total background count, and the value of p was chosen as 0.05. All data having $F_o < 3\sigma(F_o)$ were taken to be unobserved, leaving 4360 independent data (some 86.5% of the theoretical number possible). 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[8] was fully confirmed by all subsequent developments during the determination of structure. The cobalt atom was placed at the center of symmetry, taken as the origin; the position of the remaining 30 heavy atoms in the asymmetric unit of structure were readily found by Fourier syntheses.[9] Block-diagonal least-squares refinement[10] of the coordinates and isotropic thermal parameters using all 4360 independent data was followed by a difference Fourier synthesis which revealed electron density concentrations appropriately located for all hydrogen atom positions. Hydrogen atoms were then fixed in the theoretically calculated positions (C–H = 1.05 Å in the piperidine ligand, C–H = 1.0 Å otherwise, N–H = 1.0 Å). The hydrogen atom contributions[11] were subsequently included in the least-squares minimization with isotropic thermal parameters fixed one unit higher than that of its associated atom; this minimization was then carried to convergence using anisotropic thermal parameters for all other atoms. A final cycle[12] of full-matrix least-squares refinement[13] was carried out varying only the coordinates of all heavy atoms; the output of this cycle was used to obtain the elements of the inverse matrix for the calculation of standard deviations.[14] The final value of $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ was 0.043, that of $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o^2)]^{1/2}$ was 0.059, with a final data/parameter ratio of 15.7. The estimated standard deviation of an observation of unit weight was 2.2. The final parameter shifts were less than 10% of their estimated standard deviations during the last cycle. A final difference Fourier was judged to be significantly free of features with no peaks greater than 0.3 e Å^{-3}.

Atomic coordinates and the associated anisotropic thermal parameters in the asymmetric unit of structure are listed in Tables I and II, respectively. The numbering of the atoms given in Figures 1 and 2 is maintained in all tables.

Discussion

The values (with estimated standard deviations) of all structurally independent bond lengths of the por-

(4) W. R. Scheidt, *J. Amer. Chem. Soc.*, **95**, 90 (1973).

(5) (a) F. A. Walker, *ibid.*, **95**, 1150 (1973); (b) *ibid.*, **95**, 1154 (1973); (c) D. V. Stynes, H. C. Stynes, B. R. James, and J. A. Ibers, *ibid.*, **95**, 1796 (1973).

(6) J. L. Hoard and W. R. Scheidt, *Proc. Nat. Acad. Sci., U. S.*, in press.

(7) (a) M. F. Perutz, *Nature (London)*, **228**, 726 (1970); (b) M. F. Perutz and L. F. TenEyck, *Cold Spring Harbor Symp. Quant. Biol.*, **36**, 295 (1972).

(8) 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.

(9) The program ALFF written in PL/1 was used: C. R. Hubbard, C. O. Quicksall, and R. A. Jacobson, "The Fast Fourier Algorithm and the Programs ALFF, ALFFDP, ALFFPROJ, ALFTT, and FRIEDEL," IS-2625, Ames Laboratory, Iowa State University, Ames, Iowa, 1971.

(10) The program REFINE written by J. J. Park at Cornell University, was used. The function minimized was $\Sigma w(|F_o| - s|F_c|)^2$ where w is the weight ($= 1/\sigma^2$) and s is the scale factor. Atomic form factors were from D. T. Cromer and J. L. 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, *Acta Crystallogr.*, **18**, 17 (1965).

(11) The atomic form factor used for hydrogen was from C. H. MacGillavry, G. D. Rieck, and K. Lonsdale, Ed., "International Tables for X-Ray Crystallography," Vol. III, 2nd ed, The Kynoch Press, Birmingham, England, 1968.

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

(13) W. R. Busing, K. O. Martin, and H. A. Levy, "OR-FLS, a Fortran Crystallographic Least-Squares Program," ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(14) These calculations followed 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.
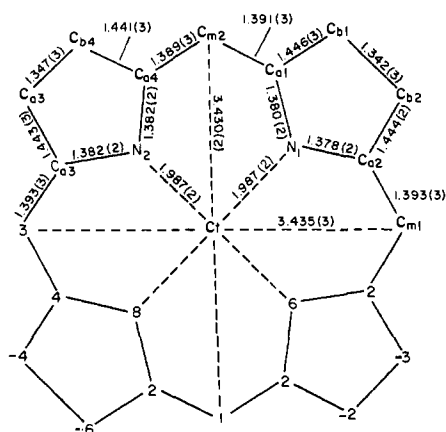
Figure 1. A diagram of the porphinato core showing, on the upper half, the structurally independent bond lengths and the numbering scheme used throughout this paper for the atoms. On the lower half of the diagram, the numbered symbols for each atom is replaced by its perpendicular displacement, in units of 0.01 Å, from the mean plane of the porphinato core.

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

Atom type[b]	Coordinates		
	10^4x	10^4y	10^4z
Co	0	0	0
N_1	−195 (1)	1584 (1)	1003 (2)
N_2	−1012 (1)	57 (1)	−2171 (2)
N_3	2195 (2)	1168 (2)	384 (2)
C_{m1}	1008 (2)	1872 (2)	3880 (2)
C_{m2}	−1616 (2)	1921 (2)	−1452 (2)
C_{a1}	−942 (2)	2222 (2)	211 (2)
C_{a2}	246 (2)	2204 (2)	2614 (2)
C_{a3}	−1360 (2)	−807 (2)	−3648 (2)
C_{a4}	−1645 (2)	899 (2)	−2552 (2)
C_{b1}	−972 (2)	3244 (2)	1352 (2)
C_{b2}	−235 (2)	3238 (2)	2828 (2)
C_{b3}	−2199 (2)	−484 (2)	−4955 (2)
C_{b4}	−2367 (2)	568 (2)	−4279 (2)
C_{11}	−2396 (2)	2719 (2)	−2090 (2)
C_{12}	−3875 (2)	4179 (2)	−3279 (3)
C_{13}	−3812 (2)	2340 (2)	−2727 (3)
C_{14}	−4542 (2)	3063 (2)	−3324 (4)
C_{15}	−1735 (2)	3841 (2)	−2073 (3)
C_{16}	−2481 (3)	4568 (2)	−2667 (3)
C_{17}	1499 (2)	2720 (2)	5573 (2)
C_{18}	2506 (3)	4273 (2)	8784 (3)
C_{19}	2548 (2)	3874 (2)	6315 (2)
C_{20}	3061 (3)	4640 (2)	7916 (3)
C_{21}	939 (2)	2368 (2)	6466 (3)
C_{22}	1435 (3)	3150 (2)	8047 (3)
C_{p1}	3340 (3)	1757 (3)	2057 (3)
C_{p2}	3915 (3)	1305 (2)	−531 (3)
C_{p3}	5098 (3)	1842 (3)	1194 (4)
C_{p4}	4665 (3)	2584 (3)	2287 (4)
C_{p5}	2610 (3)	508 (2)	696 (3)

[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 and 2.

phinato core are displayed in the upper half of the diagram in Figure 1; it also carries the values of some structurally important radii of the core, wherein $Ct\cdots N \equiv Co–N$ in this case. In the lower half of the centrosymmetric diagram, each numbered symbol for an atom is replaced by the perpendicular displacement (in units of 0.01 Å) of this atom from the mean plane of the porphinato core; each centrosymmetrically related atom in the upper half of the diagram has a displacement of the same magnitude, but with opposite

Figure 2. Computer-drawn model in perspective of centrosymmetric Pip$_2$CoTPP as it exists in the triclinic crystal. Also shown is the numbering scheme employed for atoms in the phenyl groups and the piperidine ligands.

sign. The departures from planarity of the porphinato core are of insignificant magnitude as compared with those observed in a number of other crystalline porphyrins.[15] As is usual, local flatness (within 0.02 Å)

is preserved in the trigonal carbon atoms of the inner 16-membered ring and in the pyrrole rings.

Figure 2 is a computer-drawn model of the centro-

(15) J. L. Hoard, *Science*, 174, 1295 (1971).

Table II. Thermal Parameters[a]

Atom type[b]	Anisotropic parameters, Å²					
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	3.47 (1)	2.60 (1)	2.55 (1)	1.52 (1)	1.32 (1)	0.99 (1)
N_1	3.34 (6)	2.75 (6)	2.80 (6)	1.45 (5)	1.34 (5)	1.07 (5)
N_2	3.22 (6)	2.67 (5)	2.83 (6)	1.31 (5)	1.35 (5)	1.01 (5)
N_3	4.19 (7)	3.89 (7)	3.91 (7)	1.63 (6)	2.13 (6)	1.50 (6)
C_{m1}	3.32 (7)	2.82 (6)	2.86 (6)	1.07 (5)	1.55 (6)	0.89 (5)
C_{m2}	3.01 (7)	2.79 (6)	3.33 (7)	1.36 (5)	1.39 (5)	1.35 (6)
C_{a1}	3.37 (7)	2.82 (6)	3.37 (7)	1.53 (6)	1.61 (6)	1.24 (6)
C_{a2}	3.47 (7)	2.87 (1)	3.01 (7)	1.46 (6)	1.58 (6)	0.95 (5)
C_{a3}	3.22 (7)	2.96 (7)	2.74 (6)	1.12 (6)	1.39 (6)	1.05 (5)
C_{a4}	3.06 (7)	2.86 (6)	3.08 (7)	1.24 (5)	1.28 (6)	1.31 (5)
C_{b1}	4.59 (9)	3.55 (8)	3.61 (8)	2.43 (7)	1.95 (7)	1.30 (6)
C_{b2}	4.73 (9)	3.62 (8)	3.58 (8)	2.36 (7)	2.17 (7)	1.21 (6)
C_{b3}	4.01 (8)	3.47 (7)	2.88 (7)	1.55 (6)	1.35 (6)	1.23 (6)
C_{b4}	3.92 (8)	3.39 (7)	3.03 (7)	1.58 (6)	1.23 (6)	1.31 (6)
C_{11}	3.4 (1)	3.1 (1)	3.0 (1)	1.6 (1)	1.4 (1)	1.2 (1)
C_{12}	5.4 (1)	4.7 (1)	3.8 (1)	3.2 (1)	1.6 (1)	1.8 (1)
C_{13}	3.7 (1)	4.1 (1)	6.9 (1)	1.7 (1)	2.0 (1)	2.6 (1)
C_{14}	3.6 (1)	5.0 (1)	7.1 (1)	2.2 (1)	1.5 (1)	2.5 (1)
C_{15}	4.2 (1)	3.9 (1)	5.4 (1)	2.0 (1)	2.4 (1)	2.5 (1)
C_{16}	5.7 (1)	4.4 (1)	5.6 (1)	2.7 (1)	3.0 (1)	3.0 (1)
C_{17}	3.4 (1)	3.3 (1)	2.9 (1)	1.6 (1)	1.6 (1)	1.1 (1)
C_{18}	6.5 (1)	5.1 (1)	3.3 (1)	3.4 (1)	2.3 (1)	1.1 (1)
C_{19}	4.5 (1)	3.4 (1)	3.8 (1)	1.2 (1)	2.3 (1)	1.0 (1)
C_{20}	5.6 (1)	3.8 (1)	4.2 (1)	1.2 (1)	2.0 (1)	0.4 (1)
C_{21}	4.4 (1)	4.5 (1)	4.2 (1)	1.8 (1)	2.7 (1)	1.8 (1)
C_{22}	6.5 (1)	6.1 (1)	4.4 (1)	3.9 (1)	3.8 (1)	2.9 (1)
C_{p1}	4.9 (1)	6.9 (1)	4.0 (1)	−0.4 (1)	2.4 (1)	0.0 (1)
C_{p2}	5.4 (1)	5.8 (1)	5.3 (1)	1.9 (1)	3.4 (1)	1.5 (1)
C_{p3}	4.7 (1)	5.9 (1)	6.5 (1)	1.7 (1)	2.9 (1)	2.4 (1)
C_{p4}	5.6 (1)	7.6 (1)	5.3 (1)	−0.9 (1)	3.1 (1)	−0.5 (1)
C_{p5}	5.1 (1)	5.3 (1)	4.4 (1)	1.0 (1)	2.8 (1)	0.6 (1)

[a] The number in parentheses following each datum is the estimated standard deviation in the last significant figure. [b] Atoms are identified in agreement with Figures 1 and 2.
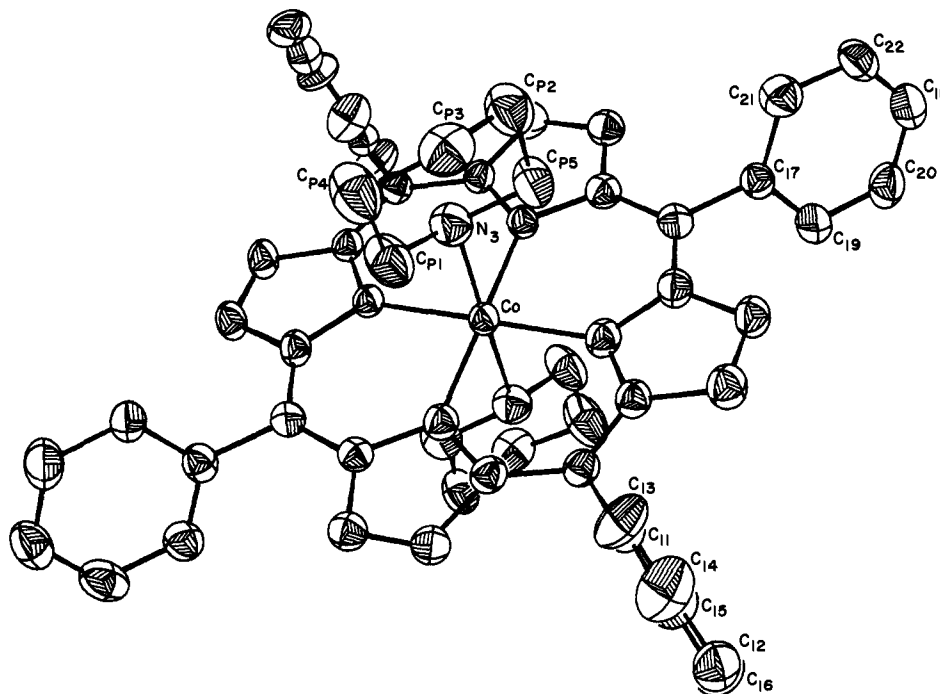
Table III. Bond Lengths in the Coordination Group, Porphinato Skeleton, and Piperidine Ligand[a]

Type[b]	Length, Å	Type[b]	Length, Å	Type[b]	Length, Å
Co–N_1	1.987 (2)	C_{m1}–C_{11}	1.494 (3)	C_{b1}–C_{b2}	1.342 (3)
Co–N_2	1.987 (2)	C_{m2}–C_{a1}	1.391 (3)	C_{b3}–C_{b4}	1.347 (3)
Co–N_3	2.436 (2)	C_{m2}–C_{a4}	1.389 (3)	N_3–C_{p1}	1.457 (3)
N_1–C_{a1}	1.380 (2)	C_{m2}–C_{17}	1.501 (2)	N_3–C_{p5}	1.465 (3)
N_1–C_{a2}	1.378 (2)	C_{a1}–C_{b1}	1.446 (3)	C_{p1}–C_{p4}	1.524 (4)
N_2–C_{a3}	1.382 (2)	C_{a2}–C_{b2}	1.444 (2)	C_{p2}–C_{p3}	1.506 (4)
N_2–C_{a4}	1.382 (2)	C_{a3}–C_{b3}	1.443 (3)	C_{p2}–C_{p5}	1.520 (4)
C_{m1}–C_{a2}	1.393 (3)	C_{a4}–C_{b4}	1.441 (3)	C_{p3}–C_{p4}	1.532 (4)
C_{m1}–C_{a3}'	1.393 (2)				

[a] The number in parentheses is the estimated standard deviation. [b] Atoms are identified in agreement with Figures 1 and 2.

symmetric ($\bar{1}$) Pip$_2$CoTPP molecule as it exists in the triclinic crystal. Each atom is represented by an ellipsoid[16] of the relative size and orientation required by the thermal parameters given in Table II.

The porphinato core exhibits nearly exact D_{4h} geometry, although not required of the molecule in the crystal, as displayed in Figure 1. 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, averaged bond lengths (Table III) for the chemically analogous bonds are Co–N (= Ct···N) = 1.987 (0, 2), N–C_a = 1.380 (2, 2), C_a–C_m = 1.392 (2, 2), C_a–C_b = 1.444 (3, 3), 3$_b$–3$_b$ = 1.344 (3, 3), and C_m–C_p = 1.498 (3, 3) Å, where the first

(16) 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 IV. Bond Angles in the Coordination Group, Porphinato Skeleton, and Piperidine Ring[a]

Angle[b]	Value, deg	Angle	Value, deg
N_2CoN_1	89.98 (7)	$N_2C_{a4}C_{m2}$	125.8 (2)
N_3CoN_2	90.83 (6)	$N_2C_{a4}C_{b4}$	110.6 (2)
N_3CoN_1	90.83 (6)	$C_{m2}C_{a4}C_{b4}$	123.6 (2)
$C_{a1}N_1C_{a2}$	104.9 (1)	$C_{b2}C_{b1}C_{a1}$	107.1 (2)
$C_{a3}N_2C_{a4}$	104.8 (1)	$C_{b1}C_{b2}C_{a2}$	107.0 (2)
$C_{a2}C_{m1}C_{a3}'$	123.3 (2)	$C_{b4}C_{b3}C_{a3}$	107.0 (2)
$C_{a2}C_{m1}C_{11}$	118.3 (2)	$C_{b3}C_{b4}C_{a4}$	107.0 (2)
$C_{a3}'C_{m1}C_{11}$	118.5 (2)	$C_{p5}N_3C_{p1}$	110.9 (2)
$C_{a4}C_{m2}C_{a1}$	123.4 (2)	$N_3C_{p1}C_{p4}$	114.2 (2)
$C_{a4}C_{m2}C_{17}$	118.5 (2)	$C_{p3}C_{p2}C_{p5}$	111.1 (2)
$C_{a1}C_{m2}C_{17}$	118.1 (2)	$C_{p2}C_{p3}C_{p4}$	108.4 (2)
$N_1C_{a1}C_{m2}$	125.9 (2)	$C_{p3}C_{p4}C_{p1}$	110.4 (2)
$N_1C_{a1}C_{b1}$	110.4 (2)	$N_3C_{p5}C_{p2}$	114.0 (2)
$C_{m2}C_{a1}C_{b1}$	123.6 (2)	CoN_1C_{a1}	127.2 (1)
$N_1C_{a2}C_{m1}$	125.8 (2)	CoN_1C_{a2}	127.5 (1)
$N_1C_{a2}C_{b2}$	110.6 (2)	CoN_2C_{a3}	127.5 (1)
$C_{m1}C_{a2}C_{b2}$	123.5 (2)	CoN_2C_{a4}	127.3 (1)
$N_2C_{a3}C_{m1}'$	125.7 (2)	CoN_3C_{p1}	115.2 (1)
$N_2C_{a3}C_{b3}$	110.5 (2)	CoN_3C_{p5}	115.4 (1)
$C_{m1}C_{a3}C_{b3}$	123.7 (2)		

[a] The number in parentheses following each datum is the estimated standard deviation in the last significant figure. [b] Atoms are identified in agreement with Figures 1 and 2.

figure in parentheses following each averaged value is the mean deviation and the second is the estimated standard deviation of an individual type.[17] The agreement in the bond angles of a given chemical type in the core is equally close (Table IV). The averaged values

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

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Table V. Bond Lengths in the Phenyl Groups[a,b]

Type I[c]	Length, Å	Type II[d]	Length, Å	Type III[e]	Length, Å
C_{11}–C_{13}	1.387 (3)	C_{13}–C_{14}	1.380 (3)	C_{12}–C_{14}	1.368 (4)
C_{11}–C_{15}	1.384 (3)	C_{15}–C_{16}	1.393 (3)	C_{12}–C_{16}	1.368 (3)
C_{17}–C_{19}	1.385 (3)	C_{19}–C_{20}	1.388 (3)	C_{18}–C_{20}	1.378 (3)
C_{17}–C_{21}	1.398 (3)	C_{21}–C_{22}	1.382 (3)	C_{18}–C_{22}	1.372 (4)
Av[b]	1.389 (5)	Av[b]	1.386 (5)	Av[b]	1.372 (3)

[a] The figure in parentheses following the length of a specified bond is the estimated standard deviation. [b] The figure in parentheses following the averaged length for a bond is the mean deviation from the average. [c] Bond set lying nearest to the molecular center. [d] Bond set lying approximately parallel to the porphinato core. [e] Bond set lying furthest from the porphinato core.

are C_aNC_a = 104.8 (0, 1), NC_aC_b = 110.5 (1, 2), NC_aC_m = 125.8 (1, 2), $C_aC_bC_b$ = 107.0 (1, 2), $C_aC_mC_a$ = 123.4 (1, 2), and $C_aC_mC_p$ = 118.4 (2, 2)°.

The dihedral angles between the plane of the porphinato core and the planes of the two phenyl groups in Pip_2CoTPP are 73.4 and 81.3°; the averaged length of the bond connecting the phenyl carbon atom to the methine carbon atom is 1.498 (3, 3) Å, and is in excellent agreement with the precisely determined value of 1.496 Å in $\alpha,\beta,\gamma,\delta$-tetraphenylporphinatodichlorotin-(IV).[18] These data are consistent with σ-bonding between a pair of trigonally hybridized carbon atoms.

The averaged value of the internal angles in the phenyl rings is 120.0 (8, 3)°. The sum of the angles subtended at C_p is 360.0 (0, 3)°, corresponding to a planar trigonal carbon atom. The individual C–C bond distances in the two structurally independent phenyl rings are foreshortened (Table V) from the standard 1.397 Å separation owing to the complex thermal motions of these peripheral groups. This pattern of foreshortening has been discussed previously.[18,19]

The piperidine ligand is in the chair form, with a CNC angle of 110.9 (2)°; the CCC angle opposite the nitrogen atom is 108.4 (2)°. The two NCC angles average to 114.1 (1, 2)°; the remaining two CCC angles average to 110.8 (4, 2)°. The excellent agreement between structurally independent, chemically analogous bond lengths is maintained in the piperidine ligand with (N–C)$_{av}$ = 1.461 (4, 3) and (C–C)$_{av}$ = 1.520 (8, 4) Å.

The octahedral CoN_6 coordination group has nearly exact D_{4h} geometry with the porphinato core as the equatorial girdle. The equatorial Co–N lengths average to 1.987 (0, 2) Å; the average NCoN angle is 90.00 (2, 7)°. The Co–N bonds to the axial piperidine ligands are tipped ~1.0° from the normal to the equatorial girdle in a plane that is perpendicular to the core and passes through C_{m2} and C_{m2}'. The N–H vector of the ligand lies in this plane. This tipping can be ascribed to minimizing the steric interactions of the ligand hydrogen atoms attached to the nitrogen and the two carbon atoms adjacent to the nitrogen atom and the atoms of the porphinato core. For the experimentally determined configuration, there are only two H$\cdots$N separations less than the critical separation of ~2.9 Å, the sum of the van der Waals radii for hydrogen (1.20 Å) and the aromatic ring (1.70 Å). The two short H$\cdots$N separations of 2.84 Å are between a hydrogen

bonded to C_{p5} or C_{p1} and the nitrogen atoms of the porphinato core. The number of H$\cdots$N(C) separations less than the critical 2.90 Å increases to six for the configuration having exact D_{4h} geometry for the coordination group or C_{2h}-2/m symmetry for the molecule as a whole. It could be argued that the slight departures from the idealized symmetry could result from packing forces in the crystal. However, of the eight C$\cdots$C separations less than 4.0 Å involving piperidine carbons, only one is less than 3.8 Å. Indeed, the fact that the Pip_2CoTPP molecule in the triclinic crystal approximates so closely the maximum symmetry allowable in the isolated species implies that there are few tight contacts between molecules. Of the 25 structurally independent, intermolecular C$\cdots$C contacts less than 4.0 Å, only five are below 3.70 Å and none are less than 3.55 Å.

The axial complexing bonds of this low-spin d^7 complex are extremely long with Co–N = 2.436 (2) Å. That these exceedingly long bonds are the direct consequence of the single unpaired electron in the d_{z^2} orbital, which points directly at the two axial nitrogen atoms, can scarcely be doubted. In the preceding report,[20] we detail the molecular stereochemistry of Pip_2CoTPP^+, a complex with the same coordination group, which is similar to Pip_2CoTPP in every respect, save for the removal of one electron (yielding low-spin Co(III)) and much shortened axial bonds. Thus, the removal of the unpaired electron (from the d_{z^2} orbital) leads to axial complexing bonds, Co–N = 2.060 (3) Å, in spite of the presence of tight steric interactions between the piperidine hydrogen atoms in each axial ligand with the porphinato core. The molecular stereochemistry of Pip_2CoTPP and the changes in stereochemistry upon removal of the unpaired electron are in accord with the qualitative predictions of crystal field theory.[21] The structure is also consistent with the esr results.[1]

The sterically unconstrained axial Co–N bond distances in a cobalt(III) porphyrin are expected to be ~1.94 Å;[22] the extension of the axial Co–N bonds in low-spin Pip_2CoTPP can be estimated as ~0.50 Å. The corresponding change in the Co–N bond lengths of high-spin $[Co(NH_3)_6]^{2+}$ and low-spin $[Co(NH_3)_6]^{3+}$ (both with O_h symmetry) is 0.178 Å.[25] It is then interesting to note that the total change in Co–N bond lengths, upon oxidation, is ~1.00 Å in the low-spin cobalt(II) porphyrin system (two bonds affected) and 1.068 Å in the high-spin cobalt(II) hexaammines (all six Co–N bonds affected).

The virtual equality of the equatorial bond lengths in Pip_2CoTPP and Pip_2CoTPP^+, Co–N = 1.987 (0, 2) and 1.978 (5, 3) Å, respectively, and the trivial differences in the two porphinato skeletons (compare Figure

(18) D. M. Collins, W. R. Scheidt, and J. L. Hoard, *J. Amer. Chem. Soc.*, **94**, 6689 (1972).

(19) L. J. Radonovich, A. Bloom, and J. L. Hoard, *J. Amer. Chem. Soc.*, **94**, 2073 (1972).

(20) W. R. Scheidt, J. A. Cunningham, and J. L. Hoard, *J. Amer. Chem. Soc.*, **95**, 8289 (1973).

(21) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Interscience, New York, N. Y., 1972, pp 555–567.

(22) The calculated $N_{eq}\cdots N_{ax}$ separations of 2.76 Å for a cobalt porphyrin having equatorial Co–N lengths of 1.98 Å and axial Co–N lengths of 1.92 Å are not unreasonable. An N$\cdots$N separation of 2.755 Å is found for nitrosyl-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatocobalt.[23] Co–N lengths of 1.92 Å are found for low-spin ethylenediaminetetraacetatocobaltate(III)[24] and 1.936 Å for low-spin hexaamminecobalt(III).[25]

(23) W. R. Scheidt and J. L. Hoard, *J. Amer. Chem. Soc.*, **95**, 8281 (1973).

(24) H. A. Weakliem and J. L. Hoard, *J. Amer. Chem. Soc.*, **81**, 549 (1959).

(25) N. E. Kime and J. A. Ibers, *Acta Crystallogr., Sect. B*, **25**, 168 (1969).

l herein with Figure 2 of the preceding report[20]) suggest that the equatorial bond radii of tetragonal low-spin cobalt(II) complexes will be essentially isodimensional with the corresponding cobalt(III) complexes.

The observation[26] that crystalline six-coordinate cobalt(II) porphyrins utilizing various amines as the axial ligands slowly decompose with loss of ligand is easily rationalized from their structure. The differing reactivities of the small molecules, O_2, and CO with cobalt(II) porphyrins are now explicable in a straightforward way. It is clear that all six-coordinate complexes of the type (amine)CoTPP(XY) in which the unpaired electron resides largely in the d_{z^2} orbital of the cobalt atom must have long axial bonds. For XY = CO, which is a poor σ-bonding ligand, the long Co–C bond will inhibit effective π overlap of the metal d_{xz} and d_{yz} orbitals with the antibonding orbitals of CO, thus limiting the amount of charge that can be removed from the cobalt atom. Consequently, a weak complexing Co–C linkage would be expected. Indeed, this molecule has never been observed.[2,27] A qualitative bonding scheme for a five-coordinate CO complex in which the restrictions of π overlap need not be as rigorous as in the six-coordinate case can be suggested. The d_{z^2} orbital of the cobalt can be combined with the σ-type orbital of CO to give a bonding orbital, which accommodates the electron pair, and an antibonding orbital which contains the unpaired electron.[28] This

accounts (*a posteriori*) for the weak carbonyl complex recently observed.[27a] The interaction of O_2 with a cobaltous porphyrin leads to the transfer of approximately one electron from the cobalt atom to the small molecule with a concomitant tightening of the axial interaction(s). This electron transfer takes place through σ-bonding orbitals. For the O_2 complex, the formal description is (amine)TPPCo^{III}(O_2^-) as has been suggested from esr experiments.[1,2]

The enthalpies for the coordination of one and two molecules of amine to cobalt porphyrins correlate satisfactorily with the structure of the five- and six-coordinate complexes. The enthalpy for the addition of one molecule of amine is −8 to 11 kcal/mol[5a,c] corresponding to the formation of a Co–N bond of ∼2.15 Å.[4] The small enthalpy for the addition of the second amine (−2 kcal/mol[5b]) is consistent with the stretching of the *first* Co–N bond from ∼2.15 to ∼2.40 Å and the formation of a second weak Co–N bond.

(26) W. R. Scheidt, unpublished observations.

(27) (a) B. B. Wayland and D. Mohajer, *J. Amer. Chem. Soc.*, **93**, 5295 (1971); (b) F. A. Walker and W. R. Scheidt, unpublished observations.

(28) A molecular orbital description similar to this has been given for high-spin five-coordinate ferric porphyrins.[29] The bonding orbital in the cobalt porphyrins need not be as strongly bonding as in the ferric porphyrins.

(29) J. L. Hoard in "Structural Chemistry and Molecular Biology," A. Rich and N. Davidson, Ed., W. H. Freeman, San Francisco, Calif., 1968, pp 573–594.