

STEREOCHEMISTRY OF LOW-SPIN COBALT PORPHYRINS. 9.
 PREPARATION AND CHARACTERIZATION OF FIVE-COORDINATE
 ORGANOCOBALT(III) DERIVATIVES

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Summary

Organocobalt(III) derivatives have been prepared by direct aerial oxidation of tetraphenylporphinatocobalt(II) in solutions containing acetone, acetophenone, and malononitrile. The molecular and crystal structure of acetyl- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinatocobalt(III) has been determined by x-ray diffraction techniques. The porphinato core provides the base of a square pyramid, with the acetyl group at the apex. $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CoTTP}$ crystallizes in the triclinic system, space group $P\bar{1}$. The unit cell has $a = 12.187$ (8) Å, $b = 14.157$ (5) Å, $c = 11.925$ (5) Å, $\alpha = 94.70$ (2)°, $\beta = 111.39$ (4)°, and $\gamma = 68.44$ (4)°. The calculated and experimental densities are 1.356 and 1.34 g/cm³ respectively for $Z = 2$, required crystal symmetry $\bar{1}$. Final discrepancy indices are $R_1 = 0.050$ and $R_2 = 0.076$. The average Co-N distance is 1.948 Å and the Co-C distance is 2.028 Å.

Introduction

In the course of attempting to prepare selected crystalline adducts of cobalt(II) porphyrins, we discovered a facile reaction between cobalt(II) porphyrins and organic substrates with active methyl or methylene groups. The reaction yields quite stable five-coordinate organocobalt(III) porphyrin species. In view of the interest in the chemistry of vitamin B₁₂ and the relative rarity of five-coordinate cobalt(III) complexes, we have investigated the spectroscopic properties and the structure of one of these compounds. We report herein the molecular structure of acetyl- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinatocobalt(III).

Experimental

(Acetonyl)CoTPP. This compound was originally prepared as large single crystals by the slow (ca. 3 weeks) evaporation of an acetone solution of CoTPP¹ containing a large molar excess of N-benzyl-2,4,5-trimethylimidazole. Subsequent preparations were performed on a larger scale. Air was bubbled through a solution of CoTPP (200 mg, 0.30 mmole) in acetone (250 mL) containing an excess of various Lewis bases (N-benzyl-2,4,5-trimethylimidazole,² 2,4,5-trimethylimidazole, or tetramethylguanidine were all found satisfactory). The acetone was replenished as necessary. After ca. 10 days, the acetone was evaporated, the residue dissolved in benzene and chromatographed on a dry-packed silica gel column. The first band eluted (benzene) was CoTPP, the second band, eluted with 20% methanol-benzene, was the desired organocobalt(III) species (67 mg, 31%). IR (KBr) ν CO, 1660 cm^{-1} . Anal. Calcd. for $\text{CoN}_4\text{OC}_{47}\text{H}_{33}$: C, 77.46; H, 4.56; N, 7.69. Found: C, 76.41; H, 4.75; N, 7.47. λ_{max} benzene (ϵ) 527 (1.33×10^4), 412 (1.41×10^5).

(Acetophenonyl)CoTPP. Air was bubbled through a solution of CoTPP (200 mg, 0.30 mmole) in 25 mL of acetophenone containing a Lewis base. After two weeks, the product was obtained and purified as above (60 mg, 25%). IR (KBr) ν CO, 1630 cm^{-1} . Anal. Calcd. for $\text{CoN}_4\text{OC}_{52}\text{H}_{35}$: C, 78.98; H, 4.46; N, 7.08. Found: C, 79.04; H, 4.96; N, 7.13. λ_{max} benzene (ϵ) 620 (1.21×10^3), 530 (1.33×10^4), 412 (1.51×10^5).

(CH(CN)₂)CoTPP. Air was bubbled through a solution of CoTPP (200 mg, 0.3 mmole) and malononitrile (500 mg, 7.6 mmole) in 50 ml of benzene and purified as above except for the use of pure benzene as eluent (75 mg, 34%). IR (KBr) ν (CN), 2225 cm^{-1} . Anal. Calcd. for $\text{CoN}_6\text{C}_{47}\text{H}_{29}$: C, 76.62; H, 3.97; N, 11.34. Found: C, 76.45; H, 4.29; N, 11.02. λ_{max} benzene (ϵ) 620 (1.31×10^3), 550 (8.34×10^3), 552 (1.58×10^4), 412 (1.06×10^5).

Instrumentation. IR spectra were recorded in KBr pellets on a Perkin-Elmer 457 and visible spectra on a Cary 15 spectrophotometer. Nmr spectra were recorded on a Varian XL-100 spectrophotometer operating in the FT mode. Magnetic susceptibilities were measured on a Cahn Faraday balance. The mass spectrum was measured on an AEI MS-902 instrument.

X-ray Structure Determination of (Acetonyl)CoTPP. All measurements were derived from a crystal with approximate dimensions of 0.2 x 0.2 x 1.0 mm. Preliminary examination on a Syntex P $\bar{1}$ diffractometer revealed no symmetry other than a center. A

Delauney reduction confirmed the assignment of the triclinic system. Lattice constants, $a = 12.187 (8) \text{ \AA}$, $b = 14.157 (5) \text{ \AA}$, $c = 11.925 (5) \text{ \AA}$, $\alpha = 94.70 (5)^\circ$, $\beta = 111.39 (4)^\circ$, and $\gamma = 68.44 (4)^\circ$, came from a least-squares refinement that utilized the setting angles of 56 reflections, collected at $\pm 2\theta$. For a cell content of $2[\text{CoN}_4\text{OC}_{47}\text{H}_{33}]$, these constants led to a calculated density of 1.356 g/cm^3 . The experimental density is 1.34 g/cm^3 .

Intensity data were measured by θ - 2θ scanning methods with graphite-monochromated Mo K α radiation. All independent data for which $\sin\theta/\lambda < 0.626 \text{ \AA}^{-1}$ were measured and the 6546 reflections for which $F_o > 3\sigma(F_o)$ were retained as observed. Backgrounds were measured at the extremes of the scan for 0.5 times the time required for the scan. Four standard reflections, measured every 50 reflections during data collection, showed no long term trends. Intensity data were reduced as described previously.³ With a $\mu = 0.56 \text{ mm}^{-1}$ and the crystal dimensions, no correction for absorption was deemed necessary.

The structure was solved by the heavy atom method and refined using block-diagonal least-squares techniques. Standard values for scattering factors were used.^{5,6} After isotropic refinement, a difference Fourier synthesis revealed electron density maxima appropriately located for porphinato hydrogen atoms. The position of hydrogen atoms were idealized (C-H = 0.95 \AA). The position of the acetyl hydrogen atoms were also determined from the Fourier maps and idealized (C-H = 1.0 \AA). All hydrogen atom parameters were included in subsequent cycles of refinement as fixed contributors. Refinement was carried to convergence using anisotropic temperature factors for all heavy atoms. Final values of the discrepancy indices were 0.050 (conventional residual) and 0.076 (weighted residual). A final difference Fourier synthesis was judged to be free of significant features; the largest peak had a density of 0.5 e/\AA^3 . Final atomic coordinates and the associated anisotropic thermal parameters in the asymmetric unit of structure are listed in Tables 1 and 2, respectively. A listing of the final observed and calculated structure factors is available from ASIS/NAPS.*

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Results and Discussion

Figure 1 is a computer drawn model of the (Acetyl)CoTPP molecule as it exists in the crystal. Each atom is represented by an ellipsoid with the relative size and orientation required by the thermal parameters given in Table 2. The hydrogen atoms of the acetyl ligand have been made artificially small. Each atom is identified by a label that is used throughout the tables. Also displayed in the figure are the bond distances of the coordination group.

Figure 2 illustrates the displacement of the atoms in the molecule from the mean plane defined by the 24-atom macrocyclic ring. The figure has essentially the same orientation as Figure 1; each atom symbol has been replaced by the value of the displacement in units of 0.01 \AA . The pattern of displacements in

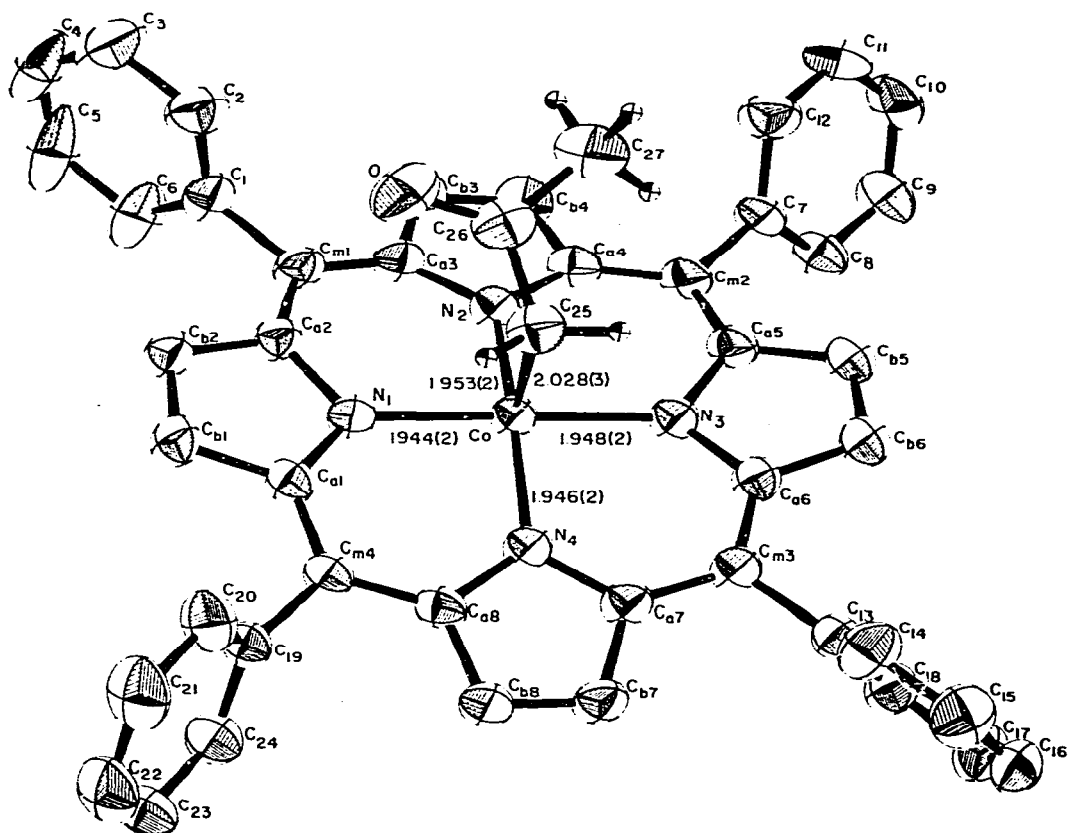


Figure 1. A computer-drawn model of the (Acetyl)CoTPP molecule. The atom labeling scheme is shown.

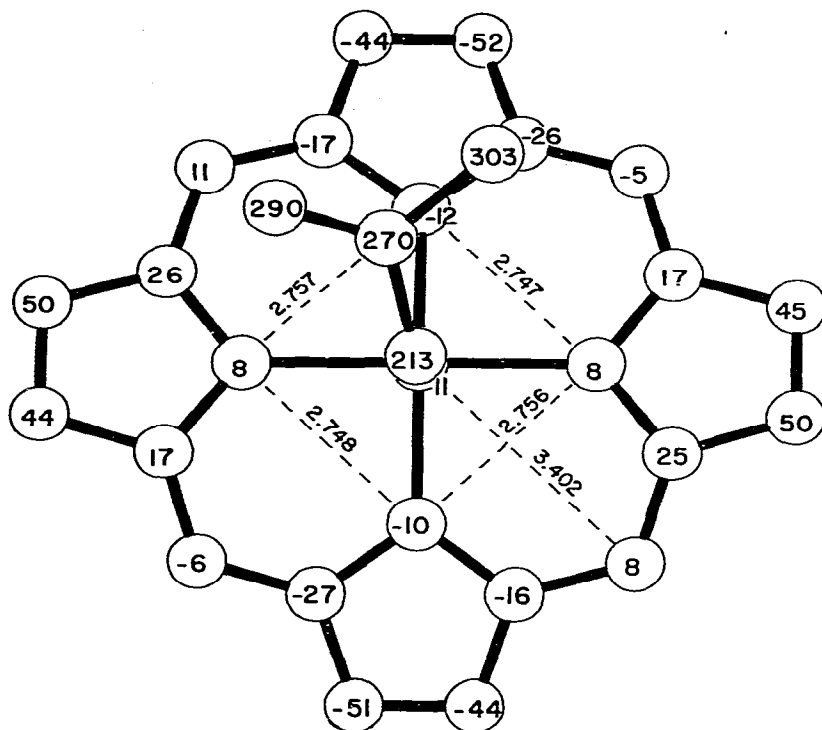


Figure 2. A diagram of the porphinato core showing displacements of the atoms, in units of 0.01 \AA , from the mean plane of the 24-atom core. This diagram has the same general orientation as that of Figure 1. The mean plane of the core and the paper are coplanar. Also displayed on the figure are the individual $\text{N}\cdots\text{N}$ distances and the average $\text{Co}\cdots\text{C}_m$ separation.

the porphinato core corresponds closely to \underline{D}_{2d} symmetry. The equatorial pseudo twofold axes pass through the methine carbon atoms (C_m 's on Figure 1) and the pseudo dihedral mirror planes pass through the nitrogen atoms and the midpoints of the $\text{C}_b\text{-C}_b$ bonds. Otherwise put, the methine carbon atoms define a plane that is coplanar with the mean plane of the four nitrogen atoms (Figure 2); the β -pyrrole carbon atoms of adjacent rings are alternatively above and below this plane. It is interesting to note that most porphyrin structures that have a \underline{D}_{2d} type of ruffled core have an alternate conformation in which the positions of the dihedral mirrors and twofold axes are reversed.

Bond parameters in the core reflect the fourfold geometry

(continued on p. 118)

Table 1. Atomic Coordinates in the Unit Cell Coordinates^a

Atom type	Coordinates		
	10^4x	10^4y	10^4z
Co	2273 (1)	- 19 (1)	42 (1)
N ₁	1921 (2)	1419 (1)	304 (2)
N ₂	559 (2)	299 (2)	-1126 (2)
N ₃	2604 (2)	-1465 (1)	- 192 (2)
N ₄	3814 (2)	- 360 (1)	1467 (2)
C ₂₅	3182 (3)	70 (2)	-1047 (3)
C ₂₆	2242 (3)	562 (2)	-2219 (3)
C ₂₇	1775 (3)	- 73 (3)	-3188 (3)
O	1847 (2)	1485 (2)	-2410 (2)
C _{a1}	2722 (2)	1857 (2)	1089 (2)
C _{a2}	931 (2)	2227 (2)	- 426 (2)
C _{b1}	2233 (3)	2938 (2)	823 (2)
C _{b2}	1141 (3)	3159 (2)	- 112 (2)
C _{a3}	- 364 (2)	1254 (2)	-1529 (2)
C _{a4}	- 8 (2)	- 375 (2)	-1749 (2)
C _{b3}	-1517 (3)	1164 (2)	-2324 (3)
C _{b4}	-1313 (3)	175 (2)	-2447 (3)
C _{a5}	1873 (2)	-1898 (2)	-1082 (2)
C _{a6}	3734 (2)	-2264 (2)	337 (2)
C _{b5}	2573 (3)	-2950 (2)	-1138 (2)
C _{b6}	3713 (3)	-3173 (2)	- 263 (3)
C _{a7}	4685 (2)	-1313 (2)	1922 (2)
C _{a8}	4254 (2)	303 (2)	2262 (2)
C _{b7}	5623 (3)	-1241 (2)	3043 (2)
C _{b8}	5362 (2)	- 260 (2)	3250 (2)
C _{m1}	- 168 (2)	2157 (2)	-1279 (2)
C _{m2}	615 (2)	-1400 (2)	-1792 (2)
C _{m3}	4709 (2)	-2214 (2)	1375 (2)

Table 1. contd.

Atom Type	Coordinates		
	10^4x	10^4y	10^4z
C _{m4}	3793 (2)	1346 (2)	2062 (2)
C ₁	-1148 (2)	3120 (2)	-1983 (3)
C ₂	-1037 (3)	3429 (2)	-2985 (3)
C ₃	-1862 (4)	4345 (3)	-3614 (3)
C ₄	-2838 (3)	4945 (2)	-3241 (4)
C ₅	-2969 (3)	4641 (3)	-2276 (4)
C ₆	-2113 (3)	3722 (2)	-1621 (3)
C ₇	- 60 (2)	-1998 (2)	-2680 (2)
C ₈	- 362 (3)	-2730 (2)	-2299 (3)
C ₉	- 978 (3)	-3281 (2)	-3121 (3)
C ₁₀	-1291 (3)	-3116 (2)	-4336 (3)
C ₁₁	-1000 (3)	-2393 (3)	-4729 (3)
C ₁₂	- 385 (3)	-1830 (2)	-3912 (3)
C ₁₃	5804 (2)	-3167 (2)	1942 (2)
C ₁₄	6987 (3)	-3336 (2)	1938 (3)
C ₁₅	7997 (3)	-4219 (3)	2495 (3)
C ₁₆	7826 (3)	-4921 (2)	3071 (3)
C ₁₇	6655 (3)	-4752 (2)	3089 (3)
C ₁₈	5633 (3)	-3877 (2)	2532 (3)
C ₁₉	4507 (2)	1931 (2)	2932 (2)
C ₂₀	5214 (3)	2346 (2)	2602 (3)
C ₂₁	5958 (3)	2807 (2)	3445 (3)
C ₂₂	5996 (3)	2858 (2)	4609 (3)
C ₂₃	5271 (3)	2464 (2)	4934 (3)
C ₂₄	4532 (3)	2004 (2)	4101 (3)

Table 2. Anisotropic Thermal Parameters.

Atom Type	Anisotropic parameters ^a						$B_{11}^{O_2^b}$
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	
Co	2.22(1)	2.42(1)	2.40(1)	-1.15(1)	0.29(1)	-0.09(1)	2.3
N ₁	2.28(8)	2.70(8)	2.59(8)	- .96(7)	0.61(7)	-0.16(7)	2.6
N ₂	2.46(9)	2.93(9)	2.93(9)	-1.29(7)	0.69(7)	-0.17(7)	2.7
N ₃	2.60(9)	2.80(9)	2.68(9)	-1.24(7)	0.57(7)	-0.17(7)	2.7
N ₄	2.53(9)	2.57(8)	2.89(9)	-1.25(7)	0.26(7)	0.06(7)	2.7
C ₂₅	3.6 (1)	3.9 (1)	3.6 (1)	-1.7 (1)	1.2 (1)	0.1 (1)	3.6
C ₂₆	3.7 (1)	4.6 (1)	4.0 (1)	-1.6 (1)	1.9 (1)	0.2 (1)	3.8
C ₂₇	5.3 (2)	6.5 (2)	4.0 (1)	-2.8 (1)	1.6 (1)	-0.4 (1)	4.9
O	5.7 (1)	4.7 (1)	5.5 (1)	-1.6 (1)	2.1 (1)	1.3 (1)	5.0
C _{a1}	2.8 (1)	2.8 (1)	3.1 (1)	-1.3 (1)	0.7 (1)	0.3 (1)	2.9
C _{a2}	2.9 (1)	2.8 (1)	2.8 (1)	-1.2 (1)	0.5 (1)	0.2 (1)	2.9
C _{b1}	3.5 (1)	2.7 (1)	3.7 (1)	-1.6 (1)	0.5 (1)	0.0 (1)	3.2
C _{b2}	3.4 (1)	2.7 (1)	3.5 (1)	-1.2 (1)	0.6 (1)	0.2 (1)	3.3
C _{a3}	2.4 (1)	3.2 (1)	3.2 (1)	-1.0 (1)	0.5 (1)	-0.0 (1)	3.0
C _{a4}	2.7 (1)	3.7 (1)	3.0 (1)	-1.8 (1)	0.8 (1)	-0.3 (1)	3.0
C _{b3}	2.5 (1)	3.9 (1)	4.9 (2)	-1.1 (1)	0.1 (1)	-0.0 (1)	3.8
C _{b4}	2.6 (1)	4.3 (1)	4.5 (1)	-1.8 (1)	0.2 (1)	-0.5 (1)	3.6
C _{a5}	3.3 (1)	3.1 (1)	2.7 (1)	-1.7 (1)	0.7 (1)	-0.3 (1)	2.9
C _{a6}	3.1 (1)	2.7 (1)	3.0 (1)	-1.3 (1)	0.6 (1)	-0.1 (1)	2.9
C _{b5}	4.0 (1)	3.1 (1)	3.3 (1)	-1.7 (1)	0.7 (1)	-0.6 (1)	3.4
C _{b6}	3.8 (1)	3.1 (1)	3.4 (1)	-1.4 (1)	0.7 (1)	-0.4 (1)	3.5
C _{a7}	2.7 (1)	2.9 (1)	2.9 (1)	-1.3 (1)	0.5 (1)	0.1 (1)	2.8
C _{a8}	2.7 (1)	3.2 (1)	2.5 (1)	-1.5 (1)	0.6 (1)	-0.4 (1)	2.7
C _{b7}	3.0 (1)	3.3 (1)	3.2 (1)	-1.4 (1)	-0.1 (1)	0.3 (1)	3.2
C _{b8}	3.0 (1)	3.3 (1)	3.1 (1)	-1.4 (1)	0.0 (1)	-0.3 (1)	3.2
C _{m1}	2.5 (1)	3.0 (1)	3.2 (1)	-0.8 (1)	0.3 (1)	0.3 (1)	3.0
C _{m2}	3.3 (1)	3.4 (1)	2.8 (1)	-2.1 (1)	0.5 (1)	-0.3 (1)	2.9
C _{m3}	2.7 (1)	2.8 (1)	3.2 (1)	-1.2 (1)	0.6 (1)	0.1 (1)	2.9
C _{m4}	2.7 (1)	2.9 (1)	2.9 (1)	-1.4 (1)	0.7 (1)	-0.4 (1)	2.8

Table 2. contd.

Atom Type	Anisotropic parameters ^a						$\underline{B}_A^{O_2^b}$
	\underline{B}_{11}	\underline{B}_{22}	\underline{B}_{33}	\underline{B}_{12}	\underline{B}_{13}	\underline{B}_{23}	
C ₁	2.6 (1)	3.2 (1)	4.0 (1)	-1.2 (1)	-0.0 (1)	0.3 (1)	3.3
C ₂	4.7 (2)	4.6 (2)	3.8 (1)	-1.6 (1)	0.2 (1)	0.6 (1)	4.5
C ₃	6.9 (2)	5.4 (2)	4.9 (2)	-3.0 (1)	-1.0 (2)	1.9 (1)	5.4
C ₄	3.9 (2)	3.7 (1)	8.7 (2)	-1.7 (1)	-1.5 (2)	1.9 (1)	4.9
C ₅	3.4 (2)	3.6 (2)	12.0 (3)	-0.7 (1)	1.7 (2)	0.3 (2)	5.6
C ₆	3.5 (1)	4.0 (2)	7.3 (2)	-0.8 (1)	1.7 (1)	0.6 (1)	4.8
C ₇	3.1 (1)	3.4 (1)	2.9 (1)	-1.7 (1)	0.5 (1)	-0.5 (1)	3.1
C ₈	4.0 (1)	4.0 (1)	3.5 (1)	-2.3 (1)	1.3 (1)	-0.9 (1)	3.5
C ₉	4.5 (2)	4.8 (2)	4.9 (2)	-3.0 (1)	1.8 (1)	-1.3 (1)	4.1
C ₁₀	3.8 (1)	4.8 (2)	4.5 (1)	-2.2 (1)	0.7 (1)	-1.8 (1)	4.1
C ₁₁	4.8 (2)	6.4 (2)	2.8 (1)	-2.5 (1)	0.3 (1)	-0.7 (1)	4.4
C ₁₂	4.6 (2)	4.8 (2)	3.2 (1)	-2.3 (1)	0.1 (1)	0.0 (1)	4.2
C ₁₃	3.2 (1)	2.6 (1)	3.1 (1)	-1.2 (1)	0.4 (1)	-0.3 (1)	3.0
C ₁₄	3.4 (1)	4.1 (1)	5.0 (2)	-1.3 (1)	1.1 (1)	0.4 (1)	4.2
C ₁₅	3.1 (1)	5.2 (2)	5.9 (2)	-0.9 (1)	1.0 (1)	-0.5 (1)	4.9
C ₁₆	4.9 (2)	3.2 (1)	4.5 (2)	-0.3 (1)	-0.3 (1)	-0.4 (1)	4.5
C ₁₇	5.5 (2)	2.9 (1)	4.8 (2)	-1.6 (1)	0.6 (1)	0.4 (1)	4.4
C ₁₈	4.3 (1)	3.0 (1)	4.0 (1)	-1.8 (1)	0.5 (1)	-0.1 (1)	3.7
C ₁₉	2.6 (1)	2.6 (1)	3.3 (1)	-1.2 (1)	0.2 (1)	-0.4 (1)	2.9
C ₂₀	4.1 (1)	3.7 (1)	4.8 (2)	-2.1 (1)	1.6 (1)	-1.0 (1)	3.9
C ₂₁	4.8 (2)	4.3 (2)	7.3 (2)	-3.1 (1)	1.7 (2)	-1.2 (1)	4.6
C ₂₂	4.4 (2)	4.6 (2)	6.1 (2)	-2.4 (1)	0.1 (1)	-1.6 (1)	4.6
C ₂₃	5.3 (2)	4.7 (2)	3.7 (1)	-2.1 (1)	0.2 (1)	-1.1 (1)	4.6
C ₂₄	3.9 (1)	3.9 (1)	3.7 (1)	-1.8 (1)	0.6 (1)	-0.5 (1)	3.8

^aThe number in parentheses following each datum is the estimated standard deviation in the last significant figure. \underline{B}_{ij} is related to the dimensionless β_{ij} employed during refinement as $\underline{B}_{ij} = 4\beta_{ij}/a_i^*a_j^*$.

^bIsotropic thermal parameters as calculated from $\underline{B} = 4[V^2\det(\beta_{ij})]^{1/3}$.

Table 3. Bond Lengths in the Coordination Group,
Porphinato Skeleton, and Acetylonyl Group^a

Bond	Value, Å	Bond	Value, Å	Bond	Value, Å
Co-N ₁	1.944 (2)	C _{a1} -C _{m4}	1.383 (4)	C _{a7} -C _{b7}	1.433 (4)
Co-N ₂	1.948 (2)	C _{a1} -C _{b1}	1.438 (3)	C _{a8} -C _{m4}	1.380 (4)
Co-N ₃	1.953 (2)	C _{a2} -C _{m1}	1.387 (4)	C _{a8} -C _{b8}	1.431 (4)
Co-N ₄	1.946 (2)	C _{a2} -C _{b2}	1.429 (4)	C _{m1} -C ₁	1.500 (4)
Co-C ₂₅	2.028 (3)	C _{a3} -C _{m1}	1.375 (4)	C _{m2} -C ₇	1.498 (4)
N ₁ -C _{a1}	1.377 (3)	C _{a3} -C _{b3}	1.424 (4)	C _{m3} -C ₁₃	1.492 (4)
N ₁ -C _{a2}	1.380 (3)	C _{a4} -C _{m2}	1.375 (4)	C _{m4} -C ₁₉	1.501 (3)
N ₂ -C _{a3}	1.385 (3)	C _{a4} -C _{b4}	1.435 (4)	C _{b1} -C _{b2}	1.335 (4)
N ₂ -C _{a4}	1.391 (3)	C _{a5} -C _{m2}	1.386 (4)	C _{b3} -C _{b4}	1.335 (4)
N ₃ -C _{a5}	1.378 (3)	C _{a5} -C _{b5}	1.428 (4)	C _{b5} -C _{b6}	1.339 (4)
N ₃ -C _{a6}	1.383 (3)	C _{a6} -C _{m3}	1.387 (4)	C _{b7} -C _{b8}	1.330 (4)
N ₄ -C _{a7}	1.375 (3)	C _{a6} -C _{b6}	1.424 (4)	C ₂₅ -C ₂₆	1.468 (4)
N ₄ -C _{a8}	1.386 (3)	C _{a7} -C _{m3}	1.379 (4)	C ₂₆ -C ₂₇	1.480 (5)
				C ₂₆ -O	1.224 (4)

^aThe numbers in parentheses are the estimated standard deviations.

with average bond distances of Co-N = 1.948 (4) Å, N-C_a = 1.382 (5) Å, C_a-C_b = 1.430 (5) Å, C_a-C_m = 1.382 (5) Å, and C_b-C_b = 1.335 (4) Å, where the number in parentheses following the averaged value is the estimated standard deviation. The average value of the individually determined C-C bond distances in the four peripheral phenyl rings is 1.38 (1) Å. Values for the bond angles are as follows: C_aNC_a = 104.5 (3)°, C_aC_mC_a = 122.6 (5)°, NC_aC_b = 110.4 (4)°, NC_aC_m = 125.0 (5)°, C_aC_bC_b = 107.3 (2)°. The values of the various bond parameters in porphinato complexes have been observed to vary as a function of the size of the central hole.⁷ The values observed in (Acetylonyl)CoTPP are in agree-

ment with these general trends. Individual values of bond distances and bond angles are listed in Tables 3 and 4.

The average Co-N bond distance of 1.948 (4) Å is at the lower end of the observed range of porphinato nitrogen-cobalt bond distances.^{7,8} It is comparable to the 1.949 Å value observed

Table 4. Bond Angles in the Coordination Group,
Porphinato Skeleton, and Acetylonyl Group^a

Angle	Value, deg	Angle	Value, deg	Angle	Value, deg
N ₁ CoN ₂	90.21 (9)	C _{a5} C _{m2} C ₇	118.2 (2)		
N ₁ CoN ₃	178.5 (7)	C _{a6} C _{m3} C ₁₃	119.2 (2)	N ₃ C _{a6} C _{b6}	110.7 (2)
N ₁ CoN ₄	89.93 (9)	C _{a7} C _{m3} C ₁₃	118.7 (2)	C _{m3} C _{a6} C _{b6}	124.3 (2)
N ₁ CoC ₂₅	89.0 (1)	C _{a1} C _{m4} C ₁₉	119.6 (2)	N ₄ C _{a7} C _{m3}	126.1 (2)
N ₂ CoN ₃	89.54 (9)	C _{a8} C _{m4} C ₁₉	117.8 (2)	N ₄ C _{a7} C _{b7}	110.0 (2)
N ₂ CoN ₄	167.1 (1)	N ₁ C _{a1} C _{m4}	124.8 (2)	C _{m3} C _{a7} C _{b7}	123.8 (2)
N ₂ CoC ₂₅	100.6 (1)	N ₁ C _{a1} C _{b1}	110.6 (2)	N ₄ C _{a8} C _{m4}	125.1 (2)
N ₃ CoN ₄	89.97 (9)	C _{m4} C _{a1} C _{b1}	124.3 (2)	N ₄ C _{a8} C _{b8}	110.0 (2)
N ₃ CoC ₂₅	92.5 (1)	N ₁ C _{a2} C _{m1}	124.5 (2)	C _{m4} C _{a8} C _{b8}	124.5 (2)
N ₄ CoC ₂₅	92.3 (1)	N ₁ C _{a2} C _{b2}	110.9 (2)	C _{a1} C _{b1} C _{b2}	107.0 (2)
C _{a1} N ₁ C _{a2}	104.3 (2)	C _{m1} C _{a2} C _{b2}	124.4 (2)	C _{a2} C _{b2} C _{b1}	107.2 (2)
C _{a3} N ₂ C _{a4}	104.6 (2)	N ₂ C _{a3} C _{m1}	124.8 (2)	C _{a3} C _{b3} C _{b4}	107.7 (2)
C _{a5} N ₃ C _{a6}	104.3 (2)	N ₂ C _{a3} C _{b3}	110.3 (2)	C _{a4} C _{b4} C _{b3}	107.4 (2)
C _{a7} N ₄ C _{a8}	104.9 (2)	C _{m1} C _{a3} C _{b3}	124.7 (2)	C _{a5} C _{b5} C _{b6}	107.1 (2)
C _{a2} C _{m1} C _{a3}	123.2 (2)	N ₂ C _{a4} C _{m2}	125.1 (2)	C _{a6} C _{b6} C _{b5}	107.2 (2)
C _{a4} C _{m2} C _{a5}	122.4 (2)	N ₂ C _{a4} C _{b4}	109.8 (2)	C _{a7} C _{b7} C _{b8}	107.6 (2)
C _{a6} C _{m3} C _{a7}	122.1 (2)	C _{m2} C _{a4} C _{b4}	124.8 (2)	C _{a8} C _{b8} C _{b7}	107.3 (2)
C _{a1} C _{m4} C _{a8}	122.5 (2)	N ₃ C _{a5} C _{m2}	125.0 (2)	C ₂₅ C ₂₆ C ₂₇	119.3 (3)
C _{a2} C _{m1} C ₁	117.0 (2)	N ₃ C _{a5} C _{b5}	110.7 (2)	C ₂₅ C ₂₆ O	121.1 (3)
C _{a3} C _{m1} C ₁	119.8 (2)	C _{m2} C _{a5} C _{b5}	124.3 (2)	C ₂₇ C ₂₆ O	119.6 (3)
C _{a4} C _{m2} C ₇	119.3 (2)	N ₃ C _{a6} C _{m3}	124.8 (2)	CoC ₂₅ C ₂₆	109.1 (2)

^aThe numbers in parentheses are the estimated standard deviations.

Table 5. ^1H NMR Spectra (τ values)

Compound ^a	Proton assignments for axial ligands					(mp)Ph (o)Ph ref
	H _a	H _b	H _c	H _d		
$\text{C}(\text{H}_c)_3\text{C}(\text{O})\text{C}(\text{H}_a)_2\text{CoTPP}$	13.68		11.78			b
$\text{PhC}(\text{O})\text{C}(\text{H}_a)_2\text{CoTPP}$	12.84				3.6	5.16 b
$(\text{CN})_2\text{C}(\text{H}_a)\text{CoTPP}$	13.45					b
$\text{C}(\text{H}_d)_3\text{C}(\text{H}_c)_2\text{C}(\text{H}_b)_2\text{C}(\text{H}_a)_2\text{Co}(\text{etio I})$	14.3	15.3	11.65	11.0		c
$\text{C}(\text{H}_b)_2(\text{CN})\text{C}(\text{H}_a)_2\text{CoOEP}$		14.28 (br)				d
$\text{cis-PhC}(\text{H}_b)=\text{C}(\text{H}_a)\text{CoOEP}$	9.94	11.3			3.50	6.10 d
$\text{trans-PhC}(\text{H}_b)=\text{C}(\text{H}_a)\text{CoOEP}$	10.12	11.0			3.79	5.10 d
$\text{C}_3(\text{H}_d)_4(\text{H}_c)\text{C}(\text{O})\text{C}(\text{H}_a)_2\text{Rh}(\text{etio I})$	16.0		14.1	11.2, 11.6		e
$\text{p-F-PhC}(\text{O})\text{C}(\text{H}_c)_2\text{C}(\text{H}_b)_2\text{C}(\text{H}_a)_2\text{Rh}(\text{etio I})$	16.15	14.9	11.18		3.3	e

a. The free bases of the porphyrin ligands are abbreviated as follows: H_2TPP , tetraphenylporphyrin; H_2OEP , octaethylporphyrin; $\text{H}_2(\text{etio I})$, etioporphyrin I.

b. This work.

c. D. A. Clark, R. Grigg and A. W. Johnson, Chem. Commun., (1966) 208.

d. Ref. 15.

e. A. M. Abeysekera, R. Grigg, J. Trocha-Grimshaw and V. Viswanatha, J.C.S. Chem. Comm., (1976) 227.

in four-coordinate CoTPP⁹ (a cobalt(II) derivative) and the 1.954-Å value found for six-coordinate (3,5-lutidine)-meso-tetraphenylporphinato(nitro)cobalt(III).¹⁰ The porphinato cores in these two derivatives are also quite ruffled and, as noted earlier,¹¹ the porphinato core conformation appears to have a greater effect on the Co-N bond distance than any other variable.

The Co-C bond distance of 2.028 (3) Å is within the range (1.93-2.05 Å) reported¹² for a variety of six-coordinate organocobalt(III) complexes. The Co-C bond distance in five-coordinate N,N'-ethylene-bis-(acetylacetoniminato)methylcobalt(III) is 1.95 (2) Å.¹³ The Rh-C bond distance in a five-coordinate porphinato derivative is 2.031 (6) Å.¹⁴ These three five-coordinate derivatives all have small metal atom displacements from the basal plane: 0.11 Å in (Acetyl)CoTPP, 0.12 Å in N,N'-ethylene-bis-(acetylacetoniminato)methylcobalt(III) and 0.05 Å in (methyl)-octaethylporphinatorhodium(III).¹⁴

Tetrahedral geometry is maintained at C₂₅ of the ligand with a Co-C₂₅-C₂₆ angle of 109.1 (2)^o and trigonal geometry at C₂₆, the carbonyl carbon atom. As can be seen from Figures 1 and 2, the C₂₅-C₂₆ bond almost projects onto the Co-N₂ bond. The dihedral angle between the C₂₅-Co-N₂ plane and the C₂₆-C₂₅-Co plane is 13.2 (2)^o. This orientation of the acetyl ligand leads to a C₂₅-Co-N₂ angle that is substantially larger than the other three C₂₅-Co-N angles. The C₂₇ atom makes two rather close nonbonded contacts of 3.3 and 3.4 Å to N₂ and C_{a4}, respectively. The (Acetyl)CoTPP molecules are well separated in the crystal with no unusual intermolecular contacts.

The preparation of organocobalt(III) porphyrin derivatives has been reported previously.^{15,16} These preparations utilized the reaction of cobalt(I) porphyrins with organic halides. Recently the preparation of organocobalt(III) porphyrin derivatives by the reaction of halocobalt(III) porphyrin species with diazoalkanes has been reported.¹⁷ The compounds reported here are the first to be prepared by the direct reaction of cobalt(II) porphyrins utilizing aerial oxidation. Such methods have been used for the preparation of other organocobalt(III) species however.^{12,18} (Acetyl)CoTPP and the other derivatives appear to be stable in the solid state and in benzene solution and relatively stable to light. They are rather unstable in chloroform solution, decomposing in a few hours to uncharacterized products.

All derivatives are found to be diamagnetic. The IR spectra of the complexes show a decrease of $\sim 55\text{-}60\text{ cm}^{-1}$ in the carbonyl stretch of the coordinated ligand. The mass spectrum of (Acetonyl)CoTPP shows as the largest peak that of CoTPP^+ (671.155 amu, observed). Peaks at 727.161 and 685.160 are assigned to $\text{CH}_2\text{C}(\text{O})\text{CH}_2\text{CoTPP}^+$ and $\text{CH}_2\text{CoTPP}^+$, respectively. Below the CoTPP^+ peak, the fragmentation pattern is typical of a metallotetra-phenylporphyrin.¹⁹

The ^1H NMR spectra of (Acetonyl)CoTPP and the related derivatives shows the porphinato hydrogen atoms at 1.27 τ (β -pyrrole), 1.85 τ (o -phenyl) and 2.3 τ (m, p -phenyl). The corresponding values for tetraphenylporphyrin itself are 1.25, 1.7 and 2.2 τ .²⁰ The observed shifts for the axial ligand protons are summarized in Table 5. The protons of the axial ligand experience the influence of the ring current of the porphyrin. As can be seen from Table 5, the shifts are comparable to those observed in a variety of closely related porphyrin derivatives.

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