Table VIII. Comparison of Some Crystallographic Data for $C_{12}H_8X$ Compounds

Compd	Crystal system	Space group	No. of molecules in Unit cell	Asymmetric unit
Dibenzotellurophene	Orthorhombic	$P2_12_12_1$	4	1
Dibenzoselenophene	Orthorhombic	*Pbca*	16	2
Dibenzothiophene	Monoclinic	$P2_1/c$	4	1
Dibenzofuran	Orthorhombic	*Pnam*	4	$^1/_2$[a]

[a] The dibenzofuran molecule is required crystallographically to have a plane of symmetry perpendicular to the C(6)–C(6′) bond at its midpoint.

In general, the four compounds have quite similar molecular structures which differ mainly because of the range of X–C distances involved. However, the crystal structures and packing arrangements differ distinctly from compound to compound. The differences are shown in condensed form in Table VIII. Of particular interest is the number of chemical molecules in the crystallographic asymmetric unit, which ranges from $^1/_2$ in dibenzofuran to 2 in dibenzoselenophene. The latter compound is unique in the series in forming loosely associated dimers with intermolecular C–C contacts as short as 3.36 Å.

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Registry No. $C_{12}H_8Te$, 244-98-4.

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 Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC50341F-11-75.

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Stereochemistry of Low-Spin Cobalt Porphyrins. VII. (3,5-Dimethylpyridine)-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatocobalt(II)

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(3,5-Dimethylpyridine)-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatocobalt(II) crystallizes in the monoclinic system, space group $P2_1/c$. The unit cell has a = 11.514 (11) Å, b = 30.939 (10) Å, c = 11.571 (11) Å, and β = 103.73 (1)° and contains four molecules. The calculated and experimental densities are 1.292 and 1.29 g/cm^3, respectively, at 20 ± 1°. Measurement of diffracted intensities employed ω scanning with graphite-monochromated Mo Kα radiation on a four-circle diffractometer. All independent reflections for $(\sin\theta)/\lambda \leq 0.602$ Å^{-1} were measured; 4435 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 0.076 and 0.092, respectively. The square-pyramidal CoN_5 coordination group has an average equatorial bond length of 2.000 Å; the axial Co–N_b bond is 2.161 (5) Å. The cobalt(II) atom is displaced 0.17 Å from the mean porphinato plane and 0.14 Å from the plane of the porphinato nitrogens.

There has been considerable recent interest in structural[1–5] and solution[6–10] studies of low-spin cobalt(II) porphyrins. This work has been stimulated by the discovery[6] that cobalt(II) porphyrins reversibly bind molecular oxygen and that cobaltohemoglobin,[11] the product of replacement in hemoglobin of the protohemes by molecules of the corresponding low-spin cobalt(II) protoporphyrin, displays reversible uptake of oxygen that is qualitatively similar in all respects to the uptake of oxygen by hemoglobin. Some controversy has attended the interpretation[12] of the cooperative oxygen binding of cobaltohemoglobin.

Solution studies[6,8,9] of cobalt(II) porphyrins have shown that alkylamines and -pyridines can add either one or two molecules of base to form five-coordinate or six-coordinate complexes. Imidazoles and substituted imidazoles, however, appear to form *only* five-coordinated complexes. This difference in reactivity between imidazoles and other nitrogenous bases has been suggested[13] to be the result of electronic effects peculiar to imidazoles.

In the process of attempting to prepare crystals of cobalt(II) porphyrins coordinated by sterically hindered bases, we unexpectedly obtained crystals of (3,5-dimethylpyridine)-

α,β,γ,δ-tetraphenylporphinatocobalt(II), to be written as (3,5-lut)CoTPP. The true identity of the complex was not discovered until near the end of the structure solution. Least-squares refinement of the crystallographic data for the complex continued to afford a comparison of the quantitative stereochemistry of the five-coordinate 3,5-lutidine adduct with those of the five-coordinate imidazole adducts[1,3,5] and other cobalt(II) porphyrins.

Experimental Section

Single crystals of (3,5-lut)CoTPP were grown by the slow evaporation of 1:1 chloroform–2,4,6-trimethylpyridine solutions; the coordinated 3,5-lutidine appears to result from an impurity in the 2,4,6-trimethylpyridine at a concentration of <0.5%.[14] Preliminary X-ray photographic examination established a four-molecule monoclinic unit cell; the systematic absences suggest the unique choice of $P2_1/c$ as the space group. Lattice constants, a = 11.514 (11) Å, b = 30.939 (10) Å, c = 11.571 (11) Å, and β = 103.73 (1)° (λ 0.71069 Å), came from a least-squares refinement that utilized the setting angles of 30 reflections, each collected at $\pm 2\theta$. These constants led to a calculated density of 1.292 g/cm^3 at 20 ± 1°. The experimental density was 1.29 g/cm^3.

Intensity data were measured on a Syntex $P\bar{1}$ diffractometer using the "wandering" ω-scan method with graphite-monochromated Mo Kα radiation using conditions previously described.[1] Four standard reflections that were well distributed in reciprocal space were used for periodic checking on the alignment and possible deterioration of the crystal; only random variations were noted. All independent data having $(\sin\theta)/\lambda \leq 0.602$ Å^{-1} were measured.

The specimen crystal had dimensions of 0.2 × 0.2 × 0.5 mm and was mounted with the ϕ axis of the diffractometer approximately parallel to the long axis of the crystal. With a linear absorption coefficient of 0.50 mm^{-1} for Mo Kα radiation, the maximum error in any structure amplitude resulting from neglect of absorption corrections was seen to be <2%. 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] and all data having $F_o < 3\sigma(F_o)$ were taken to be unobserved, leaving 4435 independent observed data (~60% of the theoretical number possible). Only the observed data were used for the determination and refinement of structure.

The structure was solved by standard heavy-atom methods.[15] Block-diagonal least-squares refinement[16] was followed by a difference Fourier synthesis which revealed electron density concentrations appropriately located for all hydrogen atom positions except those of the two methyl groups of the lutidine ligand. Hydrogen atom positions were then idealized (C–H = 0.95 Å) and 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

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

was 0.76; that of

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

was 0.092. The estimated standard deviation of an observation of unit weight was 1.92. The final parameter shifts were less than 50% of the estimated standard deviations during the final cycle,[17] 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/Å^3.

Atomic coordinates and the associated anisotropic thermal parameters in the asymmetric unit of structure are listed in Tables I and II, respectively; bond parameters[18] are listed in Tables III and IV.

Table I. Atomic Coordinates in the Unit Cell

	Coordinates^a		
Atom type	10^4x	10^4y	10^4z
Co^b	6092 (1)	1314 (0)	1737 (1)
N_1	5499 (4)	725 (1)	2010 (4)
N_2	4696 (4)	1574 (2)	2241 (4)
N_3	6536 (4)	1897 (1)	1230 (4)
N_4	7327 (4)	1053 (2)	995 (4)
C_{a1}	6023 (6)	337 (2)	1841 (6)
C_{a2}	4540 (6)	625 (2)	2482 (6)
C_{a3}	3842 (5)	1355 (2)	2681 (5)
C_{a4}	4451 (5)	2003 (2)	2317 (5)
C_{a5}	6023 (5)	2284 (2)	1422 (5)
C_{a6}	7439 (5)	2001 (2)	700 (5)
C_{a7}	8130 (5)	1270 (2)	474 (5)
C_{a8}	7575 (5)	619 (2)	924 (5)
C_{m1}	3764 (5)	911 (2)	2794 (6)
C_{m2}	5069 (5)	2343 (2)	1941 (5)
C_{m3}	8209 (5)	1711 (2)	353 (5)
C_{m4}	7012 (5)	282 (2)	1350 (5)
N_5	7229 (5)	1349 (2)	3512 (5)
C_{b1}	5366 (6)	−15 (2)	2203 (6)
C_{b2}	4456 (6)	165 (2)	2590 (6)
C_{b3}	3061 (6)	1669 (2)	3046 (6)
C_{b4}	3438 (6)	2060 (2)	2802 (6)
C_{b5}	6642 (6)	2641 (2)	984 (6)
C_{b6}	7502 (6)	2461 (2)	553 (6)
C_{b7}	8878 (6)	959 (2)	42 (6)
C_{b8}	8532 (6)	562 (2)	330 (6)
C_1	6823 (7)	1193 (3)	4444 (6)
C_2	7519 (8)	1203 (3)	5601 (7)
C_3	8678 (7)	1374 (2)	5791 (7)
C_4	9109 (7)	1529 (3)	4840 (7)
C_5	8342 (6)	1509 (2)	3728 (6)
C_6	6994 (9)	1033 (4)	6650 (8)
C_7	10335 (8)	1718 (3)	5023 (9)
C_{11}	2794 (6)	745 (2)	3337 (6)
C_{12}	1601 (6)	794 (2)	2728 (6)
C_{13}	645 (7)	663 (3)	3265 (8)
C_{14}	935 (7)	477 (3)	4416 (7)
C_{15}	2119 (8)	415 (3)	4966 (7)
C_{16}	3059 (6)	555 (2)	4453 (6)
C_{21}	4666 (5)	2797 (2)	2091 (5)
C_{22}	3985 (7)	3015 (2)	1147 (6)
C_{23}	3603 (8)	3437 (3)	1284 (7)
C_{24}	3902 (7)	3634 (2)	2357 (7)
C_{25}	4560 (8)	3411 (3)	3305 (7)
C_{26}	4963 (7)	2993 (2)	3195 (6)
C_{31}	9183 (6)	1887 (2)	−177 (6)
C_{32}	10358 (6)	1894 (2)	475 (6)
C_{33}	11256 (6)	2061 (3)	−16 (7)
C_{34}	10980 (7)	2213 (3)	−1162 (8)
C_{35}	9807 (7)	2213 (3)	−1810 (6)
C_{36}	8922 (6)	2046 (2)	−1333 (6)
C_{41}	7489 (6)	−163 (2)	1309 (6)
C_{42}	8563 (6)	−269 (2)	2121 (6)
C_{43}	9071 (7)	−680 (3)	2121 (8)
C_{44}	8442 (8)	−980 (2)	1242 (8)
C_{45}	7396 (7)	−874 (2)	448 (7)
C_{46}	6899 (7)	−469 (2)	464 (6)

^{a} Numbers in parentheses are the estimated standard deviations. ^{b} For Co 10^5x = 60917 (8), 10^5y = 13136 (3), and 10^5z = 17367 (8).

Discussion

Figure 1 is a model in perspective of the (3,5-lut)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 of the molecule. 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 (fourfold geometry) in the porphinato skeleton are N–C_a = 1.376 (7, 8), C_a–C_m = 1.384 (8, 9), C_a–C_b = 1.444 (11, 9), C_b–C_b = 1.344 (11, 10), and C_m–C_p = 1.497 (4, 8) 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.[19] The averaged bond angles of a given chemical type in the core are as follows: C_aNC_a = 106.0 (2, 5), NC_aC_b = 109.8 (4, 5), NC_aC_m = 126.2 (3, 5), $C_aC_bC_b$ = 107.2 (7, 6), $C_aC_mC_a$ =

Table II. Anisotropic Thermal Parameters[a]

Atom type	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	3.67 (4)	3.69 (4)	3.89 (4)	−0.03 (4)	1.29 (3)	0.13 (4)
N_1	3.6 (3)	2.5 (2)	3.4 (2)	−0.3 (2)	1.4 (2)	0.1 (2)
N_2	2.9 (2)	2.7 (2)	3.1 (2)	−0.0 (2)	1.3 (2)	0.0 (2)
N_3	2.9 (2)	2.2 (2)	3.4 (2)	−0.0 (2)	1.0 (2)	−0.2 (2)
N_4	2.9 (2)	2.8 (2)	3.5 (2)	0.2 (2)	1.7 (2)	0.2 (2)
C_{a1}	4.2 (3)	2.5 (3)	3.6 (3)	0.1 (3)	0.9 (3)	0.5 (2)
C_{a2}	3.4 (3)	3.3 (3)	3.8 (3)	−0.4 (2)	1.3 (3)	0.2 (2)
C_{a3}	3.0 (3)	4.2 (3)	2.9 (3)	0.3 (3)	1.4 (2)	0.1 (3)
C_{a4}	2.9 (3)	3.3 (3)	3.3 (3)	0.6 (2)	1.2 (2)	0.2 (2)
C_{a5}	3.5 (3)	2.8 (3)	3.1 (3)	−0.2 (2)	0.6 (2)	0.0 (2)
C_{a6}	3.0 (3)	2.9 (3)	3.1 (3)	−0.2 (2)	0.9 (2)	−0.2 (2)
C_{a7}	2.9 (3)	4.1 (3)	3.2 (3)	0.4 (3)	1.0 (2)	0.2 (3)
C_{a8}	2.9 (3)	3.2 (3)	3.3 (2)	0.1 (2)	0.7 (2)	−0.0 (2)
C_{m1}	3.1 (3)	3.4 (3)	3.7 (3)	0.5 (3)	−0.5 (2)	−0.2 (2)
C_{m2}	3.3 (3)	2.8 (3)	3.0 (3)	0.1 (2)	0.5 (2)	−0.2 (2)
C_{m3}	2.7 (3)	3.5 (3)	3.1 (3)	−0.2 (2)	1.0 (2)	0.2 (2)
C_{m4}	3.3 (3)	3.1 (3)	3.1 (3)	0.4 (2)	0.9 (2)	−0.1 (2)
N_5	3.7 (3)	5.0 (3)	4.5 (3)	0.0 (2)	1.1 (2)	0.1 (3)
C_{b1}	4.4 (4)	3.2 (3)	5.8 (4)	0.1 (3)	2.3 (3)	0.6 (3)
C_{b2}	4.9 (4)	3.8 (3)	5.3 (4)	−0.3 (3)	2.8 (3)	0.5 (3)
C_{b3}	4.0 (3)	4.4 (4)	4.0 (3)	0.4 (3)	1.6 (3)	0.1 (3)
C_{b4}	4.2 (3)	3.3 (3)	4.6 (3)	0.7 (3)	1.8 (3)	−0.2 (3)
C_{b5}	4.2 (3)	3.0 (3)	4.2 (3)	−0.4 (3)	1.2 (3)	−0.1 (3)
C_{b6}	3.9 (3)	3.8 (3)	4.1 (3)	−0.5 (3)	1.7 (3)	−0.1 (3)
C_{b7}	4.0 (3)	3.8 (3)	4.8 (4)	0.6 (3)	2.0 (3)	0.4 (3)
C_{b8}	4.5 (4)	3.9 (3)	5.1 (4)	1.0 (3)	2.4 (3)	0.0 (3)
C_1	5.9 (4)	6.7 (5)	3.6 (3)	0.4 (4)	1.1 (3)	0.9 (3)
C_2	6.4 (5)	6.2 (5)	5.5 (4)	−0.1 (4)	0.7 (4)	0.8 (4)
C_3	6.2 (4)	4.6 (4)	5.1 (4)	1.2 (3)	−0.1 (3)	0.1 (3)
C_4	4.5 (4)	5.5 (4)	6.5 (5)	0.9 (3)	1.0 (3)	−0.8 (4)
C_5	4.3 (4)	5.8 (4)	4.4 (4)	0.7 (3)	0.6 (3)	−0.5 (3)
C_6	10.0 (7)	12.5 (8)	4.8 (5)	−1.9 (6)	2.5 (5)	2.9 (5)
C_7	5.2 (5)	9.4 (7)	10.1 (7)	−1.6 (5)	1.1 (5)	−1.8 (5)
C_{11}	3.7 (3)	3.4 (3)	4.4 (3)	−0.5 (3)	1.6 (3)	−0.3 (3)
C_{12}	4.2 (4)	5.2 (4)	5.4 (4)	−0.7 (3)	1.6 (3)	0.0 (3)
C_{13}	4.5 (4)	5.9 (5)	8.6 (6)	−1.3 (3)	2.5 (4)	−0.6 (4)
C_{14}	6.0 (5)	6.2 (5)	6.9 (5)	−1.7 (4)	2.7 (4)	−0.3 (4)
C_{15}	8.3 (6)	7.4 (5)	4.5 (4)	−2.1 (4)	2.7 (4)	0.6 (4)
C_{16}	4.5 (4)	5.3 (4)	4.6 (4)	−0.7 (3)	1.6 (3)	0.3 (3)
C_{21}	3.2 (3)	3.1 (3)	3.8 (3)	0.4 (2)	1.2 (3)	−0.1 (2)
C_{22}	7.0 (5)	3.7 (4)	4.1 (4)	1.3 (3)	0.4 (3)	−0.0 (3)
C_{23}	7.1 (5)	4.4 (4)	5.8 (4)	1.5 (4)	0.5 (4)	0.6 (3)
C_{24}	6.5 (4)	3.7 (4)	6.7 (5)	1.4 (3)	2.4 (4)	0.2 (3)
C_{25}	8.9 (6)	5.1 (4)	6.2 (5)	1.5 (4)	1.0 (4)	−2.3 (4)
C_{26}	6.1 (4)	4.6 (4)	4.4 (4)	1.4 (3)	0.1 (3)	−0.9 (3)
C_{31}	3.5 (3)	3.0 (3)	4.2 (3)	−0.1 (2)	1.6 (3)	0.1 (2)
C_{32}	3.9 (4)	5.3 (4)	4.3 (4)	−0.3 (3)	1.4 (3)	0.4 (3)
C_{33}	3.3 (3)	6.3 (5)	6.7 (5)	−0.9 (3)	1.5 (3)	−0.0 (4)
C_{34}	6.5 (5)	5.1 (4)	8.0 (5)	−1.5 (4)	3.8 (4)	−0.1 (4)
C_{35}	5.9 (4)	6.6 (5)	4.4 (4)	−0.8 (4)	2.0 (3)	1.1 (3)
C_{36}	4.1 (4)	5.5 (4)	4.8 (4)	−0.4 (3)	1.7 (3)	0.9 (3)
C_{41}	5.6 (4)	4.3 (4)	5.2 (4)	0.6 (3)	3.0 (3)	0.8 (3)
C_{42}	4.4 (4)	3.7 (4)	5.8 (4)	0.6 (3)	1.1 (3)	0.3 (3)
C_{43}	6.1 (5)	4.2 (4)	8.7 (6)	0.9 (3)	3.0 (4)	0.8 (4)
C_{44}	9.4 (6)	3.1 (4)	10.2 (6)	0.6 (4)	7.0 (5)	0.2 (4)
C_{45}	7.6 (5)	3.8 (4)	5.7 (4)	−0.1 (3)	3.4 (4)	−0.2 (3)
C_{46}	6.9 (4)	3.1 (3)	4.4 (4)	−0.8 (3)	2.2 (3)	−0.4 (3)

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

123.4 (2, 5), $C_aC_mC_p$ = 118.3 (4, 5)°.

The departures of the atoms of the porphine core from the mean plane of the core are displayed in Figure 2, which is drawn in the same orientation as Figure 1. The departures from planarity of the porphinato core of this derivative are small relative to those in a number of other metalloporphyrins. Local flatness is preserved in the trigonal carbon atoms of the inner 16-membered ring and, of course, in the pyrrole rings. The four nitrogen atoms of the porphine skeleton are coplanar; the cobalt atom is displaced 0.144 Å from this mean plane toward the nitrogen atom of the coordinated ligand. The mean planes defined respectively by the four nitrogen atoms and the entire porphine skeleton are separated by ~0.03 Å; the cobalt atom is displaced by 0.171 Å from the mean skeletal plane.

The dihedral angles between the mean plane of the porphine skeleton and the planes of the four phenyl groups are 67.1, 77.9, 74.5, and 73.7°. The averaged value of the internal angles in the phenyl rings is 120.0°. The individually determined C–C bond distances of the four structurally independent phenyl rings average to 1.39 Å.

The equatorial Co–N lengths of the square-pyramidal CoN_5 coordination group average to 2.000 (3, 5) Å; the NCoN angles of the equatorial plane average to 89.7 (5, 2)°. The "radius of the central hole", Ct···N, is 1.995 Å. The equatorial Co–N distance and indeed even Ct···N in (3,5-lut)CoTPP are significantly longer than the equatorial Co–N distances that characterize other five-coordinate cobalt(II) porphyrins. The Co–N bond distances are 1.985 (2, 2) Å in (1,2-DiMeIm)-

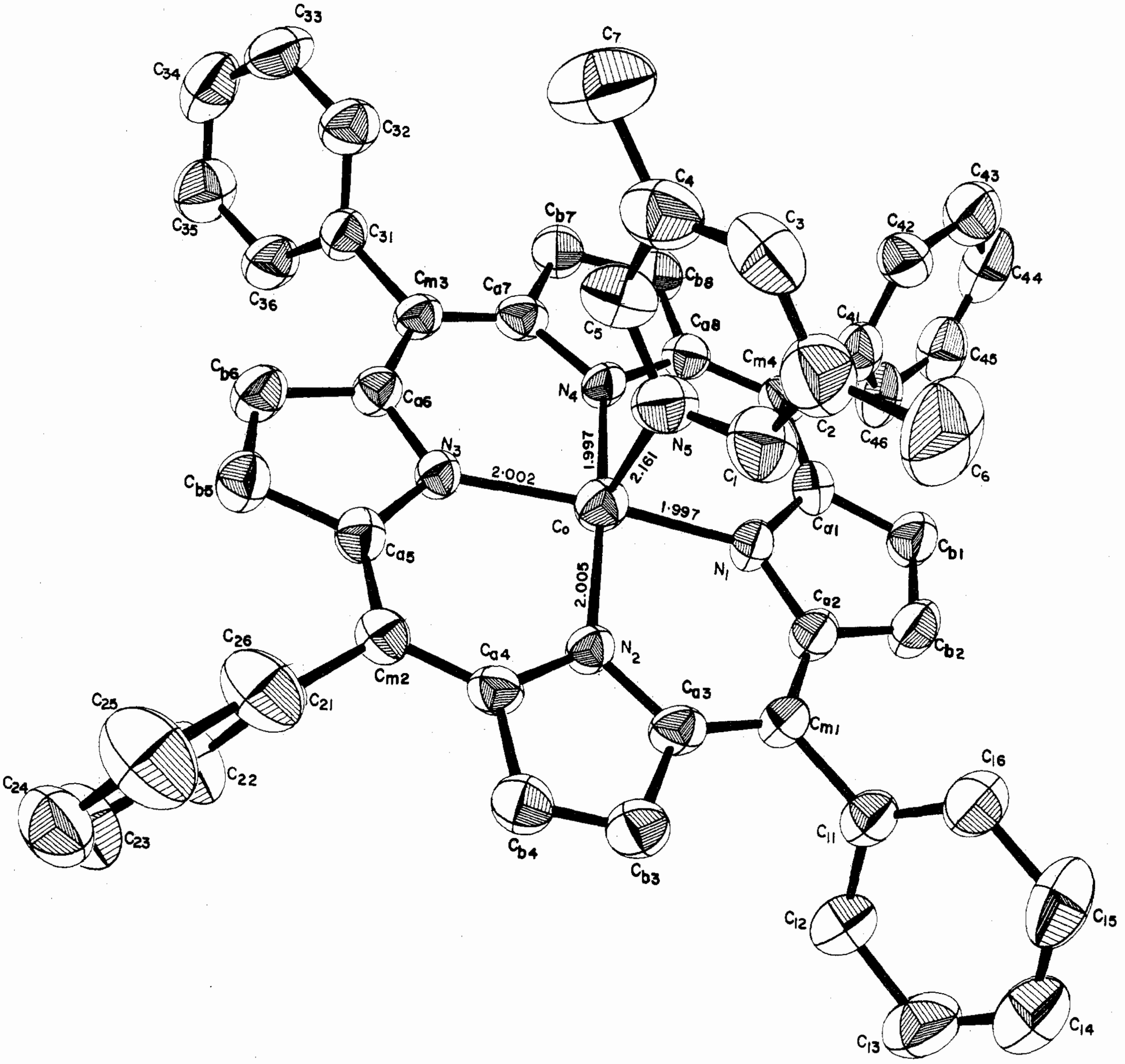

Figure 1. Computer-drawn model in perspective of the (3,5-lut)CoTPP molecule. Each atom is represented by an ellipsoid having the orientation and relative size required by the thermal parameters listed in Table II. Each atom is identified with the symbol used throughout the paper. Also displayed are the structurally independent bond distances of the coordination group.

Table III. Bond Lengths in the Coordination Group, Porphinato Skeleton, and Lutidine Ligand[a]

Bond	Value, Å	Bond	Value, Å	Bond	Value, Å
Co-N_1	1.997 (5)	C_{a2}-C_{m1}	1.365 (9)	C_{m2}-C_{21}	1.500 (8)
Co-N_2	2.005 (5)	C_{a2}-C_{b2}	1.435 (9)	C_{m3}-C_{31}	1.503 (8)
Co-N_3	2.002 (5)	C_{a3}-C_{m1}	1.386 (9)	C_{m4}-C_{41}	1.486 (9)
Co-N_4	1.997 (5)	C_{a3}-C_{b3}	1.452 (9)	C_{b1}-C_{b2}	1.352 (9)
Co-N_5	2.161 (5)	C_{a4}-C_{m2}	1.397 (9)	C_{b3}-C_{b4}	1.336 (10)
N_1-C_{a1}	1.376 (8)	C_{a4}-C_{b4}	1.421 (8)	C_{b5}-C_{b6}	1.331 (9)
N_1-C_{a2}	1.379 (8)	C_{a5}-C_{m2}	1.384 (9)	C_{b7}-C_{b8}	1.358 (10)
N_2-C_{a3}	1.386 (7)	C_{a5}-C_{b5}	1.469 (9)	N_5-C_1	1.362 (9)
N_2-C_{a4}	1.363 (8)	C_{a6}-C_{m3}	1.386 (8)	N_5-C_5	1.340 (9)
N_3-C_{a5}	1.375 (8)	C_{a6}-C_{b6}	1.437 (9)	C_1-C_2	1.39 (1)
N_3-C_{a6}	1.365 (7)	C_{a7}-C_{m3}	1.377 (9)	C_2-C_3	1.40 (1)
N_4-C_{a7}	1.391 (7)	C_{a7}-C_{b7}	1.457 (9)	C_3-C_4	1.40 (1)
N_4-C_{a8}	1.377 (8)	C_{a8}-C_{m4}	1.381 (9)	C_4-C_5	1.38 (1)
C_{a1}-C_{m4}	1.399 (9)	C_{a8}-C_{b8}	1.442 (9)	C_2-C_6	1.57 (1)
C_{a1}-C_{b1}	1.443 (9)	C_{m1}-C_{11}	1.497 (8)	C_4-C_7	1.49 (1)

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

CoTPP[3], 1.977 (5, 3) Å in (1-MeIm)CoTPP,[1] and 1.96 Å in (1-MeIm)CoOEP.[5,20] Despite the increased Co–N bond lengths in (3,5-lut)CoTPP, the displacement of the cobalt(II) atom out of plane is virtually the same in all four derivatives. The tetraphenylporphinato core in (3,5-lut)CoTPP accommodates the increased Co–N bond distances, relative to the other two tetraphenylporphinato derivatives, by increasing the C_aNC_a angle and decreasing the N–C_a bond length with C_aNC_a = 106.0 (2, 5), 104.7 (1, 2), 104.6 (1, 3)° and N–C_a = 1.376 (7, 8), 1.381 (3, 3) 1.387 (5, 5) Å for (3,5-lut)CoTPP, (1,2-DiMeIm)CoTPP, and (1-MeIm)CoTPP, respectively. Smaller adjustments in the values of the NC_aC_b and NC_aC_m angles also contribute with NC_aC_b = 109.8 (4, 5), 110.7 (1, 2), 110.7 (3, 5)° and NC_aC_m = 126.2 (3, 5), 125.9 (1, 2), 125.4 (2, 4)°, respectively, for the three derivatives.

The equatorial Co–N bonds are also longer than those observed in a number of six-coordinate cobalt(II) and -(III) porphyrins: 1.987 (0, 2) Å in $(pip)_2$CoTPP,[2,20] 1.978 (5, 3)

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

Angle	Value, deg	Angle	Value, deg	Angle	Value, deg
N_1CoN_2	89.6 (2)	$N_1C_{a1}C_{m4}$	126.2 (5)	$C_{a3}C_{b3}C_{b4}$	106.8 (6)
N_1CoN_3	171.9 (2)	$N_1C_{a1}C_{b1}$	109.8 (5)	$C_{a4}C_{b4}C_{b3}$	108.0 (6)
N_1CoN_4	90.2 (2)	$C_{m4}C_{a1}C_{b1}$	123.9 (6)	$C_{a5}C_{b5}C_{b6}$	106.3 (6)
N_1CoN_5	92.8 (2)	$N_1C_{a2}C_{m1}$	126.6 (6)	$C_{a6}C_{b6}C_{b5}$	107.8 (5)
N_2CoN_3	90.1 (2)	$N_1C_{a2}C_{b2}$	109.4 (5)	$C_{a7}C_{b7}C_{b8}$	106.4 (5)
N_2CoN_4	171.6 (2)	$C_{m1}C_{a2}C_{b2}$	124.0 (6)	$C_{a8}C_{b8}C_{b7}$	107.9 (6)
N_2CoN_5	92.8 (2)	$N_2C_{a3}C_{m1}$	125.9 (5)	$C_1N_5C_5$	118.4 (6)
N_3CoN_4	88.9 (2)	$N_2C_{a3}C_{b3}$	108.8 (5)	$N_5C_1C_2$	121.9 (7)
N_3CoN_5	95.3 (2)	$C_{m1}C_{a3}C_{b3}$	125.3 (5)	$C_1C_2C_3$	117.9 (7)
N_4CoN_5	95.5 (2)	$N_2C_{a4}C_{m2}$	125.9 (5)	$C_1C_2C_6$	120.0 (7)
$C_{a1}N_1C_{a2}$	106.3 (5)	$N_2C_{a4}C_{b4}$	110.3 (5)	$C_6C_2C_3$	122.1 (7)
$C_{a3}N_2C_{a4}$	106.1 (5)	$C_{m2}C_{a4}C_{b4}$	123.8 (6)	$C_2C_3C_4$	120.7 (7)
$C_{a5}N_3C_{a6}$	105.6 (5)	$N_3C_{a5}C_{m2}$	127.0 (5)	$C_3C_4C_5$	116.8 (7)
$C_{a7}N_4C_{a8}$	106.0 (5)	$N_3C_{a5}C_{b5}$	109.6 (5)	$C_3C_4C_7$	121.5 (7)
$C_{a2}C_{m1}C_{a3}$	123.9 (5)	$C_{m2}C_{a5}C_{b5}$	123.3 (6)	$C_7C_4C_5$	121.7 (8)
$C_{a4}C_{m2}C_{a5}$	123.3 (5)	$N_3C_{a6}C_{m3}$	125.7 (5)	$C_4C_5N_5$	124.3 (7)
$C_{a6}C_{m3}C_{a7}$	123.4 (5)	$N_3C_{a6}C_{b6}$	110.6 (5)	CoN_5C_1	119.4 (5)
$C_{a1}C_{m4}C_{a8}$	123.2 (5)	$C_{m3}C_{a6}C_{b6}$	123.6 (5)	CoN_5C_5	122.2 (4)
$C_{a2}C_{m1}C_{11}$	119.3 (5)	$N_4C_{a7}C_{m3}$	126.1 (5)	CoN_1C_{a1}	126.5 (4)
$C_{a3}C_{m1}C_{11}$	116.8 (5)	$N_4C_{a7}C_{b7}$	109.7 (5)	CoN_1C_{a2}	127.1 (4)
$C_{a4}C_{m2}C_{21}$	118.4 (5)	$C_{m3}C_{a7}C_{b7}$	124.1 (5)	CoN_2C_{a3}	126.7 (4)
$C_{a5}C_{m2}C_{21}$	118.3 (5)	$N_4C_{a8}C_{m4}$	126.5 (5)	CoN_2C_{a4}	127.0 (4)
$C_{a6}C_{m3}C_{31}$	118.3 (5)	$N_4C_{a8}C_{b8}$	110.0 (5)	CoN_3C_{a5}	126.0 (4)
$C_{a7}C_{m3}C_{31}$	118.3 (5)	$C_{m4}C_{a8}C_{b8}$	123.5 (6)	CoN_3C_{a6}	128.3 (4)
$C_{a1}C_{m4}C_{41}$	118.0 (5)	$C_{a1}C_{b1}C_{b2}$	106.6 (6)	CoN_4C_{a7}	127.2 (4)
$C_{a8}C_{m4}C_{41}$	118.8 (5)	$C_{a2}C_{b2}C_{b1}$	107.8 (6)	CoN_4C_{a8}	126.7 (4)

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

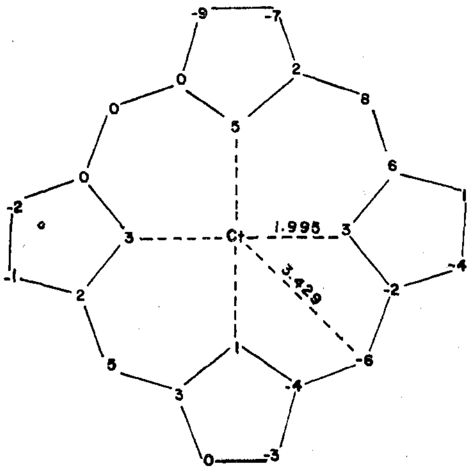

Figure 2. Formal diagram of the porphinato core with the same relative orientation as Figure 1. Each atom symbol has been replaced by its perpendicular displacement, in units of 0.01 Å, from the mean plane of the porphinato core. Ct represents the center of central hole of the macrocycle and the values of two important structural radii are displayed.

Å in (pip)$_2$CoTPP$^+$,[21] 1.954 (4, 2) Å in (3,5-lut)(NO$_2$)-CoTPP,[22] 1.992 (1, 1) Å in (3-pic)$_2$CoOEP,[4] 1.982 Å in Im$_2$CoTPP$^+$,[23] and 1.949 (3) Å in four-coordinate CoTPP.[24]

The plane of the lutidine ring makes an angle of 89.5° with the mean plane of the core; the Co–N$_5$ vector is tipped ~2.5° from the normal to the mean skeletal plane. The plane of the lutidine ring is rotated 41.1° from the N$_1$CoN$_5$ coordinate plane; a rotation of 45° corresponds to the most favorable orientation of the ligand plane. With the favorable orientation of the lutidine ligand, the nonbonded contacts between the hydrogen atoms bonded to C$_1$ and C$_5$ (Figure 1) and the porphinato core atoms are all greater than 2.7 Å. The orientation of the imidazole planes in the three imidazole-cobalt(II) porphyrins are 0° in (1-MeIm)CoTPP,[1] 10° in (1-MeIm)CoOEP,[5,25] and 20° in (1,2-DiMeIm)CoTPP.[3]

The axial Co–N$_5$ bond length is 2.161 (5) Å, insignificantly different from the 2.157 (3) Å observed in (1-MeIm)CoTPP[1] and the 2.15 (1) Å observed in (1-MeIm)CoOEP.[5] The axial bond is, however, shorter than the 2.216-Å value observed for (1,2-DiMeIm)CoTPP[3] wherein the axial bond is stretched by reason of steric interactions between the ligand atoms and the core. The displacement of the cobalt(II) atom out of plane is also quite comparable for all four five-coordinate cobalt(II) porphyrins. Thus the only real structural difference between (3,5-lut)CoTPP and the imidazolecobalt(II) porphyrins is the increase in the equatorial Co–N bond lengths in the pyridine derivative. It appears, consquently, that, in the absence of significant steric constraints, pyridine and imidazole display nearly identical behavior as complexing agents in forming five-coordinate cobalt(II) porphyrin derivatives.

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Registry No. (3,5-Lut)CoTPP, 56335-60-5.

Supplementary Material Available. A listing of structure factor amplitudes (×10) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order of $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC50422B-11-75.

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

(20) Abbreviations: 1-MeIm, 1-methylimidazole; 1,2-DiMeIm, 1,2-dimethylimidazole; OEP, octaethylporphyrin dianion; pip, piperidine, 3-pic, 3-methylpyridine.

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Reactions of Acetylenes Held Proximate to a Metal. Addition of Hydrogen Chloride to *cis*-Dichlorobis(3,3,3-trifluoropropynyldiphenylphosphine)palladium(II) and -platinum(II). X-Ray Structure of *trans*-$PdCl_2[Ph_2PCH{=}C(Cl)CF_3]_2$

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The reaction of *cis*-$MCl_2(Ph_2PC{\equiv}CCF_3)_2$ (M = Pd, Pt) with HCl in nonaqueous solutions yields predominantly the complexes *trans*-$PdCl_2(Ph_2PCH{=}C(Cl)CF_3)_2$ and *cis*-$PtCl_2(Ph_2PCH{=}C(Cl)CF_3)_2$ via trans addition to the triple bonds. The compounds have been characterized by microanalysis, ir, ^1H, ^{19}F, and ^{31}P NMR spectroscopy. The palladium complex crystallizes in the monoclinic space group $P2_1/n$ with $a = 10.202$ (3) Å, $b = 10.964$ (4) Å, $c = 14.943$ (5) Å, $\beta = 90.16$ (6)°, $Z = 2$, $d_{measd} = 1.61$ g cm^{-3}, and $d_{calcd} = 1.602$ g cm^{-3}. The structure has been solved by heavy-atom methods and refined by full-matrix least-squares techniques to a final R value of 0.040. All hydrogen atoms were located and refined. The principal structural features are the trans square-planar stereochemistry at palladium (Pd–P = 2.322 (1) Å; Pd–Cl(1) = 2.291 (1) Å) and the olefinic phosphine with H and Cl mutually trans across the double bond. A possible mechanism for the reactions is suggested.

Introduction

In the square-planar complex *cis*-$PdCl_2[Ph_2PC{\equiv}CCF_3]_2$ (I) and the platinum analog (II) (vide infra) the alkyne triple bonds are uncoordinated yet are held proximate to the coordination sphere of the metal and to one another.[1–5] The phosphorus-coordinated phosphinoacetylenes in these derivatives are activated and highly susceptible to nucleophilic attack at phosphorus or an alkyne carbon atom. These reactions have provided synthetic routes to the stabilized coordinated ligands $[R_2PO\cdots H\cdots OPR_2]^-$ and R_2POH via nucleophilic displacement at phosphorus,[6,7] to $R_2PCH{=}C(CF_3)O$ chelates and β-keto phosphines via acetylene hydration,[7] and to unsymmetrical diphosphines via base-promoted acetylene coupling[8] or R_2PH addition.[9] The apparent analogy of acetylene coupling in the formation of *cis*-$MCl_2(Ph_2PCH_2C(CF_3)CHPPh_2)$ (M = Pd, Pt) from I and II to the dimerization of adjacent alkyne groups in *o*-bis(phenylethynyl)benzene promoted by both electrophilic and nucleophilic reagents[10] together with the known[11,12] susceptibility of alkynes to electrophilic attack prompted us to investigate the addition of hydrogen chloride to I and II. Ionic additions of HCl and HBr to acetylenes appear to be strictly electrophilic reactions in which the intermediacy of vinyl carbonium ions has been adequately demonstrated.[13,14] In some cases proton-initiated alkyne dimerizations to cyclobutanes accompany simple addition to the triple bond.[13] The steric course of these reactions is very dependent on experimental conditions.[14] However, for tolan and propyne, addition is stereospecific, leading to the trans olefin.[15]

In this paper we describe the synthesis and characterization of *trans*-$PdCl_2[Ph_2PCH{=}C(Cl)CF_3]_2$ and *cis*-$PtCl_2[Ph_2PCH{=}C(Cl)CF_3]_2$ from the reactions of I and II with HCl. A single-crystal X-ray structure determination of the palladium derivative has revealed a trans addition of HCl to the phosphinoacetylene. The likely course of these reactions is discussed.

Experimental Section

Physical Measurements. Infrared spectra were measured as Nujol mulls on cesium iodide plates using a PE 180 spectrophotometer. ^1H NMR spectra in CD_2Cl_2 were obtained from a Varian HA100 spectrometer. Shifts (δ) are downfield of TMS as an internal standard. A Varian HA-60 operating at 58.3 MHz was utilized for ^{19}F measurements. Shifts are upfield of $CFCl_3$ as an internal standard. ^{31}P spectra were measured in the FT mode at 40.49 MHz on a JEOL-100 FTL instrument. Chemical shifts are upfield of external trimethyl phosphite in deuteriobenzene using dichloromethane as a solvent. Microanalyses and molecular weight measurements were carried out by Galbraith Laboratories, Knoxville, Tenn.

Synthesis of Compounds. *cis*-$PdCl_2(Ph_2PC{\equiv}CCF_3)_2$ **(I)** was prepared from *trans*-$PdCl_2(PhCN)_2$ and $Ph_2PC{\equiv}CCF_3$ as previously described.[2]