

of the endocyclic valency angles follow the same trend as those in (+)-8-bromocamphor (Bear & Trotter, 1975*a*) rather than, for example, those in (-)-3,3,4-trimethyl-1,7-dibromonorbornan-2-one, a structure with a slightly twisted norbornane skeleton (Bear & Trotter, 1975*b*). The accuracy with which the positions of the carbon atoms are known is low and hence subtle differences in C-C bond lengths may be hidden. The C(sp<sup>3</sup>)-C(sp<sup>2</sup>) distances C(1)-C(2) and C(2)-C(3) are 1.52 (4) and 1.49 (4) Å. The angles between the C(1), C(4), C(7) plane and the four-atom planes of the six-membered boat [C(1), C(2), C(3), C(4), and C(1), C(4), C(5), C(6)] are 127.6 and 124.0°, comparing reasonably well with the corresponding dihedral angles of 124.5 and 124.2° in (+)-8-bromocamphor. The C-Br distances average 1.95 (1) Å.

Fig. 2 is a stereo diagram of the contents of the unit cell. The molecules are linked into infinite chains about the twofold screw axes by C(3)-H...O interactions (broken line in Fig. 2), which may represent hydrogen bonds. Br(3), by way of the inductive effect, presumably causes H(3) to be quite acidic. The C(3)...O distance is 3.29 Å; with H(3) in its calculated position,

the H...O distance is about 2.3 Å, and the C-H...O angle is about 160°. These parameters are in agreement with those in other documented C-H...O hydrogen bonds *e.g.* O...H 2.27 Å and C-H...O 164° in 1-(4-chlorobenzyl)-1-nitroso-2-(4,5-dihydro-2-imidazolyl)-hydrazine monohydrate (Palenik, 1965). The intramolecular nonbonded Br(1)...Br(2) distance is 3.156 (7) Å, and the only other intermolecular contacts of < 3.5 Å are O...Br(2) [1 + x, y, z] 3.33 (2) Å and O...C (8) [1 - x, y - ½, -z] 3.48 (4) Å.

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## Chloro- $\alpha, \beta, \gamma, \delta$ -tetraphenylporphinatopyridinecobalt(III)

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**Abstract.** C<sub>49</sub>H<sub>33</sub>N<sub>5</sub>CoCl.½(C<sub>6</sub>H<sub>6</sub>), monoclinic, *P*2<sub>1</sub>/*n*, *a* = 14.50 (4), *b* = 23.42 (6), *c* = 13.12 (3) Å,  $\beta$  = 102.1 (3)°, *V* = 4357 (19) Å<sup>3</sup>; *D<sub>x</sub>* = 1.258 g cm<sup>-3</sup>. *R* = 7.3%, 3997 observed reflexions. The cobalt atom is in the plane of the four pyrrole nitrogen atoms and has nearly exact octahedral coordination. The porphinato core is considerably ruffled. The overall symmetry of the tetraphenyl porphinato group is  $\bar{4}$ .

**Introduction.** Several six-coordinate cobalt(III) complexes of  $\alpha, \beta, \gamma, \delta$ -tetraphenylporphyrin (TPP) have been prepared in our Institute (Yamamoto & Tonomura, 1964). The effects of axial ligands on the complexes were studied by electronic absorption and nuclear magnetic resonance spectra. The title compound [ClTPP.PyCo<sup>III</sup>] was chosen to determine the three-dimensional structure. The complex was obtained by heating Co<sup>II</sup>TPP with pyridine in a hydrochloric acidic benzene-methanol mixture. The violet metallic-lustrous prismatic crystals were identified by elemental analysis. Found: C 75.80, H 4.28, N 8.56, Co 7.18, Cl 4.25%. Calculated: C 75.71, H 4.36, N 8.49, Co 7.14, Cl 4.30%, for C<sub>52</sub>H<sub>36</sub>N<sub>5</sub>CoCl [ClTPP.PyCo.½(C<sub>6</sub>H<sub>6</sub>)].

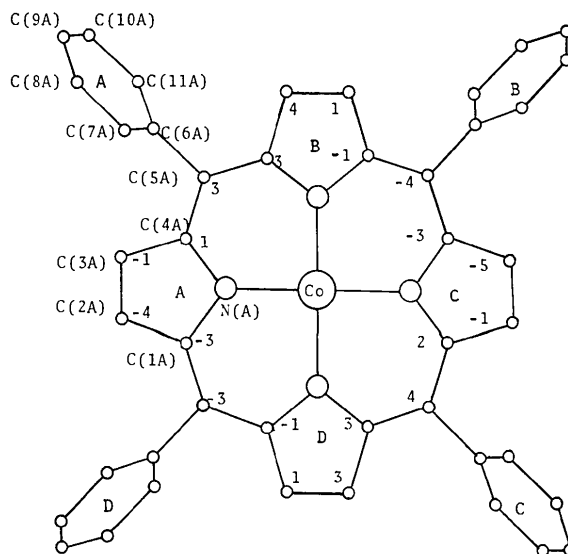


Fig. 1. The numbering scheme for the atoms used in this paper. The numerals attached to the atoms in the porphinato core represent perpendicular displacements from the mean plane in units of 0.1 Å.

X-ray diffraction intensities were measured on a Rigaku automatic four-circle diffractometer with graphite-monochromatized Mo  $K\alpha$  radiation. A crystal

of dimensions  $0.2 \times 0.2 \times 0.4$  mm was used for data collection. The crystal had a fairly large temperature factor and reflexion intensities above  $2\theta = 50^\circ$  were

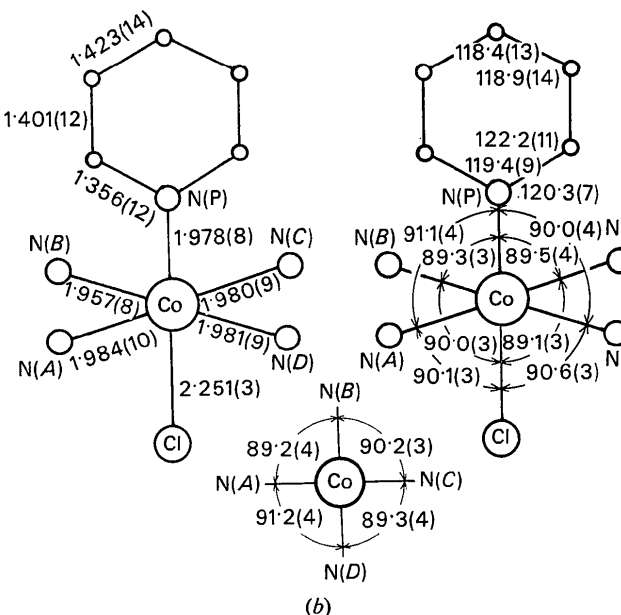
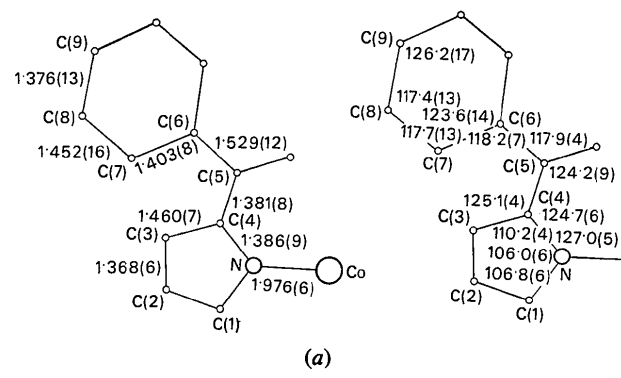


Fig. 2. Bond distances (Å) and angles ( $^\circ$ ). (a) TPP group, averaged over the chemically equivalent bonds. (b)  $Co^{III}$  coordination.

Table 1. Atomic parameters

Positional parameters are  $\times 10^4$ , thermal parameters are given by the equivalent temperature factors ( $\text{Å}^2$ ). The numbering scheme for the atoms in TPP is shown in Fig. 1. P and X represent atoms belonging to the pyridine and benzene molecules respectively. For the benzene molecule, positional parameters are  $\times 10^3$ .

	x	y	z	$B_{eq}$
Co	3964 (1)	2968 (1)	1611 (1)	2.5
Cl	2731 (2)	3521 (1)	889 (2)	4.8
N(A)	4651 (6)	3218 (4)	530 (7)	4.1
N(B)	4519 (6)	3608 (3)	2486 (6)	3.4
N(C)	3271 (6)	2730 (4)	2691 (6)	3.7
N(D)	3408 (6)	2312 (4)	741 (6)	4.2
N(P)	5039 (6)	2485 (4)	2282 (7)	4.0
C(1A)	4491 (8)	2996 (5)	-501 (8)	4.3
C(2A)	5051 (9)	3344 (5)	-1097 (9)	4.8
C(3A)	5542 (9)	3727 (5)	-428 (8)	4.5
C(4A)	5296 (8)	3644 (4)	588 (8)	3.8
C(5A)	5639 (8)	3973 (5)	1450 (8)	3.9
C(6A)	6374 (8)	4411 (4)	1358 (8)	3.8
C(7A)	7310 (9)	4268 (6)	1540 (10)	5.5
C(8A)	7964 (10)	4682 (7)	1329 (11)	6.7
C(9A)	7657 (10)	5220 (6)	979 (10)	6.2
C(10A)	6728 (10)	5372 (5)	832 (9)	5.6
C(11A)	6061 (9)	4967 (5)	1037 (9)	5.0
C(1B)	5261 (7)	3947 (4)	2348 (8)	3.7
C(2B)	5553 (9)	4342 (5)	3240 (9)	4.7
C(3B)	4917 (8)	4252 (5)	3856 (9)	4.6
C(4B)	4280 (8)	3804 (4)	3401 (8)	3.8
C(5B)	3566 (8)	3577 (5)	3824 (8)	4.1
C(6B)	3278 (8)	3900 (5)	4713 (9)	4.6
C(7B)	3567 (10)	3684 (6)	5749 (9)	5.7
C(8B)	3268 (10)	4008 (7)	6561 (10)	6.6
C(9B)	2737 (10)	4465 (6)	6354 (11)	6.4
C(10B)	2455 (12)	4697 (7)	5334 (13)	8.3
C(11B)	2742 (11)	4388 (6)	4498 (11)	6.8
C(1C)	3100 (8)	3083 (4)	3510 (8)	3.9
C(2C)	2418 (10)	2797 (6)	4000 (10)	5.8
C(3C)	2263 (10)	2257 (6)	3575 (10)	5.9
C(4C)	2790 (9)	2241 (5)	2735 (8)	4.7
C(5C)	2702 (9)	1804 (5)	2020 (9)	4.8
C(6C)	2240 (9)	1245 (5)	2285 (9)	5.1
C(7C)	2796 (11)	894 (7)	3014 (11)	7.4
C(8C)	2382 (12)	362 (7)	3283 (11)	7.7
C(9C)	1447 (11)	250 (6)	2799 (10)	6.6
C(10C)	910 (11)	592 (6)	2091 (11)	6.6
C(11C)	1300 (9)	1118 (6)	1809 (10)	5.9
C(1D)	2967 (9)	1850 (5)	1062 (9)	4.8
C(2D)	2756 (10)	1414 (6)	245 (10)	6.1
C(3D)	3083 (11)	1636 (6)	-586 (10)	6.5
C(4D)	3477 (9)	2182 (5)	-281 (8)	4.8
C(5D)	3993 (9)	2524 (5)	-855 (8)	4.5
C(6D)	4040 (11)	2309 (6)	-1965 (11)	7.1
C(7D)	4938 (13)	2128 (8)	-2094 (14)	10.1
C(8D)	4978 (15)	1909 (10)	-3189 (16)	12.2
C(9D)	4127 (14)	1946 (8)	-3850 (13)	10.0
C(10D)	3199 (14)	2098 (7)	-3754 (12)	9.9
C(11D)	3170 (13)	2290 (7)	-2714 (11)	8.1
C(2P)	5433 (9)	2115 (5)	1715 (10)	5.5
C(3P)	6179 (11)	1761 (7)	2157 (12)	7.5
C(4P)	6539 (11)	1785 (7)	3263 (13)	7.7
C(5P)	6135 (9)	2176 (6)	3849 (10)	6.0
C(6P)	5361 (8)	2506 (5)	3339 (9)	4.7
C(1X)	491 (4)	48 (3)	25 (4)	6.3
C(2X)	500 (4)	11 (3)	95 (5)	7.6
C(3X)	513 (5)	-43 (3)	74 (5)	8.2

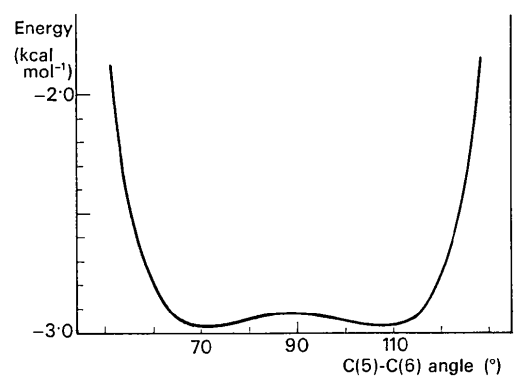


Fig. 3. Van der Waals energy between the phenyl group and the neighbouring two pyrrole groups.

very weak. 3997 significant reflexions, about 55% of the theoretically accessible data in the  $2\theta$  range  $0-50^\circ$ , were used for the structure determination. The positions of Co and Cl were obtained by the direct phasing method, and the rest of the structure was determined by successive Fourier and least-squares calculations. A difference-Fourier synthesis at an  $R$  value of 12% revealed some residual peaks near  $\frac{1}{2}, 0, 0$ , which were assigned to a half benzene molecule, although the individual peaks were not well resolved. The final  $R$  value using the block-diagonal least-squares method with anisotropic temperature factors is 7.3%.\* Final atomic parameters are shown in Table 1.

**Discussion.** Because of the chemico-physical and biological importance of the molecule, a lot of structural work has been done on porphyrins and metalloporphyrins. These were reviewed by Fleischer (1970) and Hoard (1971). The Co complexes were not studied until the recent work of Sheidt and coworkers (Sheidt & Hoard, 1973; Sheidt, Cunningham & Hoard, 1973; Sheidt, 1974), and Ibers and coworkers (Ibers, Lauher & Little, 1974; Little & Ibers, 1974; Lauher & Ibers, 1974).

The bond distances and angles in the porphinato core (Fig. 2) are not significantly different from previously reported values. The cobalt atom is in the mean plane of the pyrrole nitrogen atoms, and has nearly exact octahedral coordination. The Co-N(axial) distance of 1.978 Å is slightly longer than the minimal approach distance, 1.93 Å, of the imidazole ring to the porphyrin plane (Ibers, Lauher & Little, 1974).

Table 2. Dihedral angles ( $^\circ$ ) between pyrrole planes

	B	C	D
A	18.2	27.5	15.6
B		20.3	25.2
C			20.5

\* For the structure-factor calculation hydrogen atoms were not included and the isotropic temperature factors were used for the residual benzene. The structure factor tables and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31177 (42 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

In contrast to other Co complexes, the porphinato core is considerably ruffled. The methine carbons C(5A) and C(5C) are up, and C(5B) and C(5D) are down, as shown in Fig. 1. The local planarity is preserved in the pyrrole ring. The dihedral angles between four pyrrole rings are shown in Table 2. In many reported TPP structures, the dihedral angle between the phenyl group and the mean porphinato plane varies between  $60$  and  $90^\circ$ . The van der Waals interaction energy between the phenyl group and the porphinato group was calculated as a function of the rotation angle about C(5)-C(6). The energy curve showed two shallow minima at  $72$  and  $108^\circ$  (Fig. 3). The corresponding torsion angles in the present case are shown in Table 3. The overall symmetry of the TPP is approximately  $\bar{4}$ , as shown in the stereo drawing in Fig. 4. This  $\bar{4}$  symmetry does not always appear in the TPP group. Since the energy barrier between these two minima is very low, the angular position may easily be changed in order to satisfy the molecular packing in the crystal. The pyridine plane is almost within a vertical plane that bisects the N(A)-Co-N(D) angle. The dihedral angle between the pyridine plane and the mean porphinato plane is  $88.6^\circ$ .

Table 3. Torsion angles ( $^\circ$ ) about C(5)-C(6)

Phenyl	4-5-6-11	4-5-6-7	1-5-6-11	1-5-6-7
A	91.5 (13)	-86.0 (14)	-82.4 (14)	100.1 (13)
B	75.6 (15)	-104.9 (13)	-104.7 (14)	74.8 (14)
C	103.0 (14)	-76.2 (15)	-74.1 (16)	106.6 (14)
D	64.7 (16)	-112.1 (15)	-119.3 (14)	63.9 (17)

Calculations were carried out on the FACOM 230-75 computer of this Institute using the programs UNICS II (Sakurai *et al.*, 1974), ORTEP (Johnson, 1965), and LSAM (Main, Woolfson & Germain, 1972). The authors are grateful to Dr H. Midorikawa of this Institute for his encouragement. The research is supported, in part, by a Scientific Grant 934034 from the Ministry of Education.

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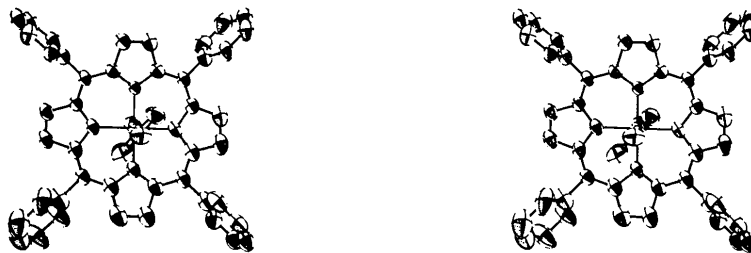


Fig. 4. Stereographic drawing of the molecule viewed along the principal axis of the largest moment of inertia. The porphinato group has approximate  $\bar{4}$  symmetry.

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## 20-Methylcholanthrene (a New Refinement)

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**Abstract.** 20-Methylcholanthrene,  $C_{21}H_{16}$ , M. W. 268.36, monoclinic  $P2_1/c$ ,  $a = 4.898$  (3),  $b = 11.36$  (1),  $c = 25.16$  (2) Å,  $\beta = 95.3$  (1)°,  $U = 1393.94$  Å<sup>3</sup>,  $D_m = 1.277$  g cm<sup>-3</sup>,  $Z = 4$ ,  $D_x = 1.294$ ,  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å. The structure was reported previously [Iball & MacDonald, *Z. Kristallogr.* (1960). **114**, 439–446]. New intensities (1974 reflexions) have been refined by least-squares calculations to a final  $R$  of 0.060. (A new  $c$  and  $\beta$  were chosen to make the cell more nearly rectangular.)

**Introduction.** The earlier determination and refinement of the structure of this carcinogenic hydrocarbon was carried out by differential Fourier syntheses (Iball & MacDonald, 1960). In the present work new and more extensive reflexion data were collected from equi-inclination Weissenberg photographs. The camera was fitted with one-dimensional integration and the spots were measured by densitometer. There were 1974 reflexions with non-zero intensities and the new value of  $R$  (=0.060) compares with 0.15 for the earlier re-

finement. The accuracy of the bond lengths and angles is correspondingly increased.

**Refinement.** The atomic parameters were refined by block-diagonal least-squares calculations and the weighting scheme was  $1/w = 1/\{1 + [(|F_o| - F^*)/G^*]^2\}^{1/2}$ ;  $F^*$  and  $G^*$  were 15 and 35 respectively. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). C atoms were refined anisotropically. The H atoms were included in the structure factor calculation but not refined until near the end when the C atoms were fixed and the H atoms (positions only, not temperature parameters) allowed to refine. In the final three cycles the H atoms were again fixed and only the C atoms allowed to refine. The final value of  $R$  was 0.060.†

Final parameters with their standard deviations are listed in Tables 1, 2, 3 and bond lengths and angles in Table 4. Fig. 1 shows the molecule with deviations from the mean plane in parentheses. The mean plane of the C atoms is given by  $-0.71275X + 0.57671Y - 0.39924Z = 1.4845$  ( $X$  is parallel to  $\mathbf{a}$ ,  $Y$  to  $\mathbf{b}$ , and  $Z$  is perpendicular to  $\mathbf{a}$  and  $\mathbf{b}$ ). The shortest intermolecular distance, 3.308 (12) Å, is between C(20) at  $(x, y, z)$  and C(20) of the molecule at  $(1-x, 1-y, -z)$ .

**Discussion.** Methylcholanthrene (Iball, 1936) is a transformation product of deoxycholic acid (Cook & Haslewood, 1934) and of cholic acid (Fieser & Newman, 1935) both of which are present in bile; it is a very potent carcinogen. The refinement confirms the essential planarity of the molecule and the short bonds

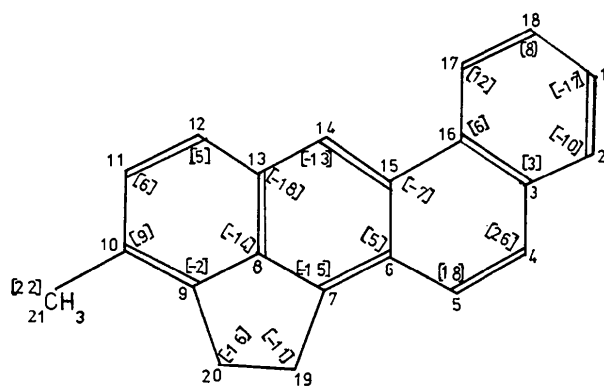


Fig. 1. 20-Methylcholanthrene: the numbering system and deviations (Å × 10<sup>3</sup>) of C atoms from the mean plane.

† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31197 (14 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.