$(CuBr.2MAN)_2$, ensemble répété en chaîne infinie par la translation **c**.

A ces caractéristiques originales s'ajoutent cependant des aspects classiques: coordinence quatre pour les atomes de cuivre, trois pour les atomes de brome, et la molécule de méthylacrylonitrile présente peu de déformation.

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Structural Studies of Metalloporphyrins. V.* Characterization and Structure of Methoxy-α,β,γ,δ-tetraphenylporphinato(pyridine)cobalt(III) Methanol Solvate

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The title compound, $C_{50}H_{36}N_5OCo.3CH_3OH$, was prepared accidentally and has been characterized by a three-dimensional X-ray structure determination. The complex crystallizes in the monoclinic space group $P2_1/n$, with $a = 18{\cdot}593$ (17), $b = 16{\cdot}537$ (33), $c = 14{\cdot}748$ (11) Å, $\beta = 94{\cdot}25$ (5)° and $Z = 4$. The structure has been refined by least-squares methods using rigid groups for the four phenyl units. The final R value was 0·092 with 1448 observed intensities. The Co–N(pyridine) and Co–O bond lengths are 1·99 and 1·92 Å. The Co–O–CH_3 bond angle is 121°. The porphyrin plane is significantly ruffled and has $\bar{4}$ overall symmetry. The Co atom is in the mean plane of the porphyrin.

Introduction

Oxygen insertion in the Co–C bond of alkyl cobalt complexes has been achieved with alkyl cobaloximes (Fontaine, Duong, Merienne, Gaudemer & Giannotti, 1972) and more recently with the alkyl cobalt porphyrins R-CoTPP, where TPP = α,β,γ,δ-tetraphenylporphinato (Perrée-Fauvet, Gaudemer, Boucly & Devynck, 1976). In the former case, the structure of the insertion product was unambiguously proven by an X-ray diffraction study (Chiaroni & Pascard, 1973). In order to establish the structure of the alkyl peroxo complexes in the porphyrin series, photochemical O insertion was carried out on CH_3–CH_2–CoTPP; the

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* Part IV: Gouédard, Riche & Gaudemer (1977).

corresponding alkyl peroxo cobalt porphyrin, CH_3—CH_2—O—O—CoTPP, was recrystallized from methanol. NMR spectroscopy of the crystals revealed that during recrystallization the expected peroxo complex had decomposed into a new complex having a methoxy group and a pyridine molecule as axial ligands. We now report the X-ray structure of this complex.

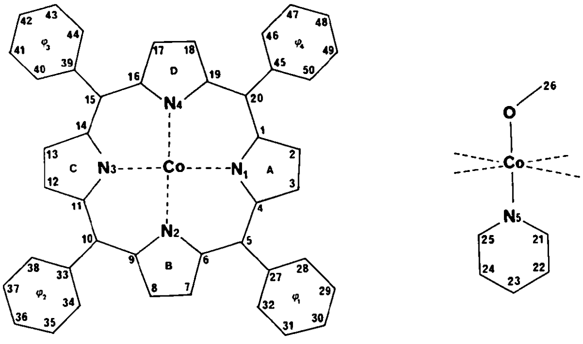
Experimental

Preparation

Ethyl(tetraphenylporphinato)cobalt(III) has been prepared by the alkylation of tetraphenylporphinatocobalt(I). Photolysis of a chloroform–pyridine solution of this compound, in the presence of molecular oxygen, yields a new complex for which the structure C_2H_5O—OCo^{III}TPP has been assumed (Perrée-Fauvet *et al.*, 1976).

$$C_2H_5CoTPP \xrightarrow[\text{visible}]{h\nu} C_2H_5O\text{—}OCoTPP$$

Recrystallization of C_2H_5O—OTPP from methanol causes decomposition to give (I), methoxytetraphenylporphinato(pyridine)cobalt(III).



(I)

Crystal data

Methoxy-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinato(pyridine)-cobalt(III) methanol solvate, $C_{50}H_{36}N_5OCo.3CH_3OH$, M_r = 786, monoclinic, $P2_1/n$, a = 18·593 (17), b = 16·537 (33), c = 14·748 (11) Å, β = 94·25 (5)°, Z = 4. Unit-cell parameters and their estimated standard deviations were determined by least-squares calculations minimizing the differences between observed and calculated θ values for 52 reflections (λ = 0·7107 Å).

Intensity data

Violet prismatic crystals, grown from methanol, decayed in air to a powder within a few minutes, probably owing to a loss of solvent of crystallization. Crystals sealed in a thin-walled capillary with a drop of mother liquor stayed in good condition during the data collection. Data were collected with a crystal of approximate dimensions 0·4 × 0·2 × 0·6 mm on a Philips PW 1100 diffractometer, using Mo $K\alpha$ graphite-monochromated radiation, a scanning speed of 0·05° s^{-1} and a scanning range of 3°. The background was counted for a time which allowed optimization of counting statistics.

The intensities of the three standard reflections displayed no observable trend; random variations were in the range ±3%. Of the 6440 reflections scanned only those 1448 unique reflections with $I > 2 \cdot 5\sigma(I)$ were used in the subsequent structure determination and refinement.

Since the data set was of poor quality additional crystals were selected but were obviously of lower quality because of excessive crystal decomposition.

Structure determination and refinement

The Co atom was located from a three-dimensional Patterson map. A series of Fourier and difference-Fourier maps revealed the positions of all non-hydrogen atoms in the porphyrin as well as those of the pyridine and methoxy groups linked to the Co atom. In addition, two molecules of methanol were found in the asymmetric unit. One of the four phenyl groups (φ_4) appeared to have high thermal motion or to be slightly disordered. The structure was refined by the least-squares method using the computer program *ORION* (André, Fourme & Renaud, 1971). The four phenyl rings were treated as rigid groups in which the methine C of the porphyrin was included (C—C = 1·40 Å and C_m—C = 1·51 Å). Thermal parameters were anisotropic for the Co atom and isotropic for the light atoms. Three cycles of refinement of all group and non-group atoms led to a value of the conventional residual R of 0·12. A difference map calculated at this stage revealed the presence of a third methanol solvent molecule, hydrogen bonded to the second. The two atoms of this molecule were introduced in the refinement with fixed B values. In addition, the B values for the atoms belonging to a rigid group were fixed at their approximate mean values. The final R factors were R = 0·10 and R_w = 0·092. The scattering factors were those of Doyle & Turner (1968).

Fractional coordinates and thermal parameters are listed in Table 1. Bond lengths and bond angles are given in Tables 2 and 3.*

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* A list of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33381 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Fractional coordinates* ($\times 10^4$) *and thermal parameters*

	x	*y*	*z*	*B* (Å^2)
Co	4007	8399	1950	*
N(1)	3097	7960	1374	2·5
N(2)	4511	7466	1495	3·1
N(3)	4924	8814	2502	2·9
N(4)	3516	9349	2403	2·9
N(5)	4164	8988	804	3·7
C(1)	2412	8236	1458	3·4
C(2)	1824	7747	1015	3·2
C(3)	2221	7208	504	3·1
C(4)	3003	7293	743	1·9
C(5)	3572	6835	502	2·6
C(6)	4280	6891	858	2·6
C(7)	4809	6331	654	5·0
C(8)	5448	6489	1268	4·6
C(9)	5211	7217	1750	2·8
C(10)	5715	7659	2283	2·0
C(11)	5572	8400	2660	3·2
C(12)	6098	8925	3166	3·0
C(13)	5813	9655	3283	2·7
C(14)	5062	9565	2943	3·0
C(15)	4530	10198	2996	2·7
C(16)	3813	10076	2756	3·0
C(17)	3253	10632	2931	4·0
C(18)	2589	10290	2738	4·3
C(19)	2744	9469	2355	4·5
C(20)	2241	8893	2009	4·7
C(21)	4702	8800	360	5·1
C(22)	4784	9101	−529	10·2
C(23)	4229	9729	−882	8·5
C(24)	3519	9921	−437	8·7
C(25)	3643	9479	411	6·1
O	3857	7851	3066	3·7
C(26)	3884	6998	3116	4·7
C(27)	3387	6239	−256	5·0
C(28)	3353	6496	−1161	5·0
C(29)	3181	5944	−1864	5·0
C(30)	3045	5135	−1661	5·0
C(31)	3080	4878	−756	5·0
C(32)	3251	5431	−53	5·0
C(33)	6455	7300	2492	5·0
C(34)	6982	7383	1870	5·0
C(35)	7669	7050	2063	5·0
C(36)	7828	6634	2878	5·0
C(37)	7301	6552	3501	5·0
C(38)	6615	6885	3307	5·0
C(39)	4748	10977	3473	5·0
C(40)	5036	11611	2987	5·0
C(41)	5238	12334	3430	5·0
C(42)	5151	12424	4358	5·0
C(43)	4863	11790	4844	5·0
C(44)	4661	11067	4401	5·0
C(45)	1472	9147	2118	7·0
C(46)	1065	9508	1392	7·0
C(47)	352	9744	1493	7·0
C(48)	46	9619	2320	7·0
C(49)	454	9258	3045	7·0
C(50)	1166	9022	2944	7·0
O(1)	3000	8345	4223	9·1
Me(1)	3324	8962	4751	8·9
O(2)	2244	7093	4672	14·3
Me(2)	1584	7038	4044	16·1
O(3)	2921	5778	5177	18·0
Me(3)	3669	5603	5376	18·0

Mean e.s.d.'s

	x	*y*	*z*
Co	0·0005	0·0005	0·0005
N, O	0·0020	0·0025	0·0030
C	0·0030	0·0035	0·0040

* $T = \exp(-0{\cdot}0020h^2 - 0{\cdot}0022k^2 - 0{\cdot}0037l^2 + 0{\cdot}0006hk - 0{\cdot}0004hl + 0{\cdot}0003kl)$.

Results and discussion

Fig. 1 is a perspective view of the molecule with phenyl groups omitted for clarity and shows the hydrogen-bonding scheme of the three methanol molecules.

In contrast to the Co^{III} porphyrin complexes with two identical axial ligands, [bis(piperidine)tetraphenylporphinatocobalt(III)]$^+$ {$[(pip)_2CoTPP]^+$, Scheidt, Cunningham & Hoard, 1973}, [bis(imidazole)tetraphenylporphinatocobalt(III)]$^+$ {$[(imid)_2CoTPP]^+$, Lauher & Ibers, 1974}, and [bis(1-phenylethylamine)-tetraphenylporphinatocobalt(III)]$^+$ {$[(PEA)_2CoTPP]^+$, Riche, Chiaroni, Gouédard & Gaudemer, 1977}, the porphinato core in the present structure [as in chlorotetraphenylporphinato(pyridine)(III) (Cl—CoTPP.Pyr, Sakurai, Yamamoto, Seino & Katsuta, 1975)] is considerably ruffled. The four pyrrole rings are planar. The least-squares planes are listed in Table 4 with the dihedral angles between them. Adjacent pyrrole rings are tilted by 17° (mean value) with respect to each other and by 12° (mean) with respect to the porphyrin mean plane. The ruffling, with overall symmetry $\bar{4}$ (Fig. 2), is a necessary consequence of steric interactions between the pyridine H atoms and the porphyrin atoms. Collins, Countryman & Hoard (1972), in their analysis of the structure of $[(imid)_2$-$FeTPP]^+$, have defined an angle φ as the dihedral angle between the imidazole plane and a plane passing through an idealized Co—N axial bond and one of the porphyrin N atoms (see Fig. 2). Steric interactions between the H atoms of the imidazole and atoms of the porphyrin ring are at a maximum for $\varphi = 0$ or $\varphi = 90°$

Table 2. *Bond distances* (Å)

Mean e.s.d. = 0·07 Å. The average values of equivalent distances assuming D_{4h} symmetry are given, together with the calculated e.s.d.'s in parentheses.

N(1)–C(1)	1·37
N(1)–C(4)	1·45
N(2)–C(6)	1·38
N(2)–C(9)	1·39
N(3)–C(11)	1·39
N(3)–C(14)	1·42
N(4)–C(16)	1·41
N(4)–C(19)	1·44
Average	1·41 (3)
C(1)–C(2)	1·47
C(3)–C(4)	1·48
C(6)–C(7)	1·40
C(8)–C(9)	1·48
C(11)–C(12)	1·47
C(13)–C(14)	1·45
C(16)–C(17)	1·43
C(18)–C(19)	1·51
Average	1·46 (3)
C(4)–C(5)	1·37
C(5)–C(6)	1·38
C(9)–C(10)	1·39
C(10)–C(11)	1·38
C(14)–C(15)	1·45
C(15)–C(16)	1·37
C(19)–C(20)	1·40
C(20)–C(1)	1·41
Average	1·39 (2)

C(2)–C(3)	1·41
C(7)–C(8)	1·46
C(12)–C(13)	1·33
C(17)–C(18)	1·37
Average	1·39 (5)
Co–N(1)	1·97
Co–N(2)	1·95
Co–N(3)	1·96
Co–N(4)	1·96
Average	1·96 (1)
Co–N(5)	1·99
Co–O	1·92
O–C(26)	1·41
N(5)–C(21)	1·27
N(5)–C(25)	1·36
C(21)–C(22)	1·42
C(22)–C(23)	1·53
C(23)–C(24)	1·54
C(24)–C(25)	1·45
O(1)–Me(1)	1·39
O(2)–Me(2)	1·49
O(3)–Me(3)	1·43

and a minimum for $\varphi = 45°$. Moreover, it has been shown (Lauher & Ibers, 1974) that shorter axial bond lengths are observed in the ions [(imid)$_2$FeTPP]$^+$ and [(imid)$_2$CoTPP]$^+$ if φ is near 45°. Steric interactions should be more severe in pyridine than in imidazole*

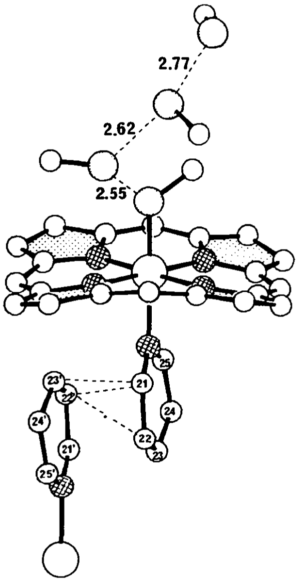

Fig. 1. Perspective view of the molecule with phenyl groups omitted for clarity.

Table 3. *Bond angles* (°)

Mean e.s.d. = 4°. The average values of the equivalent angles assuming D_{4h} symmetry are given. Calculated e.s.d.'s are in parentheses.

C(1)–N(1)–C(4)	104
C(6)–N(2)–C(9)	103
C(11)–N(3)–C(14)	103
C(16)–N(4)–C(19)	105
Average	104 (1)
N(1)–C(1)–C(2)	116
N(1)–C(4)–C(3)	107
N(2)–C(6)–C(7)	114
N(2)–C(9)–C(8)	115
N(3)–C(11)–C(12)	109
N(3)–C(14)–C(13)	113
N(4)–C(16)–C(17)	110
N(4)–C(19)–C(18)	109
Average	112 (3)
C(1)–C(2)–C(3)	101
C(4)–C(3)–C(2)	111
C(6)–C(7)–C(8)	107
C(9)–C(8)–C(7)	101
C(11)–C(12)–C(13)	110
C(14)–C(13)–C(12)	104
C(16)–C(17)–C(18)	111
C(19)–C(18)–C(17)	105
Average	106 (4)

C(4)–C(5)–C(6)	127
C(9)–C(10)–C(11)	124
C(14)–C(15)–C(16)	122
C(19)–C(20)–C(1)	124
Average	124 (2)
N(1)–C(4)–C(5)	122
C(5)–C(6)–N(2)	123
N(2)–C(9)–C(10)	125
C(10)–C(11)–N(3)	124
N(3)–C(14)–C(15)	124
C(15)–C(16)–N(4)	125
N(4)–C(19)–C(20)	124
C(20)–C(1)–N(1)	124
Average	124 (1)
C(3)–C(4)–C(5)	131
C(5)–C(6)–C(7)	123
C(8)–C(9)–C(10)	119
C(10)–C(11)–C(12)	126
C(13)–C(14)–C(15)	123
C(15)–C(16)–C(17)	125
C(18)–C(19)–C(20)	127
C(20)–C(1)–C(2)	119
Average	124 (4)

N(1)–Co–N(2)	89
N(2)–Co–N(3)	90
N(3)–Co–N(4)	89
N(4)–Co–N(1)	92
N(1)–Co–N(5)	89
N(2)–Co–N(5)	89
N(3)–Co–N(5)	90
N(4)–Co–N(5)	90
N(1)–Co–O	91
N(2)–Co–O	91
N(3)–Co–O	89
N(4)–Co–O	89
Co–N(5)–C(21)	119
Co–N(5)–C(25)	121
N(5)–C(21)–C(22)	122
C(21)–C(22)–C(23)	116
C(22)–C(23)–C(24)	125
C(23)–C(24)–C(25)	100
C(25)–N(5)–C(21)	119
Co–O–C(26)	121

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* The H atoms would be 0·4 Å nearer the porphinato core if the Co–N(pyridine) bond length were equal to Co–N(imidazole).

Table 4. *Least-squares planes through atomic positions*

Definition of the planes

P: porphyrin plane including 20 C atoms and four N atoms. Corresponding deviations are listed in Fig. 2.

A,*B*,*C*,*D*: individual pyrrole mean planes which comprise the five atoms composing the pyrrole.

Pyr: pyridine mean plane including six atoms.

Plane equations

Plane *P* $0\cdot2243x + 0\cdot4930y - 0\cdot8406z - 6\cdot0693 = 0$
Plane *A* $0\cdot0925x + 0\cdot5920y - 0\cdot7054z - 8\cdot9483 = 0$
Plane *B* $0\cdot3897x + 0\cdot5920y - 0\cdot7054z - 8\cdot9483 = 0$
Plane *C* $0\cdot3484x + 0\cdot3418y - 0\cdot8728z - 4\cdot8387 = 0$
Plane *D* $0\cdot0768x + 0\cdot3713y - 0\cdot9253z - 2\cdot9616 = 0$
Plane Pyr $0\cdot4644x + 0\cdot7768y - 0\cdot4252z + 15\cdot5719 = 0$

Deviations (Å)

Plane *A* C(1) 0·05; C(2) –0·05; C(3) 0·04; C(4) –0·01; N(1) –0·02
Plane *B* C(6) –0·03; C(7) 0·03; C(8) –0·02; C(9) 0·00; N(2) 0·01
Plane *C* C(11) 0·00; C(12) –0·03; C(13) 0·04; C(14) –0·04; N(3) 0·02
Plane *D* C(16) –0·01; C(17) 0·02; C(18) –0·02; C(19) 0·02; N(4) –0·01
Plane Pyr N(5) –0·03; C(21) 0·00; C(22) 0·05; C(23) –0·07; C(24) 0·03; C(25) 0·01

Dihedral angles (°)

A/*P*	11	*A*/*B*	18	*A*/*C*	23
B/*P*	13	*B*/*C*	17	*B*/*D*	25
C/*P*	11	*C*/*D*	16		
D/*P*	12	*D*/*A*	17		

but they are relieved by a lengthening of the axial Co—N bond with respect to the imidazole [Co—N(pyridine) = 1·99; Co—N(imidazole) = 1·93 Å] and by the ruffling of the porphyrin ring. As shown in Fig. 2, this ruffling is easily correlated with the pyridine position. In the present structure, CH_3O—CoTPP.Pyr, φ is 32° and we calculate a φ value of 42° for the structurally related Cl—CoTPP.Pyr (Sakurai *et al.*, 1975).

The axial covalent Co—O bond length is 1·92 (4) Å. This bond length may be compared with the Co—O distance of 1·909 (3) Å found for the axial ligand in the complex (cumyl peroxide)(pyridine)cobaloxime (Giannotti, Fontaine, Chiaroni & Riche, 1976). The short interactions between the C of the methoxy group and the porphyrin atoms [C(26)···N(2) 2·84, C(26)···C(6) 3·47, C(26)···N(1) 3·27, C(26)···C(4) 3·78 Å] result in a distortion of the Co—O—CH_3 bond angle (121°) from tetrahedral. Such a distortion has been previously observed in the structures of bis(dimethylamine)-etio(I)porphinatorhodium(III) chloride dihydrate (117°, Hanson, Gouterman & Hanson, 1973), and [bis(1-phenylethylamine)TPPCO^{III}]$^+$ (123°, Riche, Chiaroni, Gouédard & Gaudemer, 1977).

The dihedral angles between the mean planes of the porphinato core and the four phenyl groups are $\varphi_1 = 81$, $\varphi_2 = 84$, $\varphi_3 = 81$ and $\varphi_4 = 76°$. The pyridine group is slightly tilted by 6° with respect to the Co—N(5) bond, the Co atom being 0·20 Å out of the mean plane of the pyridine. This can be ascribed to intermolecular packing forces. As shown in Fig. 1, the stacking of the pyridine groups with respect to a centre of symmetry gives rise to short distances: C(21)···C′(23) 3·20, C(21)···C′(22) 3·60, C(22)···C′(23) 3·30, and C(22)···C′(23) 3·42 Å.

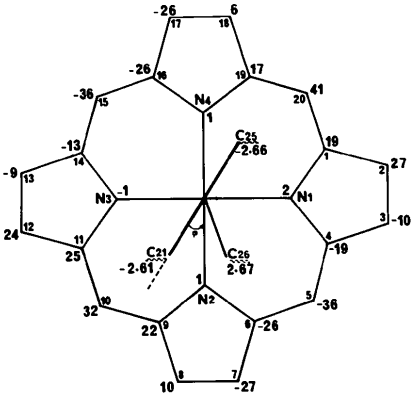

Fig. 2. Diagram illustrating the ruffling of the porphinato core. Perpendicular distances of the atoms from the mean plane are in units of 0·01 Å.

The three methanol molecules of crystallization form a hydrogen-bonded chain attached to the O atom of the methoxy group (Fig. 1). The tailed methanol molecule, only linked at one point, is highly agitated. The crystal decomposition is probably due to a loss of this molecule.

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