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Dipyridine[5,10,15,20-tetrakis(4-carboxyphenyl)-porphyrinato]cobalt(II) pyridine tetrasolvate monohydrate

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In the title compound, $[Co(C_{48}H_{28}N_4O_8)(C_5H_5N)_2]\cdot4C_5H_5N\cdot H_2O$, the Co atom lies on a fourfold inversion axis, with the N atom and one C atom of the axial pyridine ligand on a twofold axis. Four pyridine solvent molecules hydrogen bond to the carboxylate groups of the porphyrin. The structure generates a hydrophobic void that incorporates a disordered solvent water molecule whose O atom lies on another fourfold inversion axis.

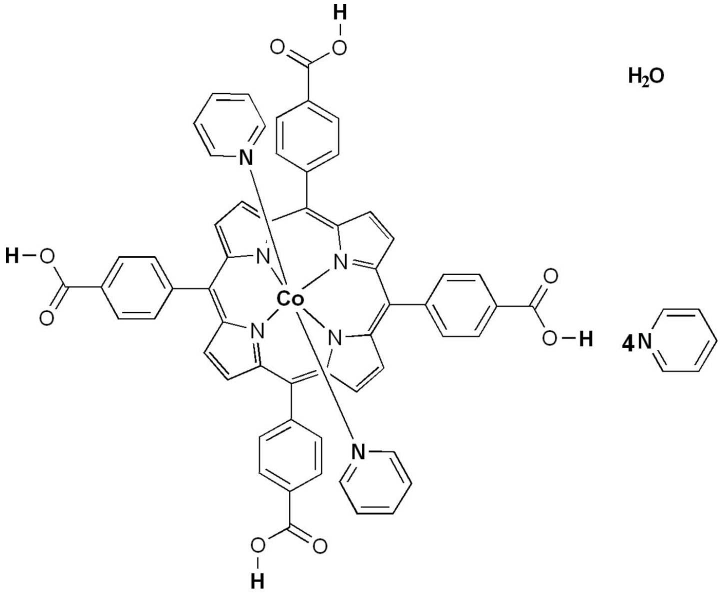
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.004 Å
H-atom completeness 97%
R factor = 0.097
wR factor = 0.326
Data-to-parameter ratio = 16.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Microporous metal–organic frameworks are currently of great interest in gas storage, separation and catalysis (Bradshaw *et al.* 2005; Kesanli *et al.*, 2003; Kitagawa *et al.*, 2004; Rowsell & Yaghi, 2004; Xiong *et al.*, 2001). Carboxyl-substituted tetraphenylporphyrins have been widely used as building blocks in the synthesis of novel microporous materials (Kosal *et al.*, 2002; Goldberg, 2000, 2002; Shmilovits *et al.*, 2004; Smithenry & Suslick, 2004). Porphyrins possess high thermal stability relative to other organic molecules, and metalloporphyrins are good oxidation catalysts for hydroxylation of alkanes and epoxidation of alkenes. Porous metalloporphyrin networks also have the potential to act as size- and shape-selective catalysts (Suslick *et al.*, 2005). We describe here the crystal structure of a cobalt(II)–5,10,15,20-tetrakis(4-carboxyphenyl)-porphyrin (TCPP) complex, (I) (Fig. 1).



(I)

The Co^{2+} ion lies at the center of the TCPP ring on a fourfold inversion axis; the Co1—N1 bond length

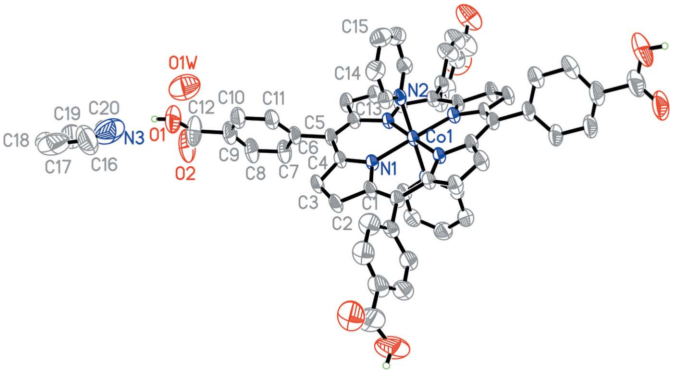


Figure 1
The molecular structure of (I), showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted for clarity. Unlabeled atoms are related to labeled atoms by $(-x, \frac{1}{2}-y, z)$, $(-\frac{1}{4}+y, \frac{1}{4}-x, \frac{3}{4}-z)$ and $(\frac{1}{4}-y, \frac{1}{4}+x, \frac{5}{4}-z)$.

[1.961 (2) Å] is consistent with those reported for other cobalt(II)–porphyrin complexes (Kim *et al.*, 1988; Terazono *et al.*, 2003). The axial sites of the cobalt coordination are occupied by pyridine molecules, with Co1—N2 bond lengths of 1.958 (3) Å. The similarity of the equatorial and axial Co—N distances shows the coordination geometry for the Co^{II} atom to be close to regular octahedral. The r.m.s. deviation from the least-squares plane of the metalloporphyrin (0.28 Å) indicates considerable distortion. The carboxyphenyl ring subtends an angle of 69.60 (8)° to the metalloporphyrin plane, while the carboxylic acid group is almost coplanar with the phenyl ring [dihedral angle = 12.7 (5)°].

The carboxylic acid substituents of the CoTCPP system do not participate in coordination to the metal, but form O1—H1*A*···N3 hydrogen bonds to the pyridine solvent molecules (Table 1), extending the porphyrin arms. These extended porphyrin units form a three-dimensional network, leaving a small void which is occupied by a disordered water molecule with its O atom lying on a fourfold inversion axis (Fig. 2). There are no intermolecular hydrogen bonds between water and the surrounding porphyrin units due to the hydrophobic nature of the void.

Experimental

meso-Tetrakis(carboxyphenyl)porphyrin (8 mg) and Co(NO$_3$)$_2$·6H$_2$O (3.2 mg) were dissolved in pyridine (5 ml). An aqueous solution (4 ml) of KOH (0.6 mg) was added. The mixture was transfered to a 23 ml Teflon-lined reactor which was heated to 423 K, and maintained at that temperature for 24 h. The reactor was then cooled to room temperature over 3 d. Purple plate-like crystals suitable for single-crystal X-ray diffraction separated from the reaction mixture.

Crystal data

[Co(C$_{48}$H$_{28}$N$_4$O$_8$)(C$_5$H$_5$N)$_2$]·4C$_5$H$_5$N·H$_2$O
M_r = 1340.29
Tetragonal, $I4_1/a$
a = 19.093 (4) Å
c = 16.916 (6) Å
V = 6167 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.35 mm^{-1}
T = 150 (1) K
0.26 × 0.15 × 0.12 mm

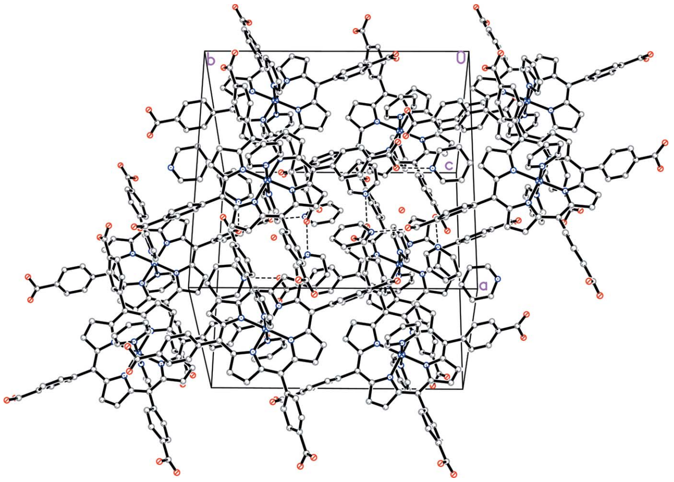


Figure 2
The three-dimensional network of (I), showing the O atoms of the solvent water molecules in voids generated by adjacent porphyrin units.

Data collection

Bruker SMART CCD 1000 diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.872, T_{max} = 0.917
26109 measured reflections
3342 independent reflections
1975 reflections with $I > 2\sigma(I)$
R_{int} = 0.103

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.097
$wR(F^2)$ = 0.326
S = 1.08
3342 reflections
205 parameters
2 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.69 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···N3	0.84	1.90	2.664 (3)	151

All H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C) for aromatic, and O—H = 0.84 Å and U_{iso}(H) = 1.5U_{eq}(O) for the carboxyl OH groups. The H atoms of water could not be located in difference Fourier maps and were therefore not included in the refinement. Atoms of the solvent pyridine molecule showed high displacement parameters and were refined using a rigid regular hexagon model with a bond length of 1.39 Å. The maximum electron-density peak is located about 0.9 Å from atom Co1.

Data collection: *SMART* (Siemens, 1994); cell refinement: *SAINT* (Siemens, 1994); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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