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Hydrogen-bonded supramolecular lattice of the 1:3:4 complex between [5,10,15,20-*meso*-tetrakis(4-hydroxyphenyl)porphyrinato-κ^4N]zinc(II), dibenzo-24-crown-8 and methanol

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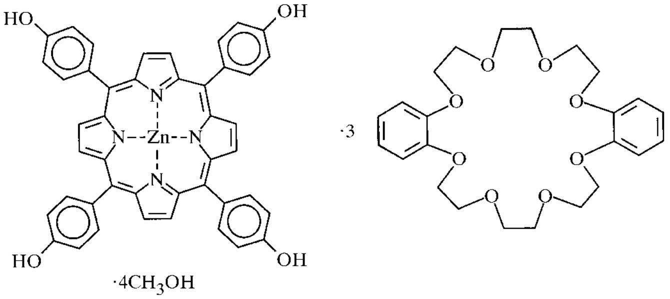
The title compound, [5,10,15,20-*meso*-tetrakis(4-hydroxyphenyl)porphyrinato-κ^4N]zinc(II) tris(dibenzo-24-crown-8) methanol tetrasolvate, $[Zn(C_{44}H_{28}N_4O_4)]\cdot3C_{24}H_{32}O_8\cdot4CH_4O$, was synthesized and its molecular structure precisely characterized by low-temperature single-crystal analysis. All the components are involved in hydrogen bonding with each other, thus forming an extensively hydrogen-bonded supramolecular lattice. The functionalized porphyrin moiety coordinates both equatorially and axially to the neighboring species.

Comment

The zinc–tetrakis(4-hydroxyphenyl)porphyrin molecule has been used previously as a potential building block for the supramolecular synthesis of multiporphyrin arrays (Goldberg *et al.*, 1995; Goldberg, 2000). The peripheral OH functional groups provide self-complementary binding sites for a simultaneous lateral association of every building block to several neighboring species by multiple hydrogen bonding. The Zn^{II} ion in the porphyrin center may allow additional coordination in the axial direction to other ligands. A relevant example of such an axial coordination of zinc– and manganese–tetraphenylporphyrin to 18-crown-6, *via* a water ligand bound to the metal ion, has been reported previously (Diskin-Posner *et al.*, 1999). The present report describes the extensive hydrogen bonding between the porphyrin moiety and the surrounding dibenzo-24-crown-8 species, either directly or through methanol bridges, in directions parallel to the porphyrin plane, as well as perpendicular to it. The resulting structure, (I), represents a fascinating supramolecular lattice composed of three different species and held together by a co-operative array of hydrogen bonds.

The central core of the porphyrin moiety is nearly planar with only a slight puckering, the deviations of the individual atoms from the mean plane of the 24-atom macrocycle being between −0.091 (6) and 0.077 (5) Å. The Zn^{II} ion is five-coordinate, deviating by 0.335 (3) Å from the plane of the four pyrrole N atoms towards the axial methanol ligand coordinated to it, and assumes a square-pyramidal coordination environment (shown in Fig. 3). The hydroxyphenyl rings are oriented in an almost perpendicular manner with respect to the porphyrin macrocycle, the corresponding dihedral angles being 76.2 (2), 73.4 (1), 75.6 (2) and 72.6 (2)°. The coordination bond lengths to the Zn^{II} ion are given in Table 1. The three dibenzo-24-crown-8 species assume a roughly flat conformation (Fig. 1), with some of the methylene groups turned inward to fill the space within the macrocyclic rings. Correspondingly, while a fully open crown structure is characterized by a *gauche* conformation about the C—C bonds and a *trans* conformation about the C—O bonds, in (I), some of the latter are also *gauche*. However, all O—C—C—O fragments preserved their *gauche* arrangement. Otherwise, the molecular geometries of the constituent species are characterized by common features.



(I)

The supramolecular structure consists of layers of species interconnected by a network of hydrogen bonds, as shown in Fig. 2. Within a given layer, every porphyrin unit is hydrogen bonded in lateral directions to four different crown-ether moieties, either directly or through bridging methanol molecules. The direct porphyrin–crown-ether interactions involve O31—H31···O82, O31—H31···O85, O45—H45···O114 and, possibly, O45—H45···O117 hydrogen bonds on opposite sides of the porphyrin framework (Table 2). In the other directions, on one side, the porphyrin hydrogen bonds to a third crown-ether species through one methanol molecule (O38—H38···O152 and O152—H152···O98), while on the other side, it links through two methanol moieties (O52—H52···O154, O154—H154···O156 and O156—H156···O146; Table 2). The layers formed consist of two different rows (extending in the $a - 2b$ direction) arranged side-by-side in an alternating manner. One row consists of crown-ether molecules only, while the other row contains paired porphyrin–crown-ether assemblies (Fig. 2). These layers are stacked along the *a* axis of the crystal in an offset manner, which also facilitates additional hydrogen bonding between the layers. The offset is along $a - 2b$ by a half vector translation in order to position the crown-ether ring of one layer above the

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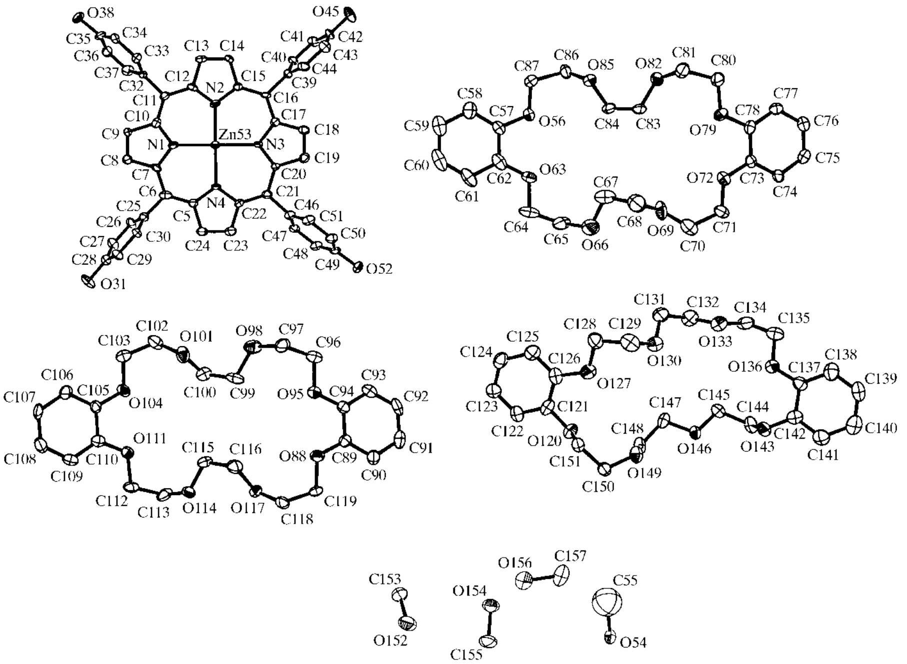

Figure 1

The molecular structure of the porphyrin, crown-ether and methanol components of the title compound, showing the atom-labeling scheme. The ellipsoids represent displacement parameters at the 50% probability level at *ca* 110 K. The methanol species labeled O54 and C55 is coordinated to zinc through atom O54. Bond lengths involving the $\mathrm{Zn^{II}}$ ion in the porphyrin core are listed in Table 1.

porphyrin-coordinated axial methanol ligand of another layer, and thus optimize the interlayer O54—H54···O149 hydrogen bond (Table 2). Figs. 3 and 4 illustrate the stacking arrangement along the *a* axis of the crystal. The resulting structure thus contains columns of alternating porphyrin and crown-ether species, as well as separate stacks of the other crown-ether moieties (Fig. 4), all of which are interconnected with each other by the methanol bridges. The efficient intermolecular hydrogen bonding yielded a relatively well packed chiral (though the analyzed crystal represents a racemic twin)

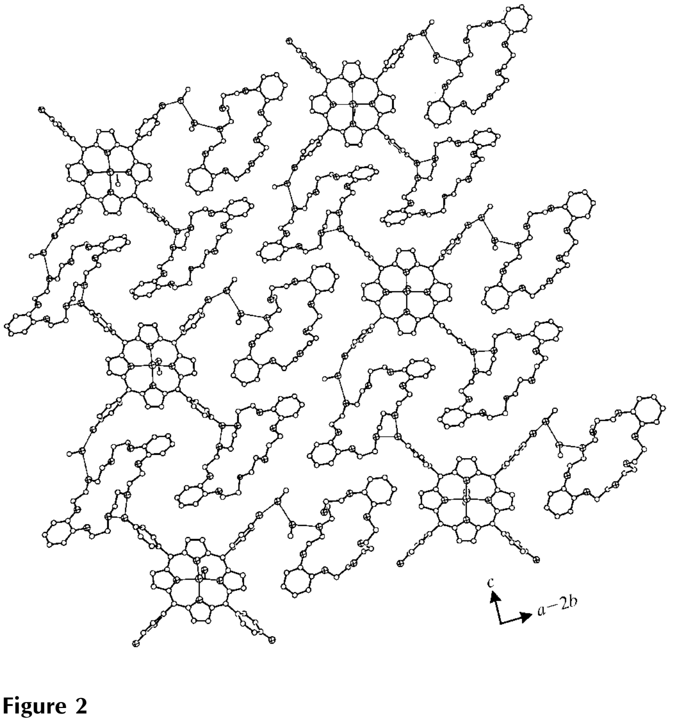

Figure 2

A perspective view of the layered molecular arrangement in the title structure, roughly down the *a* axis of the crystal (all the heteroatoms are represented by crossed circles, while C atoms are represented by open circles). All the intralayer hydrogen bonds, which interconnect between the different species, are indicated by thin lines. The translation vectors, which relate between equivalent molecules, are also marked.

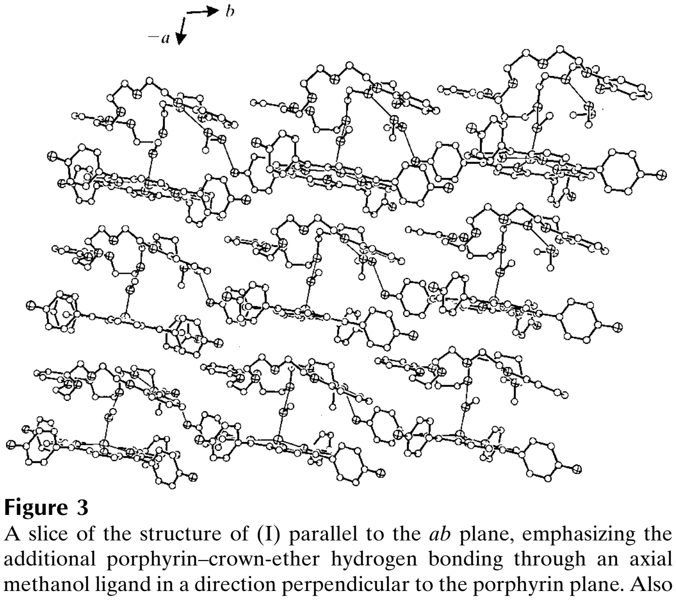

Figure 3

A slice of the structure of (I) parallel to the *ab* plane, emphasizing the additional porphyrin–crown-ether hydrogen bonding through an axial methanol ligand in a direction perpendicular to the porphyrin plane. Also illustrated is the stacked organisation of the layers shown in Fig. 2. This slice of the structure is sandwiched above and below between sections consisting of stacked crown-ether moieties only (see Fig. 4), accounting for the 1:3 ratio between the porphyrin and crown-ether components. Note the slight deviation of the $\mathrm{Zn^{II}}$ ion from the porphyrin core towards the axial ligand.

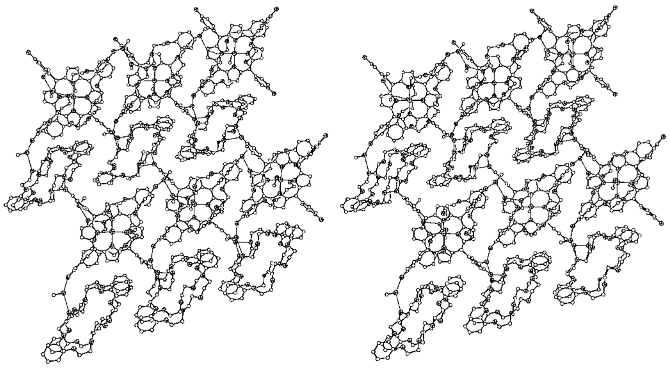

Figure 4
Stereoview of the intermolecular stacking down the *a* axis (*c* is roughly vertical). Two layers are shown. Note the separate columns of overlapping crown-ether components, and axially hydrogen-bonded porphyrin and crown-ether species. The columns are interlinked laterally by methanol bridges.

and polar structure of previously unknown supramolecular features. These results are particularly significant in the context of the crystal engineering of new supramolecular materials.

Experimental

All chemicals used were obtained commercially. Zinc–tetrakis-(4-hydroxyphenyl)porphyrin (7.5 mg, 0.01 mmol) was reacted with dibenzo-24-crown-8 (5 mg, 0.01 mmol) in warm methanol (4 ml). Toluene (10 drops) was added to this solution to control solubility. Single crystals of the title compound were then obtained by slow evaporation in air.

Crystal data

$[Zn(C_{44}H_{28}N_4O_4)]\cdot 3C_{24}H_{32}O_8\cdot$-
$4CH_4O$
$M_r = 2215.73$
Triclinic, $P1$
$a = 10.2643\ (3)$ Å
$b = 13.4878\ (4)$ Å
$c = 21.1227\ (8)$ Å
$\alpha = 86.2858\ (10)^\circ$
$\beta = 77.9955\ (13)^\circ$
$\gamma = 73.932\ (3)^\circ$
$V = 2748.51\ (15)$ Å^3

$Z = 1$
$D_x = 1.339$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 18 559 reflections
$\theta = 1.9$–27.8°
$\mu = 0.31$ mm^{-1}
$T = 110\ (2)$ K
Prism, red
0.35 × 0.30 × 0.25 mm

Data collection

Nonius KappaCCD diffractometer
0.8° φ and ω scans
15 453 measured reflections
15 453 independent reflections
13 092 reflections with $I > 2\sigma(I)$

$\theta_{\max} = 25.0^\circ$
$h = -11 \rightarrow 12$
$k = -14 \rightarrow 16$
$l = -24 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.070$
$wR(F^2) = 0.167$
$S = 1.05$
15453 reflections
1420 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0644P)^2 + 4.9932P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.136$
$\Delta\rho_{\max} = 0.96$ e Å^{-3}
$\Delta\rho_{\min} = -0.55$ e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter = 0.477 (13); 6357 Friedel reflections

Table 1
Selected interatomic distances (Å).

N1—Zn53	2.047 (5)	N4—Zn53	2.081 (5)
N2—Zn53	2.068 (5)	O54—Zn53	2.123 (4)
N3—Zn53	2.081 (5)		

Table 2
Hydrogen-bonding geometry (Å, °).

The contacts H31···O82 and H31···O85, as well as H45···O114 and H45···O117, represent either bifurcated or disordered hydrogen-bonding interactions between the porphyrin and crown-ether moieties.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O31—H31···O85^{i}	0.78	2.18	2.878 (7)	149
O31—H31···O82^{i}	0.78	2.34	2.875 (6)	127
O38—H38···O152	0.96	1.74	2.688 (7)	168
O45—H45···O114^{ii}	0.95	1.82	2.769 (6)	180
O45—H45···O117^{ii}	0.95	2.61	3.030 (7)	107
O52—H52···O154^{iii}	0.95	1.73	2.677 (7)	179
O54—H54···O149^{iv}	0.94	1.80	2.740 (6)	179
O152—H152···O98	0.94	1.93	2.872 (7)	174
O154—H154···O156	0.93	1.72	2.651 (7)	180
O156—H156···O146^{v}	0.95	1.81	2.755 (7)	180

Symmetry codes: (i) $x, y-1, z$; (ii) $x, y, 1+z$; (iii) $x, y-1, 1+z$; (iv) $1+x, y, 1+z$; (v) $1+x, y, z$.

The title compound is a racemic twin. The methyl group of the zinc-bound methanol molecule is orientationally disordered. These features, along with the somewhat high mosaicity of the analyzed crystal and the large number of available data, affected, to some extent, the precision of the crystallographic determination and resulted in somewhat high *R* factors. Atom H31 (bonded to O31) was located directly from a difference map, with an O—H distance of 0.78 Å; the remaining H atoms were placed in calculated postions, with C—H distances in the range 0.95–0.99 Å and O—H distances in the range 0.93–0.96 Å.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski, 1985); data reduction: *DENZO*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1198). Services for accessing these data are described at the back of the journal.

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