Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Supramolecular assembly of (methanol)[10,15,20-tris(4-cyanophenyl)-5-(4-pyridyl)porphyrinato]zinc(II) by intermolecular hydrogen bonding and weak coordination

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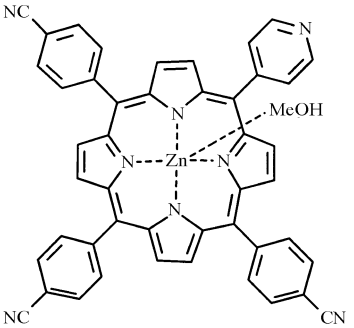
Received 24 August 2006
Accepted 30 August 2006
Online 12 September 2006

The crystal structure of the title compound, [Zn($C_{46}H_{24}N_8$)(CH_4O)], consists of two-dimensional supramolecular arrays sustained by O—H···N(pyridyl) hydrogen bonding and weak Zn···NC coordination. The interlayer organization in the crystal structure is characterized by tight stacking of the corrugated layers.

Comment

The supramolecular chemistry of porphyrins in the context of crystal engineering has been widely studied during the past decade or so. Effort has been focused mostly on the *meso*-tetra-4-pyridylporphyrin and *meso*-tetrakis(4-carboxyphenyl)porphyrin building blocks in both their free-base and metallated forms, taking advantage of the square-planar functionality of these units and the versatile coordination and hydrogen-bonding capacity of the peripheral pyridyl and carboxylic acid groups (Goldberg, 2005, and references therein; Kosal *et al.*, 2002; Diskin-Posner *et al.*, 2000; Diskin-Posner & Goldberg, 1999; Krupitsky *et al.*, 1994; Abrahams *et al.*, 1994). Attempts to induce the formation of non-centrosymmetric materials using moieties of reduced (lower than D_{4h}) symmetry have been reported as well (George *et al.*, 2006; George & Goldberg, 2006; Vinodu & Goldberg, 2003). As part of our systematic investigation of porphyrin-based crystalline solids, we have been exploring the networking capacity of porphyrin scaffolds bearing various combinations of peripheral functional groups (Goldberg, 2005). We report here on the self-assembly of the title compound, (I).

Compound (I) (Fig. 1) is characterized by its low symmetry, while bearing substituent groups suitable for hydrogen bonding as well as coordinative interactions. Both types come into play in the interesting crystal structure of (I). The molecular structure exhibits a slightly domed conformation, with the central Zn ion deviating by only 0.161 (3) Å from the mean plane of the four pyrrole N atoms towards the methanol ligand. This value should be compared with a commonly observed deviation of about 0.3 Å in otherwise unconstrained five-coordinate complexes of zinc porphyrins (*e.g.* Lipstman & Goldberg, 2006). An apparent weak coordination to the central Zn ion from the opposite axial direction (Table 1, see also below) provides an explanation for this discrepancy.



(I)

Fig. 2 depicts the supramolecular interaction scheme for (I), and the self-assembly process can be best described in a modular way. Firstly, the strongest intermolecular attraction that can be utilized in this structure is provided by hydrogen bonding between the axial methanol ligand of one porphyrin (acting as H-atom donor) and the pyridyl arm (the strongest H-atom acceptor) of an adjacent unit (Table 2). Each porphyrin molecule is involved in two such bonds in opposite directions, thus creating a hydrogen-bonded zigzag chain of the porphyrin species. However, adjacent chains combine into a layered array *via* additional weak coordinations. These involve the cyanophenyl substituent *trans* to the pyridyl group of one unit and the uncoordinated (slightly concave) face of the methanol–zinc core of an adjacent glide-related unit (Table 1). This Zn···N distance is somewhat longer than previously observed in coordination polymers of six-coordinate zinc tetrakis(4-cyanophenyl)porphyrin (2.7–2.8 Å; Krishna Kumar *et al.*, 1998), and in the present case this should

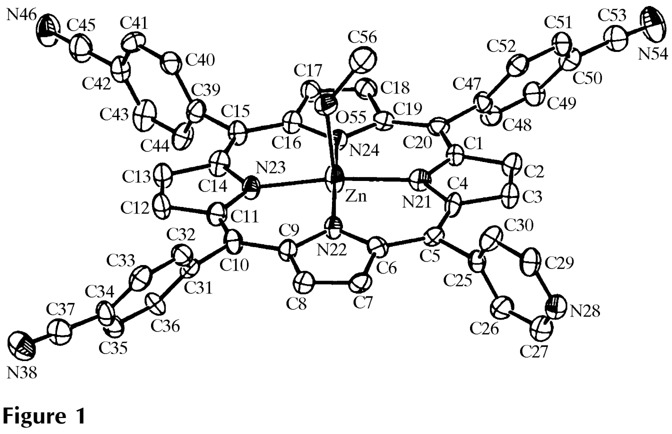


Figure 1
The molecular structure of the title compound, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level at *ca* 110 K.

be attributed to the bias introduced by the markedly stronger methanol binding to the Zn, as is also reflected in the slighly domed conformation of the porphyrin species. However, the Zn···NC attraction creates an interporphyrin 'linkage' along an axis nearly perpendicular to the O55—H55···N28 hydrogen-bonding direction, thus affording a supramolecular porphyrin array of two-dimensional connectivity.

The crystal structure of (I) naturally consists of a stacked arrangement of the two-dimensional arrays. The corrugated surfaces of neighbouring layers seem to fit effectively into one another, and no solvent is included between them. Two of the cyanophenyl substituents (related *trans* to each other) are directed at the interlayer interface from above and below, contributing stabilizing dipolar attractions between these CN dipoles of adjacent layers that point in opposite directions (Fig. 3). However, the structure of (I) is not centrosymmetric. This is consistent with our earlier correlations between the symmetry of the individual building blocks and that of the resulting crystalline architectures in porphyrin solids (George & Goldberg, 2006; Vinodu & Goldberg, 2003). The use of metalloporphyrin scaffolds of D_{4h} symmetry almost uniformly leads to centrosymmetric crystal structures, while the presence of directional inter-porphyrin interactions combined with lateral and/or axial asymmetry of the individual building blocks may afford non-centrosymmetric architectures (George *et al.*, 2006; George & Goldberg, 2006; Vinodu & Goldberg, 2003). In summary, the structure of (I) consists of uniquely assembled two-dimensional multi-porphyrin arrays, *via* a combination of hydrogen bonding and weak coordination.

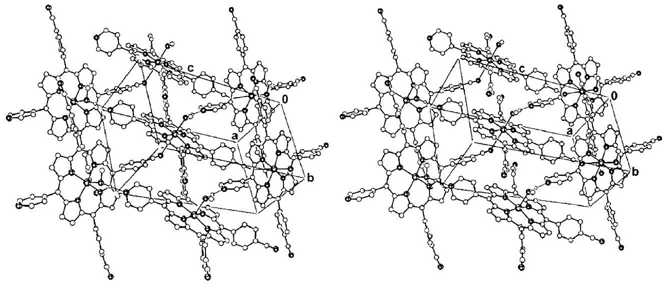


Figure 2
A stereoview of the specific intermolecular interaction scheme in (I). Zn, N and O atoms are shown as darkened spheres. The methanol-to-pyridyl O—H···N hydrogen bonds [O···N = 2.751 (6) Å] and the Zn···NC contacts [Zn···N = 3.020 (5) Å] are indicated by thin lines. Note the two-dimensional assembly that forms with a corrugated surface. H atoms have been omitted for clarity, except for the hydroxylic H atoms in four of the porphyrin units (in the lower left corner) which are involved in hydrogen bonding.

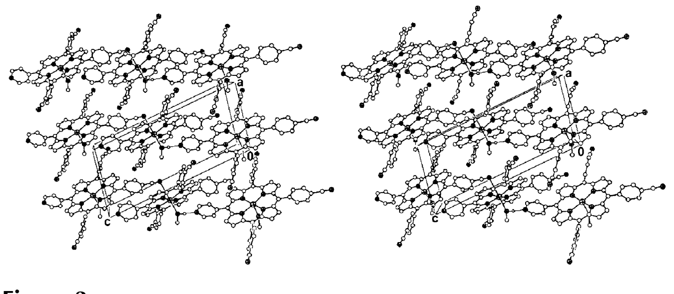


Figure 3
A stereoview of the crystalline architecture of (I), projected approximately down the *b* axis. Zn, N and O atoms are shown as darkened spheres. Note the tight solvent-free organization of the layered assemblies (three layers are viewed edge-on). The O—H···N hydrogen bonds and weak Zn···NC coordination in each layer are indicated by thin lines. H atoms have been omitted, except for the hydroxylic H atoms of the three central molecular units which are involved in hydrogen bonding.

Experimental

The free-base porphyrin compound was synthesized according to a standard literature procedure (Adler *et al.*, 1970), by condensation of a 3:1 mixture of 4-cyanobenzaldehyde and pyridine-4-carbaldehyde with distilled pyrrole in hot propionic acid. It was then separated from the mixture of the various possible substitutional isomers by elution with 2% methanol on a silica-gel column, and subsequently metallated with zinc. Both the free-base and the metalloporphyrin species were fully characterized by ^{1}H NMR, UV–vis and mass spectroscopic techniques. Crystallization of the title porphyrin was carried out by evaporation of a solution in a mixture of methanol and *N*,*N*′-dimethylacetamide (1.5 *v*/*v*).

Crystal data

$[Zn(C_{46}H_{24}N_8)(CH_4O)]$
$M_r = 786.14$
Monoclinic, *Pn*
$a = 9.2505$ (4) Å
$b = 9.6600$ (5) Å
$c = 21.1032$ (10) Å
$\beta = 101.422$ (3)°
$V = 1848.43$ (15) Å^3
$Z = 2$
$D_x = 1.412$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.72$ mm^{-1}
$T = 110$ (2) K
Prism, red
0.30 × 0.20 × 0.20 mm

Data collection

Nonius KappaCCD area-detector diffractometer
1° φ and ω scans
17749 measured reflections
7371 independent reflections
6328 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.032$
$\theta_{\rm max} = 27.9°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.063$
$wR(F^2) = 0.139$
$S = 1.11$
7371 reflections
517 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0348P)^2 + 3.736P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.013$
$\Delta\rho_{\rm max} = 0.83$ e Å^{-3}
$\Delta\rho_{\rm min} = -1.55$ e Å^{-3}
Absolute structure: Flack (1983), with 2936 Friedel pairs
Flack parameter: 0.381 (17)

Table 1
Selected geometric parameters (Å, °).

Zn—N21	2.062 (5)	Zn—N24	2.044 (4)
Zn—N22	2.042 (4)	Zn—O55	2.226 (4)
Zn—N23	2.059 (4)	Zn—N46$^{\rm i}$	3.020 (6)
N21—Zn—N22	89.86 (17)	N23—Zn—N24	90.02 (17)
N21—Zn—N23	171.0 (2)	N21—Zn—O55	95.96 (16)
N21—Zn—N24	89.09 (17)	N22—Zn—O55	95.93 (16)
N22—Zn—N23	89.61 (17)	N23—Zn—O55	93.07 (17)
N22—Zn—N24	171.0 (2)	N24—Zn—O55	93.07 (16)

Symmetry code: (i) $x + \frac{1}{2}, -y + 1, z + \frac{1}{2}$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O55—H55···N28^{ii}	1.00	1.75	2.751 (6)	175

Symmetry code: (ii) $x - \frac{1}{2}, -y, z - \frac{1}{2}$.

The H atoms were treated as riding, with C—H = 0.95–0.98 Å, O—H = 1.00 Å and $U_{iso}(H) = 1.2U_{eq}$(C,O) or $1.5U_{eq}$(methyl C). The resulting structure represents a racemic twin. Two relatively high residual peaks and troughs near the Zn atom are associated with the twinning or slight axial disorder of this atom, as reflected in its axially elongated displacement ellipsoid.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *MERCURY* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

This research was supported in part by the Israel Science Foundation (grant No. 254/04).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3047). Services for accessing these data are described at the back of the journal.

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