

Poly[[μ -5,10,15,20-tetrakis-(4-methoxycarbonylphenyl)-porphyrinato(2-)]zinc(II)] *N,N'*-dimethylacetamide disolvate]

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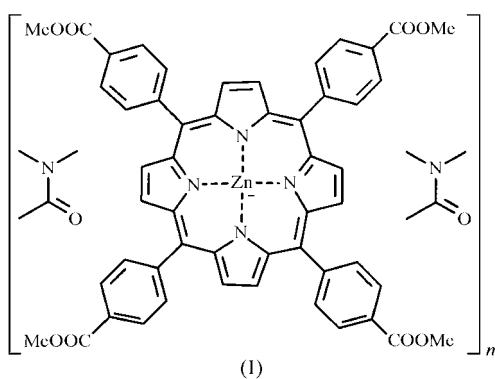
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The crystal structure of the title compound, $\{[\text{Zn}(\text{C}_{52}\text{H}_{36}\text{N}_4\text{O}_8)] \cdot 2\text{C}_4\text{H}_9\text{NO}\}_n$, consists of two-dimensional coordination polymers of the six-coordinate zinc–porphyrin unit [$\text{Zn}-\text{N} = 2.039(2)$ and $2.061(2)$ Å, and $\text{Zn}-\text{O} = 2.540(2)$ Å], which intercalate between the molecules of *N,N*-dimethylacetamide solvent. The Zn atom lies on an inversion centre.

Comment

The formulation of porphyrin network and framework solids has received increasing attention in recent years (Goldberg, 2005, and references therein; Kosal *et al.*, 2002; Diskin-Posner *et al.*, 2000; Krupitsky *et al.*, 1994; Abrahams *et al.*, 1994), due to their potential application to problems of materials storage



and separation as well as heterogeneous catalysis. Most of the supramolecular architectures reported to date involve external auxiliaries (metal ions or organic ligands) as linkers between the porphyrin units. Only a few examples of direct networking between suitably functionalized metalloporphyrins have been observed thus far, including our first robust porous solid consisting of a three-dimensional coordination polymer of zinc–tetra-4-pyridylporphyrin (Krupitsky *et al.*, 1994; Shmilovits *et al.*, 2004a; George *et al.*, 2006). As part of our systematic investigation of porphyrin-based solids, we

report here the direct coordination polymerization of the title porphyrin derivative, (I) (Fig. 1), and the intercalate-type crystal structure it forms with *N,N'*-dimethylacetamide.

The methoxycarbonyl function has not been utilized before in the supramolecular assembly of porphyrin arrays. The bond lengths and angles in (I) (Table 1) show standard values [Cambridge Structural Database, Version 5.27 (Allen, 2002) and *MERCURY* (Macrae *et al.*, 2006)], in particular for the $\text{Zn}-\text{N}$ (pyrrole) distances (Shmilovits *et al.*, 2004b).

The inter-porphyrin coordination pattern in (I) is illustrated in Fig. 2. It represents a unique two-dimensional coordination polymer obtained by direct coordination of two *trans*-related peripheral methoxycarbonyl groups of one porphyrin to the metal core of neighbouring moieties. Thus, formation of the polymeric array is effected by axial coordination of the Zn centres from above and below to the methoxycarbonyl groups of two perching units across inversion at $\text{Zn}-\text{O}(\text{C}=\text{O})$ of 2.540(2) Å. Two *trans*-related methoxycarbonylphenyl arms along a roughly perpendicular direction of the central molecule associate with the metal centres of two other neighbouring entities. Each porphyrin unit (located on an inversion centre) is thus involved in a four-point connection to the surrounding species, affording a condensed two-dimensional coordination polymer assembly. The supramolecular $\text{Zn}-\text{O}$ coordinative interactions operate between molecular units related to each other by the screw/glide symmetry (thus forming a herring-bone pattern). There are fortuitous $\text{C}-\text{H} \cdots \pi$ interactions (*PLATON*; Spek, 2003) between the adjacent methoxycarbonyl methyl atom H32A and the Zn-pyrrole ring ($\text{Zn}/\text{N11}/\text{C4}-\text{C6}/\text{N12}$) at $(x, \frac{1}{2} - y, z - \frac{1}{2})$ of 2.45 Å ($\text{C}-\text{H} \cdots \pi$ angle 167°). The resulting polymeric arrays have corrugated surfaces.

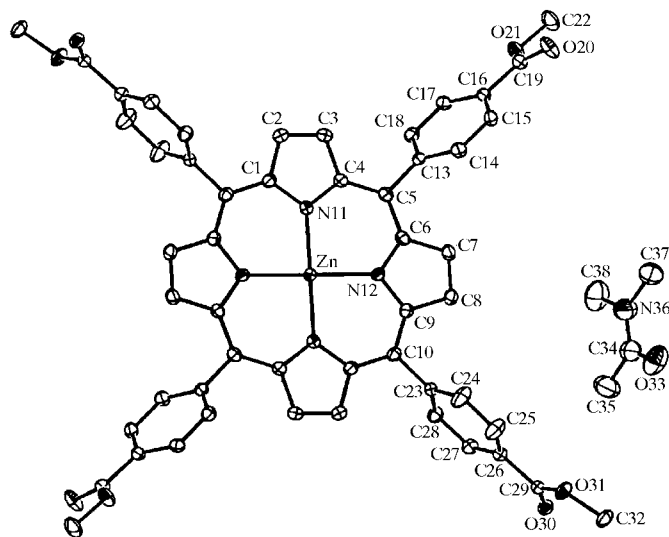


Figure 1

The molecular structure of compound (I), showing the atom-labelling scheme of the asymmetric unit. Displacement ellipsoids are drawn at the 50% probability level at ca 110 K. H atoms have been omitted for clarity. The metalloporphyrin molecule is located on a centre of inversion at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.

Similar polymer constructions have been reported previously only for the Mn-tetrakis(4-carboxyphenyl)porphyrin, with the embedded Mn ions having a distinct preference for a six-coordinate environment and exhibiting considerably shorter Mn–O axial interactions (2.2–2.3 Å; Shmilovits *et al.*, 2004a; George *et al.*, 2006). Octahedral coordination is less common for the d¹⁰ Zn ions, with lower affinity for oxo ligands than Mn, thus representing somewhat weaker though still significant interactions at Zn–O near

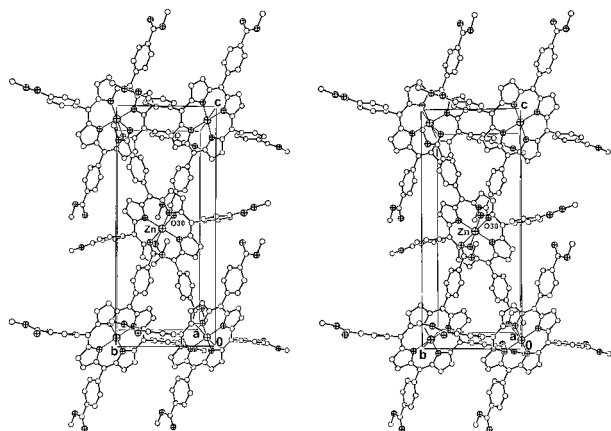


Figure 2
A stereoview, approximately down the *a* axis, of the crystal structure of (I), illustrating the coordination polymerization scheme. Each porphyrin unit is coordinated to four neighbouring species *via* two Zn–O(=C) and two (C=O)–Zn bonds of 2.540 (2) Å. The Zn, N and O atoms are indicated by darkened spheres, and the C atoms by open circles. H atoms have been omitted for clarity.

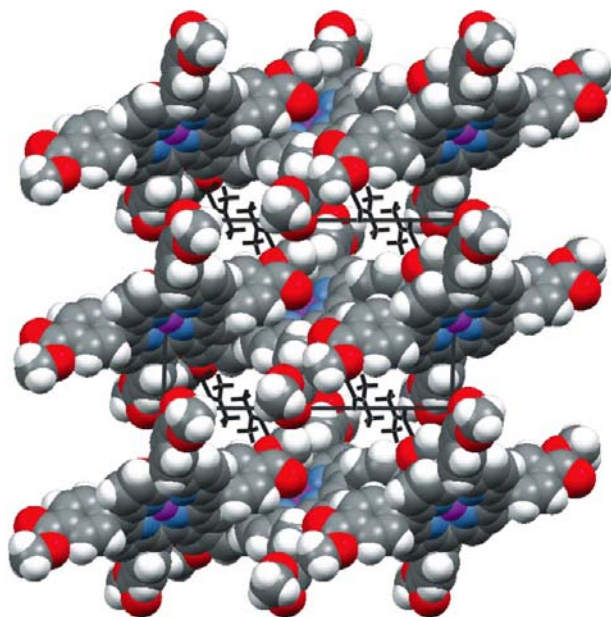


Figure 3
The crystalline architecture of (I), projected down the *b* axis of the unit cell (*c* is horizontal and *a* is vertical). The porphyrin coordination polymers (three successive corrugated layers) are shown in space-filling mode. The *N,N'*-dimethylacetamide solvent molecules intercalated between the porphyrin layers are illustrated in stick mode.

2.5 Å (Krishna Kumar *et al.*, 1998). The crystal structure of (I) consists of a stacked arrangement of the polymeric layers along the *a* axis, which do not interact directly (except by dispersion). The corresponding shortest non-bonding distance involves the terminal methoxycarbonyl substituents, with a C32...O20(2 - *x*, *y* - 3/2, 1/2 - *z*) distance of 3.351 (3) Å.

Overall, this represents an intercalated pattern, with the *N,N'*-dimethylacetamide solvent species incorporated into the interface regions parallel to the layered arrays (Fig. 3). Thus, the structure of (I) consists of uniquely assembled two-dimensional multiporphyrin arrays *via* direct coordination polymerization, which is rarely observed.

Experimental

The title porphyrin molecule was synthesized by standard literature procedures (Lindsey *et al.*, 1987; Adler *et al.*, 1970). The initially obtained free-base porphyrin derivative was fully characterized by ¹H NMR, UV-vis and MS techniques. Crystals of (I) were obtained by dissolving the metallated product in *N,N'*-dimethylacetamide, followed by slow evaporation.

Crystal data

[Zn(C₅₂H₃₆N₄O₈)]·2C₄H₉NO
M_r = 1084.46
 Monoclinic, *P*2₁/*c*
a = 13.8014 (4) Å
b = 8.9030 (4) Å
c = 21.1399 (9) Å
 β = 91.675 (3)°
V = 2596.43 (18) Å³

Z = 2
D_x = 1.387 Mg m⁻³
 Mo *K*α radiation
 μ = 0.54 mm⁻¹
T = 110 (2) K
 Needle, red
 0.45 × 0.10 × 0.10 mm

Data collection

Nonius KappaCCD area-detector diffractometer
 1° φ scans
 19518 measured reflections

6135 independent reflections
 4518 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.081
 θ_{max} = 27.9°

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.064
wR(*F*²) = 0.116
S = 1.08
 6135 reflections
 354 parameters
 H-atom parameters constrained

w = 1/[σ²(*F_o*²) + (0.0204*P*)² + 3.6188*P*]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} = 0.002
 Δρ_{max} = 0.63 e Å⁻³
 Δρ_{min} = -0.54 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Zn–N11	2.039 (2)	Zn–O30 ⁱ	2.540 (2)
Zn–N12	2.061 (2)		
N11–Zn–N12	89.63 (8)	N11 ⁱⁱ –Zn–N12	90.37 (8)

Symmetry codes: (i) -*x* + 1, *y* + 1/2, -*z* + 1/2; (ii) -*x* + 1, -*y* + 1, -*z* + 1.

The H atoms were located in calculated positions and were constrained to ride on their parent atoms, with C–H = 0.95–0.98 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C) or 1.5*U*_{eq}(methyl C).

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP III* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA3024). Services for accessing these data are described at the back of the journal.

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