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[5,10,15,20-Tetrakis(4-methoxyphenyl)-porphinato]zinc(II) 1,1,2,2-tetrachloroethane solvate

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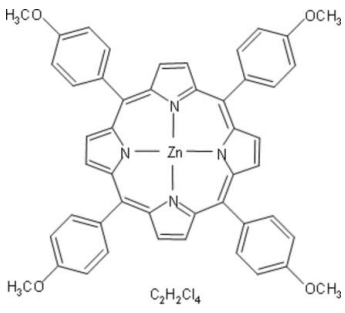
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.003 Å; disorder in main residue; R factor = 0.035; wR factor = 0.093; data-to-parameter ratio = 10.4.

In the title complex, $[Zn(C_{48}H_{36}N_4O_4)]\cdot C_2H_2Cl_4$, the Zn^{II} ion is located on an inversion centre and in an approximately square-planar coordination environment. The tetrachloroethane solvent lies across an inversion centre at the mid-point of the C—C bond. Porphyrin–porphyrin and porphyrin–solvent contacts are dominated by C—H$\cdots\pi$ and C—H$\cdots$O interactions, resulting in the formation of a clathrate-like structure. One benzene ring and its methoxy substituent are disordered over two positions, with site occupancies of 0.824 (2) and 0.176 (2). In addition, two symmetry-equivalent Cl atoms of the tetrachloroethane solvent also exhibit positional disorder, with site occupancies of 0.635 (2) and 0.365 (2).

Related literature

For background to the structural chemistry of porphyrins and metalloporphyrins, see: Senge (2000). For porphyrins that crystallize with a variety of solvents, see: Byrn *et al.* (1993). For information on C—H$\cdots\pi$ interactions, see: Nishio *et al.* (1998). For a related structure, see: Scheidt *et al.* (1986). For details of the preparation, see: Adler *et al.* (1967, 1970).



Experimental

Crystal data

$[Zn(C_{48}H_{36}N_4O_4)]\cdot C_2H_2Cl_4$
M_r = 966.01
Monoclinic, $P2_1/c$
a = 14.3347 (3) Å
b = 9.6644 (2) Å
c = 15.6369 (3) Å
β = 100.865 (1)°
V = 2127.44 (7) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.88 mm^{-1}
T = 173 (2) K
0.22 × 0.20 × 0.18 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
T_{min} = 0.830, T_{max} = 0.857
24295 measured reflections
3756 independent reflections
3427 reflections with $I > 2\sigma(I)$
R_{int} = 0.025

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.093
S = 1.08
3756 reflections
362 parameters
41 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.85 e Å^{-3}
$\Delta\rho_{min}$ = −0.66 e Å^{-3}

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C5—H5$\cdots$O2^{i}	0.93	2.51	3.273 (2)	139
C22—H22$\cdots\pi^{ii}$	0.93	2.58	3.436 (2)	153
C25—H25$\cdots\pi^{iii}$	0.93	2.69	3.598 (2)	153

Symmetry code: (i) $-x, -y, -z+3$; (ii) $-x, y-\frac{1}{2}, -z+\frac{5}{2}$; (iii) $x, y, z-1$.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2* and *SAINT-Plus* (Bruker, 2004); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-32* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2403).

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supplementary materials

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[5,10,15,20-Tetrakis(4-methoxyphenyl)porphinato]zinc(II) 1,1,2,2-tetrachloroethane solvate

P. Bhyrappa, K. Karunanithi and B. Varghese

Comment

The structural chemistry of porphyrins and metalloporphyrins is of continued interest due to the dramatic changes in the macrocycle stereochemistry that result from varying substituents at the periphery of the porphyrin (Senge, 2000). 5,10,15,20-Tetraphenylporphyrin and its metal complexes crystallize with variety of solvates resulting in the formation of porphyrin sponges (Byrn *et al.*, 1993).

The asymmetric unit of the title compound (I), comprises one half of the porphyrin unit with Zn atom on an inversion centre and one half of the 1,1,2,2,-tetrachloroethane (TCE) solvate, which is also bisected by a centre of inversion (Fig. 1). The Zn^{II} ion is four coordinate and is displaced only slightly (0.0005 (5) Å) from the mean plane of the four N atoms. This is also evident from the average angles for N1—Zn1—N2 (90.0 (6)°) and N1—Zn1—N1 (180.0 (11)°). The average Zn—N bond distance is 2.035 (12) which is similar to that reported for another ZnTPP complex (2.037 (2) Å) (Scheidt *et al.*, 1986). Further, the porphyrin ring of structure (I) showed nearly planar geometry with maximum displacement of core atoms 0.079 (2) Å only. The average Zn^{II}-to-*meso*-carbon distance 3.45 (4) Å and the average C—C bond distance in the porphyrin ring 1.404 (2) Å are comparable to those reported for the other ZnTPP complex, 3.447 (2) Å and 1.401 (3) Å respectively. The *meso* aryl groups are almost planar, oriented with an average dihedral angle of 66.9 (2)° relative to the mean plane of the porphyrin ring.

Molecular packing of the complex is stabilized by interesting intermolecular interactions. Fig. 2 shows the two-dimensional network structure formed by C—H···O and C—H···π interactions. The porphyrins shown in gray colour are *c*-translation equivalents and are interacting with two adjacent neighbors *via* a pair of C—H···O (C5—H5···O2; H5···O2 = 2.51 Å) hydrogen bonding interactions to form one-dimensional chains parallel to *c* axis. The porphyrins shown in orange colour are 2_1 screw equivalents of the gray one-dimensional chains. The angle between nearest neighbour orange and gray coloured porphyrin ring planes is 33.93°. The two one dimensional arrays are linked *via* C—H···π interactions. The interaction is formed by the H22 of the aryl group centered above the pyrrole (C3–C6/N1) unit of the neighboring porphyrin with a short H22···pyrrole (centroid) distance of 2.576 (2) Å. This is expected for C—H···π interactions (Nishio *et al.*, 1998). The two dimensional network is parallel to the *bc* plane. Further, these two dimensional networks are linked through solvate mediated C—H···π (C25—H25···C15 (aryl group)) with a H25···C15 distance of 2.695 Å (Fig. 3). This three-dimensional clathrate like structure is formed by interporphyrin and solvate-porphyrin interactions.

Experimental

5,10,15,20-tetrakis(4'-methoxy phenyl)porphyrin, $H_2T(4\text{-}OCH_3P)P$ and its $ZnT(4\text{-}OCH_3P)P$ complex were synthesized using reported literature methods (Adler *et al.*, 1967, 1970). Crystals of $ZnT(4\text{-}OCH_3P)P$ complex were grown by vapor diffusion of hexane to the 1,1,2,2-tetrachloroethane solution of the porphyrin over a period of three days.

Refinement

The C11–C16 benzene ring and its methoxy substituent are disordered over two positions. The disorder components were refined with occupancy factors 0.824 (2) and 0.176 (2) respectively. In addition, the Cl1 atom of the tetrachloroethane solvate also exhibited positional disorder and the occupancies were found to be 0.635 (2) and 0.365 (2) respectively. H atoms were placed in constrained positions with C—H = 0.90–0.98 Å) and refined using a riding model, with U_{iso}(H) = 1.2 or 1.5 times U_{eq}(C).

Figures

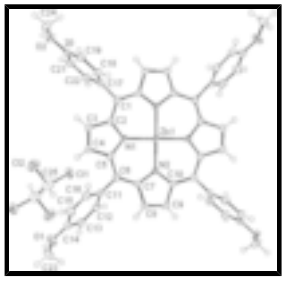

Fig. 1. The structure of (I) showing the atom numbering scheme and ellipsoids at 50% probability level. The minor disorder of the aryl ring of the asymmetric unit and Cl1' are not shown for simplicity.

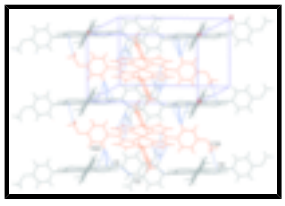

Fig. 2. Molecular packing diagram of the complex, (I). The layer structure is viewed between the *ab* and *bc* planes. Selected atoms are numbered and the molecules shown in different colors are in a slipped stack interaction. The solvates are not shown for clarity.

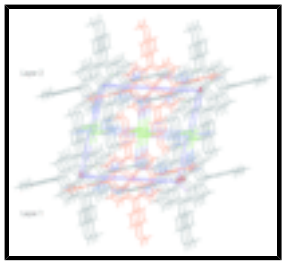

Fig. 3. Shows the bridging of two layers by solvate–porphyrin (CH···π) interactions (viewed along unit cell 'b' axis). The short contacts are shown in dotted blue lines. The TCE solvate is shown in green.

[5,10,15,20-Tetrakis(4-methoxyphenyl)porphinato]zinc(II) tetrachloroethane solvate

Crystal data

$[Zn(C_{48}H_{36}N_4O_4)]\cdot C_2H_2Cl_4$	F_{000} = 992
M_r = 966.01	D_x = 1.508 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 2458 reflections
a = 14.3347 (3) Å	θ = 2.3–28.3º
b = 9.6644 (2) Å	μ = 0.88 mm^{-1}
c = 15.6369 (3) Å	T = 173 (2) K
β = 100.865 (1)º	Plate, purple

V = 2127.44 (7) Å^3	0.22 × 0.20 × 0.18 mm
Z = 2	

Data collection

Bruker APEXII CCD area-detector diffractometer	3756 independent reflections
Radiation source: fine-focus sealed tube	3427 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.025
T = 173(2) K	θ_{max} = 25.0º
ω and φ scans	θ_{min} = 2.5º
Absorption correction: multi-scan (SADABS; Bruker, 1999)	h = −17→16
T_{min} = 0.830, T_{max} = 0.857	k = −11→11
24295 measured reflections	l = −15→18

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.035	H-atom parameters constrained
$wR(F^2)$ = 0.093	$w = 1/[\sigma^2(F_o^2) + (0.0411P)^2 + 2.7384P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.08	$(\Delta/\sigma)_{max} < 0.001$
3756 reflections	$\Delta\rho_{max}$ = 0.85 e Å^{-3}
362 parameters	$\Delta\rho_{min}$ = −0.66 e Å^{-3}
41 restraints	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
C1	0.20385 (17)	0.0792 (2)	0.98842 (15)	0.0204 (5)	
C2	0.23259 (16)	0.0947 (2)	1.07868 (15)	0.0205 (5)	

C3	0.17285 (16)	0.0793 (2)	1.13960 (15)	0.0191 (5)	
C4	0.20165 (17)	0.0936 (3)	1.23263 (15)	0.0223 (5)	
H4	0.2628	0.1115	1.2628	0.027*	
C5	0.12329 (17)	0.0763 (2)	1.26797 (15)	0.0216 (5)	
H5	0.1203	0.0821	1.3268	0.026*	
C6	0.04559 (17)	0.0472 (2)	1.19776 (14)	0.0183 (5)	
C7	−0.04665 (18)	0.0160 (2)	1.20816 (15)	0.0198 (5)	
C8	−0.12042 (17)	−0.0279 (2)	1.14119 (15)	0.0201 (5)	
C9	−0.21429 (17)	−0.0649 (3)	1.15283 (16)	0.0248 (5)	
H9	−0.2361	−0.0655	1.2052	0.030*	
C10	0.26482 (18)	0.0988 (3)	0.92600 (16)	0.0258 (5)	
H10	0.3275	0.1291	0.9379	0.031*	
C11	0.33499 (17)	0.1249 (3)	1.11235 (15)	0.0269 (6)	
C12	0.4023 (3)	0.0244 (6)	1.0961 (3)	0.0298 (9)	0.824 (4)
H12	0.3815	−0.0552	1.0649	0.036*	0.824 (4)
C13	0.4987 (2)	0.0443 (4)	1.1265 (2)	0.0322 (8)	0.824 (4)
H13	0.5424	−0.0206	1.1145	0.039*	0.824 (4)
C14	0.5297 (2)	0.1622 (6)	1.1750 (3)	0.0290 (8)	0.824 (4)
C15	0.4647 (4)	0.2595 (6)	1.1904 (3)	0.0270 (10)	0.824 (4)
H15	0.4857	0.3385	1.2223	0.032*	0.824 (4)
C16	0.3667 (4)	0.2413 (6)	1.1587 (4)	0.0296 (16)	0.824 (4)
H16	0.3237	0.3083	1.1692	0.035*	0.824 (4)
O1	0.62572 (19)	0.1691 (3)	1.20344 (19)	0.0470 (8)	0.824 (4)
C23	0.6624 (4)	0.2855 (7)	1.2535 (4)	0.0501 (14)	0.824 (4)
H23A	0.7303	0.2778	1.2692	0.075*	0.824 (4)
H23B	0.6357	0.2895	1.3053	0.075*	0.824 (4)
H23C	0.6462	0.3682	1.2200	0.075*	0.824 (4)
C12'	0.4207 (7)	0.058 (2)	1.109 (2)	0.052 (11)	0.176 (4)
H12'	0.4211	−0.0254	1.0802	0.063*	0.176 (4)
C13'	0.5058 (11)	0.118 (2)	1.1512 (11)	0.017 (4)	0.176 (4)
H13'	0.5617	0.0691	1.1525	0.021*	0.176 (4)
C14'	0.5118 (14)	0.249 (2)	1.1910 (13)	0.028 (5)	0.176 (4)
C15'	0.4331 (13)	0.333 (2)	1.1942 (9)	0.026 (4)	0.176 (4)
H15'	0.4323	0.4217	1.2167	0.032*	0.176 (4)
C16'	0.3557 (18)	0.251 (3)	1.156 (4)	0.073 (18)	0.176 (4)
H16'	0.2994	0.2959	1.1603	0.088*	0.176 (4)
O1'	0.5969 (10)	0.3082 (12)	1.2332 (8)	0.037 (3)	0.176 (4)
C23'	0.679 (2)	0.222 (3)	1.242 (2)	0.059 (9)	0.176 (4)
H23D	0.7334	0.2711	1.2721	0.089*	0.176 (4)
H23E	0.6892	0.1955	1.1851	0.089*	0.176 (4)
H23F	0.6694	0.1401	1.2742	0.089*	0.176 (4)
C17	−0.07009 (17)	0.0322 (2)	1.29712 (15)	0.0192 (5)	
C18	−0.07731 (18)	0.1626 (3)	1.33222 (15)	0.0235 (5)	
H18	−0.0643	0.2402	1.3013	0.028*	
C19	−0.10368 (18)	0.1796 (3)	1.41266 (15)	0.0238 (5)	
H19	−0.1096	0.2679	1.4347	0.029*	
C20	−0.12117 (16)	0.0641 (3)	1.45993 (14)	0.0207 (5)	
C21	−0.11288 (17)	−0.0672 (3)	1.42651 (15)	0.0230 (5)	
H21	−0.1242	−0.1447	1.4583	0.028*	

C22	−0.08777 (17)	−0.0828 (3)	1.34588 (15)	0.0230 (5)	
H22	−0.0826	−0.1712	1.3238	0.028*	
N1	0.07740 (13)	0.0496 (2)	1.11961 (12)	0.0181 (4)	
N2	0.11500 (14)	0.0388 (2)	0.94572 (12)	0.0189 (4)	
O2	−0.14729 (13)	0.06812 (18)	1.53955 (10)	0.0260 (4)	
Zn1	0.0000	0.0000	1.0000	0.01790 (13)	
C24	−0.1517 (2)	0.2008 (3)	1.57856 (17)	0.0345 (6)	
H24A	−0.1707	0.1903	1.6339	0.052*	
H24B	−0.1970	0.2576	1.5412	0.052*	
H24C	−0.0902	0.2437	1.5868	0.052*	
C25	0.5331 (2)	0.5607 (4)	0.01066 (19)	0.0591 (10)	
H25	0.5176	0.6286	−0.0364	0.071*	
Cl1	0.6542 (2)	0.5167 (3)	0.0212 (3)	0.0287 (7)	0.365 (4)
Cl1'	0.6484 (2)	0.4852 (5)	0.0185 (3)	0.1116 (16)	0.635 (4)
Cl2	0.51877 (7)	0.64070 (10)	0.10872 (6)	0.0602 (3)	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0220 (12)	0.0208 (12)	0.0196 (11)	0.0006 (9)	0.0072 (9)	−0.0011 (9)
C2	0.0206 (12)	0.0214 (12)	0.0198 (12)	0.0012 (9)	0.0041 (9)	0.0001 (9)
C3	0.0221 (12)	0.0183 (11)	0.0173 (11)	0.0010 (9)	0.0044 (9)	−0.0006 (9)
C4	0.0223 (12)	0.0261 (12)	0.0172 (11)	−0.0002 (10)	0.0007 (9)	0.0013 (9)
C5	0.0287 (13)	0.0231 (12)	0.0133 (11)	0.0010 (10)	0.0047 (9)	0.0013 (9)
C6	0.0243 (12)	0.0161 (11)	0.0152 (11)	0.0005 (9)	0.0052 (9)	0.0000 (9)
C7	0.0286 (13)	0.0168 (11)	0.0155 (11)	0.0002 (9)	0.0084 (10)	0.0006 (9)
C8	0.0250 (12)	0.0206 (11)	0.0158 (11)	−0.0003 (9)	0.0070 (9)	0.0004 (9)
C9	0.0262 (13)	0.0320 (14)	0.0184 (12)	−0.0021 (11)	0.0101 (10)	−0.0001 (10)
C10	0.0219 (12)	0.0346 (14)	0.0222 (12)	−0.0035 (10)	0.0078 (10)	−0.0012 (10)
C11	0.0223 (13)	0.0426 (15)	0.0163 (11)	−0.0027 (11)	0.0049 (10)	0.0046 (11)
C12	0.0205 (16)	0.043 (2)	0.027 (2)	0.0000 (19)	0.0052 (15)	0.0005 (18)
C13	0.0204 (16)	0.040 (2)	0.0372 (19)	0.0063 (15)	0.0070 (14)	−0.0082 (17)
C14	0.024 (2)	0.040 (3)	0.0238 (18)	−0.003 (2)	0.0055 (16)	−0.0030 (19)
C15	0.029 (3)	0.030 (3)	0.0217 (17)	−0.007 (2)	0.005 (2)	−0.0040 (16)
C16	0.029 (2)	0.044 (3)	0.0154 (19)	−0.0155 (16)	0.0049 (14)	0.0014 (15)
O1	0.0206 (14)	0.0656 (19)	0.0525 (17)	−0.0016 (13)	0.0010 (12)	−0.0158 (15)
C23	0.025 (3)	0.068 (4)	0.053 (3)	−0.013 (3)	−0.004 (2)	−0.008 (3)
C12'	0.052 (11)	0.053 (11)	0.052 (11)	−0.0004 (12)	0.010 (2)	0.0005 (12)
C13'	0.017 (4)	0.017 (4)	0.017 (4)	0.0003 (11)	0.0033 (14)	−0.0006 (11)
C14'	0.025 (12)	0.035 (13)	0.024 (9)	−0.004 (12)	0.008 (10)	−0.006 (8)
C15'	0.036 (10)	0.025 (9)	0.019 (7)	0.001 (8)	0.007 (6)	−0.002 (7)
C16'	0.073 (18)	0.074 (18)	0.073 (18)	−0.0004 (12)	0.014 (3)	0.0002 (12)
O1'	0.021 (7)	0.046 (7)	0.043 (7)	−0.002 (5)	−0.001 (5)	−0.006 (5)
C23'	0.039 (16)	0.050 (17)	0.08 (2)	0.010 (15)	0.002 (14)	−0.005 (15)
C17	0.0206 (12)	0.0236 (12)	0.0142 (11)	−0.0021 (9)	0.0055 (9)	−0.0004 (9)
C18	0.0309 (13)	0.0221 (12)	0.0183 (11)	−0.0042 (10)	0.0064 (10)	0.0033 (9)
C19	0.0320 (13)	0.0203 (12)	0.0195 (12)	−0.0022 (10)	0.0057 (10)	−0.0047 (10)
C20	0.0217 (12)	0.0264 (12)	0.0144 (11)	−0.0029 (10)	0.0044 (9)	−0.0011 (9)

C21	0.0308 (13)	0.0196 (12)	0.0195 (12)	−0.0047 (10)	0.0074 (10)	0.0031 (9)
C22	0.0302 (13)	0.0193 (12)	0.0206 (12)	−0.0018 (10)	0.0077 (10)	−0.0017 (9)
N1	0.0210 (10)	0.0199 (10)	0.0143 (9)	−0.0005 (8)	0.0060 (8)	−0.0009 (8)
N2	0.0209 (10)	0.0219 (10)	0.0144 (9)	−0.0007 (8)	0.0048 (8)	−0.0020 (8)
O2	0.0385 (10)	0.0268 (9)	0.0157 (8)	−0.0039 (8)	0.0126 (7)	−0.0028 (7)
Zn1	0.0195 (2)	0.0215 (2)	0.0137 (2)	−0.00120 (14)	0.00548 (15)	−0.00173 (14)
C24	0.0541 (18)	0.0313 (15)	0.0221 (13)	−0.0005 (13)	0.0173 (12)	−0.0059 (11)
C25	0.088 (3)	0.057 (2)	0.0350 (17)	0.002 (2)	0.0174 (18)	0.0028 (16)
Cl1	0.0267 (15)	0.0282 (11)	0.0323 (15)	0.0000 (9)	0.0084 (11)	0.0027 (8)
Cl1'	0.0485 (16)	0.205 (4)	0.082 (2)	0.0286 (19)	0.0141 (14)	0.029 (2)
Cl2	0.0749 (6)	0.0646 (6)	0.0448 (5)	−0.0015 (5)	0.0203 (4)	−0.0157 (4)

Geometric parameters (Å, °)

C1—N2	1.378 (3)	C12'—C13'	1.397 (5)
C1—C2	1.402 (3)	C12'—H12'	0.9300
C1—C10	1.440 (3)	C13'—C14'	1.399 (5)
C2—C3	1.404 (3)	C13'—H13'	0.9300
C2—C11	1.492 (3)	C14'—O1'	1.40 (2)
C3—N1	1.375 (3)	C14'—C15'	1.400 (5)
C3—C4	1.442 (3)	C15'—C16'	1.400 (5)
C4—C5	1.352 (3)	C15'—H15'	0.9300
C4—H4	0.9300	C16'—H16'	0.9300
C5—C6	1.437 (3)	O1'—C23'	1.43 (3)
C5—H5	0.9300	C23'—H23D	0.9600
C6—N1	1.383 (3)	C23'—H23E	0.9600
C6—C7	1.395 (3)	C23'—H23F	0.9600
C7—C8	1.406 (3)	C17—C18	1.386 (3)
C7—C17	1.500 (3)	C17—C22	1.398 (3)
C8—N2^{i}	1.380 (3)	C18—C19	1.390 (3)
C8—C9	1.437 (3)	C18—H18	0.9300
C9—C10^{i}	1.347 (4)	C19—C20	1.387 (3)
C9—H9	0.9300	C19—H19	0.9300
C10—C9^{i}	1.347 (4)	C20—O2	1.367 (3)
C10—H10	0.9300	C20—C21	1.386 (4)
C11—C16	1.368 (5)	C21—C22	1.383 (3)
C11—C12'	1.395 (5)	C21—H21	0.9300
C11—C16'	1.401 (5)	C22—H22	0.9300
C11—C12	1.426 (5)	N1—Zn1	2.0436 (18)
C12—C13	1.387 (6)	N2—C8^{i}	1.380 (3)
C12—H12	0.9300	N2—Zn1	2.0265 (19)
C13—C14	1.394 (6)	O2—C24	1.426 (3)
C13—H13	0.9300	Zn1—N2^{i}	2.0264 (19)
C14—O1	1.366 (5)	Zn1—N1^{i}	2.0436 (18)
C14—C15	1.377 (6)	C24—H24A	0.9600
C15—C16	1.410 (7)	C24—H24B	0.9600
C15—H15	0.9300	C24—H24C	0.9600
C16—H16	0.9300	C25—C25^{ii}	1.507 (7)

O1—C23	1.414 (7)	C25—Cl1	1.764 (4)
C23—H23A	0.9600	C25—Cl2	1.764 (3)
C23—H23B	0.9600	C25—Cl1'	1.789 (4)
C23—H23C	0.9600	C25—H25	0.9800
N2—C1—C2	126.0 (2)	C12'—C13'—H13'	118.1
N2—C1—C10	109.4 (2)	C14'—C13'—H13'	118.1
C2—C1—C10	124.6 (2)	O1'—C14'—C13'	123.8 (17)
C1—C2—C3	124.8 (2)	O1'—C14'—C15'	112.4 (15)
C1—C2—C11	117.3 (2)	C13'—C14'—C15'	123.8 (16)
C3—C2—C11	117.8 (2)	C16'—C15'—C14'	104 (2)
N1—C3—C2	125.2 (2)	C16'—C15'—H15'	128.2
N1—C3—C4	109.4 (2)	C14'—C15'—H15'	128.2
C2—C3—C4	125.4 (2)	C15'—C16'—C11	141 (2)
C5—C4—C3	107.4 (2)	C15'—C16'—H16'	109.5
C5—C4—H4	126.3	C11—C16'—H16'	109.5
C3—C4—H4	126.3	C14'—O1'—C23'	115.7 (19)
C4—C5—C6	107.2 (2)	O1'—C23'—H23D	109.5
C4—C5—H5	126.4	O1'—C23'—H23E	109.5
C6—C5—H5	126.4	H23D—C23'—H23E	109.5
N1—C6—C7	125.8 (2)	O1'—C23'—H23F	109.5
N1—C6—C5	109.6 (2)	H23D—C23'—H23F	109.5
C7—C6—C5	124.6 (2)	H23E—C23'—H23F	109.5
C6—C7—C8	125.1 (2)	C18—C17—C22	118.2 (2)
C6—C7—C17	117.9 (2)	C18—C17—C7	120.6 (2)
C8—C7—C17	117.0 (2)	C22—C17—C7	121.2 (2)
$N2^{i}$—C8—C7	125.6 (2)	C17—C18—C19	121.3 (2)
$N2^{i}$—C8—C9	109.5 (2)	C17—C18—H18	119.4
C7—C8—C9	124.9 (2)	C19—C18—H18	119.4
$C10^{i}$—C9—C8	107.4 (2)	C20—C19—C18	119.7 (2)
$C10^{i}$—C9—H9	126.3	C20—C19—H19	120.2
C8—C9—H9	126.3	C18—C19—H19	120.2
$C9^{i}$—C10—C1	107.3 (2)	O2—C20—C21	115.3 (2)
$C9^{i}$—C10—H10	126.3	O2—C20—C19	124.8 (2)
C1—C10—H10	126.3	C21—C20—C19	119.9 (2)
C16—C11—C12'	100.9 (8)	C22—C21—C20	119.9 (2)
C12'—C11—C16'	108.1 (14)	C22—C21—H21	120.0
C16—C11—C12	119.1 (4)	C20—C21—H21	120.0
C16'—C11—C12	126.2 (12)	C21—C22—C17	121.0 (2)
C16—C11—C2	123.7 (4)	C21—C22—H22	119.5
C12'—C11—C2	135.4 (8)	C17—C22—H22	119.5
C16'—C11—C2	116.5 (11)	C3—N1—C6	106.40 (18)
C12—C11—C2	117.2 (3)	C3—N1—Zn1	127.04 (15)
C13—C12—C11	120.6 (5)	C6—N1—Zn1	126.32 (15)
C13—C12—H12	119.7	C1—N2—$C8^{i}$	106.28 (19)
C11—C12—H12	119.7	C1—N2—Zn1	126.86 (15)
C12—C13—C14	119.6 (4)	$C8^{i}$—N2—Zn1	126.85 (16)
C12—C13—H13	120.2	C20—O2—C24	117.18 (19)

C14—C13—H13	120.2	$N2^{i}$—Zn1—N2	180.0
O1—C14—C15	125.6 (5)	$N2^{i}$—Zn1—$N1^{i}$	89.75 (8)
O1—C14—C13	114.5 (4)	N2—Zn1—$N1^{i}$	90.25 (8)
C15—C14—C13	119.8 (4)	$N2^{i}$—Zn1—N1	90.25 (8)
C14—C15—C16	121.0 (4)	N2—Zn1—N1	89.75 (8)
C14—C15—H15	119.5	$N1^{i}$—Zn1—N1	180.0
C16—C15—H15	119.5	O2—C24—H24A	109.5
C11—C16—C15	119.9 (5)	O2—C24—H24B	109.5
C11—C16—H16	120.0	H24A—C24—H24B	109.5
C15—C16—H16	120.0	O2—C24—H24C	109.5
C14—O1—C23	117.8 (4)	H24A—C24—H24C	109.5
O1—C23—H23A	109.5	H24B—C24—H24C	109.5
O1—C23—H23B	109.5	$C25^{ii}$—C25—Cl1	113.7 (3)
H23A—C23—H23B	109.5	$C25^{ii}$—C25—Cl2	111.2 (3)
O1—C23—H23C	109.5	Cl1—C25—Cl2	107.4 (2)
H23A—C23—H23C	109.5	$C25^{ii}$—C25—Cl1'	103.5 (3)
H23B—C23—H23C	109.5	Cl2—C25—Cl1'	112.1 (2)
C11—C12'—C13'	119.3 (13)	$C25^{ii}$—C25—H25	108.1
C11—C12'—H12'	120.4	Cl1—C25—H25	108.1
C13'—C12'—H12'	120.4	Cl2—C25—H25	108.1
C12'—C13'—C14'	123.9 (16)	Cl1'—C25—H25	113.6
N2—C1—C2—C3	−4.1 (4)	C12—C11—C12'—C13'	−175 (7)
C10—C1—C2—C3	178.2 (2)	C2—C11—C12'—C13'	−178.8 (13)
N2—C1—C2—C11	173.7 (2)	C11—C12'—C13'—C14'	−5(4)
C10—C1—C2—C11	−3.9 (4)	C12'—C13'—C14'—O1'	180 (2)
C1—C2—C3—N1	−1.3 (4)	C12'—C13'—C14'—C15'	1(3)
C11—C2—C3—N1	−179.1 (2)	O1'—C14'—C15'—C16'	−175 (3)
C1—C2—C3—C4	179.4 (2)	C13'—C14'—C15'—C16'	4(4)
C11—C2—C3—C4	1.5 (4)	C14'—C15'—C16'—C11	−6(9)
N1—C3—C4—C5	−1.6 (3)	C16—C11—C16'—C15'	20 (14)
C2—C3—C4—C5	177.8 (2)	C12'—C11—C16'—C15'	2(9)
C3—C4—C5—C6	1.6 (3)	C12—C11—C16'—C15'	3(10)
C4—C5—C6—N1	−1.1 (3)	C2—C11—C16'—C15'	−176 (6)
C4—C5—C6—C7	176.6 (2)	C13'—C14'—O1'—C23'	−6(3)
N1—C6—C7—C8	4.9 (4)	C15'—C14'—O1'—C23'	173 (2)
C5—C6—C7—C8	−172.4 (2)	C6—C7—C17—C18	71.2 (3)
N1—C6—C7—C17	−174.2 (2)	C8—C7—C17—C18	−108.0 (3)
C5—C6—C7—C17	8.6 (3)	C6—C7—C17—C22	−110.6 (3)
C6—C7—C8—$N2^{i}$	−4.2 (4)	C8—C7—C17—C22	70.3 (3)
C17—C7—C8—$N2^{i}$	174.8 (2)	C22—C17—C18—C19	−1.6 (4)
C6—C7—C8—C9	177.5 (2)	C7—C17—C18—C19	176.7 (2)
C17—C7—C8—C9	−3.4 (4)	C17—C18—C19—C20	1.4 (4)
$N2^{i}$—C8—C9—$C10^{i}$	0.4 (3)	C18—C19—C20—O2	179.9 (2)
C7—C8—C9—$C10^{i}$	178.9 (2)	C18—C19—C20—C21	−0.4 (4)
N2—C1—C10—$C9^{i}$	−2.5 (3)	O2—C20—C21—C22	179.3 (2)
C2—C1—C10—$C9^{i}$	175.5 (2)	C19—C20—C21—C22	−0.4 (4)

C1—C2—C11—C16	120.1 (4)	C20—C21—C22—C17	0.2 (4)
C3—C2—C11—C16	−61.9 (5)	C18—C17—C22—C21	0.7 (4)
C1—C2—C11—C12'	−60 (2)	C7—C17—C22—C21	−177.5 (2)
C3—C2—C11—C12'	118 (2)	C2—C3—N1—C6	−178.5 (2)
C1—C2—C11—C16'	118 (3)	C4—C3—N1—C6	1.0 (3)
C3—C2—C11—C16'	−64 (3)	C2—C3—N1—Zn1	6.9 (3)
C1—C2—C11—C12	−61.1 (4)	C4—C3—N1—Zn1	−173.64 (16)
C3—C2—C11—C12	116.9 (3)	C7—C6—N1—C3	−177.6 (2)
C16—C11—C12—C13	−0.2 (6)	C5—C6—N1—C3	0.0 (3)
C12'—C11—C12—C13	4(5)	C7—C6—N1—Zn1	−2.9 (3)
C16'—C11—C12—C13	2(3)	C5—C6—N1—Zn1	174.68 (15)
C2—C11—C12—C13	−179.0 (3)	C2—C1—N2—C8^{i}	−175.8 (2)
C11—C12—C13—C14	1.5 (6)	C10—C1—N2—C8^{i}	2.2 (3)
C12—C13—C14—O1	178.3 (4)	C2—C1—N2—Zn1	3.3 (3)
C12—C13—C14—C15	−1.7 (6)	C10—C1—N2—Zn1	−178.80 (16)
O1—C14—C15—C16	−179.3 (5)	C21—C20—O2—C24	176.7 (2)
C13—C14—C15—C16	0.7 (6)	C19—C20—O2—C24	−3.6 (3)
C12'—C11—C16—C15	−2.1 (16)	C1—N2—Zn1—N1^{i}	−178.9 (2)
C16'—C11—C16—C15	−165 (22)	C8^{i}—N2—Zn1—N1^{i}	0.0 (2)
C12—C11—C16—C15	−0.8 (8)	C1—N2—Zn1—N1	1.1 (2)
C2—C11—C16—C15	178.0 (4)	C8^{i}—N2—Zn1—N1	180.0 (2)
C14—C15—C16—C11	0.5 (8)	C3—N1—Zn1—N2^{i}	174.09 (19)
C15—C14—O1—C23	0.3 (6)	C6—N1—Zn1—N2^{i}	0.53 (19)
C13—C14—O1—C23	−179.7 (4)	C3—N1—Zn1—N2	−5.91 (19)
C16—C11—C12'—C13'	1(3)	C6—N1—Zn1—N2	−179.47 (19)
C16'—C11—C12'—C13'	4(4)		

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5···O2^{iii}	0.93	2.51	3.273 (2)	139 (2)
C22—H22···π^{iv}	0.93	2.58	3.436 (2)	153
C25—H25···π^{v}	0.93	2.69	3.598 (2)	153

Symmetry codes: (iii) −*x*, −*y*, −*z*+3; (iv) −*x*, *y*−1/2, −*z*+5/2; (v) *x*, *y*, *z*−1.

Fig. 1

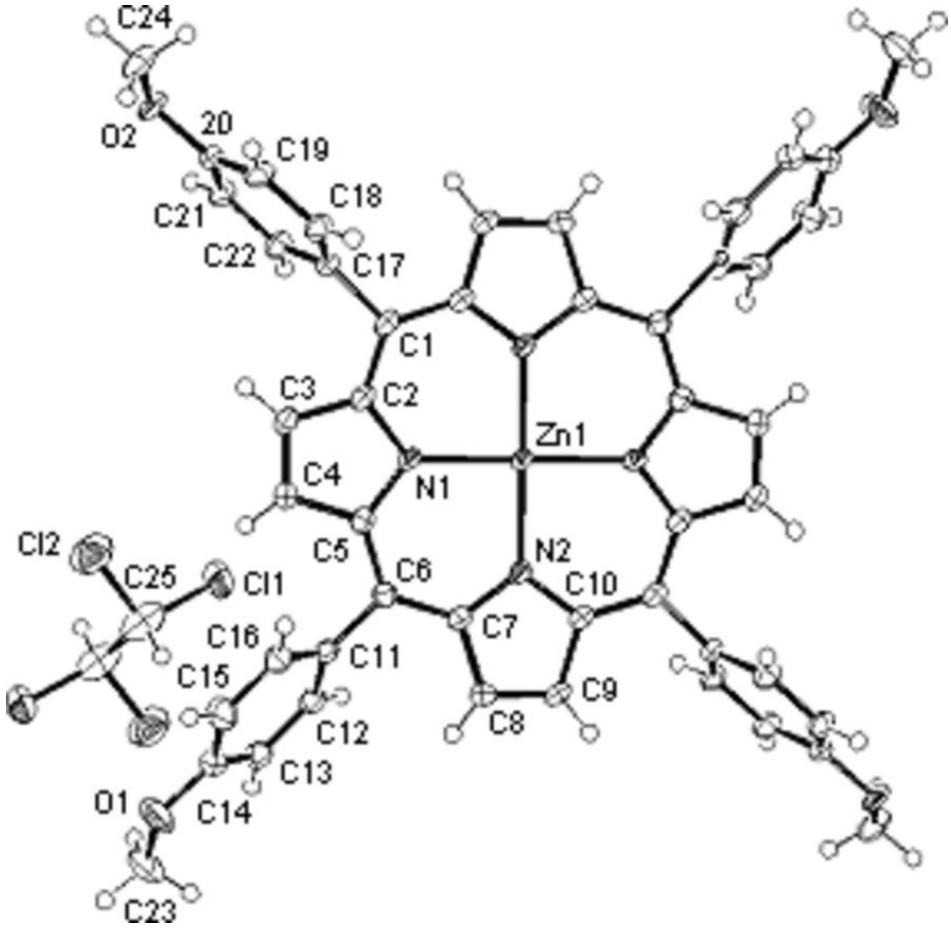
C24
O2
20
C19
C18
C21
C22
C17
C1
C3
C2
Zn1
C4
N1
Cl2
C5
N2
C25
Cl1
C6
C10
C16
C7
C11
C15
C9
C12
C8
C13
O1
C14
C23

Fig. 2

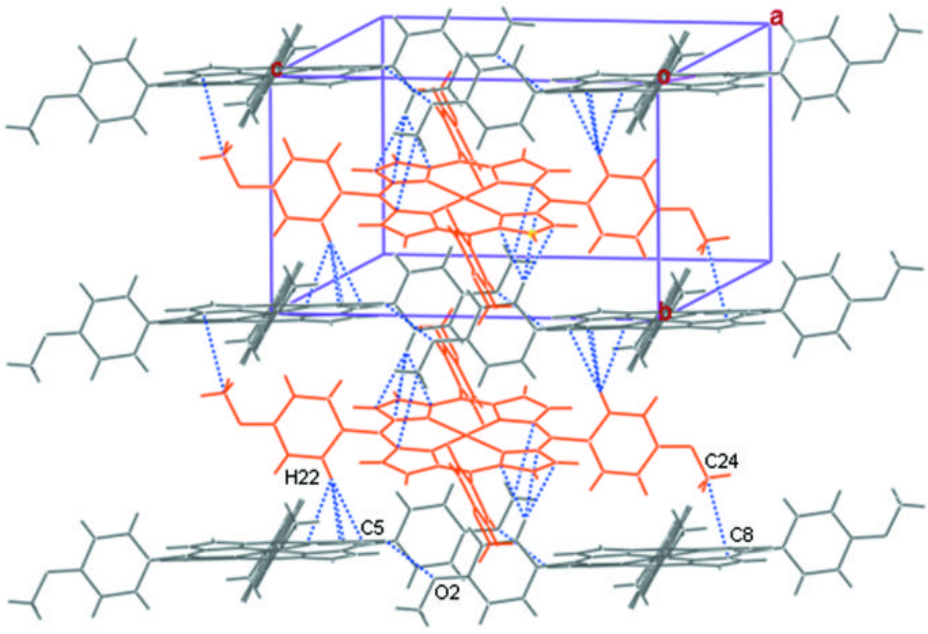

Fig. 3