

Sophia Lipstman and
Israel Goldberg*School of Chemistry, Sackler Faculty of Exact
Sciences, Tel-Aviv University, Ramat-Aviv,
69978 Tel-Aviv, Israel

Correspondence e-mail: goldberg@post.tau.ac.il

Key indicators

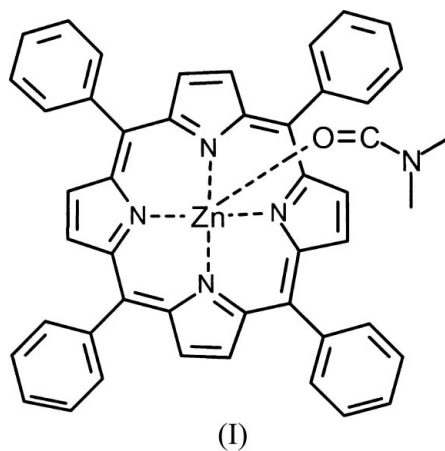
Single-crystal X-ray study
 $T = 110$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
 R factor = 0.052
 wR factor = 0.132
Data-to-parameter ratio = 17.8For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Unsolvated (dimethylformamide)(tetraphenyl-
porphyrinato)zinc(II)

The title compound, $[\text{Zn}(\text{C}_{44}\text{H}_{28}\text{N}_4)(\text{C}_3\text{H}_7\text{NO})]$, is a square-pyramidal five-coordinate zinc–porphyrin complex with N,N' -dimethylformamide as an apical ligand. The crystal structure is characterized by a layered organization of the porphyrin species with tight stacking of the corrugated layers along the b axis.

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Comment

Numerous four-, five- and six-coordinate complexes of metallo-tetraphenylporphyrins have been reported with a wide variety of crystallization solvents (many of these compounds form clathrates) and axial/apical ligands coordinated to the metal centre (Byrn, *et al.*, 1991; Byrn *et al.*, 1993). Porphyrin complexes with dimethylformamide as an axial or apical ligand include Zn^{II} -tetra(4-hydroxyphenyl)porphyrin (Goldberg *et al.*, 1995), Mn^{III} -tetraphenylporphyrin perchlorate (Hill & Williamson, 1985), Zr^{IV} -tetraphenylporphyrin dichloride (Tutass *et al.*, 2002), and Zn^{II} -tetraphenylporphyrin (Droege *et al.*, 1994). The latter crystallized as a dichloromethane solvate. The present report provides information on the title five-coordinate complex, (I) (Fig. 1), determined at low temperature (*ca* 110 K).



In the crystal structure, the porphyrin core is slightly saddled, with the inner pyrrole N atoms deviating ± 0.023 (1) Å from their mean plane. The zinc ion is displaced by 0.329 (1) Å from this N_4 plane towards the apical ligand, imparting to the metalloporphyrin entity a domed structure (Fig. 2), which is typical of many five-coordinate complexes of metallated tetraarylporphyrins (Allen, 2002).

Efficient crystal packing of the molecules of (I) (Fig. 3) is realized by corrugated layers of the metalloporphyrin species running perpendicular to the b axis. Adjacent inversion-

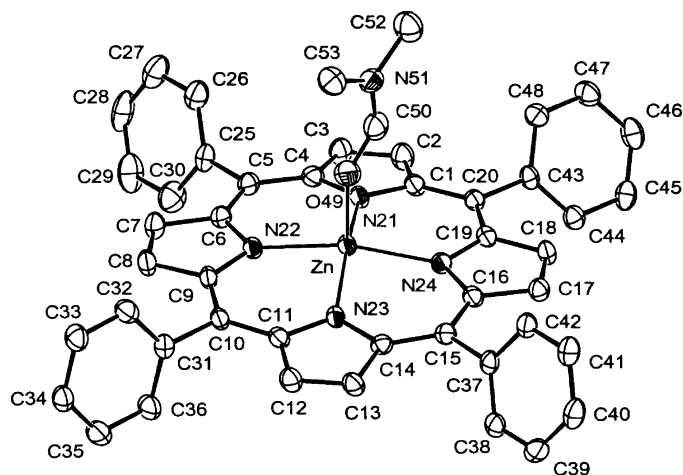


Figure 1

Molecular structure of the title compound, with the atom-labelling scheme. Displacement parameters are drawn at the 50% probability level. H atoms have been omitted.

related layers fit tightly into one another; the apical ligands of one layer are inserted between the porphyrin frameworks of neighbouring layers. The parallel offset of these layers allows a close van der Waals contact between the concave surface of a given metalloporphyrin core and a phenyl ring from another layer. The corresponding shortest non-bonding distances include: $C4 \cdots C35(1-x, -y, 2-z) = 3.583(2) \text{ \AA}$, $N22 \cdots C36(1-x, -y, 2-z) = 3.459(2) \text{ \AA}$, and $C6 \cdots C36(1-x, -y, 2-z) = 3.463(2) \text{ \AA}$. This concave surface is in van der Waals contact with one of the methyl residues from the nearest layer translated along **b**. The apical ligand from one layer penetrates through the nearest layer, approaching the porphyrin core [$N24 \cdots C52(x, 1+y, z) = 3.776(3) \text{ \AA}$]. The geometry of the coordination around the zinc ion (Table 1) shows standard values (Allen, 2002, Vinodu & Goldberg, 2004).

Experimental

The crystals of the title compound were obtained as a side product by dissolving zinc-tetraphenylporphyrin (6.8 mg, 0.01 mmol) in *N,N*-dimethylformamide (2 ml) in the presence of tris(acetoneperoxide) (2.2 mg, 0.01 mmol) while attempting to generate new porphyrin complexes.

Crystal data

$[\text{Zn}(\text{C}_{44}\text{H}_{28}\text{N}_4)(\text{C}_3\text{H}_7\text{NO})]$	$D_x = 1.371 \text{ Mg m}^{-3}$
$M_r = 751.17$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 8468 reflections
$a = 13.7419(3) \text{ \AA}$	$\theta = 2.3\text{--}28.2^\circ$
$b = 9.2278(2) \text{ \AA}$	$\mu = 0.72 \text{ mm}^{-1}$
$c = 29.3016(7) \text{ \AA}$	$T = 110(2) \text{ K}$
$\beta = 101.7186(13)^\circ$	Prism, red
$V = 3638.22(14) \text{ \AA}^3$	$0.20 \times 0.15 \times 0.15 \text{ mm}$
$Z = 4$	

Data collection

Nonius KappaCCD diffractometer	$R_{\text{int}} = 0.059$
φ and ω scans	$\theta_{\text{max}} = 28.2^\circ$
29748 measured reflections	$h = -18 \rightarrow 18$
8697 independent reflections	$k = -12 \rightarrow 12$
5627 reflections with $I > 2\sigma(I)$	$l = -38 \rightarrow 37$

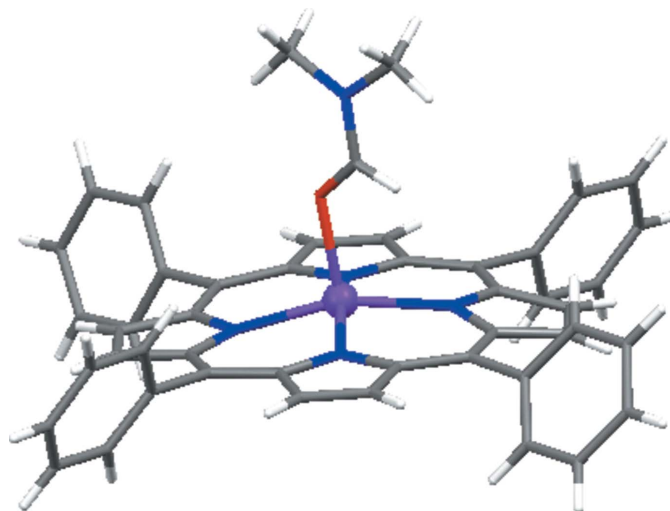


Figure 2

Stick illustration of the domed molecular structure. The Zn atom is represented by a small sphere. Colour code: C dark grey, H white, N blue, O red, Zn violet.

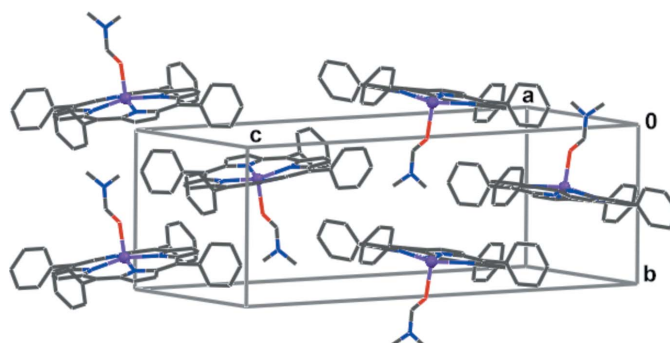


Figure 3

Crystal packing of the title compound, illustrating the tight layered intermolecular organization. H atoms have been omitted for clarity. Zn atoms are represented by small spheres. Colour code: C dark grey, N blue, O red, Zn violet.

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.052$
 $wR(F^2) = 0.132$
 $S = 1.03$
 8697 reflections
 489 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.058P)^2 + 1.2438P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.003$
 $\Delta\rho_{\text{max}} = 0.85 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.64 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

Zn—N22	2.054(2)	Zn—N21	2.091(2)
Zn—N24	2.065(2)	Zn—O49	2.150(2)
Zn—N23	2.073(2)		
N22—Zn—N24	162.90(9)	N22—Zn—O49	99.08(8)
N22—Zn—N23	88.74(8)	N24—Zn—O49	98.01(8)
N24—Zn—N23	88.64(8)	N23—Zn—O49	96.81(8)
N22—Zn—N21	88.81(8)	N21—Zn—O49	102.67(8)
N24—Zn—N21	88.04(8)	C50—O49—Zn	126.0(2)
N23—Zn—N21	160.51(9)		

H atoms were placed in calculated positions and constrained to ride on their parent atoms, with C–H distances in the range 0.95–0.98 Å and with $U_{\text{iso}}(\text{H}) = 1.2$ or 1.5 times $U_{\text{eq}}(\text{C})$.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *MERCURY* (Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997).

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