metal-organic papers

(Dimethylacetamide)(tetraphenylporphyrinato)-zinc(II)

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The title compound, [Zn($C_{44}H_{28}N_4$)(C_4H_9NO)], represents a five-coordinate zinc–porphyrin complex with N,N'-dimethyl-acetamide as an axial ligand of typical domed geometry. The latter reveals a twofold orientational disorder. The crystal structure is characterized by a layered organization of the porphyrin species. In a given layer, all axial ligands are oriented in the same direction, while neighboring layers are related to each other by crystallographic inversion.

Comment

Numerous four-, five- and six-coordinate complexes of metallo-tetraphenylporphyrin have been reported with a wide variety of axial ligands coordinating to the metal center (Byrn *et al.*, 1991, 1993). Porphyrin complexes with dimethyl-formamide as an axial ligand are known for the Zn^{II}–tetra-kis(4-hydroxyphenyl)porphyrin (Goldberg *et al.*, 1995), Mn^{III}–tetraphenylporphyrin perchlorate (Hill & Williamson, 1985), Zr^{IV}–tetraphenylporphyrin dichloride (Tutass *et al.*, 2002), Zn^{II}–tetraphenylporphyrin (Lipstman & Goldberg, 2006) and Zn^{II}–tetraphenylporphyrin dichloromethane solvate (Droege *et al.*, 1994). However, only a single report of an analogous complex with N,N'-dimethylacetamide as an axial ligand bound to tetrakis(4-pyridyl)zinc porphyrin has been recently published (Carlucci *et al.*, 2005).

(I)
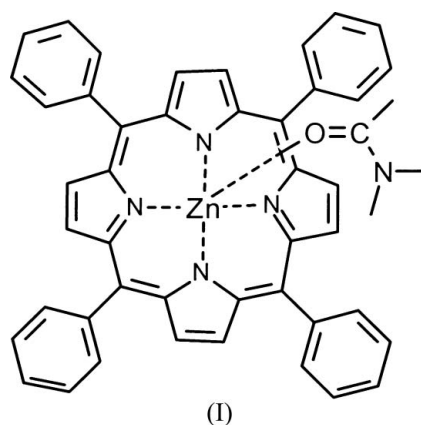
The present report provides complementary information for the five-coordinate complex of the title compound, (I), precisely analysed at *ca* 110 K (Fig. 1). In this structure, the porphyrin core is markedly saddled. This is well reflected in the dihedral angles between the planes of the *trans*-related pyrrole rings. Thus, the dihedral angle between the N21- and N23-pyrroles is 25.35 (9)°, their planes folding downward away from the axial ligand. The corresponding angle between
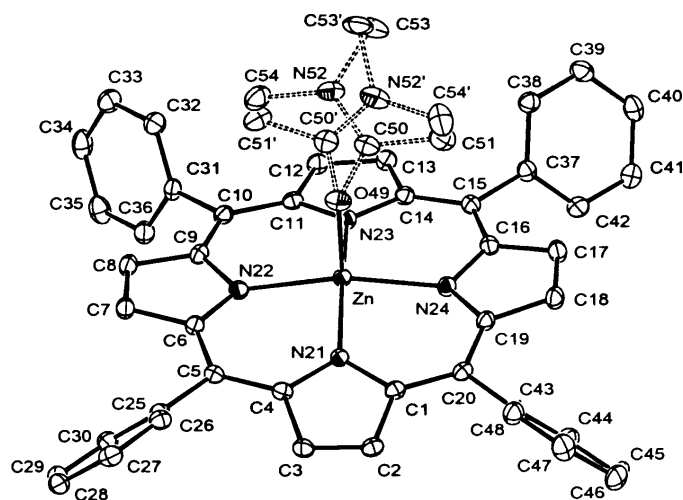
Figure 1
The molecular structure of the title compound, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probablity level at *ca* 110 K. The orientationally disordered dimethylacetamide ligand is denoted by dashed bonds. H atoms have been omitted.
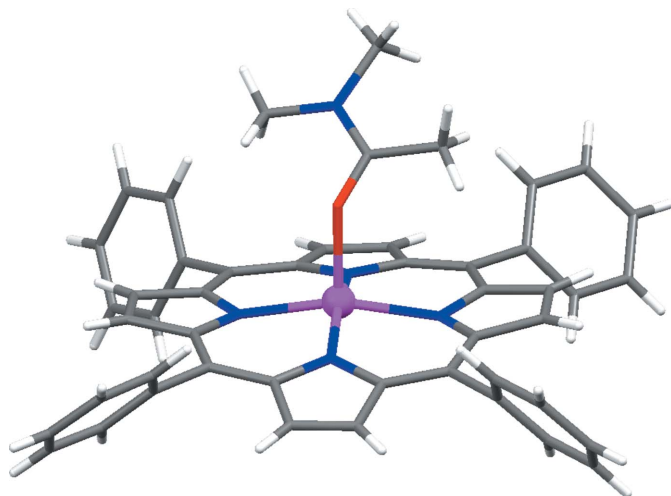

Figure 2
Stick illustration of the domed molecular structure. The Zn atom is represented by a small sphere. Color code: C dark grey, H white, N blue, O red, and Zn violet. In Figs. 2–4, the dimethylacetamide ligand is shown only in one orientation.

Figure 3
Crystal packing of the title compound, illustrating the tightly layered intermolecular organization. The H atoms have been omitted for clarity. The Zn atoms are represented by small spheres. Note the layered organization of the metalloporphyrin constituents, with all units in a given layer oriented in the same direction. Color code: C dark grey, N blue, O red, and Zn violet.

Figure 4
Detailed illustration of the parallel offset between adjacent layers. The central (yellow dotted) molecule belongs to the lower layer, while the four surrounding molecules represent a neighboring upper layer. Color code: C dark grey, H white, N blue, O red, and Zn violet.

the N22- and N24-containing rings, which bend upwards towards the dimethylacetamide is 11.96 (11)°. The four pyrrole N atoms deviate alternately ±0.0106 (7) Å from their mean plane. The central zinc ion is displaced upward by 0.3162 (7) Å from this N_4 plane, imparting to the metalloporphyrin entity a domed structure (Fig. 2), which is characteristic of many five-coordinate complexes of metallated tetraarylporphyrins with a single axial ligand (Cambridge Structural Database, Version 5.27; Allen, 2002). In this structure, the dimethylacetamide exhibits a twofold orientational disorder with nearly equal occupancies of its two orientations, which could be well resolved (Fig. 1).

The crystal packing consists of layered arrays of the metalloporphyrin units stacked approximately along the [110]
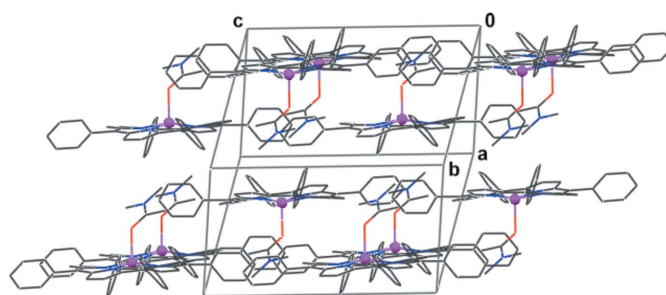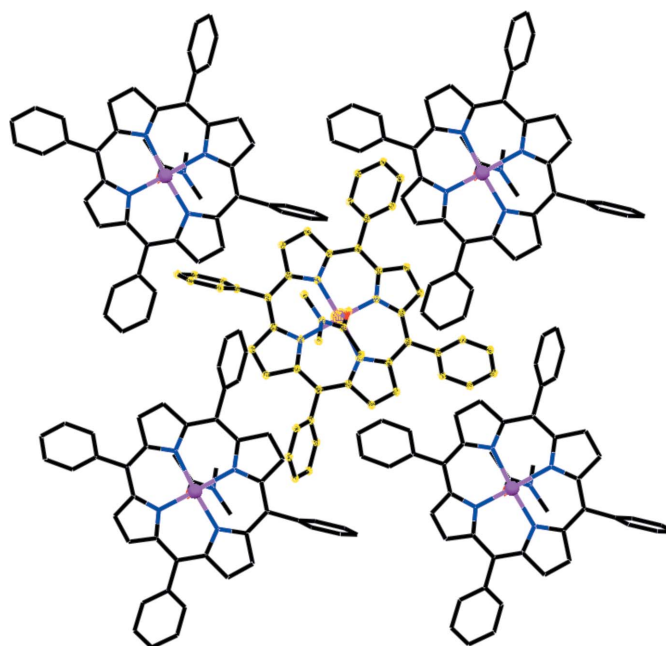
axis (Fig. 3). All porphyrin units in a given layer are oriented in the same direction. Adjacent layers are inter-related by the crystallographic inversion, stacking one on top of the other in an offset manner (Fig. 4). In the interface between the convex surfaces of the porphyrin sheets, the axial ligands of one layer penetrate into the interporphyrin voids of another layer (Figs. 3 and 4). Then, in the other interface between the layers, the phenyl rings of one layer fit into the concave porphyrin faces of the neighboring array. The corresponding shortest non-bonding distances include: $C29 \cdots N23(1-x, 1-y, 1-z) = 3.693$ (2) Å, $C30 \cdots N22(1-x, 1-y, 1-z) = 3.319$ (2) Å, $C41 \cdots N21(1-x, 1-y, -z) = 3.564$ (2) Å and $C42 \cdots N24(1-x, 1-y, -z) = 3.603$ (2) Å. The covalent parameters of the molecular structure and the coordination

around the zinc ion (Table 1) show ordinary features (Allen, 2002; Vinodu & Goldberg, 2004; Lipstman & Goldberg, 2006).

Experimental

The crystals of the title compound were obtained by dissolving zinc–tetraphenylporphyrin in N,N'-dimethylacetamide, followed by slow evaporation.

Crystal data

$[Zn(C_{44}H_{28}N_4)(C_4H_9NO)]$	$V = 1820.60\ (4)\ \text{Å}^3$
$M_r = 765.20$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 1.396\ \text{Mg m}^{-3}$
$a = 10.5914\ (1)\ \text{Å}$	Mo $K\alpha$ radiation
$b = 11.9472\ (1)\ \text{Å}$	$\mu = 0.72\ \text{mm}^{-1}$
$c = 14.7234\ (3)\ \text{Å}$	$T = 110\ (2)\ \text{K}$
$\alpha = 85.2552\ (6)°$	Prism, red
$\beta = 80.3160\ (6)°$	$0.35 \times 0.25 \times 0.20$ mm
$\gamma = 83.4235\ (5)°$	

Data collection

Nonius KappaCCD diffractometer	8687 independent reflections
φ and ω scans	7524 reflections with $I > 2\sigma(I)$
Absorption correction: none	$R_{int} = 0.029$
20517 measured reflections	$\theta_{max} = 28.2°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0468P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.036$	$+\ 0.9708P]$
$wR(F^2) = 0.096$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} = 0.089$
8687 reflections	$\Delta\rho_{max} = 0.43\ \text{e Å}^{-3}$
548 parameters	$\Delta\rho_{min} = -0.63\ \text{e Å}^{-3}$
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Zn—N22	2.0612 (14)	Zn—N23	2.0849 (14)
Zn—N21	2.0656 (13)	Zn—O49	2.1102 (12)
Zn—N24	2.0751 (13)		
N22—Zn—N21	88.53 (5)	N24—Zn—N23	87.90 (5)
N22—Zn—N24	163.00 (6)	N22—Zn—O49	99.16 (5)
N21—Zn—N24	89.05 (5)	N21—Zn—O49	101.11 (5)
N22—Zn—N23	89.19 (5)	N24—Zn—O49	97.81 (5)
N21—Zn—N23	161.88 (5)	N23—Zn—O49	97.01 (5)

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 $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}$(methyl C). The two possible orientations of the dimethylacetamide ligand, with a common position of the Zn-coordinated pivot O atom, were clearly recognizable in the initial electron density map. The corresponding atoms C50–C53 and C50′–C53′ were grouped in two different 'parts' of the structural model, which were then refined in alternating cycles of the least-squares calculations to avoid high correlations between the parameters of partly overlapping atoms C51, C53 and C54.

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*.

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