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Key indicators

Single-crystal X-ray study
 $T = 110$ K
Mean $\sigma(\text{C}-\text{C}) = 0.005$ Å
 R factor = 0.053
 wR factor = 0.147
Data-to-parameter ratio = 17.5For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

(4-Acetylpyridine)(tetraphenylporphyrinato)zinc(II)

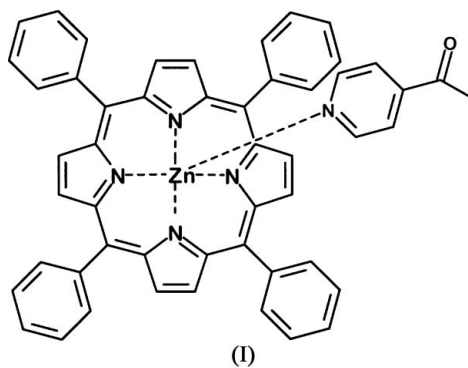
The title compound, $[\text{Zn}(\text{C}_{44}\text{H}_{28}\text{N}_4)(\text{C}_7\text{H}_7\text{NO})]$, is a square-pyramidal five-coordinate zinc–porphyrin complex with γ -acetylpyridine as the apical ligand. The intermolecular packing involves van der Waals forces, close π – π stacking and $\text{C}-\text{H}\cdots\pi$ contacts, revealing an interesting pairing of adjacent molecules related by inversion.

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Comment

This study is part of our effort to formulate ligand-bridged metalloporphyrin oligomers (Krishna Kumar *et al.*, 2000; Shukla *et al.*, 2000; Diskin-Posner *et al.*, 2001), by employing a variety of ligands that contain two or more potential coordination sites for metal ions. However, with the acetylpyridine species only the monomeric title compound, (I) (Fig. 1), was formed.



Although a large number of five-coordinate complexes of zinc–tetraphenylporphyrin are known (Byrn *et al.*, 1991, 1993), association of the latter with γ -acetylpyridine in crystal structures has not been reported. Moreover, only a single crystallographic characterization of the zinc ion coordinated by 4-acetylpyridine has been published thus far (Steffen & Palenik, 1977). In the structure of (I), the porphyrin core is slightly saddled, with the inner pyrrole N atoms deviating alternately ± 0.035 (1) Å from their mean plane. The central zinc ion deviates by 0.302 (1) Å from this N_4 plane towards the apical ligand, imparting to the metalloporphyrin entity a domed structure (Fig. 2), which is characteristic of many five-coordinate complexes of metallated tetraarylporphyrins with a single apical ligand (Allen, 2002). The saddled conformation can be characterized also by dihedral angles between the mean planes of the five-membered pyrrole rings. Thus, around the porphyrin macrocycle, the dihedral angles are 13.3 (2), 11.7 (2), 10.6 (2) and 11.1 (2)° between the pyrrole rings containing N21/N22, N22/N23, N23/N24 and N24/N21,

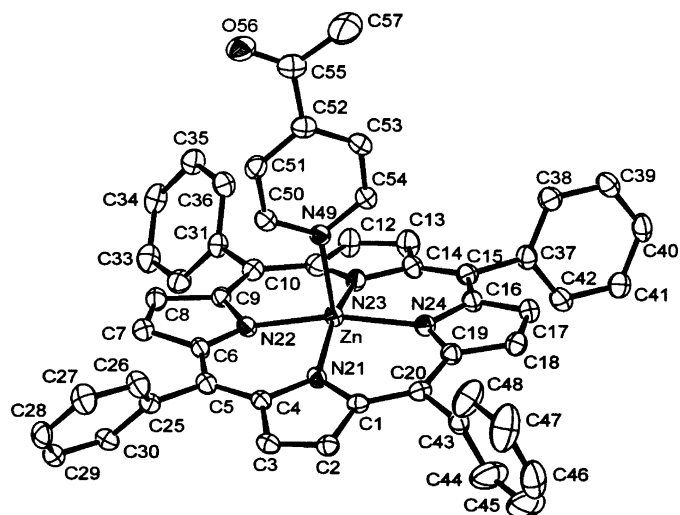


Figure 1
Molecular structure of (I), showing 50% displacement ellipsoids (H atoms omitted for clarity).

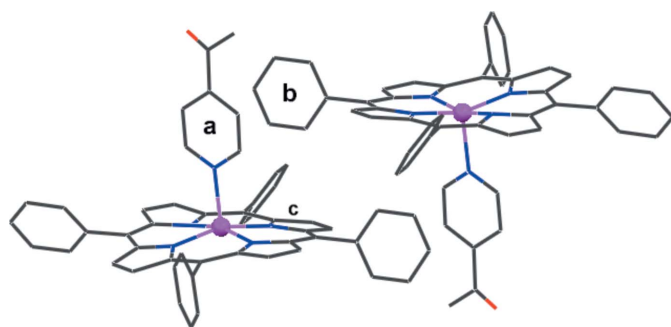


Figure 2
Stick illustration of the domed molecular structure of (I), and of the tight pairing of the molecules through face-to-face and edge-to-face aryl–aryl interactions. Ring *a* represents the N49/C50–C54 group of the axial ligand at (x, y, z) . Ring *b* represents the C37–C42 phenyl ring at $(-x, -y, 2 - z)$. Symbol *c* represents a fragment of the porphyrin macrocycle consisting of atoms C10–C14 and N23. Face-to-face stacking operates between *a* and *b*, while edge-to-face interaction operates between *b* and *c* (see text). Colour code: C dark gray, N blue, O red, Zn violet. H atoms have been omitted.

respectively. The corresponding dihedral angles between the *trans*-related pyrrole rings containing N21/N23 and N22/N24 are 20.9 (2) and 8.0 (2)°.

As shown in Fig. 2, inversion-related molecules pair tightly, with the apical ligand of one species (atoms N49 and C50 through C54) being aligned roughly parallel to a *meso*-substituted phenyl ring (atoms C37 through C42). The dihedral angle between these two planes is only 15.6 (2)°. The distance between the centroids of the N49/C50–C54 and C37–C42 [at $(-x, -y, 2 - z)$] rings is 3.766 (2) Å, the center of the C39–C40 bond lying 3.245 (3) Å above the mean plane of the N49/C50–C54 ring. The C37–C42 [at $(-x, y, 2 - z)$] ring is at the same time nearly perpendicular to, and in contact with, part of the porphyrin core (defined *e.g.* by atoms C10 through C14 and N23). The mid-point of the C38–C39 bond of the former is located 3.485 (3) Å [and the respective H atoms

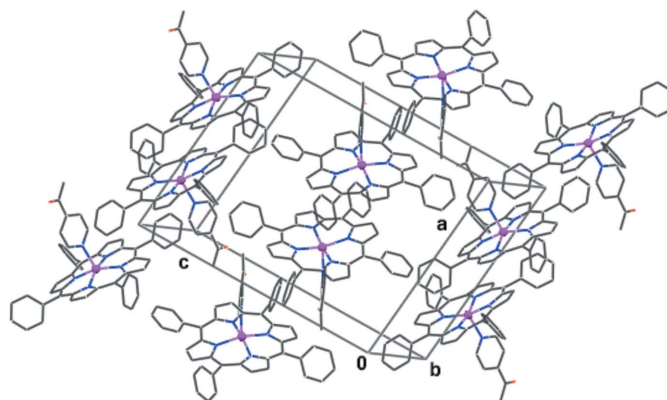


Figure 3
Crystal packing of (I). Note the columnar organization of the porphyrin molecules, and their alternating orientation in every column. Within the molecular pairs the axial ligands turn inward, while the interaction between adjacent pairs in a column involves the concave faces of the porphyrin macrocycles. Colour code: C dark gray, N blue, O red, Zn violet. H atoms have been omitted.

2.69 Å (H38) 2.69 Å and 2.63 Å (H39)] above the mean plane of the latter, the corresponding C38–H38 and C39–H39 bonds pointing directly at the π cloud of that fragment of the porphyrin core.

The crystal structure of (I) is illustrated in Fig. 3. It can be best described in terms of a columnar arrangement of such paired molecules along the *a* axis of the crystal. There is a considerable offset between adjacent pairs in each column in order to optimize the van der Waals interactions by placing edge-on a phenyl arm of one molecule (atoms C25 through C30) in close proximity to the concave face [and in particular to the N24-pyrrole ring at $(1 - x, -y, 2 - z)$] of an adjacent inversion-related molecular pair. Tight organization characterizes the side packing of the screw/glide-related molecular columns in a herringbone manner, yielding a stable crystal structure without the need to include any crystallization solvent. The covalent parameters of the molecular structure and the coordination around the zinc ion (Table 1) show ordinary features (Allen, 2002; Vinodu & Goldberg, 2004).

Experimental

Zinc tetraphenylporphyrin (2 mg) (Aldrich) was dissolved in a mixture of chloroform (4 ml) and 4-acetylpyridine (0.5 mg) (Aldrich). The dark-red solution thus formed was filtered and left to crystallize at room temperature, yielding diffraction quality crystals of (I) after a few days.

Crystal data

[Zn(C₄₄H₂₈N₄)(C₇H₇NO)]
 $M_r = 799.21$
 Monoclinic, $P2_1/c$
 $a = 16.2055$ (2) Å
 $b = 11.0902$ (2) Å
 $c = 21.4881$ (4) Å
 $\beta = 99.6311$ (6)°
 $V = 3807.46$ (11) Å³
 $Z = 4$

$D_x = 1.394$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 8863 reflections
 $\theta = 2.4$ – 28.2 °
 $\mu = 0.69$ mm⁻¹
 $T = 110$ (2) K
 Prism, red
 0.30 × 0.20 × 0.20 mm

Data collection

Nonius KappaCCD diffractometer $R_{\text{int}} = 0.080$
 φ and ω scans $\theta_{\text{max}} = 28.2^\circ$
 Absorption correction: none $h = -21 \rightarrow 21$
 34397 measured reflections $k = -14 \rightarrow 14$
 9172 independent reflections $l = -28 \rightarrow 27$
 6048 reflections with $I > 2\sigma(I)$

Refinement

Refinement on F^2 $w = 1/[\sigma^2(F_o^2) + (0.0771P)^2 + 1.2795P]$
 $R[F^2 > 2\sigma(F^2)] = 0.053$ where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.147$ $(\Delta/\sigma)_{\text{max}} = 0.001$
 $S = 1.02$ $\Delta\rho_{\text{max}} = 0.61 \text{ e } \text{Å}^{-3}$
 9172 reflections $\Delta\rho_{\text{min}} = -0.68 \text{ e } \text{Å}^{-3}$
 524 parameters
 H-atom parameters constrained

Table 1

Selected bond lengths (Å).

Zn–N22	2.064 (2)	Zn–N23	2.075 (2)
Zn–N24	2.065 (2)	Zn–N49	2.183 (2)
Zn–N21	2.070 (2)		

The H atoms were positioned geometrically (C–H = 0.95–0.98 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and $1.5U_{\text{eq}}(\text{methyl C})$. The large amplitude anisotropic displacement factors of the C43–C48 phenyl ring and the terminal C57 methyl group may be correlated with unresolved rotational disorder.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski and 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*.

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