

(4-Aminopyridine- κN^1)(phthalocyaninato- $\kappa^4 N$)zinc(II) tetrahydrofuran disolvate

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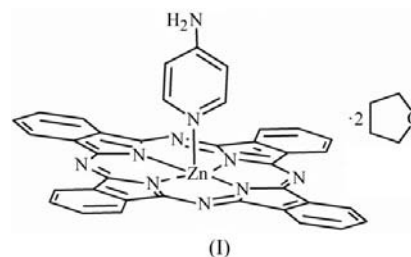
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The title compound, $[\text{Zn}(\text{C}_{32}\text{H}_{16}\text{N}_8)(\text{C}_5\text{H}_6\text{N}_2)] \cdot 2\text{C}_4\text{H}_8\text{O}$, consists of one (phthalocyaninato)zinc (ZnPc) unit, a coordinated 4-aminopyridine (4-ap) molecule and two tetrahydrofuran (THF) solvent molecules. The central Zn atom is (4+1)-coordinated by four isoindole N atoms of the Pc core and by the pyridine N atom of 4-aminopyridine. The Zn atom is displaced by 0.4464 (8) Å from the isoindole N_4 plane towards the pyridine N atom. The crystal structure is stabilized by intermolecular amine–phthalocyaninate $\text{N}-\text{H} \cdots \text{N}$ hydrogen bonds and $\pi-\pi$ interactions between the aggregated Pc rings, which form molecular layers, and by weak van der Waals interactions between the layers. As well as hindering the aggregation of ZnPc molecules by occupying an axial position, the amino group will add new interactions which will favor applications of ZnPc, for example, as a sensitizer of photodynamic therapy.

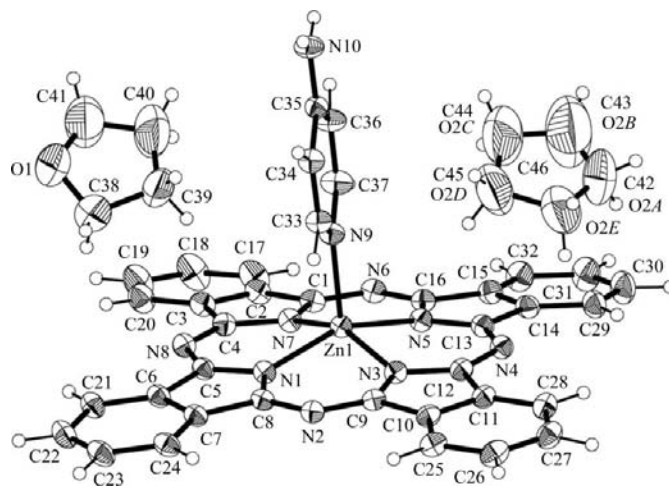
Comment

It is well known that phthalocyanines exhibit interesting optical, electrical, magnetic and catalytic properties, and they are widely used in many fields, such as dyes, catalysts, molecular materials, chemical sensors, nonlinear optical materials, *etc.* (Kadish *et al.*, 2003; McKeown, 1998; Torre *et al.*, 2001). Among those phthalocyanine compounds, the (phthalocyaninato)zinc (ZnPc) derivatives are particularly interesting owing to their unique photosensitizing properties for photodynamic therapy (PDT) (Lukyanets, 1999; Tabata *et al.*, 2000; Milgrom, 1977; Bonnett, 1995), magnetic circularly polarized luminescence (MCPL) and magnetic circular dichroism (MCD) spectra. Our interest in ZnPc derivatives is due to their photodynamic activity. Some crystal structures of (4+1)-coordinated ZnPc derivatives, such as ZnPc(*n*-hexylamine), ZnPcCl, ZnPc(dipy-pra) (dipy-pra is 1,3-di-4-pyridylpropane), ZnPc(di/tetra/hexa/octaphenyl-py) (py is pyridine), $[\text{ZnPc}(\text{H}_2\text{O})] \cdot 2\text{DMF}$ (DMF is dimethylformamide) and ZnPc(4-

Mepy) (4-Mepy is 4-methylpyridine) have been reported (Kobayashi *et al.*, 1971; Deneux *et al.*, 1985; Zeng *et al.*, 2005; Fukuda *et al.*, 2005; Cui *et al.*, 2007; Kubiak *et al.*, 2007). In this paper, we report the structure of the title compound, (I), produced by the reaction of 4-aminopyridine with zinc phthalocyanine in tetrahydrofuran (THF) solution. UV–vis and fluorescence spectral measurements and thermal gravimetric analysis were also applied to characterize this complex.



The asymmetric unit of (I) consists of a (4-aminopyridine- κN^1)(phthalocyaninato- $\kappa^4 N$)zinc(II) unit, denoted ZnPc(4-ap), and two THF solvent molecules (one of the THF molecules shows disorder) (Fig. 1). The central Zn^{II} atom exhibits (4+1)-coordination by four isoindole N atoms of the Pc ring system and the pyridine N atom of the 4-aminopyridine molecule, forming a distorted pyramid (Table 1). The Zn atom in this coordination environment assumes an sp^2d^2 hybridization. The bond distances from the azamethine N atoms of the Pc ring to the central Zn atom range from 2.0278 (15) to 2.0345 (15) Å, whereas the distance from the pyridine N atom of the axial ligand is somewhat longer at 2.0917 (16) Å. The angle between the basal Pc plane defined by the four isoindole N atoms (the N_4 plane) and the plane of the coordinated 4-aminopyridine molecule is 87.60 (6)°, thus the 4-aminopyridine molecule is almost perpendicular to the Pc plane. The central Zn atom is significantly displaced by 0.4464 (8) Å from

**Figure 1**

The crystal structure of compound (I), drawn with 30% probability displacement ellipsoids. H atoms are shown as spheres of arbitrary radii.

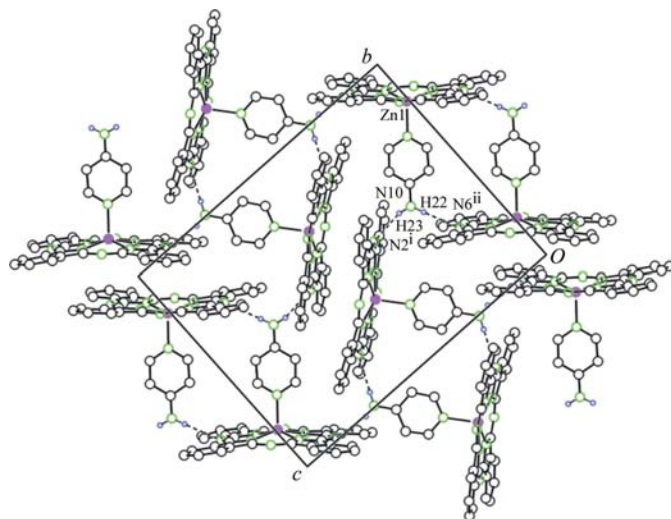


Figure 2
A view of the hydrogen-bonded structure of compound (I) and the back-to-back π - π interactions between the ZnPc(4-ap) molecules. All C-bound H atoms and the THF solvent molecules have been omitted for clarity. [Symmetry codes: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + 1, -y + 1, -z$.]

the N_4 plane towards the axially coordinated N atom of the 4-aminopyridine molecule.

For axially coordinated ZnPc complexes, a range of values have been observed for the distance between the Zn^{II} cation and the N_4 plane, the value being related to the bond strength between the metal cation and the axial ligand. For example, the Zn atom is displaced from the N_4 plane as follows: 0.2 Å in ZnPc(dipy-pra), 0.35 Å in ZnPc(4-Mepy), 0.38 Å in ZnPc(H_2O)-2DMF, 0.48 Å in ZnPc(*n*-hexylamine) and 0.59 Å in ZnPcCl (Zeng *et al.*, 2005; Kubiak *et al.*, 2007; Cui *et al.*, 2007; Kobayashi *et al.*, 1971; Deneux *et al.*, 1985); the displacement is 0.45 Å in compound (I). Additionally, the Pc ring is distorted from planarity, with small angles between the benzene rings and the N_4 plane of 8.30 (13), 4.55 (10), 4.22 (10) and 7.56 (12)° for the C2/C3/C17–C20, C6/C7/C21–C24, C10/C11/C25–C28 and C14/C15/C29–C32 rings, respectively. The small differences of these angles are related to the aggregation of the Pc rings, where the less overlapped benzene rings have slightly larger distortion angles.

The crystal structure of (I) is stabilized by hydrogen bonds and π - π interactions between Pc rings. The hydrogen-bonding interactions occur between the azamethine N2 and N6 atoms of the Pc ring as acceptors and the amino group of the 4-aminopyridine molecule as donor (Fig. 2 and Table 2). These intermolecular hydrogen bonds construct an infinite two-dimensional layer in the *bc* plane. Concurrently, in the two-dimensional layer, the Pc rings are aggregated in a back-to-back fashion, with a distance of 3.56 Å and a centre offset of 3.15 Å between two stacked N_4 planes, which indicates a strong intermolecular π - π interaction (Pauling, 1960). Finally, the THF molecules occupy the space around the axial 4-aminopyridine ligands (Figs. 1 and 3).

As further characterizations of compound (I), the electronic absorption spectrum was recorded in DMF solution. It showed

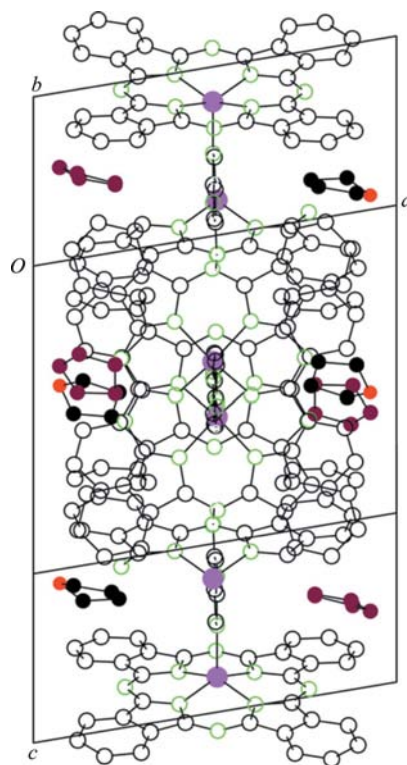


Figure 3
The molecular packing of compound (I), showing the positions of the THF solvent molecules around the 4-aminopyridine ligands. H atoms have been omitted for clarity.

intense absorption in the UV region (*B* band, 343 nm) and visible-IR region (*Q* band, 669 nm). Compared with the corresponding bands of ZnPc (340 and 669 nm), a slight red shift in the *B* band occurs in compound (I), but the *Q* band is at the same position which indicates the axial ligand has less influence on the Pc π system. In the UV-visible diffuse reflectance spectra of the solid sample, bands at 570 and 649 nm corresponded to the dimeric aggregate of molecules.

ZnPc derivatives all display strong fluorescence. Compound (I) in DMF solution exhibits two emission peaks at about 679 and 739 nm ($\lambda_{ex} = 617$ nm). In contrast to the emission wavelength (676 and 743 nm) of unsubstituted ZnPc, the small red (3 nm) and blue (4 nm) shifts can be related to the presence of the axial ligand (Ogunsipe *et al.*, 2003; Yslas *et al.*, 2005; Nitschke *et al.*, 2004).

The thermogravimetric analysis shows two characteristic steps, the first at about 339 K corresponds to the loss of the THF molecules (12.26%) and the second at about 448 K correlates with the loss of 4-aminopyridine. Finally, above 571 K, the sample decomposes.

Experimental

Pure zinc(II) phthalocyanine was prepared according to the procedure of Kobayashi *et al.* (1968). ZnPc powder was reacted with 4-aminopyridine (2:3 molar ratio) in THF solution at about 338 K for 6 h. When the solvent was evaporated slowly at room temperature, purple crystals were obtained in various sizes.

Crystal data

[Zn(C₃₂H₁₆N₈)(C₅H₆N₂)]·2C₄H₈O
M_r = 816.22
 Monoclinic, *P*2₁/*c*
a = 13.5385 (17) Å
b = 15.0756 (19) Å
c = 19.224 (3) Å
 β = 100.420 (3)°
V = 3858.9 (9) Å³
Z = 4
 Mo *K*α radiation
 μ = 0.69 mm⁻¹
T = 298 (2) K
 0.72 × 0.70 × 0.20 mm

Data collection

Rigaku Saturn 724 CCD area-detector diffractometer
 Absorption correction: numerical (NUMABS; Higashi, 2000)
*T*_{min} = 0.636, *T*_{max} = 0.874
 30133 measured reflections
 8842 independent reflections
 8208 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.028

Refinement

R[*F*² > 2σ(*F*²)] = 0.044
wR(*F*²) = 0.121
S = 1.06
 8842 reflections
 611 parameters
 H atoms treated by a mixture of independent and constrained refinement
 Δρ_{max} = 0.37 e Å⁻³
 Δρ_{min} = -0.43 e Å⁻³

Table 1
 Selected geometric parameters (Å, °).

Zn1—N3	2.0278 (15)	Zn1—N7	2.0345 (15)
Zn1—N1	2.0311 (15)	Zn1—N9	2.0917 (16)
Zn1—N5	2.0335 (15)		
N3—Zn1—N1	86.70 (6)	N5—Zn1—N7	86.47 (6)
N3—Zn1—N5	87.94 (6)	N3—Zn1—N9	103.29 (6)
N1—Zn1—N5	154.77 (6)	N1—Zn1—N9	101.89 (6)
N3—Zn1—N7	154.46 (6)	N5—Zn1—N9	103.34 (6)
N1—Zn1—N7	87.81 (6)	N7—Zn1—N9	102.25 (6)

Table 2
 Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N10—H23...N2 ⁱ	0.83 (3)	2.27 (3)	3.070 (2)	162 (2)
N10—H22...N6 ⁱⁱ	0.83 (3)	2.38 (3)	3.210 (3)	179 (3)

Symmetry codes: (i) -*x* + 1, *y* - ½, -*z* + ½; (ii) -*x* + 1, -*y* + 1, -*z*.

All H atoms bound to C and N atoms of the ZnPc(4-ap) unit were located in difference Fourier syntheses and refined. The H atoms of the THF solvent molecules were refined as riding, with C—H = 0.97 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C). One THF molecule (C42—C46/O2A—O2E) was disordered and treated statistically with the site-occupancy

factors of the C atoms at each of the five sites equal to 0.8 and the site-occupancy factors of the O atoms equal to 0.2.

Data collection: *CrystalClear* (Rigaku, 2007); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP* (McArdle, 1995); 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: HJ3088). Services for accessing these data are described at the back of the journal.

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