

Bis[μ -(*E*)-2-[(2-pyridylamino)-(2-pyridylimino)methyl]benzato]-bis[acetatozinc(II)] tetrahydrate

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Received 28 January 2008

Accepted 15 March 2008

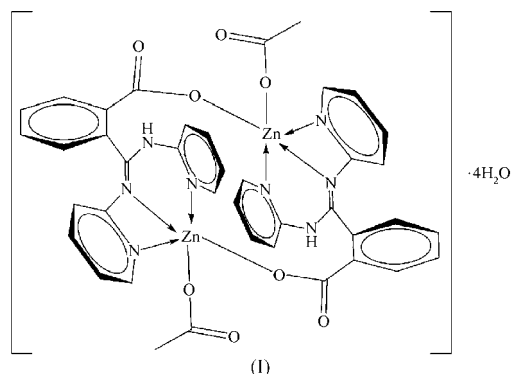
Online 29 March 2008

In the C_2 -symmetric dinuclear title complex, $[\text{Zn}_2(\text{C}_{18}\text{H}_{13}\text{N}_4\text{O}_2)_2(\text{C}_2\text{H}_3\text{O}_2)_2] \cdot 4\text{H}_2\text{O}$, each Zn^{II} ion is five-coordinated in a distorted trigonal bipyramidal fashion by one carboxylate O atom from one benzoate ligand, one imine N atom and two pyridyl N atoms from a second benzoate ligand, and one O atom from an acetate anion. The two Zn atoms are bridged by the two benzoate ligands, forming a dinuclear structure with a 14-membered macrocycle. Adjacent dinuclear units are further connected by extensive hydrogen bonds involving the solvent water molecules, giving a three-dimensional hydrogen-bonded framework. The framework can be regarded as an example of the four-connected node network of the PtS topology.

Comment

The rapidly growing area of coordination polymers based on the interactions of metal cations with organic ligands has given rise to a wide range of fascinating one-, two- and three-dimensional structures (Erxleben, 2003). In designing these polymers, the choice of appropriate organic ligands is a dominant factor in determining the structural and functional outcome of the target polymers. Organic ligands containing *N,O*-donors are of interest because of their capacity for intriguing structural features and their potential applications (Li *et al.*, 2003; Gao *et al.*, 2004; Fei *et al.*, 2005). Many studies have centred on the use of pyridine(di)carboxylate ligands, especially 3- or 4-pyridinecarboxylate ligands and 2,5-pyridinedicarboxylate (Xing *et al.*, 1998; Qin *et al.*, 2002; Garcia-Zarracino & Hopfl, 2005). However, there are few reports on the bis(pyridine)carboxylate ligands (Hemmert *et al.*, 1996; Kirin *et al.*, 2005). In order to explore further the self-assembly of coordination networks based on bis(pyridine)carboxylate ligands, we synthesized a new dinuclear zinc complex, (I), obtained by the reaction of zinc(II) acetate dihydrate and a new ligand, *viz.* (*E*)-2-[(2-pyridylamino)(2-pyridylimino)methyl]benzoic acid, in methanol solution. To

the best of our knowledge, this is the first report of a crystal structure of a metal complex containing this ligand.



The title complex has a dinuclear structure, in which the molecule is situated about a crystallographic twofold axis, as shown in Fig. 1. The unique Zn^{II} ion lies in a distorted trigonal bipyramidal coordination environment, which is completed by one carboxylate O atom from one benzoate ligand, one imine N atom and two pyridyl N atoms from a second benzoate ligand, and one O atom from an acetate anion. The equatorial plane of the trigonal bipyramid is defined by atoms N1, O3 and O1ⁱ [symmetry code: (i) $-x, y, \frac{1}{2} - z$], and the displacement of the Zn^{II} ion from the equatorial plane is 0.13 (3) Å. The axial positions are occupied by pyridyl atoms N2 and N4, and the N2–Zn1–N4 angle deviates significantly from linearity (Table 1). The distortion of the coordination polyhedron is primarily influenced by the very small bite angle imposed by the four-membered ring generated by the coordination of the imine and immediately adjacent pyridyl N atoms to the Zn^{II} ion.

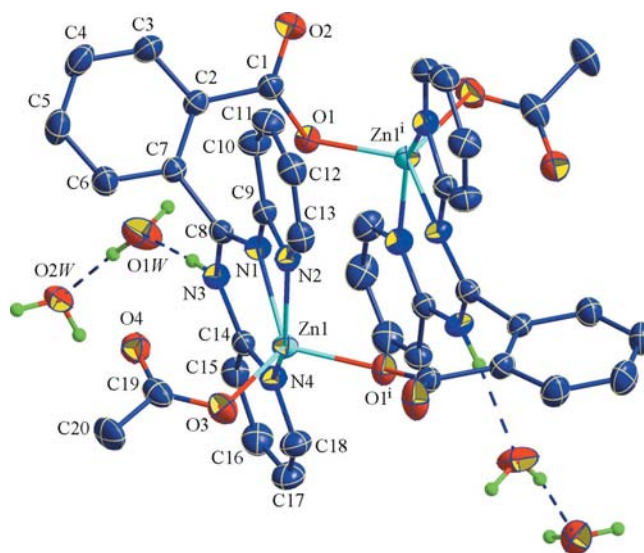


Figure 1
The molecular structure of complex (I), showing displacement ellipsoids at the 50% probability level. Hydrogen bonds are shown as dashed lines. [Symmetry code: (i) $-x, y, \frac{1}{2} - z$.]

It is noteworthy that each ligand behaves in a tetradentate coordination fashion involving one monodentate carboxylate O atom, the imine N atom and the two pyridyl N atoms, while the amine N atom is free of coordination with the Zn atoms. Within each benzoate ligand, the two pyridyl rings are nearly parallel to one another, with a dihedral angle of $9.2(2)^\circ$; however, the benzene ring is nearly perpendicular to these two pyridyl rings, with dihedral angles of $89.8(2)$ and $89.7(2)^\circ$. The two Zn atoms in the molecule are bridged by the two benzoate ligands to give a 14-membered macrometallacyclic

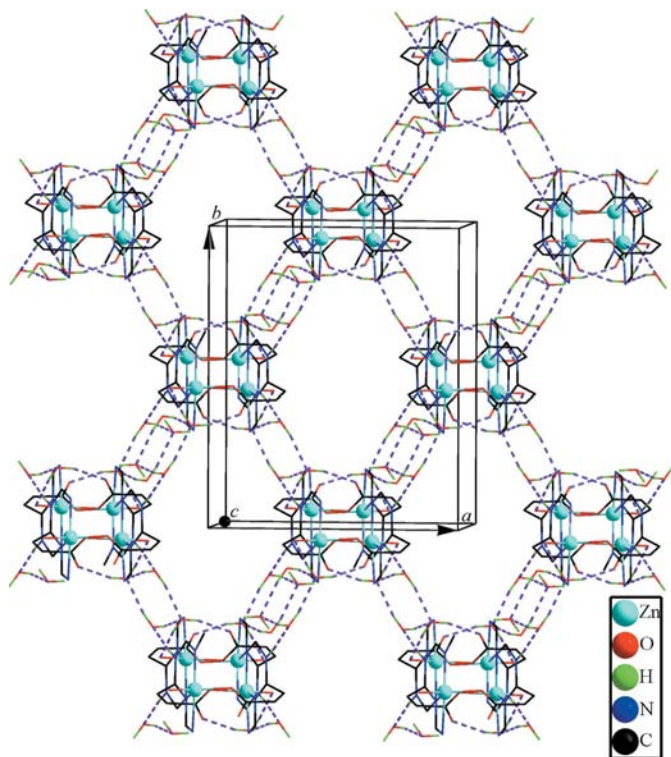


Figure 2
The three-dimensional hydrogen-bonding network structure of complex (I), with uninvolved H atoms omitted.

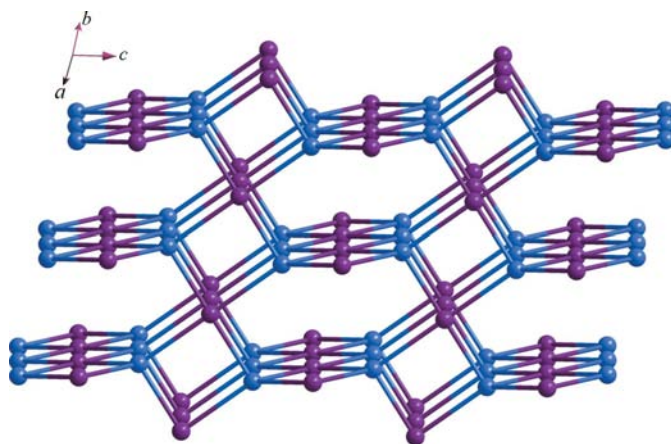


Figure 3
The PtS topology exhibited by the structure of complex (I).

ring with a Zn \cdots Zn separation of $5.0983(12)$ Å. Within the dinuclear units, π - π interactions are present between each of the pyridyl rings and their symmetry-related counterparts in the second benzoate ligand. The centroid-centroid distances are $3.573(2)$ and $3.817(2)$ Å for the pyridyl rings containing atoms N2 and N4, respectively.

The asymmetric unit of the crystal structure includes two solvent water molecules. It can be seen from Fig. 2 that the crystal structure is built up through extensive hydrogen bonds. The free water molecules of adjacent asymmetric units form hydrogen bonds amongst themselves (Table 2), which result in eight-membered centrosymmetric rhombic hydrogen-bonded rings. These rings have a graph-set motif of $R_4^2(8)$ (Bernstein *et al.*, 1995), where atom O1W acts solely as a hydrogen-bond donor through both of its H atoms and atom O2W acts solely as a hydrogen-bond acceptor. At the same time, the free water molecules also form intermolecular hydrogen bonds with adjacent Zn complex molecules. Atom O1W accepts a hydrogen bond from the uncoordinated amine N atom (N3), while atom O2W donates hydrogen bonds through its two H atoms to acetate atom O3 and carboxylate atom O2 of two different adjacent Zn complex molecules (Table 2). Taken together, the hydrogen-bonding interactions give rise to a regular three-dimensional hydrogen-bonding framework. It is noteworthy that the complex molecules do not interact with one another *via* direct hydrogen bonds but only *via* water molecules. A better insight into the nature of this intricate framework can be achieved by the application of a topological approach, reducing multidimensional structures to simple node and connection nets. As discussed above, each dinuclear unit and each eight-membered rhombic hydrogen-bonded ring of water molecules can be considered as a four-connected node. Therefore, the whole structure can be regarded as a PtS net (Wang *et al.*, 2008), as shown in Fig. 3.

Experimental

An aqueous solution of zinc(II) acetate dihydrate (0.110 g, 0.5 mmol) was added to a methanol solution of (*E*)-2-[(2-pyridylamino)(2-pyridylimino)methyl]benzoic acid (1.59 g, 5 mmol). The solution was stirred for half an hour and allowed to evaporate at room temperature. Colourless crystals were isolated from the filtered solution after four weeks. Analysis calculated for $C_{40}H_{40}N_8O_{12}Zn_2$: C 50.28, H 4.22, N 11.73%; found: C 50.24, H 4.25, N 11.77%.

Crystal data

$[Zn_2(C_{18}H_{13}N_4O_2)_2 \cdot (C_2H_3O_2)_2] \cdot 4H_2O$
 $M_r = 955.58$
 Monoclinic, $C2/c$
 $a = 13.718(3)$ Å
 $b = 15.433(3)$ Å
 $c = 20.526(4)$ Å

$\beta = 108.83(3)^\circ$
 $V = 4113.0(16)$ Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 1.24$ mm⁻¹
 $T = 295(2)$ K
 $0.36 \times 0.35 \times 0.23$ mm

Data collection

Rigaku R-Axis RAPID
 diffractometer
 Absorption correction: multi-scan
 (ABSCOR; Higashi, 1995)
 $T_{min} = 0.654$, $T_{max} = 0.744$

19669 measured reflections
 4715 independent reflections
 4200 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.025$

Refinement

$$R[F^2 > 2\sigma(F^2)] = 0.029$$

$$wR(F^2) = 0.075$$

$$S = 1.03$$

4715 reflections

293 parameters

6 restraints

H atoms treated by a mixture of independent and constrained refinement

$$\Delta\rho_{\max} = 0.30 \text{ e } \text{Å}^{-3}$$

$$\Delta\rho_{\min} = -0.34 \text{ e } \text{Å}^{-3}$$

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO* and *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

Table 1

Selected geometric parameters (Å, °).

Zn1—O1 ⁱ	1.9566 (14)	Zn1—N4	2.0890 (14)
Zn1—O3	1.9675 (13)	Zn1—N2	2.2256 (14)
Zn1—N1	2.0838 (13)		
O1 ⁱ —Zn1—O3	117.51 (6)	N1—Zn1—N4	85.59 (5)
O1 ⁱ —Zn1—N1	116.59 (6)	O1 ⁱ —Zn1—N2	98.98 (5)
O3—Zn1—N1	124.59 (6)	O3—Zn1—N2	98.52 (5)
O1 ⁱ —Zn1—N4	91.71 (5)	N1—Zn1—N2	61.86 (5)
O3—Zn1—N4	103.81 (6)	N4—Zn1—N2	147.20 (5)

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

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>
N3—H14...O1W	0.86	1.99	2.848 (2)	173
O1W—H1W1...O2W	0.85 (3)	1.996 (12)	2.833 (2)	169 (3)
O1W—H1W2...O2W ⁱⁱ	0.85 (3)	1.97 (3)	2.808 (2)	165 (3)
O2W—H2W1...O2 ⁱⁱⁱ	0.852 (9)	1.896 (13)	2.723 (2)	163 (3)
O2W—H2W2...O3 ^{iv}	0.86 (2)	1.886 (12)	2.731 (2)	168 (3)

Symmetry codes: (ii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (iii) $x + \frac{1}{2}, y - \frac{1}{2}, z$; (iv) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$.

H atoms in the complex molecule were placed in calculated positions and included in the refinement using the riding-model approximation, with pyridyl and phenyl C—H distances of 0.93 Å, methyl C—H distances of 0.96 Å and amine N—H distances of 0.86 Å, and with $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{pyridyl})$ and phenyl C and amine N) or $1.5U_{\text{eq}}(\text{methyl C})$. H atoms of the water molecules were located in a difference map and refined with O—H distance restraints of 0.85 (1) Å and with $U_{\text{iso}}(\text{H})$ values of $1.5U_{\text{eq}}(\text{O})$.

The authors thank Heilongjiang Province Natural Science Foundation (grant No. B200501), the Scientific Fund of Remarkable Teachers of Heilongjiang Province (grant No. 1054 G036) and Heilongjiang University for supporting this work.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN3090). Services for accessing these data are described at the back of the journal.

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