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The honeycomb network structure of poly[[[μ_2-1,3-bis(1*H*-benzimidazol-2-yl)benzene-κ^2N^3:$N^{3'}$](μ_2-terephthalato-κ^2O:O')zinc(II)] ethanol solvate]

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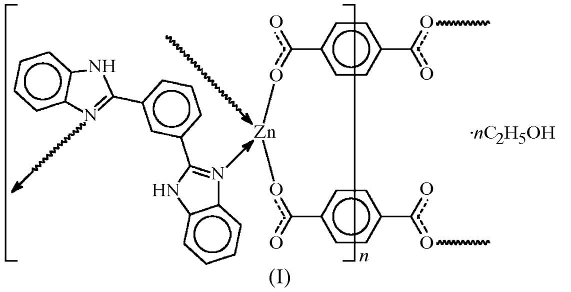
The terephthalate dianion and the bis(imidazolyl)benzene ligand of the title compound, $\{[Zn(C_8H_4O_4)(C_{20}H_{14}N_4)]\cdot C_2H_6O\}_n$, each bridges two adjacent zinc centers, resulting in a layer-type coordination polymer; the zinc center shows tetrahedral coordination. The disordered ethanol solvent molecules occupy the spaces between the layers and are hydrogen bonded to the layers. The two symmetry-independent dianions lie on different inversion sites.

Comment

Zinc terephthalate forms a number of 1:1 adducts with bidentate N-heterocyclic ligands; crystallographic studies have focused on rigid heterocycles, such as, for example, 4,4′-bipyridine (Tao *et al.*, 2000) and 1,10-phenanthroline (Sun *et al.*, 2001). As the terephthalate entity itself is rigid, the adducts adopt architectures that reflect such rigidity, *i.e.* the 4,4′-bipyridine adduct is a three-dimensional network and the 1,10-phenanthroline adduct is a linear chain. With a flexible ligand such as 1,3,4-bis(triazol-1-yl)ethane, a two-dimensional rhombic network is formed (Li *et al.*, 2004). 1,3,4-Bis(triazol-1-yl)butane affords a threefold interpenetrating diamondoid network based on a zinc center (Wang *et al.*, 2006).



(I)

1,3-Bis(benzimidazol-2-yl)benzene, an N-heterocycle that can be conveniently synthesized by condensing *m*-phenylenediamine and phthalic acid under the influence of microwaves (Song *et al.*, 2000), is a ligand that can bind to two metal centers through its two tertiary nitrogen-donor sites. Spectroscopic measurements are available for a small number of adducts with transition metals, and among the zinc complexes that have been characterized spectroscopically are the halide and perchlorate complexes (Chawla & Gill, 1997; Shivakumaraiah & Nanje Gowda, 2003), but to date no example of an adduct has been reported in the literature (CSD, Version 5.28, November 2006 release; Allen, 2002).

The title 1:1 zinc terephthalate–bis(benzimidazolyl)benzene adduct, (I), which exists as an ethanol solvate, is a coordination polymer in which the carboxylate group and benzene ligand both engage in bridging two tetrahedral zinc centers (Fig. 1), this bridging mode giving rise to a layer motif. The two symmetry-independent dianions lie on different inversion sites. The two benzimidazolyl arms are bent with respect to the phenylene ring, one (with the N1 atom) being twisted by 31.6 (1)° and the other (with the N3 atom) being twisted by 15.7 (1)°. The twist angles parallel the deviation of the metal atom from the plane of the arms, the atom being displaced by 0.807 (3) Å from the first arm and by 0.507 (3) Å from the second arm.

The topology of the layer is a (6,3)-honeycomb (Fig. 2) that is somewhat buckled as the two bridging components are of

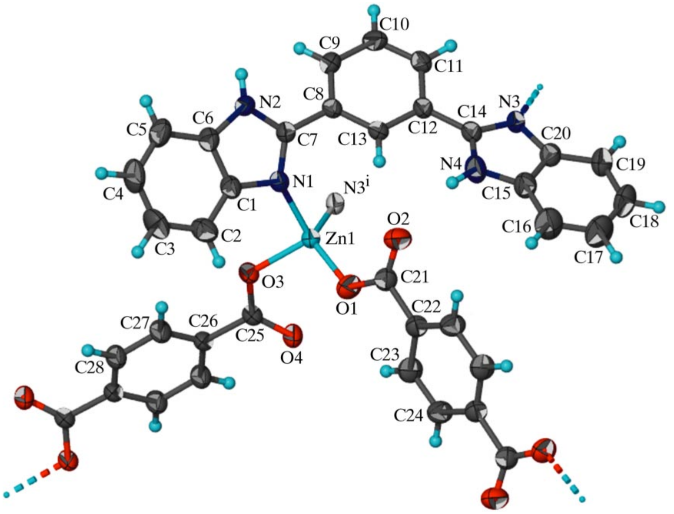


Figure 1
The tetrahedral geometry of the Zn atom in the layer structure of (I). Displacement ellipsoids are drawn at the 70% probability level. The disordered ethanol solvent molecule is not shown. [Symmetry code: (i) $-x, 1-y, 1-z$.]

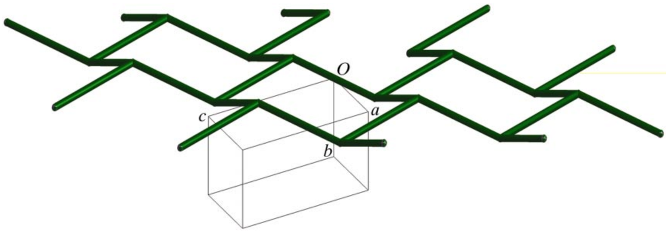


Figure 2
OLEX (Dolomanov *et al.*, 2003) depiction of the (6,3)-honeycomb topology, shown projected against the unit cell.

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different sizes. The atoms comprising the layer framework constitute only about 79% of the volume, as calculated by *PLATON* (Spek, 2003). The layers are consolidated by N—H···O hydrogen bonds (Table 2), but the space between layers is large enough to accommodate ethanol molecules.

Experimental

The N-heterocycle was prepared according to a reported procedure (Chawla & Gill, 1997). Zinc nitrate hexahydrate (0.074 g, 0.25 mmol), benzene-1,4-dicarboxylic acid (0.021 g, 0.125 mmol), 1,3-bis(benzimidazol-2-ylmethyl)benzene (0.039 g, 0.125 mmol), ethanol (2 ml) and water (15 ml) were placed in a 23 ml Teflon-lined stainless steel Parr bomb. (Neither sodium nor potassium hydroxide was added.) The bomb was heated at 433 K for 5 d and cooled to room temperature at a rate of 5 K h^{-1}. Colorless block-shaped crystals were obtained in 20% yield.

Crystal data

$[Zn(C_8H_4O_4)(C_{20}H_{14}N_4)]\cdot C_2H_6O$
$M_r = 585.90$
Triclinic, $P\overline{1}$
$a = 9.0660$ (8) Å
$b = 9.3077$ (9) Å
$c = 15.921$ (2) Å
$\alpha = 86.731$ (1)°
$\beta = 83.140$ (1)°
$\gamma = 87.931$ (1)°
$V = 1331.1$ (2) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.97$ mm^{-1}
$T = 291$ (2) K
0.28 × 0.21 × 0.18 mm

Data collection

Bruker APEX area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.712$, $T_{max} = 0.845$
10765 measured reflections
5834 independent reflections
4918 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.098$
$S = 1.03$
5834 reflections
389 parameters
31 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.38$ e Å^{-3}
$\Delta\rho_{min} = -0.41$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn1—O1	1.930 (2)	Zn1—N1	2.040 (2)
Zn1—O3	1.966 (2)	Zn1—N3^i	2.036 (2)
O1—Zn1—O3	106.0 (1)	O3—Zn1—N1	98.9 (1)
O1—Zn1—N3^i	125.1 (1)	O3—Zn1—N3^i	104.2 (1)
O1—Zn1—N1	115.7 (1)	N1—Zn1—N3^i	103.30 (7)

Symmetry code: (i) $-x, -y+1, -z+1$.

The ethanol solvent molecule is disordered in the C atoms and was refined with two ethyl components in a 0.72:0.28 ratio. The O—C distance was restrained to 1.45 (1) Å and the C—C distance to 1.50 (1) Å. The displacement parameters of the four C atoms were restrained to be nearly isotropic.

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2n···O4^{ii}	0.84 (2)	1.94 (2)	2.777 (2)	176 (3)
N4—H4n···O2	0.86 (2)	2.11 (2)	2.895 (3)	152 (3)
O5—H5o···O1	0.86 (4)	2.14 (4)	2.999 (4)	176 (7)

Symmetry code: (ii) $x, y+1, z$.

Carbon-bound H atoms were positioned geometrically (C—H = 0.93 and 0.97 Å), and were included in the refinement in the riding-model approximation, with U_{iso}(H) values set at 1.2–1.5U_{eq}(C). The water and amino H atoms were located in a difference Fourier map, and were refined with a distance restraint of O—H = N—H = 0.85 (1) Å.

Data collection: *SMART* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2007).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG3037). Services for accessing these data are described at the back of the journal.

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