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## Key indicators

Single-crystal X-ray study

T = 273 K

Mean  $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$ 

R factor = 0.024

wR factor = 0.065

Data-to-parameter ratio = 14.2

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.A two-dimensional network: poly[aqua- $\mu_2$ -1,4-diazabicyclo[2.2.2]octane- $\mu_2$ -terephthalato-zinc(II)]

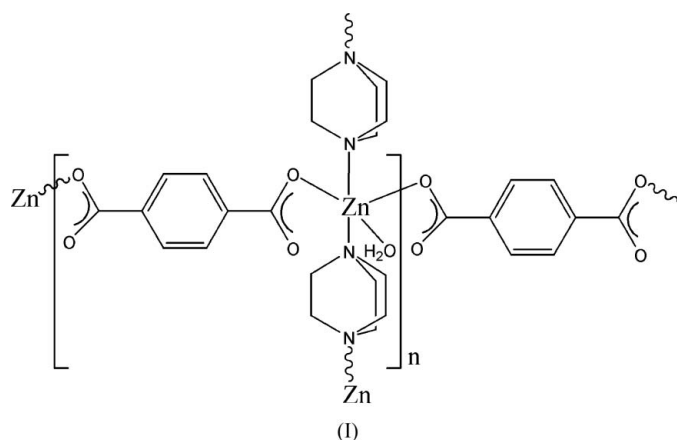
In the title complex,  $[\text{Zn}(\text{tp})(\text{dbo})(\text{H}_2\text{O})]_n$ , where tp is terephthalate ( $\text{C}_8\text{H}_4\text{O}_4$ ) and dbo is 1,4-diazabicyclo[2.2.2]octane ( $\text{C}_6\text{H}_{12}\text{N}_2$ ), each  $\text{Zn}^{\text{II}}$  atom is coordinated by three O atoms from two bis-monodentate tp ligands and one aqua ligand, and by two N atoms from two bridging dbo ligands, in a distorted trigonal-bipyramidal geometry, with the two N atoms located at the axial sites. The bridging tp ligands link the  $\text{Zn}^{\text{II}}$  atoms to form one-dimensional zigzag chains, running along [221]. These chains are assembled into layers parallel to the *ac* plane by dbo ligands, which are extended into a three-dimensional network by O—H...O hydrogen bonds and  $\pi$ – $\pi$  stacking interactions.

## Comment

Supramolecular chemistry based on the metal-ion-directed assembly of organic molecular building blocks is receiving extensive attention, owing to potential applications in the fields of catalysis, nonlinear optics, sensors, magnetism and molecular recognition (Lehn, 1995). Because the construction of a molecular architecture depends on the combination of several factors, such as the coordination geometry of the metal ions, the nature of the organic ligands, metal atoms, counter-anions and solvent, the templates, and sometimes the ratio between the metal salt and the ligand (Hirsch *et al.*, 1997), it is still a challenge to control the structure of a complex. Dicarboxylate ligands adopting a plethora of coordination modes are an important type of bridging ligand in the construction of coordination architectures. Together with different multi-N-ligands, they can give various structural coordination polymers by the reaction of transition metal ions. Studying such reaction systems is very helpful to understand how the nature of the metal ions and the structure of the ligands affect the structure of their complexes. Previous studies showed that 2,2'-bipyridine-like chelate ligands give low-dimensional coordination polymers, especially one-dimensional chains, with dicarboxylate ligands and transition metals under hydrothermal conditions (Zhang *et al.*, 2003); 4,4'-bipyridine-like N-ligands and dicarboxylate anions give infinite two-dimensional network polymers by reaction of Cu ions (Sun *et al.*, 2003) and three-dimensional network polymers with six- or seven-coordinated transition metal ions, such as zinc, cadmium and cobalt (Li *et al.*, 1999). 1,4-Diazabicyclo[2.2.2]octane gives a two-dimensional network polymer by reaction of the dicarboxylate ligands and the  $\text{Zn}^{\text{II}}$  atom, in contrast with the three-dimensional network polymer formed with 4,4'-bipyridine and the same dicarboxylate ligand and  $\text{Zn}^{\text{II}}$  atom. This indicates that the steric hindrance of the N-ligand also affects the structure of the resulting complex. We report here the crystal structure of the title complex, (I).

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In the title complex, the  $\text{Zn}^{\text{II}}$  atom and the O atom of the coordinated water molecules in the asymmetric unit lie on a twofold rotation axis, and have a partial occupancy of 0.5. Each  $\text{Zn}^{\text{II}}$  atom is coordinated by three O atoms from two bis-monodentate tp ligands, and one coordinated aqua ligand and two N atoms from two bridging dbo ligands, in a distorted trigonal-bipyramidal geometry, with the two N atoms located at the axial sites (Fig. 1, Table 1).

The bridging tp ligands link the  $\text{Zn}^{\text{II}}$  atoms to form one-dimensional zigzag chains running along [221]. These chains are assembled into layers parallel to the  $ac$  plane by the bridging dbo ligands (Fig. 2). These layers are then extended into a three-dimensional network by O—H...O hydrogen bonds and  $\pi$ – $\pi$  stacking interactions. The  $\text{Cg4} \cdots \text{Cg4}^{\text{i}}$  distance is 3.580 (2) Å, where Cg4 is the centroid of the C2–C4/C2<sup>ii</sup>–C4<sup>ii</sup> ring [symmetry codes: (i)  $1 - x, y, -\frac{1}{2} - z$ ; (ii)  $1 - x, 1 - y, -z$ ] (Fig. 3, Table 2). The network structure is further stabilized by C—H...O hydrogen bonds.

## Experimental

A mixture of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.297 g, 1.0 mmol), terephthalic acid (0.083 g, 0.5 mmol), 1,4-diazabicyclo[2.2.2]octane (0.112 g, 1.0 mmol), NaOH (0.040 g, 1.0 mmol) and water (10 ml) was stirred for 15 min in air, then transferred to and sealed in a Teflon reactor (23 ml). The reactor was heated at 433 K for 5 d and then cooled to room temperature at a rate of 5 K h<sup>-1</sup>. Colourless prisms of (I) were obtained, and these were washed with deionized water and absolute ethanol (yield >40% based on Zn). Elemental analysis for (I):  $\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_5\text{Zn}$  (359.67) requires: C 46.75, H 5.04, N 7.79%; found: C 46.70, H 5.15, N 7.82%.

### Crystal data

$[\text{Zn}(\text{C}_8\text{H}_4\text{O}_4)(\text{C}_6\text{H}_{12}\text{N}_2)(\text{H}_2\text{O})]$

$M_r = 359.67$

Monoclinic,  $C2/c$

$a = 10.854$  (3) Å

$b = 18.955$  (6) Å

$c = 7.1592$  (19) Å

$\beta = 116.23$  (2)°

$V = 1321.2$  (7) Å<sup>3</sup>

$Z = 4$

$D_x = 1.808$  Mg m<sup>-3</sup>

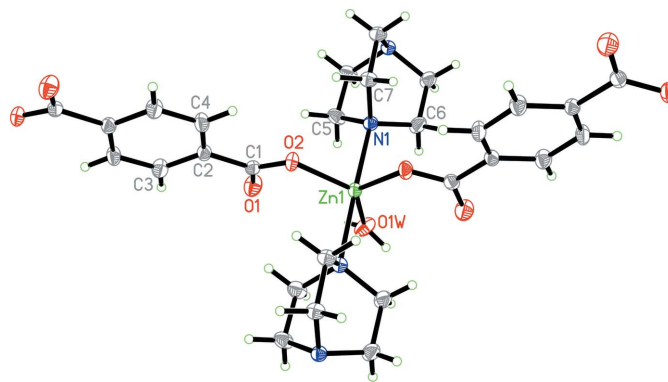
Mo  $K\alpha$  radiation

$\mu = 1.89$  mm<sup>-1</sup>

$T = 273$  (2) K

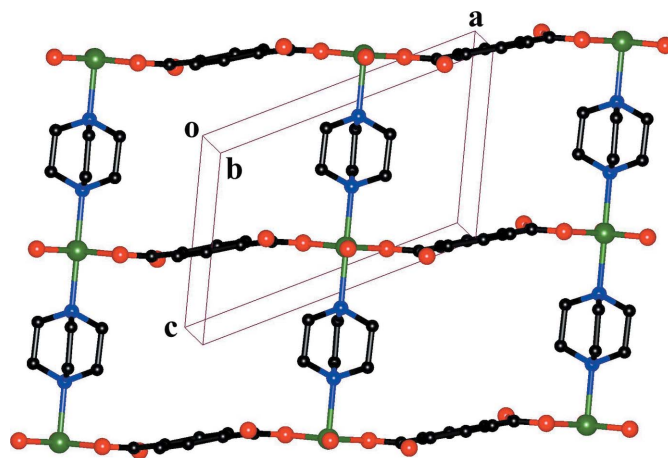
Block, colourless

$0.26 \times 0.13 \times 0.06$  mm



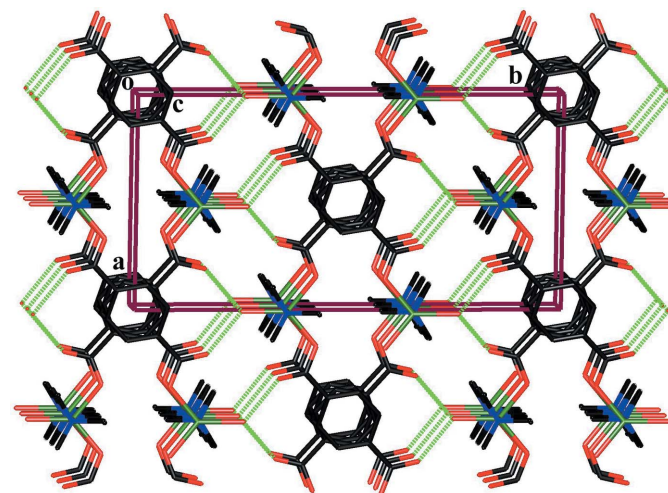
**Figure 1**

Part of the polymeric network of (I), showing 50% probability displacement ellipsoids. Symmetry operations (i)  $(2 - x, +y, \frac{1}{2} - z)$ , (ii)  $(1 - x, 1 - y, -z)$  and (iii)  $(1 + x, 1 - y, +z)$  are for O1/O2/C1–C4 and their H atoms, and operations (i), (iv)  $(2 - x + y, -\frac{1}{2} - z)$  and (v)  $(+x, +y, 1 + z)$  are for atoms N1/C5–C7 and their H atoms. The  $\text{Zn}^{\text{II}}$  atom and the O atom of the coordinated water molecules in the asymmetric unit lie on a twofold rotation axis and have a partial occupancy of 0.5.



**Figure 2**

A layer of (I), viewed along the  $b$  axis. H atoms have been omitted.



**Figure 3**

The crystal packing of (I), viewed along the  $c$  axis. H atoms have been omitted. Dashed lines indicate hydrogen bonds.

## Data collection

Bruker SMART APEX area-detector diffractometer	3966 measured reflections
$\varphi$ and $\omega$ scans	1433 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	1361 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.640$ , $T_{\max} = 0.895$	$R_{\text{int}} = 0.018$
	$\theta_{\text{max}} = 27.0^\circ$

## Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0367P)^2 + 1.1622P]$
$R[F^2 > 2\sigma(F^2)] = 0.025$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.065$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.39 \text{ e } \text{\AA}^{-3}$
1433 reflections	$\Delta\rho_{\text{min}} = -0.23 \text{ e } \text{\AA}^{-3}$
101 parameters	
H-atom parameters constrained	

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Zn1—O2	2.011 (1)	Zn1—N1	2.269 (2)
Zn1—O1W	2.034 (2)		
O2 <sup>i</sup> —Zn1—O2	101.26 (8)	O1W—Zn1—N1	87.29 (4)
O2 <sup>i</sup> —Zn1—O1W	129.37 (4)	O2—Zn1—N1 <sup>i</sup>	90.90 (5)
O2—Zn1—O1W	129.37 (4)	O1W—Zn1—N1 <sup>i</sup>	87.29 (4)
O2 <sup>i</sup> —Zn1—N1	90.90 (5)	N1—Zn1—N1 <sup>i</sup>	174.59 (7)
O2—Zn1—N1	92.54 (5)		

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

**Table 2**

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1W—H1WA $\cdots$ O1 <sup>ii</sup>	0.85	1.84	2.6891 (19)	176
C5—H5B $\cdots$ O1 <sup>ii</sup>	0.97	2.43	3.362 (2)	162

Symmetry code: (ii)  $-x + \frac{3}{2}, -y + \frac{1}{2}, -z$ .

Water H atoms were located in a Fourier difference map, adjusted to give C—H = 0.85  $\text{\AA}$ , and refined as riding on their parent atoms, with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ . C-bound H atoms were positioned geometrically, with C—H = 0.93  $\text{\AA}$  for aromatic C atoms and 0.96  $\text{\AA}$  for methylene C atoms, and refined as riding on their parent C atoms, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2002); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Bruker, 2000); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL and OLEX (Dolomanov *et al.*, 2003); software used to prepare material for publication: SHELXTL and OLEX.

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