

## Poly[ $\mu$ -aqua- $\mu_4$ -naphthalene-1,8-dicarboxylato-zinc(II)]

Yi-Hang Wen,\* Xia Feng, Yin-Hua He, You-Zhao Lan and Hong Sun

Zhejiang Key Laboratory for Reactive Chemistry on Solid Surfaces, Institute of Physical Chemistry, Zhejiang Normal University, Jinhua, Zhejiang 321004, People's Republic of China

Correspondence e-mail: wyh@zjnu.cn

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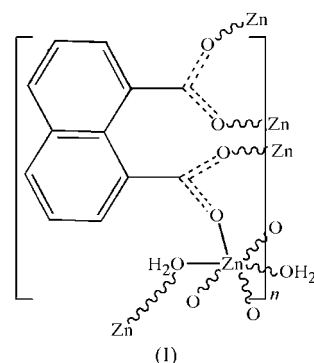
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In the title complex,  $[\text{Zn}(\text{C}_{12}\text{H}_6\text{O}_4)(\text{H}_2\text{O})]_n$ , a  $\text{Zn}^{\text{II}}$  polymer based on naphthalene-1,8-dicarboxylate (1,8-nap), the  $\text{Zn}^{\text{II}}$  atoms adopt an elongated octahedral coordination geometry. A zigzag chain is formed by  $\mu_2$ -aqua ligands and  $\mu_2$ -carboxylate groups of the 1,8-nap ligands. Adjacent parallel chains are further linked by 1,8-nap ligands, forming a twisted two-dimensional layer structure along the (100) plane.

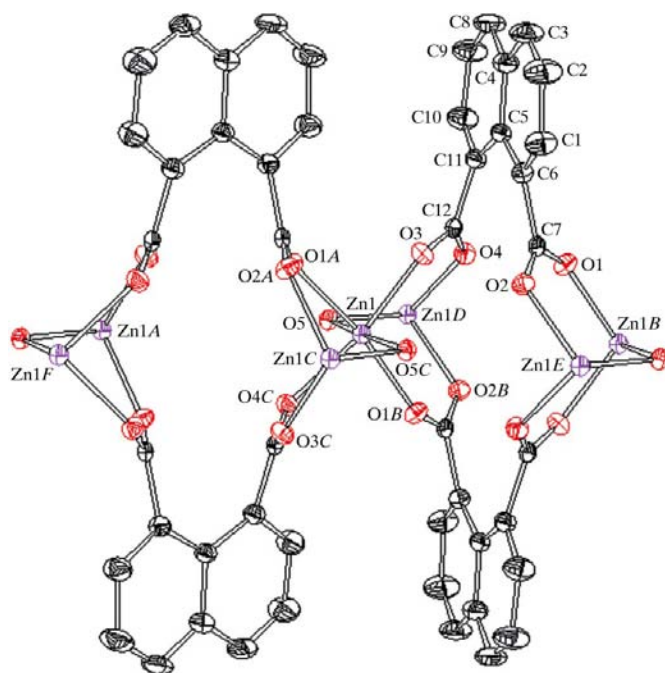
### Comment

Considerable efforts are currently devoted to the use of suitable multidentate ligands as building blocks to design metal-organic coordination polymers, not only because such ligands can construct intriguing structural topologies (Yaghi *et al.*, 1998; Hagrman *et al.*, 1999), but also because of their potential properties for eventual application as functional materials (Piguet *et al.*, 1997; Park *et al.*, 2001). Molecular self-assembly has emerged as an attractive approach to the fabrication of new materials, and in the construction of one-, two- or three-dimensional frameworks, multidentate ligands are usually used to bridge metal centers into polymeric structures (Li *et al.*, 1999; Zheng *et al.*, 2003; Wen *et al.*, 2005). It is well known that naphthyl-containing aromatic multicarboxylate ligands are versatile building blocks able to modify the structure and properties of these polymers owing to their variety of bridging abilities. Some structural reports on transition metal complexes containing naphthalenecarboxylic acid, such as naphthalene-1,4,5,8-tetracarboxylic dianhydride (Xu *et al.*, 2005), naphthalene-1,4,5,8-tetracarboxylic acid (Wang *et al.*, 2005; Chen *et al.*, 2005) and naphthalene-1,4-dicarboxylic acid (Zheng *et al.*, 2005), have been reported in the literature. One of our current lines of work focuses on the use of naphthalene-1,8-dicarboxylic anhydride, hydrolyzed under hydrothermal conditions into the naphthalene-1,8-dicarboxylate ligand (1,8-nap), as a starting material to prepare novel coordination polymers. As part of this work, we

report here a new two-dimensional Zn complex, *viz.*  $[\text{Zn}(1,8\text{-nap})(\text{H}_2\text{O})]_n$ , (I). To the best of our knowledge, (I) is the first  $\text{Zn}^{\text{II}}$  polymer containing the 1,8-nap ligand.



The asymmetric unit of (I) is composed of one Zn atom, one  $\mu_4$ -1,8-nap ligand and one bridging water molecule. As shown in Fig. 1, the  $\text{Zn}^{\text{II}}$  center is six-coordinated by four carboxylate O atoms of four 1,8-nap ligands and two water molecules, and displays a slightly distorted  $\text{ZnO}_6$  octahedral coordination geometry, with the three *trans* angles [170.58 (5), 170.66 (5) and 174.41 (4) $^\circ$ ] deviating slightly from the ideal value of 180 $^\circ$ . The four carboxylate O atoms form the equatorial plane of the octahedron [the sum of the angles is 360.0 (2) $^\circ$ ], from which atom Zn1 deviates slightly, by 0.018 Å. Finally, the two water O atoms occupy the axial positions, with an O—Zn—O angle

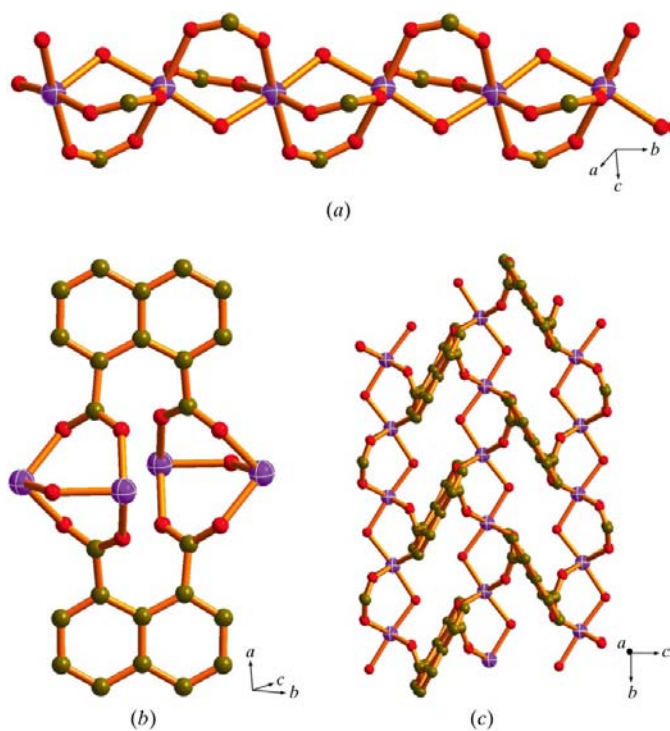


**Figure 1**

The coordination environment of the  $\text{Zn}^{\text{II}}$  atom in (I), showing the atom-numbering scheme. Displacement ellipsoids are plotted at the 30% probability level. Atoms labeled with the suffixes A–F are at the symmetry positions  $(x, \frac{1}{2} - y, -\frac{1}{2} + z)$ ,  $(1 - x, -y, 2 - z)$ ,  $(1 - x, \frac{1}{2} + y, \frac{3}{2} - z)$ ,  $(1 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$ ,  $(x, \frac{1}{2} - y, \frac{1}{2} + z)$  and  $(1 - x, 1 - y, 1 - z)$ , respectively.

of  $174.41(4)^\circ$ . The Zn—O<sub>carboxy</sub> and Zn—O<sub>water</sub> distances (Table 1) are comparable to those found in other Zn<sup>II</sup> complexes with similar coordination (Kongshaug & Fjellvag, 2002; Chun *et al.*, 2005; Muthu *et al.*, 2001). The carboxylate groups of the 1,8-nap ligand act as  $\mu_2$ -bridges to link two Zn atoms, and as a result, each 1,8-nap is coordinated by four Zn atoms. The ligands are not planar, with the carboxylate groups and the naphthalene ring system subtending dihedral angles of  $45.8(1)$  and  $45.4(1)^\circ$ , respectively.

The Zn<sup>II</sup> centers in (I) are linked *via*  $\mu_2$ -aqua and  $\mu_2$ -carboxylate groups to generate a one-dimensional linear chain propagating along the *b* axis, with a Zn···Zn separation of  $3.529(1)$  Å (Fig. 2*a*). In this chain, the ZnO<sub>6</sub> octahedra are corner-sharing *via*  $\mu_2$ -aqua ligands. One of the strong hydrogen bonds in the structure, that involving H5B as a donor and O2 as an acceptor, contributes to this process (Table 2). As shown in Fig. 2(*b*), two 1,8-nap ligands bridge simultaneously two dinuclear Zn units from two adjacent chains, thus further combining parallel chains into two-dimensional layers parallel to the (100) plane (Fig. 2*c*). This action is reinforced by the remaining hydrogen bond, involving H5A and O2 (Table 2). It is worth noting that both hydrogen bonds are felt by the corresponding Zn—O(acceptor) interactions, which end up being the longer (weaker) ones among Zn—O(carboxylate) distances. The naphthalene ring systems of the ligands are located on opposite sides of the layer, and the dihedral angles between naphthalene systems from different sides are  $59.8(1)^\circ$ .



**Figure 2**  
(*a*) A view of the chain substructure in (I); (*b*) two dinuclear Zn units from two adjacent chains bridged by two 1,8-nap ligands; (*c*) a view of the layered structure of (I).

## Experimental

A mixture of naphthalene-1,8-dicarboxylic anhydride (0.1982 g, 1 mmol), ZnSO<sub>4</sub>·7H<sub>2</sub>O (0.2857 g, 1 mmol), Na<sub>2</sub>CO<sub>3</sub> (0.053 g, 0.5 mmol) and water–ethanol (1:1, 16 ml) was sealed in a 25 ml stainless steel reactor with a Teflon liner and heated at 433 K for 3 d. On completion of the reaction, the reactor was cooled slowly to room temperature and the mixture was filtered, giving colorless single crystals suitable for X-ray analysis in 30% yield. Elemental analysis found: C 48.84, H 2.36, O 27.12%; calculated for C<sub>12</sub>H<sub>8</sub>O<sub>5</sub>Zn: H 2.39, C 48.82, O 27.11%. IR (KBr, cm<sup>-1</sup>): 3052.63 (*s*), 1771.44 (*s*), 1739.21 (*s*), 1619.59 (*sh*), 1511.94 (*s*), 1454.43 (*s*), 1388.66 (*s*), 845.35 (*s*), 775.57 (*sh*), 632.97 (*s*).

### Crystal data

[Zn(C <sub>12</sub> H <sub>8</sub> O <sub>4</sub> )(H <sub>2</sub> O)]	$V = 1065.6(4)$ Å <sup>3</sup>
$M_r = 297.55$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 15.693(3)$ Å	$\mu = 2.31$ mm <sup>-1</sup>
$b = 7.0491(14)$ Å	$T = 296(2)$ K
$c = 9.752(2)$ Å	$0.19 \times 0.15 \times 0.05$ mm
$\beta = 98.97(3)^\circ$	

### Data collection

Bruker APEXII area-detector diffractometer	9526 measured reflections
Absorption correction: empirical (using intensity measurements) (SADABS; Sheldrick, 1996)	2427 independent reflections
$T_{\min} = 0.67$ , $T_{\max} = 0.89$	2134 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.025$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.061$	$\Delta\rho_{\max} = 0.41$ e Å <sup>-3</sup>
$S = 1.07$	$\Delta\rho_{\min} = -0.43$ e Å <sup>-3</sup>
2427 reflections	
169 parameters	
3 restraints	

**Table 1**  
Selected bond lengths (Å).

Zn1—O1 <sup>i</sup>	2.0483 (13)	Zn1—O4 <sup>iii</sup>	2.0921 (13)
Zn1—O3	2.0529 (13)	Zn1—O5	2.1330 (12)
Zn1—O2 <sup>ii</sup>	2.0837 (13)	Zn1—O5 <sup>iii</sup>	2.1547 (12)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O5—H5A···O4 <sup>iv</sup>	0.813 (15)	1.955 (18)	2.6931 (19)	151 (2)
O5—H5B···O2 <sup>v</sup>	0.851 (15)	1.888 (17)	2.6757 (19)	153 (2)

Symmetry codes: (iv)  $x, -y - \frac{1}{2}, z - \frac{1}{2}$ ; (v)  $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$ .

C-bound H atoms were positioned geometrically and included in the refinement using a riding model [ $C-H = 0.93$  Å and  $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$ ]. Water H atoms were located in difference maps and their positions were refined isotropically, with distance restraints  $O-H = 0.85(2)$  Å and  $H\cdots H = 1.30(2)$  Å; their  $U_{\text{iso}}(H)$  values were set at  $1.5U_{\text{eq}}(O)$ .

Data collection: APEXII (Bruker, 2006); cell refinement: SAINT (Bruker, 2006); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine

structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2002); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG3055). Services for accessing these data are described at the back of the journal.

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