A double-layered zinc(II) coordination polymer with the ligand 3,5-bis(carboxylatomethoxy)benzoate

Zhong-Min Cen,[a] Fa-Si Li,[a] Qing-Ling Ni,[a] Xiu-Jian Wang[a]* and Bin Li[b]

[a]School of Chemistry and Chemical Engineering, Guangxi Normal University, Guilin 541004, People's Republic of China, and [b]School of Chemistry and Chemical Engineering, Guangxi University, Nanling 530004, People's Republic of China
Correspondence e-mail: wang1_xj@yahoo.com.cn

In the title compound, poly[hexaaquabis[μ_4-3,5-bis(carboxylatomethoxy)benzoato]trizinc(II)], $[Zn_3(C_{11}H_7O_8)_2(H_2O)_6]_n$, there are two crystallographically distinct Zn^{II} cations which are bridged by polycarboxylate ligands in a μ_4-bridging mode. A pair of ligands bridges adjacent Zn atoms to give centrosymmetric dimetal building blocks which act as four-connected nodes to be further interlinked into a two-dimensional double-layered framework with (4,4) topology. Other Zn atoms, lying on inversion centres, occupy the cavities of this topological structure. This submission shows a versatile polycarboxylate ligand with rigid and flexible functional groups, the co-operation and complementarity of which would meet the coordination requirements of a variety of topological structures.

Comment

Carboxylate-containing ligands have been intensively investigated are linkers in metal–organic frameworks with an intriguing variety of topologies and potential applications in gas sorption, separation and/or catalysis (Eddaoudi *et al.*, 2001; Kitagawa *et al.*, 2004; Rao *et al.*, 2004). A wide variety of metal–carboxylate architectures are obtained by varying the nature of the reactants or the synthetic conditions. Polycarboxylate ligands are good choices for such architectures because the topological structures can be adjusted not only by the location of the carboxylate groups but also by the nature of the organic spacers. Rigid spacer-based ligands such as phenylenedicarboxylate have commonly been used to design functional metal–organic frameworks since these ligands allow for a certain level of control of steric effects in the assembly process and result in predictable motifs (Bourne *et al.*, 2001; Kim *et al.*, 2001). Nevertheless, it is also known that flexible ligands have good conformational freedom, which manifests itself in the various connecting modes that offer opportunities

to create structurally diverse molecular architectures (Chen *et al.*, 2007). In addition, compounds that are capable of rotational motion in response to outside driving forces, such as light, heat or electric fields, are intriguing for the development of molecular devices (Horike *et al.*, 2006). Therefore, efforts recently focusing on manipulating flexible ligands for metal–organic frameworks have been increasing. Considering the respective advantages of rigid and flexible ligands, their co-operation has been proved to be successful in creating metal–organic architectures with intriguing topological structures and/or potential applications (Wang *et al.*, 2007; Wei *et al.*, 2008).

As part of our ongoing investigation of metal–organic frameworks involving semirigid organic ligands (Wang *et al.*, 2008), we have developed a versatile polycarboxylate ligand, 3,5-bis(carboxymethoxy)benzoic acid (H_3L), which contains non-equivalent carboxyl groups from a rigid benzoic acid group and two flexible carboxymethoxy groups. The complementarity of the coordination function and geometric conformation from these different carboxyl groups matches the requirement for structural variety in metal–organic frameworks. We report here the title compound, (I), a two-dimensional zinc-containing double-layered framework structure, prepared by reacting H_3L with $ZnAc_2 \cdot 2H_2O$ (Ac is acetate) under hydrothermal conditions.
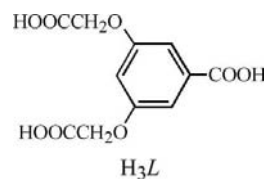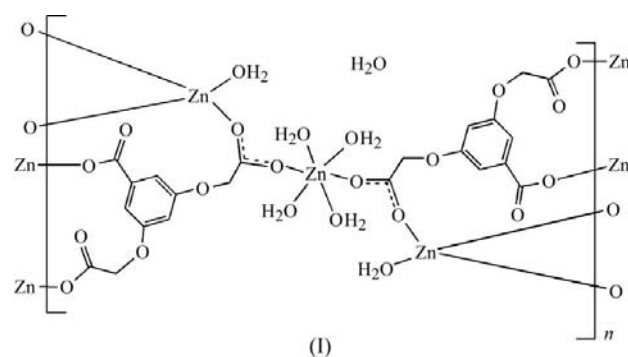

Compound (I) is a two-dimensional double-layer polymer in which the asymmetric unit contains one ligand, two crystallographically independent Zn^{II} ions, one of which lies on a centre of inversion, and three coordinated water molecules (Fig. 1). The coordination geometry of atom Zn1 can be described as a distorted tetrahedron consisting of three carboxylate O atoms from three different ligands and one aqua O atom [O7, O9, O5^i and O2^{ii}; symmetry codes: (i) $-x+2$, $-y+1$, $-z$; (ii) $x-\frac{1}{2}$, $-y+\frac{3}{2}$, $z+\frac{1}{2}$]. Atom Zn2 is located on the inversion centre at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and is coordinated by two carboxylate O atoms from two different ligands and four aqua

metal-organic compounds
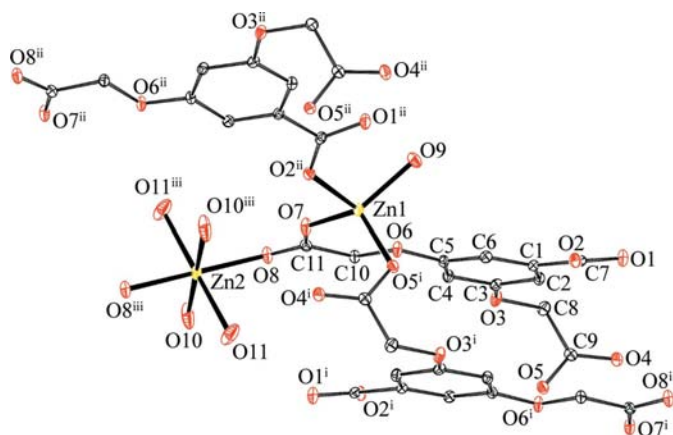
Figure 1
The local coordination of Zn^{II} cations in the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. [Symmetry codes: (i) $-x + 2$, $-y + 1$, $-z$; (ii) $x - \frac{1}{2}$, $-y + \frac{3}{2}$, $z + \frac{1}{2}$; (iii) $-x + 1$, $-y + 1$, $-z + 1$.]

O atoms [O8, O10 and O11, and their symmetry-related atoms at $(1 - x, 1 - y, 1 - z)$], giving a slightly distorted octahedral geometry. The whole ligand is completely deprotonated in this complex and acts in a μ_4-bridging mode. One carboxylato-methoxy group is approximately coplanar with the aromatic ring, with a C5—O6—C10—C11 torsion angle of 177.2 (2)°, while the other deviates from this ring, with a C3—O3—C8—C9 torsion angle of 67.0 (3)° and a dihedral angle between the carboxylate group and the aromatic ring plane of 102.8 (2)°. The carboxylate group of the coplanar carboxylatomethoxy group behaves as a *syn–anti* bidentate bridging ligand to coordinate atoms Zn1 and Zn2, while each of the other two carboxylate groups adopts a monodentate coordination mode to bridge different Zn1 atoms. The Zn1—O6 distance of 2.706 (2) Å shows some weak interaction between Zn1 and an uncoordinated ether O atom from the coplanar carboxylato-methoxy group, which may be viewed as a semichelating coordination mode. Such a weak interaction could lead to this carboxylatomethoxy group being coplanar with the benzene ring. Therefore, the environment of atom Zn1 can also be described as a significantly distorted trigonal bipyramid, with atoms O6 and O2^{ii} located at the apical positions and atoms O7, O9 and O5^i in the equatorial positions [symmetry codes: (i) $-x + 2$, $-y + 1$, $-z$; (ii) $x + \frac{1}{2}$, $-y + \frac{3}{2}$, $z + \frac{1}{2}$].

Analysis of this polymeric network suggests a functional centrosymmetric dimetallic building block unit, generated by a pair of symmetry-related ligands bridging adjacent Zn1 atoms (Fig. 2a), with its centre located on an inversion centre. The pair of ligands adopts an antiparallel mode, with a centroid–centroid distance of 3.895 (4) Å, an interplanar distance of 3.513 (2) Å and a ring-centroid slippage of 1.683 Å, indicating that the two benzene rings do not overlap. Such building blocks can be regarded as double-layered motifs and they adopt a four-connected node (each pair of connections associated with one layer) to be further interlinked through Zn1—O$_{benzoate}$ bonds into a two-dimensional double-layered framework with (4,4) topology. Four adjacent building blocks
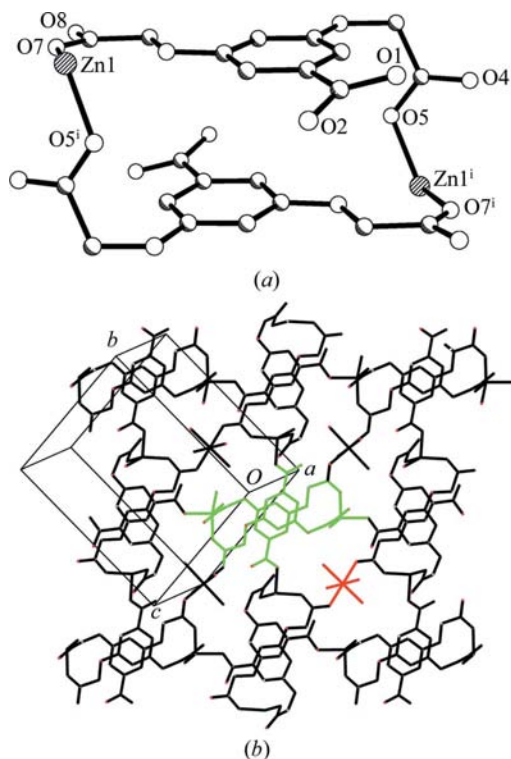
Figure 2
(a) The centrosymmetric dimetal building block [symmetry code: (i) $-x + 2$, $-y + 1$, $-z$]. (b) The two-dimensional double-layered structure consisting of four-connected building blocks. The layer formed is parallel to the (101) plane. H atoms have been omitted for clarity. In the electronic version of the paper, green indicates the building block and red the ZnO$_6$ fragment.
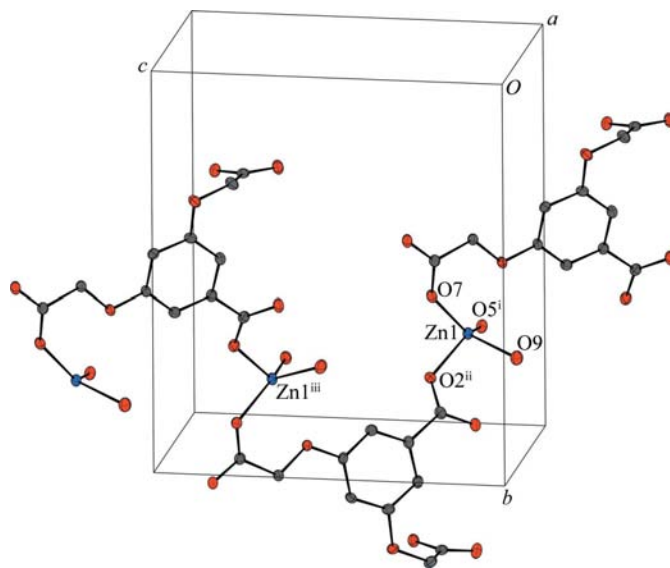
Figure 3
The independent one-dimensional zigzag metal–organic chain in each layer, constructed by Zn1 atoms and ligands. [Symmetry codes: (i) $-x + 2$, $-y + 1$, $-z$; (ii) $x - \frac{1}{2}$, $-y + \frac{3}{2}$, $z + \frac{1}{2}$; (iii) $x - \frac{3}{2}$, $-y + \frac{1}{2}$, $z - \frac{1}{2}$.]

are interlinked to form a cavity which is occupied by one octahedral Zn2 atom that links two opposite building blocks through O4 atoms at (x, y, z) and $(1 - x, 1 - y, 1 - z)$, stabilizing the cavity (Fig. 2b). Therefore, the double-layered

framework is formed by assembling the building blocks, whereas the ZnO_6 fragments occupy the cavities. Further analysis of this structure shows that each layer consists of independent one-dimensional zigzag metal–organic chains constructed by consecutive linking between atom Zn1 and the ligands through carboxylate O atoms from the benzoate and coplanar carboxylatomethoxy groups, respectively (Fig. 3). The combination of crosslinking and linking through Zn2—O bonds between chains belonging to different layers forms the double-layered framework.

All coordinated water molecules in complex (I) act as dual hydrogen-bond donors, with carboxylate O atoms acting as the acceptors (Table 2). The ether O atoms are not involved in hydrogen bonding. Atoms H9A, H10A, H10B and H11A participate in the hydrogen bonding to consolidate the two-dimensional double-layered structure, whereas atoms H9B and H11A form hydrogen bonds with carboxylate O atoms from neighbouring double-layered structures to form a three-dimensional supramolecular structure. Adjacent double-layered structures stack antiparallel in an $ABAB \ldots$ pattern.

Experimental

A mixture of $ZnAc_2 \cdot 2H_2O$ (0.0438 g, 0.2 mmol) and H_3L (0.1224 g, 0.4 mmol) in H_2O (4 ml) and tetrahydrofuran (4 ml) was sealed in a Teflon-lined steel bomb (15 ml) and then heated at 353 K for 3 d. Colourless block-shaped crystals of (I) were collected (yield: 20%). Elemental analysis calculated for $C_{22}H_{26}O_{22}Zn_3$: C 31.50, H 3.10%; found: C 31.32, H 2.92%. IR (KBr, ν, cm^{-1}): 3494 (m), 1638 (s), 1604 (s), 1546 (s), 1425 (s), 1404 (s), 1359 (m), 1324 (m), 1171 (s), 1097 (m), 1079 (m), 751 (m), 792 (m).

Crystal data

$[Zn_3(C_{11}H_7O_8)_2(H_2O)_6]$	$V = 1391.0$ (3) Å^3
$M_r = 838.54$	$Z = 2$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 8.0458$ (9) Å	$\mu = 2.67$ mm^{-1}
$b = 14.2074$ (16) Å	$T = 173$ (2) K
$c = 12.1692$ (13) Å	$0.42 \times 0.37 \times 0.19$ mm
$\beta = 90.261$ (2)°	

Data collection

Bruker SMART CCD area-detector diffractometer	7056 measured reflections
	3006 independent reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)	2581 reflections with $I > 2\sigma(I)$
$T_{min} = 0.342$, $T_{max} = 0.602$	$R_{int} = 0.021$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$	214 parameters
$wR(F^2) = 0.086$	H-atom parameters constrained
$S = 1.05$	$\Delta\rho_{max} = 0.96$ e Å^{-3}
3006 reflections	$\Delta\rho_{min} = -0.54$ e Å^{-3}

C-bound H atoms were fixed geometrically and treated as riding, with C—H = 0.97 (methylene) or 0.93 Å (aromatic) and U_{iso}(H) = $1.2U_{eq}$(C). The H atoms of the water molecules were located in a difference Fourier map and included in the subsequent refinement using the restraints O—H = 0.85 (1) Å and H$\cdots$H = 1.39 (2) Å. In the last cycles of refinement, they were treated as riding on the O atoms to which they are attached, with U_{iso}(H) = $1.5U_{eq}$(O).

Table 1
Selected geometric parameters (Å, °).

Zn1—O7	1.9335 (19)	Zn2—O8	2.0537 (19)
Zn1—O5^i	1.9457 (19)	Zn2—O10	2.094 (2)
Zn1—O9	1.973 (2)	Zn2—O11	2.104 (2)
Zn1—O2^{ii}	2.0051 (18)		
O7—Zn1—O5^i	117.63 (9)	O8^{iii}—Zn2—O10	93.82 (8)
O7—Zn1—O9	133.07 (9)	O8—Zn2—O10	86.18 (8)
O5^i—Zn1—O9	99.31 (8)	O8—Zn2—O11^{iii}	93.48 (9)
O7—Zn1—O2^{ii}	91.50 (8)	O8—Zn2—O11	86.52 (9)
O5^i—Zn1—O2^{ii}	113.10 (8)	O10—Zn2—O11	90.07 (12)
O9—Zn1—O2^{ii}	99.97 (8)	O10^{iii}—Zn2—O11	89.93 (12)

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

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

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
O9—H9$A\cdots$O1^{ii}	0.85	1.90	2.703 (3)	159
O9—H9$B\cdots$O4^{iv}	0.85	1.81	2.654 (3)	169
O10—H10$A\cdots$O5^v	0.85	2.01	2.828 (3)	161
O10—H10$B\cdots$O7^{iii}	0.85	2.16	2.742 (3)	125
O11—H11$A\cdots$O1^{vi}	0.85	1.96	2.769 (3)	159
O11—H11$B\cdots$O10	0.86	2.45	2.970 (4)	120

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

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2003), *DIAMOND* (Brandenburg, 1999) and *CAMERON* (Watkin *et al.*, 1993); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

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