

# A binuclear zinc polymer with paddlewheel building units and intersecting helical chains based on a flexible 4-[(carboxymethyl)sulfanyl]benzoic acid ligand

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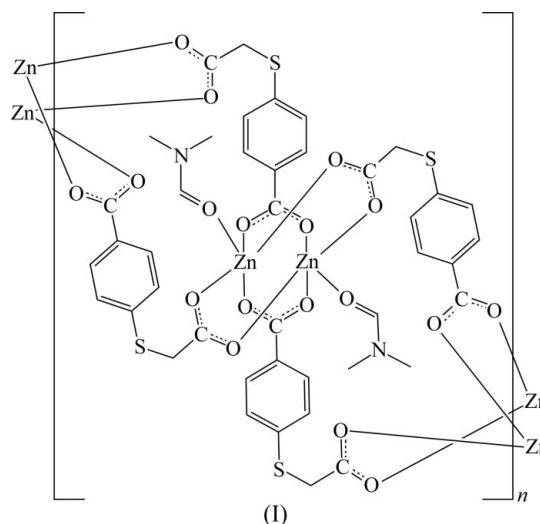
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The asymmetric unit of the title compound, poly[[ $\mu_4$ -4-[(carboxylatomethyl)sulfanyl]benzoato}(*N,N*-dimethylformamide)zinc],  $[\text{Zn}(\text{C}_9\text{H}_6\text{O}_4\text{S})(\text{C}_3\text{H}_7\text{NO})]_n$ , consists of one crystallographically independent  $\text{Zn}^{\text{II}}$  cation, one 4-[(carboxylatomethyl)sulfanyl]benzoate ( $L^{2-}$ ) ligand and one coordinated dimethylformamide (DMF) molecule. The zinc ion is coordinated by five O atoms from four separate  $L^{2-}$  ligands and one DMF molecule, and the  $\text{ZnO}_5$  unit displays a distorted square-based-pyramidal geometry. Two  $\text{ZnO}_5$  units form a binuclear zinc-tetracarboxylate paddlewheel cluster, and these are bridged by  $L^{2-}$  ligands to generate an intersecting helical chain ( $\text{Zn}^{2+}$  ions as nodes), which is composed of right-handed (*P*) and left-handed (*M*) helices. Weak C—H...O hydrogen bonds extend the one-dimensional coordinated chain into a weakly bound three-dimensional supramolecular architecture.

## Comment

The design and synthesis of metal-organic coordination polymers have attracted great interest in recent years, not only for their structural diversity and intriguing molecular topologies, but also for their potential as a new class of solid-state materials applied in the fields of separation, catalysis, gas storage and drug delivery (Kitagawa & Uemura, 2005; Dincă & Long, 2008; Choi & Suh, 2004). To construct such materials, judicious selection of bridging ligands is one of the various factors to be taken into account. Flexible ligands have been extensively explored in coordination chemistry and crystal engineering because of their numerous conformations and coordination modes observed in the coordination process (Ma *et al.*, 2008; Zhang *et al.*, 2008). In this contribution, we choose

a new flexible ligand, 4-[(carboxylatomethyl)sulfanyl]benzoate ( $L^{2-}$ ), as a bridging ligand to synthesize the coordination polymers. We report herein a new binuclear  $\text{Zn}^{\text{II}}$  polymer with paddlewheel building units and intersecting helical chains ( $\text{Zn}^{2+}$  ions as nodes), which is composed of right-handed (*P*) and left-handed (*M*) helices.



In the structure of (I) (Fig. 1 and Table 1), the  $\text{Zn}^{2+}$  centre adopts a five-coordinated mode with a distorted square-based-pyramidal geometry ( $\text{ZnO}_5$ ) via binding to one axial dimethylformamide (DMF) O atom and four O atoms from four different  $\text{CO}_2^-$  groups of  $L^{2-}$  ligands in the basal plane. The four carboxylate O atoms [O1, O2<sup>i</sup>, O3, O4<sup>i</sup>; symmetry code: (i)  $-x + 1, -y + 2, -z$ ] define an ideal plane, with an

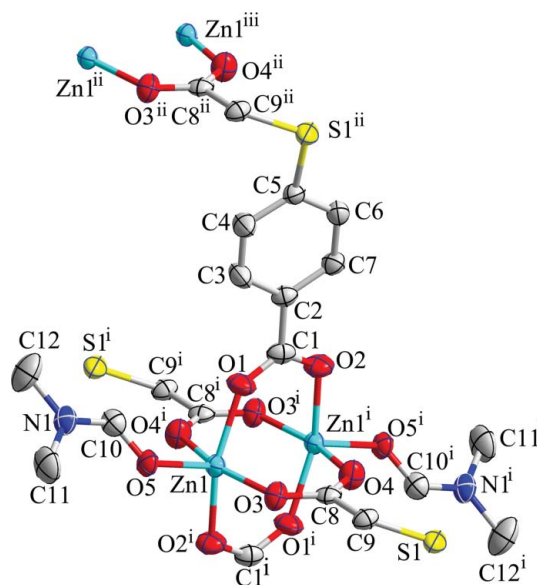
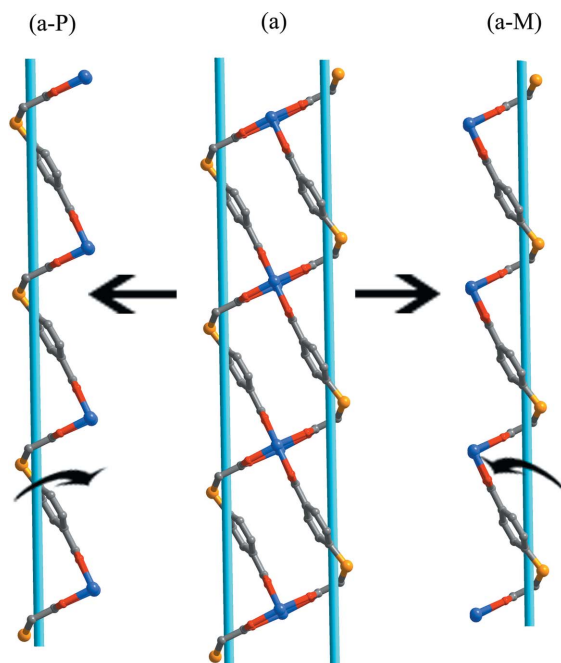


Figure 1

The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. All H atoms have been omitted for clarity. [Symmetry codes: (i)  $-x + 1, -y + 2, -z$ ; (ii)  $x, y - 1, z$ ; (iii)  $-x + 1, -y + 1, -z$ .]



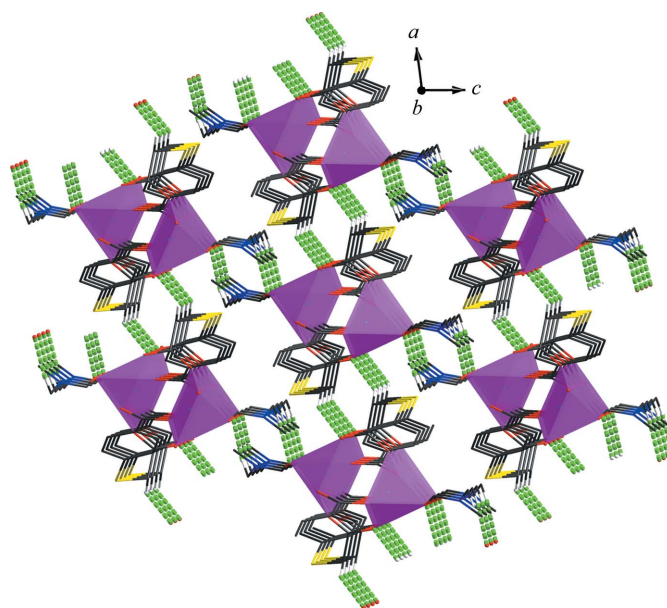
**Figure 2**

View of the intersecting helical chains in (I) composed of *P*- and *M*-handed helices with  $\text{Zn}^{2+}$  ions as nodes.

r.m.s. deviation of 0.0139 (14) Å. Each  $L^{2-}$  ligand bridges four different  $\text{Zn}^{2+}$  ions, *via* bridging carboxylate groups at each end of the ligand molecule, to form a one-dimensional coordination polymer. The two  $\text{Zn}^{2+}$  centres are bridged by four carboxylate groups from different  $L^{2-}$  ligands in a *syn-syn* bidentate mode, forming a paddlewheel secondary building unit (SBU). The intradimer  $\text{Zn} \cdots \text{Zn}$  separation is 2.9186 (11) Å, within the normal range found in other reported structures with the same paddlewheel core  $[\text{Zn}_2\text{O}_2(\text{O}_2\text{CR})_4]$  (Zhou *et al.*, 2000; Kwak *et al.*, 2009). A dramatic, almost perpendicular, twist between the two carboxylate groups in each  $L^{2-}$  ligand is observed, with a dihedral angle of 87.1 (4)° (Fig. 1).

In (I), each paddlewheel unit connects to two neighbouring paddlewheel clusters *via* bridging  $L^{2-}$  anions, which adopt a bridging tetradentate mode. It should be emphasized that because of the orientation of the carboxylate coordination sites and the flexibility of the  $L^{2-}$  ligand, the quadrates rings in the one-dimensional chain are highly distorted. Interestingly, these quadrates rings are interlinked by sharing the  $\text{Zn}^{2+}$  ions to form an intersecting helical chain, in which *P*- and *M*-handed helices can be distinguished (Fig. 2). Obviously, the twist of the  $L^{2-}$  ligand is responsible for the formation of the helical chain.

To date, only a few structures with the same paddlewheel core  $[\text{Zn}_2\text{O}_2(\text{O}_2\text{CR})_4]$  have been reported. These are the zero-dimensional Lantern-type  $[\text{Zn}_2(\text{O}_2\text{CCF}_3)_6]^{2-}$  ions (Demirhan *et al.*, 2002); the zero-dimensional dinuclear  $[\text{Zn}_2(\text{Indo})_4(\text{DMA})_2] \cdot 2\text{DMA}$  [IndoH = 1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indole-3-acetic acid and DMA = *N,N*-dimethylacetamide; Zhou *et al.*, 2000], the zero-dimensional overall 'figure-of-eight' shape  $[\text{Zn}_2(\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_4\text{S}_3)_2(\text{C}_3\text{H}_7\text{NO})_2]$  (Wang *et al.*, 2009), the two-dimensional square-grid motif



**Figure 3**

View of the weak  $\text{C}-\text{H} \cdots \text{O}$  hydrogen-bonding interactions between adjacent chains generating a three-dimensional supramolecular network. Dashed lines indicate hydrogen bonds and polyhedra represent  $\text{ZnO}_5$  groups.

$[\text{Zn}_2(\text{C}_8\text{H}_4\text{O}_2)_2(\text{H}_2\text{O})_2] \cdot 2\text{C}_4\text{H}_9\text{NO}]_n$  (Lv & Ng, 2007), the one-dimensional zigzag chain  $[\text{Zn}_2(\text{O}_2\text{CPh})_4(\text{H}_2\text{O})_2][\text{Zn}(\text{O}_2\text{CPh})_2(\text{bpe})]_n$ , (II) [bpe = 1,2-bis(4-pyridyl)ethane; Kwak *et al.*, 2009], the two-dimensional layer structure  $[\text{Zn}_2(\text{C}_8\text{H}_4\text{O}_4)_2(\text{C}_2\text{H}_6\text{OS})_2] \cdot 5\text{C}_2\text{H}_6\text{OS}$  (Yang *et al.*, 2005), the three-dimensional (3,24)-connected metal-organic framework  $[\text{Zn}_{24}(\text{L})_8(\text{H}_2\text{O})_{24}]_n$   $\{L = 5,5',5''\text{-[benzene-1,3,5-triyltris(carbonylimino)]-tris(benzene-1,3-dicarboxylic acid)}$ ; Zou *et al.*, 2008} and the three-dimensional twofold interpenetrating polyhedral metal-organic framework  $\{[\text{Zn}_3(\text{BTPCA})_2(\text{H}_2\text{O})_3] \cdot \text{py} \cdot 3\text{DMSO}\}_n$ , with a primitive cubic network [BTPCA = 1,1',1''-(benzene-1,3,5-triyl)tris(piperidine-4-carboxylic acid), py = pyridine and DMSO = dimethyl sulfoxide; Zhao *et al.*, 2009]. The chain structure of complex (I) is quite different from that of complex (II), which consists of mononuclear  $\text{Zn}(\text{O}_2\text{CC}_6\text{H}_5)_2$  units bridged by a bpe ligand to form a one-dimensional zigzag chain. Importantly, such an example of the co-existence of a binuclear  $\text{Zn}^{\text{II}}$ -tetracarboxylate paddlewheel cluster and intersecting *P*- and *M*-handed helical chains is unique, to the best of our knowledge.

Another interesting feature of complex (I) is the non-covalent interactions (Table 2). In the landmark study by Desiraju (1996),  $\text{C}-\text{H} \cdots \text{O}$  contacts occur within certain distance ( $2.30 < d < 2.84$  Å,  $3.18 < D < 3.60$  Å) and angle ( $122 < \theta < 160^\circ$ ) ranges. There are weak  $\text{C}-\text{H} \cdots \text{O}$  hydrogen bonds between two  $L^{2-}$  ligands [C9 $\cdots$ O3<sup>iv</sup>; symmetry code: (iv)  $-x, -y + 2, -z$ ], as well as between two DMF molecules [C12 $\cdots$ O5<sup>v</sup>; symmetry code: (v)  $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$ ], which link the one-dimensional helical chains to generate a weakly bound three-dimensional supramolecular architecture, as depicted in Fig. 3.

## Experimental

All reagents and solvents employed were commercially available and were used as received without further purification. A mixture of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (60 mg, 0.2 mmol),  $\text{H}_2\text{L}$  (42 mg, 0.2 mmol) and DMF (10 ml) was sealed in a 25 ml stainless steel reactor with a Teflon liner, heated to 348 K for 4 d and then cooled to room temperature. The crystals were washed with methanol to give complex (I) in about 45% yield (based on the  $\text{H}_2\text{L}$  ligand).

### Crystal data

$[\text{Zn}(\text{C}_9\text{H}_6\text{O}_4\text{S})(\text{C}_3\text{H}_7\text{NO})]$	$V = 1358.7(8) \text{ \AA}^3$
$M_r = 348.66$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 7.873(3) \text{ \AA}$	$\mu = 1.98 \text{ mm}^{-1}$
$b = 10.225(3) \text{ \AA}$	$T = 298 \text{ K}$
$c = 17.006(6) \text{ \AA}$	$0.35 \times 0.34 \times 0.24 \text{ mm}$
$\beta = 97.014(4)^\circ$	

### Data collection

Bruker SMART APEXII CCD diffractometer	5851 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	2402 independent reflections
$T_{\min} = 0.544$ , $T_{\max} = 0.648$	1855 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.032$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$	183 parameters
$wR(F^2) = 0.091$	H-atom parameters constrained
$S = 1.00$	$\Delta\rho_{\text{max}} = 0.65 \text{ e \AA}^{-3}$
2402 reflections	$\Delta\rho_{\text{min}} = -0.50 \text{ e \AA}^{-3}$

**Table 1**

Selected bond lengths ( $\text{\AA}$ ).

Zn1—O1	2.056 (3)	Zn1—O5	1.987 (2)
Zn1—O2 <sup>i</sup>	2.017 (3)	S1—C9	1.794 (4)
Zn1—O3	2.045 (3)	C5—S1 <sup>ii</sup>	1.769 (4)
Zn1—O4 <sup>i</sup>	2.057 (3)		

Symmetry codes: (i)  $-x + 1, -y + 2, -z$ ; (ii)  $x, y - 1, z$ .

**Table 2**

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{C9-H9B} \cdots \text{O3}^{\text{iii}}$	0.97	2.50	3.365 (4)	148
$\text{C12-H12B} \cdots \text{O5}^{\text{iv}}$	0.96	2.52	3.476 (6)	172

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

Methyl H atoms were constrained to an ideal geometry ( $\text{C-H} = 0.96 \text{ \AA}$ ), with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ , but were allowed to rotate freely. The remaining C-bound H atoms were refined using a riding model [ $\text{C-H} = 0.97 (\text{CH}_2)$  or  $0.93 \text{ \AA} (\text{CH})$  and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ ].

Data collection: SMART (Bruker, 2001); cell refinement: SMART; data reduction: SAINT-Plus (Bruker, 2001); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: DIAMOND (Brandenburg, 2008) and ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: PLATON (Spek, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: EM3043). Services for accessing these data are described at the back of the journal.

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