

## Distinct chiral units from an axially prochiral ligand in a photoluminescent zinc(II)–organic complex

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Received 10 October 2011

Accepted 10 February 2012

Online 3 March 2012

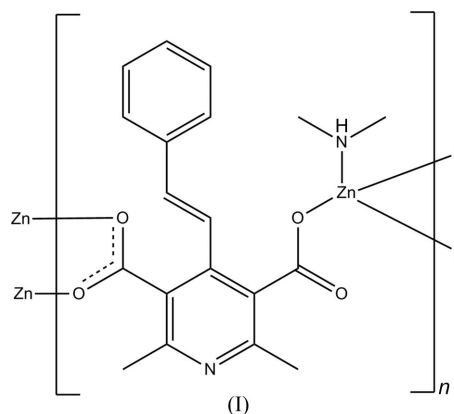
The asymmetric unit of the title compound, poly[(dimethylamine- $\kappa N$ )[ $\mu_3$ -(*E*)-2,6-dimethyl-4-styrylpyridine-3,5-dicarboxylato- $\kappa^3 O^3:O^3':O^5$ ]zinc(II)], [Zn(C<sub>17</sub>H<sub>13</sub>NO<sub>4</sub>)(C<sub>2</sub>H<sub>7</sub>N)]<sub>n</sub>, consists of one crystallographically independent distorted tetrahedral Zn<sup>II</sup> cation, one (*E*)-2,6-dimethyl-4-styrylpyridine-3,5-dicarboxylate (mspda<sup>2-</sup>) ligand and one coordinated dimethylamine molecule. Two *S*- and *R*-type chiral units are generated from the axially prochiral mspda<sup>2-</sup> ligand through C–H···O hydrogen bonds. The *R*-type chiral units assemble a left-handed (*M*) Zn–mspda helical chain, while the right-handed (*P*) Zn–mspda helical chain is constructed from neighbouring *S*-type chiral units. The *P*- and *M*-type helical chains are interlinked by carboxylate O atoms to form a one-dimensional ladder. Interchain N–H···O hydrogen bonds extend these one-dimensional ladders into a two-dimensional supramolecular architecture. The title compound exhibits luminescence at  $\lambda_{\max} = 432$  nm upon excitation at 365 nm.

### Comment

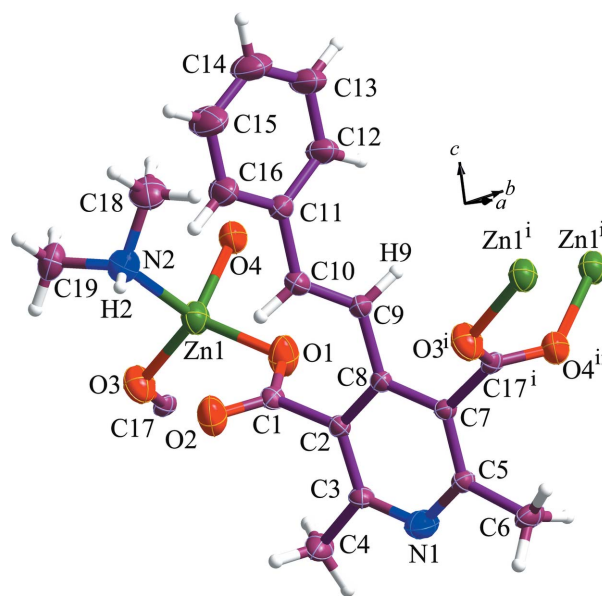
The construction of metal–organic coordination polymers has attracted intense attention, owing to their intriguing network topologies and useful properties (gas storage, catalysis, photosensitivity, molecular recognition *etc.*), which are intimately related to their structures (Yaghi *et al.*, 2003; O'Keeffe *et al.*, 2008; Ockwig *et al.*, 2005). Helices and atropisomeric units in metal complexes are two of the main aspects in the study of structural isomerism and, compared with the former, the latter has not been well explored (Kesanli & Lin, 2003; Han & Hong, 2005). For the construction of metal complexes, besides coordination bonds, secondary interactions such as hydrogen bonding and  $\pi$ – $\pi$  stacking must also be exploited.

Compared with common pyridinedicarboxylic acids (PDAs), highly substituted PDAs have not been effectively utilized in the construction of supramolecular polymers

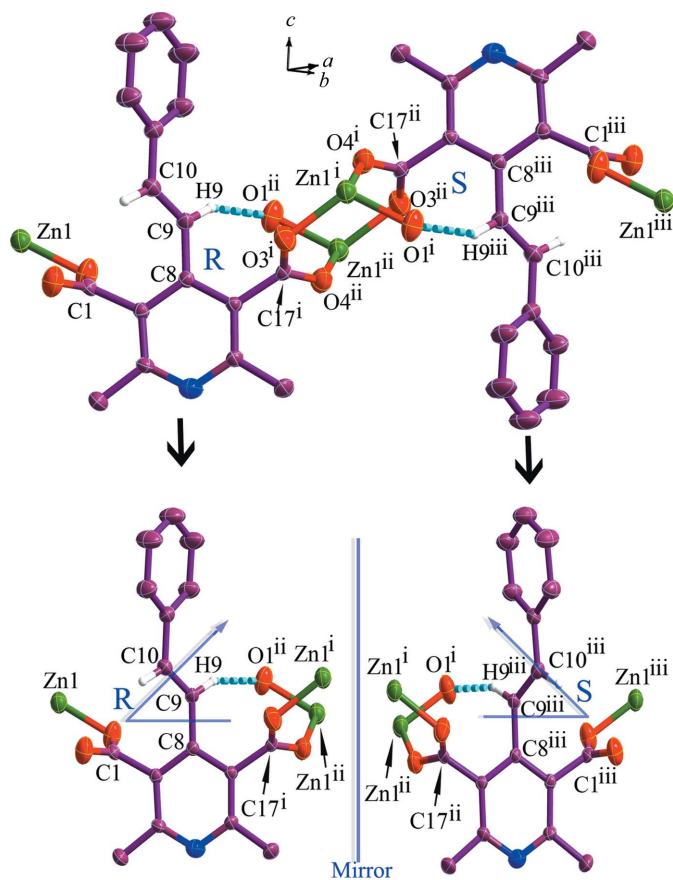
(Huang, He, Liang *et al.*, 2007). In our previous work, 2,6-dimethyl-4-(2-thiophenyl)pyridine-3,5-dicarboxylate, 2,6-dimethyl-4-phenylpyridine-3,5-dicarboxylate and 2,6-dimethyl-4-(pyridin-4-yl)pyridine-3,5-dicarboxylate were employed in the construction of luminescent metal compounds (Huang, He, Wang *et al.*, 2007). Only a few reports exist of coordination polymers related to (*E*)-2,6-dimethyl-4-styrylpyridine-3,5-dicarboxylic acid (H<sub>2</sub>mspda) (Zhang *et al.*, 2011; Huang *et al.*, 2010). In this work, we report a new photoluminescent complex, poly[(dimethylamine- $\kappa N$ )[ $\mu_3$ -(*E*)-2,6-dimethyl-4-styrylpyridine-3,5-dicarboxylato]zinc(II)], (I), with a helical motif, assembled by distinct chiral units from an axially prochiral ligand through C–H···O hydrogen bonds.



The asymmetric unit of (I) contains one crystallographically independent Zn<sup>II</sup> cation, one mspda<sup>2-</sup> ligand and one coordinated dimethylamine ligand (Fig. 1). The N–H bond of dimethylamine is confirmed by a characteristic peak (3176 cm<sup>-1</sup>) in the FT-IR spectrum of (I). It should be noted



**Figure 1**  
Part of the structure of the mspda<sup>2-</sup> ligand and Zn<sup>II</sup> centres in (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (i)  $x + 1, y, z$ ; (ii)  $-x + 1, -y + 1, -z + 1$ .]



**Figure 2**  
The absolute conformations of the chiral units comprising  $[\text{Zn}(\text{mspda})]_n$ , shown as mirror images. [Symmetry codes: (i)  $x + 1, y, z$ ; (ii)  $-x + 1, -y + 1, -z + 1$ ; (iii)  $-x + 2, -y + 1, -z + 1$ .]

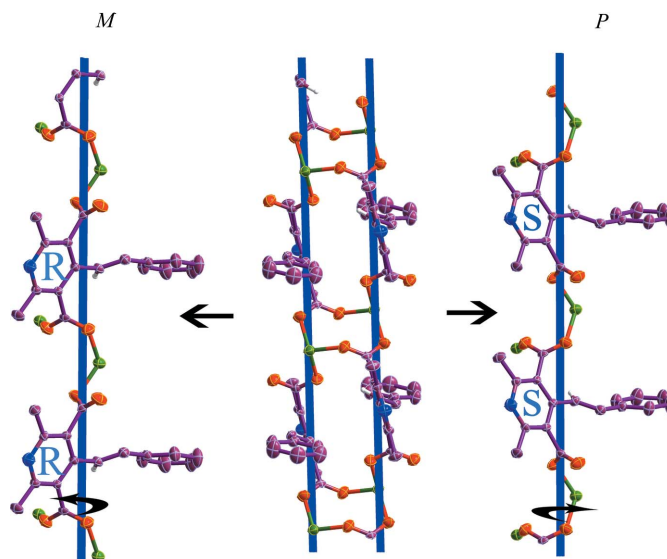
that hydrolysis of dimethylformamide is observed in the formation of (I). Similar cases have also been discovered in some anionic metal-organic frameworks with aromatic polycarboxylates (Rosi *et al.*, 2005; Chen *et al.*, 2003). The geometry around atom Zn1 is a distorted tetrahedron ( $\text{ZnNO}_3$ ), with the four binding sites occupied by three O atoms (O1, O3 and O4) from three equivalent  $\text{mspda}^{2-}$  ligands and one N atom (N2) from the coordinated dimethylamine molecule (Table 1). All the Zn–O and Zn–N bond lengths are in agreement with those reported in other  $\text{Zn}^{\text{II}}$  complexes of *N,O*-chelating ligands (Wang *et al.*, 2007).

As shown in Fig. 1, the  $\text{mspda}^{2-}$  anion serves as an *exo*-tridentate ligand and bridges three  $\text{Zn}^{\text{II}}$  centres through O1, O3 and O4, leaving the uncoordinated carboxylate O atom involved in an  $\text{N2}-\text{H2}\cdots\text{O2}^{\text{iv}}$  hydrogen bond [symmetry code: (iv)  $-x + 1, -y, -z + 1$ ]. The Zn $\cdots$ Zn separations over the  $\text{mspda}^{2-}$  bridge are 8.0331 (14) and 9.134 (2) Å. The C9–C10 bond of 1.320 (4) Å is assigned as a C=C double bond, with the  $\text{mspda}^{2-}$  ligand displaying a *trans* conformation (*E*). The  $\text{C}_6\text{H}_5-\text{CH}=\text{CH}$  dihedral angle in  $\text{mspda}^{2-}$  is 19.76 (14) $^\circ$ , and that between the pyridine and phenyl rings is 68.03 (14) $^\circ$ . Thus, the pyridine and phenyl rings in the  $\text{mspda}^{2-}$  ligand are not coplanar, with the major twist (C2–C8–C9–C10) occurring about the C8–C9 bond (Table 1).

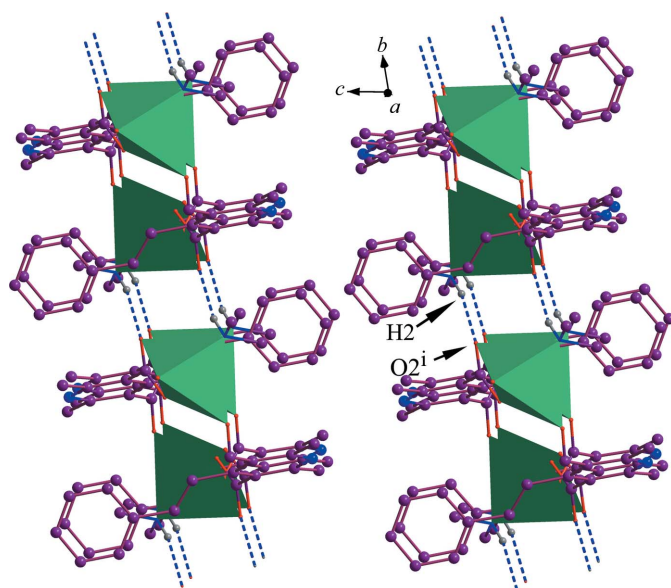
It is interesting that *S*- and *R*-type chiral units co-exist in the structure of (I) (Fig. 2). In the  $\text{mspda}^{2-}$  ligand, according to the Cahn–Ingold–Prelog sequence rule (Cahn *et al.*, 1966), atom C10 has priority over atom H9, and the two carboxylate ( $\text{CO}_2^-$ ) groups may exist in different chemical environments within the metal complex. Thus, the  $\text{mspda}^{2-}$  ligand is an axially prochiral ligand. In the structure of (I), one carboxylate group [denoted C17<sup>i</sup>; symmetry code: (i)  $x + 1, y, z$ ] of the  $\text{mspda}^{2-}$  anion is coordinated to two  $\text{Zn}^{2+}$  centres, while the other (C1) is coordinated to only one  $\text{Zn}^{2+}$  centre, and thus atom C17<sup>i</sup> has priority over atom C1. In crystal engineering, C–H $\cdots$ O contacts are electrostatic and they occur within certain distance (C–H $\cdots$ O = 3.0–4.0 Å) and angle (C–H $\cdots$ O = 90–180 $^\circ$ ) ranges (Desiraju, 1991; Taylor & Kennard, 1982). Therefore, we believe that there are reliable C–H $\cdots$ O interactions in (I) because of the C9–H9 $\cdots$ O1<sup>ii</sup> angle and the short C9 $\cdots$ O1<sup>ii</sup> distance [Table 1; symmetry code: (ii)  $-x + 1, -y + 1, -z + 1$ ]. The rotation of  $\text{C}_6\text{H}_5-\text{CH}=\text{CH}$  around the aryl-carbon bond (C8–C9) controls the C–H $\cdots$ O hydrogen bonds to a certain degree. Thus, there are two types of chiral units (*S* and *R*) that co-exist in the same crystal lattice (Fig. 3).

Another interesting feature is the presence of *P*- and *M*-type helical chains comprising the *S*- and *R*-chiral units separately. It should be emphasized that the *R*-chiral units assemble a left-handed (*M*) Zn– $\text{mspda}$  helical chain with a helical pitch of 9.134 Å, while the right-handed (*P*) Zn– $\text{mspda}$  helical chain is constructed from the connection of neighbouring *S*-chiral units (Fig. 3). Thus, the *P*- and *M*-type helices assembled separately by distinct *S*- and *R*-chiral units are interlinked by O4 to form a one-dimensional ladder. To our knowledge, such an arrangement of helical chains has only rarely been reported among Zn frameworks (Yashima *et al.*, 2008; Bishop, 2008).

The configuration of the chiral units in (I) is similar to those of atropisomeric  $[\text{M}(\text{Hsm}(\text{pdc}))_2(\text{H}_2\text{O})_4]\cdot 6\text{H}_2\text{O}$ , (II) [sm $\text{pdc}$  is



**Figure 3**  
View of the one-dimensional ladders comprising separate *P*- and *M*-type helices, which are assembled by distinct *S*- and *R*-atropisomeric units, with  $\text{Zn}^{2+}$  ions as nodes.

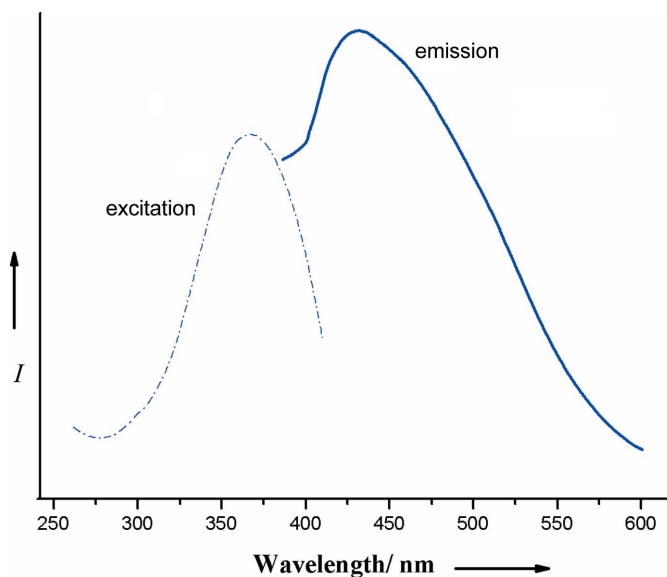


**Figure 4**  
View of the two-dimensional supramolecular network of (I). Dashed lines represent the  $N2 \cdots O2^i$  hydrogen bonds and polyhedra represent the  $ZnNO_3$  groups. [Symmetry code: (i)  $x + 1, y, z$ .]

2,6-dimethyl-4-(thiophen-2-yl)pyridine-3,5-dicarboxylate,  $M = Zn$ ; Huang, He, Liang *et al.*, 2007),  $[M(H\text{-mpypdc})Cl(H_2O)_3]_n$ , (III) [mpypdc is 2,6-dimethyl-4-(pyridin-4-yl)pyridine-3,5-dicarboxylate,  $M = Co$ ; Huang & Hu, 2007] and  $\{[Cd_3(HL)_2(\text{phen})_3(H_2O)_2] \cdot 4.25H_2O\}_n$ , (IV) [ $H_4L = p$ -terphenyl-type 4,4'-(1,4-phenylene)bis(2,6-dimethylpyridine-3,5-dicarboxylic acid) and phen is 1,10-phenanthroline; Huang *et al.*, 2009]. However, the structure of (I) is quite different from these structures. For example, (II) has an interesting hydrogen-bonded  $M^{2+}(H_2O)_8$  ionic cluster, which links the  $H\text{sm}pdc^-$  ligands into a one-dimensional supramolecular motif. Compound (III) displays wave-like motifs generated from the  $H\text{mpypdc}^-$  ligands. The  $R$ - and  $S$ -components composed of  $[M(H\text{mpypdc})]$  are arranged in an  $\dots ABAB \dots$  fashion in the one-dimensional coordination polymer. In complex (IV), the T-type secondary building units construct independent one-dimensional metal-organic nanotubes (MONTs) with  $6^3$  topology, containing distinct axially asymmetric  $[R\text{-}Cd_3(HL)$  and  $S\text{-}Cd_3(HL)]$  subunits. In (I), the construction of atropisomeric type units from axially prochiral ligands through hydrogen bonds is the major feature of interest.

Interchain hydrogen bonds between the coordinated dimethylamine molecules and  $\text{ms}pda^{2-}$  ligands ( $N2 \cdots O2^{iv}$ ) extend the one-dimensional ladders of (I) into a two-dimensional supramolecular architecture (Fig. 4).

The photoluminescent emission maximum of free  $H_2\text{ms}pda$  was observed at 496 nm (em). The emission spectra of (I) in the solid state at room temperature are shown in Fig. 5. Excitation at 365 nm leads to a broad fluorescent emission band at 432 nm. The distinct maximum emission wavelength indicates that the mechanism of photoluminescence can be assigned to ligand-metal charge transfer (LMCT) (Hu *et al.*, 2010; Zhou *et al.*, 2008).



**Figure 5**  
Photoluminescent spectra of (I) ( $\lambda_{em}$  at 432 nm, upon  $\lambda_{ex}$  at 365 nm).  $I$  is relative intensity.

## Experimental

A mixture of  $Zn(NO_3)_2 \cdot 6H_2O$  (60 mg, 0.2 mmol),  $H_2\text{ms}pda$  (59 mg, 0.2 mmol), imidazole (14 mg, 0.2 mmol),  $Et_3N$  (0.02 ml) and dimethylformamide (10 ml) was sealed in a 25 ml Teflon-lined stainless steel reactor and directly heated to 413 K for 2 d, then cooled to room temperature. The crystals were washed with methanol to yield 20 mg of (I) (yield  $\sim 25\%$  based on the  $H_2\text{ms}pda$  ligand).

### Crystal data

$[Zn(C_{17}H_{13}NO_4)(C_2H_7N)]$	$\gamma = 66.518 (4)^\circ$
$M_r = 405.76$	$V = 939.9 (4) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 9.134 (2) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 9.694 (2) \text{ \AA}$	$\mu = 1.33 \text{ mm}^{-1}$
$c = 11.735 (3) \text{ \AA}$	$T = 298 \text{ K}$
$\alpha = 80.602 (4)^\circ$	$0.28 \times 0.25 \times 0.22 \text{ mm}$
$\beta = 87.611 (4)^\circ$	

### Data collection

Bruker APEXII CCD area-detector diffractometer	5025 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	3295 independent reflections
$T_{min} = 0.707, T_{max} = 0.758$	2691 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.021$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.091$	$\Delta\rho_{max} = 0.32 \text{ e \AA}^{-3}$
$S = 1.07$	$\Delta\rho_{min} = -0.31 \text{ e \AA}^{-3}$
3295 reflections	
243 parameters	
1 restraint	

The methyl H atoms were constrained to an ideal geometry, with  $C-H = 0.96 \text{ \AA}$  and  $U_{iso}(H) = 1.5U_{eq}(C)$ , but were allowed to rotate freely. Other H atoms attached to C atoms were refined using a riding model, with  $C-H = 0.93 \text{ \AA}$  (CH) and  $U_{iso}(H) = 1.2U_{eq}(C)$ . The N-bound H atom was refined freely.

**Table 1**

Selected geometric parameters (Å, °).

Zn1—O1	1.927 (2)	Zn1—O4	2.004 (2)
Zn1—O3	1.961 (2)	Zn1—N2	2.008 (3)
O1—Zn1—O3	115.82 (10)	O1—Zn1—N2	121.58 (10)
O1—Zn1—O4	101.18 (8)	O3—Zn1—N2	105.88 (10)
O3—Zn1—O4	109.50 (9)	O4—Zn1—N2	101.31 (10)
C2—C8—C9—C10	49.1 (5)		

Data collection: *APEX2* (Bruker, 2010); cell refinement: *APEX2*; data reduction: *SAINT-Plus* (Bruker, 2008); 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).

This work was supported by Science and Technology Projects of Chongqing Municipal Education Commission (grant No. KJ100602) and Chongqing Normal University Scientific Research Foundation Project (grant Nos. 10XLZ005 and 2011XLS30).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: EM3046). Services for accessing these data are described at the back of the journal.

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**Table 2**

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N2—H2...O2 <sup>iv</sup>	0.84 (2)	2.19 (2)	3.010 (3)	167 (3)
C9—H9...O1 <sup>ii</sup>	0.93	2.41	3.258 (4)	151

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

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