

# Poly[( $\mu_5$ -2,6-dimethylpyridine-3,5-dicarboxylato)zinc]

 Ming-Xing Zhang,<sup>a\*</sup> Xin Chen<sup>a</sup> and Yi Zhu<sup>b</sup>
<sup>a</sup>College of Chemistry, Chongqing Normal University, Chongqing 400047, People's Republic of China, and <sup>b</sup>College of Life Science, Chongqing Normal University, Chongqing 400047, People's Republic of China

Correspondence e-mail: zmx0102@hotmail.com

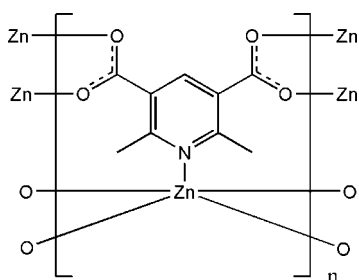
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 Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å;  $R$  factor = 0.023;  $wR$  factor = 0.067; data-to-parameter ratio = 10.3.

In the polymeric title complex,  $[\text{Zn}(\text{C}_9\text{H}_7\text{NO}_4)]_n$ , the  $\text{Zn}^{\text{II}}$  cation is located on a twofold rotation axis and is coordinated by five 2,6-dimethylpyridine-3,5-dicarboxylate (mpdc) anions in a distorted  $\text{ZnNO}_4$  trigonal-bipyramidal geometry. The mpdc anion is also located on the twofold rotation axis and bridges five  $\text{Zn}^{\text{II}}$  cations, forming the three-dimensional polymeric complex. Weak  $\text{C}-\text{H}\cdots\pi$  interactions are present in the crystal structure.

## Related literature

For a related structure, see: Huang *et al.* (2007). For background to metal-organic frameworks (MOFs), see: Long & Yaghi (2009); Zhao *et al.* (2003).



## Experimental

### Crystal data

 $[\text{Zn}(\text{C}_9\text{H}_7\text{NO}_4)]$ 
 $M_r = 258.53$ 

 Monoclinic,  $C2/c$ 
 $a = 8.578$  (7) Å

 $b = 14.016$  (11) Å

 $c = 7.382$  (7) Å

 $\beta = 112.176$  (17)°

 $V = 821.9$  (12) Å<sup>3</sup>
 $Z = 4$ 

 Mo  $K\alpha$  radiation

 $\mu = 2.98$  mm<sup>-1</sup>
 $T = 293$  K

 $0.30 \times 0.25 \times 0.16$  mm

### Data collection

Rigaku Mercury2 diffractometer

Absorption correction: multi-scan

 (*CrystalClear*; Rigaku, 2005)

 $T_{\text{min}} = 0.469$ ,  $T_{\text{max}} = 0.647$ 

2615 measured reflections

732 independent reflections

 709 reflections with  $I > 2\sigma(I)$ 
 $R_{\text{int}} = 0.022$ 

### Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.023$ 
 $wR(F^2) = 0.067$ 
 $S = 1.00$ 

732 reflections

71 parameters

1 restraint

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.50$  e Å<sup>-3</sup>
 $\Delta\rho_{\text{min}} = -0.59$  e Å<sup>-3</sup>
**Table 1**

Selected bond lengths (Å).

Zn1—O1	2.207 (3)	Zn1—N1 <sup>ii</sup>	2.089 (3)
Zn1—O2 <sup>i</sup>	1.977 (2)		

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

**Table 2**

Hydrogen-bond geometry (Å, °).

Cg is the centroid of the pyridine ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C5}-\text{H5C}\cdots\text{Cg}^{\text{ii}}$	0.96	2.67	3.573 (4)	158

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

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; 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 and figures for this paper are available from the IUCr electronic archives (Reference: XU5247).

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## supporting information

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**Poly[( $\mu_5$ -2,6-dimethylpyridine-3,5-dicarboxylato)zinc]****Ming-Xing Zhang, Xin Chen and Yi Zhu****S1. Comment**

Recently, research on metal-organic frameworks (MOFs) has become of increasing interest (Long & Yaghi, 2009). However, it is still a great challenge to assemble a predicted structure because there are numerous influences that can play decisive roles on the structure and crystal packing. Fortunately, these uncertainties can be reduced by the use of well selected spacers that have the ability to aggregate metal ions into different secondary building units (Zhao *et al.*, 2003). Herein we reports an interesting five-connected zeolite-like coordination polymer based on highly-substituted pyridinedi-carboxylates.

The title compound is a three-dimensional framework built from Zn cations that are linked by mpdc anions. From this arrangement cavities are formed. Zn1 is coordinated by four oxygen atoms from four different CO<sub>2</sub><sup>-</sup> groups of mpdc ligands and one pyridyl nitrogen atom from another mpdc ligand. The mpdc ligand bridges five different Zn atoms and favors the construction of the structure with zeolite-like topology. The topology of the title compound is identical with the reported [Cd(mpdc)]<sub>n</sub> (Huang *et al.*, 2007), but the coordination sphere of cation, the binding mode of the carboxylate group and the synthesis condition are different.

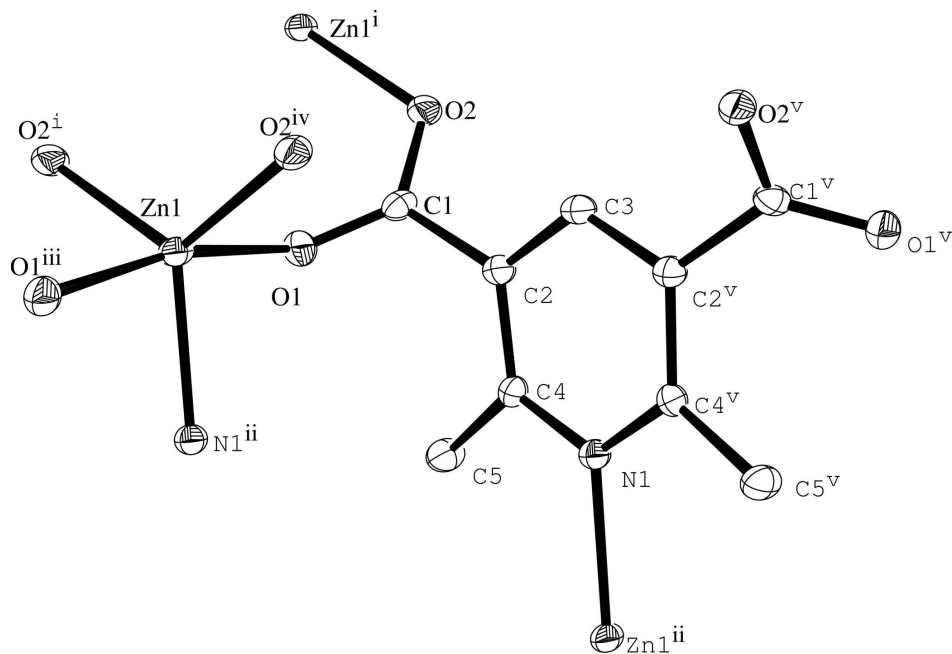
The combination of the dramatic twists between two carboxylate groups in mpdc ligands results in the formation of the intersecting double-stranded helical chain comprised of [Zn(CO<sub>2</sub>)<sub>2</sub>]<sub>n</sub> (Zn atoms as nodes).

**S2. Experimental**

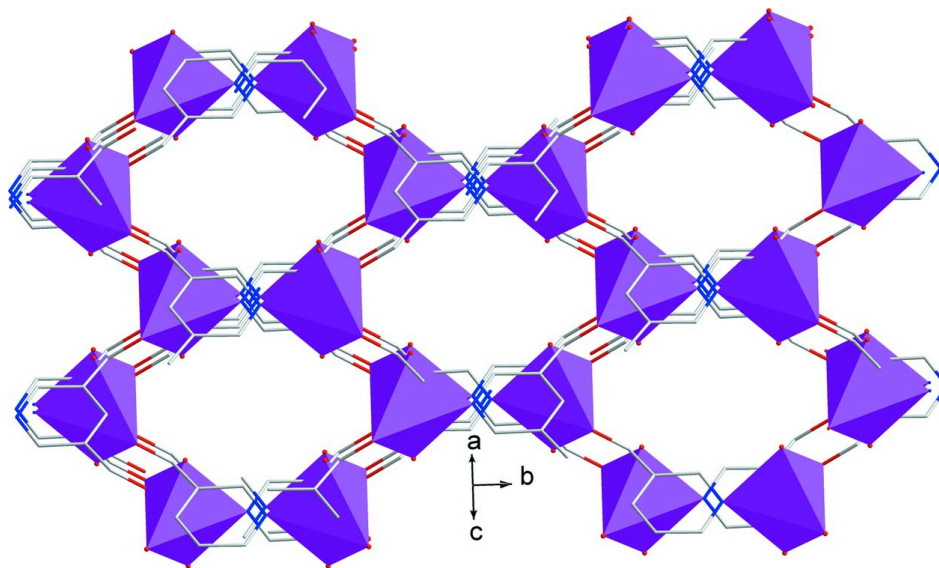
All chemicals were of reagent grade and used as purchased without further purification. A mixture of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (450 mg, 1.5 mmol), H<sub>2</sub>mpdc (97.5 mg, 0.5 mmol), (Et)<sub>3</sub>N 0.07 mL and H<sub>2</sub>O 10 mL was sealed in a 25 ml stainless steel reactor with Teflon liner and directly heated to 180 °C for 3 days, and then cooled to room temperature. The crystal samples were washed with methanol to give the title compound in about 35% yield (based on H<sub>2</sub>mpdc ligand).

**S3. Refinement**

Constraint instruction 'delu 0.001 Zn1 O1' was used in the refinement. All H atoms were placed in geometrically idealized positions (C—H = 0.93 Å) and treated as riding on their parent atoms, with U<sub>iso</sub>(H) = 1.5U<sub>eq</sub>(C) for methyl H atoms and 1.2U<sub>eq</sub>(C) for aromatic H atom.

**Figure 1**

The coordination environments of Zinc ions, showing 30% probability displacement ellipsoids and hydrogen atoms have been removed for clarity. Symmetry codes: (i)  $-x, -y, -z+1$ ; (ii)  $-x + 1/2, -y + 1/2, -z + 1$ ; (iii)  $-x, y, -z+1/2$ ; (iv)  $x, -y, z - 1/2$ ; (v)  $-x + 1, +y, -z + 3/2$ .

**Figure 2**

The presentation of the 3-D zeolite-like architecture. Methyl groups and hydrogen atoms have been removed for clarity. Polyhedra represent the  $\text{ZnNO}_4$  groups.

Poly[( $\mu_5$ -2,6-dimethylpyridine-3,5-dicarboxylato)zinc]

## Crystal data

[Zn(C<sub>9</sub>H<sub>7</sub>NO<sub>4</sub>)]  
 $M_r = 258.53$   
 Monoclinic,  $C2/c$   
 Hall symbol:  $-C\ 2yc$   
 $a = 8.578\ (7)\ \text{\AA}$   
 $b = 14.016\ (11)\ \text{\AA}$   
 $c = 7.382\ (7)\ \text{\AA}$   
 $\beta = 112.176\ (17)^\circ$   
 $V = 821.9\ (12)\ \text{\AA}^3$   
 $Z = 4$

$F(000) = 520$   
 $D_x = 2.089\ \text{Mg m}^{-3}$   
 Mo  $K\alpha$  radiation,  $\lambda = 0.71073\ \text{\AA}$   
 Cell parameters from 535 reflections  
 $\theta = 2.9\text{--}27.5^\circ$   
 $\mu = 2.98\ \text{mm}^{-1}$   
 $T = 293\ \text{K}$   
 Prism, colorless  
 $0.30 \times 0.25 \times 0.16\ \text{mm}$

## Data collection

Rigaku Mercury2  
 diffractometer  
 Radiation source: fine-focus sealed tube  
 Graphite monochromator  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan  
 (*CrystalClear*; Rigaku, 2005)  
 $T_{\min} = 0.469$ ,  $T_{\max} = 0.647$

2615 measured reflections  
 732 independent reflections  
 709 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.022$   
 $\theta_{\max} = 25.0^\circ$ ,  $\theta_{\min} = 2.9^\circ$   
 $h = -10 \rightarrow 10$   
 $k = -14 \rightarrow 16$   
 $l = -8 \rightarrow 8$

## Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.023$   
 $wR(F^2) = 0.067$   
 $S = 1.00$   
 732 reflections  
 71 parameters  
 1 restraint  
 Primary atom site location: structure-invariant  
 direct methods

Secondary atom site location: difference Fourier  
 map  
 Hydrogen site location: inferred from  
 neighbouring sites  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0519P)^2 + 0.6817P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.50\ \text{e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.59\ \text{e \AA}^{-3}$

## Special details

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn1	0.0000	0.08158 (2)	0.2500	0.01616 (18)
N1	0.5000	0.26938 (18)	0.7500	0.0137 (5)
O1	0.0625 (2)	0.09690 (11)	0.5672 (2)	0.0189 (4)
O2	0.20746 (19)	-0.00679 (11)	0.7999 (2)	0.0192 (4)

C1	0.1949 (3)	0.06763 (15)	0.6979 (3)	0.0147 (5)
C2	0.3560 (3)	0.12188 (16)	0.7360 (3)	0.0147 (5)
C3	0.5000	0.0730 (2)	0.7500	0.0168 (7)
H3	0.5000	0.0066	0.7500	0.020*
C4	0.3618 (3)	0.22210 (15)	0.7464 (3)	0.0137 (5)
C5	0.2202 (3)	0.28064 (16)	0.7589 (4)	0.0195 (5)
H5A	0.2644	0.3278	0.8596	0.029*
H5B	0.1434	0.2399	0.7893	0.029*
H5C	0.1621	0.3117	0.6358	0.029*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Zn1	0.0108 (2)	0.0106 (3)	0.0269 (3)	0.000	0.00690 (17)	0.000
N1	0.0128 (13)	0.0115 (13)	0.0166 (12)	0.000	0.0054 (10)	0.000
O1	0.0143 (8)	0.0178 (8)	0.0228 (7)	0.0007 (7)	0.0050 (7)	0.0013 (6)
O2	0.0146 (8)	0.0135 (8)	0.0277 (8)	-0.0012 (6)	0.0061 (6)	0.0048 (6)
C1	0.0143 (12)	0.0124 (11)	0.0202 (11)	-0.0012 (9)	0.0095 (9)	-0.0039 (8)
C2	0.0145 (11)	0.0121 (12)	0.0175 (10)	-0.0004 (9)	0.0058 (9)	0.0007 (8)
C3	0.0161 (17)	0.0107 (16)	0.0226 (17)	0.000	0.0064 (14)	0.000
C4	0.0111 (11)	0.0133 (11)	0.0165 (10)	-0.0011 (8)	0.0049 (8)	-0.0001 (8)
C5	0.0160 (11)	0.0150 (12)	0.0302 (12)	0.0005 (9)	0.0118 (10)	-0.0021 (9)

*Geometric parameters (Å, °)*

Zn1—O1	2.207 (3)	O2—Zn1 <sup>iii</sup>	1.977 (2)
Zn1—O1 <sup>i</sup>	2.207 (3)	C1—C2	1.507 (3)
Zn1—O2 <sup>ii</sup>	1.977 (2)	C2—C3	1.382 (3)
Zn1—O2 <sup>iii</sup>	1.977 (2)	C2—C4	1.407 (3)
Zn1—N1 <sup>iv</sup>	2.089 (3)	C3—C2 <sup>v</sup>	1.382 (3)
N1—C4	1.349 (3)	C3—H3	0.9300
N1—C4 <sup>v</sup>	1.349 (3)	C4—C5	1.497 (3)
N1—Zn1 <sup>iv</sup>	2.089 (3)	C5—H5A	0.9600
O1—C1	1.250 (3)	C5—H5B	0.9600
O2—C1	1.267 (3)	C5—H5C	0.9600
O2 <sup>iii</sup> —Zn1—O2 <sup>ii</sup>	115.94 (11)	O2—C1—C2	116.0 (2)
O2 <sup>iii</sup> —Zn1—N1 <sup>iv</sup>	122.03 (5)	C3—C2—C4	118.6 (2)
O2 <sup>ii</sup> —Zn1—N1 <sup>iv</sup>	122.03 (5)	C3—C2—C1	119.6 (2)
O2 <sup>iii</sup> —Zn1—O1	95.17 (6)	C4—C2—C1	121.69 (19)
O2 <sup>ii</sup> —Zn1—O1	90.75 (6)	C2 <sup>v</sup> —C3—C2	120.5 (3)
N1 <sup>iv</sup> —Zn1—O1	84.42 (4)	C2 <sup>v</sup> —C3—H3	119.7
O2 <sup>iii</sup> —Zn1—O1 <sup>i</sup>	90.75 (6)	C2—C3—H3	119.7
O2 <sup>ii</sup> —Zn1—O1 <sup>i</sup>	95.17 (6)	N1—C4—C2	120.30 (19)
N1 <sup>iv</sup> —Zn1—O1 <sup>i</sup>	84.42 (4)	N1—C4—C5	117.2 (2)
O1—Zn1—O1 <sup>i</sup>	168.83 (9)	C2—C4—C5	122.51 (19)
C4—N1—C4 <sup>v</sup>	121.2 (3)	C4—C5—H5A	109.5
C4—N1—Zn1 <sup>iv</sup>	119.41 (13)	C4—C5—H5B	109.5

C4 <sup>v</sup> —N1—Zn1 <sup>iv</sup>	119.41 (13)	H5A—C5—H5B	109.5
C1—O1—Zn1	124.94 (16)	C4—C5—H5C	109.5
C1—O2—Zn1 <sup>iii</sup>	117.23 (15)	H5A—C5—H5C	109.5
O1—C1—O2	125.3 (2)	H5B—C5—H5C	109.5
O1—C1—C2	118.7 (2)		
O2 <sup>iii</sup> —Zn1—O1—C1	120.17 (19)	O2—C1—C2—C4	-137.8 (2)
O2 <sup>ii</sup> —Zn1—O1—C1	4.03 (18)	C4—C2—C3—C2 <sup>v</sup>	-3.21 (13)
N1 <sup>iv</sup> —Zn1—O1—C1	-118.08 (18)	C1—C2—C3—C2 <sup>v</sup>	173.1 (2)
O1 <sup>i</sup> —Zn1—O1—C1	-118.08 (18)	C4 <sup>v</sup> —N1—C4—C2	-3.33 (14)
Zn1—O1—C1—O2	-103.1 (2)	Zn1 <sup>iv</sup> —N1—C4—C2	176.67 (14)
Zn1—O1—C1—C2	74.7 (2)	C4 <sup>v</sup> —N1—C4—C5	175.2 (2)
Zn1 <sup>iii</sup> —O2—C1—O1	-0.8 (3)	Zn1 <sup>iv</sup> —N1—C4—C5	-4.8 (2)
Zn1 <sup>iii</sup> —O2—C1—C2	-178.63 (14)	C3—C2—C4—N1	6.6 (3)
O1—C1—C2—C3	-131.9 (2)	C1—C2—C4—N1	-169.61 (17)
O2—C1—C2—C3	46.1 (3)	C3—C2—C4—C5	-171.85 (17)
O1—C1—C2—C4	44.2 (3)	C1—C2—C4—C5	11.9 (3)

Symmetry codes: (i)  $-x, y, -z+1/2$ ; (ii)  $x, -y, z-1/2$ ; (iii)  $-x, -y, -z+1$ ; (iv)  $-x+1/2, -y+1/2, -z+1$ ; (v)  $-x+1, y, -z+3/2$ .

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

Cg is the centroid of the pyridine ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C5—H5C <sup>iv</sup> ...Cg <sup>iv</sup>	0.96	2.67	3.573 (4)	158

Symmetry code: (iv)  $-x+1/2, -y+1/2, -z+1$ .