

## Ethane-1,2-diyl bis(pyridine-3-carboxylate)

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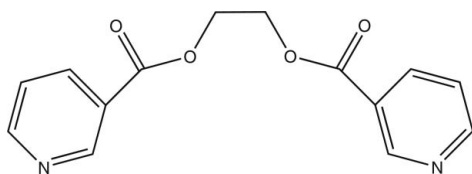
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Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.005$  Å;  $R$  factor = 0.049;  $wR$  factor = 0.131; data-to-parameter ratio = 9.6.

The title compound,  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_4$ , has twofold imposed crystallographic symmetry in the solid state. The asymmetric unit contains one half-molecule. An intramolecular  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bond is formed between the carboxylate O group and one H atom of the aromatic ring such that a five-membered ring is formed. The angle between the planes of symmetry-related aromatic rings is  $44.71(19)^\circ$ .

### Related literature

For the synthesis of ditopic flexible linkers, see: Chatterjee *et al.* (2004). For the potential of coordination polymers based on this multitopic bridging ligand and metal centers as functional materials, see: Huang *et al.* (2007). For applications, see: Matsuda *et al.* (2005); Wu *et al.* (2005); Xiang *et al.* (2005). For bond-length data, see: Allen (2002).



### Experimental

#### Crystal data

$\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_4$   
 $M_r = 272.26$   
Orthorhombic,  $P2_12_12$   
 $a = 4.0740(14)$  Å

$b = 21.3404(7)$  Å  
 $c = 7.395(6)$  Å  
 $V = 642.9(6)$  Å<sup>3</sup>  
 $Z = 2$

Mo  $K\alpha$  radiation  
 $\mu = 0.11$  mm<sup>-1</sup>

$T = 293$  K  
 $0.19 \times 0.10 \times 0.08$  mm

#### Data collection

Nonius KappaCCD area-detector diffractometer  
2298 measured reflections

874 independent reflections  
694 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.030$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$   
 $wR(F^2) = 0.131$   
 $S = 1.27$   
874 reflections

91 parameters  
H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.16$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.18$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C2}-\text{H2}\cdots\text{O1}$	0.93	2.40	2.735 (5)	101

Data collection: COLLECT (Nonius, 2000); cell refinement: DENZO-SMN (Otwinowski & Minor, 1997); data reduction: DENZO-SMN; program(s) used to solve structure: SIR97 (Altomare *et al.*, 1999); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997) and PLATON (Spek, 2009); software used to prepare material for publication: WinGX (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: OM2303).

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**supplementary materials**

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## Ethane-1,2-diyl bis(pyridine-3-carboxylate)

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### Comment

In the past decade, crystalline nanoporous coordination polymers have been extensively studied for their potential applications in magnetism (Xiang, *et al.*, 2005), catalysis (Wu, *et al.*, 2005), and gas adsorption or separation (Matsuda, *et al.*, 2005). Ethanediyl pyridinecarboxylate ligands have been used as flexible linkers to generate metallocyclic ensembles, which showed hysteretic adsorption properties (Chatterjee *et al.*, 2004). We report here the crystal structure of the title compound which has twofold imposed crystallographic symmetry in the solid state. The asymmetric unit contains one-half of the molecule (Fig. 1). This compound crystallizes in a chiral space group,  $P2_12_12$  despite the absence of a chiral center. This chirality arises from the crystal packing. A twofold rotation axis passes through the midpoint of C7 and C7(i). An intramolecular C—H $\cdots$ O hydrogen bond is formed between the carboxylate O group and one H-atom of the aromatic ring such that a five-membered ring is formed. The angle between the planes of symmetry-related aromatic rings is 44.71 (19). A search in the Cambridge Structural Database (version 5.30; Allen, 2002) for the title compound yielded two structures namely *catena*-(bis( $\mu_2$ -1,2-ethanediyl bis(3-pyridinecarboxylate)-N,N')- bis(isothiocyanato)-cobalt(ii) trihydrate) and *catena*-(bis( $\mu_2$ -1,2-ethanediyl bis(3-pyridinecarboxylate)-N,N')- bis(isothiocyanato)-cobalt(ii) tetrahydrofuran clathrate) (refcodes HEXKEB and HEXKIF, respectively) (Huang *et al.*, 2007). The most obvious differences between these coordination polymers and the uncoordinated ligand reported here are the angles between the planes of symmetry-related aromatic rings (66.80 (12) $^\circ$  and 44.71 (19) $^\circ$ , respectively) which is a consequence of the flexible organic components of the title compound.

### Experimental

Nicotinic acid (15 g, 0.122 mol) was stirred in SOCl<sub>2</sub> (40 ml) in the presence of DMF (0.6 ml) at 60  $^\circ$ C for 12 h. Excess thionyl chloride was removed in vacuo. Dried ethylene glycol (3.4 ml, 0.061 mol) was added. After the evolution of hydrogen chloride ended, the mixture was heated at 150  $^\circ$ C for 2 h. The mixture was dissolved in water, and NH<sub>4</sub>OH solution was added. After filtration, recrystallization in ethyl acetate gave colorless crystals. Yield 11.53 g (75%). Analysis calculated for C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>O<sub>4</sub>: C: 61.76, H 4.44, N: 10.29; found: C: 61.25, H: 4.58, N: 10.15. IR (KBr, cm<sup>-1</sup>): (C=O) 1723 s, (C=C) 1589 m, (Ar C—C, C=N) 1424 s, (C—O) 1287 m.

### Refinement

In the absence of anomalous scatterers, 488 Friedel pairs were merged.

H atoms were positioned geometrically at distances of 0.93 (CH) and 0.97 Å (CH<sub>2</sub>) from the parent C atoms and refined as riding with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

50 reflections were not included in the data set as they were either partially obscured by the beam stop or were eliminated during data reduction. The material was difficult to obtain in a suitable crystalline form.

## Figures

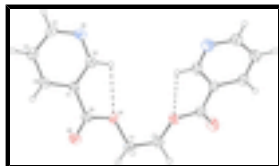


Fig. 1. A view of the molecular structure with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Intramolecular hydrogen bonds are indicated by dotted lines. Unlabeled atoms are related to labeled atoms by the symmetry code  $(-x, 1 - y, z)$ .

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### Crystal data

$C_{14}H_{12}N_2O_4$

$M_r = 272.26$

Orthorhombic,  $P2_12_12$

Hall symbol:  $P\ 2\ 2ab$

$a = 4.0740$  (14) Å

$b = 21.3404$  (7) Å

$c = 7.395$  (6) Å

$V = 642.9$  (6) Å<sup>3</sup>

$Z = 2$

$F(000) = 284$

$D_x = 1.406$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 1704 reflections

$\theta = 1.9$ – $27.5^\circ$

$\mu = 0.11$  mm<sup>-1</sup>

$T = 293$  K

Prismatic, colourless

$0.19 \times 0.10 \times 0.08$  mm

### Data collection

Nonius KappaCCD area-detector diffractometer

Radiation source: fine-focus sealed tube graphite

$\varphi$  scans, and  $\omega$  scans with  $\kappa$  offsets

2298 measured reflections

874 independent reflections

694 reflections with  $I > 2\sigma(I)$

$R_{int} = 0.030$

$\theta_{max} = 27.6^\circ$ ,  $\theta_{min} = 1.9^\circ$

$h = -5 \rightarrow 0$

$k = -27 \rightarrow 27$

$l = -9 \rightarrow 9$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.049$

$wR(F^2) = 0.131$

$S = 1.27$

874 reflections

91 parameters

0 restraints

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

$w = 1/[\sigma^2(F_o^2) + (0.0408P)^2 + 0.2469P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.002$

$\Delta\rho_{max} = 0.16$  e Å<sup>-3</sup>

$\Delta\rho_{min} = -0.18$  e Å<sup>-3</sup>

*Special details*

**Geometry.** All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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  $F^2 > 2\sigma(F^2)$  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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	-0.1685 (7)	0.44509 (9)	-0.0673 (3)	0.0399 (6)
O2	-0.1110 (9)	0.34487 (11)	-0.1477 (3)	0.0619 (9)
N1	-0.5385 (10)	0.40255 (14)	0.4274 (4)	0.0574 (10)
C1	-0.3638 (9)	0.36912 (14)	0.1334 (4)	0.0330 (8)
C2	-0.3991 (10)	0.41380 (16)	0.2682 (5)	0.0458 (10)
H2	-0.3207	0.454	0.2458	0.055*
C3	-0.6491 (10)	0.34439 (17)	0.4541 (5)	0.0497 (10)
H3	-0.7497	0.3355	0.564	0.06*
C4	-0.6241 (11)	0.29697 (17)	0.3305 (4)	0.0462 (10)
H4	-0.7058	0.2573	0.3562	0.055*
C5	-0.4756 (10)	0.30923 (15)	0.1671 (4)	0.0416 (9)
H5	-0.451	0.2778	0.0812	0.05*
C6	-0.2039 (9)	0.38335 (15)	-0.0413 (4)	0.0365 (8)
C7	0.0000 (10)	0.46502 (15)	-0.2299 (4)	0.0408 (9)
H7A	-0.1124	0.4492	-0.3362	0.049*
H7B	0.2233	0.4493	-0.2306	0.049*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.0527 (15)	0.0300 (12)	0.0371 (11)	-0.0025 (11)	0.0110 (13)	-0.0014 (10)
O2	0.102 (2)	0.0365 (13)	0.0474 (13)	0.0018 (16)	0.0250 (17)	-0.0097 (12)
N1	0.077 (2)	0.051 (2)	0.0441 (16)	-0.0096 (19)	0.015 (2)	-0.0089 (15)
C1	0.038 (2)	0.0291 (15)	0.0321 (15)	0.0021 (15)	-0.0016 (16)	-0.0008 (12)
C2	0.058 (3)	0.0334 (18)	0.0457 (19)	-0.0051 (19)	0.008 (2)	-0.0066 (15)
C3	0.057 (3)	0.054 (2)	0.0380 (18)	-0.009 (2)	0.008 (2)	0.0021 (17)
C4	0.055 (3)	0.0358 (18)	0.0478 (19)	-0.0023 (18)	0.003 (2)	0.0044 (15)
C5	0.049 (2)	0.0331 (17)	0.0423 (17)	-0.0009 (18)	0.0011 (19)	-0.0043 (15)
C6	0.042 (2)	0.0318 (17)	0.0360 (16)	0.0001 (16)	-0.0020 (17)	-0.0014 (14)
C7	0.047 (2)	0.0460 (18)	0.0294 (15)	-0.0102 (19)	0.0023 (18)	-0.0013 (14)

## supplementary materials

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### Geometric parameters (Å, °)

O1—C6	1.339 (4)	C3—C4	1.368 (5)
O1—C7	1.449 (4)	C3—H3	0.93
O2—C6	1.198 (4)	C4—C5	1.376 (5)
N1—C2	1.330 (5)	C4—H4	0.93
N1—C3	1.335 (5)	C5—H5	0.93
C1—C5	1.380 (4)	C7—C7 <sup>i</sup>	1.493 (7)
C1—C2	1.387 (4)	C7—H7A	0.97
C1—C6	1.478 (4)	C7—H7B	0.97
C2—H2	0.93		
C6—O1—C7	117.3 (2)	C5—C4—H4	120.7
C2—N1—C3	116.3 (3)	C4—C5—C1	118.7 (3)
C5—C1—C2	118.2 (3)	C4—C5—H5	120.6
C5—C1—C6	119.6 (3)	C1—C5—H5	120.6
C2—C1—C6	122.2 (3)	O2—C6—O1	123.1 (3)
N1—C2—C1	123.8 (3)	O2—C6—C1	124.9 (3)
N1—C2—H2	118.1	O1—C6—C1	112.0 (3)
C1—C2—H2	118.1	O1—C7—C7 <sup>i</sup>	107.1 (3)
N1—C3—C4	124.3 (3)	O1—C7—H7A	110.3
N1—C3—H3	117.8	C7 <sup>i</sup> —C7—H7A	110.3
C4—C3—H3	117.8	O1—C7—H7B	110.3
C3—C4—C5	118.6 (3)	C7 <sup>i</sup> —C7—H7B	110.3
C3—C4—H4	120.7	H7A—C7—H7B	108.6
C3—N1—C2—C1	-0.2 (6)	C7—O1—C6—O2	-2.0 (5)
C5—C1—C2—N1	-0.9 (6)	C7—O1—C6—C1	177.0 (3)
C6—C1—C2—N1	-179.3 (4)	C5—C1—C6—O2	-13.3 (6)
C2—N1—C3—C4	0.7 (6)	C2—C1—C6—O2	165.1 (4)
N1—C3—C4—C5	0.1 (7)	C5—C1—C6—O1	167.8 (3)
C3—C4—C5—C1	-1.3 (6)	C2—C1—C6—O1	-13.9 (5)
C2—C1—C5—C4	1.7 (6)	C6—O1—C7—C7 <sup>i</sup>	178.5 (4)
C6—C1—C5—C4	-179.9 (4)		

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

### 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>
C2—H2...O1	0.93	2.40	2.735 (5)	101

Fig. 1

