organic compounds

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

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The title compound, $C_{14}H_{12}N_2O_4$, has twofold imposed crystallographic symmetry in the solid state. The asymmetric unit contains one half-molecule. An intramolecular C—H···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)°.

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).
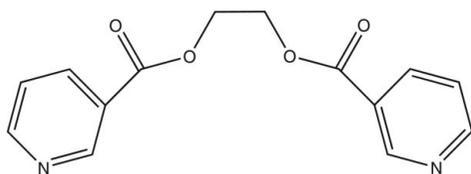
Experimental

Crystal data

$C_{14}H_{12}N_2O_4$	b = 21.3404 (7) Å
M_r = 272.26	c = 7.395 (6) Å
Orthorhombic, $P2_12_12$	V = 642.9 (6) Å^3
a = 4.0740 (14) Å	Z = 2

Mo $K\alpha$ radiation	T = 293 K
μ = 0.11 mm^{-1}	$0.19 \times 0.10 \times 0.08$ mm

Data collection

Nonius KappaCCD area-detector diffractometer	874 independent reflections
	694 reflections with $I > 2\sigma(I)$
2298 measured reflections	R_{int} = 0.030

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049	91 parameters
$wR(F^2)$ = 0.131	H-atom parameters constrained
S = 1.27	$\Delta\rho_{max}$ = 0.16 e Å^{-3}
874 reflections	$\Delta\rho_{min}$ = −0.18 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···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).

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

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supporting information

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

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S1. 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 beeen 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⋯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(μ_2-1,2-ethanediyl bis(3-pyridinecarboxylate)-N,*N′*)- bis(isothiocyanato)-cobalt(ii) trihydrate) and *catena*-(bis(μ_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 the angles between the planes of symmetry-related aromatic rings (66.80 (12)° and 44.71 (19)°, respectively) which is a consequence of the flexible organic components of the title compound.

S2. Experimental

Nicotinic acid (15 g, 0.122 mol) was stirred in $SOCl_2$ (40 ml) in the presence of DMF (0.6 ml) at 60 °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 °C for 2 h. The mixture was dissolved in water, and NH_4OH solution was added. After filtration, recrystallization in ethyl acetate gave colorless crystals. Yield 11.53 g (75%). Analysis calculated for $C_{14}H_{12}N_2O_4$: C: 61.76, H 4.44, N: 10.29; found: C: 61.25, H: 4.58, N: 10.15. IR (KBr, cm^{-1}): (C=O) 1723 s, (C=C) 1589 m, (Ar C—C, C=N) 1424 s, (C—O) 1287 m.

S3. 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 (CH₂) from the parent C atoms and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$.

  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.
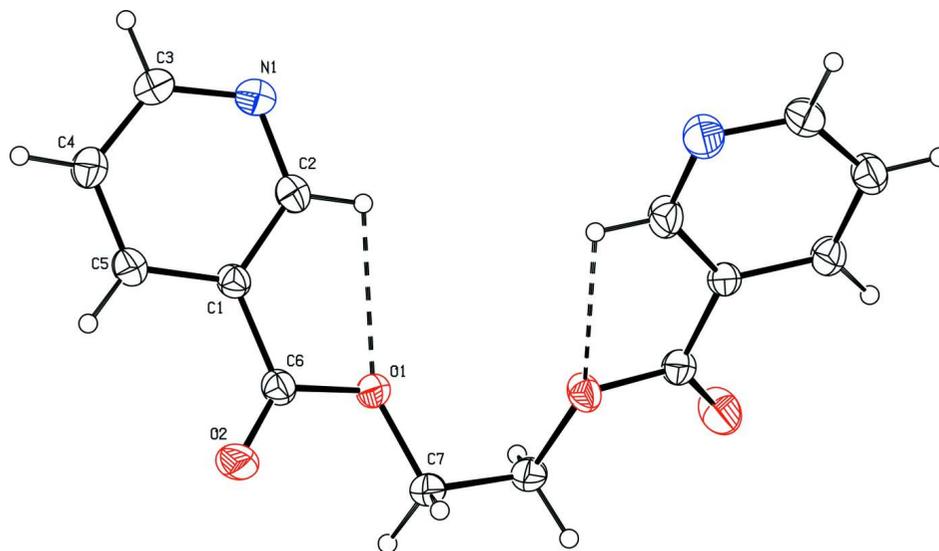
Figure 1

A view of the molecular structure with the atom-numbering scheme. Displacemenent 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

$C_{14}H_{12}N_2O_4$	$F(000) = 284$
$M_r = 272.26$	$D_x = 1.406$ Mg m^{-3}
Orthorhombic, $P2_12_12$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2 2ab	Cell parameters from 1704 reflections
$a = 4.0740\ (14)$ Å	$\theta = 1.9–27.5°$
$b = 21.3404\ (7)$ Å	$\mu = 0.11$ mm^{-1}
$c = 7.395\ (6)$ Å	$T = 293$ K
$V = 642.9\ (6)$ Å^3	Prismatic, colourless
$Z = 2$	$0.19 \times 0.10 \times 0.08$ mm

Data collection

Nonius KappaCCD area-detector diffractometer	694 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.030$
Graphite monochromator	$\theta_{max} = 27.6°$, $\theta_{min} = 1.9°$
φ scans, and ω scans with κ offsets	$h = -5 \rightarrow 0$
2298 measured reflections	$k = -27 \rightarrow 27$
874 independent reflections	$l = -9 \rightarrow 9$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.049$	
$wR(F^2) = 0.131$	
$S = 1.27$	Hydrogen site location: inferred from neighbouring sites
874 reflections	H-atom parameters constrained
91 parameters	
0 restraints	

$w = 1/[\sigma^2(F_o^2) + (0.0408P)^2 + 0.2469P]$
   where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$

$\Delta\rho_{max} = 0.16$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{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 (Å^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)

Geometric parameters (Å, º)

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^i	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^i	107.1 (3)
N1—C3—C4	124.3 (3)	O1—C7—H7A	110.3
N1—C3—H3	117.8	C7^i—C7—H7A	110.3
C4—C3—H3	117.8	O1—C7—H7B	110.3
C3—C4—C5	118.6 (3)	C7^i—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^i	178.5 (4)
C6—C1—C5—C4	−179.9 (4)		

Symmetry code: (i) −*x*, −*y*+1, *z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O1	0.93	2.40	2.735 (5)	101