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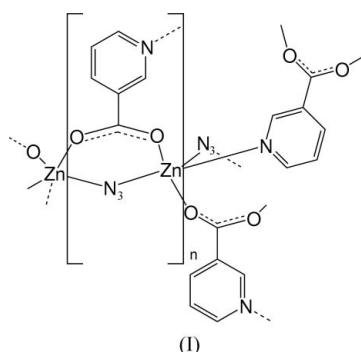
Key indicators

Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$
 R factor = 0.024
 wR factor = 0.060
Data-to-parameter ratio = 10.5For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Poly[zinc(II)- μ_2 -azido- $\kappa^2\text{N}^1:\text{N}^1$ - μ_3 -nicotinato- $\kappa^3\text{N}:\text{O}:\text{O}'$]

The title complex, $[\text{Zn}(\text{N}_3)(\text{C}_6\text{H}_4\text{NO}_2)]_n$, formed from Zn cations, nicotinate and azide groups, exhibits a three-dimensional non-centrosymmetric covalent network. The coordination sphere of the central metal ions is completed by an N_3O_2 five-coordinate coordination model showing distorted trigonal-bipyramidal geometry. Adjacent Zn atoms are bonded by μ_2 -carboxylate groups and a μ_2 -azide bridge into one-dimensional helical double-stranded chains with the six-membered ring running along the a axis, and these chains are further linked by μ_3 -nicotinate groups *via* covalent bonds, extending into two-dimensional sheets and further generating a non-centrosymmetric three-dimensional covalent network.

Comment

The design and synthesis of one-, two- or three-dimensional coordination polymers has recently been of interest due to their special properties and potential applications (Kitagawa *et al.*, 2004; Seki & Mori, 2002; Shin *et al.*, 2003). The asymmetric organic ligand, *m*-pyridinecarboxylate (nicotinate), has recently been used as a bi/tridentate bridge to build chiral coordination polymers of Cd^{II} and Zn^{II} for exploring non-linear optical materials (Lin *et al.*, 1998; Evans & Lin, 2001) and Cu^{II} and Mn^{II} for magnetic materials (Chapman *et al.*, 2001; Chen *et al.*, 2001). In these reported coordination polymers, the generation of acentricity comes from the asymmetric organic ligands, especially when the central ion is located at an inversion center (Lin *et al.*, 1998). In our recent work, two three-dimensional coordination polymers, *catenapoly*[tetrakis(μ_3 -nicotinato- N,O,O')bis(μ_2 -azido)diaqua-trimanganese(II)] (formed from nicotinate and azide bridges and Mn^{II} ions; Chen *et al.*, 2001) and polymeric hexa- μ -nicotinato-tricadmium(II) tetrahydrate (formed from nicotinate bridges and Cd^{II} ions with both seven- and six-coordination geometries in the binuclear unit; Chen, 2003), do not show non-centrosymmetric networks.

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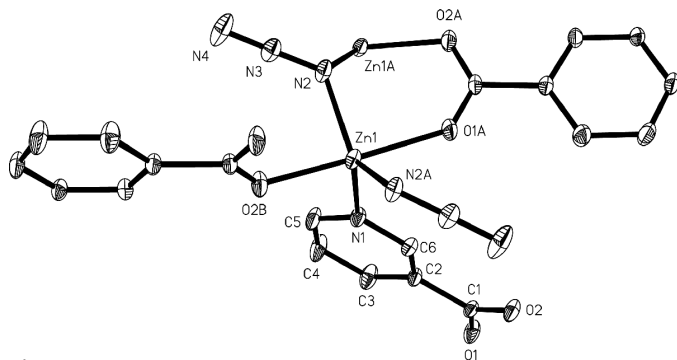


Figure 1
The coordination environment of the Zn atom in (I), showing displacement ellipsoids at the 30% probability level. [Symmetry codes: (A) $x - \frac{1}{2}, -y + \frac{1}{2}, -z$; (B) $-x + \frac{1}{2}, -y, z - \frac{1}{2}$.] H atoms have been omitted.

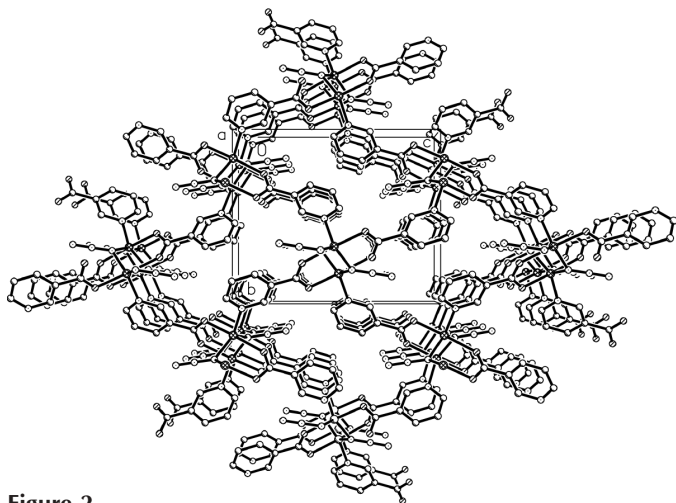


Figure 2
A view of the three-dimensional network.

In order to generate the acentricity of the three-dimensional network, we carried out an experiment to introduce azide groups into the system of nicotinate and Zn ions. In this work, we report the synthesis and structure of the three-dimensional non-centrosymmetric coordination polymer poly[zinc(II)- μ_2 -azido- $\kappa^2 N^1:N_1$ - μ_3 -nicotinato- $\kappa^3 N:O:O'$], (I), featuring mixed azide and nicotinate bridges.

In (I), the Zn atom is five-coordinate and shows a distorted trigonal-bipyramidal geometry, which is generated by three N atoms from one nicotinate and two azide groups in the triangular plane and two axial O atoms from two other nicotinate groups (Fig. 1). The bond lengths around the Zn atom range from 2.033 (3) to 2.206 (2) Å, with the longer axial distance, Zn1—O1ⁱ, being unusually long [symmetry code: (i) $x - \frac{1}{2}, -y + \frac{1}{2}, -z$]. The bond angles around the Zn atom in the triangular plane are not regular, and the Zn atom is located 0.118 (3) Å above the plane. The coordination of Zn by the two O atoms in the axial direction is nearly linear with a bond angle of 178.05 (10)°. Adjacent Zn atoms are bonded by two O atoms of the μ -carboxylate group from a nicotinate group and one terminal N atom of a μ -azide bridge to form a six-membered ring [$-\text{Zn1}-\text{N2}-\text{Zn1}^i-\text{O2}^{ii}-\text{C1}^{ii}-\text{O1}^{ii}-$; symmetry code: (ii) $-x + \frac{1}{2}, -y, z - \frac{1}{2}$], and then a one-dimensional helical double-stranded chain running along the *a*

axis (Fig. 2). In the chain, the distance between adjacent Zn atoms is 3.410 (2) Å. The bond angle of the coordinated azide group is slightly bent [$\text{N2}-\text{N3}-\text{N4} = 178.80 (4)^\circ$]. The helical double-stranded chains are connected by μ_3 -nicotinate groups *via* covalent bonds, extending into two-dimensional sheets with a distance between Zn atoms of adjacent chains of 5.995 (3) Å, and these sheets are further connected by μ_3 -nicotinate groups, generating a three-dimensional covalent network with the same Zn distance as that between adjacent chains (Fig. 2). In the title complex, only one type of coordination mode of nicotinate or azide groups is found. Comparing the title complex with the two-dimensional square grids in polymeric bis(nicotinato)zinc (Lin *et al.*, 1998), the addition of azide groups to the grids does not change the acentricity of the network, even though the dimensionality has been increased from 2 to 3.

Experimental

An aqueous solution (4 ml) of zinc nitrate hexahydrate (0.89 g, 3.0 mmol) was added to an ethanol–water (1:1 *v/v*) solution (10 ml) containing both nicotinic acid (0.49 g, 4.0 mmol) and sodium azide (0.13 g, 2.0 mmol). The reaction solution was mixed for 5 min and the pH of the solution adjusted to 7.0 by adding aqueous ammonia. The resulting solution was left at room temperature for one week to give colorless crystals of (I) suitable for X-ray analysis. The yield was 37% based on zinc nitrate hexahydrate. IR (cm^{-1}): 3373 (*w*), 3327 (*m*), 3061 (*m*), 2093 (*vs*, azide group), 1607 (*vs*, carboxylic group), 1550 (*vs*), 1399 (*vs*, carboxylic group), 1300 (*m*), 1227 (*w*), 1176 (*w*), 1059 (*s*), 851 (*w*), 783 (*m*), 695 (*m*). Elemental analysis found: C 31.42, H 1.80, N 24.38%; calculated for $\text{C}_6\text{H}_4\text{N}_4\text{O}_2\text{Zn}$: C 31.40, H 1.76, N 24.42%.

Crystal data

$[\text{Zn}(\text{N}_3)(\text{C}_6\text{H}_4\text{NO}_2)]$
 $M_r = 229.50$
Orthorhombic, $P2_12_12_1$
 $a = 5.995 (4) \text{ \AA}$
 $b = 10.540 (4) \text{ \AA}$
 $c = 12.586 (6) \text{ \AA}$
 $V = 795.3 (7) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.917 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
Cell parameters from 25 reflections
 $\theta = 6.5\text{--}15.0^\circ$
 $\mu = 3.06 \text{ mm}^{-1}$
 $T = 293 (2) \text{ K}$
Prism, colorless
 $0.28 \times 0.24 \times 0.19 \text{ mm}$

Data collection

Siemens R3m diffractometer
 ω scans
Absorption correction: ψ scan
(Kopelman & Huber, 1968)
 $T_{\text{min}} = 0.454, T_{\text{max}} = 0.560$
1268 measured reflections
1247 independent reflections
1157 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.017$
 $\theta_{\text{max}} = 29.0^\circ$
 $h = 0 \rightarrow 8$
 $k = 0 \rightarrow 14$
 $l = -1 \rightarrow 17$
2 standard reflections
every 200 reflections
intensity decay: <0.1%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.024$
 $wR(F^2) = 0.060$
 $S = 1.02$
1247 reflections
119 parameters
H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0354P)^2 + 0.2937P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.50 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.29 \text{ e \AA}^{-3}$
Extinction correction: SHELXL97
Extinction coefficient: 0.0066 (18)
Absolute structure: Flack (1983),
1276 Friedel pairs
Flack parameter = $-0.01 (2)$

Table 1
Selected geometric parameters (Å, °).

Zn1—N2 ⁱ	2.032 (3)	Zn1—O2 ⁱⁱ	2.067 (2)
Zn1—N2	2.048 (3)	Zn1—O1 ⁱⁱⁱ	2.206 (2)
Zn1—N1	2.057 (3)		
N2 ⁱ —Zn1—N2	128.61 (8)	N2—Zn1—O1 ⁱⁱⁱ	88.05 (10)
N2 ⁱ —Zn1—N1	118.42 (11)	N1—Zn1—O1 ⁱⁱⁱ	86.64 (10)
N2—Zn1—N1	111.95 (13)	O2 ⁱⁱ —Zn1—O1 ⁱⁱⁱ	178.07 (9)
N2 ⁱ —Zn1—O2 ⁱⁱ	94.79 (11)	N3—N2—Zn1	121.3 (3)
N2—Zn1—O2 ⁱⁱ	90.34 (10)	Zn1 ^{iv} —N2—Zn1	112.93 (13)
N1—Zn1—O2 ⁱⁱ	94.95 (9)	N4—N3—N2	178.8 (4)
N2 ⁱ —Zn1—O1 ⁱⁱⁱ	85.39 (11)		

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

H atoms of the nicotinate groups were placed in calculated positions (N—H = 0.86, C—H = 0.93–0.96 Å) and allowed to ride on their respective parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2$ or 1.5 times $U_{\text{eq}}(\text{parent atom})$.

Data collection: *P3/P4-PC* (Siemens, 1991); cell refinement: *P3/P4-PC*; data reduction: *XDISK* (Siemens, 1991); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Siemens, 1990); software used to prepare material for publication: *SHELXL97*.

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