Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

A novel two-dimensional zinc(II) coordination polymer with 6-mercaptonicotinic acid

Yong Wang, Dong-Xia Zhu, Zhong-Min Su,* Kui-Zhan Shao and Ya-Hui Zhao

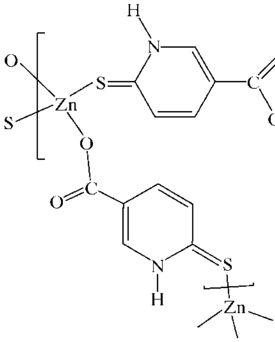
Institute of Functional Material Chemistry, Department of Chemistry, Northeast Normal University, Changchun 130024, People's Republic of China
Correspondence e-mail: zmsu@nenu.edu.cn

Received 23 October 2007
Accepted 27 November 2007
Online 14 December 2007

The novel title Zn^{II} coordination polymer, poly[bis(μ-6-thioxo-1,6-dihydropyridine-3-carboxylato-κ^2S:O)zinc(II)], $[Zn(C_6H_4NO_2S)_2]_n$, consists of two crystallographically independent zinc centers and two 6-mercaptonicotinate ($Hmna^-$) ligands. Each Zn^{II} atom is four-coordinated and lies at the center of a distorted tetrahedral ZnS_2O_2 coordination polyhedron, bridged by four $Hmna^-$ ligands to form a two-dimensional (4,4)-network. Each $Hmna^-$ ion acts as a bridging bidentate ligand, coordinating to two Zn^{II} atoms through the S atom and a carboxyl O atom. The metal centers reside on twofold rotation axes. The coordination mode of the S atoms and N—H···O hydrogen-bonding interactions between the protonated N atoms and the uncoordinated carboxyl O atoms give the extended structure a wavelike form.

Comment

In recent years, research on coordination polymers has expanded rapidly because of their fascinating structural diversity and potential applications as functional materials (Batten & Robson, 1998; Moulton & Zaworotko, 2001). Multifunctional carboxylates and related species provide an effective means of designing novel hybrid materials with porous structures and other interesting properties (Kitagawa *et al.*, 2004; Yaghi *et al.*, 2003). In contrast with the large amount of work on ligands containing O- or N-atom donors, there have been fewer reports of studies based on organothiolate ligands. Three types of organothiolate ligands, *viz.* thiolatopyridine (Han *et al.*, 2004; Su *et al.*, 2000), thiolatobenzoate (Cave *et al.*, 2002) and thiolatopyridinecarboxylate (Humphrey *et al.*, 2005, 2006) have been explored to construct structures with luminescent or magnetic properties. 6-Mercaptonicotinic acid (H_2mna), which exists in solution as an equilibrium mixture of thiol and thione tautomeric forms, is an interesting ligand in the thiolatopyridinecarboxylate system because of its potential coordination possibilities, which include (*a*) an *S*,*N*-donor chelate and carboxyl uncoordinated mode (Nomiya *et al.*, 2003), (*b*) an *S*,*N*-donor chelate and carboxyl multidentate mode (Humphrey *et al.*, 2005, 2006), (*c*) an *S*,*N*-donor chelate and *O*,*O*-chelation bridging mode (Humphrey *et al.*, 2005, 2006), (*d*) a single *S*-donor and carboxyl monodentate mode, and (*e*) an *S*,*N*-donor chelate and carboxyl monodentate mode. In addition, it can act not only as a hydrogen-bond donor but also as a hydrogen-bond acceptor, owing to the existence of deprotonated and/or protonated carboxyl groups and pyridine N atoms, as well as the thiol or thione group. These considerations prompted our interest in the structure patterns of the H_2mna ligand. In this paper, we report the preparation and crystal structure of a novel two-dimensional coordination polymer, *viz.* $[Zn(Hmna)_2]_n$, (I).



(I)

The asymmetric unit of (I) consists of two zinc centers and two $Hmna^-$ ligands (Fig. 1). Each Zn^{II} atom sits on a twofold rotation axis and is coordinated by two O atoms and two S atoms from four different $Hmna^-$ ligands in a typical distorted tetrahedral coordination geometry (Table 1). The bond lengths and angles involving Zn, O and S atoms are similar to those in analogous zinc coordination polymers (Humphrey *et al.*, 2004). The two $Hmna^-$ ligands in the asymmetric unit adopt the same coordination mode, *i.e.* the thione coordinates to the Zn atoms and the carboxylate group links the Zn atoms in a monodentate coordination fashion [mode (*d*) above]. To the best of our knowledge, (I) is the first example with this

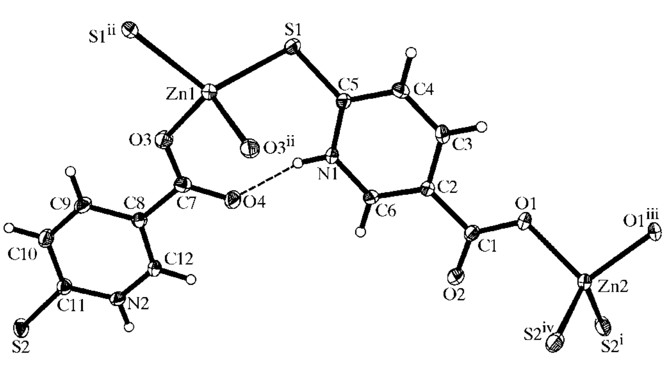


Figure 1
A view of the local coordination of the Zn^{II} atom, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+1, y, -z+\frac{3}{2}$; (iii) $-x, y, -z+\frac{1}{2}$; (iv) $x-1, -y+1, z-\frac{1}{2}$.]

DOI: 10.1107/S0108270107063962

coordination mode (*d*) of the H_2mna ligand. In the molecular structure, the C5—S1 and C11—S2 bond lengths [1.728 (3) and 1.723 (3) Å] are indicative of double bonds, similar to those in a number of structures reported previously (Chung *et al.*, 2003; Lobana *et al.*, 2005). The C5—S1—Zn1 and C11—S2—Zn2^{i} [symmetry code: (i) $-x + 1, -y + 1, -z + 1$] angles are 100.44 (9) and 111.71 (9)°, respectively.

The molecules of (I) form an extended two-dimensional network involving coordination frameworks of (4,4)-topology (Fig. 2). In the grid, adjacent Zn···Zn distances (linked by Hmna$^-$ ligands) are 10.015 and 9.618 Å, so each 4 × 4 unit is an approximate rhombus. Considering the Zn^{II} atoms as three-connected nodes, the corrugated metal–organic framework can be represented as a two-dimensional distorted sheet of (4,4)-topology in the *ac* plane. These layers are then stacked on top of each other to give rise to the final structure (Fig. 3).

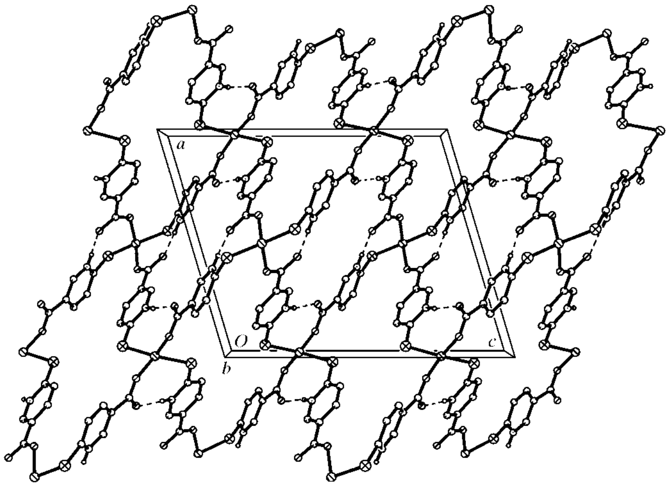


Figure 2
The two-dimensional single-layer (4,4)-network in (I). N—H···O hydrogen bonds are shown as dashed lines and H atoms bonded to C atoms have been omitted for clarity.

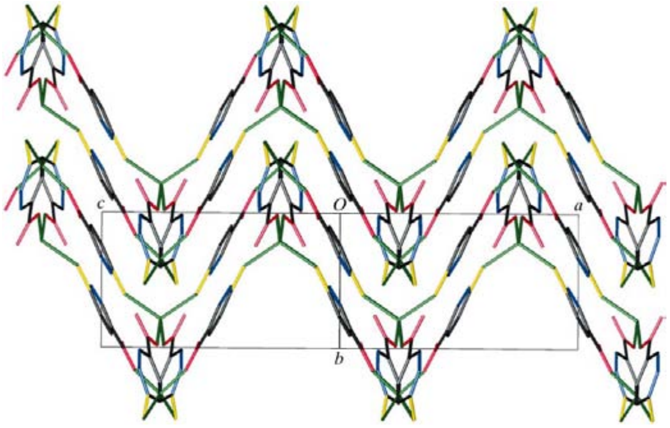


Figure 3
A view of the sine wave sheets in (I), along the (010) plane.

There are some significant hydrogen-bonding interactions between the protonated N atoms of the Hmna$^-$ ligands (owing to the thiol–thione tautomerism) and the uncoordinated carboxyl O atoms (Table 2). The coordination mode of the S atoms and the hydrogen-bonding interactions lead the complex to form a wavelike extended structure along the (010) plane (Fig. 3).

Experimental

A mixture of $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.0658 g), H_2mna (0.0466 g), NaOH (0.012 g) and water (10 ml) was stirred for 20 min in air. The mixture was then transferred to a 23 ml Teflon reactor and kept at 438 K for 3 d under autogenous pressure, then cooled to room temperature at a rate of 5 K h^{-1}. Colorless block-like crystals of (I) were obtained; these were washed with distilled water and dried at room temperature (yield *ca* 50% based on Zn). Elemental analysis found: C 38.64, H 2.10, N 7.62%; calculated: C 38.57, H 2.16, N 7.50%.

Crystal data

$[Zn(C_6H_4NO_2S)_2]$
$M_r = 373.69$
Monoclinic, $P2/c$
$a = 13.4079 (8)$ Å
$b = 6.5765 (4)$ Å
$c = 16.0390 (9)$ Å
$\beta = 106.283 (1)°$
$V = 1357.54 (14)$ Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 2.13$ mm^{-1}
$T = 293 (2)$ K
0.23 × 0.19 × 0.14 mm

Data collection

Bruker SMART APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
$T_{min} = 0.640, T_{max} = 0.755$
8024 measured reflections
3222 independent reflections
2531 reflections with $I > 2\sigma(I)$
$R_{int} = 0.037$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.094$
$S = 1.00$
3222 reflections
191 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.42$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn1—O3	1.9757 (19)	Zn2—O1	1.9648 (18)
Zn1—S1	2.3119 (7)	Zn2—S2^{i}	2.3367 (8)
O3—Zn1—O3^{ii}	107.26 (12)	O1^{iii}—Zn2—O1	98.72 (11)
O3—Zn1—S1	119.38 (6)	O1—Zn2—S2^{iv}	94.59 (6)
O3^{ii}—Zn1—S1	97.41 (6)	O1—Zn2—S2^{i}	126.23 (6)
S1—Zn1—S1^{ii}	117.00 (4)	S2^{iv}—Zn2—S2^{i}	117.98 (4)

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+1, y, -z+\frac{3}{2}$; (iii) $-x, y, -z+\frac{1}{2}$; (iv) $x-1, -y+1, z-\frac{1}{2}$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O4	0.86	1.85	2.686 (3)	163
N2—H2···O2^{i}	0.86	1.87	2.706 (3)	164

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

All H atoms were generated geometrically and included as riding atoms [C—H = 0.93 Å, N—H = 0.86 Å and U_{iso}(H)= $1.2U_{eq}$(C,N)].

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.

The authors gratefully acknowledge financial support from the National Natural Science Foundation of China (project Nos. 20373009, 20571029 and 20573016).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3111). Services for accessing these data are described at the back of the journal.

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