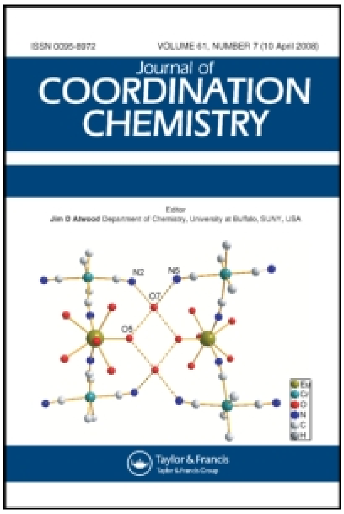

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Hydrothermal synthesis and crystal structure of a layered coordination polymer: $[Zn_2(C_2O_4)_2(C_3N_2H_4)_2]_n$

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A new metal-organic coordination polymer $[Zn_2(C_2O_4)_2(C_3N_2H_4)_2]_n$ (**1**) has been hydrothermally synthesized with $ZnCl_2 \cdot 2H_2O$, oxalic acid and imidazole. The compound has a 2D network, consisting of infinite zinc(II) oxalate chains connected to each other by three-coordinate oxygen atoms. Within the chains, the zinc atoms are each octahedrally coordinated by one nitrogen atom from imidazole and five oxygen atoms from oxalate groups. Furthermore, there are two coordination modes of oxalate to zinc ions: chelate bis-bidentate and chelate/bridging bis-bidentate in compound **1**, and the latter is rare among related compounds. Crystal data: monoclinic, $P2(1)/c$, $a = 8.4310(17)$, $b = 9.4060(19)$, $c = 8.2790(17)$ Å, $\beta = 93.15(3)^\circ$, $V = 655.5(2)$ Å^3, $Z = 2$, $R_1 = 0.0322$, $wR_2 = 0.0850$.

Keywords: Zn(II) complex; Oxalate complex; Hydrothermal synthesis; Crystal structure

1. Introduction

In recent years, much interest has been focused on the design and synthesis of metal-directed extended networks, for their interesting structural motifs and their potential applications in catalysis, medicine, host-guest chemistry and molecular-based magnetic materials [1–3]. Many important properties of coordination polymers depend largely on their structures and topology. Therefore, the key to the construction of a desired framework is the selection of inorganic and organic building blocks [4]. In fabricating these kinds of complexes, organic N-donors such as imidazole and related species [5–8] are often chosen as ligands to bind the metal centers. On the other hand, the oxalate ion has been known to function as a bis-bidentate ligand, and its coordination to transition metal ions has been widely examined due to its remarkable ability to mediate strong

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magnetic interactions between metal centers [9–11]. However, metal-organic frameworks based on both oxalate and other organic ligands have been rarely explored [3, 4, 10–12]. Utilizing the hydrothermal synthesis methodology, here we report a layered coordination polymer, $[Zn_2(C_2O_4)_2(C_3N_2H_4)_2]_n$ (**1**), which consists of infinite zinc(II) oxalate chains connected to each other by three-coordinate oxygen atoms. The coordination modes of oxalate to metal ions are various [13, 14], but the general mode to zinc is only chelate bis-bidentate. In compound **1** there are two coordination modes: chelate bis-bidentate and chelate/bridging bis-bidentate.

2. Experimental

2.1. *Physical measurements*

All reagents were purchased commercially and used without further purification. Elemental analyses (C, H and N) were measured on a CARCO ERBA EA1110 element analyzer. The Zn content was determined by an IRIS Intrepid IIXSP instrument. An IR spectrum was recorded in the range 4000–400 cm^{-1} on Nicolet Impact 410 FTIR Spectrophotometer using a KBr pellet. Thermogravimetric analyses for compound **1** were preformed on a SDT Q600 V5.0 Build 63 thermal analyzer from room temperature to 800°C under nitrogen at a heating rate of 10°C min^{-1}.

2.2. *Syntheses*

In a typical synthesis, $ZnCl_2 \cdot 2H_2O$ (0.6 g) was added to deionized water (10 mL) by stirring for 10 min to form a homogeneous solution; then oxalic acid (0.555 g) was added, followed by addition of imidazole (0.608 g) with stirring. The mixture became homogeneous, transferred into a Teflon-lined stainless-steel autoclave and heated at 433 K for 3 days. The crystallization products were cleaned with distilled water several times, and dried at room temperature. Yields: 60% based on the initial $ZnCl_2 \cdot 2H_2O$. Anal. Calcd for $C_{10}H_8N_4O_8Zn_2$ (%): C, 27.1; H, 1.8; N, 12.7; Zn, 29.5. Found: C, 26.8; H, 2.0; N, 13.2; Zn, 30.3. IR (cm^{-1}): 3400(m), 3149(m), 3074(w), 1647(s), 1611(s), 1550(w), 1516(w), 1451(w), 1377(m), 1078(m), 835(m), 806(m), 757(m), 658(m), 621(w), 505(m).

2.3. *X-ray crystallography*

The single crystal with dimensions $0.489 \times 0.222 \times 0.111\ mm^3$ for compound **1** was selected for structure determination. Data was collected at 293 K on a Bruker P4 diffractometer with the θ–2θ scan mode in the range $2.0 < 2\theta < 55.0°$. The data was corrected for LP effects and an absorption correction was performed empirically ($T_{min–max} = 0.199–0.333$). 1504 independent reflections were applied for the structure determination and refinement. The structure was solved by direct methods and refined by full-matrix least-squares on F2 using the SHELXL-97 software. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located from difference Fourier maps. Crystallographic details for the structure of **1** are summarized in table 1; selected bond lengths and angles are listed in table 2.

Table 1. Crystal data and structure refinement for compound **1**.

Identification code	shx97
Empirical formula	C10 H8 N4 O8 Zn2
Formula weight	442.94
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2(1)/c$
Unit cell dimensions	$a = 8.4310(17)$ Å $\alpha = 90^\circ$
	$b = 9.4060(19)$ Å $\beta = 93.15(3)^\circ$
	$c = 8.2790(17)$ Å $\gamma = 90^\circ$
Volume	655.5(2) $Å^3$
Z	2
Density (calculated)	2.244 $Mg\,m^{-3}$
Absorption coefficient	3.715 mm^{-1}
$F(000)$	440
Crystal size	$0.489 \times 0.222 \times 0.111$ mm^3
Theta range for data collection	2.42–27.49.
Index ranges	$-10 \le h \le 10$, $-1 \le k \le 12$, $-10 \le l \le 1$
Reflections collected	2010
Independent reflections	1504 [R(int) = 0.0379]
Completeness to $\theta = 27.49^\circ$	100.0%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1504/0/111
Goodness-of-fit on F^2	1.079
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0322$, $wR_2 = 0.0850$
R indices (all data)	$R_1 = 0.0378$, $wR_2 = 0.0884$
Extinction coefficient	0.020(3)
Largest diff. peak and hole	0.989 and −0.776 e $Å^{-3}$
Type of experimental absorption correction	Psi-scan
Absorption correction	Empirical
Maximum and Minimum transmission	0.333, 0.199
Final mean shift/esd	0.000

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Zn–N(1)	2.025(2)	N(1)–C(3)	1.316(3)	C(4)–O(1)	1.248(3)
Zn–O(1)	2.0454(16)	N(1)–C(1)	1.375(3)	C(4)–O(2)	1.259(3)
Zn–O(4)#1	2.0735(16)	N(2)–C(3)	1.336(3)	C(4)–C(4)#2	1.567(4)
Zn–O(3)	2.0770(16)	N(2)–C(2)	1.370(4)	C(5)–O(3)	1.245(3)
Zn–O(2)#2	2.2946(16)	N(2)–H(4)	0.8600	C(5)–O(4)	1.252(3)
Zn–O(2)#3	2.4096(16)	C(1)–C(2)	1.356(3)	C(5)–C(5)#1	1.554(4)
N(1)–Zn–O(1)	99.17(8)	O(4)#1–Zn–O(3)	80.64(6)	N(1)–Zn–O(2)#3	96.61(7)
N(1)–Zn–O(4)#1	170.71(7)	N(1)–Zn–O(2)#2	94.68(7)	O(1)–Zn–O(2)#3	92.11(6)
O(1)–Zn–O(4)#1	89.62(7)	O(1)–Zn–O(2)#2	76.79(6)	O(4)#1–Zn–O(2)#3	86.00(6)
N(1)–Zn–O(3)	90.43(7)	O(4)#1–Zn–O(2)#2	84.34(7)	O(3)–Zn–O(2)#3	90.01(6)
O(1)–Zn–O(3)	169.87(6)	O(3)–Zn–O(2)#2	99.31(6)	O(2)#2–Zn–O(2)#3	165.30(7)

Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y+1, -z$; #2 $-x+1, -y, -z$; #3 $-x+1, y+1/2, -z+1/2$; $^{\#4}$ $-x+1, y-1/2, -z+1/2$.

3. Results and discussion

X-ray crystallographic analysis shows that compound **1** exhibits a novel 2D layered network, which consists of zinc oxalate chains and organic imidazole ligands, as shown in figure 1. There is only one crystallographically unique Zn center in the crystal structure. The Zn center displays a distorted octahedral geometry, which is completed by one nitrogen atom from imidazole with Zn–N bond length of 2.025(2) Å,

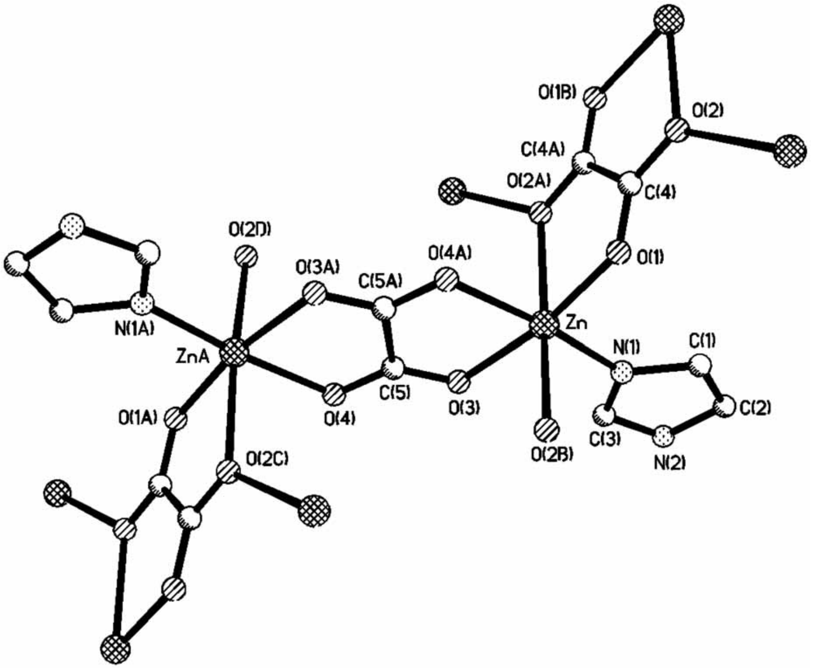

Figure 1. The ORTEP view of the $[Zn_2(C_2O_4)_2]_\infty$ chain with imidazole molecules with displacement ellipsoids (50% probability) and atomic labelling in **1**.

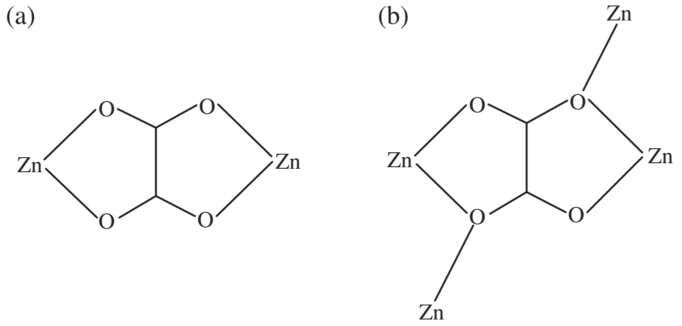

Figure 2. Coordination modes of oxalate to zinc ions: (a) chelate bis-bidentate; (b) chelate/bridging bis-bidentate.

three oxygen atoms (O(1), O(3), O(4)) from oxalate groups with Zn–O distance of 2.0454(16)–2.0770(16) Å, and two three-coordinate oxygen atoms (O(2A), O(2B)) also from oxalate groups with Zn–O bond length of 2.2946(16)–2.4096(16) Å. The O–Zn–O angles range from 76.79(6)–169.87(6)°, while N–Zn–O angles are in the range of 90.43(7)–170.71(7)°. There are two coordination modes of oxalate to zinc: chelate bis-bidentate (formed by oxalate I) and chelate/bridging bis-bidentate (formed by oxalate II) in compound **1**, as shown in figure 2. The latter is rare among zinc oxalate compounds. The Zn centers are connected by the oxalate ligands to form an infinite $[Zn_2(C_2O_4)_2]_\infty$ chain along b axis (figure 3). Oxalate I and II alternate

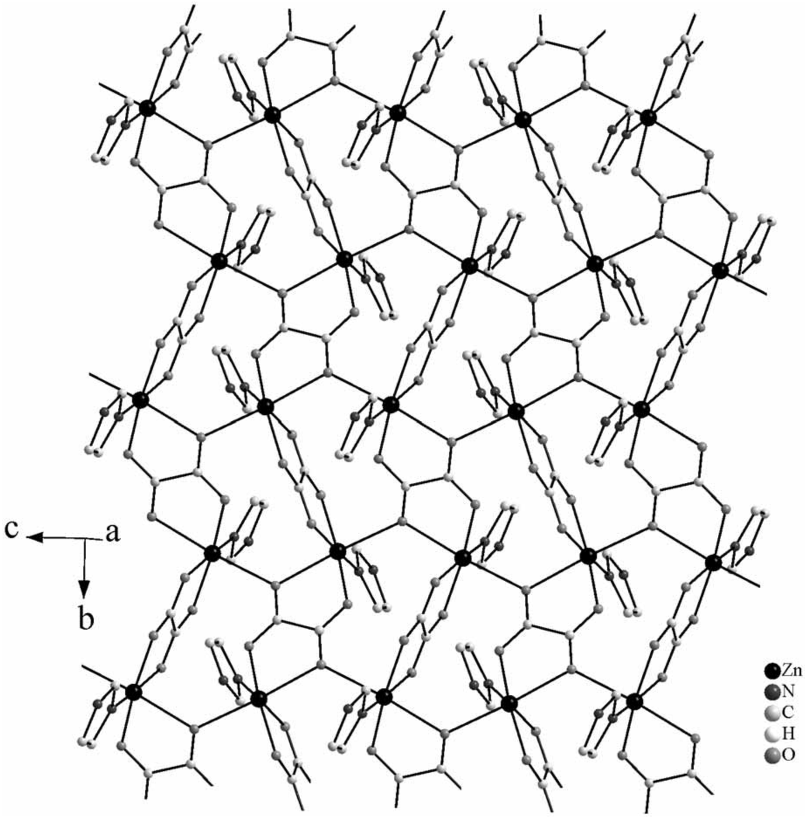

Figure 3. The 2D layered network of compound **1**.

in the chain, and moreover, they are not on the same plane, forming an angle of 86.84(8)°. The adjacent 1D chains are linked by the three-coordinate oxygen atoms from oxalate to form a 2D layered network along *bc* plane. The imidazole molecules act as terminal ligands by employing only one N-donor to coordinate with Zn centers.

In addition, there exist C–H $\cdots$ O hydrogen bonding (C $\cdots$ O distance is 2.953 Å), N–H $\cdots$ O hydrogen bonding (N $\cdots$ O distance is 2.815 Å) and π–π stacking interactions between the adjacent 2D layers (the distance between the aromatic groups is about 3.42 Å). These interactions enhance the stability of compound **1**.

The infrared spectra of compound **1** exhibit characteristic bands for both imidazole and oxalate. The bands in the region 621–1078 $\mathrm{cm^{-1}}$ can be assigned to the C–H in-plane or out-of-plane bend, ring breathing and ring deformation adsorption of imidazole. The aromatic C–C and C–N stretching vibrations appear at 1611, 1550, 1516 and 1451 $\mathrm{cm^{-1}}$. The peaks at 3149, 3074 $\mathrm{cm^{-1}}$ are attributed to the N–H stretching vibration of imidazole [3, 5, 10]. In addition, the absorptions of the coordinated oxalate group occur at 1647($\nu_{\mathrm{asym(CO)}}$), 1377($\nu_{\mathrm{sym(CO)}}$) and 835 $\mathrm{cm^{-1}}$($\delta_{\mathrm{(O–C–O)}}$) [13].

The TGA data showed that the framework of **1** did not lose weight upon heating to ca. 120°C, and then, in the range of 120–600°C, it went through a series of complicated multiple weight losses (releasing of two oxalate ions and two imidazole ligands) with elevating temperature to give the final product that should be a ZnO solid according to the residual weight (observed: 38.08%, calculated: 36.75%).

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