Synthesis, Crystal Structure, and Thermal Stability of 1D Coordination Polymer $[Zn(BDOA)(Py)_2(H_2O)]_n^1$

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Abstract—A new coordination polymer, $[Zn(BDOA)(Py)_2(H_2O)]_n$ (I) (BDOA = benzene-1,4-dioxylacetate, Py = pyridine), has been prepared via self-assembly of benzene-1,4-dioxylacetate with zinc nitrate under mild conditions and characterized by IR spectra, elemental analysis and X-ray diffraction single-crystal analysis. The complex crystallizes in the monoclinic system, space group C2/c with a = 15.5751(9), b = 6.0898(4), c = 21.7133(13) Å, V = 1991.9(2) Å³, $\beta = 104.719(1)^\circ$, Z = 4. The zinc atoms are bridged by BDOA ligand, forming a one-dimensional chain along the z axis. A two-dimensional layer structure is formed by the intermolecular hydrogen bonds. The thermal decomposition profile of the complex is reported as well.

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INTRODUCTION

Metal organic frameworks (MOFs) have attracted a great deal of recent interest not only for the potential discovery of novel functional materials, which may have applications in the areas including gas storage, molecular sieves, ion-exchange, catalysis, magnetism, and optoelectronics, but also for their intriguing variety of architectures and topologies, such as molecular grids, bricks, herringbones, ladders, rings, boxes, diamondoids, and honeycombs [1-5]. Two kinds of these ligands have been generally used in this field, either flexible ligands, such as butanedioic and glutaric acids and such analogous compounds [6-8], or rigid ligands, such as benzenedicarboxylate, benzenetricarboxylate, and so on [9, 10]. Although many ligands with characteristics of both flexibility and rigidity have been reported, here the ligands refer to those containing both a benzene ring and an aliphatic acid group, reports of which are comparatively rare; these ligands are very important in the development of so-called third-generation coordination polymers with dynamic frameworks and striking functions. In this context, we report the synthesis, characterization and thermal studies of a new Zn(II) coordination polymer $[Zn(BDOA)(Py)_2(H_2O)]_n(I)$, where BDOA = benzene-1,4-dioxylacetate.

EXPERIMENTAL

All reagents were commercially available and were used without further purification. FT-IR spectra (KBr pellets) were taken on a Nicolet 380 infrared spectrometer. Elemental analysis (CHN) were performed on a Heraeus CHN-O-RAPID elemental analyzer. TG analysis were recorded with a NETZSCH TG-209 microanalyzer under nitrogen atmosphere at a heating rate of 10°C/min.

Synthesis of ligand BDOA. Hydroquinone 5.5 g (0.05 mol) was dissolved in 50 mL 2 M NaOH (aq), the mixture was heated to 70°C with stiring. Then 25 mL 5 M monochloroacetic acid was added, adjusted pH 11 with 4 M NaOH and heated to 120°C for 3 h (4 M NaOH was dropped in continuously to keep pH 8), cooling to room temperature, acdic with 6 M HCl. The resulting white solid was filtered and washed with water and ethanol and dried. The yield was 6.057 g (53%); mp 250–251°C; ¹H NMR (600 MHz; DMSO; δ , ppm): 4.703 (s., 4H), 6.985 (d, J = 7.2 Hz, 4H), 13.019 (s., 2H).

For $C_{10}H_{10}O_6$		
anal. calcd., %:	C, 53.10;	Н, 4.43.
Found, %:	C, 53.48;	Н, 4.29.

Synthesis of I. A solution of BDOA (0.03 mM), NaOH (0.06 mM) in pyridine $-H_2O(1:1, 2.5 \text{ mL})$ was carefully layered on the top of a solution of Zn(NO₃)₂ · $6H_2O(0.03 \text{ mM})$ in DMF $-H_2O(1:1, 2.5 \text{ mL})$. The yellow crystals suitable for X-ray diffraction were obtained in a few weeks. The yield was 48%.

For C ₂₀ H ₂₀ N ₂ O ₇	Zn		
anal. calcd., %:	C, 51.57;	Н, 4.33;	N, 6.01.
Found, %:	C, 51.82;	H, 4.16;	N, 6.28.

X-ray crystallography. Single crystals of I suitable for X-ray diffraction study were collected on a Bruker

¹ The article is published in the original.

Parameter	Value	
Formula weight	465.75	
Temperature, K	296(2)	
Crystal system	Monoclinic	
Space group	C2/c	
<i>a</i> , Å	15.5751(9)	
b, Å	6.0898(4)	
<i>c</i> , Å	21.7133(13)	
Volume, Å ³	1991.9(2)	
$\rho_{calcd}, mg/m^3$	1.553	
Absorption coefficient, mm ⁻¹	1.279	
<i>F</i> (000)	960	
Crystal size, mm	$1.10\times0.73\times0.51$	
θ Range, deg	1.94-28.20	
Limited indice	$\begin{array}{c} -20 < h < 17, -8 < k < 7, \\ -28 < l < 21 \end{array}$	
Reflections collected	6972	
Independent reflection	3774 ($R_{\rm int} = 0.0223$)	
Completeness to $\theta = 28.20^{\circ}$, %	99.9	
Parameters	273	
Goodness-of-fit on F^2	1.061	
Final <i>R</i> indices, $(I > 2\sigma(I))$	$R_1 = 0.0243, wR_2 = 0.0605$	
R indices, all data	$R_1 = 0.0270, wR_2 = 0.0619$	
Largest diff. peak and hole, $e \text{ Å}^{-3}$	0.229 and -0.284	

 Table 1. Crystallographic data and X-ray experiment details for complex I

SMART APEX-II CCD diffractometer equipped with a graphite crystal and incident beam monochromator using Mo K_{α} radiation ($\lambda = 0.71073$ Å) at room temperature. Data processing was accomplished with the SAINT processing program. The structure was solved by direct methods and refined on F^2 by full matrix least-squares analysis with SHELXTL-97 [11]. The



Fig. 1. A segment of the polymeric structure of complex I with displacement ellipsoids drawn at the 30% probability level.

non-hydrogen atoms were located in successive difference Fourier syntheses and with the hydrogen atoms at calculated position riding on the carbon atoms. Crystallographic data and experimental details for structure analysis are summarized in Table 1. Bond lengths and bond angles of the complex are listed in Table 2. The atomic coordinates and other parameters of structure have been deposited with the Cambridge Crystallographic Data Centre (no. 836460; deposit@ ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Singel-crystal X-ray structure analysis reveals that the asymptotic unit of I contains one Zn(II) atom, one BDOA ligand, two coordination pyridine molecules and one coordination water molecule. Figure 1 shows the view of the local coordination geometries around the Zn(II) atom. The Zn(II) atom is five-coordinated in a distorted square-pyramidal arrangement, with two O atoms of different carboxylate groups and two N atoms of two pyridine molecules in basal positions and a water O atom at the apex. The distortion of the regular square-pyramidal geometry is due to the big angle of the three coordination molecules; O(4)Zn(1)N(1) (and O(4)Zn(1)N(1A) have the same chelate angles 99.72(4)°. The bis-monodentate BDOA ligand has inversion symmetry and acts as bridge to link the Zn(II) atoms to form an infinite zigzag chain along the z axis, as shown in Fig. 2. And the distance between two adjacent Zn(II) atoms in the same chain is half the length of the z axis.

It should be noted that the O–H...O hydrogen bonds (Fig. 3), which are between the coordinated water molecule and the free carboxylate O atoms, link the zigzag chains into two-dimensional layers. Simultaneously, between the pyridyl rings there exist supramolecular weak interactions $\pi-\pi$ stacking (Fig. 2). They are probably an important factor in the supramolecular assembly and stabilization of the layer [11].



Fig. 2. The crystal structure of complex **I**, viewed down the y axis. All H atoms have been omitted for clarity.

Bond	d, Å	Bond	d, Å
Zn(l)-O(4)	2.0088(16)	O(4)-H(4A)	0.78
Zn(1)–O(1)	2.0387(13)	C(1)–C(2)	1.518(2)
Zn(1) - N(1)	2.1454(13)	$C(3)-C(5)^{\#1}$	1.382(2)
N(l)-C(6)	1.332(2)	C(3)–C(4)	1.388(2)
N(l)-C(10)	1.340(2)	C(4)–C(5)	1.390(2)
O(1)–C(1)	1.259(2)	C(6)–C(7)	1.381(3)
O(2)–C(1)	1.226(2)	C(7)–C(8)	1.369(3)
O(3)–C(3)	1.3748(19)	C(8)–(9)	1.378(3)
O(3)–C(2)	1.4162(19)	C(9)–C(10)	1.373(3)
Angle	ω, deg	Angle	ω, deg
O(4)Zn(1)O(1)	93.16(4)	O(1)C(1)C(2)	113.96(15)
O(1)Zn(1)O(1) ^{#1}	173.68(8)	O(3)C(2)C(1)	114.62(13)
O(4)Zn(1)N(1)	99.72(4)	O(3)C(3)C(5) ^{#1}	115.39(14)
O(1)Zn(1)N(1)	87.83(5)	O(3)C(3)C(4)	125.28(14)
$N(1)^{#1}Zn(1)N(1)$	160.56(8)	$C(5)^{#1}C(3)C(4)$	119.30(15)
C(6)N(1)C(10)	117.32(15)	C(3)C(4)C(5)	119.65(14)
C(6)N(1)Zn()	122.81(11)	$C(3)^{\#1}C(5)C(4)$	121.05(15)
C(10)N(1)Zn(1)	119.87(12)	N(1)C(6)C(7)	122.77(17)
C(1)O(1)Zn(1)	115.60(12)	C(8)C(7)C(6)	119.62(18)
C(3)O(3)C(2)	117.71(12)	C(7)C(8)C(9)	117.92(18)
Zn(1)O(4)H(4A)	124	C(10)C(9)C(8)	119.49(18)
O(2)C(l)O(l)	125.97(16)	N(1)C(10)C(9)	122.85(18)
O(2)C(1)C(2)	120.07(15)		

Table 2. Bond lengths and bond angles of complex I

Note: ${}^{\#1}-x+2, -y+1, -z+1$.

IR analysis shows that peaks appearing at 1601 and 1502 cm^{-1} are attributed to the asymmetric vibrations of carboxylated groups. The bands of 1445 and 1413 cm⁻¹ should be assigned to the symmetric vibrations of carboxylated groups. The broad band at 3257 cm⁻¹ belongs to the typical band of hydroxyl group, confirming the presence of water molecule in

the compounds. A further confirmation of this was obtained from the single crystal X-ray structure of the complex.

The thermogravimetric analyses (TGA) of the complex was conducted under N_2 atmosphere in the temperature range of 25–800°C at a rate of 10°C/min



Fig. 3. The two-dimensional layer linked by intermolecular hydrogen bonds.



Fig. 4. The thermogravimetric curves of complex I.

RUSSIAN JOURNAL OF COORDINATION CHEMISTRY Vol. 39 No. 2 2013



Fig. 5. XRPD pattern of complex I.

(Fig. 4). For the complex, it loses coordinated water molecules in the range of $101-130^{\circ}$ C (obsd. 4.17%, calcd. 3.87%). Two pyridine molecules have lost within the scope of 140–380°C (obsd. 34.12%, calcd. 33.98%). The BODA thermal decomposite in the range of 390–450°C (obsd. 42.61%, calcd. 44.73%). The final solid residue formed at about 460°C is thus suggested to be ZnO (obsd. 19.10%, calcd. 17.42%).

In order to confirm the phase purity of the bulk materials, X-ray powder diffraction (XRPD) experiment has been carried out for complex I. The XRPD of I determined by experiment is in a good agreement with the simulated one of single crystal, which shows that the bulk synthesized material has the same components and structure as those of single crystals (Fig. 5).

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