

## Synthesis, Crystal Structure and Characterization of Zn(II) Complex Constructed from 2,2'-Bisbenzimidazole

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A new complex associated with Zn ion,  $[\text{Zn}(\text{OH}-\text{H}_2\text{Bdc})(\text{Bibim})]_n$  (**1**), (OH-H<sub>2</sub>Bdc = 5-hydroxyisophthalic acid, Bibim = 2,2'-bisbenzimidazole) has been synthesized under hydrothermal conditions and characterized by elemental analysis, FT-IR spectroscopy, TG/DTG and fluorescence spectra. X-ray crystallographic studies reveal that complex  $[\text{Zn}(\text{OH}-\text{H}_2\text{Bdc})(\text{Bibim})]_n$  (**1**) crystallizes in a monoclinic space group P2<sub>1</sub>/n, each Zn atom is five-coordinated and adopts a distorted square-pyramidal coordination environment. There exists a 2-D supramolecular network linked by hydrogen bonds and face-to-face  $\pi-\pi$  interactions between adjacent benzene rings (3.768 Å) and imidazole rings (3.742 Å). A three-dimensional supramolecular network is further constructed through  $\pi-\pi$  stacking and hydrogen-bonding interactions between the helices. The TG/DTG shows that it collapsed with total loss of 84.8 (calc. 86.3 %). Blue fluorescent emission of the complex was determined at 506 nm in the solid state.

**Keywords:** Zinc(II) complex, 2,2'-Bisbenzimidazole, Crystal structure, Fluorescent property.

### INTRODUCTION

The design and synthesis of novel coordination polymers have received remarkable attention not only due to their intriguing variety of structures and topologies, but also to their potential applications in many fields such as ion exchange, catalysis and for the development of optical, electronic and magnetic devices<sup>1-4</sup>. However, it is still a challenge to construct coordination polymer, which may be affected by many factors, such as metal ions, organic ligands, metal-to-ligand ratios, reaction temperature, solvents, and counter ions<sup>5-7</sup>. Among these factors, metal ions and organic ligands play crucial roles in synthesizing new coordination polymer. So various multicarboxylate ligands have been used to produce coordination polymer, due to their versatile bridge modes and excellent coordination capacities. As a rigid and versatile bridging ligand, 5-hydroxyisophthalic acid has been extensively studied for designing new coordination polymer because its two carboxylic groups can bond with metal centers and the hydroxyl group, an electron-withdrawing group coexisting in isophthalic acid, can not only act as a hydrogen bond acceptor, can but also take on some spatial effects<sup>8,9</sup>. On the other hand, benzimidazole derivatives contain multiple nitrogen-donor sites with the possibility of reversible protonation and deprotonation properties and can be coordinated to a transition metal in

various forms, which has been utilized in coordination polymer for the preparation of different networks<sup>10-12</sup>. Herein, we report the synthesis, X-ray crystal structure, thermal and optical spectral properties of a novel zinc(II) complex  $[\text{Zn}(\text{OH}-\text{H}_2\text{Bdc})(\text{Bibim})]_n$  (**1**).

### EXPERIMENTAL

All solutions and chemicals were commercial reagents and used without further purification. Elemental analysis was carried out on a PE 1700 CHN auto elemental analyzer. The solid infrared spectra (IR) were obtained from a Bruker IFS66V vacuumtype FT-IR spectrophotometer using KBr pellets. Thermogravimetry (TG) analysis was measured on a Perkin Elmer TG/DTA 6300 thermal analyzer under flowing N<sub>2</sub> at a heating rate of 10 °C min<sup>-1</sup>. Fluorescence measurements were performed on a Model RF-5 spectrofluorimeter. The crystal structure was determined using a Bruker APEX area-detector diffractometer and SHELXL crystallographic software.

**Synthesis of  $[\text{Zn}(\text{OH}-\text{H}_2\text{Bdc})(\text{Bibim})]_n$  (**1**):** For the hydrothermal reaction of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.5 mmol), bisbenzimidazole (0.25 mmol), 5-hydroxyisophthalic acid (0.25 mmol), and water (15 mL), the mixture was stirred for 10 min in air, then transferred and sealed into a 23 mL Teflon reactor, which was heated at 100 °C for two days and then cooled to room temperature. Colorless crystals were obtained (yield 48 %

based on Zn), filtered off, washed with distilled water and dried in air. Elemental analysis (%): Anal. Calcd. C, 55.08; H, 2.94; N, 11.68; found C, 54.96; H, 3.11; N, 11.87. IR (KBr,  $\nu_{\max}$ ,  $\text{cm}^{-1}$ ): 3379, 1607, 1588, 1539, 1395, 1349, 1259, 1149, 1116, 1001, 976, 921, 776, 744.

**X-ray crystallography:** The diffraction data were collected on a Bruker Smart Apex CZN diffractometer with graphite-monochromated  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 296 K. Absorption correction was applied by SADABS<sup>13</sup>. The structure was solved by Direct Methods and refined with full-matrix least-squares technique using SHELXTL<sup>14</sup>. All non-hydrogen atoms were refined with anisotropic displacement parameters. Complete crystallographic data (CCDC 827564) has been deposited at The Cambridge Crystallographic Data Centre and may be obtained free of charge *via* www.ccdc.cam.ac.uk/data-request/cif. The crystal data, details on the data collection and refinement are summarized in Table-1, and selected bond lengths and angles are presented in Table-2. The hydrogen bond lengths (nm) and bond angles (deg) are listed in Table-3. Figs. 1-3 illustrate the structure of **1**.

TABLE-1  
CRYSTAL DATA AND STRUCTURE  
REFINEMENT FOR COMPLEX **1**

Empirical formula	$\text{C}_{22}\text{H}_{14}\text{N}_4\text{O}_2\text{Zn}$
Formula weight	479.77
Temp. (K)	296(2)
Crystal system	Monoclinic
Space group	$\text{P2}_1/\text{n}$
a ( $\text{\AA}$ )	7.4211(14)
b ( $\text{\AA}$ )	12.278(2)
c ( $\text{\AA}$ )	21.550(4)
$\alpha$ ( $^\circ$ )	90
$\beta$ ( $^\circ$ )	95.515(3)
$\gamma$ ( $^\circ$ )	90
V ( $\text{\AA}^3$ )	1954.5(6)
Cryst size (mm)	$0.18 \times 0.20 \times 0.22$
Z	4
$D_c$ ( $\text{g cm}^{-3}$ )	1.630
$\mu$ (cm)	13.0
F(000)	976
Limiting indices	$-7 \leq h \leq 8; -13 \leq k \leq 14; -23 \leq l \leq 25$
Reflections	10253
Independent	3436
Observed data	2614
Npar	290
$R_{\text{int}}$	0.070
GOF	1.03
$R_1^a$ ( $I > 2\sigma(I)$ )	0.0392
$wR_2^a$ (all data)	0.1139
Max/min electron density ( $\text{e \AA}^{-3}$ )	0.58/-0.46
Theta range ( $^\circ$ )	1.9, 25.0

<sup>a</sup> $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ , <sup>b</sup> $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$

## RESULTS AND DISCUSSION

Single-crystal X-ray crystallographic studies reveal that complex **1** crystallizes in a monoclinic space group  $\text{P2}_1/\text{n}$ , which is made up of one Zn(II), one Bibim and one Bdc (Bdc = 5-hydroxyisophthalate) molecule. Each Zn atom is five-coordinated and adopts a distorted square-pyramidal coordination

TABLE-2  
SELECTED BOND LENGTHS ( $\text{\AA}$ ) AND  
BOND ANGLES ( $^\circ$ ) FOR COMPLEX **1**

Zn1-O1	2.264(3)	Zn1-N1	2.146(3)
Zn1-O2	2.068(2)	Zn1-N3	2.046(3)
Zn1-O3	1.984(3)	-	-
O1-Zn1-O2	60.59(9)	O2-Zn1-C15	30.76(11)
O1-Zn1-O3	89.64(9)	O3-Zn1-N1	96.33(10)
O1-Zn1-N1	171.05(10)	O3-Zn1-N3	144.45(12)
O1-Zn1-N3	98.36(9)	O3-Zn1-C15	93.38(10)
O1-Zn1-C15	30.09(10)	N1-Zn1-N3	80.62(10)
O2-Zn1-O3	101.40(11)	N1-Zn1-C15	142.23(12)
O2-Zn1-N1	111.48(11)	N3-Zn1-C15	110.73(10)
O2-Zn1-N3	112.74(11)	-	-

environment (Fig. 1). Two N atoms are from one Bibim ligand and three O atoms from two Bdc ligands. The Zn-O distances are in the range of 1.984(3)-2.264(3)  $\text{\AA}$ , and the Zn-N distances are in the range of 2.046(3)-2.146(3)  $\text{\AA}$ , respectively. In the structure, the Bdc ligand adopts  $\mu_3$ -bridging coordination fashion: one carboxylate group adopts chelating/bridging mono-bidentate coordination mode to chelate the Zn(II) centers, and another carboxylate group acts as a mono-dentate ligand, while Bibim ligand acts as a chelating ligand. Each pair of adjacent Zn atoms is bridged by Bdc ligands to form a helical chain running along a direction with a long pitch of 7.36  $\text{\AA}$ . These chains are decorated with Bibim ligands, positioning alternately on two sides and pointing outwards, as depicted in Fig. 2. The adjacent helices are alternately packed through hydrogen bonds involving Bdc and Bibim ligands (Table-3) and face-to-face  $\pi$ - $\pi$  interactions between adjacent benzene rings (3.768  $\text{\AA}$ ) and imidazole rings (3.742  $\text{\AA}$ ) to sustain the 2D-assembly extended in the ab plane, as illustrated in Fig. 3. A three-dimensional supramolecular network is further constructed through  $\pi$ - $\pi$  stacking and hydrogen-bonding interactions between the helices.

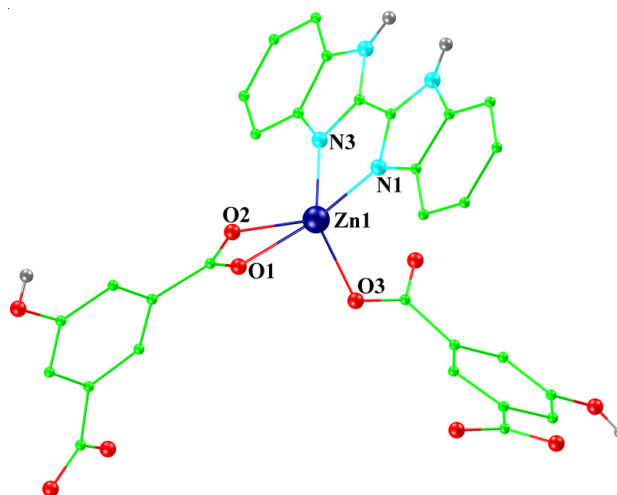


Fig. 1. Coordination environment of Zn(II) ion in **1**

Thermogravimetric analysis was carried out to examine the thermal stability of complex **1** (Fig. 4). The crushed single-crystal sample was heated up to 1000  $^\circ\text{C}$  in  $\text{N}_2$  at a heating rate of 10  $^\circ\text{C min}^{-1}$ . The TG and DTG curves for **1** show that it collapsed with total loss of 84.8 % (calc. 86.3 %), consistent with the pyrolysis of mixed-ligands. The pyrolysis of mixed-

TABLE-3  
 DISTANCES (Å) AND ANGLES (°) OF HYDROGEN BONDS FOR COMPLEX 1

D-H...A	d(D-H)	d(H...A)	d(D...A)	∠(D-H...A)	
N2-H2...O2	0.8607	2.2765	2.851(4)	124.26	-x, 2-y, 1-z
N2-H2...O4	0.8607	2.5409	3.251(4)	140.46	1/2 + x, 3/2-y, -1/2 + z
N4-H4...O4	0.8595	1.9153	2.709(4)	152.91	1/2 + x, 3/2-y, -1/2 + z
O5-H5...O1	0.8209	1.9798	2.707(4)	147.30	-1 + x, y, z
C7-H7...O5	0.9308	2.4592	3.358(5)	162.21	1/2-x, 1/2 + y, 3/2-z
C22-H22...O5	0.9297	2.4343	3.326(4)	160.72	1 + x, y, z

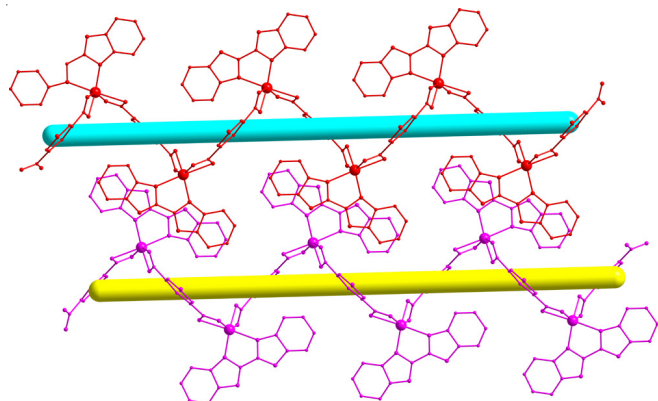
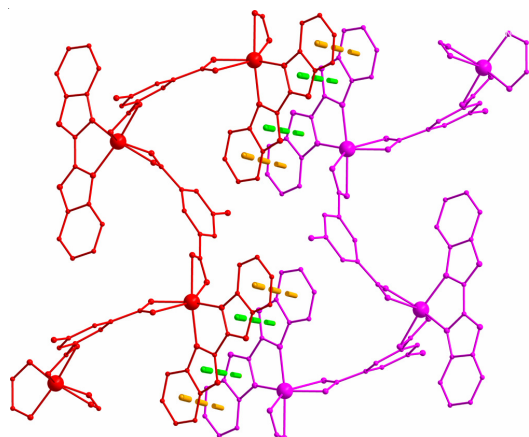


Fig. 2. 1D helical chain of 1

Fig. 3.  $\pi$ - $\pi$  interactions from two nearest 1D chains of 1

ligands occurred in the temperature range 100-800 °C. The above different thermal behaviours may attribute to their structural features, the presence of a number of coordination bond of carboxylate ligands and the chelating effect of five-membered rings, which change the bite angles for chelating, resulting in the formation of a rich variety of polymeric structures.

The emission spectrum of complex 1 in the solid state is investigated at room temperature. Excitation at 365 nm leads to strong blue-fluorescent emission band at 506 nm for 1. The emission is neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal transfer (LMCT) in nature since the Zn(II) ions are difficult to oxidize or to reduce due to their  $d^{10}$  configuration. For the free  $H_2Bdc$  ligand, the emission band at 387 nm ( $\lambda_{ex} = 351$  nm) can be assigned to  $\pi$ - $\pi^*$  transition. In addition, for the free Bibim, the main emission band at 498-nm ( $\lambda_{ex} = 490$  nm), is assigned to the intraligand  $\pi$ - $\pi^*$  transition. Therefore, we assign the emission described above for 1 to LLCT (ligand-ligand charge transfer) excited states.

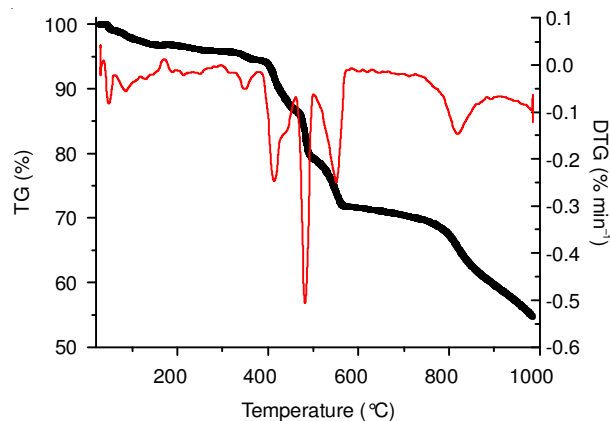


Fig. 4 TG-DTG curve of Zn(II) complex

In summary, a zinc(II) coordination polymer based on  $OH-H_2Bdc$  and Bibim was hydrothermally synthesized and exhibits intense blue photoluminescent emission. The TG/DTG shows that it collapsed with total loss of 84.8 %. The complex is promising as a blue-light emitting material for its high thermal stability and the insolubility in common solvents.

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