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**CRYSTAL STRUCTURE AND FLUORESCENCE OF A 1D ZINC(II) COORDINATION POLYMER BASED ON A SEMI-RIGID bis(BENZIMIDAZOLE) LIGAND****W.-L. Hou<sup>1</sup>, G.-Y. Dong<sup>2</sup>, X.-X. Wang<sup>2</sup>, K. Van Hecke<sup>3</sup>**<sup>1</sup>*Analysis and Test Center, Hebei Normal University of Science and Technology, Qinhuangdao, Hebei, P. R. China*

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A new Zn(II) coordination polymer,  $\{[\text{Zn}(\text{npht})(\text{L})_{0.5}(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}\}_n$  (**L** = 1,4-bis(2-methylbenzimidazol-1-ylmethyl)benzene,  $\text{H}_2\text{npht}$  = 3-nitrophthalic acid) has been hydrothermally synthesized and characterized by elemental analysis, IR, XRPD, and single-crystal X-ray diffraction. The Zinc(II) coordination compound exhibits a 1D linear chain, which is further assembled into a 2D supramolecular layer via two modes of classical hydrogen bonding interactions. The fluorescence properties and thermal stability of the complex have been investigated in the solid state.

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**Key words:** bis(benzimidazole) ligand, crystal structure, fluorescence, zinc(II) complex.**INTRODUCTION**

In recent years, the design and synthesis of metal-organic coordination polymers (MOCPs) have been the subject of extensive research, not only due to the variety of their structures and interesting properties, but also their potential applications in luminescence, gas adsorption, molecular sieves, ion exchange, corrosion inhibition and antitumor agents [1–4]. However, the controllable synthesis of these complexes with desired architectures and properties is still a great challenge, which is because a lot of factors show significant effect on this framework, such as the nature of organic ligands, pH, central metal ion, temperature, solvents etc. [5–8]. Moreover, the selection of appropriate organic ligands is the key point in manipulating the structures of the coordination polymers [9]. Therefore, significant interest has arisen in the structural tuning of MOCPs via rational selection of the bridging ligands. The organic aromatic carboxylate ligands as O-donor bridging ligands have been widely used to construct novel metal-organic coordination polymers owing to their versatile coordination modes and remarkable stability such as 3-nitrophthalic acid ( $\text{H}_2\text{npht}$ ), where the nitro group as an electron-withdrawing component shows the steric hindrance, which may restrict extension of the whole networks and result in the formation of supramolecular structures [10–12]. Flexible bis(benzimidazole) derivatives have attracted great attention for crystal engineering and supramolecular chemistry in our and other groups, due to their remarkable coordination ability and flexible conformations [13–15]. However, the complexes based on the combination of flexible bis(2-methylbenzimidazole)-based ligands with 3-nitrophthalic acid are relatively scarce [16]. Herein we selected a semi-rigid bis(benzimidazole) ligand and  $\text{H}_2\text{npht}$  co-ligands to construct one new MOCP, namely  $\{[\text{Zn}(\text{npht})(\text{L})_{0.5}(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}\}_n$  (**L** = 1,4-bis(2-methylbenzimidazol-1-ylmethyl)benzene). Thermogravimetric analyses and solid state luminescence properties of the complexes are reported.

## EXPERIMENTAL SECTION

**Materials and physical measurements.** All reagents and solvents were obtained from commercial sources and used without further purification. The ligand **L** was prepared by the published method [17]. Elemental analyses were obtained on a Perkin-Elmer 240C elemental analyzer. FT-IR spectra were recorded from KBr pellets in the range of 4000–400  $\text{cm}^{-1}$  on an Avatar 360 (Nicolet) spectrophotometer. Thermogravimetric analysis (TGA) was carried out on a NETZSCH TG 209 thermal analyzer from room temperature to 800 °C with a heating rate of 10°/min under  $\text{N}_2$  atmosphere. The luminescence spectra for the powdered solid samples were measured at room temperature on a Hitachi F-7000 fluorescence spectrophotometer. The X-ray powder diffraction (XRPD) data collection was executed on a D/MAX 2500PC X-ray diffractometer using  $\text{CuK}\alpha$  radiation ( $\lambda = 0.1542 \text{ nm}$ ) in the  $2\theta$  range of 5–50° with a step size of 0.02° and a scanning rate of 10°/min.

**X-ray crystallography.** X-ray diffraction data for the colorless single crystal with dimensions of 0.22×0.19×0.18 mm was obtained at room temperature on an Agilent SuperNova Dual Source diffractometer with graphite-monochromated  $\text{MoK}\alpha$  radiation ( $\lambda = 0.7107 \text{ \AA}$ ) and  $\omega$ - $2\theta$  scan mode at 293(2) K. Semi-empirical absorption corrections were applied using the SADABS program [18]. The structure was solved by direct methods, and all non-hydrogen atoms were refined anisotropically with the SHELXTL package using a full-matrix least-squares procedure based on  $F^2$  values [19]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms bonded to carbon atoms were placed in their geometrically calculated positions. The crystal parameters, data collection, and refinement results are summarized in Table 1. The selected bond lengths and bond angles are listed in Table 2. The complex showed disorder of O6 atom from carboxyl group of the nphl ligand, and this positions were refined with a split model with site occupation factor 0.48. The atomic coordinates and other parameters of structure have been deposited with the CCDC 998605; deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>.

Table 1

## Crystal data and structure refinements for the complex

Empirical formula	$\text{C}_{32}\text{H}_{29}\text{ZnN}_5\text{O}_8$
$M$ , g/mol	676.97
$T$ , K	293(2)
Wavelength, $\text{Å}$	0.7107
Crystal system	Triclinic
Unit cell dimensions $a$ , $b$ , $c$ , $\text{Å}$	10.9199(4), 12.3499(7), 12.7067(7)
$\alpha$ , $\beta$ , $\gamma$ , deg.	66.491(5), 77.835(4), 70.484(4)
Space group	$P-1$
Volume, $\text{Å}^3$	1475.15(13)
$Z$	2
Calculated density, $\text{g/cm}^3$	1.524
Absorption coefficient, $\text{mm}^{-1}$	0.895
$F(000)$	700
Crystal size, mm	0.22×0.19×0.18
$\theta_{\text{min}}$ — $\theta_{\text{max}}$ , deg.	2.99—25.02
Limiting indices	$-12 \leq h \leq 12$ , $-14 \leq k \leq 14$ , $-15 \leq l \leq 15$
Reflections collected / unique [ $R_{\text{int}}$ ]	27400 / 5176 [0.0895]
Data / restraints / parameters	5176 / 3 / 427
Goodness-of-fit on $F^2$	1.007
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0468$ , $wR_2 = 0.0994$
$R$ indices (all data)	$R_1 = 0.0718$ , $wR_2 = 0.1170$
Residual peak and hole, $\text{e/Å}^3$	0.422 and $-0.595$

Table 2

Selected bond lengths (Å) and angles (deg.) for the complex

Zn(1)—O(3)	1.966(2)	O(5)A—Zn(1)—O(1W)	106.19(11)	O(3)—Zn(1)—N(1)	117.13(11)
Zn(1)—O(5)A	1.952(2)	O(3)—Zn(1)—O(1W)	104.78(10)	C(1)—N(1)—Zn(1)	129.3(2)
Zn(1)—O(1W)	1.978(2)	O(5)A—Zn(1)—N(1)	112.38(10)	C(2)—N(1)—Zn(1)	125.1(2)
Zn(1)—N(1)	1.994(3)	O(1W)—Zn(1)—N(1)	104.25(11)	C(32)—O(3)—Zn(1)	110.9(2)
		O(5)A—Zn(1)—O(3)	110.97(10)	C(31)—O(5)—Zn(1)A	121.9(2)

Symmetry code for A:  $2-x, 2-y, -z$ .

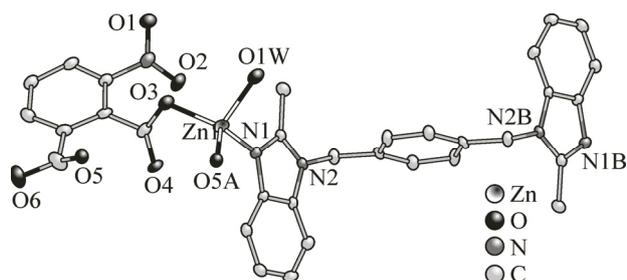
**Synthesis of  $\{[\text{Zn}(\text{npht})(\text{L})_{0.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ .** A mixture of  $\text{Zn}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$  (0.2 mmol, 59.4 mg), **L** ligand (0.1 mmol, 36.6 mg),  $\text{H}_2\text{npht}$  (0.2 mmol, 42.2 mg) and NaOH (0.2 mmol, 0.8 mg) in 15 mL  $\text{H}_2\text{O}$  was stirred for 25 min in air. The mixture was sealed in a 25 mL Teflon-lined stainless steel vessel and heated at 140 °C for three days under autogenous pressure. Colorless block crystals of the complex suitable for X-ray diffraction were isolated by manual separation from an amorphous solid in 55 % yield based on  $\text{Zn}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ . Anal. Calcd. for  $\text{C}_{32}\text{H}_{29}\text{N}_5\text{O}_8\text{Zn}$  (%): C 56.77, H 4.32, N 10.34. Found (%): C 56.32, H 4.65, N 10.03. IR (KBr,  $\text{cm}^{-1}$ ): 3438w, 1622s, 1527m, 1453m, 1363s, 750s, 711w, 492w.

## RESULTS AND DISCUSSION

**Description of crystal structure.**  $\{[\text{Zn}(\text{npht})(\text{L})_{0.5}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ . Single crystal X-ray diffraction analysis reveals that the complex crystallizes in a triclinic space group  $P-1$ . The asymmetric unit contains one Zn(II) ion, one  $\text{npht}^{2-}$  anion, half a **L** ligand, one coordinated and one lattice water molecule. As shown in Fig. 1, each Zn atom is four-coordinated by N1 atom from **L** ligand, O3 atom from carboxyl group of one  $\text{npht}^{2-}$  ligand, O5A atom (Symmetry code:  $A = 2-x, 2-y, -z$ ) from a carboxylate group of other distinct  $\text{npht}^{2-}$  ligands and O1W from water molecule to give a tetrahedral geometry. The Zn—N bond distance is 1.994(3) Å, the Zn—O bond distances are in the range of 1.952(2)—1.978(2) Å. The bond angles at the Zn center range from 104.25(11)° to 117.13(11)°, which are comparable to the values observed for similar zinc(II) complexes [16,20].

In the structure of the complex, two  $\text{npht}^{2-}$  ligands show a coordination fashion with bimonodentate coordination mode connecting two neighboring Zn atoms to form  $[\text{Zn}_2(\text{npht})_2]$  units. The **L** ligand adopts *trans*-conformation, with the dihedral angle between the mean planes of the two benzimidazole rings being 0°, linking the  $[\text{Zn}_2(\text{npht})_2]$  units and developing a 1D linear chain (Fig. 2) with a distance between adjacent Zn atoms of 14.055(10) Å. The 1D chain is further extended into a 2D supramolecular architecture by two kinds of classical hydrogen bonding modes in which water molecules serve as hydrogen bonding donors. The selected hydrogen bond lengths and bond angles for the complex are given in Table 3, the distance of  $\text{N}\cdots\text{O}$  is 2.677(4) Å and the length of  $\text{O}\cdots\text{O}$  is 2.866(4) Å. As shown in Fig. 3, the dashed lines indicate  $\text{O}-\text{H}\cdots\text{N}$  and  $\text{O}-\text{H}\cdots\text{O}$  bonds, respectively. In addition, the 2D framework is further strengthened by  $\pi-\pi$  stacking interactions between the benzimidazole rings from distinct **L** ligands with the center-to-center separations of 3.504(6) Å

Fig. 1. The coordination environment around the Zn atom in the complex. (Symmetry codes: A:  $2-x, 2-y, -z$ ; B:  $1-x, 1-y, -z$ )



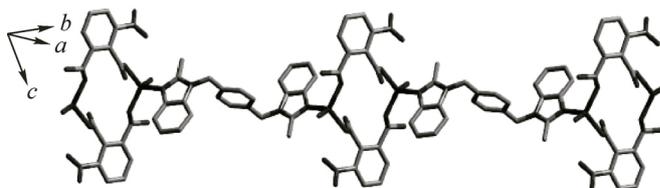


Fig. 2. The 1D linear chain of the complex

T a b l e 3

Hydrogen bond lengths (Å) and bond angles (deg.)				
D—H···A	d(D—H)	d(H···A)	d(D···A)	∠DHA
O1W—H1WA···N3C	0.850	1.85	2.677(4)	165
O2W—H2WA···O3D	0.850	2.04	2.866(4)	163

Symmetry codes for C: 1-x, 1-y, -1-z; D: 1-x, 2-y, 1-z.

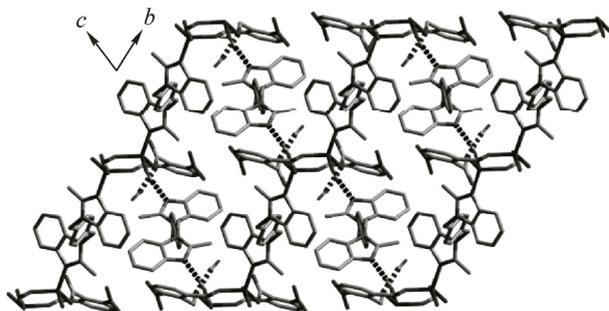


Fig. 3. The 2D supramolecular structure constructed by O—H···N and O—H···O hydrogen bonding interactions of the complex

Found: 85.11 %). The residue weight can be assigned to ZnO (Calcd: 12.02 %; Found: 12.15 %).

**Fluorescence properties.** It is well-known that metal-organic coordination polymers of  $d^{10}$  metal centers are potential candidates for photochemistry [23]. The solid-state photoluminescence spectrum of the compound was measured at room temperature. The complex exhibits a fluorescent emission band with maximum at 426 nm upon excitation at 210 nm, while the main emission peak of the free **L** ligand is 309 nm ( $\lambda_{\text{ex}} = 293$  nm) [16], which can be assigned to  $\pi-\pi^*$  transitions [24]. When comparing the title complex with the free **L** ligand, the emission band of the complex is red-shifted by 117 nm, and is tentatively ascribed as to the ligand-to-metal charge-transfer band [25].

and the slipping angles of  $\beta$  ( $\gamma$ ) of  $16.57^\circ$  (Cg1: N3—C12—N4—C19—C13, symmetry code: E = 1-x, -y, 1-z).

**IR spectrum.** In the IR spectra, a broad band centered at  $3438\text{ cm}^{-1}$  can be attributed to the stretching vibrations of lattice water molecules, coordination water molecules or strong hydrogen bonds [21]. The presence of the expected characteristic bands at  $1527\text{ cm}^{-1}$  is due to the  $\nu_{\text{C=N}}$  stretching of the benzimidazole ring. There is no characteristic band at around  $1700\text{ cm}^{-1}$ , demonstrating that all carboxyl groups in the complex are completely deprotonated. The bands at  $1622\text{ cm}^{-1}$  and  $1363\text{ cm}^{-1}$  can be assigned to asymmetric and symmetric vibrations of the carboxyl groups. The  $\Delta\nu[\nu_{\text{as}}(\text{COO}) - \nu_{\text{s}}(\text{COO})]$  is  $259\text{ cm}^{-1}$ , indicating monodentate bridging coordination of the carboxylate group to the metal center [22].

**Thermal analysis.** Thermogravimetric analyses (TGA) were performed to explore the thermal stability of the title compound. The TG curve of the complex contains two steps. In the first step the weight losses range from  $140^\circ\text{C}$  to  $153^\circ\text{C}$  can be assigned to the water molecule (Calcd: 2.66 %; Found: 2.74 %). The second step occurs at  $283^\circ\text{C}$  and remains stable up to  $550^\circ\text{C}$ , which is attributed to the removal of **L** and  $\text{npht}^{2-}$  ligands (Calcd: 85.32 %;

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