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A Novel Zn(II) Complex Based on 1H-1,2,3-Benzotriazol-1-Ylacetic Acid and 1H-1,2,3-Benzotriazole Ligands: Synthesis, Crystal Structure, and Photoluminescent Property[1]

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Abstract—A novel complex formulated as $[Zn(HBTA)_2(L)_2] \cdot 2H_2O$ (I), where HL = 1H-1,2,3-benzotriazol-l-ylacetic acid, HBTA = 1H-1,2,3-benzotriazole, has been synthesized and structurally characterized by single crystal X-ray diffraction. Complex I shows a mononuclear structure, which is assembled into 1D chain via intermolecular π···π interactions and N–H···O hydrogen bonds. Different chains are linked by C–H···O hydrogen bonds into 2D layer. The photoluminescence property of the complex has been investigated.

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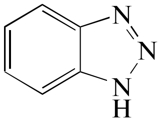
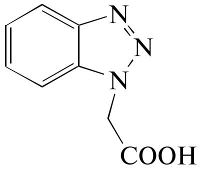
INTRODUCTION

The benzotriazole (HBTA) is well known for its multifunctional linking groups in the coordination chemistry. The HBTA has been found to act as a monodentate [1], bridging bidentate [2] and bridging tridentate [3] ligand. Many multinuclear complexes based on HBTA ligand had been reported [4]. 1H-1,2,3-Benzotriazol-1-ylacetic acid (HL) is a derivative of HBTA, in which the carboxylate group was introduced into the structure of HBTA. HL is rich in coordination model and has ever been used to construct metal-organic frameworks (MOFs). Wang et al. have made an investigation on the Zn(II), Ag(I), Cd(II), Ni(II) and Mn(II) complexes based on HL [5–8].

The structures of HBTA and HL ligands are given below:



(HBTA)



(HL)

The conjugated π system in HBTA leads to its potential application in the construction of luminescent materials [9]. The Zn(II) or Cd(II) complexes also attracted interest for their appealing structures and photoluminescent properties [10]. In the present work, a novel Zn(II) complex based on HBTA and HL ligands has been successfully synthesized and structurally characterized by single crystal X-ray diffraction. The photoluminescence property of the complex has been investigated.

EXPERIMENTAL

The ligand HL was synthesized according to the literature [5]. All materials of reagent grade were commercially purchased and used without further purification. C, H and N elemental analyses were performed on a Perkin-Elmer 240c Elemental Analyzer. Solid-state photoluminescent spectrum of the title complex was measured at room temperature with an Edinburgh FLS920 fluorescence spectrometer. Infrared spectrum was recorded as KBr pellet on a Nicolet 170SXFT-IR spectrometer. TGA was performed on a NETZSCH STA 449C thermogravimetric analyzer in flowing N_2 with a heating rate of 10°C min^{-1}.

Synthesis of $[Zn(HBTA)_2(L)_2] \cdot 2H_2O$ (I). The solution A: 0.1 mmol $Zn(NO_3)_2 \cdot 6H_2O$ (0.030 g) was dissolved in 2 mL H_2O–CH_3OH mixed solution (1 : 1 v/v), then added 3 mL aqueous solution of 0.1 mmol HBTA (0.012 g). During this process, a little white sediment was formed. The solution B: 0.1 mmol HL (0.020 g) and 0.1 mmol NaOH (0.004 g) were dissolved in 6 mL mixed solution of H_2O–CH_3OH (1 : 2 v/v). Then, the solution A was layered on the solution B, colorless block single crystals appear in a few days. The crystals were collected by filtration, washed by distilled water and dried in air at room temperature. One of the crystals was used for X-ray crystallographic analysis. The yield was 0.029 g (42% based on Zn).

IR (KBr; ν cm^{-1}): 3365 s, 3092 w, 2991 w, 2962 w, 2710 w, 1934 w, 1622 s, 1497 w, 1455 w, 1426 w, 1410 w,

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[1] The article is published in the original.

Table 1. Crystal data and structure refinements for complex **I**

Parameter	Value
Empirical formula	$C_{28}H_{22}N_{12}O_6Zn$
M	687.97
Crystal system	Monoclinic
Space group	$C2/c$
a, Å	18.3271(3)
b, Å	9.1444(2)
c, Å	19.0464(4)
α, deg	90.00
β, deg	106.526(2)
γ, deg	90.00
V/Å^3	3060.13(11)
Z	4
ρ_{calcd}, g cm^{-3}	1.493
Crystal size, mm	0.30 × 0.24 × 0.20
μ, mm^{-1}	0.866
F(000)	1408
Scan mode	φ and ω scans
θ Range for date collection	2.32–25.00
Limited indices h, k, l	$-21 \le h \le 21$, $-10 \le k \le 9$, $-22 \le l \le 22$
Reflections collected/unique	6950/2640
(R_{int})	(0.0242)
Reflections with $I > 2\sigma(I)$	2132
GOOF	1.017
Parameters	217
R_1, wR_2 ($I > 2\sigma(I)$)	0.0315, 0.0881
R_1, wR_2 (all date)	0.0402, 0.0898
Largest diff. peak and hole, e Å^{-3}	0.506 and –0.363

1391 m, 1330 w, 1311 w, 1297 w, 1271 w, 1230 m, 1163 w, 1143 w, 1113 w, 1030 m, 998 w, 971 w, 907 m, 932 w, 800 w, 780 w, 767 w, 752 m, 721 w, 670 w, 637 w, 587 w, 542 w. The broad band at 3365 cm^{-1} is assigned to the O–H stretching of water. The peaks of carboxylate groups at 1622–1391 cm^{-1} are assigned to the ν_{as}(COO) and ν_s(COO) stretching vibrations, respectively.

For $C_{28}H_{22}N_{12}O_6Zn$

anal. calcd., %:	C, 48.9;	H, 3.2;	N, 24.4.
Found, %:	C, 48.8;	H, 2.9;	N, 24.6.

X-ray crystallography. Single-crystal X-ray data for complex **I** was collected on an Oxford Xcalibur Eos diffractometer using graphite monochromated MoK_α (λ = 0.71073 Å) radiation at room temperature. Empirical absorption correction was applied. The structures were solved by direct methods and refined by the full-matrix least-squares methods on F^2 using the SHELXTL-97 software [11]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in the calculated positions. The crystal data and structure refinement for complex **I** is summarized in Table 1. Selected bond lengths and angles for the title complex are listed in Table 2. Supplementary material for complex **I** has been deposited with the Cambridge Crystallographic Data Centre (no. 800781; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULT AND DISCUSSION

As shown in Fig. 1, the asymmetric unit of complex **I** contains one unique Zn(II) atom, one HBTA ligand, one deprotonated ligand (L) and one water ligand. Zn(II) atom adopts a distorted tetrahe-

Table 2. Selected bond lengths (Å) and angles (deg) for complex **I***

Bond	d, Å	Bond	d, Å
Zn(1)–O(2)$^{\#1}$	1.949(2)	Zn(1)–N(1)	2.016(2)
O(1)–C(14)	1.230(3)	O(2)–C(14)	1.263(3)
N(4)–N(5)	1.306(3)	N(5)–N(6)	1.346(3)
N(6)–C(7)	1.362(3)	N(3)–C(2)	1.354(3)
N(2)–N(1)	1.315(3)	N(l)–C(1)	1.375(3)
Angle	**ω, deg**	**Angle**	**ω,deg**
O(2)$^{\#1}$Zn(l)O(2)	134.87(1)	O(2)$^{\#1}$Zn(1)N(l)$^{\#1}$	99.66(7)
O(2)Zn(1)N(1)$^{\#1}$	104.94(7)	N(1)$^{\#1}$Zn(1)N(1)	112.64(2)
C(14)O(2)Zn(1)	114.44(2)	N(5)N(4)C(8)	108.4(1)
N(5)N(6)C(7)	110.2(2)	C(7)N(6)C(1)	130.0(2)
N(2)N(1)C(1)	109.19(2)	N(2)N(1)Zn(1)	119.39(2)
C(1)N(1)Zn(1)	131.40(2)	N(1)C(1)C(2)	106.9(2)
N(3)C(2)C(3)	133.3(2)	N(3)C(2)C(1)	104.9(2)

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

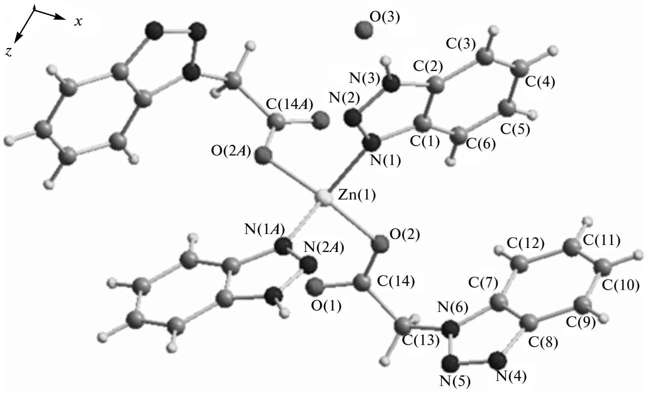

Fig. 1. The coordination environment of the Zn(II) center of complex **I**. Symmetry transformation used to generate equivalent atoms: (*A*) $-x, y, 0.5 - z$.

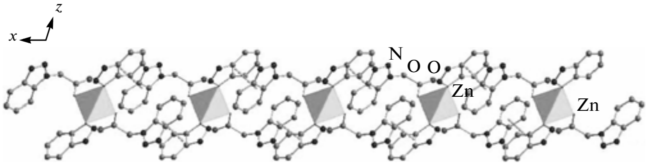

Fig. 2. 1D chain constructed by the intermolecular π···π interactions in complex **I**, π···π interactions are indicated by turquiose dotted lines, hydrogen atoms and non-coordination oxygen atoms are omitted for clarity.

dral geometry coordinated by two N atoms (N(1) and N(1*A*)) from two different HBTA ligands and two O atoms (O(2) and O(2*A*)) from two carboxylate groups of two different deprotonated L ligand. The Zn—O distance is 1.950(2) Å, and Zn—N distance is 2.019(2) Å. The HBTA ligand has been found to act as a monodentate ligand and the deprotonated L ligand exhibits a monodentate coordination mode in the structure of the title compound. As depicted in Fig. 2, strong π···π interactions and N—H···O hydrogen bonds are observed between different mononuclear Zn(II) units resulting in a 1D chain. For example, the centroid-to-centroid and perpendicular distances between the HBTA plane constructed by N(1*A*)—N(3*A*)/C(1*A*)—C(6*A*) and the plane constructed by N(4*B*)—N(6*B*)/C(7*B*)—C(12*B*) from the L ligand are 3.55 and 3.46 Å, respectively (atom with additional labels *A*, *B* refer to the symmetry operations: (*A*) $1 - x, -1 + y, 0.5 - z$; (*B*) $0.5 + x, -0.5 + y, z$). O(3)···*H*(3) 1.63, N(3)—H(3)' 1.04, O(3)···N(3) 2.66 Å, angle N(3)—H(3)'···O(3) 168.19°. Different chains are linked by C—H···O hydrogen bonds into a 2D supramolecular layer (Fig. 3). For example, O(3*C*)···H(4*D*) 4.38 Å, C(4*D*)—H(4*D*) 0.93 Å, O(3*C*)···C(4*D*) 4.29 Å, angle C(4*D*)—H(4*D*)···O(3*C*) 78.03° (atom with additional labels *C*, *D* refer to the symmetry operations: (C) $1 - x, 3 - y, 1 - z$; (*D*) $1 + x, 1 + y, 1 + z$).

The thermal stability of complex **I** was examined by TG. The experiment was carried out in a N_2 atmosphere with a heating rate of 10°C/min. As shown in Fig. 4, the first weight loss occurs between 100 and 168°C, corresponding to the loss of the lattice water molecules (obsd. 4.7%, calcd. 4.6%).

The solid-state photoluminescence of complex **I** was investigated at room temperature. The intense emission peak is observed at 389 nm ($\lambda_{ex} = 320$ nm), which may be attributed to the ligand-to-metal charge transfer (LMCT) [12]. The free HL and HBTA ligands exhibit weak flourescence emissions with maxima at 356 ($\lambda_{ex} = 325$) and 378 nm ($\lambda_{ex} = 278$ nm), respectively [8, 13]. The photoluminescent intensity of the title complex is much stronger than those of the free HL and HBTA ligands, indicating the photolumines-

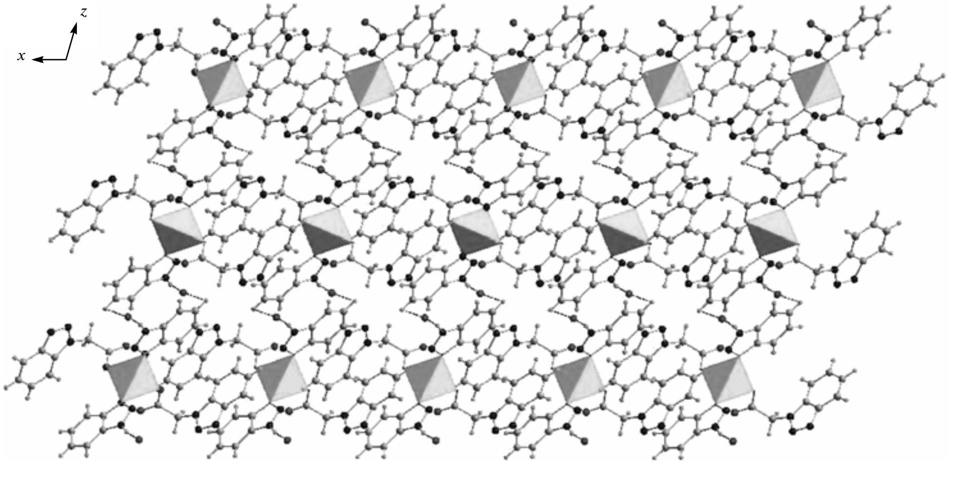

Fig. 3. 2D supramolecular layer of complex **I** with C—H···O hydrogen bonds.

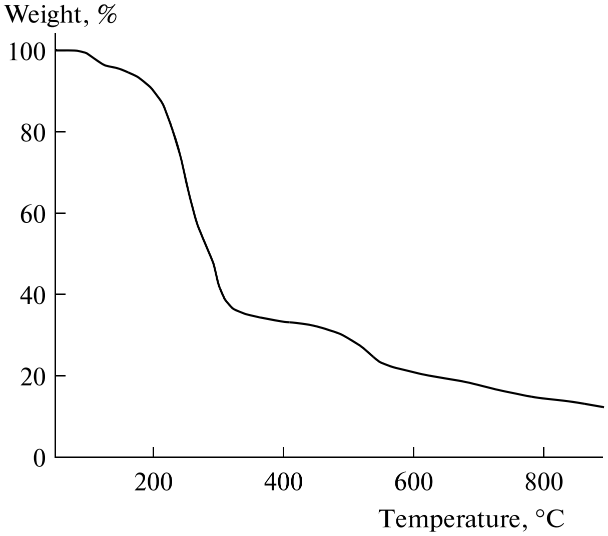

Fig. 4. The TG curve of complex **I**.

cence is enhanced by the coordination of the HL and the HBTA to Zn^{2+} ion, which effectively increases the rigidity of the coordination polymer and reduces the loss of energy by radiationless decay [13, 14].

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