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Hydrothermal Synthesis, Crystal Structural, and Thermal Properties of a 1D Zinc Coordination Polymer Based on Benzoate and Flexible Bis(benzimidazole) Ligands[1]

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Abstract—A new coordination polymer, $[Zn(PhCOO)_2(Bbbm)]_n$ (**I**), where Bbbm = 1,1'-(1,4-butanediyl)bis-1H-benzimidazole, has been synthesized under hydrothermal conditions and characterized by elemental analysis, IR, TG and X-ray single-crystal diffraction. The complex crystallizes in the monoclinic system with space group $P2_1/n$, the unit cell parameters: $a = 10.815(3)$, $b = 20.516(6)$, $c = 12.802(4)$ Å, $\beta = 102.025(3)°$, $V = 2778.2(14)$ Å^3, $Z = 4$. In this structure, the Zn^{2+} ion is in a distorted tetrahedral geometry, one-dimensional linear chain is constructed by Bbbm ligand with bis(monodentate) coordination mode.

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INTRODUCTION

During the past few decades, the rational design and synthesis of metal-organic coordination polymers has attracted significant attention. The creation of metal-organic coordination networks based on complexes of transition metals and multifunctional bridging ligands, such as polypyridyl and polyacid ligands, has proven to be a fertile field due to the intriguing network topologies and potential functions as new classes of materials [1–6]. Especially benzimidazole-containing heterocyclic moieties have found extensive use and captured the attention of chemists for years [7–14] Among of them, the 1,4-bis(N-benzimidazolyl)butane (Bbbm) is a good choice of N-donor ligands, the flexible nature of spacers allows the ligand to bend and rotate when coordinating to metal centers so as to conform to the coordination geometries of metal ions [15–18]. Hence, we select this bis-monodentate ligand Bbbm as main ligand to construct metal-organic polymer at the presence of an organic benzoate anion served as secondary ligand to react with zinc acetate and obtain a new one-dimensional metal-organic polymer enzimidazole derivatives with organic carboxylates as the secondary ligands [4]. $[Zh(PhCOO)_2(Bbbm)]_n$ (**I**). This work is part of our ongoing effort to synthesize and characterize an extensive series of transition metal complexes based on benzimidazole derivatives with organic carboxylates as the secondary ligands [4].

EXPERIMENTAL

Materials and measurements. Solvents and raw materials for synthesis were commercially available and used without further purification. Ligand Bbbm was prepared according to the literature [19]. Elemental analyses were taken on a PerkinElmer 240C analyzer. IR spectra (KBr pellet) in a range 4000–400 cm^{-1} were performed on a FT-IR 170 SX (Nicolet) spectrometer. Thermal stability (TG–DTA) studies were carried out on a NETZSCH TG 209 thermal analyzer from 10 to 800°C.

Synthesis of compound I. A mixture of $Zn(OAC)_2 \cdot 2H_2O$ (213 mg, 1 mmol), Bbbm ligand (290 mg, 1 mmol), benzoic acid (122 mg, 1 mmol), NaOH (40 mg, 1 mmol), and H_2O (10 mL) was placed in a teflon-lined stainless vessel and heated to 140°C for 5 days under autogenously pressure and then cooled to room temperature at a rate of 10°C/h. The resulting colorless block crystals of **I** were obtained by filtration, washed with distilled water, and dried at ambient temperature (the yield was ~75%).

For $C_{32}H_{28}N_4O_4Zn$ (**I**)

anal. calcd., %:	C, 64.28;	H, 4.72;	N, 9.37.
Found, %:	C, 64.59;	H, 4.61;	N, 9.23.

X-ray crystal determination. The single-crystal X-ray diffraction measurement was carried out on a Bruker Smart 1000 CCD diffractometer using graphite-monochromatized MoK_α radiation (λ = 0.71073 Å) with co scan mode in the range of $2.17° < \theta < 26.46°$. Unit cell dimensions were obtained with least-squares refinements and semi-empirical absorption corrections were applied using

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SADABS program [20], The structure was solved by direct method [21] and refined on F^2 were performed by full-matrix least-squares methods using SHELXL-97 program package [22]. All of the non-hydrogen atoms were refined anisotropically. All other hydrogen atoms were placed in geometrically ideal positions and constrained to ride on their parent atoms. Crystallographic data and experimental details for structural analyses are summarized in Table 1, and the selected bond lengths and angles are listed in Table 2.

The atomic coordinates and other parameters of structure have been deposited with the Cambridge Crystallographic Data Centre (no. 837268); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

In this work, compound **I** was obtained from the reaction of Bbbm with $Zn(OAC)_2 \cdot 2H_2O$, benzoic acid and NaOH in aqueous. The results of elemental analysis for the complex **I** are in good agreement with the theoretical requirements of their compositions (X-ray analysis). This compound is stable in air. The IR spectrum of the title complex shows very strong bands at 1620 and 1360 cm^{-1} which can be attributed to C=O symmetry and asymmetry stretching vibration, respectively. The bands at 1570, 1520, 1470, 1260, 761 and 722 cm^{-1} arise from the C=C and C=N stretching vibrations of the Bbbm ligand.

The X-ray single crystal analysis reveals that complex **I** crystallizes in monoclinic system, space group $P2_1/n$. The asymmetric unit of **I** contains one Zn^{2+} ion, one Bbbm and two $PhCOO^-$ ligands (Fig. 1). Each Zn ion is four-coordinated by two nitrogen atoms from two different Bbbm ligands and two oxygen atoms from distinct $PhCOO^-$ ligands, to furnish distorted ZnN_2O_2 tetrahedral geometry. The corresponding bond distances, Zn–O bond lengths ranging from 1.929(2) to 1.964(2) Å, and Zn–N bond lengths are 2.004(2) and 2.054(2) Å. The bond lengths in the coordination polyhedron of **I** are normal [15–18]. The bond angles in the region 92.68(8)°–122.82(8)° deviate from the value of 109°28′ for an ideal tetrahedron. The crystallographically distinct benzoate anions monodentately coordinate to metal atoms, further more, the carboxylate groups are no longer co-planar with the bearing benzene ring due to coordination effect, and the corresponding dihedral angles between of them are 8.0° and 15.6°, respectively. In complex **I**, the Bbbm ligand acts as a bridging bis(monodentate)ligand and connects with two adjacent units $[Zn(PhCOO)_2]$ forming a 1D infinite linear chain formulated as $[Zn(PhCOO)_2(Bbbm)]$ with the Zn–Zn separation being 12.802(4) Å through the Bbbm ligand (Fig. 2). The resulting chains extend infinitely along [001] direction.

Table 1. Crystallographic data and experimental details for complex **I**

Parameter	Value
Formula weight	597.95
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions:	
a, Å	10.815(3)
b, Å	20.516(6)
c, Å	12.802(4)
β, deg	102.025(3)
V, Å^3	2778.2(14)
Z	4
ρ_{calcd}, g cm^{-3}	1.430
Absorption coefficient, mm^{-1}	0.929
F(000)	1240
Crysral size, mm	0.21 × 0.19 × 0.15
θ Range, deg	2.17–26.46
Index range h, k, l	−13/13, −25/25, −16/16
Reflections collected	23529
Independent reflections, R_{int}	5730 (0.0492)
Parameters	370
Goodness-of-fit on F^2	1.047
Final R indeces, ($I > 2\sigma(I)$)	$R_1 = 0.0406$, $wR_2 = 0.0989$
Largest diff. peak and hole, e Å^{-3}	0.43 and −0.26

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

Bond*	d, Å	Bond	d, Å
Zn(1)–O(1)	1.929(2)	N1)–C(1)	1.323(3)
Zn(1)–O(3)	1.964(2)	N(2)–C(1)	1.334(3)
Zn(1)–N(3)	2.004(2)	N(3)–C(12)	1.325(3)
Zn(1)–N(1)	2.054(2)	N(4)–C(11)	1.466(3)
Angle	ω, deg	Angle	ω, deg
O(1)Zn(1)O(3)	106.91(9)	O(1)Zn(1)N(3)	122.82(8)
O(3)Zn(1)N(3)	118.51(9)	O(1)Zn(1)N(1)	105.24(9)
O(3)Zn(1)N(1)	92.68(8)	N(3)Zn(1)N(1)	105.39(9)
C(12)N(3)Zn(1)	128.22(18)	C(13)N(3)Zn(1)	126.03(16)
C(1)N(1)Zn()	123.48(18)	C(2)N(1)Zn(1)	131.28(16)
C(19)O(1)Zn(1)	123.84(18)	C(26)O(3)Zn(1)	110.31(18)
C(12)N(4)C(11)	128.7(2)	C(18)N(4)C(11)	124.2(2)
C(1)N(2)C(8)	125.1(2)	C(7)N(2)C(8)	128.0(2)
N(2)C(8)C(9)$^{\#2}$	115.4(2)	C(8)$^{\#1}$C(9)C(10)	108.8(2)
C(1)C(10)C(9)	112.4(2)	N(1)C(1)N(2)	113.7(2)

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

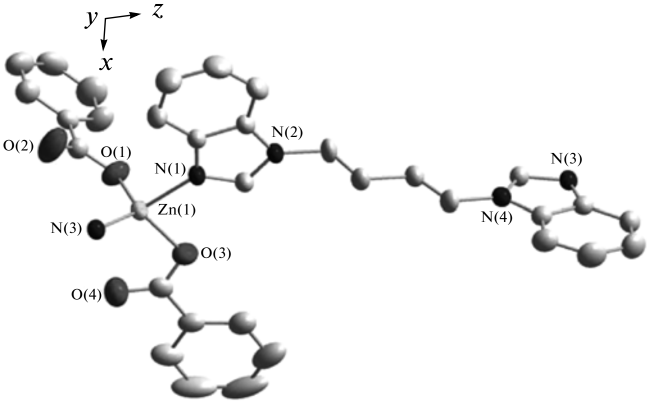

Fig. 1. Coordination arrangements of Zn^{2+} ion in complex **I** (hydrogen were omitted for clarity).

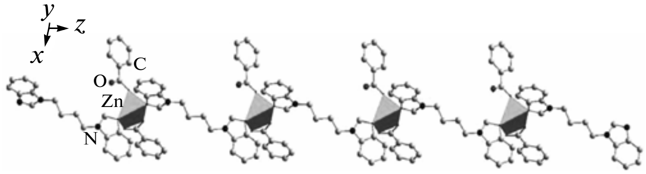

Fig. 2. 1D infinite linear chain of complex **I**.

The thermogravimetric analysis of complex **I** was carried out from 10 to 800°C under nitrogen atmosphere at the heating rate of 10°C min^{-1}. There is no weight loss between 10 and 275°C, indicating that the polymer **I** remains stable up to 275°C. Decomposition of the polymer begins from 275°C with two-steps weight losses. In the temperature range 275–415°C, the first weight loss of 47.8% of the total weight occurs, which can be assigned to the decomposition of Bbbm ligand (calc. 48.5%) and the collapse of the whole framework. The second weight loss of 39.5% between 416 and 566°C corresponds to the removal of benzoate ligand (calc. 40.1%) and the final residual weight is 13.3% corresponding to that of ZnO (calc. 13.6%).

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