

КРАТКИЕ СООБЩЕНИЯ

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CRYSTAL STRUCTURAL AND THERMAL PROPERTIES OF A 1D CADMIUM COORDINATION POLYMER
[Cd(PhCOO)₂(bbbm)]_n

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A new 1D cadmium coordination polymer [Cd(PhCOO)₂(bbbm)]_n (**1**) (bbbm = 1,1'-(1,4-butanediyl)bis-1H-benzimidazole) is synthesized under hydrothermal conditions and characterized by elemental analysis, IR, TG, and X-ray single-crystal diffraction. Compound **1** crystallizes in the triclinic system, space group *P*-1 with *a* = 10.4289(17) Å, *b* = 12.5198(9) Å, *c* = 12.6130(9) Å, α = 118.4260(10)°, β = 95.1990(10)°, γ = 94.3820(10)°, *V* = 1428.8(3) Å³, *Z* = 2. In the structure of **1**, each cadmium center is six-coordinated in a strongly distorted octahedron by two N and four O atoms; an infinite one-dimensional linear chain was built by the flexible bbbm ligand that adopts a bis-monodentate bridging mode linking Cd^{II} atoms.

Key words: bis(benzimidazole), hydrothermal, cadmium(II), 1D coordination polymer.

Introduction. Coordination polymers based on metal and organic building blocks have attracted considerable attention as new functional materials because of their intriguing variety of architectures and interesting properties [1, 2]. These materials are usually produced by simple self-assembly process that is governed by the subtle interplay of metal, ligands, solvents, temperature, and counterions [3]. Of these factors, a judicious choice of organic ligand is one of the main strategies. The use of azoles as ligands has been comprehensively studied; benzimidazole and its derivatives as a typical embranchment have attracted the interest of various research groups due to its synthetic utility and a broad range of pharmacological activities [4]. Among of them, the flexible dibenzimidazole ligand of bbbm (bbbm = 1,1'-(1,4-butanediyl)bis-1H-benzimidazole) has been explored, and several coordination polymers based on it have been reported [5]. Up to now, we and other groups [6, 7] have focused on the synthesis and structural exploration of coordination polymers with mixed carboxylates and neutral N-containing ligands. In continuation of our work, we chose benzoic acid, which has antibacterial and anti-fungal properties, as a co-ligand. The preparation and crystal structure of a new 1D cadmium(II) coordination polymer of the bbbm (bbbm = 1,1'-(1,4-butanediyl)bis-1H-benzimidazole) ligand with this organic acid, namely [Cd(PhCOO)₂(bbbm)]_n, were presented with a view to understanding how the nature of a metal ion and ligand structures affect the architectures assembled via coordination bonds.

Experimental. Reagents and apparatus. All commercially available starting materials were of analytical grade and used without further purification. The bbbm ligand was prepared according to the literature method with some modification [8]. Elemental analyses were taken on a Perkin-Elmer 240C analyzer. IR spectra (KBr pellet) in a range 4000–400 cm⁻¹ were obtained on a FT-IR 170 SX (Nicolet) spectrometer. Thermal stability (TG-DTA) studies were carried out on a NETZSCH TG 209 thermal analyzer from room temperature to 800 °C. The single crystal X-ray diffraction measurement was carried out on a Bruker Smart 1000 CCD diffractometer equipped with a graphite crystal mono-

Table 1

Crystal data and structure refinement for 1

Empirical formula	C ₃₂ H ₂₈ CdN ₄ O ₄
CCDC number	838751
Molecular weight	644.98
Temperature, K	293(2)
Wavelength, Å	0.71073
Crystal system	Triclinic
Space group	<i>P</i> -1
Unit cell dimensions <i>a</i> , <i>b</i> , <i>c</i> , Å; α , β , γ , deg.	10.4289(17), 12.5198(9), 12.6130(9); 118.4260(10), 95.1990(10), 94.3820(10)
Volume, Å ³	1428.8(3)
<i>Z</i>	2
<i>d</i> _x , g/cm ³	1.499
μ , mm ⁻¹	0.808
<i>F</i> (000)	656
Crystal size, mm	0.22×0.20×0.19
θ range, deg.	2.51 to 26.24
Crystal color and shape	Colorless block
Range of <i>h</i> , <i>k</i> , <i>l</i>	-12 ≤ <i>h</i> ≤ 12, -15 ≤ <i>k</i> ≤ 15, -15 ≤ <i>l</i> ≤ 15
Reflections collected/unique	9163 / 4400
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	4400 / 0 / 370
Goodness-of-fit on <i>F</i> ²	1.085
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0310, <i>wR</i> 2 = 0.0918
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0348, <i>wR</i> 2 = 0.0945
Residual peak and hole, e/Å ³	0.846 and -0.434

chromator situated in the incident beam for data collection at 293(2) K. Intensities of reflections were measured using graphite-monochromatized MoK α radiation ($\lambda = 0.71073$ Å) with ω scan mode in the range $2.51 < \theta < 26.24^\circ$. Unit cell dimensions were obtained with least-squares refinements, and semi-empirical absorption corrections were applied using the SADABS program [9]. The structure was solved by a direct method [10], and non-hydrogen atoms were obtained in successive difference Fourier syntheses. The final refinements were performed by full-matrix least-squares methods on *F*² using the SHELXL-97 program package [11]. All non-hydrogen atoms were refined anisotropically. All 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. CCDC-838751 contains the supplementary crystallographic data for polymer **1**. These data can be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk.

Preparation of [Cd(PhCOO)₂(bbbm)]_n **1.** A mixture of cadmium(II) acetate dihydrate (0.1 mmol, 26.6 mg), bbbm ligand (0.1 mmol, 29.0 mg), benzoic acid (0.1 mmol, 12.2 mg), NaOH (0.1 mmol, 4.0 mg), EtOH (2 ml), and H₂O (8 ml) was placed in a Teflon-lined stainless vessel and heated to 140 °C for 5 days under autogenous pressure, and then cooled to room temperature with a rate of 10 °C/h. The resulting colorless block crystals of **1** were obtained by filtration, washed with distilled water, and dried at ambient temperature; 48 % yield based on Cd. Anal. calcd. for CdC₃₂H₂₈N₄O₄ (%): C, 59.59; H, 4.38; N, 8.69. Found (%): C, 59.48; H, 4.26; N, 8.43. IR (KBr pellet, cm⁻¹): 3428(w), 2936(w), 1596(m), 1538(s), 1467(m), 1395(vs), 1194(m), 852(m), 722(m), 676(m).

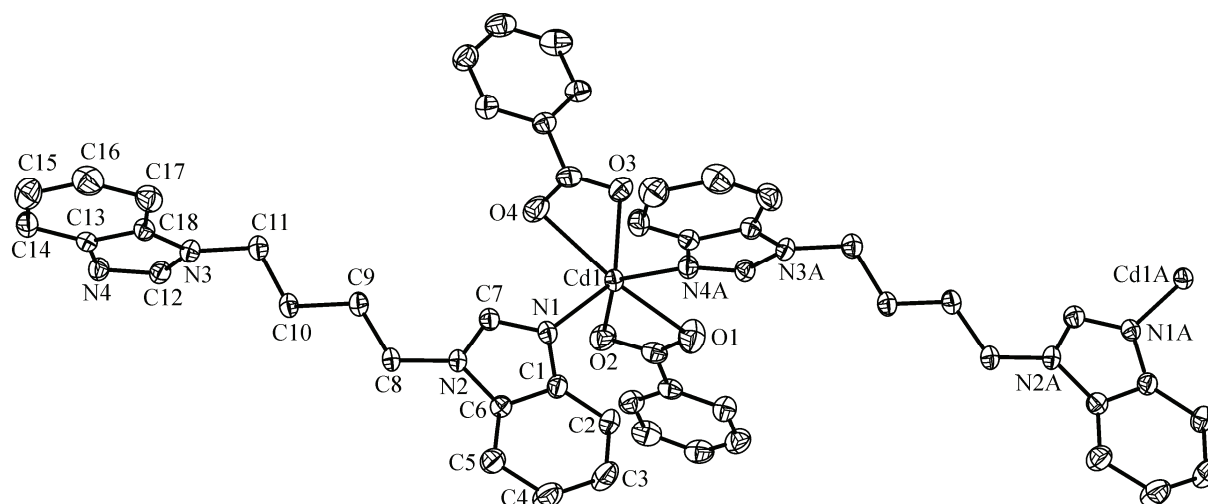


Fig. 1. Coordination arrangement of the Cd(1) ion in complex **1** (symmetry code: A = x, y+1, z+1; hydrogen atoms were omitted for clarity)

Results and discussion. Syntheses and general methods. Reactions of $\text{Cd}(\text{OAC})_2 \cdot 2\text{H}_2\text{O}$ with bbbm and benzoic acid in the 1:1:1 molar ratio at pH = 7–8, under hydrothermal conditions, gave rise to a one-dimensional chain coordination polymer $[\text{Cd}(\text{PhCOO})_2(\text{bbbm})]_n$ that is stable in air. The band at 2936 cm^{-1} in the IR spectra can be attributed to stretching vibrations of C—H. Strong absorption bands at 1596 cm^{-1} and 1538 cm^{-1} can be attributed to C=O symmetry and asymmetry stretching vibrations respectively. They clearly indicate that PhCOO^- ligands adopt chelating coordination to the metal ion. The characteristic bands at 1538 cm^{-1} , 1467 cm^{-1} , 1395 cm^{-1} , 1194 cm^{-1} , and 722 cm^{-1} can be regarded as the C=C and C=N stretching vibrations of the bbbm ligand.

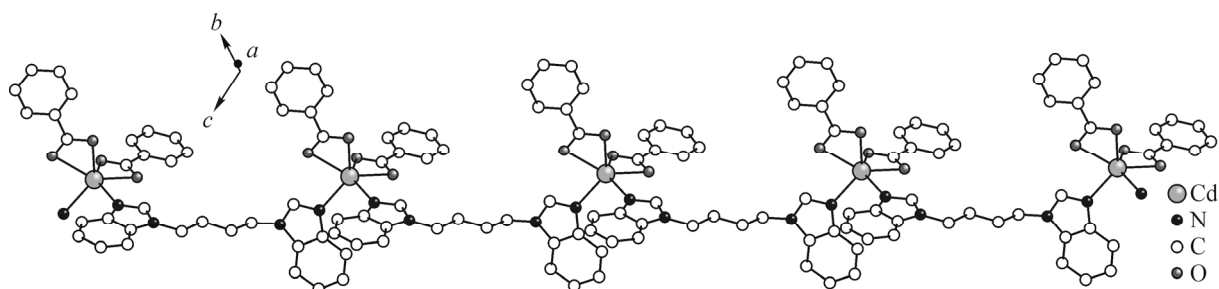
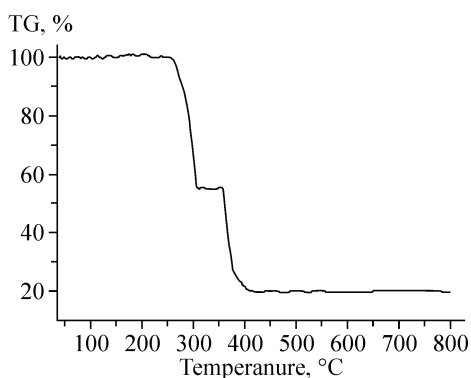
Description of the crystal structure. A view of the structure is shown in Fig. 1; principal bond lengths and angles are summarized in Table 2. X-ray single-crystal analysis reveals that **1** crystallizes in the triclinic crystal system, space group *P*-1. The asymmetric unit of **1** contains one Cd(II) ion, one bbbm and two benzoate anions. Each Cd(II) ion is six-coordinated by two nitrogen atoms from two different bbbm ligands and four oxygen atoms from two PhCOO^- ligands to furnish distorted CdN_2O_4 octahedral geometry. O1, O4, O2, and N4A (A = x, y+1, z+1) occupy the equatorial plane; bond lengths vary from $2.277(3)\text{ \AA}$ to $2.468(3)\text{ \AA}$ and the diagonal ones are $\text{O1—O4} = 4.6726(40)\text{ \AA}$ and $\text{O2—N4A} = 4.2229(56)\text{ \AA}$ respectively. The coordination bond angles are: $\text{O}(2)\text{—Cd}(1)\text{—O}(1) = 54.35(10)^\circ$, $\text{O}(2)\text{—Cd}(1)\text{—O}(4) = 104.25(12)^\circ$, $\text{N}(4\text{A})\text{—Cd}(1)\text{—O}(4) = 118.81(12)^\circ$, $\text{N}(4\text{A})\text{—Cd}(1)\text{—O}(1) = 82.38(9)^\circ$. While N1 and O3 complete the apical positions, Cd1—N1 bond lengths are:

Table 2

Selected bond lengths (Å) and angles (deg.) for polymer **1**

Cd(1)—N(1)	2.278(3)	N(1)—Cd(1)—O(2)	96.70(11)	O(4)—Cd(1)—O(1)	148.12(11)
Cd(1)—O(2)	2.280(3)	O(2)—Cd(1)—N(4A)	135.82(9)	N(1)—Cd(1)—N(4A)	96.73(9)
Cd(1)—N(4A)	2.277(3)	O(2)—Cd(1)—O(3)	99.42(11)	N(1)—Cd(1)—O(3)	138.25(9)
Cd(1)—O(3)	2.347(3)	N(1)—Cd(1)—O(4)	84.47(10)	N(4A)—Cd(1)—O(3)	97.91(10)
Cd(1)—O(4)	2.391(3)	N(4A)—Cd(1)—O(4)	118.81(12)	O(2)—Cd(1)—O(4)	104.25(12)
Cd(1)—O(1)	2.468(3)	N(1)—Cd(1)—O(1)	118.43(12)	O(3)—Cd(1)—O(4)	54.30(10)
		N(4A)—Cd(1)—O(1)	82.38(9)	O(2)—Cd(1)—O(1)	54.35(10)
				O(3)—Cd(1)—O(1)	102.16(12)

Symmetry code: A = x, y+1, z+1.

Fig. 2. 1D infinite linear chain of complex **1**Fig. 3. TG plot for **1**

$\text{Cd}(1)\text{—N}(1) = 2.278(3) \text{ \AA}$ and $\text{Cd}1\text{—O}3 = 2.347(3) \text{ \AA}$. All the bond lengths are shorter than the reported ones [12] except $\text{Cd}1\text{—O}1 = 2.468(3) \text{ \AA}$. The coordination bond angles between the axial and equatorial planes are $54.30 \sim 118.43^\circ$ and deviate from the value of 90° for an ideal octahedron, indicating a strong distortion. All bbbm ligands are bidentate; the two benzimidazolyl moieties at the end of each ligand provide one N atom coordinating to the metal ions. Each benzoate anion offers two O atoms coordinating bidentately to one Cd^{2+} ion, leading to a closure of a four-membered chelate CdO_2C ring. Two O atoms of the benzoate anion chelating to a metal ion cause the formation of smaller bond angles of 54.30° and 54.35° . In complex **1**, each neutral bbbm serves as a bridging ligand to link two secondary building

$[\text{Cd}(\text{PhCOO})_2]$ units made up of one Cd^{2+} connecting two adjacent benzoate anions, giving rise to an infinite linear one-dimensional coordination polymer formulated as $[\text{Cd}(\text{PhCOO})_2(\text{bbbm})]$, with the $\text{Cd}1\text{—Cd}1A$ ($A = x, y+1, z+1$) separation being $12.8644(7) \text{ \AA}$ (Fig. 2).

The thermogravimetric analysis of complex **1** was carried out from room temperature to 800°C under the nitrogen atmosphere at a heating rate of $10^\circ\text{C} \cdot \text{min}^{-1}$, as shown in Fig. 3. There is no weight loss between room temperature and 256.4°C , indicating that complex **1** remains stable up to 256.4°C . The decomposition of the polymer begins from 256.4°C with two-step weight losses. In the temperature range $256.4\text{—}305.8^\circ\text{C}$, the first weight loss of 44.98 % of the total weight occurs, which can be assigned to the decomposition of the bbbm ligand (calc. 45.02 %). The second weight loss of 35.07 % between 357.2°C and 406.2°C corresponds to the removal of two PhCOO^- anions (calc. 35.08 %), and the final residual weight is 19.90 %, corresponding to that of CdO (calc. 19.91 %) (Fig. 3).

In summary, a new one-dimensional coordination polymer $[\text{Cd}(\text{PhCOO})_2(\text{bbbm})]_n$ based on the bbbm ligand has been hydrothermally prepared and structurally characterized by single crystal X-ray diffraction analysis. Each $\text{Cd}(\text{II})$ atom in the complex is six-coordinated in a slightly distorted octahedral geometry.

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