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**CRYSTAL STRUCTURE AND FLUORESCENCE OF A 2D CADMIUM(II)
COORDINATION POLYMER BASED ON FLEXIBLE
bis(2-METHYLBENZIMIDAZOLE) AND BENZENEDICARBOXYLATE Co-LIGANDS**

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A new coordination polymer, $\{[\text{Cd}(\text{bbmb})(\text{bdc})]\}_n$ (bbmb = 1,1'-(1,4-butanediyl)bis-(2-methylbenzimidazole), H_2bdc = 1,3-benzenedicarboxylic acid) was synthesized under hydrothermal conditions. The complex was structurally characterized by single crystal X-ray diffraction analyses, infrared spectroscopy (IR), elemental analyses. The compound crystallizes in the monoclinic system, space group $P2_1/c$ with $a = 10.860(6) \text{ \AA}$, $b = 13.115(7) \text{ \AA}$, $c = 21.009(9) \text{ \AA}$, $\beta = 120.94(2)^\circ$, $V = 2567(2) \text{ \AA}^3$, $Z = 4$, $\text{C}_{28}\text{H}_{26}\text{CdN}_4\text{O}_4$, $M_r = 594.93$, $D_c = 1.540 \text{ g/cm}^3$, $\mu = 0.893 \text{ mm}^{-1}$. Each cadmium center is six coordinated with four O atoms from two bdc²⁻ anions, and two N atoms of two bbmb ligands. The complex features a 4-connected 2D (4, 4) sheet with a point symbol $\{4^2.6^2\}$. Fluorescence properties of the title complex were investigated.

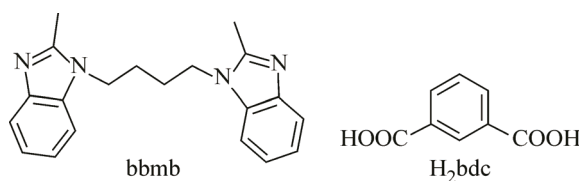
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Keywords: bis(benzimidazole), Cd(II) complex, crystal structure, fluorescence.

INTRODUCTION

Crystal engineering of coordination polymers has received growing interest in recent years, which not only stems from their intriguing architectures but also from their potential applications in catalysis, adsorption, magnetism and luminescent materials [1–4]. The assembly and structures of coordination polymers are greatly affected by the organic ligands, the nature of the metal ions, the pH value, the solvent system, and so on [5, 6]. The selection of appropriate organic ligands is undoubtedly the vital one and considerable effort has been devoted to design linkers containing N- and O-donors [7–9]. The flexible bis(2-methylbenzimidazole) ligands with $(-\text{CH}_2-)_n$ ($n = 2, 3, 4, 5, 6$) spacers, representing of classic N-containing organic linkers, have been widely used for the construction of metal coordination polymers with charming structures, owing to the flexible nature of the alkyl spacer, which allows those ligands to bend and rotate freely so as to conform to the coordination geometries of central metal ions and exhibit versatile coordination conformations [10, 11]. In addition, organic polycarboxylate anions have been used extensively in the construction of coordination polymers, due to their remarkable coordination ability and diverse coordination modes [12, 13]. The polycarboxylate-bis(benzimidazole) system is an important and flourishing branch in the constructing mixed-ligand metal coordination polymers [14, 15].

As a part of our ongoing studies [16], herein we selected flexible 1,1'-(1,4-butane)bis-(2-methylbenzimidazole) (bbmb) as the main ligand, and 1,3-benzenedicarboxylic acid (H_2bdc) (Scheme 1) as the co-ligands, and a Cd(II) complex based on this mixed system was hydrothermally synthesized and characterized. The fluorescence properties were also investigated.



Scheme 1. The ligands used in this paper

EXPERIMENTAL SECTION

Materials and physical measurements. All reagents and solvents for syntheses were commercially available and used without further purification. The ligand bbmb was prepared according to the literature [17]. Elemental analyses were performed on a Perkin-Elmer 240C automatic analyzer. IR spectra were recorded on a Nicolet FT-IR Avatar 360 spectrophotometer in 4000—400 cm^{-1} region in KBr pellets. Fluorescence spectrum was recorded with a Hitachi F-7000 fluorescence spectrophotometer at room temperature in solid state.

X-ray crystallography. A single crystal with dimensions of 0.17×0.16×0.15 mm was selected for the X-ray diffraction. The data collection was carried out on a Bruker Smart 1000 CCD diffractometer with graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) and ω -2 θ scan mode at 293(2) K. A total of 8273 reflections were collected with 2659 unique ones ($R_{\text{int}} = 0.0307$). A semi-empirical absorption correction was applied using the SADABS program [18]. The structure was solved by direct methods with SHELXS-97 program and refined by full-matrix least squares on F^2 with SHELXTL [19]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions. The final refinement converged at $R = 0.0316$ and $wR = 0.0790$ ($w = 1/[s^2(F_0^2) + (0.0834P)^2]$, where $P = (F_0^2 + 2F_c^2)/3$), $(\Delta\rho)_{\text{max}} = 0.82 \text{ e/\AA}^3$, $(\Delta\rho)_{\text{min}} = -1.04 \text{ e/\AA}^3$, $S = 1.14$. The selected bond distances and angles are listed in Table 1. CCDC 1000351 contains the supplementary crystallographic data for complex. This 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.

RESULTS AND DISCUSSION

Description of crystal structure $\{[\text{Cd}(\text{bbmb})(\text{bdc})]\}_n$. Single-crystal X-ray diffraction analysis has revealed that the title complex crystallizes in the monoclinic system, space group $P2_1/c$. In the asymmetric unit of the complex, there exists one crystallographically independent Cd^{2+} ion, one bbmb ligand and one bdc^{2-} anion. As illustrated in Fig. 1, the Cd(II) center exhibits a distorted octahedral geometry coordinated by three oxygen atoms (O1, O3A, and O4A) from two different bdc^{2-} anions and one nitrogen atom (N3) from one bbmb ligand composing the equatorial plane (symmetry codes: $A = -x, y+1/2, -z+1/2$), one oxygen atom (O2) and one nitrogen atom (N1) from another bbmb ligand located in the axial sites with the angle of N1—Cd1—O2 of $150.220(2)^\circ$. The Cd—O/N bond

Table 1

Selected bond lengths (\AA) and angles (deg.)

Cd1—N1	2.252(5)	N1—Cd1—O2	150.2(2)	O4A—Cd1—N3	90.3(2)	N1—Cd1—O1	96.5(2)
Cd1—O2	2.269(5)	N1—Cd1—O4A	109.1(2)	N1—Cd1—O3A	95.59(19)	O2—Cd1—O1	53.81(19)
Cd1—O4A	2.303(6)	O2—Cd1—O4A	98.2(2)	O2—Cd1—O3A	90.2(2)	O4A—Cd1—O1	141.58(19)
Cd1—N3	2.331(6)	N1—Cd1—N3	95.1(2)	O4A—Cd1—O3A	55.25(18)	N3—Cd1—O1	116.1(2)
Cd1—O3A	2.491(5)	O2—Cd1—N3	96.5(2)	N3—Cd1—O3A	145.5(2)	O3A—Cd1—O1	95.1(2)
Cd1—O1	2.548(7)						

Symmetry code: $A = -x, y+1/2, -z+1/2$.

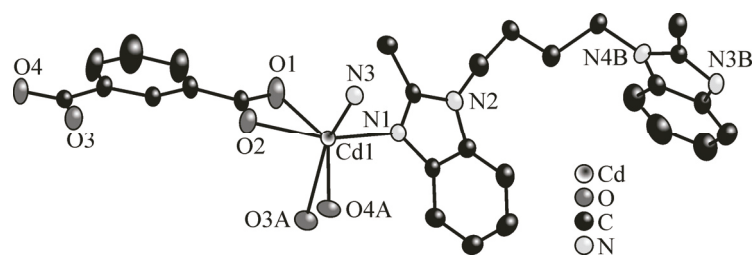


Fig. 1. The coordination environment around cadmium centers in the complex (symmetry code: A = $-x, y+1/2, -z+1/2$)

lengths are in the range of 2.269(5)—2.548(7) Å and 2.252(5)—2.331(6) Å, respectively, which are comparable to those in similar cadmium complexes [20, 21].

The flexible bbmb ligands adopt bis(monodentate) coordination mode and connect adjacent Cd(II) atoms adopting a twisted conformation to generate right-handed helical chains with the dihedral angles between the mean planes of the two benzimidazole rings of entire bbmb ligand of 84.668(2)°. Additionally and interestingly, the completely deprotonated bdc²⁻ anions, as auxiliary ligands, with μ_2 - η^2 : η^2 coordination mode, connect neighbouring Cd(II) atoms, forming left-handed helical chains. This two kinds of helical chains are present in 1:1 ratio and are further interlinked into an unevenly extended 2D (4,4) net (Fig. 2, a), in which each 38-membered circuit contains four cadmium(II) atoms at the corners and the two kinds of ligands making up four edges, generating an irregular [Cd₄(bbmb)₂(bdc)₂] unit. The dimensions of each unit are 12.805(5)×9.628(4) Å, with angles of 61.608(8)°, 85.859(1)°, 106.02(1)°, as determined by through-space Cd⋯Cd distances and Cd—Cd—Cd angles (Fig. 2, b). Topology analysis indicates that the 2D layer can be portrayed as a uninodal 4-connected undulated sql/Shubnikov tetragonal plane net with {4⁴.6²} topology [22].

IR spectrum. The main features in the IR spectra concern the carboxylate groups and the N-containing ligands. The band at 1507 cm⁻¹ may be tentatively assigned to the C=N stretching vibrations of the benzimidazolyl groups. There is no strong absorption peaks around 1700 cm⁻¹, which indicates that all carboxylic groups are completely deprotonated. The characteristic bands of the carbo-

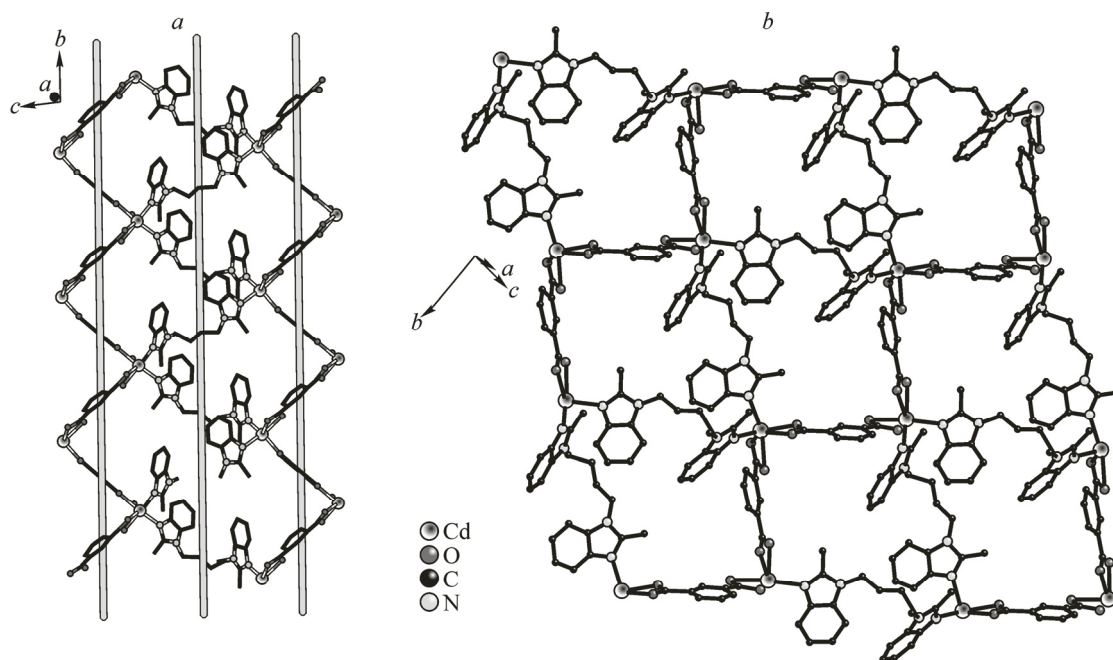


Fig. 2. The left-handed and right-handed helical chains in the 2D layer of the complex (a), the 2D layer in the complex (b)

xylate anions occur at 1604 cm^{-1} and 1412 cm^{-1} for the asymmetric and symmetric vibrations, respectively. The $\Delta\nu$ value ($\Delta\nu = \nu_{\text{as}}(\text{COO}) - \nu_{\text{s}}(\text{COO})$) is 192 cm^{-1} , indicating the presence of bidentate chelating coordination mode [23].

Fluorescence properties. As is well-known, the Cd(II) complexes, with d^{10} electronic configurations, exhibit interesting luminescence properties [24, 25]. Therefore, the luminescent behavior of the title compound and of free bbmb ligand were studied in the solid state at room temperature. Intense emission of the complex occurs at 356 nm upon excitation with 280 nm wavelength. Free bbmb, upon excitation at 300 nm, exhibited strong photoluminescence with emission maximum at 368 nm, a slightly red shifted compared to free bbmb ligand, which is attributed to $\pi \rightarrow \pi^*$ transitions [26]. In addition, a weak emission peak of free H₂bdc ligand was reported at 369 nm ($\lambda_{\text{ex}} = 310\text{ nm}$), resulting from the $\pi^* \rightarrow n$ transition. The carboxylate ligands contribute little to the fluorescent emission in the presence of the N-donor ligand [27]. What is more, the Cd(II) ions are difficult to oxidize or reduce [28], thus, the emission band for the complex can be assigned mainly to a $\pi \rightarrow \pi^*$ transition within the coordinated bbmb ligands.

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