

Synthesis, Structural Characterization, and Properties of a Cd(II) Complex with a Carboxylate- and Benzimidazolyl-Containing Ligand¹

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Abstract—The hydrothermal reaction of cadmium salt with 3,5-bis(benzimidazol-1-ylmethyl)benzoic acid (HL) forms a new complex $[\text{Cd}(\text{L})_2] \cdot 3\text{H}_2\text{O}$ (**I**). This complex has been characterized by single-crystal X-ray diffraction, IR, elemental and thermogravimetric analyses and shows 3D flu framework structure with 2-nodal (3,6)-connected $(4^2.6)_2(4^4.6^2.8^3)$ topology. Luminescent property of **I** was investigated. Moreover, single crystals of HL were obtained accidentally in the hydrothermal reaction of the HL with MnSO_4 at 160°C, and its crystal structure has been characterized by single-crystal X-ray diffraction (CIF files CCDC nos. 1020274 (HL) and 1020275 (**I**)).

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INTRODUCTION

The assembly of coordination polymers has received remarkable attention in recent years because of their fascinating structures and potential applications in magnetism, optical material, catalysis, and adsorption [1]. Generally, the syntheses of complexes involves the metal centers and bridging ligands to fabricate overall architectures, which can be influenced by many factors, such as the nature of metal ions and ligands, solvent, the auxiliary ligands, and the reaction temperature [2]. It is known that the functional properties of the resultant complexes may have a close relation with the intrinsic features of the metal centers and the ligands [3]. And thus, the selection of ligands becomes very important task for the exploration of new crystalline materials. Among the well utilized buildings, N- and O-donors are always regarded as excellent candidates in the construction of desirable frameworks.

Some N- and O-donor ligands, such as 3,5-di(1*H*-imidazol-1-yl)benzoate, 3,5-di(pyridine-4-yl)benzoate, and 5-(isonicotinamido)isophthalate, have been found to be efficient organic building blocks in the construction of new complexes with fascinating structures in the reported literatures [4–6]. However, ligands containing both sterically hindered N-donor groups, such as benzimidazolyl and carboxylate groups, have also been paid increasing attention because of their distinctive features. Hitherto, 5-(benzimidazol-1-ylmethyl)isophthalic acid and 4-(benzimidazol-1-ylmethyl)benzoic acid have already been selected as organic ligands to assemble new complexes with diverse intriguing structures [7–9],

which attracts us to undertake further study on this kind of ligands for the comprehension of the correlation between the synthetic conditions and the structure of resultant complexes.

Recently we have been focusing our attention on the utilization of a benzimidazol-1-yl and carboxylate-containing ligand 3,5-bis(benzimidazol-1-ylmethyl)benzoic acid (HL) as a building block for the construction of coordination polymers. The arene-cored ligand HL possesses two functional groups, namely carboxylate and sterically hindered benzimidazol-1-yl groups. Due to mutable coordination patterns of the carboxylate, such as $\mu_1\text{-}\eta^1\text{:}\eta^0$ -monodentate, $\mu_1\text{-}\eta^1\text{:}\eta^1$ -chelating and $\mu_2\text{-}\eta^1\text{:}\eta^1$ -bridging modes, the HL can show various coordination modes which is helpful to achieve structural diversification [10]. Moreover, the sterically hindered benzimidazolyl group may induce new structural evolution and its large conjugated system is very important for seeking for new fluorescent materials. Herein we report the synthesis and structural characterization of a new complex $[\text{Cd}(\text{L})_2] \cdot 3\text{H}_2\text{O}$ (**I**). The thermal stability and fluorescence have been investigated.

EXPERIMENTAL

Materials and methods. All commercially available chemicals were of reagent grade and used as received without further purification. According to the reported literature [7–9], a slightly revised experimental procedure was used to synthesize the HL ligand. Elemental analyses of C, H, and N were taken on a Perkin Elmer 240C elemental analyzer. Infrared spectra (IR)

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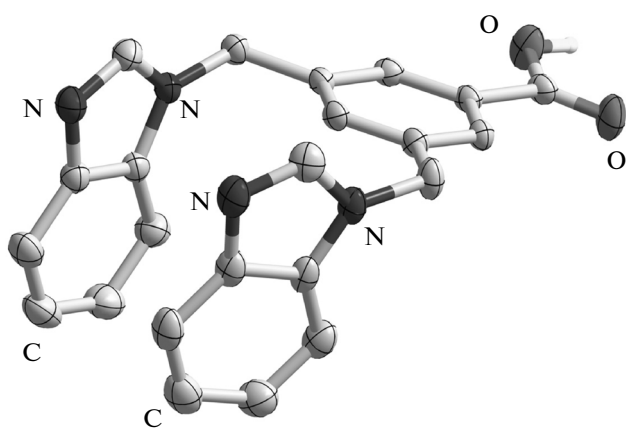


Fig. 1. Molecular structure of HL in the single crystal of HL · H₂O with the ellipsoids drawn at the 30% probability level. The hydrogen atoms are omitted for clarity.

were recorded on a Bruker Vector22 FT-IR spectrophotometer by using KBr pellets. Thermogravimetric analysis (TGA) was performed on a simultaneous SDT 2960 thermal analyzer under nitrogen atmosphere with a heating rate of 10°C min⁻¹. The luminescence spectra for the powdered solid samples were measured on an Aminco Bowman Series 2 spectrofluorometer with a xenon arc lamp as the light source. In the measurements of emission and excitation spectra the pass width was 5 nm, and all measurements were carried out under the same experimental conditions.

Synthesis of I. Reaction mixture of Cd(ClO₄)₄ · 6H₂O (41.9 mg, 0.1 mmol), HL (19.1 mg, 0.1 mmol) and KOH (5.6 mg, 0.1 mmol) in 10 mL H₂O was stirred for 30 min. Then reaction mixture was placed in a 16 mL Teflon-lined stainless steel container and heated at 180°C for 48 h. And then the oven was shut off and cooled down naturally at ambient temperature. After cooling to the room temperature, block colorless crystals of **I** were obtained with the yield of 40% based on HL.

For C₄₆H₄₀N₈O₇Cd (*M* = 929.26)

anal. calcd., %: C, 59.45; H, 4.34; N, 12.06.

Found, %: C, 59.62; H, 4.26; N, 11.95.

IR data (ν, cm⁻¹): 1655 ν(C=O), 1612 ν_{as}(COO⁻), 1597 ν_{as}(COO⁻), 1500 ν_s(COO⁻), 1458 ν_s(COO⁻).

X-ray structure determinations. The crystallographic data collections for the complex **I** and HL · H₂O were carried out on a Bruker Smart ApexII CCD area-detector diffractometer using graphite-monochromated MoK_α radiation (λ = 0.71073 Å) at 200 K. The diffraction data were integrated by using the program SAINT [11], which was also used for the intensity corrections for Lorentz and polarization effects. Semi-empirical absorption corrections were applied using the program

SADABS [12]. The structures of **I** and HL · H₂O were solved by direct methods, and all non-hydrogen atoms were refined anisotropically on *F*² by the full-matrix least-squares techniques using the SHELXL-97 crystallographic software package [13]. In **I** and HL, all hydrogen atoms at C atoms were generated geometrically. The hydrogen atoms at O atoms in HL could be found at a reasonable position in the difference Fourier maps and fixed there. The crystal water in **I** is badly disordered and could not be modeled and has been removed from the structure by SQUEEZE in PLATON. The suggested number of crystal water molecules was determined according to elemental and thermogravimetric analyses. The details of crystal parameters, data collection, and refinements are summarized in Table 1, selected bond lengths and angles are listed in Table 2.

Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 1020274 (HL) and 1020275 (**I**); deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

RESULTS AND DISCUSSION

Cd(ClO₄)₂ · 6H₂O reacts with 3,5-bis(benzimidazol-1-ylmethyl)benzoic acid (HL) under hydrothermal conditions at 180°C to yields the complex [Cd(L)₂] · 3H₂O (**I**). Moreover, single crystals of HL were obtained accidentally in the hydrothermal reaction of the HL with MnSO₄ at 160°C. Complex **I** and single crystals of HL are stable in air.

The accidentally obtained single crystals the asymmetrical unit of HL · H₂O consists of one HL and one crystal water. Because containing two flexible benzimidazolyl groups, the HL ligand can display the *cis*- and *trans*-molecule conformations, respectively. In the accidentally obtained single crystal of HL · H₂O, its molecular conformation is a *cis*-conformation (Fig. 1), while in complex **I**, the L⁻ ligand displays a *trans*-one (Fig. 2a).

Structural analysis shows that complex **I** exhibits a 3D flu framework structure. The HL molecule was deprotonated to the L⁻ anionic ligand. In the asymmetrical unit of there are one centrosymmetric Cd²⁺ ion with occupancy of 0.5, one L⁻ ligand, and 1.5 crystal water molecules. Unfortunately, all the crystal water is badly disordered and could not be modeled, which was thus removed from the structural mode of **I** by SQUEEZE in PLATON. The suggested number of crystal water was determined by elemental and thermogravimetric analyses.

As shown in Fig. 2a, Cd²⁺ ion is six-coordinated by four benzimidazolyl N atoms from four different L⁻ and two carboxylate O atoms from two different L⁻ to furnish a distorted octahedral coordination geometry [CdN₄O₂]: O(1), O(1E), N(11A), and N(11D) define the equatorial plane; N(31B) and N(31C) occupy the axial positions. The bond distances around Cd²⁺ ion

Table 1. Crystallographic data and structure refinement for complex **I**

Parameter	Value	
	I	HL · H ₂ O
Formula	C ₄₆ H ₄₀ N ₈ O ₇ Cd	C ₂₃ H ₂₀ N ₄ O ₃
<i>M</i>	929.26	400.43
Crystal size, mm	0.20 × 0.18 × 0.18	0.20 × 0.10 × 0.10
Crystal system	Orthorhombic	Triclinic
Space group	<i>Fddd</i>	<i>P</i> $\bar{1}$
<i>a</i> , Å	18.5913(12)	9.112(5)
<i>b</i> , Å	25.9762(16)	10.826(6)
<i>c</i> , Å	33.167(2)	11.417(6)
α , deg	90	65.464(7)
β , deg	90	80.188(7)
γ , deg	90	71.480(7)
<i>V</i> , Å ³	16017.6(17)	970.6(9)
<i>Z</i>	16	2
ρ_{calcd} , g cm ⁻³	1.54	1.37
$\mu(\text{MoK}\alpha)$, cm ⁻¹	0.61	0.093
<i>F</i> (000)	7616	420
Limiting indices <i>hkl</i>	$-22 \leq h \leq 23, -23 \leq k \leq 32, -41 \leq l \leq 40$	$-10 \leq h \leq 10, -12 \leq k \leq 12, -13 \leq l \leq 9$
θ Range, deg	1.99–26.60	1.96–25.01
Reflections measured	22341	4921
Reflections unique	4198	3358
<i>R</i> _{int}	0.0693	0.0438
Parameter refined	267	271
<i>R</i> (<i>F</i>)/ <i>wR</i> (<i>F</i> ²)* (all data)	0.0612/0.0686	0.1037/0.2255
GOOF (<i>F</i> ²)	1.000	1.033
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$, e Å ⁻³	0.74/–0.69	0.22/–0.30

* $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = \sqrt{\sum w(|F_o|^2 - |F_c|^2)^2} / \sum w(F_o)^2$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = (F_o^2 + 2F_c^2)/3$.

are from 2.300(3) to 2.402(3) Å. The carboxylate group of the L⁻ ligand exhibit the terminal $\mu_1\text{-}\eta^1\text{:}\eta^0$ monodentate mode and each benzimidazolyl group coordinates to a Cd²⁺ ion. So the L⁻ just acts as μ_3 -bridge. Each Cd²⁺ ion is coordinated by six L⁻ ligands. The interconnection of Cd²⁺ and L⁻ repeat in-

finitely to construct a 3D framework (Fig. 2b). In the viewpoint of topology, each Cd²⁺ ion can be viewed as a 6-connected node; each L⁻ ligand can be considered as a 3-connector bridge. Therefore, the 3D framework of **I** can be simplified as a 2-nodal (3,6)-connected flu network with (4².6)₂(4⁴.6².8⁹) topology (Fig. 2c).

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

Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
Cd(1)–O(1)	2.353(3)	Cd(1)–N(31) ^{#2}	2.300(3)
Cd(1)–N(11) ^{#3}	2.402(3)		
Angle	ω, deg	Angle	ω, deg
O(1)Cd(1)O(1) ^{#1}	113.44(13)	O(1)Cd(1)N(31) ^{#2}	90.15(9)
O(1)Cd(1)N(11) ^{#3}	86.51(9)	O(1) ^{#1} Cd(1)N(31) ^{#2}	81.41(9)
O(1) ^{#1} Cd(1)N(11) ^{#3}	156.09(9)	N(11) ^{#3} Cd(1)N(31) ^{#2}	85.69(9)
N(31) ^{#5} Cd(1)N(31) ^{#2}	164.62(13)	N(11) ^{#3} Cd(1)N(11) ^{#4}	77.94(8)
N(31) ^{#5} Cd(1)N(11) ^{#4}	106.46(9)		

* Symmetry transformations used to generate equivalent atoms: ^{#1} 5/4 – *x*, *y*, 1/4 – *z*; ^{#2} 1 – *x*, 1/4 + *y*, 1/4 + *z*; ^{#3} 3/4 – *x*, 3/4 – *y*, *z*; ^{#4} 1/4 – *x*, 9/4 – *y*, *z*; ^{#5} 1/4 + *x*, 1/4 + *y*, 2 – *z*.

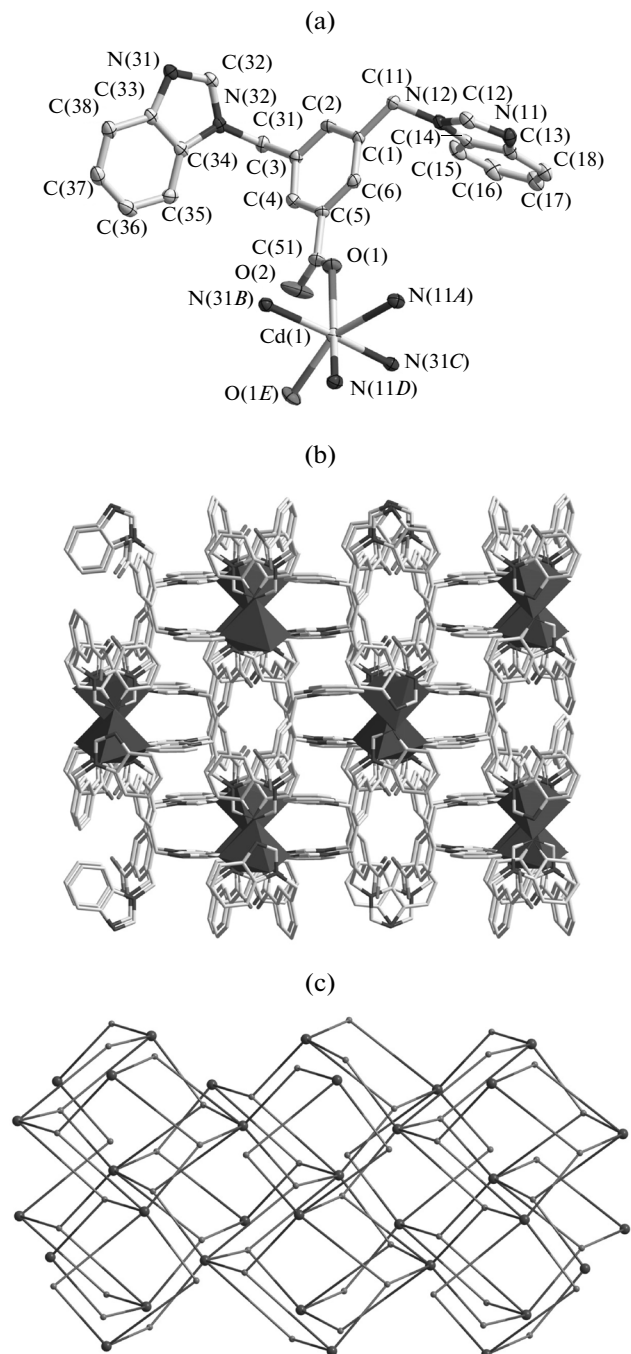


Fig. 2. The coordination environment of the Cd²⁺ ions in **I** with ellipsoids drawn at the 30% probability level, the hydrogen atoms are omitted for clarity (a); view of the 3D framework structure of **I** (b); topological view of the 3D architecture of **I** (c).

TGA was carried out for complex **I**, and the result is shown in Fig. 3: there is a weight loss of 5.9% from 98 to 150°C corresponding to the release of crystal water (calcd. 5.8%) and the decomposition of the framework of **I** can be observed at 380°C.

Due to the outstanding luminescent property of Cd(II) coordination polymers, the photoluminescence of complex **I** was investigated in the solid state at room temperature for its potential application as photoactive materials. As shown in Fig. 4, intense bands were observed at 410 nm ($\lambda_{\text{ex}} = 325$ nm) for **I** and 405 nm ($\lambda_{\text{ex}} = 332$ nm) for HL. As for the source of fluorescence of the complex, it may be assigned to intraligand transition of the coordinated L[–] ligands since a similar emission can be observed for HL [14, 15]. The red shift of the emission maximum in **I** compared with

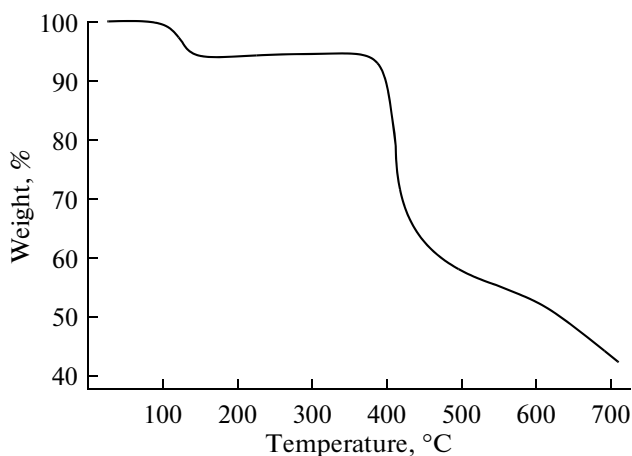


Fig. 3. TGA curve of complex **I**.

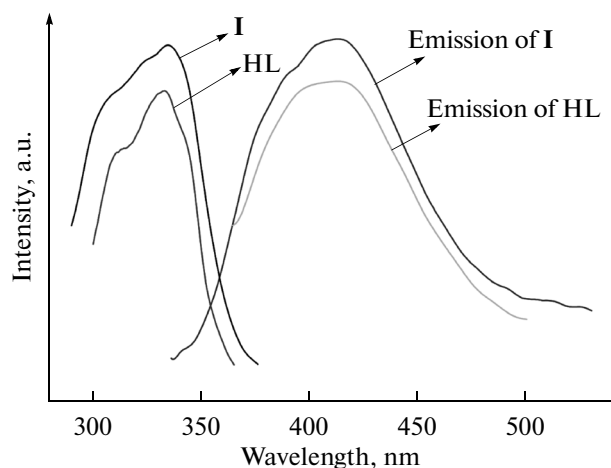


Fig. 4. Emission and excitation spectra of **I** and **HL** in the solid state at room temperature.

free HL ligand may originate from the coordination of the ligands to the metal centers [16, 17].

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