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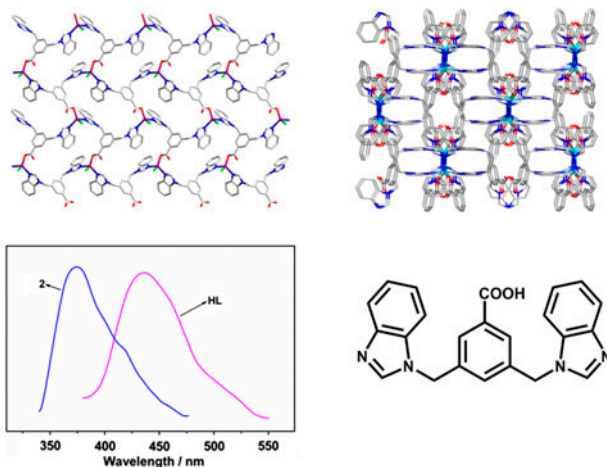
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Co(II) and Cd(II) coordination polymers from a semirigid N- and O-mixed donor-containing ligand: Synthesis, characterization, and property

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Co(II) and Cd(II) salts react with 3,5-bis(benzimidazol-1-ylmethyl)benzoic acid (HL) under hydrothermal conditions to yield two new complexes, $[\text{Co}(\text{L})(\text{Cl})]_n$ (**1**) and $\{[\text{Cd}(\text{L})_2] \cdot 2.5\text{H}_2\text{O}\}_n$ (**2**), which have been characterized by single-crystal and powder X-ray diffractions, IR, element, and thermogravimetric analysis. Complexes **1** and **2** exhibit structural diversity dependent on different metal salts; **1** has 2-D undulating sheet-like structure with (6^3) **hcb** topology and **2** is a 3-D 2-nodal $(3,6)$ -connected **flu** framework with $(4^2 \cdot 6)_2(4^4 \cdot 6^2 \cdot 8^9)$ topology. Luminescence of **2** was investigated.

Keywords: Cobalt and cadmium; Coordination polymers; Characterization; Fluorescence

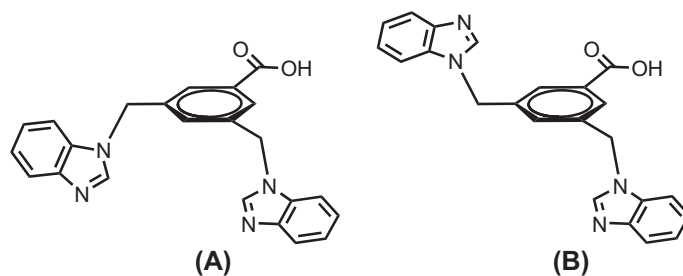
1. Introduction

Coordination polymers have attracted attention from chemists in view of intriguing architectures and topologies as well as potential applications in many fields [1].

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Consequently, many coordination polymers with interesting functional properties have been prepared via employing a variety of organic building blocks and are discussed in some comprehensive reviews [2]. Current efforts have mainly been focused on the exploration of such crystalline materials with intriguing structures and properties, such as catalytic, absorbent, magnetic, and electric properties, and fluorescence and nonlinear optical effects [3]. Functional properties of complexes are largely dependent on the nature of the metal centers and bridging ligands, and their architectures [4]. Previous studies have also shown that many factors can exert subtle influence on the structure of resultant complexes such as the coordination geometry of metal center, the intrinsic nature of organic ligand, anion, solvent, and sometimes the ratio of metal salt to ligand [5]. Thus, it is crucial for exploitation of new solid state materials to try different experimental conditions including employment of various ligands and metal salts for the pursuit of structural diversity. It is still a challenge to synthesize complexes with targeted structures and properties for complicated influential factors in the assembling process, but architectures and properties of complexes seem tunable, providing us an impetus to try more experimental conditions to structurally diversify complexes. Among many influential factors, the intrinsic nature of ligand has been documented to play a crucial role in determining the resulted structures [6].

The ligand 3,5-bis(benzimidazol-1-ylmethyl)benzoic acid (HL) was employed as an organic building block for new frameworks. In previously reported studies, rigid carboxylate-containing ligands such as 1,3-benzenedicarboxylate and 1,3,5-benzenetricarboxylate have been extensively studied in construction of complexes due to their coordination capacities and varied coordination modes [7]; flexible sterically hindered N-donors, especially those containing benzimidazolyl groups such as 1,4-bis(benzimidazol-1-ylmethyl)-2,3,5,6-tetramethylbenzene and 1,3,5-tri(benzimidazol-1-ylmethyl)-2,4,6-trimethylbenzene have also been well employed to assemble complexes [8]. However, a combination of carboxylate and flexible benzimidazolyl groups within one ligand remains less developed. Therefore, we designed the semi-rigid N- and O-mixed donor-containing ligand, HL which can exhibit several distinctive features in construction of complexes. The carboxylate can adopt mutable coordination patterns [9]; HL can have different conformations as illustrated in scheme 1 and the steric hindrance of benzimidazolyl groups may engender subtle impact on the formation of complexes. We, herein, report synthesis and structural characterization of $[\text{Co}(\text{L})_2(\text{Cl})_n]$ (**1**) and $\{[\text{Cd}(\text{L})_2] \cdot 2.5\text{H}_2\text{O}\}_n$ (**2**). The structures depend on metal centers. Luminescence of **2** was also examined.



Scheme 1. Different conformations of HL: (A) syn and (B) anti.

2. Experimental

2.1. Materials and methods

Commercially available chemicals are of reagent grade and were used as received. According to the reported literature [10], a slightly revised experimental procedure was used to synthesize HL, namely, DMSO was used as solvent for higher yields. Elemental analysis of C, H, and N were taken on a Perkin-Elmer 240C elemental analyzer. Infrared spectra (IR) were recorded on a Bruker Vector22 FT-IR spectrophotometer using KBr pellets. Thermogravimetric analysis (TGA) was performed on a simultaneous SDT 2960 thermal analyzer under nitrogen with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$. Powder X-ray diffraction (PXRD) patterns were measured on a Shimadzu XRD-6000 X-ray diffractometer with $\text{Cu K}\alpha$ ($\lambda = 1.5418\text{ \AA}$) radiation at room temperature. 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 is 5 nm; and all the measurements were carried out under the same experimental conditions.

2.2. Preparation of $[\text{Co}(\text{L})(\text{Cl})]_n$ (**1**)

Reaction mixture of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (23.8 mg, 0.1 mM), HL (19.1 mg, 0.1 mM), and NaOH (4.0 mg, 0.1 mM) in 10 mL H_2O was stirred for 30 min, then placed in a 16 mL Teflon-lined stainless steel container and heated at $180\text{ }^{\circ}\text{C}$ for 72 h. Then the oven was shut off and cooled down naturally to ambient temperature. After cooling to room temperature, dark purple block crystals of **1** were obtained in 35% yield (16.6 mg) based on HL. Anal. Calcd for $\text{C}_{23}\text{H}_{17}\text{ClN}_4\text{O}_2\text{Co}$ (%): C, 58.06; H, 3.60; N, 11.78. Found (%): C, 58.32; H, 3.80; N, 11.66. IR (KBr pellet, cm^{-1}): 1616 (s), 1585 (s), 1506 (s), 1462 (s), 1382 (s), 1293 (m), 1263 (m), 1224 (m), 1190 (m), 1120 (w), 1094 (w), 1011 (w), 915 (w), 786 (s), 744 (m), 746 (s), 678 (w).

2.3. Preparation of $\{[\text{Cd}(\text{L})_2] \cdot 2.5\text{H}_2\text{O}\}_n$ (**2**)

Complex **2** was obtained by hydrothermal procedure as used for the preparation of **1** except using CdCl_2 (18.3 mg, 0.1 mM) instead of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and raising the quantity of HL to 0.2 mM. After cooling to room temperature, colorless block crystals of **2** were obtained in 30% yield (27.6 mg) based on HL. Anal. Calcd for $\text{C}_{46}\text{H}_{39}\text{N}_8\text{O}_{6.50}\text{Cd}$ (%): C, 60.04; H, 4.27; N, 12.18. Found (%): C, 60.12; H, 4.33; N, 12.12. IR (KBr pellet, cm^{-1}): 3385 (m), 1617 (m), 1551 (s), 1501 (s), 1455 (s), 1438 (m), 1376 (s), 1290 (m), 1261 (m), 1193 (m), 1011 (w), 977 (w), 909 (w), 806 (w), 778 (m), 738 (s), 669 (w).

2.4. Preparation of single crystals HL (**3**)

Single crystals of HL were obtained accidentally in the hydrothermal reaction of HL (19.1 mg, 0.1 mM) with stoichiometric amount of $\text{MnCl} \cdot 4\text{H}_2\text{O}$ (19.8 mg, 0.1 mM) in DMF/ H_2O (1 : 1, 10 mL) in a 16 mL Teflon-lined stainless steel container at $100\text{ }^{\circ}\text{C}$ for 72 h. After cooling to room temperature, colorless block single crystals of HL (2.86 mg, 0.015 mM) can be obtained.

2.5. X-ray crystallography

The crystallographic data collections for **1**, **2**, and HL were carried out on a Bruker Smart ApexII CCD area-detector diffractometer using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293(2) K. The diffraction data were integrated using SAINT [11], which was also used for intensity corrections for Lorentz and polarization effects. Semi-empirical absorption correction was applied using SADABS [12]. The structures of **1**, **2**, and HL were solved by Direct Methods and all non-hydrogen atoms were refined anisotropically on F^2 by full-matrix least-squares using the SHELXL-97 crystallographic software package [13].

Table 1. Crystallographic data and structure refinement details for **1**, **2**, and HL.

| | 1 | 2 | HL |
|---|--|---|---|
| Empirical formula | C ₂₃ H ₁₇ ClN ₄ O ₂ Co | C ₄₆ H ₃₉ N ₈ O _{6.50} Cd | C ₂₃ H ₂₀ N ₄ O ₃ |
| Formula weight | 475.79 | 920.25 | 400.43 |
| Temperature, K | 293(2) | 293(2) | 293(2) |
| Crystal system | Orthorhombic | Orthorhombic | Triclinic |
| Space group | <i>Pbca</i> | <i>Fddd</i> | <i>P-1</i> |
| <i>a</i> , Å | 11.9277(14) | 18.6387(15) | 9.189(5) |
| <i>b</i> , Å | 16.5330(19) | 25.816(2) | 10.829(5) |
| <i>c</i> , Å | 21.172(2) | 32.706(3) | 11.434(5) |
| α , ° | 90.00 | 90.00 | 65.708(5) |
| β , ° | 90.00 | 90.00 | 80.014(5) |
| γ , ° | 90.00 | 90.00 | 71.386(5) |
| <i>V</i> , Å ³ | 4175.2(8) | 15,738(2) | 981.6(8) |
| <i>Z</i> , <i>D</i> _{Calcd} , Mg/m ³ | 8, 1.514 | 16, 1.554 | 2, 1.355 |
| <i>F</i> (000) | 1944 | 7536 | 420 |
| θ Range, ° | 2.31–28.38 | 1.48–25.01 | 1.96–26.00 |
| Reflections collected | 25,152 | 19,450 | 5421 |
| Independent reflections | 5162 | 3478 | 3800 |
| Goodness-of-fit on F^2 | 1.015 | 1.081 | 1.048 |
| <i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)] ^a | 0.0411 | 0.0596 | 0.0526 |
| <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)] ^b | 0.0973 | 0.1479 | 0.1360 |

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

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

Table 2. Selected bond lengths [Å] and angles [°] for **1** and **2**.

| 1 | | | |
|----------------------|------------|-----------------------|------------|
| Co(1)–Cl(1) | 2.2509(8) | Co(1)–O(1) | 1.9912(17) |
| Co(1)–N(11)#1 | 2.062(2) | Co(1)–N(31)#2 | 2.041(2) |
| Cl(1)–Co(1)–O(1) | 126.21(6) | Cl(1)–Co(1)–N(11)#1 | 104.98(6) |
| Cl(1)–Co(1)–N(31)#2 | 101.03(6) | O(1)–Co(1)–N(11)#1 | 97.65(7) |
| O(1)–Co(1)–N(31)#2 | 117.87(8) | N(11)#1–Co(1)–N(31)#2 | 107.21(8) |
| 2 | | | |
| Cd(1)–N(11) | 2.305(4) | Cd(1)–N(31)#1 | 2.403(5) |
| Cd(1)–O(1)#4 | 2.342(4) | | |
| N(11)–Cd(1)–N(31)#1 | 107.70(15) | N(11)–Cd(1)–N(31)#2 | 84.89(15) |
| N(11)–Cd(1)–N(11)#3 | 163.99(14) | O(1)#4–Cd(1)–N(11) | 80.27(14) |
| O(1)#5–Cd(1)–N(11) | 91.31(15) | N(31)#1–Cd(1)–N(31)#2 | 78.96(17) |
| O(1)#5–Cd(1)–N(31)#1 | 153.73(16) | O(1)#4–Cd(1)–N(31)#1 | 85.04(16) |
| O(1)#4–Cd(1)–O(1)#5 | 116.68(15) | | |

Symmetry transformations used to generate equivalent atoms: for **1**, #1 $1/2 - x, -1/2 + y, z$; #2 $3/2 - x, -1/2 + y, z$; for **2**, #1 $1 - x, 1/2 - y, 1/2 - z$; #2 $-1/4 + x, 1/2 - y, 1/4 + z$; #3 $3/4 - x, y, 3/4 - z$; #4 $1/4 + x, -1/4 + y, 1/2 - z$; #5 $1/2 - x, -1/4 + y, 1/4 + z$.

In **1**, **2**, and HL, all hydrogens on carbon were generated geometrically, while hydrogens on O2 and O3 in HL were found at reasonable positions in the difference Fourier maps and fixed there. The water of solvation in **2** is badly disordered and could not be modeled and has been removed from the structure by SQUEEZE in PLATON. The number of lattice water molecules was determined according to elemental and TGA. According to the literature [14], C–O bond distances in **2** were constrained to specific lengths (1.26 Å for C51–O1 and 1.25 Å for C51–O2), employing instructions of “dfix 1.26 0.01 C51 O1” and “dfix 1.25 0.01 C51 O2.” The details of crystal parameters, data collection, and refinements for the complexes are summarized in table 1; selected bond lengths and angles are listed in table 2.

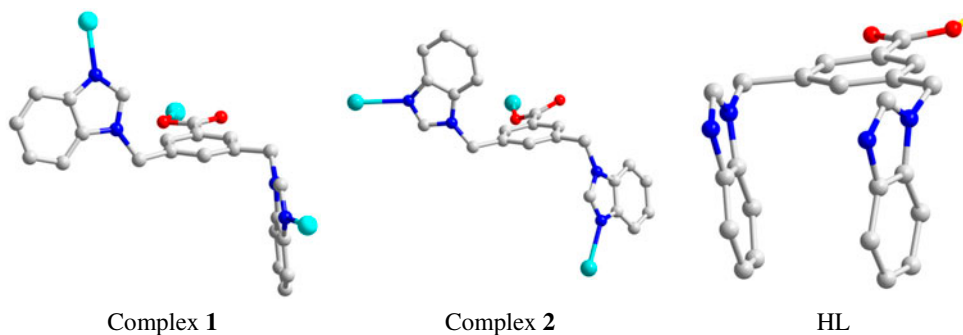
3. Results and discussion

3.1. Preparation

The hydrothermal reactions of stoichiometric amount of Co(II) and Cd(II) salt with HL at 180 °C provided single-crystalline materials **1** and **2**, which are stable in air. Scheme 2 exhibits varied molecule conformations of L[−]/HL in **1**, **2**, and HL.

3.2. Crystal structure description of [Co(L)(Cl)]_n (**1**)

Crystallographic analysis revealed that **1** crystallizes in the orthorhombic system with space group *Pbca* (table 1). It exhibits a 2-D undulating sheet-like structure based on Co(II), Cl[−], and L[−] ligand. The asymmetrical unit is composed of one Co(II), one Cl[−], and one L[−]. Each Co(II) is tetrahedrally coordinated by two benzimidazolyl nitrogens from two different L[−] ligands with bond lengths of Co–N 2.041(2) and 2.062(2) Å (table 2), one carboxylate oxygen [Co–O = 1.9912(17) Å], and one chloride [Co–Cl = 2.2509(8) Å] to furnish a slightly distorted tetrahedral coordination geometry [figure 1(a)]. The corresponding bond distances [Co–O, Co–N, and Co–Cl] are all within normal parameters [15]. The carboxylate in L[−] adopts a $\mu_1-\eta^1:\eta^0$ monodentate mode coordinating to cobalt; each benzimidazolyl is bound to a Co(II) ion, so L[−] in **1** can be defined as $\mu_3-\eta^1:\eta^0-\eta^1-\eta^1$ tridentate coordination. Each L[−] connects three cobalt centers, and each cobalt bridges three L[−] ligands; this



Scheme 2. The coordination modes (or conformation) of L[−]/HL appearing in **1**, **2** and HL.

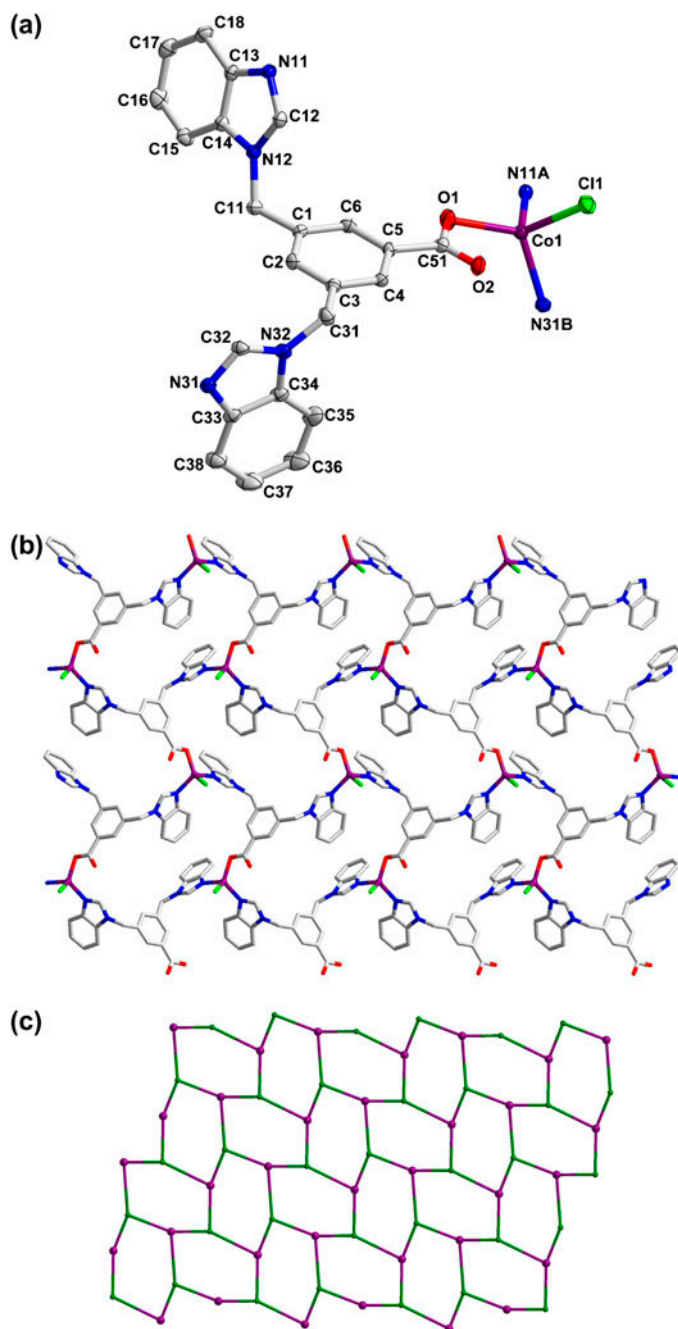


Figure 1. (a) The coordination environment of Co(II) in **1** with the ellipsoids drawn at the 30% probability level. Hydrogens are omitted for clarity. (b) The 2-D network of **1**. (c) Schematic representation of the uninodal 3-connected (6³) 2-D **hcb** net of **1**.

interconnection extends infinitely, leading to formation of the 2-D network structure [figure 1(b)]. For clarity, topological analysis was carried out to simplify the structure of **1**. Each metal center can be viewed as a 3-connected node and each L^- can also be considered as a 3-connector bridge. Then the molecular structure of **1** can be simplified into a uninodal 3-connected **hcb** network with (6^3) topology [figure 1(c)] [16].

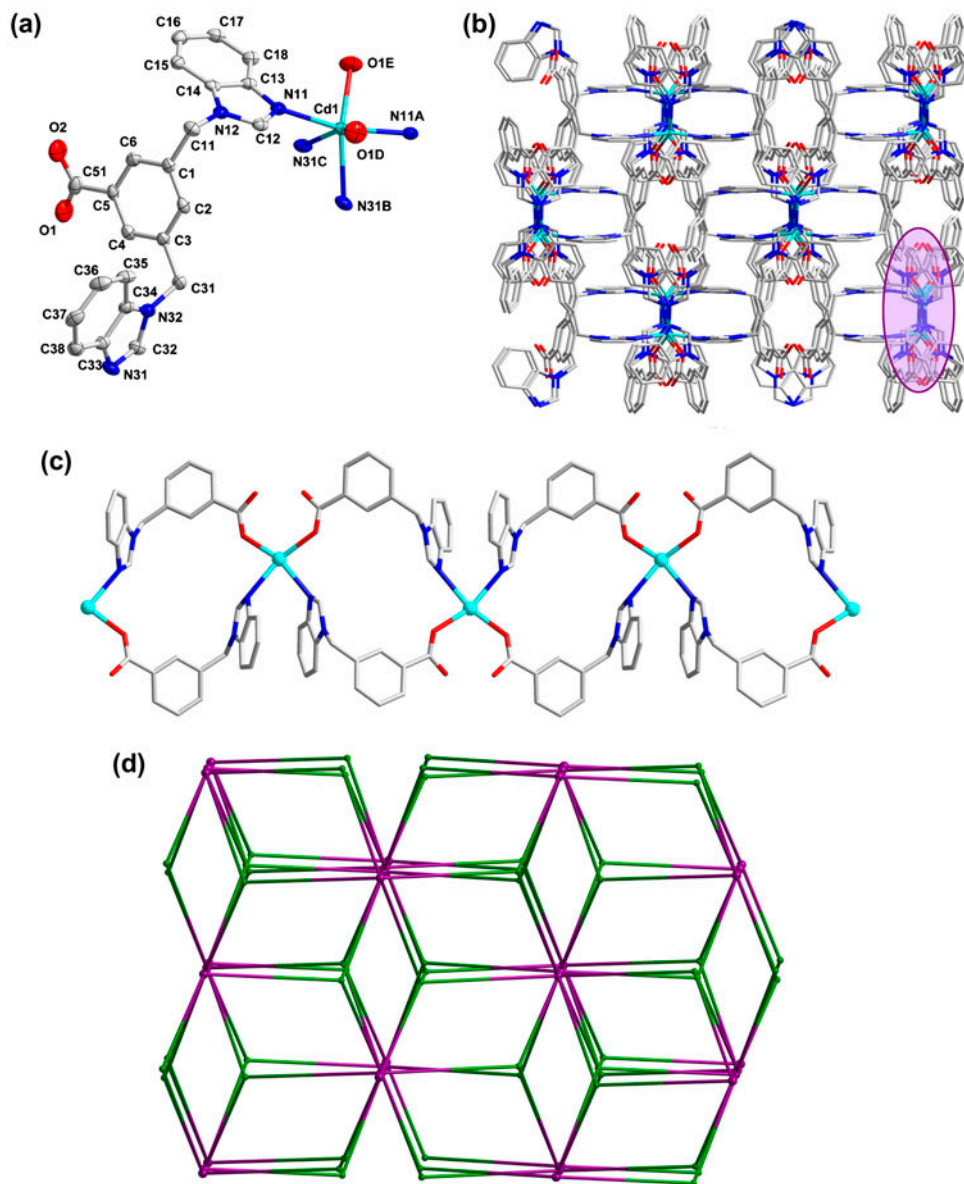


Figure 2. (a) The coordination environment of Cd(II) in **2** with the ellipsoids drawn at the 30% probability level. Hydrogens are omitted for clarity. (b) View of the 3-D framework architecture of **2**. The circle is to emphasize the existing 1-D chain. (c) The 1-D chain in **2**. (d) Schematic representation of 2-nodal (3,6)-connected **flu** network of **2** with $(4^2 \cdot 6)_2(4^4 \cdot 6^2 \cdot 8^9)$ topology.

3.3. Crystal structure description of $\{[Cd(L)_2] \cdot 2.5H_2O\}_n$ (**2**)

When $CdCl_2$ was introduced into the hydrothermal reaction system, **2** was obtained. Single-crystal X-ray structural analysis shows that **2** crystallizes in orthorhombic crystal system with $Fddd$ space group. In its asymmetric unit, there are one L^- , one Cd(II) residing on an inversion center, and 1.25 lattice waters. All the lattice waters were badly disordered and could not be modeled, and were thus removed from the structural mode of **2** by SQUEEZE in PLATON. The suggested number of lattice waters was determined by elemental and TGA. According to calculation by PLATON, total potential solvent area volume of the framework is 970.0 \AA^3 per unit cell volume 15737.0 \AA^3 , namely, accessible pore volume ratio is 6.2%. As shown in [figure 2(a)], each six-coordinate Cd(II) is bound by four benzimidazolyl nitrogens and two carboxylate oxygens from six different L^- ligands and exhibits a distorted octahedral coordination geometry and two apex positions occupied by centrosymmetric N11 and N11A with Cd–N distance of $2.305(4) \text{ \AA}$. The average bond distances around Cd(II), involving Cd–N [$2.305(4)$ and $2.403(5) \text{ \AA}$] and Cd–O [$2.342(4) \text{ \AA}$], is 2.350 \AA , are comparable to previously reported Cd(II) complexes [14]. The carboxylate group in L^- exhibits $\mu_1-\eta^1:\eta^0$ -monodentate coordination and each benzimidazolyl N was bonded to cadmium, and thus L^- has $\mu_3-\eta^1:\eta^0-\eta^1-\eta^1$ coordination as a 3-connector bridging rod in **2**; meanwhile, each cadmium is coordinated by six different L^- ligands. This kind of interconnection expands infinitely to generate a 3-D supramolecular architecture [figure 2(b)]. Within the 3-D framework, there exist different 1-D chains [figure 2(c)], which were circled in [figure 2(b)] for emphasis. To better understand the complicated 3-D structure of **2**, topological analysis was carried out. Each metal center can be viewed as a 6-connected node since it links six different L^- ligands, and each L^- ligand can be considered as a 3-connector bridge. Such connectivity repeats infinitely to simplify the 3-D framework of **2** as a 2-nodal (3,6)-connected flu network with $(4^2 \cdot 6)_2(4^4 \cdot 6^2 \cdot 8^9)$ topology [figure 2(d)].

3.4. Coordination modes of HL and structural comparison of **1** and **2** with previously reported Co(II) and Cd(II) complexes

According to crystal structure and infrared spectroscopy (vide infra), HL was completely deprotonated to generate L^- and displays a different molecule conformation in **1** and **2** (scheme 2). In **1** and **2**, L^- have $\mu_3-\eta^1:\eta^0-\eta^1-\eta^1$ tridentate coordination as 3-connectors to bridge metal(II) ions. In **1** and **2**, L^- ligands display anti-conformation, while in the accidentally obtained crystal structure of HL, its molecular conformation is syn (figure 3).

To further comprehend the coordination chemistry of Co(II) and Cd(II) complexes with benzimidazole/imidazole and carboxylate-containing ligands, we would here like to carry out a structural comparison of **1** and **2** with previously reported Co(II) and Cd(II) complexes with N- and O-mixed donor-containing ligand.

Three Co(II) polymers will be taken, for example: $[Co(L^1)_2] \cdot H_2O$ (**R1**) [$HL^1 = 4$ -(benzimidazol-1-ylmethyl)benzoic acid], $[Co(L^2)(NO_3)]$ (**R2**) and $[Co(L^2)(H_2O)_2]ClO_4$ (**R3**) [$HL^2 = 3,5$ -di(1H-imidazol-1-yl)benzoic acid] [15]. Carboxylate shows $\mu_1-\eta^1:\eta^0$ -monodentate coordination mode in **R1** and $\mu_1-\eta^1:\eta^1$ -chelating in **R2** and **R3**. Co(II) is four-coordinate in **R1** and six-coordinate in **R2** and **R3**. Therefore, as the benzimidazolyl-containing ligand complexes, **1** is more similar to **R1** in carboxylate coordination mode and metal coordination number. As for bond distances around Co(II) atoms, Co–O_{carboxylate} distances are $2.016(2)$ and $2.037(2) \text{ \AA}$ in **R1**, $2.071(2) \text{ \AA}$ in **R2**, and $2.083(2)$ and $2.099(3) \text{ \AA}$ in **R3**; Co–N distances are $2.067(2)$ and $2.079(2) \text{ \AA}$ in **R1**, $2.100(3) \text{ \AA}$ in **R2**, and $2.106(3)$ and $2.115(3) \text{ \AA}$

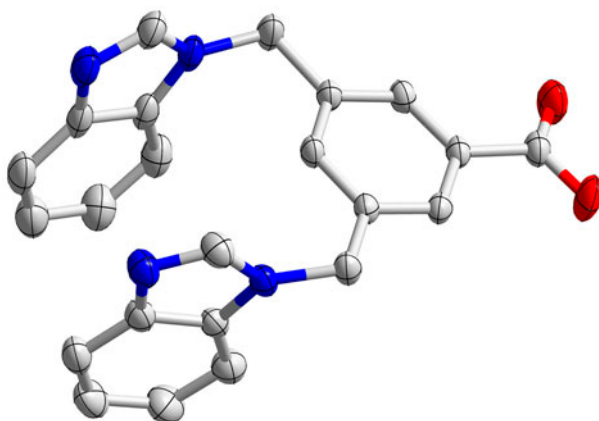


Figure 3. Molecular structure of the single crystal of HL with the ellipsoids drawn at the 30% probability level. Hydrogens are omitted for clarity.

in **R3**. In **1**, the Co–N distances are 2.062(2) and 2.041(2) Å and Co–O_{carboxylate} distance is 1.9912(17) Å, comparable to the aforementioned Co(II) complexes.

Meanwhile, four Cd(II) polymers will also be taken, for example: [Cd(L³)(py)₂(H₂O)] (**R4**), [Cd(L³)(DMF)(H₂O)] (**R5**), [Cd(L³)] (**R6**), and [Cd(L³)] (**R7**) [H₂L³ = 5-(1H-benzotriazol-1-ylmethyl)isophthalic acid] [14]. In **R4–R7**, carboxylate coordination modes are $\mu_2\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1$, $\mu_2\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^0$, $\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1$ and $\mu_3\text{-}\eta^2\text{:}\eta^1\text{:}\eta^1$, respectively. So, only **R5** contains the same $\mu_1\text{-}\eta^1\text{:}\eta^0$ -monodentate mode as in **2**. Metal coordination numbers in **R4–R7** are 7, 6, 5, and 6, respectively. Obviously, **R5** and **R7** are the same as **2**. Cd–O_{carboxylate} distances are 2.387(3), 2.598(3), 2.566(3), and 2.314(3) Å in **R4**, 2.3343(12), 2.3445(11), and 2.2148(11) Å in **R5**, 2.284(2), 2.3273(18), 2.220(18), and 2.1747(17) Å in **R6**, and 2.496(3), 2.246(3), 2.357(3), 2.355(3), and 2.257(3) Å in **R7**. In **2**, the Cd–O distance is [2.342(4) Å] comparable to the aforementioned Cd(II) complexes. Cd–N distances are 2.352(4) and 2.323(4) Å in **R4**, 2.3921(13) Å in **R5**, 2.243(2) Å in **R6**, and 2.275(4) Å in **R7**, which are comparable to the ones in **2** [2.305(4) and 2.403(5) Å].

3.5. PXRD, IR, and TGA

The phase purity of **1** and **2** could be proved by PXRD analyses. As shown in figure 4, each pattern of the bulk sample was in agreement with the simulated pattern from the corresponding single-crystal data.

The absence of bands from 1680 to 1760 cm⁻¹ indicates complete deprotonation of carboxylic groups of HL in **1** and **2**. Characteristic bands of carboxylates for asymmetric stretches are at 1616 and 1585 cm⁻¹ for **1** and 1617 and 1551 cm⁻¹ for **2**. Characteristic bands of carboxylates for symmetric stretches appear at 1462 and 1382 cm⁻¹ for **1** and 1438 and 1376 cm⁻¹ for **2**. The values of $\Delta\nu = \nu_{\text{as}}(\text{COO}) - \nu_{\text{s}}(\text{COO})$ are 178 and 177 cm⁻¹ for **1** and **2**, closely related with the coordination modes of carboxylate, usually following the order $\Delta\nu_{\text{monodentate}} > \Delta\nu_{\text{ionic}} > \Delta\nu_{\text{bridging}} > \Delta\nu_{\text{chelate}}$ [17].

TGA were carried out for **1** and **2**, and the results of TGA are shown in figure 5. For **1**, no obvious weight loss can be observed before the framework decomposition at 400 °C, which further confirms no solvent in the structure. Complex **2** shows continuous weight loss of 4.80% from 55 to 140 °C corresponding to release of lattice water (Calcd 4.89%), which

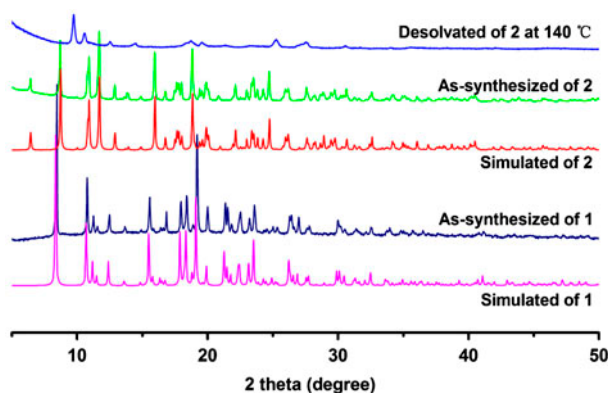


Figure 4. The PXRD patterns of **1** and **2**.

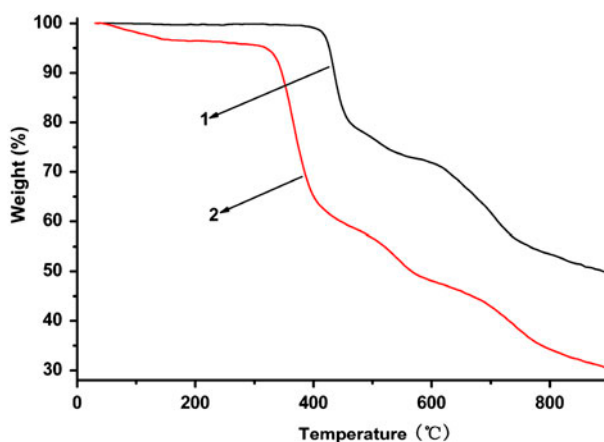


Figure 5. The TGA curves of **1** and **2**.

is just equivalent to 2.5 water molecules. Further decomposition occurred at 312 °C. The continuous decomposition of **1** and **2** does not terminate above 900 °C, so the final residuals for them have not been characterized.

According to TGA, **2** can lose water molecules entirely at 140 °C. PXRD shows that **2** lost its crystallinity after desolvation at 140 °C (figure 4).

3.6. Luminescence

Previous studies have shown that coordination compounds containing d^{10} metal centers such as Cd(II) may exhibit excellent luminescence and have potential applications as photoactive materials [18]. In the present work, luminescence of **2** and HL has been investigated in the solid state at room temperature. As shown in figure 6, intensive fluorescent emission can be observed with emission bands at 372 nm ($\lambda_{\text{ex}} = 320$ nm) for **2** and 442 nm ($\lambda_{\text{ex}} = 360$ nm) for HL. The fluorescent emission of **2** may be tentatively assigned to intra-ligand transition of coordinated ligands, since similar emission was observed for free HL [19]. The observed blue shift of the emission maximum between **2**

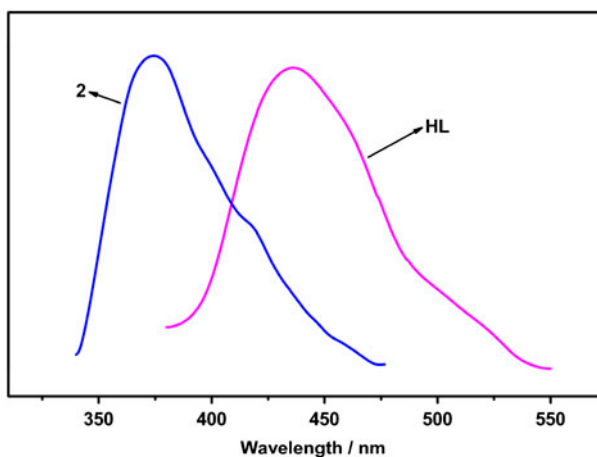


Figure 6. Emission spectra of **2** and HL in the solid state at room temperature.

and HL may be considered to mainly originate from the coordination interactions between metal atoms and ligands [20].

4. Conclusion

A semirigid N- and O-mixed donor ligand, 3,5-bis(benzimidazol-1-ylmethyl)benzoic acid (HL), was selected as organic blocks with potential variable molecule conformation and coordination. Hydrothermal reactions of HL with Co(II) and Cd(II) salts provide two new complexes, $[\text{Co}(\text{L})(\text{Cl})]_n$ (**1**) and $\{[\text{Cd}(\text{L})_2] \cdot 2.5\text{H}_2\text{O}\}_n$ (**2**), exhibiting 2-D and 3-D structures, respectively. The results show that metal center can efficiently influence structures of resultant complexes. Cadmium complex emits intensive fluorescence.

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Supplementary data

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication [CCDC-989494 (for **1**), CCDC-989495 (for **2**), and CCDC-989496 (for HL)]. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336 033; Email: deposit@ccdc.cam.ac.uk). Supplemental data for this article can be accessed <http://dx.doi.org/10.1080/00958972.2014.988149>.

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