Cadmium(II) and cobalt(II) complexes generated from benzimidazole-5-carboxylate: Self-assembly by hydrogen bonding and $\pi-\pi$ interactions

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Abstract

Self-assembly of L^- (HL = benzimidazole-5-carboxylic acid) with Cd(II) and Co(II), respectively, by layer-separating diffusion method at ambient temperature gives rise to two new supramolecular architectures $[(CdL_2 \cdot H_2O) \cdot 2CH_3OH]_n$ (**1**) and $\{[CoL_2(H_2O)_2] \cdot 2H_2O\}_n$ (**2**), both of which are stabilized by the hydrogen bonding interactions and the intermolecular $\pi-\pi$ interactions. **1** crystallizes in the triclinic system, space group $P-1$, with cell parameters $M = 516.78$, $a = 9.084(2)$ Å, $b = 10.063(10)$ Å, $c = 11.533(8)$ Å, $\alpha = 90.21(11)°$, $\beta = 99.48(6)°$, $\gamma = 98.34(9)°$, $V = 1028.4(12)$ Å^3, $Z = 2$, $R_1[I > 2\sigma(I)] = 0.0257$, $wR_2[I > 2\sigma(I)] = 0.0719$. **2** crystallizes in the monoclinic system, space group $C2/c$, with cell parameters $M = 453.27$, $a = 16.119(2)$ Å, $b = 8.8952(13)$ Å, $c = 14.195(2)$ Å, $\beta = 118.507(2)°$, $V = 1788.5(4)$ Å^3, $Z = 4$, $R_1[I > 2\sigma(I)] = 0.0802$, $wR_2 [I > 2\sigma(I)] = 0.1515$. Complex **1** displays a remarkable three-dimensional (3-D) structure with unusual channels generated from the interlayer voids. Complex **2** exhibits the 3-D structure consisting of 1-D zigzag chains. The thermal and fluorescence properties associated with their crystal structures have been measured, and complex **1** displays intense blue emission in the solid state.

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1. Introduction

The understanding of various molecular interactions [1,2] plays a major role in supramolecular chemistry and crystal engineering [2–6]. The knowledge of structural motifs generated by such interactions can be utilized in the design of novel materials with desirable physical and chemical properties [7]. Hydrogen bonding and $\pi-\pi$ stacking interactions are by far the most well-studied interactions [8–12]. These interactions are employed to control the conformational and topological features

of the molecular assembly in the solid state [13–19]. Many scientists have been involved in the analysis of weak interactions focusing on benzimidazole derivatives due to their relevance to DNA, proteins, and other biological systems [20–23]. In the last decade, the structure of benzimidazole-5(6)-carboxylic acid (HL) was widely used in the design of therapeutic agents, such as diuretic and natriuretic [24], antiparasitic, serotonin antagonist, antineoplastic and antiflarial [25], herbicidal, and antihypertensive [26] compounds. The analysis of various interactions in drugs has attracted considerable interest for their wide-ranging antiviral activity and the possibility of forming supramolecular aggregates with transition-metal ions. However, to the

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best of our knowledge, up to now few of attention has been attached on the coordination behavior of benzimidazole-5(6)-carboxylic acid (HL).
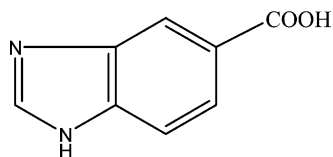
From a structural point of view, L^- possesses three interesting characteristics: (1) the nitrogen atom in benzimidazole ring and the oxygen atoms in carboxylate group are both potential sites of the hydrogen bonding interactions, given that the presence of solvent molecules, such as water or methanol, might serve as possible hydrogen bond donors [27]; (2) due to the benzimidazole rings, we can predict that the $\pi-\pi$ interactions might devote greatly to the formation of crystal structures [28]; (3) the relatively large π-conjugated system in benzimidazole ring might contribute much to the desirable fluorescence property. Herein, we report the construction of two new, self-assembling supramolecular aggregates from cadmium(II) and cobalt(II) complexes of L^- as building blocks, by the hydrogen bonding interactions and the intermolecular $\pi-\pi$ stacking interactions: $[(CdL_2 \cdot H_2O) \cdot 2CH_3OH]_n$ (**1**) and $\{[CoL_2(H_2O)_2] \cdot 2H_2O\}_n$ (**2**).

2. Experimental

2.1. General

HL were purchased from Acros Ltd. Company and used without further purification, the other reagents were commercially available and used as purchased. The IR spectra as KBr discs were recorded on a Magna 750 FT-IR spectrophotometer. C, H, and N analysis were determined on an Elementary Vario ELIII elemental analyzer. Fluorescent spectra were measured on an Edinburgh Instruments analyzer model FL920. Thermal analyses were performed in N_2 from 30 to 1200 °C at 10 °C/min, using a Thermal Analyst 2100 TA Instrument and a SDT 2960 Simultaneous TGA-DTA Instrument.

2.2. Synthesis of $[(CdL_2 \cdot H_2O) \cdot 2CH_3OH]_n$ (*1*)

A solution of L^- (0.016 g, 0.10 mmol) in MeOH (5 mL), which was obtained from the neutralization of L^- and NaOH by the mole ratio 1:1, was carefully layered on a solution of $CdBr_2 \cdot 4H_2O$ (0.034 g, 0.10 mmol) in H_2O (5 mL). Diffusion between the two phases over a period of 2 weeks produced light yellow block crystals. Yield: 0.012 g (46% based on HL);

Elementary analysis: calcd. for $C_{18}H_{20}CdN_4O_7$ (516.79): C, 41.83; H, 3.90; N, 10.84%; found: C, 41.78; H, 3.94; N, 10.81%. IR (KBr, cm^{-1}): 3345 (m), 2925 (w), 1626 (m), 1597 (s), 1538 (s), 1491 (m), 1390 (vw), 1293 (w), 1243 (vw), 1125 (w), 967 (w), 844 (vw), 784 (m), 755 (w), 699 (w), 621 (m), 589 (vw), 532 (w).

2.3. Synthesis of $\{[CoL_2(H_2O)_2] \cdot 2H_2O\}_n$ (*2*)

A solution of L^- (0.016 g, 0.10 mmol) in MeOH (5 mL), which was obtained from the neutralization of L^- and NaOH by the mole ratio 1:1, was carefully layered on a solution of $CoCl_2 \cdot 6H_2O$ (0.024 g, 0.10 mmol) in H_2O (5 mL). Diffusion between the two phases over a period of 1 month produced pink block crystals. Yield: 0.014 g (62% based on HL); Elementary analysis: calcd. for $C_{16}H_{18}CoN_4O_8$ (453.27): C, 42.38; H, 4.00; N, 12.36%; found: C, 42.45; H, 3.94; N, 12.32%. IR (KBr, cm^{-1}): 3414 (s), 3123 (s), 2925 (m), 2865 (m), 1624 (w), 1547 (s), 1496 (m), 1416 (s), 1295 (w), 1262 (vw), 1150 (vw), 1122 (vw), 1034 (vw), 962 (w), 780 (m), 688 (w).

2.4. X-ray crystallography

The single crystal X-ray diffraction measurement was carried out on a Siemens Smart CCD area detector. Intensities of reflections were measured using graphite-monochromatized Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å). with ω scan mode at 273(2) K in the range of $2.05° < \theta < 27.48°$ for **1** and $2.70° < \theta < 25.02°$ for **2**, respectively. Unit cell dimensions were obtained with least-squares refinements, and semi-empirical absorption corrections were applied using SADABS program [29]. The structure was solved by direct method [30] 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 by SHELXL-97 program package [31]. For both **1** and **2**, Water H-atom coordinates were located from difference maps and refined isotropically, other hydrogen atoms were generated geometrically and treated as riding. The crystallographic data for **1–2** are summarized in Table 1, and the selected bond distances and angles are listed in Table 2.

3. Result and discussion

Part of the structure of **1** is shown in Fig. 1. The hexacoordinate Cd(II) ion lies in a slightly distorted environment, consisting of two oxygen donors from one bidentate carboxylate group, one oxygen donor from the other monodentate carboxylate group, one oxygen donor from a water molecule, and two benzimidazole nitrogen atoms from two ligands. The bond distances

Table 1
Crystallographic data for complexes **1** and **2**

Compound	**1**	**2**
Formula	$C_{18}H_{20}CdN_4O_7$	$C_{16}H_{18}CoN_4O_8$
Formula weight	516.78	453.27
Crystal size (mm)	$0.50 \times 0.30 \times 0.30$	$0.40 \times 0.25 \times 0.25$
Crystal system	Triclinic	Monoclinic
Space group	$P\text{-}1$	$C2/c$
a (Å)	9.084(2)	16.119(2)
b (Å)	10.063(10)	8.8952(13)
c (Å)	11.533(8)	14.195(2)
α (°)	90.21(11)	90
β (°)	99.48(6)	118.507(2)
γ (°)	98.34(9)	90
V (Å^3)	1028.4(12)	1788.5(4)
Z	2	4
D_c (Mg m^{-3})	1.669	1.683
μ (mm^{-1})	1.110	1.016
F (000)	520	932
T (K)	173(2)	173(2)
Reflns. collected	7733	2798
Reflns. unique	4585	1562
Parameters	292	150
Goodness-of-fit on F^2	1.185	1.285
R (int)	0.0142	0.0434
R_1, wR_2 $[I>2\sigma(I)]^a$	0.0257, 0.0719	0.0802, 0.1515
R_1, wR_2 (all data)^b	0.0276, 0.0729	0.0935, 0.1577
Max, Min $\Delta\rho$ (e Å^{-3})	0.726, -0.451	0.480, -0.662

$^a R = \Sigma||F_0| - |F_c||)/\Sigma|F_0|$.
$^b _w R = [\Sigma w(F_0^2 - F_c^2)^2/\Sigma w(F_0^2)^2]^{1/2}$.

Table 2
Selected bond lengths (Å) and angles (°) for **1** and **2**

1

Cd(1)–N(2)	2.265(3)	Cd(1)–O(1)	2.374(3)
Cd(1)–O(4A)	2.266(2)	Cd(1)–O(2)	2.390(3)
Cd(1)–N(3B)	2.269(3)	Cd(1)–O(5)	2.391(3)
N(2)–Cd(1)–O(4A)	88.60(8)	N(3B)–Cd(1)–O(2)	105.89(9)
N(2)–Cd(1)–N(3B)	96.13(12)	O(1)–Cd(1)–O(2)	55.22(8)
O(4B)–Cd(1)–N(3B)	107.93(10)	N(2)–Cd(1)–O(5)	171.35(7)
N(2)–Cd(1)–O(1)	92.06(13)	O(4A)–Cd(1)–O(5)	83.89(8)
O(4A)–Cd(1)–O(1)	89.71(11)	N(3B)–Cd(1)–O(5)	90.28(12)
N(3B)–Cd(1)–O(1)	160.66(8)	O(1)–Cd(1)–O(5)	83.63(12)
N(2)–Cd(1)–O(2)	100.71(11)	O(2)–Cd(1)–O(5)	83.01(11)
O(4A)–Cd(1)–O(2)	143.65(8)		

2

Co(1)–O(1)	2.100(6)	Co(1)–N(2A)	2.140(6)
Co(1)–O(1A)	2.100(6)	Co(1)–O(2B)	2.171(6)
Co(1)–N(2)	2.140(6)	Co(1)–O(2C)	2.171(6)
O(1)–Co(1)–O(1A)	180.0(3)	N(2)–Co(1)–O(2B)	95.3(2)
O(1)–Co(1)–N(2)	95.3(2)	N(2A)–Co(1)–O(2B)	84.7(2)
O(1A)–Co(1)–N(2)	84.7(2)	O(1)–Co(1)–O(2C)	91.8(2)
O(1)–Co(1)–N(2A)	84.7(2)	O(1A)–Co(1)–O(2C)	88.2(2)
O(1A)–Co(1)–N(2A)	95.3(2)	N(2)–Co(1)–O(2C)	84.7(2)
N(2)–Co(1)–N(2A)	180.000(1)	N(2A)–Co(1)–O(2C)	95.3(2)
O(1)–Co(1)–O(2B)	88.2(2)	O(2B)–Co(1)–O(2C)	180.0(3)
O(1A)–Co(1)–O(2B)	91.8(2)		

Symmetry codes: For **1**: A: $x-1, y, z$; B: $x, y+1, z$; For **2**: A: $-x+2, -y+2, -z$; B: $x, -y+2, z-1/2$; C: $-x+2, y, -z+1/2$.
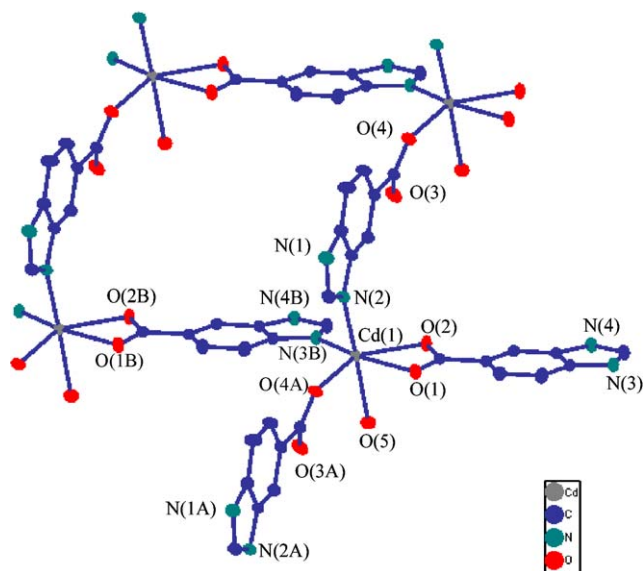

Fig. 1. The 30-membered ring of the (4, 4) networks in **1**; the uncoordinated methanol molecules are omitted for clarity.

around the Cd(II) center are typical of other cadmium-based carboxylates containing benzimidazole nitrogen donor ligands [32,33]. There are two crystallographically independent L$^-$ molecules in **1**. Along the *a*-axis orientation, its carboxylate group coordinates to Cd(II) center as bidentate, while the nitrogen atom bonds to the other Cd(II) center. Instead, L$^-$, along the *b*-axis orientation, bonds to one Cd(II) cation in a monodentate fashion with the nitrogen atom coordinating to the other Cd(II) center. As a result, each L$^-$ molecule is coordinated to two Cd(II) ions, bridging the metal ions to form infinite (4, 4) networks that contain 30-membered rings with a metal ion at each corner and a molecule of L$^-$ at each edge. The lengths of the opposite edges are equal (the edge lengths are 10.063(10) Å and 9.084(2) Å) and the diagonal distances are 14.5(6) Å and 12.5(7) Å.

The intriguing feature of **1** is that the hydrogen bonding interactions play an important structure-directing role. The related hydrogen bonding geometries with the symmetry codes are given in Table 3. All values involved with hydrogen bonding interaction fall in the normal range. Two crystallographically different methanol molecules act as bridges to connect the adjacent sheets with N(1)–H(1)···O(6), O(6)–H(6A)···O(5) of interlayer A and N(4)–H(4)···O(7), O(7)–H(7)···O(3) of interlayer B (Fig. 2b). On the other hand, the intermolecular O(5)–H(5A)···O(2) hydrogen bonding interactions between one oxygen atom of the bidentate carboxylate group and another oxygen atom of the coordinated water further strengthen the link of interlayer B. Besides, the role of π−π interactions cannot be ignored in completing the three-dimensional (3-D) architecture. Interestingly, Cd(II) ions and L$^-$ ligands

Table 3
H-bond lengths (Å) and bond angles (°) for **1** and **2**

1

D–H..A	d(D–H)	d(H..A)	∠ DHA	d(D..A)	Symmetry code
O(6)–H(6A)···O(5)	0.84(0)	1.93(0)	167(3)	2.758(4)	$x+1, y, z$
O(7)–H(7)···O(3)	0.84(0)	1.89(0)	174(7)	2.727(4)	x, y, z
N(1)–H(1)···O(6)	0.87(4)	1.95(4)	169(3)	2.816(3)	$-x+1, -y+1, -z+2$
N(4)–H(4)···O(7)	0.81(4)	1.98(4)	174(4)	2.790(4)	$-x+1, -y+1, -z+1$
O(5)-H(5A)···O(2)	0.78(4)	1.90(4)	176(4)	2.683(3)	$-x, -y+1, -z+1$
O(5)–H(5B)···O(3)	0.92(5)	1.72(5)	162(4)	2.610(3)	$x-1, y, z$
O(5)–H(5B)···O(4)	0.92(5)	2.64(5)	113(3)	3.115(4)	$x-1, y, z$

2

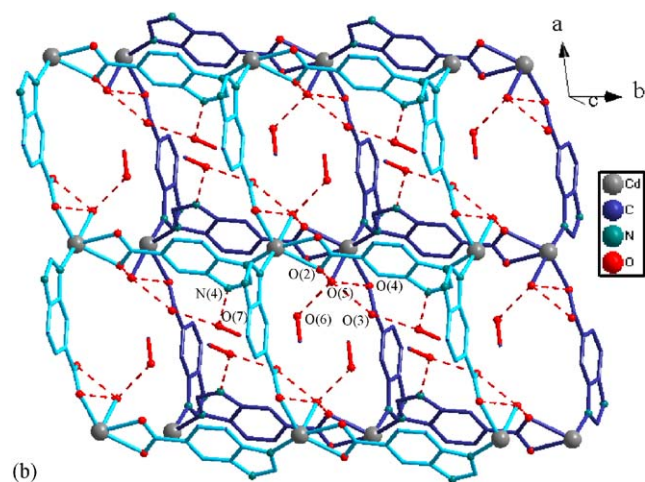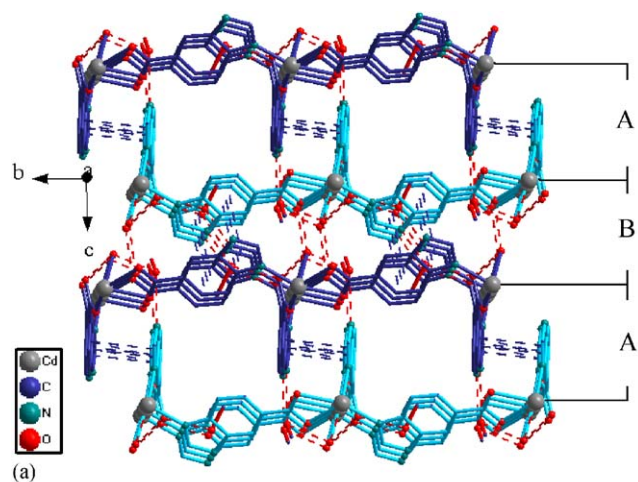| D–H..A	d(D–H)	d(H..A)	∠ DHA	d(D..A)	Symmetry code
O(1)–H(1B)···O(3)	0.82(0)	1.96(0)	146(9)	2.687(7)	$x, -y+2, z-1/2$
N(1)–H(1)···O(3)	0.84(7)	2.00(7)	167(7)	2.829(7)	$x, -y+1, z-1/2$
O(1)–H(1A)···O(4)	0.86(6)	1.87(6)	177(6)	2.732(7)	$x, y+1, z$
O(4)–H(4B)···O(2)	0.84(2)	1.96(3)	164(9)	2.777(7)	$x, y-1, z$
O(4)–H(4B)···O(3)	0.85(2)	1.98(3)	172(2)	2.825(8)	$x+3/2, y-1/2, -z+1/2$

Fig. 2. (a) Three-dimensional framework stabilized by the $\pi-\pi$ interactions and the hydrogen bonding interactions in complex **1**. (b) The hydrogen bonding interactions at interlayer B. ($\pi-\pi$ interactions and hydrogen bonding interactions are indicated by blue and red dot lines, respectively. The methanol molecules are illustrated with red color. The hydrogen atoms in the hydrogen bonding interactions have been omitted for clarity.)

Table 4
Parameters for the $\pi-\pi$ interactions in **1** and **2**

	D_{cc} (Å)	D_{pp} (Å)	α (°)	β (°)
1				
Interlayer A				
Phenyl···Imidazole	3.922(4)	3.524(1)	25.85(4)	0
Phenyl···Phenyl	3.626(4)	3.524(1)	13.04(5)	0
Interlayer B				
Phenyl···Imidazole	3.748(3)	3.400(1)	24.88(5)	0
2				
Phenyl···Imidazole	3.736(3)	3.561(2)	17.75(7)	0
Phenyl···Phenyl	3.692(3)	3.561(2)	15.73(7)	0

β, the angle between the relevant π planes; the other parameters are illustrated in Fig. 3.

form cross arch bridges in almost two perpendicular directions in the same layer. The planes of the interacting rings both at interlayer A and at interlayer B are offset between the adjacent layers with a face-to-face separation with centroid to centroid distances from 3.626(4) to 3.922(4) Å. The offsets of the barycenters separated by interplanar distances from 3.400(1) to 3.524(1) Å indicates the multiple $\pi-\pi$ interactions, which are responsible for the formation of the 3-D network. (Fig. 2a). All related data about the $\pi-\pi$ interactions are summarized in Table 4 (Fig. 3). It is noteworthy that the packing at interlayer B is much tighter than that at interlayer A in term of hydrogen bonding interactions and $\pi-\pi$ interactions. Although it appears difficult to tell which interlayer has the stronger interactions since there are more $\pi-\pi$ interactions at interlayer A but more hydrogen bonding interactions at interlayer B, published calculation for the energy of $\pi-\pi$ interactions is ~2 KJ/mol [28], which is very weak compared to coordination of the transition metal
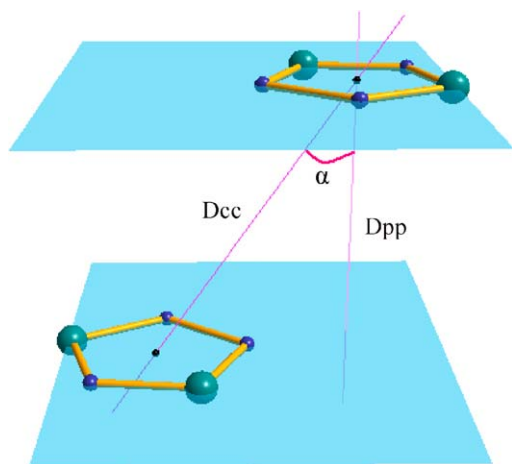
Fig. 3. Scheme for the parameters of $\pi-\pi$ interactions. α, the angle between the ring normal vectors and the centroid–centroid vectors; D_{cc}, the distances between two centroids; D_{pp}, the distance between two π planes.
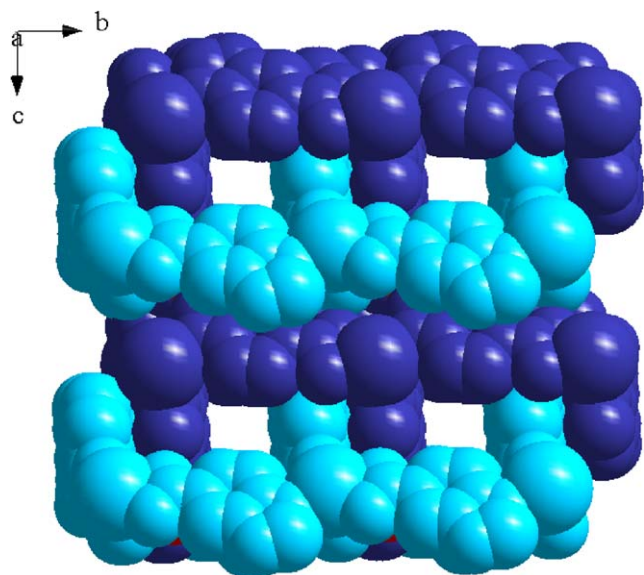

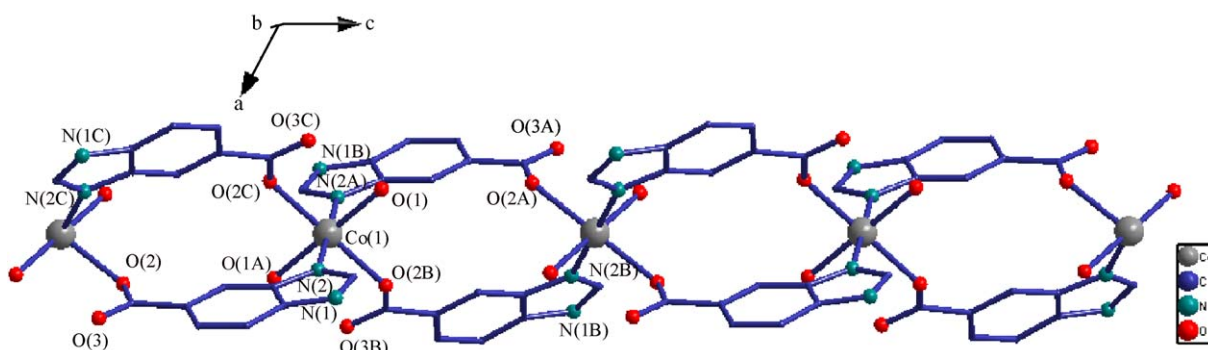Fig. 4. Space-filling views of **1** along the *a*-axis demonstrating the channels in 3-D architecture.

cations and, especially, the hydrogen bonds when it comes to crystal packing. And also, the values of D_{cc} at interlayer A and interlayer B are at the rather high levels. This fact can be also observed from the architecture that there are voids at interlayer A and vice versa at interlayer B.

Further analysis of the crystal packing reveals that complex **1** contains large solvent accessible channels (ca. $5.4 \times 6.5\,\text{Å}$) in the lattice (Fig. 4). It is worth noting that the channels are born from the interlayer voids, and the periphery of the voids comprises not only covalent bonds and dative bonds but also hydrogen bonding and $\pi-\pi$ interactions, differing from most of those previously reported architectures including channels [34–37].

Part of the structure of complex **2** is shown in Fig. 5. Each cobalt ion is coordinated to two *trans* N atoms from two different L^- ligands, to two *trans* O atoms of two distinct carboxylate groups as well as to two water molecules in a *trans* arrangement, leading to an octahedral coordination polyhedron. Selected bond distances in close agreement with previous reported for Co(II) carboxylates containing nitrogen aromatic heterocyclic ligands are given in Table 2 [38–41]. The L^- ligands connect the Co(II) centers resulting in two neutral 1-D polymeric chain propagated in direction of the crystallographic *c*-axis. The dihedral angle between the benzimidazole rings of adjacent zigzag chains is 50.4°. The 1-D zigzag chain presents a period equivalent to the unit cell length *c* of 14.195(2) Å. In addition, the shortest intrachain Co···Co separation is 9.205(1) Å.

As conveniently shown in Fig. 6a, the prominent structural feature of **2** is that the 3-D framework is formed from each adjacent 1-D butterfly-shaped chain extending in a parallel arrangement in the *ab*-plane by hydrogen-bonding and $\pi-\pi$ interactions. Similar to **1**, the multiple $\pi-\pi$ interactions are responsible for the formation of the 2-D architecture as can be seen from Fig. 6b and Table 4. It is necessary to point out that these multiple $\pi-\pi$ interactions in benzimidazole rings are not frequently observed in previously reported

Fig. 5. Two intersecting 1-D zigzag chains in **2** propagate in the direction of *c*-axis; uncoordinated water molecules are omitted for clarity.
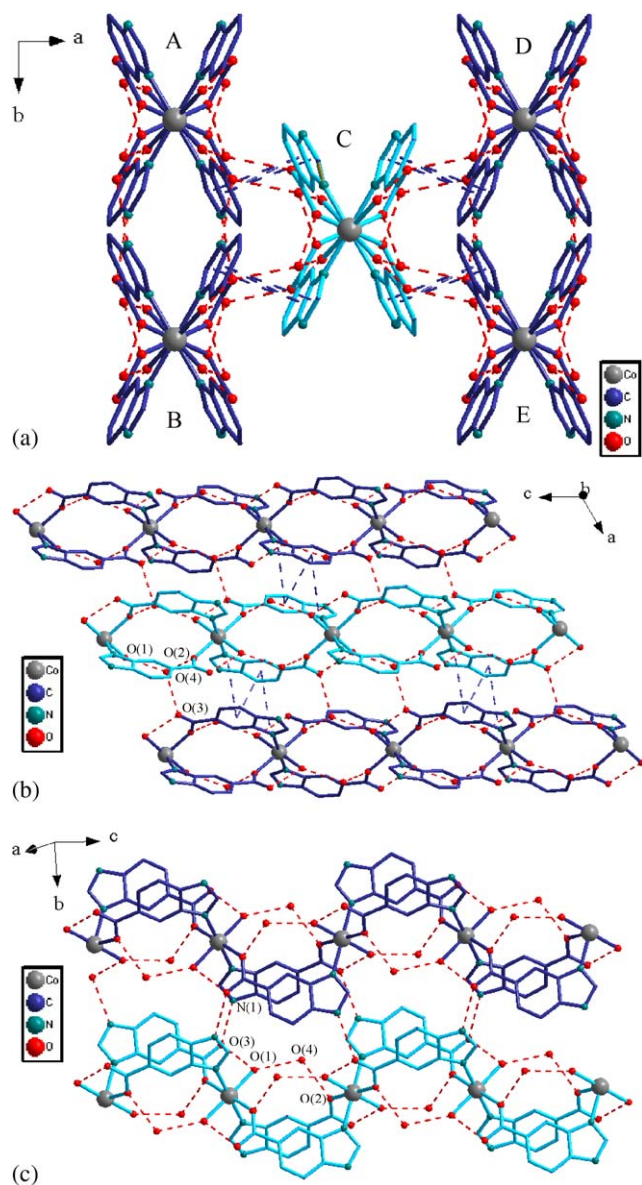
(a)

(b)

(c)

Fig. 6. (a) Three-dimensional framework constructed by hydrogen bonding and $\pi-\pi$ interactions in complex **2**. (b) The hydrogen bonding and $\pi-\pi$ interactions among chain A, C, and D (guest water molecules are omitted for clarity). (c) The hydrogen-bonding interactions between chain A and B. ($\pi-\pi$ interactions and hydrogen-bonding are indicated by blue and red dot lines, respectively. The methanol molecules are illustrated with red color. The hydrogen atoms in the hydrogen bonding interactions have been omitted for clarity.)

Fig. 7. Fluorescent spectra of complex **1** (solid line) and HL (dash line) in the solid state at room temperature.

architectures. In addition, the hydrogen bonding interactions also exert the vital impact on the connection of the adjacent chains (Fig. 6). The intermolecular hydrogen bonding interactions exist between the unligated carboxylic oxygen atom and the nitrogen atom of benzimidazole ring in the other chain, namely, N(1)–H(1)···O(3), correlating the parallel chains along the direction of *b*-axis. By the same token, the
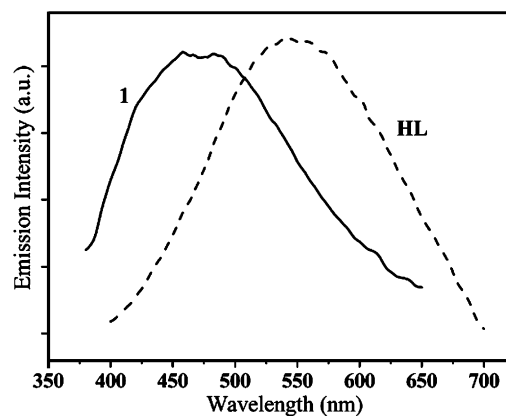
uncoordinated water molecule also bridges the neighboring chains to complete the formation of 3-D structure: O(4)–H(4B)···O(2), O(4)–H(4B)···O(3), and O(1)–H(1A)···O(4).

To study the thermal stability of **1** and **2**, thermogravimetric analysis (TGA) was performed on polycrystalline samples under a nitrogen atmosphere. The result showed the well-seperated weight loss steps: a total weight loss of 9.63% occurred over the temperature range 30–165 °C, corresponding to the loss of one water molecule and one methanol molecule per formula (calcd. 9.69%). Subsequent to this, no obvious weight loss occurred from 165 to 321 °C, following by a loss of 6.75% during 321–378 °C, corresponding to the loss of the one free methanol molecule per formula unit (calcd. 6.20%). Immediately above this point, the samples began to lose the L⁻ ligands, and the whole frameworks collapse in continuous fashion. The TGA result of **2** reveals that all of the coordinated and crystalline water molecules are lost in the temperature range of ~120–254 °C and the dehydrated compound remains stable up to ~312 °C and then upon further heating decomposes to unidentified products.

Metal-organic polymer compounds with a d^{10} configuration (such as Zn^{2+} and Cd^{2+}) have been found to exhibit photoluminescent properties [42]. Here, we examined the photoluminescence of **1** and showed the solid-state emission spectra in Fig. 7. It can be observed that the free HL has an emission at 550 nm in the solid state upon excitation at 380 nm. In contrast, complex **1** exhibits an intense broad emission pure blue with an emission maximum at ca. 480 nm when irradiated with 370 nm. Generally, the intraligand fluorescence emission wavelength is determined by the energy gap between the π and π^* molecular orbitals of the free ligand, which is simply related to the extent of π conjugation in the system [43]. As for the metal complexes, the unexpected blue shift emission compared to free HL can be tentatively assigned to $\pi \rightarrow 5s$ ligand-to-metal charge

transfer (LMCT). The chelation of the ligand to the metal center results in the larger π-conjugated systems and thus influences on the loss of the energy through a radiationless pathway.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 249673 for **1** and no. CCDC 259840 for **2**. 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; E-mail: deposit@ccdc.cam.ac.uk).

Acknowledgments

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