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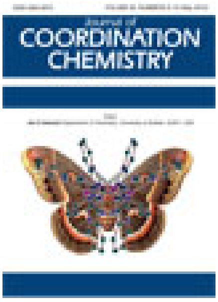

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Self-assembly of three Cd(II) complexes: 0-D, 1-D, and 3-D structures based on 2-(1H-imidazol-1-methyl)-1 H-benzimidazole

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Self-assembly of three Cd(II) complexes: 0-D, 1-D, and 3-D structures based on 2-(1*H*-imidazol-1-methyl)-1*H*-benzimidazole

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Three new complexes, $[Cd(L)I_2]_2$ (**1**), $\{[Cd(L)I_2]\cdot DMF\}_n$ (**2**), and $[Cd_2(L)_4(\mu_2\text{-}I)I(H_2O)]_n$ (**3**), have been obtained through self-assembly of an unsymmetrical ligand 2-(1*H*-imidazol-1-methyl)-1*H*-benzimidazole (L) with Cd(II) salts. Single-crystal X-ray diffraction shows that **1** displays a dimeric structure in which two Cd(II) ions are bridged by two bidentate bridging L. Complex **2** exhibits a 1-D chain structure (···Cd–L–Cd–L···) constructed by L bridging Cd(II) ions. In **3**, the Cd(II) ions are five-connected nodes and linked by L and iodide leading to the 3-D network. Complexes **2** and **3** are synthesized maintaining the same solvents and stoichiometric ratio of metal and ligand at different reaction temperature. The different structures of the complexes indicate that the temperature plays a significant role in construction of the complexes. Luminescent properties of **1**–**3** have been investigated in the solid state at room temperature.

Keywords: Cadmium complex; Crystal structure; Temperature influence

1. Introduction

Metal–organic frameworks [1], especially with *N*-heterocyclic ligands [2] of various structures have been synthesized from transition metal ions with pyridine-based ligands [3], imidazole-based ligands [4], benzimidazole-based ligands [5], and benzotriazole-based ligands [6]. However, it remains a challenge to control metal–organic architectures [7]. Control in constructing complexes with well-defined structures and useful functions still remains a distant prospect in crystal engineering owing to the influence of many factors, such as coordination characteristics of the central metal, geometry and flexibility of ligands, solvent, temperature, ratio of ligand to metal ion, and crystallization method [8–13]. Selection of ligands is extremely important since changing the structure of the ligand can control structures of the complexes [14, 15]. Flexible *N*-heterocyclic ligand, which can adopt various conformations, may induce complexes with different structures under different conditions. 2-(1*H*-imidazole-

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1methyl)-1*H*-benzimidazole (L), which has abundant *N*-donor sites, possesses several interesting characteristics. First, there are three potential nitrogen donors with Mulliken charges, −0.251 for N1, −0.264 for N3, and −0.353 for N4 (scheme 1 in the Supplementary material) [16]. Therefore L can be used as a monodentate or bridging ligand [17]. If the reaction conditions are appropriate or N4 can be deprotonated, it can be used as a tridentate ligand. Second, L can act as both hydrogen-bond acceptors and donors due to the presence of the amino group of benzimidazole ring to construct supramolecular frameworks. Third, the aromatic rings can easily generate π–π interactions and extend the structure to higher dimensionality. Fourth, L has a flexible methylene group, which allows L to have better adaptability, and thus can provide various possible complexes. Cadmium ion is a favorable building block, easy to coordinate to *N* or *O*-containing ligands, and the closed-shell d^{10} Cd–Cd interaction can give intriguing supramolecular motifs and properties [18, 19]. Temperature can dramatically affect the extended structure of a network. In order to further explore the influences of temperature on the formation of complexes several temperature-dependent Cd(II) complexes are prepared.

Here, we use the flexible *N*-heterocyclic ligand 2-(1*H*-imidazole-1-methyl)-1*H*-benzimidazole (L) to assemble with Cd(II) salts and three new complexes $[Cd(L)I_2]_2$ (**1**), $\{[Cd(L)I_2]\cdot DMF\}_n$ (**2**), and $[Cd_2(L)_4(\mu_2\text{-}I)I(H_2O)]_n$ (**3**) are obtained. Their infrared (IR), elemental analysis, single-crystal X-ray diffraction and fluorescent properties have also been investigated.

2. Experimental

2.1. *General information and materials*

2-(1*H*-imidazole-1-methyl)-1*H*-benzimidazole (L) was synthesized according to the literature method [20]. All chemicals were of AR Grade from commercial sources and used without purification. IR data were recorded on a BRUKER TENSOR 27 spectrophotometer with KBr pellets from 400 cm^{-1} to 4000 cm^{-1}. Elemental analyses (C, H, and N) were carried out on a FLASH EA 1112 elemental analyzer. PXRD patterns were recorded using Cu-Kα radiation on a PANalytical X'Pert PRO diffractometer. ^1H NMR spectra were recorded on a Bruker AV-400 spectrometer at room temperature in DMSO. Steady-state fluorescence measurements were performed using a Fluoro Max-P spectrofluorimeter at room temperature in the solid state and in ethanol solution.

2.2. *Synthesis of $[Cd(L)I_2]_2$ (1)*

A water solution (6 mL) of CdI_2 (0.1 mmol) was added dropwise into a 2 mL methanol solution of L (0.1 mmol) to give a clear solution, then the mixture was put aside at room temperature for 7 weeks. Colorless block crystals suitable for X-ray analysis were obtained (yield: 65% based on Cd). Anal. Calcd for $C_{11}H_{10}CdI_2N_4$ (564.43) (%): C, 23.41; H, 1.79; N, 9.93. Found (%): C, 23.32; H, 1.72; N, 9.96. IR (KBr, cm^{-1}): 3232(m), 3121(w), 3092(w), 1601(w), 1518(s), 1465(w), 1402(w), 1326(m), 1277(m), 1237(s), 1194(w), 1090(s), 1028(w), 938(m), 839(m), 750(s), 652(m), 613(w), 478(w), 433(w). ^{1}H NMR (400 mol L^{-1}, DMSO) δ: 12.67(imidazol from benzimidazole, 1H), 8.04(imidazol, 1H), 7.56(benzimidazole, 2H), 7.40(imidazol, 1H), 7.20(benzimidazole, 2H), 7.05(imidazol, 1H), 5.58(CH_2, 2H).

2.3. *Synthesis of $\{[Cd(L)I_2]\cdot DMF\}_n$ (2)*

A mixture of CdI_2 (0.1 mmol), L (0.1 mmol), DMF (1 mL), methanol (2 mL), and water (5 mL) was placed in a 25 mL Teflon-lined stainless steel vessel and heated at 80°C for 72 h, and was then cooled to room temperature. Colorless block crystals were collected, washed with distilled water, and dried in air (yield: 76% based on Cd). Anal. Calcd for $C_{14}H_{17}CdI_2N_5O$ (637.53) (%): C, 26.38; H, 2.69; N, 10.99. Found (%): C, 26.56; H, 2.63; N, 10.84. IR (KBr, cm^{-1}): 3117(m), 1657(s), 1621(m), 1514(s), 1493(w), 1466 (m), 1447(m), 1407(m), 1383(s), 1336(w), 1278(w), 1234(m), 1191(w), 1089(s), 1038(m), 939(w), 895(w), 840(m), 747(s), 667(s), 651(m). ^{1}H NMR (400 mol L^{-1}, DMSO) δ: 12.69(imidazol from benzimidazole, 1H), 8.08(imidazol, 1H), 7.95(DMF, 1H), 7.57(benzimidazole, 2H), 7.42(imidazol, 1H), 7.20(benzimidazole, 2H), 7.07(imidazol, 1H), 5.60(CH_2, 2H), 2.89(DMF, 3H), 2.73(DMF, 3H).

2.4. *Synthesis of $[Cd_2(L)_4(\mu_2\text{-}I)I(H_2O)]_n$ (3)*

The preparation of **3** was similar to that of **2** except that the temperature is increased from 80°C to 160°C. Colorless crystals of **3** were collected (yield: 43% based on Cd). Anal. Calcd for $C_{44}H_{42}Cd_2I_2N_{16}O$ (1289.54) (%): C, 40.98; H, 3.28; N, 17.38. Found (%): C, 40.82; H, 2.33; N, 17.53. IR (KBr, cm^{-1}): 3431(w), 3120(w), 1721(s), 1619(s), 1582(m), 1546(s), 1445(s), 1363(s), 1278(w), 1238(w), 1136(w), 1099(m), 1023(w), 936(w), 849(w), 796(w), 741(s), 722(m), 652(m).

2.5. *Single-crystal structure determination*

A suitable single crystal of each compound was carefully selected and glued to a thin glass fiber. Crystal structure determination by X-ray diffraction was performed on a Rigaku Saturn 724 CCD area detector with graphite monochromator for the X-ray source (Mo-Kα radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 40 mA. The data were collected by ω scan mode at 293(2) K; the crystal-to-detector distance was 45 mm. An empirical absorption correction was applied. The data were corrected for Lorentz-polarization effects. The structures were solved by direct methods and refined by full-matrix least-squares and difference Fourier techniques, based on F^2, using SHELXS-97 [21]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were positioned geometrically and refined using a riding model. All hydrogen atoms were included in the final refinement. Crystallographic parameters and structural refinement for complexes are summarized in table 1. Selected bond lengths and angles are listed in table 2. Hydrogen bonds are listed in table 3.

Table 1. Crystal data and structural refinement of **1**–**3**.

Complex	**1**	**2**	**3**
Empirical formula	$C_{11}H_{10}CdI_2N_4$	$C_{14}H_{17}CdI_2N_5O$	$C_{44}H_{42}Cd_2I_2N_{16}O$
Formula weight	564.43	637.53	1289.54
Temperature (K)	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Tetragonal
Space group	$P2_1/n$	$P2_1/c$	$P4nc$
Unit cell dimensions (Å, °)			
a	9.1195(18)	9.778(2)	11.8957(17)
b	11.965(2)	13.687(3)	11.8957(17)
c	13.522(3)	17.395(5)	14.869(3)
α	90	90	90
β	92.05(3)	120.93(2)	90
γ	90	90	90
Volume (Å^3), Z	1474.4(5), 4	1996.9(8), 4	2104.1(6), 2
F(000)	1032	1192	1256
Crystal size (mm^3)	$0.19 \times 0.18 \times 0.14$	$0.24 \times 0.18 \times 0.14$	$0.18 \times 0.17 \times 0.14$
R(int)	0.0284	0.0333	0.0306
Data/restraints/parameters	3499/0/163	4761/0/210	1801/1/152
Goodness-of-fit on F^2	1.025	1.113	1.066
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0353$, $wR_2 = 0.0916$	$R_1 = 0.0360$, $wR_2 = 0.0746$	$R_1 = 0.0773$, $wR_2 = 0.1945$
R indices (all data)	$R_1 = 0.0376$, $wR_2 = 0.0936$	$R_1 = 0.0408$, $wR_2 = 0.0773$	$R_1 = 0.0777$, $wR_2 = 0.1955$

Table 2. Selected bond lengths (Å) and angles (°) for **1**–**3**.

1					
Cd(1)–N(1)#1	2.246(4)	Cd(1)–N(3)	2.284(4)	Cd(1)–I(1)	2.7260(7)
Cd(1)–I(2)	2.7290(7)				
N(1)#1–Cd(1)–N(3)	90.38(15)	N(1)#1–Cd(1)–I(1)	110.40(11)	N(3)–Cd(1)–I(1)	111.97(10)
N(1)#1–Cd(1)–I(2)	117.95(10)	N(3)–Cd(1)–I(2)	115.25(10)	I(1)–Cd(1)–I(2)	109.72(3)
2					
I(1)–Cd(1)	2.7286(7)	I(2)–Cd(1)	2.7151(7)	Cd(1)–N(1)	2.244(3)
Cd(1)–N(3)#1	2.265(3)				
N(1)–Cd(1)–N(3)#1	110.42(11)	N(1)–Cd(1)–I(2)	108.84(9)	N(3)#1–Cd(1)–I(2)	107.84(7)
N(1)–Cd(1)–I(1)	105.74(8)	N(3)#1–Cd(1)–I(1)	107.43(7)	I(2)–Cd(1)–I(1)	116.52(2)
3					
Cd(1)–O(1)	2.22(5)	Cd(1)–N(1)#1	2.315(4)	Cd(1)–N(1)	2.315(4)
Cd(1)–N(1)#2	2.315(4)	Cd(1)–N(1)#3	2.315(4)	Cd(1)–I(1)	2.640(7)
Cd(2)–N(3)#4	2.433(4)	Cd(2)–N(3)	2.433(4)	Cd(2)–N(3)#5	2.433(4)
Cd(2)–N(3)#6	2.433(4)	Cd(2)–I(2)	2.645(4)	Cd(2)–I(1)#7	2.647(6)
O(1)–Cd(1)–N(1)#1	87.36(17)	O(1)–Cd(1)–N(1)	87.36(17)	N(1)#1–Cd(1)–N(1)	89.878(16)
O(1)–Cd(1)–N(1)#2	87.36(17)	N(1)#1–Cd(1)–N(1)#2	174.7(3)	N(1)–Cd(1)–N(1)#2	89.878(16)
O(1)–Cd(1)–N(1)#3	87.36(17)	N(1)#1–Cd(1)–N(1)#3	89.878(16)	N(1)–Cd(1)–N(1)#3	174.7(3)
N(1)#2–Cd(1)–N(1)#3	89.878(16)	O(1)–Cd(1)–I(1)	180.000(3)	N(1)#1–Cd(1)–I(1)	92.64(17)
N(1)–Cd(1)–I(1)	92.64(17)	N(1)#2–Cd(1)–I(1)	92.64(17)	N(1)#3–Cd(1)–I(1)	92.64(17)
N(3)#4–Cd(2)–N(3)	89.939(9)	N(3)#4–Cd(2)–N(3)#5	89.939(10)	N(3)–Cd(2)–N(3)#5	176.3(3)
N(3)#4–Cd(2)–N(3)#6	176.3(3)	N(3)–Cd(2)–N(3)#6	89.939(10)	N(3)#5–Cd(2)–N(3)#6	89.939(9)
N(3)#4–Cd(2)–I(2)	91.87(14)	N(3)–Cd(2)–I(2)	91.87(14)	N(3)#5–Cd(2)–I(2)	91.87(14)
N(3)#6–Cd(2)–I(2	91.87(14)	N(3)#4–Cd(2)–I(1)#7	88.13(14)	N(3)–Cd(2)–I(1)#7	88.13(14)
N(3)#5–Cd(2)–I(1)#7	88.13(14)	N(3)#6–Cd(2)–I(1)#7	88.13(14)	I(2)–Cd(2)–I(1)#7	180.000(1)

Symmetry transformations used to generate equivalent atoms: For **1**: #1 $-x+2$, $-y+1$, $-z+1$. For **2**: #1 x, $-y-1/2$, $z-1/2$. For **3**: #1 y, $-x+1$, z; #2 $-y+1$, x, z; #3 $-x+1$, $-y+1$, z; #4 $-y$, x, z; #5 $-x$, $-y$, z; #6 y, $-x$, z; #7 $-x+1/2$, $y-1/2$, $z+1/2$.

Table 3. Hydrogen bonds of **1** and **2**.

D–H···A	d(D–H) (Å)	d(H···A) (Å)	d(D···A) (Å)	(D–H···A) (°)
1				
N(4)–H(4A)···I(2)#2	0.86	2.85	3.630(4)	151.4
2				
N(4)–H(4A)···O(1)#3	0.86	1.87	2.701(4)	161.8

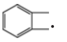
Symmetry transformations used to generate equivalent atoms: For **1**: #2 $x-1/2$, $-y+3/2$, $z-1/2$. For **2**: #3 $-x+1$, $y+1/2$, $-z-1/2$.

3. Results and discussion

3.1. *Synthesis of the complexes*

To explore the influence of temperature on formation of complexes, **1** was obtained by the reaction of CdI_2 (0.1 mmol) with L (0.1 mmol) in methanol and water ($V_{\mathrm{methanol}} : V_{\mathrm{water}} = 1:3$) at room temperature. When the temperature of system **1** is increased from room temperature to 80°C or 160°C, the same complex is obtained. Furthermore, we can also get **1** when solvent is completely water at 80°C or 160°C. However, with the other experimental conditions unchanged, introduction of DMF in the reaction system of **1** ($V_{\mathrm{DMF}} : V_{\mathrm{methanol}} : V_{\mathrm{water}} = 1:2:5$) at 80°C gives a new complex **2**, with a different structure than **1**. When the temperature of system **2** is increased from 80°C to 160°C, a new complex **3** is obtained. This indicates that the outcome of the reactions between the Cd^{2+} and L shows clear dependence on the reaction temperature.

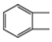
3.2. *IR spectroscopy of 1–3*

The main IR frequencies of **1**–**3** and the band assignments are listed in table 4. Absorption at 3431 cm^{-1} for **3** can be attributed to the stretch of O–H. Absorptions at 3117–3121 cm^{-1} for **1**–**3** can be attributed to Ar–H stretch. Three sharp absorptions at 1601–1621 cm^{-1}, 1514–1546 cm^{-1}, and 1445–1493 cm^{-1} for **1**–**3** are stretching vibrations of C=C and C=N. Absorptions at 1277 cm^{-1} and 1278 cm^{-1} for **1**–**3** are due to C–N stretches. Absorptions at 741–750 cm^{-1} for **1**–**3** correspond to stretching vibrations of . These analyses are consistent with the results of the X-ray diffraction.

3.3. *Crystal structures of complexes*

3.3.1. Crystal structure of $[Cd(L)I_2]_2$ (1). Single-crystal X-ray diffraction analysis reveals that **1** crystallizes in the monoclinic space group $P2_1/n$. Figure 1(a) depicts the coordination geometry of Cd(II). Each Cd(II) is in a distorted tetrahedral coordination environment with two nitrogen atoms (N1A, N3) from two L and two terminal iodides (I1, I2). The bond lengths of Cd1–N are 2.246(4) Å and 2.284(4) Å, which are close to those in $[CdI_2(pbbm)]_2$ (pbbm = 1,1′-(1,5-pentanediyl)bis-1*H*-benzimidazole, Cd–N: 2.247(3) and 2.299(3) Å) [22]. The Cd1–I1 and Cd1–I2 bond lengths are 2.7260(7) and

Table 4. Main IR frequencies of **1**–**3** (cm^{-1}).

Complexes	O–H	Ar–H	C=C, C=N	C–N	
1	–	3121	1601, 1518, 1465	1277	750
2	–	3117	1621, 1514, 1493	1278	747
3	3431	3120	1619, 1546, 1445	1278	741

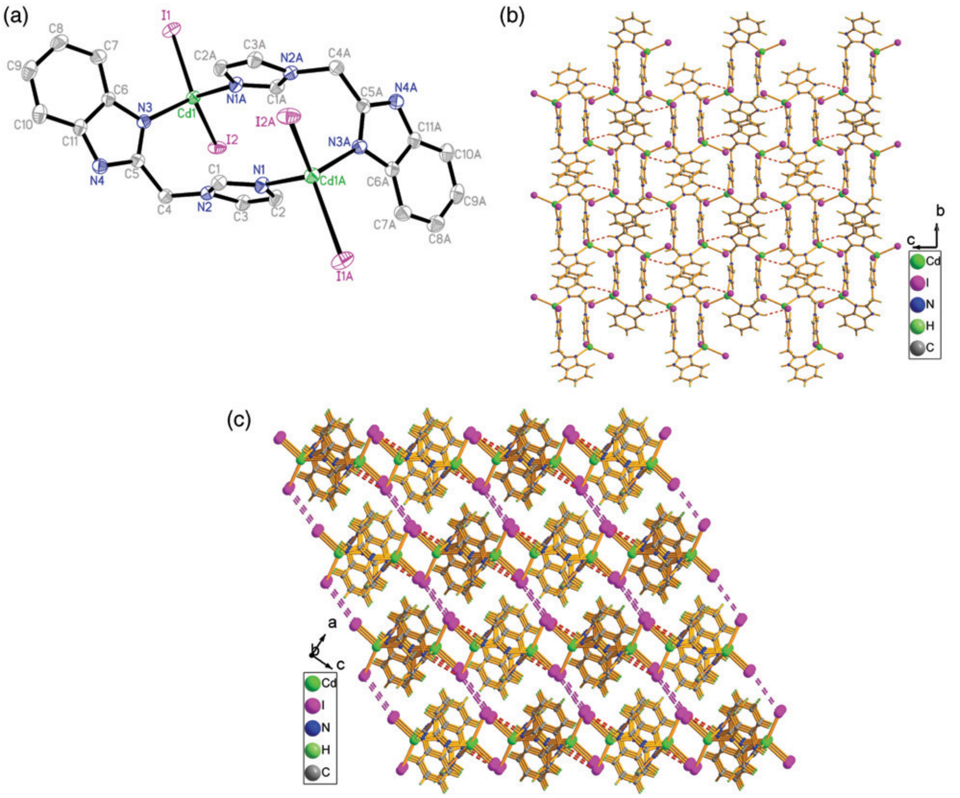


Figure 1. (a) Coordination environment of Cd(II) in **1** with the atom-numbering scheme. Hydrogen atoms are omitted for clarity. (b) View of the 2-D structure of **1** supported by hydrogen bonds. (c) 3-D structure of **1** in the solid state supported by π–π interactions, hydrogen bond, and I $\cdots$ I interactions.

2.7290(7) Å, respectively, normal for terminal iodides. Bond angles around Cd1 range from 90.38(15)° to 117.95(10)°. Cd1 and Cd1A are bridged through two bidentate bridging L in *cis*-conformation (N1–C4–C5–N3 = 72.0°) leading to a dinuclear structure, in which the Cd1 $\cdots$ Cd1A distance is 6.673 Å. There are π–π interactions between benzimidazole rings of adjacent $[Cd(L)I_2]_2$ units [23]. These benzimidazole rings are parallel to each other with distance of 3.3772 Å. In **1** there are N–H $\cdots$ I hydrogen bonds between NH of the benzimidazole ring and I^- with bond length of 3.630(4) Å and bond angle of 151.4°. Binuclear units $[Cd(L)I_2]_2$ are linked by N–H $\cdots$ I hydrogen bonds and π–π interactions forming a 2-D structure along the *bc*-plane (figure 1b). The 2-D networks are further connected into a 3-D supramolecular framework through I···I (4.253 Å) interactions as shown in figure 1(c) [24].

3.3.2. Crystal structure of $\{[Cd(L)I_2]\cdot DMF\}_n$ (2). With the other experimental conditions unchanged, introduction of DMF in the reaction system of **1** at 80°C, **2** is obtained. The architecture of **2** is different from **1**; DMF molecules cocrystallize with the complex, but do not coordinate to Cd(II). X-ray crystallographic analysis reveals that **2** crystallizes in the monoclinic space group $P2_1/c$. As shown in figure 2(a), Cd(II) ions adopt a distorted tetrahedral coordination geometry. Each Cd(II) is four-coordinate with two nitrogen atoms from two L (Cd1–N1 = 2.244(3) Å and Cd1–N3 = 2.265(3) Å) and two terminal iodides (Cd1–I1 = 2.7286(7) Å and Cd1–I2 = 2.7151(7) Å); the Cd–N and Cd–I bond lengths are close to those in **1**. Though the coordination mode of L in **2** is similar to **1**, the conformation of L in **2** is different from that in **1**. The L bridge Cd(II) in *trans*-conformation (N1A–C4A–C5–N3 = 117.7°) to form a 1-D···Cd–L–Cd–L···chain in **2** (figure 2b), while Cd(II) ions are connected through bridging L in *cis*-conformation leading to a dinuclear structure in **1**. The intrachain Cd···Cd distance separated by L is 8.701 Å. In **2** there are N–H···O hydrogen bonds between NH of the benzimidazole ring and O from free DMF with 2.701(4) Å bond length and bond angle of 161.8°. These 1-D chains are connected by hydrogen bonds as well as π–π interactions between benzimidazole rings which are parallel to each other and have an interplanar distance of 3.4518 Å leading to the 3-D structure (figure 2c).

3.3.3. Crystal structure of $[Cd_2(L)_4(\mu_2\text{-}I)I(H_2O)]_n$ (3). When the reaction temperature is increased from 80°C to 160°C, a new complex **3** is isolated with a different structure than **2**. In **3**, there are no uncoordinated DMF molecules. Single-crystal X-ray diffraction analysis reveals that **3** crystallizes in the tetragonal space group $P4nc$. As illustrated in figure 3(a), there are two crystallographical independent Cd(II) centers, one L, two iodides, and one water molecule in which all Cd(II) centers display an approximately octahedral coordination geometry. However, coordinations of two Cd(II) centers are different. Cd1 is bonded to four nitrogen atoms from imidazole rings of four L (Cd1–N1 = Cd1–N1A = Cd1–N1B = Cd1–N1C = 2.315(4) Å), one oxygen from water (Cd1–O1 = 2.22(5) Å), and one bridging iodide (Cd1–I1 = 2.640(7) Å). Cd2 bonds four nitrogen atoms from benzimidazole of four L (Cd2–N3 = Cd2–N3A = Cd2–N3B = Cd2–N3C = 2.433(4) Å), one bridging iodide (Cd2–I1A = 2.647(6) Å), and one terminal iodide (Cd2–I2 = 2.645(4) Å). In Cd1, the apical positions are occupied by water and iodide with the four nitrogen atoms of the four imidazole rings located in the equatorial plane. However, in Cd2 the axial positions are occupied by two iodides; the equatorial plane is still formed by four nitrogen atoms from four benzimidazoles. In **3**, L in *trans*-conformation (N1–C4–C5–N3 = −147.8°) coordinates bidentate bridging to Cd(II) and each Cd is bridged by four L leading to an infinite 2-D (4,4) layer along the *ab*-plane (figure 3b). Adjacent layers are linked in parallel in an ABAB fashion, and these layers further extend to the 3-D structure through interlamellar iodides as pillars. Thus, Cd(II) ions are five-connected nodes, linked by L and iodide to form the 3-D network (figure 3c). Topological analysis shows that **3** can be described

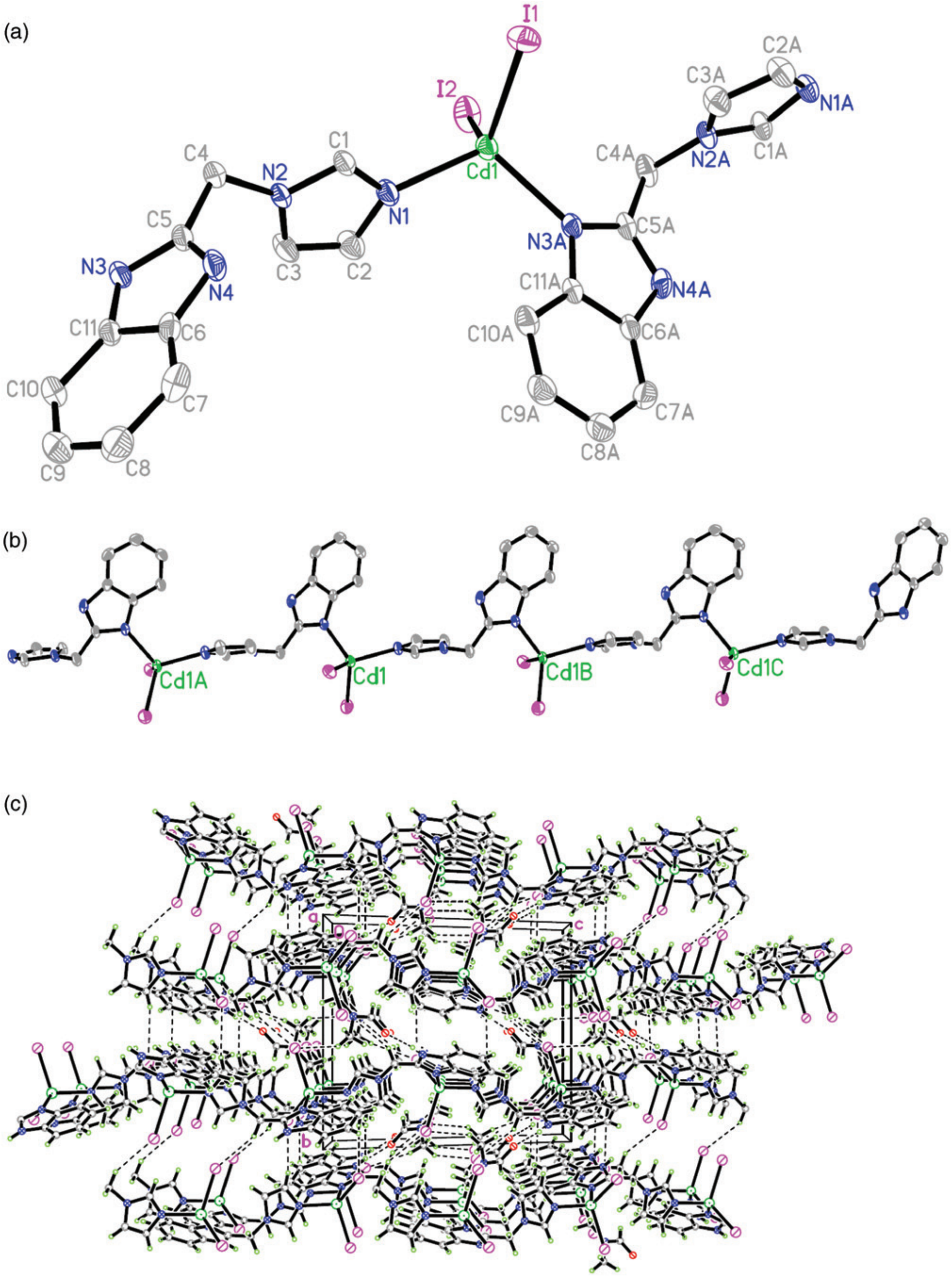


Figure 2. (a) Coordination environment of Cd(II) in **2** with the atom-numbering scheme. (b) View of the 1-D chain structure of **2**. Hydrogen atoms and uncoordinated DMF are omitted for clarity. (c) 3-D structure of **2** in the solid state supported by hydrogen bond and π–π interactions.

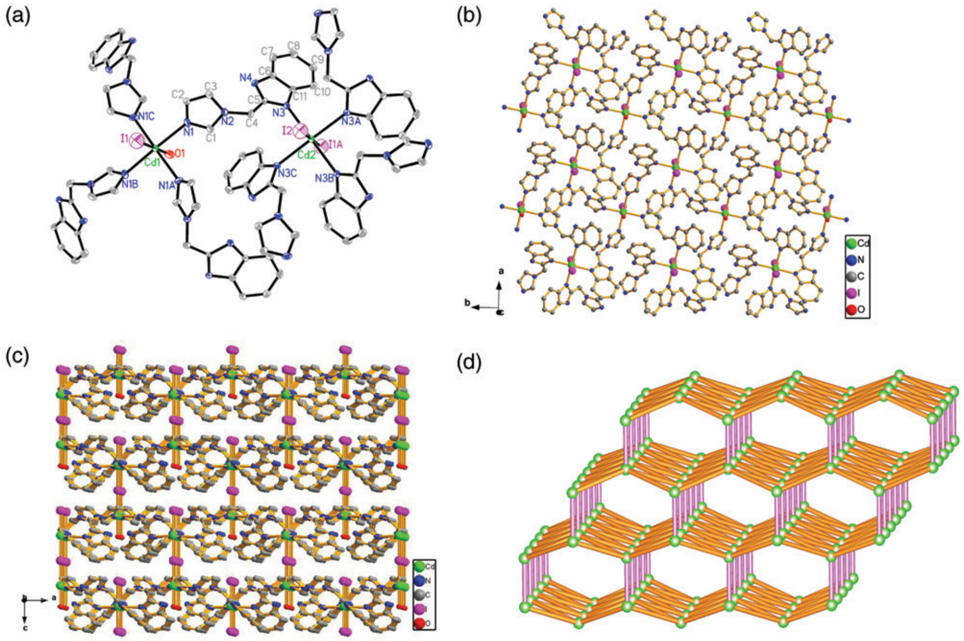


Figure 3. (a) Coordination environment of Cd(II) in **3** with the atom-numbering scheme. Hydrogen atoms are omitted for clarity. (b) View of a 2-D (4,4) layer structure in **3** along the *c*-axis. (c) View of a 3-D structure along the *b*-axis in **3**. (d) Schematic representation of a 5-connected 3-D sqp-net in **3**, which is constructed by iodide pillaring (4,4) sheets.

as a non-uniform 5-connected binodal ($4^4 \cdot 6^6$) topological sqp-network predicted by Wells, as shown in figure 3(d).

3.4. *XRD patterns*

To confirm the phase purity of these complexes, PXRD patterns were recorded for **1**–**3**, and they were comparable to the corresponding simulated ones calculated from the single-crystal diffraction data (figure S1 in the Supplementary material), indicating a pure phase of each bulk sample.

3.5. *Fluorescence*

Polynuclear d^{10} transition metal complexes, such as Zn(II) and Cd(II) complexes, exhibit interesting luminescence [25, 26]. Hence, the solid-state and solution photoluminescent behaviors of L and the solid-state photoluminescent behaviors of **1**–**3** are investigated at room temperature. As illustrated in figure S2(a) and S2(b) (Supplementary material), the free L gives an emission band at 301 nm upon excitation at 285 nm in the solid state and shows an emission band with a maximum at 294 nm ($\lambda_{ex} = 275$ nm, $\varepsilon = 2.574 \times 10^7$ L mol^{-1} cm^{-1}) in ethanol. Comparing bands for free L in solid state and in ethanol solution, the emission spectra bathochromically shift in the solid state. Fluorescence of **1**–**3** (figure S2(c) and S2(d) in the Supplementary material) shows no clear photoluminescence. This may be attributed to the competitive quenching effect of iodide [27].

4. Conclusion

The above discussion indicates that change of solvents or temperature can influence the coordination environment of Cd(II) and the conformations of L, and thus influence the architectures of complexes. Herein we have synthesized three Cd(II) complexes containing a flexible ligand by using different solvents or temperature. Complex **1** displays a dimeric structure in which two Cd(II) ions are bridged through two bidentate bridging L in methanol and water at room temperature. Introduction of DMF at 80°C results in the 1-D polymeric chain complex **2** with bidentate bridging L and uncoordinated DMF. When the temperature of system **2** is increased from 80°C to 160°C, a 3-D network **3** with bidentate bridging ligands is isolated.

Supplementary material

Crystallographic data reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication. CCDC numbers are 8480100, 848099, and 848098. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336 033).

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