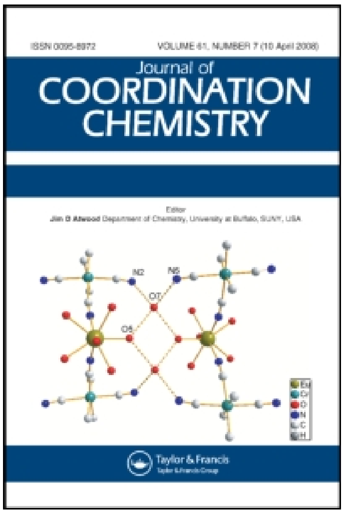

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# Syntheses and crystal structures of two cadmium coordination polymers [Cd(2-mBIM)(NCS)(SCN)]$_{\text{<i>n</i>}}$ and [Cd$_2$(2-mBIM)$_2$(NO$_3$)$_2$(C$_4$H$_4$O$_4$)(H$_2$O)$_5$]*<sub>n</sub>* based on bis(2-methylimidazol-1-yl)methane

Ji-Jun Xu[a]; Zhu Zhu[a]; Shao-Min Shi[a]; Juan Zhou[a]; Chuan-Ming Jin[a]
[a] Hubei Key Laboratory of Pollutant Analysis and Reuse Technology, College of Chemistry and Environmental Engineering, Hubei Normal University, Huangshi, Hubei 435002, P.R. China

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# Syntheses and crystal structures of two cadmium coordination polymers [Cd(2-mBIM)(NCS)(SCN)]$_n$ and [Cd$_2$(2-mBIM)$_2$(NO$_3$)$_2$(C$_4$H$_4$O$_4$)(H$_2$O)$_5$]$_n$ based on bis(2-methylimidazol-1-yl)methane

JI-JUN XU, ZHU ZHU, SHAO-MIN SHI, JUAN ZHOU
and CHUAN-MING JIN*

Hubei Key Laboratory of Pollutant Analysis and Reuse Technology,
College of Chemistry and Environmental Engineering, Hubei Normal
University, Huangshi, Hubei 435002, P.R. China

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Two cadmium(II) coordination polymers, [Cd(2-mBIM)(NCS)(SCN)]$_n$ (**1**) and [Cd$_2$(2-mBIM)$_2$(NO$_3$)$_2$(C$_4$H$_4$O$_4$)(H$_2$O)$_5$]$_n$ (**2**) (2-mBIM = bis(2-methylimidazo-1-yl)methane, C$_4$H$_4$O$_4$ = succinate), have been synthesized and characterized by X-ray diffraction. Complex **1** crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.0770(5)$ Å, $b = 9.4043(4)$ Å, $c = 19.8720(9)$ Å, $\alpha = 101.551(1)°$, $\beta = 93.498(1)°$, $\gamma = 108.484(1)°$, $V = 1562.02(13)$ Å$^3$, and $Z = 2$. Each Cd(II) is octahedrally coordinated and connected with two adjacent Cd(II)'s by double end-to-end thiocyanate bridges, resulting in the formation of 1-D zigzag chains, linked to each other *via* bridging 2-mBIM giving a 2-D supramolecular framework. Complex **2** crystallizes in the monoclinic space group *P2(1)/n* with $a = 12.6543(6)$ Å, $b = 7.7128(4)$ Å, $c = 17.3089(9)$ Å, $\beta = 109.3980(10)°$, $V = 1593.45(14)$ Å$^3$, and $Z = 2$. Cd(II) is coordinated with oxygen and nitrogens from two independent 2-mBIM, in a *cis*-configuration to form a 1-D helical structure. A 3-D supramolecular network comprised of succinate anion bridged 1-D helical chains, and weak hydrogen bonds between dimer waters gave 2-D layers.

*Keywords*: Crystal structure; Cadmium; Bis(2-methylimidazol-1-yl)methane; Thiocyanate bridges; Helix chain

## 1. Introduction

Construction of solid-state architectures and crystal engineering have been rapidly developed in supramolecular chemistry [1–5]. Several molecular architectures have been designed and synthesized by judicious combination of a metal "node" and an organic ligand "spacer". Counter anions and solvents also play significant roles in supramolecular self-assembly. Supramolecular molecules exhibit a variety of 0-D, 1-D, 2-D, and 3-D frameworks, possessing interesting structural features and fascinating functional properties that can be exploited in magnetism, catalysis, nonlinear optics, molecular separation, toxic materials adsorption, and molecular sensors [6–10].

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*Corresponding author. Email: cmjin@email.hbnu.edu.cn; Jincm1999@yahoo.com

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Multidentate N-donor spacer ligands play key roles in molecular materials as well as crystal engineering due to their molecular geometry and flexibility. As examples, 4,4′-bipyridine, 1,2-bis(4-pyridyl)ethane, and *trans*-bis-(4-pyridyl)ethene can form various coordination polymers with distinct structural features [11, 12]. A flexible N-donor ligand, i.e., bis(imidazo-1-yl)methane (BIM), has attracted considerable attention in crystal engineering recently. Several coordination compounds of BIM based on Cu(II), Zn(II), Cd(II), or Ag(I) have been reported [13, 14]. However, to date, bis(2-methylimidazo-1-yl)methane (2-mBIM), as a structural analog of BIM, has not been well studied. We have shown in previous studies that coordination polymers with interesting topological structures can be obtained *via* self-assembling 2-mBIM with proper metal ions [15]. As an extension of previous work, we report herein the synthesis of a thiocyanato-bridged cadmium(II) coordination polymer $[Cd(2\text{-mBIM})(NCS)(SCN)]_n$ (**1**) and a 3-D cadmium(II) coordination polymer $[Cd_2(2\text{-mBIM})_2(NO_3)_2(C_4H_4O_4)(H_2O)_5]_n$ (**2**) containing a helix chain structure.

## 2. Experimental

### 2.1. *Materials and methods*

All the chemicals were commercially available and used as received without purification. 2-mBIM was prepared by the literature method [16]. Fourier transform infrared (FT-IR) spectra were recorded from KBr pellets from 4500 to 400 $cm^{-1}$ on a Bio-Rad FTS 3000 Excalibur series infrared spectrometer. Thermogravimetric analyses (TGA) were made using a thermal analysis (TA) instrument TA50. Samples were heated at 10°C $min^{-1}$ from 40°C to 800°C in a dynamic nitrogen atmosphere. Elemental analyses were performed on a Perkin Elmer 2400 CHN elemental analyzer. Photoluminescence measurements were carried out on crystalline samples at room temperature and the spectra were collected with a Hitachi F-4500 spectrophotometer.

### 2.2. *Synthesis of $[Cd(2\text{-mBIM})(NCS)(SCN)]_n$ (1)*

Ethanol solution (5 mL) of 2-mBIM (89 mg, 0.5 mmol) was slowly diffused into an aqueous solution (5 mL) of $Cd(NO_3)_2 \cdot 4H_2O$ (77 mg, 0.25 mmol) and $NH_4SCN$ (38 mg, 0.5 mmol) in a test tube. Colorless crystals of $[Cd(2\text{-mBIM})(NCS)(SCN)]_n$ were formed at the interface of the solvent in 2 weeks in 62% yield. Anal. Calcd for $C_{22}H_{24}Cd_2N_{12}S_4$ (%): C, 32.64; H, 2.99; and N, 20.76; Found (%): C, 31.94; H, 2.79; and N, 20.92; infrared (IR) (KBr, $cm^{-1}$): $\nu = 3123$ w, 3106 w, 2920 w, 2118 s, 2098 s, 2076 s, 2048 s, 1627 s, 1504 s, 1422 m, 1385 w, 1364 w, 1266 s, 1139 m, 865 w, 748 s, 652 s, and 416 w.

### 2.3. *Synthesis of $[Cd_2(2\text{-mBIM})_2(NO_3)_2(C_4H_4O_4)(H_2O)_5]_n$ (2)*

A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (154 mg, 0.5 mmol), succinic acid (59 mg, 0.5 mmol), NaOH (40 mg, 1.0 mmol), and 2-mBIM (89 mg, 0.5 mmol) was dissolved in $H_2O$ (10 mL). The resultant mixture was transferred and sealed in a 25 mL Teflon-lined stainless steel autoclave under autogenous pressure at 160°C for 2 days and then slowly cooled to room temperature at a rate of 5°C h$^{-1}$. Light yellow crystals of $[Cd_2(2\text{-mBIM})_2(NO_3)_2(C_4H_4O_4)(H_2O)_5]_n$ suitable for X-ray analysis were obtained in 54% yield. Anal. Calcd for $C_{22}H_{40}Cd_2N_{10}O_{15}$ (%): C, 29.05; H, 4.43; and N, 15.40; Found (%): C, 29.60; H, 4.68; and N, 15.72; IR (KBr, cm$^{-1}$): $\nu = 3329$ s, 3131 m, 3021 m, 1595 s, 1542 m, 1504 m, 1455 s, 1369 s, 1312 m, 1269 s, 1218 s, 1142 s, 1087 s, 1039 s, 1002 s, 934 w, 813 m, 755 s, and 669 m.

### 2.4. *Crystal structure determination*

A single crystal of **1** and **2** with dimensions of $0.5 \times 0.3 \times 0.2\,\text{mm}^3$ and $0.2 \times 0.1 \times 0.1\,\text{mm}^3$ were removed from the test tube and covered with a layer of hydrocarbon oil, mounted to a glass fiber, and data were collected at 153(2) K for **1** and 272(2) K for **2**, using a Bruker/Siemens SMART APEX instrument (Mo-K$\alpha$ radiation, $\lambda = 0.71073$ Å). Data were measured using a $\omega$–$\varphi$ scan mode in the range of $3.0 < \theta < 27.5$ for **1**. A total of 15,343 reflections were collected with 7078 unique ones ($R_{\text{int}} = 0.035$), of which 6026 reflections with $I > 2\sigma(I)$ were observed. For **2**, in the range of $1.8 < \theta < 27.0$, a total of 15,782 reflections were collected with 3468 unique ($R_{\text{int}} = 0.0767$), of which 2964 with $I > 2\sigma(I)$ were observed. Cell parameters were retrieved using SMART software [17] and refined using SAINTPlus [18] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS [19]. The structure was solved by direct methods and refined by least squares on $F^2$ using the SHELXTL program package [20] with $R = 0.034$ and $wR = 0.093$ ($w = [\sigma^2(F_o^2) + (0.0492P)^2 + 1.5086P]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3)$, $S = 1.00$, $(\Delta/\delta)_{\max} = 0.002$, $(\Delta\rho)_{\max} = 0.78$, and $(\Delta\rho)_{\min} = -1.19\,\text{e}\,\text{Å}^{-3}$ for **1** and $R = 0.039$, and $wR = 0.092$ ($w = [\sigma^2(F_o^2) + (0.0544P)^2 + 0.0000P]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3)$, $S = 1.00$, $(\Delta/\delta)_{\max} < 0.001$, $(\Delta\rho)_{\max} = 1.16$, and $(\Delta\rho)_{\min} = -0.77\,\text{e}\,\text{Å}^{-3}$ for **2**. All the non-hydrogen atoms were refined anisotropically and hydrogens were placed in riding model. No decomposition was observed during data collection. The crystallographic data and structure refinement parameters are presented in table 1. Selected bond distances and angles are given in tables 2 and 3.

## 3. Results and discussion

### 3.1. *Description of the crystal structure of 1*

Single-crystal X-ray diffraction revealed that **1** crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit of **1** consisted of a cadmium(II), two thiocyanates, and two 2-mBIM. The crystal structure of **1** along with the atom-numbering scheme is shown in figure 1. Each Cd(II) was octahedrally coordinated by two nitrogens from imidazolyl rings of two different 2-mBIM, as well as two nitrogens and two sulfurs from four bridging thiocyanates with Cd–N and Cd–S distances in the ranges of 2.284–2.385 Å and 2.711–2.808 Å, respectively. The octahedral geometry around Cd(II) was slightly distorted with $\text{N} \cdots \text{Cd} \cdots \text{N}$ angles from 84.2° to 100.9°, deviating significantly from the ideal one. Adjacent Cd(II) ions were related by inversion centers and linked by double end-to-end thiocyanate bridges resulting in a 1-D zigzag chain with $\text{Cd} \cdots \text{Cd}$

Table 1. Crystal data and structure refinement summary for $[Cd(2\text{-}mBIM)(NCS)(SCN)]_n$ (**1**) and $[Cd_2(2\text{-}mBIM)_2(NO_3)_2(C_4H_4O_4)(H_2O)_5]_n$ (**2**).

| Compound number | **1** | **2** |
|---|---|---|
| Empirical formula | $C_{22}H_{24}Cd_2N_{12}S_4$ | $C_{22}H_{40}Cd_2N_{10}O_{15}$ |
| CCDC deposit number | 689346 | 689344 |
| Formula weight | 809.57 | 909.44 |
| Temperature (K) | 153(2) | 292(2) |
| Wavelength (Å) | 0.71073 | 0.71073 |
| Crystal system | Triclinic | Monoclinic |
| Space group | $P\bar{1}$ | *P2(1)/n* |
| Unit cell dimensions (Å, °) | | |
| $a$ | 9.0770(5) | 12.6543(6) |
| $b$ | 9.4043(4) | 7.7128(4) |
| $c$ | 19.8720(9) | 17.3089(9) |
| $\alpha$ | 101.551(1) | 90 |
| $\beta$ | 93.498(1) | 109.3980(10) |
| $\gamma$ | 108.484(1) | 90 |
| Volume (Å$^3$), $Z$ | 1562.02(13), 2 | 1593.45(14), 2 |
| Calculated density (g cm$^{-3}$) | 1.721 | 1.895 |
| Absorption coefficient (mm$^{-1}$) | 1.66 | 1.42 |
| $F(000)$ | 800 | 916 |
| Crystal size (mm$^3$) | $0.50 \times 0.31 \times 0.20$ | $0.20 \times 0.10 \times 0.08$ |
| $\theta$ range for data collection (°) | 3.0–27.5 | 2.4–27.60 |
| Limiting indices | $-11 \le h \le 11$; $-12 \le k \le 11$; $-25 \le l \le 25$ | $-14 \le h \le 16$; $-9 \le k \le 9$; $-22 \le l \le 22$ |
| Reflections collected | 15,343 | 15,782 |
| Independent reflection | 7078 [$R$(int) = 0.035] | 3468 [$R$(int) = 0.085] |
| Absorption correction | SADABS | SADABS |
| Max. and min. transmission | 0.732 and 0.490 | 0.895 and 0.764 |
| Refinement method | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 7078/102/605 | 3468/0/246 |
| Goodness-of-fit on $F^2$ | 1.00 | 1.00 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.0341$, $wR_2 = 0.0891$ | $R_1 = 0.0394$, $wR_2 = 0.0861$ |
| $R$ indices (all data) | $R_1 = 0.0425$, $wR_2 = 0.0931$ | $R1 = 0.0476$, $wR_2 = 0.0919$ |
| Largest difference peak and hole (e Å$^{-3}$) | 0.78 and −1.19 | 1.16 and −0.77 |

distances of 5.795 and 5.765 Å (figure 2). In the double end-to-end thiocyanate-bridged $Cd(NCS)_2Cd$, the two end-to-end thiocyanate bridges were parallel and thus formed a $(NCS)_2$ plane. The dihedral angle between the planes of $(NCS)_2$ and N–Cd–S plane was 3.5°, indicating a slight deformation toward the chair conformation of the Cd–$(NCS)_2$–Cd ring (figure 2). The dihedral angle between two adjacent $Cd(NCS)_2Cd$ planes in the same zigzag chain was 57.8°. Such 1-D zigzag chains were interconnected to form a 2-D network *via* 2-mBIM ligands, which bridged two Cd(II) centers of adjacent zigzag chains (figure 3). The 2-mBIM ligands are disordered and each Cd was coordinated with two 2-mBIM ligands in a *cis*-configuration to form a helix structure along the *a*-axis (figure 3). This structure is different from the structures of the previously reported $[Cd(SCN)_2L_2]$ (where L are nitrogen-containing ligands) [21], which showed *trans*-coordination for nitrogen-containing ligands. Complex **1** was air-stable and insoluble in water and common organic solvents. IR spectra of **1** clearly showed the presence of bridging thiocyanate. The peaks at 2048, 2076, 2098, and 2118 cm$^{-1}$ can be attributed to C=N of thiocyanate, suggesting the presence of end-to-end NCS-bridged ligands [22]. The bands at 1627, 1504, and 1422 cm$^{-1}$ can be assigned to C=C and C=N groups in the aromatic rings.

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

| | | | |
|---|---|---|---|
| Cd(1)–N(1) | 2.329(3) | Cd(1)–N(5) | 2.342(5) |
| Cd(1)–N(10)$^{i}$ | 2.322(3) | Cd(1)–N(9)$^{ii}$ | 2.324(3) |
| Cd(1)–S(1) | 2.7583(9) | Cd(1)–S(2) | 2.7106(9) |
| Cd(2)–N(4) | 2.313(4) | Cd(2)–N(12)$^{iii}$ | 2.284(4) |
| Cd(2)–N(11)$^{iv}$ | 2.296(3) | Cd(2)–N(8)$^{v}$ | 2.385(5) |
| Cd(2)–S(4) | 2.7555(10) | Cd(2)–S(3) | 2.8084(11) |
| N(10)$^{i}$–Cd(1)–N(9)$^{ii}$ | 84.20(12) | N(10)$^{i}$–Cd(1)–N(1) | 92.55(12) |
| N(1)–Cd(1)–N(9)$^{ii}$ | 85.24(12) | N(10)$^{i}$–Cd(1)–N(5) | 96.27(16) |
| N(5)–Cd(1)–N(9)$^{ii}$ | 173.70(15) | N(1)–Cd(1)–N(5) | 88.47(15) |
| N(10)$^{i}$–Cd(1)–S(2) | 98.47(8) | S(2)–Cd(1)–N(9)$^{ii}$ | 88.95(9) |
| N(1)–Cd(1)–S(2) | 166.97(10) | N(5)–Cd(1)–S(2) | 97.18(13) |
| N(10)$^{i}$–Cd(1)–S(1) | 178.70(9) | S(1)–Cd(1)–N(9)$^{ii}$ | 96.87(8) |
| N(1)–Cd(1)–S(1) | 86.80(9) | N(5)–Cd(1)–S(1) | 82.59(13) |
| S(1)–Cd(1)–S(2) | 82.31(3) | N(12)$^{iii}$–Cd(2)–N(11)$^{iv}$ | 88.47(15) |
| N(12)$^{iii}$–Cd(2)–N(4) | 99.45(13) | N(11)$^{iv}$–Cd(2)–N(4) | 85.50(12) |
| N(12)$^{iii}$–Cd(2)–N(8)$^{v}$ | 100.94(18) | N(11)$^{iv}$–Cd(2)–N(8)$^{v}$ | 168.89(15) |
| N(8)$^{v}$–Cd(2)–N(4) | 87.12(15) | N(12)$^{iii}$–Cd(2)–S(4) | 96.72(10) |
| N(11)$^{iv}$–Cd(2)–S(4) | 85.11(9) | N(4)–Cd(2)–S(4) | 161.05(10) |
| N(8)$^{v}$–Cd(2)–S(4) | 99.48(13) | N(12)$^{iii}$–Cd(2)–S(3) | 173.80(11) |
| N(11)$^{iv}$–Cd(2)–S(3) | 95.16(8) | N(4)–Cd(2)–S(3) | 85.87(10) |
| N(8)$^{v}$–Cd(2)–S(3) | 76.01(14) | S(4)–Cd(2)–S(3) | 78.63(4) |

Symmetry transformations used to generate equivalent atoms: $^{i}-x+2, -y+2, -z+1$; $^{ii}-x+1, -y+2, -z+1$; $^{iii}-x, -y+1, -z+2$; $^{iv}-x+1, -y+1, -z+2$; and $^{v}x-1, y, z$.

Table 3. Bond lengths (Å) and angles (°) for **2**.

| | | | |
|---|---|---|---|
| Cd(1)–O(6) | 2.256(2) | Cd(1)–N(1) | 2.317(3) |
| Cd(1)–O(3) | 2.381(3) | Cd(1)–O(2) | 2.386(3) |
| Cd(1)–O(1) | 2.474(3) | Cd(1)–N(4)$^{i}$ | 2.317(3) |
| O(6)–Cd(1)–N(1) | 91.33(9) | O(6)–Cd(1)–N(4)$^{i}$ | 172.00(9) |
| N(1)–Cd(1)–N(4)$^{i}$ | 93.95(9) | O(6)–Cd(1)–O(3) | 97.51(9) |
| N(1)$^{i}$–Cd(1)–O(3) | 122.57(9) | N(4)$^{i}$–Cd(1)–O(3) | 84.69(9) |
| O(6)–Cd(1)–O(2) | 83.37(9) | N(1)$^{i}$–Cd(1)–O(2) | 157.95(10) |
| N(4)$^{i}$–Cd(1)–O(2) | 89.51(9) | O(3)–Cd(1)–O(2) | 79.42(9) |
| O(6)–Cd(1)–O(1) | 83.09(9) | N(1)–Cd(1)–O(1) | 82.23(10) |
| N(4)$^{i}$–Cd(1)–O(1) | 91.67(10) | O(3)–Cd(1)–O(1) | 155.08(10) |

Symmetry transformations used to generate equivalent atoms: $^{i}-x+3/2, y-1/2, -z+1/2$.

### 3.2. *Description of the crystal structure of 2*

Single-crystal X-ray diffraction revealed that **2** crystallizes in a monoclinic space group *P2(1)/n*. The asymmetric unit of **2** consists of a cadmium(II), one nitrate, two coordinated waters, a half uncoordinated water, a half succinate, and a 2-mBIM ligand. The crystal structure of **2** together with the atom-numbering scheme is shown in figure 4. Each Cd(II) was octahedrally coordinated by two nitrogens of imidazolyl rings from two individual 2-mBIM ligands, an oxygen (O3) of nitrate, a monodentate oxygen (O6) of succinate, and two independent waters (O1 and O2). The octahedral geometry around Cd(II) was slightly distorted with N–Cd–N, N–Cd–O, and O–Cd–O angles being in the range of 75.89(10)°–97.51(9)°, deviating significantly from ideal.

Two independent 2-mBIM ligands were coordinated with each Cd through a *cis*-configuration and each 2-mBIM bridged two different Cd's with a Cd1–Cd1A distance 9.772 Å to form a 1-D helical structure along the *b*-axis (figure 5). The pitch of

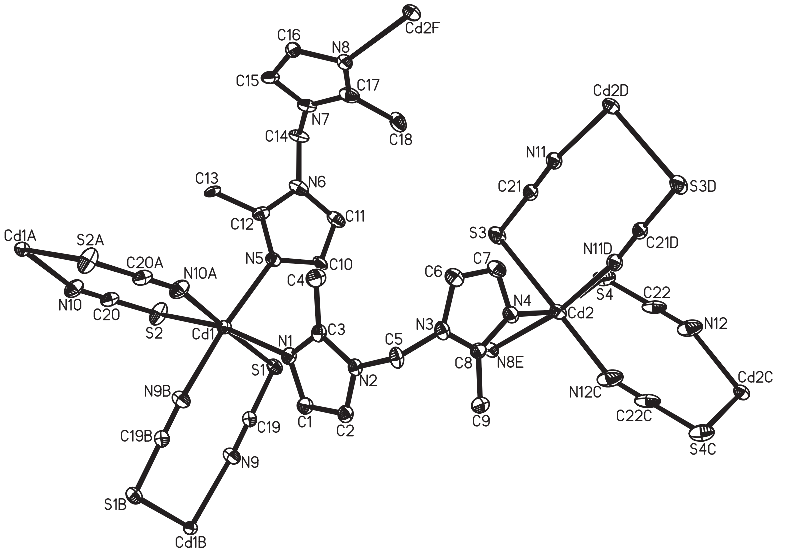

Figure 1. ORTEP of **1** with atom-numbering scheme. The thermal ellipsoids were drawn at 30% probability. Hydrogen atoms were omitted for clarity.

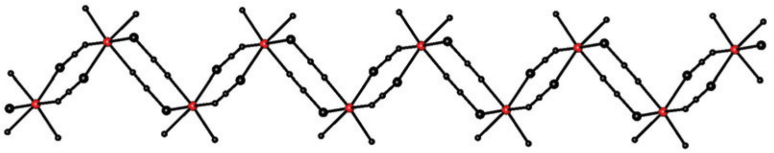

Figure 2. The double end-to-end thiocyanate-bridged 1-D zigzag chain with a slight chair conformation of $Cd(NCS)_2Cd$ units in **1**.

the helix was 7.713 Å. Such 1-D helix structures subsequently formed a 2-D layer by monodentate succinate which connected two Cd(II) centers between two adjacent helical chains (figure 5). The uncoordinated water (O8) was encapsulated in the middle of two adjacent succinates through hydrogen bond between water O8 and uncoordinated carboxylic oxygen O7 (figure 6). The 2-D layers further interacted with each other through weak hydrogen bonds (C–H $\cdots$ O and O–H $\cdots$ O) to form an overall 3-D supramolecular network (table 4).

IR spectra of **2** showed absorption bands resulting from skeletal vibrations of aromatic rings in the range of 1455–1595 $cm^{-1}$. Relatively weak absorptions around 3131 and 3027 $cm^{-1}$ were probably due to C–H vibrations of aromatic rings as well as methylene groups bridging two imidazole rings, respectively, while bands in the range 669–1087 $cm^{-1}$ can be assigned to the bending of C–H groups in or out of the aromatic plane.

### 3.3. *Thermal and photoluminescent properties of 1 and 2*

TGA under nitrogen showed that **1** possesses a high decomposition temperature at 285°C. The 41.4% weight loss from 285°C to 330°C can be attributed to the loss of

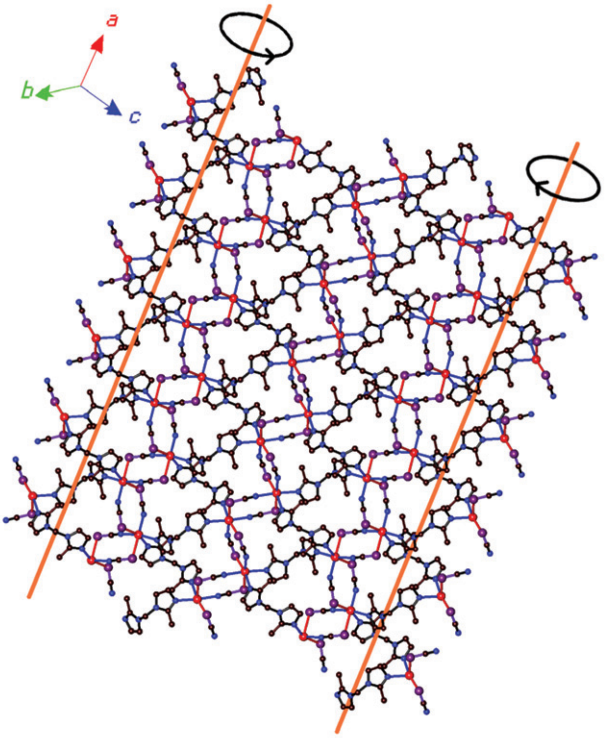

Figure 3. The 2-D network containing a helix *via cis*-coordination of 2-mBIM to Cd in **1**.

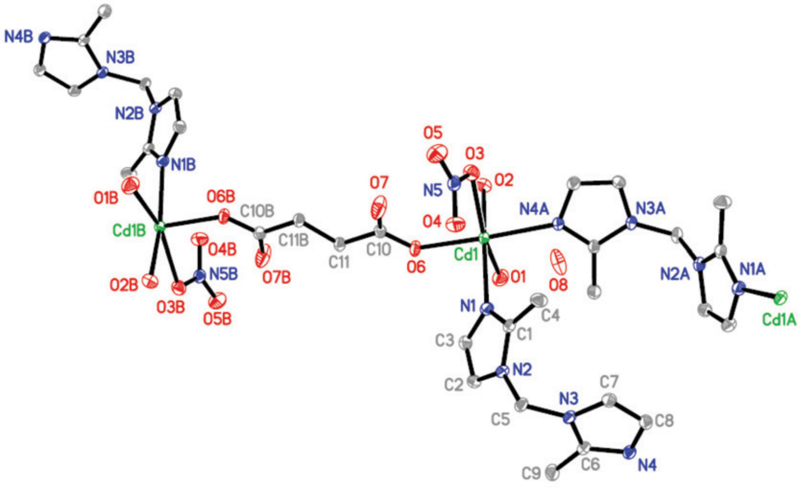

Figure 4. View of the local coordination environment around Cd at 30% probability ellipsoids in **2**.

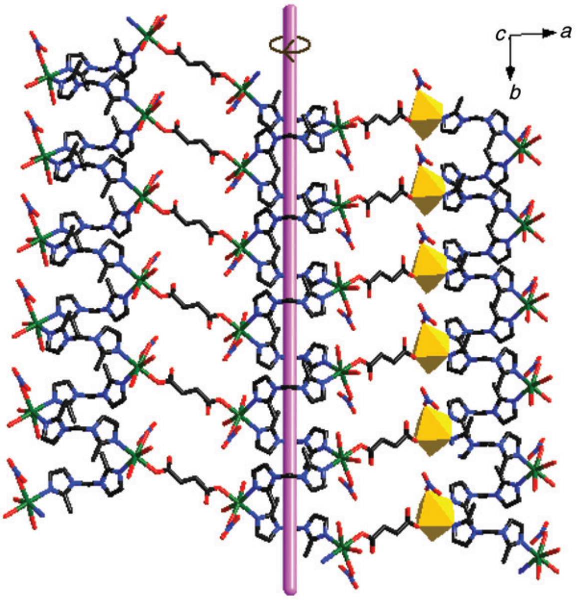

Figure 5. View of the 2-D layer comprised of 1-D helical chains in **2**.

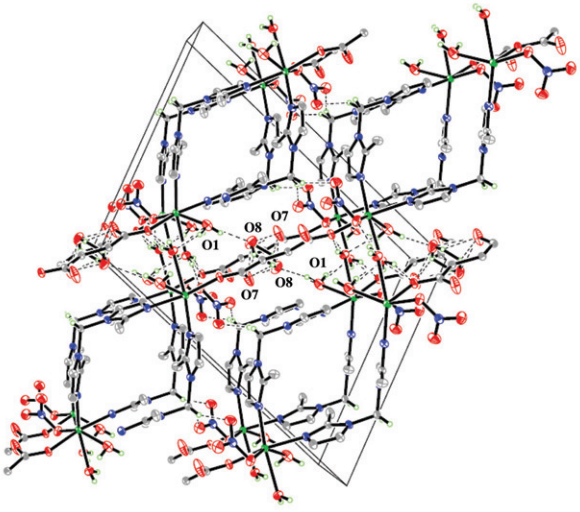

Figure 6. View of the 3-D supramolecular network formed *via* weak hydrogen bonds in **2**.

2-mBIM (Calcd 43.5%) (Supplementary material). A three-step weight loss can be indentified in **2**. The first step from 80°C to 110°C with a weight loss of 10.1% can be attributed to the loss of water (Calcd 9.9%), while the second step with a weight loss of 36.6% from 294°C to 342°C corresponds to the loss of 2-mBIM (Calcd 38.7%). The third step from 465°C to 580°C with a residual weight of 26.0% probably corresponds to the complete decomposition of **2** at 580°C.

Table 4. Hydrogen-bond geometry for **2** (Å, °).

| D–H $\cdots$ A | D–H | H $\cdots$ A | D $\cdots$ A | D–H $\cdots$ A |
|---|---|---|---|---|
| C9–H9A $\cdots$ O1$^{iii}$ | 0.96 | 2.50 | 3.298(5) | 140 |
| C8–H8 $\cdots$ O3$^{iii}$ | 0.93 | 2.54 | 3.101(4) | 120 |
| C5–H5B $\cdots$ O5$^{iv}$ | 0.97 | 2.57 | 3.509(5) | 163 |
| C5–H5A $\cdots$ O4$^{v}$ | 0.97 | 2.51 | 3.441(5) | 161 |
| O8–H8B $\cdots$ O7$^{vi}$ | 0.81(9) | 2.07(9) | 2.760(9) | 142(7) |
| O8–H8A $\cdots$ O8$^{vii}$ | 0.81(9) | 1.59(7) | 1.920(13) | 101(5) |
| O2–H2A $\cdots$ O6$^{viii}$ | 0.81(5) | 1.86(5) | 2.632(4) | 158(4) |
| O8–H8A $\cdots$ O7$^{ix}$ | 0.81(9) | 1.91(8) | 2.673(10) | 155(7) |
| O2–H2B $\cdots$ O3$^{ix}$ | 0.82(5) | 2.01(5) | 2.822(4) | 170(5) |
| O1–H1A $\cdots$ O2$^{ix}$ | 0.82(6) | 1.99(6) | 2.791(4) | 164(5) |

Symmetry codes: $^{iii}-x+3/2, y+1/2, -z+1/2$; $^{iv}-x+1, -y, -z$; $^{v}-x+1, -y+1, -z$; $^{vi}x+1/2, -y+1/2, z+1/2$; $^{vii}-x+1, -y+1, -z+1$; $^{viii}-x+1/2, y-1/2, -z+1/2$; $^{ix}-x+1/2, y+1/2, -z+1/2$.

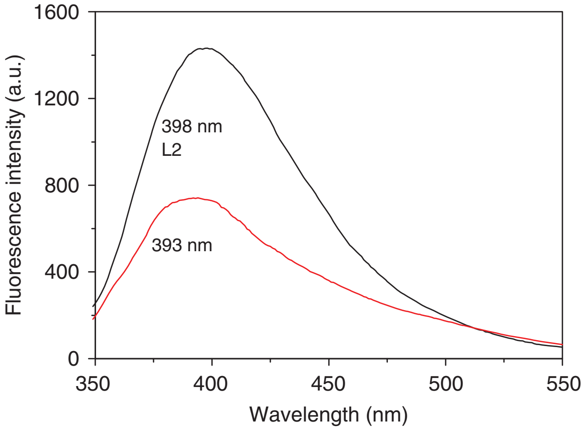

Figure 7. Solid-state luminescence spectra of **2** (red) and free 2-mBIM (black).

The photoluminescent properties of **2** and 2-mBIM were also investigated. Emission spectra at room temperature in the solid state are shown in figure 7. Compound **2** exhibited photoluminescence upon photoexcitation at 328 nm, with the main emission peak at 393 nm, which can be attributed to intraligand $\pi$–$\pi$* transitions, since a similar emission peak at 398 nm was also found in free 2-mBIM. However, the fluorescence intensity of **2** was significantly lower than that of free 2-mBIM ligand, possibly due to the ligand-to-metal charge transfer (LMCT) transitions; a similar result was observed previously [23]. No luminescence has been observed for **1** under the experimental conditions.

## 4. Conclusions

Two coordination polymers, $[Cd(2\text{-mBIM})(NCS)(SCN)]_n$ (**1**) and $[Cd_2(2\text{-mBIM})_2(NO_3)_2(C_4H_4O_4)(H_2O)_5]_n$ (**2**), were synthesized using $Cd(NO_3)_2$ and 2-mBIM in the presence of $NH_4SCN$ or succinic acid. Both complexes possessed a slightly distorted octahedral Cd(II) and each Cd(II) was *cis*-coordinated by two 2-mBIM ligands to form 1-D helical structures. Such 1-D helical chain structures were connected to each other *via* either double end-to-end thiocyanate bridges (in **1**) or the succinate (in **2**), leading to the formation of a 2-D framework. An overall 3-D supramolecular network was formed in **2** *via* weak hydrogen bond interactions between dimer waters and the 2-D layers. Compounds **1** and **2** exhibited new structural features and good stabilities. Compound **2** also exhibited fluorescent emission.

## Supplementary material

Additional crystallographic details and complete bond lengths and angles, coordinates, and displacement parameters have been deposited at the Cambridge Crystallographic Data Center (CCDC) as supplementary publication no: CCDC 689346 for **1** and CCDC 689344 for **2**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: +(44) 1223 336 033; Email: deposit@ccdc.cam.ac.uk).

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## References

[1] (a) G. Férey. *Chem. Soc. Rev.*, **37**, 191 (2008); (b) S. Leininger, B. Olenyuk, P.J. Stang. *Chem. Rev.*, **100**, 853 (2000); (c) X.M. Chen, M.L. Tong. *Acc. Chem. Res.*, **40**, 162 (2007).

[2] R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O'Keeffe, O.M. Yaghi. *Science*, **319**, 939 (2008).

[3] C.F. Lee, D.A. Leigh, R.G. Pritchard, D. Schultz, S.J. Teat, G.A. Timco, R.E.P. Winpenny. *Nature*, **458**, 314 (2009).

[4] M. Kawano, M. Fujita. *Coord. Chem. Rev.*, **251**, 2592 (2007).

[5] (a) A.J. Cairns, J.A. Perman, L. Wojtas, V.C. Kravtsov, M.H. Alkordi, M. Eddaoudi, M.J. Zaworotko. *J. Am. Chem. Soc.*, **130**, 1560 (2008); (b) S. Kitagawa, R. Kitaura, S. Noro. *Angew. Chem. Int. Ed.*, **43**, 2334 (2004).

[6] (a) H.B. Cui, B. Zhou, L.S. Long, Y. Okano, H. Kobayashi, A. Kobayashi. *Angew. Chem. Int. Ed.*, **47**, 3376 (2008); (b) Y. Hou, W.T. Yin, X.D. Xie, X. Chen, J.R. Zhou, H.R. Zuo, Q. Huang, L.M. Yang, C.L. Ni, X.L. Hu. *Inorg. Chim. Acta*, **363**, 424 (2010).

[7] (a) D.F. Sun, S.Q. Ma, Y.X. Ke, D.J. Collins, H.C. Zhou. *J. Am. Chem. Soc.*, **128**, 3896 (2006); (b) H.J. Park, M.P. Suh. *Chem. Commun.*, **46**, 610 (2010).

[8] (a) A. Morsali, Z.R. Ranjbar, M.G. Amiri, A. Askarinejad, H.P. Xiao. *J. Coord. Chem.*, **59**, 961 (2006); (b) J.P. Zou, X.M. Liu, L.S. Yan, A.M. Deng, Q.J. Xing, M.H. Chen. *J. Coord. Chem.*, **63**, 56 (2010); (c) M.Y. Duan, J. Li, Y. Xi, X.F. Lu, J.Z. Liu, G. Mele, F.X. Zhang. *J. Coord. Chem.*, **63**, 90 (2010).

[9] O.S. Jung, Y.J. Kim, Y.A. Lee, J.K. Park, H.K. Chae. *J. Am. Chem. Soc.*, **122**, 9921 (2000).

[10] E.Q. Gao, S.Q. Bai, C.H. Yan. *J. Am. Chem. Soc.*, **125**, 4984 (2003).

[11] (a) S.A. Barnett, N.R. Champness. *Coord. Chem. Rev.*, **246**, 145 (2003); (b) K. Biradha, M. Sarkar, L. Rajput. *Chem. Commun.*, 4169 (2006).

[12] (a) N.G. Pschirer, D.M. Curtin, M.D. Smith, W.H.F. Bunz, H.-C. Zur Loye. *Angew. Chem. Int. Ed.*, **41**, 583 (2002); (b) P. Lama, A. Aijaz, E.C. Sañudo, P.K. Bharadwaj. *Cryst. Growth Des.*, **10**, 283 (2010).

[13] (a) G.H. Cui, J.R. Li, J.L. Tian, X.H. Bu, S.R. Batten. *Cryst. Growth Des.*, **5**, 1775 (2005); (b) N. Masciocchi, C. Pettinari, E. Alberti, R. Pettinari, C.D. Nicola, A.F. Albisetti, A. Sironi. *Inorg. Chem.*, **46**, 10501 (2007); (c) N. Masciocchi, A.F. Albisetti, A. Sironi, C. Pettinari, C.D. Nicola, R. Pettinari. *Inorg. Chem.*, **48**, 5328 (2009).

[14] (a) S.W. Jin, W.Z. Chen. *Polyhedron*, **26**, 3074 (2007); (b) S.W. Jin, W.Z. Chen, H.Y. Qiu. *Cryst. Growth Des.*, **7**, 2071 (2007).

[15] (a) C.M. Jin, H. Lu, L.Y. Wu, J. Huang. *Chem. Commun.*, 5039 (2006); (b) C.M. Jin, L.Y. Wu, H. Lu, Y. Xu. *Cryst. Growth Des.*, **8**, 215 (2008); (c) C.M. Jin, Z.F. Chen, C.Y. Cheng, J.H. Dong. *J. Coord. Chem.*, **62**, 390 (2009); (d) C.M. Jin, Z. Zhu, M.X. Yao, X.G. Meng. *CrystEngComm*, **12**, 358 (2010).

[16] S. Julia, P. Sala, J. Del Mazo, M. Sancho, C. Ochoa, J. Elguero. *J. Heterocycl. Chem.*, **19**, 1141 (1982).

[17] Bruker Advanced X-ray Solutions. *SMART: Bruker Molecular Analysis Research Tool (Version 5.626)*, Bruker AXS Inc., Madison, WI (2002).

[18] Bruker Advanced X-ray Solutions. *SAINTPlus: Data Reduction and Correction Program (Version 6.45a)*, Bruker AXS Inc., Madison, WI (2003).

[19] Bruker Advanced X-ray Solutions. *SADABS: An Empirical Absorption Correction Program (Version 2.01)*, Bruker AXS Inc., Madison, WI (2004).

[20] G.M. Sheldrick. *SHELXTL: Structure Determination Software Suite (Version 6.10)*, Bruker AXS Inc., Madison, WI (2001).

[21] F. Jin, H.P. Zhou, X.C. Wang, Z.J. Hu, J.Y. Wu, Y.P. Tian, M.H. Jiang. *Polyhedron*, **26**, 1338 (2007).

[22] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York (1978).

[23] M.D. Allendorf, C.A. Bauer, R.K. Bhakta, R.J.T. Houk. *Chem. Soc. Rev.*, **38**, 1330 (2009).