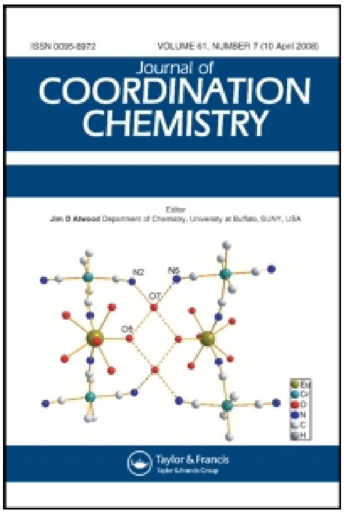

**Journal of Coordination Chemistry**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

# Syntheses, crystal structures and properties of two cadmium coordination polymers containing <i>bis</i>(2-methylimidazol-1-yl)methane(2-mBIM) and <i>bis</i>(imidazol-1-yl)methane (BIM) ligands

Chuan-Ming Jin[a]; Zhan-Fen Chen[a]; Cai-Yuan Chen[a]; Jing-Hua Dong[a]
[a] Hubei Key Laboratory of Bioanalytic Technique, Department of Chemistry and Environmental Engineering, Hubei Normal University, Huangshi, Hubei 435002, P.R. China

**To cite this Article** Jin, Chuan-Ming , Chen, Zhan-Fen , Chen, Cai-Yuan and Dong, Jing-Hua(2009) 'Syntheses, crystal structures and properties of two cadmium coordination polymers containing <i>bis</i>(2-methylimidazol-1-yl)methane(2-mBIM) and <i>bis</i>(imidazol-1-yl)methane (BIM) ligands', Journal of Coordination Chemistry, 62: 3, 390 — 399, First published on: 10 December 2009 (iFirst)

**To link to this Article: DOI:** 10.1080/00958970802244984

**URL:** http://dx.doi.org/10.1080/00958970802244984

*Journal of Coordination Chemistry*
Vol. 62, No. 3, 10 February 2009, 390–399

# Syntheses, crystal structures and properties of two cadmium coordination polymers containing *bis*(2-methylimidazol-1-yl) methane(2-mBIM) and *bis*(imidazol-1-yl)methane (BIM) ligands

CHUAN-MING JIN*, ZHAN-FEN CHEN, CAI-YUAN CHEN and JING-HUA DONG

Hubei Key Laboratory of Bioanalytic Technique, Department of Chemistry and Environmental Engineering, Hubei Normal University, Huangshi, Hubei 435002, P.R. China

(*Received 11 November 2007; in final form 11 April 2008*)

Coordination polymers, $\{[Cd(2\text{-mBIM})_3](ClO_4)_2\}_n$ (**1**) and $[Cd(BIM)_2(NO_3)_2]_n$ (**2**), have been prepared from the reaction of *bis*(2-methylimidazol-1-yl)methane(2-mBIM) with $Cd(ClO_4)_2$ and *bis*(imidazol-1-yl)methane (BIM) with $Cd(NO_3)_2$ in ethanol and water, respectively. Their structures were characterized by single crystal X-ray diffraction and IR spectroscopy. Compound **1** crystallizes in the rhombohedral space group *R*-3*c* with $a = b = 12.3617(5)$ Å, $c = 38.896(3)$ Å, $\gamma = 120°$, $V = 5147.5(5)$ Å$^3$, $z = 6$. The $Cd^{II}$ occupies a crystallographic inversion center and is coordinated by six *N* atoms from six distinct 2-mBIM ligands to form a slightly distorted octahedral geometry. Each 2-mBIM is coordinated to two $Cd^{II}$ cations, linking alternatively four $Cd^{II}$ cations, resulting in a 32-membered $M_4L_4$ macrometallacycle. Compound **2** crystallizes in the monoclinic space group $C2/m$ with $a = 14.400(3)$ Å, $b = 9.3894(18)$ Å, $c = 8.6926(17)$ Å, $\beta = 123.499(2)°$, $V = 980.1(3)$ Å$^3$, $z = 2$. The Cd coordinates to four nitrogen atoms from four different BIM and two nitrates to form a slightly distorted octahedral geometry. The BIM ligands bridge to form a 1-D infinite double-bridged chain structure with 16-membered $M_2L_2$ macrometallacyclic structural units.

*Keywords*: Crystal structure; Cadmium; *Bis*(2-methylimidazol-1-yl)methane; *Bis*(imidazol-1-yl) methane (BIM); Macrometallacycle

## 1. Introduction

Inorganic supramolecular networks and coordination polymers are topical due to fundamental interest in self-assembly processes, supramolecular chemistry and crystal engineering [1–8]. Coordination polymers attract attention because of their structural properties and potential applications in magnetism, electrical conductivity, ion exchange, separation, and catalysis [9–15]. Studies in this field have been focused on the design and construction of coordination frameworks and on the examination of the relationships between structures and properties. Many coordination polymers with architectures such as linear or zigzag chains, helices, honeycombs, square grids, ladders,

---

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

*Journal of Coordination Chemistry*
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970802244984

brick walls and interwoven diamondoid have been developed [16–20]. The framework motifs are primarily dependent upon the coordination preferences of the metal and the functionality of the ligand. However, the counter-anion also plays a significant role in influencing the network structure, either as a coordinating or non-coordinating building block [21, 22]. Some complexes have been reported through self-assembly of metals and BIM [23]. We described a one-dimensional double-bridged chain polymer structure with a 16-membered macrometallacyclic motif [23c], in which the nitrate anions coordinated with cadmium. Herein, we report a coordination polymer with similar structure motif from *bis*(imidazol-1-yl)methane (BIM) and $Cd(NO_3)_2$; a crystal structure of the metal-organic framework containing $CdN_6$ octahedra with 32-membered $M_4L_4$ macrometallacyclic structural motif is formed by the addition of a solution of *bis*(2-methylimidazol-1-yl)methane (2-mBIM) to $Cd(ClO_4)_2$.

## 2. Experimental

### 2.1. *Materials and methods*

All solvents and reagents were purchased from commercial sources and used without further purification. The ligands 2-mBIM and BIM were prepared as previously described [24]. The infrared spectra were recorded in the 500–4000 $cm^{-1}$ range using KBr disks on a Nicolet 5700 FT-IR spectrometer. Thermogravimetric analysis (TGA) measurements were made using a Pyris diamond TG/DTA Thermogravimetric/differential Thermal Analyzer. The sample was heated from 50–800°C at 10°C $min^{-1}$ in a nitrogen atmosphere with a flow rate of 70 cc $min^{-1}$. 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.

***Caution:*** *Although we have not experienced any problems in handling perchlorate compounds, they should be handled with extreme care.*

### 2.2. *Synthesis of* $\{[Cd(2\text{-}mBIM)_3](ClO_4)_2\}_n$ *(1)*

An ethanol solution (5 mL) of 2-mBIM (91 mg, 0.5 mmol) was slowly diffused into an aqueous solution (5 mL) of $Cd(ClO_4)_2 \cdot 6H_2O$(105 mg, 0.25 mmol) in a test tube. The mixture stood at room temperature for two weeks and block-shaped colorless single crystals of $\{[Cd(2\text{-}mBIM)_3](ClO_4)_2\}_n$ were obtained in 83% yield based on ligand 2-mBIM by slow evaporation. Anal. Calcd for $C_{27}H_{36}CdCl_2N_{12}O_8$: C, 38.61; H, 4.32; N, 20.01. Found: C, 38.21; H, 4.61; N, 19.72. IR (KBr, $cm^{-1}$): $\upsilon = 3141$m, 3005m, 2915w, 2486w, 2361w, 2016w, 1583w, 1535s, 1498s, 1443m, 1391m, 1365s, 1341m, 1261s, 1193w, 1089s, 991s, 940w, 856m, 776w, 737s, 674m, 655m, 636s.

### 2.3. *Synthesis of* $[Cd(BIM)_2(NO_3)_2]_n$ *(2)*

An ethanol solution (5 mL) of BIM (74 mg, 0.5 mmol) was slowly diffused into an aqueous solution (5 mL) of $Cd(NO_3)_2 \cdot 4H_2O$ (154 mg, 0.5 mmol) in a test tube.

Colorless crystals of $[Cd(BIM)_2(NO_3)_2]_n$ were formed at the interface of solvent in two weeks in 87% yield. Anal. Calcd for $C_{14}H_{16}CdN_{10}O_6$: C, 31.56; H, 3.03; N, 26.29. Found (%): C, 31.31; H, 3.23; N, 26.10. IR (KBr, $cm^{-1}$): $\upsilon = 3119s$, 3037m, 2576w, 2427w, 1613w, 1511s, 1419s, 1239s, 1142m, 1101s, 1040s, 937s, 860s, 830m, 768s, 722s, 666s, 625m.

### 2.4. *Crystal structure determination*

A single crystal of **1** or **2** with dimensions 0.2 mm × 0.1 mm × 0.1 mm was removed from the test tube and covered with a layer of hydrocarbon oil, attached to a glass fiber and data was collected at 292(2) K using a Bruker/Siemens SMART APEX instrument (Mo-K$\alpha$ radiation, $\lambda = 0.71073$ Å). Data were measured using a $\omega$-$\phi$ scan mode in the range $2.2 < \theta < 26.3$ for **1**. A total of 15600 reflections were collected with 1419 unique ones ($R_{\text{int}} = 0.056$), of which 1142 reflections with $I > 2\sigma(\text{I})$ were observed. For **2**, in the range $2.75 < \theta < 27.0$, a total of 5469 reflections were collected with 1141 unique ones ($R_{\text{int}} = 0.0767$), of which 1124 reflections with $I > 2\sigma(\text{I})$ were observed. Cell parameters were retrieved using SMART software [25] and refined using SAINTPlus [26] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS [27]. The structure was solved by direct methods and refined by least squares on $F^2$ using the SHELXTL program package [28] with $R = 0.059$, $wR = 0.178$ $\{w = [\sigma^2(F_{\text{O}}^2) + (0.1042P)^2 + 21.8399P]^{-1}$, where $P = (F_{\text{o}}^2 + 2F_{\text{c}}^2)/3\}$, $S = 1.05$, $(\Delta/\delta)_{\max} < 0.001$, $(\Delta\rho)_{\max} = 1.19$ and $(\Delta\rho)_{\min} = -0.40\,\text{e}\,\text{Å}^{-3}$ for **1** and $R = 0.0284$, $wR = 0.0681$ $\{w = [\sigma^2(F_{\text{o}}^2) + (0.0423P)^2 + 0.1030P]^{-1}$, where $P = (F_{\text{o}}^2 + 2F_{\text{c}}^2)/3\}$, $S = 1.117$, $(\Delta/\delta)_{\max} = 0.000$, $(\Delta\rho)_{\max} = 0.448$ and $(\Delta\rho)_{\min} = -0.340\,\text{e}\,\text{Å}^{-3}$ for **2**. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in riding model. No decomposition was observed during data collection. The crystallographic data and structure refinement is 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*

As revealed by single-crystal X-ray diffraction analysis, in **1**, each $Cd^{II}$ occupies a crystallographic inversion center and is coordinated by six *N* atoms from six distinct 2-mBIM ligands in slightly distorted octahedral geometry. An ORTEP drawing of $\{[Cd(2\text{-mBIM})_3](ClO_4)_2\}_n$ is shown in figure 1. Perchlorate anions are not coordinated. Each 2-mBIM is coordinated to two $Cd^{II}$ cations acting as a bridge to form a one-dimensional zigzag chain polymer with Cd–Cd separation of 9.643(2) Å (figure 2). The dihedral angle between two imidazole rings of the same 2-mBIM ligand is 69.4°. The conformation of 2-mBIM in **1** is considerably different from that of 2-mBIM in $[Cd(2\text{-mBIM})_2(NO_3)_2]_n$ [23], since the two methyl groups of imidazole in the same ligand point to opposite direction (see figure 1). However, it is similar to free 2-mBIM [29]. Two different conformations of 2-mBIM cause the formation of coordination polymers $\{[Cd(2\text{-mBIM})_3](ClO_4)_2\}_n$ and $[Cd(2\text{-mBIM})_2(NO_3)_2]_n$ with different structural motifs.

Table 1. Crystal data and structure refinement summary for **1** and **2**.

| Compound number | **1** | **2** |
|---|---|---|
| Empirical formula | $C_{27}H_{36}CdCl_2N_{12}O_8$ | $C_{14}H_{16}CdN_{10}O_6$ |
| CCDC Deposit No. | 664653 | 626178 |
| Formula weight | 839.98 | 532.77 |
| Temperature | 292(2)K | 292(2)K |
| Wavelength | 0.71073 Å | 0.71073 Å |
| Crystal system | Rhombohedral | Monoclinic |
| Space group | *R*-3*c* | *C*2/*m* |
| Unit cell dimensions (Å, °) | | |
| *a* | 12.3617(5) | 14.400(3) |
| *b* | 12.3617(5) | 9.3894(18) |
| *c* | 38.896(3) | 8.6926(17) |
| $\alpha$ | 90° | 90° |
| $\beta$ | 90° | 123.499(2)° |
| $\gamma$ | 120° | 90° |
| Volume (Å$^3$) | 5147.5(5) | 980.1(3) |
| *Z* | 6 | 2 |
| $D_{\mathrm{Calcd}}$ (Mg m$^{-3}$) | 1.626 | 1.805 |
| Absorption coefficient (mm$^{-1}$) | 0.86 | 1.172 |
| *F*(000) | 2568 | 532 |
| Crystal size (mm$^3$) | 0.20 × 0.10 × 0.10 | 0.20 × 0.10 × 0.10 |
| $\theta$ range for data collection | 2.2–26.3° | 2.75–27.00° |
| Index ranges | $-16 \le h \le 16$, $-16 \le k \le 16$, $-51 \le l \le 45$ | $-18 \le h \le 18$, $-11 \le k \le 11$, $-11 \le l \le 11$ |
| Reflections collected | 15600 | 5469 |
| Independent reflections | 1142 [*R*(int) = 0.056] | 1124 [*R*(int) = 0.0767] |
| Absorption correction | SADABS | SADABS |
| Max. and min. transmission | 0.9191 and 0.8471 | 0.8918 and 0.7994 |
| Refinement method | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ |
| | 1419/0/78 | 1141/0/80 |
| Data/restraints/parameters | 1.05 | 1.117 |
| Goodness-of-fit on $F^2$ | $R_1 = 0.0591$, $wR_2 = 0.1688$ | $R_1 = 0.0284$, $wR_2 = 0.0681$ |
| Final *R* indices [$I > 2\sigma(I)$] | $R_1 = 0.0705$, $wR_2 = 0.1782$ | $R_1 = 0.0291$, $wR_2 = 0.0684$ |
| *R* indices (all data) Largest diff. peak and hole (e Å$^{-3}$) | 1.19 and −0.40 | 0.448 and −0.340 |

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

| | | | |
|---|---|---|---|
| Cd(1)–N(1) | 2.444(4) | Cd(1)–N(1)$^{\mathrm{iii}}$ | 2.444(4) |
| Cd(1)–N(1)$^{\mathrm{i}}$ | 2.444(4) | Cd(1)–N(1)$^{\mathrm{iv}}$ | 2.444(4) |
| Cd(1)–N(1)$^{\mathrm{ii}}$ | 2.444(5) | Cd(1)–N(1)$^{\mathrm{v}}$ | 2.444(5) |
| N(1)$^{\mathrm{i}}$–Cd(1)–N(1) | 96.13(17) | N(1)$^{\mathrm{ii}}$–Cd(1)–N(1)$^{\mathrm{iv}}$ | 96.14(17) |
| N(1)$^{\mathrm{i}}$–Cd(1)–N(1)$^{\mathrm{ii}}$ | 96.13(17) | N(1)$^{\mathrm{iii}}$–Cd(1)–N(1)$^{\mathrm{iv}}$ | 96.14(17) |
| N(1)–Cd(1)–N(1)$^{\mathrm{ii}}$ | 83.87(17) | N(1)$^{\mathrm{i}}$–Cd(1)–N(1)$^{\mathrm{v}}$ | 83.86(17) |
| N(1)$^{\mathrm{i}}$–Cd(1)–N(1)$^{\mathrm{iii}}$ | 180.00(16) | N(1)–Cd(1)–N(1)$^{\mathrm{v}}$ | 96.14(17) |
| N(1)–Cd(1)–N(1)$^{\mathrm{iii}}$ | 83.87(17) | N(1)$^{\mathrm{ii}}$–Cd(1)–N(1)$^{\mathrm{v}}$ | 179.995(1) |
| N(1)$^{\mathrm{ii}}$–Cd(1)–N(1)$^{\mathrm{iii}}$ | 83.87(17) | N(1)$^{\mathrm{iii}}$–Cd(1)–N(1)$^{\mathrm{v}}$ | 96.14(17) |
| N(1)$^{\mathrm{i}}$–Cd(1)–N(1)$^{\mathrm{iv}}$ | 83.86(17) | N(1)$^{\mathrm{iv}}$–Cd(1)–N(1)$^{\mathrm{v}}$ | 83.86(17) |
| N(1)$^{\mathrm{i}}$–Cd(1)–N(1)$^{\mathrm{iv}}$ | 179.994(1) | | |

Symmetry transformations used to generate equivalent atoms: (i) $y+1/3$, $-x+y+2/3$, $-z+2/3$; (ii) $-x+y+1$, $-x+1$, $z$; (iii) $-y+1$, $x-y$, $z$; (iv) $-x+4/3$, $-y+2/3$, $-z+2/3$; (v) $x-y+1/3$, $x-1/3$, $-z+2/3$; (vi) $y+2/3$, $x-2/3$, $-z+5/6$.

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

| | | | |
|---|---|---|---|
| Cd(1)–N(2) | 2.3083(18) | Cd(1)–N(2)$^{\mathrm{iv}}$ | 2.3083(18) |
| Cd(1)–N(2)$^{\mathrm{ii}}$ | 2.3083(18) | Cd(1)–O(1)$^{\mathrm{ii}}$ | 2.433(3) |
| Cd(1)–N(2)$^{\mathrm{iii}}$ | 2.3083(18) | Cd(1)–O(1) | 2.433(3) |
| N(2)–Cd(1)–N(2)$^{\mathrm{ii}}$ | 180.0 | N(2)$^{\mathrm{iii}}$ –Cd(1)–O(1)$^{\mathrm{ii}}$ | 82.11(6) |
| N(2)–Cd(1)–N(2)$^{\mathrm{iii}}$ | 96.54(9) | N(2)$^{\mathrm{iv}}$ –Cd(1)–O(1)$^{\mathrm{ii}}$ | 97.89(6) |
| N(2)$^{\mathrm{ii}}$–Cd(1)–N(2)$^{\mathrm{iii}}$ | 83.46(9) | N(2)–Cd(1)–O(1) | 97.89(6) |
| N(2)–Cd(1)–N(2)$^{\mathrm{iv}}$ | 83.46(9) | N(2)$^{\mathrm{ii}}$ –Cd(1)–O(1) | 82.11(6) |
| N(2)$^{\mathrm{ii}}$ –Cd(1)–N(2)$^{\mathrm{iv}}$ | 96.54(9) | N(2)$^{\mathrm{iii}}$ –Cd(1)–O(1) | 97.89(6) |
| N(2)$^{\mathrm{iii}}$ –Cd(1)–N(2)$^{\mathrm{iv}}$ | 180.00(6) | N(2)$^{\mathrm{iv}}$ –Cd(1)–O(1) | 82.11(6) |
| N(2)–Cd(1)–O(1)$^{\mathrm{ii}}$ | 82.11(6) | O(1)$^{\mathrm{ii}}$ –Cd(1)–O(1) | 180.00(5) |
| N(2)$^{\mathrm{ii}}$ –Cd(1)–O(1)$^{\mathrm{ii}}$ | 97.89(6) | | |

Symmetry transformations used to generate equivalent atoms: (i) $x$, $-y+2$, $z$; (ii) $-x+2$, $-y+1$, $-z$; (iii) $x$, $-y+1$, $z$; (iv) $-x+2$, $y$, $-z$.

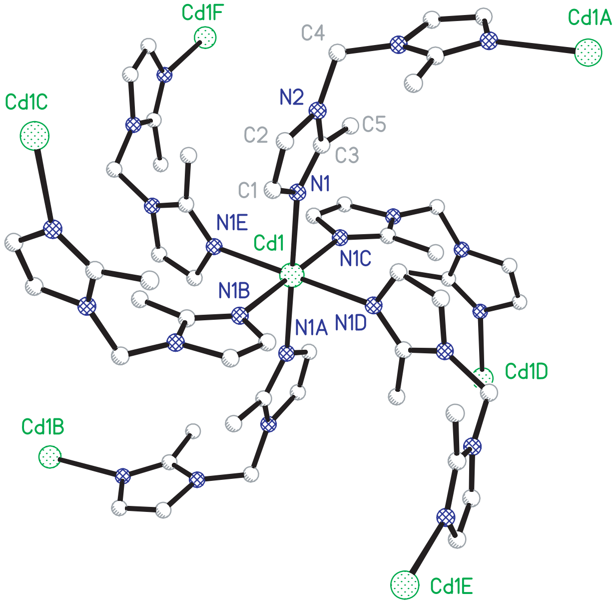

Figure 1. The coordination environment of Cd in {[Cd(2-mBIM)$_3$](ClO$_4$)$_2$}$_n$ showing the atom-numbering scheme [symmetry codes: (A) $y+1/3$, $-x+y+2/3$, $-z+2/3$; (B) $-x+y+1$, $-x+1$, $z$; (C) $-y+1$, $x-y$, $z$; (D) $-x+4/3$, $-y+2/3$, $-z+2/3$; (E) $x-y+1/3$, $x-1/3$, $-z+2/3$; (F) $y+2/3$, $x-2/3$, $-z+5/6$].

Each group of four 2-mBIM ligands are linked alternatively to each other by four Cd$^{\mathrm{II}}$ cations, resulting in a 32-member M$_4$L$_4$ macrometallacycle with the distance between opposite pairs of Cd–Cd being about 14.802 and 12.360 Å (figure 3). Each Cd$^{\mathrm{II}}$ exists in six different macrometallacycles, propagating the coordination polymer to three-dimensional networks. The perchlorate anions fill the voids by weak C–H–O and C–H–N interactions (table 4). Some examples of three-dimensional coordination polymers have been reported that form through self-assembly of Cd$^{\mathrm{II}}$ and rigid or flexible bridging ligands containing N donors [30, 31]. Complex **1** appears to be the first polymeric centrosymmetric three-dimensional network containing CdN$_6$

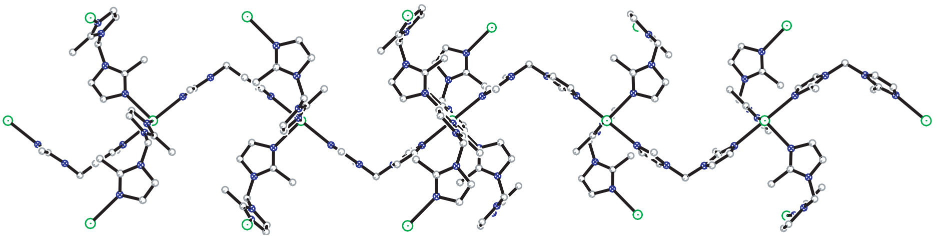

Figure 2. A view of Cd$^{II}$ center and 1-D zigzag polymer chain structure along the c axis for **1**. H-atoms and anions have been omitted for clarity.

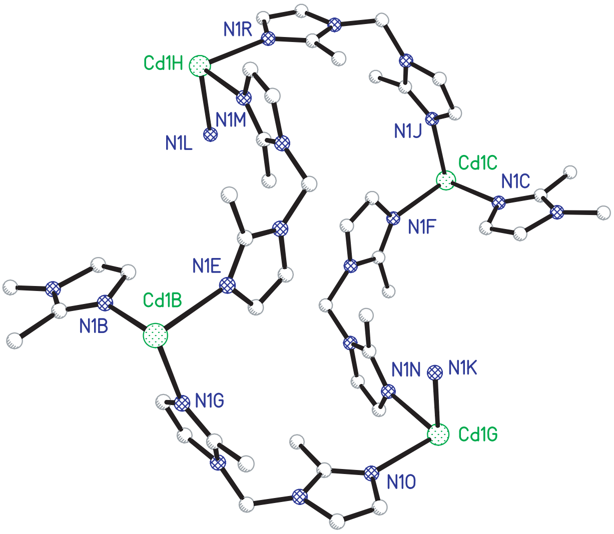

Figure 3. A view of the 32-membered $M_4L_4$ macrometallocycle structure in **1**.

Table 4. Hydrogen-bond geometry for **1**.

| D–H$\cdots$A | D–H | H$\cdots$A | D$\cdots$A | D–H$\cdots$A |
|---|---|---|---|---|
| C1–H1$\cdots$N1$^{iii}$ | 0.93 | 2.56 | 3.163 (8) | 123 |
| C4–H4A$\cdots$O2$^{vii}$ | 0.97 | 2.34 | 3.304 (7) | 176 |
| C4–H4B$\cdots$O2$^{viii}$ | 0.97 | 2.34 | 3.304 (7) | 176 |
| C5–H5A$\cdots$N1$^{i}$ | 0.96 | 2.49 | 3.393 (9) | 158 |

Symmetry codes: (iii) $-y+1$, $x-y$, $z$; (vii) $-x+2$, $-x+y+1$, $-z+1/2$; (viii) $-x+y+5/3$, $-x+4/3$, $z+1/3$; (i) $y+1/3$, $-x+y+2/3$, $-z+2/3$.

octahedral structure unit with 32-membered macrometallacyclic structural motif. $CdN_6$ octahedra have finite structures or coordination polymers with six different *N*-containing ligands [32–37].

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

Single crystal X-ray analysis indicated that **2** has a 1-D polymeric chain structure with units of [Cd(BIM)$_2$(NO$_3$)$_2$] (figure 4). Each Cd$^{II}$ is six-coordinate by four nitrogen atoms from four different BIM ligands and two $NO_3^-$ anions to form a slightly distorted octahedral geometry. The *cis* coordination angles vary from 83.46(9)° to 96.54(9)°; four nitrogen donors lie in the equatorial plane and two coordinated $NO_3^-$ in the apical positions. The Cd–N distance of 2.3083(18) Å is within the range expected for such species [38]. The axial Cd–O distance is 2.433(3) Å. Two $Cd^{II}$ centers are bridged by two BIM ligands to form a 16-membered $M_2L_2$ macrometallacyclic structure with a Cd–Cd separation of 9.389 Å. The dihedral angle between two imidazole rings in the same BIM ligand is 68.9°. The metallacycle units of **2** were repeated to generate an infinite 1-D double-bridged chain structure along the *b* axis. Such 1-D double-bridged chain run parallel to each other in the extended network (figure 5).

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

Thermogravimetric analysis (TGA) shows that **1** is thermally stable to 310°C and displayed a weight loss in the range of 310°C to 397°C, attributed to loss of ligands and counter anions. The weight of the residue (16.6%) corresponds to cadmium oxide (Calcd: 15.3%). $[Cd(BIM)_2(NO_3)_2]_n$ (**2**) displayed a weight loss of 54.4% in the range of 324°C to 369°C.

The photoluminescent properties of **1** and **2** have been investigated. Emission spectra at room temperature in the solid state are shown in figure 6. Compounds **1** and **2** exhibit weak photoluminescence upon photoexcitation at 301 nm and 334 nm, respectively. The main emission peaks are located at 333 nm for **1** and 386 nm for **2**. The emission of **1** and **2** may be due to σ-donation from the coordination environment of the Cd(II) centers and thus be assigned as ligand-to-metal charge-transfer (LMCT) [39].

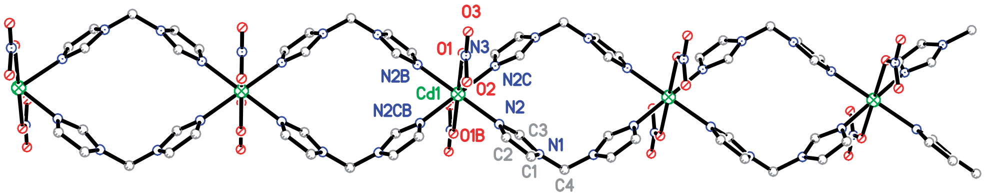

Figure 4. ORTEP drawing of compound $[Cd(BIM)_2(NO_3)_2]_n$ showing the local coordination environment of Cd(II) with thermal ellipsoids. Hydrogens are omitted for clarity [symmetry codes: (A) $x, -y+2, z$; (B) $-x+2, -y+1, -z$; (C) $x, -y+1, z$; (D) $-x+2, y, -z$].

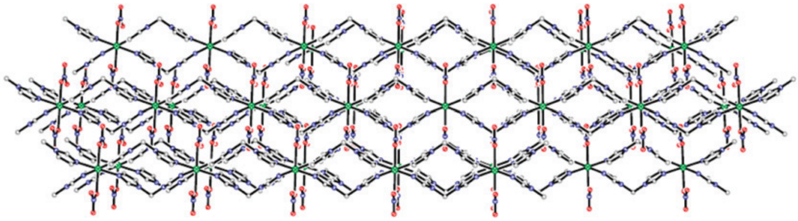

Figure 5. The packing arrangement of compound **2** along the *c* axis.

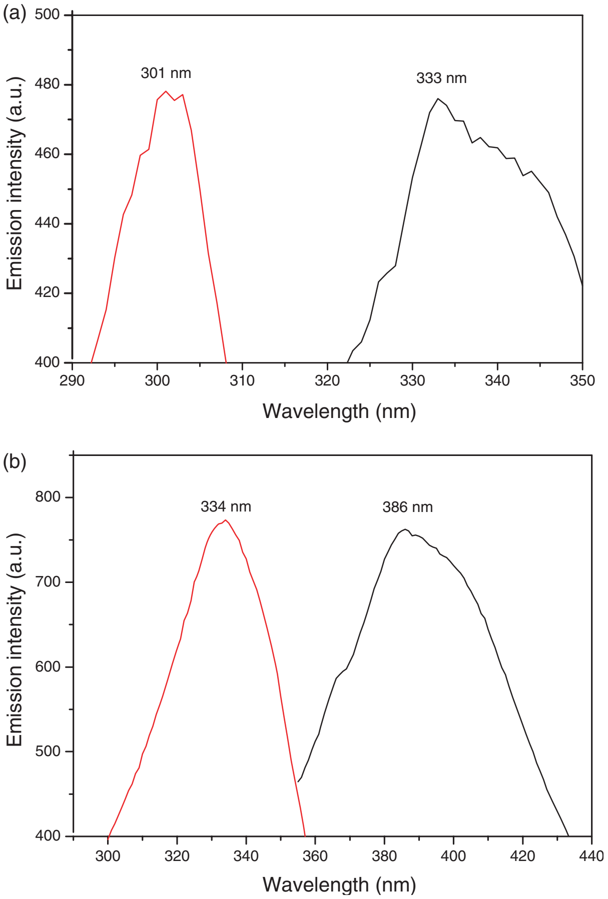

Figure 6. Solid-state emission spectra for (a) **1** and (b) **2**.

## 4. Conclusions

In summary, using $Cd(ClO_4)_2$ and 2-mBIM, we synthesized a coordination polymer, $\{[Cd(2\text{-mBIM})_3](ClO_4)_2\}_n$ as a centrosymmetric three-dimensional framework containing $CdN_6$ octahedral structural unit with 32-membered $M_4L_4$ macrometallacyclic structural motif. $[Cd(BIM)_2(NO_3)_2]_n$ (**2**), a 1-D infinite double-bridged chain structure with a repeated 16-membered $M_2L_2$ macrometallacyclic unit, was formed when BIM and $Cd(NO_3)_2$ were used. Compounds **1** and **2** show new structural features and exhibit good stabilities and fluorescent emissions.

## Supplementary material

Complete bond lengths and angles, coordinates and displacement parameters have been deposited at the Cambridge Crystallography Data Centre. Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting deposition number 664653 for $\{[Cd(2\text{-}mBIM)_3](ClO_4)_2\}_n$ (**1**) and CCDC 626178 for $[Cd(BIM)_2(NO_3)_2]_n$ (**2**).

## Acknowledgements

This work was financially supported by the Natural Science Funds for Distinguished Young Scholars of Hubei Province, P.R. China (Grant No. 2006ABB038), the outstanding Mid-young Scholars' Science and Technology Programs, Hubei Provincial Department of Education (2007B003) and The Project sponsored by SRF for ROCS, SEM (200724).

## References

[1] G.R. Desiraju. *Angew. Chem. Int. Ed. Engl.*, **34**, 2311 (1995).
[2] S.R. Batten, R. Robson. *Angew. Chem. Int. Ed. Engl.*, **37**, 1460 (1998).
[3] S. Leininger, B. Olenyuk, P.J. Stang. *Chem. Rev.*, **100**, 853 (2000).
[4] G.F. Swiegers, T.J. Malefetse. *Chem. Rev.*, **100**, 3484 (2000).
[5] B. Moulton, M.J. Zaworotko. *Chem. Rev.*, **101**, 1629 (2001).
[6] J.-M. Lehn. *Supramolecular Chemistry – Concepts and Perspectives*, VCH, Weinheim (1995).
[7] L. Carlucci, G. Ciani, D. Proserpio. *Coord. Chem. Rev.*, **246**, 247 (2003).
[8] J.-C. Bunzli, C. Piguet. *Chem. Rev.*, **102**, 1897 (2002).
[9] C.J. Kepert, M.J. Rosseinsky. *Chem. Commun.*, 375 (1999).
[10] A.J. Fleetcher, E.J. Cussen, T.J. Prior, M.J. Rosseinsky, C.J. Kepert, K.M. Thomas. *J. Am. Chem. Soc.*, **123**, 10001 (2001).
[11] W. Lin, O.R. Evans. *Acc. Chem. Res.*, **35**, 511 (2002).
[12] R. Wang, M. Hong, J. Luo, R. Cao, J. Weng. *Chem. Commun.*, 1018 (2003).
[13] M. Yoshizawa, M. Nagao, K. Umemoto, K. Biradha, M. Fujita, S. Sakamoto, K. Yamaguchi. *Chem. Commun.*, 1808 (2003).
[14] O.M. Yaghi, C.E. Davis, G. Li, H. Li. *J. Am. Chem. Soc.*, **119**, 2861 (1997).
[15] P. Ren, J. Qin, C. Chen. *Inorg. Chem.*, **42**, 8 (2003).
[16] C.K.V. Sharma, R.D. Rogers. *Chem. Commun.*, 83 (1999).
[17] R. Wang, M. Hong, J. Weng, W. Su, R. Cao. *Inorg. Chem. Commun.*, **3**, 486 (2000).
[18] A.N. Khlobystov, A.J. Blake, N.R. Champness, D.A. Lemenovskii, A.G. Majouga, N.V. Zyk, M. Schroder. *Coord. Chem. Rev.*, **222**, 155 (2001).
[19] D.M.L. Goodgame, A.M. Menzer, S. Menzer, A.J.P. White, D.J. Williams. *Inorg. Chim. Acta*, **355**, 314 (2003).
[20] M. Fujita, O. Sasaki, K.Y. Watanabe, K. Ogura, K. Yamaguchi. *New. J. Chem.*, 189 (1998).
[21] O.-S. Jung, Y.-J. Kim, Y.-A. Lee, J.K. Park, H.K. Chae. *J. Am. Chem. Soc.*, **122**, 9921 (2000).
[22] M.-L. Tong, B.-H. Ye, J.-W. Cai, X.-M. Chen, S.W. Ng. *Inorg. Chem.*, **37**, 2645 (1998).
[23] (a) C.M. Jin, L.Y. Wu, H. Lu, Y. Xu. *Cryst. Growth Des.*, **8**, 215 (2008); (b) C.M. Jin, H. Lu, L.Y. Wu, J. Huang. *Chem. Commun.*, 5039 (2006); (c) C.M. Jin, C.Y. Chen, W.D. Wang, L.Y. Wu. *Acta Cryst. C*, **63**, m454 (2007); (d) G.H. Cui, J.R. Li, J.L. Tian, X.H. Bu, S.R. Batten. *Cryst. Growth Des.*, **5**, 1775 (2005); (e) S.W. Jin, W.Z. Chen. *Polyhedron*, **26**, 3074 (2007); (f) N. Masciocchi, C. Pettinari, E. Alberti, R. Pettinari, C.D. Nicola, A.F. Albisetti, A. Sironi. *Inorg. Chem.*, **46**, 10501 (2007).
[24] E. Diez-Barra, A.D.L. Hoz, A. Sanchez-Migallon, J. Tejeda. *Heterocycles*, **34**, 1365 (1992).
[25] *SMART: v. 5.626, Bruker Molecular Analysis Research Tool*, Bruker AXS, Madison, WI (2002).
[26] *SAINTPlus: v. 6.45a, Data Reduction and Correction Program*, Bruker AXS, Madison, WI (2003).
[27] *SADABS: v. 2.01, An Empirical Absorption Correction Program*, Bruker AXS Inc., Madison, WI (2004).
[28] *SHELXTL: v. 6.10, Structure Determination Software Suite*, G.M. Sheldrick, Bruker AXS Inc., Madison, WI (2001).
[29] C.M. Jin, C.R. Gong. *Acta Cryst. E*, **61**, o1494 (2005).
[30] J.Y. Han, J. Fang, H.Y. Chang, Y. Dong, S. Liang. *Acta Cryst. C*, **61**, m2667 (2005).
[31] M.J. Plater, M.R. St J. Foreman, J.M.S. Skakle. *Cryst. Eng.*, **4**, 293 (2001).
[32] A. Morsali, Z.R. Ranjbar, M.G. Amiri, A. Askarinejad, H.P. Xiao. *J. Coord. Chem.*, **59**, 961 (2006).

[33] J.Y. Han, J. Fang, H.Y. Chang, Y. Dong, S. Liang. *Acta Cryst. E*, **61**, m2667 (2005).
[34] D.L. Reger, R.F. Semeniuc, M.D. Smith. *Cryst. Growth Des.*, **5**, 1181 (2005).
[35] H. Yoshikawa, S. Nishikiori, T. Watanabe, T. Ishida, G. Watanabe, M. Murakami, K. Suwinska, R. Luboradzki, J. Lipkowski. *J. Chem. Soc., Dalton Trans.*, 1907 (2002).
[36] B. Gunes, H. Soylu, S. Ozbey, Y. Tufan, N. Karacan. *Acta Cryst. C*, **52**, 2425 (1996).
[37] E.-Q. Gao, Z.-M. Wang, C.-S. Liao, C.-H. Yan. *New J. Chem.*, 1096 (2002).
[38] X. Li, R. Cao, W.H. Bi, D.Q. Yuan, D.F. Sun. *Eur. J. Inorg. Chem.*, 3156 (2005).
[39] X.-M. Ouyang, D.-J. Liu, T. Okamura, H.-W. Bu, W.-Y. Sun, W.-X. Tang, N. Ueyama. *J. Chem. Soc., Dalton Trans.*, 1836 (2003).