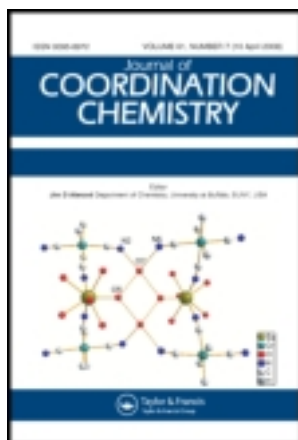


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Two coordination polymers based on 2,2'-biimidazoles and d¹⁰ metal ions: syntheses, structures, and luminescence

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Two d¹⁰ metal coordination polymers, [Zn(μ-Me₂biim)Cl₂]_n (**1**) and [Cd₃(MeHbiim)₂(1,4-BDC)₃]_n (**2**) (Me₂biim = N,N'-dimethyl-2,2'-biimidazole, MeHbiim = N-methyl-2,2'-biimidazole, 1,4-BDC = 1,4-benzenedicarboxylate), were synthesized under hydrothermal conditions and characterized by elemental analysis, infrared spectroscopy, thermogravimetric analysis, and single-crystal X-ray crystallography. Complex **1** features an infinite neutral zigzag 1-D chain. Interchain hydrogen-bonding interactions further extend the 1-D arrangement to generate a 2-D supramolecular architecture. Complex **2** features a 3-D coordination polymer with α-Po net topology, based on linear trinuclear {Cd₃O₁₄N₄} clusters. Both complexes have high thermal stability and exhibit strong luminescence at room temperature.

Keywords: N-methyl-2,2'-biimidazole; N,N'-dimethyl-2,2'-biimidazole; d¹⁰ Metal coordination polymers; α-Po net topology; Luminescent properties

1. Introduction

Metal organic frameworks (MOFs) have received much attention in supramolecular chemistry and crystal engineering because of their diverse structures and promising applications in catalysis, nonlinear optics, luminescent materials, porous materials, and microelectronics [1–5]. Design of MOFs is influenced by the coordination geometry of the central atom, the structural characteristics of the ligand, the counter anion, the pH of the reaction solutions, the symmetry of the solvent system, the reaction conditions, etc. [6–10].

2,2'-Biimidazole (H₂biim) is a bidentate ligand. In its chelating complexes, the two imidazole rings are nearly coplanar. Coordinated H₂biim is able to act as a hydrogen-bond donor *via* hydrogens at N–H [11–19]. Replacement of N–H with bulky groups is favorable for bridging coordination [20–28] and polymer motifs. Even methyl groups are large enough to force the imidazole rings out of plane, thus reducing the tendency of R₂biim to chelate. Despite the increased steric hindrance, some chelating

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N,N'-substituted methylimidazoles can be synthesized [29–31]. However, little investigation has been performed on the role of secondary ligands in N-methyl-2,2'-biimidazole (MeHbiim) and N,N'-dimethyl-2,2'-biimidazole (Me₂biim) complexes by far. Coordination of auxiliary ligands could affect the overall architecture and functions of the target MOFs. As a rigid and versatile bridging ligand, 1,4-benzenedicarboxylate (1,4-BDC) has been extensively studied for designing new materials, which also bears a complementary functional group linked to N–H entities [32–34]. Therefore, to explore the coordination of the aromatic polycarboxylate on the resulting MOFs, hydrothermal reactions of MeHbiim or Me₂biim in the presence of Cd²⁺ or Zn²⁺ as Lewis acid and 1,4-BDC as auxiliary ligand gave two coordination polymers [Zn(μ-Me₂biim)Cl₂]_n (**1**) and [Cd₃(MeHbiim)₂(1,4-BDC)₃]_n (**2**). [Cd₃(MeHbiim)₂(1,4-BDC)₃]_n is the first coordination polymer of MeHbiim.

2. Experimental

2.1. Materials

All chemicals were used as purchased without purification except that MeHbiim and Me₂biim were prepared by literature methods [35] with some modifications of prolonging the reaction time at reflux to enhance the yield.

2.2. Physical measurements

Elemental analyses (C, H, and N) were performed by a Vario EL-III instrument. Infrared (IR) spectra were recorded on an Equinox55 spectrophotometer from 4000 to 400 cm⁻¹ using a KBr pellet. Fluorescence spectra were measured with a Perkin-Elmer LS55. Thermogravimetric analysis (TGA) was performed on a Netzsch STA 449C instrument in flowing N₂ with a heating rate of 10°C min⁻¹.

2.3. Synthesis

2.3.1. [Zn(μ-Me₂biim)Cl₂]_n (1**).** Complex **1** was obtained by the reaction of ZnCl₂, Me₂biim, H₂BDC, and KOH in molar ratio of 1:1:1:2 mixed with 15 mL of water under hydrothermal conditions (at 160°C for 5 days and cooled to room temperature at 10°C h⁻¹). The colorless block crystals were washed with water and ethanol, and dried in air. Yield: 35% (based on Zn). Anal. Found for C₈H₁₀Cl₂N₄Zn (%): C 32.82, N 19.05, H 3.56. Calcd (%) C 32.21, N 18.79, H 3.36. IR spectrum (KBr; cm⁻¹): 3120(s), 2953(m), 1640(s), 1455(s), 1373(s), 680(w), 508(w).

2.3.2. [Cd₃(MeHbiim)₂(1,4-BDC)₃]_n (2**).** The synthesis of **2** was similar to that described for **1** except using CdCl₂·2.5H₂O instead of ZnCl₂, and the pink block crystals of **2** were obtained. The crystals were washed with water and ethanol, and dried in air. Yield: 55% (based on Cd). Anal. Found for C₃₈H₂₈Cd₃N₈O₁₂ (%): C 39.95,

Table 1. The crystal parameters of **1** and **2**.

Complex	1	2
Empirical formula	C ₈ H ₁₀ Cl ₂ N ₄ Zn	C ₃₈ H ₂₈ Cd ₃ N ₈ O ₁₂
Formula weight	298.47	1125.88
Temperature (K)	293(2)	296(2)
Crystal system	Orthorhombic	Triclinic
Space group	<i>Pnna</i>	<i>P</i> $\bar{1}$
Unit cell dimensions (Å, °)		
<i>a</i>	14.472(3)	9.9096(16)
<i>b</i>	9.894(2)	10.3188(17)
<i>c</i>	8.1226(16)	11.819(3)
α	90	100.165(3)
β	90	113.120(4)
γ	90	109.184(2)
Volume (Å ³), <i>Z</i>	1163.0(4), 4	982.7(3), 1
Density (g cm ⁻³)	1.705	1.902
<i>F</i> (000)	600	552
Crystal size (mm ³)	0.64 × 0.38 × 0.19	0.16 × 0.13 × 0.07
Absorption coefficient (mm ⁻¹)	2.543	1.683
Goodness-of-fit on <i>F</i> ²	1.095	0.998
Reflections collected (independent)	5375/1038	5018/3443
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0191, <i>wR</i> ₂ = 0.0517	<i>R</i> ₁ = 0.0285, <i>wR</i> ₂ = 0.0610
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0206, <i>wR</i> ₂ = 0.0525	<i>R</i> ₁ = 0.0429, <i>wR</i> ₂ = 0.0642

H 2.34, N 9.38. Calcd (%) C 40.57, H 2.49, N 9.96%. IR spectrum (KBr; cm⁻¹): 3151(m), 3063(m), 2921(m), 1640(w), 1445(s), 1376(s), 682(s), 517(m).

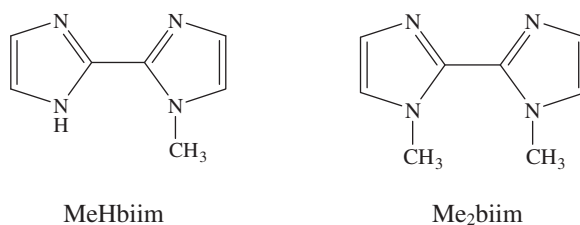
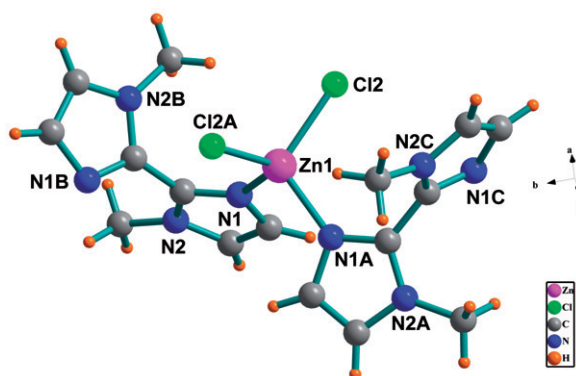
2.4. X-ray crystallography

Diffraction data for **1** and **2** were collected on a Bruker Smart Apex CCD diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at 298 K. The structures were solved by direct methods and refined by full-matrix least-square on *F*² using the SHELXL-97 crystallographic software package [36]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogens were placed in calculated positions with fixed C–H and N–H distances (C–H, 0.97 Å; N–H, 0.89 Å). The crystallographic data for **1** and **2** are summarized in table 1.

3. Results and discussion

3.1. Synthesis

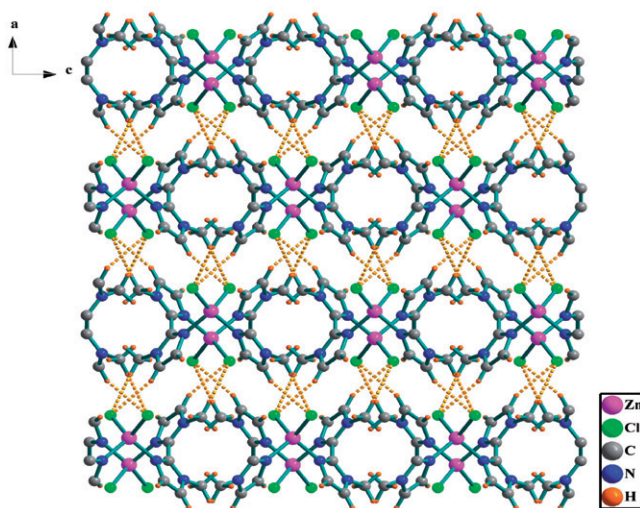
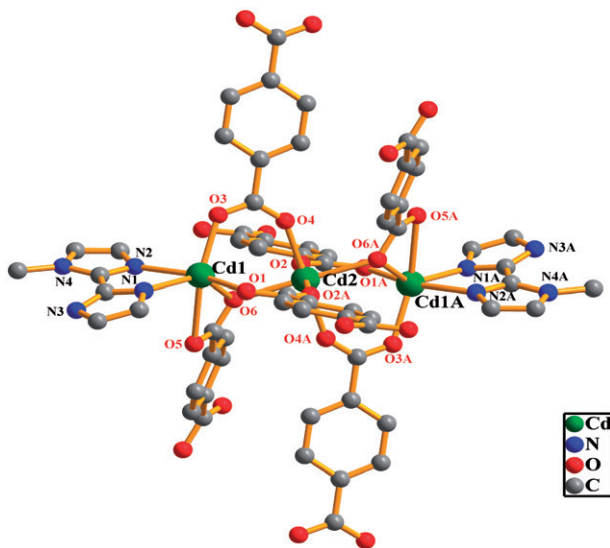
Although many coordination polymers of zinc and cadmium containing BIM or BDC have been published [37–42], syntheses of **1** and **2** are more attractive. The N-substituted 2,2'-biimidazole derivatives such as MeHbiim, Me₂biim possess different shapes (scheme 1), which may play a crucial role in the construction of coordination polymers. These ligands connect metal centers in two manners with chelating and bridging coordination. When 1,4-BDC is introduced as a co-ligand of

Scheme 1. The structures of MeHbiim and Me₂biim.Figure 1. The structure of **1** with 30% thermal ellipsoids (A: $x, 1.5-y, 2.5-z$; B: $0.5-x, 2-y, z$; C: $0.5-x, -0.5+y, 2.5-z$).

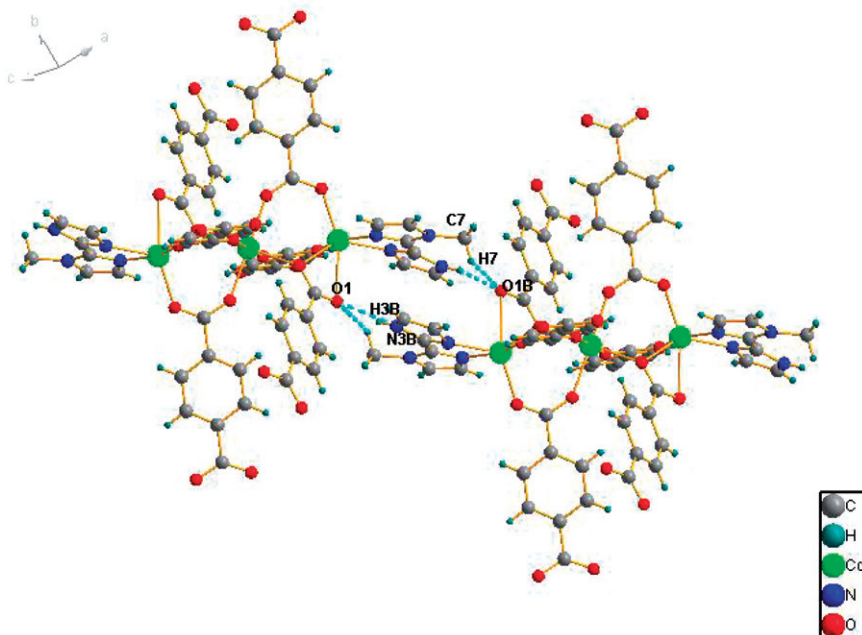
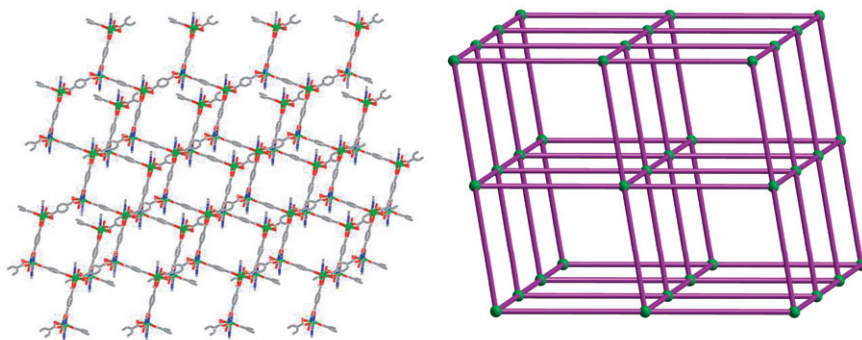
methyl-substituted biim in the presence of metal ions, interesting inorganic–organic frameworks may be produced. Indeed, **1** and **2** were obtained by the reactions of metal salts, MeHbiim/Me₂biim, and 1,4-BDC under hydrothermal conditions, **1** is a 1-D zigzag chain and **2** is a 3-D coordination polymer. These may be attributed to the different shapes of the methyl-substituted biim ligands. The Me₂biim has two methyl substituents with steric hindrance on the aromatic ring, in comparison with the MeHbiim, favoring the formation of bridging coordination polymers. As a result, 1,4-BDC as an ancillary ligand, although present in the reaction mixture, did not participate in the formula of **1**.

3.2. Crystal structures

The structures of **1** and **2** with atom labeling schemes and crystal packing are illustrated in figures 1–5; selected bonds and angles are listed in tables 2–5. Complex **1** has a 1-D structure as illustrated in figure 1. The central Zn has distorted tetrahedral coordination with two nitrogens from two different Me₂biim's and two chlorides. Me₂biim links two neighboring ZnCl₂ into a zigzag infinite chain. The N–Zn–N angle ($100.65(9)^\circ$) and the

Figure 2. The 2-D structure of **1**.Figure 3. The structure of **2** (A: $-x, -y+2, -z+2$).

Cl–Zn–Cl angle ($108.60(3)^\circ$) are considerably smaller than in $[\text{Zn}_2\text{Cl}_4(\mu\text{-Me}_2\text{biim})_2]$ ($112.02(10)^\circ, 118.17(4)^\circ$) [23], but the Cl–Zn–Cl angle is similar to $\text{Zn}(\text{H}_2\text{biim})\text{Cl}_2$ ($109.8(2)^\circ$) [43]. The Zn–Cl and Zn–N distances ($2.2346(6)$ and $2.0296(15)$ Å) are close to those in $[\text{Zn}_2\text{Cl}_4(\mu\text{-Me}_2\text{biim})_2]$ (average 2.240 and 2.025 Å). Steric requirements between methyls force the two imidazole rings to form a dihedral angle of 77.7° . C(1) and C(2) of the imidazole have weak interactions with Cl(2) *via* nonclassical hydrogen

Figure 4. Hydrogen-bonds of **2** (B: $-x, -y+1, -z+1$).Figure 5. The 3-D network (left) and the α -Po topology structure (right) of **2**.Table 2. Selected bond lengths (\AA) and angles ($^\circ$) of **1**.

Zn(1)–N(1)	2.0296(15)	Zn(1)–Cl(2)	2.2346(6)
N(1)#1–Zn(1)–N(1)	100.65(9)	N(1)–Zn(1)–Cl(2)#1	111.73(5)
N(1)–Zn(1)–Cl(2)	112.01(5)	N(1)–C(4)–C(4)#2	127.24(17)
Cl(2)#1–Zn(1)–Cl(2)	108.60(3)	N(2)–C(4)–C(4)#2	122.00(16)
N(1)–C(4)–N(2)	110.56(15)	C(4)–N(1)–C(1)	105.93(15)
C(4)–N(1)–Zn(1)	131.10(12)	C(1)–N(1)–Zn(1)	122.83(13)

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

Table 3. The bond lengths (Å) and angles (°) of hydrogen bonds of **1**.

D–H...A	<i>d</i> (D–H)	<i>d</i> (H...A)	<i>d</i> (D...A)	∠(DHA)
C(1)–H(1)...Cl(2)	0.93	2.76	3.659(2)	163
C(2)–H(2)...Cl(2)	0.93	2.92	3.737(2)	146

Table 4. Selected bond lengths (Å) and angles (°) of **2**.

Cd(1)–O(1)	2.562(3)	O(4)–Cd(2)–O(6) ^A	92.56(10)
Cd(1)–O(3)	2.196(3)	O(6) ^A –Cd(2)–O(2) ^A	92.91(10)
Cd(1)–N(1)	2.305(3)	O(6)–Cd(2)–O(2) ^A	87.09(10)
Cd(1)–O(2)	2.347(3)	O(5)–Cd(1)–O(3)	100.12(13)
Cd(1)–N(2)	2.352(3)	O(5)–Cd(1)–N(1)	88.86(11)
Cd(1)–O(5)	2.169(3)	O(3)–Cd(1)–N(1)	119.17(12)
Cd(2)–O(4)	2.236(3)	O(5)–Cd(1)–O(2)	102.91(11)
Cd(2)–O(6)	2.351(3)	O(3)–Cd(1)–O(2)	97.53(11)
Cd(2)–O(2)	2.308(2)	N(1)–Cd(1)–O(2)	138.98(10)
C(3)–C(4)	1.463(5)	O(5)–Cd(1)–N(2)	161.51(11)
N(1)–C(3)–C(4)	119.2(3)	O(3)–Cd(1)–N(2)	91.25(12)
N(3)–C(3)–C(4)	130.2(4)	N(1)–Cd(1)–N(2)	72.82(11)
O(2)–Cd(1)–O(1)	53.14(9)	O(2)–Cd(1)–N(2)	89.87(10)
N(1)–Cd(1)–O(1)	87.34(11)	O(1)–Cd(1)–O(5)	94.07(12)
		O(3)–Cd(1)–O(1)	149.86(11)

Symmetry transformations used to generate equivalent atoms: ^A $-x, -y+2, -z+2$.

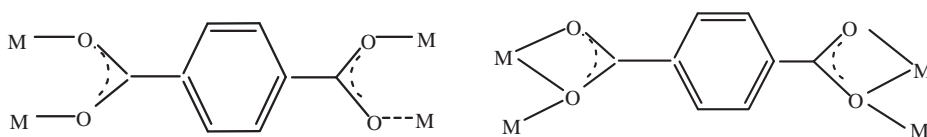
Table 5. The bond lengths (Å) and angles (°) of hydrogen bonds of **2**.

D–H...A	<i>d</i> (D–H)	<i>d</i> (H...A)	<i>d</i> (D...A)	∠(DHA)
N(3)–H(3)...O(1) ^B	0.86	1.95	2.792(6)	163
C(7)–H(7)...O(1)	0.96	2.56	3.196(6)	123

Symmetry transformations used to generate equivalent atoms: ^B $-x, -y+1, -z+1$.

bonds, C(1)–H(1)...Cl(2) distance of 3.659(2) Å (\angle C–H...Cl = 163°) intrachain and C(2)–H(2)...Cl(2) (3.734 Å, \angle C–H...Cl = 146°) interchain, forming 2-D supramolecular framework of **1** as displayed in figure 2.

The structural unit of **2**, given in figure 3, is significantly different from that in **1**. N-substituted 2,2'-biimidazole (MeHbiim) is a terminal chelating ligand and 1,4-BDC is a co-ligand. Complex **2** consists of a linear trinuclear cluster, where Cd(1) is bridged by three 1,4-BDC to the central Cd(2), which is located at an inversion center. The coordination environment of Cd(1) is distorted octahedral with two nitrogens of a MeHbiim [Cd(1)–N(1) 2.305(3) and Cd(1)–N(2) 2.352(3) Å] and four oxygens [Cd(1)–O(1) 2.562(3), Cd(1)–O(3) 2.196(3), Cd(1)–O(5) 2.169(3), and Cd(1)–O(2) 2.347(3) Å] from three different 1,4-BDC ligands; Cd(2) has ideal octahedral geometry with six oxygens from six 1,4-BDC ligands. Therefore, two 1,4-BDC's bridge bis-bidentate and the third chelates/bridges bis-bidentate (scheme 2). The distance

Scheme 2. The coordination modes of the 1,4-BDC ligands in complex **2**.

between the two metal centers [$\text{Cd}(1) \cdots \text{Cd}(2)$] is 3.682(9) Å, slightly longer than that observed in $[\text{Cd}_3(\text{H}_2\text{biim})_2(1,4\text{-bdc})_3] \cdot 2\text{H}_2\text{O}$ (3.658 Å) [44].

For MeHbiim, ring closure induces in-plane distortions to improve overlap between metal orbitals and ligand δ lone pairs, leading to a large difference between the $\text{N}(1)\text{--C}(3)\text{--C}(4)$ and $\text{N}(3)\text{--C}(3)\text{--C}(4)$ angles ($\sim 119^\circ$ vs. $\sim 130^\circ$). The central $\text{C}(3)\text{--C}(4)$ bond length is 1.463(5) Å, which is similar to that observed in $[\text{Pt}(\text{MeHbiim})\text{Cl}_2] \cdot \text{Et}_4\text{NCl}$ (1.467 Å) [45]. For **2**, although the two independent imidazole rings remain individually planar, the MeHbiim molecule is bent slightly about the $\text{C}(3)\text{--C}(4)$ bond, leading to a dihedral angle of $14.388(2)^\circ$ between the two imidazole rings.

An interesting feature of this structure is the presence of hydrogen-bonding. The $\text{N}(3)\text{--H}(3)$ and --CH_3 of each MeHbiim form hydrogen bonds to $\text{O}(1)$ of a chelating/bridging bis-bidentate 1,4-BDC. The $\text{N}(3)\text{--H}(3) \cdots \text{O}(1)$ hydrogen bond is quite strong, since the $\text{N--H} \cdots \text{O}$ unit is nearly linear ($\sim 163^\circ$) and the $\text{N} \cdots \text{O}$ separation averages 2.792 Å [46]; the --CH_3 has weak interaction with $\text{O}(1)$ via a nonclassical hydrogen bond ($\text{C}(7)\text{--H}(7) \cdots \text{O}(1) = 3.196(6)$ Å), as illustrated in figure 4. These hydrogen bonds stabilize the crystal packing.

The trinuclear units are interconnected through six 1,4-BDC ligands to yield a robust 3-D supramolecular architecture in a $\alpha\text{-Po}$ topology (figure 5). Although similar linear trinuclear complexes have been reported [44, 47–52], this type of complex with terminal MeHbiim has not been found.

3.3. Luminescence

Polymeric complexes of d^{10} metal cations, such as ZnII , CdII , and polyimidazole heterocyclic ligands, possess interesting luminescent properties [53], which can be used as DNA photocleavage agents, chemical probes, and cation-induced photoswitch. Thus, luminescence of the free ligands, **1** and **2** in DMSO were investigated at room temperature.

Emission spectra of **1**, **2**, Me_2biim , and MeHbiim are depicted in figure 6. Apparently, emission spectra of **1** and **2** resemble their free ligands except for emission intensity, indicating that fluorescence of **1** and **2** may be assigned to ligand-based emission. Maximum emission is at 342 nm for **1** and 343 nm for **2** (under 290 nm excitation), attributed to n/π^* or π/π^* transitions of ligands [54, 55]. By comparing with the emission spectra of the corresponding ligand, the fluorescence intensity enhancement of **2** was stronger than that of **1**. A possible explanation is that there is strong conformational rigidity for a 3-D supramolecular network constructed by coordination interactions and hydrogen bonds compared with those of **1** [56].

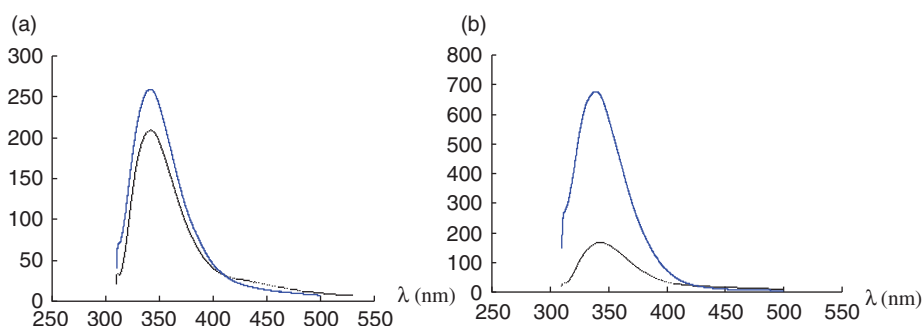


Figure 6. (a) Fluorescence emission spectra of Me_2biim (dashed line) and **1** (full line); (b) Fluorescence emission spectra of MeHbiim (dashed line) and **2** (full line).

3.4. Thermogravimetric analyses

The TGA of **1** and **2** under nitrogen indicate that the framework of **1** is stable to 355°C . When the temperature is higher than 355°C , the organic ligands were removed leading to collapse of the framework. No weight loss was observed in the TGA curve of **2** to 400°C ; obvious weight loss ended at 676°C . The TGA curves show that the solid-state structure of **2** is highly robust.

4. Conclusions

The syntheses, structures, and fluorescence of two d^{10} complexes with N-substituted 2,2'-biim and auxiliary 1,4-BDC are presented. The different N-substituted methyl groups have different angles between imidazole rings, which may exhibit different geometries of the coordination polymers. The steric hindrance of the methyl substituents is responsible for the distortion of the coordination sphere of the metals in **1** and **2**. The present results demonstrate that the template effect of the auxiliary ligand plays an important role in the construction of topological nets. The complexes display strong fluorescence, indicating that they may have potential applications such as optical materials.

Supplementary material

Crystallographic data for the structure of the complexes $[\text{Zn}(\mu\text{-Me}_2\text{biim})\text{Cl}_2]_n$ and $[\text{Cd}_3(\text{MeHbiim})_2(1,4\text{-BDC})_3]_n$ have been deposited with the Cambridge Crystallographic Data Centre as supplementary Nos CCDC 603834 and 603835, respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif

Acknowledgments

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