



Two three-dimensional cadmium supramolecular architectures containing extensive hydrogen-bonding networks based on CdSO₄ and bis-imidazole ligands

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HIGHLIGHTS

- ▶ Two interesting architectures containing different extensive hydrogen-bonding networks.
- ▶ Compound **1** has an infinite 1D double chain structure and **2** contains an infinite 1D helix channel.
- ▶ Subtle changes in the ligand structure may have a strong influence on architectures of MOF.

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ABSTRACT

In this study, two novel three-dimensional (3D) supramolecular networks, [Cd(BIM)₂(SO₄)(H₂O)]·(C₂H₅OH) (H₂O)₂ (**1**) and [Cd(2-mBIM)(SO₄)(H₂O)₃]·H₂O (**2**) [BIM = bis(imidazol-1-yl)-methane, 2-mBIM = bis(2-methylimidazol-1-yl)methane], were synthesized by the reactions of CdSO₄ with BIM or 2-mBIM ligand *via* solvent diffusion methods. The networks were then characterized by elemental analyses, IR, TGA, and X-ray diffraction. Both compounds **1** and **2** have a 3D hydrogen-bonding network with an infinite one-dimensional (1D) double chain structure and an infinite 1D helix channel, respectively. These results suggest that the subtle change in the ligand structure may have a strong influence on the resulting architectures of the metal–organic frameworks. The solid-state luminescent spectra of compounds **1** and **2** indicate weak fluorescent emissions at *ca.* 338 and 389 nm, respectively.

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1. Introduction

In recent years, metal–organic frameworks (MOFs) with well-regulated network structures have received remarkable attention as functional materials with potential applications in fields such as gas adsorption [1–3], ion exchange [4,5], magnetism [6], heterogeneous catalysis, luminescence, and nonlinear optics [7–10]. The rational design, synthesis, and characterization of new metal–organic architectures has been elusive and still remains a major challenge in this field because the self-assembly process is frequently influenced by various factors such as the number, type, and spatial disposition of binding sites on the ligand, anions, template, geometric requirements of metal atoms, temperature, and medium [11–14]. The most effective and facile approach for the controlled

preparation of functional MOFs is appropriate selection of well-designed organic ligands containing multidentate nitrogen and oxygen donor ligands, together with metal centers with various coordination preferences [15–17].

So far, flexible ligands have been widely used in the construction of MOFs with interesting topologies and attractive properties. This is because flexible ligands have variable coordination modes and can adopt a variety of conformations according to the restrictions imposed by the coordination geometry of the metal ion. Among them, flexible multidentate ligands with imidazole nitrogen donors have been found to be one of the most useful organic building blocks for the construction of MOFs with versatile topologies such as cages, honeycombs, interpenetrating networks, and multidimensional frameworks architectures [18–20]. In our previous work, we have reported many fascinating structures based on bis(imidazol-1-yl) methane derivative ligands. The results of these investigations have shown that the bis(imidazol-1-yl) methane derivative ligands are good candidates for the construction of coordination polymers exhibiting interesting architectures. In addition, subtle changes in the ligand structure may have a strong influence on the resulting

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

Complex code	1	2
Empirical formula	C ₁₆ H ₂₈ CdN ₈ O ₈ S	C ₉ H ₂₀ CdN ₄ O ₈ S
Formula weight	604.92	456.75
Temperature (K)	200(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	P2(1)/c	P-1
A (Å)	9.2649(2)	7.6095(6)
B (Å)	14.9855(3)	12.2202(10)
C (Å)	16.5599(4)	18.4300(16)
α (°)	90.000(0)	86.326(1)
β (°)	95.328(1)	82.807(1)
γ (°)	90.000(0)	73.908(1)
V (Å ³)	2289.23(9)	1632.9(2)
Z	4	4
De (g/cm ³)	1.755	1.858
μ (mm ⁻¹)	1.11	1.51
F(000)	1232	920
Crystal size (mm)	0.30 × 0.10 × 0.10	0.18 × 0.16 × 0.12
Crystal color and habit	Colorless block	Colorless block
θ range (°)	1.8–26.0	2.0–29.1
Index ranges	–11 ≤ h ≤ 11, –18 ≤ k ≤ 16 –20 ≤ l ≤ 18	–10 ≤ h ≤ 10, –15 ≤ k ≤ 16 –19 ≤ l ≤ 24
Reflections collected	14480	10186
Independent reflections	4475 [R(int) = 0.112]	7524 [R(int) = 0.013]
Max. and min. transmission	0.895 and 0.876	0.840 and 0.773
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data/restraints/parameters	4475/24/349	7524/16/463
Goodness-of-fit on F ²	1.14	1.02
Final R indices [I > 2σ(I)]	R1 = 0.0390, wR2 = 0.0977	R1 = 0.0265, wR2 = 0.0677
R indices (all data)	R1 = 0.0458, wR2 = 0.1147	R1 = 0.0304, wR2 = 0.0698
Largest diff. peak and hole	0.83 and –0.77 e Å ⁻³	0.91 and –0.47 e Å ⁻³

architectures of the MOFs [21]. Herein, we report the syntheses, crystal structures, and photoluminescence properties of two cadmium three-dimensional (3D) supramolecular architectures containing extensive hydrogen-bonding networks, [Cd(BIM)₂(SO₄)(H₂O)] (C₂H₅OH)(H₂O)₂ (**1**) and [Cd(2-mBIM)(SO₄)(H₂O)₃·H₂O (**2**).

2. Experimental section

2.1. Materials and measurements

All chemicals were obtained commercially available and used as received without further purification. Ligand bis(imidazol-1-yl)methane (BIM) and bis(2-methyl-imidazol-1-yl)methane (2-mBIM) were prepared by literature's methods [22]. The FT-IR spectra were recorded from KBr pellets in the range of 4500–500 cm⁻¹ on a Nicolet 5700 infrared spectrometer. Thermogravimetric analysis (TGA) measurements were made using a Pyris diamond TG/DTA Thermogravimetric differential Thermal Analyzer. Samples were heated at 10 °C/min from 40 to 800 °C in a dynamic nitrogen atmosphere. Elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer. The 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(BIM)₂(SO₄)(H₂O)]·(C₂H₅OH)(H₂O)₂ (**1**)

An ethanol solution (5 ml) of BIM (74 mg, 0.5 mmol) was slowly diffused into an aqueous solution (5 ml) of CdSO₄·8/3H₂O (64 mg,

Table 2
Selected bond lengths [Å] and angles [°] for complex **1** and **2**.

1			
Cd(1)–O(1)	2.244(3)	Cd(1)–N(1)	2.323(3)
Cd(1)–N(4)	2.325(3)	Cd(1)–N(8)	2.327(3)
Cd(1)–N(5)	2.337(3)	Cd(1)–O(5)	2.375(3)
N(1)–Cd(1)–O(1)	95.38(13)	O(1)–Cd(1)–N(4)	99.78(12)
N(1)–Cd(1)–N(4)	91.04(11)	O(1)–Cd(1)–N(8)	91.46(13)
N(1)–Cd(1)–N(8)	173.1(10)	N(4)–Cd(1)–N(8)	86.37(11)
N(5)–Cd(1)–O(1)	82.81(12)	N(1)–Cd(1)–N(5)	90.58(11)
N(4)–Cd(1)–N(5)	176.80(10)	N(8)–Cd(1)–N(5)	91.71(11)
O(1)–Cd(1)–O(5)	165.43(12)	N(1)–Cd(1)–O(5)	83.66(10)
N(4)–Cd(1)–O(5)	94.77(10)	N(8)–Cd(1)–O(5)	90.08(10)
N(5)–Cd(1)–O(5)	82.67(10)		
2			
Cd(1)–N(2) ⁱ	2.285(2)	Cd(1)–O(5)	2.296(2)
Cd(1)–O1W	2.299(2)	Cd(1)–N(5)	2.303(2)
Cd(1)–O3W	2.328(2)	Cd(1)–O4W	2.347(2)
Cd(2)–N(8)	2.263(2)	Cd(2)–O5W	2.273(2)
Cd(2)–N(4)	2.293(2)	Cd(2)–O(3)	2.298(2)
Cd(2)–O2W	2.340(2)	Cd(2)–O6W	2.456(2)
Cd(1) ⁱⁱ –N2	2.285(2)		
O(5)–Cd(1)–N(2) ⁱ	92.85(8)	O1W–Cd(1)–N(2) ⁱ	176.89(8)
O(5)–Cd(1)–O1W	89.57(8)	N(2) ⁱ –Cd(1)–N(5)	92.59(8)
O(5)–Cd(1)–N(5)	86.42(7)	O1W–Cd(1)–N(5)	89.51(8)
N(2) ⁱ –Cd(1)–O3W	93.49(8)	O(5)–Cd(1)–O3W	87.12(7)
O1W–Cd(1)–O3W	84.68(8)	N(5)–Cd(1)–O3W	171.34(8)
N(2) ⁱ –Cd(1)–O4W	86.33(8)	O(5)–Cd(1)–O4W	169.37(7)
O1W–Cd(1)–O4W	90.92(8)	N(5)–Cd(1)–O4W	104.20(8)
O3W–Cd(1)–O4W	82.35(8)	N(8)–Cd(2)–O5W	174.72(8)
N(8)–Cd(2)–N(4)	98.07(8)	N(4)–Cd(2)–O5W	87.12(8)
N(8)–Cd(2)–O(3)	89.69(8)	O5W–Cd(2)–O(3)	88.49(7)
N(4)–Cd(2)–O(3)	99.26(8)	N(8)–Cd(2)–O2W	98.08(8)
O5W–Cd(2)–O2W	82.78(7)	N(4)–Cd(2)–O2W	90.75(8)
O(3)–Cd(2)–O2W	166.39(9)	N(8)–Cd(2)–O6W	87.07(8)
O6W–Cd(2)–O5W	87.82(7)	N(4)–Cd(2)–O6W	173.53(7)
O(3)–Cd(2)–O6W	84.64(8)	O2W–Cd(2)–O6W	84.61(8)

Symmetry codes: (i) x + 1, y, z; (ii) x – 1, y, z for **2**.

0.25 mmol) in test tube. Colorless crystals of **1** were formed at the interface of solvent in two weeks and were obtained in ca. 80% yield. Anal. Calcd for C₁₆H₂₈CdN₈O₈S: C 31.77, H 4.67, N 18.52; Found: C 31.51, H 4.56, N 18.83; IR (KBr, cm⁻¹): ν = 3400s, 3109s, 2990 m, 1648s, 1502s, 1384s, 1290s, 1236s, 1137s, 1082s, 930s, 865 m, 768s, 706 m, 656 m, 610s.

2.3. Synthesis of [Cd(2-mBIM)(SO₄)(H₂O)₃]·H₂O (**2**)

An ethanol solution (5 ml) of 2-mBIM (89 mg, 0.5 mmol) was slowly diffused into an aqueous solution (5 ml) of CdSO₄·8/3H₂O (64 mg, 0.25 mmol) in test tube. Colorless crystals of **2** were formed at the interface of solvent in two weeks and were obtained in ca. 75% yield. Anal. Calcd for C₉H₂₀CdN₄O₈S: C 23.67, H 4.41, N 12.27; Found: C 23.51, H 4.56, N 12.93; IR (KBr, cm⁻¹): ν = 3410s, 3113s, 1651s, 1548s, 1507 m, 1470w, 1430 m, 1381 m, 1278s, 1131s, 1080s, 773s, 613s.

2.4. X-ray crystallography

Crystals of complexes **1** and **2** were removed from test tube and covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber and data for **1** and **2** were collected at 200(2) K for **1** and 293(2) K for **2** using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, λ = 0.71073 Å). An empirical absorption was applied using SADABS program [23]. The structures were solved by direct methods using the program SHELXL 97 and refined by full-matrix least-squares methods on F² using the SHELXL 97 crystallographic software package [24]. All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms

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