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Research paper

Three new 3D metal-organic frameworks based on the tetrakis(imidazol-1-ylmethyl)methane and 1,4-benzenedicarboxylic acid ligands with transition metal (Zn/Cd/Co) and properties research

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ABSTRACT

Three novel 3D metal-organic frameworks, $\{[Zn_2(L)(BDC)_2]\cdot H_2O\}_n$ (**1**), $\{[Cd_2(L)_2(BDC)]\cdot(BDC)\cdot 7.7(H_2O)\}_n$ (**2**), and $\{[Co(L)(H_2O)_2]\cdot(BDC)\cdot 5(H_2O)\}_n$ (**3**) (L = tetrakis(imidazol-1-ylmethyl)methane, H_2BDC = 1,4-benzenedicarboxylic acid), have been successfully synthesized by self-assembly of transition-metal salts with a flexible N-containing ligand and 1,4-dicarboxybenzene ligand. Complexes **1**–**3** have 3D structures with various topologies. In complex **1**, the L connects Zn(II) atoms to form 2D layers, which are linked by two kinds of 1D $[Zn(BDC)]_n$ chains to generate a 4-connected three-dimensional structure with $(6\cdot8^5)(6^4\cdot8^2)(8^6)$ topology. In complex **2**, Cd(II) atoms are coordinated by L to furnish a 2D layer, and the adjacent layers are linked by BDC ligands as bridging ligands to general a new (4,5)-connected three-dimensional network with a point symbol of $(4^4\cdot6^2)(4^4\cdot6^6)$. In Complex **3**, the L ligands act as 4-connected linkers connecting Co(II) ions to display a 4-connected three-dimensional structure with $4\cdot6^5$ topological net directly. In addition, the solid-state fluorescence, infrared spectra, magnetic property and thermal stability of these complexes have also been investigated.

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1. Introduction

In recent years, metal-organic frameworks (MOFs) have received much attention not only due to structural diversity, but also their great potential application value in many fields, such as, ion exchange [1,2], catalysis [3–5], gas adsorption and separation [6–8], luminescence [9–11], magnetism [12,13] etc. To date, though lots of MOFs have been reported and studied within the past decades, the establishment of novel structures remain a big challenge in the long term [14]. Generally, the self-assembly of MOFs is dominated by various factors such as organic ligand, metal ions, anions, reaction solvent, temperature, pH value, and so on. Then it is so important to select the organic ligand in the construction of MOFs [15–17]. For the past few years, using flexible ligands to create MOFs is a common tactics, especially the study of tetrakis (imidazol-1-ylmethyl)methane ligand has been a lot. In the previous studies, Ma and co-workers systematically reported several 2D or 3D coordination complexes containing tetrakis(imidazol-1-ylmethyl)methane (L) ligand and other anions with different transition metals(Co/Zn/Cd/Ni) ions [18–21]. The L ligand is a good candidate for the construction of coordination polymers with interesting topologies. And the proper subsidiary bridging linkers are also critical in constructing coordination polymers. 1,4-benzenedicarboxylic acid (H_2BDC), may act as bridging ligands and has been extensively used [22–24].

In this work, we report the synthesis and structures of three metal-organic frameworks with the formulas $\{[Zn_2(L)(BDC)_2]\cdot H_2O\}_n$ (**1**), $\{[Cd_2(L)_2(BDC)]\cdot(BDC)\cdot 7.7(H_2O)\}_n$ (**2**), $\{[Co(L)(H_2O)_2]\cdot(BDC)\cdot 5(H_2O)\}_n$ (**3**) using tetrakis(imidazol-1-ylmethyl)methane (L, as shown in Scheme 1) ligand as organic linker, 1,4-benzenedicarboxylic acid (H_2BDC, as shown in Scheme 1) as bridging linker, divalent transitional-metal ions Zn(II), Cd(II), Co(II) as connecters respectively. And the three coordination modes between H_2BDC and metal ions are shown in Scheme 2. All Complexes are characterized by elemental analysis, X-ray crystallography, and thermal stability. The luminescent properties of Complexes **1** and **2** have been investigated. The magnetism of complex **3** also has been studied.

2. Experimental section

2.1. General

All the reagents were used as received from commercially purchased without any further purification. The ligand tetrakis(imida-

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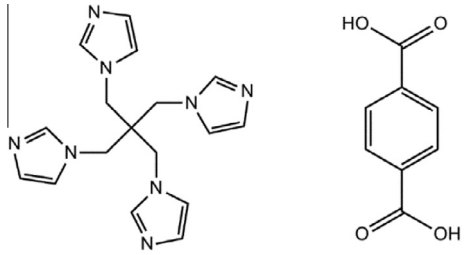
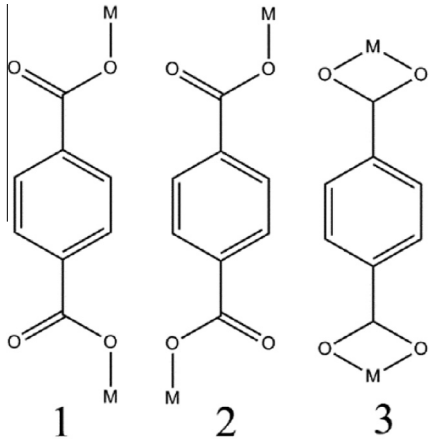


Scheme 1. The L ligand and H_2BDC.



Scheme 2. Three coordinated modes of H_2BDC in the text.

zol-1-ylmethyl)methane (L) was synthesized and purified as reported previously [18]. Elemental analysis was carried out with an Elementar vario ELIII analyzer. Infrared spectra were recorded with a Bruker Tensor 27 FT-IR spectrometer using KBr pellets in the 400–4000 cm^{-1} region. PXRD patterns of the samples were collected on a Bruker D8-Advance diffractometer equipped with Cu Kα radiation (λ = 1.5406 Å) at a scan speed of 10 °/min. Thermogravimetric (TG) analysis datas were collected on a simultaneous SDT thermal analyzer at a heating rate of 10 °C/min under a N_2 atmosphere (N_2 flow rate = 0.06 L/min). The emission spectrum and luminescent decay of Complexes **1** and **2** were measured on a Hitachi FL-7000 Fluorescence Spectrometer. Magnetic data of complex **3** was collected using a Quantum Design vibrating sample magnetometer in Physical Property Measurement System.

2.2. Syntheses of $\{[Zn_2(L)(BDC)_2]\cdot H_2O\}_n$ (**1**).

A mixture of L (0.1 mmol, 0.0336 g), $Zn(NO_3)_2\cdot 6H_2O$ (0.2 mmol, 0.0595 g), H_2BDC (0.2 mmol, 0.0332 g), 5 mL H_2O and a drop of DMF was stirred for 0.5 h, then transferred to a 20 mL Teflon-lined stainless steel container, heated at 120 °C for 2 days, and then cooled to room temperature slowly. Colorless crystals of **1** can be obtained. Yield: 28% based on Zn^{II}. Elemental analysis (%) for $C_{33}H_{30}Zn_2N_8O_9$ (813.39). Calcd: C, 48.73; H, 3.72; N, 13.78. Found: C, 48.57; H, 3.79; N, 13.68. IR (KBr, cm^{-1}): 3459(s), 3118(s), 1599 (s), 1338(s), 1103(s), 1024(w), 948(m), 881(m), 826(m), 740(s), 658(m), 630(w), 569(w), 514(w).

2.3. Syntheses of $\{[Cd_2(L)_2(BDC)]\cdot(BDC)\cdot 7.7(H_2O)\}_n$ (**2**)

A mixture of L (0.2 mmol, 0.0673 mg), $Cd(NO_3)_2\cdot 4H_2O$ (0.4 mmol, 0.1234 g), H_2BDC (0.4 mmol, 0.0664 g), 8 mL H_2O, 3 mL DMF and 10% sodium hydroxide solution (0.1 mL) was stirred for 0.5 h, then transferred to a 20 mL Teflon-lined stainless steel container, heated at 130 °C for 3 days, and then cooled to room temperature slowly. Colorless crystals of **2** can be obtained. Yield: 47% based on Cd^{II}. Elemental analysis (%) for $C_{50}H_{63.4}Cd_2N_{16}O_{15.7}$ (1364.59). Calcd: C, 44.01; H, 4.68; N, 16.42. Found: C, 44.71; H, 4.98; N, 16.09. IR (KBr, cm^{-1}): 3423(s), 3127(w), 2922(w), 1558 (s), 1382(s), 1242(m), 1093(s), 1024(m), 932(m), 830(m), 751(m), 657(m), 624(w), 515(w).

2.4. Syntheses of $\{[Co(L)(H_2O)_2]\cdot(BDC)\cdot 5(H_2O)\}_n$ (**3**)

The similar synthetic method for **1** was used except that Cd $(NO_3)_2\cdot 4H_2O$ was replaced by $Co(NO_3)_2\cdot 6H_2O$ (0.4 mmol, 0.1164 g). Colorless crystals of **3** can be obtained. Yield: 46% based on Co^{II}. Elemental analysis (%) for $C_{25}H_{38}CoN_8O_{11}$ (685.56). Calcd: C, 43.80; H, 5.59; N, 16.35; Found: C, 43.52; H, 5.51; N, 16.37. IR (KBr, cm^{-1}): 3385(s), 3133(w), 1565(s), 1455(m), 1384(s), 1292 (m), 1241(s), 1089(s), 1026(m), 938(m), 824(m), 752(s), 663(s), 623(w), 508(w).

2.5. Crystallographic data collection and refinement

Single-crystal X-ray diffraction measurements for Complexes **1**–**3** were carried out on a Bruker Smart APEX II CCD at 298 K with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Empirical absorption corrections were carried out using the SADABS program. The structures were solved by direct methods and refined on F2 by the full-matrix least-squares technique by using the SHELXL-97 program [25,26]. The hydrogen atoms on the water molecule were generated geometrically. The details on crystallographic data collection refinement parameters are shown in Table 1.

3. Results and discussion

3.1. Crystal structure of complex **1**

Complex **1** crystallizes in the $Pca2_1$ space group and in a triclinic system. As shown in Fig. 1a, there are two unique Zn(II) atoms (Zn1 and Zn2), one L ligand, two BDC ligands, and one lattice water molecule in the asymmetric unit of **1**. Both Zn1 and Zn2 have the same coordinated environment, while each Zn(II) atom is four-coordinated by two N atoms from two individual L ligands [Zn1-N4 = 2.013(6) Å and Zn1-N7 = 2.058(7) Å; Zn2-N2 = 2.016 (5) Å and Zn2-N5 = 2.027(6) Å], two O atoms from two BDC ligands [Zn1-O1 = 1.961(5) Å and Zn1-O3$^{\#1}$ = 1.970(5) Å; Zn2-O5 = 1.959 (6) Å and Zn2-O7$^{\#2}$ = 1.953(6) Å] to form two distorted tetrahedron coordination geometry respectively.

Along *a* axis and *c* axis, every BDC ligand connects two adjacent Zn atoms to form a 1D flat $[Zn(BDC)]_n$ chains with the neighbouring Zn distances being 10.952 Å and 10.910 Å, respectively (Fig. 1b). There are $\pi\cdots\pi$ interactions between the phenyls of BDC anions with centroid distance of 3.8960 Å and 3.9120 Å in Fig. S1. In this Complex, the BDC ligands adopt mode 1 connecting Zn1 atoms and mode 2 bridging Zn2 atoms severally to form 1D chains. And each L ligand coordinated four Zn atoms through its four imidazole groups to form a 2D layer structure (Fig. 1c). Adjacent layers are linked by the 1D chains to form one 3D framework structure (Fig. 1d). From a topological view point, the Zn atoms and the L ligands can be all considered as a four-connected node, so the 3D structure of Complex **1** is simplified to a 4-connected net with the point symbol $(6\cdot 8^5)(6^4\cdot 8^2)(8^6)$ (Fig. 1e).

3.2. Crystal structure of complex **2**

The result of XRD showed that the Complex **2** is in the $P2_1/c$ space group, a triclinic system. As shown in part of Fig. 2a, the

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