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Hydrothermal synthesis and structure characterization of two six-connected metal–organic frameworks based on the mixed ligands

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ABSTRACT

Two metal–organic frameworks, namely, $[Ni_2(BIMB)_2(ndd)_2\cdot H_2O]_n$ (**1**) and $[Zn_3(ndd)_{2.5}(\mu_3\text{-}OH)(1,3\text{-}dpp)]_n$ (**2**) (H_2ndd = 2,2′-(naphthalene-1,5-diylbis(oxy))diacetic acid, BIMB = 1,4-*bis*[(1H-imidazol-1-ly)methyl]benzene, 1,3-dpp = 1,3-di(pyridin-4-yl)propane) have been synthesized under hydrothermal conditions and characterized by single-crystal X-ray diffraction and thermogravimetric analysis. Compound **1** presents a two-dimensional network with point symbol of $(3^6\cdot4^6\cdot5^3)$-**hxl** topology. Moreover, compound **2** displays a novel 2-fold interpenetrated structure with the point symbol of $(4^{12}\cdot6^3)$-**pcu** topology based on the hexanuclear $[Zn_6(CO_2)_{10}(N)_4]$ unit as a six-connected node. Meanwhile, compound **2** shows good fluorescence property in the solid state at room temperature.

1. Introduction

The current interest in metal–organic frameworks not only stems from their potential applications in microelectronics, nonlinear optics, porous materials, and catalysis, but also from their intriguing variety of topologies and entanglement motifs [1]. In recent years, a number of metal–organic frameworks with various structural types and topological features has been documented [2]. Generally, the topological architectures of the metal–organic frameworks can be controlled by the deliberate design and judicious choice of the organic ligands and coordination geometries of the metal ions. In this aspect, the structural features of the organic ligands, such as shape, functionality, flexibility, symmetry, length, and substituent group, can influence the final structure types of the coordination polymers directly [3]. Among the reported structures, organic ligands with carboxylate groups are particularly interesting because of their various coordination modes to metal ions [4]. Thus, we have designed a multi-carboxylate ligand, 2,2′-(naphthalene-1,5-diylbis(oxy))diacetic acid (H_2ndd, Scheme 1), possessing flexibility owing to the presence of $-O-CH_2-$ group between the phenyl ring and carboxyl moiety, to construct novel coordination polymers.

On the other hand, many research have been concerned with the synthesis of metal–organic frameworks by incorporating a second organic ligand such as 2,2′-bipyridine, 4,4′-bipyridine or 1,10-phenanthroline into the structures of coordination polymers [5]. As a continuation of our search for new coordination network, a fairly effective way to construct desirable networks is the introduction of the flexible N-donor ligands, such as 1,4-*bis*((1H-imidazol-1-ly)methyl)benzene, 1,3-di(pyridin-4-yl)propane. Herein, two new complexes, $[Ni_2(BIMB)_2(ndd)_2\cdot H_2O]_n$ (**1**), $[Zn_3(ndd)_{2.5}(\mu_3\text{-}OH)(1,3\text{-}dpp)]_n$ (**2**), have been synthesized from the reactions of the Ni(II) or Zn(II) with 2,2′-(naphthalene-1,5-diylbis(oxy))diacetic acid in the presence of flexible N-donor auxiliary ligands. Compound **1** shows 2D grid with the $(3^6\cdot4^6\cdot5^3)$-**hxl** topology based on the binuclear cluster as a six-connected node. Compound **2** exhibits the 2-fold interpenetrating 3D structure with point symbol of the $(4^{12}\cdot6^3)$-**pcu** topology.

2. Experimental sections

2.1. Materials and methods

All reagents and solvents employed were commercially available and used as received without further purification. The ligand of H_2ndd, BIMB and 1,3-dpp was synthesized readily by the procedure reported in the literature [6]. Elemental analyses (C, H and N) were performed with a Perkin–Elmer 240C elemental analyzer. The FT-

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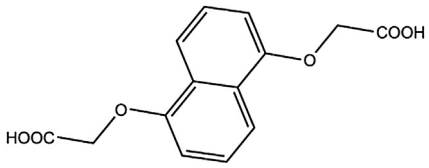

2,2'-(naphthalene-1,5-diylbis(oxy))diacetic acid

Scheme 1. The structure of H_2ndd ligand.

IR spectra were recorded from KBr pellets in the range of 4000–400 cm^{-1} on a Mattson Alpha–Centauri spectrometer (Figs. S1 and S2 in the Supporting Information). Solid-state luminescent spectra were measured on a Cary Eclipse spectrophotometer (Varian) equipped with a xenon lamp and quartz carrier at room temperature. Thermogravimetric (TG) analysis was performed with a Perkin–Elmer TG-7 analyzer heated from 40 to 1000 °C under nitrogen.

2.2. Synthesis of complex

2.2.1. Synthesis of $[Ni_2(BIMB)_2(ndd)_2\cdot H_2O]_n$ (1)

A mixture of $Ni(NO_3)_2\cdot 6H_2O$ (0.058 g, 0.2 mmol), H_2ndd (0.055 g, 0.2 mmol) BIMB (0.048 g, 0.2 mmol) in H_2O (14 mL) was sealed in a 25 mL Teflon-lined stainless steel container, which was heated at 150 °C for 3 days and then cooled down to room temperature at a rate of 5 °C h^{-1}. Yellow green crystals of **1** were collected and washed with distilled water and dried in air to give the product; yield, 42.6% (based on Ni^{II} salts). Elemental analyses calcd (%) for $C_{56}H_{50}N_8O_{13}Ni_2$ (1160.43): C, 57.96; H, 4.34; N, 9.66%. Found: C, 56.85; H, 4.01; N, 9.32% IR (KBr pellet, cm^{-1}): 3420.43(m), 3031.44(m), 2970.20(m), 2899.39(m), 2315.93(s), 1641.13(w), 1509.98(w), 1401.63(w), 1357.18(m), 1321.58(w), 1271.27(w), 1174.85(w), 1097.31(w), 938.12(m), 879.58(m), 791.30(m), 714.95(w), 683.18(m), 630.81(w), 537.70(s).

2.2.2. Synthesis of $[Zn_3(ndd)_{2.5}(\mu_3\text{-}OH)(1,3\text{-}dpp)]_n$ (2)

A mixture of $Zn(Ac)_2\cdot 2H_2O$ (0.044 g, 0.2 mmol), H_2ndd (0.055 g, 0.2 mmol), 1,3-dpp (0.040 g 0.2 mmol) in H_2O (14 mL) was sealed in a 25 ml Teflon-lined stainless steel container, which was heated at 150 °C for 3 days and then cooled down to room temperature at a rate of 5 °C h^{-1}. Yellow crystals of **2** were collected and washed with distilled water and dried in air to give the product; yield, 43.2% (based on Zn^{II} salts). Elemental analyses calcd (%) for $C_{48}H_{40}N_2O_{16}Zn_3$ (1097.06): C, 52.55; H, 3.68; N, 2.55%. Found: C, 52.05; H, 3.41; N, 2.14%. IR (KBr pellet, cm^{-1}): 3666.21(m), 3415.79(m), 3062.10(m), 2908(m), 1951.29(m), 1600(w), 1549.16(w), 1508.59(w), 1410.49(w), 1302.56(w), 1252.58(w), 1168.47(w), 1141.60(w), 1066.16(w), 857.46(w), 784.20(w), 699.27(w), 507.35(w), 473.07(w).

2.3. X-ray crystallography

Data collection of compounds **1** and **2** was performed on a Bruker Smart Apex II CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at room temperature. All absorption corrections were performed by using the SADABS program. The crystal structure was solved by direct methods and refined with full-matrix least-squares (SHELXTL-97) with atomic coordinates and anisotropic thermal parameters for all nonhydrogen atoms [7]. The hydrogen atoms of aromatic rings were included in the structure factor calculation at idealized positions by using a riding model. In compound **2**, H atoms of water molecules could not be introduced in the refinement but were included in the structure factor calculation. The detailed crystallographic data and structure refinement parameters for compounds **1** and **2** are summarized in Table S1 (in the Supporting Information). Selected bond lengths and angles are given in Table S2 (in the Supporting Information).

3. Results and discussions

3.1. Syntheses

Complexes **1**–**2** were successfully synthesized by reacting Ni(II) or Zn(II) salts, H_2ndd ligand and different secondary N-containing ligands at 150 °C for 3 days under hydrothermal conditions. When the semi-rigid BIMB was introduced into the reaction system, the two-dimensional compound **1** was obtained. When the flexible 1,3-dpp bridging ligand was adopted, one three-dimensional compound **2** was produced. The infrared spectra of **1** and **2** were consistent with their formulations. Features corresponding to the skeletal vibrations of aromatic rings and heterocyclic rings for these complexes were observed in the range of 1321–1440 cm^{-1} for **1** and 1302–1410 cm^{-1} for **2**. The absorption bands 1509 and 1641 cm^{-1} in **1**, 1508 and 1600 cm^{-1} in **2** in the IR spectra are attributed to the characteristic asymmetric stretching vibration of coordinated carboxylic groups due to the formation of Ni(II)–O and Zn(II)–O coordination bonds of carboxylic oxygen atom in the ligand.

3.2. Description of structures

3.2.1. $[Ni_2(BIMB)_2(ndd)_2\cdot H_2O]$ (**1**)

Single-crystal X-ray diffraction analysis reveals that compound **1** crystallizes in the monoclinic space group $P2_1/n$ and the structure of **1** contains two Ni^{II} ions, two BIMB ligands, two ndd ligands and one coordinated water molecule in the asymmetric unit. Compound **1** shows a six-connected 2D network which is built from the dinuclear Ni_2 unit. Meanwhile, each Ni^{II} ion in the dinuclear motif is coordinated by three carboxylic oxygen atoms of three ndd ligands (Ni–O 2.039(3)–2.094(3) Å), one oxygen atom of a water molecule (Ni–O 2.108(3) Å) and two nitrogen atoms of two BIMB ligands (Ni–N 2.074(4)–2.094(3) Å) to furnish a distorted octahedral geometry (Fig. S3 in the Supporting Information) [8]. Two symmetry-related Ni^{II} centers are bridged by two bidentate carboxylate groups from two ndd^{2-} anions and one bridging H_2O molecule to furnish $[Ni_2(CO_2)_4N_2]$ fragment in which the Ni···Ni distance is 3.566(17) Å (Fig. 1a). The axis sites of each Ni_2 are occupied by four additional BIMB ligands via nitrogen atom. Although each metal cluster is ligated by eight bridging ligands, it is virtually linked to six nearest-neighbors (six $\{Ni_2\}$ cluster) with distances of 13.611(25)–15.905(5) Å (center–center) (Fig. 1b). The extension of this structure results in a 2D layer structure (Fig. 1c).

From the topological point of view, the dinuclear Ni^{II} cluster is treated as a single node, each node can be considered as a six-connected node, because the two BIMB ligands form two "double-bridges". The ndd and BIMB ligands can be seen as a linear linker between two nodes. Thus, the whole structure can be represented to a 2D network with point symbol of the $(3^6\cdot 4^6\cdot 5^3)$-**hxl** topology (Fig. 1d).

In addition, there are the hydrogen-bonding interactions between the coordinated water molecules and carboxylic oxygen atoms (O1W–H···O13A, 2.649 Å; O1W–H···O8A, 2.601 Å, A, $-1+x$, y, z) in the identical 2D layers. Meanwhile, there are also strong interactions between imidazole ring from one network and imidazole ring from the other in the adjacent 2D layers (Parallel stacking with distances face–face of 3.2067(17) Å, centroid–centroid of 3.576(2) Å) which extend the 2D layers into a 3D supramolecular structure. Both the hydrogen bonds and π–π interactions make the