Inorganic Chemistry Communications 31 (2013) 13–17

Contents lists available at SciVerse ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Metal ion-driven assembly of 3D coordination polymers with 5-oxyacetate isophthalic acid and 4,4′-bis(1-imidazolyl)bibenzene

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ARTICLE INFO

Article history:
Received 28 November 2012
Accepted 4 February 2013
Available online 16 February 2013

Keywords:
Nickel(II) coordination polymer
Cadmium(II) coordination polymer
5-Oxyacetate isophthalic acid
4,4′-Bis(1-imidazolyl)bibenzene
Hydrothermal reactions
Crystal structures

ABSTRACT

Hydrothermal reactions of $NiCl_2\cdot6H_2O$ or $CdCl_2\cdot2.5H_2O$ with 4,4′-bis(1-imidazolyl)bibenzene (bimb) and 5-oxyacetate isophthalic acid (H_3OAIP) resulted in the formation of two coordination polymers $[Ni_2(HOAIP)_2(bimb)_3(H_2O)_2]_n$ (**1**) and $[Cd_3(OAIP)_2(bimb)(H_2O)_2]_n\cdot2nH_2O$ (**2**), respectively. Compounds **1** and **2** were characterized by elemental analysis, IR, powder X-ray diffraction, and single-crystal X-ray diffraction. **1** exhibits three-fold interpenetrating 3D architecture with a $(4^4\cdot6^5\cdot8)$ Schläfli symbol in which 1D $[Ni(HOAIP)]_n$ chains are interlinked by bimb ligands. In **2**, the two $[Cd_2(OAIP)_4]$ and $[Cd_2(OAIP)_4(H_2O)_4]$ units are interconnected by OAIP and bimb to afford a 3D network with a unique $(4\cdot8^2)_4(4^2\cdot6^8\cdot8^5)_2(8^6)$ Schläfli symbol. The results showed that metal ions did exert great influence upon the coordination modes and the geometrical conformations of ligands and the topological structures of the final products. Their thermal and photoluminescent properties were also investigated.

The design and construction of functional coordination polymers presently have attracted much attention not only for their intriguing architectures [1] but also for their potential applications in absorption [2], separation [3], magnetism [4], luminescence [5], catalysis [6], drug delivery [7], proton conduction [8], etc. Among numerous strategies for constructing these extended networks, the self-assembly of transition metal salts with organic ligands under solvothermal conditions has become an effective approach [9]. The topological networks of the resulting coordination polymers are intimately related to both the coordination environment favored by the transition metal ions and the geometry of the organic ligands [10]. Metal ions can be preselected in order to impart various chemical properties or predictable coordination geometries [1h,5a]. Rigid or flexible ligands have been used widely to construct coordination polymers with fascinating topologies, which offers us the opportunity to systematically study the relationship between the geometry of the ligands and the architecture of the generated networks [11]. Flexible ligands in the assembly procedure adopt a variety of conformations according to the restrictions imposed by the coordination requirement of the metal ions, while rigid ligands are normally robust and show geometric predictability [12]. If we introduce rigid groups and flexible groups on an identical ligand, can the resulting ligand in the assembly procedure combine the merits of both rigid ligands and flexible ones, to produce different topological structures and properties? With this in mind, we selected 5-oxyacetate isophthalic acid (H_3OAIP), which possesses one flexible and two rigid carboxylic acids [13] and is expected to have different coordination modes (Scheme 1). We carried out its reactions with $NiCl_2\cdot6H_2O$ and $CdCl_2\cdot2.5H_2O$ in the presence of a rigid N-donor ligand, 4,4′-bis(1-imidazolyl)bibenzene (bimb) under the hydrothermal conditions, and two unique 3D coordination polymers with different conformations and coordination modes of OAIP ligands, $[Ni_2(HOAIP)_2(bimb)_3(H_2O)_2]_n$ (**1**) and $[Cd_3(OAIP)_2(bimb)(H_2O)_2]_n\cdot2nH_2O$ (**2**) were isolated. Herein, we report their syntheses, crystal structures, thermal and photoluminescent properties.

The hydrothermal reaction of $NiCl_2\cdot6H_2O$ with H_3OAIP and bimb in a 1:1:1 molar ratio at 170 °C for one day gave rise to green block crystals of **1** in 72% yield based on bimb [14]. Analogous reaction of $CdCl_2\cdot2.5H_2O$ with H_3OAIP and bimb afforded colorless block crystals of **2** (41% yield based on Cd) [14]. At lower temperatures, the reaction gave the products in a lower yield. As described later in this paper, compounds **1** and **2** have different topological structures that may be ascribed to different metal ions. In **1**, each Ni(II) center takes an octahedral coordination geometry while in **2** some Cd(II) centers adopt a normal octahedral geometry and some have a pseudo pentagonal bipyramidal coordination geometry. It is such a small difference in the coordination geometry of Ni(II) or Cd(II) in **1** and **2** that led to the formation of different coordination modes and conformations of the HOAIP/OAIP ligands (Scheme 1), different terminal N-to-N distances of the bimb ligands, different metal ions/carboxylate units such as 1D

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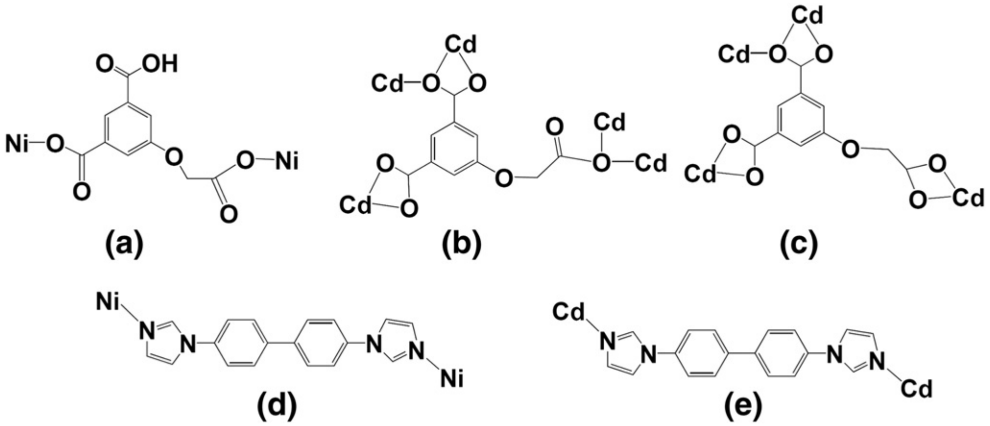
http://dx.doi.org/10.1016/j.inoche.2013.02.013



Scheme 1. The coordination modes of HOAIP in **1** (a), OAIP in **2** (b), OAIP in **2** (c), and bimb in **1** or **2** (d).

chain $[Ni(HOAIP)]_n$ (**1**), 4-connected $[Cd_2(OAIP)_4(H_2O)_4]$ unit and 6-connected $[Cd_2(OAIP)_6]$ unit (**2**) and different 3D topological structures of **1** and **2**.

Compounds **1** and **2** are air-stable and insoluble in common solvents. The elemental analysis was consistent with their chemical formulas. The IR spectra of **1** and **2** showed strong peaks in the ranges of 1560–1637 cm^{-1} and 1307–1435 cm^{-1}, indicating that they all contain coordinated carboxylic groups. The strong peaks at ca. 1060 cm^{-1} and 650 cm^{-1} mean the existence of imidazolyl groups in **1** and **2**. In the IR spectra of **1**, the strong absorption at 1701 cm^{-1} and 1410 cm^{-1} could be assigned to be the $\nu(C{=}O)$ vibration of the uncoordinated –COOH group [15]. The PXRD showed that the experimental patterns for each compound correlate well with its simulated one generated from single-crystal X-ray diffraction data (Fig. S1). The identities of **1** and **2** were further confirmed by single crystal X-ray diffraction analysis [16].

Compound **1** crystallizes in the monoclinic space group $P2_1/c$ and its asymmetric unit consists of half a $[Ni_2(HOAIP)_2(bimb)_3(H_2O)_2]$ molecule. In **1**, each Ni atom is octahedrally coordinated by two O atoms from one rigid and one flexible carboxyl group of two different OAIP ligands, one O atom from the coordinated H_2O, and three N atoms from three different bimb ligands (Fig. 1a). The average chelating Ni–O(OAIP) and Ni–O(H_2O) bond lengths (2.056(2) Å vs 2.086(3) Å) in **1** are somewhat shorter than those of the corresponding ones in $\{[Ni(bpea)(bim)_{1.5}(H_2O)]\cdot 3(bim)\}_n$ (2.087(5) Å vs 2.103(3) Å, H_2bpea = biphenylethene-4,4′-dicarboxylic acid, bim = 1,4-bis(1-

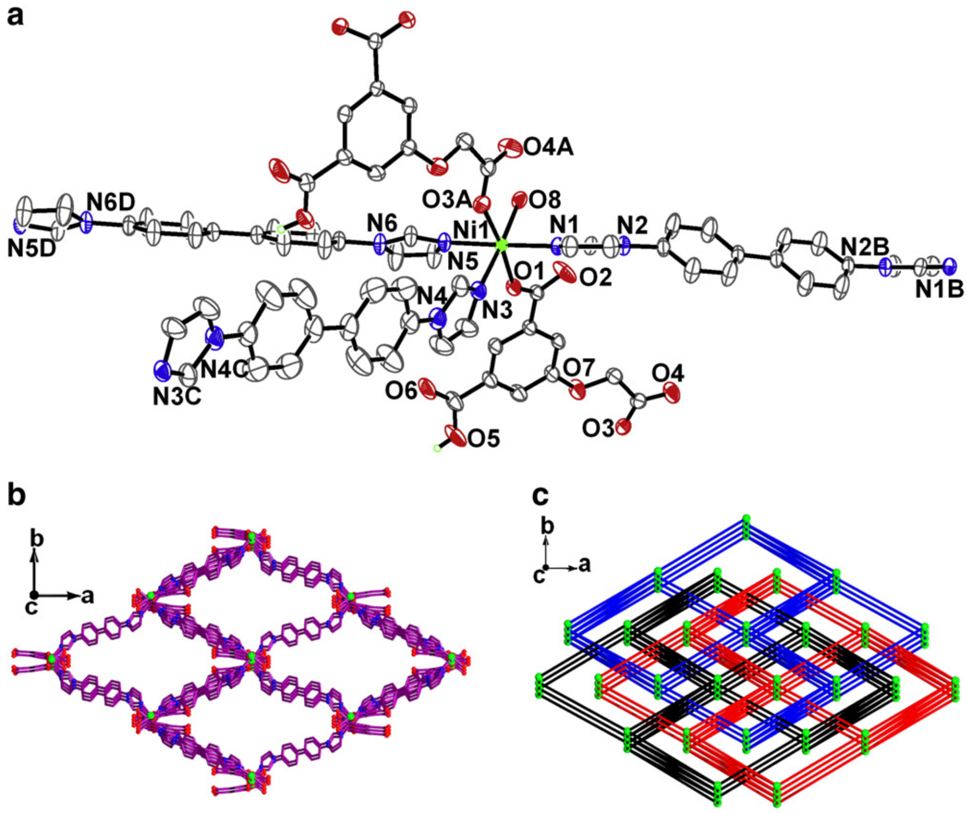


Fig. 1. (a) View of the coordination environment of Ni(1) in **1** with a labeling scheme and 40% thermal ellipsoids. All H atoms except one from the uncoordinated carboxyl group were omitted for clarity. Symmetry codes: (A) $x, y+3/2, z+1/2$; (B) $-x-1, -y+2, -z$; (C) $-x+2, -y+2, z+1$; (D) $-x+2, -y+2, -z+1$. (b) The 3D net of **1** (looking down the c axis). (c) View of 3-fold interpenetrating mode of **1** looking down the c axis. The red, gray, blue and green balls represent O, H, N and Ni atoms.