



A novel 3D (4,5,14)-connected layer-pillared metal-organic framework containing rare planar hexnuclear cadmium(II) clusters

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ARTICLE INFO

Article history:

Received 7 February 2012

Accepted 23 March 2012

Available online 2 April 2012

Keywords:

Imidazole-4,5-dicarboxylic acid

1,4-benzenedicarboxylic acid

Metal-organic frameworks (MOFs)

Mixed-ligands

Luminescence

ABSTRACT

A novel 3D layer-pillared metal-organic framework of $[\text{Cd}_3(\text{IDC})(\text{BDC})_{1.5}(\text{H}_2\text{O})]_n$ (**1**), (H_3IDC = imidazole-4,5-dicarboxylic acid, H_2BDC = 1,4-benzenedicarboxylic acid) was obtained by hydrothermal reaction, which contains rare planar hexnuclear Cd(II) cluster structural units and represents an unprecedented trinodal (4,5,14)-connected topology network. Furthermore, the thermal stability and luminescent property of **1** have also been examined.

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In the past decade, the rational design and assembly of metal-organic frameworks (MOFs) have received remarkable attention due to their potential applications in many fields [1,2]. Among thousands of MOFs investigated, a large number of MOFs are assembled from metal ions with single ligand, such as benzenecarboxylates [3,4] or N-heterocyclic carboxylates [5,6]. Besides, some MOFs constructed from mixed-ligands have also been reported [7,8]. For example, the introduction of rod-like neutral ligands such as 4,4'-bipyridine, pyrazine, or flexible bis-imidazole, piperazine and so on into MOFs often lead to the formation of new MOFs with more intriguing architectures and desired function properties [7b,8a,9–11].

Imidazole-4,5-dicarboxylic acid (H_3IDC), containing two nitrogen atoms in the imidazole ring and four oxygen atoms in the carboxylate group, shows strong coordination abilities and diverse coordination modes, and thus attracts much interest in the field of coordination chemistry [6,9b,10–14]. Therefore, a number of function MOFs based on H_3IDC have been synthesized and reported by our group and others during the past several years [6,9b,10–14]. For instance, by using H_3IDC and oxalic acid (H_2OX) to react with $\text{Ln}(\text{NO}_3)_3$ under hydrothermal conditions, we have synthesized a series of unique 3D lanthanide MOFs of $\{\text{K}_5[\text{Ln}_5(\text{IDC})_4(\text{OX})_4]\}_n \cdot 20n\text{H}_2\text{O}$ ($\text{Ln} = \text{Gd}, \text{Tb}, \text{and Dy}$) with 1D channels containing K^+ ions, and found that the exchange of guest K^+ ions with various cations can lead to variation of the luminescent properties [13b]. Very recently, we found that introduction of rod-like neutral N,N'-donor pillared ligands into the

metal- H_3IDC layer system can generate novel layered-pillared MOFs [10,11], which show interesting luminescent properties. Encouraged by these successful results, we use another second ligand of 1,4-benzenedicarboxylic acid (H_2BDC), which has been proved a good candidate for weaving luminescent MOFs with high dimensionality [4b,9c,15a,16], instead of N,N'-donor ligands to construct new MOFs. Fortunately, we obtained a layer-pillared MOF based on H_3IDC and H_2BDC , $[\text{Cd}_3(\text{IDC})(\text{BDC})_{1.5}(\text{H}_2\text{O})]_n$ (**1**), which contains rare planar hexnuclear cadmium(II) clusters and represents an unprecedented trinodal (4,5,14)-connected topology network. In this communication, we report its synthesis, crystal structure, thermal stability and luminescent property.

Colorless crystals of **1** were hydrothermally prepared by reacting $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ with H_3IDC , H_2BDC , and KOH at 170°C for 4 days, and characterized by elemental analysis (EA), infrared spectra (IR) [17], and single crystal X-ray diffraction analysis [18]. The result of single-crystal X-ray diffraction analysis reveals that **1** crystallizes in the triclinic system with space group $P\bar{1}$. The asymmetrical unit contains three crystallographically independent Cd(II) ions, one $\mu_4\text{-IDC}^{3-}$ anion (Fig. 1a), one $\mu_6\text{-BDC}^{2-}$ anion (Fig. 1b), half $\mu_8\text{-BDC}^{2-}$ anion (Fig. 1c) as well as one coordinated water molecule. As shown in Fig. 2a, the three Cd(II) ions display similar six-coordinated distorted octahedral geometries. Cd(1) is coordinated by one nitrogen atom and one oxygen atom from one $\mu_4\text{-IDC}^{3-}$ ligand, two oxygen atoms from two individual $\mu_8\text{-BDC}^{2-}$ ligands, and two oxygen atoms from two individual $\mu_6\text{-BDC}^{2-}$ ligands, Cd(2) is bonded with one nitrogen atom and one oxygen atom from one $\mu_4\text{-IDC}^{3-}$ ligand, one oxygen atom from one $\mu_8\text{-BDC}^{2-}$ ligand, and three oxygen atoms from three individual $\mu_6\text{-BDC}^{2-}$ ligands, and Cd(3) is completed by

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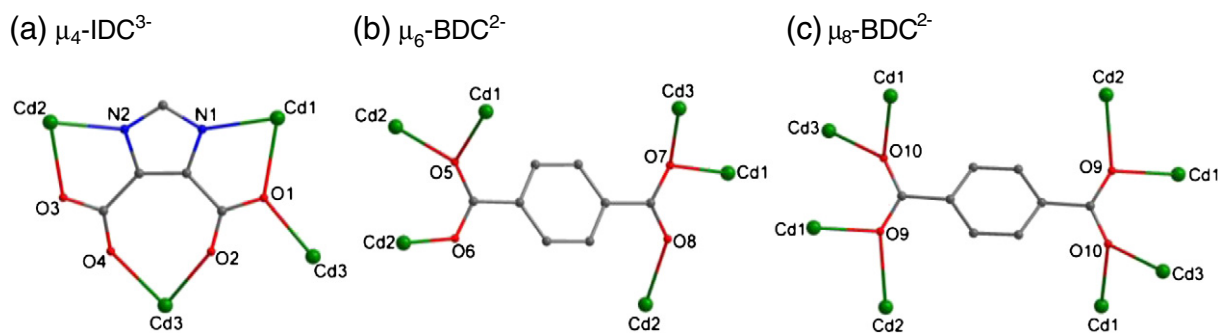


Fig. 1. The coordination modes of the IDC^{3-} and BDC^{2-} ligands observed in **1**.

six oxygen atoms from two $\mu_4\text{-IDC}^{3-}$ ligands, one $\mu_6\text{-BDC}^{2-}$ ligand, and one coordinated water molecule. The ligand IDC^{3-} anion employs μ_4 -coordination mode, connecting four Cd(II) ions, and the BDC^{2-} anions adopt μ_6 - and μ_8 -coordination modes, linking six Cd(II) ions and eight Cd(II) ions, respectively. To the best of our knowledge, among numerous H_2BDC -based coordination polymers, these in which the BDC^{2-} anions employ the coordination modes like in **1** are very limited [4b,9c,15a,16]. The Cd–N distances of 2.202(6)–2.286(6) Å and Cd–O distance of 2.230(5)–2.509(5) Å are in good agreement with literature values (Table S2) [4,11].

Through the linking of two $\mu_4\text{-IDC}^{3-}$ ligands, two Cd(1), two Cd(2) and two Cd(3) are connected together to generate a dimeric unit of $[\text{Cd}_3(\mu_4\text{-IDC})]_2$ (hexanuclear Cd(II) cluster, Fig. 2b and c), which should be regarded as secondary building unit (SBU). It is interesting to find the six Cd(II) ions are nearly in the same plane, with the mean plane deviation value of 0.0193 Å. Each hexanuclear SBU connects four $\mu_8\text{-BDC}^{2-}$ ligands (Fig. 3a), and each $\mu_8\text{-BDC}^{2-}$ ligand links four SBUs (Fig. 3b), resulting in a 2D undulated (4,4)-connected layer along the *ab* plane (Fig. 3c and d). The adjacent 2D layers are further pillared by $\mu_6\text{-BDC}^{2-}$ ligands (Fig. 4a) to fabricate a 3D complicated layer-pillared framework (Fig. 4c).

To well understand the architecture of **1**, the topological method was used to simplify and analyze this complicated framework. Obviously, the hexanuclear Cd(II) cluster, $\mu_8\text{-BDC}^{2-}$ and $\mu_6\text{-BDC}^{2-}$

anions should be considered as three nodes. Therefore, each $\mu_8\text{-BDC}^{2-}$ and $\mu_6\text{-BDC}^{2-}$ anion connecting four and five hexanuclear Cd(II) clusters, can be regarded as 4-connected node (Fig. 3b) and 5-connected node (Fig. 4a), respectively, and each hexanuclear Cd(II) clusters connecting four $\mu_8\text{-BDC}^{2-}$ anions and ten $\mu_6\text{-BDC}^{2-}$ anions, should be viewed as a 14-connected node (Fig. 4b). The 4-connected nodes, 5-connected nodes, and 14-connected nodes are in the ratio of 1:2:1. Therefore, each 14-connected node links four 4-connected nodes and ten 5-connected nodes, each 4-connected node and 5-connected node links four and five 14-connected nodes, respectively, creating a novel trinodal (4,5,14)-connected 3D framework (Fig. 4d), and the point symbol of the framework is $(4^{10})_2(4^{54}\cdot 6^{36}\cdot 8)(4^5\cdot 6)$ analyzed by TOPOS [19]. This framework represents the first 14-connected network utilizing hexanuclear Cd(II) clusters SBUs as building blocks among thousands of reported MOFs.

Compound **1** is air stable under ambient conditions and insoluble in water and common organic solvents. The phase purity of the bulk sample of the as-synthesized **1** was identified by powder X-ray diffraction (PXRD). Fig. S1 shows the measured PXRD pattern of **1** at room temperature and the simulated PXRD pattern generated from the single-crystal X-ray diffraction data. Obviously, the peak positions displayed in the measured pattern closely match to those in the simulated one, which indicates that single phase of **1** was formed.

To estimate the thermal stability of **1**, thermogravimetric analysis (TGA) experiment was carried out from 20 °C to 600 °C in an air

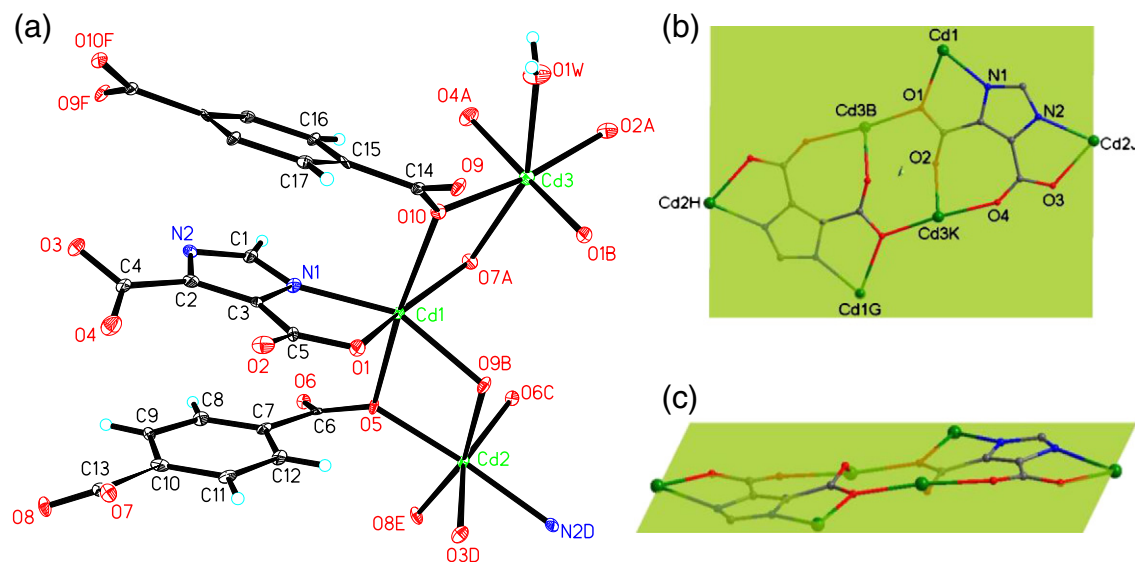


Fig. 2. (a) The coordination environment of the Cd(II) ions in **1** (thermal ellipsoids were drawn at the 30% level). (b) Top view and (c) side view of the dimeric unit of $[\text{Cd}_3(\mu_4\text{-IDC})]_2$ (planar hexanuclear cluster structural unit, the plane that goes through all the Cd(II) ions is in yellow-green) in **1**. Symmetry codes: A $x+1, y, z$; B $-x+1, -y+2, -z+1$; C $-x+1, -y+2, -z+2$; D $x, y+1, z$; E $-x, -y+2, -z+2$; F $-x+1, -y+1, -z+1$; G $-x, -y+2, -z+1$; H $-x, -y+3, -z+1$; J $x, -y+1, z$; K $x+1, y, z$.

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