

Bilayer and 3-D open framework: Pillared metal-organic frameworks based on zinc and cadmic (6,3)-layers



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ARTICLE INFO

Article history:

Received 8 July 2014

Received in revised form 12 August 2014

Accepted 20 August 2014

Available online 21 August 2014

Keywords:

Metal-organic frameworks

Pillared open framework

Bilayer

(6,3)-layer

ABSTRACT

The (6,3)-layers of transition metals and 3,5-pyridinecarboxylate (3,5-PDC) containing terminal coordinated molecules offer a great potential for obtained porous frameworks via the “pillaring” approach. In this work, we have successfully obtained two porous frameworks based on the zinc and cadmic (6,3)-layers (compounds **1** and **2**, respectively) pillared by 4,4'-pyridine (bipy). Interestingly, different metal centers of Zn(II) and Cd(II) in the (6,3)-layers lead to the pillared frameworks into bilayers with $\{6^3\}\{6^6\}$ topology (compound **3**) and 3-D open framework with $\{6^3\}\{6^9 \cdot 8\}$ **hms** topology (compound **4**), respectively. It is believed that this work deserves further focus to enrich the design strategy of novel porous crystalline metal-organic frameworks (MOFs).

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Over the last decade, metal-organic frameworks (MOFs) have been developed into a promising class of multifunctional porous materials due to their numerous structures with variable properties and potential applications [1–6]. The design and construction of MOFs are of continuous interest by judiciously designing the organic ligands as linkers and carefully selecting metal centers as nodes. One of the limitations is the enumeration of the possible predetermined frameworks accessible from predefined building blocks [7–9]. As we know, for the self-assembly processes of MOFs, many experimental parameters such as metal/ligand ratio, temperature, pH values, solvents and templates can affect the resulting topology of MOFs. Nevertheless, if the external environment is well defined, the synthetic strategies would play the key role in the formation of these materials. The “pillaring” strategy is widely employed and proved to be one of the most effective ways to obtain predicted structures [10–15]. Especially, for a 2-D network which possess terminal coordinated molecules on the two sides of the layer, N-donor auxiliary ligands such as piperazine, 1,4-diaza-bicyclo[2.2.2]octane (dabco), 4,4'-bipyridine (bipy) or anions such as SiF_6^{2-} and TiF_6^{2-} could be employed to pillar the network and porous frameworks could be obtained. One of the features of the “pillaring” strategy is that the pore size and internal surface between layers could be tuned through the pillar substitution [16].

In this work, we focused on the 2-D (6,3) network of transition metals and 3,5-pyridinecarboxylate (3,5-PDC) which contains coordinated molecules besides the two sides of the layer and offer a great potential for obtained porous frameworks via the “pillaring” approach. It is

well known that the (6,3) network, also known as honeycomb topology, is the default 2-D structure constructed from tri-connected nodes [17]. The (6,3) network constructed from 3,5-PDC and many divalent transition metals such as Mn, Co, Ni, and Cd were reported very earlier [18–22]. Herein, we report the synthesis of the (6,3) network of 3,5-PDC with Zn(II) and Cd(II) (compounds **1**, **2**, respectively) under solvothermal conditions in DMF and discuss their structures in detail. We adopted the “pillaring” strategy to construct porous frameworks based on these two layers with 4,4'-pyridine (bipy) as pillars. Interestingly, different metal centers of Zn(II) and Cd(II) in the (6,3)-layers lead to the pillared frameworks into bilayers with $\{6^3\}\{6^6\}$ topology (compound **3**) and 3-D open framework with $\{6^3\}\{6^9 \cdot 8\}$ **hms** topology (compound **4**).

The (6,3) network of 3,5-PDC and Zn(II) and Cd(II) formulated as $\text{M}(3,5\text{-PDC})(\text{DMF})(\text{H}_2\text{O})$ ($\text{M} = \text{Zn}$ for compound **1**, Cd for compound **2**, respectively) were synthesized under similar conditions by heating a solution of $\text{M}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.15 mmol) and 3,5-PDC (0.15 mmol) in DMF (10 ml) with a little triethylamine (TEA, 0.05 ml) at 60 °C for 3 days. Single-crystal X-ray analysis reveals that compound **1** crystallizes in the space group $P2_1/c$ (No. 14) while compound **2** in Cc (No. 9) [23]. As shown in Fig. 1, compounds **1** and **2** contain similar layers. To form 2-D (6,3) network in both compounds, each metal connects three 3,5-PDC ligands by the coordination of carboxylate oxygens and nitrogen, and each 3,5-PDC links three metals. Additionally, the axial positions of the metal coordination environment in both of them are occupied by water and DMF (Fig. 1c and d). However, carefully examining their structures, it can be found that the coordination modes of metals to carboxylates are different in them. Zn(II) center in compound **1** is five-coordinated in a trigonal bipyramidal coordination environment,

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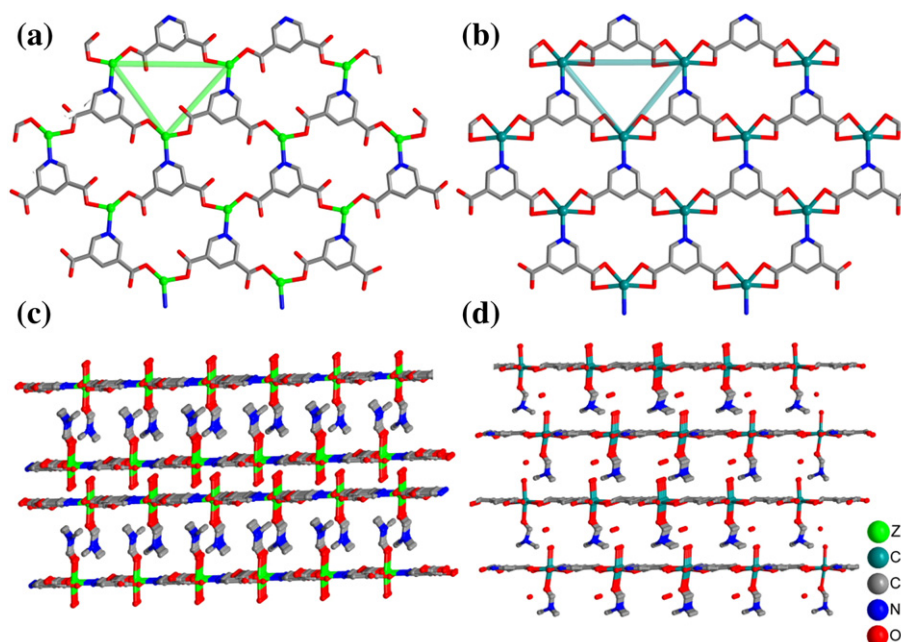


Fig. 1. (a, b) One of the (6,3) network layers of compounds **1** and **2**, respectively (terminal DMF and water have been omitted for clarity); (c, d) the packing view of compounds **1** and **2**, respectively.

while Cd(II) center in compound **2** is seven-coordinated in a distorted pentagonal bipyramidal coordination environment owing to its flexible coordination ability. What's more, bond lengths between Cd(II) and two oxygens from one carboxylate group are not equivalent (Cd1-O1 2.264 Å, Cd1-O2 2.524 Å, Table S2). As shown in Fig. 1a and b, the difference between these two layers is that Zn(II) coordinate with 3,5-PDC to form scalene triangle gridding while Cd(II) to form isosceles triangle gridding. Compared to the (6,3) networks of transit metals and 3,5-PDC reported, the kind of layer in compound **2** was more commonly seen such as Mn(3,5-pdc)·2(H₂O) [18], Co(3,5-pdc)(H₂O)₂ [19], Cu(3,5-PDC)(py)₂·H₂O·EtOH [19] and Cd(3,5-pdc)(H₂O)₂ [21], while

the similar layer to compound **1** was only seen in Cu(3,5-PDC)(py)₂ [22]. The layers in these two compounds were both stack in AB fashion, where each metal is situated between the hexagonal pores of neighboring layers. However, the packing modes of these two kinds of layers are different in the orient directions of terminal molecules, as shown in Fig. 1c and d.

The pillared frameworks formulated as Zn₂(3,5-PDC)₂(H₂O)₂(bipy) (compound **3**) and Cd(3,5-PDC)(bipy) (compound **4**) were obtained under similar conditions to the respective layer structures only with bipy (0.15 mmol) instead of TEA. Single-crystal X-ray analysis reveals that compound **3** crystallizes in the space group C2/c (No. 15) while

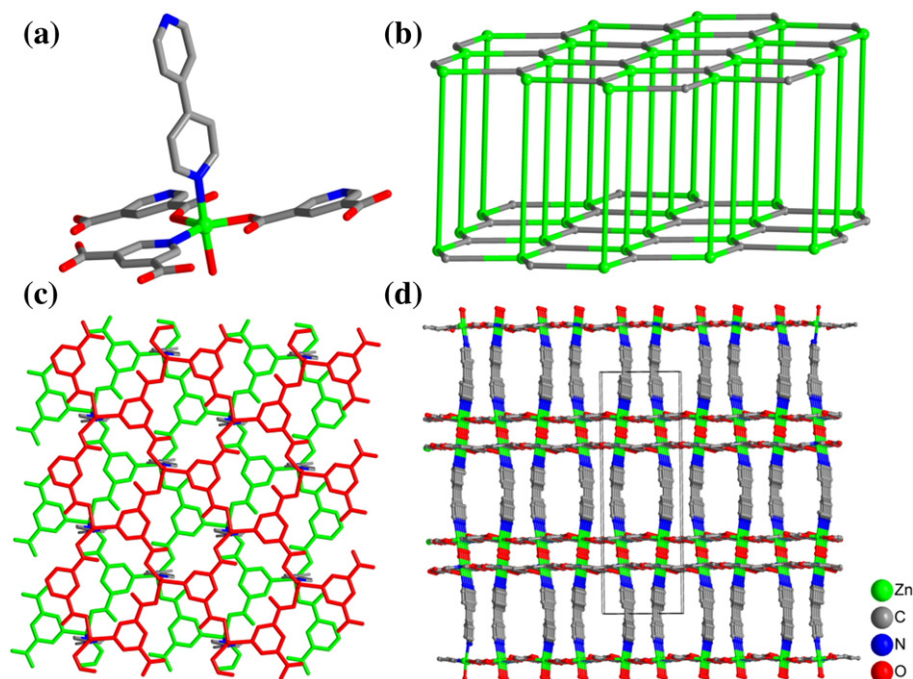


Fig. 2. (a) Coordination environment of Zn in compound **3**; (b) 2-D (3,4)-connected net; (c) the bilayer viewed vertically with the up layer in red and the bottom layer in green; (d) the packing diagram of compound **3**. Hydrogen has been omitted for clarity.

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