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A 2D zinc-organic network being easily exfoliated into isolated sheets

Guihong Yu, Ruiqing Li, Zhihua Leng, Shucai Gan*

College of Chemistry, Jilin University, Changchun 130026, China

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ABSTRACT

A metal-organic aggregate, namely $\{Zn_2Cl_2(BBC)\}_n$ (BBC = 4,4′,4″-(benzene-1,3,5-triyl-tris(benzene-4,1-diyl))tribenzoate) was obtained by solvothermal synthesis. Its structure is featured with the $Zn_2(COO)_3$ paddle-wheels with two chloride anions on axial positions and hexagonal pores in the layers. The exclusion of water in the precursor and the solvent plays a crucial role in the formation of target compound. This compound can be easily dissolved in alkaline solution and exfoliated into isolated sheets, which shows a novel way for the preparation of 2D materials.

1. Introduction

Coordination polymers have attracted increasing attentions due to their diverse structures and potential applications [1]. It is well known that the bi- or multidentate organic ligands as the linkers and metals or clusters as the nodes are essential for the construction of coordination polymers. Tritopic tricarboxylate ligands are turned out to be a kind of efficient linkers for the construction of coordination polymers, especially metal-organic frameworks (MOFs). Emblematically, the most investigated and commercially available HKUST-1 metal–organic framework was constructed by linking Cu paddle-wheel clusters with benzene-1,3,5-tricarboxylate (BTC) [2]. On the other hand, the Zn carboxylate clusters such as dinuclear Zn_2 [3], trinuclear Zn_3 [4], tetranuclear Zn_4 [5,6], hexanuclear Zn_6 [7] and even higher nuclearity clusters [3c,7] were reported to be the secondary building units (SBUs) to build up coordination polymers. The combination of Zn clusters and tricarboxylates would lead to the formation of varieties of compounds. For instance, Feng et al. reported two MOFs with Zn clusters and BTC, one featured with Zn_8 clusters and the other with Zn_2 clusters and interpenetrating networks [3c]. Lah et al. presented a two-fold interpenetrated (3,6)-connected MOF with Zn_4 SBUs as the nodes and 4,4′,4″-[1,3,5-benzenetriyltris (carbonylimino)]tribenzoate as the linkers [8]. 4,4′,4″-(Benzene-1,3,5-triyl-tris(benzene-4,1-diyl))tribenzoate (BBC) ligand is a further elongated homologue of BTC. Zhou et al. prepared two porous MOFs $Zn_4(OH)_2(H_2O)_2(py)_2(BBC)_2$ (py = pyridine) and $Zn_8(OH)_4(BBC)_4$ with Zn_4 clusters and Zn_8 clusters, respectively [9]. Yaghi et al. reported a highly porous material MOF-200 with Zn_4 clusters as SBUs and BBC as the linker [10]. Kaskel et al. reported four zinc coordination polymers containing two 2D layered structures $[Zn_2(H_2O)_2(BBC)](NO_3)(DEF)_6$ (DUT-40) and $[Zn_3(H_2O)_3(BBC)_2]$ (DUT-41) and two 3D networks $[(C_2H_5)_2NH_2][Zn_2(BBC)(TDC)](DEF)_6(H_2O)_7$ (DUT-42) and $[Zn_{10}(BBC)_5(BPDC)_2(H_2O)_{10}](NO_3)(DEF)_{28}(H_2O)_8$ (DUT-43) with hydrated zinc nitrate as the zinc source [11]. Han et al. obtained a 2D (6,3) net $[Zn(BBC)(H_2O)_2](Me_2NH_2)\cdot 12DMF$ and a 3D three-fold interpenetrating (3,5)-connected network $[Zn_2(BBC)(NH_2\text{-}BDC)](Me_2NH_2)\cdot 10DMF$ using hydrated zinc nitrate as the zinc source [12].

Here we present a 2D layered coordination polymer based on the dinuclear Zn_2 clusters as the nodes and 4,4′,4″-(benzene-1,3,5-triyl-tris(benzene-4,1-diyl)) tribenzoate (BBC) as the linker. Because anhydrous zinc chloride was chosen as the zinc source instead of hydrated zinc nitrate, the Zn-BBC layers in the title compound were bonded by additional chloride anions instead of water molecules in the reported 2D networks [11,12]. Notedly, this compound can be dissolved in alkaline solution so that the layer structure can be exfoliated into some isolated sheets which were observed by AFM. This work would show a novel way to prepare 2D materials for their potential application as electrodes, semiconductors and photovoltaics.

* Corresponding author.
E-mail address: ghyu@ciac.ac.cn (S. Gan).

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2. Experimental section

2.1. Materials and measurements

All the reagents were purchased from commercial sources and used as received. TG-DSC measurement was performed on a PYRIS DIAMOND from room temperature to 800 °C, with a heating rate of 10 °C min^{-1} under atmosphere. FT-IR spectra (KBr pellets) were taken on a Bruker Vertex 70 spectrometer. Elemental analysis for C, H, N was recorded on a VarioEL instrument. N_2 adsorption measurement for $\{Zn_2Cl_2(BBC)\}_n$ was performed on a Micromeritics ASAP 2020M automatic volumetric instrument. Atomic-force microscopy (AFM) measurements were performed using Nanoscope V multimode atomic force microscope (Veeco Instruments, USA). Tapping mode was used to acquire the images under ambient conditions.

2.2. Preparation of $\{Zn_2Cl_2(BBC)\}_n$

Anhydrous $ZnCl_2$ (0.10 g, 0.7 mmol), H_3BBC (0.067 g, 0.1 mmol), N,N'-diethylformamide (DEF) (4 ml) and triethylamine (several drops) were placed in a 20 ml Teflon-lined autoclave which was kept at 130 °C for 3 days and then slowly cooled to room temperature at about 4 °C/h. Colorless block crystals of the title compound were obtained (yield: 53 mg, 61% based on H_3BBC). Elemental analysis: calculated (%) for $C_{45}H_{28}Cl_2O_6Zn_2$: C 62.33, H 3.23; found (%): C 62.85, H 3.07. FT-IR (cm^{-1}): 2935(m), 2864(m), 1651(s), 1603(s), 1547(w), 1383(s), 1252(m), 1180(w), 1181(s), 829(m), 785(s).

2.3. X-ray crystallography

The intensity data were recorded on a Bruker APEX CCD system with Mo-Kα radiation ($\lambda = 0.71073$ Å). The crystal structures were solved by means of Direct Methods and refined employing full-matrix least squares on F^2 (SHELXL-2014/7) [13]. Crystal data for $\{Zn_2Cl_2(BBC)\}_n$: $C_{45}H_{28}Cl_2O_6Zn_2$, $M = 866.31$ g/mol, hexagonal, $P6_122$, $a = 23.995$ (7) Å, $c = 28.351$ (10) Å, $V = 14136$ (10) $Å^3$, $Z = 6$, $D_{calcd} = 0.611$ g cm^{-3}, $\mu = 0.586$ mm^{-1}, $T = 293$ (2) K,

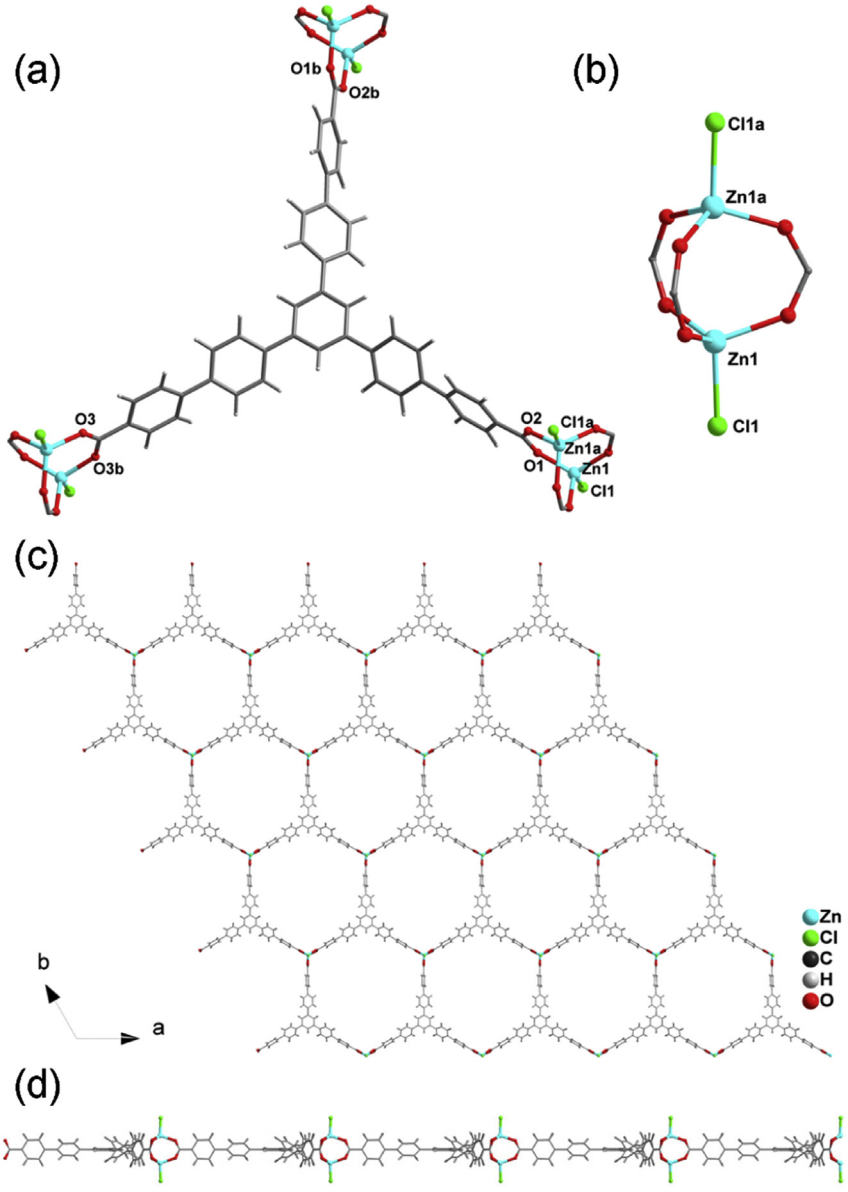

Fig. 1. Coordination of the BBC ligand and Zn center in $\{Zn_2Cl_2(BBC)\}_n$ compound (a), $Zn_2(COO)_3$ paddle-wheel SBU (b), 2D honeycomb network based on BBC and $Zn_2(COO)_3$ paddle-wheels (c), and the side view of the layer structure (d). The symmetry code in (a) −y, -x, 1/6-z; (b) 1−y, 1-x, 1/6-z.