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The synthesis and characterization of a new 3-D inorganic–organic hybrid framework porous material $\text{Zn}_3(\text{bbdc})_3(4,4'\text{-bpy}) \cdot 2(\text{DMF}) \cdot 4(\text{H}_2\text{O})$

Qianrong Fang, Xin Shi, Gang Wu, Ge Tian, Guangshu Zhu, Runwei Wang,
and Shilun Qiu*

Department of chemistry, Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun 130023, China

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Abstract

A new 3-D inorganic–organic hybrid framework microporous material $\text{Zn}_3(\text{bbdc})_3(4,4'\text{-bpy}) \cdot 2(\text{DMF}) \cdot 4(\text{H}_2\text{O})$ (1), which is constructed by coordination of zinc ions with 4,4'-bibenzene-dicarboxylic acid (H_2bbdc) and 4,4'-bipyridine (4,4'-bpy), was obtained at mild synthesis condition. Crystallographic data for the compound (1), $\text{C}_{58}\text{H}_{54}\text{N}_4\text{O}_{18}\text{Zn}_3$, orthorhombic, space group *Pbcn*, $a = 14.532(3)$ Å, $b = 25.037(5)$ Å, $c = 18.184(4)$ Å, $Z = 4$, $V = 6616(2)$ Å³.

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Keywords: Inorganic–organic hybrid framework; Porous material; 4,4'-bibenzene-dicarboxylic acid

1. Introduction

Porous inorganic–organic hybrid framework materials have attracted much attention for their great potential in flexible structure designs and wide applications in selective gas adsorption, recognising molecule, gas storage, heterogeneous catalysis etc. [1–6]. In general, *N,N'*-donors and oxygen donors are always used to lead to inorganic–organic hybrid frameworks. Bidentate ligands such as 4,4'-bipyridine (4,4'-bpy) and bi- or tricarboxylic acid are very common [7–16]. Especially, the metal-organic frameworks (MOFs), constructed by transition metal ions with organic carboxylate ligands, not only possess zeolite-like microporous framework, but also keep their rigid structures after removing the guest molecules [11,12]. Recently, some complexes of the 4,4'-bibenzene-dicarboxylate (bbdc) ligand having 2-D, 3-D framework have been reported by other groups [17–21]. Intrigued by the beauty of structural design, we introduce 4,4'-bibenzene-dicarboxylate (bbdc) and 4,4'-bpy simultaneously as linkers with zinc ions to lead to a new 3-D open framework.

2. Experimental

2.1. Synthesis

The synthesis of the compound $\text{Zn}_3(\text{bbdc})_3(4,4'\text{-bpy}) \cdot 2(\text{DMF}) \cdot 4(\text{H}_2\text{O})$ (1) was performed under near room temperature. Reaction of H_2bbdc (0.12 g, 0.5 mmol), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.15 g, 0.5 mmol) and a small quantity of 4,4'-bipyridine (4,4'-bpy) in a solvent mixture of *N,N*-dimethylformamide (DMF) (50.0 mL), ethanol (10.0 mL) and water (1.0 mL) at 65°C for five days produced large colorless block crystals in 19% yield. The elemental analysis was performed on a Perkin-Elmer 2400 element analyzer and inductively coupled plasma (ICP) analysis on a Perkin-Elmer Optima 3300 DV ICP spectrometer. The result of ICP showed that the compound (1) contained 15.23% Zn. The elemental analysis found: C, 54.01%; H, 4.20%; N, 4.22%; O, 22.34% (calculated: C, 53.95%; H, 4.22%; N, 4.34%; O, 22.30%).

The IR spectra were obtained on a Nicolet Impact 410 FTIR spectrometer. The TGA analysis was carried out in nitrogen atmosphere on a Perkin-Elmer DTA 1700 differential thermal analyzer.

*Corresponding author. Fax: +86-431-567-1974.

E-mail address: sqiu@mail.jlu.edu.cn (S. Qiu).

2.2. Crystallography

A single crystal of compound (1) with $0.333 \times 0.573 \times 0.260$ mm was mounted on a Rigaku RAXIAS-RAPID diffractometer with $\text{MoK}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation. Intensity data were collected at 293(2) K using multi-scan technique. The structure was solved by the direct methods and refined by the full-matrix least-squares method against F^2 (SHELXL-97). Crystal data for compound (1): orthorhombic, space group $Pbcn$, $F_w = 1291.16$, $Z = 4$, $V = 6616(2) \text{ \AA}^3$, $D_c = 1.296 \text{ Mg/m}^3$, 14395 reflections collected ($\theta = 1.62\text{--}27.48^\circ$), 7593 of which were used in the refinement to give the final $R_1 = 0.0705$, $wR_2 = 0.2056$. The goodness-of-fit on F^2 is 0.896.

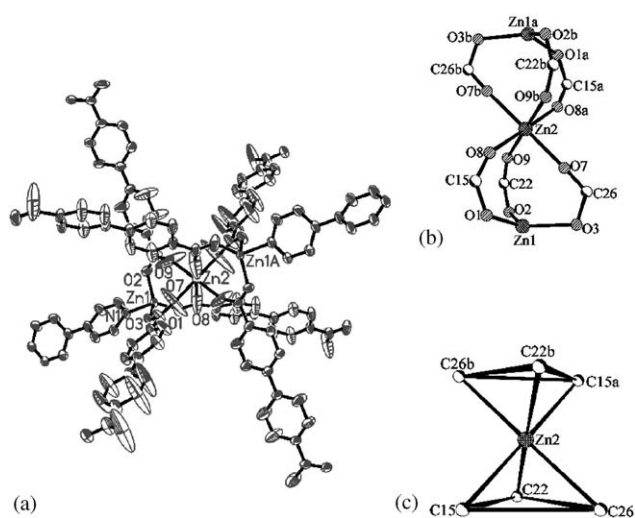


Fig. 1. (a) The building unit of $\text{Zn}_3(\text{bbdc})_3(4,4'\text{-bpy}) \cdot 2(\text{DMF}) \cdot 4(\text{H}_2\text{O})$. The $\text{Zn}_3(\text{CO}_2)_6$ cluster (b) can be seen as a sharing-vertex trigonal bipyramid SBU (c) of the titled compound.

Table 1
The crystallographic data for compound (1)

Empirical formula	$\text{C}_{58}\text{H}_{54}\text{N}_4\text{O}_{18}\text{Zn}_3$
F_w	1291.16
Space group	$Pbcn$
T/K	293(2)
$a/\text{Å}$	14.532(3)
$b/\text{Å}$	25.037(5)
$c/\text{Å}$	18.184(4)
$\alpha/^\circ$	90.000(0)
$\beta/^\circ$	90.000(0)
$\gamma/^\circ$	90.000(0)
$V/\text{Å}^3$	6616(2)
Z	4
$D_c/\text{g cm}^{-3}$	1.296
$\lambda/\text{Å}$	0.71073
μ/mm^{-1}	1.145
R_1	0.0705
wR_2	0.2056

3. Results and discussion

3.1. Crystal structures

3.1.1. $\text{Zn}_3(\text{bbdc})_3(4,4'\text{-bpy}) \cdot 2(\text{DMF}) \cdot 4(\text{H}_2\text{O})$ (1)

In order to understand the structures of the coordination polymer in solid-state, single crystal X-ray diffraction study was carried out for compound (1). The building unit of the three-dimensional structure of compound (1) is shown in Fig. 1(a). Crystallographic data, structural parameter such as selected bond distances and angles of compound (1) are listed in Tables 1 and 2, respectively.

Table 2
Selected bond lengths (Å) and angles ($^\circ$) for compound (1)

Bond lengths (Å)	
Zn(1)–O(3)	1.935(4)
Zn(1)–O(2)	1.938(4)
Zn(1)–O(1)	1.951(4)
Zn(1)–N(1)	2.080(4)
Zn(2)–O(7)#1	1.970(5)
Zn(2)–O(7)	1.970(5)
Zn(2)–O(9)	1.973(6)
Zn(2)–O(9)#1	1.973(6)
Zn(2)–O(8)#1	2.046(5)
Zn(2)–O(8)	2.046(5)
N(1)–C(5)	1.330(8)
N(1)–C(1)	1.341(7)
N(2)–C(29)	1.246(14)
N(2)–C(28)	1.384(19)
N(2)–C(27)	1.386(19)
O(1)–C(15)	1.235(7)
O(2)–C(22)	1.222(7)
O(3)–C(26)	1.241(7)
O(5)–C(29)	1.234(16)
O(7)–C(26)	1.202(7)
O(8)–C(15)	1.166(8)
Bond angles ($^\circ$)	
O(3)–Zn(1)–O(2)	116.86(19)
O(3)–Zn(1)–O(1)	121.4(2)
O(2)–Zn(1)–O(1)	113.1(2)
O(3)–Zn(1)–N(1)	96.24(17)
O(2)–Zn(1)–N(1)	97.19(18)
O(1)–Zn(1)–N(1)	106.2(2)
O(7)#1–Zn(2)–O(7)	88.8(6)
O(7)#1–Zn(2)–O(9)	179.2(3)
O(7)–Zn(2)–O(9)	90.7(6)
O(7)#1–Zn(2)–O(9)#1	90.7(6)
O(7)–Zn(2)–O(9)#1	179.2(3)
O(9)–Zn(2)–O(9)#1	89.7(9)
O(7)#1–Zn(2)–O(8)#1	89.3(4)
O(7)–Zn(2)–O(8)#1	87.6(3)
O(9)–Zn(2)–O(8)#1	91.3(4)
O(9)#1–Zn(2)–O(8)#1	91.8(4)
O(7)#1–Zn(2)–O(8)	87.6(3)
O(7)–Zn(2)–O(8)	89.3(4)
O(9)–Zn(2)–O(8)	91.8(4)
O(9)#1–Zn(2)–O(8)	91.3(4)
O(8)#1–Zn(2)–O(8)	175.7(7)

Symmetry transformations used to generate equivalent atoms: #1: $-x + 1, y, -z + 1/2$, #2: $-x + 1, y, -z - 1/2$, #3: $-x + 3/2, y + 1/2, z$, #4: $-x, y, -z + 1/2$, #5: $-x + 3/2, y - 1/2, z$.

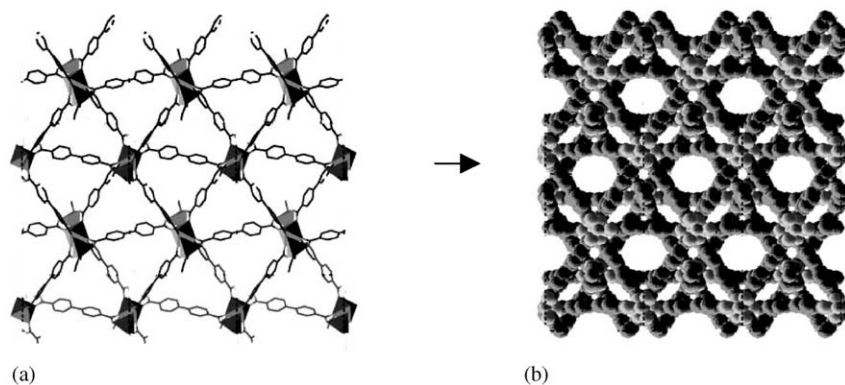


Fig. 2. (a) View from *c*-axis, 2-D network was constructed by six-coordinated zinc ions with bbdc ligands along the *ab* plane; (b) The 3-D double interpenetrating framework was formed from 2-D networks (a) upheld by 4,4'-bpy molecules along the *c*-axis.

In the building unit, there are three zinc, three bbdc ligands and one 4,4'-bpy. Three zinc(II), with an inversion center on Zn2, are bridged by three symmetry-equivalent bbdc bidentate ligands. Zn2 atom has octahedral coordination environment with six oxygen atoms (O7, O8, O9, O7b, O8a and O9b) from carboxylate groups of six bbdc ligands, while Zn1 and Zn1a are coordinated to three oxygen atoms (O1, O2, O3 and O1a, O2b, O3b) from carboxylate groups of bbdc ligands and one nitrogen atom (N1 and N1a) of a 4,4'-bpy molecule to form a tetrahedral geometry. The Zn–O_{carb} distances are between 1.935(4)–2.046(5) Å. The Zn–N_{bpy} distance is 2.080(4) Å. The bond angles around the Zn center range from 87.6(3)° to 179.2(3)°. The bond angles of O(3)–Zn(1)–N(1), O(2)–Zn(1)–N(1) and O(1)–Zn(1)–N(1) are 96.24(17)°, 97.19(18)°, 106.2(2)°, respectively. The above bond distances and bond angles are similar to those in Zn(tp)(4,4'-bpy) [22].

Three zinc centers form an Zn₃(CO₂)₆ cluster (Fig. 1(b)), which can be seen as a secondary building unit (SBU), sharing-vertex(Zn2) trigonal bipyramid with Zn2 as an inversion center (Fig. 1(c)). The six vertexes of the SBUs are linked via 4,4'-biphenylene organic groups to form a 2-D network along *ab* plane at first (Fig. 2(a)). Then the two poles (Zn1 and Zn1a) of the cluster are connected through 4,4'-bipyridine molecules along the *c*-axis, leading to a 3-D double interpenetrating framework (Fig. 2(b)). In a word, coordination of bbdc ligands with zinc ions forms a 2-D network along *ab* plane, while 4,4'-bpy as pillars uphold the 2-D network to lead to a 3-D framework along *c*-axis. There are 3 × 5 Å 1-D channels along *c*-axis occupied by the guest DMF and H₂O molecules.

3.2. IR spectrum

The IR spectrum of the compound (1) displays the asymmetric and symmetric stretching vibrations of the carboxylate group at 1538 and 1394 cm⁻¹. The band at 1606 cm⁻¹, the broad bands at 3068 cm⁻¹, bands at 856,

680 cm⁻¹ and band at 771 cm⁻¹ are attributed to the aromatic skeleton vibration of benzene ring, ν_{C-H} of benzene, δ_{C-H} out of the face of benzene, and 1,4-substitute of benzene ring, respectively. The bands at 1668 and 2929 cm⁻¹ are due to $\nu_{C=O}$ and asymmetric stretching vibration of the methyl group of the guest DMF molecule, respectively. The broad band at 3392 cm⁻¹ belongs to the typical band of the guest H₂O molecules. The absence of a band at 1006 cm⁻¹ is typical band of vibration of the pyridine ring of the 4,4'-bpy ligand.

3.3. Thermogravimetric analysis

To study the stability of the compound (1), Thermogravimetric tri-analysis (TGA) was performed. The result of TGA showed the following separated weight loss steps. The first weight loss of 9.18% at about 140°C is for evacuation of one DMF molecule and two H₂O molecules from the cavity (9.23% calculated). The second weight loss of 29.81% at about 300°C corresponds to the loss of one 4,4'-bpy molecule and one bbdc ligand (30.16% calculated). The third weight loss of 28.79% at about 500°C corresponds to the loss of two bbdc ligands (29.10% calculated).

After the titled compound was heated for two hours at 140°C under vacuum condition, the powder XRD pattern showed that the main peaks still remained, but the intensity decreased. After further heated for 6 h, the powder XRD pattern of the titled compound showed that there was no peak left. It was suggested that the framework of the compound collapsed after removing the guest molecules, DMF and H₂O.

4. Conclusions

A 3-D microporous material Zn₃(bbdc)₃(4,4'-bpy)·2(DMF)·4(H₂O) (1) was synthesized at mild condition. In this structure, bbdc ligands bridge zinc ions into 2-D

nets, which are further pillared by 4,4'-bpy molecules to generate a 3-D double interpenetrating framework with a $3 \times 5 \text{ \AA}$ channels.

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