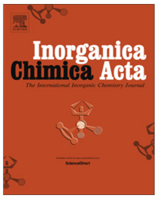
Inorganica Chimica Acta 471 (2018) 180–185

Contents lists available at ScienceDirect

Inorganica Chimica Acta

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



Research paper

Temperature-tuned topologies and interpenetrations of two 3D porous copper(II)-organic frameworks and gas adsorption behaviors

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ARTICLE INFO

Article history:
Received 28 September 2017
Received in revised form 27 October 2017
Accepted 29 October 2017
Available online 2 November 2017

Keywords:
Copper(II)-organic frameworks
Interpenetrating structure
Gas adsorption
X-ray crystallography

ABSTRACT

In this article, two novel three-dimensional (3D) Copper(II)-organic frameworks $[Cu(PC)_2]_n \cdot 2DMF$(**1**) and $[Cu(PC)_2]_n \cdot DMF$ (**2**) (HPC = 4-(2-(pyridin-4-yl)vinyl)benzoic acid) were obtained from the same reaction mixture but tuned by different solvothermal temperature, The product **1**, which was obtained at 160 °C, is a rare fivefold interpenetrating **lvt** framework, whereas the product **2**, obtained at 120 °C, exhibits a sevenfold interpenetrating **dia** framework. Their structures have been characterized by single crystal X-ray diffraction, infrared spectroscopy (IR), powder X-ray diffraction (PXRD), elemental analysis and thermogravimetric analysis (TGA). The N_2 adsorption isotherm revealed that the BET surface areas of **1** and **2** were 780 and 464 m^2/g, respectively. Regrettably, no adsorption of CO_2, CH_4 or N_2 was observed at 273 K.

1. Introduction

Metal organic frameworks (MOFs) as microporous materials were focused on the unpredictable structural variations as well as application in the adsorption and separation of gases [1–3] and nonlinear optics (NLO) [4–5] and catalyst/catalyst support [6–7]. The elongated ligands always have been employed to constructed the MOFs with the expected large pores last two decades. While unfortunately, it is easy to get interpenetrated MOFs rather than the designed large-pore MOFs when the elongated ligands were used due to minimizing the systematic energy [8] Of course, the interpenetrated MOFs also exhibited unexpected properties in gas separation [9–10] and NLO [4–5]. Although it is still a challenge, the study of how to control interpenetration of MOFs has attracted much attention. Therefore, the crystal engineering strategies are always employed to tune the structures, topologies and interpenetration degree of interpenetrated MOF via changing the sizes of solvent molecules and counterions (template-directed control), reaction temperatures and some other reaction factors [8]. The suitable templates reduce the empty space to could remarkably enhance the stabilities of frameworks, not only by filling into void space but also weakening repulsive forces that serve to prevent from large-pore MOFs collapsing [8,11]. Accordingly, the larger template molecules or counterions always bring about the lower degree interpenetrated and even non-interpenetrated MOFs, while the smaller ones always lead to high degree interpenetrated MOFs. Moreover, reaction temperature also can modulate the interpenetrated of MOFs, higher temperatures favor interpenetrated and compact frameworks, while lower temperatures prefer to non-interpenetrated and even large-pore frameworks [8,12]. Actually, there are not many examples of successfully regulating the interpenetration degree of MOFs. It is very expected that more rational approaches and successful manipulation to synthesize samples of interpenetration degree of MOFs [8].

The ligand HPC containing N, O donors often was employed to assembly coordination polymers. Early, the Zinc and Cadmium coordination polymers based on HPC as the NLO materials were investigated [4,5,13]. Recently, the microporous coordination polymers constructed by HPC mostly were used in the filed of gas storage and separation [14]. In this work, we investigated the influence of temperature in the system of HPC and $Cu(NO_3)_2$. Fortunately, two three-dimensional Cu(II)-organic frameworks with different topologies and pore sizes and shapes were obtained and characterized. Compounds **1** and **2** are the only reported Copper coordination polymers constructed only with HPC ligand [14c,d]. Compound **1** is a rare fivefold interpenetrating **lvt** framework with BET surface area of 776 cm^3/g, while **2** exhibits a sevenfold interpenetrating **dia** framework with BET surface area of 464 cm^3/g. Unfortunately, very limited adsorption of CO_2, CH_4 or N_2 was observed at 273 K.

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https://doi.org/10.1016/j.ica.2017.10.039
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2. Experimental section

2.1. Materials and physical measurements

All solvents and reagents for the syntheses were of analytical grade and were used as received from commercial sources without further purification. The HPC (Scheme 1) synthesis routine was according to literature [14c]. The yield of HPC is 64% base on 4-formylbenzoic acid. The elemental analyses (C, H and N) were carried out applying a Perkin-Elmer 240C elemental analyzer. Powder X-ray diffraction (PXRD) data were collected using a BRUKER D8 ADVANCE diffractometer using CuKα(λ = 1.542 Å). The IR spectra in the 4000–400 cm^{-1} region were measured using a Nicolet IR-408 spectrometer and KBr pellets. Thermogravimetric (TG) curves were recorded from room temperature to 800 °C with the heating rate of 10 °C/min on a Netzsch TG 209 instrument under nitrogen atmosphere. The N_2 adsorption isotherm were measured by V-Sorb 2800TP surface area and pore size analyzer at 77 K. CO_2, CH_4 and N_2 adsorption experiments were carried on Autosorb iQ Station 2 at 273 K.

2.2. Syntheses of compounds

2.2.1. Synthesis of **1**

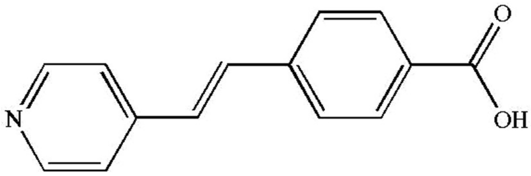
$Cu(NO_3)_2{\cdot}3H_2O$(0.120 g, 0.5 mmol) and HPC (0.2252 g, 1.0 mmol) were added in DMF (10 mL). Then, the mixture was transferred into a Teflon-lined stainless steel autoclave, which was subsequently heated at 160 °C for 24 h and cooled to room temperature in 24 h. The purple acicular crystal precipitate was separated by centrifugation, washed with DMF for several times and dried 40 °C for 12 h in vacuum drying oven. The yield is about 76% calculated based on $Cu(NO_3)_2$. Elemental Anal. (%) Calc for $C_{34}H_{32}CuN_4O_6$: C; 61.23, H; 4.92; N, 8.53; Found: C, 61.10; H, 5.11; N, 8.49. IR (KBr, cm^{-1}): 3405(m), 1612(s), 1595(w), 1373(s), 777(vw).

2.2.2. Synthesis of **2**

The synthetic route to compounds **2** was similar to that of **1**. Only reaction temperature was replaced by 120 °C. After cooling to room temperature naturally, the mother liquor was decanted and green acicular crystal were filtered off, washed with DMF for several times and dried under 40 °C for 12 h in vacuum drying oven. The yield is about 85% calculated based on $Cu(NO_3)_2$. Elemental Anal. (%) Calc For $C_{31}H_{27}CuN_3O_5$: C, 63.63; H, 4.65; N, 7.18; Found: C, 63.46; H, 4.35; N, 7.06. IR (KBr, cm^{-1}): 3446(vw), 2921(vw), 1610(vs), 1375(vs), 1025(m), 845(s).

2.3. X-ray crystallography

A suitable crystal of 1 was selected and fixed on a SuperNova, Single source at offset/far, Eos diffractometer. The crystal was kept at 121(2) K during data collection. Crystallographic data of **2** was carried out on a Bruker SMART Apex CCD diffractometer using graphite-monochromated Mo Kα radiation (0.71073 Å) at 293 K in the ω-2θ scan mode. Using Olex2 [15], the structure was solved by the ShelXS structure solution program [16], and refined with the XLrefinement package [16] using Least Squares minimisation. Hydrogen atoms were riding on carbon atoms geometrically. The crystallographic data for X-ray diffraction analysis are listed in Table 1.



Scheme 1. The structure of 4-(2-(pyridin-4-yl)vinyl)benzoic acid (HPC).

3. Results and discussion

3.1. Description of the structure

3.1.1. Structural description of complex **1**

The result of X-ray structural analysis reveals that **1** crystallizes in tetragonal crystal system, a space group of $I4_1/a$ with an asymmetric unit of half Cu(II) cation and a PC anion. As is shown in Fig. 1a, the Cu (II) cation is located in the center of parallelogram which was constructed by two O atoms (O1 and O1A, A = –X, –Y,–Z) from two ligands and two N atoms (N1B and N1C, B = 0.25 – y, –0.25 + x, –1.25 + z; C = –0.25 + y, 0.25 – x, 1.25 – z) from the other two ligands. The Cu–O and Cu–N bond lengths are 1.9521(67) Å and 2.0918(67) Å, respectively. Each Cu(I) connected four PC ligands to give a three dimensional framework with a one channel with side length of about 15.0 Å along c axis, which is similar to the channel shape of fsc-5-NDS constructed by HPC and 1,5-Naphthalenedisulfonate [14b] (Fig. 2 (a)). According to the simplified regulation of topology, Cu(II) cations and PC ligands can be regarded as 4-connected nodes and lines. Thus, topology of **1** can be simplified to a rare fivefold interpenetrating 4-connected **lvt**-$4^2{\cdot}8^4$ framework (Fig. 3b and d). **lvt**-type net [18] is relatively rare reported comparing to the other well-known four-connected **dia** [4b,19], **nbo** [20] and **sra** [21] nets. The interpenetration number of **lvt**-type net were mainly two- and threefold, while the higher interpenetrated structures were rarely reported [21]. The highest interpenetrated number with lvt net was fivefold, compound **1** is the second sample [18]. Although high interpenetration have happened in **1**, the channel sizes and sharps have not been changed (Fig. 2(c)). The calculation of the void volume with PLATON [17] revealed that there was a free volume of about 4203.9 Å^3 in **1**, which represents 51.4% of the unit cell volume of 8171.0 Å^3.

3.1.2. Structural description of complex **2**

Complex **2** crystallized in monoclinic crystal system with a *Cc* space group. The asymmetric unit of **2** contained a crystallographic

Table 1
Crystallographic data for compounds **1** and **2**.

Compound	1	2
Empirical formula	$C_{34}H_{32}CuN_4O_6$	$C_{31}H_{27}CuN_3O_5$
Formula weight	656.18	585.11
Crystal system	tetragonal	monoclinic
Space group	$I4_1/a$	*Cc*
a/Å	38.7920(9)	13.261(18)
b/Å	38.7920(9)	25.14(3)
c/Å	5.5144(2)	8.476(11)
α/°	90.00	90.00
β/°	90.00	98.396(16)
γ/°	90.00	90.00
Volume/Å^3	8298.2(4)	2796(6)
Z	8	4
$D_{calc.}$ (g cm^{-3})	1.050	1.390
GOOF	1.074	1.055
F(0 0 0)	2728.0	1212.0
R_1[a] [I > 2σ (I)]	0.0936	0.1000
wR_2 [I > 2σ(I)]	0.2354	0.1843
R_1 (all data)	0.1086	0.1311
wR_2[b] (all data)	0.2491	0.2076
(Δρ)max (e/Å^3)	1.09	1.26
(Δρ)min (e/Å^3)	–0.65	–0.45

[a] $R_1 = Fo\ Fc/Fo$.

[b] $wR_2 = [[w(Fo^2\ Fc^2)^2] / w(Fo^2)^2]^{1/2}$.