$[Ni_3(cit)_2(pyz)(H_2O)_4](H_2O)_4$: A New Three-dimensional Porous Coordination Polymer with a Pillared Layer Structure

Ting Yu, Yunqi Tian, Zhenxia Chen, Jinxi Chen, Linhong Weng, and Dongyuan Zhao*
Department of Chemistry and Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200433, P. R. China

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Reaction of $NiCl_2 \cdot 4H_2O$ with citric acid and pyrazine affords a new three-dimensional (3-D) porous coordination polymer, which adopts a pillared layer structure with $(4^26^28^2)(46^48)_2$ topology and contains 3-D intersected channels.

Recently a great deal of attention has been focused on the design and construction of porous coordination polymers because of their potential applications in gas storage, catalysis, magnetism, and enantioselective sorption.[1–8] Up to now, a variety of net topologies have been found with their chemical entities in coordination polymers, which employ suitable metal ions and organic ligands with specific geometry and coordination configuration as nodes and/or linkers.[8] A useful strategy on construction of various coordination networks is to employ mixed linkers with different affinity to central metal ion. However, there are still rare examples concerning multiple linkers assembly in the domain of coordination polymers. To address this motif, deliberate choice of ligands as different linkers is carried out.

Citric acid has previously been reported in construction of transition-metal clusters and hydrophilic porous coordination polymers,[9,10] whose structures exhibit the coordination versatility of carboxylate groups of citric acid and its inherent chelating coordination mode as well. On the other hand, employing pyrazine to form pillared layer structures is one of approaches for producing high-dimensional porous coordination polymers.[2,11] Herein, our attempt to incorporate pyrazine with nickel citrate results in a new coordination polymer, $[Ni_3(cit)_2(pyz)(H_2O)_4]$-$(H_2O)_4$, (cit = citrate, pyz = pyrazine) (**1**), that is confirmed by X-ray diffraction study and elemental analysis.

The synthesis of **1** was carried out under hydrothermal condition: Nickel chloride tetrahydrate (0.5 mmol) and citric acid (0.5 mmol) were stirred in 5 mL of H_2O for 1 h and transferred into 25-mL Teflon-lined autoclave. After layered 5 mL of *n*-butanol containing pyrazine (0.5 mmol), the autoclave was sealed and left at 130 °C for 5 days. Then pale green block-shaped crystals were collected, washed with ethanol and dried in air. Elemental analysis (%): Calcd. for $Ni_3C_{16}H_{30}N_2O_{22}$: C, 24.68; H, 3.88; N, 3.60%; Found: C, 24.82; H, 3.81; N, 3.74%. IR(KBr): 474(s), 566, 639, 850, 1067, 1284, 1388, 1430, 1577, 1625, 3343(br) cm^{-1}.

The X-ray single-crystal structural analysis reveals that **1** is a 3-D coordination polymer with a pillared layer structure, where pyrazine, μ_2-bridged carboxylate and the whole skeleton of citrates can be viewed as three different linkers.[12–14] There are two crystallographically independent Ni(II) ions with slightly distorted octahedral coordination environment (Figure 1a). Ni(1) is coordinated with its equatorial positions occupied by four oxygen atoms from carboxylate group of different citrate anions and its axial positions coordinated by two water molecules. The coordination sphere of Ni(2) contains one N atom from pyrazine, one water molecule, two carboxylate oxygen atoms and one hydroxy oxygen atom from the same citrate anion and one unidentate carboxylate oxygen atom from another citrate anion. The distance between two neighboring Ni(2) linked by pyrazine is about 6.974 Å. It is worthy noting that the citrate anion serves as a hexadentate ligand in **1**. The triionized citrate ion forms a tridentate ligand, in which one terminal carboxylate, the central carboxylate, and the protonated hydroxy group are coordinated to Ni(2) ion. Furthermore, the carboxylate groups, which take part in chelating Ni(2) ion, act as linkers between Ni(2) and Ni(1) (*d*(Ni(1)···Ni(2) = 5.375 Å), the left terminal carboxylates are coordinated to another Ni(2) centers in an unidentate way (*d*(Ni(2)···Ni(2C) = 5.474 Å).

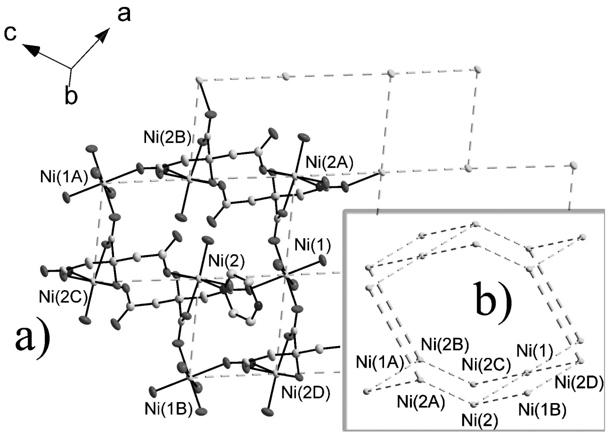

Figure 1. a) View of Ni_3cit_2 layer of **1**. b) Schematic view of the $4^26^48^2$ cage unit showing the pillared 2D layers.

The 3-D framework of the Ni(II) coordination polymer with $(4^26^28^2)(46^48)_2$ topology is shown in Figure 1.[12] Nickel ions linked by citrate ions form two-dimensional (2-D) layers (Figure 1a), which are further pillared by pyrazine into 3-D framework. Figure 1b shows that the schematic illustration of the cage unit, designated as $4^26^48^2$, consist of two 4-rings, four 6 rings and two 8 rings, where layers of 4 rings and 6 rings represent the Ni_3cit_2 and the four struts refer to pyrazine. This porous coordination polymer contains a 3-D channel system, where the channel openings in the [001] and the [010] directions are 8.8 × 4.5 and 5.5 × 5.6 Å, respectively, while the channel opening in the [100] direction is composed of Ni_4–pyz–Ni_4–pyz, which has approximately the size of 7.2 × 10.1 Å. However, this channel opening is partially obstructed by carbon skeletons of citrate ligands. Four water molecules are accommodated in the $4^26^48^2$ cage unit.

The thermal behavior of **1** was characterized by thermogravimetric analysis (TGA) under air environment. The first step of weight loss observed up to 150 °C corresponds to the four lattice

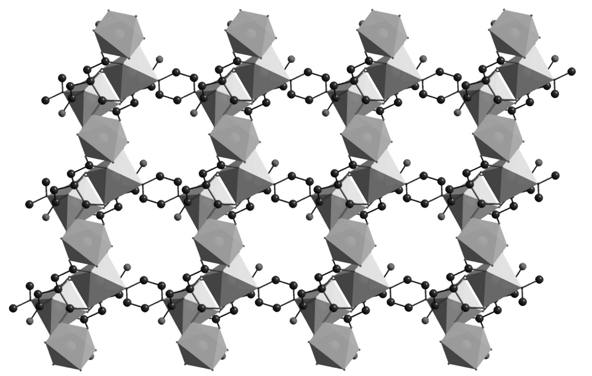

Figure 2. The crystal structure projection of 1 along the *c* axis direction (NiO_6, octahedral), where channels window of (5.5×5.6 Å) are observed with water occupied (water omitted for clarity).

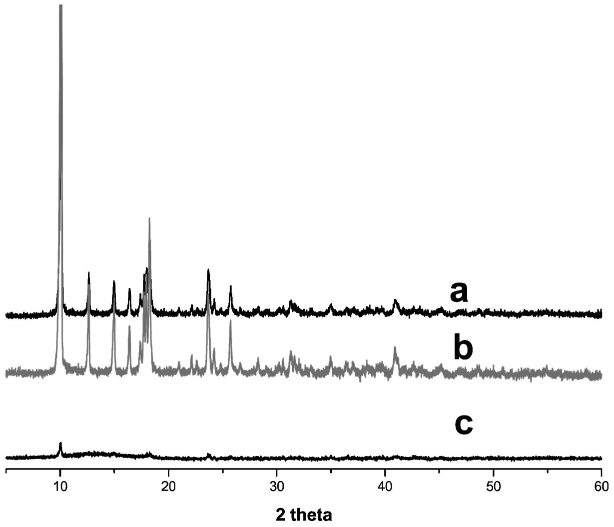

Figure 3. Powder XRD patterns for **1** (a) taken after rehydrating of the heated sample, (b) as-synthesized, (c) after heated at 180 °C for 8 h.

water molecules and two coordinated ones (found, 13.1 wt %; calcd, 13.8 wt %). The following gradual weight loss until 300 °C refers to the other two coordinated water molecules (found, 4.6 wt %; calcd, 4.6 wt %). The structure collapses between 330 and 400 °C. In order to further study the thermal stability, the sample of **1** was heated at 180 °C for 8 h. Powder X-ray diffraction (PXRD) analyses (Figure 3) show that the diffraction intensity of the sample is almost lost which may suggest the generation of amorphous phase. But after stored under water-saturate air for one night, PXRD (Figure 3) pattern of the rehydrated sample is similar to that of as-synthesized. This phenomenon suggests a recovery of the crystalline structure of **1** and the water sorption property of the amorphous phase of the dehydrated **1**.

In summary, we have deliberately chosen citrate and pyrazine serving as three different linkers to construct a new 3-D porous coordination polymer, $[Ni_3(cit)_2(pyz)(H_2O)_4](H_2O)_4$ with a pillared layer structure of $(4^26^28^2)(46^48)_2$ topology. This method may result distorted networks due to the different length of linkers. Yet it offers more opportunities to create novel networks because of the versatile approaching manners of multiple linkers to metal ion. We are now continuing to look for the possible new networks by applying this strategy to other metal ions.

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15 Single crystal X-ray data were collected on a Bruker Smart APEX diffractometer at room temperature. Mo Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods (SHELXTL Version 5.10), and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms from citrate anion were then found by successive difference Fourier maps. Hydrogen atoms from the water molecules and hydroxy group of citrate were not included in the structural model. Crystal data for **1**. $Ni_3C_{16}H_{30}N_2O_{22}$ (298 K). $M_r = 381.21$, Triclinic, space group $P\bar{1}$, $a = 7.495(8)$ Å, $b = 9.668(11)$ Å, $c = 11.102(12)$ Å, $\alpha = 113.484(13)°$, $\beta = 109.727(10)°$, $\gamma = 90.000(13)°$, $V = 686.1(13)$ Å^3, $Z = 2$, $D_{calcd.} = 1.392\,g/cm^3$, absorption coefficient = 2.136 mm^{-1}, total reflections collected 2904, unique 2393 (Rint = 0.0357), GOF = 1.144, $R1 = 0.0577$, $R_w = 0.1666$ ($I > 2\sigma(I)$), $R1 = 0.0616$, $R_w = 0.1695$ for all data. Crystallographic data (excluding structure factors) for **1** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 245793. Copies of the data can be obtained free of charge in application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk).

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