



Amine-templated synthesis of two metal phosphonates based on 5-phosphononicotinic acid



Jintang Li^{*}, Rongyi Chen, Xue Zeng, Chaonan Wang, Yuqing Chen, Xuetao Luo^{*}

Fujian Key Laboratory of Advanced Materials, College of Materials, Xiamen University, Xiamen, Fujian 361005, PR China

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ABSTRACT

Two metal phosphonates, namely $[\text{Co}_3(\text{OOC}_5\text{H}_3\text{NPO}_3)_2(\text{H}_2\text{O})_6] \cdot 2(\text{H}_2\text{O})$ (**1**) and $[\text{Ni}_5(\text{OOC}_5\text{H}_3\text{NPO}_3)_2(\text{OOC}_5\text{H}_3\text{NPO}_3)_2(\text{H}_2\text{O})_8] \cdot 2(\text{H}_2\text{O})$ (**2**) were hydrothermally synthesized by reacting 5-phosphononicotinic acid with corresponding metal sulfate in the presence of organic amines as templates. In compound **1**, bicobaltic clusters are corner-shared with $\{\text{CPO}_3\}$ tetrahedrons and subsequently connected by phosphonyl and pyridyl groups into layered structures. These layers are further linked with $\{\text{Co}_3\text{O}_6\}$ octahedrons through carboxyl groups forming a three dimensional pillared layered frameworks. In compound **2**, $\{\text{NiO}_6\}$ and two $\{\text{NiO}_5\text{N}\}$ octahedrons are linked by $\mu\text{-OH}_2$ bridge of water forming a trimeric cluster of Ni_3 . Subsequently, Ni_3 clusters are corner-shared with $\{\text{CPO}_3\}$ tetrahedron and link to $\{\text{Ni}_3\text{O}_5\text{N}\}$ octahedron forming a double-chain structure. These double-chains are further connected to a three dimensional structure by three functional groups of ligands. Magnetic property of compound **2** was investigated.

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1. Introduction

Metal–organic frameworks (MOFs) are now receiving increasing interests due to their diverse structures and potential applications as functional materials in many fields. However, it is still a challenge to rational design and controllable synthesis of the MOFs with expected structures. An effective approach directing porous structures was using organic amines as templates in synthesis of MOFs [1]. Careful selection of organic amine templates with different sizes and shapes can adjust pore size, pore volume and pore shape of MOFs [2].

Phosphonates ligands are widely used to assemble MOFs due to their numerous possible modes of coordination and myriad different arrangements of structures. Compared to carboxylate-based MOFs, MOFs based on phosphonates are more stable both thermally and chemically due to their stronger bonds between phosphonyl groups and metal atoms. In the last two decades, metal phosphonates are receiving increasing interests due to their potential applications in catalysis [3], absorption and separation [4,5], proton conductors [6,7], optics [8], magnetism [9] and electronics [10], biotechnology [11] etc. However, building microporosity in phosphonate based MOFs is not an easy task because of the presence of three oxygen atoms in the phosphonate ligands tending to

forming more condensed structures. During the past few years, diverse phosphonic acids with additional functional groups were designed and involved in the phosphonate based MOFs, such as amino [12], carboxylate [13,14], pyridyl [15,16], hydroxyl [17], triazole [18], imidazole [19], etc. Also different kind of organic amines were used as templates in growth of single crystals with phosphonates. For example, Zhao et al. reported preparing a series of zinc phosphonates using organic amines as templates [20]. We also synthesized two phosphonate compounds in the presence of 4,4'-bipyridine and 1,4-diazabicyclo[2.2.2] octane (DABCO) [21]. Nevertheless, in these cases, organic amines were involved in the structures and resulted in very small pore size.

In present work, we choose a multifunctional phosphonate ligand, namely 5-phosphononicotinic acid (5- H_3PN) combining pyridyl, carboxyl and phosphonyl groups in one ligand which is seldom explored [22,23]. 5- H_3PN has diverse coordination modes and is expected to form many interesting structures. Here in, We present the two MOFs based on the 5- H_3PN with interesting structures under directing of organic amine templates, namely, $[\text{Co}_3(\text{OOC}_5\text{H}_3\text{NPO}_3)_2(\text{H}_2\text{O})_6] \cdot 2(\text{H}_2\text{O})$ (**1**) and $[\text{Ni}_5(\text{OOC}_5\text{H}_3\text{NPO}_3)_2(\text{OOC}_5\text{H}_3\text{NPO}_3)_2(\text{H}_2\text{O})_8] \cdot 2(\text{H}_2\text{O})$ (**2**). In compound **1**, we use DABCO as template and get a pillared layered structure. While in compound **2**, monoamine tetrapropylammonium bromide leads to a porous structure. Both organic amines are not involved in the structures. Magnetic studies of compound **2** shows an antiferromagnetic ally coupled between a ferromagnetic nickel chain trimer Ni_3 cluster and two paramagnetic Ni atoms.

^{*} Corresponding authors. Tel.: +86 18030105513 (J. Li), +86 13515963818 (X. Luo).

E-mail addresses: leejt@xmu.edu.cn (J. Li), xuetao@xmu.edu.cn (X. Luo).

2. Experiments

2.1. Materials and instruments

All starting materials were of reagent quality and were obtained from commercial sources without further purification. The 5-phosphononicotinic acid (5-H₃PN) was synthesized according to the literature [23,24]. Elemental analyses for C, H, and N were performed on a Vario EL III elemental analyzer. The powder X-ray diffraction patterns of samples were carried out by Bruker-Axs D8 Advance X-ray diffractometer with a Cu K α radiation ($\lambda = 0.15406$ nm), operating at 40 kV and 40 mA. The IR spectra (KBr pellets) were recorded in the range 400–4000 cm⁻¹ with a Thermo Scientific Nicolet iS10 FTIR spectrometer. The thermal behavior of samples were studied by thermogravimetry (TG) (Netzsch STA 449 F3 Jupiter[®], Germany) from 30 °C to 800 °C in nitrogen atmosphere at the heating rate of 10 °C/min. Magnetic susceptibility measurements were carried out on a Quantum Design MPMSXL7 SQUID magnetometer in the 2–300 K temperature range and under a magnetic field of 1000 Oe.

2.2. Preparations

2.2.1. [Co₃(OOCCH₂H₃NPO₃)₂(H₂O)₆] \cdot 2(H₂O) (**1**)

A mixture of CoSO₄ \cdot 7H₂O (28.3 mg, 0.10 mmol), 5-phosphononicotinic acid (20.3 mg, 0.1 mmol), DABCO (16.8 mg, 0.15 mmol) and H₂O (10 mL) was mixed and stirred for 20 min then transferred to a Teflon-lined stainless steel vessel (25 mL) and heated at 140 °C for 2 days. After slowly cooling to room temperature, small block purple crystals were obtained. Yield: 0.0087 g (36.2% based on Co). *Anal.* found (calcd) for C₁₂H₂₂N₂O₁₈P₂Co₃: C, 19.92 (19.99); H, 3.02(3.08); N, 3.88 (3.89)%. IR (KBr, cm⁻¹): 3377(vs), 1602(s), 1587(s), 1552(s), 1420(w), 1390(vs), 1302(w), 1243(w), 1207(m), 1131(vs), 1095(vs), 1059(s), 1030(vs), 977(vs), 963(s), 923(w), 789(w), 694(m), 606(m), 567(m), 550(m), 467(w).

2.2.2. [Ni₅(OOCCH₂H₃NPO₃H)₂(OOCCH₂H₃NPO₃)₂(H₂O)₈] \cdot 2(H₂O) (**2**)

NiSO₄ \cdot 6H₂O (28.3 mg, 0.10 mmol), 5-phosphononicotinic acid (20.3 mg, 0.1 mmol), Tetrapropylammonium bromide (79.8 mg, 0.30 mmol) and H₂O (10 mL) were mixed in a Teflon-lined stainless steel vessel (25 mL) and heated at 200 °C for 2 days. After slowly cooling to room temperature, small needle green crystals were obtained. Yield: 0.0126 g (48.0% based on Ni). *Anal.* found (calcd) for C₂₄H₃₈N₄O₃₂P₄Ni₅: C, 21.94 (21.97); H, 2.98 (2.92); N, 4.34 (4.27)%; IR (KBr, cm⁻¹): 3247(vs), 1628(vs), 1583(s), 1560(m), 1433(m), 1396(vs), 1296(w), 1209(m), 1100(vs), 1080(vs), 1054(vs), 989(vs), 941(w), 885(w), 790(m), 766(m), 698(m), 572(s), 500(w), 460(w).

2.3. Crystallographic studies

Single crystals of dimensions 0.21 \times 0.18 \times 0.13 mm³ for **1** and 0.33 \times 0.08 \times 0.04 mm³ for **2** were used for structural determinations on a Bruker SMART APEX CCD diffractometer using graphite-monochromatized Mo K α radiation ($\lambda = 0.71073$ Å) at 173 \pm 2 K. A hemisphere of data was collected in the θ range 2.99–25.25° for **1** and 3.08–25.34° for **2** using a narrow-frame method with scan widths of 0.30° in ω and an exposure time of 5 s/frame. Numbers of observed and unique [$I > 2\sigma(I)$] reflections are 9024 and 3935 ($R_{\text{int}} = 0.0397$) for **1** and 9830 and 3643 ($R_{\text{int}} = 0.0750$) for **2**, respectively. The data were integrated using the Siemens SAINT program [25] with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. Empirical absorption corrections were applied. The structures were solved by direct methods and were refined on F^2 by full matrix

least squares using SHELXTL [26]. All the non-hydrogen atoms were located from the Fourier maps, and were refined anisotropically. All H atoms were refined isotropically, with the isotropic vibration parameters related to the non-H atom to which they are bonded. Additionally, the lattice water O18 in compound **1** is disordered. Crystallographic and refinement details of **1** and **2** are listed in Table 1. Selected bond lengths and angles are given in Tables S1 and S2.

3. Results and discussion

3.1. Description of structure

Compound **1** crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit consists of three Co atoms, two 5-PN³⁻, six coordinated water molecules and two lattice water molecules (Fig. 1). There are three crystallographically distinguishable Co atoms. The Co1 atom has a distorted pentahedral environment. Three sites are occupied by two phosphonate oxygen atoms and one nitrogen atom (O3A, O3B, N1) from three equivalent phosphonate ligands. The remained two sites are occupied by the fourth phosphonate (O7) oxygen and water (O11). The Co2 atom coordinated with four phosphonate oxygen atoms (O1C, O2, O8D, O8E) from four phosphonate ligands, one nitrogen atom (N2) and water (O12) forming a distorted octahedral geometry. The Co3 atom is linked with two carboxyl oxygen atoms (O4, O10F) and surrounded by four water molecules. The Co–O bond lengths fall in the range of 1.964(2)–2.175(2) Å. The Co1–N1 and Co2–N2 bond lengths are 2.144(3) Å and 2.096(3) Å respectively.

There are two different 5-PN³⁻ ligands, one serves as a hexadentate ligand by using its nitrogen, three phosphonate and one carboxylate oxygen atoms, another serves as a penta-dentate ligand with one phosphonate oxygen unoccupied (Scheme S1). In the former ligand, the phosphonate oxygen O3 acts as μ_2 -O bridge and links two Co1 atoms. The remaining two phosphonate oxygen atoms (O1, O2) are each coordinated to a single Co2 atom. The later ligand is similar to the former except one phosphonate oxygen atom (O6) without coordinated to metal atoms. Hence two {Co1O₄-N} pentahedrons and two {Co2O₅N} octahedrons are edge-shared forming bimetallic cluster respectively. These bimetallic clusters are corner-shared with {CPO₃} tetrahedrons forming one dimensional chain along the *b* axis. Subsequently, one dimensional chains are connected by phosphonate and pyridine groups into a two-dimensional layer along the *a* axis (Fig. 2). Along the *c* axis, these

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

Compound	1	2
Empirical formula	C ₁₂ H ₂₂ N ₂ O ₁₈ P ₂ Co ₃	C ₂₄ H ₃₈ N ₄ O ₃₂ P ₄ Ni ₅
F_w	721.05	1312.01
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2(1)/n$
<i>a</i> (Å)	8.7167(5)	10.7845(9)
<i>b</i> (Å)	9.7520(7)	9.5855(7)
<i>c</i> (Å)	13.8642(7)	19.8249(16)
α (°)	84.030(2)	90.00
β (°)	79.446(2)	94.398(3)
γ (°)	73.029(2)	90.00
<i>V</i> (Å ³)	1106.54(12)	2043.4(3)
<i>Z</i>	2	2
ρ_{calcd} (g cm ⁻³)	2.164	2.132
$F(000)$	726	1332
Goodness-of-fit (GOF) on F^2	1.010	1.013
R_1 , wR_2 [$I > 2\sigma(I)$] ^a	0.0337, 0.0720	0.0403, 0.0716
R_1 , wR_2 (All data) ^a	0.0557, 0.0793	0.0805, 0.0811
$(\Delta\rho)_{\text{max}}$, $(\Delta\rho)_{\text{min}}$ (e Å ⁻³)	–0.500, 0.545	–0.568, 0.553

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

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