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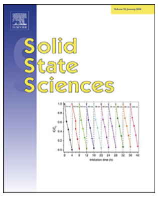

Assembly of two novel inorganic–organic hybrid solids based on 3-(aminomethyl)pyridine ligand

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ABSTRACT

Two new inorganic–organic hybrids, (H*ampy*)$Zn_2(PO_4)$ (HPO_3) (**1**) and (*ampy*)$Zn_2(HPO_3)_2$ (**2**), where *ampy* = 3-(aminomethyl)pyridine, have been solvothermally prepared and structurally characterized. Compound **1** exhibits an unusual two-dimensional layer structure, which possesses a central 4.8^2 zincophosphate sheet wrapped by infinite zincophosphite chains. Left- and right-handed helical chains participate in the formation of the zincophosphate layer. Compound **2** features a three-dimensional pillared-layer structure, in which two-dimensional $Zn^{II}(HPO_3)$ inorganic sheets were cross-linked by *ampy* ligands. The simultaneous occurrence of zinc-amine helical chains in **2** is unique and, to the best of our knowledge, firstly encountered in phosphite/phosphate hybrid materials. Different coordination modes and roles of the same *ampy* ligand were observed in the formation of the hybrid structures.

1. Introduction

The investigation of new microporous materials has attracted huge interest for their abundant structural beauty and potential applications in the areas of catalysis, absorption, ion-exchange and separation, etc [1–3]. As one branch of these materials, metal phosphites gained more and more attention in part due to their relationship to metal phosphates with a significant amount of rich compositions and structures [4,5]. The substitution of four-connected phosphate groups in metal phosphate frameworks by three-connected HPO_3 units can greatly reduce the M–O–P connectivity and favors the formation of large-pore materials. Typical examples in this system include CoHPOCJ2 with 18R channels [6], TJPU-3 with 20R channels [7], Cr-NKU-24, ZnHPO-CJn (n = 1–4), $[HR]_2[Zn_3(HPO_3)_4]$ (R = CHA, CHPA), and SCU-24 with extra-large 24R channels [8–12], bimetallic phosphite NTHU-5 with 26R channels [13]. More recently, the upper limit of the channel size (26R) was expanded by a family of fascinating zinc-gallium heterometallic phosphites with larger 28-, 40-, 56-, 64- and 72Rchannels [14].

As an effective and promising method, hydro(solvo)thermal route has been well used to produce phosphite-based materials with organic amines as templates or SDAs (structure-directing agents). In most cases, these organic molecules are protonated and act as charge-balancers and/or space-fillers. By contrast, hybrid frameworks with both inorganic and organic components as subunits, are still scarce. For example, the ethanediamine template in $[H_2N(CH_2)_2NH_2]_{0.5}\cdot ZnHPO_3$, is neutral and coordinates to Zn^{II} ions to create an inorganic–organic architecture with two-fold interpenetration [15]; $Zn_9(TPT)_3(H_2PO_4)_2(HPO_4)_4(HPO_3)_4\cdot 6H_2O$, employing tris(4-pyridyl)triazine (= TPT) as bridging ligands to connect framework zinc atoms, features a hybrid material with interesting fluorescent and photosensitive properties [16]; $[C_6N_2O_2H_{16}][Zn(HPO_3)]_2$ firstly used long and flexible aliphatic 1,2-bis(2-aminoethoxy)ethane polyamines acting as pillaring ligands instead of amine templates [17]. Further, a few hybrid phosphite materials have been realized by using multifunctional organic ligands with N-donor or O-donor groups, such as piperazine, bipyridine, imidazole and natural amino acid, etc [18–22]. We have recently been interested in the study of templating effects in the synthesis of microporous materials. Our earlier study on phosphate/phosphite based materials indicated the possibility of exploiting different framework structures by subtle introduction of various templates generated by *in situ* strategy or the use of the same template under a variety of synthetic conditions [23–25]. For the study of the inorganic–organic hybrid phosphite frameworks, herein we used a semi-rigid 3-(aminomethyl)pyridine (*ampy*)

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ligand and successfully synthesized two new hybrid phases, (H*ampy*)$Zn_2(PO_4)$ (HPO_3) (**1**) and (*ampy*)$Zn_2(HPO_3)_2$ (**2**).

2. Experimental section

2.1. Materials and methods

All chemicals were commercially available, and used as purchased without further purification. CHN analyses were performed on a Perkin-Elmer 240C analyzer (Perkin-Elmer, USA). Infrared spectra were obtained from sample powder pelletized with KBr on a MAGNA-560 (Nicolet) FT-IR spectrometer over a range 400–4000 cm^{-1}. Powder X-ray diffraction (PXRD) spectra were collected on a Bruker D8 FOCUS diffractometer with a Cu-target tube and a graphite monochromator. Thermogravimetric analyses (TGA) were conducted on a Rigaku standard TG-DTA analyzer with a heating rate of 10 °C min^{-1} from ambient temperature to 800 °C.

2.2. Synthesis

(H*ampy*)$Zn_2(PO_4)$ (HPO_3) (**1**): A mixture of $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.2184 g), H_3PO_3 (0.1666 g), 3-(aminomethyl)pyridine (0.27 mL), methanol (2.5 mL) and H_2O (3.5 mL) was sealed in a Teflon-lined autoclave and heated at 145 °C for 7 days. After cooling to room temperature, filtration and washing with distilled water, colorless crystals of **1** were obtained and dried in air (77.4% yield based on zinc). Anal. Elemental analysis (%) calcd for $C_6H_{10}N_2O_7P_2Zn_2$: C, 17.37; H, 2.42; N, 6.75. Found: C, 17.77; H, 2.74; N, 6.49. IR (KBr pellets, cm^{-1}): 3434(m), 3053(w), 2954(w), 2363(w), 1622(s), 1557(s), 1431(s), 1335(s), 1125(m), 1070(m), 841(w), 779(m), 713(m), 644(w), 621(w), 571(w), 541(w), 512(w), 466(w).

(*ampy*)$Zn_2(HPO_3)_2$ (**2**): It was prepared using the same procedure as described for **1** with ZnO (0.0821 g), H_3PO_3 (0.1181 g), 3-(aminomethyl)pyridine (0.16 mL), methanol (1 mL) and H_2O (4.5 mL). Colorless crystals were collected in 83.6% yield on the basis of zinc. Anal. Elemental analysis(%) calcd for $C_6H_{10}N_2O_6P_2Zn_2$: C, 18.06; H, 2.52; N, 7.02. Found: C, 18.27; H, 2.80; N, 6.78. IR (KBr pellets, cm^{-1}): 3427(m), 3051(w), 2952(w), 2361(w), 2332(w), 1626(s), 1559(s), 1431(s), 1336(s), 1126(m), 1071(w), 1025(w), 839(w), 778(m), 711(m), 677(w), 647(w), 619(w), 516(w), 464(w).

The X-ray powder diffraction profiles of compounds **1** and **2** match well with the simulated patterns from single crystal X-ray structure data, indicating the purity of the as-synthesized samples (Fig. 1).

2.3. Determination of crystal structure

The single-crystal X-ray diffraction data for **1** and **2** were collected on a Rigaku SCX-mini diffractometer at 293(2) K with Mo-Kα radiation (λ = 0.71073 Å) by ω scan mode. The program *CrystalClear* was used for the integration of the diffraction profiles [26]. All structures were solved by direct method using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL (semi-empirical absorption corrections were applied by using the SADABS program) [27]. Heavy metal atoms in each compound were located from the *E*-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters. The hydrogen atoms residing on the phosphorous were located by Fourier maps and the remaining hydrogen atoms were placed geometrically and refined in a riding model. All of the non-hydrogen atoms were refined anisotropically. Detailed crystallographic data are summarized in Table 1. CCDC 1422693 (**1**) and 1422694 (**2**) contain the supplementary crystallographic data for this paper.

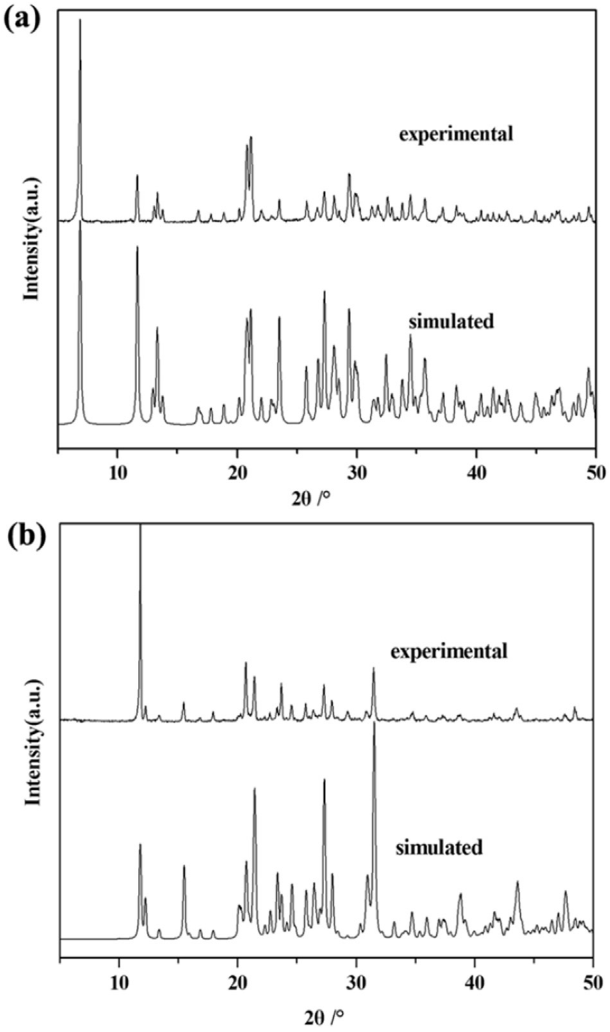

Fig. 1. Simulated and experimental X-ray powder diffraction patterns of compounds (a) and **2** (b).

Table 1
Crystal data and structure refinement parameters for compounds **1** and **2**.

	1	**2**
Formula	$C_6H_{10}N_2O_7P_2Zn_2$	$C_6H_{10}N_2O_6P_2Zn_2$
Mr (g mol^{-1})	414.84	398.88
Space group	$P2_1/c$	$P2_1/c$
Crystal system	Monoclinic	Monoclinic
a (Å)	13.5147(7)	9.3492(3)
b (Å)	9.3947(2)	15.0050(8)
c (Å)	10.4636(2)	8.7498(7)
α(°)	90	90
β(°)	107.918(5)°	109.260(5)°
γ(°)	90	90
V ($Å^3$)	1264.09(7)	1158.76(12)
Z	4	4
F(000)	824	792
Dc (gcm^{-3})	2.180	2.286
μ (mm^{-1})	4.076	4.436
R_{int}	0.0481	0.1211
limiting indices	$-16 \leq h \leq 16$ $-11 \leq k \leq 11$ $-13 \leq l \leq 13$	$-12 \leq h \leq 12$ $-19 \leq k \leq 19$ $-11 \leq l \leq 11$
Collected reflections	12065	11904
Unique reflections	2604	2651
GOF on F^2	1.143	1.075
$R_1, wR_2[I > 2\sigma(I)]$[a]	0.0382, 0.0788	0.0743, 0.1211

[a] $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$.