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Solvent-free synthesis of new metal phosphites with double-layered, pillared-layered, and framework structures

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ABSTRACT

Three new metal phosphites, formulated as $(H_3O)_2 \cdot Mn_2(HPO_3)_3$ (**1**), Co(bpy) (H_2O) (HPO_3) (**2**), and $H_2tmpda \cdot Zn_3(HPO_3)_4$ (**3**), have been synthesized under solvent-free conditions, where bpy = 4,4′-bipyridine, and tmpda = N,N,N′,N′-tetramethyl-1,3-propanediamine. Compound **1** has a double-layered structure with a thickness of 5.68 Å. Compound **2** has an inorganic-organic hybrid framework with cobalt phosphite layers pillared by bpy ligands. Compound **3** has a three-dimensional open-framework structure containing 8-ring channels. The temperature dependence of the magnetic susceptibility of compounds **1** and **2** were also investigated.

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1. Introduction

Crystalline microporous inorganic solids, such as zeolites and aluminophosphate molecular sieves, are of current interest due to their potential applications in catalysis, separation, and ion-exchange processes [1–3]. Since the pioneering work reporting the synthesis of open-framework zinc phosphites by Clearfield in 1989, great efforts have been devoted to preparing new framework structures containing HPO_3 pseudo pyramids [4–8]. Different from 4-connected PO_4 tetrahedra, HPO_3 unit often makes three linkages with metal ions [9–11]. It is believed that the substitution of PO_4 tetrahedra by HPO_3 pseudo pyramids in zeotype material synthesis may help to make new interrupted frameworks, especially those with extra-large channels [12–16]. Notable examples are the family of gallium zincophosphites (denoted as NTHU-13) with pore sizes ranging from 24-membered ring (24 R) and 28 R–40 R, 48 R, 56 R, 64 R, and 72 R [17].

Open-framework compounds are usually synthesized under hydro/solvothermal conditions [18–22]. The use of ionic liquids as both solvents and structure-directing agents for zeotype material synthesis has also been studied [23–26]. Recently, we develop a solvent-free approach for the synthesis of crystalline metal phosphites, metal oxalates, metal phosphate-oxalates, and metal phosphite-oxalates [27–30]. Single-crystal X-ray diffraction analyses reveal that most as-prepared compounds possess new structures, demonstrating the potential of this synthetic method in the discovery of new open-framework compounds and related inorganic-organic hybrid solids. Along this line of research, three new metal phosphites, formulated as $(H_3O)_2 \cdot Mn_2(HPO_3)_3$ (**1**), $Co_2(bpy)_2(H_2O)_2(HPO_3)_2$ (**2**), and $H_2tmpda \cdot Zn_3(HPO_3)_4$ (**3**), have been prepared under solvent-free conditions, where bpy = 4,4′-bipyridine, and tmpda = N,N,N′,N′-tetramethyl-1,3-propanediamine. Herein, we describe their syntheses, crystal structures, and characterizations.

2. Experimental

2.1. Materials and methods

Reagents were purchased commercially and used without further purification. Powder X-ray diffraction (XRD) data were collected using a Rigaku D/MAX-rA diffractometer with Cu-Kα radiation ($\lambda = 1.5418$ Å). The CHN analyses were carried out on a Euro EA3000 analyzer. The thermogravimetric analyses were performed on a Netzsch STA 449c analyzer in a flow of N_2 with a heating rate of 10 °C/min. Magnetic measurements were performed at 1000 Oe in the temperature range 2–300 K with a SQUID MPMS-7 magnetometer manufactured by Quantum Design.

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2.2. Synthesis

2.2.1. $(H_3O)_2{\cdot}Mn_2(HPO_3)_3$ (**1**)

A mixture of $Mn(OAc)_2{\cdot}2H_2O$ (0.490 g), H_3PO_3 (0.328 g), and guanidinium carbonate (0.360 g) was sealed in a Teflon-lined steel autoclave and heated at 150 °C for 8 days. After cooling to room temperature, light-pink crystals of **1** were separated from the resulting product by sonication, washed with distilled water, and then dried in air (67.2 wt% yield based on manganese).

2.2.2. Co(bpy) (H_2O) (HPO_3) (**2**)

A mixture of $Co(OAc)_2{\cdot}4H_2O$ (0.498 g), H_3PO_3 (0.164 g), and bpy (0.312 g) was sealed in a Teflon-lined steel autoclave and heated at 150 °C for 9 days. After cooling to room temperature, red crystals of **2** were separated from the resulting product by sonication, washed with distilled water, and then dried in air (57.4 wt% yield based on cobalt). $C_{10}H_{11}CoN_2O_4P$: calcd. C, 38.36; H, 3.54; N, 8.95. Found C, 37.92; H, 3.46; N, 8.91.

2.2.3. $H_2dmpda{\cdot}Zn_3(HPO_3)_4$ (**3**)

A mixture of $Zn(OAc)_2{\cdot}2H_2O$ (0.223 g), H_3PO_3 (0.183 g), and dmpda (0.128 g) was sealed in a Teflon-lined steel autoclave and heated at 150 °C for 7 days. After cooling to room temperature, colorless crystals of **3** were obtained together with a large amount of unidentified powders. The crystals of **3** were separated from the resulting product by sonication, washed with distilled water and dried in air (25.6 wt% yield based on zinc). $C_7H_{24}N_2O_{12}P_4Zn_3$: calcd. C, 12.97; H, 3.73; N, 4.32. Found C, 12.85; H, 3.66; N, 4.29.

2.3. Crystal structure determination

A suitable single crystal of each compound was carefully selected under an optical microscope and glued to a glass fiber with epoxy resin. Data collection was performed on a Siemens SMART CCD diffractometer or an Oxford Xcalibur diffractometer with graphite-monochromated MoK$_\alpha$ ($\lambda = 0.71073$ Å) radiation at room temperature. The crystal structures were solved by direct methods. The structures were refined on F^2 by full-matrix least-squares methods using the *SHELXTL* program package [31]. All non-hydrogen framework atoms were refined anisotropically. The crystallographic data for compounds **1**–**3** are summarized in Table 1.

3. Results and discussion

Three new metal phosphites were obtained as good quality single crystals without the addition of liquid solvents in the reaction systems. Powder X-ray diffraction pattern of each compound is in good agreement with the simulated one on the basis of single crystal data, indicating the phase purity of as-synthesized compounds.

Table 1
Crystal data and structure refinement for **1**–**3**.

	1	**2**	**3**
Empirical formula	$H_9Mn_2O_{11}P_3$	$C_{10}H_{11}CoN_2O_4P$	$C_7H_{24}N_2O_{12}P_4Zn_3$
Formula weight	387.86	313.11	648.27
Crystal system	hexagonal	monoclinic	orthorhombic
Space group	$P6_3/mmc$	$P2_1$	*Pnma*
a, Å	5.4749(7)	10.6164(3)	16.7654(9)
b, Å	5.4749(7)	10.3572(3)	14.3933(9)
c, Å	19.086(5)	11.5205(3)	8.5453(6)
β, °	90	100.699(2)	90
Volume, Å^3	495.45(16)	1244.73(6)	2062.1(2)
Z	2	4	4
D_c, g/cm^3	2.600	1.671	2.088
μ (Mo-Kα), mm^{-1}	3.081	1.514	3.830
Total data	2265	4982	5428
Unique data	207	3105	2191
Data, I > 2σ(I)	199	2610	1848
Final R_1, wR_2 [I > 2σ (I)]	0.0392, 0.1057	0.0316, 0.0724	0.0323, 0.0703

A single-crystal structural analysis reveals that compound **1** crystallizes in the hexagonal space group $P6_3/mmc$ (no. 194). There are one crystallographically independent manganese atom and two crystallographically independent phosphorus atoms in the asymmetric unit. The manganese atom is octahedrally coordinated by six oxygen atoms with the Mn–O bond lengths in the region 2.157(4)–2.273(5) Å. Of the two crystallographically independent phosphorus atoms, P(1) atom makes three P–O–Mn connections to adjacent manganese atoms. P(2) atom is disordered over two positions with equal occupancy, which make six P–O–Mn connections to adjacent manganese atoms. The P–O bond lengths are between 1.515(4) Å and 1.517(6) Å. The linkages between manganese atoms and HPO_3 units create a double-layered structure with a thickness of 5.68 Å, as shown in Fig. 1(a),(b). Such layered structure can be understood as the packing of two different layered structures: a hcb-type layer (Fig. 1(c)) and a kgd-type layer (Fig. 1(d)). The manganese phosphite layers are stacked along the [001] direction in an ABAB sequence. The H_3O^+ cations are orderly within the interlayer region, which occupy 13.4% of the unit cell volume. They interact with each other through hydrogen bonds, forming a supramolecular layer with a hcb topology (Fig. 1(e)). The O···O distance is 3.439 Å. It should be noted that a series of triple-layered manganese phosphites have been prepared by using linear diamines as the structure-directing agents [32]. The thick inorganic layer consists of two hcb layers and one kgd layer as its building blocks. From the viewpoint of structural chemistry, it is expected that other slab-like layers, such as quadruple-layered $[Mn_4(HPO_3)_5]$ structure, can be obtained if more hcb layers are incorporated into the structures.

Compound **2** crystallizes in the monoclinic space group $P2_1$ (no. 4). The asymmetric unit contains two cobalt atoms, two HPO_3 pseudo pyramids, two water molecules, and two bpy ligands. Each cobalt atom is octahedrally coordinated by three oxygen atoms of HPO_3 units, one oxygen atom from a water molecule, and two nitrogen atoms from byp ligands. Each HPO_3 pseudo pyramids share three oxygen corners with adjacent CoO_4N_2 octahedra. The Co–O(N) bond lengths varying from 2.039(3) Å to 2.230(3) Å, and the P–O bond lengths is in the region 1.483(3)–1.521(3) Å. The strictly alternating CoO_4N_2 octahedra and HPO_3 pseudo pyramids give rise to layered structures parallel to the *ab* plane, which have a hcb topology (Fig. 2(a)). The inorganic layers are further pillared by bpy ligands, forming a three-dimensional structure (Fig. 2(b)). By regarding cobalt atoms as 5-connected nodes and phosphorus atoms as 3-connected nodes, the whole framework can be topologically represented as a (3,5)-connected hms topology (Fig. 2(c)). The point symbol for the net is (6^3) $(6^9.8)$, as analyzed by the TOPOS program [33].

Previously, several pillared layered structures, such as $(VO)_4(4,4'\text{-bpy})_2(HPO_3)_4$ [34], $[Zn_2(HPO_3)_2](ppz)]_n$ [35], $[C_6N_2O_2H_{16}][Zn(HPO_3)]_2$ [36], $Zn(O_3PH)$ $(4,4'\text{-bpy})_{0.5}$ [37], $Co(O_3PH)$ $(4,4'\text{-bpy})_{0.5}(H_2O)$ [37] and $[Co_3(PO_3)_2(4,4'\text{-bpy})_3(H_2O)_6]{\cdot}3H_2O$ [38], were prepared under hydrothermal or solvothermal conditions. Careful analysis of their structures reveals that the former four compounds contain inorganic layers with a fes topology, $Co(O_3PH)$ $(4,4'\text{-bpy})_{0.5}(H_2O)$ contains cobalt phosphite layers with a hcb topology, and $[Co_3(PO_3)_2(4,4'\text{-bpy})_3(H_2O)_6]{\cdot}3H_2O$ contains cobalt phosphite layers with a kgm topology. Among these compounds, $Co(O_3PH)$ $(4,4'\text{-bpy})_{0.5}(H_2O)$ shares many common structural features with compound **2**. Both compounds have the same hcb-type inorganic layers pillared by the same organic molecules. The main difference between the two structures is that, the cobalt phosphite layers in $Co(O_3PH)$ $(4,4'\text{-bpy})_{0.5}(H_2O)$ are stacked in an AAAA sequence, whereas in compound 2, an ABAB stacking mode for these inorganic layers has been found.

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