Inorganic Chemistry Communications 95 (2018) 8–11

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

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

Short communication

Solvent-free synthesis of inorganic-organic hybrid solids with chainlike, layered, and open-framework structures

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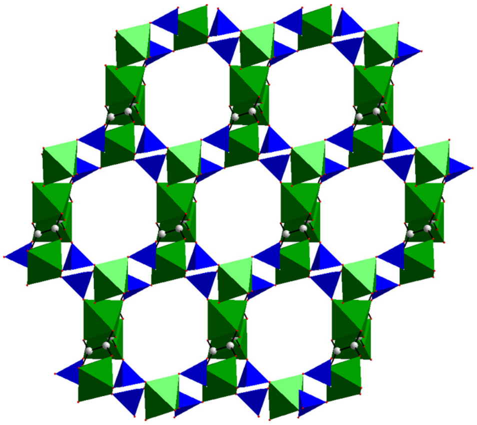
GRAPHICAL ABSTRACT

An open-framework indium phosphite-oxalate with multidirectional 12-ring channels was prepared under solvent-free conditions. The hybrid framework is intriguing since it may serve a structural model to illustrate that the wall of a dia-type framework can be thickened by using larger inorganic building blocks.



ARTICLE INFO

Keywords:
Solvent-free synthesis
Metal phosphite-oxalate
Open framework
Second harmonic generation
Magnetism

ABSTRACT

Three inorganic-organic hybrid solids, namely, $Cd_2(phen)_2(H_2PO_4)(H_2PO_3)(C_2O_4)$ (**1**), $(H_2dab)_{0.5}\cdot Co(H_2PO_3)(C_2O_4)$ (**2**), and $Hdbu\cdot In_2(HPO_3)_2(C_2O_4)_{1.5}$ (**3**), were prepared under solvent-free conditions, where phen = 1,10-phenanthroline, dab = 1,4-diaminobutane, and dbu = 1,8-diazabicyclo[5.4.0]undec-7-ene. These compounds have chainlike, layered, and three-dimensional structures, respectively. Compound **1** shows a weak second harmonic generation response. The temperature dependence of the magnetic susceptibility of compound **2** was also investigated.

Open-framework metal phosphites are an important class of solid state materials that have diverse structures and many appealing properties such as luminescence, magnetism, and gas adsorption [1–3]. Different from zeolite molecular sieves with 4-connected nets, metal phosphites often possess interrupted frameworks [4–8]. Illustrative compounds include the chiral zinc phosphite $Na_4[Zn_3(HPO_3)_5]\cdot 2H_2O$ with 20-membered ring (20 MR) channels, the low-density beryllium phosphite SCU-24 with 24 MR channels, and the bimetallic phosphites NTHU-13 with tunable pore apertures [9–11]. During the past two decades, a great deal attention has been paid to the structure-directing role of amines and the coordination geometries of metal ions. Much less work has been carried out to incorporate organic ligands into metal phosphite frameworks [12–15].

Microporous and open-framework materials are usually prepared

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https://doi.org/10.1016/j.inoche.2018.06.022
Received 20 May 2018; Received in revised form 26 June 2018; Accepted 27 June 2018

under hydrothermal and solvothermal conditions. The replacement of water or molecular organic solvents by ionic liquids has resulted in the formation of a large number of new open-framework materials [16–19]. Recently, solvent-free method has attracted considerable attention because it offers new opportunities for the synthesis of crystalline materials by removing the effect of solvent on the framework structure [20–25]. In our previous studies, two open-framework metal phosphite-oxalates with diamondoid and pillared-layered structures were prepared by a solvent-free approach using guanidinium carbonate as the structure-directing agent [26]. Along this line of research, here we report the solvent-free synthesis of three inorganic-organic hybrid solids, namely, $Cd_2(phen)_2(H_2PO_4)(H_2PO_3)(C_2O_4)$ (**1**), $(H_2dab)_{0.5}{\cdot}Co(H_2PO_3)(C_2O_4)$ (**2**), and $Hdbu{\cdot}In_2(HPO_3)_2(C_2O_4)_{1.5}$ (**3**), where phen = 1,10-phenanthroline, dab = 1,4-diaminobutane, and dbu = 1,8-diazabicyclo[5.4.0]undec-7-ene. These compounds have chainlike, layered, and three-dimensional structures, respectively [27]. The successful synthesis of compound **1** provides a rare example that three different types of anions (i.e., phosphate, phosphite, and oxalate) can coexist in the same structure. This compound crystallizes in a chiral space group and shows a weak second harmonic generation response. Topological analyses reveal that compounds **2** and **3** have hcb and dia nets, respectively.

Yellow crystals of compound **1** were obtained by heating a mixture of $Cd(OAc)_2{\cdot}2H_2O$, H_3PO_3, $H_2C_2O_4{\cdot}2H_2O$, and 1,10-phenanthroline at 150 °C for 8 days. This compound crystallizes in the triclinic space group *P*1 (No. 1). The asymmetric unit contains two cadmium atoms, one H_2PO_4 unit, one H_2PO_3 unit, one oxalate ligand, and two phen molecules. The presence of $H_2PO_4{}^-$ unit in the structure indicates that the phosphorous acid can be oxidized or disproportionated into $H_2PO_4{}^-$ anion under the solvent-free conditions. This phenomenon was also observed in the syntheses of several zinc phosphate-phosphites [28,29]. The linkages between cadmium atoms, H_2PO_4 unit, and H_2PO_3 unit gave rise to linear $Cd_2(H_2PO_4)(H_2PO_3)$ tetramers, which are further bridged by oxalate ligands to produce inorganic-organic hybrid chains running along the [100] direction (Fig. 1). Phen molecules attach to the chains through Cd—N bonds to complete the octahedral coordination of cadmium atoms. The hybrid structure of compound **1** is reminiscent of the manganese phosphate-oxalate $Mn(phen)(H_2PO_4)(C_2O_4)_{0.5}$, which has a similar chainlike structure containing $Mn_2(H_2PO_4)_2$ tetramers. It is worth noting that the manganese phosphate-oxalate crystallizes in the centrosymmetric space group *P*-1, while compound **1** crystallizes in the chiral space group *P*1. We believe that the presence of both $H_2PO_4{}^-$ and $H_2PO_3{}^-$ units in the structure of **1** is helpful for the symmetry breaking.

Red crystals of compound **2** were obtained by heating a mixture of $Co(OAc)_2{\cdot}4H_2O$, H_3PO_3, $H_2C_2O_4{\cdot}2H_2O$, and 1,4-diaminobutane at 150 °C for 6 days. This compound crystallizes in the triclinic space group *P*-1 (No. 2). There are one cobalt atom, one H_2PO_3 unit, two halves of oxalate ligands, and one half of an H_2dab cation in the asymmetric unit. The linkages between cobalt atoms and H_2PO_3 units give rise to cyclic $Co_2(H_2PO_3)_2$ tetramers, which are further bridged by oxalate ligands to produce honeycomb-like layers with 12 MR windows (Fig. 2). Each 12 MR window has a pore size of 7.5 × 7.8 $Å^2$ and hosts one H_2dab cation within its free void. By regarding cobalt atoms as 3-connected nodes, the layered structure can be represented as an hcb net with a point symbol of 6^3.

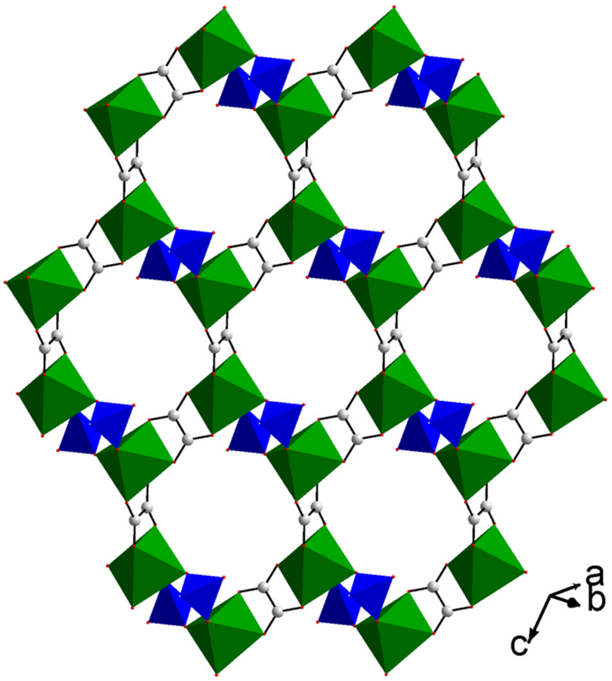

Fig. 2. View of the layered structure of compound **2** with honeycomb-like windows.

Colorless crystals of compound **3** were obtained by heating a mixture of In_2O_3, H_3PO_3, $H_2C_2O_4{\cdot}2H_2O$, and 1,8-diazabicyclo[5.4.0]undec-7-ene at 150 °C for 5 days. This compound crystallizes in the triclinic space group *P*-1 (No. 2). The asymmetric unit contains two crystallographically independent indium atoms and two crystallographically independent phosphorus atoms. Each indium atom is surrounded by six oxygen atoms with the In—O bond length in the region 2.067(5)–2.248(4) Å. Each phosphorus atom makes three P—O—In linkages to adjacent indium atoms, with the fourth vertex occupied by a hydrogen atom. The strict alternation of InO_6 octahedra and HPO_3 pseudo pyramids produces double-chain building blocks running along the [100] direction. The indium phosphite double-chains are bridged by oxalate ligands along the [010] direction to form double-layers. Such a double-layer can be understood as the assembly of two hcb-type layers. Then, the double-layers are further pillared by oxalate ligands along the

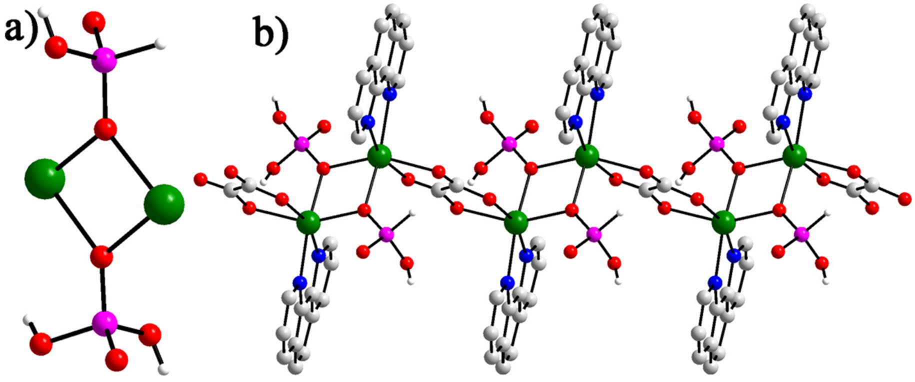

Fig. 1. (a) The linear $Cd_2(H_2PO_4)(H_2PO_3)$ tetramer. (b) The chainlike structure of compound **1**.