Two Neutral Open-framework Metal Phosphites with Ten-ring Channels Constructed by Three-, Four-, and Five-connected Centers

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Neutral open-structured metal phosphites of Al and In are hydrothermally synthesized; they are structural analogues that constructed by HPO_3 and MO_6 groups with intersecting eight- and 10-ring channels. The two metal sites serve as four- and five-connected centers, respectively, with the rest oxygen atoms belonging to the coordinated water molecules.

Open-framework materials have attracted much attention for their structural diversities and wide applications in catalysis, absorption, separation, ion-exchange, and host–guest chemistry.[1] Recently, using three-connected centers, such as $HOPO_3{}^{2-}$, $O{=}PO_3{}^{3-}$, $SeO_3{}^{2-}$, and $BO_3{}^{3-}$, replacing the four-connected units, has shown fascinating ability to construct novel open-structures with new topologies or low framework densities due to the reduced connection modes.[2] The occurrence of $HOPO_3$ and $O{=}PO_3$ groups in some large pore zeolitic compounds also verified its possibility. From this view, replacing tetrahedral phosphate groups by pseudo-pyramidal phosphite units has been considerably explored and resulted in a new family of metal phosphites in the past decade.[3] Notably, several novel compounds with extralarge pores have been isolated, including TJPU-3 with 20-ring apertures, ZnHPO–CJ1 and Cr–NKU-24 with 24-ring openings, and NTHU–5 with the largest 26-ring micropores.[4]

As well known, many documented open-framework aluminophosphates and indium phosphates with large pores contain hydrogenphosphate groups that act as three-connected units. However, open-structured phosphites of aluminum and indium are seldom.[5] By using 1,3-cyclohexane bis(methylamine) as the trial templates, two isostructural phosphites of Al and In, $[Al_2(H_2O)_3(HPO_3)_3]\cdot H_2O$ (denoted as TJPU-7Al, TJPU represents Tianjin Polytechnic University) and $[In_2(H_2O)_3(HPO_3)_3]\cdot H_2O$ (TJPU-7In) were synthesized.

TJPU-7Al and TJPU-7In were hydrothermally synthesized by heating a mixture of $Al(NO_3)_3$ or $InCl_3\cdot 4H_2O$, H_3PO_3, cyclohexanebis(methylamine) (CHBMA) and H_2O at 180 °C for 6 days. Typically, TJPU-7Al was isolated from 0.21 g of $Al(NO_3)$, 2.05 g of H_3PO_3, 1.462 g of CHBMA, and 10 mL of H_2O with the pH value of 2. TJPU-7In was prepared from 0.294 g of $InCl_3\cdot 4H_2O$, 0.595 g of H_3PO_3, 0.213 g of CHBMA, and 8 mL of H_2O with the pH value of 1.5. Although organoamines were used as the trial templates, no organic species were detected by elemental analyses. Organoamines solely served as pH adjustment in the formation of TJPU-7. EDAX measurement for metal and phosphorus contents gave a value of 1.5 for both P:Al in TJPU-7Al and P:In in TJPU-7In, respectively. Both of the powder X-ray diffraction patterns of these two compounds were in good agreement with those simulated from the structure data, indicating the monophasic feature of the as-synthesized materials. Also, powder XRD patterns revealed that TJPU-7Al and TJPU-7In were structural analogues, which were further verified by single crystal structural refinement.

Because single crystal structure refinements disclose that TJPU-7Al and TJPU-7In are structural analogues,[6,7] only structure of TJPU-7Al is described in detail. TJPU-7Al crystallizes in the monoclinic space group $P2_1$. The asymmetric unit contains two aluminum atoms, three phosphites ($HPO_3{}^{2-}$) and four water molecules (Figure 1), of which one is the noncoordinated solvent of crystallization. All phosphorus atoms are phosphite groups, serving as three-connected centers. The P–O bond lengths are in the range of 1.5136(19)–1.5264(19) Å with the bond angles of 109.24(11)–113.87(11)°. The presence of phosphite groups is also confirmed by a sharp IR peak at $2424\,cm^{-1}$. As well known, aluminum atoms are generally in tetrahedral geometry in open-framework aluminophosphates. In TJPU-7Al, however, both of two unique aluminum atoms are hexagonally coordinated by six oxygen atoms with bond lengths of 1.8512(19)–1.9994(20) Å and bond angles of 85.47(8)–177.50(9)°. Although aluminum atoms are all in octahedral environment similar to those in some documented aluminophosphites, Al(1) serves as five-connected center and Al(2) is a four-connected group owing to the presence of coordinated water molecules. O(4) and O(5) that bonded to Al(2) and O(9) to Al(1) are assigned to coordinated water molecules with the elongated Al–O bond lengths of 1.9865(20) and 1.9994(20) Å for Al(2)–O(5) and Al(2)–O(4) and 1.9574(22) Å for Al(2)–O(9), respectively. Hence, TJPU-7Al is formulated as $[Al_2(H_2O)_3(HPO_3)_3]\cdot H_2O$.

The extended structure of TJPU-7Al is a three-dimensional neutral architecture of $[Al_2(H_2O)_3(HPO_3)_3]$ with inclusive water molecules that are constructed by AlO_6 octahedral and HPO_3 pseudo pyramids. Unlike some documented aluminum phosphites are constructed by six-connected AlO_6 moieties and three-connected HPO_3 groups, TJPU-7Al is built from HPO_3, AlO_4, and AlO_5 moieties regardless of the coordinated water molecules (Figure 2). The structure can be elucidated in two

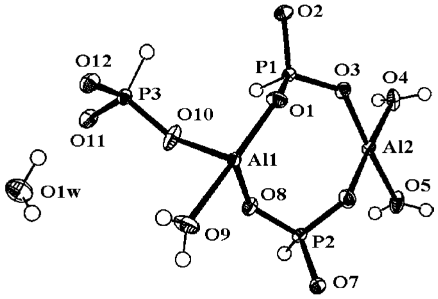

Figure 1. ORTEP view of TJPU-7Al with labeling scheme.

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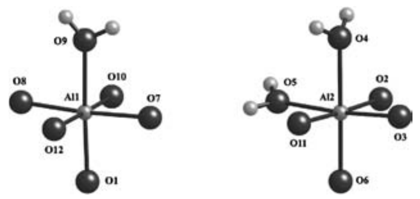

Figure 2. Coordination mode for Al(1) and Al(2) in TJPU-7 showing the four- and five-connected style of aluminum.

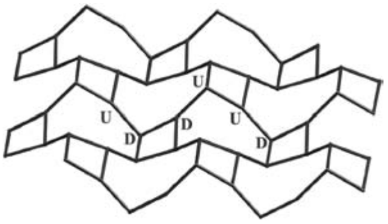

Figure 3. Layer structure of the 4.8^2 network. The oxygen atoms are omitted for clarity.

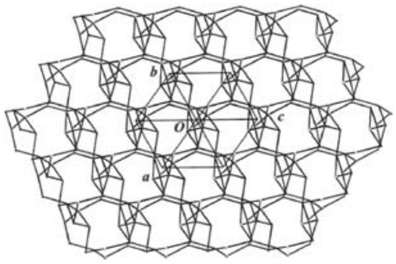

Figure 4. Structure of TJPU-7Al viewed along (111) direction showing the distorted 10-ring channels. The O and H atoms are omitted for clarity.

different ways. First, Al(2) and P(1) are bridged by oxygen atoms to generate a helical chain running along *b* axis. The connection of Al(1)O_6, HP(2)O_3, and HP(3)O_3 groups produces a corner-shared four-ring chain along *b* direction by using Al(1) as the vertex of each four-ring. Each four-ring unit relates to its neighbors by 2_1 symmetry within a four-ring chain. The connections of the alternative four-ring chains and helices create a three-dimensional architecture with intersecting eight- and 10-ring channels. The 10-ring channels run along 111 direction with dimensions of 7.772 Å [O(6)–O(1)] × 6.824 Å [O(11)–O(3)].

The structure of TJPU-7Al can be also elucidated as a pillared layer structure. The connections of Al(1)O_6, Al(2)O_6, HP(1)O_3, and HP(2)O_3 groups create a layer of 4.8^2 network (Figure 3). The vertexes of the neighbored eight-rings are alternatively up (U) and down (D) in the DUUDDUUD and UDDUUDDU arrangement. Similar arrangements are observed in zeolite GIS (UUUUDDDD) and ABW (UUDUDDUD). But the different arrangements direct to different structures. This arrangement gives rise to an undulating layer structure in (101) plane. Using HP(3)O_3 as pillar, stacking of this layer generates an extended structure with intersecting eight- and 10-ring channels (Figure 4).

Thermogravimetric analyses indicate two-step weight loss for both TJPU-7Al and TJPU-7In. TJPU-7Al and TJPU-7In, transforming into unknown dense phases after annealing at 200 °C for 2 h.

In a summary, two isostructural open-framework phosphites of aluminum and indium are hydrothermally synthesized and structurally determined. The structures are constructed by three-, four-, and five-connected centers to form three-dimensional frameworks with intersecting eight- and 10-membered ring channels.

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6 Crystal data for TJPU-7Al: $[Al_2(H_2O)_3(HPO_3)_3]{\cdot}H_2O$, $M_r = 731.92$, monoclinic space group $P2_1$, $a = 7.6472(18)$ Å, $b = 9.951(2)$ Å, $c = 8.1146(19)$ Å, $\beta = 111.970(4)°$, $V = 572.6(2)$ Å^3, $Z = 2$, $D_{calcd} = 2.122\,g\,cm^{-3}$, μ (Mo Kα) = 0.740 mm^{-1}. Direct phase determination yielded the positions of Al, P, and a part of oxygen atoms, and the rest oxygen atoms were located in successive difference Fourier syntheses. The hydrogen atoms of HPO_3 and water molecule were found in the final difference Fourier map. The final residual wR_2 (for all data) was 0.0689 and R_1 was 0.0298 with $S = 1.054$.

7 Crystal data of TJPU-7Al: $[In_2(H_2O)_3(HPO_3)_3]{\cdot}H_2O$, $M_r = 1083.28$, monoclinic space group $P2_1$, $a = 8.0075(16)$ Å, $b = 10.388(2)$ Å, $c = 8.4641(17)$ Å, $\beta = 113.36(3)°$, $V = 646.3(2)$ Å^3, $Z = 2$, $D_{calcd} = 2.783\,g\,cm^{-3}$, μ (Mo Kα) = 3.998 mm^{-1}. The final residual wR_2 (for all data) was 0.0375 and R_1 was 0.0179 with $S = 0.977$.

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