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Ionothermal Synthesis and Crystal Structures of Novel Aluminum Phosphates with in Situ Generated Templates

Shanshan Man, Zenglong Wang, Boya Zhao, Lei Liu* and Jinxiang Dong.

Protic ionic liquids (PILs) are subgroup of ionic liquids and easily formed by proton transfer from a Brønsted acid to a Brønsted base. Two new crystalline aluminophosphates, \([\text{C}_6\text{H}_{16}\text{N}_2][\text{Al}((\text{PO}_4)\text{HPO}_4)]\) (AlPO-PIL1) and \([\text{C}_6\text{H}_{16}\text{N}_2][\text{Al}(\text{OH}_2)\text{(PO}_4)_2]\) (AlPO-PIL2), have been successfully prepared for the first time from a protic ionic liquid, 3-dimethylaminopropylamine acetate. Their structures were determined from single-crystal X-ray diffraction data. It was found that HF in the reaction mixture is crucial to determine the selectivity of phase. In the absence of HF, AlPO-PIL1 with one-dimensional chain structure was synthesized by templating the protonated 3-dimethylaminopropylamine cation of the PIL. Upon addition of HF to the initial reaction mixture, AlPO-PIL2 was obtained by templating the protonated \(\text{N},\text{N}'\text{-dimethyl-1,3-propenediamine}\), which was in situ generated from the protonated 3-dimethylaminopropylamine through migration of methyl groups during the crystallization. AlPO-PIL2 has a novel layered structure with 3-connected 4.8.8 2-dimensional network which has never been found in the previous reported layered aluminophosphates.

Introduction

Since the discovery of microporous aluminophosphates by Wilson and co-workers\(^1\) in 1982, many open-framework aluminophosphates with various architectures have been synthesized. Most of these materials were achieved in the presence of organic amines by using hydro/solvothermal method, and it was found that the solvents and organic amines are crucial to obtain the aluminophosphates with novel structures.\(^2-4\)

Ionothermal synthesis, using ionic liquids or eutectic mixtures as solvent and template, was firstly reported by Morris in 2004.\(^5\) Nowadays, this emerging synthetic approach has been shown a great potential to prepare crystalline solids with novel structures or improve the known phases for specific purposes.\(^6-14\)

Also, these synthetic procedures can be performed at ambient pressure, thus it could eliminate safety concerns associated with high solvent pressures and provide more conveniences to study the crystalline mechanism.\(^15-16\)

It is well known that the species and structure of ionic liquids are very rich and dynamic, but so far many of the work on ionothermal synthesis has concentrated predominantly on the use of the imidazole-based ionic liquids and deep eutectic mixtures.\(^5-7\) Many of these ionic liquids are structurally related to each other and often template the same frameworks. Protic ionic liquids (PILs) are a subset of ionic liquids and are formed through proton transfer from a Bronsted acid to a Bronsted base.\(^17-18\) Compared to imidazole-based ionic liquids, these ionic liquids are generally lower cost and can be easily prepared in high purity. Also, the cations of the PILs can be made up of primary, secondary and tertiary ammonium, and this will give us more possibilities of preparing novel metal phosphates by choosing a suitable ionic liquid as solvent and template.

More recently, using a protic ionic liquid as solvent and template, we have synthesized two zinc phosphates, both are known framework structures.\(^19\) But the efforts encourage us to further extend the possibility of application of PILs for the synthesis of other metal phosphates. Herein, another protic ionic liquid, 3-dimethylaminopropylamine acetate, was used to synthesize aluminophosphates for the first time. As a result, two novel crystalline aluminum phosphates, \(\text{[C}_6\text{H}_{16}\text{N}_2][\text{Al}((\text{PO}_4)\text{HPO}_4)\text{]}\) and \(\text{[C}_6\text{H}_{16}\text{N}_2][\text{Al}(\text{OH}_2)\text{(PO}_4)_2]\), have been successfully synthesized and their structures were determined from the single crystal diffraction data. The powder XRD, SEM, TG-DSC and CHN analysis were also used to characterize the two materials.

Experimental

Raw materials

Aluminum hydroxide \(\text{(Al(OH)}_3\), 99.5wt\%\), orthophosphoric acid \((\text{H}_3\text{PO}_4\), 85 wt\% in water), 3-dimethylaminopropylamine \(\text{(C}_6\text{H}_{16}\text{N}_2\), 99.5wt\%\), acetic acid \((\text{CH}_3\text{COOH}\), 99.5wt\%) and absolute alcohol \((\text{C}_2\text{H}_5\text{CH}_2\text{OH}\), 99.5wt\%) were purchased from Aladdin Reagent (China) Co., Ltd and used without further purification.

Synthesis

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The protic ionic liquid, 3-dimethylaminopropylamine acetate (designated as (HDMAPA)(Ac)), was prepared by neutralization of 3-dimethylaminopropylamine (DMAPA) with acetic acid as shown in Scheme S1. A flask was charged with DMAPA and placed in water bath, then an equimolar acetic acid was slowly added with stirring in N₂ atmosphere, (HDMAPA)(Ac) can be obtained after reaction for 24 hours. The purity of PIL was confirmed using ¹H and ¹³C nuclear magnetic resonance (NMR) (Figure S1 and S2), and its melting point is roughly 45°C which was measured by melting-point apparatus.

Aluminum phosphates were prepared with the following typical procedure: a Teflon-lined autoclave (15 mL) was charged with Al(OH)₃, (HDMAPA)(Ac) and H₂PO₄, and heated at 180°C for 3 days. The solid product was recovered by dissolving the reaction mixture in water and subsequent filtration, then washed thoroughly with absolute alcohol and dried at room temperature. Detailed synthesis conditions and reaction results are presented in Table S1. It was found that P/Al ratios in initial mixture have no obvious influence on the reaction results are presented in Table S1. It was found that P/Al ratios in initial mixture have no obvious influence on the resulting phases, A IPO-PIL1 could be obtained with P/Al ratio in the range of 2 to 7, but upon the addition of a small amount of HF, another phase was formed. The typical formulations in molar ratio for AlPO₅PIL1 and AlPO₅PIL2, which are used for single crystal structure determination, are 1Al(OH)₃:4H₂PO₄:10PIL and 1Al(OH)₃:1H₂PO₄:10PIL:0.5HF, respectively.

Characterization

Powder X-ray diffraction (XRD) patterns were collected on a RigakuMiniflex II X-ray diffractometer with Cu-Kα radiation (λ = 1.5418 Å) in the 2θ range of 20°C-80°C with a scan rate of 2°/min. Temperature measurement was accomplished using a thermocouple. The heating rate of 5°C/min. SEM images were obtained on a Hitachi, TM53000 scanning electron microscope. Thermogravimetric analysis (TGA) was recorded on a SETARAM Labsys Evo instrument in air atmosphere with a heating rate of 10°C/min. SEM images were obtained on an ElementarVario EL analyzer. X-ray diffraction data were collected on a Bruker SMART10000 CCD area detector system using graphite monochromated Mo-Kα (λ = 0.71073 Å). The experimental XR D patterns were compared with simulated patterns from single crystal X-ray structure data (Figure S3), proving the phase purity of the as-synthesized products. The difference in reflection intensities between the simulated and experimental patterns was due to the variation in preferred orientation of the powder sample. The results of elemental analysis (wt %) also confirmed the phase purity in each case (for AlPO₅PIL1: Caled. C, 16.69; N, 7.98; H, 5.19. Found: C, 16.28; N, 8.12; H, 4.87. For AlPO₅PIL2: Caled. C, 15.70; N, 7.33; H, 4.71. Found: C, 15.32; N, 7.12; H, 4.20). The SEM images (Figure S4) show the different crystal morphologies of AlPO₅PIL1 and AlPO₅PIL2, also indicating the purity of the as-synthesized samples.

For AlPO₅PIL1, its asymmetric unit (Figure 1a) contains 18 non-hydrogen atoms, of which 11 atoms belong to the aluminum phosphate chain and 7 atoms belong to the organic specie, diprotonated DMAPA. There are one crystallographically distinct Al and two P atoms in the asymmetric unit. The Al atom is tetrahedrally coordinated by four O atoms belonging to four different PO₄ tetrahedra, with Al-O bond lengths between 1.7284(18) Å and 1.7442(17) Å, and O-Al-O bond angles in the range of 105.92(9)°-112.51(9)°. PO₄ tetrahedra share two O atoms with adjacent AlO₅ tetrahedra and the other two O atoms exist in the form of terminal linkage, and the P-O distances vary from 1.5106(18) to 1.5479(17) Å and from 1.4755(18) to 1.5642(18) Å for the P1 and P2 phosphate groups, respectively. This dispersion is attributable to multiple-bond character and is often observed in the low dimensional aluminophosphates.

Structure Determination

The single crystals for AlPO₅PIL1 and AlPO₅PIL2 with a suitable size were selected, then sets of single crystal X-ray diffraction data were collected on a Bruker SMART10000 CCD area detector system using graphite monochromated Mo-Kα radiation(λ = 0.71073 Å). The crystal structures were solved by direct methods and refined by full-matrix least-squares with SHELXTL97 software package.[20] The aluminum and phosphorus atoms were determined directly, and then the carbon, nitrogen, and oxygen atoms were found in the difference Fourier map. All non-hydrogen atoms were refined with anisotropic thermal parameters and the hydrogen atoms were geometrically placed. A summary of the crystallographic data and structure details is presented in Table 1.

Results and discussion

1. Crystal structures

From the PIL (HDMAPA)(Ac), two aluminophosphates, [C₃H₁₆N₂][Al₂(OH)₃(PO₄)₂] (AlPO₅PIL1) and [C₃H₁₆N₂][Al₂(OH)₃(PO₄)₂] (AlPO₅PIL2), have been obtained in the absence and presence of HF in initial mixture, respectively. Their structures were determined from single-crystal X-ray diffraction data. The experimental XRD patterns for the two compounds are in good agreement with the simulated patterns from single crystal X-ray structure data (Figure S3), proving the phase purity of the as-synthesized products. The difference in reflection intensities between the simulated and experimental patterns was due to the variation in preferred orientation of the powder sample. The results of elemental analysis (wt %) also confirmed the phase purity in each case (for AlPO₅PIL1: Caled. C, 16.69; N, 7.98; H, 5.19. Found: C, 16.28; N, 8.12; H, 4.87. For AlPO₅PIL2: Caled. C, 15.70; N, 7.33; H, 4.71. Found: C, 15.32; N, 7.12; H, 4.20). The SEM images (Figure S4) show the different crystal morphologies of AlPO₅PIL1 and AlPO₅PIL2, also indicating the purity of the as-synthesized samples.

<Figure 1>

AlPO₅PIL1 has one-dimensional chain structure with 4-membered rings constructed from strictly alternating AlO₄ and PO₄/PO₄(OH) units, the inorganic chains [Al₂O₅H₂]²⁻ were separated by diprotonated DMAPA (Figure 2). The organic cations between the chains not only balance the negative charges of the macroionic chains, but also interact with the terminal oxygen atoms of PO₄ tetrahedral through N-H···O hydrogen bonds, with N···O distances in the range of 2.657 to 2.783 Å.

<Figure 2>

In ionothermal synthesis, fluoride has often been used as a mineralizer for crystallization of the desired aluminophosphate materials, which seems to be important in determining the phase selectivity of the reaction.[5] In addition, there is evidence that fluoride could result in the variation of the bulk ionic liquid during the crystallization process.[23] In the present study, on addition of HF to the reaction mixture, a novel layered aluminophosphate, [C₃H₁₆N₂][Al₂(OH)₃(PO₄)₂], was obtained. It is interesting to note that the organic species in AlPO₅PIL2 are the protonated N,N’-dimethyl-1,3-propanediamine (DMPDA) instead of the original ionic liquid, the protonated 3-dimethylaminopropylamine (DMAPA). It is believed that the DMPDA is in situ generated from the protonated DMAPA through intramolecular methyl migration during the crystallization. Intramolecular methyl migration is well known
in the organometallic reactions and in the rearrangements of the carbonium ions, intramolecular methyl migration in the protonated DMAPA and DMPDA were found to proceed by a high-energy inversion mechanism.\[24,25\]

The single-crystal structure analysis shows that AlPO-PIL2 involves a novel layer topology. Its asymmetric unit (Figure 1b) contains one crystallographically independent Al and P atoms. Each P atom is tetrahedrally coordinated by four oxygen atoms, three of them bridge to adjacent Al atoms with P-O bond lengths within 1.522(3) Å-1.536(2) Å, the fourth oxygen atom exists in the form of a terminal P-O linkage with P-O bond length being 1.494(3) Å, which is very similar to those in other layered aluminophosphates containing terminal P=O bonds.\[21,26\]

Each Al atom exists in the form of AlO\(_2\)(OH) tetrahedra, which shares three oxygen atoms with adjacent P atoms and leaves one vertex for the terminal hydroxyl groups. The Al-OH bond length is 1.657(2) Å, shorter than other Al-O bonds in this structure with the average value being 1.726 Å. There are some examples containing Al-OH groups in the previously reported AlPO\(_5\)PIL1, AlPO\(_5\)PIL2, and AlPO\(_5\)PIL3.\[27\] and AlPO\(_5\)PIL4.\[28,29\] However, the Al coordination in these compounds is more than four and the OH ligands are found to connect the adjacent Al atoms in the form of Al-(OH)-Al linkages.

**<Figure 3>**

The structure (Figure 3a) is made up of macroionionic layers of empirical formula \[\text{Al}_n(\text{PO}_4)_2(\text{OH})_2\]\(^2\) with diprotonated DMPDA cations between the interlayer. The organic cations located in the interlayer region not only balance the negative charges of the macroionionic layers, but also hold the anionic layers together through hydrogen-bonds in different ways. The diprotonated DMPDA cations interact with the terminal O atoms of PO\(_4\) and AlO\(_2\)(OH) units through N-H⋯O hydrogen bonds, respectively, with N⋯O distances in the range of 2.721 to 3.078 Å. Each P atom in the structure is connected with three Al atoms through oxygen bridges and vice versa. PO\(_4\) and AlO\(_2\)(OH) tetrahedra are linked in a strict alternation to form a single chain with corner-sharing Al\(_2\)P\(_2\) four-membered rings (Figure 3c). The connectivity between the chains via Al–O–P linkages leads to the anionic \[\text{Al}_n\text{P}_2\text{O}_4(\text{OH})_2\]\(^2\) layer with eight-membered rings, parallel to the bc plane (Figure 3b). In fact, this structure can be regarded as a 3-connected 4.8.8 2-dimensional network which could be found in 3-dimensional open-framework aluminophosphates and zeolites such as AlPO\(_4\)-C, AlPO\(_4\)-15, GIS, MER and PHI structures.\[30\] This is the first example for the layered aluminophosphate with 3-connected 4.8.8 2-dimensional network. As far as we know, only 4.6.12-, 4.6.8-, 4.6-, 4.8-, 4.20- and 4.12 nets were reported for the layered aluminophosphates with various stoichiometries.\[2,4\]

**2. Thermal analysis**

To investigate the thermal stability of the two materials, thermogravimetric analysis (TG-DSC) and powder XRD measurement were performed. For AlPO-PIL1, TG-DSC curves (Figure S5a) show an obvious weight loss of ca. 31 wt % in the region of 240-350°C, accompanied with a marked exothermic peak, resulting from the remove of organic species between chains with calculated value of 32 wt%. Above 350°C, there is a gradual weight loss with about 4.5 wt%, corresponding to the dehydroxylation from the P-OH. For AlPO-PIL2, TG-DSC curves (Figure S5b) show a major weight loss occurring around 310°C accompanied by a marked endothermic effect. The total weight loss of the compound between 240 and 600°C is about 28.6%, in accordance with the calculated value on the basis of the empirical formula (23.8% for the decomposition of the template, 4.7% for dehydroxylation of Al-OH). Powder XRD patterns of the two samples heated in air or N\(_2\) atmosphere at different temperatures (Figure S6 and S7) show that, their structures are retained on calcinations at 250°C, and become amorphous phase beyond 300°C.

**3. The effect of the crystallization time**

For ionothermal synthesis, generally the starting materials were almost completely dissolved in the liquid phase at crystallization temperatures, and the synthesis mechanism is a crystallization from solution rather than a solid-to-solid transformation.\[5\] To describe the crystallization process, powder XRD patterns (Figure S8) were recorded for the samples after different crystallization times. For AlPO-PIL1, the nucleation and crystallization rate of the crystal are very fast, the crystallinity can reach a high level after reaction for 6h. By contrast, the nucleation rate for AlPO-PIL2 seems to proceed in a slow manner, the crystal nucleation was gradually generated and began to grow after reaction for 12h. The reasons may attribute to the formation of the new template agents for AlPO-PIL2, the protonated DMPDA needs a period of time to be formed from the protonated DMAPA through intramolecular methyl migration at initial crystallization process.

**Conclusions**

In conclusion, it was the first time that two novel aluminophosphates, AlPO-PIL1 and AlPO-PIL2, were successfully synthesized from the protic ionic liquid. The former has a one-dimensional chain structure, and the latter has a novel layered structure with 3-connected 4.8.8 2-dimensional network which has never been found in the previous reported layered aluminophosphates. AlPO-PIL2 was obtained by templating the protonated N,N'-dimethyl-1,3-propanediamines, which was in situ generated from the protonated 3-dimethylaminopropylamine through migration of methyl groups upon the addition of HF to the initial reaction mixture. Protic ionic liquids are a subset of ionic liquids and can be easily prepared from prolific and available amine precursors. In our study, we proved the feasibility for the ionothermal synthesis of aluminophosphates from the protic ionic liquid, and this will give us the more opportunities of preparing novel crystalline materials by choosing a suitable ionic liquid as solvent and template.

**Acknowledgements**

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**Notes and references**
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†Electronic Supplementary Information (ESI) available: 1H-NMR and 13C-NMR spectra of (HDMAPA)(Ac), powder XRD patterns, SEM images and two CIF files for the two aluminophosphate materials. See DOI:10.1039/b000000x/

Table 1 Crystal data and structure refinement for AIPO-PIL1 and AIPO-PIL2

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Figure captions

**Figure 1.** Thermal ellipsoid plot (50% probability) of a section of the structure of AlPO-PIL1 (a) and AlPO-PIL2 (b), showing the atom labeling, the coordination about the independent Al and P atoms and the various organic templates.

**Figure 2.** The structure of the AlPO-PIL1, [C5H16N2][Al(PO4)(HPO4)], (a) projection along the a axis showing the chain and the deprotonated DMAPA between the chains; (b) a clear view of the chain structure built up from AlO4 and PO4 tetrahedra; (c) projection along the c axis showing the polyhedral connectivity. (PO4/P: pink, AlO4/Al: turquoise, O: red, C: grey, N: blue, H: white)

**Figure 3.** Projection of the structure of AlPO-PIL2, [C5H16N2][Al2(OH)2(PO4)2]: (a) view of the structure along b axis, showing the inorganic layers intercalated by the diprotonated DMPDA cations. (b) an individual layer with 4.8.8 nets viewed along the a axis, the O and H atoms are omitted for clarity. (c) the single chain with corner-sharing Al2P2 four-membered rings. (PO4/P: pink, AlO4/Al: turquoise, O: red, C: grey, N: blue, H: white)

![Figure 1](image-url)