



Aluminophosphates prepared using in situ generated tetramethylammonium cations as structure directing agents



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ABSTRACT

A series of aluminophosphates (AlPOs) with open architectures, namely $[dmdabco][Al_2(HPO_4)_4]$ (**1**, $dmdabco = N,N$ -dimethyl-1,4-diazabicyclo[2,2,2]octane), $[tmpip]_{0.5}[Al(HPO_4)_2]$ (**2**, $tmpip = N,N,N,N$ -tetramethylpiperazinium) and $[tmpip][Al_6(PO_4)_6(HPO_4)]$ (**3**) have been solvothermally synthesized and structurally characterized. The *in situ* generated templates ($dmdabco^{2+}$ and $tmpip^{2+}$) originated from the methylation reactions between methanol solvent and their corresponding aliphatic organic-amine parents: 1,4-diazabicyclo[2,2,2]octane (*dabco*) for **1**, 1-methylpiperazine for **2** and **3**. Such a characteristic *in situ* methylation is distinct from conventional Eschweiler–Clarke methylation with excessive formic acid and formaldehyde. Compounds **1** and **2** possess the same infinite inorganic chains, which are further linked by hydrogen bonds to form 3D supramolecular framework. Compound **3** is built from Al_6P_6 and Al_6P_8 building units, giving rise to an open architecture with three-dimensional channel system.

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1. Introduction

Crystalline materials with regular microporous structures have been extensively studied due to their diverse structural chemistry and potential applications in catalysis, absorption, ion-exchange and separation, etc [1–3]. Since the discovery of the aluminophosphate molecular sieves in 1982 by Wilson et al. [4], aluminophosphates (AlPOs) have become an important family of zeolite materials. To date, a large variety of novel composition of AlPOs with zero-dimensional (0D) cluster, one-dimensional (1D) chains or ladders, two-dimensional (2D) layers and three-dimensional (3D) architectures have been prepared and characterized [5–13]. They are traditionally synthesized by using hydrothermal or solvothermal synthetic methods with organic amines as the structure directing agents (SDAs). Recently, ionothermal synthesis in which ionic species (an ionic liquid or eutectic mixture) are used as both solvent and template, has been proven to be a promising technique in preparing porous materials with novel structures and special properties [14–16]. Notable examples include DNL-1(CLO framework type, 20-ring) [17], JIS-3 (18-ring) [18], SIZ-13 containing unusual Co–Cl bonds in framework [19], NIS-4 with non-

centrosymmetric architecture and helical channels [20], NTHU-9 with dual photogenerated features [21], and other SIZ-n type materials with interrupted frameworks [8,22]. In comparison with those protonated organic amines as SDAs commonly encountered in traditional hydrothermal or solvothermal systems, the organic cations of ionic liquids present in ionothermal reaction usually featured alkyl-substituted groups (e.g. alkyl imidazolium or tetraalkylammonium). Therefore, it would be highly expected to design new alternatives as SDAs for the synthesis of zeolitic and other porous materials. In this aspect, hydrothermal *in situ* alkylation transformations of readily available organic species may be a promising option. As expected, some crystalline porous solids have been successfully prepared by using *in situ* formed SDAs, including zinc phosphates/phosphites and gallium phosphates [23–25]. All these encourage us to further explore the possibility of *in situ* generated SDAs for making novel aluminium phosphates. Herein, three new organically templated AlPOs, $[dmdabco][Al_2(HPO_4)_4]$ (**1**), $[tmpip]_{0.5}[Al(HPO_4)_2]$ (**2**) and $[tmpip][Al_6(PO_4)_6(HPO_4)]$ (**3**), have been successfully obtained by using *in situ* template generation route. Notably, the organic *dmdabco* and *tmpip* molecules were generated by *in situ* methylation reactions of CH_3OH solvent and *dabco* and *pip* precursors respectively. Compound **1** and **2** are isostructural and exhibit infinite inorganic chain built from AlO_4 and HPO_4 tetrahedra; compound **3** features an rarely observed Al/P ratio of 6/7 and has a three-dimensional open-framework

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constructed from AlO_4 , AlO_5 , PO_4 and HPO_4 units.

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 data were obtained from sample powder pelletized with KBr on a MAGNA-560 (Nicolet) FT-IR spectrometer over a range $400\text{--}4000\text{ cm}^{-1}$. Powder X-ray diffraction (PXRD) data 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 $10\text{ }^\circ\text{C min}^{-1}$ from ambient temperature to $800\text{ }^\circ\text{C}$.

2.2. Synthesis

[*dmdabco*][$\text{Al}_2(\text{HPO}_4)_4$] (**1**) A mixture of $\text{Al}(\text{i-PrO})_3$ (0.1222 g, 0.6 mmol), H_3PO_4 (0.33 mL, 5 mmol), 1,4-diazabicyclo[2,2,2]octane (0.662 g, 3 mmol), methanol (3.0 mL, 75 mmol) and H_2O (2.0 mL, 111 mmol) was sealed in a Teflon-lined autoclave and heated at $145\text{ }^\circ\text{C}$ for 6 days. After cooling to room temperature, filtration and washing with distilled water, colorless crystals of **1** were obtained and dried in air (83.4% yield based on Al). Anal. Elemental analysis (%) calcd for $\text{C}_8\text{H}_{22}\text{N}_2\text{O}_{16}\text{P}_4\text{Al}_2$: C, 16.56; H, 3.82; N, 4.82. Found: C, 16.32; H, 3.36; N, 4.43. IR (KBr pellets, cm^{-1}): 3436(m), 3052(w), 2954(w), 2924(w), 1625(s), 1556(s), 1431(s), 1334(s), 1132(m), 1045(m), 840(w), 786(m), 712(s), 650(m), 610(m), 515(w), 456(w).

[*tmpip*] $_{0.5}$ [$\text{Al}(\text{HPO}_4)_2$] (**2**) A mixture of $\text{Al}(\text{OH})_3$ (0.0923 g, 1.2 mmol), H_3PO_3 (0.2976 g, 3.6 mmol), 1-methylpiperazine (0.22 mL, 2 mmol) and methanol (4.5 mL, 113 mmol) was sealed in a Teflon-lined autoclave and heated at $170\text{ }^\circ\text{C}$ for 6 days. After cooling to room temperature, filtration and washing with distilled water, colorless crystals of **2** were obtained and dried in air (66.8% yield based on Al). Anal. Elemental analysis (%) calcd for $\text{C}_4\text{H}_{12}\text{NO}_8\text{P}_2\text{Al}$: C, 16.51; H, 4.12; N, 4.81. Found: C, 16.26; H, 3.62; N, 4.32. IR (KBr pellets, cm^{-1}): 3423(m), 3056(w), 3008(w), 2920(m), 2852(m), 1642(m), 1480(m), 1378(m), 1334(s), 1154(m), 1052(s), 916(m), 712(w), 651(m), 617(m), 461(m).

[*tmpip*][$\text{Al}_6(\text{PO}_4)_6(\text{HPO}_4)_2 \cdot (\text{H}_2\text{O})$] (**3**) A mixture of $\text{Al}(\text{OH})_3$ (0.0796 g, 1 mmol), H_3PO_4 (0.33 mL, 5 mmol), 1-methylpiperazine (0.27 mL, 2.5 mmol), methanol (3.0 mL, 75 mmol) and H_2O (2.0 mL, 111 mmol) was sealed in a Teflon-lined autoclave and heated at $175\text{ }^\circ\text{C}$ for 6 days. After cooling to room temperature, filtration and washing with distilled water, colorless crystals of **3** were obtained and dried in air (78.2% yield based on Al). Anal. Elemental analysis (%) calcd for $\text{C}_8\text{H}_{23}\text{N}_2\text{O}_{29}\text{P}_7\text{Al}_6$: C, 9.71; H, 2.34; N, 2.83. Found: C, 9.38; H, 2.18; N, 2.26. IR (KBr pellets, cm^{-1}): 3429(m), 3054(w), 2953(w), 2872(w), 1636(s), 1554(s), 1431(s), 1331(s), 1130(m), 1045(m), 839(w), 779(m), 711(s), 650(m), 616(m), 514(w), 454(w).

The X-ray powder diffraction profiles of compounds **1–3** are in agreement 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

Single-crystal X-ray diffraction data were collected on a Rigaku SCX-mini diffractometer at 293(2) K with Mo- $K\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) 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]. The aluminum and phosphorus atoms were first located, whereas the carbon, nitrogen and oxygen atoms were found in the successive Fourier difference maps. The O(7) and O(8) atoms in **2** are found to be disordered over two positions with an equal site-occupation factor (SOF), and the SOF values of 0.7 and 0.3 are assigned to the O1W and O2W in **3** respectively. All hydrogen atoms associated with the terminal P–O groups and the organic template cations were placed geometrically and refined using a riding model. All of the non-hydrogen atoms were refined anisotropically. Detailed crystallographic data are summarized in Table 1. CCDC 1443166 (**1**), 1443167 (**2**) and 1443168 (**3**) contain the supplementary crystallographic data for this paper.

3. Results and discussion

3.1. Syntheses

Hydro(solvo)thermal synthesis has been well explored in the synthesis of AlPOs. Among the various factors to affect the structures of AlPOs, organic SDAs undoubtedly played important role in tuning targeted architecture owing to their diverse species, polarity, size, charge and shape, etc. However, the commercially available organic amine is limited and the synthesis of complicated organic amine is time-consuming and high-cost. It is energetic to enlarge the scope of organic SDAs with readily availability from synthetic aspect. The *in situ* modulation of existing organic amines may be a promising avenue to obtain new SDAs. Recent studies have testified that *in situ* ligand reactions occasionally occur in hydro(solvo)thermal synthesis [23–25,28]. Many novel coordination complexes driven by *in situ* synthesized ligands has also been reported [29–31]. There is of course no reason why this *in situ* strategy cannot be utilized to generate new organically templated AlPOs. Herein, two familiar cyclic aliphatic amines are selected as precursors to investigate the *in situ*-template-generation of AlPOs. As expected, 1,4-diazabicyclo[2,2,2]octane (*dabco*) and 1-methylpiperazine are *in situ* transformed into structure-related N,N-dimethyl-1,4-diazabicyclo[2,2,2]octane (in **1**) and N,N,N,N-tetramethylpiperazinium (in **2** and **3**). Undoubtedly, solvothermal *in situ* methylation occurred between methanol and corresponding organic parents (Scheme 1). To our knowledge, *in situ* alkylation of amine has been previously observed in the fabrication of AlPO-CJ8 [32], in which N,N'-diisopropylethylenediamine template was formed by the dehydration reaction between isopropylamine and the solvent ethylene glycol. The mechanism for alkylation in this work is distinct from that found in AlPO-CJ8. Although compounds **2** and **3** have the same SDAs, their resultant structures exhibit obvious diversities owing to the different initial stoichiometric ratio of reactants and solvent used. Compared with traditional Eschweiler-Clarke methylation of the primary or secondary amine with excess formic acid and formaldehyde [33], the simplicity and environmental friendliness of the *in situ* direct methylation transformation is noteworthy.

3.2. Structural description

Single-crystal X-ray diffraction analysis reveals that both compounds **1** and **2** crystallize in the triclinic *P*-1 space group, and present similar one-dimensional chain-like structure. As shown in Fig. 2a, the asymmetric unit of **1** contains two Al^{3+} ions, four HPO_4^{2-} groups and one [*dmdabco*] $^{2+}$ cation, while the asymmetric unit of **2** consists of one Al^{3+} ion, two HPO_4^{2-} groups and half of one [*tmpip*] $^{2+}$ cation (Fig. 2b). In both structures, the Al^{3+} ions are tetra-coordinated by O atoms from phosphate, forming typical

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