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

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

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, $[\text{C}_5\text{H}_{16}\text{N}_2][\text{Al}(\text{PO}_4)(\text{HPO}_4)]$ (AIPO-PIL1) and $[\text{C}_5\text{H}_{16}\text{N}_2][\text{Al}_2(\text{OH})_2(\text{PO}_4)_2]$ (AIPO-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, AIPO-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, AIPO-PIL2 was obtained by templating the protonated N,N'-dimethyl-1,3-propanediamine, which was in situ generated from the protonated 3-dimethylaminopropylamine through migration of methyl groups during the crystallization. AIPO-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]

Ionochemical 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 much 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 Brønsted acid to a Brønsted 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 the 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 these 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, $[\text{C}_5\text{H}_{16}\text{N}_2][\text{Al}(\text{PO}_4)(\text{HPO}_4)]$ and $[\text{C}_5\text{H}_{16}\text{N}_2][\text{Al}_2(\text{OH})_2(\text{PO}_4)_2]$, 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 ($\text{Al}(\text{OH})_3$, 99.5wt%), orthophosphoric acid (H_3PO_4 , 85 wt% in water), 3-dimethylaminopropylamine ($\text{C}_5\text{H}_{14}\text{N}_2$, 99.5wt%), acetic acid (CH_3COOH , 99.5wt%) and absolute alcohol ($\text{CH}_3\text{CH}_2\text{OH}$, 99.5wt%) were purchased from Aladdin Reagent (China) Co., Ltd and used without further purification.

Synthesis

The protic ionic liquid, 3-dimethylaminopropylamine acetate (designed 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.

Aluminium phosphates were prepared with the following typical procedure: a Teflon-lined autoclave (15 mL) was charged with Al(OH)₃, (HDMAPA)(Ac) and H₃PO₄, 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 resulting phases, AIPO-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 AIPO-PIL1 and AIPO-PIL2, which are used for single crystal structure determination, are 1Al(OH)₃:4H₃PO₄:10PIL and 1Al(OH)₃:1H₃PO₄:10PIL:0.5HF, respectively.

Characterization

Powder X-ray diffraction (XRD) patterns were collected on a Rigaku Miniflex II X-ray diffractometer with Cu-Kα radiation (λ=1.5418 Å) in the 2θ range of 3-50° and with a scan rate of 2°/min. ¹H and ¹³C NMR spectra for PIL in CDCl₃ were recorded using a DRX300 NMR spectrometer. CHN element analysis was carried out on an Elementar Vario EL analyzer. Thermogravimetric analysis (TGA) was recorded on SETARAM Labsys Evo instrument in air atmosphere with a heating rate of 5°C/min. SEM images were obtained on a Hitachi, TM-3000 scanning electron microscope.

Structure Determination

The single crystals for AIPO-PIL1 and AIPO-PIL2 with a suitable size were selected, then sets of single crystal X-ray diffraction data were collected on a Bruker SMART-1000 CCD area detector system using graphite-monochromated Mo-Kα radiation (λ=0.71073 Å). The crystal structures were solved by using 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.

<Table 1>

Results and discussion

1. Crystal structures

From the PIL (HDMAPA)(Ac), two aluminophosphates, [C₅H₁₆N₂][Al(PO₄)(HPO₄)] (AIPO-PIL1) and

[C₅H₁₆N₂][Al₂(OH)₂(PO₄)₂] (AIPO-PIL2), 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 AIPO-PIL1: Calcd. C, 18.63; N, 8.69; H, 5.28. Found: C, 18.29; N, 8.39; H, 5.12; for AIPO-PIL2: Calcd. 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 AIPO-PIL1 and AIPO-PIL2, also indicating the purity of the as-synthesized samples.

For AIPO-PIL1, 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) 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 AlO₄ tetrahedra and the other two O atoms exist in the form of a 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.^[21-22]

<Figure 1>

AIPO-PIL1 has one-dimensional chain structure with 4-membered rings constructed from strictly alternating AlO₄ and PO₄/PO₃(OH) units, the inorganic chains [AlP₂O₈H]²⁻ were separated by diprotonated DMAPA (Figure 2). The organic cations between the chains not only balance the negative charges of the macroanionic 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, [C₅H₁₆N₂][Al₂(OH)₂(PO₄)₂], was obtained. It is interesting to note that the organic species in AIPO-PIL2 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 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 AIPO-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 AlO₃(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 2-D layered aluminophosphates, such as [C₄H₁₂N₂][Al₂P₂O₈(OH)₂]^[27] and (C₃N₂H₁₂)[AlPO₄(OH)]₂·H₂O^[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 macroanionic layers of empirical formula [Al₂(PO₄)₂(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 macroanionic 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 PO₄ and AlO₃(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. PO₄ and AlO₃(OH) tetrahedra are linked in a strict alternation to form a single chain with corner-sharing Al₂P₂ four-membered rings (Figure 3c). The connectivity between the chains via Al-O-P linkages leads to the anionic [Al₂P₂O₈(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 AIPO₄-C, AIPO₄-15, 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 AIPO-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 AIPO-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 N₂ 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 ionic liquid 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 AIPO-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 AIPO-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 AIPO-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, AIPO-PIL1 and AIPO-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. AIPO-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

This work was financially supported by the National Natural Science Foundation (21276174, 21322608), Shanxi Province Science Foundation for Youths (2014021005), Program for New Century Excellent Talents in University (NCET-11-1038), and A Foundation for the Author of National Excellent Doctoral Dissertation of PR China (No. 201350).

Notes and references

Research Institute of Special Chemicals, Taiyuan University of Technology, Taiyuan 030024, Shanxi, P. R. China. Fax: +86-351-6111178; Tel: +86-351-6010550-5; E-mail: liulei@tyut.edu.cn.

†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/

1. S. T. Wilson, B. M. Lok, C. A. Messian, T. R. Cannan and E. M. Flanigen, *J. Am. Chem. Soc.*, 1982, **104**, 1146.
2. J. H. Yu and R. R. Xu, *Acc. Chem. Res.*, 2003, **36**, 481.
3. J. H. Yu and R. R. Xu, *Chem. Soc. Rev.*, 2006, **35**, 593.
4. R. Murugavel, A. Choudhury, M. G. Walawalkar, R. Pothiraja and C. N. R. Rao, *Chem. Rev.*, 2008, **108**, 3549.
5. E. R. Cooper, C. D. Andrew, P. S. Wheatley, P. B. Webb, P. Wormald and R. E. Morris, *Nature.*, 2004, **430**, 1012.
6. E. R. Parnham and R. E. Morris, *Acc. Chem. Res.*, 2007, **10**, 1005.
7. R. E. Morris, *Chem. Commun.*, 2009, 2990.
8. E. R. Parnham and R. E. Morris, *J. Am. Chem. Soc.*, 2006, **128**, 2204.
9. H. Z. Xing, J. Y. Li, W. F. Yan, P. Chen, Z. Jin, J. H. Yu, S. Dai and R. R. Xu, *Chem. Mater.*, 2008, **20**, 4179.
10. H. Z. Xing, W. T. Yang, T. Su, Y. Li, J. Xu, T. Nakano, J. H. Yu and R. R. Xu, *Angew. Chem. Int. Ed.*, 2010, **49**, 2328.
11. T. Su, H. Z. Xing, J. Xu, J. H. Yu and R. R. Xu, *Inorg. Chem.*, 2011, **50**, 1073.
12. L. Liu, S. Ferdov, C. Coelho, K. Kong, L. Mafra, J. P. Li, J. X. Dong, U. Kolitsch, R. S. Ferreira, E. Tillmanns, J. Rocha and Z. Lin, *Inorg. Chem.*, 2009, **48**, 4598.
13. L. Liu, Z. F. Chen, H. B. Wei, Y. Li, Y. C. Fu, H. Xu, J. P. Li, M. Z. S. Alexandra and J. X. Dong, *Inorg. Chem.*, 2010, **49**, 8270.
14. Y. Wei, Z. J. Tian, H. Gies, R. S. Xu, H. J. Ma, Pei, R. Y.; W. P. Zhang, Y. P. Xu, L. Wang, K. D. Li, B. C. Wang, G. D. Wen and L. W. Lin, *Angew. Chem. Int. Ed.*, 2010, **49**, 5367.
15. H. J. Ma, Z. J. Tian, R. S. Xu, B. C. Wang, Y. Wei, L. Wang, Y. P. Xu, W. P. Zhang and L. W. Lin, *J. Am. Chem. Soc.*, 2008, **130**, 8120.
16. D. S. Wragg, P. J. Byrne, G. Giriat, B. L. Ouay, R. Gyepes, A. Harrison, A. G. Whittaker and R. E. Morris, *J. Phys. Chem. C*, 2009, **113**, 20553.
17. T. L. Greaves and C. J. Drummond, *Chem. Rev.*, 2008, **108**, 206.
18. B. Nuthakki, T. L. Greaves, I. Krodkiewska, A. Weerawardena, M. I. Bugar, R. J. Mulder and C. J. Drummond, *Aust. J. Chem.*, 2007, **60**, 21.
19. S. Y. Li, W. Wang, L. Liu and J. X. Dong, *CrystEngComm.*, 2013, **15**, 6424.
20. G. M. Sheldrick, SHELXS-97, Program for crystal structure solution; University of Göttingen: Göttingen, 1997.
21. S. Oliver, A. Kuperman, A. Lough and G. A. Ozin, *Inorg. Chem.*, 1996, **35**, 6373.
22. S. Oliver, A. Kuperman, A. Lough and G. A. Ozin, *Chem. Mater.*, 1996, **8**, 2391.
23. E. R. Parnham and R. E. Morris, *Chem. Mater.*, 2006, **18**, 4882.
24. X. Zhang, S. J. Yao and Y. L. Guo, *J. Mass Spectrom.*, 2008, **270**, 31.
25. B. P. Callahan and R. Wolfenden, *J. Am. Chem. Soc.*, 2003, **125**, 310.
26. S. Oliver, A. Kuperman, A. Lough and G. A. Ozin, *Chem. Commun.*, 1996, **35**, 1761.
27. K. X. Wang, J. H. Yu, P. Miao, Y. Song, J. Y. Li, Z. Shi and R. R. Xu, *J. Mater. Chem.*, 2001, **11**, 1898.
28. A. Tuel, V. Gramlich, C. Baerlocher, *Microporous Mesoporous Mater.*, 2000, **41**, 217.
29. H. M. Yuan, J. S. Chen, Z. Shi, W. Chen, Y. Wang, P. Zhang, J. H. Yu and R. R. Xu, *J. Chem. Soc. Dalton Trans.*, 2000, 1981.
30. C. Baerlocher, L. B. McCusker and D. H. Olson, *Atlas of Zeolite Framework Types*; Elsevier: Amsterdam, 2007.

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

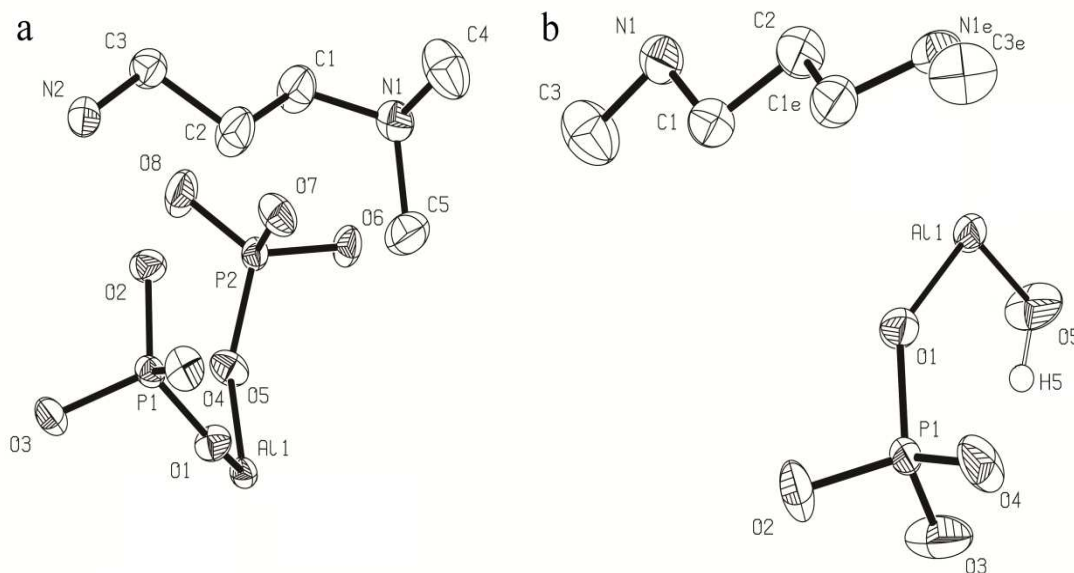
Compounds	AIPO-PIL1	AIPO-PIL2
Chemical formula	[C ₅ H ₁₆ N ₂][Al(PO ₄)(HPO ₄)]	[C ₅ H ₁₆ N ₂][Al ₂ (OH) ₂ PO ₄] ₂
Formula weight	322.13	382.11
Temperature (K)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2(1)/ <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	8.8966(8)	15.5986(13)
<i>b</i> (Å)	17.6602(16)	9.6662(7)
<i>c</i> (Å)	8.3738(9)	10.0576(9)
β (°)	102.590(2)	100.048(2)
Volume (Å ³)	1284.0(2)	1493.2 (2)
<i>Z</i>	4	4
ρ_{calc} (mg. m ⁻³)	1.666	1.700
μ (mm ⁻¹)	0.441	0.458
<i>F</i> (000)	672	792
Crystal size (mm)	0.45×0.23×0.20	0.50×0.38×0.37
θ range (°)	2.75 – 25.02	2.65 – 25.02
Index ranges	-10 ≤ <i>h</i> ≤ 8, -21 ≤ <i>k</i> ≤ 16, -9 ≤ <i>l</i> ≤ 9	-18 ≤ <i>h</i> ≤ 18, -11 ≤ <i>k</i> ≤ 11, -11 ≤ <i>l</i> ≤ 7
Reflections collected	6321	3621
Independent reflections	2258 [<i>R</i> _{int} = 0.0310]	1301 [<i>R</i> _{int} = 0.0464]
Absorption correction	'multi-scan'	'multi-scan'
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Goodness-of-fit on <i>F</i> ²	1.112	1.066
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0327, <i>wR</i> ₂ = 0.0819	<i>R</i> ₁ = 0.0409, <i>wR</i> ₂ = 0.1164
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0423, <i>wR</i> ₂ = 0.0890	<i>R</i> ₁ = 0.0457, <i>wR</i> ₂ = 0.1208
Largest diff. peak and hole [e·Å ⁻³]	0.257 and -0.338	0.493 and -0.636
CCDC number	974277	974278

Figure captions

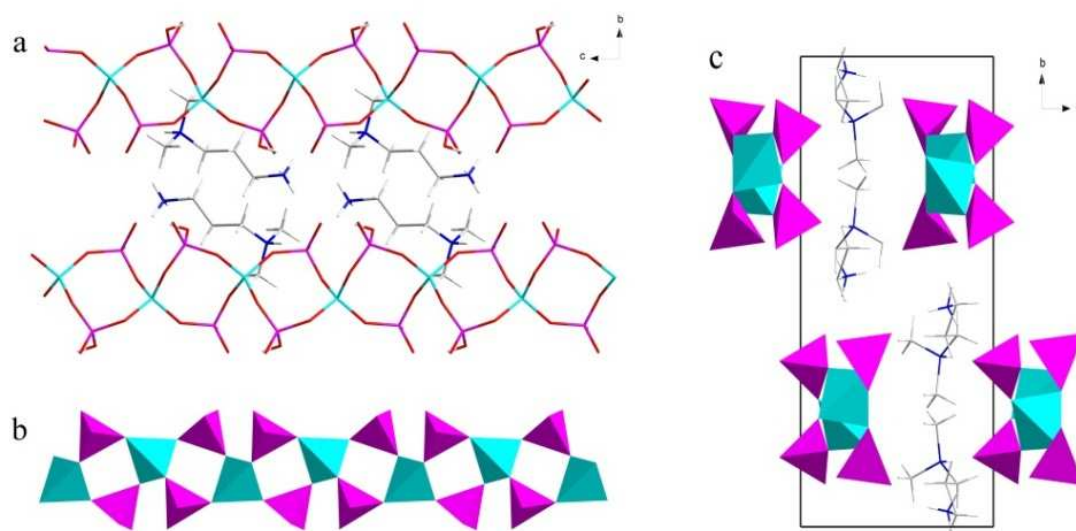
Figure 1. Thermal ellipsoid plot (50% probability) of a section of the structure of AIPO-PIL1 (a) and AIPO-PIL2 (b), showing the atom labeling, the coordination about the independent Al and P atoms and the various organic templates

Figure 2. The structure of the AIPO-PIL1, $[C_5H_{16}N_2][Al(PO_4)(HPO_4)]$. (a) projection along the a axis showing the chain and the deprotonatedDMAPA 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)

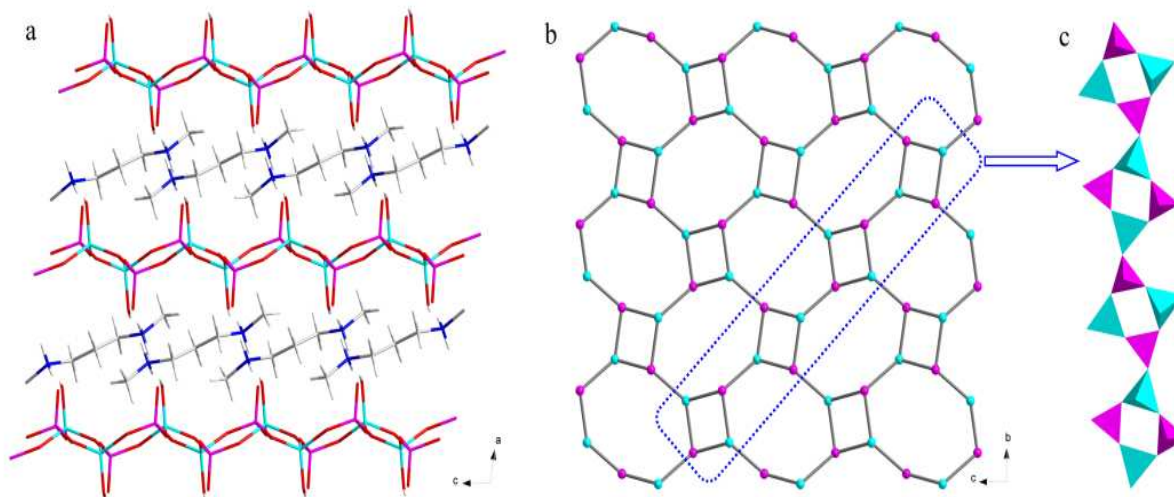
Figure 3. Projection of the structure of AIPO-PIL2, $[C_5H_{16}N_2][Al_2(OH)_2(PO_4)_2]$: (a) view of the structure along b axis, showing the inorganic layers intercalated by the diprotonated DMPDA cations. (b) an individual layer with 4.8.8 nets viewed along the a axis, the O and H atoms are omitted 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>



<Figure 2>



<Figure 3>