The ionothermal synthesis of SIZ-6—a layered aluminophosphate†

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A new layered open framework aluminophosphate has been prepared by ionothermal synthesis using an ionic liquid as the reaction solvent and structure-directing agent.

Hydrothermal[1] and solvothermal[2] synthesis has led to a rich array of organically structure-directed[3] aluminophosphate (AlPO) materials, from one-dimensional chains[4,5] to two-dimensional layers[6,7] and three-dimensional frameworks with molecular sieving properties.[8] Recently we have reported the first examples of ionothermal synthesis as a new route to making AlPOs,[9] which involves using an ionic liquid as both the solvent and organic structure-directing agent (SDA). This approach has many advantages over traditional hydrothermal and solvothermal synthesis, including the fact that the solvent is also the SDA, reducing any competition between the two, and that the low vapour pressure of ionic liquids means that the preparations can take place at high temperature whilst pressure is maintained at ambient levels.

The different chemistry of the ionothermal solvent system produces conditions under which novel types of structures may be accessible. For example, the first material reported using the ionothermal method, SIZ-1,[9] has an unusual interrupted structure with hanging P–O bonds (*i.e.* where not all oxygen atoms are part of Al–O–P linkages) and contains aluminium in both 4- and 5-coordinations. Other SIZ-*n* type materials have either known zeolite frameworks or are new materials. On the limited evidence so far it seems that unusual structures are particularly prevalent in conditions where water is present in only small amounts.[9]

Here we report the synthesis of SIZ-6, $Al_4(OH)(PO_4)_3(HPO_4)(H_2PO_4)(H_2O)_{0.2}\cdot C_6H_{11}N_2$, a very unusual layered material where the ionic liquid, 1-ethyl-3-methylimidazolium bromide (mp 83 °C) acted as both solvent and SDA. A PTFE-lined autoclave (volume 23 ml) was charged with $Al[OCH(CH_3)_2]_3$ (0.100 g, 0.49 mmol, Aldrich) and H_3PO_4 (0.173 g, 1.50 mmol, 85 wt% in H_2O, Aldrich). This was then heated to 50 °C on a hotplate for 2 h to remove excess water and any propan-2-ol formed during the reaction. The 1-ethyl-3-methylimidazolium bromide (4.25 g, 22.23 mmol) was added and the reaction heated at 200 °C for four days. The product (yield 35–50% from different preparations), is recovered as a white crystalline solid.

The crystal size (max. 100 × 20 × 20 μm) proved too small for single crystal data collection on a conventional laboratory diffractometer, so data was collected on Station 9.8 at the Synchrotron Radiation Source (SRS), Daresbury Laboratories, Cheshire, UK using a wavelength of 0.6933 Å.‡ Details of atomic coordinates, bond distances and angles, and refinement details can be found in the supplementary material.

The asymmetric unit of SIZ-6 consists of 7 independent phosphorus and 5 aluminium atoms (Fig. 1). All the phosphorus atoms show the expected tetrahedral coordination by oxygen, while 3 aluminium atoms are 4-coordinated in a regular tetrahedron by oxygen and one in a regular octahedron. The remaining aluminium atom (Al2, Fig. 1) is predominantly five coordinate, but the single crystal X-ray refinement revealed a Fourier peak that refined successfully as a partially occupied oxygen atom (occupancy factor 0.2), indicating that in the majority (∼80%) of the asymmetric units Al2 is 5-coordinate but in the remainder it is 6-coordinate. The extra oxygen atom is most likely part of a water molecule remaining from the phosphoric acid source. The ^{27}Al MAS NMR shows the octahedral coordination (resonance at −23.6 ppm) and the tetrahedral coordination (resonance at 38.9 ppm). In addition there is a resonance at 18.9 ppm that can be ascribed to the 5-coordinate aluminium.[10] The bond distances and angles around the regular 4- and

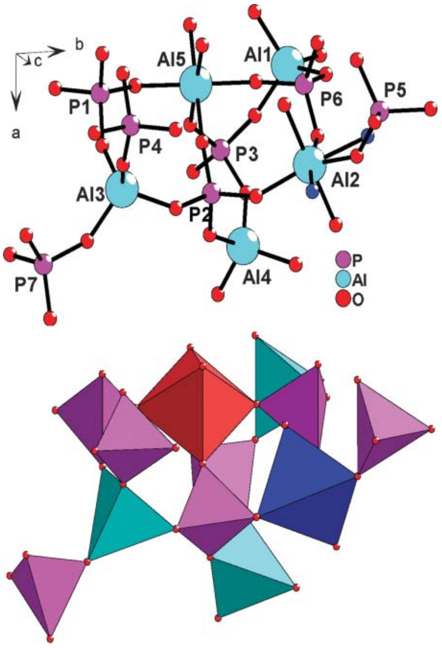

Fig. 1 (Top) The asymmetric unit of SIZ-6 showing the five independent aluminium and seven independent phosphorus atoms. Symmetry equivalent oxygen atoms have been included to complete the coordination spheres and the minor atoms of the disorder present around Al2 are shown in blue. (Bottom) Polyhedral representation of the asymmetric unit showing three tetrahedral (cyan), one octahedral (red) and one pentacoordinate (blue) aluminium (excluding minor component).

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† Electronic supplementary information (ESI) available: NMR spectra and TGA for SIZ-6. See DOI: 10.1039/b513458g

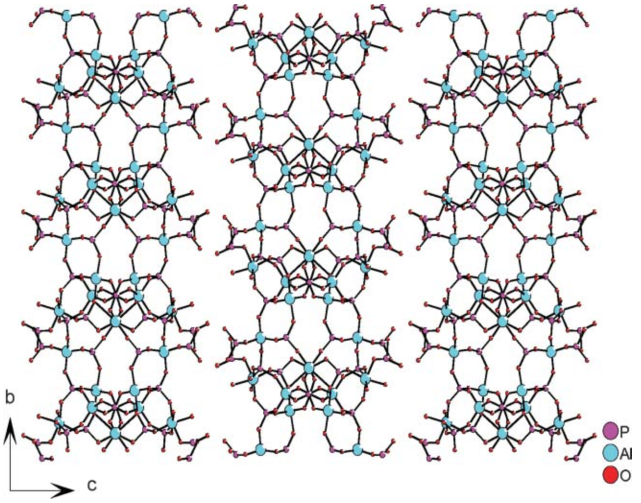

Fig. 2 The layered structure of SIZ-6 illustrating the thick aluminophosphate layers and the HPO_4 dimers that hold the layers together though hydrogen bonding.

6-coordinate aluminium atoms are as expected for such a structure (see supplementary material‡), but the coordination around the remaining aluminium is less regular. The disorder (*i.e.* the presence or absence of the extra water molecule) around Al2 leads to large anisotropic displacement parameters for two of the oxygens that form part of the coordination sphere of P5. We were able to refine a split atom on one of these two oxygens (Fig. 1) but this was not possible for the other. That disorder affects the coordination sphere of P5 more than any other is not surprising given that P5 has two hanging P–O bonds while the two other P–O bonds form part of Al–O–P units, and this unit is therefore not held as tightly as the others near to Al5. The ^{31}P MAS NMR spectrum of SIZ-6 shows at least four resolved sites in a broad envelope between −6.6 and −34.4 ppm.

The overall structure of SIZ-6 is shown in Fig. 2, and comprises 13.5 Å thick anionic aluminophosphate layers of chemical composition $Al_4(OH)(PO_4)_3(HPO_4)(H_2PO_4)^-$ (the distance is measured from the centres of the oxygens forming the surfaces of the layers). The layers themselves consist of rings containing 4, 6 and 8 nodes (aluminium or phosphorus atoms). The 8-ring windows shown in Fig. 3 are large enough to make the layers potentially porous to small molecules. The layers are held together *via* some relatively strong hydrogen bonding. This occurs because two H_2PO_4 groups, one each from two adjacent layers, form dimeric units with O–O distances across the hydrogen bond of 2.441 Å. In addition, the negative charge on the layers is compensated for by one 1-ethyl-3-methylimidazolium cation, which occupies the interlayer space. Unfortunately, while it is possible to find parts of these cations crystallographically they are severely disordered and we were unable to model all the electron density in the interlayer region satisfactorily. However, the program Squeeze contained within the PLATON[11] package of crystallographic tools indicates that the total number of electrons per $Al_4(OH)(PO_4)_3(HPO_4)(H_2PO_4)$ in the interlayer region is approximately 58.8, which compares extremely well with the 60 electrons required by one 1-ethyl-3-methylimidazolium cation. The ^{13}C MAS NMR shows five distinct resonances in the expected regions, confirming that the SDA remains intact.

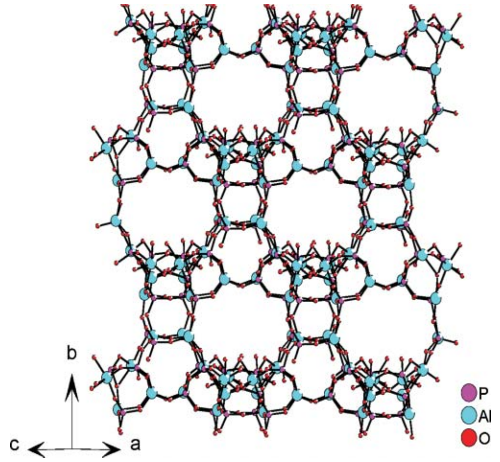

Fig. 3 A view of a single layer showing the 8-ring windows.

Thermogravimetric analysis shows an initial mass loss of about 3.6% between 200 and 330 °C and a second mass loss between 350 and 450 °C of 16.3%. These values agree reasonably well with the values expected for the loss of 1 mole of 1-ethyl-3-methylimidazolium per $Al_4(OH)(PO_4)_3(HPO_4)(H_2PO_4)$ formula unit (15.9%) plus water lost from condensation of the hanging P–OH bonds and the small amount of water bound to the aluminium in the sample (~3.0%). Unfortunately, the material breaks down after the condensation of the phosphate groups takes place.

The structure of SIZ-6 is noteworthy in that it is rare to have such a thick layer in aluminophosphate systems. It is also interesting that there are 4-, 5- and 6-coordinate aluminium atoms in the same material. The synthesis mixture here is relatively dry, the only water coming from that present in the phosphoric acid. Under such conditions ionothermal synthesis of aluminophosphates seems to favour the formation of interrupted structures. Addition of water to the system tends to promote the formation of Al–O–P bonds and produce zeolitic frameworks.[9] Further work to more fully understand the properties of ionothermal synthesis, and particularly the role of small amounts of water present, is currently underway.

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Notes and references

‡ *Crystal data* for SIZ-6: $Al_4(OH)(PO_4)_3(HPO_4)(H_2PO_4)(H_2O)_{0.2}\cdot C_6H_{11}N_2$, orthorhombic, space group *Cmca* (no. 64), a = 17.5472(14), b = 18.0516(15), c = 35.5602(29) Å, $\alpha = \beta = \gamma = 90°$, U = 11263.87(16) Å^3, T = 150 K, D_c = 1.65 g cm^{-3}, Z = 16, μ = 0.502 mm^{-1}. Inspection of the data indicated that there was essentially no scattering beyond ~41° 2θ and the data were truncated at this value, 3077 reflections measured, 2525 observed (R_{int} = 0.0815). Final wR($F^2_{\text{all data}}$) was 0.1424 and R(F$_{\text{observed data}}$) was 0.057. CCDC 285931. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b513458g

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