Synthesis and structure of a three-dimensional open-framework aluminophosphate $[NH_2(CH_2)_3NH_3]^+[HAl_3P_3O_{14}]^-\cdot H_2O$, containing AlO_5 and AlO_6 polyhedra

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The novel, open-framework aluminophosphate, $[NH_2(CH_2)_3NH_3]^+[HAl_3P_3O_{14}]^-\cdot H_2O$, designated SBM-6, contains five- and six-coordinate aluminum but, unlike other AlPOs, no AlO_4 tetrahedra.

Nanoporous materials have attracted widespread attention because of their applications in catalysis, gas separation, *etc.* After the seminal work of Flanigen and co-workers on the synthesis of nanoporous aluminophosphates (AlPOs),[1] a flurry of research activity on related materials resulted in the discovery of gallophosphates (GaPOs),[2,3] and other new types of frameworks. Recently, synthetic routes involving transition-metal coordination complexes as structure-directing agents have been shown to be promising.[4–6] The main advantages lie in the wide variety of shapes (including chiral ones) and charges offered by these complexes, as well as the possibility of introducing a transition-metal directly into the pores. Indeed, even though the question of the location of the metal in such materials after calcination remains open, this approach could facilitate much better control and enrichment of the nanoporous compound in the transition-metal ion compared to materials obtained by cation exchange. We report here the synthesis, in the presence of a diamine transition-metal complex, and the X-ray single-crystal structure of a new, open-framework aluminophosphate designated SBM-6, $[H_2N(CH_2)_3NH_3]^+$-$[HAl_3P_3O_{14}]^-\cdot H_2O$.

The compound SBM-6 was synthesized under hydrothermal conditions. The starting material consisted of phosphoric acid (85 mass%, 1.153 g) with water (8 ml) and hydrated aluminium oxide (0.92 g, 55 mass% Al_2O_3, 45 mass% H_2O). The mixture was stirred until homogeneous, followed by the addition of the tris nickel complex of 1,3-diaminopropane[7] (prepared by rotary evaporation of the filtrate of a mixture of $[Ni(pn)_3]_2Cl_2$ and an excess of Ag_2O). The gel was stirred again to homogeneity, sealed in a Teflon-lined stainless autoclave (23 ml), and heated at 160 °C for 2 days, under autogenous pressure. The resulting product, consisting of large colourless single crystalline platelets and some greenish amorphous material, was filtered off and dried at 80 °C. Finally, the two phases were separated using ultrasonification. Thermogravimetric analysis shows three mass losses at 120 (3.7%), 250 (4.3%) and 320 °C (14.78%). These losses probably correspond to the desorption of surface and occluded water, followed by the hydrogen-bonded water (calc. 3.8%), and finally the organic template (calc. 15.25%). The powder diffraction pattern of a sample heated in oxygen at 600 °C showed it to be the aluminium phosphate analogue of quartz, *i.e.* berlinite.

The structure was solved by single-crystal X-ray diffraction.† The asymmetric unit contains 26 non-hydrogen independent atoms [Fig. 1(*a*)]: three phosphate groups, with P–O distances in the range 1.515–1.540 Å, are linked *via* oxygen to three aluminium atoms to form the building block of the framework. Al(1) is at the centre of a quasi-regular octahedron, with Al–O distances in the range 1.873–1.894 Å; Al(2) and Al(3) have a distorted trigonal-bipyramidal coordination, with Al–O equatorial distances of 1.761–1.807 Å and Al–O apical distances of 1.863–1.916 Å. Although all connections between the polyhedra are made *viá* vertex-bridged oxygen atoms, the framework cannot be described by a simple alternation of phosphate tetrahedra with aluminium-centred polyhedra. In particular, there are vertex-bridged oxygen atoms, O(14) and O(13), between Al(1) and, Al(2) and Al(3), respectively. Note also that a hydrogen atom is found on O(13) in the Fourier map. The absence of nickel atoms within the structure is confirmed by an electron microprobe analysis.

The building blocks are connected along [100] to form zigzag columns, which in turn are connected along [001] to create planes containing seven ring apertures [Fig. 1(*b*)]. From the linking of these planes along [010] *via* four-rings emerges the formation of crosslinked ten- and eight-membered channels parallel to [100] and [101], [10$\bar{1}$], respectively (Fig. 2). The

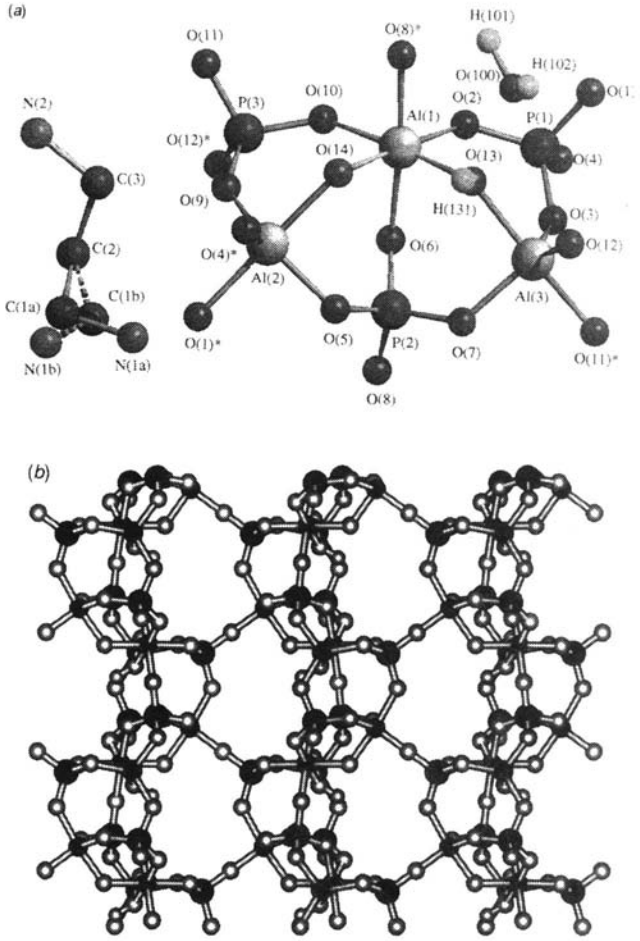

Fig. 1 (*a*) Asymmetric unit of SBM-6. Selected and average bond lengths (Å): P–O 1.532(8), Al–O_{eq} 1.79(2), Al–O_{ap} 1.89(2), Al(1)–O 1.886(8). (*b*) The plane-building unit seen along [010], (P, large black spheres; Al, small black spheres; O, white spheres).

diamine ligands [Fig. 1(*a*)] and water molecules are located at the intersections of these channels (Fig. 2), locked in position by hydrogen bonds. The location of the water molecule, between N(2) and the framework, indicates that a similar structure could be obtained with diaminobutane, the additional CH_2 group replacing the water molecule; such a material has been synthesized and will be reported elsewhere. Note that only one of the amine groups of the diamine molecule, N(1), is protonated, and that the branch C(1)–N(1) is disordered over two different conformations (labelled a and b) with respective occupancies of 0.88 and 0.12. This difference of population comes from the difference in the number of hydrogen bonds in which they are involved: two for N(1a) [N(1a)–H(1a)···O(1) 1.921(6), N(1a)–H(2a)···O(3) 1.932(6) Å] and only one for N(1b) [N(1b)–H(1b)···O(8) 2.078(3) Å].

Although Al–O–Al bridges and trigonal bipyramidal aluminium are now well known in AlPOs,[8–10] to our knowledge SBM-6 is the first AlPO structure in which there is no tetrahedral aluminium. However, such framework structures have been previously described in the GaPOs.[11,12] In particular, ULM-3 exhibits essentially the same framework architecture as SBM-6, albeit in a system where fluorine is involved in the Ga–F–Ga bridges.[10] Clearly, neither fluorine nor the larger Ga^{3+} ion are required in order to stabilize a structure with only five- and six-coordinated Al/Ga. Since fluorine was not used in our synthesis, we presume that the use of the nickel complex, rather than the pure amine itself, helped in stabilising the higher coordination for aluminium in SBM-6. It is already known that the use of diamine often leads to layered structures.[13,14] When 1,3-diaminopropane is used instead of the diamine complex in our synthesis, a different phase is obtained. In the synthesis of SBM-6, nickel ions arising from the decomposition of the complex are assumed to end up in the amorphous phase, as indicated by its greenish colour. It seems very likely, therefore, that the role of the nickel is to control the availability of the free amine in solution. Further work is under way in order to characterise and evaluate the role of such diamine complexes in the synthesis of ALPOs and related phases.

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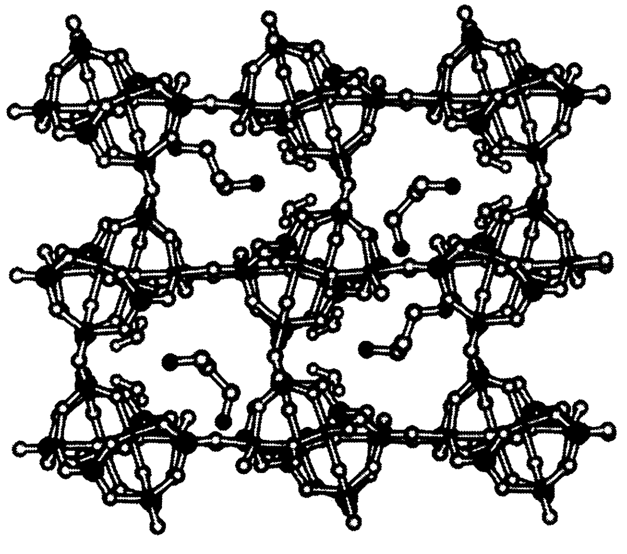

Fig. 2 View of the structure of SBM-6 along [100]. For clarity, only one conformation for the diamine is shown in each channel and only the hydrogen atoms on water are represented (same framework atoms representation as Fig. 1).

Footnote

† A typical single crystal (0.050 × 0.075 × 0.300 mm) was selected for X-ray diffraction analysis from the whole batch by careful observation under stereoscopic and polarizing microscopes. Crystal data for $[H_2N(CH_2)_3NH_3]^+[HAl_3P_3O_{14}]^-\cdot H_2O$: orthorhombic, space group *Pbca*, $a = 10.0583(8)$, $b = 18.085(1)$, $c = 15.6192(8)$ Å, $U = 2841.2(3)$ Å^3; $Z = 8$, $M = 491.9554$, graphite monochromated Cu-Kα radiation, $\lambda = 1.54180$ Å, $T = 293$ K, $D_c = 2.300$ g cm^{-3}. Data collection was performed on an Enraf-Nonius CAD4-MACH four-circle diffractometer equipped with a Rigaku rotating anode using ω–2θ scans with a width of $\Delta\omega = (1.0 + 0.15 \tan\theta)°$ extending 25% on each side for background measurement; horizontal counter aperture $\Delta l = (2.0 + 0.10 \tan\theta)$ mm, vertical aperture 4.0 mm, prescan speed 2.75° min^{-1}, $\sigma(I)/I = 0.010$, maximum time for final scan 120 s, 2θ range 1–144°. The unit-cell constants were determined from 25 centred reflections within the 2θ range 8.8–31.6°. A total of 6659 reflections were collected, of which 2688 were unique ($R_{int} = 2.48$), and 1960 had $I > 3.0\sigma(I)$ for 260 parameters. The data were corrected for decay (3.8%) and for absorption ($\mu = 49.5$ cm^{-1}) by a semi-empirical method based on Ψ-scans. The structure was solved by direct methods (SHELXS86) and difference Fourier syntheses. All of the hydrogen positions were located from difference Fourier maps and then held in the 'riding' mode. Full-matrix least-squares structure refinement was carried out using the CRYSTALS package of programs. Anisotropic thermal parameters were used for all non-hydrogen atoms, except for C(1b) and N(1b) for which the small occupation factors precluded such refinement. Final $R_F = 0.0349$, $R_w = 0.0392$ (unit weights), $S = 1.72$, $(\Delta/\sigma)_{max} = 0.00$. The final difference Fourier map had a minimum and maximum of -0.61 and 0.43 e Å^{-3}, respectively. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/74.

References

1 S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Cannan and E. M. Flanigen, *J. Am. Chem. Soc.*, 1982, **104**, 1146.

2 R. Xu, J. Chen and S. Feng, *Stud. Surf. Sci. Catal.*, 1990, **60**, 63.

3 J. L. Guth, H. Kessler, J. M. Higel, J. M. Lamblin, J. Patarin, A. Seive, J. M. Chezeau and R. Wey, *ACS Symp. Ser.*, 1989, **398**, 176.

4 K. J. Balkus, C. D. Hargis and S. Kowalak, *ACS Symp. Ser.*, 1992, **499**, 347.

5 K. Morgan, G. Gainesford and N. Milestone, *J. Chem. Soc., Chem. Commun.*, 1995, 425.

6 D. A. Bruce, A. P. Wilkinson, M. G. White and J. A. Bertrand, *J. Chem. Soc., Chem. Commun.*, 1995, 2059.

7 *Comprehensive Inorganic Chemistry*, ed. J. C. Bailar Jr., H. J. Emelèus, R. Nyholm and A. F. Trotman-Dickenson, Pergamon, Oxford, 1973, pp. 1139; N. Milestone, personal communication.

8 L. Li, L. Wu, J. Chen and R. Xu, *Acta Crystallogr., Sect. C*, 1991, **47**, 246.

9 A. M. Chippindale, A. V. Powell, L. M. Bull, R. H. Jones, A. K. Cheetham, J. M. Thomas and R. Xu, *J. Solid State Chem.*, 1992, **96**, 199.

10 A. M. Chippindale, A. V. Powell, R. H. Jones, J. M. Thomas, A. K. Cheetham, Q. Huo and R. Xu, *Acta Crystallogr., Sect. C*, 1994, **50**, 1537.

11 T. Loiseau, R. Retoux, P. Lacorre and G. J. Ferey, *J. Solid State Chem.*, 1994, **111**, 427.

12 X. Yin and L. F. Nazar, *J. Chem. Soc., Chem. Commun.*, 1994, 2349.

13 A. M. Chippindale, S. Natarajan, J. M. Thomas and R. H. Jones, *J. Solid State Chem.*, 1994, **111**, 18.

14 J. M. Thomas, R. H. Jones, J. Chen, R. Xu, A. M. Chippindale, S. Natarajan and A. K. Cheetham, *J. Chem. Soc., Chem. Commun.*, 1992, 929.

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