Organo-template control of inorganic structures: a low-symmetry two-dimensional sheet aluminophosphate3$[NH_3CHMeCH_2NH_3][Al_6P_8O_{32}]\cdot H_2O$

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A new low-symmetry two-dimensional AlPO network is found for $[Al_3P_4O_{16}]^{3-}$ with $[NH_3CHMeCH_2NH_3]^{2+}$ as the templating cation; calculations show that all existing AlPO two-dimensional nets are of comparable energy and that several hypothetical nets are energetically feasible.

The synthesis of new inorganic framework materials in which fine control is exercised by the use of organic templates, or structure-directing agents, is of fundamental interest for the design of microporous solids with specifically tailored properties.[1] Previously we and others have prepared a number of low-dimensional AlPO materials,[2–6] including several two-dimensional anionic aluminophosphates of general empirical formula $[Al_3P_4O_{16}]^{3-}$ in which the inorganic layers were separated by a variety of organo-ammonium or -diammonium ions. Three different two-dimensional networks have been found previously for the $[Al_3P_4O_{16}]^{3-}$ sheets [Fig. 1(*a*)–(*c*)], which we designate here as either 4.6, 4.6.8 or 4.6.12 nets, depending on the number of Al/P atoms in each ring.[2–4] We now wish to report a new low-symmetry 4.6 network in this family, which demonstrates the powerful yet subtle control exercised by the organic templates upon the inorganic sheet.

The title compound **1** $3[NH_3CHMeCH_2NH_3][Al_6P_8O_{32}]\cdot H_2O$ was synthesized from a predominantly non-aqueous system using ethylene glycol (EG) as solvent, a racemic mixture of (±)1,2-diaminopropane (DAP) as the templating organic base and aluminium triisopropoxide, $Al(OPr^i)_3$, and 85% H_3PO_4 as the Al and P precursors.† A specimen of *ca.* ⩾30 μm dimension was chosen and a single-crystal structure analysis‡ carried out using a rotating anode X-ray source.§ As for the previous structures of $[Al_3P_4O_{16}]^{3-}$ the inorganic layer consists of AlO_4 and PO_4 tetrahedra, with one terminal P=O group for each phosphate and all other oxygens bridging between Al and P. This connectivity pattern thus dictates the 3 : 4 Al : P ratio in the formula.

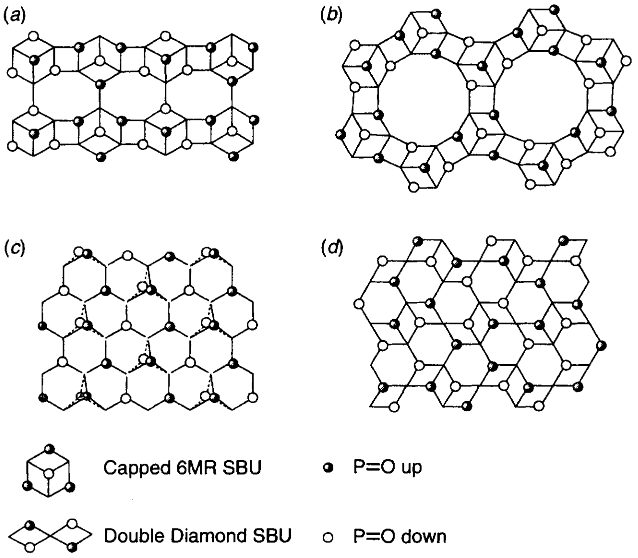

Fig. 1 Two-dimensional networks of the aluminophosphate anion $[Al_3P_4O_{16}]^{3-}$; (*a*) 4.6.8 network templated by $[NH_3CH_2CH_2NH_3]^{2+}$, (*b*) 4.6.12 network templated by $[NH_3CH_2CH_2CH_2CH_2NH_3]^{2+}$, (*c*) 4.6 network templated by $[Co(en)_3]^{3+}$, (*d*) 4.6 network templated by $[NH_3CHMeCH_2NH_3]^{2+}$

Compound **1** has a new Al_3P_4 structural building unit (SBU) which can be viewed as a 'double-diamond' *i.e.* two 4-membered rings sharing a common vertex. Morgan's 4.6 net contains a SBU with a P_2Al_3 trigonal-bipyramidal core[2] and the SBU for both the 4.6.8 and 4.6.12 nets is a phosphate capped Al_3P_3 ring, which will be referred to as 'capped 6MR'. The polyhedral arrangement of the sheet anion for **1** is shown in Fig. 2.

The structure of **1** may be contrasted to that templated by the dication $[NH_3CH_2CH_2NH_3]^{2+}$ for which a 4.6.8 net is formed. In both cases a complex system of hydrogen bonds is formed between the organo-ammonium ions and the P=O groups of the sheet.¶ The space group for **1** is non-centrosymmetric *Ia* (a non-standard setting of *Cc*), which has only translational symmetry elements. The asymmetric unit contains the formula unit $3[NH_3CHMeCH_2NH_3][Al_6P_8O_{32}]\cdot H_2O$ with 8 P=O groups which serve as hydrogen-bond acceptors and 6 $[NH_3R]^+$ hydrogen-bond donor functionalities. A total of 18 N–H···O=P hydrogen bonds, characterised by [O···N] separations between 2.66 and 2.93 Å, are formed between these functionalities per asymmetric unit, with 9 above and 9 below the sheet. In addition there is one molecule of disordered water which acts as a hydrogen-bond donor to P=O.

The low symmetry of the cation appears to transfer itself to the two-dimensional sheet which may be assigned to the plane group pg which contains only a glide symmetry element. The sheet itself appears more highly puckered than typical for the

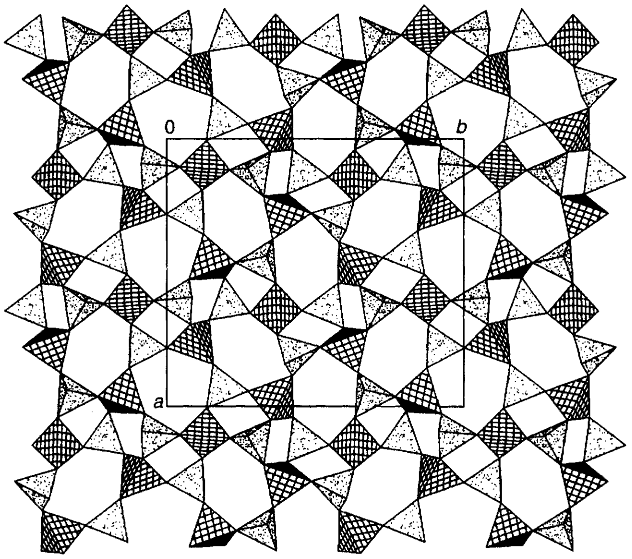

Fig. 2 Polyhedral framework of the crystal structure of **1** viewed along the *c* axis

previous nets, with maximum deviations of ±2.1 Å from the least-squares plane of the Al and P atoms for P(2) and P(6). The bond angles at the bridging oxygens in **1** also vary more widely than for the other sheets, in which the typical Al–O–P angle is *ca.* 140°. For example Al(6)–O(66)–P(6) is 170.1° and several others are > 160°. These features demonstrate a considerable level of flexibility of the two-dimensional network, which is utilised in order to optimise the inter-lamellar system of hydrogen bonds.

Discovery of the new 4.6 net has led us to search for alternate networks of the $[Al_3P_4O_{16}]^{3-}$ anion. Using either the double-diamond or capped 6MR SBUs, or a combination of both, an infinite number of two-dimensional sheets can be constructed which obey the required connectivity rules at Al and P. For example since the capped 6MR structure can be connected *via* three 4MR to other such units, as in the 4.6.12 net, it can be connected using all 66 known three-connected two-dimensional networks.[8] This has important implications for the synthesis of sheet AlPOs with rings of even larger size. Our studies have not yet revealed a topologically chiral net[3d] and imply such is not possible.

Interestingly, two of the 1,2-diammoniumpropane cations in **1** are disordered, with the 1- and 2-NH_3 groups interchangeable, having the observed effect of switching Me group positions with H. This implies that small van der Waals effects can affect the structure directing ability of the cations, since ethylenediamine should also be capable of forming this 4.6 net. We have therefore investigated the energy of a number of $[Al_3P_4O_{16}]^{3-}$ sheets, comparing both hypothetical and known networks. The results are summarised in Table 1. Hypothetical nets were constructed by us and geometry optimization performed using the Cerius^2 software package.[9,10]

The results indicate little intrinsic energy difference between the four known nets, with 4.6.12 being least stable. Of the hypothetical nets several were of the same order of stability of the known structures including a 4.8 net made from the double-diamond units. The variation of total energy was found to be dependent mainly on two factors. Several nets require unfavourable alignment of neighbouring P=O groups on the same side of the sheet, thereby increasing the angular strain and increasing the unfavourable Urey–Bradley or 1,3 interaction energy. Secondly, structures with larger rings, such as the 8.16 net, are also less stable as a result of lowered van der Waals interactions. Nets taken from crystal structure coordinates were typically > 10 kcal mol^{-1} (cal = 4.184 J) less stable than their geometry-optimised values, showing the extent of distortion made to fully optimise the hydrogen-bond network with the counter-ions.

Table 1 Calculated relative energies[a] for $[Al_3P_4O_{16}]^{3-}$ networks

Nets	Relative energies/kcal mol^{-1}				Remarks
	Total	Bond	Urey-B	vdW	
4.6 (a)	0.0	0.2	0.8	0.0	Hypothetical
4.6 (b)	1.8	0.1	0.4	3.2	This work
4.6 (c)	2.0	0.2	0.7	3.0	Ref. 2
4.8 (a)	3.4	0.2	0.8	4.4	Hypothetical
4.6.8	3.8	0.0	0.0	5.8	Ref. 3
4.6.12	4.9	0.0	0.0	6.8	Ref. 4
4.6.8 (x)	13.9	3.5	5.4	5.9	From ref. 3(*a*)
4.6 (x)	15.1	5.4	8.0	2.7	This work
4.6.12 (x)	16.6	7.4	4.3	5.8	From ref. 4(*a*)
8.16	19.2	1.7	15.6	2.8	Hypothetical
4.8 (b)	53.4	4.4	48.0	3.1	Hypothetical

[a] Calculations carried out using the Cerius^2 package (ref. 10) with Burchart 1.01-Dreiding 2.02 force-field (ref. 9). (x) Indicates from X-ray structure coordinates, and all others optimized geometry. (a), (b) and (c) indicate different topological isomers.

In conclusion, the ability of $[NH_2CHMeCH_2NH_2]$ to create a layered aluminophosphate network with low symmetry demonstrates the subtlety and importance of organic–inorganic interfaces in this field. Our examination of a wide number of hypothetical nets for these two-dimensional AlPOs indicate that many more may yet be synthesized, and we are now examining templating of such networks so that their rational synthesis may be pursued. The results are also highly encouraging for the idea of creating surfaces with highly specific recognition properties *via* information transfer from organic to inorganic materials.

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Footnotes

† *Typical reaction conditions*: A homogeneous mixture of composition $Al(OPr^i)_3 : 10H_3PO_4 : 5$ DAP : 90.0 EG : 5 H_2O was heated at 180 °C for 20 d resulting in fine crystals of **1** of *ca.* 30 μm dimension in 80% yield.

‡ *Crystal data for* **1**: $[C_9H_{36}N_6][Al_6P_8O_{32}]\cdot H_2O$, M_r = 1168.1, monoclinic, space group *Ia* (no. 9), a = 18.119(2), b = 16.236(2), c = 14.736(2) Å, β = 91.35(1)°, U = 4333.8(1.0) Å^3, Z = 4, D_c = 1.79 Mg m^{-3}, μ(Mo-Kα) = 0.55 mm^{-1}, R = 0.040, R_w = 0.045, GOF = 1.26 for 4451 data with $F \geqslant 4\sigma(F)$.

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 182/102.

§ Data were collected using a Siemens P4-RA system and all subsequent analysis carried out using the SHELXTL-PLUS package, © G. M. Sheldrick, Siemens Analytical Instruments, 1993.

¶ Note: The formation of a specific set of hydrogen bonds in these salts leads us to use the term template for the organic ions in these structures, rather than merely structure directing ions, as discussed by Davis and Lobo in ref. 1(*b*).

References

1 (*a*) R. M. Barrer, *Hydrothermal Chemistry of Zeolites*, Academic Press, London, 1982, p. 44; (*b*) M. E. Davis and R. F. Lobo, *Chem. Mater.*, 1992, **4**, 759.

2 K. Morgan, G. Gainsford and N. Milestone, *J. Chem. Soc., Chem. Commun.*, 1995, 425.

3 (*a*) R. H. Jones, J. M. Thomas, R. Xu, Q. Huo, A. K. Cheetham and A. V. Powell, *J. Chem. Soc., Chem. Commun.*, 1991, 1266; (*b*) A. M. Chippindale, S. Natarajan, J. M. Thomas and R. H. Jones, *J. Solid State Chem.*, 1994, **111**, 18; (*c*) R. H. Jones, A. M. Chippindale, S. Natarajan and J. M. Thomas, *J. Chem. Soc., Chem. Commun.*, 1994, 565; (*d*) D. A. Bruce, A. P. Wilkinson, M. G. White and J. A. Bertrand, *J. Chem. Soc., Chem. Commun.*, 1995, 2059.

4 (*a*) J. M. Thomas, R. H. Jones, R. Xu, J. Chen, A. M. Chippindale, S. Natarajan and A. K. Cheetham, *J. Chem. Soc., Chem. Commun.*, 1992, 929; (*b*) A. Kuperman, S. Nadimi, S. Oliver, G. A. Ozin, J. M. Garces and M. M. Olken, *Nature*, 1993, **365**, 239; (*c*) P. A. Barrett and R. H. Jones, *J. Chem. Soc., Chem. Commun.*, 1995, 1979.

5 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.

6 R. H. Jones, J. M. Thomas, R. Xu, Q. Huo, Y. Xu, A. K. Cheetham and D. Bieber, *J. Chem. Soc., Chem. Commun.*, 1990, 1170; I. D. Williams, K. N. Hui, Q. Gao, J. Chen and R. Xu, unpublished work.

7 Q. Gao, S. Li, J. Chen, R. Xu, I. D. Williams, L.-Y. Ngai, Z. Lin, J. Zheng, Z. Tang and D. J. Barber, *J. Solid State Chem.*, in preparation.

8 J. V. Smith, *Proc. 8th Intl. Zeolite Conf.*, 1989, pp. 29–47, ed. P. A. Jacobs and R. van Santen, Elsevier; (*b*) J. V. Smith, *Chem. Rev.*, 1988, **88**, 149.

9 E. de Vos Burchart, H. van Bekkum, B. van de Graff and E. T. C. Vogt, *J. Chem. Soc., Faraday Trans.*, 1992, **88**, 2761.

10 Cerius^2. © Molecular Simulations/Biosym Corporation, 1995.

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