

Synthesis and crystal structure of ULM-6, a new open-framework fluorinated aluminium phosphate with encapsulated 1,3-diaminopropane: $[\text{N}_2\text{C}_3\text{H}_{12}]^{2+}[\text{Al}_4(\text{PO}_4)_4\text{F}_2(\text{H}_2\text{O})]^{2-}$

Nathalie Simon, Thierry Loiseau* and Gérard Férey

Institut Lavoisier, UMR CNRS 173, Université de Versailles — St Quentin en Yvelines, 45 Avenue des Etats-Unis, 78035 Versailles Cedex, France. E-mail: loiseau@chimie.uvsq.fr; Fax: 33 1 39 25 43 58

Received 5th October 1998, Accepted 5th February 1999

The compound $[\text{N}_2\text{C}_3\text{H}_{12}]^{2+}[\text{Al}_4(\text{PO}_4)_4\text{F}_2(\text{H}_2\text{O})]^{2-}$ or ULM-6, a new fluorinated aluminium phosphate, has been obtained by hydrothermal synthesis at 180 °C for 14 d with 1,3-diaminopropane as a structure-directing agent. The gallium form of ULM-6 was also obtained. The structure of the aluminium compound was characterized by means of single-crystal X-ray diffraction analysis. It consists of the alternation of corner-linked PO_4 tetrahedra with $\text{AlO}_4(\text{H}_2\text{O})$, AlO_4F trigonal bipyramids and AlO_4F_2 octahedra. The connection of these building units generates 8-ring channels running along [100] and [010] in which the diprotonated diamine is located. Crystal data: triclinic, space group $P\bar{1}$ (no. 2), $Z = 1$, $a = 9.5581(3)$, $b = 9.7661(3)$, $c = 10.4724(3)$ Å, $\alpha = 68.370(1)$, $\beta = 80.509(1)$, $\gamma = 89.506(1)^\circ$, $V = 894.82(5)$ Å³, $R1(F) = 0.0556$, $wR2(F^2) = 0.1516$ for 3827 reflections with $I > 2\sigma(I)$.

Introduction

Microporous solids are of great interest for their potential applications in heterogeneous catalysis, molecular sieving and ion exchange. Much research has been devoted to the hydrothermal synthesis of new open-framework materials such as aluminosilicate zeolites and phosphate-based compounds.¹ Organic molecules such as amines or alkylammonium ions are usually required for the formation of three-dimensional frameworks and act as structure directing or templating agents. During the last decade, several works reported the use of fluorine during the hydrothermal treatment in order to increase the crystallinity of the resulting product. These studies, first developed by Guth *et al.*,² offered new opportunities for the elaboration of new topologies. For instance, the extra large pore fluorinated gallium phosphate cloverite³ exhibits a three-dimensional 20-membered ring channel system. Fluorine is encapsulated in the centres of the cubic-like D4R cage and seems to stabilize this type of building block. Very recently, other structures based on this D4R cage have been characterized with various dimensionalities: the D4R units can appear as isolated clusters (Mu-1⁴), form chains (Mu-3⁵), layered structures (ULM-18⁶) and three-dimensional frameworks (Mu-2⁷). Besides this specific behaviour, fluorine can belong to the co-ordination sphere of the aluminium or gallium atoms. In the ULM-*n* series⁸ or the TREN-GAPO $\{[\text{N}_4\text{C}_6\text{H}_{21}]^{3+}_{0.5}[\text{NC}_5\text{H}_6]^+_{0.5}[\text{Ga}_3(\text{PO}_4)_3\text{F}_2]^{2-}\}$ ⁹ fluorine is incorporated into the inorganic network. The metal atom is five- or six-co-ordinated, generating more complex topologies than those usually found in zeolite-like materials.

In our systematic study of the synthesis of fluorinated phosphates, we found that the formation of compounds labelled ULM-3, ULM-4 and ULM-5 depends on the length of the diamine.⁸ It has been mentioned that the ULM-4 type can be obtained in the gallium system with a small amount of another phase, named ULM-6,¹⁰ by using 1,3-diaminopropane as the structure directing agent. The same reaction is observed for the synthesis of the aluminium form of ULM-4.¹¹ Here we present the synthesis and the X-ray diffraction characterization of a new three-dimensional open-framework phosphate $[\text{N}_2\text{C}_3\text{H}_{12}]^{2+}[\text{Al}_4(\text{PO}_4)_4\text{F}_2(\text{H}_2\text{O})]^{2-}$ or ULM-6. Such a solid can be obtained either with aluminium or gallium during the crystal-

lisation of the ULM-4 type phase, but the single-crystal quality of the gallium compound was not good enough and prevented us from determining the structure properly. Only the structure of the aluminium form is reported in this paper. The open-framework of ULM-6 contains channels delimited by eight polyhedra and is more dense than that of ULM-4.

Experimental

Synthesis

The two compounds were synthesized hydrothermally under autogenous pressure with 1,3-diaminopropane as a structure directing agent. The starting mixture contains aluminium oxide (Al_2O_3 , Prolabo) or gallium oxide (Ga_2O_3 , Merck, 99%+), phosphoric acid (H_3PO_4 , 85% in water, Prolabo RP Normapur), hydrofluoric acid (HF, 40% in water, Prolabo RP Normapur), 1,3-diaminopropane (99%+, Aldrich, hereafter noted DAP) and deionized water. The molar ratios were 1 Al (0.18 g):1 P (0.23 ml):1.5 F (0.24 ml):0.5 DAP (0.15 ml):80 H_2O (5 ml) and 1 Ga (0.65 g):2 P (0.92 ml):1 F (0.32 ml):0.5 DAP (0.30 ml):40 H_2O (5 ml) for the aluminophosphate and the gallophosphate, respectively. The mixtures were sealed in a polytetrafluoroethylene-lined stainless steel autoclave (Parr) and heated at 180 °C for 14 d for the aluminium phosphate and 3 d for the gallium phosphate. The pH of the reaction was 5 for the aluminium compound and 1–2 for the gallium ones. The resulting product was filtered off, washed with deionized water and dried at room temperature. The reaction yield is very low (<10%) and these phases crystallize with a large amount of the phase called ULM-4.^{10,11} For the aluminium system, MIL-12¹² is also formed together with ULM-6 and ULM-4. In order to increase the reaction yield, different attempts for both systems have been done by changing the pH value or concentration of the reactants. Under more acidic conditions, a mixture of ULM-4 and quartz type phosphate ($\alpha\text{-MPO}_4$, M = Al or Ga) is obtained, while at higher pH the ULM-4 can be prepared as a pure phase. Nevertheless, examination under an optical microscope indicated that the ULM-6 compounds exhibit well defined multifaceted crystals with a spherical shape. The ULM-4 or MIL-12 phases grow as needles and, therefore, some

crystals of ULM-6 can be isolated from the main product of the reaction by observation under an optical microscope.

Crystallography

A suitable single crystal of the aluminium compound was carefully selected under a polarizing microscope and glued at the top of a thin glass fiber with araldite adhesive. X-Ray diffraction intensities were recorded on a Siemens SMART three-circle diffractometer equipped with a CCD bidimensional detector using monochromatized radiation of wavelength $\lambda(\text{Mo-K}\alpha) = 0.71073 \text{ \AA}$. The crystal-to-detector distance was 45 mm allowing for data collection up to $60^\circ (2\theta)$. Slightly more than one hemisphere of data was recorded and the acquisition time per frame was 30 s. An empirical absorption correction was applied using the SADABS program.¹³

The structure was solved by direct methods and refined by full-matrix least squares using the SHELXTL package.¹⁴ The phosphorus and aluminium atoms were located by direct methods and all the other non-hydrogen atoms (F, O, C, N) placed from subsequent Fourier-difference map calculations. The location of fluorine atoms was deduced from the analysis of the anisotropic thermal parameters, the absence in the Fourier-difference map of any residue due to the hydrogen atoms (of OH group) close to the corresponding atoms, and bond valence calculations. The hydrogen atoms of the amine molecule were placed with geometrical restraints in the riding mode. All the non-hydrogen atoms were refined anisotropically. The final refinement converged at $R1(F) = 0.0556$ and $wR2(F^2) = 0.1516$ for 3827 reflections [$I > 2\sigma(I)$]. The remaining difference Fourier map residues (2.961 e \AA^{-3}) are randomly located within the pores of the structure. They do not fit with the configuration of another trapped linear diamine or other water molecules since they are close to the anions ($< 1.5 \text{ \AA}$) of the framework.

The observed cell parameters of the gallium compound are similar to those of the aluminium form [$a = 9.6830(4)$, $b = 9.8679(4)$, $c = 10.6223(4) \text{ \AA}$, $\alpha = 68.638(1)$, $\beta = 81.258(1)$, $\gamma = 89.82(1)^\circ$, $V = 932.76(6) \text{ \AA}^3$]. The structure was refined by starting from the atomic coordinates of the aluminium phase with gallium replacing the aluminium. With this model, the reliability factors for the gallium one are $R1(F) = 0.1132$ and $wR2(F^2) = 0.2783$ and refinements performed from direct methods led to the same results. These values are quite high and some uncertainties occur in this structural arrangement. This is the reason why the structure is not presented.

Crystal data and details of the data collection for the aluminium compound are summarized in Table 1. The resulting atomic coordinates are listed in Table 2, selected bond distances and angles in Table 3 and positions of hydrogen atoms in Table 4.

CCDC reference number 186/1343.

Results and discussion

ULM-6 is a new three-dimensional open framework of chemical formula $[\text{Al}_4(\text{PO}_4)_4\text{F}_2(\text{H}_2\text{O})]^{2-}$ in which the diprotonated 1,3-diaminopropane molecule $[\text{N}_2\text{C}_3\text{H}_{12}]^{2+}$ is encapsulated. In the inorganic framework the P–O distances of all the PO_4 tetrahedra range from 1.50 to 1.56 \AA . The aluminium atoms exhibit two types of co-ordination. The Al(2) and Al(3) atoms are five-co-ordinated corresponding to a very distorted trigonal bipyramid. The Al–O equatorial distances are in the range 1.700–1.769 \AA . The Al–O and Al–F apical distances are much longer. For the Al(3) atom the distances are Al(3)–O(13) 1.808(3) and Al(3)–F(1) 2.297(3) \AA . Atom F(1) is shared between three metal atoms which explains the large value observed for this Al–F bond length. For the Al(2) atom, the Al–O apical distances are Al(2)–O(9) 1.799(3) and Al(2)–OW 2.312(6). The water molecule, which completes the co-

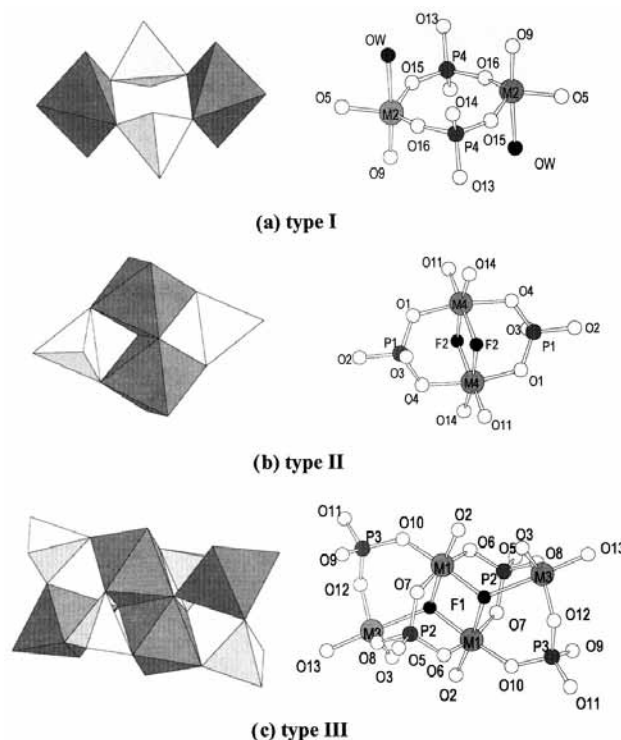


Fig. 1 Secondary building units: (a) type I [$\text{Al}_2\text{P}_2\text{O}(\text{H}_2\text{O})_2$]; (b) type II ($\text{Al}_2\text{P}_2\text{O}_7$); (c) type III ($\text{Al}_4\text{P}_4\text{O}_7$).

ordination sphere of the Al(2) metal atom, is in a terminal position. Bond valence calculations¹⁵ performed on the framework confirm the presence of a water molecule on this site (calculated valence: 0.17, instead of the expected value 0.4 for H_2O). The two other metallic atoms (Al) are in octahedral coordination, as had been observed in other compounds of the ULM-*n* series⁸ (ULM-3, ULM-4, ULM-16). These two atoms, Al(1) and Al(4), are surrounded by four oxygen atoms ($\langle \text{Al–O} \rangle$ 1.86 \AA) and two fluorine atoms ($\langle \text{Al(1)–F(1)} \rangle$ 1.96 and $\langle \text{Al(4)–F(4)} \rangle$ 1.89 \AA) in *cis* positions in the octahedra.

The open-framework of ULM-6 is built up from the connection of PO_4 tetrahedra with AlO_4X ($\text{X} = \text{F}$ or H_2O) trigonal bipyramids and AlO_4F_2 octahedra. This topology is composed of three distinct building units. One, noted type I [Fig. 1(a)], consists of the connection of two $\text{Al(2)O}_4(\text{H}_2\text{O})_2$ trigonal bipyramids with two P(4)O_4 tetrahedra by corner sharing. The two bipyramids have no common vertex. The unit noted type II [Fig. 1(b)] is also tetrameric but it is formed with two P(1)O_4 tetrahedra connected to a group of two edge-shared $\text{Al(4)O}_4\text{F}_2$ octahedra, the common edge corresponding to two fluorine atoms. Each phosphate group shares two of its vertices with the bioctahedral entity. The existence of such a building species had been reported in other fluorinated aluminophosphates, e.g. chabazite (CHA)¹⁶ and gismondine (GIS)¹⁷ types and in fluorinated gallium phosphates such as in ULM-1.⁸ The building unit of type III [Fig. 1(c)] is octameric (Al_4P_4). It is based on a tetramer of metal-centred (Al) polyhedra formed by edge-sharing octahedra [Al(1)]; this edge, corresponding to two fluorine atoms F(1) as in the unit II, is then corner-linked to two trigonal bipyramids [Al(3)]. Four PO_4 tetrahedra share either three [P(2)] or two [P(3)] of their corners with this defined tetramer. This structural unit was also encountered in the gallium phosphate GaPO_4 -14.¹⁸ In the latter the gallium atoms are exclusively surrounded by oxygen atoms and hydroxide groups link the common edge of the bioctahedral entity to the trigonal bipyramids. Some similar geometrical units are encountered in the frameworks of AlPO_4 -12¹⁹ and AlPO_4 -15.²⁰ In type 12 the tetramers are formed by two edge sharing trigonal bipyramids and the common edge is linked to two additional trigonal bipyramids. The three-dimensional frameworks of types 12 and

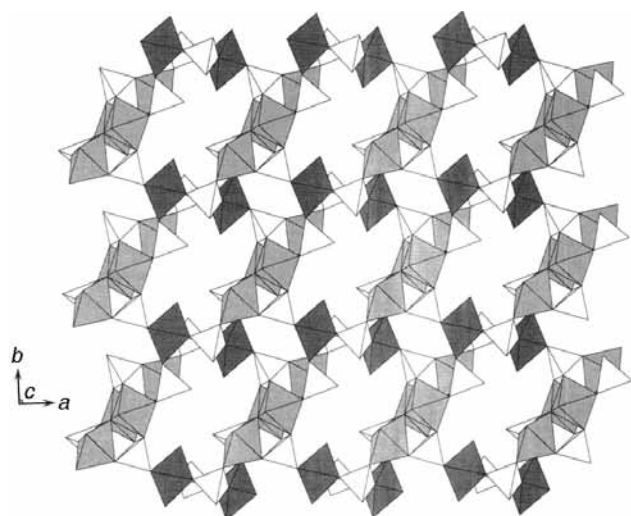


Fig. 2 Structure of ULM-6 showing the view of the layer along [001]. Dark polyhedra indicate trigonal bipyramids of the units of type I; grey the trigonal bipyramids and the octahedra of the units of type III; PO₄ groups are represented by white tetrahedra.

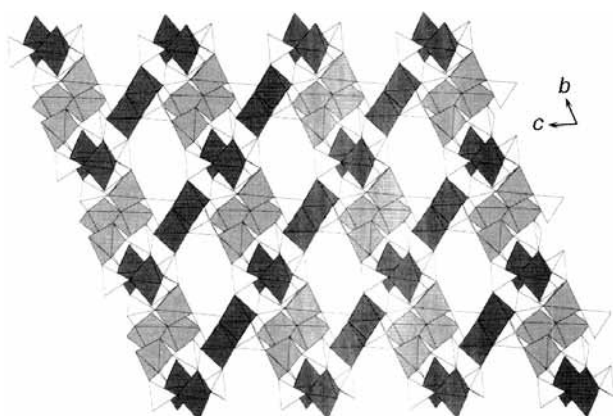


Fig. 3 View of the three-dimensional framework of ULM-6 along [100]. The bi-octahedral units of type II connecting the layers are indicated by dark polyhedra.

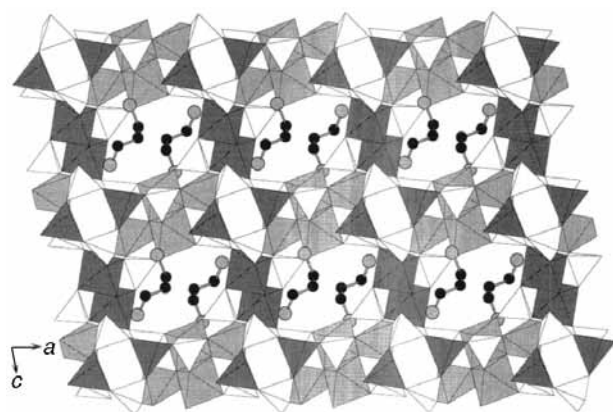


Fig. 4 View of the structure of ULM-6 along [010] showing the disposition of the molecule of 1,3-diaminopropane in the 8-ring channels. Hydrogen atoms have been omitted for clarity.

14 are built up from the connection of metal-centred tetramers with PO₄ and AlO₄ tetrahedra. In AlPO₄-15, which is related to the structure of the mineral leucophosphate,²¹ the building unit is exclusively composed of metal-centred octahedra sharing a common edge which connects two additional octahedra. The connection of these octahedra-based units with PO₄ groups forms the three-dimensional framework.

The structure can be described in term of infinite sheets

Table 1 Crystal data and structure refinement for ULM-6 (Al)

| | |
|--|---|
| Identification code | ULM-6 (Al) |
| Empirical formula | C ₆ H ₂₆ Al ₈ F ₈ N ₄ O ₃₄ P ₈ |
| Formula weight | 1313.91 |
| <i>T</i> /K | 293(2) |
| Crystal system | Triclinic |
| Space group | <i>P</i> $\bar{1}$ (no. 2) |
| <i>a</i> /Å | 9.5581(3) |
| <i>b</i> /Å | 9.7661(3) |
| <i>c</i> /Å | 10.4724(3) |
| α /° | 68.370(1) |
| β /° | 80.509(1) |
| γ /° | 89.506(1) |
| <i>V</i> /Å ³ , <i>Z</i> | 894.82(5), 1 |
| <i>D_c</i> /Mg m ⁻³ | 2.438 |
| μ /mm ⁻¹ | 0.759 |
| <i>F</i> (000) | 658 |
| Crystal size/mm | 0.30 × 0.20 × 0.16 |
| θ Range for data collection/° | 2.12 to 29.69 |
| Limiting indices | -12 ≤ <i>h</i> ≤ 12, -13 ≤ <i>k</i> ≤ 13, -10 ≤ <i>l</i> ≤ 14 |
| Reflections collected | 6331 |
| Independent reflections | 4480 [<i>R</i> (int) = 0.0167] |
| Data [<i>I</i> > 2 σ (<i>I</i>)] | 3827 |
| Parameters | 292 |
| Goodness of fit on <i>F</i> ² | 1.061 |
| Final <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)] (all data) | 0.0556, 0.1516 0.0643, 0.1579 |
| Extinction coefficient | 0.001(2) |
| Largest difference peak and hole/ e Å ⁻³ | 2.961 and -1.524 |

Table 2 Atomic coordinates (×10⁴) and equivalent isotropic displacement parameters (Å² × 10³) for ULM-6 (Al); *U*_{eq} is defined as one third of the trace of the orthogonalized *U*_{ij} tensor

| Atom | <i>x</i> | <i>y</i> | <i>z</i> | <i>U</i> _{eq} |
|-------|----------|----------|----------|------------------------|
| P(1) | 7265(1) | 4383(1) | 3454(1) | 9(1) |
| P(2) | 9683(1) | 7858(1) | -1031(1) | 12(1) |
| P(3) | 12790(1) | 6805(1) | 1457(1) | 13(1) |
| P(4) | 5458(1) | -323(1) | 2181(1) | 16(1) |
| Al(1) | 10134(1) | 5069(1) | 1378(1) | 11(1) |
| Al(2) | 7186(1) | 9833(2) | -730(1) | 22(1) |
| Al(3) | 7196(1) | 2466(1) | 1651(1) | 13(1) |
| Al(4) | 5246(1) | 3713(1) | 6148(1) | 9(1) |
| F(1) | 8724(3) | 4509(3) | 478(2) | 20(1) |
| F(2) | 5619(2) | 5775(2) | 5423(2) | 12(1) |
| O(1) | 6938(3) | 3628(3) | 5043(3) | 14(1) |
| O(2) | 8882(3) | 4663(3) | 2996(3) | 13(1) |
| O(3) | 6708(3) | 3379(3) | 2780(3) | 17(1) |
| O(4) | 6548(3) | 5868(3) | 2950(3) | 12(1) |
| O(5) | 8780(3) | 9203(3) | -1311(3) | 22(1) |
| O(6) | 9252(3) | 6862(3) | -1758(3) | 13(1) |
| O(7) | 9569(3) | 7014(3) | 543(3) | 15(1) |
| O(8) | 11224(3) | 8491(3) | -1691(3) | 16(1) |
| O(9) | 12165(3) | 8266(3) | 1420(3) | 23(1) |
| O(10) | 11607(3) | 5572(3) | 2054(3) | 15(1) |
| O(11) | 13973(3) | 6438(3) | 2306(3) | 16(1) |
| O(12) | 13453(3) | 6966(3) | -58(3) | 17(1) |
| O(13) | 5996(3) | 868(3) | 2631(3) | 17(1) |
| O(14) | 5353(3) | -1797(3) | 3364(3) | 16(1) |
| O(15) | 4036(4) | 111(4) | 1764(5) | 42(1) |
| O(16) | 6577(4) | -415(4) | 964(4) | 37(1) |
| OW | 6509(5) | 7350(7) | 96(5) | 70(2) |
| N(1) | 6826(5) | 7505(5) | 6726(5) | 41(1) |
| N(2) | 8876(6) | 8053(6) | 2754(6) | 53(1) |
| C(1) | 9208(10) | 7337(8) | 4224(8) | 63(2) |
| C(2) | 9040(8) | 8441(7) | 4944(6) | 50(2) |
| C(3) | 7584(8) | 8762(8) | 5474(6) | 52(2) |

connected to each other by the isolated building units of type II. The layer, along (001), consists of the connection of the structural units of type I with those of type III *via* corners. As shown in Fig. 2, each block of type III is linked to four units of type I with respect to the strict M/P alternation and *vice versa*. The

Table 3 Bond lengths (Å) and angles (°) for ULM-6 (Al)

| | | | | | |
|--------------------------|----------|--------------------------------|------------|--------------------------------|------------|
| P(1)–O(1) | 1.529(3) | O(1)–P(1)–O(2) | 108.5(1) | O(1)–P(1)–O(4) | 111.4(1) |
| P(1)–O(2) | 1.536(3) | O(1)–P(1)–O(3) | 109.7(2) | O(2)–P(1)–O(4) | 109.2(1) |
| P(1)–O(3) | 1.545(3) | O(2)–P(1)–O(3) | 109.8(2) | O(3)–P(1)–O(4) | 108.2(2) |
| P(1)–O(4) | 1.546(3) | | | | |
| P(2)–O(5) | 1.529(3) | O(5)–P(2)–O(6) | 110.8(2) | O(6)–P(2)–O(8) | 108.7(2) |
| P(2)–O(6) | 1.533(3) | O(5)–P(2)–O(8) | 105.1(2) | O(7)–P(2)–O(6) | 111.6(2) |
| P(2)–O(7) | 1.532(3) | O(5)–P(2)–O(7) | 110.2(2) | O(7)–P(2)–O(8) | 110.3(2) |
| P(2)–O(8) | 1.548(3) | | | | |
| P(3)–O(9) | 1.532(3) | O(9)–P(3)–O(10) | 109.5(2) | O(11)–P(3)–O(9) | 110.9(2) |
| P(3)–O(10) | 1.535(3) | O(9)–P(3)–O(12) | 108.8(2) | O(11)–P(3)–O(10) | 110.8(2) |
| P(3)–O(11) | 1.513(3) | O(10)–P(3)–O(12) | 109.7(2) | O(11)–P(3)–O(12) | 107.1(2) |
| P(3)–O(12) | 1.558(3) | | | | |
| P(4)–O(13) | 1.528(3) | O(15)–P(4)–O(14) | 111.9(2) | O(14)–P(4)–O(13) | 109.6(2) |
| P(4)–O(14) | 1.505(3) | O(15)–P(4)–O(13) | 107.2(2) | O(14)–P(4)–O(16) | 107.3(2) |
| P(4)–O(15) | 1.505(3) | O(15)–P(4)–O(16) | 112.8(2) | O(13)–P(4)–O(16) | 108.0(2) |
| P(4)–O(16) | 1.552(4) | | | | |
| Al(1)–O(2) | 1.818(3) | O(2)–Al(1)–O(10) | 94.01(12) | O(6)–Al(1)–F(1) | 85.66(11) |
| Al(1)–O(10) | 1.823(3) | O(2)–Al(1)–O(6) | 96.91(12) | O(7)–Al(1)–F(1) | 85.52(12) |
| Al(1)–O(6) | 1.888(3) | O(10)–Al(1)–O(6) | 91.62(12) | O(2)–Al(1)–F(1 ¹) | 172.74(12) |
| Al(1)–O(7) | 1.891(3) | O(2)–Al(1)–O(7) | 94.53(12) | O(10)–Al(1)–F(1 ¹) | 93.12(11) |
| Al(1)–F(1) | 1.953(3) | O(10)–Al(1)–O(7) | 95.91(13) | O(6)–Al(1)–F(1 ¹) | 84.27(11) |
| Al(1)–F(1 ¹) | 1.964(3) | O(6)–Al(1)–O(7) | 165.83(13) | O(7)–Al(1)–F(1 ¹) | 83.35(11) |
| | | O(2)–Al(1)–F(1) | 92.46(11) | F(1)–Al(1)–F(1 ¹) | 80.46(11) |
| | | O(10)–Al(1)–F(1) | 173.24(12) | | |
| Al(2)–O(16) | 1.700(4) | O(16)–Al(2)–O(15) | 117.9(2) | O(5)–Al(2)–O(9) | 94.26(14) |
| Al(2)–O(15) | 1.707(4) | O(16)–Al(2)–O(5) | 124.2(2) | O(16)–Al(2)–OW | 81.5(2) |
| Al(2)–O(5) | 1.739(3) | O(15)–Al(2)–O(5) | 111.1(2) | O(15)–Al(2)–OW | 80.6(2) |
| Al(2)–O(9) | 1.799(3) | O(16)–Al(2)–O(9) | 100.8(2) | O(5)–Al(2)–OW | 81.7(2) |
| Al(2)–OW | 2.312(6) | O(15)–Al(2)–O(9) | 101.0(2) | O(9)–Al(2)–OW | 175.9(2) |
| Al(3)–O(3) | 1.732(3) | O(3)–Al(3)–O(12) | 119.23(14) | O(8)–Al(3)–O(13) | 96.67(13) |
| Al(3)–O(12) | 1.769(3) | O(3)–Al(3)–O(8) | 120.97(14) | O(3)–Al(3)–F(1) | 82.87(11) |
| Al(3)–O(8) | 1.767(3) | O(12)–Al(3)–O(8) | 115.56(14) | O(12)–Al(3)–F(1) | 83.05(11) |
| Al(3)–O(13) | 1.808(3) | O(3)–Al(3)–O(13) | 95.32(13) | O(8)–Al(3)–F(1) | 83.48(11) |
| Al(3)–F(1) | 2.297(3) | O(12)–Al(3)–O(13) | 98.70(13) | O(13)–Al(3)–F(1) | 177.95(12) |
| Al(4)–O(11) | 1.815(3) | O(11)–Al(4)–O(14) | 100.81(13) | O(1)–Al(4)–F(2 ²) | 86.98(11) |
| Al(4)–O(14) | 1.825(3) | O(11)–Al(4)–O(1) | 96.46(12) | F(2)–Al(4)–F(2 ²) | 79.48(10) |
| Al(4)–O(1) | 1.867(3) | O(14)–Al(4)–O(1) | 95.26(12) | O(11)–Al(4)–O(4) | 90.80(12) |
| Al(4)–F(2) | 1.885(2) | O(11)–Al(4)–F(2) | 91.13(12) | O(14)–Al(4)–O(4) | 91.67(12) |
| Al(4)–F(2 ²) | 1.897(2) | O(14)–Al(4)–F(2) | 167.75(12) | O(1)–Al(4)–O(4) | 168.84(12) |
| Al(4)–O(4) | 1.918(3) | O(1)–Al(4)–F(2) | 86.03(11) | F(2)–Al(4)–O(4) | 85.36(10) |
| | | O(11)–Al(4)–F(2 ²) | 169.78(12) | F(2 ²)–Al(4)–O(4) | 84.47(10) |
| | | O(14)–Al(4)–F(2 ²) | 88.41(11) | | |
| N(1)–C(3) | 1.505(8) | C(2)–C(1)–N(2) | 109.5(5) | | |
| N(2)–C(1) | 1.525(8) | C(2)–C(3)–N(1) | 113.7(5) | | |
| C(1)–C(2) | 1.521(9) | C(3)–C(2)–C(1) | 118.7(6) | | |
| C(2)–C(3) | 1.486(9) | | | | |

Symmetry transformations used to generate equivalent atoms: $1 - x + 2, -y + 1, -z$; $2 - x + 1, -y + 1, -z + 1$.**Table 4** Hydrogen coordinates^a ($\times 10^4$) and isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for ULM-6 (Al)

| Atom | <i>x</i> | <i>y</i> | <i>z</i> | <i>U</i> _{eq} |
|-------|----------|----------|----------|------------------------|
| H(1A) | 6542(45) | 6804(24) | 6457(8) | 62 |
| H(1B) | 6073(29) | 7831(12) | 7129(29) | 62 |
| H(1C) | 7413(16) | 7137(34) | 7331(23) | 62 |
| H(2A) | 7944(9) | 7967(52) | 2783(9) | 79 |
| H(2B) | 9327(46) | 7606(39) | 2215(15) | 79 |
| H(2C) | 9163(52) | 9004(15) | 2405(22) | 79 |
| H(1D) | 8567(10) | 6477(8) | 4752(8) | 76 |
| H(1E) | 173(10) | 7017(8) | 4181(8) | 76 |
| H(2D) | 9544(8) | 8093(7) | 5726(6) | 60 |
| H(2E) | 9518(8) | 9367(7) | 4294(6) | 60 |
| H(3A) | 7027(8) | 8999(8) | 4732(6) | 63 |
| H(3B) | 7642(8) | 9623(8) | 5718(6) | 63 |

^a The N–H and C–H distances have been fixed at 0.89 and 0.97 Å, respectively.

sheets are joined *via* Al–O–P bonding to the bioctahedra-based unit Al₂P₂ (type II) to generate cross-linking channels along [100] and [010] (Fig. 3). These tunnels are delimited by eight polyhedra and encapsulate the molecules of 1,3-diaminopropane which are diprotonated to balance the two negative charges of the framework (Fig. 4). The 1,3-diaminopropane molecule interacts with the inorganic network *via* N–H⋯O and N–H⋯F weak hydrogen bonds. The most significant hydrogen bonds are N(1)⋯F(2) 2.88(1), N(1)⋯O(6) 2.96(1), N(2)⋯O(7) 2.84(1) and N(2)⋯O(4) 3.03(1) Å.

In conclusion a new fluorinated open-framework aluminium phosphate, called ULM-6, has been prepared hydrothermally in the presence of 1,3-diaminopropane. The structure features interconnected 8-ring channels along [100] and [010] in which diprotonated 1,3-diaminopropane is located. This structure offers a new example of the complexity of topologies based on the connection of phosphate groups with trigonal bipyramidal and octahedral entities.

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Paper 8/07731B