The synthesis and structure of two novel layered aluminophosphates containing interlamellar cyclohexylammonium

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The synthesis of aluminophosphates from a nonaqueous tetraethylene glycol–cyclohexylamine medium yields two new layered materials that have been solved by single-crystal X-ray diffraction.

While the synthesis and physicochemical characterization of three-dimensional framework aluminophosphate materials has been an actively pursued area of materials chemistry, only in recent years have the structures of one- and two-dimensionally extended aluminophosphate solids been reported.[1–7] Within the last year, the number of reported aluminophosphate layered structures continued to grow.[8–10]

In the course of our synthetic work on the nonaqueous synthesis of aluminophosphate materials, we have discovered a series of new one-, two- and three-dimensional structures, which we denote UT-*n* (University of Toronto, Structure No. *n*).[11–13] In this report, we focus on the tetraethylene glycol (TEG)–cyclohexylamine synthesis system that has yielded two new crystalline layered aluminophosphates, UT-4 and UT-5.

The materials were prepared from similar synthesis mixtures using slightly different reaction conditions. Continuous stirring was used throughout the preparation of the reaction mixtures. Hydrated alumina in the form of pseudoboehmite (Dispal 23N4-80, Vista) was dispersed in a pre-weighed TEG solvent, followed by the slow, dropwise addition of phosphoric acid (85 mass% H_3PO_4–15 mass% H_2O). Finally, cyclohexylamine (99%, Aldrich) was added, causing the slurry to gel and form an opaque, slightly yellow mixture. The gels were loaded into Teflon-lined stainless-steel autoclaves and treated under static conditions at the synthesis temperature. For UT-4 synthesis, the ideal reaction mixture molar composition is: 14 TEG : 0.9 $Al_2O_3{\cdot}nH_2O$: 1.8 ($P_2O_5{\cdot}4.9H_2O$) : 5.9 $C_6H_{11}NH_2$. The crystalline product was obtained after 4 days at 180 °C. For UT-5 synthesis, the ideal composition of the reaction mixture is: 14 TEG : 0.9 $Al_2O_3{\cdot}nH_2O$: 1.8 ($P_2O_5{\cdot}4.9H_2O$): 3.7 $C_6H_{11}NH_2$, and the material was made at 180 °C in 3 days.

The molecular formula for both structures is $[Al_2P_3O_{12}H]^{2-}{\cdot}2[C_6H_{11}NH_3{}^+]$. The materials are built of inorganic anionic layers that contain tetrahedral Al and P centres connected through bridging oxygens and separated by double layers of cyclohexylammonium cations. As observed in the optical and scanning electron microscope images, the crystals of UT-4 are elongated hexagonal plates, while those of UT-5 are thinner rectangular plates. The UT-5 crystals have a thickness of < 100 μm, but their millimetre size in other dimensions allows the structure to be solved by single-crystal X-ray diffraction (SC-XRD).‡

By varying conditions such as time, temperature, and reagent amounts of water, other new phases may be prepared from the same synthesis mixture. Also, by changing the above parameters, the relative amounts of phases in the product mixture can be altered. For example, under the conditions given above, a small amount of UT-4 or UT-5 will coprecipitate, judging by the powder X-ray diffraction (PXRD) patterns of the products (Fig. 1, Ni-filtered Cu-Kα radiation, λ = 1.54178 Å). Performing the UT-4 synthesis given above at 200 °C rather than 180 °C, gives approximately an equal yield of UT-4 and UT-5 by mass, as evidenced by PXRD data. It is possible that the indexed PXRD pattern of UT-4 is identical to that of a reported unknown aluminophosphate obtained from an aqueous cyclohexylamine system.[14]

The layer architecture of UT-4 may be thought of as a two-dimensional net of three-connected Al and P centres. Rows of edge-sharing six-rings of T atoms (T = Al, P) in an alternating A,B arrangement with respect to the *c*-axis, are connected by four- and eight-rings [Fig. 2(*a*)]. To define a framework $AlPO_4$-*n* material, the fourth vertices of the tetrahedral P and Al centres would be defined by oxygens connecting to the next 'layer'. For UT-4, however, the P atoms each possess one terminal oxygen as a phosphonyl group [P–O 1.487(4), 1.494(3) Å]. The fourth oxygens of the aluminium tetrahedra are defined by doubly bridging phosphate groups that essentially 'cap' the layers from connecting to an adjacent layer. These phosphate groups reside exclusively on the six-rings, and alternate above and below the plane of the layers with respect to the *z*-axis [Fig. 2(*a*)]. Since they are doubly bridging, they possess two terminal oxygens [P–O 1.494(3), 1.552(3) Å].

The latter O is protonated, which has been resolved by a difference Fourier electron density map. This proton is involved in an intralayer hydrogen bond to an adjacent phosphate group. All of the terminal phosphate oxygens are involved in an intricate hydrogen-bonding network with the interlamellar cyclohexylammoniums. Each O accepts two hydrogen bonds from N–H bonds of the template ammonium head group. The chair-conformation cyclic ammoniums are arranged in a bilayer-like manner, which separate the anionic aluminophosphate layers and define the hydrophobic interlayer region.

UT-5 is isostructural with UT-3, a layered aluminophosphate obtained from the TEG–cyclopentylammonium system.[11] The bilayer-like cyclic amines reside in the same positions for both

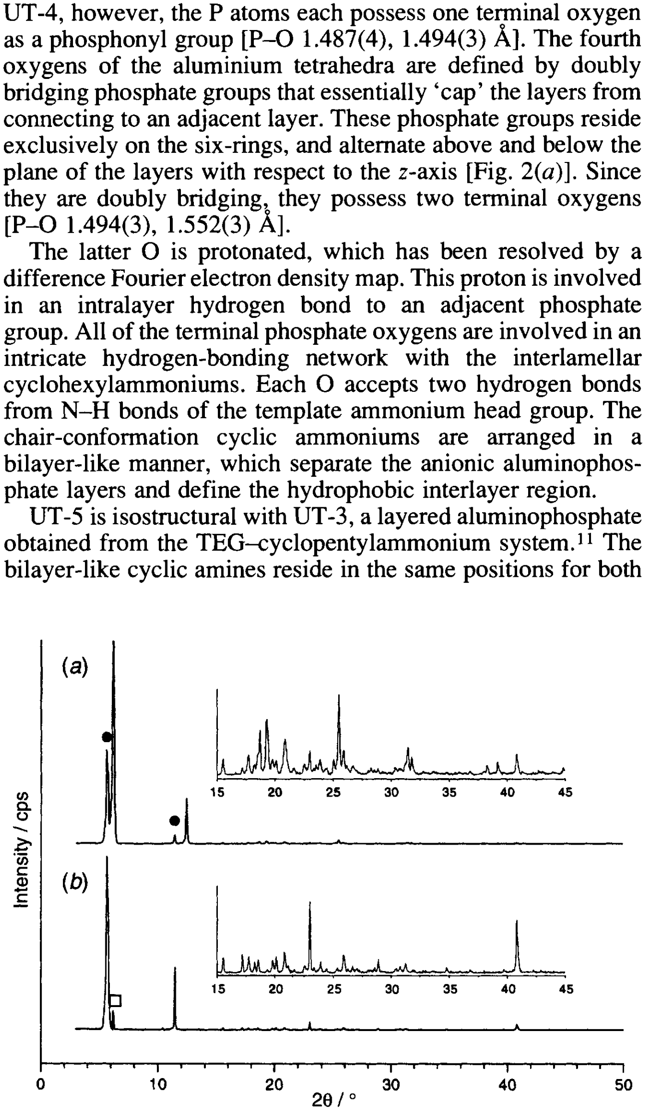

Fig. 1 Experimental PXRD patterns of the two layered compounds. (*a*) UT-4. UT-5 coprecipitates in the product (●); (*b*) UT-5. UT-4 coprecipitates in the product (□). Inset: expanded higher-angle region, showing the large number of peaks observed for each phase.

structures, and are involved in an isostructural hydrogen-bonding network. Not surprisingly, the d_{0k0} peaks in the PXRD of UT-5 shift to lower angles with respect to UT-3, corresponding to the expansion of the unit cell in the *b*-dimension to accommodate the larger cyclohexylammoniums.

UT-5 also consists of a two-dimensional net of alternating, three-connected Al and P centres, where the fourth vertices are occupied by 'capping' phosphate groups and terminal oxygens, respectively [Fig. 2(*b*)]. However, UT-5 contains only six-rings in the layer. Similar to UT-4, the capping phosphate groups alternate above and below the plane of the layers, residing only on six-rings, but the rows of six-rings in this case are connected on opposite sides of the hexagons [Fig. 2(*b*)]. Again, they are singly protonated, as found for both UT-3 and UT-4 [P–O 1.494(3), 1.575(3) Å]. The arrangement of six-rings is the same as for the previously reported $Al_2P_3O_{12}H$ layer,[5] but the capping phosphate groups are of a unique arrangement in the case of UT-4.

Preliminary studies of the properties of these new materials demonstrate that they have moderate thermal stability. TGA and *in situ* high-temperature PXRD show that both materials transform at *ca.* 200 °C to an amorphous layered material with a very similar value of *d*-spacing. Upon further heating, this lamellar phase collapses into $AlPO_4$ tridymite at about 350 °C. High-temperature PXRD experiments also revealed that UT-5 appears to be transforming to a new crystalline phase with the 100% peak at slightly lower *d*-spacing, 14–15 Å. However, both UT-5 and this new phase decompose before the transformation is complete. Further thermal studies under less rigorous conditions may elucidate the transformation of UT-5, possibly to a different or new crystal structure.

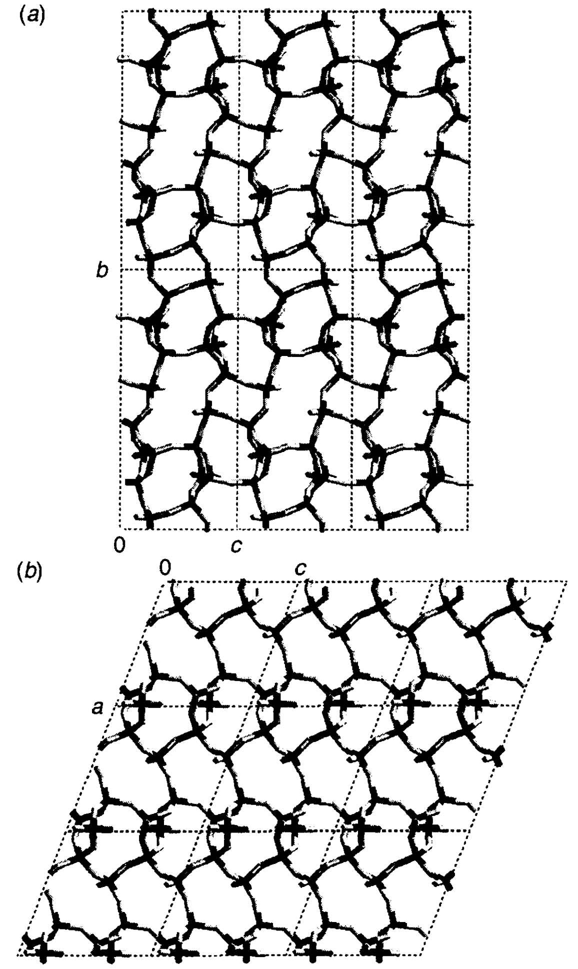

Fig. 2 Cerius™ representations of the two structures. The template cations have been omitted for clarity. Shading scheme: oxygen, white; phosphorus and aluminium, black. (*a*) [100] projection of the UT-4 layer containing four-, six- and eight-rings; (*b*) [010] projection of UT-5. Excluding the doubly bridging phosphates, the layer defines a graphite-like geometry of edge-sharing six-rings.

UT-4 and UT-5 represent novel layered structures in the aluminophosphate compositional domain. The same synthesis system yields several other phases which can be obtained by varying the synthesis conditions. Further study of this and similar systems should readily yield more novel chain, layered and framework crystal structures.

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Footnotes

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‡ *Crystal data*: for UT-4, $C_{12}H_{29}Al_2N_2O_{12}P_3$, M = 540.24, monoclinic, space group $P2_1/c$, a = 14.739(3), b = 18.837(4), c = 8.601(2) Å, β = 105.89(3)°, U = 2296.7(9) Å^3, Z = 4, D_c = 1.562 g cm^{-3}, μ(Mo-Kα) = 3.96 cm^{-1}. Data were collected on an Enraf-Nonius CAD4 diffractometer in the range $5.2 < 2\theta < 52.6°$. 4958 reflections were collected, of which 4637 were unique and 3147 observed independent reflections [$I < 2\sigma(I)$]. Crystal size 0.52 × 0.50 × 0.21 mm, refinement of 284 parameters by full-matrix least squares on F^2; R_1 = 0.0604, wR_2 = 0.1947. For UT-5, $C_{12}H_{29}Al_2N_2O_{12}P_3$, M = 540.24, monoclinic, space group $P2_1/c$, a = 9.104(3), b = 30.848(11), c = 9.004(3) Å, β = 111.17(3)°, U = 2357.9(14) Å^3, Z = 4, D_c = 1.522 g cm^{-3}, μ(Mo-Kα) = 3.86 cm^{-1}. Data were collected on a Siemens P4 diffractometer in the range $5.0 < 2\theta < 50.0°$. 4412 reflections were collected, of which 4137 were unique and 2319 observed independent reflections [$I < 2\sigma(I)$]. Crystal size 0.48 × 0.42 × 0.08 mm, refinement of 279 parameters by full-matrix least squares on F^2; R_1 = 0.0976, wR_2 = 0.2974. 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 182/143.

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