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Synthesis and structural characterisation of a new layered aluminophosphate $[C_3H_{12}N_2][Al_2P_2O_8(OH)_2]\cdot H_2O$

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A new layered aluminophosphate $[C_3H_{12}N_2][Al_2P_2O_8(OH)_2]\cdot H_2O$ has been synthesized hydrothermally by using racemic 1,2-diaminopropane as the structure-directing agent. Its structure, solved by single-crystal X-ray diffraction analysis, consists of $[Al_2P_2O_8(OH)_2]^{2-}$ macroanionic sheets stacked in an ABAB sequence, and diprotonated racemic 1,2-diaminopropane cations lying between the inorganic sheets. Hydrogen bonds exist between the oxygen atoms in the sheets and nitrogen atoms of the diprotonated 1,2-diaminopropane molecules. The as-synthesized product has also been characterised by powder X-ray diffraction, inductive coupled plasma analysis, IR spectroscopy, TGA and DTA.

Introduction

Following the discovery of microporous crystalline aluminophosphates $AlPO_4$-*n*,[1] the rational design and synthesis of microporous materials continue to be an important research subject because these materials have enormous potential as catalysts, ion exchangers, adsorbents and as hosts for host–guest assembly.[2] Most open-framework aluminophosphates whose structures are constructed from alternating AlO_4 and PO_4 tetrahedral units were prepared by hydrothermal techniques.[3,4] However, a large number of novel 1-D chain, 2-D layer and 3-D open-framework aluminophosphates have also been obtained using a non-aqueous solvent as the reaction medium.[5–8] It is known that non-aqueous systems favour the formation of low-dimensional materials whereas in aqueous media three-dimensional compounds are easier to crystallise.[6,9] The organo-templated layered aluminophosphate family not only exhibit rich diversity in both structure and composition, but also help in understanding the role of organic templates in the process of the formation of 3-D microporous aluminophosphate materials.[9,10]

So far, there are a number of aluminophosphate sheets with distinct stoichiometries, and among them are $[Al_3P_4O_{16}]^{3-}$,[11–18] $[Al_2P_3O_{12}]^{3-}$,[19,20] $[Al_4P_5O_{20}H]^{2-}$,[21] $[AlP_2O_8]^{3-}$ [18,22,23] and $[Al_2P_2O_9]^{2-}$.[24,25] Most of the 2-D nets are built up from alternating AlO_4 and $PO_3(=O)$ tetrahedral units with the exception of $[2N_2C_3H_5]\cdot[Al_3P_4O_{16}H]$,[18] $[Al_4P_5O_{20}H]^{2-}$,[21] $[NH_3(CH_2)_2NH_3][Al_2P_2O_9]$,[24] $[NH_3(CH_2)_3NH_3][Al_2P_2O_9]$[24] and $[NH_3(CH_2)_2NH_3][Al_2(OH)_2(PO_4)_2(H_2O)]\cdot H_2O$ [25] which contain five-coordinate Al atoms. Usually, an aluminophosphate with an Al : P ratio of unity possesses a 3-D open-framework structure, and very few aluminophosphates with P : Al = 1 : 1 are of layered structure.[24–26] Furthermore, no large single crystals of organo-templated layered aluminophosphate compounds with Al : P = 1 : 1 have been isolated before the present work.[24–26] Here we report the synthesis and structural characterisation of large single crystals of a new layered aluminophosphate with a P : Al ratio of 1 : 1 by using racemic 1,2-diaminopropane as the structure-directing agent. All the Al atoms in this compound are five-co-ordinated and the racemic 1,2-diaminopropane molecules occupy the interlayer region. It is noteworthy that, unlike most of the low-dimensional templated aluminophosphates reported previously, our compound was formed from a hydrothermal reaction system instead of from a non-aqueous medium.

Experimental

The title compound was synthesized by hydrothermally treating a reaction mixture of aluminium triisopropoxide ($Al(i\text{-}PrO)_3$), phosphoric acid (85 wt%) and racemic 1,2-diaminopropane. A typical synthesis was as follows: a reaction mixture with an empirical molar composition of $Al(i\text{-}PrO)_3 : 2H_3PO_4 : 3NH_2CH_2CH(NH_2)CH_3 : 139H_2O$ was prepared by combining 2.1 g aluminium triisopropoxide and 25 ml distilled water, 1.44 ml orthophosphoric acid (85 wt%) and 2.5 ml racemic 1,2-diaminopropane with continuous stirring. The mixture was stirred until homogeneous, sealed in a Teflon-lined stainless steel autoclave and then heated at 180 °C for two days under autogenous pressure. The resulting large single crystals were collected by filtration, washed with distilled water and dried in air at ambient temperature.

The powder X-ray diffraction (XRD) data were collected on a Siemens D5005 diffractometer with Cu-Kα radiation ($\lambda = 1.5418$ Å). The elemental analyses were conducted on a Perkin-Elmer 2400 element analyser. Inductively coupled plasma (ICP) analysis was performed on a Perkin-Elmer Optima 3300DV spectrometer. A Perkin-Elmer DTA 1700 differential thermal analyser was used to obtain the differential thermal analysis (DTA) curve and a Perkin-Elmer TGA 7 thermogravimetric analyser to obtain the thermogravimetric analysis (TGA) curve in air. The infrared spectrum was recorded within the 400–4000 cm^{-1} region on a Nicolet Impact 410 FTIR spectrometer using KBr pellets.

The single crystal structure was solved by direct methods. The aluminium and phosphorus atoms were first located, and the carbon, nitrogen, oxygen atoms and the hydrogen atoms residing on the amine molecules were found in Fourier difference maps. The full-matrix least-squares refinements were against F^2 and included anisotropic displacement parameters for all non-hydrogen atoms. The SHELXTL program system was used to perform the structure solution and refinement.[27] We have tested the possibility of racemic twinning by refining

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the structure as a twin crystal, and the refinement resulted in the batch scale factor 0.41.

CCDC reference number 186/1967.

See http://www.rsc.org/suppdata/dt/b0/b000685h/ for crystallographic files in .cif format.

Results and discussion

The ICP analysis for the compound gives an Al : P ratio of unity, whereas the element analysis indicates that the contents of C, H and N are 10.31, 4.45 and 8.24%, respectively, corresponding well to the values (9.7, 4.3 and 7.5%) on the basis of the single crystal structure formula (see Table 1).

The powder X-ray diffraction pattern for $[C_3H_{12}N_2][Al_2P_2O_8(OH)_2]\cdot H_2O$ is in good agreement with that simulated on the basis of the single crystal structure (Fig. 1). The diffraction peaks on both patterns correspond well in position, suggesting that the as-synthesized sample is pure. The difference in reflection intensity between the simulated and experimental patterns is due to a certain degree of preferred orientation of the powder sample during data collection.

The IR spectrum of the compound exhibits broad bands at 3165, 3400, and 3614 cm^{-1} due to stretching vibrations of CH_2, water (or OH), and NH_2 groups. The bands at 1540 and 1627 cm^{-1} can be assigned to the bending vibrations of the NH_2 and CH_2 groups. The bands at 2130 and around 2500–2900 cm^{-1} are also characteristic of a diamine in its protonated form.[28,29] The main bands observed in the range of 504–1154 cm^{-1} are associated with the asymmetric stretching and bending vibrations of PO_4 units.[29]

The thermogravimetric analysis shows a major weight loss occurring at about 260 °C accompanied by a distinct endothermic effect (Fig. 2). Following the major weight loss is a gradual one at higher temperatures. The total weight loss of the compound is about 36%, in accordance with the calculated value on the basis of the empirical formula (20.4% for the decomposition of the template, 4.8 and 9.1% for dehydration and dehydroxylation, respectively). The TGA curve exhibits two weight losses: one is about 5% occurring from 50 to 260 °C and the other about 31% appearing between 260 and 700 °C. The former is assigned to dehydration whereas the latter is attributed to the the decomposition of the template and dehydroxylation. The sample calcined in the air at different temperatures was monitored by powder X-ray diffraction. It was shown that the compound heated at 240 °C for one hour retains its structure. It transforms into an amorphous phase after heating at 350 °C for two hours and remains amorphous up to 700 °C, indicating that the structure collapses in the absence of the amine molecules and OH groups occluded in the structure.

A summary of the crystallographic data is presented in Table 1. There are two independent P and two independent Al atoms in the asymmetric unit of the compound (Fig. 3). The P atoms are all tetrahedrally co-ordinated by oxygen atoms. Each Al atom is in a distorted trigonal bipyramid environment formed by O atoms. The two crystallographically distinct P atoms each share three oxygen atoms with adjacent Al atoms and the P–O bond lengths vary within 1.522(3)–1.545(3) Å with the average value being 1.532 Å The terminal P–O bond lengths 1.516(3) and 1.511(3) Å are longer than those (*ca.* 1.49 Å) in other layered aluminophosphates containing terminal P=O bonds;[5,13,31] P–O distances of about 1.51 Å have also been observed in other aluminophosphates such as $AlPO_4$-15,[32] senegalite[33] and berlinite,[34] and in a zirconium phosphate compound.[35] Obviously, the two terminal P–O groups in the present compound do not involve typical double bonds, and they might be regarded as a mixture of P=O and $P\text{–}O^-$ species. The value of the O–P–O bond angle lies within a narrow range (106.77(18) to 111.77(17)°), indicating that the two distinct P atoms lie at the centre of a quite regular tetrahedron formed by

Table 1 Crystal data and structure refinement for $[C_3H_{12}N_2][Al_2P_2O_8(OH)_2]\cdot H_2O$

Empirical formula	$[C_3H_{12}N_2][Al_2P_2O_8(OH)_2]\cdot H_2O$
Formula weight	372.08
T/K	293(2)
Crystal system	Orthorhombic
Space group	$Pca2_1$
a/Å	10.001(3)
b/Å	6.7120(13)
c/Å	18.633(2)
V/Å^3	1250.8(4)
Z	4
D_c/Mg m^{-3}	1.976
μ/mm^{-1}	0.550
Reflections collected/unique	2716/1642 [*R*(int) = 0.0320]
Final R, R_w indices [$I > 2\sigma(I)$]	0.0269, 0.0648
(all data)	0.0306, 0.0667

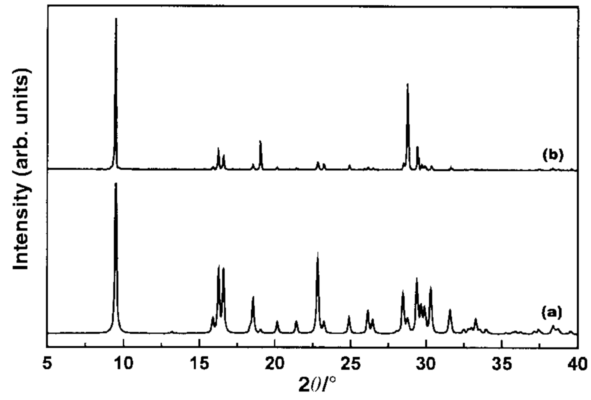

Fig. 1 Simulated (a) and experimental (b) powder X-ray diffraction patterns for $[C_3H_{12}N_2][Al_2P_2O_8(OH)_2]\cdot H_2O$.

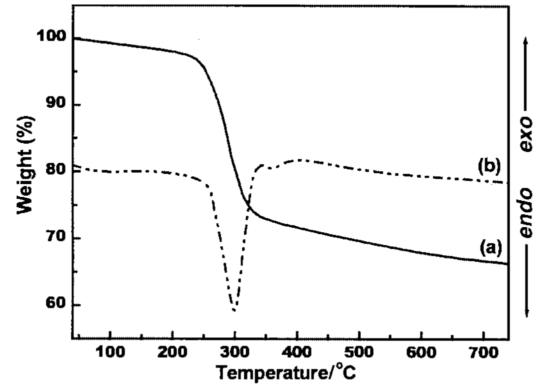

Fig. 2 Thermogravimetric analysis (a) and differential thermal analysis (b) curves for $[C_3H_{12}N_2][Al_2P_2O_8(OH)_2]\cdot H_2O$ in air.

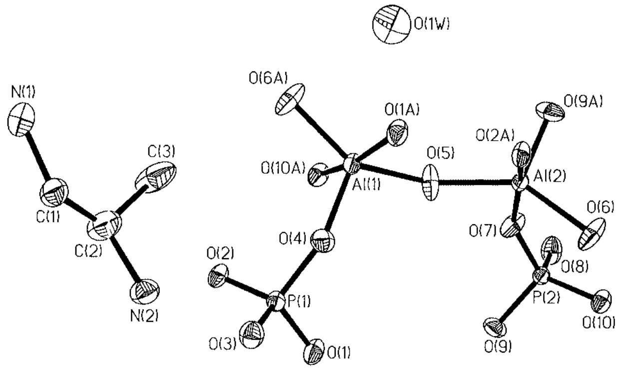

Fig. 3 An ORTEP[30] drawing of the asymmetric unit of $[C_3H_{12}N_2][Al_2P_2O_8(OH)_2]\cdot H_2O$. Thermal ellipsoids are shown at 50% probability.

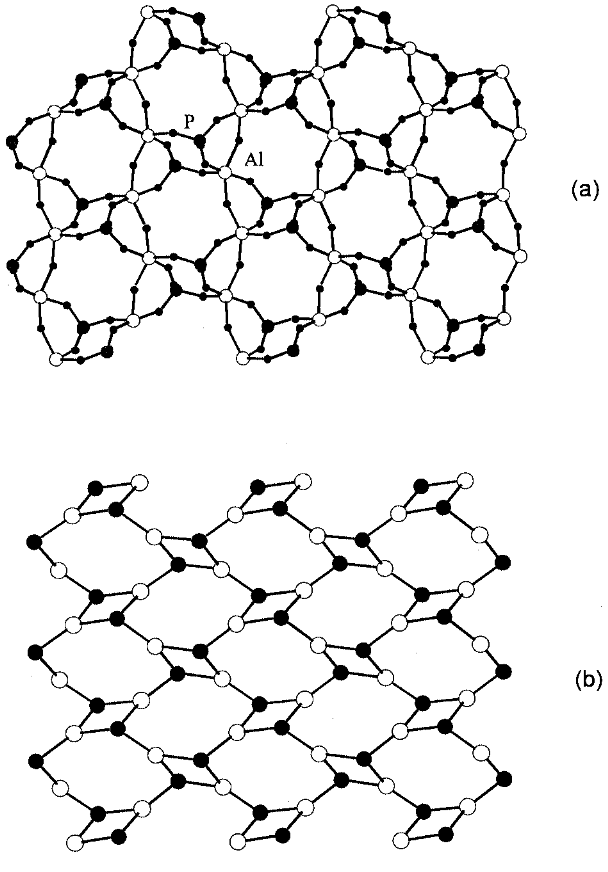

Fig. 4 (a) The structure of an individual layer for $[C_3H_{12}N_2][Al_2P_2O_8(OH)_2]\cdot H_2O$ viewed along the [001] direction. (b) A 3-connected 4.8.8 2-D net formed by removal of hydroxyl groups between Al atoms (O atoms are omitted for clarity).

Table 2 Hydrogen bonds (Å) for $[C_3H_{12}N_2][Al_2P_2O_8(OH_2]\cdot H_2O$

N(1)···O(3)#7	2.838(5)	N(2)···O(3)	2.764(5)
N(1)···O(4)#2	3.020(6)	N(2)···O(8)#9	3.002(5)
N(1)···O(8) # 8	2.740(5)	N(2)···O(8)#10	2.937(6)

Symmetry codes: #2 $x, y - 1, z$; #7 $-x + \frac{3}{2}, y - 2, z + \frac{1}{2}$; #8 $x + \frac{1}{2}, -y, z$; #9 $-x + \frac{3}{2}, y - 1, z + \frac{1}{2}$; #10 $-x + 1 -y + 1, z + \frac{1}{2}$.

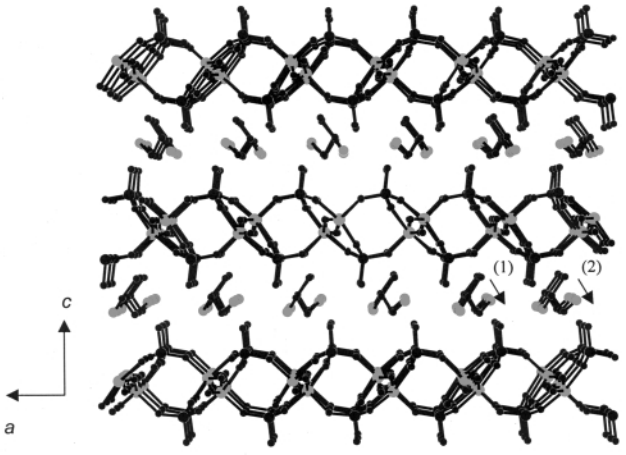

Fig. 5 A view along the crystallographic *b* axis showing the arrangement of template molecules between inorganic sheets with each row of rows (1) and (2) containing a particular enantiomer (dark circle, P; gray, Al; small dark, C; gray; N).

four oxygen atoms. Each of the Al atoms shares three oxygen atoms with adjacent P atoms and two hydroxyl groups with adjacent Al atoms. Bridging OH ligands between two Al atoms have also been found for 3-D open-framework aluminophosphates such as as-synthesized $AlPO_4$-12, -14, -15, -17 and -21.[10] However, of the previously reported organo-templated 2-D layered aluminophosphates few contain OH groups.[25] The Al(1)–O(5) and Al(1)–O(6) distances in the present compound are 1.845(3) and 1.846(4) Å and those of Al(2)–O(5) and Al(2)–O(6) are 1.836(3) and 1.847(3) Å (O(5) and O(6) are the O atoms of the bridging OH groups); other Al–O distances are in the range 1.786(3)–1.858(3) Å.

The structure consists of macroanionic layers of empirical formula $[Al_2P_2O_8(OH)_2]^{2-}$ and diprotonated 1,2-diaminopropane cations located in the interlayer region. In addition, there is one water molecule (occupancy: 0.5) that is disordered in the six-membered ring of the inorganic sheet. Individual layers are formed from a network of distorted trigonal bipyramidal AlO_5 and tetrahedral PO_4 units connected through oxygen bridges (Fig. 4a). The macroanionic sheets are held together in an ABAB stacking sequence, and the terminal P(1)–O(3) and P(2)–O(8) groups alternate above and below the plane of the inorganic sheets. The individual layer contains six-membered rings each of which is surrounded by a series of distorted four-membered rings and three-membered rings generated by linking hydroxyl groups between Al atoms (*i.e.* the layer can be regarded as a 3 × 4 × 6 2-D network). To our knowledge, the known layered aluminophosphates with various stoichiometries consist of 4 × 6, 4 × 8, 4 × 6 × 8, 4 × 6 × 12, 8 × 8 and 4 × 20 2-D networks,[22,36] and only one 3 × 4 × 6 2-D net has been reported previously.[25] By removal of linkages of hydroxyl groups between Al atoms, the structure of the present compound becomes a 2-D three-connected net (each Al atom is connected with three P atoms through oxygen bridges and *vice versa*) (Fig. 4b). Interestingly, the above-mentioned distorted layer arrangement corresponds to a 3-connected 4.8.8 2-D net envisioned in 3-D open-framework aluminophosphates and zeolites such as $AlPO_4$-C, $AlPO_4$-D, $AlPO_4$-15, GIS, MER, ABW and PHI structures.[37] In other words, these 3-D aluminophosphates or zeolites can also be regarded as networks formed by crosslinking of the 3-connected 4.8.8 2-D nets.[38] This is reminiscent of the situation for $AlPO_4$-5, MAPO-46, CoAPO-50 and $AlPO_4$-12 which can be thought of as 3-D networks built up from corresponding $[Al_3P_4O_{16}]^{3-}$ layers by removing the capping-phosphoryl groups followed by crosslinking of the layers through bridging O atoms.[9]

In the organo-templated layered aluminophosphates the macroanionic sheets are held together through hydrogen-bonds in different ways. Therefore, hydrogen-bonds are critical to determining the structural features of these layered aluminophosphates. The bond lengths for the present compound are reported in Table 2. The diprotonated 1,2-diaminopropane supplies H atoms to form hydrogen-bonds with the nearest O atoms in the macroanionic inorganic layers. It is noteworthy that the organic amine molecules exist in either a left-hand or a right-hand form in between the inorganic sheets. They are arranged alternately in two rows with each row containing only one type of enantiomer (Fig. 5), in a way similar to that for $[\text{DL-Co(en)}_3][Al_3P_4O_{16}]$.[14] Recently, we synthesized a new layered aluminophosphate in which racemic isopropanolamine molecules are arranged in a double layer fashion with each layer containing one type of enantiomer between inorganic sheets.[39] Therefore, by variation of recipes and reaction conditions, not only new layer structures can be obtained but also new arrangements of chiral template molecules arise.

Conclusion

The present compound represents a new member of layered aluminophosphates, and it is demonstrated that the use of a chiral amine as the structure-directing agent can result in the formation of layered aluminophosphates with new structural features. By removal of the hydroxyl groups bridging two adjacent Al atoms, the 2-D inorganic net of this compound can be regarded as being constructed from a 4.8.8 net which is related to the 2-D nets in open-framework compounds. Further investigation of the structural relationship between the layered and 3-D compounds may shed light on the formation mechanism of microporous crystalline materials.

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