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Synthesis and structure of an aluminium 3-aminopropylphosphonate sulfate hydrate

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A new aluminium 3-aminopropylphosphonate sulfate hydrate has been prepared using hydrothermal methods, and its structure solved using microcrystal X-ray diffraction at a synchrotron source. The structure consists of one-dimensional chains of aluminium 3-aminopropylphosphonate with sulfate anions occluded between the chains. It is unusual in compounds of this type to have anionic groups between positively charged aluminium phosphonate units. Further characterisation of the compound has been carried out using magic angle spinning NMR.

Introduction

Metal phosphonates ($M(RPO_3)_x$) are a versatile group of compounds due to the possibility of incorporating a wide variety of organic groups into an inorganic framework. Consequently, the properties of the resulting materials can cover a range far more diverse than would be available from their purely inorganic counterparts.

Since metal phosphonates were first reported in a publication by Yamanaka in 1976,[1] most research has been concentrated on a limited number of systems, notably those incorporating Zr, V and Zn as a result of their properties such as charge storage,[2] proton conduction[3–5] and intercalation.[6–8] Interest has also been directed towards their use as non-linear optical materials[9,10] and the fact that it is possible to grow analogues of Langmuir–Blodgett films from some of these phosphonates.[11,12] However, research has largely been restricted to tetra- and di-valent metals. Tetravalent metal phosphonates tend to be layered and porosity can be introduced through diphosphonic acids, which act as pillars.[13] For divalent metal phosphonates there are several known examples of microporous materials[14–18] in addition to a range of layered compounds.

The investigation into aluminium phosphonates started after it was realised that the close relation to the group of aluminium phosphates made them likely to form similar structures. So far, accounts have been published of materials containing methyl,[18–21] carboxymethyl,[22] phenyl,[23–26] benzyl[23,27] and bromobenzyl groups.[23] Two of the methylphosphonates are microporous with a pore diameter of approx. 5.8 Å.[18,19,28] These materials are thermally stable up to 600 °C and show some unusual thermal behaviour in the presence of water.[29] Furthermore, Harvey *et al*. recently reported the preparation of a microporous aluminium ethylenediphosphonate from the pyridine–HF system.[30] This material contains channels with a cross-section of approx. 5.7 Å × 5.3 Å. Apart from the two microporous methylphosphonates and the ethylenediphosphonate, all other aluminium(III) phosphonates have layered structures. They were prepared under either hydrothermal conditions,[18–20,22,25,29] under reflux[24–26] or by melting an aluminium salt together with a phosphonic acid.[21]

In this article, we report the synthesis and full structural characterisation of a new aluminium 3-aminopropylphosphonate phase (AlaPrPO-I). The chain structure occludes sulfate ions that are attached to the framework by hydrogen bonding.

Experimental

Synthesis of aluminium 3-aminopropylphosphonate sulfate hydrate (AlaPrPO-I)

Aluminium 3-aminopropylphosphonate sulfate hydrate was prepared from aluminium sulfate ($Al_2(SO_4)_3{\cdot}18H_2O$, Aldrich, 98%) and 3-aminopropylphosphonic acid (Aldrich, 99%) under hydrothermal conditions. The aluminium to phosphorus molar ratio was varied between 1 : 1 and 1 : 10 and the pH adjusted to values ranging from 2.0 to 7.0. Reactions took place at 160 °C and 150 °C over periods of 3 to 29 days. A typical synthesis (Al : P 1 : 10) was carried out by dissolving 7.2×10^{-4} mol of phosphonic acid and 3.6×10^{-3} mol of aluminium sulfate in 5 ml of deionised water in a Teflon-lined stainless steel autoclave with a volume of 23 ml. The pH value was then adjusted to 3.6 by addition of 0.16 ml of 5 M sodium hydroxide solution and the autoclave closed and heated in an oven at 150 °C for 11 days. After it was allowed to cool down, the crystalline white product was removed by filtration, washed with water and acetone and left to dry in air at 60 °C.

Powder X-ray diffraction data

A powder X-ray diffraction pattern was recorded on a STOE diffractometer with a position-sensitive linear detector covering 6° in 2θ and employing Ge-monochromated Cu-Kα1 radiation (λ = 1.54056 Å). The sample was mounted in a glass capillary in order to reduce any preferred orientation effects, where such are observed. Indexing of the powder pattern was carried out using the program TREOR90 (P.-E. Werner, University of Stockholm, Sweden, 1990).

In addition, high resolution data were collected at room temperature on Station 2.3 of the Synchrotron Radiation Source in Daresbury, Cheshire, UK, using an X-ray wavelength of 1.0011 Å. The sample was mounted in a silica capillary and spun at high speed on a modified STOE spinner.

Single-crystal X-ray diffraction data

Microcrystal X-ray diffraction data were collected at low temperature (160 K) using a Bruker AXS SMART CCD

area-detector diffractometer on the high-flux single-crystal diffraction station 9.8 at CCLRC Daresbury Laboratory Synchrotron Radiation Source, Cheshire, UK. The experiment used X-rays of wavelength 0.68870 Å selected by a horizontally focusing silicon (111) monochromator and vertically focused by a cylindrically bent palladium-coated zerodur mirror. The data set covered more than a hemisphere of reciprocal space with several series of exposures, each series with a different crystal orientation and each exposure taken over 0.15° rotation. Corrections were made for the synchrotron beam intensity decay as part of standard inter-frame scaling procedures.

CCDC reference number 165782.

See http://www.rsc.org/suppdata/dt/b1/b103911n/ for crystallographic data in CIF or other electronic format.

Thermogravimetric analysis (TGA)

The TGA experiment was carried out on a TA Instruments SDT 2960 thermogravimetric analyser. Samples were heated in an alumina crucible, at a rate of 10 °C min^{-1}, to a maximum temperature of 1200 °C, in an atmosphere of flowing oxygen (100 ml min^{-1}). Recalcined aluminium oxide was used as the reference material.

Solid state NMR spectroscopy

^{27}Al, ^{31}P, ^{15}N and ^{13}C MAS NMR experiments were carried out using the EPSRC Solid State Service (Durham) on a Varian Unityplus 300 spectrometer at 7.0 T. All spectra were recorded on 'as-made' samples (*i.e.* there was no isotopic enrichment). Chemical shifts are reported with respect to 1 M aqueous $AlCl_3$, 85% H_3PO_4, CH_3NO_2 and TMS for ^{27}Al, ^{31}P, ^{15}N and ^{13}C spectra respectively. Experimental details for ^{27}Al; frequency 78.157 MHz, acquisition time 20.0 ms, relaxation delay 0.2 s, no. of scans 7600, spin rate 10200 Hz, no decoupling. Details for ^{31}P; frequency 121.421 MHz, acquisition time 20.2 ms, relaxation delay 60.0 s, no. of scans 16, spin rate 10200 Hz, direct polarisation. Details for ^{15}N; frequency 30.399 MHz, acquisition time 20.0 ms, relaxation delay 2.0 s, no. of scans 27456, spin rate 4000 Hz, cross polarisation with flip-back. Details for ^{13}C; frequency 75.430 MHz, acquisition time 15.0 ms, relaxation delay 1.0 s, no. of scans 1312, spin rate 3780 Hz, cross polarisation with flip-back. All experiments were carried out at room temperature.

Microanalysis (CHN analysis)

The CHN analyses were obtained on a Carlo Erba model 1106 elemental analyser.

Results and discussion

Synthesis of aluminium 3-aminopropylphosphonates

The preparation of aluminium 3-aminopropylphosphonates was attempted using four different aluminium sources (aluminium sulfate, chloride, nitrate and gibbsite), but only the use of aluminium sulfate produced any crystalline products. All other reactions yielded clear solutions.

When aluminium sulfate is used, the main product is AlaPrPO-I for most reactions. Powder X-ray diffraction data give an indication that there are another two phases with larger interlayer spacings (*d* approx. 9.5 Å and 15.5 Å for AlaPrPO-III and -II respectively). However, these phases usually occur in mixtures with AlaPrPO-I and could not be further characterised. Samples that consisted of mixtures of phases II and III only showed little crystallinity.

The formation of different phases/phase mixtures was influenced by the pH value at which the reaction was carried out. Reactions at pH 2.0 and 2.5 always yielded pure AlaPrPO-I. Reactions at pH 3.5 tended to yield mixtures of AlaPrPO-I and -II or -I and -III or of all three phases. Reactions between pH 4.5 and 5.5 always led to mixtures between phases I and II or II and III. Reaction mixtures at pH values above 5.5 produced either amorphous materials or clear solutions.

The ratio of aluminium to phosphorus in the reaction vessel seemed to have little influence on the outcome of the reaction. An increase in the reaction time enhanced the crystallinity of the samples and in one case also led to an inversion of the respective relative amounts of two phases in a sample. The reaction temperature did not have any influence on the products. A few experiments carried out under reflux in an increased amount of water did not show any significant differences to similar samples prepared in an autoclave.

The structure of $Al(O_3P(CH_2)_3NH_3)\cdot SO_4\cdot 3H_2O$ (AlaPrPO-I)

Initially, only microcrystalline powders were available from the preparations described above. The unit cell was therefore indexed using TREOR90 and the structure solved by direct methods *ab initio* from the powder X-ray diffraction data using EXPO.[31] Subsequently however, small single crystals (size 0.1 × 0.01 × 0.01 mm) of AlaPrPO-I were recovered from one of the hydrothermal preparations, and data were collected using station 9.8 at the Daresbury Synchrotron Radiation Source. The data collected from a needle-shaped crystal were then used to solve and refine the structure with direct methods and least-square techniques.

The final crystal data for $Al(O_3P(CH_2)_3NH_3)\cdot SO_4\cdot 3H_2O$ (AlaPrPO-I) are: M_r = 315.16 g mol^{-1}, orthorhombic, *Pnma*, a = 10.3082(10) Å, b = 6.2577(6) Å, c = 16.486(2) Å, Z = 4, μ = 0.650 mm^{-1}, 7189 reflections measured between 4.52 and 58.68° 2θ (λ = 0.68870 Å), 1632 unique reflections, of which 1204 were observed according to the criterion that $I > 2\sigma(I)$. The final cycles of least-square refinement against F^2 included anisotropic thermal displacement parameters for Al, P, S, O, N and C atoms. Where possible, hydrogen atoms were placed using geometric methods and their positions recalculated at the end of each cycle of least-squares refinement. Their isotropic temperature factors were calculated based on the carbon atoms they are bonded to. Final agreement factors for the refinement were $R(F^2)$ = 0.0717, $wR(F^2_{obs\ data})$ = 0.1929 and S = 1.073. Fractional coordinates and equivalent isotropic temperature factors for AlaPrPO-I are available from the CIF file.

The asymmetric unit of AlaPrPO-I consists of an octahedrally coordinated aluminium atom and a tetrahedrally coordinated phosphorus atom. The phosphorus atom is connected to three different aluminium atoms *via* its three oxygen atoms. The aluminium is coordinated by three oxygens from three different phosphorus atoms and a further three oxygens from water molecules. The fourth bond of the phosphorus atoms is formed with the carbon of the aminopropyl chain (Fig. 1). The sulfur ion is coordinated by four oxygens (Fig. 2). One of those oxygens forms a hydrogen bond with a neighbouring amino group (distance 2.94 Å).

The overall structure of AlaPrPO-I consists of phosphonate chains along the *b*-axis, with the aminopropyl chains pointing along the *c*-axis. The sulfate groups lie between those chains, each of them close to one NH_3 group (Fig. 2). The chains consist of edge-sharing four-membered ring units in a ladder-like arrangement (Fig. 1). They are made up from alternating aluminium octahedra and phosphorus tetrahedra on each strand, connected by corner-sharing oxygens. The chains are held together by hydrogen bonding and ionic interactions between the positively charged nitrogen and the negatively charged sulfate ion as well as hydrogen bonds between the water molecules and the sulfate ions, and between the water molecules and the nitrogen of the protonated amine.

The symmetry of the X-ray diffraction model is consistent with the data collected from NMR experiments. The ^{27}Al MAS

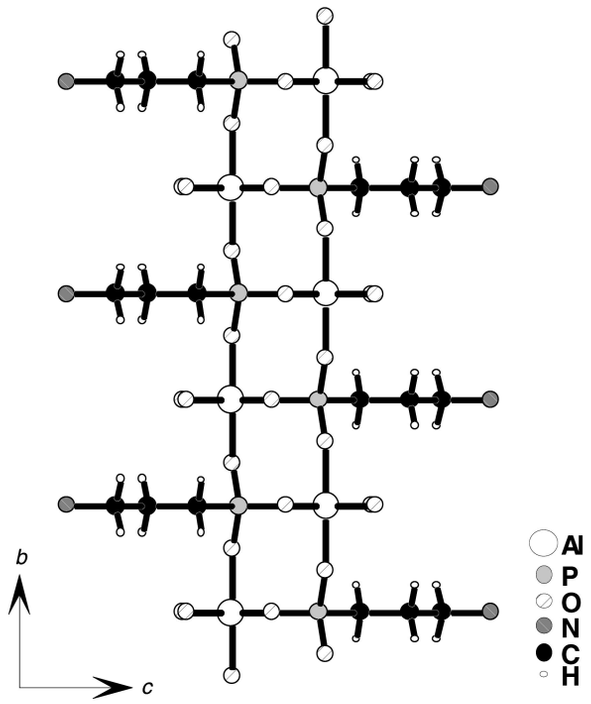

Fig. 1 Ladder-like structure of the AlaPrPO-I chains viewed parallel to the crystallographic *a*-axis.

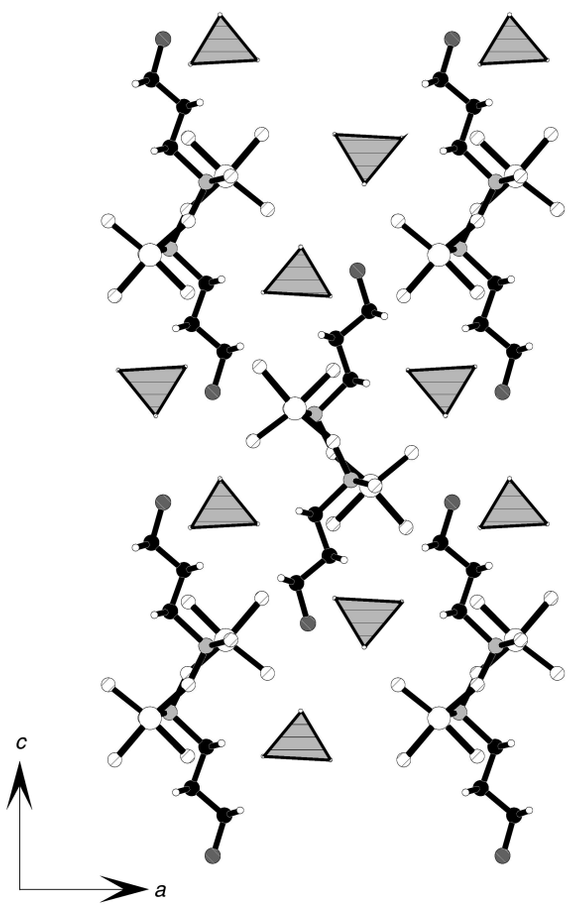

Fig. 2 Arrangement of the AlaPrPO-I chains viewed parallel to the *b*-axis. The sulfate groups are shown as tetrahedra. The assignment of the atoms is the same as in Fig. 1.

NMR spectrum (Fig. 3) shows one aluminium resonance at $\delta = -13.05$. The ^{31}P NMR spectrum (Fig. 4) also indicates only one independent phosphorus atom ($\delta = 6.20$), but there is a small impurity in the sample. The peak in the ^{15}N NMR

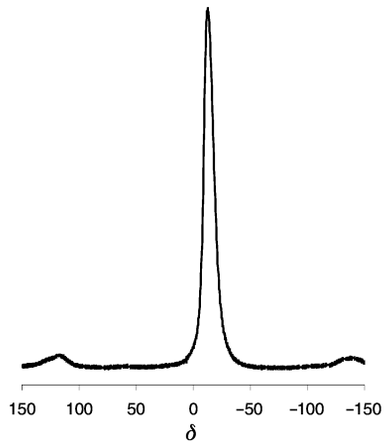

Fig. 3 ^{27}Al NMR of AlaPrPO-I.

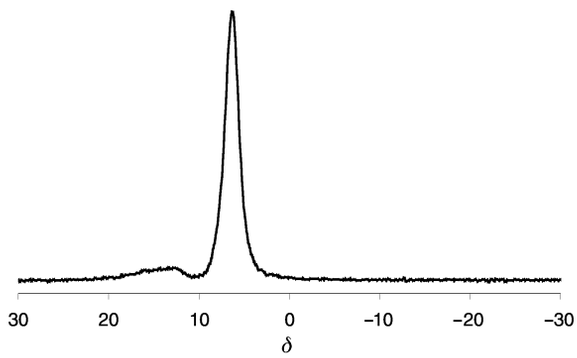

Fig. 4 ^{31}P NMR of AlaPrPO-I. The peak at $\delta \approx 13$ is an amorphous impurity.

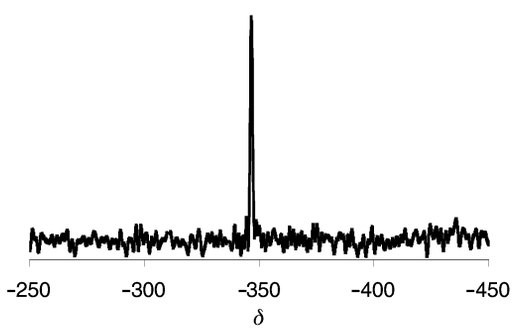

Fig. 5 ^{15}N NMR of AlaPrPO-I.

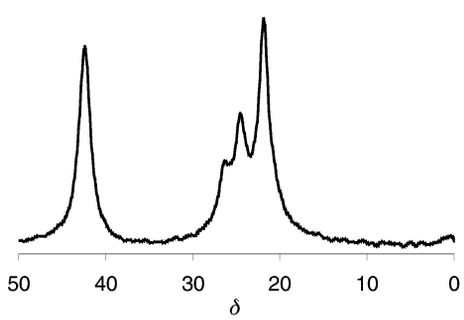

Fig. 6 ^{13}C NMR of AlaPrPO-I.

spectrum (Fig. 5) has a chemical shift of $\delta = -346.6$. This is within the range expected for protonated primary amines ($\delta = -255$ to -355).[32] The ^{13}C NMR (Fig. 6) consists of a singlet at $\delta = 43.40$, a doublet at $\delta = 27.37$ and 25.53 respectively, and another singlet at $\delta = 22.90$. These peaks can be assigned as follows; the singlet that is furthest downfield is caused by the carbon that is deshielded by the nitrogen. The doublet results from coupling of the carbon to the phosphorus next to it. The

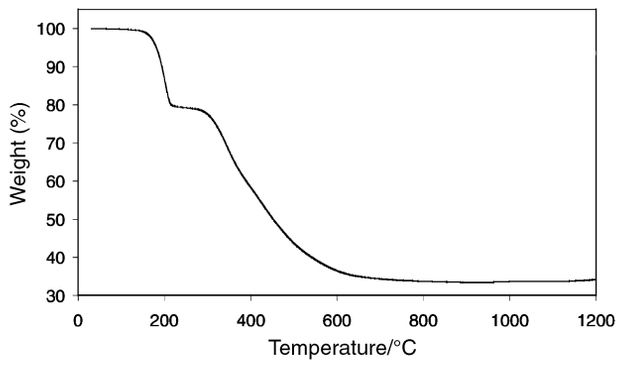

Fig. 7 TGA of AlaPrPO-I under O_2.

remaining singlet is due to the carbon in the middle of the propyl chain.

The results of thermogravimetric analysis are also fairly consistent with the X-ray diffraction structure (Fig. 7). The first step was calculated to be 17.15% for a loss of three molecules of water per formula unit. The observed value (20.69%). For the second step, a weight loss of 45.56% was observed, compared with the calculated 44.16%. The observed value for the residue is 33.75%, compared with a calculated value of 38.69% for one molecule of $AlPO_4$ per formula unit. X-Ray powder diffraction on the TGA residue confirmed it to be aluminium phosphate. The results of the CHN analysis (10.85% C, 4.80% H, 4.14% N) are within 0.6% of the values calculated for $Al(O_3P(CH_2)_3NH_3)\cdot SO_4\cdot 3H_2O$ (11.43% C, 4.80% H, 4.44% N).

The structure of AlaPrPO-I is unusual in that it contains chains of aluminium phosphonate, rather than the much more common layered arrangements. Also unusual, by virtue of the protonation of the amine nitrogen atoms under the acidic reaction conditions, is that the aluminium phosphonate chain is positively charged. Normally in phosphonate chemistry the units are neutral or negatively charged, although there is one example of a positively charged lithium aluminium phosphonate layer.[33]

In aluminium phosphates, the inorganic frameworks also tend to be either neutral or negatively charged (when doped with aliovalent M^{2+} cations or fluoride ions). This allows the use of positively charged structure directing agents to be occluded into the structure. In the case of AlaPrPO-I, the positive charge on the 3-aminopropylphosphonate unit is balanced by occlusion of the negatively charged sulfate group between the chains. This type of synthetic approach leading to positively charged 'framework' aluminium phosphonate species opens up the possibility of using anions of different sizes as 'structure directing agents' in a similar fashion to the use of protonated/quaternary amines in the synthesis of chain, layered and microporous aluminium phosphates.

Furthermore, the inclusion of protonated amino groups enables a wide range of possible subsequent reactions on the material, such as ion exchange, amidation or intercalation. The presence of positive charges on the framework should thereby enable the introduction of negatively charged or polar compounds that could not previously be used in negatively charged or neutral frameworks. This would lead to a further diversification of the range and characteristics of aluminium phosphonates that are available by direct synthesis or through post-synthetic modification.

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