

Synthesis of a family of aluminium benzylphosphonates†

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A family of four aluminium benzylphosphonate phases has been synthesised using hydrothermal methods. The effect of changing the synthetic conditions (starting pH, starting Al:P ratio, aluminium source *etc.*) has been studied and full structural characterisation of two of the phases by NMR, TGA and X-ray diffraction methods has been completed; Al(OH)(O₃PCH₂C₆H₅)·H₂O, monoclinic *P*2₁/*c*, *a* = 14.985(9), *b* = 7.066(5), *c* = 9.613(9) Å, β = 113.9(3)°, and Al₃H(PO₃CH₂C₆H₅)₅·H₂O, monoclinic *P*2₁/*c*, *a* = 17.2497(13), *b* = 25.7851(18), *c* = 9.4339(7) Å, β = 103.567(1)°.

Introduction

Metal phosphonates are a diverse group of solids that display varied and potentially important properties. The fact that the phosphonate group (RPO₃) contains both an inorganic part, which can form part of an inorganic framework, and an organic part, allows the preparation of novel materials. The choice of the organic group, R, can greatly affect the properties of the resulting material. The vast majority of these solids are layered, although there are a number now known that have microporous architectures. Several systems have been under investigation for many years, especially those containing Zr, V and Zn, due to their interesting intercalation,^{1,2} ionic conduction³ and charge storage properties.⁴ There is also interest in their properties as non-linear optical materials.^{5,6} These materials are almost exclusively layered, with the organic groups lining the layers. Microporous solids can be formed from the layers by introducing diphosphonic acids, thus creating a covalently bonded “bridge” between the layers.⁷

Soon after the discovery of the first tetravalent metal phosphonates,^{8,9} research into divalent metal phosphonates began.^{10–17} Like the metal(IV) phosphonates, these materials are generally layered, but there are also examples of microporous compounds, *e.g.* Cu(CH₃PO₃),¹⁸ Pb₃{O₂C(CH₂)₂PO₃}₃¹⁹ and Zn(O₃PC₂H₄NH₂).²⁰ The inside of the phosphonate solids is lined with the organic groups, which leads to a surface with greatly different chemical properties compared to those the purely inorganic compound would have.

Research into aluminium phosphonates has begun only fairly recently. A major reason for studying these materials is the assumption that there are similarities between the phosphonates and the microporous family of aluminium phosphates, and that interesting materials might possibly be prepared in this system. The syntheses of two microporous aluminium phosphonates, AlMePO-α^{21,22} and AlMePO-β,²³ were published for the first time by Maeda and co-workers in 1994 and 1995, respectively. These reports were followed closely by several other publications in the area of aluminium phosphonates.^{24–26} The compounds prepared by Maeda and co-workers have pore sizes in a similar range to that of medium-pore zeolites, such as ZSM-5. Their properties include

thermal stability up to 600 °C and some unusual thermal behaviour in the presence of water²⁷ and they are attracting some interest for applications in catalysis and adsorption processes.

Besides the two microporous aluminium methylphosphonates^{21–23,27} mentioned above and layered aluminium methylphosphonates^{25,28} there are other functionalities that have been introduced into aluminium phosphonates. These include carboxymethyl²⁹ and phenyl groups.^{24,30,31} Most aluminium methylphosphonates were synthesised hydrothermally,^{21–23,25,27} both in the absence and presence of organic molecules, which appear to have some structure-directing influence. The carboxymethylphosphonate²⁹ was synthesised hydrothermally. The aluminium phenylphosphonates were prepared partly under reflux^{24,30,31} and partly hydrothermally.³⁰ A third approach to aluminium phosphonates is by melting a phosphonic acid together with an aluminium salt, either of which ought to have a melting point around or below 100 °C. This concept was employed to prepare other types of aluminium methylphosphonates.²⁸

Work by Cabeza *et al.*³⁰ on aluminium phenylphosphonates illustrated the rich variety of phases that can be prepared hydrothermally. Recently, an article was published by Chaplais *et al.*³² that mentioned the preparation of an aluminium benzylphosphonate with the same molecular formula, Al(OH)(O₃PCH₂C₆H₅)·H₂O, and similar cell parameters to one of the compounds studied here. However, although the authors noted the similarity between the unit cell parameters of this material with those of an aluminium bromobenzylphosphonate they reported in the same paper, no structural information was given. In this paper, we report the results of our efforts to prepare new aluminium benzylphosphonate phases by variation of the reaction conditions, and demonstrate that four phases can be prepared in this way. This synthetic work forms part of a larger project aimed at producing phosphonate materials with different functionality compared to those previously prepared and to evaluate their potential for adsorption and catalytic uses. The influence of the reaction conditions on the resulting phases and phase mixtures is detailed and the full structural characterisation of two of the phases has been carried out by X-ray diffraction.

Experimental

Synthesis of aluminium benzylphosphonates

For the preparation of aluminium benzylphosphonates from benzylphosphonic acid *via* hydrothermal synthesis (adapted

†Electronic supplementary information (ESI) available: powder diffraction data for AlBzPO-I. See <http://www.rsc.org/suppdata/jm/b0/b004177g/>.

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from Maeda *et al.*²³), qualitative and quantitative reaction parameters were varied. The qualitative factor was represented by the aluminium source [gibbsite (aluminium hydroxide), aluminium chloride, nitrate and sulfate]. The quantitative parameters included the Al:P ratio (varied between 1:1 and 1:50), the pH value (1.5, 2.5 or 4.5), the absolute concentration of starting material per autoclave (0.3 g or 1.7 g) and the reaction time (2 to 13 d). The reaction temperature was kept constant at 160 °C. The procedure was the same for the preparation of all samples, *e.g.* the sample containing the AlBzPO-II [$\text{Al}_3\text{H}(\text{PO}_3\text{CH}_2\text{C}_6\text{H}_5)_5\cdot\text{H}_2\text{O}$] single crystals was prepared as follows: 9.6×10^{-3} mol benzylphosphonic acid and 4.8×10^{-4} mol gibbsite were ground together in a mortar and pestle. The mixture was then transferred into a Teflon-lined stainless steel autoclave with a volume of 23 ml and mixed with 10 ml of water. After adjusting the pH to 1.5 with dilute (0.1 M) NaOH solution under stirring and addition of 0.5 ml of acetone, the autoclave was closed and left in an oven at 160 °C for 13 d. The white crystalline product was removed by filtration, washed with water and acetone and dried in air at 60 °C.

Powder X-ray diffraction

Powder X-ray diffraction patterns were recorded on a Phillips diffractometer equipped with a Xe proportional detector and utilising Cu-K α radiation. Patterns suitable for Rietveld refinement were re-recorded on a STOE diffractometer with a position-sensitive linear detector covering 6° in 2 θ and employing Ge-monochromated Cu-K α_1 radiation ($\lambda = 1.54056$ Å). Samples were mounted in a glass capillary in order to reduce any preferred orientation effects, where such are observed. Indexing of powder patterns was carried out using the program Treor-90,³³ and Rietveld refinement carried out using the GSAS³⁴ suite of programs. (See ESI† for details of powder X-ray diffraction study of AlBzPO-I.)

Single crystal X-ray diffraction data

Microcrystal X-ray diffraction data were collected at low temperature (160 K) using a Bruker AXS SMART CCD areadetector 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 0.6944 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 0.2 rotation. Corrections were made for the synchrotron beam intensity decay as part of standard inter-frame scaling procedures.

CCDC reference number 1145/238. See <http://www.rsc.org/suppdata/jm/b0/b004177g/> for crystallographic files in .cif format.

Thermogravimetric analysis (TGA)

The TGA experiments were carried out on a TA Instruments SDT 2960 simultaneous DTA-TGA 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). Re-calcined aluminium oxide was used as the reference material.

Solid state NMR spectroscopy

²⁷Al, ³¹P and ¹³C MAS NMR experiments were carried out using the EPSRC Solid State Service (Durham) on a Varian Unityplus 300 spectrometer. Chemical shifts are reported with

respect to 1 M aqueous AlCl₃, 85% H₃PO₄ and TMS for ²⁷Al, ³¹P and ¹³C spectra, respectively.

Microanalysis (CHN analysis)

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

Results and discussion

Synthesis of aluminium benzylphosphonates

Depending on the synthesis conditions, a variety of different phases can be obtained. The pH, Al:P ratio and aluminium source all have dramatic effects on the nature of the phases produced. Fig. 1 shows the effect of pH and Al:P ratio on the phases prepared from gibbsite. One of the phases was present in all samples, and in a number of cases was the only phosphorus containing product (however some Al-containing starting material was still present in a number of preparations). This phase has been identified as Al(OH)(O₃PCH₂C₆H₅)·H₂O and is referred to as AlBzPO-I. The unit cell of this phase has been indexed and a model for the structure elucidated from the X-ray powder diffraction data (see below). At lower Al:P ratios, phases with increasing phosphorus content are also evident. However, the presence of AlBzPO-I in almost all the preparations as a minor phase complicates the characterisation of these phases considerably and only in the case of Al₃H(PO₃CH₂C₆H₅)₅·H₂O (AlBzPO-II), where small single crystals suitable for X-ray diffraction at a synchrotron source were recovered, was full structural characterisation possible (see below). The mixtures can include two more phases, AlBzPO-III and AlBzPO-IV, identified from their different powder X-ray diffraction patterns. AlBzPO-III is the major phase prepared at low pH and at Al:P ratios between 1:5 and 1:10 and a minor phase at higher phosphorus concentrations. Unfortunately, we have, as yet, been unable to prepare this material either as a pure phase or as single crystals suitable for structural characterisation. AlBzPO-IV has only been observed as a minor phase in combination with AlBzPO-I prepared from synthesis mixtures with starting pH higher than 2.5 and at Al:P ratios around 1:1.

Many of the samples prepared at Al:P ratios between 1:1 and 1:2 also contain pseudo-boehmite [AlO(OH)].

The variety of phases/phase mixtures that can be obtained also depends strongly on the aluminium source. With aluminium nitrate and sulfate, only AlBzPO-I is observed. When aluminium chloride is used, mixtures of AlBzPO-I and AlBzPO-III can be prepared. For aluminium chloride, the phase diagram is similar to the pattern for gibbsite: AlBzPO-III

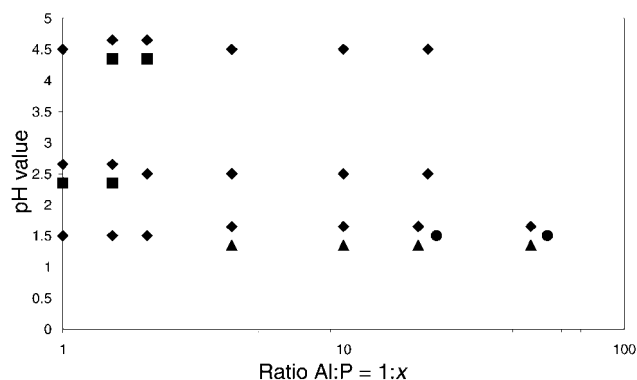


Fig. 1 The phases produced from syntheses of aluminium benzylphosphonates by varying the pH and Al:P ratio of the starting material, all other conditions were kept constant between experiments, as described in the text. The aluminium source is gibbsite in all cases. Key: AlBzPO-I (◆), AlBzPO-II (●), AlBzPO-III (▲) and AlBzPO-IV (■).

can be found in products prepared at pH 1.5 for Al:P ratios between 1:4 and 1:10.

Although the reaction time for most experiments was left constant at 2 d, there seems to be an influence on the composition of the product if the reaction time is increased. Samples with an Al:P ratio of 1:20 and an absolute concentration of 1.7 g of material per autoclave at pH 1.5 were left in the oven for 2, 5 and 10 d. The first and the second sample each yielded a mixture of AlBzPO-III with some AlBzPO-I, whereas the third contained mainly AlBzPO-II accompanied by AlBzPO-III and AlBzPO-I.

The structure of $\text{Al}(\text{OH})(\text{O}_3\text{PCH}_2\text{C}_6\text{H}_5)\cdot\text{H}_2\text{O}$ (AlBzPO-I)

Samples of AlBzPO-I were synthesised as described above, and the small single crystals that were recovered investigated using single crystal X-ray diffraction. Unfortunately however, closer inspection of the thin plates indicated that they were not single, and consisted of very thin lamellar sections, which had grown into one another. A laboratory powder X-ray diffraction data set was subsequently collected and the resulting powder pattern indexed with a monoclinic unit cell; the final refined lattice parameters are $a=14.985(9)$, $b=7.066(5)$, $c=9.613(9)$ Å, $\beta=113.9(3)^\circ$. The systematic absences were consistent with spacegroup $P2_1/c$ (no. 14). Initial attempts to solve the structure *ab initio* using direct methods were unsuccessful. However, the indexed unit cell is very similar in two directions to that for the aluminium methylphosphonate $\text{Al}(\text{OH})(\text{O}_3\text{PCH}_3)\cdot\text{H}_2\text{O}$, solved by Wright *et al.*²⁵ This suggests that AlBzPO-I is layered, with the same layer structure as aluminium methylphosphonate, but with a larger interlayer spacing to accommodate the bulky benzyl group. The atomic positions for aluminium methylphosphonate,²⁵ suitably modified to take into account the difference in interlayer spacing between aluminium methyl and benzylphosphonates, were used as a starting point for Rietveld refinement against the powder X-ray diffraction data. The remaining six carbons of the phenyl group were then located from difference Fourier maps. This process was not straightforward and, despite finding possible positions for the benzyl group, the refinement is not entirely satisfactory. This may be due to some unresolvable disorder in the benzyl group, similar to that seen in AlBzPO-II (see below), or may simply be due to the inherent lack of information presented by powder X-ray diffraction. The refinement was also complicated by the presence of a small amount of non-phosphorus containing impurity that was identified as pseudo-boehmite. Considering these difficulties, it is not surprising that the final refinement required reasonably strong chemical restraints to remain stable. The final Rietveld refinement least-squares cycles led to agreement factors of $R_p=0.100$ and $R_{wp}=0.133$. Because of the need for restraints and the slight uncertainty in the carbon positions, the model proposed here should be regarded as a rough estimate of the benzyl carbon positions rather than a detailed structural determination. However, considering the consistency of the results with the other experimental techniques (see below), and the similarity between the unit cells of AlBzPO-I, aluminium methylphosphonate²⁵ and aluminium bromobenzylphosphonate,³² together with reasonable refinement of the layer itself, leads us to believe that the layered model is indeed a good representation of this structure. To obtain information on the finer details of the structure would require an improved sample and further experiments.

The asymmetric unit contains one crystallographically independent benzylphosphonate group and one aluminium atom. The structure of AlBzPO-I is made up of layers (Fig. 2) that contain chains of *trans* vertex-sharing AlO_6 octahedra, which are linked together into layers by bridging phosphonate units (Fig. 3). The shared vertices of the aluminium-centred

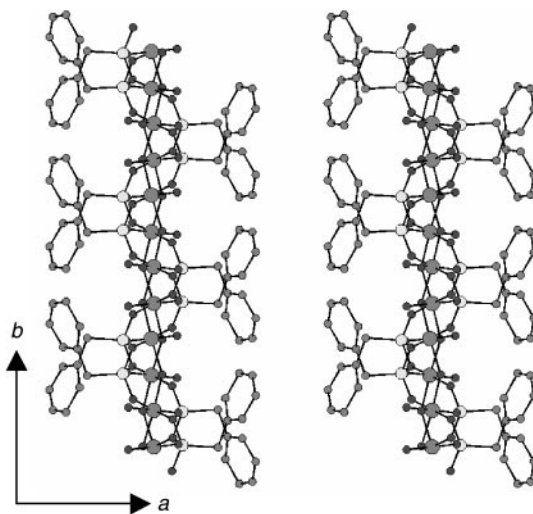


Fig. 2 Proposed structure of AlBzPO-I viewed parallel to the c -axis. Atom identities are as shown in Fig. 6.

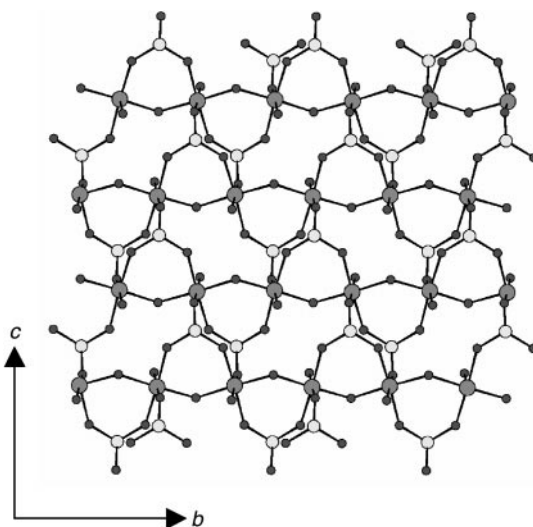


Fig. 3 One of the layers present in the structure of AlBzPO-I viewed parallel to the a -axis. For clarity, carbon atoms of the benzyl groups are not shown. The Al–OH–Al chains run parallel to the b -axis and are linked into layers by bridging phosphonate groups. Atom identities are as shown in Fig. 6.

octahedra are hydroxide. The benzyl groups point into the interlayer region of the structure. The Al–O–Al chains run parallel to the crystallographic b -axis of the structure and the layers are parallel to the ab -plane of the unit cell.

The symmetry of this X-ray diffraction model structure is consistent with NMR experiments. The ^{27}Al MAS and MQM NMR spectra clearly show one octahedral aluminium atom (together with a small amount of a second octahedral site from a pseudoboehmite impurity, which is also just detectable in the XRD experiments). From a simulation of the bands shape, the site was determined to have a quadrupole coupling of 6.4 MHz, an asymmetry of 0.76 and an isotropic chemical shift of $\delta_{\text{Al}} 0.0$. These values are very similar to those for $\text{Al}(\text{OH})(\text{O}_3\text{PCH}_3)\cdot\text{H}_2\text{O}$,²⁵ confirming the similar coordination environment of the aluminium in both materials. There is only one resonance present in the ^{31}P MAS NMR (δ 10.27 ppm) spectrum, indicating only one crystallographically independent phosphorus atom, again consistent with the X-ray structure (Fig. 4a). As expected, the ^{13}C MAS NMR spectrum shows the peaks for the phenyl carbons between 120 and 140 ppm and the resonance for the methylene group as a broad doublet centred at δ 35.96 ppm.

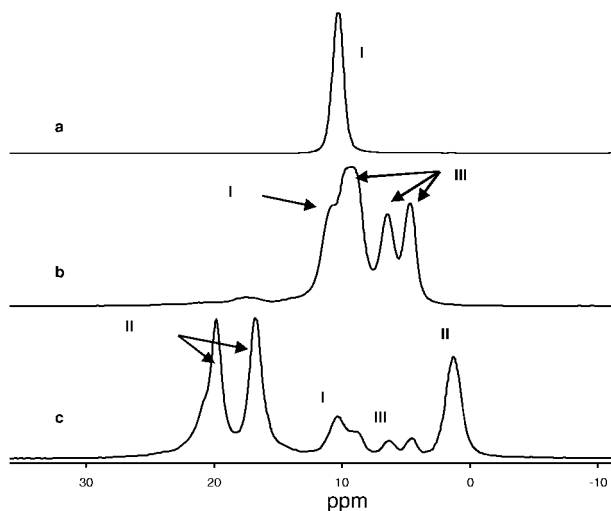


Fig. 4 ^{31}P MAS NMR of: (a) a pure sample of AlBzPO-I, (b) a mixture of AlBzPO-I and -III, and (c) a mixture of AlBzPO-I, -II and -III. Resonances due to each of the phases are labelled.

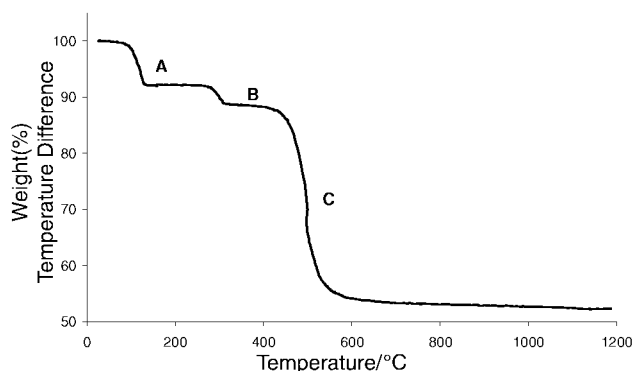


Fig. 5 TGA trace for AlBzPO-I. Individual weight losses A, B and C are described in the text.

Thermogravimetric analysis of AlBzPO-I is also consistent with the X-ray diffraction structure. The mass losses observed in the TGA of AlBzPO-I (see Fig. 5) are within 1% of those calculated for $\text{Al}(\text{OH})(\text{O}_3\text{PCH}_2\text{C}_6\text{H}_5)\cdot\text{H}_2\text{O}$. The three mass losses in the TGA correspond to the loss of one molecule of water per formula unit at 130 °C (A in Fig. 5; observed 7.8%, calculated 7.72%), the loss of half a molecule of water per formula unit (arising from the condensation of two hydroxyl groups; B in Fig. 5; observed 3.7%, calculated 3.88%) at 300 °C and finally, the combustion of the phosphonate groups at 500 °C (C in Fig. 5; observed 35.92%, calculated 35.82%). The mass of the residue corresponds to the value calculated for one molecule of AlPO_4 per formula unit. This is confirmed by the X-ray powder pattern of the residue, which shows it to be a mixture of two AlPO_4 phases. The results of the CHN analysis of AlBzPO-I were also consistent with the formula mentioned above. The observed contents are C 36.33 and H 4.20%. The composition calculated for $\text{Al}(\text{OH})(\text{O}_3\text{PCH}_2\text{C}_6\text{H}_5)\cdot\text{H}_2\text{O}$ is C 36.22 and H 4.34%.

The structure of $\text{Al}_3\text{H}(\text{PO}_3\text{CH}_2\text{C}_6\text{H}_5)_5\cdot\text{H}_2\text{O}$ (AlBzPO-II)

AlBzPO-II was synthesised at relatively low starting Al:P ratios (<1:5) and at relatively acidic pH. Unfortunately, despite numerous attempts, we have been unable to prepare this material as a single pure phase; it is always contaminated to some extent with AlBzPO-I and another phase, AlBzPO-III. However, it was possible to pick out some very small (<20 μm maximum dimension) crystals from some of these mixtures, which were suitable for single crystal X-ray

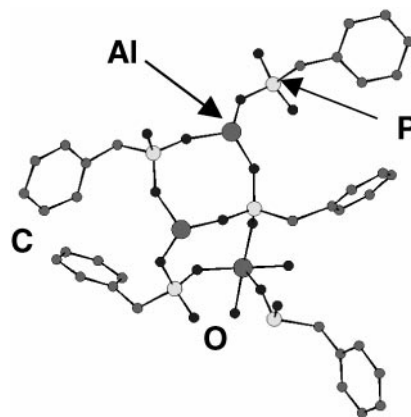


Fig. 6 The asymmetric unit of AlBzPO-II. For clarity, only one orientation for each of the disordered benzyl groups is shown.

diffraction experiments using station 9.8 at the Daresbury synchrotron radiation laboratory. Data were collected on a plate-like crystal of approximate dimensions $15 \times 15 \times 5 \mu\text{m}$, and the structure solved and refined using direct methods and least-squares techniques. The small size of the crystal, even for synchrotron techniques, led to fairly weak data with no appreciable scattering beyond $40^\circ 2\theta$. The paucity of data, together with the disorder that is present in some of the benzyl groups, is probably the cause of the need for restraints on the aromatic rings and thermal displacement parameters, and the fact that the precision on the atomic positions (and consequently the bond distances and angles) is slightly worse than would be expected for a more strongly diffracting crystal. However, the bond distances and angles are of a magnitude expected for a structure of this type.

The final single crystal X-ray diffraction data for compound AlBzPO-II, $\text{Al}_3\text{H}(\text{PO}_3\text{CH}_2\text{C}_6\text{H}_5)_5\cdot\text{H}_2\text{O}$, are: $M_r=950.48$, monoclinic $P2_1/c$, $a=17.2497(13)$, $b=25.7851(18)$, $c=9.4339(7)$ Å, $\beta=103.567(1)^\circ$, $Z=4$, $\mu=0.378 \text{ mm}^{-1}$, 12898 reflections measured between 4 and $40^\circ 2\theta$ ($\lambda=0.6944$ Å), 3800 unique reflections, of which 2389 were observed according to the criterion that $F > 4\sigma(F)$. The final cycles of least-squares refinement against F^2 included anisotropic thermal displacement parameters for Al, P, O 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. The final cycle of refinement also included restraints to ensure planarity of the aromatic rings in the structure, and some light restraints to prevent non-positive definite thermal parameters. Final agreement factors for the refinement were $R(F^2)=0.083$, $wR(F^2_{\text{obs data}})=0.181$, $S=1.197$.

The asymmetric unit of AlBzPO-II (Fig. 6) consists of two aluminium atoms in tetrahedral coordination, and one in octahedral coordination, together with five phosphorus atoms, all of which are present as benzylphosphonate units. Three of these phosphonate units have all three of their oxygen atoms bound to aluminium atoms, while the remaining phosphonates have only two of their oxygen atoms bound to aluminium atoms. The hydrogen atom needed for charge balancing the structure is most likely situated between these two hanging oxygens, which are 2.72 Å apart, a good distance for a hydrogen bond. Two of the five benzyl groups are disordered into two distinct positions that could be resolved in the experiment. A third benzyl group showed significantly larger thermal displacement parameters than the others, probably indicating some unresolvable disorder. The other two benzyl rings show no evidence of disorder.

The overall structure of AlBzPO-II (Fig. 7) consists of unusual undulating layers that run parallel to the bc -plane of the crystallographic unit cell, with the undulations running

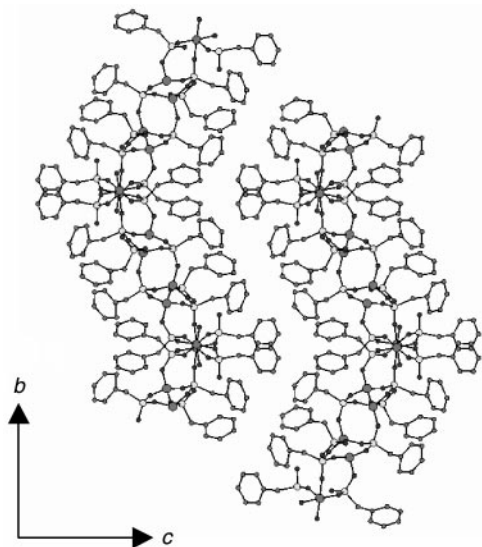


Fig. 7 The undulating layer structure of AlBzPO-II. For clarity, only one orientation for each of the disordered benzyl groups is shown.

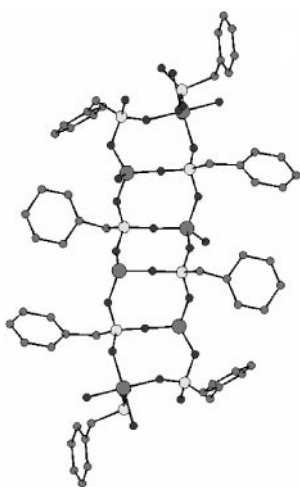


Fig. 8 The four-ring units in AlBzPO-II. For clarity, only one orientation for each of the disordered benzyl groups is shown.

parallel to the *b*-axis. The pitch of the undulations is equal in length to the *b*-parameter (25.785 Å). As in AlBzPO-I, the benzyl groups are oriented towards the interlamellar region. A similar undulating structure has been reported previously for $\text{Co}[(\text{CH}_3)_3\text{CPO}_3] \cdot \text{H}_2\text{O}$.³⁵ The layers themselves consist of small subunits comprising five edge sharing four-ring units in a short ladder-like arrangement (Fig. 8). These units are linked into a two-dimensional array to form the layers (Fig. 9). Unlike AlBzPO-I, the arrangement of aluminium and phosphorus is strictly alternating (*i.e.* there are no Al–O–Al linkages). The water molecule, which is coordinated to the octahedral aluminium, is enclosed within the layer, hydrogen bonding to two oxygens of different phosphonate groups, one of which is a hanging oxygen.

As described above, AlBzPO-II has only been synthesised as an impure sample in combination with two other phases AlBzPO-I and AlBzPO-III, and so analysis of the NMR spectra is complicated. However, the ³¹P resonances of AlBzPO-I and AlBzPO-III can be identified from the spectra of pure AlBzPO-I and the spectra of a mixture of AlBzPO-I and AlBzPO-III (Fig. 4a and b). Discounting these resonances leaves three resolvable peaks at 1.27, 16.79 and 19.75 ppm (Fig. 4c), which is at least not inconsistent with the multiple (five) phosphorus sites expected from the single crystal X-ray

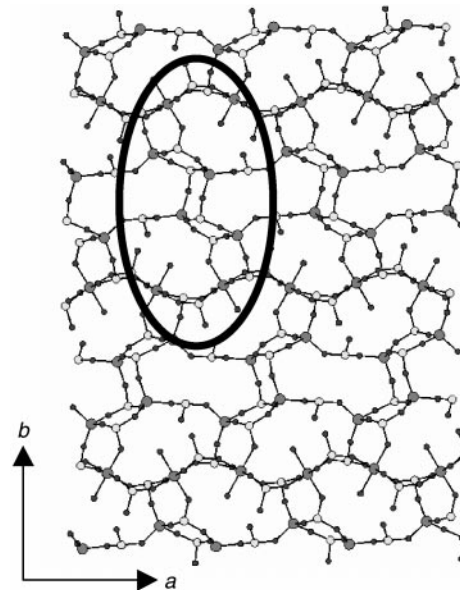


Fig. 9 The inorganic structure of the layers in AlBzPO-II. For clarity, carbon and hydrogen atoms have been omitted. The positions of one of the units shown in Fig. 8 is circled.

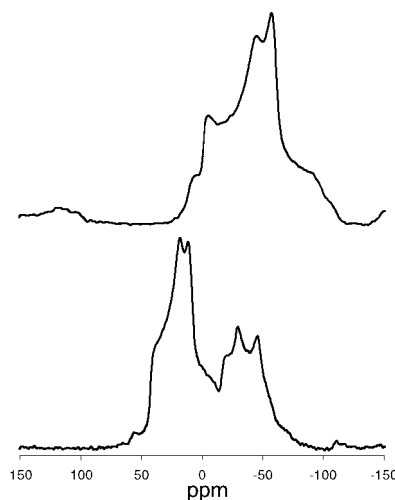


Fig. 10 ²⁷Al MAS NMR spectra for AlBzPO-I (top) and a mixture of AlBzPO-I and AlBzPO-III (bottom). The top spectrum can be modelled as one octahedral aluminium site, in accordance with the proposed X-ray structure, while the bottom spectrum shows clear evidence of both tetrahedral and octahedral aluminium species.

diffraction study. The ¹³C spectra show the expected broadening of signals when compared with the spectra of AlBzPO-I, while the complicated ²⁷Al MAS and MQM NMR spectra show the presence of multiple aluminium environments, with both octahedral and tetrahedral resonances visible.

AlBzPO-III and AlBzPO-IV

Since no pure phase or single crystal materials are available for AlBzPO-III, structural conclusions can be based only on NMR data. The ³¹P NMR spectrum of a mixture of AlBzPO-III and AlBzPO-I (Fig. 4b) shows three resonances at 4.64, 6.45 and 9.17 ppm (from AlBzPO-III), and a low field shoulder at about 10.3 ppm that can be identified as resulting from AlBzPO-I. This indicates that there are at least three crystallographically independent P atoms present in the structure and, since the peak at 9.17 ppm seems significantly broader than the others, it may be that there are more than three. The ²⁷Al spectra show clear evidence of the presence of

both octahedral and tetrahedral aluminium (Fig. 10). Since AlBzPO-I contains only octahedral Al, we can conclude that AlBzPO-III has tetrahedral Al and possibly some octahedral. The fact that it is synthesised from mixtures with high P concentrations, but not as high as AlBzPO-II, means that it is certainly possible that the Al:P ratio in the solid is somewhere between 1:1 and 3:5 (the Al:P ratios of AlBzPO-I and -II, respectively). In the case of AlBzPO-IV, which is only ever found as a very minor phase, it is difficult at the moment to draw any conclusions on its composition and structure. Further work is continuing in an attempt to synthesise and characterise these two phases.

Conclusions

The aluminium benzylphosphonate family shows a richness of the same type as the aluminium phenylphosphonate family previously prepared by Cabeza *et al.*³⁰ However, it seems that it is extremely difficult, at least under the synthetic conditions we have so far attempted, to produce these materials as pure phases. This, of course, affects the ease with which characterisation of the various phases can be accomplished, especially in the absence of single crystals large enough for routine laboratory X-ray diffraction experiments. In this work, we have reported two rather difficult structural elucidations, one from powder X-ray diffraction data on an impure sample, and one on a very small single crystal that required the use of synchrotron radiation. By comparing the results from the X-ray diffraction data with NMR spectra and TGA traces we have ascertained that the models we have found are consistent with the diffraction models. In order to fully complete the characterisation of all the phases it is necessary to, at the very least, find synthetic conditions where single crystals can be grown. This task is made somewhat easier by the availability of single crystal diffraction facilities at synchrotron sources, such as Daresbury in the UK, where the lower limit of crystal size is dramatically reduced compared with laboratory instruments. However, the real goal of synthesis would be to prepare pure samples of phases, whereupon structure–property relationships could be better studied. Further work on this family of materials is needed in order to establish if the synthesis of pure phases is at all possible, *e.g.* by variation of the reaction temperature, for aluminium benzylphosphonates. This work is continuing.

In summary, we have prepared a family of aluminium benzylphosphonates, and structurally elucidated two of the materials using X-ray diffraction techniques.

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