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Ab initio structure solution of a novel aluminium methylphosphonate from laboratory X-ray powder diffraction data†

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A novel aluminium methylphosphonate, with unit cell composition $[Al(OH)PO_3Me{\cdot}H_2O]_4$, has been prepared hydrothermally; the structure consists of parallel chains of aluminium–oxygen octahedra linked *via* bridging oxygens and methylphosphonate groups to give inorganic sheets partially covered on both surfaces by methyl groups.

The structure solution from laboratory X-ray diffraction (XRD) data of the large number of inorganic solids available only as microcrystalline powders remains an important challenge, particularly for those composed of microporous frameworks or inorganic layers. Considerable success has been achieved *via* model-building approaches,[1,2] especially when supplemented by structural data from other sources. It has also been shown that structures of moderate complexity can be solved *ab initio* using direct methods from powder diffraction data. Success in solving structures from powder data was first achieved with the high resolution available at synchrotron sources,[3] and more recently high resolution laboratory X-ray sources have been shown to be of sufficient quality.[4–8] We describe in this communication an *ab initio* structure solution of a novel aluminium methylphosphonate using laboratory X-ray data. Metal alkylphosphonates, where the metal may be di-,[8,9] tri-[10] or tetra-valent,[11,12] are a diverse group of solids that display varied and potentially important adsorption and catalytic properties. Most such solids are layered structures, although recently aluminium methylphosphonates with microporous frameworks have been reported.[13,14] The aluminium methylphosphonate structure given below is the first reported layered material of this composition, and further broadens the range of structure types in the metal alkylphosphonate family.

Multinuclear NMR of $Al(OH)PO_3Me{\cdot}H_2O$‡ is consistent with the structure derived from XRD data.§ Phosphorus gave a resonance at δ 13.55 that is within the range of phosphorus resonances observed for other aluminium methylphosphonates.[13] Aluminium gave an asymmetric peak characteristic of a quadrupolar nucleus in a distorted octahedral environment.[22] The crystal structure shows the aluminium surrounded by a distorted octahedron of oxygens with a maximum deviation of 8° in the O–Al–O bond angles. Fitting of the peak shape gave an asymmetry parameter of the electric field gradient of 1.0, a quadrupolar coupling constant of 5.86 MHz and an isotropic chemical shift of δ −0.16. The carbon signal was a doublet (J = 139.5 Hz) of chemical shift δ 15.23. Both the splitting and the chemical shift are within the ranges observed for other aluminium methylphosphonates.[13,14] Infrared spectroscopy reveals two sharp peaks at 3480 and 3650 cm^{-1} which may be assigned to O–H stretches. There is also a broad peak, characteristic of an H-bonded O•••H stretch, with a maxi-

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† *Supplementary data available* (No. SUP 57155, 4 pp.): NMR spectroscopy data, atomic coordinates, thermal parameters, profile parameters and bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

‡ The compound $Al(OH)PO_3Me{\cdot}H_2O$ was synthesised under hydrothermal conditions from a homogeneous gel made from aluminium hydroxide hydrate (Aldrich), methylphosphonic acid (Avocado) and water mixed in the ratio 1:1:40 and kept at 160 °C for 50 h. Upon filtering, washing and drying a colourless crystalline powder was obtained containing irregular hexagonal plate crystals *ca.* 0.03 mm across. Powder X-ray diffraction was performed on a STOE diffractometer with a linear position-sensitive detector covering 6° in 2θ and employing Ge monochromated Cu-Kα_1 radiation (λ = 1.540 56 Å). Samples were prepared by mounting between two sheets of milar as rotating discs in the X-ray beam. Carbon-13, ^{31}P and ^{27}Al NMR were performed using Magic Angle Spinning (MAS) on a Bruker 400 MHz spectrometer. Infrared spectra were recorded on a wavelength dispersive instrument, and the sample prepared as a suspension in Nujol mull. Thermogravimetric analysis was performed from 30 to 600 °C at 10 °C min^{-1} and X-ray fluorescence analysis was performed using a Philips PW 1450/20 X-ray spectrometer using Rh-Kα (λ = 0.613 279 Å) radiation.

§ The X-ray powder diffraction pattern was indexed using the Visser indexing package,[15] giving a monoclinic unit cell with a = 9.474, b = 7.07, c = 7.865 Å and β = 106.6°. Systematic absences indicated the space group to be $P2_1/a$. Subsequent data analysis, structure solution and Rietveld[16] structure refinement were performed using both the GSAS package[17] and the structural modelling routines within the INSIGHT software[18] and also the SIRPOW direct methods program.[19] Reflection intensities were extracted from the diffraction pattern, using the method of Le Bail,[20] and SIRPOW used in default mode on these data to examine the ranges 10–60, 10–70 and 10–80° in 2θ. (Although extending the data range should help the statistics of the process, the increased peak overlap at higher scattering angles reduces the reliability of individual extracted intensities.) The resulting sets of suggested atomic positions were input to INSIGHT and assessed using a Silicon Graphics terminal display. It was possible to assign electron density peaks directly to Al, P and 3O atoms. Bond distances expected for octahedral aluminium and tetrahedral phosphorus (as indicated by MAS NMR) were given soft constraints and the atomic positions refined to convergence. Fourier-difference maps were used to find the remaining oxygens and the methyl carbon. Thermal parameter refinement revealed a negative value for the non-bridging oxygen attached to Al. A Fourier-difference map suggested the presence of hydrogen atoms around this oxygen. Subsequently, modelling and soft constraints were used to determine and refine hydrogen positions whilst keeping the bond distances and angles realistic. This resulted in a marked improvement in the thermal parameter refinement of the non-bridging oxygen atom which was taken to belong to a water molecule. The refinement of a preferred orientation resulted in a negligible change in the quality of the fit and has been neglected. All soft constraints other than O–H and C–H bond lengths (1.03 and 1.07 Å respectively) were removed for the final profile fit resulting in a refinement of 63 variables. The resulting unit-cell composition was not charge balanced, and bond valence sum calculations[21] on an oxygen bridging two aluminiums suggested a proton should be attached to this oxygen. This gives a final unit-cell composition of $[Al(OH)PO_3Me{\cdot}H_2O]_4$. The ratio of aluminium to phosphorus was as determined by X-ray fluorescence measurements (32.54 weight % Al_2O_3 and 44.39 weight % P_2O_5, corresponding to an Al:P ratio of 1:1.02). The final profile fit is shown in Fig. 1 and atomic positions, thermal parameters and profile coefficients have been deposited (SUP 57155).

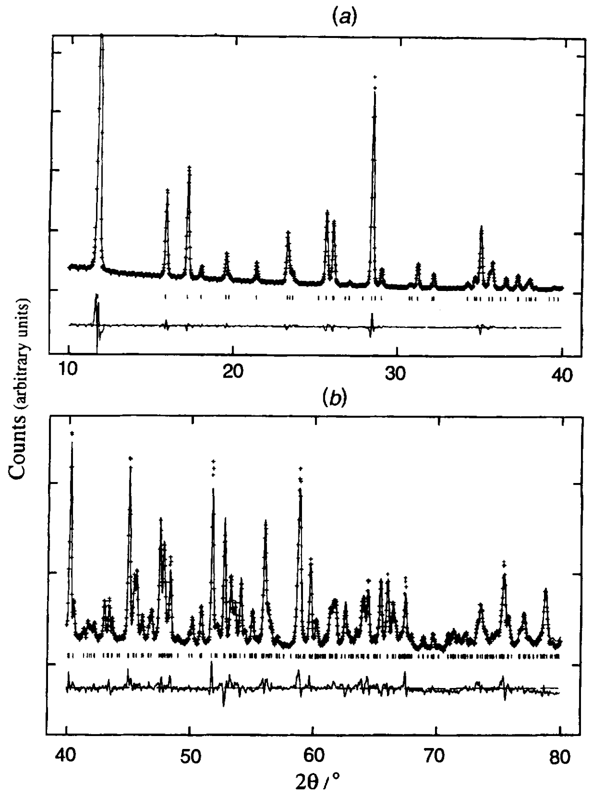

Fig. 1 Final Rietveld profile fit (λ = 1.540 56 Å) of the laboratory X-ray powder data collected on AlMePO over the ranges (*a*) 2θ 10–40° and (*b*) 2θ 40–80°, with experimental data (crosses) and calculated profile (unbroken line) on the same axes, and a difference plot below. The fit has χ^2 5.4 and a weighted profile *R* factor (R_{wp}) of 7.85%

mum at *ca.* 3300 cm^{-1}. However, the details of the H-bonding interaction indicated by the broader peak are unclear and it should be noted that considerable uncertainty in the H positions is to be expected.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) gave two incompletely separated endothermic processes with DTA maxima at 325 and 370 °C and losses in mass of about 12.5 and 5.1% respectively. Loss of bound water from the structure gives a theoretical mass loss of 11.6% so the first process is likely to be desorption of this water. The second event is envisaged to be a dehydroxylation removing half of the hydroxyls completely and hydrogen from the other half, thus releasing two molecules of water per unit cell. The total mass loss of the two suggested processes comes to 17.6% compared with 17.4% observed. Heating the material to 600 °C renders the sample amorphous.

The AlMePO structure [Fig. 2(*a*) and 2(*b*)] is made up of layers which contain chains of AlO_6 octahedra, crosslinked by phosphonate groups, the methyl groups of which point upwards and downwards from the inorganic sheet. The chains of corner-sharing AlO_6 octahedra run parallel to the *b* axis; the aluminium methylphosphonate layers are stacked obliquely along the *c* axis.

Each chain of octahedra consists of a quasi-linear array of aluminiums linked by bridging hydroxide groups, with Al–O–Al angles of 140° and Al–Al distances of 3.54 Å. In addition to these oxygen links, each aluminium is connected to its two nearest neighbours by phosphonate bridges (Al–O–P–O–Al). Moving along a chain, each successive phosphonate group is translated and rotated 180° from the last by the screw axis running through the aluminiums. This results in methyl groups pointing up and down from successive phosphonates. As well as bridging two aluminium octahedra in the same chain, each phosphonate is linked to an octahedron in the chain adjacent. This gives a planar network of stacked chains of aluminium octahedra linked within chains by bridging oxygens and phosphonate tetrahedra and with interchain links comprised only of phosphonates. The lower and upper surfaces of the layers are covered partially with methyl groups. Within the layers there is a cavity in the framework created by a ring of 12 atoms: two pairs of hydroxide-bridged aluminiums and four oxygens and two phosphorus atoms from two linking phosphonates [Fig. 2(*b*)] and making up the octahedral co-ordination of the aluminiums, two water molecules protrude into the cavity.

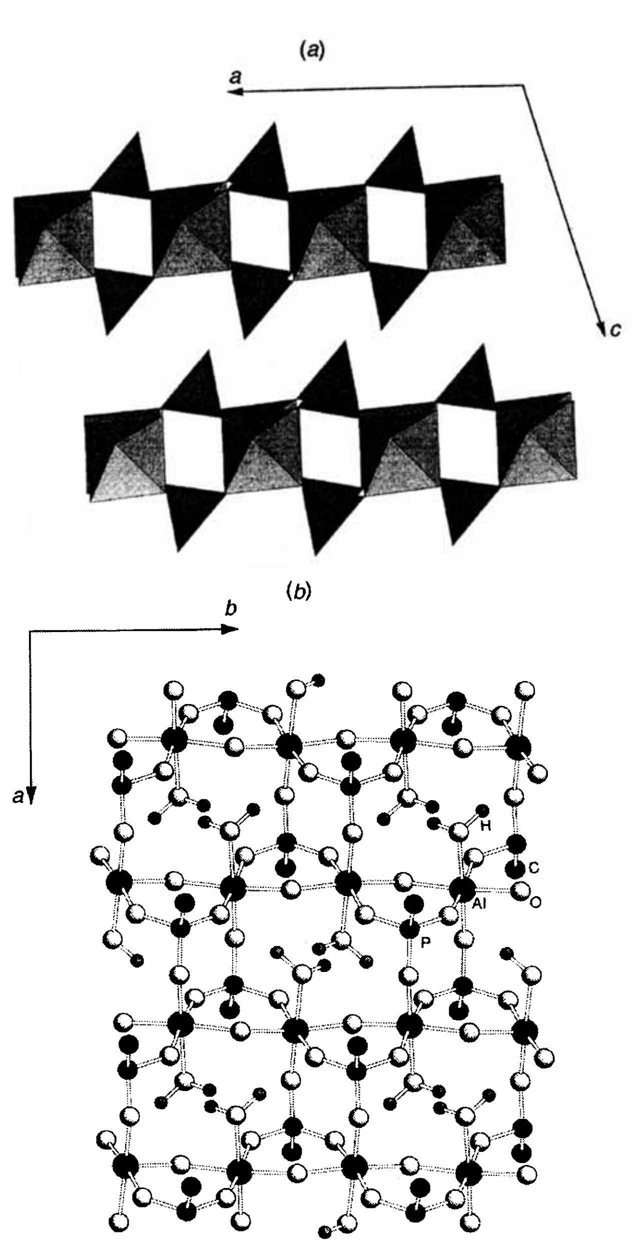

Fig. 2 Representations of the AlMePO structure. (*a*) Viewed along the *b* axis, parallel to the chains of AlO_6 octahedra. Phosphonate tetrahedra point alternatively up and down, so that inorganic layers are 'lined' on both sides with methyl groups (hydrogen atoms have been omitted from the methyl groups for clarity). (*b*) A view onto the inorganic layer in the *ab* plane (protons on the bridging Al–O–Al oxygens have been omitted for clarity). Note the 12-membered ring 'cavity' containing water molecules co-ordinated to Al

The structure has much in common with other layered metal alkylphosphonates but is, to our knowledge, the first such compound in which the metal is aluminium. The capping of the metal–oxygen polyhedra by phosphonate groups resulting in composite inorganic–organic layers is a recurrent feature of these materials. A range of divalent metal phosphonates with

M : P ratios of 1:1 [$M(O_3PMe)\cdot H_2O$, M = Mg, Mn, Zn, Ca or Cd] synthesised by Cao *et al.*[8] exhibited a similar structure type in which layered networks of metal octahedra linked by capping phosphonate tetrahedra are surrounded above and below by the organic group. A related structure is adopted by copper methylphosphonate.[9] The magnesium, calcium, manganese, zinc and cadmium methylphosphonates differ principally from the aluminium methylphosphonate in that they do not contain M–O–M links or hydroxide ions. There are Cu–O–Cu links in the copper methylphosphonate, but the oxygen bridge is not a hydroxide group but the vertex of a bridging phosphonate tetrahedron from an adjacent chain. Also, the copper is five-coordinated and although there are chains of metal atoms linked by bridging oxygens, each chain is made up of edge-sharing square-based CuO_5 pyramids. A possible explanation for the differences in the structures is the difference in valency of the metals coupled with the tendency of Cu^{II} towards Jahn–Teller distortion. The greater valency of aluminium allows the structure to maintain one extra hydroxide group per metal and its bridging action has a great influence on the nature of the structure.

The structure is to our knowledge both the first reported aluminium alkylphosphonate with a layered structure and the first to have an Al : P ratio of 1 : 1. Two microporous three-dimensional framework aluminium methylphosphonates (Al : P 1 : 1.5) have been prepared from similar gels,[13,14] the main difference being the aluminium source. Varying the synthesis temperature and the Al : P ratio in our own laboratory has resulted in several novel aluminium methylphosphonates, the structural characterisation of which is underway.

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