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Structure solution of a novel aluminium methylphosphonate using a new simulated annealing program and powder X-ray diffraction data†

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The structure of a novel layered aluminium methylphosphonate, formula $Al_2(CH_3PO_3)_3$, has been solved from laboratory X-ray powder diffraction data by simulated annealing of five independent structural sub-units, revealing a combination of four- and five-fold coordinated aluminiums within the inorganic lamellae that is unique for this kind of solid.

Organic–inorganic hybrid solids, such as metal phosphonates and carboxylates, can crystallise to give coordination polymers or inorganic layer or framework structures lined with organic groups. These organic moieties can be chosen to dictate the hydrophobicity of internal surfaces (as in the microporous framework aluminium methylphosphonates AlMePO-α and -β[1,2]) or to impart chemical[3] or electronic[4] properties to the solids. The structures of these materials can be considered in terms of linked, well-defined, building units. For metal phosphonates these units are the phosphonate anions, metal cations and additional species (such as hydroxy groups or water molecules) that may be bound to the metal cations or occluded within the pore space. This 'building block' composition suggests that materials of this kind should be amenable to structural solution by the computational real-space manipulation (*e.g.* simulated annealing) of the known sub-units, combined with fitting of X-ray powder diffraction data with the evolving, simulated structure. Such methods have been outstandingly successful for molecular solids[5–7] and one-dimensionally connected polymers[8] but have been successfully applied more rarely for extended lattice structures, although examples of *ab initio* structure solution using simulated annealing[9] (*via* a cost function involving geometric terms in addition to profile fitting) or via a combination of direct methods and simulated annealing[10] or model building and simulated annealing[11] have been reported.

We report here the structure solution of a novel aluminium methylphosphonate that is the third polymorph of composition $Al_2(CH_3PO_3)_3$ to have been prepared, the others being the microporous AlMePO-α and AlMePO-β.[1,2] The new material, designated AlMePO-γ, was prepared *via* a hydrothermal route‡ as colourless crystals large enough but of insufficient quality for structure determination by single crystal diffraction. Individual crystals gave diffraction maxima characterised by streaking rather than well defined spots. A powder X-ray diffraction trace was indexed using the algorithm of Löuer available within the Stoe XPOW software,[12] in a triclinic unit cell, a = 13.2979(7), b = 9.6570(7), c = 5.0725(3), α = 89.601(5), β = 111.242(4), γ = 92.088(4)°.

The contents of the unit cell were determined through a combination of elemental analysis, NMR, thermogravimetric analysis and density measurement. The ratio of aluminium to phosphorus was determined by EDX analysis to be 2 : 3. Solid-state ^{27}Al MAS NMR spectroscopy identified two aluminium signals, at 48 and 19 ppm, characteristic of tetrahedrally and five-fold coordinated aluminium, respectively. The line shapes are also characteristic, the low-field signal displaying a classic quadrupolar splitting of 1.8 MHz and an asymmetry factor, η = 0.3, evident from the line shape. The high-field signal is rather narrow and symmetric, and there is no evidence for an asymmetry factor ($\eta \rightarrow 0$). Quadrupolar splitting in the latter signal is not observed directly, but the linewidth suggests the existence of a small unresolved quadrupolar coupling of 1.2 MHz. The ^{31}P MAS NMR spectrum revealed three signals of equal intensity that correlate to three signals observed in the ^{13}C NMR spectrum (split by a $^1J_{C-P}$ scalar coupling), indicating the presence of three crystallographically inequivalent CH_3PO_3 units. Thermogravimetric analysis showed no weight loss below 600 °C, at which temperature the methyl groups decomposed. This indicates no additional molecules were included within the structure and precludes the presence of hydroxy groups or water. The experimental density was measured to be 1.87 ± 0.03 g cm^{-3}, consistent with a unit cell composition of $Al_4(CH_3PO_3)_6$ (calculated density 1.843 g.cm^{-3}). The NMR observation of two inequivalent aluminiums and three inequivalent phosphonate groups is consistent with the space group being $P\bar{1}$, with the aluminium and phosphorus atoms in general positions.

Initially, structure factors were extracted from the diffraction profile over the d-spacing range 17.5–1.2 Å using the Le Bail method[13] and a direct methods program adapted for powder data (SIRPOW[14]) was used to try to obtain a suitable starting model. However, no obvious partial solution was obtained. The modular nature of the structure suggested AlMePO-γ to be an obvious candidate for application of a new simulated annealing computational approach (FOX), that has been recently made freely available.[15] The FOX program allows molecular fragments to be defined and placed within the unit cell. These are subsequently moved by a series of translations and rotations to produce a model that gives a diffraction profile that best fits the observed pattern (using an index of fit R-factor as a cost function). Initial positions and orientations for the three CPO_3 fragments and positions of the two aluminium atoms within the cell were chosen at random and defined as variables, with soft constraints on the bond lengths and bond angles and with the dihedral angles held fixed. Use of the simulated annealing algorithm within the FOX program produced a model where the aluminiums were located in tetrahedral and trigonal bipyramidal coordination environments. To gauge the robustness of this method, all five fragments were relocated at the origin to prevent the possibility of biasing of the result. The annealing process resulted in the same model. A second more complex strategy of defining five fragments (AlO_4 tetrahedra, AlO_5 trigonal bipyramids and three C–P units) was also tried, using

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† Electronic supplementary information (ESI) available: Tables S1–3: atomic coordinates, bond lengths and bond angles. Figs. S1–3: ^{27}Al MAS, ^{13}C-CP MAS and ^{31}P MAS NMR spectra for AlMePO-γ. Figs. S4–7: Rietveld plots. See http//www.rsc.org/suppata/cc/b2/b200318j/

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both random starting positions and the approach of starting all units at the origin. For each case the same structural model was produced. At this point the model was refined against the X-ray powder profile using Rietveld refinement within the GSAS suite of programs.[16] Soft constraints were placed on P–O bond lengths and hydrogens added and fixed in a staggered conformation. An acceptable fit to the data was achieved with $\chi^2 = 8.87$, $R_{wp} = 10.68\%$, $R_p = 8.09\%$.

The structure of AlMePO-γ consists of 'corrugated' lamellae that run parallel to the *ac* plane (Fig. 1a), from both sides of which methyl groups protrude. The inorganic layers are made up of tetrahedral AlO_4 and trigonal bipyramidal AlO_5 units linked by phosphonate groups. Each aluminium can be thought of as existing as a distinct polyhedral unit, corner-sharing oxygen atoms with CH_3PO_3 groups. Along *a*, four aluminium polyhedra are arranged in the order $Al_{tetr}Al_{fivefold}Al_{fivefold}Al_{tetr}$, the chain is then 'kinked' and the four unit pattern is repeated. In this way the corrugated appearance is achieved. Within the lamellae two arrays of infinite edge-sharing four-rings (a 'four-ring' contains 2 Al and 2 P atoms) intersect to yield 'eight-ring' units (Fig. 1b). The lamellae layers stack along the *b*-axis, with registry of the kinks between one layer and the next.

In order to examine the thermodynamic stability of the structure, and to compare the relative stability of the three AlMePO polymorphs α, β and γ, the lattice energy of the γ polymorph was calculated using a periodic implementation of the semi-empirical Hamiltonian AM1 within program GULP (V 2.0).[17] Coulombic terms were handled using the approach previously used to model successfully the α and β polymorphs,[18] including a short-range cut-off of 12 Å. The minimised energies per formula unit $Al_2(CH_3PO_3)_3$ are: α, -3895.23 eV, β, -3895.10 eV, γ, -3894.65 eV. This indicates that the crystallisation of AlMePO-γ must be favoured over that of α and β under the conditions of this experiment by kinetic rather thermodynamic factors. Indeed, pure AlMePO-α can be prepared directly at 220 °C in preparations where large concentration gradients of reactants are present.[19] The computational energy-minimised model of AlMePO-γ is in good agreement with the refined structure.

The success of the FOX algorithm in solving the structure of AlMePO-γ where programs based on direct methods were unsuccessful underlines the growing opportunities for structure solution of extended layer and framework materials by programs based on real space manipulation of building units with known geometry that are known to be present. Specifically, the solution of AlMePO-γ involved the free movement of five independent structural units that could be defined either in terms of phosphonate units and aluminium ions (with no predetermined knowledge regarding the aluminium coordination) or in terms of aluminate polyhedra (the geometry of which can be tentatively estimated from single and multiple-quantum ^{27}Al MAS NMR) and C–P units. AlMePO-γ is one of the more complex structures to be solved entirely by simulated annealing in this way.

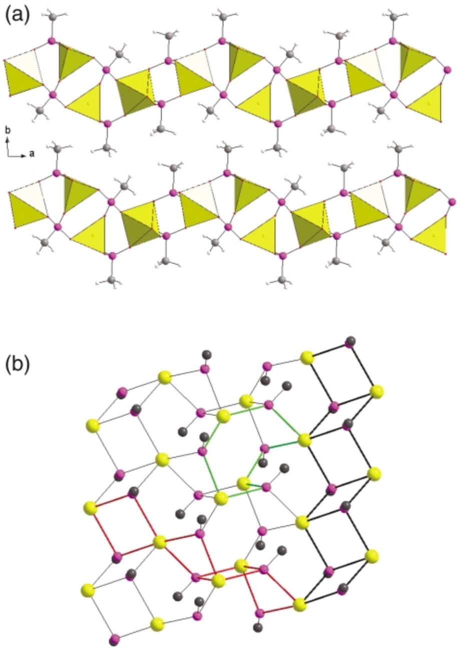

Fig. 1 The structure of AlMePO-γ, (a) displaying the lamellar nature of the material looking along the *c* axis (Al tetrahedra and trigonal bipyramids (yellow), phosphorus (purple) carbon (grey) hydrogen (white)), and (b) displaying the connectivity within the lamellar sheets, omitting oxygen atoms in the latter for clarity, using P–Al links to highlight the chains of edge-sharing 'four-membered' rings (outlined in red and black), that intersect to yield eight-ring units (outlined in green).

Notes and references

‡ *Experimental details*: AlMePO-γ is prepared using a homogenised aqueous gel composition of molar ratio $Al(OH)_3 : CH_3PO_3H_2 : H_2O = 1 : 1.5 : 40$, heated at 220 °C for three days in a Teflon-lined autoclave, filtered, washed and dried in air. (A similar gel composition, when heated at 160 °C and in the presence of dioxane, gives AlMePO-β.)

Crystal data: X-Ray powder diffraction data were collected over 16 h from 5–80° 2θ using a Stoe Stadi/p diffractometer in Debye–Scherrer geometry with the sample held in a 0.7 mm quartz glass capillary. $Al_2(CH_3PO_3)_3$: $M = 336$, $a = 13.282(3)$, $b = 9.643(2)$, $c = 5.066(1)$ Å, $\alpha = 89.601(4)$, $\beta = 111.238(3)$, $\gamma = 92.084(3)°$, $V = 604.4(3)$ Å^3, $T = 298$ K, space group $P\bar{1}$ (no. 2), λ(Cu–Kα_1) = 1.54056 Å, 733 reflections measured. The final R_{wp} was 10.68%. Soft constraints were maintained on P–O, Al–O, P–C bond lengths and thermal parameters of P and Al were constrained to be the same, as were those of O and C atoms. CCDC reference number 179576. See http://www.rsc.org/suppdata/cc/b2/b200318j/ for crystallographic data in CIF or other electronic format.

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