

Synthesis and characterisation of $\text{Al}(\text{O}_3\text{PCH}_2\text{CO}_2)\cdot 3\text{H}_2\text{O}$, a layered aluminium carboxymethylphosphonate

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Microcrystal X-ray diffraction has enabled the structure solution of a layered carboxylate–phosphonate in which aluminium atoms in the same layer are coordinated by both the carboxylic and phosphonic functional groups.

Crystalline inorganic–organic hybrid materials are attracting increased attention because of the possibilities which exist for tuning the chemistry of a solid in order to target a specific property. One class of hybrid solid that has attracted particular attention is the metal phosphonates, which are of interest in many fields of chemistry.¹ Their potential has been recognised in catalysis, ion exchange, charge storage and many other areas and they show great promise for future applications.^{2,3} The vast majority of phosphonates known to date incorporate tetravalent metals, especially zirconium, and divalent metals such as copper and zinc. Surprisingly, it is only recently that aluminium phosphonates have been reported in the literature, with crystal structures for only a handful of aluminium–methyl- and -phenyl-phosphonate solids having been published.^{3–7}

The syntheses and characterisation of carboxylate–phosphonates of zinc,⁸ copper⁹ and cobalt¹⁰ have recently been reported in the literature. In these materials the carboxylic acid group of the phosphonate anion is coordinated to the metal centres contained within the material. Copper and zinc carboxyethylphosphonates^{8,9} have layered structures and the phosphonate groups bridge across the interlayer region in order for the carboxylic acid group to coordinate to the metal centres in an adjacent layer. Coordination is *via* the carbonyl oxygen, and consequently there is a reduction in the observed stretching frequency of the carbonyl, from $\approx 1700\text{ cm}^{-1}$ to 1583 cm^{-1} . Cobalt carboxyethylphosphonate,¹⁰ however, is a three dimensional framework structure, and in this material, it is the deprotonated oxygen atoms that coordinate to the metal centres leaving the carbonyl group as non-bonding. In contrast to this work, Bujoli and co-workers have described the structure determination of a gallium hydroxy carboxyethylphosphonate where the carboxy group is not coordinated to a metal, although they also report a similar hydrated solid, characterised by infrared spectroscopy and solid state NMR, where they propose that the carboxy group coordinates to a gallium atom in an adjacent layer forming a pillared layer structure similar to the copper and zinc phosphonates described earlier.¹¹

This paper reports the synthesis and characterisation, using microcrystal diffraction at a synchrotron X-ray source, of a novel aluminium carboxymethylphosphonate. This structure is different to the carboxyethylphosphonates prepared previously in that the phosphonate unit coordinates to an aluminium and a phosphorus atom in the same layer, rather than bridging across adjacent layers. This difference in structure can be explained by the shorter length of the carboxymethylphosphonate ligand when compared with the carboxyethylphosphonate ligand.

Aluminium carboxymethylphosphonate was hydrothermally synthesised from a gel with composition $\text{Al}(\text{OH})_3$ [gibbsite] (0.53 g): $\text{H}_2\text{O}_3\text{PCH}_2\text{CO}_2\text{H}$ (0.95 g): *n*-butylamine (0.498 g):

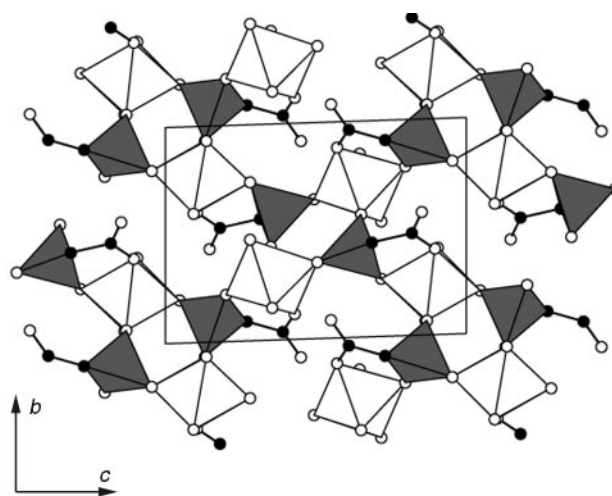


Fig. 1 Projection, perpendicular to one of the layers, viewed in the (100) direction. The AlO_6 octahedra and the CPO_3 tetrahedra are shown as open and shaded polyhedra respectively. Oxygen atoms are shown as open spheres and carbon atoms as filled spheres.

H_2O (15 ml) in the ratio 1:1:1:120. The gel was stirred until homogeneous and heated in a Teflon-lined stainless steel autoclave of 24 ml volume at 160°C for 48 hours. Immediately before heating the gel had a pH of 3.5. Products were recovered by filtration, washed with distilled water and dried in air at 60°C . Inspection of the recovered sample revealed the presence of small crystals amongst a polycrystalline phase.

The crystals were too small for single crystal X-ray data collection using a standard laboratory four circle diffractometer, so diffraction data (crystal size $\approx 30 \times 20 \times 10\ \mu\text{m}$) 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 using a wavelength of $0.6045\ \text{\AA}$. The single crystal structure determination[†] revealed that the material is layered. The composition calculated from the diffraction study, $\text{Al}(\text{O}_3\text{PCH}_2\text{CO}_2)\cdot 3\text{H}_2\text{O}$, is consistent with the microanalysis results (measured 10.99% C, 3.56% H, calculated 11.02% C, 3.69% H).

The structure of $\text{Al}(\text{O}_3\text{PCH}_2\text{CO}_2)\cdot 3\text{H}_2\text{O}$ comprises layers made up from square sub-units formed by coordination of two Al atoms by two oxygens from each of two PO_3^{2-} groups (Fig. 1). The third oxygen from these sub-units then coordinates to an Al atom in an adjacent square to form the basic layer structure. The P–C bonds from the two phosphonate groups in each square, are directed one above and one below the plane of the layer. The C–C bonds are then directed away from the square in which the PO_3^{2-} group is bound and the terminal carboxylate group is then coordinated to an Al atom in an adjacent sub-unit (Fig. 1). This Al atom is the same one to which the cross-linking P–O bond is attached. The octahedral coordination about the

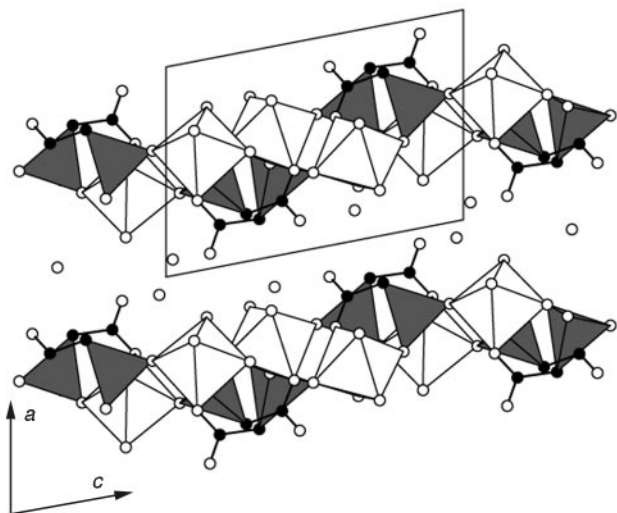


Fig. 2 The layered structure viewed in the (010) direction. The interlamellar water molecules can clearly be seen. The key for atom and polyhedra types is as in Fig. 1.

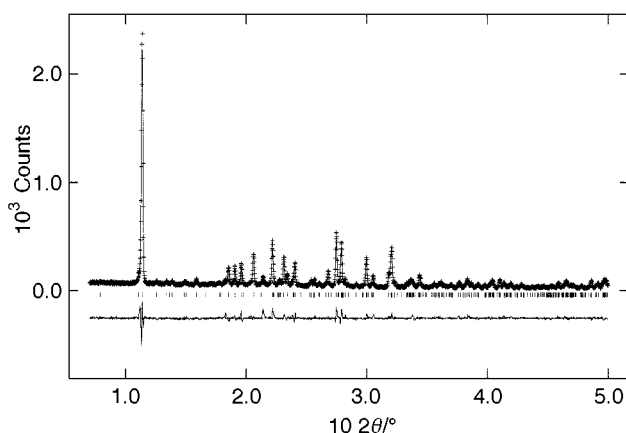


Fig. 3 Final observed (crosses), calculated (solid line) and difference plots for the Rietveld refinement against powder X-ray diffraction data.

Al atoms is completed by two water molecules, one above and one below the plane of the layer. The unbound oxygens of the carboxylate groups are directed alternately above and below the plane of the layer. The two C–O bond lengths from each of the carboxylate groups are in the range 1.248–1.283 Å, values which are between those expected for a C=O bond (1.16–1.21 Å) and a single C–O bond (1.34–1.43 Å), indicating that there is no distinct carbonyl group. The acidic oxygens are fully deprotonated, to leave a carboxylate anion, which is coordinated to the aluminium through one of the oxygen atoms. This observation is consistent with the single crystal X-ray diffraction experiments reported for zinc carboxyethylphosphonates⁷ and is confirmed by the IR spectrum of the material (see below). The layers are held together by hydrogen bonding between water molecules situated in the interlayer region, coordinated water molecules and carboxylate oxygen atoms (Fig. 2). Rietveld refinement of the structural model against powder X-ray diffraction data (Cu-K α , $\lambda = 1.5406$ Å) confirms the structure of $\text{Al}(\text{O}_3\text{PCH}_2\text{CO}_2) \cdot 3\text{H}_2\text{O}$, and verifies that the as-made sample contains only one crystalline phase (Fig. 3).[‡]

Thermogravimetric analysis indicates that there are four stepwise mass losses. The first two, seen at 148 °C and 202 °C are accounted for by the loss of six water molecules. The ratio of these losses is 1:2. This can be rationalised by considering that the lower temperature event is the loss of the two water molecules in the interlayer region, and the higher temperature event is the loss of the two water molecules coordinated to each of the Al atoms (making four in total). There is then a further

loss at 253 °C of approximately 1.93 mass%. This is tentatively assigned as a loss of $1/2\text{O}_2$, arising from a condensation between two carboxylate groups. The final mass loss is centred at 430 °C and corresponds to removal of the organic part of the material to leave AlPO_4 .

X-Ray powder diffraction studies show that removal of the water molecules results in a collapse of the structural integrity of the material. This is not surprising considering that removal of the water will result in a change in coordination number from six to four. It might be expected that the extended interlayer hydrogen bonding would indicate an ability to intercalate organic molecules such as amines. Attempts were made to intercalate *n*-butylamine into the structure both by placing the sample in an atmosphere containing *n*-butylamine vapour, and by contacting the sample with an aqueous solution of the amine. The powder pattern of the samples recovered, however, showed no changes from the profile of the original sample. This seems to underline the importance of the interlayer water molecules in maintaining the structure.

The IR spectrum of aluminium carboxymethylphosphonate contains clear information regarding the nature of the carboxylic acid group and its coordination of the metal centre. The broad peaks observed at 1652 and 1398 cm^{-1} arise from the symmetric and asymmetric stretching mode of the C–O bonds of the carboxy group. This is a lower frequency than one would expect to find for such a band were it to arise from a C=O stretch in an aliphatic carboxylic acid, typically in the region 1725–1700 cm^{-1} . This shift to lower frequency is similar to that seen for zinc carboxyethylphosphonate⁸ where the carboxylate group is coordinated to the zinc through one oxygen. The broad feature in the region 3700–2800 cm^{-1} indicates the large amount of hydrogen bonding in this material, presumably through the interlayer water molecules which are responsible for holding the structure together. The extent of hydrogen bonding is also evident by the width of the carboxylate stretching bands.

The ^{31}P MAS NMR spectrum of aluminium carboxymethylphosphonate indicates the presence of two crystallographically distinct phosphorus environments. Peaks are observed at $\delta -1.8$ and -7.4 , indicating two slightly different P environments, which is consistent with the single crystal data.

In conclusion, this work reports the synthesis and characterisation of an aluminium phosphonate with a novel layered architecture. The structure is unique in that the carboxymethylphosphonate group bridges a phosphorus and an aluminium atom in the same layer. This is in contrast to the carboxyethylphosphonate materials previously reported where the phosphonate ligand bridges a phosphorus and an aluminium in adjacent layers, producing a three dimensional material, or, as in the case of gallium carboxyethylphosphonate, the carboxyl group is not coordinated to a metal. The length of the carbon spacer is obviously important in determining how the carboxyl functional group coordinates. Carboxyethylphosphonates, with two carbon atoms in the chain, are too long to easily bridge neighbouring phosphorus and aluminium atoms in the same layer, whereas carboxymethyl phosphonates, with only one carbon, can.

Acknowledgements

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Notes and references

[‡] Crystal structure determination of $\text{Al}(\text{O}_3\text{PCH}_2\text{CO}_2) \cdot 3\text{H}_2\text{O}$: $M = 218.04$, triclinic, space group $P\bar{1}$, $a = 8.1200(2)$, $b = 8.2536(2)$, $c = 11.2848(3)$, $\alpha = 89.032(1)$, $\beta = 79.231(1)$, $\gamma = 74.733(1)^\circ$, $U = 716.34(3)$ Å³, $Z = 4$, $T = 160$ K, 2986 reflections of which 2337 observed. Final refinement of the 97 least-squares parameters converged to $wR(F^2_{\text{obsd data}}) = 0.23$, $R(F_{\text{obsd data}}) = 0.088$, $S(F^2_{\text{all data}}) = 1.226$. CCDC reference number 186/1156.

‡ Rietveld refinement of $\text{Al}(\text{O}_3\text{PCH}_2\text{CO}_2)_3 \cdot 3\text{H}_2\text{O}$: Stoe STADIP transmission diffractometer in capillary mode. Ge-monochromated Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$). Final profile refinement $R_{wp} = 0.1351$, $R_F = 0.1004$ for 251 reflections in the range $5 < 2\theta < 50^\circ$.

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