

Synthesis and structure of $\text{Li}_2\text{Al}_3(\text{HO}_3\text{PMe})_2(\text{O}_3\text{PMe})_4\text{Cl}\cdot 7\text{H}_2\text{O}$, an ionic, layered lithium aluminium methylphosphonate

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A new layered mixed metal methylphosphonate, which contains interlayer chloride anions, has been prepared by contacting an LDH with molten methylphosphonic acid, and its structure solved using microcrystal X-ray diffraction at a synchrotron source.

It is only recently that aluminium phosphonates have been reported in the literature.^{1–8} The breakthrough was made by Maeda *et al.*, who reported the synthesis of two crystalline microporous aluminium methylphosphonates, $\text{AlMePO-}\beta$ ^{1,2,4,7} and $\text{AlMePO-}\alpha$.³ Subsequently, two layered methylphosphonates,^{7,8} several phenyl phosphonates^{6,9} and a carboxymethylphosphonate¹⁰ have been reported.

A previous attempt at using layered double hydroxides (LDHs) in the preparation of mixed metal phosphonates by Vichi and Alves¹¹ succeeded in introducing both phenyl- and carboxymethylphosphonate groups. The crystal structures of the materials formed were not solved, however, and there was no evidence that the anion initially present in the LDH remained in the products after intercalation of the phosphonate groups.

The overwhelming majority of aluminium phosphonates are formed by hydrothermal syntheses,^{1–7,9,10} with only a few examples prepared by other methods (*e.g.* refluxing^{6,9} or contacting an aluminium source with a molten phosphonic acid⁸). The title compound was synthesised by grinding the layered double hydroxide, $\text{LiAl}_2(\text{OH})_6\text{Cl}\cdot\text{H}_2\text{O}$ ¹² with methylphosphonic acid (such that the Al:P ratio in the reaction mixture was 1:3.5). The mixture was placed in a sealed glass tube and heated at 110 °C (the melting point of methylphosphonic acid is 104 °C) for 5 days. Products were recovered, washed with distilled water and dried in air at 60 °C.

Inspection of the recovered sample under a microscope revealed the presence of small crystals amongst a polycrystalline phase. One of these crystals was removed from the sample and used in a single crystal determination of the structure.

The crystals were too small (max. size $20 \times 20 \times 10 \mu\text{m}$) for single crystal X-ray data collection using a standard laboratory four-circle diffractometer, so diffraction data were collected at low temperature (150 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.

As a result of the single crystal structure determination,[†] the material was found to possess a stoichiometry of $\text{Li}_2\text{Al}_3(\text{HO}_3\text{PMe})_2(\text{O}_3\text{PMe})_4\text{Cl}\cdot 7\text{H}_2\text{O}$. It is believed that this is the first example of a layered phosphonate, which is charged and contains interlayer anions. Comparison of a calculated powder XRD pattern with that obtained from the bulk product shows that the bulk contains a quantity of $\text{Al}(\text{HO}_3\text{PMe})(\text{O}_3\text{PMe})\cdot\text{H}_2\text{O}$ as an impurity phase.⁸ This necessarily means that an accurate analysis of the composition of the material by conventional methods (*e.g.* XRF, chemical analysis) is not possible.

Single crystal structure determination[†] revealed that the material is layered, with the lamellae stacking in the (100) direction (Fig. 1). All three of the Al atoms in the structure are

octahedrally coordinated by oxygen. The six phosphonate groups possess tetrahedral coordination about the P atom. Two of the phosphonate groups, however, are monoanionic, $[\text{HO}_3\text{PMe}]^-$, whilst the other four are di-anionic, $[\text{O}_3\text{PMe}]^{2-}$. The layers are made up from corner sharing of the equatorial positions of the Al octahedra with the four dianionic phosphonate groups. The P–C bonds of these four methylphosphonate groups are oriented perpendicular to the plane of the layers (Fig. 2).

The axial positions of the octahedral Al coordination sphere are occupied by water molecules, or oxygens shared with the two remaining protonated methylphosphonate groups. One Al

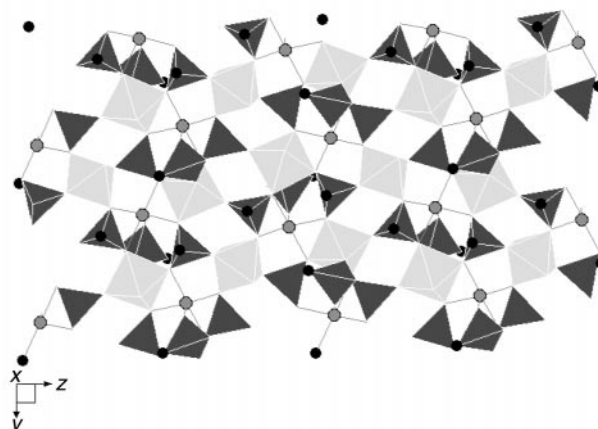


Fig. 1 A view of the layers along the (100) direction. The CPO_3 tetrahedra and the AlO_6 octahedra are shown as dark grey and light grey polyhedra respectively. Carbon atoms are shown as small black circles and lithium atoms as small grey circles. The interlayer water molecules and chlorine atoms are omitted for clarity.

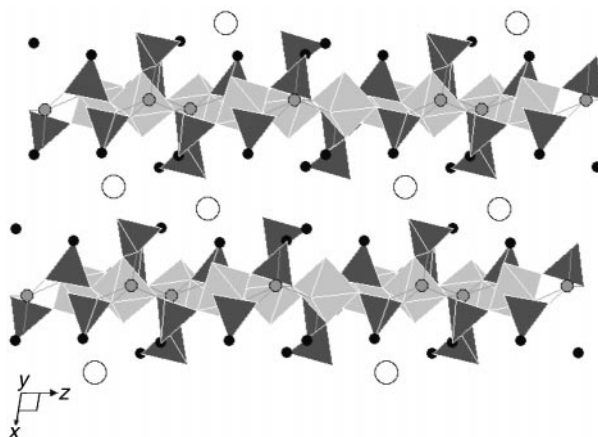


Fig. 2 Polyhedral view along the (010) direction showing the lamellae separated by interlayer chloride anions, and the different orientations adopted by the methylphosphonate groups. The CPO_3 tetrahedra and the AlO_6 octahedra are shown as dark grey and light grey polyhedra respectively. Carbon atoms are shown as small black circles, chlorine atoms as large white circles, and lithium atoms as small grey circles. The interlayer water molecules have been omitted for clarity.

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