Synthesis and structure of Li₂Al₃(HO₃PMe)₂(O₃PMe)₄Cl·7H₂O, **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, AlMePO- β ^{1,2,4,7} and AlMePO- α .³ Subsequently, two layered methylphosphonates,7,8 several phenyl phosphonates6,9 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 carboxyethylphosphonate 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.* refluxing6,9 or contacting an aluminium source with a molten phosphonic acid8). The title compound was synthesised by grinding the layered double hydroxide, $LiAl₂(OH)₆Cl·H₂O¹²$ 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 $20 \times 20 \times 10 \,\mu$ 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 $Li₂Al₃(HO₃P Me₂(O₃PMe)₄Cl·7H₂O$. 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 $Al(HO_3PMe)(O_3PMe)·H_2O$ 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, $[HO_3PMe]^-$, whilst the other four are di-anionic, $[O_3PMe]^{2-}$. 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 CPO₃ tetrahedra and the AIO_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 CPO₃ tetrahedra and the AlO6 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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atom is coordinated by two water molecules in axial positions, whilst the other two have only one coordinated water molecule. The remaining axial positions of these two octahedra are occupied by an O from a methylphosphonate. The P–C bonds of those phosphonate groups attached to the axial positions of the Al atoms, are oriented parallel to the direction of the layers (Fig. 2). This has also been observed in another aluminium methylphosphonate, which we reported previously.8

The Li atoms are situated inside six-membered rings within the layers. The Li atom is coordinated by five oxygen atoms (Fig. 3), in a distorted square pyramidal environment. The axial oxygen atom is attached to the phosphonate group which is also attached to the axial position of one of the Al atoms. Bond valence calculations (using the method of Brown and Altermatt)¹³ yielded values of 1.000 and 1.045 for the two Li ions, hence showing that the Li cations are in good coordination spheres.

Fig. 3 Representation of the coordination about the Li ions, showing the phosphonate group bridging the Al and Li atoms.

The chloride anions are located in the interlayer region along with the three remaining water molecules. Hydrogen bonding between the interlayer species and the water molecules coordinated to the Al atoms hold the layers together.

TG experiments, carried out upon a sample of the crystals separated manually from the reaction product, show stepwise mass losses upon heating. The loss of water beginning around 90 °C and ending around 350 °C is complex, but peaks in the derivative of the weight loss curve indicating that the losses are centred at 162 and 296 °C. This can be rationalised by considering that the lower temperature event is the loss of the three 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. There is then a further exothermic weight loss at 550 °C of *ca*. 7.8 mass%, which is associated with decomposition of the methyl groups. The final mass loss is centred at 1100 °C and corresponds to removal of P_2O_5 from the material to leave a mixture of AlPO₄, Li₂O and LiCl (as shown by XRD).

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Notes and references

^{\dagger} *Crystal data* for Li₂Al₃(HO₃PMe)₂(O₃PMe)₄Cl·7H₂O: $M_w = 822.40$, monoclinic, space group $P2_1$ (no. 4), $a = 10.1220(3)$, $b = 9.4659(2)$, $c =$ 15.7849(1) Å, $\beta = 95.805(1)$ ^o, $U = 1504.66(2)$ Å³, $T = 150$ K, $D_c = 1.82$ g cm⁻³, $Z = 2$, $\lambda = 0.6894$ Å, $\mu = 0.611$ mm⁻¹, 15374 reflections measured, 8145 reflections unique, 7936 reflections observed (R_{int} = 0.0874) which were used in all calculations. The final $wR(F2_{\text{all data}})$ was 0.138 and $R(F_{all data})$ was 0.055. The crystal structure was solved using direct methods and refined by full-matrix least squares on *F*2. The positions of the Li atoms were refined isotropically. Corrections were made for synchrotron beam intensity decay as part of the standard interframe scaling procedure.

CCDC 182/1451. See http://www.rsc.org/suppdata/cc/1999/2421/ for crystallographic files in .cif format.

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