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$Al_2[O_3PC_2H_4PO_3](H_2O)_2F_2{\cdot}H_2O$: a novel aluminium diphosphonate†

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The synthesis and crystal structure of the novel aluminium diphosphonate $Al_2[O_3PC_2H_4PO_3](H_2O)_2F_2{\cdot}H_2O$ is described; the material consists of chains of AlO_4F_2 octahedra linked together by ethylenediphosphonate units to form a structure with channels running parallel to the *a* axis which contain extra-framework water molecules that can be desorbed.

Metal phosphonate chemistry has received considerable interest in recent years because of the wide variety of accessible structure types and their potential applications in areas such as ion-exchange, catalysis and non-linear optics.[1] Early work focussed primarily on utilising phosphonic acids for the synthesis of new materials, this has been extended to include the use of diphosphonic acids ($(HO)_2OPRPO(OH)_2$, where R is an organic group). The attraction of the incorporation of the diphosphonic acid is that through careful selection of the R group the interlamellar distance, or pore size, and potentially the shape selective properties within the resulting structure can be controlled. Metal diphosphonates containing various metal cations have been synthesised; these include those of the alkaline earth, transition, and rare earth metals.[2,3] As far as the authors are aware, no reports of aluminium diphosphonates have hitherto been reported, which is surprising considering the possible chemical similarities between this type of material and the important aluminophosphate family of compounds. Studies on aluminium phosphonates have only recently been initiated. In 1995 Maeda *et al.* reported the synthesis of the first microporous aluminium methylphosphonates, designated AlMepO-β and AlMepO-α.[4,5] The syntheses of three layered methylphosphonates,[6–8] and a carboxymethylphosphonate,[9] have subsequently been reported. We report here the synthesis and structural characterisation of the novel aluminium diphosphonate, $Al_2[O_3PC_2H_4PO_3](H_2O)_2F_2{\cdot}H_2O$.

The title compound was synthesised hydrothermally using the pyridine/HF solvent system that has been found to be particularly fruitful in the preparation of novel microporous alumino- and gallofluorophosphates.[10,11] The reagents, aluminium sulfate ($Al_2(SO_4)_3{\cdot}18H_2O$, Aldrich), ethylenediphosphonic acid (Lancaster), HF/pyridine (70 wt%, Aldrich), pyridine (Aldrich), and de-ionised water were mixed together to form a reagent mixture of molar ratio: 1 : 2.16 : 8.7 : 54 : 144. The reagent mixture was loaded in a 23 ml Teflon-lined steel autoclave and heated for 5 days at 170 °C. The crystalline product was separated by suction filtration and had the form of colourless microcrystals. Microprobe analysis on the crystals indicated an Al : P ratio of 1 : 1 and that fluorine was present in the material. A suitable microcrystal was mounted on a Bruker AXS SMART CCD area detector diffractometer on the high-flux single-crystal diffraction station 9.8 at the CCLRC, Daresbury Laboratory, Synchrotron Radiation Source, UK.‡

The structure of $Al_2[O_3PC_2H_4PO_3](H_2O)_2F_2{\cdot}H_2O$ is shown in Fig. 1. The structure consists of chains of corner sharing AlO_4F_2 octahedra running parallel to the *b* axis with bridging fluorine atoms linking the octahedra. These chains contain two types of AlO_4F_2 octahedra. The first type contains aluminium, Al(1), coordinated to two fluorine atoms (2 × Al(1)–F(1) 1.823(5) Å) in a *trans* configuration with the other corners of the octahedron being occupied by four of the oxygen atoms of the diphosphonate groups, (2 × Al(1)–O(2) 1.873(5) Å; 2 × Al(1)–O(3) 1.894(5) Å) as shown in Fig. 2(a). The second octahedron consists of a central aluminium atom, Al(2), bound to two fluorine atoms in a *cis* fashion (2 × Al(2)–F(1) 1.825(5) Å) with the other two equatorial positions being occupied by two diphosphonate oxygen atoms (2 × Al(2)–O(1) 1.821(6) Å). The remaining axial positions are filled by two water molecules (Al(2)–O(4) 1.94(1) Å; Al(2)–O(5) 1.946(9) Å).

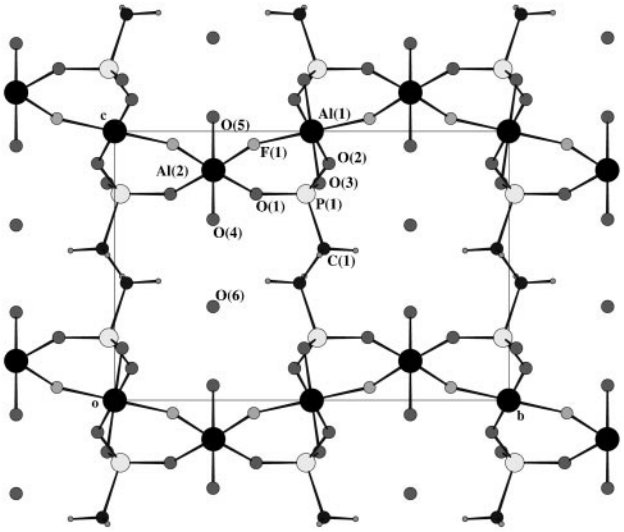

Fig. 1 Atomic representation of the structure of $Al_2[O_3PC_2H_4PO_3]$-$(H_2O)_2F_2{\cdot}H_2O$ viewed along the [100] direction. Selected bond lengths (Å): Al(1)–F(1) 1.823(5), Al(1)–O(2) 1.873(5), Al(1)–O(3) 1.894(5), Al(2)–F(1) 1.825(5), Al(2)–O(1) 1.821(6), Al(2)–O(4) 1.94(1), Al(2)–O(5) 1.946(9), P(1)–O(1) 1.530(6), P(1)–O(2) 1.541(5), P(1)–O(3) 1.518(6), P(1)–C(1) 1.780(8), C(1)–C(1) 1.52(2).

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†Electronic supplementary information (ESI) available: ^{19}F MAS SSNMR and TGA plots for $Al_2[O_3PC_2H_4PO_3](H_2O)_2F_2{\cdot}H_2O$. See http://www.rsc.org/suppdata/jm/b0/b006851i/

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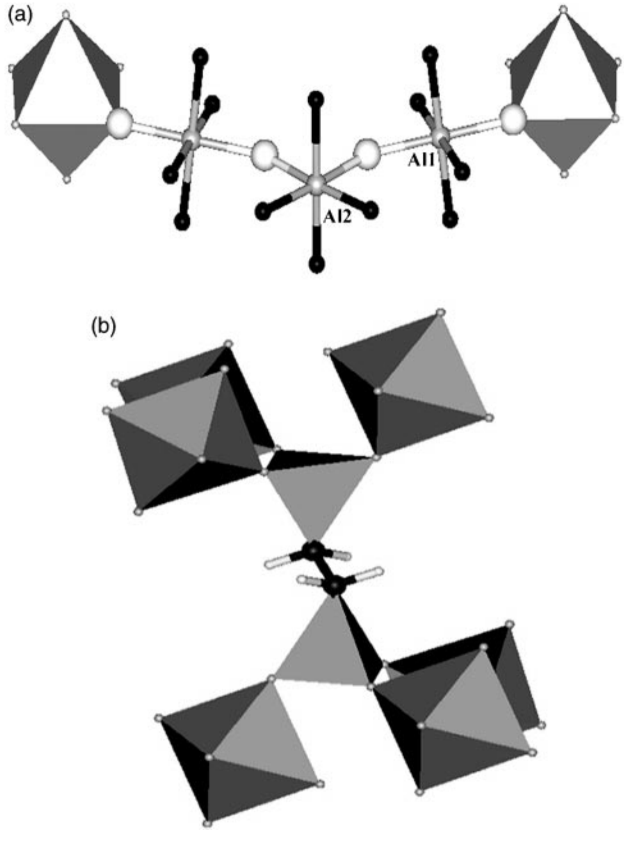

Fig. 2 (a) Polyhedral/ball and stick view of the Al octahedral chains, highlighting the alternating *cis–trans* configuration of fluorine atoms across Al(2) and Al(1) respectively (F in white, Al in grey, O in black). (b) Polyhedral view along the [010] direction showing how the diphosphonate units link the Al centred octahedral chains together.

Bond valence calculations[12] on the longer Al–O bond distances agree with the assignation of O(4) and O(5) as the oxygen atoms of water molecules. The Al–O, Al–F and Al–OH_2 distances observed are similar to those reported in the literature.[13] The ethylenediphosphonate groups link the octahedral chains in the [100] and [001] directions, as shown in Fig. 2(b). The structure formed contains small channels (5.68 Å [O(4)–O(5)] × 5.26 Å [C(1)–C(1)]) running along the [100] direction, within these channels are found extra-framework water molecules, O(6). The presence of one crystallographically independent fluorine site was confirmed by the observation of a singlet at -144.2 ppm in the ^{19}F MAS solid state NMR of the material, in agreement with the crystal structure determination. This chemical shift value is similar to that found for other bridging fluorine atoms found in aluminium centred octahedra.[13]

Thermal gravimetric analysis of $Al_2[O_3PC_2H_4PO_3](H_2O)_2F_2 \cdot H_2O$ shows a weight loss of 18% between 100 and 380 °C corresponding to the removal of the extra-framework and coordinated water molecules (calculated weight loss is 16%). Above 380 °C weight losses associated with degradation of the organic components of the ethylenediphosphonate group occur and the structure becomes an X-ray amorphous material. Heating the sample to 190 °C, corresponding to the weight loss associated with the extra-framework water, followed by cooling to room temperature and storing in a humidifier for 22 hours, resulted in no readsorption of the extra-framework water. The lack of reversible removal/adsorption of the extra-framework water is due to the hydrophobic nature and small dimensions of the channels.

An isostructural gallium form of the title compound, $Ga_2[O_3PC_2H_4PO_3](H_2O)_2F_2 \cdot H_2O$, has also been synthesised following the same preparative procedure. This material shows similar thermal properties to the aluminium analogue. However, heating the sample to 170 °C, corresponding to the weight loss associated with the extra-framework water, followed by cooling to room temperature and storing in a humidifier for 22 hours, resulted in readsorption of approximately 40% of the extra-framework water. The reversible readsorption of the extra-framework water results from the increase in channel dimensions produced by replacing the Al^{3+} cations by the larger Ga^{3+} cations in the structure which is also reflected in the larger cell dimensions of $Ga_2[O_3PC_2H_4PO_3](H_2O)_2F_2 \cdot H_2O$ ($a = 5.04881(3)$ Å, $b = 12.37065(7)$ Å, $c = 8.25492(4)$ Å, $\beta = 92.064(1)^\circ$, $V = 515.244(6)$ Å^3).

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Notes and references

‡Crystal data for $Al_2[O_3PC_2H_4PO_3](H_2O)_2F_2 \cdot H_2O$: monoclinic, space group $P21/m$, $a = 4.978(3)$ Å, $b = 12.002(1)$ Å, $c = 8.189(6)$ Å, $\beta = 91.97(3)^\circ$, $V = 488.9(2)$ Å^3, $T = 150$ K, $Z = 2$, $M_w = 331.98$, $D_c = 2.255$ g cm^{-3}, $\mu = 0.696$ cm^{-1}, $\lambda = 0.6942$ Å, crystal dimensions $10 \times 10 \times 5$ μm, 2749 reflections measured, 1338 unique reflections, 868 reflections observed ($I > 3\sigma(I)$), $R_{int} = 0.06$. The microcrystals formed were twinned and gave several sets of reflections corresponding to the individual twins. The unit cell of the most intense twin was determined using the unit cell previously obtained by auto-indexing the powder X-ray diffraction data collected on a polycrystalline sample. The structure was solved by direct methods,[14] the Al, P, C, F and framework O atoms were found first and the extra-framework O was located from difference Fourier maps. The hydrogen atoms were geometrically placed and refined in riding mode. Refinement of 39 variables was by full-matrix least-squares analysis,[15] with isotropic thermal parameters. The final residuals ($I > 3\sigma(I)$) were $R(F) = 0.104$, and $R_w(F) = 0.107$. The final residuals are higher than usual because the data set could not be de-twinned and some reflections had a contribution to their intensity from other twins. Corrections were made for synchrotron beam intensity decay as part of the standard interframe scaling procedure. CCDC 1145/250. See http://www.rsc.org/suppdata/jm/b0/b006851i/ for crystallographic files in .cif format.

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