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Linear chain aluminium(III) carboxymethylphosphonate with encapsulated ammonium ions[†]

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An aluminium carboxymethylphosphonate of composition $(NH_4)_2Al(H_{1/2}O_3PCH_2CO_2)_2$ has been prepared hydrothermally. The aluminium cation is chelated by six membered rings formed from bonding by both the carboxylate and phosphonate oxygens. These chelate rings in turn form larger eight membered rings by connecting to similar chelate groups to form chains running along the *a*-axis.

The use of phosphonic acids as ligands in the design and synthesis of metal organophosphonate-type MOFs are attractive not only because they complex metal atoms in several ways by loss of one or both protons, but also because their complexing ability can be modified by choice of organic functional groups.^{1,2} One problem in metal phosphonate chemistry is that many metal phosphonates form poorly crystalline compounds. Phosphonic acids with additional carboxylic functional groups are interesting ligands because they provide more coordination sites that may increase the solubility of the metal phosphonates in water and improve the crystallinity of their metal complexes.^{2,3} The use of phosphonocarboxylic acid in the synthesis of metal carboxylate-phosphonate materials has resulted in the formation of a number of twodimensional layered and three-dimensional network structures.⁴⁻¹² Surprisingly, reports on lower dimensional structures are scarce 13,14 While considerable progress has been made in the understanding of the chemical self-assembly of the building units (0D and 1D), into structures of higher dimensionality in the domain of the metal phosphates,¹⁵ such structural build-up in the phosphonate system still remains a challenge.¹⁶

We have attempted making metal carboxylate-phosphonates with lower dimensionality to study the possibility of assembling them into hierarchical more complex structures, and succeeded in obtaining a one-dimensional aluminium carboxymethylphosphonate of the formula $(NH_4)_2Al(H_{1/2}O_3PCH_2CO_2)_2$ I, comprising a dimeric $Al_2O_4P_2$ eight-membered ring. This paper reports the hydrothermal synthesis and characterization of this new aluminium carboxylate-phosphonate.

Compound I was prepared hydrothermally starting from Al(OH)₃ and HO₃PCH₂CO₂H in the presence of NH₃ solution[‡]. Originally we added no base but no crystallization was obtained in acidic solution. The structure of I consists of a unique aluminium(III) ion at the center of a crystallographic inversion with octahedral geometry as shown in Fig. 1. The aluminium atom is six-fold coordinated to four different carboxymethylphosphonates, where two moieties chelate to the aluminium center through one oxygen atom from each phosphonate and carboxylate group (P(1)–O(3) and C(2)–O(5)). The neighbouring phosphonate groups chelating to equivalent aluminium atoms, occupy the two remaining coordination sites (O1 and O1B), forming $\{Al_2O_4P_2\}$ dimeric units with an eight-membered ring. The dimeric unit forms chains running through the [100] direction with aluminium ions at the unit cell corners (Fig. 2). The Al-O distances are in the range 1.8650(12)-1.9301(14) Å (Al-O_{av} = 1.893 Å). The P-O distances are in the range 1.5172(13)-1.5384(12) Å, with the longest bonded to the protonated oxygen atom O(2). The fractional occupancy of this hydrogen reflects the disorder possibilities. The C-O bond distances from each of the carboxylate groups are in the range 1.245(2)-1.2813(19) Å. These values are between the expected value for a C=O double bond (1.16-1.21 Å) and a C-O single bond (1.34-1.43 Å), indicating complete deprotonation of the acidic oxygen atoms giving a CO₂²⁻ anion that coordinates



Fig. 1 Ball and stick representation of I showing the coordination around the metal center and dimeric $\{Al_2O_4P_2\}$ eight-membered ring.

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Fig. 2 Structure of I viewed along [100] direction showing the aluminium ions at the unit cell corners.

the aluminium through one of the oxygen atoms. The noncoordinating oxygen O4 is involved in hydrogen bond formation with the ammonium ion $[O4 \cdots N1 = 2.891 \text{ Å}; N1-H3 \cdots O4 =$ $172.79^{\circ}]$ as shown in Fig. 3. The framework stoichiometry of $Al(H_{\frac{1}{2}}O_3PCH_2CO_2)_2^{2-}$ with a net charge of -2 is balanced by the incorporation of two ammonium ions.



Fig. 3 Structure of I viewed along the *ab*-plane showing the individual chains with ammonium ions residing in the interspace.

The infrared spectrum of the as-synthesized compound contains peaks at 1624, 1578 and 1390 cm⁻¹, which are assigned to the asymmetric and symmetric stretching mode of C-O bonds of the carboxyl group. This is lower than that of the free ligand for C=O stretch in the region 1725–1700 cm⁻¹. The corresponding $\Delta [v_{asym}(CO_{2-}) - v_{sym}(CO_{2-})]$ value of 211 cm⁻¹ indicates the presence of carboxylate groups in a unidentate coordination mode,¹⁷ thus supporting the single-crystal X-ray data. The stretching vibrations of the tetrahedral -CPO₃ groups are indicated by the presence of intense bands in the region 1135-900 cm⁻¹, while the O-P-O bending vibrations are observable in the region 832-630 cm⁻¹. The absorption band at 1135 cm⁻¹ is assigned to v_{asym} (P–O) while peaks at 1090, 1001, 961 and 932 cm⁻¹ corresponds to v_{sym} (P–O). The broad absorption band in the region 3400-3000 cm⁻¹ centered at 3265 cm⁻¹ indicates the large amount of hydrogen bonding in this material, through the ammonium ions which are responsible for holding the structure together. The bands centered at 2370 and 1050 cm⁻¹ are attributed to P–OH vibrations due to unprotonated POH groups in the compound. The various assignments are in agreement with similar compounds in the literature.¹⁷

The ³¹P MAS NMR spectrum of aluminium phosphonoacetate contains a single peak at δ –8.0, and its associated spinning sidebands at –39.2 and 23.2 ppm, which clearly suggests the presence of one crystallographically independent phosphorus atom. The thermogravimetric analysis results (Fig. S4†) indicates that the compound is stable up to about 200 °C after which two steps of mass losses occur. The first mass loss in the region 234–266 °C is attributed to the loss of two molecules of ammonia. The observed value of 8.26% is lower compared with the calculated value of 10.05% reflecting the small impurity seen in the bulk PXRD pattern. The second mass loss of 23.67% (calc. 23.68%) between 303–479 °C corresponds to the loss of 2CO and $\frac{1}{2}O_2$. The total mass loss of 36.66% (calc. 35.49%) corresponds to the removal of the organic part of the ligand with the final product being AlPO₄.

In conclusion, a new linear chain aluminium carboxymethylphosphonate possessing dimeric $\{Al_2O_4P_2\}$ eightmembered rings has been synthesized under hydrothermal conditions in the presence of NH₃. In the mechanism proposed for the formation of open-framework aluminium phosphates,²⁰ the corner-shared chain structure has been identified as the primary building unit. We therefore speculate that through hydrolysis and condensation process, the present chain structure can be transformed into 2D and 3D frameworks. We are currently investigating the possibility of transforming this corner-shared chain with dimeric units into a more complex structure and the results will be published elsewhere.

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Notes and references

‡ In a typical synthesis of I, 0.117 g of Al(OH)₃ was dissolved in 2 ml of distilled water followed by the addition of 0.26 ml of HCl as mineralizer. To this mixture 0.42 g $(HO)_2OPCH_2CO_2H$ was added under continuous stirring followed by 1 ml of concentrated ammonia solution (28.0%wt NH₃) to adjust the pH to 4. The resulting gel with the molar composition Al(OH)₃ : 2HCl : 2(HO)₂OPCH₂CO₂H : 80H₂O was sealed in a Teflon-lined autoclave and heated at 160 °C for 120 h. The resulting colorless plate-like crystals of I were filtered by vacuum filtration, washed with distilled water and dried under ambient conditions. Initial characterization was carried out by powder X-ray diffraction (PXRD), ³¹P MAS NMR, thermogravimetric analysis (TGA), elemental CHN analysis and IR spectroscopy. The Powder X-ray diffraction pattern has an extra peak at $2\theta = 14.585^{\circ}$ which could not be indexed, thus indicating the presence of a small impurity in the bulk sample. The CHN analysis results (C 12.46%, H 3.55%, N 7.08%) on the bulk sample is lower compared with the calculated values from single-crystal X-ray data, (NH₄)₂Al(H_{1/2}O₃PCH₂CO₂)₂ (338.08 g mol⁻¹): C 14.21%, H 3.88%, N 8.29%. ATR-FTI R data (cm⁻¹), 1: $v_{(N-H)}$ (involved in hydrogen bonding interactions) = 3275s, (very broad), $v(C-H \text{ in - }CH_2-)=2972\text{ w}, v_{asym}(CO_2^-)=$ 1624s, 1578sh; $v_{sym}(CO_2^-) = 1390s$, v(C-O) = 1322s, $v_{asym}(P-O) = 1135s$; $v_{sym}(P-O) = 1090w, v_{sym}(P-OH) = 1050vs v(P-C) = 832s.$ A single crystal was mounted on a Bruker-AXS Apex II CCD X-ray

diffractometer (Mo-K α radiation, $\lambda = 0.71073$ Å) operating at 110 K. The structure was solved by direct methods (SHELXTL) and refined by the full-matrix least-squares technique against F^2 with the anisotropic displacement parameters for all non-hydrogen atoms.¹⁸ A semi-empirical method was applied for the absorption correction (SADABS).¹⁹ Hydrogen atoms were added in calculated positions and refined using a riding model with $U_{iso} = nU_{eq}$ for the carbon atoms connected to the relevant H-atom (n = 1.2). Hydrogen atoms for the nitrogen atom were found in the difference

Fourier map and refined with individual isotropic thermal parameters. For charge balance, the hydrogen atom for the phosphonate oxygen has half occupancy and was found with the difference Fourier map. It was refined using a riding model with $U_{\rm iso} = nU_{\rm eq}$ for the oxygen atom connected to the relevant H-atom (n = 1.5). The bond distance was changed with the HIMP command to 0.95 A. Anisotropic displacement parameters were established for all non-hydrogen atoms.

Crystal data: $M_r = 388.08$, triclinic, space group P(-1), a = 4.757(2), b = 8.231(4), c = 8.524(4) Å, $\alpha = 61.184(7)^\circ$, $\beta = 79.059(5)^\circ$, $\gamma = 85.228(5)^\circ$, V = 287.2(2) Å³, Z = 2, T = 110(2)K, $\rho_c = 1.955$ Mg m⁻³. A total of 3192 reflections were collected in the θ range 2.77–27.00 and merged to give 1235 unique data [R(int) = 0.0170] of which 1143 with $I > 2\sigma(I)$ were considered to be observed. Final R indices (all data); $R_1 = 0.0271$, $wR_2 = 0.0702$ and GOF = 1.086 were obtained for 105 parameters. Detailed experimental data and selected bond lengths and angles are given in the ESI.†

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