

# Synthesis and characterization of two novel organocation containing group 13 metal ethylenediphosphonates

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## Abstract

Two novel group 13 metal diphosphonates:  $(\text{H}_3\text{NC}_3\text{H}_6\text{NH}_3)_2[\text{Al}_2\text{F}_6(\text{O}_3\text{PC}_2\text{H}_4\text{PO}_3)] \cdot \text{H}_2\text{O}$  (**1**) (monoclinic,  $C2/c$ ,  $a = 16.9697(7) \text{ \AA}$ ,  $b = 8.0273(4) \text{ \AA}$ ,  $c = 16.3797(8) \text{ \AA}$ ,  $\beta = 117.762(2)^\circ$ ,  $Z = 4$ ,  $R_1 = 4.66\%$ ,  $wR_2 = 11.82\%$ ), and  $(\text{H}_3\text{NC}_3\text{H}_6\text{NH}_3)[\text{Ga}_2\text{F}_4(\text{O}_3\text{PC}_2\text{H}_4\text{PO}_3)]$  (**2**) (triclinic,  $P-1$ ,  $a = 5.398(7) \text{ \AA}$ ,  $b = 8.122(6) \text{ \AA}$ ,  $c = 15.839(18) \text{ \AA}$ ,  $\alpha = 78.89(4)^\circ$ ,  $\beta = 89.60(7)^\circ$ ,  $\gamma = 79.35(6)^\circ$ ,  $Z = 2$ ,  $R_1 = 2.90\%$ ,  $wR_2 = 3.17\%$ ) have been synthesized by solvothermal methods in the presence of the propyldiammonium cations and their structures determined using single and micro-crystal X-ray diffraction data, respectively. The structures of **1** and **2** are closely related and contain dimers of edge-sharing trivalent metal centered octahedra that are linked together by the ethylenediphosphonate groups to form chains and aperture-containing layers, respectively. The propyldiammonium cations surround the aluminum diphosphonate chains in **1** and separate the gallium diphosphonate layers in **2**. Both compounds **1** and **2** are examples of metal phosphonate materials containing only one type of octahedral–tetrahedral secondary building unit (SBU-4).

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## 1. Introduction

Research into the field of inorganic–organic hybrid materials continues to be an emerging theme within materials chemistry [1–3]. The attraction of these hybrid materials stem from the benefits introduced by inclusion of both the inorganic and organic components into the product. In particular, the incorporation and modification of the organic groups within structures allows the possibility of rationally designing materials with specific chemical functionality, properties and structures [4]. Phosphonic acids [ $\text{RPO}(\text{OH})_2$ , where  $R$  is an organic group] and diphosphonic acids [ $(\text{HO})_2\text{OPRPO}(\text{OH})_2$ ], are excellent precursors for the preparation of such hybrid materials and have been used as building units in the synthesis of a host of novel materials with one-, two-, and three-dimensionally extended structures [5–8].

These and other metal phosphonate materials are finding potential application in areas such as, sorption, ion-exchange, sensing, charge storage and catalysis [9–15].

Structural features that were found in solely inorganic materials are now being discovered within members of this raft of new hybrid materials, and because of the presence of the organic groups within these hybrid materials the linkage of these known structural features and their spatial arrangement are often found to be subtly or significantly modified. An example of this type of structural modification, occurring after the inclusion of an organic group, is found for materials containing the inorganic  $[\text{M}(\text{OH}/\text{F})(\text{PO}_4)_2]_\infty^{2-}$  chain that is present within the mineral Tancoite and its many solely inorganic analogues [16,17]. The inclusion of diphosphonate moieties into these materials has yielded Tancoite-like hybrid chains  $[\text{M}(\text{OH}/\text{F})(\text{O}_3\text{PC}_n\text{H}_{2n}\text{PO}_3)]_\infty^{2-}$  in which the interactions of the hydrophobic alkyl groups of the diphosphonate groups

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and other components of the material exert a large influence on the arrangements of the chains within the final crystal structure. The incorporation of different length alkyl spacers into the diphosphonate groups of the Tancoite-like chains also allows greater manipulation over the spatial arrangement of units within the chains, such as, the separation of the P-centered tetrahedra within the Tancoite-like chains [5,7,17]. This type of inclusion of organic groups into such materials will lead to more subtle control over the structure, and properties, of the resultant solid-state materials.

One structural unit that is not currently known, to the best of our knowledge, in trivalent metal diphosphonate materials is the octahedral–tetrahedral secondary building unit SBU-4 [18]. The use of secondary building units to describe framework structures is common in pure tetrahedral aluminosilicate and phosphate structures and, more recently, has been extended to describe octahedral–tetrahedral frameworks [18]. The structure of the SBU-4 unit is shown in Fig. 1 and consists of two metal centered edge-sharing octahedra and two non-metal centered tetrahedra that bridge the octahedra. This unit has been identified as one of the secondary building units in the structure of  $\text{Ga}_3(\text{PO}_4)(\text{HPO}_4)_2\text{F}_3(\text{OH}) \cdot \text{C}_6\text{N}_2\text{H}_{14} \cdot 0.5\text{H}_2\text{O}$  [19] and the only secondary building unit in the layered material  $[\text{C}_{10}\text{N}_4\text{H}_{28}][\{\text{FeF}(\text{OH})(\text{HAsO}_4)\}_4]$  [20]. In metal diphosphonate chemistry, compounds containing isolated dimers of edge-sharing divalent iron and cobalt cation centered octahedra [21,22] and chains of edge-sharing gallium octahedra [23] with various modes of coordination by the phosphonate ( $\text{PO}_3\text{C}$ ) tetrahedra are known but none that contain the SBU-4 unit.

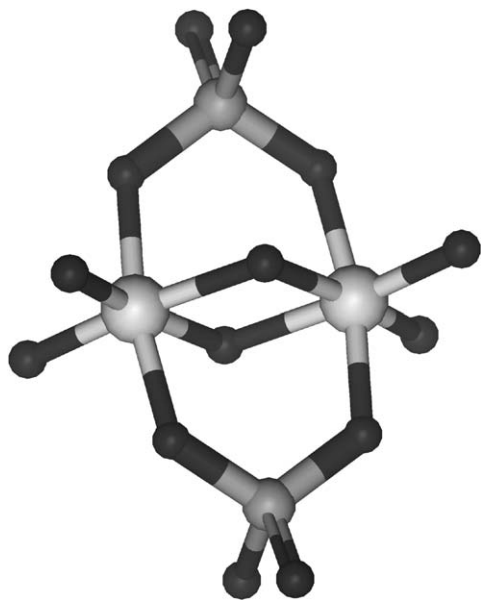


Fig. 1. Ball and stick representation of the octahedral–tetrahedral secondary building unit SBU-4 consisting of a pair of edge sharing octahedra bridged by two tetrahedra.

During the course of our program to prepare new diphosphonates of group 13 metals in the presence of charge compensating cationic species we have discovered the two novel materials:  $(\text{H}_3\text{NC}_3\text{H}_6\text{NH}_3)_2[\text{Al}_2\text{F}_6(\text{O}_3\text{PC}_2\text{H}_4\text{PO}_3)] \cdot \text{H}_2\text{O}$  (**1**) and  $(\text{H}_3\text{NC}_3\text{H}_6\text{NH}_3)[\text{Ga}_2\text{F}_4(\text{O}_3\text{PC}_2\text{H}_4\text{PO}_3)]$  (**2**). The materials are structurally related to each other and contain dimers of edge-sharing trivalent metal cation centered octahedra linked by ethylenediphosphonate groups to form one- and two-dimensionally extended structures and are examples of metal phosphonate materials containing only one type of secondary building unit (SBU-4).

## 2. Experimental section

### 2.1. Synthesis and initial characterization

The reagents used to synthesize both materials were  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  (Aldrich),  $\text{Ga}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  (Alfa Aesar), ethylenediphosphonic acid (Lancaster), HF/pyridine (70 wt%, Aldrich), pyridine (Aldrich) and propyldiamine (Aldrich). All the aforementioned reagents were used without further purification.

The sample of  $(\text{H}_3\text{NC}_3\text{H}_6\text{NH}_3)_2[\text{Al}_2\text{F}_6(\text{O}_3\text{PC}_2\text{H}_4\text{PO}_3)] \cdot \text{H}_2\text{O}$  **1** used for structure determination was synthesized by mixing together  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , ethylenediphosphonic acid, HF, pyridine, propyldiamine and de-ionized water to form a reagent mixture of molar ratio: 1:2.16:8.65:54.5:13.4:144 which after stirring had an initial pH of 10.9. This reagent mixture was loaded in a 23 mL Teflon-lined steel autoclave and heated for 2 days at 130°C. The product was washed with ethanol and acetone, separated by suction filtration and had the form of colorless, plate-like single crystals. A subsequent synthesis conducted at 160°C for 4 days resulted in the recovery of a polycrystalline powder sample, the powder X-ray diffraction pattern of which is shown in Fig. 2. This product was judged to be monophasic from the good agreement between the experimental powder X-ray diffraction pattern and that calculated from the atomic coordinates obtained from the single-crystal analysis of compound **1**. This powdered sample was used for all, non-crystallographic analyses.

A sample of  $(\text{H}_3\text{NC}_3\text{H}_6\text{NH}_3)[\text{Ga}_2\text{F}_4(\text{O}_3\text{PC}_2\text{H}_4\text{PO}_3)]$  **2** was synthesized by mixing together  $\text{Ga}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , ethylenediphosphonic acid, HF, pyridine, propyldiamine and de-ionized water to form a reagent mixture of molar ratio: 1:2.44:9.77:61.6:15.1:163 which after stirring had an initial pH of 9.45. This reagent mixture was loaded in a 23 mL Teflon-lined steel autoclave and heated for 4 days at 200°C. The product was washed with ethanol and acetone, separated by suction filtration and contained small colorless, plate-like micro-crystals. The sample was not monophasic and contained small

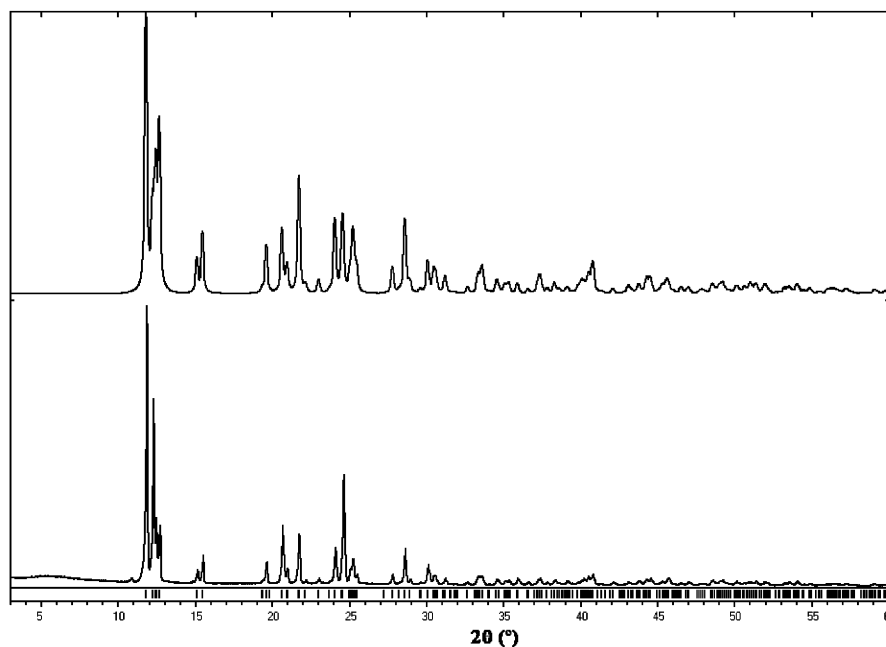


Fig. 2. The observed (bottom) and simulated (top) powder X-ray diffraction patterns of  $(\text{H}_3\text{NC}_3\text{H}_6\text{NH}_3)_2[\text{Al}_2\text{F}_6(\text{O}_3\text{PC}_2\text{H}_4\text{PO}_3)] \cdot \text{H}_2\text{O}$  **1**. Tick-marks show reflection positions.

amounts of one or more unidentified additional phases, although compound **2** was the main phase present.

### 2.2. Magic angle spinning solid-state NMR (MAS SS NMR) measurements

MAS SS NMR spectra were recorded for sample **1** using a Bruker MSL 300 spectrometer. The spectrum collected for  $^{31}\text{P}$  nuclei was referenced to an 85% solution of  $\text{H}_3\text{PO}_4$  with the spectrometer operating at a frequency of 121.50 MHz, a sample spinning speed of 24 kHz, and recycle delays of 30 s. For  $^{19}\text{F}$  nuclei a  $\text{CFCl}_3$  reference was used with the spectrometer operating at a frequency of 282.4 MHz, a sample spinning speed of 24 kHz, and recycle delays of 5 s.

### 2.3. Single-crystal X-ray structure solutions

Single-crystal X-ray data were collected from a colorless, plate-like single crystal of compound **1** mounted on a Nonius Kappa CCD diffractometer with a Nonius FR591 rotating anode generator at the EPSRC National Crystallography Service, Southampton, UK and from a single, colorless, prismatic crystal of compound **2** mounted on a Bruker AXS SMART CCD diffractometer at the high-flux single-crystal diffraction station 9.8 at CCLRC, Daresbury Laboratory Synchrotron Radiation Source, UK. The structures of both compounds were solved by direct methods and refined by full-matrix least-squares using the SHELX programs

[24]. The atomic displacement parameters of all of the non-hydrogen atoms were refined anisotropically. All the non-water hydrogen atoms of **1** and **2** were found from difference Fourier maps and the hydrogen atoms of the water molecule in **1** were geometrically placed using the method of Nardelli [25]. The hydrogen atoms in **1** were refined in riding mode with all their atomic displacement parameters refined isotropically and constrained to have the same value during refinement. The hydrogen atoms of the ethylenediphosphonate groups in **2** were refined in riding mode with their atomic displacement parameters refined isotropically and constrained to have the same value during refinement. The hydrogen atoms of the propyldiammonium cations were refined freely with their atomic displacement parameters refined isotropically. The elemental assignment of the terminal and bridging atoms within the dimers of the edge-sharing metal-centered octahedra in both structures was as fluorine, and not hydroxide or water groups, due to the significant improvement in residuals with this assignment and the failure to find any hydrogen atoms in the vicinity of these atoms by Fourier mapping. The crystallographic data and structure refinement parameters for compounds **1** and **2** are given in Table 1, atomic coordinates and equivalent isotropic atomic displacement factors are given in Table 2, and selected bond distances and angles are presented in Tables 3–5. The asymmetric units of compounds **1** and **2** are shown in Figs. 3 and 4, respectively.

Table 1

Crystallographic data and structure refinement parameters for  $(\text{H}_3\text{NC}_3\text{H}_6\text{NH}_3)_2[\text{Al}_2\text{F}_6(\text{O}_3\text{PC}_2\text{H}_4\text{PO}_3)] \cdot \text{H}_2\text{O}$  **1** and  $(\text{H}_3\text{NC}_3\text{H}_6\text{NH}_3)[\text{Ga}_2\text{F}_4(\text{O}_3\text{PC}_2\text{H}_4\text{PO}_3)]$  **2**

Compound	<b>1</b>	<b>2</b>
Formula	$\text{C}_8\text{H}_{30}\text{Al}_2\text{F}_6\text{N}_4\text{O}_7\text{P}_2$	$\text{C}_5\text{H}_{16}\text{Ga}_2\text{F}_4\text{N}_2\text{O}_6\text{P}_2$
Formula weight	524.26	477.58
Crystal size (mm)	$0.1 \times 0.04 \times 0.05$	$0.3 \times 0.02 \times 0.01$
Temperature (K)	150	150
Wavelength (Å)	0.71073 (MoK $\alpha$ )	0.6889
Crystal system	Monoclinic	Triclinic
Space group	$C2/c$	$P-1$
<i>a</i> (Å)	16.9697(7)	5.398(7)
<i>b</i> (Å)	8.0273(4)	8.122(6)
<i>c</i> (Å)	16.3797(8)	15.839(18)
$\alpha$ (deg)	—	78.89(4)
$\beta$ (deg)	117.762(2)	89.60(7)
$\gamma$ (deg)	—	79.35(6)
<i>V</i> (Å <sup>3</sup> )	1974.4(2)	669.3(13)
<i>Z</i>	4	2
<i>D<sub>c</sub></i> (g cm <sup>-3</sup> )	1.764	2.370
$\mu$ (cm <sup>-1</sup> )	0.406 (MoK $\alpha$ )	3.341
$2\theta_{\text{max}}$ (deg)	54.92	58.8
Data/parameters	2252/133	3594/238
<i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )], <i>R</i> <sub>1</sub> (all data) <sup>a</sup>	0.0466, 0.0811	0.0290, 0.0817
<i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )], <i>wR</i> <sub>2</sub> (all data) <sup>b</sup>	0.1182, 0.1366	0.0317, 0.0836
<i>S</i> on <i>F</i> <sup>2</sup>	0.847	1.043

$$^a R_1 = \sum |F_o| - |F_c| / \sum |F_o|$$

$$^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2} \quad \text{with } w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP], \quad P = [2F_c^2 + \text{Max}(F_o^2, 0)] / 3, \quad \text{where } a = 0.0875 \quad \text{and } b = 2.6883 \text{ for } \mathbf{1} \text{ and } 0.0493 \text{ and } 0.0409 \text{ for } \mathbf{2}.$$

### 3. Results and discussion

#### 3.1. Structural description of

#### $(\text{H}_3\text{NC}_3\text{H}_6\text{NH}_3)_2[\text{Al}_2\text{F}_6(\text{O}_3\text{PC}_2\text{H}_4\text{PO}_3)] \cdot \text{H}_2\text{O}$ (**1**)

The structure of  $(\text{H}_3\text{NC}_3\text{H}_6\text{NH}_3)_2[\text{Al}_2\text{F}_6(\text{O}_3\text{PC}_2\text{H}_4\text{PO}_3)] \cdot \text{H}_2\text{O}$  **1** is shown in Fig. 5. The main structural feature of **1** are the dimeric clusters of edge-sharing  $\text{AlO}_2\text{F}_4$  octahedra linked through the diphosphonate groups to form 1-dimensional  $[\text{Al}_2\text{F}_6(\text{O}_3\text{PC}_2\text{H}_4\text{PO}_3)]_\infty^{4-}$  chains that extend along the [010] direction. The  $\text{AlO}_2\text{F}_4$  octahedra consist of fluorine atoms in all the equatorial positions with two symmetry equivalent F(1) atoms bridging the two Al centers, and F(2) and F(3) occupying the remaining equatorial positions, in an unbound terminal configuration. These atoms were assigned as F atoms from the crystal structure refinement results, mentioned previously, and the presence of three distinct resonances in the <sup>19</sup>F SSNMR spectrum of **1** as shown in Fig. 6a. The three resonances are centered at -127.88, -149.99, and -159.33 ppm in the spectrum, and their integrals are similar, confirming the presence of three crystallographically independent fluorine sites of equal multiplicity. The observed chemical shifts are

Table 2

Fractional atomic coordinates and equivalent isotropic atomic displacement parameters (Å<sup>2</sup>) for compounds **1** and **2**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub> <sup>a</sup>
<b>Compound 1</b>				
Al(1)	0.1721(1)	0.2813(1)	-0.876(1)	0.017(1)
P(1)	0.2202(1)	0.5383(1)	0.0669(1)	0.016(1)
O(1)	0.1512(1)	0.4597(2)	-0.0232(1)	0.019(1)
O(2)	0.2886(1)	0.4091(2)	0.1301(1)	0.019(1)
O(3)	0.1754(1)	0.6246(2)	0.1171(1)	0.025(1)
F(1)	-0.2077(1)	0.8394(2)	-0.0229(1)	0.018(1)
F(2)	0.1593(1)	0.4068(2)	-0.1812(1)	0.028(1)
F(3)	0.0627(1)	0.2169(2)	-0.1315(1)	0.030(1)
C(1)	-0.2807(2)	1.3079(3)	-0.0392(2)	0.020(1)
O(4)	0.0000	1.0511(4)	0.2500	0.042(1)
N(1)	0.0406(2)	1.4888(3)	0.1397(2)	0.025(1)
N(2)	0.1882(2)	0.9426(3)	0.1833(2)	0.025(1)
C(2)	0.0291(2)	1.3108(4)	0.1110(2)	0.030(1)
C(3)	0.1147(2)	1.2150(4)	0.1629(2)	0.023(1)
C(4)	0.1056(2)	1.0365(4)	0.1268(2)	0.024(1)
<b>Compound 2</b>				
Ga(1)	0.8051(1)	1.1508(1)	0.5129(1)	0.007(1)
Ga(2)	0.3011(1)	1.1534(1)	1.0030(1)	0.007(1)
P(1)	0.1810(1)	0.8964(1)	0.8917(1)	0.007(1)
P(2)	0.3237(1)	1.0754(1)	0.6152(1)	0.007(1)
F(1)	0.2503(2)	1.3766(1)	0.9427(1)	0.011(1)
F(2)	0.7586(2)	1.3808(1)	0.4611(1)	0.011(1)
F(3)	1.1036(2)	1.0933(2)	0.4411(1)	0.009(1)
F(4)	0.6027(1)	1.0811(2)	0.9369(1)	0.010(1)
O(1)	0.1315(3)	1.0732(2)	0.9155(1)	0.009(1)
O(2)	0.5188(3)	1.1849(2)	0.5822(1)	0.009(1)
O(3)	-0.0210(3)	0.7936(2)	0.9257(1)	0.010(1)
O(4)	0.4450(3)	0.7905(2)	0.9209(1)	0.011(1)
O(5)	0.0565(2)	1.1787(2)	0.5945(1)	0.010(1)
O(6)	0.3717(3)	0.9044(2)	0.5834(1)	0.010(1)
C(1)	0.3587(3)	1.0283(2)	0.7315(1)	0.010(1)
C(2)	0.1638(4)	0.9271(2)	0.7753(1)	0.011(1)
N(1)	0.7580(3)	0.5870(2)	0.5879(1)	0.013(1)
N(2)	0.7416(3)	0.4590(2)	0.9103(1)	0.013(1)
C(3)	0.6919(4)	0.4789(3)	0.6684(1)	0.014(1)
C(4)	0.7716(4)	0.5322(3)	0.7498(1)	0.015(1)
C(5)	0.6996(4)	0.4089(3)	0.8261(1)	0.015(1)

<sup>a</sup> *U*<sub>eq</sub> is defined as one-third of the trace of the orthogonalized *U*<sub>ij</sub> tensor.

similar to those found for other fluorine atoms found in aluminum centered octahedra [26,27]. The average Al–O bond distance of 1.915 Å agrees well with those reported for Al in octahedral environments in other aluminophosphates and aluminophosphonates [17,27]. The average Al–F distance of 1.811 Å is consistent with those given for fluoraluminophosphates and phosphonates [17,26,27].

Each phosphonate, -PO<sub>3</sub>, group of the ethylenediphosphonate moiety bridge the two metal centers of each dimer to form SBU-4 units and provide the axial oxygen apices, (O(1) and O(2)), of each  $\text{AlO}_2\text{F}_4$  octahedra, as seen in Fig. 5a. The third oxygen atom of each phosphonate group, O(3), is unbound and forms hydrogen bonds to the propyldiammonium cations.

Table 3  
Selected bond distances (Å) for compounds **1** and **2**

<b>1</b>		<b>2</b>	
Al(1)–F(3)	1.727(2)	Ga(1)–F(2)	1.861(2)
Al(1)–F(2)	1.761(2)	Ga(1)–O(2)	1.899(2)
Al(1)–F(1) <sup>a</sup>	1.869(2)	Ga(1)–F(3) <sup>a</sup>	1.947(2)
Al(1)–F(1) <sup>b</sup>	1.888(2)	Ga(1)–O(5) <sup>b</sup>	1.953(2)
Al(1)–O(1)	1.907(2)	Ga(1)–O(6) <sup>c</sup>	1.969(2)
Al(1)–O(2) <sup>c</sup>	1.923(2)	Ga(1)–F(3)	2.001(2)
P(1)–O(3)	1.523(2)	Ga(2)–F(1)	1.851(2)
P(1)–O(1)	1.529(2)	Ga(2)–O(3) <sup>d</sup>	1.915(2)
P(1)–O(2)	1.541(2)	Ga(2)–F(4) <sup>e</sup>	1.936(2)
P(1)–C(1) <sup>d</sup>	1.794(3)	Ga(2)–O(1)	1.941(2)
C(1)–C(1) <sup>e</sup>	1.534(5)	Ga(2)–F(4)	1.987(2)
N(1)–C(2)	1.487(4)	Ga(2)–O(4) <sup>c</sup>	2.002(2)
N(2)–C(4)	1.475(4)	P(1)–O(3)	1.527(2)
C(2)–C(3)	1.507(4)	P(1)–O(1)	1.531(2)
C(3)–C(4)	1.531(4)	P(1)–O(4)	1.545(2)
		P(1)–C(2)	1.813(3)
		P(2)–O(2)	1.527(2)
		P(2)–O(5)	1.531(2)
		P(2)–O(6)	1.545(2)
		P(2)–C(1)	1.812(3)
		C(1)–C(2)	1.534(3)
		N(1)–C(3)	1.484(3)
		N(2)–C(5)	1.498(3)
		C(3)–C(4)	1.524(3)
		C(4)–C(5)	1.512(3)

For **1**: <sup>a</sup> $x + 1/2, y - 1/2, z$ ; <sup>b</sup> $-x, -y + 1, -z$ ; <sup>c</sup> $-x + 1/2, -y + 1/2, -z$ ; <sup>d</sup> $-x, -y + 2, -z$ ; <sup>e</sup> $-x - 1/2, -y + 5/2, -z$ .

For **2**: <sup>a</sup> $-x + 2, -y + 2, -z + 1$ ; <sup>b</sup> $x + 1, y, z$ ; <sup>c</sup> $-x + 1, -y + 2, -z + 1$ ; <sup>d</sup> $-x, -y + 2, -z + 2$ ; <sup>e</sup> $-x + 1, -y + 2, -z + 2$ .

Table 4  
Selected bond angles (deg) for compounds **1** and **2**

<b>1</b>		<b>2</b>	
F(3)–Al(1)–F(2)	97.8(1)	F(2)–Ga(1)–O(2)	92.98(8)
F(3)–Al(1)–F(1) <sup>a</sup>	171.31(9)	F(2)–Ga(1)–F(3) <sup>a</sup>	172.26(5)
F(2)–Al(1)–F(1) <sup>a</sup>	90.57(9)	O(2)–Ga(1)–F(3) <sup>a</sup>	94.71(8)
F(3)–Al(1)–F(1) <sup>b</sup>	92.71(9)	F(2)–Ga(1)–O(5) <sup>b</sup>	91.60(8)
F(2)–Al(1)–F(1) <sup>b</sup>	169.46(9)	O(2)–Ga(1)–O(5) <sup>b</sup>	97.7(1)
F(1) <sup>a</sup> –Al(1)–F(1) <sup>b</sup>	78.90(9)	F(3) <sup>a</sup> –Ga(1)–O(5) <sup>b</sup>	86.46(8)
F(3)–Al(1)–O(1)	90.84(9)	F(2)–Ga(1)–O(6) <sup>c</sup>	91.97(8)
F(2)–Al(1)–O(1)	94.13(9)	O(2)–Ga(1)–O(6) <sup>c</sup>	96.3(1)
F(1) <sup>a</sup> –Al(1)–O(1)	86.21(8)	F(3) <sup>a</sup> –Ga(1)–O(6) <sup>c</sup>	88.11(8)
F(1) <sup>b</sup> –Al(1)–O(1)	85.05(8)	O(5) <sup>b</sup> –Ga(1)–O(6) <sup>c</sup>	165.37(6)
F(3)–Al(1)–O(2) <sup>c</sup>	95.62(9)	F(3) <sup>a</sup> –Ga(1)–O(6) <sup>c</sup>	91.70(8)
F(2)–Al(1)–O(2) <sup>c</sup>	93.60(9)	O(2)–Ga(1)–F(3)	174.91(5)
F(1) <sup>a</sup> –Al(1)–O(2) <sup>c</sup>	86.14(8)	F(3) <sup>a</sup> –Ga(1)–F(3)	80.65(8)
F(1) <sup>b</sup> –Al(1)–O(2) <sup>c</sup>	85.96(8)	O(5) <sup>b</sup> –Ga(1)–F(3)	84.2(1)
O(1)–Al(1)–O(2) <sup>c</sup>	169.2(1)	O(6) <sup>c</sup> –Ga(1)–F(3)	81.6(1)
O(3)–P(1)–O(1)	111.0(1)	F(1)–Ga(2)–O(3) <sup>d</sup>	91.44(9)
O(3)–P(1)–O(2)	110.7(1)	F(1)–Ga(2)–F(4) <sup>e</sup>	173.03(5)
O(1)–P(1)–O(2)	111.7(1)	O(3) <sup>d</sup> –Ga(2)–F(4) <sup>e</sup>	94.60(9)
O(3)–P(1)–C(1) <sup>d</sup>	108.2(1)	F(1)–Ga(2)–O(1)	93.78(9)
O(1)–P(1)–C(1) <sup>d</sup>	108.1(1)	O(3) <sup>d</sup> –Ga(2)–O(1)	99.3(1)
O(2)–P(1)–C(1) <sup>d</sup>	107.0(1)	F(4) <sup>e</sup> –Ga(2)–O(1)	88.70(9)
C(1) <sup>e</sup> –C(1)–P(1) <sup>d</sup>	112.5(3)	F(1)–Ga(2)–F(4)	93.17(8)
N(1)–C(2)–C(3)	111.2(2)	O(3) <sup>d</sup> –Ga(2)–F(4)	175.04(5)
C(2)–C(3)–C(4)	111.3(2)	F(4) <sup>e</sup> –Ga(2)–F(4)	80.69(8)
N(2)–C(4)–C(3)	109.8(2)	O(1)–Ga(2)–F(4)	82.2(1)
		O(3) <sup>d</sup> –Ga(2)–O(4) <sup>c</sup>	95.0(1)
		F(4) <sup>e</sup> –Ga(2)–O(4) <sup>c</sup>	86.94(9)
		O(1)–Ga(2)–O(4) <sup>c</sup>	165.34(6)
		F(1)–Ga(2)–O(4) <sup>c</sup>	89.06(9)
		F(4)–Ga(2)–O(4) <sup>c</sup>	83.3(1)
		O(3)–P(1)–O(1)	111.8(1)
		O(3)–P(1)–O(4)	109.7(1)
		O(1)–P(1)–O(4)	113.8(1)
		O(3)–P(1)–C(2)	106.8(1)
		O(1)–P(1)–C(2)	107.6(1)
		O(4)–P(1)–C(2)	106.8(1)
		O(2)–P(2)–O(5)	110.4(1)
		O(2)–P(2)–O(6)	111.9(1)
		O(5)–P(2)–O(6)	113.8(1)
		O(2)–P(2)–C(1)	106.4(1)
		O(5)–P(2)–C(1)	105.9(1)
		O(6)–P(2)–C(1)	108.1(1)
		C(2)–C(1)–P(2)	112.9(1)
		C(1)–C(2)–P(1)	112.9(2)
		N(1)–C(3)–C(4)	113.5(2)
		C(5)–C(4)–C(3)	107.6(2)
		N(2)–C(5)–C(4)	112.9(2)

For **1**: <sup>a</sup> $x + 1/2, y - 1/2, z$ ; <sup>b</sup> $-x, -y + 1, -z$ ; <sup>c</sup> $-x + 1/2, -y + 1/2, -z$ ; <sup>d</sup> $-x, -y + 2, -z$ ; <sup>e</sup> $-x - 1/2, -y + 5/2, -z$ .

For **2**: <sup>a</sup> $-x + 2, -y + 2, -z + 1$ ; <sup>b</sup> $x + 1, y, z$ ; <sup>c</sup> $-x + 1, -y + 2, -z + 1$ ; <sup>d</sup> $-x, -y + 2, -z + 2$ ; <sup>e</sup> $-x + 1, -y + 2, -z + 2$ .

The second phosphonate group of each diphosphonate moiety binds to an adjacent metal cluster in an identical manner and so links the otherwise isolated SBU-4 units

Table 5  
Selected hydrogen bond distances (Å) and angles (deg) for compounds **1** and **2**

Donor–H...Acceptor	D–H	H...A	D...A	D–H...A
<b>1</b>				
N(1)–H(3)...F(2)	0.89	2.00	2.803(3)	149
N(1)–H(4)...F(3)	0.89	2.21	2.909(3)	135
N(1)–H(4)...O(1)	0.89	2.13	2.937(4)	151
N(1)–H(5)...O(3)	0.89	1.86	2.712(4)	161
N(2)–H(12)...O(2)	0.89	2.02	2.904(3)	172
N(2)–H(13)...F(2)	0.89	1.98	2.873(4)	176
N(2)–H(14)...O(3)	0.89	1.86	2.745(3)	177
O(4)–H(16)...F(3)	0.85	2.07	2.769(3)	139
O(4)–H(15)...O(2)	0.85	2.67	3.390(4)	143
<b>2</b>				
N(1)–H(5)...O(6)	0.90(2)	2.14(3)	2.990(4)	157(2)
N(1)–H(5)...F(3)	0.90(2)	2.22(3)	2.787(4)	121(2)
N(2)–H(7)...F(1)	0.97(3)	1.81(3)	2.731(4)	158(2)
N(1)–H(10)...F(2)	0.89(3)	1.90(3)	2.761(4)	162(2)
N(2)–H(11)...O(4)	0.92(2)	1.98(2)	2.901(4)	177(2)
N(2)–H(11)...F(1)	0.92(2)	2.50(2)	2.903(4)	107(2)
N(1)–H(12)...F(2)	1.00(3)	1.92(3)	2.852(4)	154(3)
N(1)–H(12)...F(2)	1.00(3)	2.50(3)	2.851(4)	100(2)
N(2)–H(14)...F(1)	0.92(3)	2.39(3)	2.872(4)	112(2)
N(2)–H(14)...O(4)	0.92(3)	2.39(3)	3.302(5)	172(3)

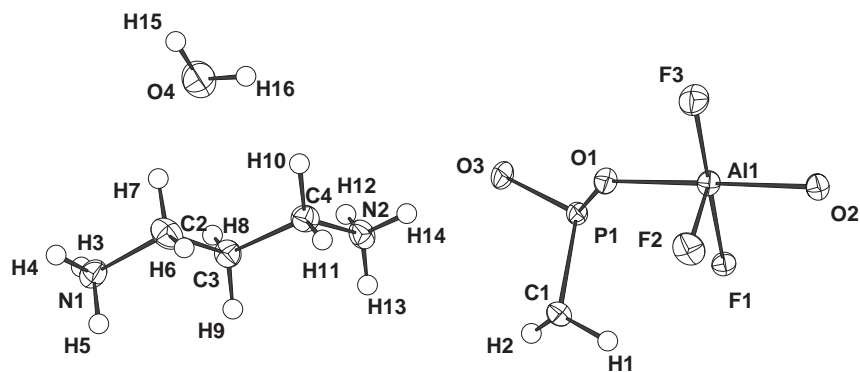


Fig. 3. The asymmetric unit of  $(\text{H}_3\text{NC}_3\text{H}_6\text{NH}_3)_2[\text{Al}_2\text{F}_6(\text{O}_3\text{PC}_2\text{H}_4\text{PO}_3)] \cdot \text{H}_2\text{O}$  **1**. Thermal ellipsoids are shown at 50% probability.

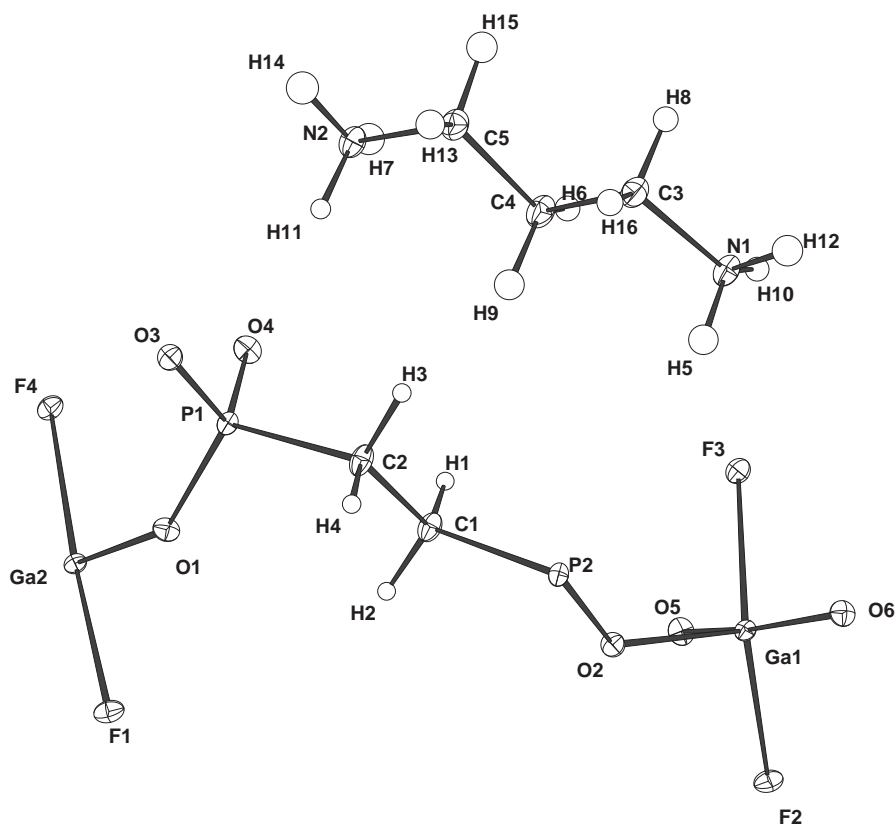


Fig. 4. The asymmetric unit of  $(\text{H}_3\text{NC}_3\text{H}_6\text{NH}_3)[\text{Ga}_2\text{F}_4(\text{O}_3\text{PC}_2\text{H}_4\text{PO}_3)]$  **2**. Thermal ellipsoids are shown at 50% probability.

together to form the  $[\text{Al}_2\text{F}_6(\text{O}_3\text{PC}_2\text{H}_4\text{PO}_3)]_\infty^{4-}$  chains. The  $[\text{Al}_2\text{F}_6(\text{O}_3\text{PC}_2\text{H}_4\text{PO}_3)]_\infty^{4-}$  chains contain only one type of secondary building unit that is linked by ethyl spacers to form the chain structure. The tetrahedral  $\text{PO}_3\text{C}$  units display average P–O distances of 1.531 Å and a P–C distance of 1.795 Å, values typically found in other metal diphosphonates [17,27]. The  $^{31}\text{P}$  SSNMR spectrum of compound **1** is presented in Fig. 6b and shows a single resonance centered at 25.85 ppm, suggesting the presence of a single crystallographically independent phosphorus site in agreement with the structure determination. The chemical shift of the

resonance is typical to that observed in other metal phosphonates [17,28].

The propyldiamine molecules in the synthesis gel are present as propyldiammonium cations within the structure of **1**. These dicationic species align themselves along the *b*-axis and surround the  $[\text{Al}_2\text{F}_6(\text{O}_3\text{PC}_2\text{H}_4\text{PO}_3)]_\infty^{4-}$  chains. Each propyldiammonium cation has significant electrostatic interactions with three separate  $[\text{Al}_2\text{F}_6(\text{O}_3\text{PC}_2\text{H}_4\text{PO}_3)]_\infty^{4-}$  chains, as shown in Fig. 5b, so forming the three-dimensional crystal structure of **1**. The organocations form hydrogen bonds with the terminal F atoms of the metal centered dimers and the



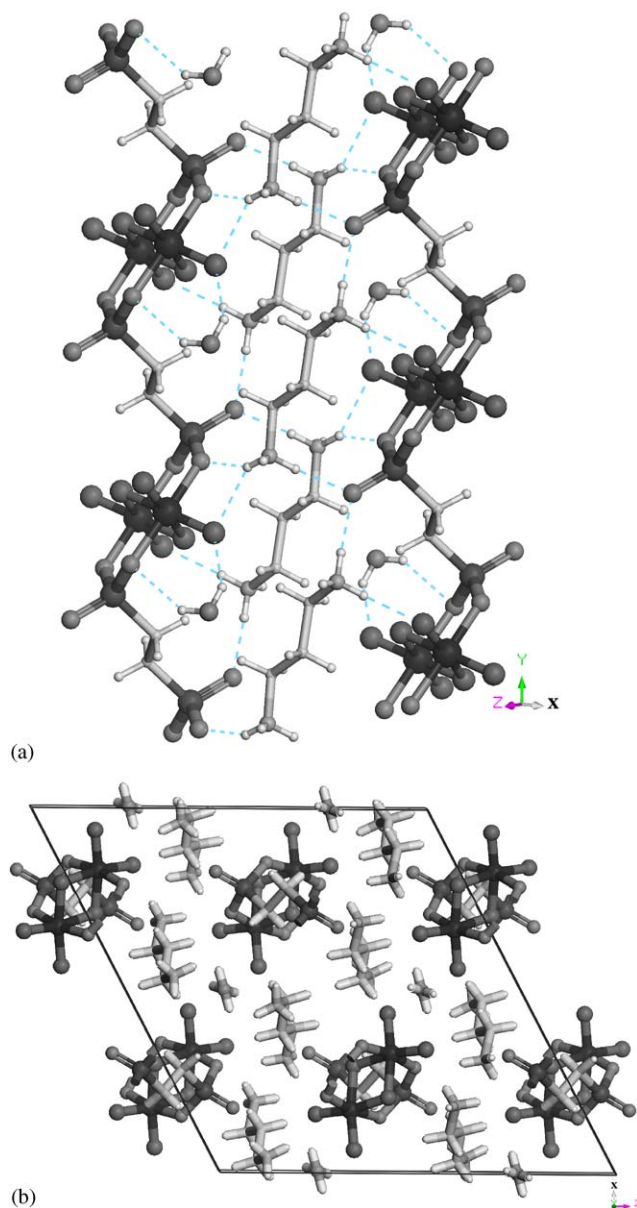


Fig. 5. The structure of **1** viewed (a) along the  $z$ -axis and (b) along the  $y$ -axis. The atoms are represented by balls that decrease in size and become lighter in the order Al, P, F, O, N, C, H. Hydrogen bonds are represented by dotted lines.

O atoms of the diphosphonate groups with a donor–acceptor distance range of 2.712 (4)–2.9937(4) Å and donor–H–acceptor angular range of 135–177°. These distance and angles indicate the hydrogen bonds are of moderate strength and mostly electrostatic in character [29]. The strongest hydrogen bonds formed involve the unbound O(3) atom of each  $-\text{PO}_3$  group, as indicated by the hydrogen bond distances and angles in Table 5. Water molecules reside between the  $[\text{Al}_2\text{F}_6(\text{O}_3\text{PC}_2\text{H}_4\text{PO}_3)]_4^{4-}$  chains and the propyldiammonium cations and are bound to the F(3) atoms by hydrogen bonds that are of moderate strength and mostly electrostatic in character, see Table 5.

### 3.2. Structural description of $(\text{H}_3\text{NC}_3\text{H}_6\text{NH}_3)[\text{Ga}_2\text{F}_4(\text{O}_3\text{PC}_2\text{H}_4\text{PO}_3)]$ (**2**)

The structure of  $(\text{H}_3\text{NC}_3\text{H}_6\text{NH}_3)[\text{Ga}_2\text{F}_4(\text{O}_3\text{PC}_2\text{H}_4\text{PO}_3)]$  **2** is shown in Fig. 7, and consists of aperture-containing layers formed from dimeric clusters of edge-sharing  $\text{GaO}_3\text{F}_3$  octahedra linked by the ethylenediphosphonate groups. Again, the cluster formed from the edge-sharing  $\text{GaO}_3\text{F}_3$  octahedra linked by the two  $\text{PCO}_3$  tetrahedra is a SBU-4 unit. The  $[\text{Ga}_2\text{F}_4(\text{O}_3\text{PC}_2\text{H}_4\text{PO}_3)]_\infty^{2-}$  layers lie along the (101) plane. The  $\text{GaO}_3\text{F}_3$  octahedra consist of fluorine atoms in three of the equatorial positions with two symmetry equivalent F atoms bridging the two Ga centers, and an F atom occupying one of the remaining terminal equatorial positions. These atoms were assigned as F atoms from the crystal structure refinement results as described previously. Each phosphonate,  $-\text{PO}_3$ , group of the ethylenediphosphonate moiety bridge the two metal centers of each dimer and provide the axial oxygen apices of each  $\text{GaO}_3\text{F}_3$  octahedra, as seen in Fig. 7a. The third oxygen atom of each phosphonate group bridges pairs of dimers and occupies the remaining axial position of each  $\text{GaO}_3\text{F}_3$  octahedron. The second phosphonate group of each diphosphonate moiety binds to an adjacent pair of metal clusters in an identical manner and so links the otherwise isolated dimeric clusters together to form the  $[\text{Ga}_2\text{F}_4(\text{O}_3\text{PC}_2\text{H}_4\text{PO}_3)]_\infty^{2-}$  layers. Again the  $[\text{Ga}_2\text{F}_4(\text{O}_3\text{PC}_2\text{H}_4\text{PO}_3)]_\infty^{2-}$  layers contain only one type of secondary building unit that is linked directly and by ethyl spacers to other SBU-4 units to form the layer structure. The apertures within the layers are 2.550 Å (H(4)⋯H(1)) wide and 6.533 Å (F(3)⋯F(4)) long. The average Ga–O bond distance of 1.947 Å agrees well with those reported for Ga in octahedral environments in other gallophosphonates and gallophosphates [30,31]. The average Ga–F distance of 1.930 Å is consistent with those given for fluorogallophosphates [32]. The tetrahedral  $\text{PO}_3\text{C}$  units display average P–O distances of 1.534 Å and a P–C distance of 1.813 Å, values typically found in other metal phosphonates and diphosphonates [17,30].

The propyldiamine molecules in the synthesis gel are present as propyldiammonium cations within the structure of **2**. These dications align themselves along the  $c$ -axis and occupy the interlamellar space between the  $[\text{Ga}_2\text{F}_4(\text{O}_3\text{PC}_2\text{H}_4\text{PO}_3)]_\infty^{2-}$  layers, as shown in Fig. 7b. Each propyldiammonium cation has significant electrostatic interactions with adjacent  $[\text{Ga}_2\text{F}_4(\text{O}_3\text{PC}_2\text{H}_4\text{PO}_3)]_\infty^{2-}$  layers so forming the three-dimensional crystal structure of **2**. The organocations form hydrogen bonds with the terminal F atoms of the metal centered dimers and the O atoms of the diphosphonate groups with a donor–acceptor distance range of 2.731(4)–3.302(5) Å and donor–H–acceptor angular range of 100(2)–177(2)°. These distance and angles

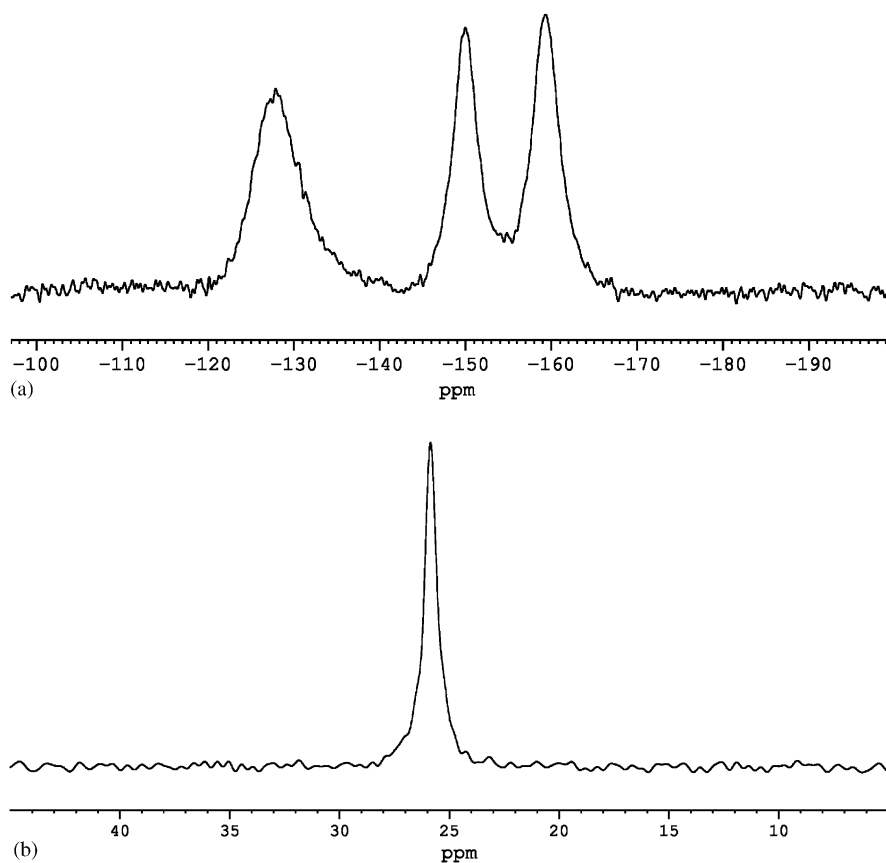


Fig. 6. The (a)  $^{19}\text{F}$  and (b)  $^{31}\text{P}$  MAS SSNMR spectrum of **1**.

indicate the hydrogen bonds are of moderate to weak strength and predominantly electrostatic in character [29].

A structural comparison of compounds **1** and **2** indicate that the structures are extremely closely related. Both contain  $[\text{M}_2\text{F}_4\text{X}_2(\text{O}_3\text{PC}_2\text{H}_4\text{PO}_3)]_\infty^{n-}$  chains consisting of pairs of edge sharing octahedra linked together by the ethylenediphosphonate groups that bridge both the octahedra within each dimer and pairs of dimers. In **1** the chains are separated by the propyldiammonium cations with the unbonded O atom of each diphosphonate  $-\text{PO}_3$  group hydrogen bonding to the propyldiammonium cation, while in **2** the remaining oxygen atoms of the  $-\text{PO}_3$  group fuse the chains together to form an aperture-containing layer. The close relation between structure **1** and **2**, and the similarity of the chemistry of aluminum and gallium, suggest that it maybe possible, under suitable reaction conditions and using the same metal species, to convert structure **1** to structure **2** through a condensation reaction. This reaction may proceed by the unbound O atom of each diphosphonate  $-\text{PO}_3$  group of the chains found in **1**, acting as a nucleophile, and substituting for one of the terminal F atoms of each of the metal dimers to fuse the chains together to form the aperture-containing layer of the type found in **2**, as shown in the reaction scheme

presented in Fig. 8. Such processes are believed to underpin the building-up principle of the formation of open-framework metal phosphate and oxalate structures [33,34].

The solitary type of octahedral–tetrahedral secondary building unit, SBU-4, found in structures **1** and **2** are closely related to those found in the phosphate and arsenate materials reported by Ferey [19] and Natarajan [20], respectively. These SBU-4 units provide an example of the occurrence of such units, known for inorganic materials, in hybrid extended structure metal phosphonate materials. Inclusion of such units into a hybrid system provides the possibility to control their spatial arrangement by incremental amounts through synthesizing analogous materials with diphosphonate groups containing longer alkyl chains and so may lead to more control over the structure, and properties, of the resulting solid-state materials.

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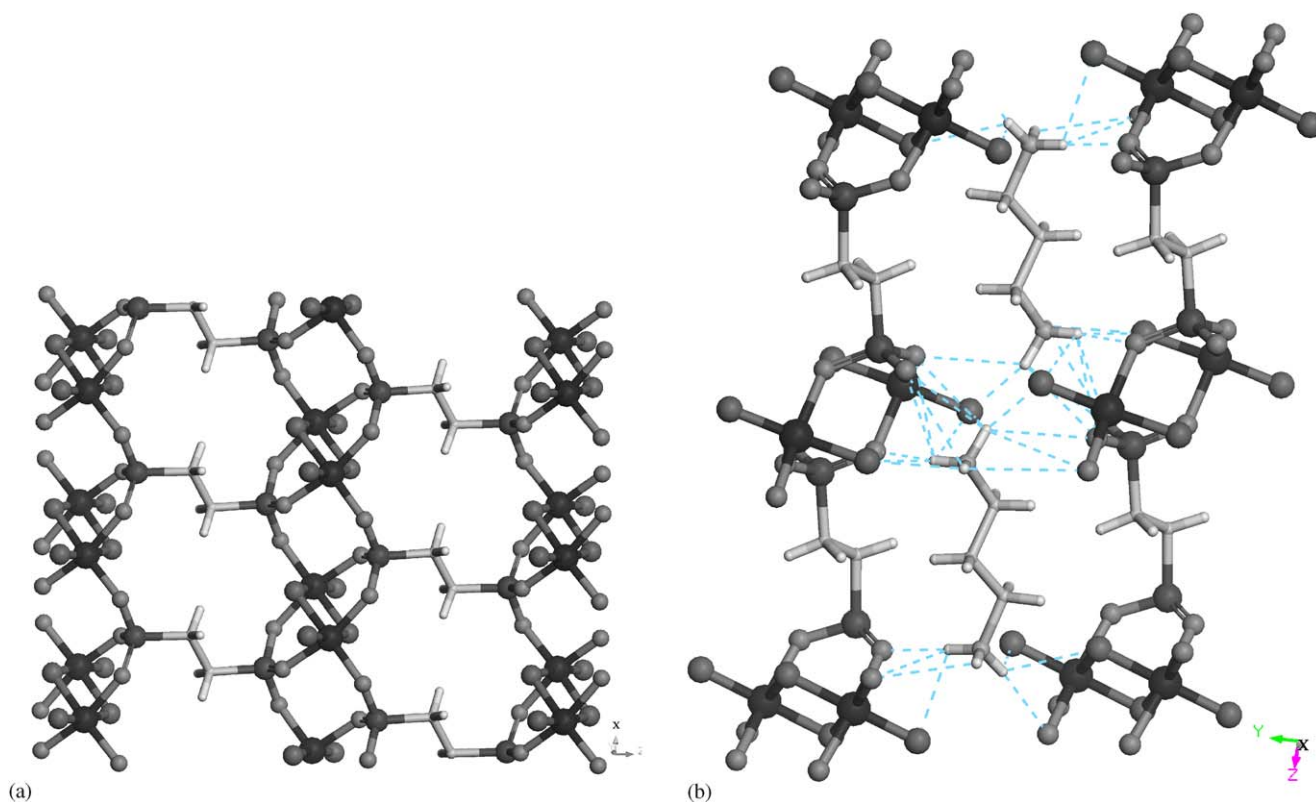


Fig. 7. The structure of **2** viewed (a) along the  $y$ -axis and (b) along the  $x$ -axis. The atoms are represented by balls that decrease in size and become lighter in the order Ga, P, F, O, N, C, H. Hydrogen bonds are represented by dotted lines.

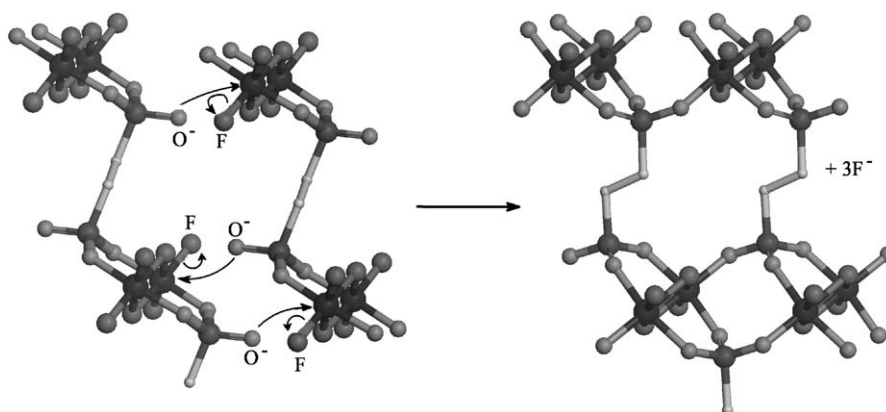


Fig. 8. A representation of the possible mechanism for the fusion of a section of the chains found in **1** to form the aperture-containing layer of the type found in **2**. The atoms are represented by balls that decrease in size and become lighter in the order  $M$  (Al or Ga), P, F, O, N. Hydrogen atoms are omitted for clarity.

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**Supporting information available:** Crystallographic data (excluding structure factors) for the structures **1** and **2** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 230020 and 230021. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2

1EZ, UK (fax: +44-1223 336-033; [mailto: deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

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