

# Synthesis and characterization of two novel pyridine-containing framework gallium ethylenediphosphonates

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## Abstract

Two novel gallium diphosphonates,  $(\text{C}_5\text{H}_5\text{N})\text{Ga}_3\text{F}(\text{O}_3\text{PC}_2\text{H}_4\text{PO}_3)_2$  (**I**) (triclinic,  $P-1$ ,  $a = 8.2880(12) \text{ \AA}$ ,  $b = 11.7197(16) \text{ \AA}$ ,  $c = 11.7601(17) \text{ \AA}$ ,  $\alpha = 71.589(3)^\circ$ ,  $\beta = 70.577(3)^\circ$ ,  $\gamma = 77.313(3)^\circ$ ,  $V = 1013.7(2) \text{ \AA}^3$ ,  $Z = 2$ ,  $R_1 = 0.0352$ ,  $wR_2 = 0.0980$ ) and  $(\text{C}_5\text{H}_5\text{NH})_2[\text{Ga}_4\text{F}_2(\text{O}_3\text{PC}_2\text{H}_4\text{PO}_3)_3]$  (**II**) (triclinic,  $P-1$ ,  $a = 8.670(4) \text{ \AA}$ ,  $b = 9.742(3) \text{ \AA}$ ,  $c = 10.406(2) \text{ \AA}$ ,  $\alpha = 81.44(3)^\circ$ ,  $\beta = 65.83(5)^\circ$ ,  $\gamma = 67.16(3)^\circ$ ,  $V = 739.0(4) \text{ \AA}^3$ ,  $Z = 2$ ,  $R_1 = 0.0600$ ,  $wR_2 = 0.1495$ ) have been synthesised by solvothermal methods in the presence of pyridine and their structures determined using single-crystal X-ray diffraction data. Both compounds **I** and **II** are composed of various Ga-centered polyhedra and ethylenediphosphonate groups that link together to form framework materials with one- and two-dimensional channel systems, respectively. The two structures are formed in the presence of structure-directing pyridine molecules that are directly bound to some of the Ga atoms in **I**, and are protonated as pyridinium cations in **II**. Compound **I** has a charge-neutral framework, while compound **II** has an anionic framework. Both materials provide rare examples of organically structure-directed framework metal diphosphonate materials.

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**Keywords:** Gallium; Diphosphonate; Pyridine; Framework; Hybrid material; Template

## 1. Introduction

Enormous growth in the field of hybrid framework materials has occurred over the last 10 years due to the huge possibilities available for designing materials with specific chemical functionality, internal surface properties and framework structures. These materials are exhibiting potentially exploitable properties for use in applications such as sorption and gas storage, ion-exchange, sensing, electroluminescence, non-linear optics and catalysis [1,2]. A major subset of this type of material is coordination polymers, which are extended arrays composed of metal atoms or clusters bridged by polyfunctional organic molecules [3]. An established family of framework coordination polymers is that of metal diphosphonates [4],

for which the possible designs of the precursor diphosphonic acid  $[(\text{HO})_2\text{OPRPO}(\text{OH})_2]$  allow a diverse group of materials with varied chemistry and structure to be formed. Examples of such framework diphosphonates include  $\{M[\text{O}_3\text{PCH}_2\text{NH}(\text{C}_2\text{H}_4)\text{NHCH}_2\text{PO}_3]\} \cdot \text{H}_2\text{O}$  ( $M = \text{Mn}, \text{Co}$ ) [5],  $\text{Na}_2\text{Zn}(\text{O}_3\text{PCH}_2\text{PO}_3) \cdot \text{H}_2\text{O}$  [6],  $\text{Na}[\text{Zn}_2(\text{OH})(\text{O}_3\text{PCH}_2\text{PO}_3)] \cdot 1.5\text{H}_2\text{O}$  [7] and  $(\text{NH}_4)_4[(\text{V}^{\text{IV}}\text{O})_3(\text{O}_3\text{PCH}_2\text{PO}_3)_4(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}$  [8].

The structures adopted by metal diphosphonates are dependent upon many factors. For any particular metal and diphosphonic acid combination, one important factor is whether there are any additional molecules or charge-compensating cations present that influence the formation of, and are occluded within, the final structure. The occluded species may be charge-compensating inorganic or organic cations, or neutral molecules, as exemplified by microporous aluminosilicate materials where all the aforementioned species have been found to direct the structure of the resultant framework material [9–11]. In the area of metal diphosphonate chemistry there are examples of

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framework structures containing inorganic cations [5–8] but relatively few examples are known for which structure-directing organic cations or molecules are incorporated into the final material. One example of the latter is  $[\text{NH}_3(\text{CH}_2)_2\text{NH}_3]\{\text{Zn}_3[\text{O}_3\text{P}(\text{CH}_2)_2\text{PO}_3]_2\}$  [12], although there are more numerous examples of hydrogen-bonded framework structures with occluded structure-directing organic species, for instance,  $[\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{Zn}_2[\text{CH}_3\text{C}(\text{OH})(\text{PO}_3)(\text{PO}_3\text{H})]_2 \cdot 2\text{H}_2\text{O}$ , ( $n = 4, 5$ ) [13] and  $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3]\text{Fe}_2[\text{CH}_3\text{C}(\text{OH})(\text{PO}_3)(\text{PO}_3\text{H})]_2 \cdot 2\text{H}_2\text{O}$  [14].

Surprisingly, the use of organic cationic or molecular species in the formation of gallium phosphonates/diphosphonates has been limited despite the routine use of such species to form new microporous gallium phosphates/fluorophosphates [15,16]. Organic cations have been used to direct the structure of the layered gallium phosphonate/diphosphonates and the hydrogen-bonded framework materials  $(\text{C}_5\text{H}_5\text{NH})[\text{Ga}_2(\text{H}_2\text{O})_2(\text{O}_3\text{PCH}_2\text{PO}_3)(\text{O}_3\text{PCH}_2\text{PO}_3\text{H})]$  and  $[(\text{CH}_3)_4\text{N}][\text{Ga}_2(\text{H}_2\text{O})_2(\text{O}_3\text{PCH}_2\text{PO}_3)(\text{O}_3\text{PCH}_2\text{PO}_3\text{H})]$  [17–19]. However, no framework gallium diphosphonate materials containing organic cationic or molecular species have been reported in the literature.

During the course of our program to investigate the structural chemistry of group 13 metal diphosphonates we have discovered two novel framework materials,  $(\text{C}_5\text{H}_5\text{N})\text{Ga}_3\text{F}(\text{O}_3\text{PC}_2\text{H}_4\text{PO}_3)_2$  (**I**) and  $(\text{C}_5\text{H}_5\text{NH})_2[\text{Ga}_4\text{F}_2(\text{O}_3\text{PC}_2\text{H}_4\text{PO}_3)_3]$  (**II**). These compounds represent the first framework gallium diphosphonate materials to be synthesized in the presence of structure-directing organic species. The materials contain a wide variety of gallium-centered polyhedral species that combine with the diphosphonate groups to form framework structures containing pore systems of different dimensionality. The compounds contain structure-directing pyridine species that are occluded in the resultant materials in differing manners to form the neutral and anionic frameworks of **I** and **II**, respectively.

## 2. Experimental section

### 2.1. Synthesis and initial characterization

The reagents used in the synthesis of both materials were  $\text{Ga}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  (Alfa Aesar), ethylenediphosphonic acid (Lancaster), HF (48 wt% in  $\text{H}_2\text{O}$ , Aldrich), pyridine (Aldrich), *N, N, N', N', N''*-pentamethyldiethylenetriamine (pmdeta), (Aldrich) and tris(2-aminoethyl)amine (Aldrich). All the aforementioned reagents were used without further purification.

The sample of  $(\text{C}_5\text{H}_5\text{N})\text{Ga}_3\text{F}(\text{O}_3\text{PC}_2\text{H}_4\text{PO}_3)_2$  (**I**) used for structure determination was synthesized under solvothermal conditions. Initially  $\text{Ga}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  (0.769 mmol) was dissolved in a solution of distilled water (111 mmol), pyridine (32.9 mmol) and HF (4.56 mmol), followed by the addition of ethylenediphosphonic acid (3.83 mmol) and pmdeta (12.9 mmol) to the subsequent mixture. The resultant mixture contained  $\text{Ga}_2(\text{SO}_4)_3$ , ethylenediphosphonic acid, HF,  $[(\text{CH}_3)_2\text{NCH}_2\text{CH}_2]_2\text{NCH}_3$ , pyridine and water in the molar ratio: 1:4.98:5.93:16.8:42.8:170 and, after stirring, had a pH of 9.58. The reagent mixture was loaded in a 23 ml Teflon-lined steel autoclave, heated at 180 °C for 8 days and slowly cooled in air to room temperature. The resultant solid product was washed with de-ionized water, separated by suction filtration and contained colourless, needle-like single crystals. The sample was not monophasic and contained one or more unidentified additional phases, although compound **I** was the predominant phase present. Microprobe analysis on crystals of compound **I** indicated a Ga:P ratio of 1:1.39 and that fluorine was present in the crystals.

A sample of  $(\text{C}_5\text{H}_5\text{NH})_2[\text{Ga}_4\text{F}_2(\text{O}_3\text{PC}_2\text{H}_4\text{PO}_3)_3]$  (**II**) was synthesized in a similar manner to compound **I**. Initially  $\text{Ga}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  (0.768 mmol) was dissolved in a solution of distilled water (111 mmol), pyridine (32.9 mmol) and HF (4.32 mmol), followed by the addition of ethylenediphosphonic acid (3.25 mmol) and tris(2-aminoethyl)amine (8.70 mmol) to the subsequent mixture. The resultant mixture contained  $\text{Ga}_2(\text{SO}_4)_3$ , ethylenediphosphonic acid, HF, tris(2-aminoethyl)amine, pyridine and water in the molar ratio: 1:4.24:5.62:11.3:42.8:170 and, after stirring, had a pH of 11.16. This reagent mixture was loaded in a 23 ml Teflon-lined steel autoclave and heated for 12 days at 150 °C and slowly cooled in air to room temperature. The resultant solid product was washed with de-ionized water, separated by suction filtration and consisted of colorless, plate-like single crystals. The powder X-ray diffraction pattern of this product is provided in the Supporting Information and was judged to be monophasic from the excellent agreement between the experimental powder X-ray diffraction pattern and that calculated using the Le Bail profile analysis [20] starting with the unit cell parameters obtained from the single-crystal analysis of compound **II**. Microprobe analysis on crystals of compound **II** indicated a Ga:P ratio of 1:1.5 and that fluorine was present in the crystals.

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

The MAS SS NMR spectrum was collected from compound **II** using a Varian Unity Inova spectrometer with a 7.05 T Oxford Instruments magnet. The spectrum collected for  $^{31}\text{P}$  nuclei was reference to an 85% solution of  $\text{H}_3\text{PO}_4$  with the spectrometer operating at a frequency of 121.37 MHz, a sample spinning speed of 12 kHz, recycle delays of 300 s, and an acquisition time of 20.2 ms.

### 2.3. Thermogravimetric analysis

Thermogravimetric analysis (TGA) data were collected on compound **II** using a TA Instruments Thermal Analysis 2000 system. The sample was contained in a platinum holder and heated under a flow of air from room

temperature to 200 °C at a heating rate of 2 °C min<sup>-1</sup> and from 200 to 900 °C at a heating rate of 1 °C min<sup>-1</sup>.

#### 2.4. Single-crystal X-ray diffraction

Single-crystal X-ray data were collected from a colorless, needle-like single microcrystal of compound **I** mounted on a Bruker SMART CCD diffractometer at the high-flux single-crystal diffraction station 9.8 at CCLRC Daresbury Laboratory Synchrotron Radiation Source, UK and from a single, colorless, plate-like crystal of compound **II** mounted on a Nonius KappaCCD diffractometer. The structures of both compounds were solved by direct methods and refined by full-matrix least squares using the SHELXTL suite of programs [21].

The gallium and phosphorus atom positions were determined directly from the structure solution, and the carbon, nitrogen, oxygen and fluorine atoms were located subsequently from difference Fourier maps. The atomic displacement parameters of all of the non-hydrogen atoms were refined anisotropically. All the hydrogen atoms of structure **I** and **II** were geometrically placed except the hydrogen atom attached to the pyridine nitrogen atom in structure **II**, which was found in a difference Fourier map and refined freely. All the other hydrogen atoms were refined in riding mode with their isotropic atomic displacement factors fixed at values of 1.2 times  $U_{eq}$  of the carbon or nitrogen atoms to which they were directly connected. The elemental assignment of the bridging atoms between the gallium-centered polyhedra in both structures was as fluorine, and not hydroxide or water groups, due to the significant improvement in residuals with this assignment, the failure to find any hydrogen atoms in the vicinity of these atoms in different Fourier maps or any potential hydrogen-bond acceptors at an appropriate distance, and the fact that the observed bond distances are more appropriate for bridging F than for bridging OH, based on an analysis of structures in the Cambridge Structural Database (version 5.26 with 2 updates, May 2005) [22]. Additionally, microprobe analysis on crystals of **I** and **II** indicated that fluorine was present in both materials. The crystallographic data and structure refinement parameters for structures **I** and **II** 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 compound **I** and **II** are shown in Figs. 1 and 2, respectively.

### 3. Results and discussion

#### 3.1. Structural description of

##### $(C_5H_5N)Ga_3F(O_3PC_2H_4PO_3)_2$ (**I**)

The crystal structure of  $(C_5H_5N)Ga_3F(O_3PC_2H_4PO_3)_2$  (**I**) is shown in Fig. 3. The main structural constituent of **I** is shown in Fig. 4 and is a cluster containing three different

Table 1

Crystallographic data and structure refinement parameters for  $(C_5H_5N)Ga_3F(O_3PC_2H_4PO_3)_2$  (**I**) and  $(C_5H_5NH)_2[Ga_4F_2(O_3PC_2H_4PO_3)_3]$  (**II**)

Compound	<b>I</b>	<b>II</b>
Formula	$C_9H_{13}FGa_3NO_{12}P_4$	$C_{16}H_{24}F_2Ga_4N_2O_{18}P_6$
Formula weight	679.24	1035.08
Crystal size (mm)	$0.1 \times 0.05 \times 0.02$	$0.2 \times 0.05 \times 0.05$
Temperature (K)	120(2)	150(2)
Wavelength (Å)	0.6898	0.71073 (MoK $\alpha$ )
	(synchrotron)	
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1
<i>a</i> (Å)	8.2880(12)	8.670(4)
<i>b</i> (Å)	11.7197(16)	9.742(3)
<i>c</i> (Å)	11.7601(17)	10.406(2)
$\alpha$ (deg)	71.589(3)	81.44(3)
$\beta$ (deg)	70.577(3)	65.83(5)
$\gamma$ (deg)	77.313(3)	67.16(3)
<i>V</i> (Å <sup>3</sup> )	1013.7(2)	739.0(4)
<i>Z</i>	2	2
<i>d</i> <sub>c</sub> (g cm <sup>-3</sup> )	2.225	2.326
$\mu$ (mm <sup>-1</sup> )	4.343	4.030
$2\theta_{min}$ – $2\theta_{max}$ (deg)	3.6–59.0	8.2–55.0
Data/parameters	5469/271	3320/220
<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>	0.0352, 0.0396	0.0600, 0.1132
<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>	0.0956, 0.0980	0.1323, 0.1495
S on <i>F</i> <sup>2</sup>	1.050	1.091
Electron density min/max ( <i>e</i> Å <sup>-3</sup> )	–0.70/1.95	–1.13/1.69

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

$$^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)]^2 / \sum [w(F_o^2)]^2 \}^{1/2} \text{ with } w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP], P = [2F_c^2 + \text{Max}(F_o^2, 0)] / 3, \text{ where } a = 0.0545 \text{ and } b = 0.7031 \text{ for } \mathbf{I} \text{ and } a = 0.0634 \text{ and } b = 2.3580 \text{ for } \mathbf{II}.$$

types of gallium-centered polyhedron and four phosphorus-centered PO<sub>3</sub>C tetrahedra. The latter are derived from the ethylenediphosphonate ligands within the compound. The Ga-centered polyhedra within each cluster are a Ga(2)O<sub>4</sub> tetrahedron, a Ga(1)O<sub>4</sub>F trigonal bipyramid and a Ga(3)O<sub>4</sub>FN octahedron. The oxygen atoms at the vertices of all the Ga-centered polyhedra are those from the –PO<sub>3</sub> groups of the diphosphonate ligands. The Ga(1)O<sub>4</sub>F trigonal bipyramid contains a fluorine atom, F(1), at one of its axial sites that forms a bridge to the Ga(3)O<sub>4</sub>FN octahedron to give a corner-sharing Ga-centered polyhedral pair within each cluster. The nitrogen atom N(1) in the Ga(3)O<sub>4</sub>FN octahedron occupies an axial position located *trans* to F(1). N(1) forms part of the pyridine ring which is coordinated directly to Ga(3). The three Ga-centered polyhedra are connected in the cluster by the four PO<sub>3</sub>C tetrahedra. Three of the PO<sub>3</sub>C tetrahedra use two of their oxygen atoms to bind to two different Ga atoms within the cluster. The remaining O and C atoms within these PO<sub>3</sub>C groups are involved in forming P–O–Ga and P–CH<sub>2</sub>–CH<sub>2</sub>–P bridges to other clusters identical to that shown in Fig. 4. The fourth PO<sub>3</sub>C group in the cluster uses all three O atoms to bind to the three Ga atoms in a cluster, leaving

Table 2

Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for compounds **I** and **II**

Atom	x	y	z	$U_{\text{eq}}^a$
<b>Compound I</b>				
Ga(1)	0.87195(4)	0.53134(2)	0.69524(3)	0.00706(8)
Ga(2)	0.65792(4)	0.84009(3)	0.48732(3)	0.00746(8)
Ga(3)	0.54675(4)	0.71350(2)	0.87805(3)	0.00631(8)
P(1)	0.75840(8)	0.45741(6)	0.98711(6)	0.0066(1)
P(2)	0.75088(9)	0.56548(6)	0.45882(6)	0.0068(1)
P(3)	0.87935(9)	0.79653(6)	0.67302(6)	0.0072(1)
P(4)	0.66355(9)	1.09191(6)	0.31110(6)	0.0068(1)
O(1)	0.5612(3)	1.1377(2)	0.2183(2)	0.0090(4)
O(2)	0.6525(3)	0.5811(2)	0.9860(2)	0.0093(4)
O(3)	0.7900(3)	0.4974(2)	0.5832(2)	0.0088(4)
O(4)	0.8273(3)	0.4357(2)	0.8558(2)	0.0103(4)
O(5)	0.6646(2)	0.3523(2)	1.0773(2)	0.0083(4)
O(6)	0.7606(3)	0.79023(2)	0.8038(2)	0.0091(4)
O(7)	0.9706(3)	0.6720(2)	0.6542(2)	0.0105(4)
O(8)	0.6746(3)	0.6978(2)	0.4547(2)	0.0118(4)
O(9)	0.9062(3)	0.5615(2)	0.3466(2)	0.0113(4)
O(10)	0.7119(3)	0.9528(2)	0.3357(2)	0.0092(4)
O(11)	0.7927(3)	0.8636(2)	0.5687(2)	0.0105(4)
O(12)	0.5691(3)	1.1221(2)	0.4376(2)	0.0095(4)
F(1)	0.6402(2)	0.6367(2)	0.7395(2)	0.0112(3)
N(1)	0.4706(3)	0.7955(2)	1.0212(2)	0.0131(5)
C(1)	0.3037(5)	0.8304(3)	1.0722(4)	0.0260(7)
C(2)	0.5877(5)	0.8139(4)	1.0665(4)	0.0278(8)
C(3)	0.3731(6)	0.9040(4)	1.2161(4)	0.0369(9)
C(4)	0.5441(6)	0.8686(4)	1.1628(4)	0.0368(9)
C(5)	0.2510(6)	0.8833(4)	1.1709(4)	0.040(1)
C(6)	0.8584(3)	1.1580(2)	0.2576(3)	0.0099(5)
C(7)	1.0439(4)	0.8858(2)	0.6433(3)	0.0102(5)
C(8)	0.5855(3)	0.4961(3)	0.4483(3)	0.0098(5)
C(9)	0.9403(3)	0.4516(2)	1.0413(3)	0.0112(5)
<b>Compound II</b>				
Ga(1)	0.1324(1)	1.14930(9)	0.86246(8)	0.0079(2)
Ga(2)	0.1199(1)	1.54631(9)	0.84910(9)	0.0072(2)
P(1)	−0.7588(3)	1.8029(2)	0.8824(2)	0.0082(4)
P(2)	0.1994(3)	1.3580(2)	0.5908(2)	0.0093(4)
P(3)	−0.2877(3)	1.7193(2)	0.9901(2)	0.0085(4)
F(1)	0.0010(6)	1.3929(5)	0.9371(4)	0.0098(9)
O(1)	−0.7600(7)	1.9481(5)	0.8019(5)	0.009(1)
O(2)	−0.8961(7)	1.8403(6)	1.0365(5)	0.009(1)
O(3)	−0.7982(7)	1.7082(6)	0.8052(5)	0.011(1)
O(4)	−0.2854(7)	1.8498(6)	1.0568(6)	0.011(1)
O(5)	−0.3112(7)	1.5935(6)	1.0965(5)	0.010(1)
O(6)	−0.1206(7)	1.6653(6)	0.8534(5)	0.010(1)
O(7)	0.3623(8)	1.3043(6)	0.4555(6)	0.017(1)
O(8)	0.1722(8)	1.2249(6)	0.6872(6)	0.013(1)
O(9)	0.2148(7)	1.4743(6)	0.6654(5)	0.011(1)
C(1)	0.691(1)	1.024(1)	0.5482(0)	0.025(2)
C(2)	0.791(1)	0.952(1)	0.6272(9)	0.026(2)
C(3)	0.834(1)	1.034(1)	0.6957(9)	0.025(2)
C(4)	0.778(1)	1.186(1)	0.683(1)	0.028(2)
C(5)	0.674(1)	1.254(1)	0.6051(9)	0.022(2)
C(6)	−0.487(1)	1.8051(8)	0.9515(8)	0.009(2)
C(7)	−0.004(1)	1.4403(8)	0.5561(8)	0.011(2)
C(8)	−0.541(1)	1.7063(8)	0.8890(8)	0.009(2)
N(1)	0.6359(0)	1.1730(9)	0.5389(8)	0.019(2)

<sup>a</sup>  $U_{\text{eq}}$  is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

Table 3

Selected bond distances ( $\text{\AA}$ ) for compounds **I** and **II**

Compound I		Compound II	
Ga(1)–O(3)	1.844(2)	Ga(1)–F(1)	2.293(4)
Ga(1)–O(4)	1.827(1)	Ga(1)–O(1) <sup>i</sup>	1.891(5)
Ga(1)–O(7)	1.856(2)	Ga(1)–O(2) <sup>ii</sup>	1.849(5)
Ga(1)–O(9) <sup>i</sup>	1.914(2)	Ga(1)–O(4) <sup>iii</sup>	1.842(5)
Ga(1)–F(1)	2.046(1)	Ga(1)–O(8)	1.808(5)
Ga(2)–O(8)	1.793(2)	Ga(2)–F(1)	2.038(4)
Ga(2)–O(10)	1.835(1)	Ga(2)–F(1) <sup>iii</sup>	2.098(4)
Ga(2)–O(11)	1.803(2)	Ga(2)–O(3) <sup>iv</sup>	1.895(5)
Ga(2)–O(12) <sup>ii</sup>	1.814(2)	Ga(2)–O(5) <sup>iii</sup>	1.927(5)
Ga(3)–O(1) <sup>ii</sup>	1.966(1)	Ga(2)–O(6)	1.938(5)
Ga(3)–O(2)	1.920(1)	Ga(2)–O(9)	1.868(5)
Ga(3)–O(5) <sup>iii</sup>	1.914(1)	P(1)–O(1)	1.531(5)
Ga(3)–O(6)	1.972(2)	P(1)–O(2)	1.548(5)
Ga(3)–F(1)	1.961(1)	P(1)–O(3)	1.518(5)
Ga(3)–N(1)	2.050(3)	P(1)–C(8)	1.775(8)
P(1)–O(2)	1.519(1)	P(2)–O(7)	1.506(6)
P(1)–O(4)	1.541(2)	P(2)–O(8)	1.549(6)
P(1)–O(5)	1.515(1)	P(2)–O(9)	1.539(5)
P(1)–C(9)	1.803(3)	P(2)–C(7)	1.796(8)
P(2)–O(3)	1.531(1)	P(3)–O(4)	1.546(5)
P(2)–O(8)	1.532(2)	P(3)–O(5)	1.541(6)
P(2)–O(9)	1.511(2)	P(3)–O(6)	1.531(5)
P(2)–C(8)	1.795(3)	P(3)–C(6)	1.785(8)
P(3)–O(6)	1.514(2)	C(1)–C(2)	1.36(1)
P(3)–O(7)	1.536(2)	C(2)–C(3)	1.38(1)
P(3)–O(11)	1.539(2)	C(3)–C(4)	1.37(1)
P(3)–C(7)	1.777(3)	C(4)–C(5)	1.37(1)
P(4)–O(1)	1.499(1)	C(5)–N(1)	1.33(1)
P(4)–O(10)	1.547(1)	C(1)–N(1)	1.34(1)
P(4)–O(12)	1.545(2)	C(6)–C(8)	1.54(1)
P(4)–C(6)	1.781(3)	C(7)–C(7) <sup>vii</sup>	1.52(2)
N(1)–C(1)	1.340(4)		
N(1)–C(2)	1.335(4)		
C(1)–C(5)	1.386(5)		
C(2)–C(4)	1.382(5)		
C(3)–C(4)	1.374(6)		
C(3)–C(5)	1.383(7)		
C(6)–C(7) <sup>iv</sup>	1.531(4)		
C(8)–C(8) <sup>v</sup>	1.537(5)		
C(9)–C(9) <sup>vi</sup>	1.539(5)		

Symmetry codes for **I**: (i)  $2-x, 1-y, 1-z$ ; (ii)  $1-x, 2-y, 1-z$ ; (iii)  $1-x, 1-y, 2-z$ ; (iv)  $2-x, 2-y, 1-z$ ; (v)  $1-x, 1-y, 1-z$ ; (vi)  $2-x, 1-y, 2-z$ .Symmetry codes for **II**: (i)  $1+x, -1+y, z$ ; (ii)  $-1-x, 3-y, 2-z$ ; (iii)  $-x, 3-y, 2-z$ ; (iv)  $1+x, y, z$ ; (v)  $-1+x, 1+y, z$ ; (vi)  $-1+x, y, z$ ; (vii)  $-x, 3-y, 1-z$ .

only the C atom to form a P–CH<sub>2</sub>–CH<sub>2</sub>–P bridge to another cluster. Each cluster binds to seven other identical clusters through P–O–Ga and P–CH<sub>2</sub>–CH<sub>2</sub>–P bridges to form the framework structure shown in Fig. 3. The average Ga–O<sub>tetrahedral</sub>, Ga–O<sub>trigonal–bipyramidal</sub> and Ga–O<sub>octahedral</sub> bond distances of 1.811, 1.860 and 1.943 Å, respectively, agree well with those reported in other gallophosphate and gallium diphosphonates [23–26]. The Ga–F<sub>trigonal–bipyramidal</sub> and Ga–F<sub>octahedral</sub> bond distances of 2.046(1), and 1.961(1) Å, respectively, agree well with those reported in other gallofluorophosphate and gallium diphosphonates [25,26]. The Ga–N<sub>octahedral</sub> bond distance of 2.050(3) Å agrees well



Table 4  
Selected bond angles (deg) for structures **I** and **II**

Compound I	Compound II
O(3)–Ga(1)–O(4)	118.83(9)
O(3)–Ga(1)–O(7)	121.07(9)
O(3)–Ga(1)–O(9) <sup>i</sup>	95.62(9)
O(3)–Ga(1)–F(1)	86.08(8)
O(4)–Ga(1)–O(7)	119.53(9)
O(4)–Ga(1)–O(9) <sup>i</sup>	90.22(8)
O(4)–Ga(1)–F(1)	90.57(8)
O(7)–Ga(1)–O(9) <sup>i</sup>	91.64(9)
O(7)–Ga(1)–F(1)	85.89(8)
O(9) <sup>i</sup> –Ga(1)–F(1)	177.48(8)
O(8)–Ga(2)–O(10)	106.62(9)
O(8)–Ga(2)–O(11)	121.92(9)
O(8)–Ga(2)–O(12) <sup>ii</sup>	105.57(9)
O(10)–Ga(2)–O(11)	103.41(9)
O(10)–Ga(2)–O(12) <sup>ii</sup>	106.89(9)
O(11)–Ga(2)–O(12) <sup>ii</sup>	111.51(9)
O(1) <sup>ii</sup> –Ga(3)–O(2)	172.35(9)
O(1) <sup>ii</sup> –Ga(3)–O(5) <sup>iii</sup>	87.31(8)
O(1) <sup>ii</sup> –Ga(3)–O(6)	86.10(8)
O(1) <sup>ii</sup> –Ga(3)–F(1)	94.83(8)
O(1) <sup>ii</sup> –Ga(3)–N(1)	86.83(9)
O(2)–Ga(3)–O(5) <sup>iii</sup>	95.88(8)
O(2)–Ga(3)–O(6)	91.51(8)
O(2)–Ga(3)–F(1)	92.15(8)
O(2)–Ga(3)–N(1)	85.96(9)
O(5) <sup>iii</sup> –Ga(3)–O(6)	170.54(8)
O(5) <sup>iii</sup> –Ga(3)–F(1)	89.57(8)
O(5) <sup>iii</sup> –Ga(3)–N(1)	95.19(10)
O(6)–Ga(3)–F(1)	84.23(8)
O(6)–Ga(3)–N(1)	91.22(9)
F(1)–Ga(3)–N(1)	175.04(9)
O(2)–P(1)–O(4)	112.02(11)
O(2)–P(1)–O(5)	114.18(11)
O(2)–P(1)–C(9)	107.81(13)
O(4)–P(1)–O(5)	109.05(11)
O(4)–P(1)–C(9)	108.27(13)
O(5)–P(1)–C(9)	105.12(11)
O(3)–P(2)–O(8)	111.92(12)
O(3)–P(2)–O(9)	113.16(11)
O(3)–P(2)–C(8)	107.33(12)
O(8)–P(2)–O(9)	109.31(12)
O(8)–P(2)–C(8)	105.64(12)
O(9)–P(2)–C(8)	109.17(12)
O(6)–P(3)–O(7)	113.26(11)
O(6)–P(3)–O(11)	114.10(11)
O(6)–P(3)–C(7)	109.01(13)
O(7)–P(3)–O(11)	109.88(12)
O(7)–P(3)–C(7)	106.67(12)
O(11)–P(3)–C(7)	103.16(12)
O(1)–P(4)–O(10)	110.07(12)
O(1)–P(4)–O(12)	113.77(11)
O(1)–P(4)–C(6)	112.12(12)
O(10)–P(4)–O(12)	108.52(11)
O(10)–P(4)–C(6)	107.78(12)
O(12)–P(4)–C(6)	104.24(13)
C(1)–N(1)–C(2)	118.5(3)
N(1)–C(1)–C(5)	121.6(4)
N(1)–C(2)–C(4)	122.7(4)
C(4)–C(3)–C(5)	118.5(4)
C(2)–C(4)–C(3)	119.0(4)
C(1)–C(5)–C(3)	119.6(4)
P(4)–C(6)–C(7) <sup>iv</sup>	110.97(18)
P(3)–C(7)–C(6) <sup>iv</sup>	113.10(18)

Table 4 (continued)

Compound I	Compound II
P(2)–C(8)–C(8) <sup>v</sup>	114.2(3)
P(1)–C(9)–C(9) <sup>vi</sup>	113.9(2)

Symmetry code for **I**: (i)  $2-x, 1-y, 1-z$ ; (ii)  $1-x, 2-y, 1-z$ ; (iii)  $1-x, 1-y, 2-z$ ; (iv)  $2-x, 2-y, 1-z$ ; (v)  $1-x, 1-y, 1-z$ ; (vi)  $2-x, 1-y, 2-z$ .

Symmetry code for **II**: (i)  $1+x, -1+y, z$ ; (ii)  $-1-x, 3-y, 2-z$ ; (iii)  $-x, 3-y, 2-z$ ; (iv)  $1+x, y, z$ ; (v)  $-1+x, 1+y, z$ ; (vi)  $-1+x, y, z$ ; (vii)  $-x, 3-y, 1-z$ .

Table 5

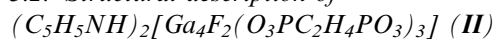
Hydrogen bond distance (Å) and angle (deg) for structure **II**.

Donor–H...Acceptor	D–H	H...A	D...A	D–H...A
N(1)–H(9)...O(7)	0.79(10)	1.89(10)	2.649(10)	161(10)

with those reported in other hybrid gallophosphate compounds containing Ga–N bonds [23,27–29]. The tetrahedral PO<sub>3</sub>C units display average P–O distances of 1.527 Å and P–C distances of 1.789 Å, values typically found in other gallium diphosphonates [19,26].

The resultant framework contains a one-dimensional channel system in which the channels run parallel to the [100] direction. The channels are bounded by rings of 12 polyhedra and also contain some of the ethylene chains of the diphosphonate groups. This results in channels whose surface contains both hydrophobic and hydrophilic portions. The channels are occupied by the pyridine molecules that are directly coordinated to the Ga(3) atoms within the framework.

### 3.2. Structural description of



The crystal structure of (C<sub>5</sub>H<sub>5</sub>NH)<sub>2</sub>[Ga<sub>4</sub>F<sub>2</sub>(O<sub>3</sub>PC<sub>2</sub>H<sub>4</sub>PO<sub>3</sub>)<sub>3</sub>] (**II**) is shown in Fig. 5a and b. The main structural constituent of **II** is shown in Fig. 6 and is a cluster containing two Ga-centered octahedra, two Ga-centered trigonal bipyramids and four P-centered PO<sub>3</sub>C tetrahedra. The tetrahedra are derived from the ethylenediphosphonate ligands within the compound. The Ga-centered octahedra and trigonal bipyramids within each cluster are linked directly to form a tetramer of Ga-centered polyhedra. This tetramer contains a dimer of edge-sharing Ga(2)O<sub>4</sub>F<sub>2</sub> octahedra, in which the fluorine atoms, F(1), occupy the two edge-sharing vertices of the Ga(2)O<sub>4</sub>F<sub>2</sub> octahedra. Each of these F atoms also makes a bridging bond to a Ga(1)O<sub>4</sub>F trigonal bipyramid and forms one of the axial vertices of this polyhedron, resulting in each Ga(1)O<sub>4</sub>F trigonal bipyramid corner sharing with one of the edge-sharing vertices of the dimer, as shown in Fig. 6. All the O atoms at the vertices of all the Ga-centered polyhedra in the tetramer are donated by the –PO<sub>3</sub> groups of the diphosphonate ligands. The tetramer of Ga-centered

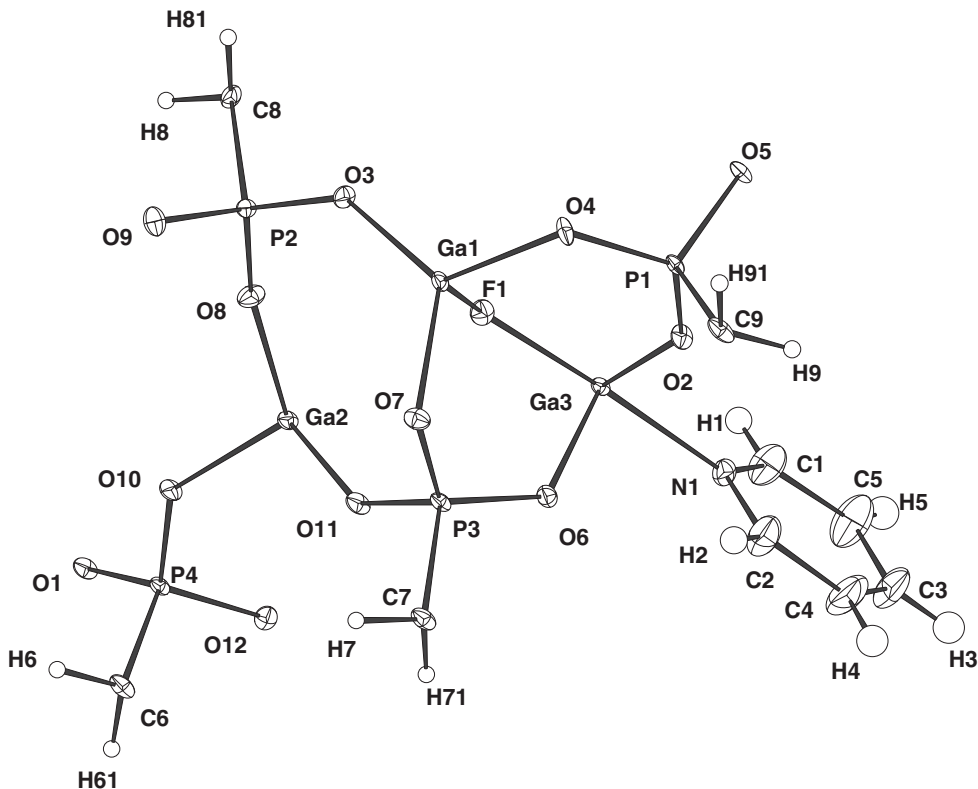


Fig. 1. The asymmetric unit of  $(C_5H_5N)Ga_3F(O_3PC_2H_4PO_3)_2$  I. Displacement ellipsoids are shown at the 50% probability level.

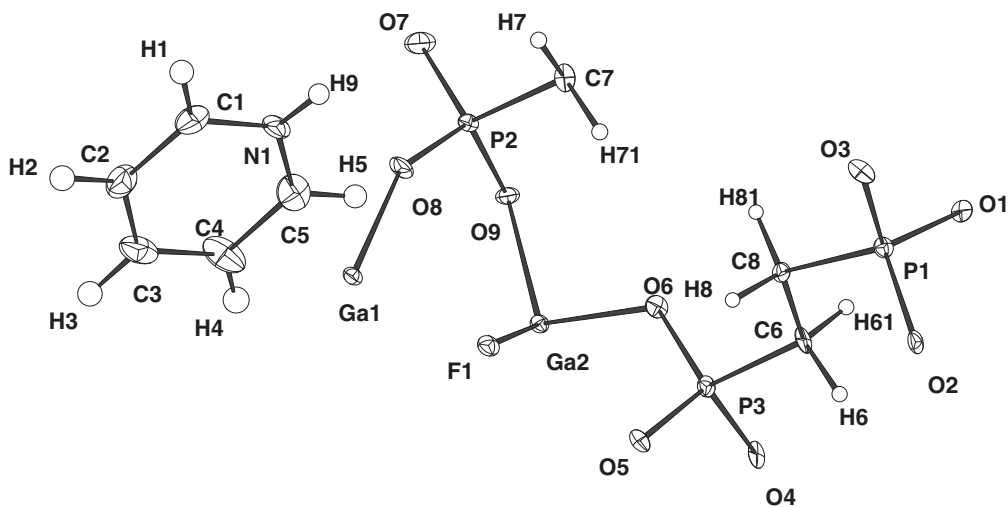


Fig. 2. The asymmetric unit of  $(C_5H_5NH)_2[Ga_4F_2(O_3PC_2H_4PO_3)_3]$  II. Displacement ellipsoids are shown at the 50% probability level.

polyhedra is connected in the cluster by six  $PO_3C$  tetrahedra. Two of the  $PO_3C$  tetrahedra use two of their oxygen atoms to bind to two different Ga atoms within the cluster. The remaining O and C atoms within these  $PO_3C$  groups are involved in forming P–O–Ga and P–CH<sub>2</sub>–CH<sub>2</sub>–P bridges to other clusters identical to that shown in Fig. 6. Two of the  $PO_3C$  tetrahedra use two of their O atoms to bind to two different Ga atoms within the cluster and the C atom to form a P–CH<sub>2</sub>–CH<sub>2</sub>–P bridge to another identical cluster. The remaining O(7) atom within

these  $PO_3C$  groups is not directly bound to any other atom. Two  $PO_3C$  groups in the cluster use all three O atoms to bind to three Ga atoms in a cluster, leaving only the C atom to form a P–CH<sub>2</sub>–CH<sub>2</sub>–P bridge to another cluster. Each cluster binds to two clusters along the *b*-axis through P–O–Ga bridges to form chains of clusters. These chains are bound to four other chains through P–CH<sub>2</sub>–CH<sub>2</sub>–P bridges to form the framework structure shown in Fig. 5. The six  $PO_3C$  groups within a cluster are derived from three crystallographically independent P atoms present in

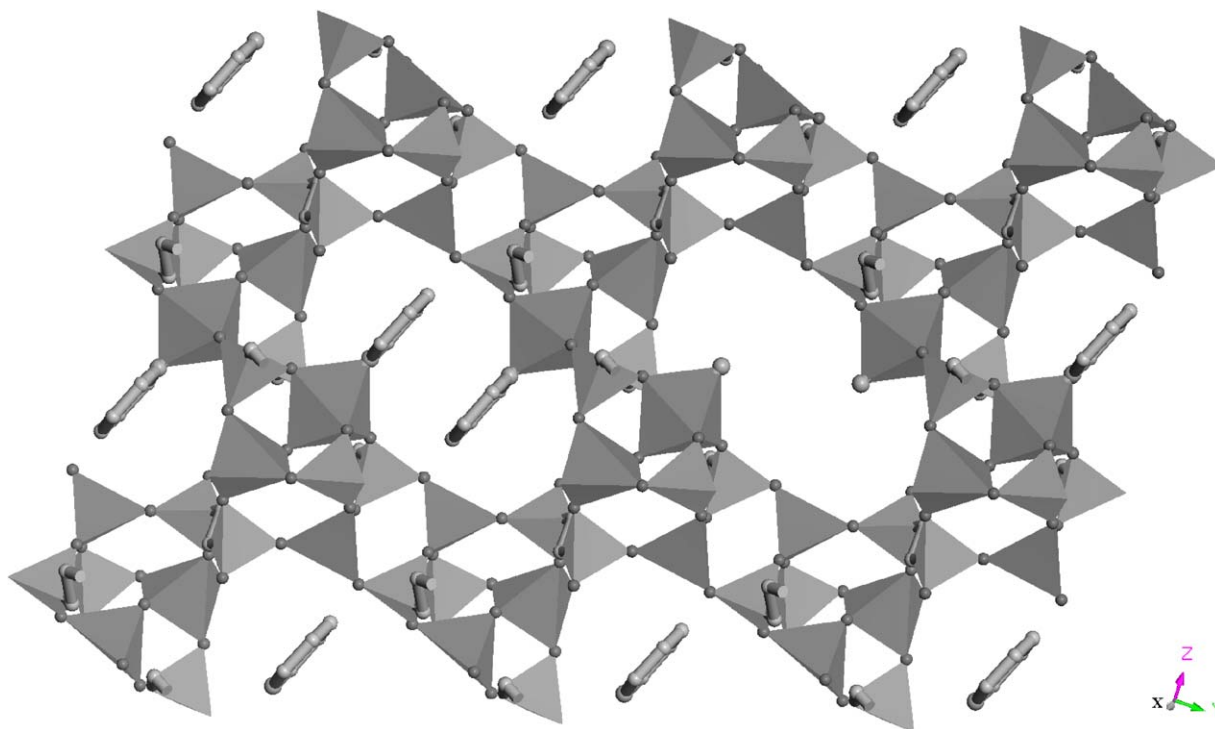


Fig. 3. A polyhedral representation of the structure of I viewed along the  $a$ -axis. The polyhedra become paler in the order: Ga-centered polyhedra,  $\text{PO}_3\text{C}$  tetrahedra. The pyridine molecules are omitted from one channel to aid visualization of the structure of a channel. All hydrogen atoms are omitted for clarity.

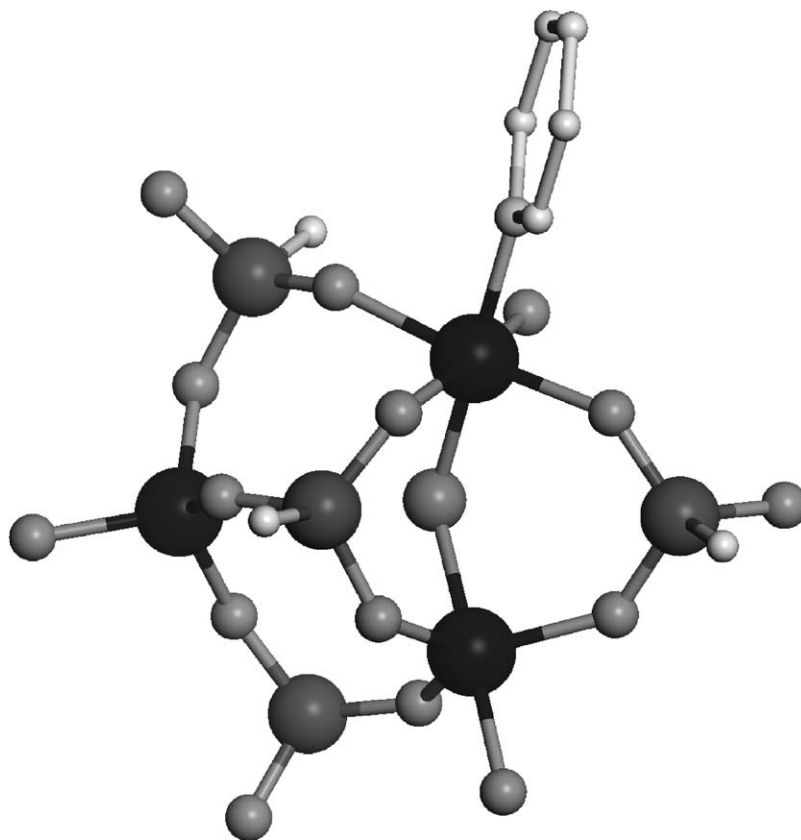


Fig. 4. A ball and stick representation of the cluster of polyhedra that forms the main building constituent of structure I. The atoms are represented by balls that decrease in size and become lighter in the order Ga, P, F, O, N, C. All hydrogen atoms are omitted for clarity.

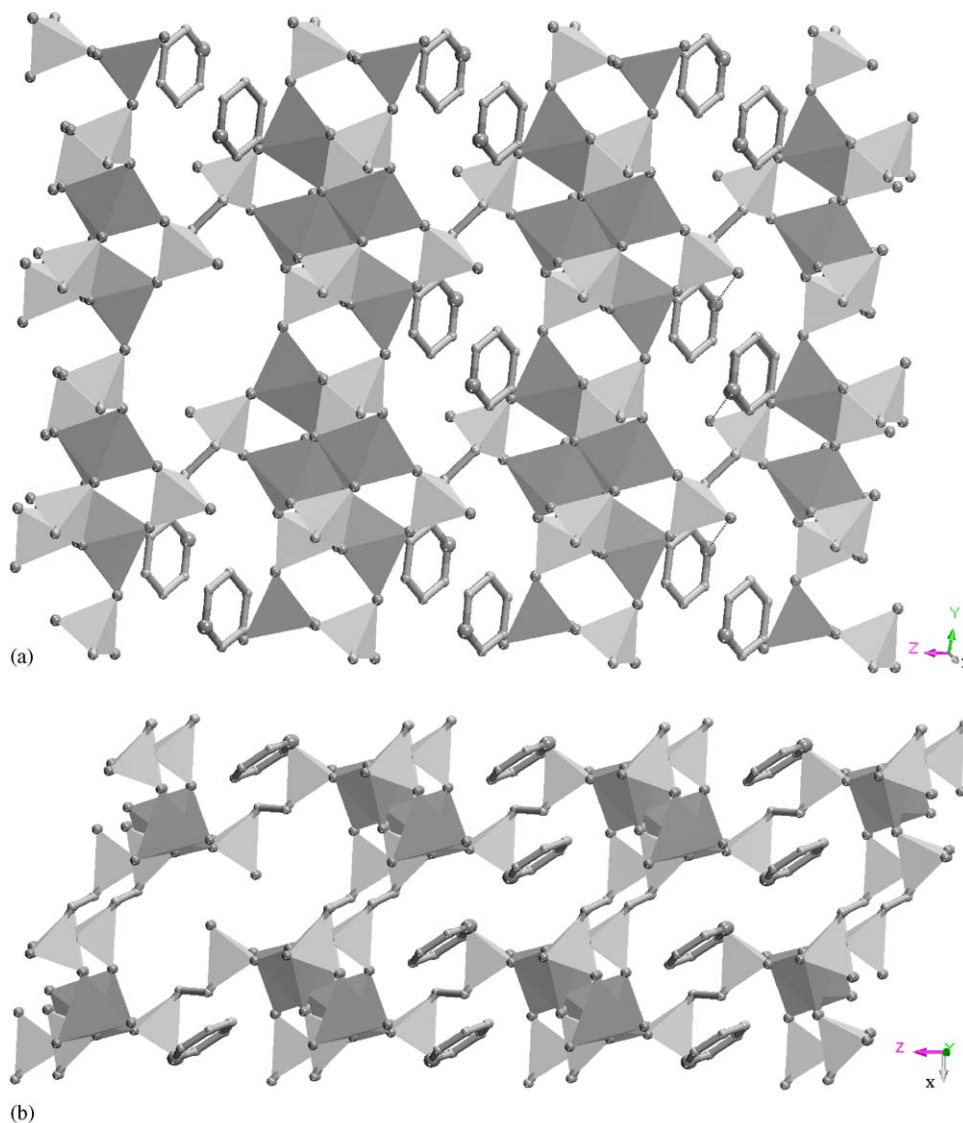


Fig. 5. A polyhedral representation of the structure of **II** viewed (a) along the  $a$ -axis and (b) along the  $b$ -axis. The polyhedra become paler in the order: Ga-centered polyhedra,  $\text{PO}_3\text{C}$  tetrahedra. The pyridium cations are omitted from one channel to aid visualization of the structure of a channel. The  $\text{N}(1)\text{--H}(9)\cdots\text{O}(7)$  hydrogen bonds are represented by dotted lines in some of the channels in (a). All hydrogen atoms are omitted for clarity.

the asymmetric unit of **II**. The  $^{31}\text{P}$  SS NMR spectrum of compound **II** is presented in Fig. 7 and shows three resonances centered at 14.7, 27.1 and 32.0 ppm, suggesting the presence of three crystallographically independent phosphorus sites, in agreement with the structure determination. The chemical shift values of the resonances are typical of those observed in other metal phosphonates [19,26]. The average  $\text{Ga}\text{--O}_{\text{trigonal-bipyramidal}}$  and  $\text{Ga}\text{--O}_{\text{octahedral}}$  bond distances of 1.848 and 1.907 Å, respectively, agree well with those reported in other gallophosphate and gallium diphosphonates [19,30]. The  $\text{Ga}\text{--F}_{\text{trigonal-bipyramidal}}$  and  $\text{Ga}\text{--F}_{\text{octahedral}}$  bond distances of 2.293(4), and 2.068 Å, respectively, agree well with those reported in other gallofluorophosphates and gallium diphosphonates [19,30]. The tetrahedral  $\text{PO}_3\text{C}$  units display average  $\text{P}\text{--O}$  distances of 1.534 Å and  $\text{P}\text{--C}$  distances of

1.785 Å, values typically found in other gallium diphosphonates [19,26].

The framework structure of **II** contains a two-dimensional channel system in which the channels run parallel to the [100] and [010] directions, as shown in Fig. 5a and b. The channels in compound **II** are bounded by purely hydrophobic (the ethylene groups) and hydrophilic sections that results in channels whose surface contains both hydrophobic and hydrophilic portions. The channels are occupied by pyridinium cations that have significant electrostatic interactions with the  $[\text{Ga}_4\text{F}_2(\text{O}_3\text{PC}_2\text{H}_4\text{PO}_3)_3]^{2-}$  framework. The protonated nitrogen atom of the pyridinium cation, N(1), forms a moderately strong hydrogen bond to the unbound atom O(7) of the  $\text{P}(1)\text{O}_3\text{C}$  tetrahedron with a donor $\cdots$ acceptor distance of 2.65(1) Å and a donor $\text{--H}\cdots$ acceptor angle of 161(10)°. These geometric parameters indicate



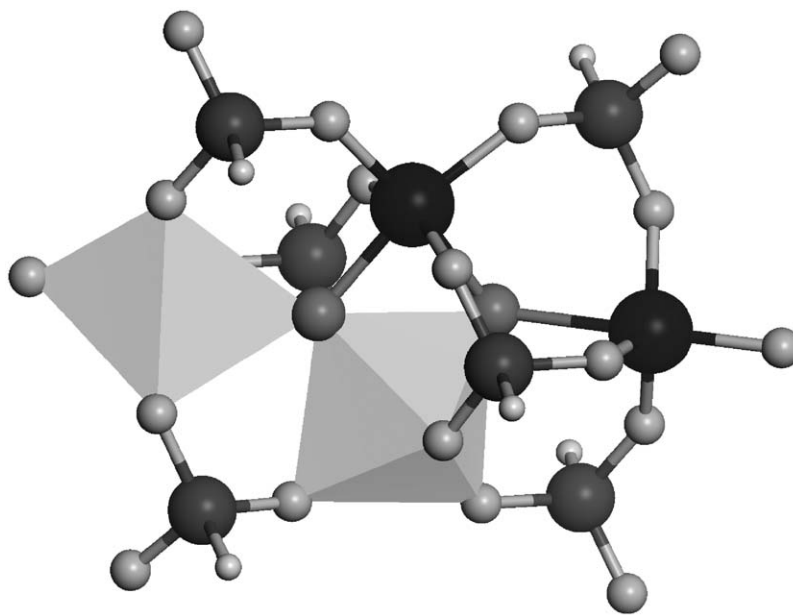


Fig. 6. A ball and stick/polyhedral representation of the cluster of polyhedra that forms the main building constituent of structure II. One  $\text{GaO}_4\text{F}_2$  octahedron and one  $\text{GaO}_4\text{F}$  trigonal bipyramid are represented as polyhedra. The atoms are represented by balls that decrease in size and become lighter in the order Ga, P, F, O, C. All hydrogen atoms are omitted for clarity.

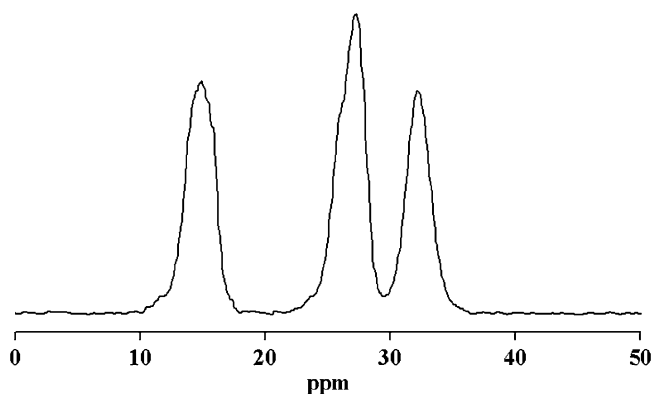


Fig. 7. The  $^{31}\text{P}$  MAS SS NMR spectrum of II.

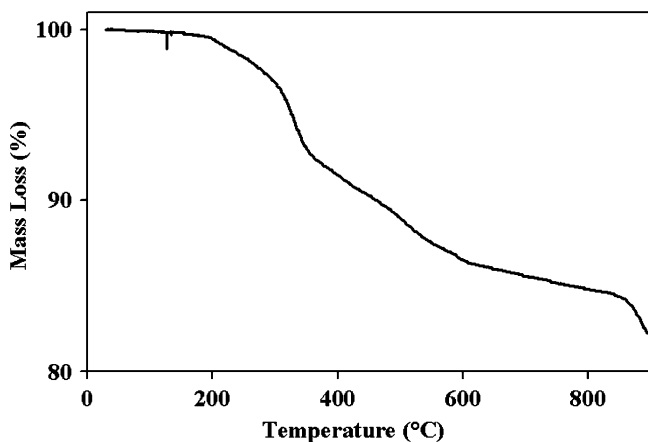


Fig. 8. The thermogravimetric trace of compound II.

the hydrogen bond is of moderate strength and mostly electrostatic in character [31].

The thermogravimetric trace for compound II is shown in Fig. 8. No observed mass loss occurs until 160 °C. The first mass loss region occurs over the temperature range from 160 to 550 °C and consists of a sharp loss (160–363 °C) followed by a more gradual loss (360–550 °C). The total loss in this region has a magnitude of 12.4% and is attributed to the partial removal and decomposition of the pyridine molecules (calculated 15.3%). The second region of mass loss occurs over the range 550–900 °C and has a magnitude of 5.3%, which is accounted for by the partial decomposition of the organic component of the ethylenediphosphonate groups (calculated mass loss 8.1%) and the remainder of the pyridine molecules. The black color of the resulting crystalline solid also indicated that the organic component of the ethylenediphosphonate group had been only partially removed. This crystalline solid was found to be multiphasic, with the major and only identifiable phase being  $\text{GaPO}_4$ . A similar thermal decomposition behavior is found for other pyridinium-containing hydrogen-bonded framework gallium diphosphonate materials [18].

The pyridine molecules and pyridinium cations must direct the formation of the resultant framework structures of compounds I and II, respectively, as these species are incorporated into the final products and occupy the void space within the frameworks. The role of the pmdeta or tris(2-aminoethyl)amine species present in the synthesis gels is less certain. These species increase the pH of the reaction mixture and they may also be involved in more

subtle effects within the synthesis mixture, for instance influencing the polar nature of the reactant mixture or being involved in the formation of transient species that are required in order to form the final products.

The resultant structures of compounds **I** and **II** provide an interesting direct comparison of the possible modes through which N-containing species can act to direct the framework structure of a particular chemical system. The pyridine molecules in compound **II** are protonated and behave in the manner most commonly observed for structure-directing species in the formation of framework solids, in that they exist in a cationic form and are bound to the negatively charged framework through electrostatic interactions and hydrogen bonds only. The pyridinium cations act as space-fillers around which the framework structure grows. The pyridinium cation is most closely associated with the terminal atom O(7) of the P(3)O<sub>3</sub>C tetrahedra. As the O(7) atoms are now prevented from forming P–O–Ga linkages, this means that less cross-linking in the framework of **II** occurs, resulting in the formation of an open framework with a two-dimensional channel system. The pyridine molecules in compound **I** behave in a less common fashion for a structure-directing agent. These molecules form a direct coordinative bond to the Ga(3) atoms in the framework. Indeed, the pyridine molecules can be thought of as forming part of the framework structure, as other molecules, for example, water, commonly do in framework materials [18,26]. However, the size of the pyridine molecule leads to these molecules simultaneously acting in a structure-directing capacity, as their presence forces the framework to develop around their large bulk. Thus, the bound pyridine molecules act in a spacing-filling mode to direct the formation of the framework structure within this material. This phenomenon of directly bound amine or N-containing heterocyclic molecules has been reported for several gallium phosphate/phosphatooxalate materials where each contains a direct covalent bond between the N atom of the occluded molecule and the Ga atom of the framework [23,32]. The resultant framework of compound **I** is charge neutral. All the O atoms of the PO<sub>3</sub>C tetrahedra of compound **I** are involved in forming Ga–O–P linkages within the resultant material and this reduces the openness of the resultant framework structure of **I** in comparison to compound **II**.

The formation of (C<sub>5</sub>H<sub>5</sub>N)Ga<sub>3</sub>F(O<sub>3</sub>PC<sub>2</sub>H<sub>4</sub>PO<sub>3</sub>)<sub>2</sub> (**I**) and (C<sub>5</sub>H<sub>5</sub>NH)<sub>2</sub>[Ga<sub>4</sub>F<sub>2</sub>(O<sub>3</sub>PC<sub>2</sub>H<sub>4</sub>PO<sub>3</sub>)<sub>3</sub>] (**II**) demonstrates that it is possible to form novel framework gallium diphosphate structures by using the structure-directing influences of N-containing species. The N-containing species may be occluded within the final structure in different modes and may yield resultant neutral or anionic frameworks. These results suggest that such an approach will lead to the formation of a rich variety of novel framework materials for this chemical system, as has been demonstrated for other chemical systems [33].

## Supporting information available

The experimental and calculated (Le Bail fitting) profile powder X-ray diffraction pattern of compound **II**. Crystallographic data (excluding structure factors) for the structures **I** and **II** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 293687 and 293688. 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; deposit@ccdc.cam.ac.uk).

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## Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2006.03.002.

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