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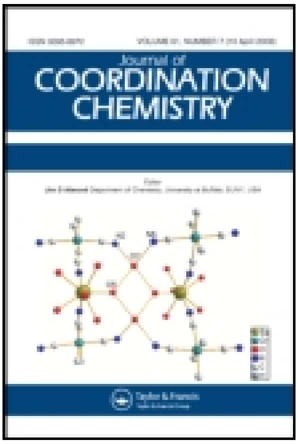

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Syntheses, characterization, and crystal structures of two fluorinated gallium phosphates templated by organic amines

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Syntheses, characterization, and crystal structures of two fluorinated gallium phosphates templated by organic amines

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Two fluorinated gallium phosphates templated by organic amines, $(C_4H_{15}N_3)[Ga_3F_2(PO_4)_3]$ (**1**) and $[(C_2H_{10}N_2)(C_2H_9N_2)][Ga_3F_4(HPO_4)_4]$ (**2**), have been synthesized under hydrothermal and solvothermal conditions, respectively. The compounds were characterized by elemental analyses, FT-IR spectroscopy, and powder X-ray diffraction. Their crystal structures were determined from single-crystal X-ray diffraction. The crystal structure of **1** has a 3-D framework with 10-membered ring channels along the *b*-axis. The crystal structure of **2** is an infinite 1-D chain structure, further forming a 3-D supramolecular structure with pseudo 10-membered ring channels along the *a*-axis through O–H $\cdots$ O hydrogen bonds. The protonated organic amine cations are located in the inorganic channel and interact with the polyanion framework both electrostatically and *via* N–H $\cdots$ O and N–H $\cdots$ F hydrogen bonds.

Keywords: Gallium phosphate; Organic amine; Synthesis; Crystal structure

1. Introduction

Since the discovery of microporous aluminum phosphates, hydrothermal synthesis, and structural characterization of new open-framework solids templated by organic molecules have attracted considerable attention. Many metal and nonmetal phosphates with open-framework structures have been synthesized owing to their rich structural chemistry and potential applications in ion exchange, adsorption, separation, and catalysis [1]. Gallium phosphates constitute an important family that exhibits rich structural and compositional diversity. Fluorides have also been incorporated in many inorganic open frameworks, following the synthetic route opened by Guth *et al*. [2]. Some fluorinated gallium phosphates templated by organic base have been reported, such as $[H_3N(CH_2)_6NH_3]_4[Ga_{16}F_7(PO_4)_{14}(HPO_4)_2(OH)_2] \cdot 6H_2O$ [3], $[H_3N(CH_2)_3NH_3][Ga_3F_2P_3O_{12}] \cdot H_2O$ [4], $[C_5H_{14}N_2]_2[Ga_3F(PO_4)_4]_3 \cdot 5.25H_2O$, $[(R)\text{-}C_5H_{14}N_2]_2[Ga_3F(PO_4)_4]_3 \cdot 5.5H_2O$, $[(S)\text{-}C_5H_{14}N_2]_2[Ga_3F(PO_4)_4]_3 \cdot 4.75H_2O$ [5], $[NH_3(CH_2)_3NH_3][GaF(HPO_4)_2] \cdot 2H_2O$ [6], $[NH_3(CH_2)_3NH_3]GaF(HPO_4)_2$ [7], $[(C_2H_7N)_3N][Ga(HPO_4)(PO_4)(OH)] \cdot H_2O$ [8], $(C_6H_{20}N_4)_{2.5}[Ga_{10}(PO_4)_2(HPO_4)_{12}(OH)_5] \cdot 4.5H_2O$ [9], and

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$(C_3H_{12}N_2)_6[Ga_{12}P_{16}O_{64}]\cdot 4.3H_2O$ [10]. In this article, we report the syntheses and crystal structures of two fluorinated gallium phosphates templated by organic amines, $(C_4H_{15}N_3)[Ga_3F_2(PO_4)_3]$ (**1**) and $[(C_2H_{10}N_2)(C_2H_9N_2)][Ga_3F_4(HPO_4)_4]$ (**2**).

2. Experimental

2.1. *Synthesis and characterization*

$(C_4H_{15}N_3)[Ga_3F_2(PO_4)_3]$ (**1**) was synthesized from a mixture of 0.0949 g of Ga_2O_3, 0.1402 g of B_2O_3, 1.2387 g of H_3BO_3, 1 mL of diethylenetriamine, 0.4 mL of H_3PO_4 (85%), 3.5 mL of HF (40%), and 2 mL of H_2O. This mixture was sealed in 15 mL of Teflon-lined stainless-steel vessels, heated at 170°C for about 15 days under autogenous pressure, and then cooled to room temperature. The resulting columnar colorless crystals were collected and dried in air at ambient temperature.

$[(C_2H_{10}N_2)(C_2H_9N_2)][Ga_3F_4(HPO_4)_4]$ (**2**) was synthesized from a mixture of 0.1495 g of Ga_2O_3, 0.1850 g of 4,4′-bipyridine, 1 mL of H_2O, 3 mL of methanol, 0.75 mL of ethylenediamine, 0.5 mL of HF (40%), and 0.65 mL of H_3PO_4 (85%). The mixture was heated in a 15 mL of Teflon-lined stainless-steel autoclave at 185°C for 3 days under autogenous pressure and then cooled to room temperature. The resulting colorless crystals were obtained by filtration, washed with deionized water and alcohol, and dried in air to a constant mass at ambient temperature.

The obtained samples have been characterized by elemental analyses (determined on a Vario EL III Elemental Analyzer), FT-IR spectroscopy (recorded from 400 to $4000\,cm^{-1}$ on a Nicolet NEXUS 670 spectrometer with KBr pellets at room temperature), and X-ray powder diffraction (XRPD, Rigaku D/MAX-IIIC with Cu target at $8°\,min^{-1}$).

2.2. *Determination of crystal structures*

Crystals of **1** (columnar, dimensions of 0.46 mm × 0.42 mm × 0.36 mm) and **2** (block, dimensions of $0.35 \times 0.30 \times 0.28\,mm^3$) were selected for crystal structure measurements at room temperature. X-ray diffraction intensities were recorded by a Bruker Smart-1000 CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.071073$ nm) in the ω scanning mode at room temperature. An empirical absorption correction was applied using SADABS [11]. The structures were both solved by direct methods. The gallium, phosphorus, fluorine, oxygen, carbon, and nitrogen were found in the final difference Fourier map. Positions of hydrogens attached to nitrogens in ethylenediaminium cations were estimated from the difference Fourier map, and all other hydrogens in **1** and **2** were geometrically placed. The structures were refined on F^2 by full-matrix least-squares using the SHELXL-97 program package [12]. All non-hydrogen atoms were refined anisotropically. Crystal data and conditions of the intensity measurements are given in table 1. The main bond lengths and angles for **1** and **2** are listed in table 2.

Table 1. Crystal data and structure refinement for $(C_4H_{15}N_3)[Ga_3F_2(PO_4)_3]$ (**1**) and $[(C_2H_{10}N_2)(C_2H_9N_2)][Ga_3F_4(HPO_4)_4]$ (**2**).

Compounds	**1**	**2**
Empirical formula	$C_4H_{15}F_2Ga_3N_3O_{12}P_3$	$C_4H_{23}F_4Ga_3N_4O_{16}P_4$
Formula weight	637.26	792.30
Crystal system	Orthorhombic	Triclinic
Space group	*Pbca*	$P\bar{1}$
Unit cell dimensions (Å, °)		
a	16.0206(19)	5.2016(6)
b	10.1070(12)	9.8396(10)
c	18.533(2)	9.9885(11)
α	90	79.8830(10)
β	90	85.440(2)
γ	90	87.185(2)
Volume (Å^3), Z	3000.9(6), 8	501.36(9), 1
Calculated density (Mg m^{-3})	2.821	2.624
Absorption coefficient (mm^{-1})	5.768	4.449
$F(000)$	2496	392
Goodness-of-fit on F^2	1.114	1.075
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0576$, $wR_2 = 0.1598$	$R_1 = 0.0223$, $wR_2 = 0.0572$

3. Results and discussion

3.1. *Elemental analysis*

Found (Calcd) for **1** (%): C, 7.78 (7.54); H, 2.49 (2.37); N, 6.53 (6.59). For **2** (%): C, 5.88 (6.06); H, 3.15 (2.93); N, 7.49 (7.07). The results are consistent with calculated values based on the formula given by single-crystal X-ray diffraction.

3.2. *FT-IR spectra*

The FT-IR spectra (Supplementary material) exhibit absorptions assigned referring to literature data [13–15]. The broad medium absorptions of **1** at 3500–2500 cm^{-1} are due to N–H and C–H stretches. Medium absorptions at 1609 and 1516 cm^{-1} are bending modes of NH_3^+ from amine ions, and the bending mode of CH_2 gives the band at 1444 cm^{-1}. The strong band at 1000 cm^{-1} can be attributed to ν(P–O). Absorption bands at 700–430 cm^{-1} can be attributed to ν(Ga–O). Absorption bands of **2** at 3560 and 3141 cm^{-1} are due to N–H, O–H, and C–H stretches. The band at 2349 cm^{-1} might arise from stretches of CO_2 in the air [16]. Bands at 1621, 1540, and 1466 cm^{-1} are assigned to bending modes of NH_3^+ and CH_2 of ethylenediaminium ions. The strong absorption at 1050 cm^{-1} is attributed to ν(P–O) and the band at 457 cm^{-1} to ν(Ga–O).

3.3. *X-ray diffraction*

XPRD patterns of as-synthesized compounds and the simulated patterns on the basis of single-crystal structures of **1** and **2** are found in Supplementary material. The diffraction peaks on patterns corresponded well in position, indicating the phase purities of the as-synthesized samples.

Table 2. Selected bond lengths (Å) and angles (°) for $(C_4H_{15}N_3)[Ga_3F_2(PO_4)_3]$ (**1**) and $[(C_2H_{10}N_2)(C_2H_9N_2)][Ga_3F_4(HPO_4)_4]$ (**2**).

1			
Ga(1)–O(9)	1.931(6)	Ga(2)–O(2)	1.871(6)
Ga(1)–O(1)	1.943(6)	Ga(2)–O(6)	1.941(6)
Ga(1)–O(3)#1	1.946(6)	Ga(2)–F(2)#3	2.019(5)
Ga(1)–F(1)	1.949(5)	Ga(3)–O(7)	1.847(6)
Ga(1)–O(5)	1.950(6)	Ga(3)–O(12)#3	1.860(6)
Ga(1)–F(2)	1.974(5)	Ga(3)–O(4)#1	1.868(7)
Ga(2)–O(8)#2	1.830(6)	Ga(3)–O(11)#4	1.934(6)
Ga(2)–O(10)#3	1.851(6)	Ga(3)–F(1)	2.016(5)
P(1)–O(3)	1.521(6)	P(2)–O(6)	1.531(6)
P(1)–O(1)	1.532(7)	P(2)–O(7)	1.539(7)
P(1)–O(4)	1.538(7)	P(3)–O(11)	1.526(7)
P(1)–O(2)	1.543(7)	P(3)–O(9)	1.532(6)
P(2)–O(8)	1.527(7)	P(3)–O(10)	1.534(6)
P(2)–O(5)	1.530(7)	P(3)–O(12)	1.543(6)
O(9)–Ga(1)–O(1)	87.7(3)	O(8)#2–Ga(2)–O(6)	96.8(3)
O(9)–Ga(1)–O(3)#1	88.6(3)	O(10)#3–Ga(2)–O(6)	92.4(3)
O(1)–Ga(1)–O(3)#1	175.2(3)	O(2)–Ga(2)–O(6)	91.5(3)
O(9)–Ga(1)–F(1)	175.0(2)	O(8)#2–Ga(2)–F(2)#3	89.3(3)
O(1)–Ga(1)–F(1)	96.0(2)	O(10)#3–Ga(2)–F(2)#3	85.8(2)
O(3)#1–Ga(1)–F(1)	87.6(2)	O(2)–Ga(2)–F(2)#3	85.5(3)
O(9)–Ga(1)–O(5)	94.4(3)	O(6)–Ga(2)–F(2)#3	173.8(2)
O(1)–Ga(1)–O(5)	94.6(3)	O(7)–Ga(3)–O(12)#3	130.0(3)
O(3)#1–Ga(1)–O(5)	88.7(3)	O(7)–Ga(3)–O(4)#1	115.4(3)
F(1)–Ga(1)–O(5)	88.8(2)	O(12)#3–Ga(3)–O(4)#1	114.3(3)
O(9)–Ga(1)–F(2)	91.7(2)	O(7)–Ga(3)–O(11)#4	91.3(3)
O(1)–Ga(1)–F(2)	88.1(2)	O(12)#3–Ga(3)–O(11)#4	95.0(3)
O(3)#1–Ga(1)–F(2)	89.1(2)	O(4)#1–Ga(3)–O(11)#4	89.4(3)
F(1)–Ga(1)–F(2)	84.9(2)	O(7)–Ga(3)–F(1)	87.2(2)
O(5)–Ga(1)–F(2)	173.4(2)	O(12)#3–Ga(3)–F(1)	86.4(2)
O(8)#2–Ga(2)–O(10)#3	112.8(3)	O(4)#1–Ga(3)–F(1)	90.8(2)
O(8)#2–Ga(2)–O(2)	111.3(3)	O(11)#4–Ga(3)–F(1)	178.4(2)
O(10)#3–Ga(2)–O(2)	134.9(3)		
O(3)–P(1)–O(1)	110.9(4)	O(8)–P(2)–O(7)	104.5(4)
O(3)–P(1)–O(4)	111.3(4)	O(5)–P(2)–O(7)	112.5(4)
O(1)–P(1)–O(4)	106.6(4)	O(6)–P(2)–O(7)	110.6(4)
O(3)–P(1)–O(2)	110.8(4)	O(11)–P(3)–O(9)	108.4(4)
O(1)–P(1)–O(2)	109.1(4)	O(11)–P(3)–O(10)	109.7(4)
O(4)–P(1)–O(2)	108.0(4)	O(9)–P(3)–O(10)	113.3(4)
O(8)–P(2)–O(5)	109.9(4)	O(11)–P(3)–O(12)	109.3(4)
O(8)–P(2)–O(6)	107.9(4)	O(9)–P(3)–O(12)	108.3(4)
O(5)–P(2)–O(6)	111.1(4)	O(10)–P(3)–O(12)	107.7(4)
2			
Ga(1)–F(2)#1	1.9522(18)	P(1)–O(1)	1.525(2)
Ga(1)–F(2)	1.9522(18)	P(1)–O(2)	1.513(2)
Ga(1)–O(5)#1	1.958(2)	P(1)–O(3)	1.5344(19)
Ga(1)–O(5)	1.958(2)	P(1)–O(4)	1.577(2)
Ga(1)–O(1)	1.9859(19)	P(2)–O(5)	1.540(2)
Ga(1)–O(1)#1	1.9859(19)	P(2)–O(6)	1.533(2)
Ga(2)–O(8)#2	1.9319(19)	P(2)–O(7)	1.552(2)
Ga(2)–F(1)	1.9328(16)	P(2)–O(8)	1.516(2)
Ga(2)–F(2)	1.9405(18)	Ga(2)–O(6)	1.943(2)
Ga(2)–O(2)	1.9803(19)	Ga(2)–O(3)#2	2.0100(19)
F(2)#1–Ga(1)–F(2)	180.000(1)	F(1)–Ga(2)–O(2)	83.55(7)
F(2)#1–Ga(1)–O(5)#1	90.19(8)	F(2)–Ga(2)–O(2)	91.73(8)
F(2)–Ga(1)–O(5)#1	89.81(8)	O(8)#2–Ga(2)–O(2)	169.31(8)
F(2)#1–Ga(1)–O(5)	89.81(8)	O(6)–Ga(2)–O(2)	92.71(8)

(*Continued*)

Table 2. Continued.

F(2)–Ga(1)–O(5)	90.19(8)	O(8)#2–Ga(2)–O(3)#2	87.75(8)
O(5)#1–Ga(1)–O(5)	180.00(12)	F(1)–Ga(2)–O(3)#2	87.89(8)
F(2)#1–Ga(1)–O(1)	88.02(8)	F(2)–Ga(2)–O(3)#2	92.81(8)
F(2)–Ga(1)–O(1)	91.98(8)	O(6)–Ga(2)–O(3)#2	176.20(8)
O(5)#1–Ga(1)–O(1)	88.68(8)	O(2)–Ga(2)–O(3)#2	87.04(8)
O(5)–Ga(1)–O(1)	91.32(8)	O(2)–P(1)–O(1)	113.20(11)
F(2)#1–Ga(1)–O(1)#1	91.98(8)	O(2)–P(1)–O(3)	112.18(11)
F(2)–Ga(1)–O(1)#1	88.02(8)	O(1)–P(1)–O(3)	111.38(11)
O(5)#1–Ga(1)–O(1)#1	91.32(8)	O(2)–P(1)–O(4)	109.27(11)
O(5)–Ga(1)–O(1)#1	88.68(8)	O(1)–P(1)–O(4)	103.66(12)
O(1)–Ga(1)–O(1)#1	180.000(1)	O(3)–P(1)–O(4)	106.56(11)
O(8)#2–Ga(2)–F(1)	86.94(8)	O(8)–P(2)–O(6)	111.60(12)
O(8)#2–Ga(2)–F(2)	97.84(8)	O(8)–P(2)–O(5)	111.65(12)
F(1)–Ga(2)–F(2)	175.19(7)	O(6)–P(2)–O(5)	111.29(11)
O(8)#2–Ga(2)–O(6)	91.87(8)	O(8)–P(2)–O(7)	107.50(11)
F(1)–Ga(2)–O(6)	88.31(8)	O(6)–P(2)–O(7)	108.25(11)
F(2)–Ga(2)–O(6)	90.99(8)	O(5)–P(2)–O(7)	106.27(12)

Symmetry transformations used to generate equivalent atoms for **1**: #1: $-x$, $y+1/2$, $-z+1/2$; #2: $-x+1/2$, $y-1/2$, z; #3: $-x$, $y-1/2$, $-z+1/2$; #4: x, $-y+3/2$, $z-1/2$; for **2**: #1: $-x+3$, $-y+3$, $-z+1$; #2: $x+1$, y, z.

3.4. *Description of crystal structures*

3.4.1. Crystal structure of 1. Single-crystal X-ray analysis demonstrated that **1** is orthorhombic with space group *Pbca*, $a = 16.0206(19)$ Å, $b = 10.1070(12)$ Å, $c = 18.533(2)$ Å, $\beta = 90°$, $V = 3000.9(6)$ Å^3, $Z = 8$. The asymmetric structure of **1** consists of a protonated diethylenetriamine $[C_4H_{15}N_3]^{2+}$ and a polyanion $[Ga_3F_2(PO_4)_3]^{2-}$, as shown in figure 1, which also shows the coordination environments of P and Ga. In this polyanion, galliums have two different coordination modes: Ga(1) is octahedrally coordinated with four oxygens and two fluorines. The Ga(1)–O (O1, O3A, O5, and O9) distances vary from 1.931(6) to 1.950(6) Å with the mean of 1.943 Å. The Ga(1)–F (F1 and F2) distances vary from 1.949(5) to 1.974(5) Å with the mean of 1.962 Å. Both Ga(2) and Ga(3) are five coordinate by four oxygens and one fluorine. The Ga(2)–O (O8A, O10A, O2, and O6) distances vary from 1.830(6) to 1.941(6) Å with the mean of 1.943 Å. The Ga(2)–F (F2A) distance is 2.019(5) Å. The Ga(3)–O (O7, O12A, O4A, and O11A) distances vary from 1.847(6) to 1.934(6) Å with a mean of 1.877 Å, and the Ga(3)–F(F1) distance is 2.016(5) Å. These gallium polyhedra (two trigonal bipyramids and one octahedron) are separated from each other by three types of PO_4 tetrahedra with P–O distances within 1.521(6)–1.543(7) Å, forming the basic building unit of $[Ga_3F_2(PO_4)_3]$.

The $[Ga_3F_2(PO_4)_3]^{2-}$ are also connected through oxygens shared by both gallium and phosphorus to neighboring units forming a 3-D framework with 10-membered ring channels along the *b*-axis (figure 2). This channel is formed through a strict alternation of GaOF polyhedra and PO_4 tetrahedra. The pore aperture and size are shown in figure 3(a). The $[C_4H_{15}N_3]^{2+}$ cations are located in the inorganic channel to compensate the negative charges and interact with the polyanion framework both electrostatically and *via* N–H ⋯ O and N–H ⋯ F hydrogen bonds. The details of hydrogen bonds for **1** are given in table 3.

This fluorinated gallium phosphate polyanion $[Ga_3F_2(PO_4)_3]^{2-}$ was also present in $[H_3N(CH_2)_3NH_3][Ga_3P_3O_{12}F_2] \cdot H_2O$ [4]. But there are some differences between their

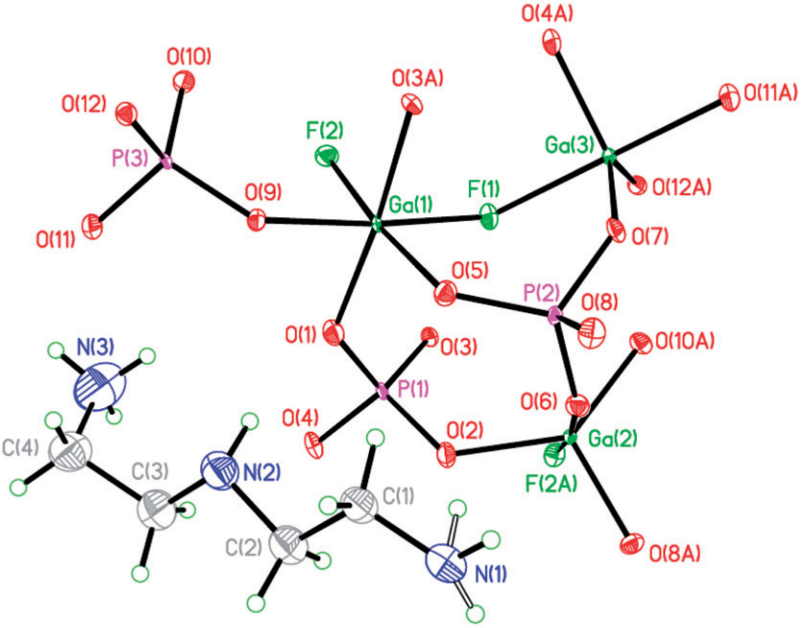

Figure 1. The molecular structure of **1** drawn at 50% probability level.

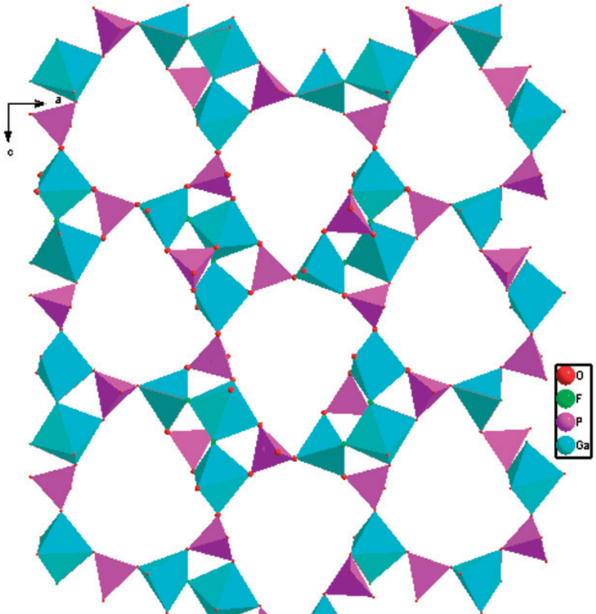

Figure 2. Packing view along the *b*-axis of **1**, showing the 3-D framework with large channels, where all $[C_4H_{15}N_3]^{2+}$ are omitted for clarity.

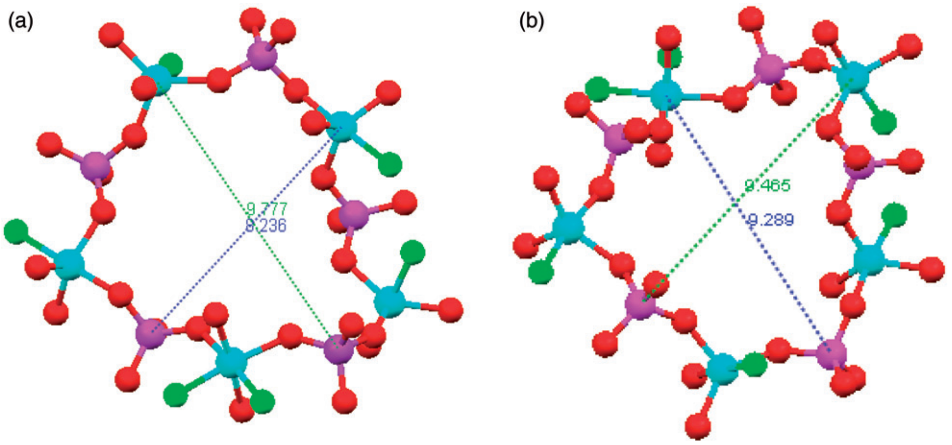

Figure 3. The pore aperture and size of (a) **1** and (b) $[H_3N(CH_2)_3NH_3]Ga_3F_2P_3O_{12} \cdot H_2O$.

Table 3. Details of hydrogen bonds for **1**.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	∠DHA (°)
N1–H1A···F2#1	0.890	2.133	2.981	159.04
N1–H1B···O5#2	0.890	2.487	3.130	129.55
N1–H1B···O2	0.890	2.649	3.342	135.52
N1–H1C···O9#2	0.890	2.193	2.959	143.92
N1–H1C···F1#1	0.890	2.395	2.922	118.17
N1–H1C···O3#1	0.890	2.516	3.032	117.58
N1–H1C···O12#2	0.890	2.553	3.238	134.34
N1–H1D···O6	0.890	2.300	3.050	141.85
N1–H1D···O2	0.890	2.622	3.342	138.61
N1–H1E···O5#2	0.890	2.304	3.130	154.26
N1–H1E···O3#1	0.890	2.367	3.032	131.64
N1–H1E···O9#2	0.890	2.399	2.959	121.12
N1–H1R···F2#1	0.890	2.132	2.981	159.29
N1–H1R···F1#1	0.890	2.345	2.922	122.61
N2–H2···O1	0.900	2.028	2.916	168.85
N3–H3A···O4#3	0.890	2.085	2.937	160.01
N3–H3A···O1#3	0.890	2.147	2.788	128.29
N3–H3B···O11#3	0.890	2.259	3.106	159.01

Symmetry transformations used to generate equivalent atoms: #1: $x+1/2$, y, $-z+1/2$; #2: $-x+1/2$, $y-1/2$, z; #3: $-x$, $-y+1$, $-z+1$.

crystal structures. In the literature compound, there exists a lattice water molecule and 10-membered ring channels along the *a*-axis, while **1** has no lattice water and has 10-membered ring channels along the *b*-axis. The pore size of **1** (9.777×8.236 Å^2) is a little smaller than that of the literature compound (9.465×9.289 Å^2) (figure 3b), which can be attributed to the different templates used.

3.4.2. Crystal structure of 2. Single-crystal X-ray analysis demonstrated that **2** is triclinic with space group $P\bar{1}$, $a = 5.2016(6)$ Å, $b = 9.8393(10)$ Å, $c = 9.9885(11)$ Å,

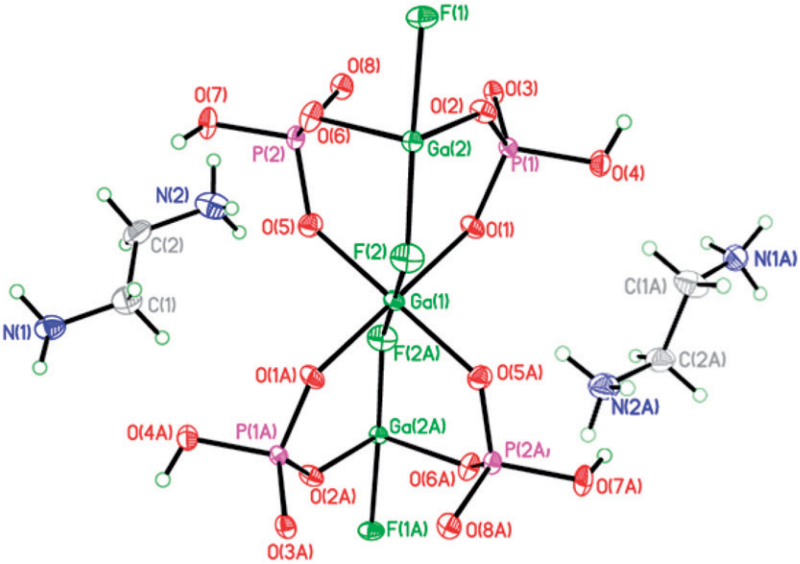

Figure 4. The molecular structure of **2** drawn at 50% probability level.

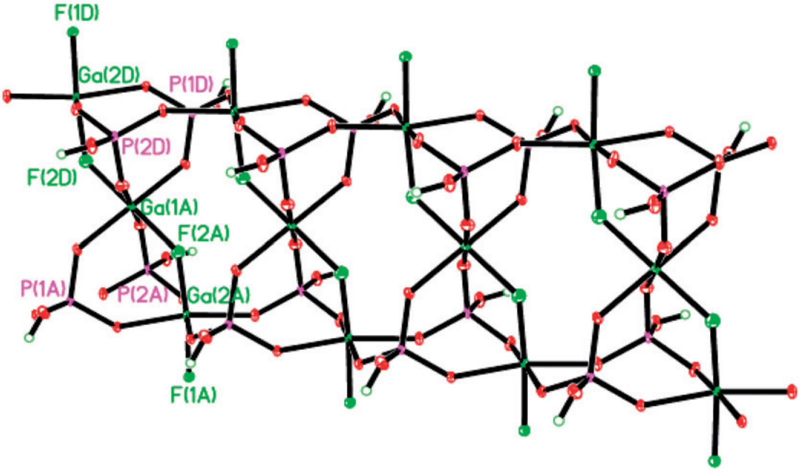

Figure 5. Packing view along the *b*-axis of **2**, showing the 1-D chain, where $[(C_2H_{10}N_2)(C_2H_9N_2)]^{3+}$ are omitted for clarity.

$\alpha = 79.8830(10)^\circ$, $\beta = 85.440(2)^\circ$, $\gamma = 87.185(2)^\circ$, $V = 507.36(9)\,\text{Å}^3$, $Z = 1$. As shown in figure 4, the molecular structure of **2** consists of a $[Ga_3F_4(HPO_4)_4]^{3-}$, one double-protonated and one single-protonated ethylenediamine cations, combined as $[(C_2H_{10}N_2)(C_2H_9N_2)]^{3+}$. There are two crystallographically distinct sites for gallium and phosphorus atoms; Ga(1) is octahedrally coordinated with four oxygens (O1, O1A, O5, O5A) from adjacent HPO_4 tetrahedra and two bridging fluorines (F2, F2A). The Ga(1)–O distances vary from 1.958(2) to 1.9859(19) Å with a mean of 1.972 Å and

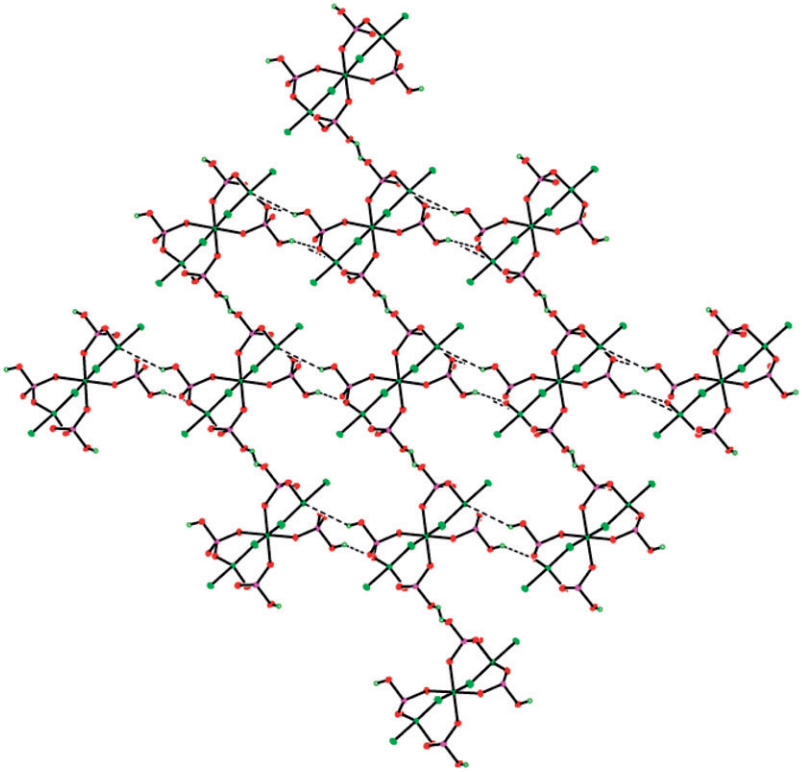

Figure 6. View along the *a*-axis showing pseudo 10-membered rings constructed by O–H ··· O hydrogen bonds, where $[(C_2H_{10}N_2)(C_2H_9N_2)]^{3+}$ are omitted for clarity.

Ga(1)–F distance is 1.9522(18) Å. Ga(2) is also octahedrally coordinated with four oxygens (O2, O6, O3B, O8B) from adjacent HPO_4 tetrahedra and two fluorines, in which F1 is terminal and F2 is bridging. The Ga(2)–O distances vary from 1.9319(19) to 2.0100(19) Å with a mean of 1.9663 Å. The Ga(2)–F1 distance is 1.9328(16) Å and Ga(2)–F2 distance is 1.9405(18) Å.

In the crystal, four HPO_4 tetrahedra, two distorted GaO_4F_2 octahedra, and a shared GaO_4F_2 octahedron are connected through bridging O and F forming the dumbbell-shaped basic structure unit of $[Ga_3F_4(HPO_4)_4]^{3-}$. $[Ga_3F_4(HPO_4)_4]^{3-}$ is a new type of fluorinated gallium phosphate anion. These building units are connected by bridging O(3) and O(8) forming an infinite 1-D chain structure (figure 5), which contains a six-membered ring along the *b*-axis.

Multipoint hydrogen-bond interactions play an important role in the formation and stability of low-dimensional structures. In **2**, $[Ga_3F_4(HPO_4)_4]^{3-}$ are further connected by O–H ··· O hydrogen bonds among the hydroxyl groups forming a 3-D structure with pseudo 10-memberd ring channels along the *a*-axis (figure 6), with O ··· O distances of 2.434–3.002 Å. The $[(C_2H_{10}N_2)(C_2H_9N_2)]^{3+}$ cations are located in these pseudo inorganic channels to compensate the negative charges and interact with the framework both electrostatically and *via* N–H ··· F and N–H ··· O hydrogen bonds forming a stable 3-D supramolecular system (figure 7), with N ··· F distances in the range

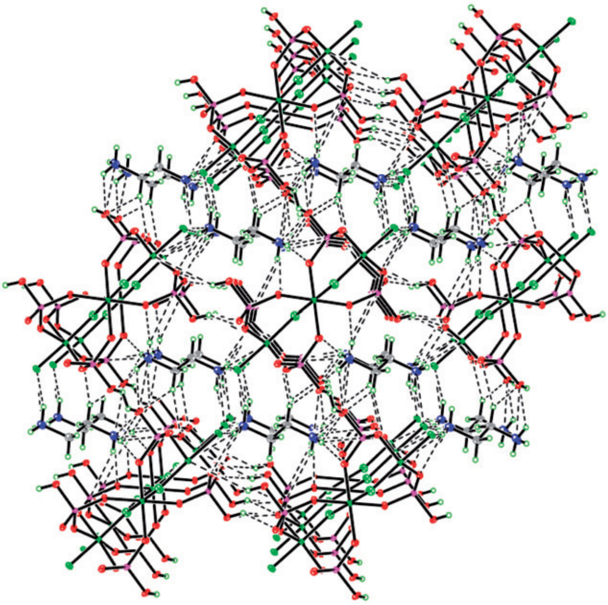

Figure 7. Packing of **2** along the *a*-axis showing the 3-D supramolecular system constructed by O–H ··· O, N–H ··· F, and N–H ··· O hydrogen bonds.

Table 4. Hydrogen bond detail for **2**.

D–H ··· A	D–H (Å)	H ··· A (Å)	D ··· A (Å)	∠DHA (°)
N1–H1A ··· F1#1	0.890	1.961	2.792	154.85
N1–H1B ··· F1	0.890	2.006	2.835	154.49
N1–H1B ··· O2	0.890	2.234	2.887	129.84
N1–H1C ··· F1#2	0.890	1.955	2.801	158.26
N1–H1C ··· O3	0.890	2.648	3.269	127.76
N2–H2A ··· O5#3	0.890	2.170	3.033	163.11
N2–H2A ··· O7#3	0.890	2.240	2.848	125.24
N2–H2B ··· O7#4	0.890	2.252	2.952	135.40
N2–H2C ··· O1#5	0.890	1.937	2.804	164.13
N2–H2C ··· O4#5	0.890	2.642	3.294	130.90
O4–H4 ··· O3#5	0.820	1.999	2.771	156.71
O4–H4 ··· O2#6	0.820	2.570	3.002	114.29
O7–H7 ··· O7#7	0.820	1.664	2.434	155.33

Symmetry transformations used to generate equivalent atoms: #1: $-x+3$, $-y+2$, $-z+2$; #2: $x-1$, y, z; #3: x, y, $z+1$; #4: $-x+2$, $-y+2$, $-z+2$; #5: $-x+2$, $-y+3$, $-z+2$; #6: $-x+3$, $-y+3$, $-z+2$; #7: $-x+3$, $-y+2$, $-z+1$.

2.792–2.835 Å and N ··· O distances of 2.804–3.294 Å. The details of hydrogen bonds for **2** are given in table 4.

4. Conclusions

We have synthesized two fluorinated gallium phosphates templated by organic amines, $(C_4H_{15}N_3)[Ga_3F_2(PO_4)_3]$ (**1**) and $[(C_2H_{10}N_2)(C_2H_9N_2)][Ga_3F_4(HPO_4)_4]$ (**2**).

Compound **1** has a 3-D framework with 10-membered ring channels along the *b*-axis. Compound **2** has a 3-D supramolecular structure with pseudo 10-membered ring channels along the *a*-axis, constructed by O–H $\cdots$ O hydrogen bonds. $[C_4H_{15}N_3]^{2+}$ in **1** and $[(C_2H_{10}N_2)(C_2H_9N_2)]^{3+}$ in **2** are located in the inorganic channels and interact with the polyanion framework both electrostatically and *via* N–H $\cdots$ O and N–H $\cdots$ F hydrogen bonds.

Supplementary material

"CCDC 750125 and 727098" contain the supplementary crystallographic data for this article. These data can be obtained free of charge at www.ccdc.cam.ac.uk [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44(0)1223-336033; Email: deposit@ccdc.cam.ac.uk].

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References

[1] J.X. Jiang, J.H. Yu, A. Corma. *Angew. Chem. Int. Ed.*, **49**, 3120 (2010).
[2] J.L. Guth, H. Kessler, R. Wey. *Stud. Surf. Catal.*, **28**, 121 (1986).
[3] T. Loiseau, G. Ferey. *J. Solid State Chem.*, **111**, 403 (1994).
[4] T. Loiseau, R. Retoux, P. Lacorre, G. Ferey. *J. Solid State Chem.*, **111**, 427 (1994).
[5] S.J. Choyke, S.M. Blau, A.A. Larner, A.N. Sarjeant, J. Yeon, P.S. Halasyamani, A.J. Norquist. *Inorg. Chem.*, **48**, 11277 (2009).
[6] R.I. Walton, F. Millange, D. O'Hare, A. Le Bail, T. Loiseau, C. Serre, G. Ferey. *Chem. Commun.*, **3**, 203 (2000).
[7] C. Paulet, T. Loiseau, G. Ferey. *Chem. Mater.*, **12**, 1997 (2000).
[8] F. Serpaggi, T. Loiseau, G. Ferey. *Acta Cryst.*, **C53**, 1568 (1997).
[9] T. Loiseau, G. Ferey. *Solid State Sci.*, **7**, 1556 (2005).
[10] S. Lohmeier, M. Wiebcke, P.Z. Behrens. *Anorg. Allg. Chem.*, **634**, 147 (2008).
[11] G.M. Sheldrick. *A Program for the Siemens Area Detector ABSorption Correction*, University of Göttingen, Germany (1997).
[12] G.M. Sheldrick. *SHELXL97, Program for Crystal Structure Refinement*, University of Göttingen, Germany (1997).
[13] L. Wang, T.Y. Song, Y. Fan, Z.F. Tian, Y. Wang, S.H. Shi, J.N. Xu. *J. Solid State Chem.*, **179**, 3400 (2006).
[14] L. Wang, T.Y. Song, Y. Fan, Y. Wang, J.N. Xu, S.H. Shi, T. Zhu. *J. Solid State Chem.*, **179**, 824 (2006).
[15] S. Fernandez, J.L. Mesa, J.L. Pizarro, L. Lezama, M.I. Arriortua, T. Rojo. *J. Solid State Chem.*, **177**, 765 (2004).
[16] G. Herzberg. *Molecular Spectra and Molecular Structure*, van Nostrand Reinhold, New York (1950).