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Synthesis and characterization of a new open-framework fluorinated gallium phosphite with three-dimensional intersecting channels

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Abstract

$(C_4N_2H_{12})[Ga_2F_3(HPO_3)_2(H_2PO_3)]$ **1** is a new open-framework fluorinated gallium phosphite obtained by mild hydrothermal synthesis using piperazine as template agent and characterized by single crystal X-ray diffraction (XRD), powder XRD, infra-red spectroscopy, inductively coupled plasma, thermogravimetric and elemental analyses. The three-dimensional (3D) anionic framework of compound **1** is constructed from two distinct motifs, a 1D tancoite chain and a single 4-ring (S4R) unit, which contains four intersecting channels running throughout the structure as 8, 12-member rings channels along to the *a*-axis and 12-member ring channels along the *b*- and *c*-axis, respectively. The well-ordered, diprotonated piperazine cations occupy all the channels, and interact with the fluorinated gallium-phosphite framework by strong hydrogen bonds.

Keywords: Open-framework; Crystal structure; Hydrothermal synthesis; Gallium phosphite; Organic template

1. Introduction

Over the past several decades, the synthesis of metal phosphates with open-framework structures has been an area of intense research due to their rich structural chemistry and the potential applications in ion exchange, separation and catalysis [1]. Among metal phosphates, gallium phosphates constitute an important family that exhibits a rich structural and compositional diversity. This class of materials is usually prepared hydrothermally under mild condition by using organic amines as structure-directing agents. In addition to the three-dimensional (3D) networks, numerous layered or chain-like structures have been reported. A most famous example is the synthesis of cloverite, which contains extra large 20-ring channels [2]. More recently, the pseudo-pyramidal phosphite $[HPO_3^{2-}]$ group has been investigated as a possible replacement for the traditional phosphate tetrahedron with great success [3–12]. It is well known that the pyramidal hydrogen phosphite group $[HPO_3^{2-}]$, different from phosphate $[PO_4^{3-}]$, only links three adjacent cations via P–O–M (M = metal) bonds, so it provides variety and novelty to the structure. In contrast to the large numbers of gallium phosphates, the reports on organically templated gallium phosphites are rare. So far, only an organically templated gallium-doped chromium phosphite $(C_2H_{10}N_2)[Ga_{0.98}Cr_{0.02}(HPO_3)F_3]$ has been reported [13]. With the aim of searching novel organically templated phosphites, we conducted our study on the hydrothermal synthesis in gallium-phosphite-amine systems. We have isolated a new 3D open-framework fluorinated gallium phosphite with diethylenetriamine as templated agent [14]. In this work, we describe the synthesis and crystal structure of a novel organically templated fluorinated gallium phosphite, $(C_4N_2H_{12})[Ga_2F_3(HPO_3)_2(H_2PO_3)]$ **1**, which contains four channels running throughout the structure with intersecting 8, 12-member ring channels along the *a*-axis and 12-member ring channels along the *b*- and *c*-axis, respectively.

2. Experimental

2.1. Materials and instrumentation

All chemicals were obtained from commercial sources and used without further purification. The elemental

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analysis was conducted on a Perkin Elmer 2400 elemental analyzer. Inductively coupled plasma (ICP) analysis was performed on a Perkin Elmer Optima 3300 DV ICP instrument. Powder X-ray diffraction (XRD) data were obtained using SHIMADAZU XRD-6000 diffractometer with Cu$K\alpha$ radiation ($\lambda = 1.5418$ Å), with the step size and the count time of 0.02° and 4 s, respectively. FT-IR spectrum was recorded on a Nicolet Impact 410 spectrometer between 400 and 4000 $\mathrm{cm^{-1}}$ using the KBr pellet method. Thermogravimetric analysis (TGA) was conducted on a SHIMADAZU DTG 60 thermogravimetric analyzer with a heating rate of 10 °C $\mathrm{min^{-1}}$ up to 1000 °C under nitrogen gas.

2.2. Synthesis

The compound **1** was synthesized hydrothermally by a typical solution mediated reaction: 0.05 g Ga_2O_3, 0.80 ml H_3PO_3, 0.50 g piperazine, 0.60 ml HF and 2 ml of water was stirred for 30 min at room temperature, then the mixture was transferred to a 23 ml PTFE-lined stainless-steel hydrothermal autoclave at a filling capacity of ~9% and heated at 180 °C for 3 d under autogenous pressure. The initial and final pH of reaction mixture was ~1. Fine rod-shaped crystals, were filtered off, washed with water and dried at room temperature (yield = 60% based on Ga).

2.3. Crystal structure determination

A suitable single crystal with dimensions 0.30 × 0.18 × 0.12 mm was selected for XRD analysis. The intensity data were collected on a Simens SMART CCD diffractometer with graphite-monochromated Mo$K\alpha$ ($\lambda = 0.71073$ Å) radiation at a temperature of 298 ± 2 K. No significant decay was observed during the data collection. Data processing was accomplished with the saint-processing program. The structure was solved by direct method using the SHELXTL crystallographic software package. The gallium and phosphorus atoms were first located, whereas the carbon, nitrogen, oxygen and fluorine atoms were found in the difference Fourier maps. The hydrogen atoms residing on the amine molecules and phosphorus were placed geometrically. A total of 5044 reflection intensities, of which 3434 were independent ($R_{\mathrm{int}} = 0.0506$), were collected within the range $1.83^\circ < \theta < 28.31^\circ$ for the compound. The final cycle of refinement performed on F_0^2 afforded residuals $R = 0.0350$ and $R_w = 0.0840$. The crystal belongs to triclinic space group P-1. Crystallographic data for this compound is listed in Table 1. Selected bond distances are summarized in Table 2. CCDC-293768 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44 1223/336 033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1
Crystallographic data for compound **1**

Empirical formula	$C_4H_{16}N_2O_9F_3P_3Ga_2$
F_w	525.54
Crystal system	Triclinic
Space group	$P-1$
a [Å]	7.1072(3)
b [Å]	9.4094(6)
c [Å]	11.7847(5)
α [°]	71.602(3)
β [°]	78.165(3)
γ [°]	70.296(3)
V [Å^3]	699.72(6)
Z	2
D_c [g cm^{-3}]	2.494
μ [mm^{-1}]	4.279
Crystal size [mm]	0.30 × 0.18 × 0.12
θ range [°]	1.83–28.31
Reflections collected/unique	5044/3434 [R(int) = 0.0506]
Data/restraints/parameters	3434/0/226
Goodness-of-fit on F^2	1.002
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0350$, w$R_2 = 0.0840$
R indices (all data)	$R_1 = 0.0479$, w$R_2 = 0.0885$
Largest diff. peak/hole [e Å^{-3}]	1.328 and −1.174

3. Results and discussion

3.1. Synthesis

Reactions of phosphite acid with the gallium oxide in the presence of HF under mild hydrothermal conditions afforded a new compound with 3D open-framework. The most characteristic synthetic results were summarized in Table 3. It should be noted that the presence of fluorine ions is of prime importance for the formation of compound **1**. As seen in runs 1–5, despite increasing the amount of phosphite, no crystal of compound **1** was obtained in absence of fluoride ions except for amorphism or thick gel. Fluoride ions act as ligands since their presence can be detected in finally prepared material. The formation of compound **1** is also greatly influenced by the amount of water. The microcrystal of compound **1** was synthesized in gels with molar ratios of 0.3 Ga_2O_3:5.0 H_3PO_3:3.0 piperazine:30 HF:278 H_2O. When decreasing the molar amount of H_2O to 111 and keeping other conditions unchanged, the rod-like crystals of compound **1** was obtained, while increasing the molar amount of H_2O more than 444, no crystals of compound **1** were prepared except for clear liquids.

3.2. Characterizations

The XRD pattern of this compound is consistent with the simulated one on the basis of single-crystal structure, indicating the phase purity of the as-synthesized sample. ICP analysis for the product gave the gallium:phosphorus ratio of the title compound was ca. 0.67, which is in good agreement with the value of 2:3 obtained from

Table 2
Selected bond lengths and angles [Å, °] and hydrogen bonds for compound **1**

Ga(1)–F(1)	1.895(2)		Ga(2)–F(3)	1.9509(2)
Ga(1)–F(2)	1.889(2)		Ga(2)–O(6)	1.938(2)
Ga(1)–O(1)	1.995(3)		Ga(2)–O(7)	1.960(2)
Ga(1)–O(2)	1.956(2)		Ga(3)–F(3)	1.966(2)
Ga(1)–O(3)	1.961(3)		Ga(3)–O(8)	1.940(2)
Ga(1)–O(4)	1.966(2)		Ga(3)–O(9)	1.941(3)
P(1)–O(1)^c	1.512(3)		P(2)–O(2)	1.521(3)
P(1)–O(3)	1.524(3)		P(2)–O(8)^b	1.521(3)
P(1)–O(5)	1.564(3)		P(2)–O(7)^b	1.531(3)
P(1)–H(1)	1.35(4)		P(2)–H(2)	1.28(4)
P(3)–O(4)	1.529(3)		P(3)–O(9)^a	1.516(3)
P(3)–O(6)	1.523(3)		P(3)–H(3)	1.39(6)
P(1)–O(3)–Ga(1)	124.83(16)		P(3)–O(6)–Ga(2)	131.82(15)
P(2)–O(2)–Ga(1)	140.13(16)		P(2)^b–O(8)–Ga(3)	133.32(15)
P(1)^c–O(1)–Ga(1)	132.57(16)		P(3)^a–O(9)–Ga(3)	136.77(16)
P(3)–O(4)–Ga(1)	140.82(15)		P(2)^b–O(7)–Ga(2)	130.72(16)
D–H···A	D(D–H)	D(H···A)	D(D···A)	<(DHA)
O(5)–H(4)···O(1)^d	0.85(6)	2.51(6)	3.076(4)	125(5)
O(5)–H(4)···F(1)^d	0.85(6)	1.85(6)	2.662(4)	159(6)
N(1)–H(1B)···O(7)^a	0.90	1.99	2.816(4)	151.5
N(2)–H(5B)···F(2)^e	0.90	1.78	2.677(4)	174.5

Symmetry transformations used to generate equivalent atoms: (a) $-x+2, -y, -z+1$; (b) $x-1, y+1, z$; (c) $-x+1, -y+1, -z+2$; (d) $x+1, y, z$; (e) $-x+1, -y, -z+2$.

Table 3
Lists of the synthesis conditions and results of compound **1**

Gel molar compositions						
Run	Ga_2O_3	H_3PO_3	Piperazine	HF	H_2O	Results
1	0.3	5.0	3.0	0	278	Amorphous
2	0.3	6.3	3.0	0	278	Amorphous
3	0.3	7.5	3.0	0	278	Amorphous
4	0.3	8.8	3.0	0	278	Amorphous
5	0.3	10.0	3.0	0	278	Amorphous
6	0.3	5.0	3.0	10	278	Amorphous
7	0.3	5.0	3.0	20	278	Amorphous
8	0.3	5.0	3.0	30	278	Microcrystal of 1
9	0.3	5.0	3.0	30	111	Compound 1
10	0.3	5.0	3.0	30	444	Clear liquid

single-crystal XRD analysis. Elemental analysis showed that C, H, and N are 9.17%, 3.97%, and 5.37%, respectively, in agreement with the expected values of 9.13, 3.04 and 5.33 wt% of C, H and N on the basis of the empirical formula given by the single-crystal structure analysis. F^- content was determined using a fluoride ion-selective electrode after mineralization and analysis data (exp. 10.90 wt%) is in good agreement with the value (calcd. 10.85 wt%) deduced from the single-crystal XRD analysis.

The IR (KBr) spectrum of compound **1** showed the stretching vibrations of N–H and C–H bonds at 2996, 2918, 2841, 2766, 2730 and 2632 cm^{-1}, while the medium absorption bonds at 1625 and 1464 cm^{-1} were assigned to the bending vibrations of N–H and C–H, respectively. The absorptions at 2398 cm^{-1} were observed as well due to the stretching vibrations of the P–H groups in phosphite anions. The strong absorptions at 1180, 1116, 1075, 1055 and 975 cm^{-1} can be attributed to P–O vibrations.

Thermogravimetric analysis (TGA) was conducted under nitrogen gas with a heating rate of 10 °C min^{-1}. The TG curve (Fig. 1) shows 2 events between 25 and 1000 °C. The first weight loss (18.72 wt%) occurring between 300 and 600 °C is attributed to the dehydration of H_2PO_3 groups (calc. 1.71%) and the departure of organic amine cations (calc. 16.74%). Powder XRD indicates that the structure is collapsed after the removal of the organic part. The second weight loss which is continuously observed from 600 to 1000 °C for compound **1** may correspond to a part of the removal of HF (exp.: 7.56%). The final decomposition product (73.72 wt%) is amorphous after the calcination and its phase is

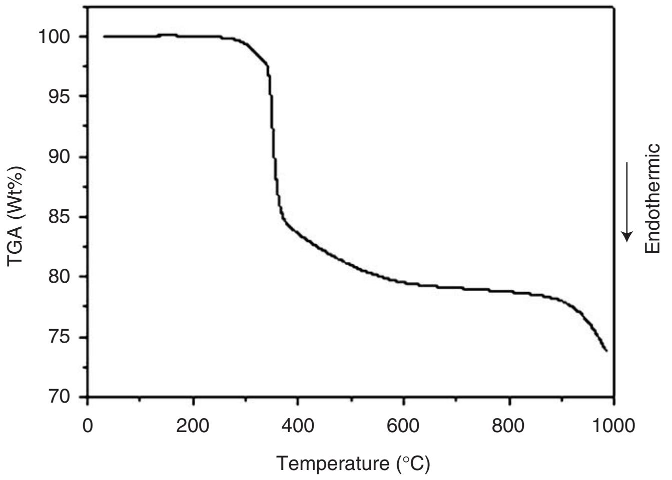

Fig. 1. Thermogravimetric curve of compound **1**.

unidentified. The presence of fluorine in compound **1** that allow for the formation of a more porous framework, would be a significant drawback for the thermal behavior.

3.3. Structural description

The asymmetric unit of **1**, contains 24 non-H atoms, including three gallium atoms, three phosphorus atoms, nine oxygen atoms, three fluorine atoms, four carbon atoms, and two nitrogen atoms, as shown in Fig. 2. All Ga atoms adopt six-coordination geometry by four O atoms and two F atoms, but they present two types of coordination environment. Ga(1) bonds to four bridging O atoms from the adjacent P atoms with Ga(1)–O(1), Ga(1)–O(2), Ga(1)–O(3), and Ga(1)–O(4) bond lengths being 1.995(3), 1.956(2), 1.961(3) and 1.966(2) Å, respectively, and two F atoms are the terminal atoms with Ga(1)–F(1), Ga(1)–F(2) bond length being 1.895(2) and 1.889(2) Å, respectively. Such a shorter Ga(1)–F(1) and Ga(1)–F(2) bond length is previously reported in the fluorine gallium phosphates $GaPO_4$–CJ2 [15] or ULM-9 [16] in which one of the fluorine atoms points toward the ammonium groups. The terminal Ga–F distances are 1.903 Å for $GaPO_4$-CJ2 and 1.800 Å for ULM-9 and correspond to the shortest distances within the coordination polyhedron. For Ga(2) and Ga(3) octahedra, the F atoms are in bridging positions corresponding to Ga(2)–F(3) and Ga(3)–F(3) bond lengths being 1.951(2) and 1.966(2) Å, respectively. The P atoms adopt pseudo-pyramidal coordination geometry, each bond to three oxygen atoms and one hydrogen atom. All oxygen atoms bridge the Ga atoms with the exception of one, which we have identified as a terminal OH group on the basis of its long associated bond length P(1)–O(5) = 1.564(3) Å. The terminal P–H bond lengths are 1.28(4), 1.35(4) and 1.39(6) Å, respectively, which are similar to the P–H bond length that is reported in metal phosphite previously [17]. The existence of P–H bond is also verified by IR spectrum, which exhibits strong absorption at 2398 cm^{-1} [3].

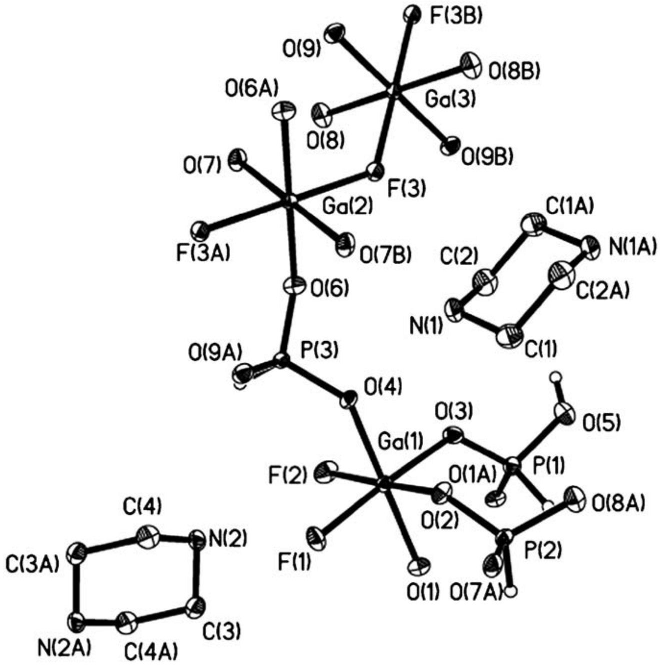

Fig. 2. ORTEP drawing of the asymmetric of compound **1** (50% thermal elipsolids).

The 3D anionic framework of compound **1** is constructed from two distinct motifs, a 1D tancoite chain and a single 4-ring (S4R) unit. $Ga(2)O_4F_2$ and $Ga(3)O_4F_2$ octahedra are linked through their fluorine vertexes forming an infinite 1D Ga–F–Ga chain. The $HP(2)O_3$ and $HP(3)O_3$ pseudo-pyramids are grafted alternatively up and down on to this central octahedral chain giving rise to a new 1D chain $[Ga_2P_4]_\infty$ which is similar to the tancoite-type chain which represent a common feature of many minerals and synthetic materials [18]. The main difference between them comes from the presence of phosphite pseudo-pyramids linked to the adjacent gallium octahedra in the infinite chains of compound **1**. The second building block is a S4R unit constructed by $Ga(1)O_4F_2$ octahedra and $H_2P(1)O_3$ pseudo-pyramids via vertex-sharing Ga–O–P bonds as seen in Fig. 3. The present S4R units are obviously different from the existing twos in gallium phosphates [19,20], one of them is built from two GaO_4 tetrahedra and two PO_4 tetrahedra, the other is composed of one GaO_6 octahedron, one GaO_4 tetrahedron and two PO_4 tetrahedra. So these two building units are connected to each other via O(2) and O(3) atoms whilst conserving strict Ga–P alternation to generate an anionic $[Ga_2F_3(HPO_3)_2(H_2PO_3)]^{3-}$ three dimensional framework which contains four intersecting channels running throughout the structure as 8, 12-member rings channels along to the *a*-axis and 12-member ring channels along the *b*- and *c*-axis (Fig. 3).

The well-ordered, diprotonated piperazine cations occupy the 8- and 12-ring windows and interact with the fluorinated gallium-phosphite framework by way of N–H…O and N–H…F hydrogen bonds, respectively (Fig. 4).

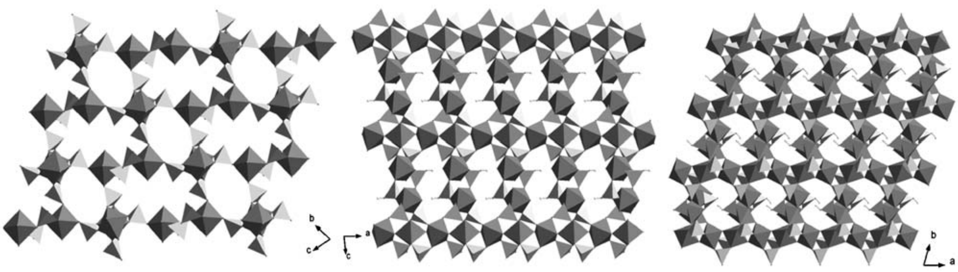

Fig. 3. Polyhedral view of 8, 12-member rings channels of compound **1** along the *a*-axis and 12-member ring channels of compound **1** along the *b*- and *c*-axis, respectively.

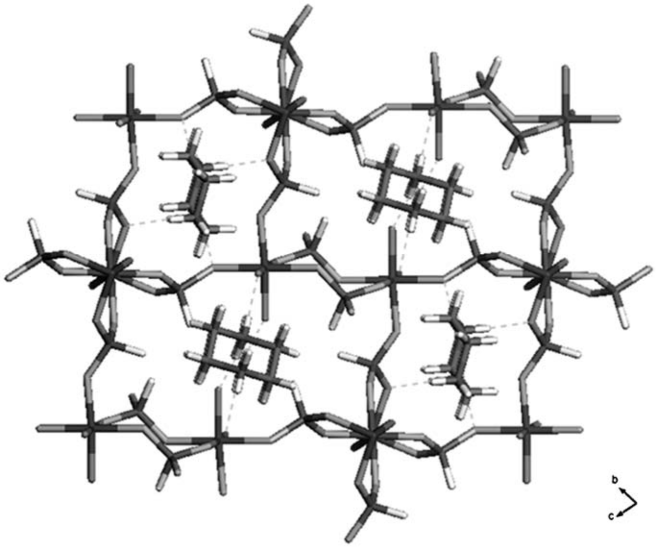

Fig. 4. View of 8- and 12-ring windows of compound **1** with template to framework hydrogen bonds indicated by dotted lines.

Based on the geometrical placement of hydrogen atoms described above, all of the N–H moieties are involved in template-to-framework hydrogen bonds, as evidenced by the short N–H$\cdots$O and N–H$\cdots$F distances: N(1)–H$\cdots$O(7) = 2.816(4) Å, N(2)–H$\cdots$F(2) = 2.677(4) Å, and the larger N–H$\cdots$O and N–H$\cdots$F angles: N(1)–H$\cdots$O(7) angles of 151.5°, N(2)–H$\cdots$F(2) angles of 174°. The interactions occur between fluorine and the ammonium groups of the template as already found in other phases of the ULM-*n* series [21,22]. There is no hydrogen bonding interactions involving the P–H bond, which is expected, as this *H* atom does not show acidic behavior [23].

The fluoride method, pioneered by Kessler et al. allows the incorporation of fluoride atoms within the inorganic framework and has led to the discovery of numerous new fluoro-gallophosphates with novel topologies such as in cloverite, a fluorinated gallophosphate with a large-pore 20-member ring structure. In compound **1**, the fluorine plays important role in the unusual framework and channel architectures. The F atoms are coordinated to all gallium atoms of the structure with both terminal and bridging environments. By occupying bridging sites, they allow the gallium polyhedra to connect together. In addition, the terminal fluorides are not merely spectator ligands, but they are involved in the formation of the hydrogen bond network to the channel counterions.

4. Conclusions

In summary, the hydrothermal synthesis and crystal structure of a novel organically templated fluorinated gallium phosphite, $(C_4N_2H_{12})[Ga_2F_3(HPO_3)_2(H_2PO_3)]$ has been described. The structure can be viewed as vertex-linking two distinct motifs 1D tancoite chain and a single 4-ring (S4R) unit to generate a 3D framework with four channels running throughout the structure as 8, 12-member ring channels along to the *a*-axis and intersecting 12-member ring channels along the *b*- and *c*-axis where the organic amines reside. Recent exploratory syntheses of metal phosphite reveal a rich structural chemistry. Because the μ_3-coordination for the phosphite is different from the traditional μ_4-coordination for the phosphate, so it presents further challenges in the hydrothermal synthesis of organically templated open-framework metal phosphites. Our investigation shows that it is possible to prepare structural complex open-framework gallium phosphites possessing cavity size, limiting apertures, and framework densities rivaling those of gallium phosphates under appropriate reaction conditions. Further investigation of gallium phosphite compounds is in progress.

Acknowledgments

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