

Ga₃(HPO₃)₄F₄(H₃DETA) (DETA = diethylenetriamine): A new open-framework fluorinated gallium phosphite with pentameric building unit

Li Wang^a, Tianyou Song^a, Yong Fan^a, Ying Wang^a, Jianing Xu^a, Suhua Shi^{a,*}, Tao Zhu^b

^aKey Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun 130012, China

^bKey Laboratory for Supramolecular Structure and Materials of Ministry of Education, Jilin University, Changchun 130012, China

Received 9 October 2005; received in revised form 28 November 2005; accepted 4 December 2005

Available online 10 January 2006

Abstract

Ga₃(HPO₃)₄F₄(H₃DETA) is a new open-framework fluorinated gallium phosphite obtained by mild hydrothermal synthesis using diethylenetriamine as templated agent and characterized by single crystal X-ray diffraction, the powder X-ray diffraction, IR spectroscopy, TGA, ICP and elemental analyses. It crystallizes in the monoclinic space group *C2/c*, *a* = 12.741(6) Å, *b* = 12.068(6) Å, *c* = 11.988(5) Å, β = 94.902(8)°, *V* = 1836.6(15) Å³, *Z* = 4. The construction of 3D open-framework structure in the title compound may be viewed as the assembly of pentameric building units and HPO₃ groups. The pentameric building unit is the first to be found, which lead to form the three types of channels along *a*-, *b*- and *c*-axes, respectively, in gallium phosphite. The triprotonated DETA cations are inserted within the 10-membered ring channels and interact with anions of the framework via hydrogen bonds.

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

1. Introduction

In the past decades, metal phosphates with open-framework structures have been synthesized owing to their rich structural chemistry and the potential applications in ion exchange, separation and catalysis [1]. More recently, the pseudo-pyramidal phosphite [HPO₃] group has been investigated as a possible replacement for the traditional phosphate tetrahedral with great success. It is well known that the pyramidal hydrogen phosphite group [HPO₃²⁻], different from phosphate [PO₄³⁻], only link three adjacent cations via P-O-*M* (*M* = metal) bonds, so it provides variety and novelty to the structures. Since the vanadium phosphite with piperazinium cation as structurally directing agent (H₂NC₄H₈NH₂)[(VO)₃(HPO₃)₄(H₂O)₂] were synthesized by Zubieta et al. [2], a number of studies on the metal phosphites containing Zn, Co, Fe, V, Mn and Cr have been carried out [3]. However, only three of the

organically templated main block metal phosphites, (H₂NC₆H₁₂NH₂)[Al(OH)(H(HPO₃))₂] [4], (H₃NC₃H₆NH₃)[Be₃(HPO₃)₄] [5] and (H₃NC₂H₄NH₃)[In(OH)₃(HPO₃)] [6] have been reported. Various open-framework gallium phosphates containing organic templates have been prepared [8], but the pure gallium phosphites are underdeveloped. So far, only gallium (III)-doped chromium (III) fluorophosphite (C₂H₁₀N₂)[Ga_{0.98}Cr_{0.02}(HPO₃)F₃] [7] has been reported. In this paper, we report the hydrothermal synthesis and characterization of a new purely gallium phosphite templated by diethylenetriamine (DETA), Ga₃(HPO₃)₄F₄(H₃DETA), which, to our knowledge, is the first organically templated gallium phosphite with 3D open-framework structure.

2. Experimental

2.1. Materials and instrumentation

All chemicals were obtained from commercial sources, and used without further purification. The elemental analysis was conducted on a Perkin-Elmer 2400 elemental

*Corresponding author.

E-mail address: shish@mail.jlu.edu.cn (S. Shi).

analyzer. Inductively coupled plasma (ICP) analysis was performed on a Perkin-Elmer Optima 3300DV ICP instrument. Powder X-ray diffraction (XRD) data were obtained using SHIMADAZU XRD-6000 diffractometer with Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$), 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 cm^{-1} , using the KBr pellet method. Thermogravimetric analysis (TGA) was conducted on a SHIMADAZU DTG 60 thermogravimetric analyzer with a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ up to $800 \text{ }^\circ\text{C}$ under nitrogen gas.

2.2. Synthesis

The title compound was synthesized hydrothermally by a typical solution-mediated reaction: 0.05 g Ga₂O₃, 0.80 g H₃PO₃, 0.10 ml DETA, 0.40 ml HF and 8 ml of water were stirred for 30 min at room temperature, then the mixture was transferred to a 23 ml PTFE-lined stainless-steel hydrothermal autoclave with a filling capacity of $\sim 35\%$ and heated at $170 \text{ }^\circ\text{C}$ for 5 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 single crystal of the title compound (size: $0.30 \times 0.18 \times 0.13 \text{ mm}$) was mounted on a thin glass fiber with cyanoacrylate adhesive. The intensity data were collected on a Siemens Smart CCD diffractometer equipped with graphite-monochromated Mo-K α ($\lambda = 0.71073 \text{ \AA}$) radiation in the ω scanning mode at room temperature. No significant decay was observed during the data collection. Data were processed on a Pentium PC using Bruker AXS Windows NT SHELXTL software package (version 5.10) [9, 10]. Empirical absorption correction was applied using the SADABS program. The structure was solved by direct method, and refined with full-matrix least squares. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed geometrically and located in the difference Fourier map. The crystal belongs to monoclinic space group *C2/c*. The crystal data are summarized in Table 1, while the selected bond lengths/angles data are presented in Table 2.

CCDC-283103 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].

3. Results and discussion

3.1. Characterizations

The XRD pattern of this compound is consistent with the simulated one on the basis of single-crystal structure,

Table 1
Crystallographic data for the title compound

Empirical formula	C ₄ H ₂₀ N ₃ O ₁₂ F ₄ P ₄ Ga ₃
Formula weight	711.27
Crystal system	Monoclinic
Space group	<i>C2/c</i>
<i>a</i> (Å)	12.741(6)
<i>b</i> (Å)	12.068(6)
<i>c</i> (Å)	11.988(5)
β (Å)	94.902(8)
<i>V</i> (Å ³)	1836.6(15)
<i>Z</i>	4
<i>D_c</i> (g cm ⁻³)	2.572
μ (mm ⁻¹)	4.825
Reflections collected/unique	5350/1990
	[<i>R</i> (int) = 0.0627]
Data/restraints/parameters	1990/0/145
Goodness-of-fit on <i>F</i> ²	1.061
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0456, <i>wR</i> ₂ = 0.0799
Largest diff. peak/hole [eÅ ⁻³]	0.902 and -0.749

$$R_1 = \sum ||F_o| - |F_{cs}|| / \sum |F_o|, \quad wR_2 = \sqrt{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]}^{1/2}.$$

Table 2
Selected bond lengths (Å) and angles (°) for the title compound

Ga(1)–F(1)	1.871(3)	Ga(2)–F(2)	1.947(3)
Ga(1)–F(2)	1.968(3)	Ga(2)–F(2) ^a	1.947(3)
Ga(1)–O(1)	1.949(3)	Ga(2)–O(2)	1.945(3)
Ga(1)–O(4)	1.942(4)	Ga(2)–O(2) ^a	1.945(3)
Ga(1)–O(5)	1.958(3)	Ga(2)–O(3)	1.934(3)
Ga(1)–O(6)	1.972(4)	Ga(2)–O(3) ^a	1.934(3)
P(1)–O(3) ^d	1.520(3)	P(2)–O(1) ^b	1.522(3)
P(1)–O(4) ^c	1.518(4)	P(2)–O(2)	1.505(3)
P(1)–O(5)	1.519(3)	P(2)–O(6)	1.516(4)
P(1)–H(1)	1.33(4)	P(2)–H(2)	1.34(4)
F(1)–Ga(1)–O(1)	90.62(13)	O(3) ^a –Ga(2)–O(3)	178.4(2)
F(1)–Ga(1)–O(4)	92.58(14)	O(3) ^a –Ga(2)–O(2)	93.03(15)
F(1)–Ga(1)–O(5)	92.89(13)	O(3)–Ga(2)–O(2)	88.09(14)
F(1)–Ga(1)–O(6)	84.55(13)	O(3)–Ga(2)–O(2) ^a	93.03(15)
F(1)–Ga(1)–F(2)	177.19(12)	O(2)–Ga(2)–O(2) ^a	88.5(2)
O(4)–Ga(1)–F(2)	88.20(13)	O(3) ^a –Ga(2)–F(2)	88.20(13)
O(1)–Ga(1)–F(2)	92.06(12)	O(3)–Ga(2)–F(2)	90.68(13)
O(5)–Ga(1)–F(2)	86.43(12)	O(2)–Ga(2)–F(2)	91.91(13)
F(2)–Ga(1)–O(6)	92.74(13)	O(2) ^a –Ga(2)–F(2)	176.28(12)
O(1)–Ga(1)–O(5)	86.19(14)	O(3)–a(2)–F(2) ^a	88.20(13)
O(4)–Ga(1)–O(1)	91.60(15)	O(2) ^a –Ga(2)–F(2) ^a	91.91(13)
O(4)–Ga(1)–O(5)	174.12(15)	F(2)–Ga(2)–F(2) ^a	87.91(16)
O(4)–Ga(1)–O(6)	90.98(15)	Ga(2)–F(2)–Ga(1)	132.87(14)
O(1)–Ga(1)–O(6)	174.62(14)	O(5)–Ga(1)–O(6)	91.68(14)
O(4) ^c –P(1)–O(5)	109.9(2)	O(2)–P(2)–O(6)	113.07(19)
O(4) ^c –P(1)–O(3) ^d	113.8(2)	O(2)–P(2)–O(1) ^b	114.5(2)
O(5)–P(1)–O(3) ^d	109.85(19)	O(6)–P(2)–O(1) ^b	110.57(19)
O(4) ^c –P(1)–H(1)	106.5(17)	O(2)–(2)–H(2)	104.4(17)
O(5)–P(1)–H(1)	107.9(16)	O(6)–P(2)–H(2)	107.5(18)
O(3) ^d –P(1)–H(1)	108.7(17)	O(1) ^b –P(2)–H(2)	106.1(17)

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

indicating the phase purity of the as-synthesized sample (Fig. 1). ICP analysis for the product gave the gallium: phosphorus ratio of the title compound as ca. 0.75, which is

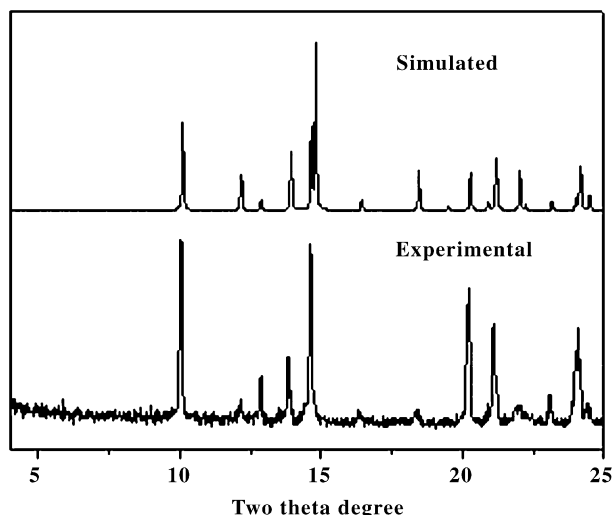


Fig. 1. Simulated and experimental power X-ray diffraction patterns of the title compound.

in good agreement with the value of 3:4 obtained from the single-crystal X-ray diffraction analysis. Elemental analysis data were satisfactory (C obsd (%), calcd (%), 6.80, 6.75; H, 2.92, 2.81; N, 6.07, 5.90). F^- content was determined using a fluoride-ion-selective electrode after mineralization and analysis data (exp. 10.72 wt%) is in good agreement with the value (calcd. 10.68 wt%) deduced from the single-crystal X-ray diffraction analysis.

The IR spectrum of the product phase exhibited a broad medium absorption band in the range $3500\text{--}2800\text{ cm}^{-1}$ due to the NH_3^+ vibration stretching as well as CH_2 groups, while the medium absorption bands at 1580 and 1625 cm^{-1} due to the bending modes of NH_3^+ , and the bending modes of CH_2 groups can be observed at 1465 cm^{-1} . The absorptions at 2402 cm^{-1} were observed as well due to the stretching vibrations of the P–H groups in phosphite anions. The strong absorptions in the region $1400\text{--}1000\text{ cm}^{-1}$ can be attributed to P–O vibrations.

The TG curve of the materials is given in Fig. 2. The total weight loss occurs in three steps. The first weight loss (0.4 wt%) occurring below 200°C can be assigned to absorbed water molecules at the surface of materials. The second weight loss occurring between 280 and 580°C (15.3 wt%) is attributed to the removal of DETA cations (calcd 14.9 wt%). The third weight loss, which is observed between 580 and 800°C (10.2 wt%) can correspond to the removal of fluorine (weight loss expected 10.6 wt%).

3.2. Structural description

Single-crystal X-ray analysis indicates that the compound possesses three-dimensional open framework with pentameric building unit. As shown in Fig. 3, there are two crystallographically distinct sites for the Ga atoms and P atoms, respectively, in the asymmetric unit of the title compound. Both Ga atoms adopt six-coordination geometry by four O atoms and two F atoms, but they present

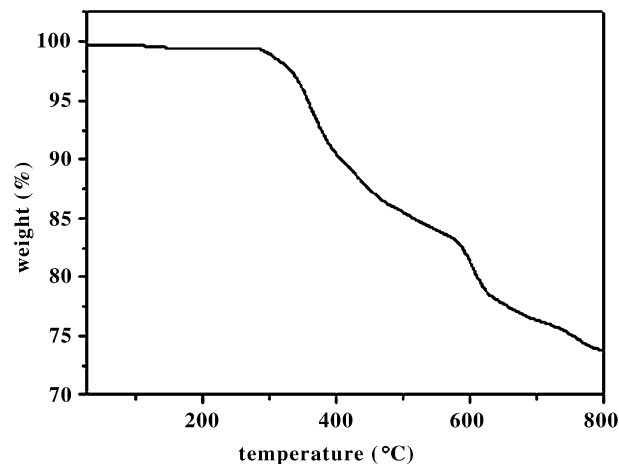


Fig. 2. Thermal analysis of the title compound under nitrogen gas.

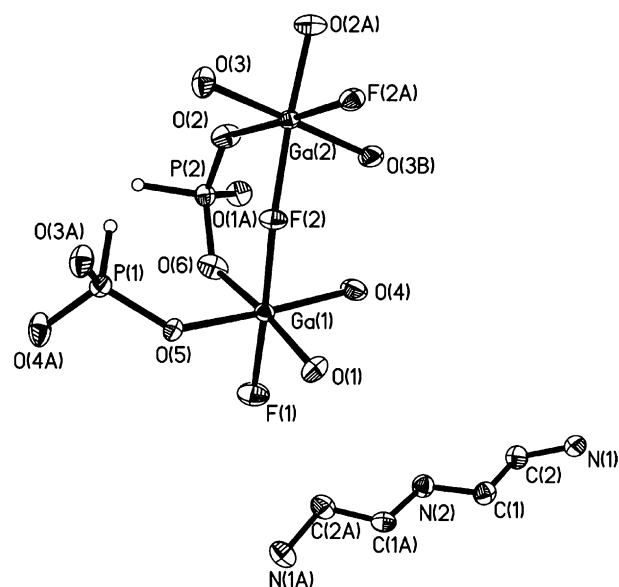


Fig. 3. Local coordination of the framework atoms shows the atom-labeling scheme (50% thermal ellipsoids).

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(4), Ga(1)–O(5), and Ga(1)–O(6) with bond lengths being 1.949(4), 1.943(4), 1.958(3) and 1.974(4) Å, respectively, and two F atoms are located in the apical vertices, one of them is the terminal atom and the other is bridging atom with Ga(1)–F(1) and Ga(1)–F(2) with bond length being 1.871(3) and 1.968(3) Å, respectively. For Ga(2) polyhedron, two F atoms are in bridging positions corresponding to Ga(2)–F(2) with bond length being 1.947(3) Å. Such a shorter Ga(1)–F(1) bond length was previously reported in the fluorine gallium phosphates $\text{GaPO}_4\text{-CJ2}$ [11] or ULM-9 [12] in which one of the fluorine atoms points toward the ammonium groups. The terminal Ga–F distances were 1.903 Å for $\text{GaPO}_4\text{-CJ2}$ and 1.800 Å for ULM-9, and correspond to the shortest distances within the coordination polyhedra. The identification of

these as F^- , rather than as OH^- bridges, is crystallographically difficult; however, refinement of the bridging atoms as oxygens lead to nonpositive defined anisotropic thermal parameters. In addition, bond valence sum calculations provide strong support for the level of fluorination we propose [13]. If the terminal and bridging atoms are assumed to be fluorines, rather than as oxygen-based ligands, the two independent Ga centers each give values close to the expected +3 valence. In contrast, calculations for all oxygen coordination environments lead to considerable deviations from this value. The P atoms adopt pseudo-pyramidal coordination geometry, which are coordinated to three O atoms with P–O bond length being 1.505(4)–1.521(3) Å, thus there are no terminal, “pendant” P–O or P–OH bonds [14], and a P–H bond makes up the fourth vertex of each $[HPO_3]^{2-}$ tetrahedron. The terminal P–H bond lengths are 1.33(4) and 1.34(4) Å, respectively, which are similar to the P–H bond length reported in H_3PO_3 previously [2]. The existence of P–H bond is also verified by IR spectrum, which exhibits strong absorption at 2402 cm^{-1} [3]. There is one triprotonated diethylenetriamine molecule in asymmetric unit.

The construction of 3D open-framework structure in the title compound may be viewed as the assembly of pentameric building unit and HPO_3 group. As shown in Fig. 4, the pentameric building unit is built by three GaO_4F_2 octahedra and two HPO_3 pseudo-pyramids. Within the pentameric building unit, the $Ga(2)O_4F_2$ octahedron is in a central position, and linked to the two $Ga(1)O_4F_2$ octahedra and two $HP(2)O_3$ pseudo-pyramids by corner-sharing via F(2), O(2) and O(6) atoms, respectively. These pentameric building units are connected to each other by bridging O(1) atoms while conserving strict Ga–P alternation in order to generate a sheet of composition $[Ga_3(HPO_3)_2F_4]$ in the ab plane (Fig. 4). In this layer, four adjacent pentameric building units are connected to form the 10-membered ring window. The free space within the 10-membered ring is slightly reduced

because the terminal Ga–F bonds attached to two Ga(1) atoms extend toward the center of the 10-membered ring. These layers are interconnected by sharing vertex-oxygen atoms with $HP(1)O_3$ pseudo-pyramids to generate 3D inorganic open-framework structure $[Ga_3(HPO_3)_4F_4]^{3-}$ with 8-, 6-, and 10-membered ring along the a -, b -, and c -axis, respectively (Fig. 5). And the organic template DETA molecules are fully protonated in order to balance the negative charge of the anionic framework.

The well-ordered triprotonated DETA cations occupy all of the 10-membered ring channels, and interact with the fluorinated gallium-phosphite framework by strong hydrogen bonds. On the basis of 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...O distances ~ 2.8 – 3.1 Å and N–H...F distances ~ 2.6 – 2.8 Å. And the hydrogen-bonding interactions are listed in Table 3. The interactions occur between fluorine and the ammonium groups of the template as already found in other phases of the ULM- n series [15,16]. There are no hydrogen-bonding interactions involving the P–H bond, which is expected, as this H atom does not show acidic behavior [17].

To our knowledge, the title compound is the first organically templated gallium phosphite with 3D open-framework structure. It is obviously different from the gallium (III)-doped chromium (III) fluorophosphite $(C_2H_{10}N_2)[Ga_{0.98}Cr_{0.02}(HPO_3)F_3]$ [7]. The structure of the latter consists of $[Ga_{0.98}Cr_{0.02}(HPO_3)F_3]^{2-}$ anionic chains, which are constructed from MO_3F_3 isolated octahedra and pseudo-pyramidal $(HPO_3)^{2-}$ phosphite oxoanions by sharing the *trans*-O(1), O(3) atoms running along the [001] direction. The ethylenediammonium cations are displayed in the cavities of the structure delimited by three different chains, and establish both hydrogen bonds and ionic interactions with the anionic chains.

The presence of the pentameric building unit in this structure is noteworthy. Although the pentameric unit has

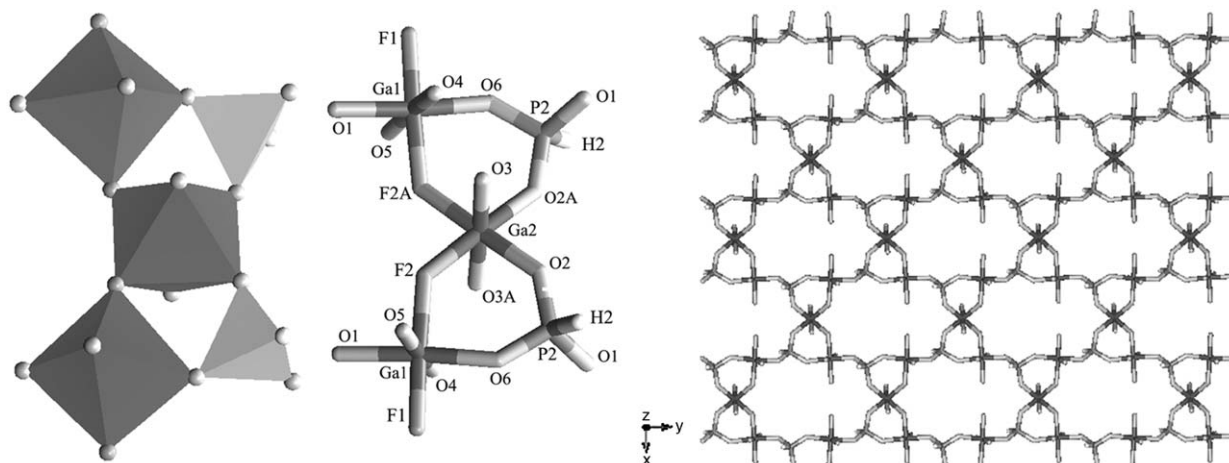


Fig. 4. The pentameric building unit built by sharing-corner GaO_4F_2 octahedra and HPO_3 pseudo pyramids (left) and a 2D layer viewed along the b -axis with 10-membered ring channels (right).

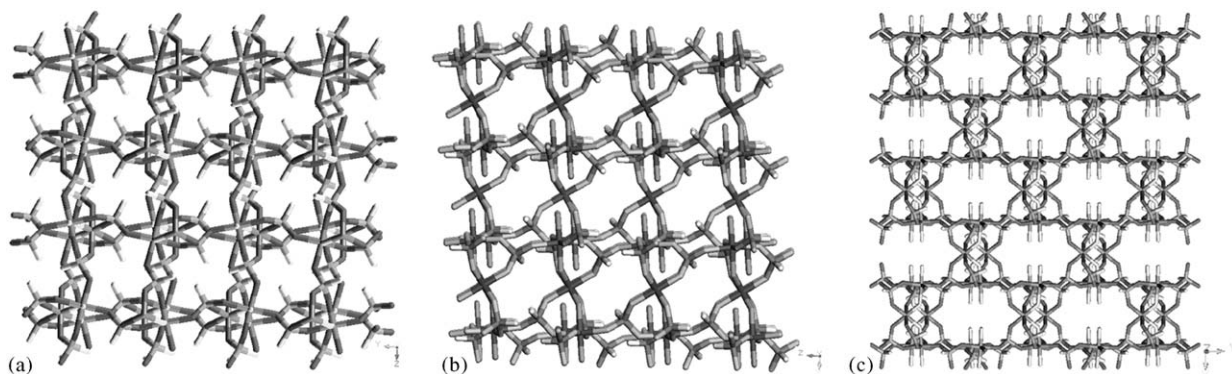


Fig. 5. Perspective view of the structure of the title compound show 8-, 6- and 10-membered ring channels along [100] (a), [010] (b) and [001] (c), respectively.

Table 3
Hydrogen bonds for the title compound (Å and °)

D–H...A	<i>d</i> (D–H)	<i>d</i> (H...A)	<i>d</i> (D...A)	∠(DHA)
N(2)–H(2A)...F(1) ^a	0.90	1.95	2.741(6)	146.1
N(2)–H(2A)...O(6) ^a	0.90	2.37	3.103(4)	139.3
N(2)–H(2B)...F(1) ^b	0.90	1.95	2.741(6)	146.1
N(2)–H(2B)...O(6) ^b	0.90	2.37	3.103(4)	139.3
N(1)–H(1A)...F(1) ^c	0.89	1.80	2.685(5)	170.6
N(1)–H(1B)...O(3) ^d	0.89	2.13	2.810(6)	133.0
N(1)–H(1B)...O(2) ^d	0.89	2.18	2.917(6)	140.0
N(1)–H(1C)...O(5) ^c	0.89	2.41	2.904(5)	115.6

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

been reported in gallium phosphite MIL-46, $\text{Ga}_9(\text{PO}_4)_8\text{F}_{7.3}(\text{OH})_{0.24}\text{NC}_5\text{H}_{12}\cdot 0.5\text{H}_3\text{O}\cdot 3.5\text{H}_2\text{O}$ [18], there are distinct differences between them. In MIL-46, the pentameric unit $\text{Ga}_3(\text{PO}_4)_2\text{F}_4$ consists of three Ga atoms and two P atoms. The central gallium atom is octahedrally coordinated with four fluorine atoms and two oxygen atoms (GaO_2F_4). It is linked to the two phosphate groups by the oxygen atoms and to two other gallium atoms by the fluorine atoms. These four anions are located in one square plane of the octahedron, the fluorine atoms being placed in *cis* position. One of the two remaining fluorine atoms is terminal, and the other fluorine atom is in bridging position between two octahedral gallium atoms belonging to two adjacent pentameric units. The two other gallium atoms are coordinated with three oxygen atoms and one fluorine atom (GaO_3F). In the title compound, the pentameric building unit is built by three GaO_4F_2 octahedra and two HPO_3 pseudo-pyramids. The octahedral $\text{Ga}(2)\text{O}_4\text{F}_2$ is located at the center and links to the two $\text{Ga}(1)\text{O}_4\text{F}_2$ octahedra and two HPO_3 pseudo-pyramids by F atoms and O atoms, respectively. In $\text{Ga}(2)\text{O}_4\text{F}_2$ octahedron, the fluorine atoms are all in bridging position; but in $\text{Ga}(1)\text{O}_4\text{F}_2$ octahedron, one fluorine atom is in bridging position, the other is in terminal position. So, it is the different coordination codes of phosphate and phosphite and gallium between them that led to form the different structures.

phite and gallium between them that led to form the different structures.

Addition of fluorine to the preparative mixtures can allow polyhedral connectivity between metal atoms through bridging, thereby assisting network formation of the metal phosphates, such as in cloverite, a fluorinated gallophosphate with a large-pore 20-membered ring structure [19]. In the title compound, 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, helping to create special pentameric building units within the structure. In addition, the terminal fluorides are not merely spectator ligands, but they are involved in the formation of a hydrogen bond network to the channel counterions.

4. Conclusions

In summary, the hydrothermal synthesis and crystal structure of a new organically templated gallium phosphite with formula $\text{Ga}_3(\text{HPO}_3)_4\text{F}_4(\text{H}_3\text{DETA})$ have been described. The structure consists of GaO_4F_2 octahedra and HPO_3 pseudo-pyramids and can be viewed as stacking of the gallium phosphite layers along the *c*-axis linked by HPO_3 pseudo-pyramid to generate a 3D framework with 6-, 8- and 10-membered ring channels along *b*-, *a*- and *c*-axis, respectively, the organic triamine residing in the larger one. And the presence of the pentameric building unit built by sharing-corner GaO_4F_2 octahedra and HPO_3 pseudo-pyramids in this structure is noteworthy. This pentameric building unit is the first be found in the gallium phosphates and phosphites. Recent exploratory syntheses of metal phosphite reveal a rich structural chemistry. Our investigation shows that it is possible to form novel gallium phosphites 3D open-framework materials containing removable organic templates which might have many potential applications. And as the μ_3 -coordination for the phosphite is different from the traditional μ_4 -coordination for the phosphate, it presents further challenges in the

hydrothermal synthesis of organically templated open-framework gallium phosphites. Further investigation of gallium phosphite compounds is in progress.

Acknowledgments

This work was supported by the State Basic Research Project (G2000077507), and the National Science Foundation of China (No.29873017 and 20101004).

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