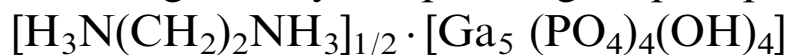


# Hydro(solvo)thermal synthesis and structural characterization of a new organically templated gallophosphate:



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## Abstract

A new three-dimensional open-framework gallophosphate:  $[\text{H}_3\text{N}(\text{CH}_2)_2\text{NH}_3]_{1/2} \cdot [\text{Ga}_5 (\text{PO}_4)_4(\text{OH})_4]$  has been prepared by hydro(solvo)thermal synthesis in presence of ethylenediamine (en) as structure-directing agent. Its structure was determined by means of single-crystal X-ray diffraction analysis with the following crystal data: monoclinic space group  $C2/m$ ,  $a = 10.1604(9) \text{ \AA}$ ,  $b = 12.0085(15) \text{ \AA}$ ,  $c = 7.1892(7) \text{ \AA}$ ,  $\beta = 90.797(6)^\circ$ ,  $V = 877.08(16) \text{ \AA}^3$ ,  $Z = 2$ ,  $R_1 = 0.0264$ ,  $wR_2 = 0.0764$ . The total numbers of measured reflections and unique reflections were 3508 and 1300, respectively. It is built up from a new secondary building unit (SBU)  $\text{Ga}_4\text{P}_4\text{O}_{20}(\text{OH})_4$ , in which Ga atoms exhibit distorted trigonal bipyramidal coordination and P atoms are in tetrahedral coordination. The SBU  $\text{Ga}_4\text{P}_4\text{O}_{20}(\text{OH})_4$  are linked into a layer by bridge oxygen atoms. The  $\text{GaO}_4(\text{OH})_2$  octahedra link the layers into a three-dimensional framework. Diprotonated ethylenediamine was found in the channel of the framework. The material was characterized by IR spectroscopy,  $^1\text{H}$  NMR spectra, thermogravimetric and differential thermal analyses and elemental analysis. © 2005 Elsevier Inc. All rights reserved.

**Keywords:** Hydro(solvo)thermal synthesis; Gallophosphate; Template; Structure

## 1. Introduction

Microporous solids continue to be the focus of much attention because of catalytic and shape-selective absorptive properties, which find widespread application in diverse areas [1]. The class of material was dominated by aluminosilicate until the discovery of porous aluminophosphates by Flanigen et al. [2]. Following, Parise reported several microporous gallophosphates [3]. The gallophosphate family was developed by Xu et al. who used nonaqueous solvent such as

alcohols, glycols, amines [4] and by Kessler et al. using fluorine method which led to the synthesis of a vast number of fluorogallophosphates with new framework topologies [5–8]. Gallium atom can exhibit 4-, 5-, 6-coordination in oxygen-based polyhedra, leading to a wide variety of new architectures different from the zeolites and AIPO. GaPO frameworks exhibit great structural diversity: many chain (1D), layered (2D) and three-dimensional (3D) structures are known. In these structures, the secondary building units (SBU) have been found [9], such as the single four-ring (4R) [10], the double four-ring (D4R) [11], the double six-ring (D6R) [12] and the single six-ring (6R) [13].

This paper describes a novel open-framework gallophosphate  $[\text{H}_3\text{N}(\text{CH}_2)_2\text{NH}_3]_{1/2} \cdot [\text{Ga}_5 (\text{PO}_4)_4(\text{OH})_4]$  synthesized with ethylenediamine (en) as template and obtained in presence of fluorine in the reaction medium.

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The compound reported here has a new SBU  $\text{Ga}_4\text{P}_4\text{O}_{20}(\text{OH})_4$ . We present its synthesis conditions, crystal structure and thermal behavior.

## 2. Experimental

### 2.1. Synthesis and characterization

The reactants were en, phosphorous acid (AR), 40% aqueous hydrofluoric acid, tetraethoxysilane ( $\text{Si}(\text{OEt})_4$ ), boric acid. The gallium source was an amorphous gallium oxide hydroxide prepared from the reaction of metallic gallium with deionized water at 200 °C for 3 days. The role of  $\text{Si}(\text{OEt})_4$ ,  $\text{H}_3\text{BO}_3$  and HF is unknown but that's a minor point on what is basically a nice structure. The title compound cannot be made in their absence. The starting mixture, with a molar ratio 1  $\text{GaO}(\text{OH})$ :5  $\text{H}_3\text{PO}_3$ :0.45  $\text{Si}(\text{OEt})_4$ :4.85  $\text{H}_3\text{BO}_3$ :220  $\text{H}_2\text{O}$ :5.75 HF:72  $\text{HOCH}_2\text{CH}_2\text{OH}$ :1.49 en, was placed in a Teflon-lined stainless-steel autoclave and heated at 180 °C for 7 days. As an example, the gel was prepared by mixing 0.103 g of the gallium source with 4 ml of  $\text{H}_2\text{O}$ , 4 ml of ethylene glycol, 0.3 g of boric acid and 0.1 ml of  $\text{Si}(\text{OEt})_4$ . After homogenization, 0.41 g of phosphorous acid and 0.1 ml of hydrofluoric acid were added successively. The mixture was stirred for 5 min before the addition of 0.1 ml of en. The gel was stirred at room temperature for 1 hour and transferred to a Teflon-lined stainless-steel autoclave. After crystallization, the autoclave was cooled down to room temperature and the colorless rod-shaped single crystal was separated by sonication, further washed by distilled water and dried at air. The phosphite is oxidised to phosphate at 180 °C in the presence of organic amine.

The elemental analyses were performed on a Perkin-Elmer 2400 element analyzer. The inductively couple plasma (ICP) analysis was carried out on a Perkin-Elmer Optima 3300DV ICP instrument. The ICP and elemental analysis results of the bulk product were also consistent with the theoretical values. Anal. Calcd. for the compound: Ga, 42.13; P, 14.98; C, 1.44; H, 1.09; N, 1.69%. Found: Ga, 42.18; P, 15.07; C, 1.39; H, 1.02; N, 1.63%.

The infrared (IR) spectrum was recorded within the 400–4000  $\text{cm}^{-1}$  region on a Nicolet Impact 410FTIR spectrometer using KBr pellets in air. The IR spectra of the compounds showed typical OH peaks. Strong absorption bands for O–H bending and stretching vibrations was observed from 3419  $\text{cm}^{-1}$ . The large band at 1099  $\text{cm}^{-1}$  arose from P–O stretching vibrations. It is in well agreement with the structure.

A Perkin-Elmer DTA 1700 differential thermal analyzer was used to obtain the differential thermal analysis (DTA) and a Perkin-Elmer TGA 7 thermogravimetric analyzer to obtain thermogravimetric analysis (TGA)

Table 1  
Crystal data and structure refinement parameters for  $[\text{H}_3\text{N}(\text{CH}_2)_2\text{NH}_3]_{1/2} \cdot [\text{Ga}_5(\text{PO}_4)_4(\text{OH})_4]$

Empirical formula	$\text{CH}_9\text{Ga}_5\text{NO}_{20}\text{P}_4$
Formula weight	827.57
Space group	$C2/m$
$T$ (K)	293(2)
$\lambda$ (Å)	0.71073
$a$ (Å)	10.1604(9)
$b$ (Å)	12.0085(15)
$c$ (Å)	7.1892(7)
$\beta$ (deg)	90.797(6)
$V$ (Å <sup>3</sup> )	877.08(16)
$Z$	2
$\rho_{\text{calc}}$ (mg $\text{m}^{-3}$ )	3.134
$\mu$ ( $\text{mm}^{-1}$ )	8.056
$R_1$ [ $I \geq 2\sigma(I)$ ]	0.0264
$wR_2$ [ $I \geq 2\sigma(I)$ ]	0.0764

$$R_1 = \frac{\sum \|F_0\| - |F_c|}{\sum \|F_0\|}; wR_2 = \left\{ \frac{\sum [w(F_0^2 - F_c^2)^2]}{\sum [w(F_0^2)^2]} \right\}^{1/2}$$

curves in an atmospheric environment with a heating rate of 10 °C  $\text{min}^{-1}$ . The  $^1\text{H}$  NMR spectra of the compound was collected on a Varian Unity-400 NMR spectrometer.

### 2.2. Determination of crystal structure

A suitable single crystal with dimensions  $0.22 \times 0.16 \times 0.15$  mm was selected for single-crystal X-ray diffraction analysis. Structural analysis was performed on a Siemens SMART CCD diffractometer using graphite monochromated  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073$  Å). The data were collected at temperature of  $20 \pm 2$  °C. The total numbers of measured reflections and unique reflections were 3508 and 1300, respectively ( $-14 \leq h \leq 13$ ,  $-9 \leq k \leq 16$ ,  $-9 \leq l \leq 10$ ). The agreement factor between equivalent reflections ( $R_{\text{int}}$ ) was 0.0263. Data processing was accomplished with the SAINT processing program [14]. The structure was solved in the space group  $C2/m$  by the direct methods and refined on  $F^2$  by full-matrix least-squares using SHELXTL97 [15]. The heaviest atoms Ga and P were easily located. O, C and N atoms were subsequently located in the difference Fourier maps, H atoms were placed geometrically. Experimental details for the structure determination are presented in Table 1. The final atomic coordinates, the selected bond distances, bond angles and hydrogen bonds are presented in Tables 2–4, respectively. The presence of hydrogen atoms was deduced from bond valence calculations performed with the Brese and O'Keeffe formulation [16]. As shown in Table 3, the analysis of the bond valence calculations also evidenced a lack of the valence on O(1) and O(6), which should consequently correspond to the hydroxyl group. The presence of hydroxyl group was confirmed by  $^1\text{H}$  NMR spectrum.

### 3. Results and discussion

#### 3.1. Characterization

The TGA studies indicate that the weight loss occurred in one step for compound. The release of the

template amine from the structure was observed to be exothermic. In the compound (Fig. 1a), a mass loss of 3.5% in the range 300–320 °C corresponds to the loss of the amine (calcd. 3.75%). The DTA curve exhibits the exothermic peaks for the decomposition of the organic template in air. The structure collapsed and converted to an amorphous phase after the calcination at 600 °C for 2 h.

Table 2

Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) [ $\text{H}_3\text{N}(\text{CH}_2)_2\text{NH}_3$ ] $_{1/2} \cdot [\text{Ga}_5(\text{PO}_4)_4(\text{OH})_4]$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>(eq)</sub>
Ga(1)	−1661(1)	1315(1)	3243(1)	19(1)
Ga(2)	0	0	0	12(1)
P(1)	1178(1)	1941(1)	2513(1)	14(1)
O(1)	−3177(5)	0	3705(7)	51(1)
O(2)	−252(2)	2307(2)	2901(3)	20(1)
O(3)	−3061(2)	1983(2)	2090(3)	24(1)
O(4)	−1829(2)	1369(2)	5782(3)	22(1)
O(5)	1231(2)	1156(2)	868(3)	19(1)
O(6)	1006(3)	0	−2372(4)	17(1)
N(1)	−4251(10)	0	−2475(16)	71(5)
C(1)	−4318(15)	0	−514(15)	50(4)

Table 4

Hydrogen bonds for [ $\text{H}_3\text{N}(\text{CH}_2)_2\text{NH}_3$ ] $_{1/2} \cdot [\text{Ga}_5(\text{PO}_4)_4(\text{OH})_4]$  [ $\text{\AA}$  and deg.]

D–H...A	d(D–H)	d(H...A)	d(D...A)	<(DHA)
N(1)–H(1A)...O(1)#8	0.89	2.52	2.969(12)	112.1
N(1)–H(1A)...O(4)#8	0.89	2.52	3.227(9)	136.8
N(1)–H(1A)...O(4)#9	0.89	2.52	3.227(9)	136.8
N(1)–H(1B)...O(2)#10	0.89	2.51	3.286(3)	146.3
N(1)–H(1C)...O(2)#11	0.89	2.51	3.286(3)	146.3

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

Table 3

Selected interatomic distances ( $\text{\AA}$ ) and angles (deg) in [ $\text{H}_3\text{N}(\text{CH}_2)_2\text{NH}_3$ ] $_{1/2} \cdot [\text{Ga}_5(\text{PO}_4)_4(\text{OH})_4]$

Ga(1)–O(1)	2.234(4)	P(1)–O(2)	1.548(2)
Ga(1)–O(2)	1.881(2)	P(1)–O(3)#4	1.539(2)
Ga(1)–O(3)	1.822(2)	P(1)–O(4)#5	1.545(2)
Ga(1)–O(4)	1.837(2)	P(1)–O(5)	1.514(2)
Ga(1)–O(6)#1	1.8278(16)	O(1)–Ga(1)#2	2.234(4)
Ga(2)–O(5)	1.965(2)	O(3)–P(1)#6	1.539(2)
Ga(2)–O(5)#1	1.965(2)	O(4)–P(1)#5	1.545(2)
Ga(2)–O(5)#2	1.965(2)	O(6)–Ga(1)#3	1.8278(16)
Ga(2)–O(5)#3	1.965(2)	O(6)–Ga(1)#1	1.8278(16)
Ga(2)–O(6)	2.000(3)	N(1)–C(1)	1.412(15)
Ga(2)–O(6)#1	2.000(3)	N(1)–H(1A)	0.8900
O(2)–Ga(1)–O(1)	174.05(12)	O(6)#1–Ga(1)–O(4)	114.22(12)
O(3)–Ga(1)–O(1)	80.97(14)	O(6)#1–Ga(1)–O(2)	102.79(12)
O(3)–Ga(1)–O(2)	104.63(11)	O(6)#1–Ga(1)–O(1)	72.25(13)
O(3)–Ga(1)–O(4)	110.69(11)	O(5)–Ga(2)–O(5)#1	180.00
O(3)–Ga(1)–O(6)#1	120.66(13)	O(5)–Ga(2)–O(5)#2	89.93(14)
O(4)–Ga(1)–O(1)	78.64(16)	O(5)#1–Ga(2)–O(5)#2	90.07(14)
O(4)–Ga(1)–O(2)	100.90(10)	O(5)–Ga(2)–O(5)#3	90.07(14)
O(5)#1–Ga(2)–O(5)#3	89.93(14)	O(3)#4–P(1)–O(4)#5	108.61(13)
O(5)#2–Ga(2)–O(5)#3	180.0	O(4)#5–P(1)–O(2)	112.11(14)
O(5)–Ga(2)–O(6)	86.56(9)	O(5)–P(1)–O(2)	111.18(13)
O(5)#1–Ga(2)–O(6)	93.44(9)	O(5)–P(1)–O(3)#4	110.17(13)
O(5)#2–Ga(2)–O(6)	86.56(9)	O(5)–P(1)–O(4)#5	108.87(14)
O(5)#3–Ga(2)–O(6)	93.44(9)	Ga(1)–O(1)–Ga(1)#2	89.96(19)
O(5)–Ga(2)–O(6)#1	93.44(9)	P(1)–O(2)–Ga(1)	124.18(14)
O(5)#1–Ga(2)–O(6)#1	86.56(9)	P(1)#6–O(3)–Ga(1)	132.13(15)
O(5)#2–Ga(2)–O(6)#1	93.44(9)	P(1)#5–O(4)–Ga(1)	139.35(16)
O(5)#3–Ga(2)–O(6)#1	86.56(9)	P(1)–O(5)–Ga(2)	131.18(14)
O(6)–Ga(2)–O(6)#1	180.00	Ga(1)#3–O(6)–Ga(1)#1	119.57(17)
O(3)#4–P(1)–O(2)	105.84(14)	Ga(1)#3–O(6)–Ga(2)	118.99(8)
		Ga(1)#1–O(6)–Ga(2)	118.99(8)

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

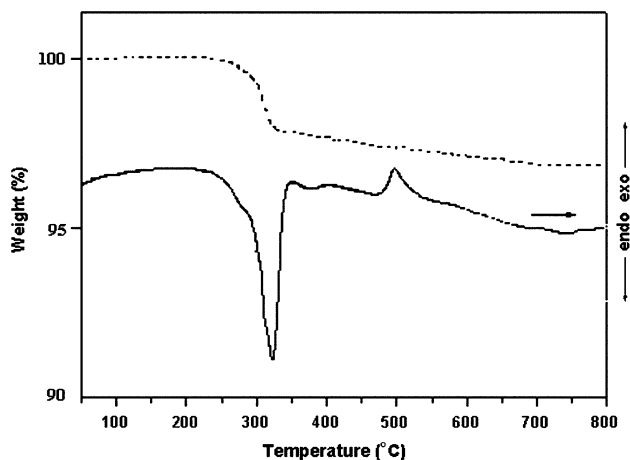


Fig. 1. TG-DTA curves of the  $[H_3N(CH_2)_2NH_3]_{1/2} \cdot [Ga_5(PO_4)_4(OH)_4]$ . The weight loss occurred in one step corresponds to the loss of the amine. The release of the template amine from the structure was observed to be exothermic.

$^1H$  NMR spectrum shows three signals at 1.2, 3.6, and 4.9 ppm. The peak at 4.9 ppm can be assigned to OH. The signal at 3.6 ppm corresponds to  $-NH$  and the signal at 1.2 ppm corresponds to  $-CH_2-$ . It is in well agreement with the structure.

### 3.2. Crystal structure of $[H_3N(CH_2)_2NH_3]_{1/2} \cdot [Ga_5(PO_4)_4(OH)_4]$

The asymmetric unit of the compound contains 11 non-hydrogen atoms, of which 9 atoms belong to the framework and 2 atoms to the guest amine molecule (Fig. 2). The gallium atoms exhibit two types of coordination. The Ga(1) is distorted trigonal bipyramidally coordinated by three oxygen atoms (Ga(1)–O(3) 1.822(2) Å, Ga(1)–O(2) 1.881(2) Å, Ga(1)–O(4) 1.837(2) Å) and two hydroxyl groups (O(1), O(6)) with the distances of Ga(1)–O(1), Ga(1)–O(6) 2.234(4), 1.8278(16) Å, respectively. Ga(2) is octahedrally coordinated by four equatorial oxygen atoms and two hydroxyl groups in axial position (axial Ga(2)–O(6) = 2.000(3) Å, equatorial Ga(2)–O(5) = 1.965(2) Å). The Ga(2)–O(5) distances are longer than those found in the trigonal bipyramid  $GaO_3(OH)_2$ , as usually observed for gallium in six-fold coordination. The  $PO_4$  tetrahedron is fairly regular with P–O bonds ranging from 1.514(2) to 1.548(2) Å and O–P–O angles from 105.84 (14)° to 112.11(14)°. Each of P atom links three Ga(1) atoms and one Ga(2) atom via P–O–Ga linking (bond angles ranging from 124.18(14)° to 139.35(16)°). The structure has a hydroxyl group (O(6)) linking three adjacent gallium atoms, two Ga(1) and one Ga(2), with the bond angles Ga(1)#3–O(6)–Ga(1)#1 119.57(17)°, Ga(1)#3–O(6)–Ga(2) 118.99(8)°, Ga(1)#1–O(6)–Ga(2) 118.99(8)°, also present in  $GaPO_4-C_3$  [17]. O(1) is a bridge hydroxyl group linking two Ga(1) with the bond

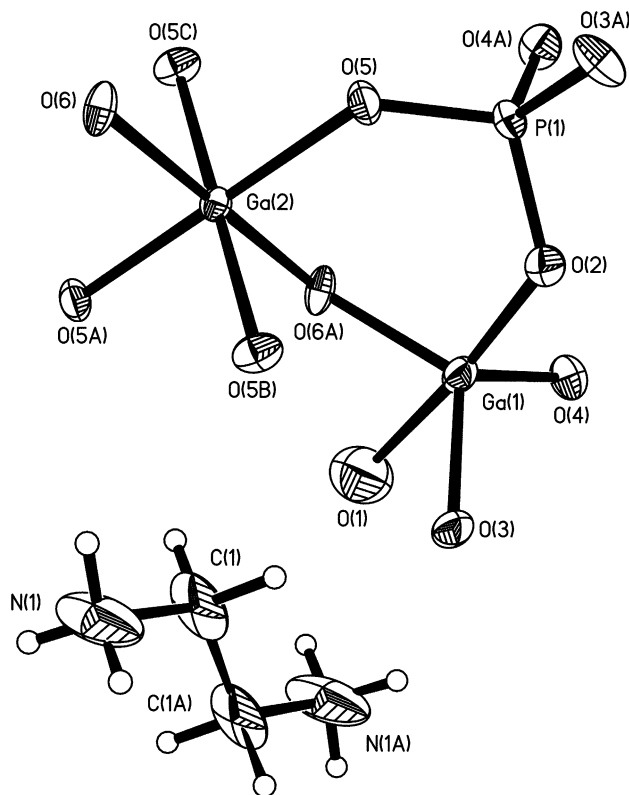


Fig. 2. An ORTEP plot of the asymmetric unit of the  $[H_3N(CH_2)_2NH_3]_{1/2} \cdot [Ga_5(PO_4)_4(OH)_4]$  showing 50% probability thermal ellipsoids and the atom labeling scheme. Note that O(1) and O(6) are hydroxyl group. The hydrogen atoms have been omitted for clarity.

angle Ga(1)–O(1)–Ga(1)#2 89.96(19)°. The Ga- and P-based polyhedra are linked in an alternating manner to give an open three-dimensional framework of formula  $[Ga_5(PO_4)_4(OH)_4]^-$  containing cavities in which the amino cations reside. The nitrogen atom of the amino cation is within hydrogen bonding distance of a number of framework oxygen atoms (N(1)...O distances 2.969(12), 3.227(9), and 3.286(3) Å to O(1), O(4), and O(2), respectively).

The 3D framework of title compound is characterized by a new SBU  $Ga_4P_4O_{20}(OH)_4$  (Fig. 3). The three-dimensional structure can be derived from two-dimensional layers (*ab*-plane) composed of  $Ga(O)_3(OH)_2$  and  $PO_4$  polyhedra. The layer is built up from the new SBU, in which four Ga atoms are in five-coordinated distorted trigonal bipyramid geometry. The SBU unit reported here is unusual, shown as scheme 1(a). In this SBU, adjacent Ga(1) and P(1) are bridged by O(2) and O(4) to form a single 4-ring (Ga–P–Ga–P). Two such single 4-rings are joined by bonds Ga–O(1)–Ga and Ga–O(6)–Ga to form 6-rings that have four common T-atoms, all of which are Ga(1) atoms. The similar structures of  $Ga_4P_4O_{20}(OH)_4$ , D4R and bifurcated hexagonal-square (bhs) unit are shown in Scheme 1. D4R (Scheme 1b) unit can be considered as a cube of corner shared polyhedral,

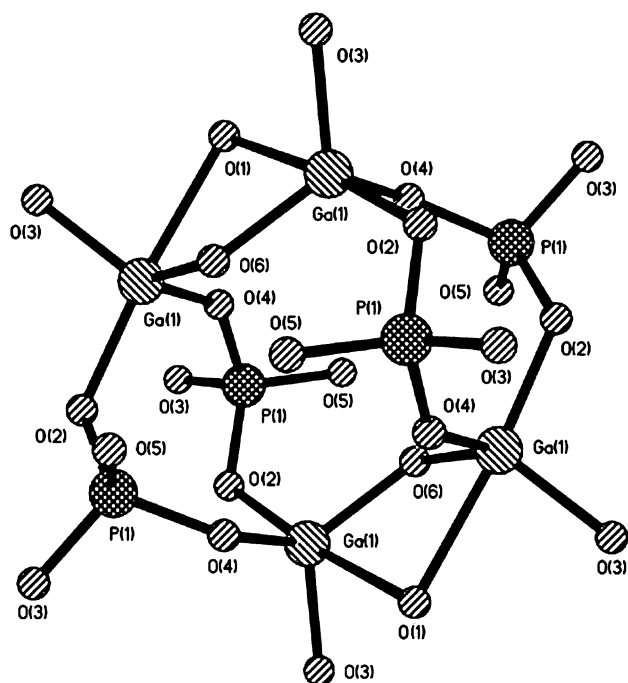
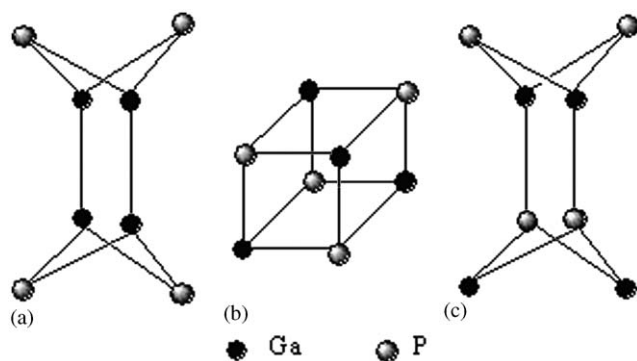


Fig. 3. The SBU Ga<sub>4</sub>P<sub>4</sub>O<sub>20</sub>(OH)<sub>4</sub> of compound. In the SBU, all Ga are 5-coordinate.



Scheme 1. Comparison to D4R and bifurcated hexagonal-square (bhs) structure: (a) The structure of the SBU unit. (b) The structure of D4R unit. (c) The structure of the bifurcated hexagonal-square.

alternatively occupied by P and Ga. The bhs unit (Scheme 1c) is composed of a pair of 4-rings with apices pointing up and down alternatively [18]. Each pair of 4-rings are joined so that two 6-rings having four common T-atoms, which are composed of two Ga atoms and two P atoms. The Ga atoms are in four-coordinated geometry that is different from our SBU.

The SBU Ga<sub>4</sub>P<sub>4</sub>O<sub>20</sub>(OH)<sub>4</sub> are linked into a 1D chain by O(3) bridging Ga(1) and P(1). Each 1D chain is joined directly to two other chains to form a layer (*ab*-plane) (Fig. 4a). The formation of such a layer leads to the creation of 4-rings of a new type between these chains in addition to the creation of 10-rings. The layer

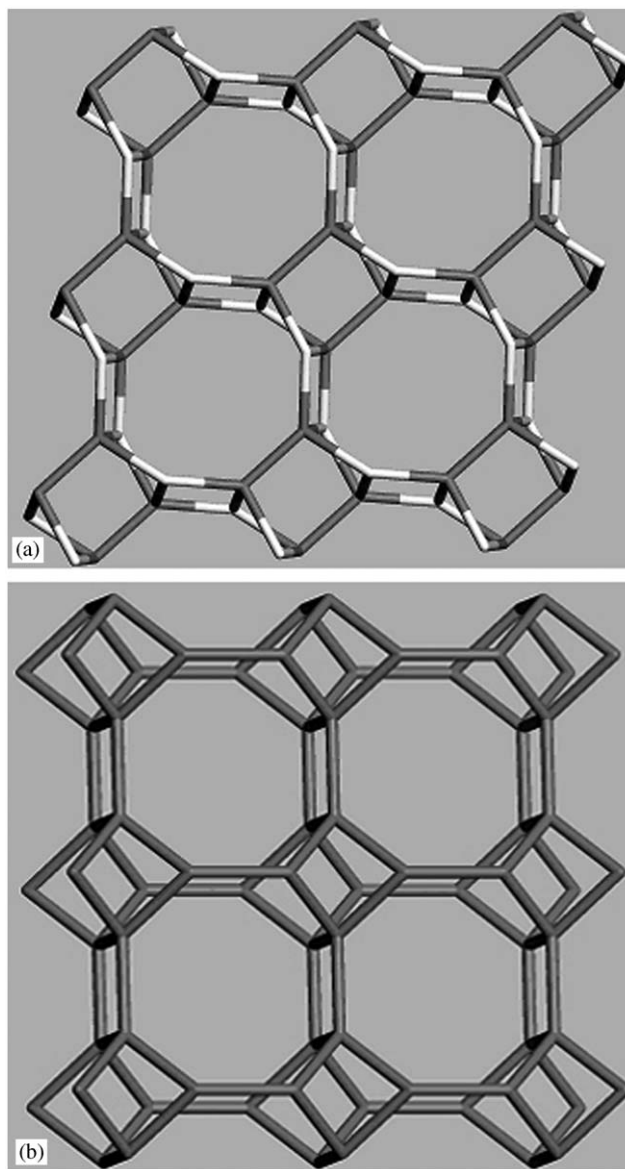


Fig. 4. Comparison to framework topology of DFT: (a) A view of [H<sub>3</sub>N(CH<sub>2</sub>)<sub>2</sub>NH<sub>3</sub>]<sub>1/2</sub> · [Ga<sub>5</sub>(PO<sub>4</sub>)<sub>4</sub>(OH)<sub>4</sub>] in *ab*-plane. Note that in the layer all Ga are 5-coordinate. (b) A view of DFT in the plane in which all Ga are 4-coordinate.

of title compound is very similar to the DFT topology (Fig. 4b) in the cobalt phosphate DAF-2 [19], the zinc arsenate UCSB-3ZnAs [18], the gallium germanate UCSB-3GaGe [20]. The different compounds with the DFT topology have in common that they all have been synthesized with ethylenediamine as organic template. The metals in the layers have 5 coordinations in the title compound but all are 4-coordinate in DFT.

Along *c* axes, shown as Fig. 5a, the layers are linked into a 3D framework by Ga(2)O<sub>4</sub>(OH)<sub>2</sub> octahedra sharing two O(6) and four O(5) with the Ga<sub>4</sub>P<sub>4</sub>O<sub>20</sub>(OH)<sub>4</sub> SBU. Viewing along the [0 0 1], shown as Fig. 5b, we find the 4-, 6-, and 10-membered channels and diprotonated



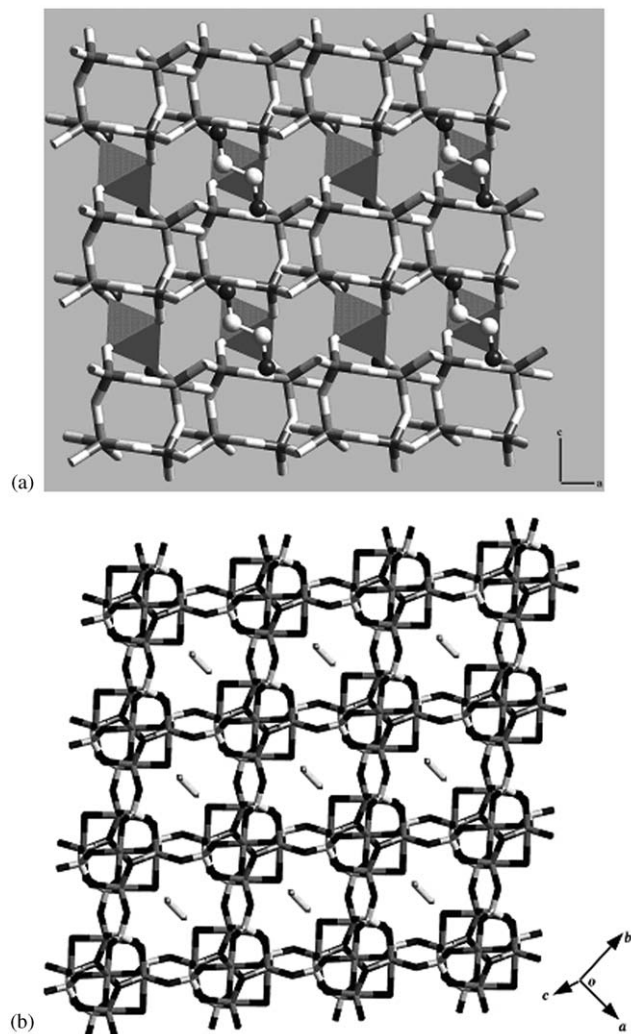


Fig. 5. The 3D framework of the compound  $[\text{H}_3\text{N}(\text{CH}_2)_2\text{NH}_3]_{1/2} \cdot [\text{Ga}_5(\text{PO}_4)_4(\text{OH})_4]$ . The lighter and P-based polyhedra and the black represent Ga-based polyhedra: (a) A view of the compound along the [010]. The layers are linked into a 3D framework by  $\text{Ga}_2\text{O}_4(\text{OH})_2$  octahedra. (b) A view of the compound along the [001]. The 4-, 6-, and 10-membered channels are found and diprotonated ethylenediamine fill in the 10-membered channel.

ethylenediamine is filled in the 10-membered channel by hydrogen bonding interactions.

#### 4. Conclusions

A novel three-dimensional open-framework gallophosphate,  $[\text{H}_3\text{N}(\text{CH}_2)_2\text{NH}_3]_{1/2} \cdot [\text{Ga}_5(\text{PO}_4)_4(\text{OH})_4]$  has

been prepared by hydro(solvo)thermal synthesis and characterized by single crystal X-ray diffraction. The interesting feature of this new structure is the presence of the new SBU  $\text{Ga}_4\text{P}_4\text{O}_{20}(\text{OH})_4$ . Its three-dimensional structure exists 4-, 6-, 10-membered channels. Diprotonated ethylenediamine is filled in the 10-membered channels. The network has a Ga/P ratio of 5/4.

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#### References

- [1] R.I. Walton, F. Millange, T. Loiseau, D. O'Hare, G. Férey, *Angew. Chem. Int. Ed. Engl.* 39 (2000) 4552.
- [2] S.T. Wilson, B.M. Lok, C.A. Messina, T.R. Cannan, E.M. Flanigen, *J. Am. Chem. Soc.* 104 (1982) 1146.
- [3] J.B. Parise, *Chem. Comm.* 606 (1985).
- [4] Q. Kan, F.P. Glasser, R. Xu, *J. Mater. Chem.* 3 (1993) 983.
- [5] H. Kessler, *Stud. Surf. Sci. Catal.* 52 (1989) 17.
- [6] G. Férey, *J. Fluorine Chem.* 72 (1995) 187.
- [7] M. Esterman, L.B. McCusker, C. Baerlocher, A. Merrouche, H. Kessler, *Nature* 352 (1991) 320.
- [8] T. Loiseau, G. Férey, *J. Solid State Chem.* 111 (1994) 403.
- [9] S. Oliver, A. Kuperman, G.A. Ozin, *Angew. Chem. Int. Ed. Engl.* 37 (1998) 46.
- [10] M.R. Mason, R.M. Matthews, M.S. Mashuta, J.F. Richardson, *Inorg. Chem.* 35 (1996) 5756.
- [11] T. Wessels, L.B. McCusker, Ch. Baerlocher, P. Reinert, J. Patarin, *Microporous Mesoporous Mater.* 23 (1998) 67.
- [12] J.L. Kissick, A.R. Cowley, A.M. Chippindale, *J. Solid State Chem.* 167 (2002) 17.
- [13] Y. Yang, J. Pinkas, M. Noltemeyer, H.W. Roesky, *Inorg. Chem.* 37 (1998) 6404.
- [14] SMART and SAINT; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1996.
- [15] SHELXTL, Version 5.1; Siemens Industrial Automation, Inc., 1997.
- [16] N.E. Brese, M. O'Keeffe, *Acta Crystallogr. B* 47 (1991) 192.
- [17] G. Yang, S. Feng, R. Xu, *Chem. Comm.* 1254 (1987).
- [18] X. Bu, P. Feng, T.E. Gier, G.D. Stucky, *J. Solid State Chem.* 136 (1998) 210.
- [19] J. Chen, R.H. Jones, S. Natarajan, M.B. Hursthouse, *Angew. Chem. Int. Ed. Engl.* 33 (1994) 639.
- [20] X. Bu, P. Feng, T.E. Gier, D. Zhao, G.D. Stucky, *J. Am. Chem. Soc.* 120 (1998) 13389.