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# A new sodium hydroxygallophosphate containing tetrameric gallium units: $\text{Na}_3[\text{Ga}_4\text{O}(\text{OH})(\text{H}_2\text{O})(\text{PO}_4)_4] \cdot \text{H}_2\text{O}$

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## Abstract

A new sodium hydroxygallophosphate,  $\text{Na}_3\text{Ga}_4\text{O}(\text{OH})(\text{H}_2\text{O})(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ , has been prepared by hydrothermal synthesis. Its structure has been determined from a single-crystal X-ray diffraction study. It crystallizes in the  $P2_1/c$  space group with the cell parameters  $a = 9.445(2) \text{ \AA}$ ,  $b = 9.028(1) \text{ \AA}$ ,  $c = 19.209(3) \text{ \AA}$ ,  $\beta = 102.08(2)^\circ$ ,  $V = 1603.4(4) \text{ \AA}^3$ . Its three-dimensional framework can be described from  $\text{PO}_4$  monophosphate groups sharing their apices with original  $\text{Ga}_4\text{O}_{16}(\text{OH})(\text{H}_2\text{O})$  tetrameric building units, which result from the assembly of one  $\text{GaO}_4$  tetrahedron, one  $\text{GaO}_5$  trigonal bipyramid and two octahedra:  $\text{GaO}_5(\text{OH})$  and  $\text{GaO}_4(\text{OH})(\text{H}_2\text{O})$ . The sodium cations and one water molecule are located in tunnels running along **b**.

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**Keywords:** Sodium gallium monophosphate; Three-dimensional tunnel structure; Tetrameric building units; Hydrothermal synthesis; Structure determination; Single crystal; X-ray diffraction

## 1. Introduction

Gallium based phosphates have been the subject of numerous investigations in order to discover open frameworks similar to those obtained for aluminum phosphates. Large families of microporous gallium phosphates and fluorophosphates containing amines in their cavities have been discovered (see for example Refs. [1–11] and references therein). These studies have shown the extraordinarily rich chemistry of gallium, which is able to adopt different kinds of coordination, i.e., octahedral, tetrahedral and trigonal bipyramidal. It is remarkable that the synthesis of such diverse structures requires the presence of organic templates and/or the introduction of fluorine on the oxygen sites. In contrast, the number of pure inorganic gallium phosphates or hydroxyphosphates is, comparatively, rather limited: only six anhydrous gallium phosphates ( $\text{GaPO}_4$  [12,13],  $\text{Na}_3\text{GaP}_8\text{O}_{23}$  [14],  $\text{Ga}(\text{PO}_3)_3$  [15],  $\text{Ga}_3\text{PO}_7$  [16],  $3[\text{NH}_4][\text{Ga}_2(\text{PO}_4)_3]$  [17] and  $\text{Cs}_2\text{GaP}_3\text{O}_{10}$  [18]), six hydroxygallophosphates ( $\text{NaGa}_2(\text{OH})(\text{PO}_4)_2$

[19],  $\text{LiGaPO}_4(\text{OH})$  [20],  $\text{CsGaHP}_3\text{O}_{10}$  [21],  $\text{Na}_3\text{Ga}(\text{OH})(\text{HPO}_4)(\text{PO}_4)$  [22],  $\text{Ba}_2\text{GaH}(\text{P}_2\text{O}_7)_2$  [23] and  $[\text{NH}_4]\text{Ga}(\text{PO}_4)(\text{OH})$  [17]) and seven hydrated hydroxygallophosphates (formulated  $\text{GaH}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  [24],  $\text{GaPO}_4 \cdot 2\text{H}_2\text{O}$  (two forms [25,26]),  $\text{NH}_4[\text{Ga}_2(\text{PO}_4)_2(\text{OH})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$  [27],  $\text{Rb}(\text{GaPO}_4)_2(\text{OH})(\text{H}_2\text{O}) \cdot \text{H}_2\text{O}$  [28],  $\text{Na}_3\text{Ga}_5(\text{PO}_4)_4\text{O}_2(\text{OH})_2 \cdot 2\text{H}_2\text{O}$  [29] and  $\text{Rb}_2[\text{Ga}_4(\text{HPO}_4)(\text{PO}_4)_4] \cdot 0.5\text{H}_2\text{O}$  [30], respectively) have been synthesized to date. Nevertheless the structural diversity of these latter inorganic hydrated hydroxyphosphates is quite remarkable. One indeed observes for gallium either exclusively octahedral coordination [24–28], or two kinds of coordination, octahedral and trigonal bipyramidal [29] or even three kinds of coordination: octahedral, trigonal bipyramidal and tetrahedral [30] in the same structure. This suggests that the crystal chemistry of inorganic gallium hydroxyphosphates is not so far very completely explored and that many new frameworks remain to be discovered. For this reason we have continued the investigation of the “Na–Ga–P–O–H” system, using hydrothermal synthesis. We report here on a new sodium hydroxygallophosphate,  $\text{Na}_3\text{Ga}_4\text{O}(\text{OH})(\text{H}_2\text{O})(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ , with a unique structure built up of tetrameric units “ $\text{Ga}_4\text{O}_{16}(\text{OH})(\text{H}_2\text{O})$ ”.

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## 2. Experimental section

### 2.1. Synthesis

The single crystal used for the structure determination of the title compound was extracted from a preparation synthesized hydrothermally in the following way: a mixture of NaOH (Carlo Erba, 97.5%), Ga<sub>2</sub>O<sub>3</sub> (ChemPur, 99.99%), H<sub>3</sub>PO<sub>4</sub> (Prolabo Rectapur, 75%) and H<sub>2</sub>O, in the respective molar ratio 1:1:2:28 (pH = 1), was placed in a 23 mL Teflon-lined autoclave, heated for 24 h under autogeneous pressure at 473 K and cooled at 10 K/h to 303 K. The pH value after reaction was 5. The resulting product was filtered off, washed with water and dried in air. Colorless crystals were obtained, whose structure determination and chemical analysis revealed the formula Na<sub>3</sub>[Ga<sub>4</sub>O(OH)(H<sub>2</sub>O)(PO<sub>4</sub>)<sub>4</sub>]·H<sub>2</sub>O.

Many attempts were made to prepare the title compound as a single phase. However, despite the use of different precursors, the modification of the acidobasic character of the initial solution, or the change of the synthesis temperature and heating cycle, we always obtained mixtures. The best result was obtained using the following procedure. In a first step, Na<sub>2</sub>CO<sub>3</sub> (Prolabo, 85%), Ga<sub>2</sub>O<sub>3</sub> (ChemPur, 99.99%) and (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> (Prolabo Rectapur, 99%) were weighted in the respective molar ratio 3:4:4, mixed in an agate mortar, placed in a platinum crucible and heated in air at 673 K for a few hours in order to decompose the sodium carbonate and the diammonium hydrogenophosphate. Once the correct weight loss was reached, the mixture was ground and placed in a 23 mL Teflon-lined autoclave with 1 mL water (the measured value of pH of the solution was 11). It was heated at 473 K for 24 h and cooled at 2 K/h. The final pH value was 6. The resulting white product was filtered off, washed with water and dried in air. The examination of its X-ray powder diffraction pattern (registered with a PHILIPS PW 1830 diffractometer using the CuK $\alpha$  radiation in the angular range  $5^\circ \leq 2\theta \leq 110^\circ$  with a step of  $0.02^\circ$  and with 10 s/step) evidenced the presence of Na<sub>3</sub>[Ga<sub>4</sub>O(OH)(H<sub>2</sub>O)(PO<sub>4</sub>)<sub>4</sub>]·H<sub>2</sub>O as the major phase, but also of NaGa<sub>2</sub>(OH)(PO<sub>4</sub>)<sub>2</sub> [19] as a secondary phase (ca. 15 wt% as confirmed from the EDS analysis performed using an EDS analyser mounted on a JEOL 2010 CX transmission electron microscope).

### 2.2. Structure determination

The semi-quantitative EDS analysis of one of the colorless stick-like crystals obtained as mentioned above was performed with an OXFORD 6650 microprobe mounted on a PHILIPS XL30 FEG scanning electron microscope: it revealed the presence of Na, Ga and P elements.

Table 1

Summary of crystal data, intensity measurements and structure refinement parameters for Na<sub>3</sub>Ga<sub>4</sub>O(OH)(H<sub>2</sub>O)(PO<sub>4</sub>)<sub>4</sub>·H<sub>2</sub>O

(1) <i>Crystal data</i>	
Crystal dimensions (mm <sup>3</sup> )	0.386 × 0.032 × 0.028 mm <sup>3</sup>
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i> (No. 14)
Cell dimensions	<i>a</i> = 9.445(2) Å <i>b</i> = 9.028(1) Å <i>c</i> = 19.209(3) Å $\beta$ = 102.08(2)° <i>V</i> = 1603.4(4) Å <sup>3</sup>
Volume (Å <sup>3</sup> )	
<i>Z</i>	4
$\rho_{\text{calc}}$ (g cm <sup>-3</sup> )	3.301
(2) <i>Intensity measurements</i>	
$\lambda$ (MoK $\alpha$ )	0.71073 Å
Scan mode	$\omega - 2\theta$
Scan width (deg)	1.20 + 0.35 tan $\theta$
Slit aperture (mm)	1.36 + tan $\theta$
Max $\theta$ (deg)	45
Standard reflections	3 every 3600 s
Measured reflections	26817
Reflections with $I > 3\sigma$	6857
Independent reflections with $I > 3\sigma$	4155
$\mu$ (mm <sup>-1</sup> )	7.245
(3) <i>Structure solution and refinement</i>	
Parameters refined	292
Agreement factors	<i>R</i> = 0.035 <i>R</i> <sub>w</sub> = 0.034
Weighting scheme	$w = 1/\sigma^2$
$\Delta/\sigma_{\text{max}}$	< 10 <sup>-3</sup>

Several crystals were then optically selected to be tested by the oscillation and Weissenberg methods using the CuK $\alpha$  radiation. A single crystal with dimensions 0.386 × 0.032 × 0.028 mm<sup>3</sup> was thus chosen for the structure determination and refinement. The cell parameters reported in Table 1 were determined and refined by diffractometric techniques at 293 K using a least-square method based upon 25 reflections in the range  $18^\circ \leq \theta \leq 22^\circ$ . The data were collected on a CAD4 ENRAF-NONIUS diffractometer using the MoK $\alpha$  radiation for  $-18 \leq h \leq +18$ ,  $-17 \leq k \leq +17$ ,  $0 \leq l \leq +38$  with the parameters listed in Table 1. The reflections were corrected for Lorentz and polarization effects, and for absorption and secondary extinction. The structure was solved in the *P*2<sub>1</sub>/*c* space group (No. 14) deduced from the systematic extinctions  $l = 2n + 1$  for  $h0l$  and  $k = 2n + 1$  for  $0k0$ , using the heavy atom method and successive difference synthesis and Fourier synthesis, with the Xtal 3.7 program [31]. The refinement of atomic coordinates and anisotropic thermal parameters of all atoms led to the reliability factors *R* = 0.039 and *R*<sub>w</sub> = 0.038, but with a very high value of the equivalent isotropic thermal factor of the Na(3) atom which was refined to  $U_{\text{eq}} = 0.099 \text{ \AA}^2$ . Fig. 1a gives an ORTEP view of the Na(3) atom at this stage of the refinement: one can notice that the ellipsoid is very elongated. Moreover, two residual peaks were found on the difference

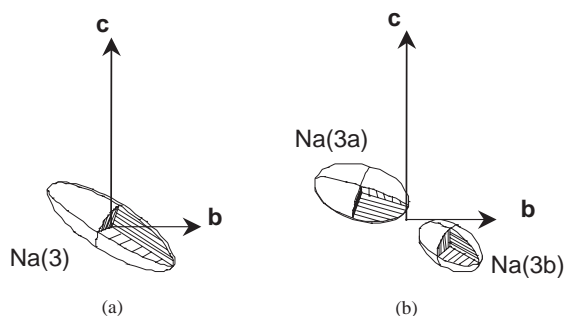


Fig. 1. ORTEP representations projected along [100]: (a) Na(3) before its splitting; (b) Na(3a) and Na(3b). Ellipsoids are drawn at the 50% probability level [34].

Table 2

Positional parameters and their estimated standard deviations in  $\text{Na}_3\text{Ga}_4\text{O}(\text{OH})(\text{H}_2\text{O})(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$ ( $\text{\AA}^2$ )	Occupancy
Ga(1)	0.04923(5)	0.00907(6)	0.16053(3)	0.0069(2)	1
Ga(2)	0.36062(5)	0.22818(6)	0.17294(3)	0.0067(2)	1
Ga(3)	0.08857(5)	0.20949(6)	0.42840(3)	0.0074(2)	1
Ga(4)	0.76362(6)	0.30588(6)	0.42669(3)	0.0101(2)	1
P(1)	0.1717(1)	0.4774(1)	0.07617(6)	0.0083(5)	1
P(2)	0.7480(1)	0.0257(1)	0.06116(6)	0.0086(5)	1
P(3)	0.6303(1)	0.3955(1)	0.27503(6)	0.0068(5)	1
P(4)	0.1406(1)	0.2517(1)	0.27982(6)	0.0070(5)	1
Na(1)	0.7028(2)	0.0458(3)	0.2351(1)	0.019(1)	1
Na(2)	0.8754(3)	0.3764(3)	0.1583(1)	0.027(1)	1
Na(3a)	0.4429(5)	0.1238(7)	0.3539(3)	0.031(3)	0.70(1)
Na(3b)	0.420(1)	0.219(2)	0.3816(7)	0.04(1)	0.27(1)
O(1)	0.0289(3)	0.1792(4)	0.2212(2)	0.010(2)	1
O(2)	0.1955(3)	0.1145(4)	0.1221(2)	0.010(2)	1
O(3)	0.2123(3)	-0.0803(4)	0.2324(2)	0.009(2)	1
O(4)	0.0620(3)	-0.1575(4)	0.0935(2)	0.010(2)	1
O(5)	-0.0871(3)	-0.0927(4)	0.2075(2)	0.010(2)	1
O(6)	-0.1048(4)	0.0980(4)	0.0892(2)	0.013(2)	1
O(7)	0.2801(4)	0.4264(4)	0.1422(2)	0.013(2)	1
O(8)	0.4369(3)	0.2085(4)	0.0837(2)	0.011(2)	1
O(9)	0.2903(3)	0.2655(4)	0.2601(2)	0.010(2)	1
O(10)	0.4460(3)	0.0419(4)	0.2184(2)	0.011(2)	1
O(11)	0.5523(3)	0.3106(4)	0.2104(2)	0.011(2)	1
O(12)	-0.0307(4)	0.0274(4)	0.4037(2)	0.013(2)	1
O(13)	0.1453(4)	0.1496(4)	0.5227(2)	0.013(2)	1
O(14)	0.2372(4)	0.3613(4)	0.4572(2)	0.015(2)	1
O(15)	0.1665(4)	0.1592(4)	0.3494(2)	0.012(2)	1
O(16)	0.7617(4)	0.1100(4)	0.4578(2)	0.014(2)	1
O(17)	0.6284(3)	0.2982(4)	0.3423(2)	0.011(2)	1
O(18)	0.6779(3)	0.3963(4)	0.4904(2)	0.013(2)	1
O(19)	0.6486(4)	0.0459(4)	0.1128(2)	0.018(2)	1
O(20)	0.6292(5)	0.4395(5)	0.0761(2)	0.036(3)	1

All atoms were refined anisotropically and are given in the form of the isotropic equivalent displacement parameter  $U_{\text{eq}}$  defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

synthesis performed after this refinement: the first one was located on Na(3), corresponding to an electronic density of  $2.6 \text{ e}\text{\AA}^{-3}$ ; the second one, of  $2.4 \text{ e}\text{\AA}^{-3}$ , was distant of  $1.15 \text{ \AA}$  from Na(3). All these results suggested a splitting of the Na(3) site over two positions. In order to verify this hypothesis, the Na(3) atom was removed,

and the shape of the residual electronic density observed on the difference synthesis maps was carefully examined. The presence of two close (but distinct) maxima was thus evidenced: they corresponded to  $13.1$  and  $4.4 \text{ e}\text{\AA}^{-3}$  respectively and were distant one from the other of ca.  $1 \text{ \AA}$ . This led us to consider that there were two partially occupied Na(3a) and Na(3b) sites (instead of one fully occupied Na(3) site). The refinement of their occupancy rates was performed without any constraint, leading to  $70(1)\%$  and  $27(1)\%$  for the Na(3a) and Na(3b) sites, respectively (Table 2). Their anisotropic thermal parameters could also be refined without any constraint: Fig. 1b shows the ORTEP representation of Na(3a) and Na(3b) atoms. The final agreement factors were  $R = 0.035$  and  $R_w = 0.034$ . They correspond to the atomic coordinates, equivalent isotropic thermal factors and occupancy ratio given in Table 2 and to the anisotropic thermal parameters available as supplementary material. The chemical formula deduced from these results is “ $\text{Na}_3\text{Ga}_4\text{P}_4\text{O}_{20}$ ”: in order to have a correct charge balance, five hydrogen atoms per formula unit are needed. Despite the good quality of the refinement, their positions could not be determined in the structure from the crystal X-ray diffraction study.

Further details of the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; <mailto:crysdata@fiz-karlsruhe.de>) on quoting the depository number CSD-413070.

### 2.3. Localization of the hydroxyl groups and water molecules

The presence of hydrogen atoms was deduced from bond valence calculations performed with the Brese and O’Keeffe formulation and  $R_{ij}$  values for Na, Ga and O [32] and with  $R_{ij}$  value determined by Leclaire et al. for P [33]. As shown from Table 3, the calculated valences are ranging from 3.08 to 3.15 for the gallium atoms, from 4.95 to 4.99 for the phosphorus atoms and from 0.78 to 0.96 for the sodium atoms. These results are in agreement with the expected values. However, the analysis of the bond valence calculations also evidenced lacks of one valence on O(2) and of two valences on O(8) and O(20). Consequently, O(2) should correspond to an hydroxyl group OH, whereas O(8) and O(20) form  $\text{H}_2\text{O}$  molecules. These results lead for the studied compound to the following formula:  $\text{Na}_3[\text{Ga}_4\text{O}(\text{OH})(\text{H}_2\text{O})(\text{PO}_4)_4] \cdot \text{H}_2\text{O}$ .

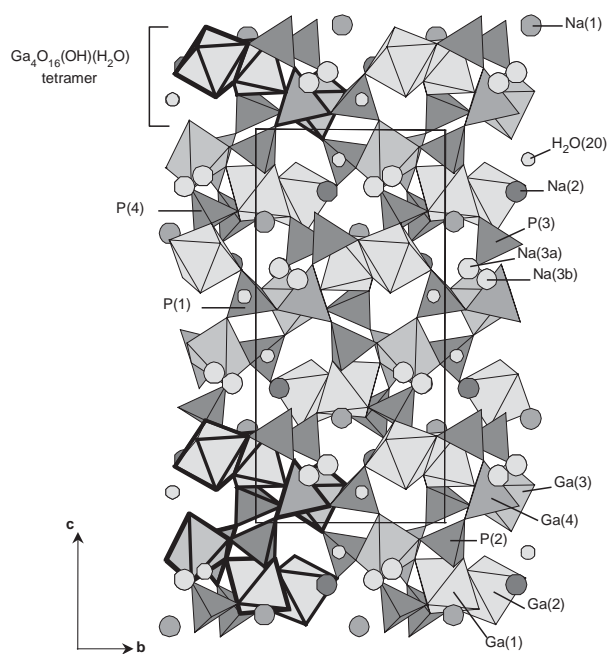
## 3. Description of the structure and discussion

The projections of the structure of  $\text{Na}_3\text{Ga}_4\text{O}(\text{OH})(\text{H}_2\text{O})(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$  along [100] (Fig. 2) and [010] (Fig. 3) evidence the three-dimensional character of its frame-

Table 3

Electrostatic valence distribution for non-hydrogen atoms in  $\text{Na}_3\text{Ga}_4\text{O}(\text{OH})(\text{H}_2\text{O})(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ 

	Ga(1)	Ga(2)	Ga(3)	Ga(4)	P(1)	P(2)	P(3)	P(4)	Na(1)	Na(2)	Na(3a)	Na(3b)	$\sum v_i^-$
O(1)	0.54							1.29		0.17			2.00
O(2)	0.56	0.55											<b>1.11</b>
O(3)	0.47						1.22			0.18			1.87
O(4)	0.48		0.74	0.82									2.04
O(5)	0.55							1.26	0.15				1.96
O(6)	0.55					1.26				0.05			1.86
O(7)		0.50			1.27				0.13		0.03		1.92
O(8)		0.48											<b>0.48</b>
O(9)		0.54						1.21	0.14		0.19	0.18	2.08
O(10)		0.50					1.28		0.21		0.09		2.05
O(11)		0.55					1.31		0.07		0.03		1.95
O(12)			0.49		1.25					0.16			1.90
O(13)			0.71		1.28								1.99
O(14)			0.54			1.23						0.07	1.79
O(15)			0.67					1.19		0.12	0.11	0.20	2.12
O(16)				0.69	1.16								1.85
O(17)				0.74			1.14				0.20	0.21	2.08
O(18)				0.83		1.19							2.02
O(19)						1.31			0.26			0.04	1.58
O(20)										0.12	0.24	0.08	<b>0.31</b>
$\sum v_i^+$	3.15	3.12	3.15	3.08	4.96	4.99	4.95	4.95	0.96	0.80	0.89	0.78	

Fig. 2. Projection of the structure of  $\text{Na}_3\text{Ga}_4\text{O}(\text{OH})(\text{H}_2\text{O})(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$  along [100].

work. The  $[\text{Ga}_4\text{P}_4\text{O}_{19}\text{H}_3]_\infty$  host lattice, which results from the assembly of the different coordination polyhedra of the gallium and phosphorus atoms by corner sharing, presents cages (Fig. 2) and also rather elongated tunnels parallel to the [010] direction (Fig. 3). The sodium cations and one water molecule are located in these cavities.

The main characteristic of this framework deals with the presence of three different coordination polyhedra for the gallium atoms: Ga(1) and Ga(2) present an octahedral environment, corresponding to  $\text{GaO}_5(\text{OH})$  and  $\text{GaO}_4(\text{OH})(\text{H}_2\text{O})$  respectively, whereas Ga(3) sits in a trigonal bipyramid  $\text{GaO}_5$  and Ga(4) in a tetrahedron  $\text{GaO}_4$ . Moreover, these four polyhedra are connected in order to form a  $\text{Ga}_4\text{O}_{16}(\text{OH})(\text{H}_2\text{O})$  tetrameric unit: Ga(1) octahedron, Ga(3) trigonal bipyramid and Ga(4) tetrahedron share indeed one common apex, corresponding to the oxygen atom O(4) which is thus triply bonded; the Ga(2) and Ga(1) octahedra share one OH group labelled O(2) (Fig. 4a). The  $[\text{Ga}_4\text{P}_4\text{O}_{19}\text{H}_3]_\infty$  framework results from the connection of such  $\text{Ga}_4\text{O}_{16}(\text{OH})(\text{H}_2\text{O})$  tetramers through  $\text{PO}_4$  monophosphate groups (Figs. 2 and 3).

One can however notice that there are two sorts of  $\text{Ga}_4\text{O}_{16}(\text{OH})(\text{H}_2\text{O})$  units in the structure, deduced one from the other through the inversion centers of the  $P2_1/c$  space group. Two enantiomorphic  $\text{Ga}_4\text{O}_{16}(\text{OH})(\text{H}_2\text{O})$  tetramers form with two  $\text{P}(2)\text{O}_4$  tetrahedra a  $\text{Ga}_8\text{P}_2\text{O}_{34}(\text{OH})_2(\text{H}_2\text{O})_2$  double unit (Fig. 4b), and the three-dimensional host-lattice results from the assemblage of such double-units through the  $\text{P}(1)\text{O}_4$ ,  $\text{P}(3)\text{O}_4$  and  $\text{P}(4)\text{O}_4$  monophosphate groups. Each of the three latter tetrahedra is indeed shared between two  $\text{Ga}_8\text{P}_2\text{O}_{34}(\text{OH})_2(\text{H}_2\text{O})_2$  double units, contrary to  $\text{P}(2)\text{O}_4$  which exclusively belongs to one double-unit. Fig. 4c illustrates the way the different monophosphate groups are connected to the  $\text{Ga}_4\text{O}_{16}(\text{OH})(\text{H}_2\text{O})$  tetramers in the structure: one can notice the presence at the center of the resulting  $\text{Ga}_8\text{P}_{12}\text{O}_{52}(\text{OH})_2(\text{H}_2\text{O})_2$  entity of a small cavity

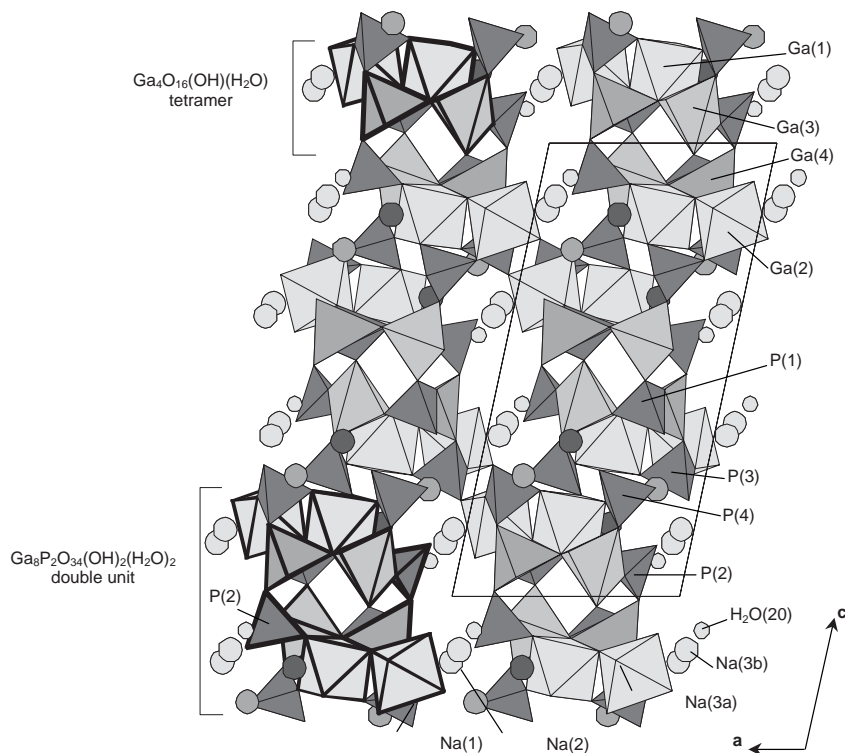


Fig. 3. Projection of the structure of  $\text{Na}_3\text{Ga}_4\text{O}(\text{OH})(\text{H}_2\text{O})(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$  along  $[010]$ .

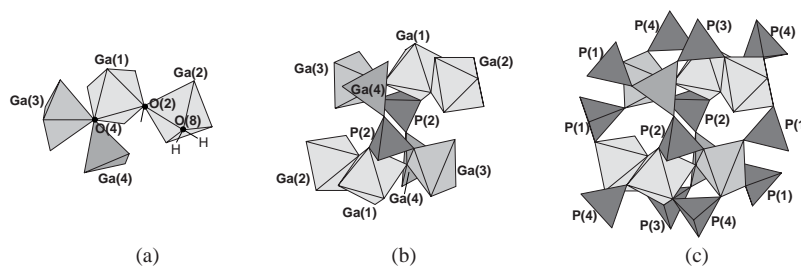


Fig. 4. (a)  $[\text{Ga}_4\text{O}_{16}(\text{OH})(\text{H}_2\text{O})]$  tetramer built from two octahedra (Ga(1) and Ga(2)), one trigonal bipyramid (Ga(3)) and one tetrahedra (Ga(4)). (b)  $[\text{Ga}_8\text{P}_2\text{O}_{34}(\text{OH})_2(\text{H}_2\text{O})_2]$  double unit resulting from the association of two enantiomeric  $[\text{Ga}_4\text{O}_{16}(\text{OH})(\text{H}_2\text{O})]$  tetramers with two  $\text{P}(2)\text{O}_4$  monophosphate groups. (c)  $[\text{Ga}_8\text{P}_{12}\text{O}_{52}(\text{OH})_2(\text{H}_2\text{O})_2]$  entity, showing the connectivity of the  $\text{PO}_4$  tetrahedra with the  $[\text{Ga}_4\text{O}_{16}(\text{OH})(\text{H}_2\text{O})]$  tetramers.

delimited by 12 polyhedra (i.e., four  $\text{PO}_4$  tetrahedra and the eight polyhedra of two enantiomeric  $\text{Ga}_4\text{O}_{16}(\text{OH})(\text{H}_2\text{O})$  tetramers). However, this cage is empty, since the sodium cations and water molecules are located in the largest cages and in the tunnels generated by the assembly of the  $\text{Ga}_8\text{P}_2\text{O}_{34}(\text{OH})_2(\text{H}_2\text{O})_2$  double units through the  $\text{P}(1)\text{O}_4$ ,  $\text{P}(3)\text{O}_4$  and  $\text{P}(4)\text{O}_4$  tetrahedra (Figs. 2 and 3).

It must be noticed that the framework of the title compound could also have been described from building units in the sens of Férey [35], by considering a very original “ $\text{Ga}_4\text{P}_4$ ” octameric BU which involves the above described  $\text{Ga}_4\text{O}_{16}(\text{OH})(\text{H}_2\text{O})$  tetramer and the four independent phosphate groups (Fig. 5). The

structure is indeed formed from such “ $\text{Ga}_4\text{P}_4$ ” octameric BUs linked through their apices (Figs. 2 and 3).

The sodium cations are distributed over three sites: Na(1) and Na(2) are located in open cages communicating with the tunnels running along **b**, which host the water molecule and the Na(3) site splitted over two positions labelled Na(3a) and Na(3b) (see above the “crystal studies” section). There are six oxygen atoms in the environment of Na(1) (Fig. 6a) with Na(1)–O distances ranging from 2.296(4) to 2.772(4) Å (Table 4). Na(2) is in a seven-fold coordination (Fig. 6b), the oxygen atoms sitting at distances ranging from 2.445(4) to 2.927(4) Å. The Na(3a) site is 70% occupied and is surrounded by six oxygen atoms and the

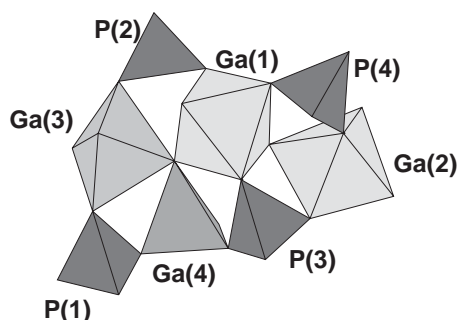


Fig. 5. One “ $\text{Ga}_4\text{P}_4$ ” octameric building unit, resulting from the corner-sharing of one  $[\text{Ga}_4\text{O}_{16}(\text{OH})(\text{H}_2\text{O})]$  tetramer with the four phosphate groups.

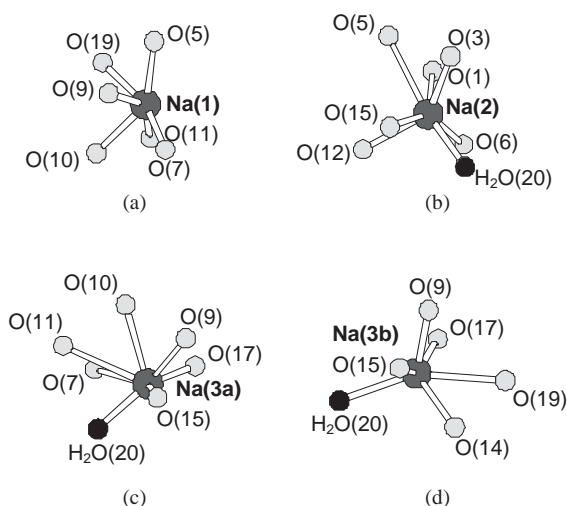


Fig. 6. Sodium environments: (a) Na(1); (b) Na(2); (c) Na(3a); (d) Na(3b).

water molecule  $\text{H}_2\text{O}$  labelled O(20), whereas the sodium atom in the Na(3b) site (ca. 30% occupied) has five oxygen atoms and the O(20) water molecule as neighbors (Fig. 6c); the Na(3)–O distances are ranging from 2.328(7) to 3.156(6) Å (Table 4).

The geometry of the  $\text{PO}_4$  tetrahedra is similar to that usually observed for monophosphate groups, with P–O distances ranging from 1.514(3) to 1.566(4) Å and O–P–O angles ranging from 105.5(2)° to 112.5(2)° (Table 4). One can however notice that the distribution of the P–O distances is slightly different in the P(2) tetrahedron compared to the three others. As a matter of fact, the P(2)–O(19) bond (1.51 Å) is shorter than the three other P(2)–O distances: it corresponds indeed to a free apex of the tetrahedron, pointing towards the [010] tunnels (Fig. 3). In contrast, in the P(1) and P(3) tetrahedra, which share all their apices with gallium polyhedra, there is one P–O distance larger than the three others (1.56 and 1.57 Å for O(16) and O(17), respectively) (Table 4): it corresponds to the oxygen atom shared with

the Ga(3) trigonal bipyramid. Finally, the P(4) tetrahedron is the most regular of the four monophosphate groups, with P–O bonds ranging from 1.521(3) to 1.551(4) Å.

The Ga(1) and Ga(2) octahedra, as well as the Ga(3) trigonal bipyramid, have geometries consistent with the results expected from previous observations performed in the gallium phosphates, since they exhibit gallium–oxygen distances ranging from 1.84 to 1.99 Å for Ga(3) and from 1.95 to 2.01 Å for both octahedra.

The geometry of the gallium tetrahedron Ga(4) is less regular, with Ga–O bonds included between 1.799(4) and 1.868(4) Å and, moreover, O–Ga–O angles ranging from 100.1(2)° to 128.8(2)°. This suggests that the gallium atom is off-centered in the tetrahedron, especially if one considers the rather homogeneous O–O distances (from 2.81 to 2.97 Å). Note that such a large Ga–O distance of 1.86 Å has already been observed in the tetrahedron of another gallium phosphate,  $\text{Rb}_2[\text{Ga}_4(\text{HPO}_4)(\text{PO}_4)_4] \cdot 0.5\text{H}_2\text{O}$  [30], but with more usual O–P–O angles (from 102° to 117°).

The main characteristic of this framework deals with the nature of its  $\text{Ga}_4\text{O}_{16}(\text{OH})(\text{H}_2\text{O})$  tetrameric units. It is thus difficult to compare the Ga–Ga distances with those of other gallium phosphates, but one can remark that they are quite shorter than those usually observed when gallium polyhedra share corners: here, Ga(1)–Ga(2) = 3.51 Å, whereas the published Ga–Ga distances between two sharing-corner  $\text{GaO}_6$  octahedra are ranging from 3.58 Å in  $\text{Na}_3\text{Ga}_5(\text{PO}_4)_4\text{O}_2(\text{OH})_2 \cdot 2\text{H}_2\text{O}$  [29], to 3.75 and 3.79 Å for  $\text{GaPO}_4 \cdot 2\text{H}_2\text{O}$  [25] and  $(\text{NH}_4)[\text{Ga}_2(\text{PO}_4)_2(\text{OH})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$  [27], respectively. Concerning the distance between the gallium atoms of one octahedron and one trigonal bipyramid sharing one apex, it is of 3.75 and 3.82 Å in the mixed units of  $\text{NaGa}_2(\text{OH})(\text{PO}_4)_2$  [20] but only of 3.32 Å between Ga(1) and Ga(3) in the structure of the title compound. Finally, the Ga(1)–Ga(4) distance (i.e., between one of the octahedra and the tetrahedron) is even shorter, with 3.25 Å.

Very few non-fluorinated gallium phosphates containing amine or not exhibit indeed several kinds of coordinations in the same framework. The present hydroxygallophosphate is the second after  $\text{Rb}_2[\text{Ga}_4(\text{HPO}_4)(\text{PO}_4)_4] \cdot 0.5\text{H}_2\text{O}$  [30] which involves the three sorts of gallium polyhedra, i.e., octahedra, trigonal bipyramids and tetrahedra in the same structure. But the unique feature of  $\text{Na}_3[\text{Ga}_4\text{O}(\text{OH})(\text{H}_2\text{O})(\text{PO}_4)_4] \cdot \text{H}_2\text{O}$  is that these three different Ga polyhedra share their apices, forming tetrameric units, whereas in  $\text{Rb}_2[\text{Ga}_4(\text{HPO}_4)(\text{PO}_4)_4] \cdot 0.5\text{H}_2\text{O}$  they are isolated one from the others by sharing corners with  $\text{PO}_4$  groups. This ability to form mixed tetrameric “ $\text{Ga}_4$ ” units is rare, and has only been observed in pure inorganic phosphates for  $\text{NaGa}_2(\text{OH})(\text{PO}_4)_2$  [19]. However, for this compound, only two sorts of gallium polyhedra share their apices

since there is no  $\text{GaO}_4$  tetrahedron in the structure, so that one obtains  $\text{Ga}_4\text{O}_{16}(\text{OH})_2$  units instead of  $\text{Ga}_4\text{O}_{16}(\text{OH})(\text{H}_2\text{O})$  units.

#### 4. Conclusion

The structure of  $\text{Na}_3[\text{Ga}_4\text{O}(\text{OH})(\text{H}_2\text{O})(\text{PO}_4)_4] \cdot \text{H}_2\text{O}$  is unique in that it exhibits tetrameric “ $\text{Ga}_4$ ” units built

up of three different kinds of gallium polyhedra, never observed in any other gallium phosphate, including fluorinated and amine-containing structures. This great ability to associate three sorts of Ga polyhedra in the same structure is very rare and suggests that many other purely inorganic hydroxy phosphates, susceptible to host other univalent or divalent cations should be possibly generated by hydrothermal synthesis.

Table 4  
Selected bond distances (Å) and angles (deg) in  $\text{Na}_3\text{Ga}_4\text{O}(\text{OH})(\text{H}_2\text{O})(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$

Ga(1)	O(1)	O(2)H	O(3)	O(4)	O(5)	O(6)
O(1)	<b>1.961(3)</b>	2.776(5)	2.895(5)	3.959(5)	2.679(5)	2.687(4)
O(2)H	90.5(1)	<b>1.947(4)</b>	2.732(5)	2.764(5)	3.896(5)	2.781(5)
O(3)	93.6(1)	87.3(1)	<b>2.010(3)</b>	2.834(4)	2.773(4)	3.960(4)
O(4)	176.3(1)	88.9(1)	90.0(1)	<b>2.000(4)</b>	2.902(5)	2.786(5)
O(5)	86.4(1)	174.9(1)	88.8(1)	94.5(1)	<b>1.952(4)</b>	2.828(5)
O(6)	86.8(1)	91.0(1)	178.3(2)	89.7(1)	92.9(1)	<b>1.951(3)</b>
Ga(2)	O(2)H	O(7)	O(8)H <sub>2</sub>	O(9)	O(10)	O(11)
O(2)H	<b>1.951(3)</b>	2.930(5)	2.679(5)	2.949(4)	2.762(4)	3.872(4)
O(7)	96.2(1)	<b>1.986(3)</b>	2.833(5)	2.675(5)	3.961(5)	2.832(4)
O(8)H <sub>2</sub>	85.3(1)	90.6(2)	<b>2.001(4)</b>	3.954(5)	2.978(5)	2.616(4)
O(9)	98.0(1)	85.5(1)	175.1(2)	<b>1.956(4)</b>	2.716(5)	2.865(5)
O(10)	89.1(1)	171.4(1)	96.6(1)	87.1(1)	<b>1.987(3)</b>	2.642(5)
O(11)	165.7(2)	92.0(1)	82.9(1)	94.3(1)	84.3(1)	<b>1.952(3)</b>
Ga(3)	O(4 <sup>i</sup> )	O(12)	O(13)	O(14)	O(15)	
O(4 <sup>i</sup> )	<b>1.842(3)</b>	2.861(5)	3.166(4)	2.798(5)	3.098(5)	
O(12)	96.4(1)	<b>1.994(3)</b>	2.760(4)	3.933(5)	2.607(5)	
O(13)	117.6(2)	91.5(2)	<b>1.858(3)</b>	2.539(5)	3.378(5)	
O(14)	94.8(2)	168.8(1)	83.4(2)	<b>1.958(4)</b>	2.736(5)	
O(15)	112.9(2)	84.6(2)	129.5(2)	91.0(2)	<b>1.876(4)</b>	
Ga(4)	O(4 <sup>ii</sup> )	O(16)	O(17)	O(18)		
O(4 <sup>ii</sup> )	<b>1.802(4)</b>	2.974(5)	2.956(4)	2.974(5)		
O(16)	108.3(2)	<b>1.868(4)</b>	2.868(5)	2.812(5)		
O(17)	108.4(2)	101.2(2)	<b>1.843(3)</b>	2.921(5)		
O(18)	128.8(2)	100.1(2)	106.7(2)	<b>1.799(4)</b>		
P(1)	O(7)	O(12 <sup>i</sup> )	O(13 <sup>iii</sup> )	O(16 <sup>ii</sup> )		
O(7)	<b>1.526(3)</b>	2.510(5)	2.478(4)	2.506(5)		
O(12 <sup>i</sup> )	110.4(2)	<b>1.532(4)</b>	2.524(5)	2.519(5)		
O(13 <sup>iii</sup> )	108.7(2)	111.3(2)	<b>1.525(4)</b>	2.504(5)		
O(16 <sup>ii</sup> )	108.7(2)	109.2(2)	108.6(2)	<b>1.559(4)</b>		
P(2)	O(6 <sup>iv</sup> )	O(14 <sup>v</sup> )	O(18 <sup>iii</sup> )	O(19)		
O(6 <sup>iv</sup> )	<b>1.530(3)</b>	2.542(5)	2.489(4)	2.512(5)		
O(14 <sup>v</sup> )	111.8(2)	<b>1.539(4)</b>	2.471(5)	2.522(6)		
O(18 <sup>iii</sup> )	107.8(2)	106.2(2)	<b>1.551(3)</b>	2.481(5)		
O(19)	111.2(2)	111.4(2)	108.1(2)	<b>1.514(4)</b>		
P(3)	O(3 <sup>ii</sup> )	O(10 <sup>ii</sup> )	O(11)	O(17)		
O(3 <sup>ii</sup> )	<b>1.540(3)</b>	2.534(5)	2.472(4)	2.537(5)		
O(10 <sup>ii</sup> )	111.6(2)	<b>1.524(4)</b>	2.642(5)	2.521(5)		
O(11)	108.1(2)	110.4(2)	<b>1.514(3)</b>	2.489(5)		
O(17)	109.5(2)	109.3(2)	107.8(2)	<b>1.566(4)</b>		

Table 4 (continued)

P(4)	O(1)	O(5 <sup>i</sup> )	O(9)	O(15)
O(1)	<b>1.521(3)</b>	2.471(5)	2.550(4)	2.539(4)
O(5 <sup>i</sup> )	108.1(2)	<b>1.530(3)</b>	2.493(5)	2.536(5)
O(9)	112.5(2)	108.3(2)	<b>1.545(4)</b>	2.464(5)
O(15)	111.5(2)	110.8(2)	105.5(2)	<b>1.551(4)</b>

Na(1)–O(19) = 2.296(4) Na(2)–O(3<sup>ii</sup>) = 2.445(4)

–O(10) = 2.382(4) –O(1<sup>iv</sup>) = 2.449(4)

–O(5<sup>iv</sup>) = 2.496(4) –O(12<sup>ii</sup>) = 2.483(5)

–O(9<sup>v</sup>) = 2.532(4) –O(15<sup>ii</sup>) = 2.583(4)

–O(7<sup>v</sup>) = 2.566(4) –O(20)H<sub>2</sub> = 2.588(5)

–O(11) = 2.772(4) –O(6<sup>iv</sup>) = 2.867(4)

–O(5<sup>ii</sup>) = 2.926(4)

Na(3a)–O(20<sup>v</sup>)H<sub>2</sub> = 2.328(7) Na(3b)–O(17) = 2.37(1)

–O(17) = 2.402(6) –O(15) = 2.40(1)

–O(9) = 2.424(6) –O(9) = 2.43(1)

–O(15) = 2.616(6) –O(20<sup>ii</sup>)H<sub>2</sub> = 2.72(2)

–O(10) = 2.712(6) –O(14) = 2.79(2)

–O(11<sup>v</sup>) = 3.089(6) –O(19<sup>ii</sup>) = 3.03(2)

–O(7<sup>v</sup>) = 3.156(6)

Symmetry codes: (i)  $-x, 1/2 + y, 1/2 - z$ ; (ii)  $1 - x, 1/2 + y, 1/2 - z$ ; (iii)  $x, 1/2 - y, -1/2 + z$ ; (iv)  $1 + x, y, z$ ; (v)  $1 - x, -1/2 + y, 1/2 - z$ .

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