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A sodium gallophosphate with an original tunnel structure: $NaGa_2(OH)(PO_4)_2$

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Abstract

A new sodium gallophosphate, $NaGa_2(OH)(PO_4)_2$, has been obtained by hydrothermal synthesis under autogeneous pressure at 473 K. It crystallizes in the $P2_1/n$ space group with the cell parameters $a = 8.9675(8)$ Å, $b = 8.9732(5)$ Å, $c = 9.2855(7)$ Å, $\beta = 114.812(6)^\circ$, $V = 678.2$ Å^3 ($Z = 4$). In its original three-dimensional framework, monophosphate groups share their apices with $[Ga_4O_{16}(OH)_2]$ tetrameric units, which are built from two $GaO_5(OH)$ octahedra and two $GaO_4(OH)$ trigonal bipyramids. The sodium cations are located in tunnels running along **a**, whereas the tunnels running along **b** are empty.

Keywords: Gallium monophosphate; Hydrothermal synthesis; Single crystal; X-ray diffraction; Structure determination; Tunnel structure; Tetrameric units

1. Introduction

Gallium phosphates have been extensively studied during the past 10 years owing to their similarity with aluminium phosphates and their potential applications in the fields of ion-exchange, catalysis and separation technologies. Numerous oxides and oxifluorides with microporous three-dimensional frameworks have thus been isolated ([1–2] and references therein), most of them involving organic templates. In the structures of these compounds, the coordination polyhedra of the gallium atoms can either be tetrahedral, trigonal bipyramidal, or octahedral. This explains the great diversity of the Ga–P mixed frameworks, which are usually described from building units resulting from the assembly of the above-mentioned gallium polyhedra with PO_4 tetrahedra by corner-sharing. Many kinds of such building units have thus been reported in the literature, especially for fluorinated gallophosphates which have been particularly studied according to the well known mineralizing role of the fluoride ions ([1–5] and references therein). However, there are only two non-fluorinated inorganically templated gallophosphates that involve different sorts of gallium polyhedra in their framework [6,7]. We report here the synthesis and the structure of a novel inorganic gallophosphate involving sodium, $NaGa_2(OH)(PO_4)_2$, the framework of which presents original $[Ga_4O_{16}(OH)_2]$ tetrameric building units.

2. 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_2O_3 (Chem-Pur, 99.99%), H_3PO_4 (Prolabo Rectapur, 75%) and H_2O, in the respective molar ratio 1:1:2:388 (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 resulting product was filtered off, washed with water and dried in air. A white powder containing colourless crystals was obtained.

3. Crystals studies

The semi-quantitative EDS analysis of one of the colourless stick-like crystals was performed with an

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Table 1
Summary of crystal data, intensity measurements and structure refinement parameters for $NaGa_2(OH)(PO_4)_2$

Crystal data	
Crystal dimensions (mm^3)	$0.090 \times 0.064 \times 0.051\,mm^3$
Space group	$P2_1/n$
Cell dimensions	$a = 8.9675(8)$ Å
	$b = 8.9732(5)$ Å
	$c = 9.2855(7)$ Å
	$\beta = 114.812(6)°$
Volume	$V = 678.2$ Å^3
Z	4
Formula weight	$369.4\,g\,mol^{-1}$
ρ_{calc}	$3.616\,g\,cm^{-3}$
Intensity measurements	
λ(MoKα)	0.71069 Å
Scan strategies	φ and ω scans
	0.5°/frame
	30 s/deg.
	2 iterations
Crystal-detector distance, D_x	34 mm
θ range for data collection	$2.65° \leqslant \theta \leqslant 45°$
Limiting indices	$-17 \leqslant h \leqslant 17$
	$-16 \leqslant k \leqslant 17$
	$-16 \leqslant l \leqslant 18$
Measured reflections	16612
Reflections with $I > 3\sigma$	5580
Independent reflections with $I > 3\sigma$	3039
μ (mm^{-1})	8.51
Extinction coefficient	0.302
Structure solution and refinement	
Parameters refined	128
Agreement factors	$R = 0.036$
	$R_w = 0.032$
Weighting scheme	$w = 1/\sigma^2$
Δ/σ max	$< 2.10^{-2}$

Table 2
Positional parameters and their estimated standard deviations in $NaGa_2(OH)(PO_4)_2$

Atom	x	y	z	$U_{eq.}$ (Å^2)
Ga(1)	0.35292(3)	0.41438(2)	0.38251(3)	0.00602(7)
Ga(2)	0.27051(3)	0.23315(2)	0.92946(3)	0.00672(8)
P(1)	0.05964(7)	0.61167(5)	0.22905(7)	0.0059(2)
P(2)	0.10297(7)	0.95161(5)	0.76664(7)	0.0060(2)
Na	0.2266(1)	0.1203(1)	0.5216(1)	0.0167(4)
O(1)	0.3977(2)	0.6218(1)	0.4787(2)	0.0071(5)
O(2)	0.3269(2)	0.3622(2)	0.5780(2)	0.0083(5)
O(3)	0.4291(2)	0.4910(2)	0.2278(2)	0.0075(5)
O(4)	0.3346(2)	0.2091(1)	0.3284(2)	0.0080(5)
O(5)	0.1264(2)	0.4528(1)	0.2512(2)	0.0077(5)
O(6)	0.1209(2)	0.3901(1)	0.8936(2)	0.0077(5)
O(7)	0.4124(2)	0.3536(2)	0.8739(2)	0.0092(5)
O(8)	0.4382(2)	0.1770(2)	1.1169(2)	0.0092(5)
O(9)	0.2170(2)	0.0862(2)	0.7770(2)	0.0090(5)

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

Table 3
Electrostatic valence distribution for non-hydrogen atoms in $NaGa_2(OH)(PO_4)_2$

	Ga(1)	Ga(2)	P(1)	P(2)	Na	$\sum vi-$
O(1)	0.44 0.38	0.24				1.06
O(2)	0.51			1.20	0.24	1.95
O(3)	0.54			1.21	0.18	1.93
O(4)	0.64		1.19		0.15	1.98
O(5)	0.61		1.24			1.85
O(6)		0.67	1.19		0.19	2.05
O(7)		0.63		1.22	0.12	1.97
O(8)		0.77	1.19			1.96
O(9)		0.73		1.13	0.18	2.04
$\sum vi+$	3.12	3.04	4.81	4.76	1.06	

OXFORD 6650 microprobe mounted on a PHILIPS XL30 FEG scanning electron microscope: it revealed the presence of Na, Ga and P elements.

Several crystals were then optically selected to be tested by the oscillation and Weissenberg methods using the CuKα radiation. A single crystal with dimensions $0.090 \times 0.064 \times 0.051\,mm^3$ was chosen for the structure determination and refinement. The data were collected with a Bruker–Nonius Kappa CCD four-circle diffractometer equipped with a bidimensional CCD detector and using the MoKα radiation. A strategy using φ and ω scans with 0.5° per frame, 30 s per degree and 2 iterations was determined. A crystal-detector distance $D_x = 34$ mm was fixed. The cell parameters reported in Table 1 were accurately determined from the whole registered frames. Data were then reduced and corrected for Lorentz and polarization effects with the EvalCCD program. The observed systematic extinctions $h\,0\,l$: $h + l = 2n + 1$ and $0\,k\,0$: $k = 2n + 1$ led to the $P2_1/n$ space group. The structure was solved with the JANA 2000 program [8] using the heavy atom method and successive difference synthesis and Fourier synthesis. Absorption and secondary extinction effect corrections were performed; the atomic coordinates and the anisotropic thermal parameters of all atoms were refined, leading to the reliability factors $R = 0.036$ and $R_w = 0.032$. Resulting atomic parameters are listed in Table 2.

Further details of the crystal structure investigations (including anisotropic displacement parameters) can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (fax: (49) 7247-808-666; e-mail: mailto:crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-412733.

4. Localization of the hydrogen atoms

The presence of hydrogen atoms was deduced from bond valence calculations performed with the Brese and O'Keeffe formulation [9]. As shown in Table 3, the calculated valencies range from 3.04 to 3.12 for the gallium atoms, from 4.76 to 4.81 for the phosphorus atoms and a value of 1.06 was obtained for the sodium atom. These results are thus in agreement with the expected values. However, the analysis of the bond valence calculations also evidenced a lack of one valence on O(1), which should consequently correspond to an hydroxyl group OH. As a result, the formula of the studied compound is $NaGa_2(OH)(PO_4)_2$.

5. Powder studies

Many attempts, involving various synthesis conditions, have been performed in order to prepare $NaGa_2(OH)(PO_4)_2$ as a monophasic sample, but they always led to mixtures. The best result was obtained starting from Na_2CO_3 (Prolabo, 85%), Ga_2O_3 (Chem-Pur, 99.99%), and $(NH_4)_2HPO_4$ (Prolabo Rectapur, 99%): first, they were 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 diamonium 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 was 7). It was heated at 473 K for 24 h and cooled at 10 K/h. The resulting white product was filtered off, washed with water and dried in air (final pH value: 5). Its X-ray powder diffraction pattern was registered with a PHILIPS PW 1830 diffractometer using the CuKα radiation in the angular range $5 \leqslant 2\theta \leqslant 120°$ with a step of 0.02° and with 9 s/step. Despite the fact that most of the diffraction peaks were indexed in the monoclinic cell deduced from the single crystal study of the title compound, the presence of a few non-indexed peaks indicated that the sample was not monophasic. However, we could not identify any minor phase from this powder X-ray diffraction study. The analysis of the sample was thus performed using a EDS analyser mounted on a JEOL 2010 CX transmission electron microscope: it confirmed the presence of $NaGa_2(OH)(PO_4)_2$ as a major phase in the sample (ca. 70%) and allowed the determination of the cationic composition of an unknown impurity, which was found to be "$Na_6Ga_9P_7$".

6. Description of the structure and discussion

As shown on the projections of the structure of $NaGa_2(OH)(PO_4)_2$ along [100] (Fig. 1) and [001] (Fig. 2), its framework results from the assembly of three sorts of coordination polyhedra: PO_4 tetrahedra, $GaO_5(OH)$ octahedra and $GaO_4(OH)$ trigonal bipyramids. These polyhedra share corners and edges, generating a three-dimensional host-lattice.

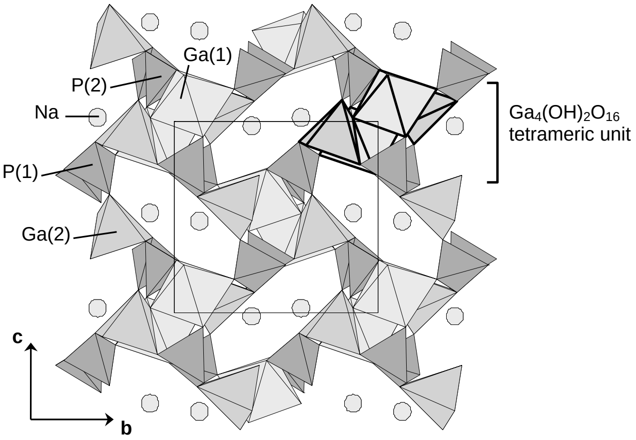

Fig. 1. Projection of the structure of $NaGa_2(OH)(PO_4)_2$ along [100].

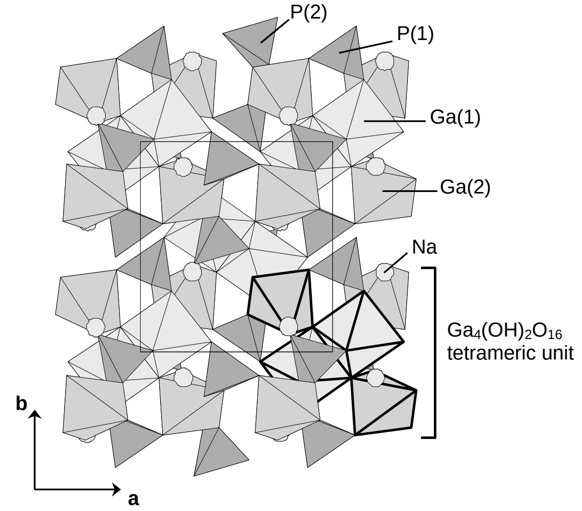

Fig. 2. Projection of the structure of $NaGa_2(OH)(PO_4)_2$ along [001].

The $[Ga_2(OH)(PO_4)_2]_\infty$ framework consists of $Ga_4(OH)_2O_{16}$ mixed-units (Fig. 3), built up of two $GaO_5(OH)$ octahedra sharing their O(1)–O(1) edge and two $GaO_4(OH)$ trigonal bipyramids grafted to the same O(1) apices (Fig. 3a and b). As a result, O(1) is quadruply bonded: it is indeed linked to three gallium atoms of the tetramer and to one hydrogen atom. This is also observed in the leucophosphite type structure [10] adopted by $(NH_4)[Ga_2(PO_4)_2(OH)(H_2O)] \cdot H_2O$ [11], which presents comparable units involving four gallium coordination polyhedra. However, in the latter framework all the gallium atoms have an octahedral environment, leading to "pure octahedral" $Ga_4(OH)_2(H_2O)_2O_{16}$ tetrameric units (Fig. 3c). The comparison between the two kinds of tetramers clearly shows that they only differ by the absence in the titled compound of the water molecule which constitutes the sixth corner of the corner-sharing gallium octahedra in the "pure

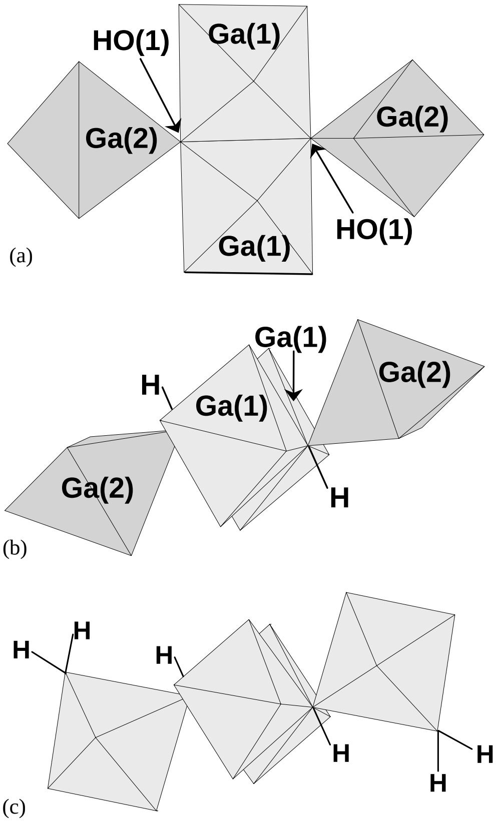

Fig. 3. (a) and (b) Two different views of the $Ga_4(OH)_2O_{16}$ mixed-unit of $NaGa_2(OH)(PO_4)_2$. (c) The $Ga_4(OH)_2(OH_2)_2O_{16}$ octahedral unit observed in the structure of $(NH_4)[Ga_2(PO_4)_2(OH)(H_2O)]\cdot H_2O$.

octahedral" unit (Fig. 3b and c). To our knowledge, a $Ga_4(OH)_2O_{16}$ tetramer involving two different sorts of gallium coordination polyhedra has never been described previously. Moreover, if the presence of different gallium coordination polyhedra forming mixed building units have already been reported in numerous oxyfluorinated gallophosphates ([1–5] and references therein), it is worth pointing out that only three non-fluorinated gallium phosphates presenting this feature are reported in literature:

(i) The first one is an organically templated compound, $Ga_3(PO_4)_3H_2O(C_3H_9N)$ [12], in which there are two GaO_5 trigonal bipyramids sharing one apex and one GaO_4 isolated tetrahedron;
(ii) the second one, $Rb_2[Ga_4(HPO_4)(PO_4)_4]0.5H_2O$ [6], has been prepared by high temperature–high pressure hydrothermal synthesis; it contains one GaO_6 octahedron, one GaO_5 trigonal bipyramid and two GaO_4 tetrahedra, all these polyhedra being separated from the others by phosphate groups;
(iii) finally, in $Na_3Ga_5(PO_4)_4O_2(OH)_2\cdot 2H_2O$ [7] there are GaO_6 octahedra sharing one vertex and isolated GaO_5 trigonal bipyramids.

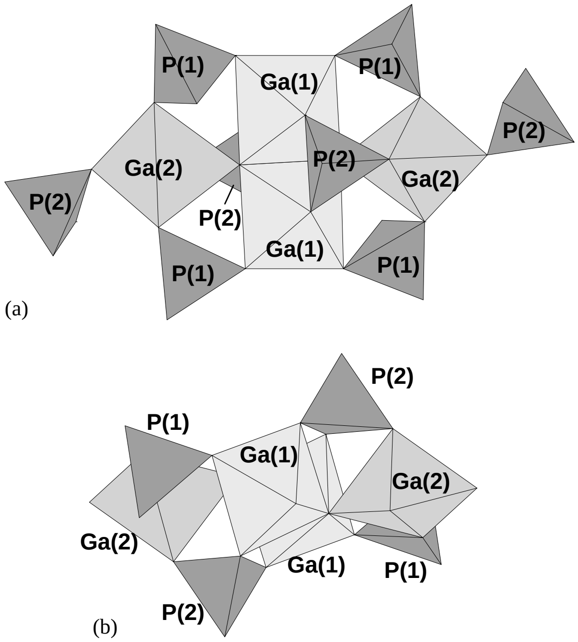

Fig. 4. (a) The eight PO_4 tetrahedra linked to each $Ga_4(OH)_2O_{16}$ tetramer, which ensure the connection with the eight other units. (b) $Ga_4P_4(OH)_2O_{24}$ octameric building unit.

The existence in the structure of $NaGa_2(OH)(PO_4)_2$ of tetrameric building units formed by two sorts of gallium polyhedra constitutes thus a very unusual feature. However, the geometry of the Ga(1) edge-sharing octahedra of the title compound is similar to that observed in the "pure octahedral" units: in both cases, the two largest Ga–O distances observed in the octahedra correspond to the bonding oxygen atoms of the units. One can nevertheless remark that these distances are even larger in the "pure octahedral" tetramers: in the edge-sharing octahedra of $(NH_4)[Ga_2(PO_4)_2(OH)(H_2O)]\cdot H_2O$ [11] and $GaPO_4\cdot 2H_2O$ [13], the two largest Ga–O distances are ranging from 2.10 to 2.17 Å, whereas they are equal to 2.030(2) and 2.086(2) Å in $NaGa_2(OH)(PO_4)_2$ (Table 4). The distortion is even more accentuated in the $Ga(2)O_4(OH)$ trigonal bipyramid: the Ga(2)–O(1) distance is indeed very long, with 2.254(2) Å, whereas the four other ones are ranging from 1.829(2) to 1.899(2) Å. The Ga–Ga distances in the $Ga_4(OH)_2O_{16}$ mixed tetrameric units are similar to that observed in the "pure octahedral" tetramers: the distance existing between the two Ga(1) atoms of the central edge-sharing octahedra is of 3.0413(3) Å (to be compared to 3.11 and 3.06 Å in $(NH_4)[Ga_2(PO_4)_2(OH)(H_2O)]\cdot H_2O$ and $GaPO_4\cdot 2H_2O$, respectively); the Ga(1)–Ga(2) distances are of 3.7520(4) and 3.8204(4) Å (versus 3.78 and 3.75 Å in $(NH_4)[Ga_2(PO_4)_2(OH)(H_2O)]\cdot H_2O$ and $GaPO_4\cdot 2H_2O$, respectively).

These $Ga_4(OH)_2O_{16}$ tetramers are connected via PO_4 tetrahedra by corner sharing, in such a way that each Ga

Table 4
Selected bond distances (Å) and angles (°) in $NaGa_2(OH)(PO_4)_2$

Ga(1)	O(1)	O(1^{i})	O(2)	O(3)	O(4)	O(5)
O(1)	2.030(2)	2.774(2)	2.678(2)	2.726(3)	3.914(2)	2.893(2)
O(1^{i})	84.73(6)	2.086(2)	2.736(3)	2.704(3)	2.769(2)	3.996(2)
O(2)	83.76(7)	84.54(7)	1.981(2)	3.905(3)	2.720(2)	2.920(2)
O(3)	86.28(7)	83.93(7)	165.39(6)	1.956(2)	2.942(2)	2.833(3)
O(4)	170.13(6)	87.92(6)	89.00(7)	99.51(7)	1.899(2)	2.768(2)
O(5)	94.37(6)	177.98(7)	97.18(8)	94.20(7)	93.18(6)	1.912(2)

Ga(2)	O(1^{ii})	O(6)	O(7)	O(8)	O(9)
O(1^{ii})	2.254(2)	2.719(2)	4.139(3)	2.803(2)	2.874(3)
O(6)	81.82(7)	1.876(2)	2.716(3)	3.331(2)	3.107(3)
O(7)	170.54(6)	92.02(7)	1.899(2)	2.687(2)	2.884(2)
O(8)	86.05(7)	128.08(7)	92.21(7)	1.829(2)	3.050(2)
O(9)	88.48(7)	117.66(6)	100.76(8)	112.21(6)	1.845(2)

P(1)	O(4^{iii})	O(5)	O(6^{ii})	O(8^{iv})
O(4^{iii})	1.541(2)	2.485(2)	2.539(2)	2.517(3)
O(5)	108.2(1)	1.526(2)	2.492(2)	2.545(2)
O(6^{ii})	111.02(9)	108.73(8)	1.540(2)	2.473(2)
O(8^{iv})	109.68(9)	112.27(9)	106.9(1)	1.539(2)

P(2)	O(2^{iv})	O(3^{v})	O(7^{iv})	O(9^{vi})
O(2^{iv})	1.536(2)	2.542(2)	2.524(2)	2.540(2)
O(3^{v})	111.8(1)	1.535(2)	2.446(3)	2.523(3)
O(7^{iv})	110.81(8)	105.86(9)	1.531(2)	2.510(2)
O(9^{vi})	110.31(8)	109.29(8)	108.7(1)	1.559(2)

Na–O(2) = 2.324(2)
Na–O(6^{vii}) = 2.419(2)
Na–O(9) = 2.429(2)
Na–O(3^{viii}) = 2.438(2)
Na–O(4) = 2.500(2)
Na–O(7^{ix}) = 2.575(2)

Symmetry codes.
(i) $1-x$; $1-y$; $1-z$; (ii) $-x$; $1-y$; $1-z$; (iii) $\frac{1}{2}-x; y+\frac{1}{2}; \frac{1}{2}-z$; (iv) $\frac{1}{2}-x; y+\frac{1}{2}; \frac{3}{2}-z$; (v) $x-\frac{1}{2}; \frac{3}{2}-y; z+\frac{1}{2}$; (vi) x; $1+y$; z; (vii) $\frac{1}{2}-x; y-\frac{1}{2}; \frac{1}{2}-z$; (viii) $\frac{1}{2}-x; y-\frac{1}{2}; \frac{3}{2}-z$; (ix) $x-\frac{1}{2}; \frac{1}{2}-y; -z-\frac{1}{2}$.

tetramer is linked to its eight next neighbours via eight PO_4 tetrahedra (four P(1) and four P(2) tetrahedra), as shown in Fig. 4a. In this way, each P(1) tetrahedron shares two apices with this tetramer and two apices with the next one, whereas each P(2) tetrahedron shares three apices with a tetramer and only one apex with the next one. As a result each PO_4 tetrahedron is linked to two Ga octahedra and two Ga trigonal bipyramids whatever its nature, but for P(1) the Ga octahedra belong to two different tetramers, whereas for P(2) they belong to the same tetramer. The geometry of the PO_4 tetrahedra is similar to that usually observed for monophosphate groups. However, P(1) presents four rather homogeneous P–O distances ranging from 1.526(2) to 1.541(2) Å, whereas one observes in the P(2) tetrahedron three P–O distances ranging from 1.531(2) to 1.536(2) Å and one larger bond of 1.559(2) Å (Table 5). This difference can be explained by the different mode of connection of the P(1) and P(2) tetrahedra with the $Ga_4(OH)_2O_{16}$ tetramers, as described above (Fig. 4a).

Thus the $[Ga_2P_2O_8(OH)]_\infty$ tridimensional framework results from the assembly of $Ga_4(OH)_2O_{16}$ tetramers via PO_4 tetrahedra by corner sharing. One can, however, notice an alternative description, involving $Ga_4P_4(OH)_2O_{24}$ building units (Fig. 4b) connected through the apices of their polyhedra: the resulting structure can then be considered as a monoclinic distorted *cc* type arrangement of these octameric building blocks (Figs. 1 and 2), similar to that Loiseau et al. observed in $(NH_4)[Ga_2(PO_4)_2(OH)(H_2O)] \cdot H_2O$ [11].

The host-lattice of the title compound delimits tunnels running along **a** and occupied by sodium (Fig. 1). The Na^+ cation is surrounded by six oxygen atoms forming a slightly distorted trigonal prism and situated at distances ranging from 2.324(2) to 2.575(2) Å (Table 4).

In conclusion, the presence in the framework of $NaGa_2(OH)(PO_4)_2$ of different sorts of gallium polyhedra ($GaO_5(OH)$ octahedra and $GaO_5(OH)$ trigonal bipyramids) assembled to form a mixed $[Ga_4O_{16}(OH)_2]$

tetramer constitutes a very original feature. It confirms the great diversity of the structures offered by mixed frameworks compounds and suggests that, as in the organically templated fluorinated gallophosphates, many original Ga–P–O frameworks involving other mixed building units should exist. The opened character of this structure suggests the possibility of cationic mobility. The latter could not be checked to date, due to the difficulty to synthesize well sintered and pure samples.

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