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$Rb(GaPO_4)_2(OH)(H_2O)\cdot H_2O$: a hydrated rubidium gallium phosphate analogue of $GaPO_4\cdot 2H_2O$ and leucophosphite

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Crystals of the title hydrated rubidium gallium phosphate, rubidium aqua-μ_3-hydroxo-di-μ-phosphato-digallium hydrate, were synthesized hydrothermally at 453 K under autogenous pressure. The solid crystallizes in the monoclinic system and its structure was determined from single-crystal X-ray diffraction analysis. It is similar to dihydrated gallium phosphate, $GaPO_4\cdot 2H_2O$, which is isostructural with the mineral leucophosphite. The structure is built up from a three-dimensional anionic framework composed of corner-linked octameric $Ga_4(PO_4)_4(OH)_2(H_2O)_2$ units. The Ga atom is in an octahedral coordination. Connection of the Ga_4P_4 species generates eight-ring channels, in which are encapsulated the Rb^+ cations and water molecules.

Comment

Microporous aluminium phosphates have been widely studied, because they find many potential applications in diverse areas such as catalysis, gas separation or ionic exchange. The replacement of Al by Ga yields open-framework solids. Some of these are isostructural with the aluminophosphate analogues and others exhibit novel three-dimensional topologies (Cheetham *et al.*, 1999). For example, the gallium phosphates MIL-31 (Sassoye *et al.*, 2000), cloverite (Estermann *et al.*, 1991) or $Ga_2(DETA)(PO_4)_2\cdot 2H_2O$ (DETA is diethylenetriamine; Lin *et al.*, 2001) are characterized by unique extra-large open frameworks delimited by 18-, 20- and 24-ring channels, respectively. While these materials are typically prepared by means of organic structure-directing agents (amines, tetraalkylammonium salts, *etc.*), there have been a few reports concerning the use of alkali cations for the formation of phosphate-based porous solids. To date, several gallium phosphates have been synthesized with Na (Attfield *et al.*, 1995), K (Harrison *et al.*, 1995) or Rb (Lii, 1996; Hammond & Zubieta, 1999) as cations. In these compounds, the alkali cations reside within small cavities delimited by six-, seven- or eight-membered rings.

In our recent work, we have focused our attention on the reactivity of alkali cations in the hydrothermal synthesis of open-framework gallium phosphates (Beitone *et al.*, 2001). In this context, we describe here the synthesis and characterization of the title compound, $Rb(GaPO_4)_2(OH)(H_2O)\cdot H_2O$, (I).

The structure of (I) is similar to the hydrated gallium phosphate $GaPO_4\cdot 2H_2O$ (Mooney-Slater, 1966), the gallium phosphates $GaPO_4$-C7 (Wang *et al.*, 1989) and $NH_4[Ga_2(PO_4)_2(OH)(H_2O)]\cdot H_2O$ (Loiseau & Ferey, 1994), and the aluminophosphate $AlPO_4$-15 (Pluth *et al.*, 1984). These structures all belong to the leucophosphite structural type (Moore, 1972; Dick & Zeiske, 1997) corresponding to a potassium iron phosphate.

The structure of (I) is built up from the connection through their vertices of PO_4 tetrahedra and $GaO_4(OH)(OH,H_2O)$ octahedra (Fig. 1). The two types of P atoms are tetrahedrally coordinated to O atoms, with typical P—O distances ranging from 1.515 (2) to 1.554 (2) Å. One of the two Ga atoms (Ga1) is connected to four O atoms and two OH (O9—H1) groups (in the *cis* position). The two Ga1—O9H distances [2.131 (2) and 2.141 (2) Å] are longer than the Ga1—O distances [Ga—O 1.905 (2)–1.925 (2) Å].

The Ga1 octahedra share an edge corresponding to the OH groups, each OH being also connected to atom Ga2. This second Ga atom is coordinated to four O atoms, one OH group (O9—H1) and one water molecule (H2—O10—H3). The water molecule attached to Ga2 is terminal [Ga2—O10 2.018 (2) Å], in the *cis* position with respect to the OH group. The bond-valence sums (O'Keeffe & Brese, 1992) for atoms O9 and O10 are 0.997 and 0.459, respectively, omitting the O—H bonds. These calculations confirm the occurrence of a hydroxyl group (O9) and a water molecule (O10).

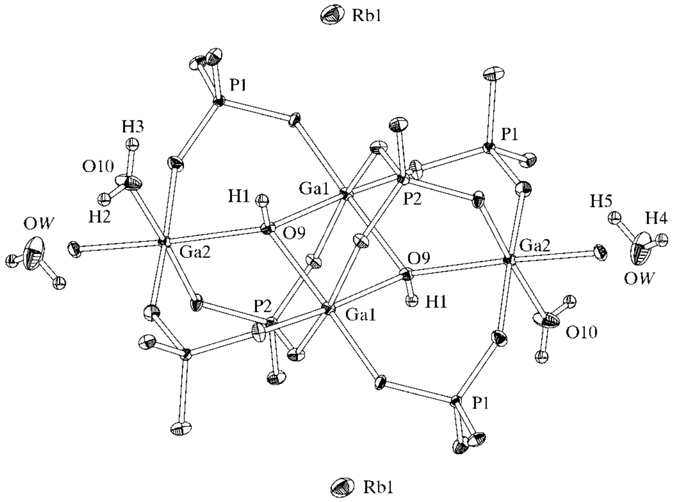

Figure 1
Displacement ellipsoid plot (50% probability) of the $Ga_4(PO_4)_4(OH)_2(H_2O)_2$ building unit of (I), showing the Rb^+ cations and the free water molecule, *OW*.

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The connection of the gallium octahedra forms a tetrameric unit which is linked to four phosphate groups. Two of them (P2) have bonds to three adjacent Ga atoms, whereas the other two (P1) connect to only two Ga centres. This results in the formation of an octameric $Ga_4(PO_4)_4(OH)_2(H_2O)_2$ cluster, corresponding to the basic building unit encountered in the leucophosphite structural type. This moiety was also observed in the extra-large-pore gallium phosphate, $Ga_4(HPO_4)(PO_4)_3(OH)_3 \cdot 4N_2C_4H_{14} \cdot 6H_2O$, whose structure exhibits channels bounded by 20-ring windows (Chippindale *et al.*, 1999; Walton *et al.*, 2000). The arrangement of these blocks, connected to each other through all the remaining free O atoms (except O10, which is terminal), describes a three-dimensional framework delimiting eight-ring channels running along [010] (Fig. 2) and [001].

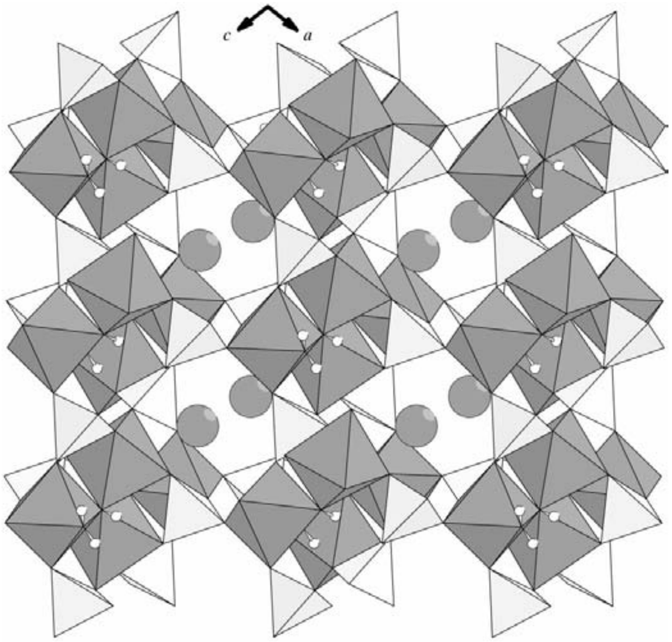

Figure 2
A polyhedral projection of the structure of (I) along [010], showing the eight-ring channels incorporating the Rb^+ cations (large grey circles). Dark-grey octahedra denote $GaO_4(OH)(OH,H_2O)$ units, light-grey tetrahedra denote PO_4 groups and small open circles denote H atoms.

The Rb^+ cation (Rb1) and a water molecule (O*W*) are encapsulated within the [010] and [001] tunnels, respectively. The Rb^+ cation is coordinated to ten O atoms, two of them belonging to the water molecules O10 and O*W*. The solvent water molecule (O*W*) is hydrogen bonded to O9 *via* H1 [O9—H1···O*W* 2.25 (1) Å] and to the ligand water molecule O10 *via* atom H2 [O10—H2···O*W* 1.988 (1) Å].

An aluminophosphate containing Rb^+ cations and which is isostructural with leucophosphite has recently been described by Nandini Devi & Vidyasagar (1999), but this compound differs in the *A*:*M* ratio (*A* is Rb and *M* is Al or Ga). This ratio was observed to be 3:4 in the aluminophosphate, whereas it is 1:2 in the present gallium-based phase, (I).

Experimental

The title compound was prepared hydrothermally from a mixture of gallium oxide, phosphoric acid, rubidium hydroxide and deionized water in the molar ratio 0.5:1:0.5:80. This mixture was sealed in a Teflon-lined Parr autoclave and then heated for 36 h at 453 K under autogenous pressure. The pH was 2 during the synthesis. After cooling to room temperature, the solid was separated from the liquid phase by filtration, washed with water and then dried in air. A single crystal of (I) was selected optically for the diffraction study and glued to a glass fibre.

Crystal data

$Rb(GaPO_4)_2(OH)(H_2O) \cdot H_2O$
$M_r = 467.89$
Monoclinic, $P2_1/n$
$a = 9.6384$ (5) Å
$b = 9.6723$ (5) Å
$c = 9.7512$ (5) Å
$\beta = 102.465$ (1)°
$V = 887.63$ (8) Å^3
$Z = 4$
$D_x = 3.501$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5336 reflections
$\theta = 2.7$–29.6°
$\mu = 11.93$ mm^{-1}
$T = 293$ (2) K
Octahedral, colourless
0.24 × 0.20 × 0.16 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{min} = 0.098$, $T_{max} = 0.148$
5966 measured reflections
2228 independent reflections
2069 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$
$\theta_{max} = 29.6°$
$h = -9 \rightarrow 13$
$k = -12 \rightarrow 11$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.062$
$S = 0.98$
2228 reflections
166 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0383P)^2 + 2.8975P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 2.47$ e Å^{-3}
$\Delta\rho_{min} = -1.57$ e Å^{-3}
Extinction correction: Larson (1970)
Extinction coefficient: 0.0047 (5)

Table 1
Principal interatomic distances (Å).

Rb1—O6^{i}	2.847 (2)	Ga1—O9^{v}	2.141 (2)
Rb1—O2	2.900 (2)	Ga2—O2	1.905 (2)
Rb1—O8	2.923 (2)	Ga2—O1	1.917 (2)
Rb1—O5	2.991 (2)	Ga2—O7	1.918 (2)
Rb1—O3^{i}	3.001 (2)	Ga2—O5	1.937 (2)
Rb1—O7^{ii}	3.017 (2)	Ga2—O10	2.018 (2)
Rb1—O1^{ii}	3.229 (2)	Ga2—O9^{vi}	2.163 (2)
Rb1—OW^{iii}	3.276 (4)	P1—O2^{vii}	1.528 (2)
Rb1—O10^{iv}	3.437 (3)	P1—O1^{viii}	1.528 (2)
Rb1—O5^{iv}	3.570 (2)	P1—O3^{i}	1.535 (2)
Ga1—O3	1.905 (2)	P1—O4	1.554 (2)
Ga1—O4	1.921 (2)	P2—O5	1.515 (2)
Ga1—O8	1.921 (2)	P2—O6^{v}	1.541 (2)
Ga1—O6	1.925 (2)	P2—O7^{ix}	1.549 (2)
Ga1—O9	2.131 (2)	P2—O8	1.551 (2)

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

Data collection: *SMART* (Siemens, 1994); cell refinement: *SMART*; data reduction: *SHELXTL* (Sheldrick, 1994); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 1996); software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1379). Services for accessing these data are described at the back of the journal.

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