inorganic compounds

RbGa₃(P₃O₁₀)₂: a new gallium phosphate isotypic with RbAl₃(P₃O₁₀)₂

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Rubidium trigallium bis(triphosphate), $RbGa_3(P_3O_{10})_2$ has been synthesized by solid-state reaction and studied by single-crystal X-ray diffraction at room temperature. This compound is the first anhydrous gallium phosphate containing both GaO_4 tetrahedra (Ga1) and GaO_6 octahedra (Ga2 and Ga3). The three independent Ga atoms are located on sites with imposed symmetry 2 (Wickoff positions $4a$ for Ga1 and $4b$ for Ga2 and Ga3). The GaO_4 and GaO_6 polyhedra are connected through the apices to triphosphate groups and form a three-dimensionnal host lattice. This framework presents inter-secting tunnels running along the [001] and <110> directions, where the Rb^{2+} cations are located on sites with imposed symmetry 2 (Wickoff position $4a$). The structure also exhibits remarkable features, such as infinite helical columns created by the junction of GaO_4 and PO_4 tetrahedra.

Comment

Against a background of synthesizing original mixed frameworks, we have explored the A_2O–M_2O_3–P_2O_5 pseudo-ternary system by solid-state reaction. M has been chosen to be a trivalent metal such as Al or Ga, which can present octahedral, tetrahedral or bipyramidal coordination, and A is a large alkaline cation such as Cs or Rb. Notably, such compounds can have applications as molecular sieves (Cheetham *et al.*, 1999; Davis, 1997). Our previous experiments using the cationic composition 10:30:60 for A:M:P led to the characterization of several new phases. In particular, for M = Al, two closely related original structures were discovered, namely CsAl₃-(P₃O₁₀)₂ and RbAl₃(P₃O₁₀)₂ (Lesage *et al.*, 2005). The gallium analogue of the caesium aluminium compound has not been synthesized, since experiments produced the pentaphosphate, *viz.* CsGa₂P₅O₁₆ (Lesage *et al.*, 2004). However, the structure of RbGa₃(P₃O₁₀)₂, which is isotypic with RbAl₃(P₃O₁₀)₂, is presented here.

The projections of the structure along c (Fig. 1) and [110] show that the Rb cation sits at the intersection of tunnels running along [001] and <110> in the $[Ga_3P_6O_{20}]_\infty$ three-dimensional framework. The latter is built from P_3O_{10} triphosphate groups, which share their corners with both GaO_4 tetrahedra and GaO_6 octahedra. More precisely, one can observe that the connection between triphosphate groups and GaO_4 tetrahedra forms infinite isolated $[GaP_6O_{20}]_\infty$ tetrahedral columns (Fig. 2). In fact, such columns are composed of helical GaP_6O_{22} elements built up of GaO_4 linked through the apices with two P_3O_{10} triphosphate groups (Fig. 3). Their junction through the 2_1 screw axis parallel to c gives rise to two interlaced infinite helical chains of tetrahedra (Fig. 2). The entire framework results from the assembly of these helical tetrahedral columns through the GaO_6 octahedra (Fig. 1).

The geometry of the P_3O_{10} group (Table 1) is close to that commonly observed in other triphosphates (Averbuch-Pouchot & Durif, 1996); as expected, the average values for PO_4 tetrahedra are 1.54 Å for P—O bonds and 109.3° for O—P—O angles. Moreover, two sets of distances can be distinguished, since the P—O bonds corresponding to the two P—O—P bridges of the P_3O_{10} group are significantly larger
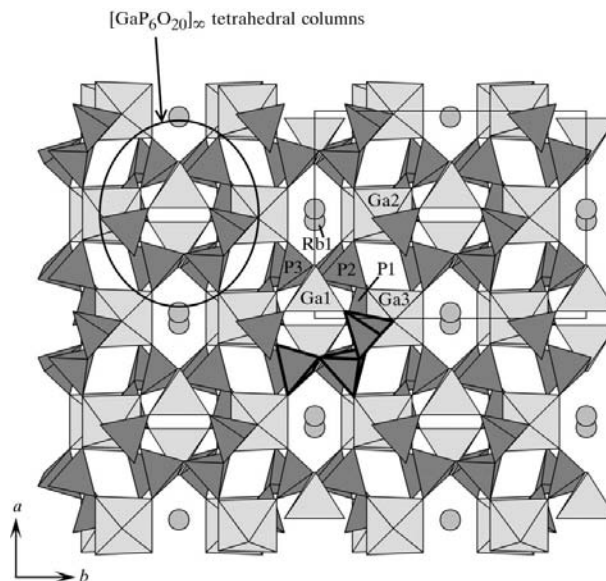

Figure 1
A projection of $RbGa_3(P_3O_{10})_2$ along c. One triphosphate group is highlighted in bold.
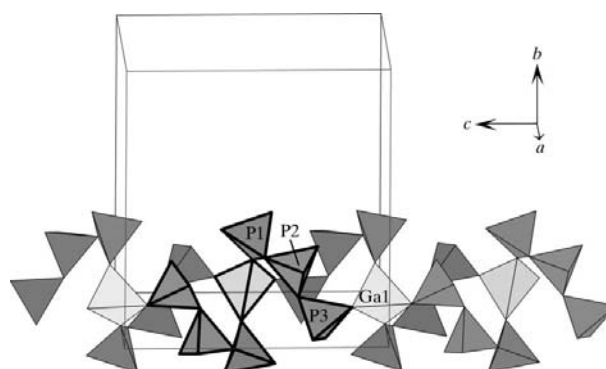
Figure 2
A perspective view of an isolated $[GaP_6O_{20}]_\infty$ tetrahedral column. One helical GaP_6O_{22} element is highlighted in bold.
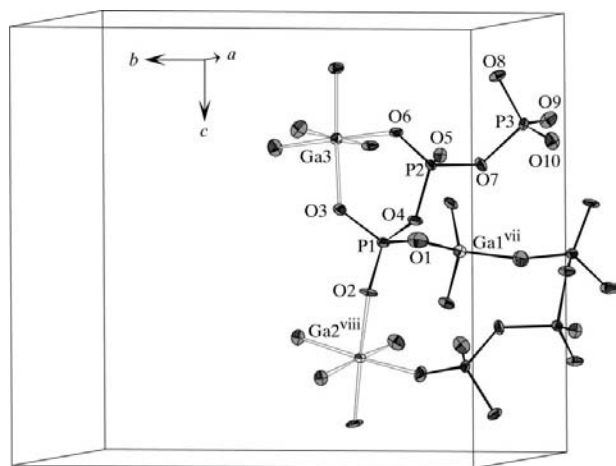
Figure 3
A perspective view of one helical GaP_6O_{22} element (filled lines) linked to two GaO_6 octahedra (unfilled lines). For clarity, only one triphosphate group has been labelled. Displacement ellipsoids are drawn at the 70% probability level. [Symmetry codes: (vii) $-x, -y, \frac{1}{2} + z$; (viii) $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z$.]

[1.591 (3)–1.632 (2) Å] than the other P—O bonds [1.485 (2)–1.540 (3) Å]. The geometries of GaO_4 and GaO_6 polyhedra are rather regular, with Ga—O distances of 1.793 (2) and 1.830 (2) Å for GaO_4, and ranging from 1.919 (2) to 1.981 (2) Å for GaO_6 (Table 1). Finally, the Rb cation is surrounded by eight O atoms, with distances ranging from 2.9764 (15) to 3.269 (2) Å. These distances are also in agreement with bond-valence-sum calculations (Brese & O'Keeffe, 1991), as reported in Table 2, since the Rb, Ga and P cations and O anions have calculated valences close to the theoretical values (1, 3, 5 and 2, respectively).

The Rb—O distances (Table 1) are very similar in the two isotypic structures, since they range from 2.958 (3) to 3.306 (2) Å for $RbAl_3(P_3O_{10})_2$. However, a significant variation in the cell volume of the two phases is observed [1579.42 (17) Å^3 for $RbGa_3(P_3O_{10})_2$ versus 1516.75 (18) Å^3 for $RbAl_3(P_3O_{10})_2$]. This is in agreement with the increase of the ionic radius of the corresponding trivalent element. This is also evidenced by examination of the Ga—O distances, which are indeed significantly larger than the Al—O distances [1.715 (3)–1.746 (2) Å in AlO_4 and 1.847 (3)–1.911 (3) Å in AlO_6].

The triphosphate groups show similar geometries in the two isotypic compounds, with average P···P distances of 2.858 and 2.845 Å, respectively, and a P···P···P angle of 126.24 and 126.32°, respectively (Table 3). This geometry is induced by the fact that the P_2O_7 group belonging to the triphosphate shares two apices with the same GaO_6 octahedron in these phases, as discussed by Lesage et al. (2005) for the $AAl_3(P_3O_{10})_2$ (A = Cs or Rb) structures (Fig. 3).

$RbGa_3(P_3O_{10})_2$ is the second gallium triphosphate after $Cs_2GaP_3O_{10}$ (Guesdon et al., 2002) to be synthesized by a solid-state reaction, i.e. not containing H atoms. Furthermore, it is noteworthy that it is the first gallium phosphate to be prepared in this way which presents two types of coordination for Ga in the same structure.

Experimental

The single crystal of $RbGa_3(P_3O_{10})_2$ used for the determination was extracted from a preparation of nominal composition $Rb_3Ga_5P_{12}O_{39}$ synthesized in two steps. First, $RbNO_3$ (Chempur, 99.9%), Ga_2O_3 (Alfa Aesar, 99.9%) and $(NH_4)_2HPO_4$ (Prolabo Normapur, 99.5%) were mixed in an agate mortar. This white mixture was placed in a platinum crucible and heated in air at about 770 K for a few hours until the correct weight loss was reached, i.e. when $RbNO_3$ and $(NH_4)_2HPO_4$ had decomposed. In a second step, the resulting powder was finely ground in an agate mortar and placed in a silica tube, which was then evacuated and sealed. The silica tube was heated at 1103 K for 20 h before being slowly cooled at a rate of 1 K h^{-1} to 1063 K and then at a rate of 10 K h^{-1} to 863 K. A white powder containing small colourless crystals was thus obtained. Semiquantitative analysis of a colourless crystal extracted from the preparation was performed with an Oxford 6650 microprobe mounted on a Philips XL30 FEG scanning electron microscope. The cationic composition obtained was in agreement with the expected theoretical value of 10:30:60 for the Rb, Ga and P cations, respectively. Several crystals were then selected optically for testing.

Crystal data

$RbGa_3(P_3O_{10})_2$	Mo $K\alpha$ radiation
$M_r = 800.5$	Cell parameters from 14 620
Orthorhombic, $C222_1$	reflections
$a = 10.0017 (8)$ Å	$\theta = 6.0–42.0°$
$b = 13.0822 (8)$ Å	$\mu = 8.88$ mm^{-1}
$c = 12.0710 (4)$ Å	$T = 298$ K
$V = 1579.42 (17)$ Å^3	Polyhedron, colourless
$Z = 4$	$0.08 \times 0.06 \times 0.05$ mm
$D_x = 3.365$ Mg m^{-3}	

Data collection

Nonius CCD area-detector diffractometer	5415 independent reflections
φ and ω scans	2778 reflections with $I > 3\sigma(I)$
Absorption correction: Gaussian (JANA2000; Petříček & Dušek, 2000)	$R_{int} = 0.088$
	$\theta_{max} = 42.0°$
	$h = -18 \rightarrow 18$
$T_{min} = 0.703$, $T_{max} = 0.849$	$k = -24 \rightarrow 24$
14 620 measured reflections	$l = -22 \rightarrow 19$

Refinement

Refinement on F	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.035$	$\Delta\rho_{max} = 1.36$ e Å^{-3}
$wR(F^2) = 0.034$	$\Delta\rho_{min} = -1.24$ e Å^{-3}
$S = 0.90$	Absolute structure: Flack & Bernardinelli (1999), with 2364 Friedel pairs
5415 reflections	
139 parameters	
$w = 1/[\sigma^2(F) + 0.0001F^2]$	Flack parameter: $-0.009 (7)$

Table 1
Selected interatomic distances (Å).

Rb1—O3^i	2.9764 (15)	P1—O1	1.516 (3)
Rb1—O5	3.208 (3)	P1—O2	1.492 (3)
Rb1—O8^{ii}	3.051 (2)	P1—O3	1.504 (2)
Rb1—O10	3.269 (2)	P1—O4	1.632 (3)
Ga1—O1^{iii}	1.793 (2)	P2—O4	1.591 (3)
Ga1—O8	1.830 (2)	P2—O5	1.492 (2)
Ga2—O2^{iv}	1.941 (2)	P2—O6	1.489 (2)
Ga2—O5	1.981 (2)	P2—O7	1.593 (3)
Ga2—O9	1.945 (2)	P3—O7	1.618 (3)
Ga3—O3	1.959 (2)	P3—O8	1.540 (3)
Ga3—O6	1.9401 (17)	P3—O9	1.485 (2)
Ga3—O10^{vi}	1.919 (2)	P3—O10	1.487 (2)

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

Table 2
Results of bond-valence-sum calculations for $RbGa_3(P_3O_{10})_2$.

	Rb1	Ga1	Ga2	Ga3	P1	P2	P3	$\Sigma(v-)$
O1		0.843 0.843			1.269			2.11
O2			0.565 0.565		1.354			1.92
O3	0.144 0.144			0.539 0.539	1.310			1.99
O4					0.927	1.036		1.96
O5	0.077 0.077		0.507 0.507			1.354		1.94
O6				0.567 0.567		1.365		1.93
O7						1.030	0.963	1.99
O8	0.118 0.118	0.763 0.763					1.189	2.07
O9			0.559 0.559				1.379	1.94
O10	0.065 0.065			0.600 0.600			1.372	2.04
$\Sigma(v+)$	0.81	3.21	3.26	3.41	4.86	4.78	4.90	

Table 3
Comparison of the geometry (Å, °) of the P_3O_{10} triphosphate groups in $RbGa_3(P_3O_{10})_2$ and $RbAl_3(P_3O_{10})_2$.

	$RbGa_3(P_3O_{10})_2$†	$RbAl_3(P_3O_{10})_2$‡
P1—P2	2.8541 (11)	2.8344 (11)
P2—P3	2.8619 (11)	2.8556 (12)
P1—P2—P3	126.24 (3)	126.32 (4)

† This work.   ‡ Lesage *et al.* (2005).

Three crystals were studied. The structure was determined using the heavy-atom method and successive difference and Fourier syntheses for the first crystal, then starting from the data previously determined for the other two crystals. The existence conditions hkl: $h + k = 2n$ and $00l$: $l = 2n$ are consistent with the non-centrosymmetric space group $C222_1$ (No. 20). As a consequence, the compound may adopt two enantiomorphic structures. Structure determinations and refinements showed that one of the crystals studied is a pure enan-tiomorph, whereas the other two are twinned by inversion. We present here only the results for the pure enantiomorph. The Flack parameter (Flack & Bernardinelli, 1999) was refined to −0.009 (7). For the other two crystals, the results of which are not presented here, the Flack parameter is close to 0.5. The harmonic displacement parameters also have significantly higher values in the twinned crystals than in the pure one, with $U_{iso,eq} \simeq 0.02$ Å^2 instead of 0.01 Å^2 for the O atoms.

Data collection: *EVALCCD* (Duisenberg *et al.*, 2003); cell refinement: *EVALCCD*; data reduction: *JANA2000* (Petříček & Dušek, 2000); program(s) used to solve structure: *JANA2000*; program(s) used to refine structure: *JANA2000*; molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *JANA2000*.

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