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Notes

$Rb_2[Ga_4(HPO_4)(PO_4)_4]\cdot 0.5H_2O$: A New Gallium Phosphate Containing Four-, Five, and Six-Coordinated Gallium Atoms

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Introduction

Aluminum phosphates have been extensively studied because they find applications in such diverse fields as catalysis, corrosion protection, and medicine.[1] Gallium phosphates have also been the subject of numerous studies in order to discover new materials with open-framework structures. The replacement of aluminum by gallium yields both novel structures[2−8] and phases that are analogous to known aluminum phosphates.[9−14] Gallium phosphates have a rich structural chemistry due to the propensity of gallium to adopt a more variable and expanded coordination environment compared to alluminum. Most of the gallium phosphates reported to date have Ga:P ratios of 1:1. Recently, a novel gallium phosphate, $[Me_2NH(CH_2)_2NHMe_2][Ga_4P_5O_{20}H]\cdot H_2O$,[8] with a Ga:P ratio of 4:5 was reported. Its 3D framework consists of GaO_4 tetrahedra, GaO_6 octahedra, and phosphate tetrahedra which, by sharing corners, form an open structure containing large cavities that house the organic cations. Here I report the synthesis and characterization of $Rb_2[Ga_4(HPO_4)(PO_4)_4]\cdot 0.5H_2O$, of which the structure is unique and consists of four-, five-, and six-coordinated gallium atoms, although its framework stoichiometry is identical with that of the organically templated gallium phosphate.

Experimental Section

Synthesis and Initial Characterization. High temperature, high pressure hydrothermal synthesis was performed in gold ampules contained in a Leco Tem-Pres autoclave where pressure was provided by water. Colorless acicular crystals of $Rb_2[Ga_4(HPO_4)(PO_4)_4]\cdot 0.5H_2O$ with a small amount of colorless equant crystals of $GaPO_4$ were obtained by heating RbH_2PO_4 (0.375 mL, 3 M), H_3PO_4 (0.375 mL, 3 M) and Ga_2O_3 (0.0937 g) (molar ratio Rb: P = 0.5) in a sealed gold ampule (7 cm × 0.485 cm inside diameter) at 600 °C and an estimated pressure of 35 000 psi for 40 h, cooled at 5 °C/h to 275 °C, and quenched to room temperature by removing the autoclave from the furnace. Equant $GaPO_4$ crystals were formed as the major product at the Rb:P ratio of 0.4. Energy-dispersive X-ray fluorescence analysis of several acicular crystals established the presence of Rb, Ga, and P. The distinct shape of $Rb_2[Ga_4(HPO_4)(PO_4)_4]\cdot 0.5H_2O$ crystals allowed for hand sorting of enough sample for further measurements. The X-ray powder pattern of a powdered sample of manually selected acicular crystals agreed well with that calculated from single-crystal data.

Table 1. Crystallographic Data for $Rb_2[Ga_4(HPO_4)(PO_4)_4]\cdot 0.5H_2O$

empirical formula	$Ga_4H_2O_{20.5}P_5Rb_2$	V, Å^3	898.45(6)
fw	934.685	Z	2
color; habit	colorless; acicular	D_{calc}, g cm^{-3}	3.455
size, mm	0.05 × 0.05 × 0.65	T, °C	23
cryst syst	monoclinic	λ(Mo Kα), Å	0.710 73
space group	$P2_1$ (No. 4)	μ(Mo Kα), cm^{-1}	118.7
a, Å	5.0607(1)	T_{min}, T_{max}	0.551, 0.941
b, Å	21.6431(6)	R^a	0.048
c, Å	8.2067(2)	$R_w{}^b$	0.056
β, deg	91.768(1)		

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. Weighting scheme $w^{-1} = \sigma^2(F) + gF^2$, where $g = 0.000\,652$.

Thermogravimetric analysis (TGA) for $Rb_2[Ga_4(HPO_4)(PO_4)_4]\cdot 0.5H_2O$ was performed on a Perkin Elmer TGA7 thermal analyzer: the sample was heated to 950 °C at 10 °C/min in air. Infrared data were collected on a Perkin-Elmer 882 infrared spectrometer (KBr method). Second harmonic generation (SHG) response of powder $Rb_2[Ga_4(HPO_4)(PO_4)_4]\cdot 0.5H_2O$ was measured in a reflection mode. A Q-switch pulsed Nd:YAG laser (Continuum Powerlite 8020) operating at 1064 nm with a repetition rate of 20 Hz and a pulse width of 6−8 ns was used as source radiation. The average power incident on the reflector was 10−20 mW before focus. The sample was loaded in a capillary of inner diameter 1 mm.

Single-Crystal X-ray Diffraction. Most of the acicular crystals were not suitable for single-crystal X-ray structure analysis as indicated from peak profile analysis. Many were selected before a satisfactory crystal was obtained. A crystal of dimensions 0.05 × 0.05 × 0.65 mm was mounted on a Siemens Smart-CCD diffractometer equipped with a normal focus, 3 kW sealed tube X-ray source. Intensity data were collected in 1271 frames with increasing ω (width of 0.3° per frame). The orientation matrix and unit cell dimensions were determined by a least-squares fit of 3440 reflections with $50 > 2\theta > 5°$. Octants collected: $\pm h, \pm k, +l$. 2θ range: 2−53.5°. Agreement between equivalent reflections (R_{int}): 0.033. Absorption correction was based on 2377 symmetry-equivalent reflections using the SHELXTL PC program package (T_{min}, T_{max} = 0.551, 0.941). The structure was solved by direct methods (SHELXTL-PLUS): the metal and phosphorus atoms were first located, and all the oxygen atoms were found in difference Fourier maps. The O(21) position, which was at a distance of 2.76 and 2.93 Å from Rb(2), refined to an occupancy of 0.48(4). Bond-valence calculations indicated that O(20) and O(21) had valence sums of 1.36 and 0.43, respectively, and all other oxygen atoms had values close to 2. These values indicated that O(20) was a hydroxo oxygen and O(21) was the oxygen atom of a half-occupied water molecule. The hydrogen atoms could not be located from difference Fourier maps. The presence of hydrogen bonding was not detected because the observed O(20)···O and O(21)···O distances were longer than the van der Waals contact distance, 2.8 Å.[15] Refinement (2197 unique reflections and 184 parameters) was performed by full-matrix least-squares analysis, with anisotropic thermal parameters for all metal and phosphorus atoms and isotropic thermal parameters for all oxygen atoms. Neutral-atom scattering factors for all atoms were used.[16]

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Table 2. Atomic Coordinates and Thermal Parameters (Å^2) for $Rb_2[Ga_4(HPO_4)(PO_4)_4]\cdot 0.5H_2O$

atom	*x*	*y*	*z*	U_{eq}[a]
Rb(1)	0.9823(3)	0	0.831(2)	0.0279(6)
Rb(2)	0.0067(4)	0.7241(1)	0.4274(2)	0.0292(6)
Ga(1)	0.0423(3)	0.6795(1)	0.9800(2)	0.0102(5)
Ga(2)	0.4625(3)	0.5872(1)	0.5384(2)	0.0099(5)
Ga(3)	0.9666(3)	0.9230(1)	0.3399(2)	0.0111(6)
Ga(4)	0.4771(3)	0.8430(1)	0.8359(2)	0.0119(6)
P(1)	0.0030(8)	0.8294(2)	0.0490(5)	0.011(1)
P(2)	−0.0314(8)	0.5602(2)	0.7484(5)	0.009(1)
P(3)	0.5072(8)	0.9371(2)	0.5451(4)	0.011(1)
P(4)	0.5401(8)	0.7102(2)	0.7407(5)	0.010(1)
P(5)	−0.4609(7)	0.6249(2)	0.1743(5)	0.011(1)
O(1)	0.088(2)	0.7633(6)	0.060(1)	0.022(3)
O(2)	0.074(2)	0.8612(6)	0.214(1)	0.017(3)
O(3)	0.153(2)	0.8637(6)	−0.085(1)	0.022(3)
O(4)	−0.297(2)	0.8389(6)	0.008(1)	0.015(2)
O(5)	−0.332(2)	0.5602(6)	0.712(1)	0.014(2)
O(6)	0.069(2)	0.4938(5)	0.780(1)	0.008(2)
O(7)	0.027(2)	0.5931(6)	0.909(1)	0.013(2)
O(8)	0.109(2)	0.5874(6)	0.600(1)	0.013(3)
O(9)	0.561(2)	0.9131(6)	0.717(1)	0.017(3)
O(10)	0.609(2)	0.0021(6)	0.541(1)	0.016(2)
O(11)	0.205(2)	0.9319(6)	0.513(1)	0.014(2)
O(12)	0.651(2)	0.8969(6)	0.423(1)	0.021(3)
O(13)	0.369(2)	0.6838(6)	0.870(1)	0.015(2)
O(14)	0.498(2)	0.6745(6)	0.579(1)	0.017(2)
O(15)	0.472(2)	0.7780(7)	0.699(1)	0.023(3)
O(16)	0.837(2)	0.7082(5)	0.792(1)	0.014(3)
O(17)	−0.258(2)	0.6694(5)	0.123(1)	0.009(2)
O(18)	−0.375(2)	0.5983(5)	0.344(1)	0.017(3)
O(19)	−0.738(2)	0.6517(5)	0.171(1)	0.015(2)
O(20)	−0.459(2)	0.5648(6)	0.064(1)	0.015(2)
O(21)[b]	−0.517(5)	0.771(2)	0.328(3)	0.037(8)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. All oxygen atoms were refined with isotropic thermal parameters. [b] The occupancy factor for O(21) is 0.5.

Table 3. Bond Lengths (Å) for $Rb_2[Ga_4(HPO_4)(PO_4)_4]\cdot 0.5H_2O$

Rb(1)−O(10)	2.991(0.011)	Rb(1)−O(3)	3.145(0.013)
Rb(1)−O(6)	3.213(0.009)	Rb(1)−O(9)	2.972(0.012)
Rb(1)−O(9)	3.630(0.012)	Rb(1)−O(11)	3.231(0.011)
Rb(1)−O(18)	3.273(0.011)	Rb(1)−O(19)	3.509(0.011)
Rb(1)−O(20)	3.141(0.011)	Rb(1)−O(20)	2.900(0.011)
Rb(2)−O(1)	3.171(0.012)	Rb(2)−O(2)	3.466(0.012)
Rb(2)−O(8)	3.316(0.013)	Rb(2)−O(14)	2.949(0.011)
Rb(2)−O(15)	3.401(0.012)	Rb(2)−O(17)	3.038(0.010)
Rb(2)−O(18)	3.398(0.012)	Rb(2)−O(21)[a]	2.930(0.028)
Rb(2)−O(14)	3.087(0.012)	Rb(2)−O(16)	3.158(0.011)
Rb(2)−O(19)	2.954(0.011)	Rb(2)−O(21)[a]	2.760(0.029)
Ga(1)−O(7)	1.960(0.013)	Ga(1)−O(13)	1.908(0.011)
Ga(1)−O(1)	1.941(0.014)	Ga(1)−O(16)	1.936(0.011)
Ga(1)−O(17)	1.959(0.010)	Ga(1)−O(19)	1.986(0.011)
Ga(2)−O(8)	1.872(0.010)	Ga(2)−O(14)	1.926(0.014)
Ga(2)−O(5)	1.836(0.011)	Ga(2)−O(10)	1.984(0.013)
Ga(2)−O(18)	1.836(0.011)	Ga(3)−O(12)	1.845(0.013)
Ga(3)−O(2)	1.785(0.012)	Ga(3)−O(6)	1.829(0.011)
Ga(3)−O(11)	1.846(0.010)	Ga(4)−O(9)	1.863(0.012)
Ga(4)−O(15)	1.797(0.014)	Ga(4)−O(3)	1.836(0.012)
Ga(4)−O(4)	1.792(0.010)		
P(1)−O(1)	1.497(0.015)	P(1)−O(2)	1.550(0.012)
P(1)−O(3)	1.548(0.013)	P(1)−O(4)	1.557(0.011)
P(2)−O(5)	1.539(0.011)	P(2)−O(6)	1.544(0.012)
P(2)−O(7)	1.516(0.012)	P(2)−O(8)	1.544(0.012)
P(3)−O(9)	1.517(0.012)	P(3)−O(11)	1.547(0.011)
P(3)−O(12)	1.527(0.013)	P(3)−O(10)	1.499(0.014)
P(4)−O(13)	1.505(0.012)	P(4)−O(14)	1.544(0.013)
P(4)−O(15)	1.542(0.015)	P(4)−O(16)	1.546(0.011)
P(5)−O(17)	1.480(0.011)	P(5)−O(18)	1.553(0.012)
P(5)−O(19)	1.517(0.011)	P(5)−O(20)	1.585(0.013)

[a] The occupancy factor for O(21) is 0.5.

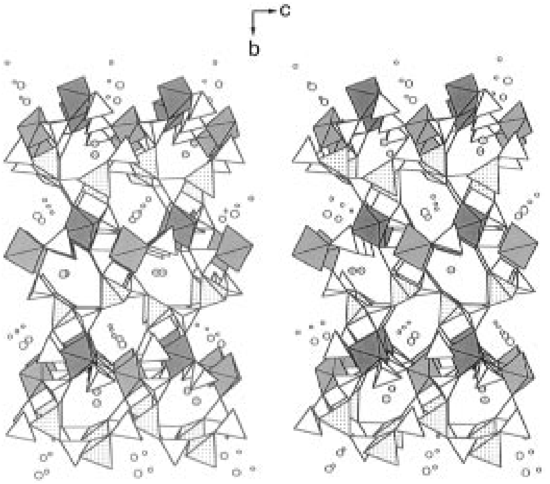

Figure 1. Stereoscopic view of the structure of $Rb_2[Ga_4(HPO_4)(PO_4)_4]\cdot 0.5H_2O$ along the [100] direction. The polyhedra, in order of increased shading, are phosphate tetrahedra, $Ga(3)O_4$ and $Ga(4)O_4$ tetrahedra, $Ga(2)O_5$ trigonal bipyramids, and $Ga(1)O_6$ octahedra. Stippled circles are Rb(1); large open circles are Rb(2); small open circles are water oxygen atoms.

Anomalous dispersion and secondary extinction corrections were applied. The absolute configuration could not be determined from the results of refining a parameter, η, which multiplied all $\Delta f''$ values. The reliability factors converged to $R = 0.0480$ and $R_w = 0.0562$. The value of extinction parameter was 0.00181. The crystallographic data are summarized in Table 1.

Results and Discussion

Physical Measurements. Thermogravimetric analysis in air showed weight loss in two steps near 250 and 600 °C. The first weight loss (0.95%) corresponds to the loss of water of hydration and can be compared with the calculated value of 0.963%. The second weight loss of 1.04% occurs at higher temperature and is attributed to the dehydration of HPO_4. The infrared spectrum shows three distinct bands at 3640, 3570, and 3350 cm^{-1}. The sharp band at 3640 cm^{-1} can be assigned to the υ(OH)-stretching of HPO_4 and suggests the absence of hydrogen bonds. The bands at 3570 (w) and 3350 cm^{-1} (br) are attributable to the lattice water molecule. The $Rb_2[Ga_4(HPO_4)(PO_4)_4]\cdot 0.5H_2O$ powder sample had a SHG signal about the same as that of quartz. The sample gave a clearly positive SHG, indicating that the structure had no center of symmetry.

Crystal Structure. The atomic coordinates, thermal parameters and bond lengths are given in Tables 2 and 3, respectively. The structure of $Rb_2[Ga_4(HPO_4)(PO_4)_4]\cdot 0.5H_2O$, viwed along the [100] direction, is shown in Figure 1. It consists of a network of Ga−O polyhedra and phosphate tetrahedra which, by sharing corners, form an open structure containing infinite channels in which the rubidium cations and water molecules reside. Of the four crystallographically distinct Ga atoms, one is octahedrally coordinated to oxygen (range of Ga(1)−O bond lengths 1.908−1.986 Å; O−Ga(1)−O bond angles 85.2−96.1°), two tetrahedrally coordinated (range of Ga−O bond lengths 1.785−1.846, 1.792−1.863 Å; O−Ga−O bond angles 107.5−112.5, 102.0−116.6°), and one trigonal bipyramidally coordinated (axial Ga(2)−O bond lengths 1.926, 1.984 Å; range of equatorial Ga(2)-O bond lengths 1.836−1.872 Å). All the vertices of Ga−O polyhedra are shared with phosphate units. All phosphate oxygen atoms except for the hydroxo group of HPO_4 are coordinated to gallium atoms. Two types of channels with eight-membered windows are formed along [100]. Each window is formed by the edges of one GaO_6 octahedron, one GaO_5 trigonal bipyramid, two GaO_4 tetrahedra, three PO_4 tetrahedra, and one HPO_4 group, and shows a strict alternation

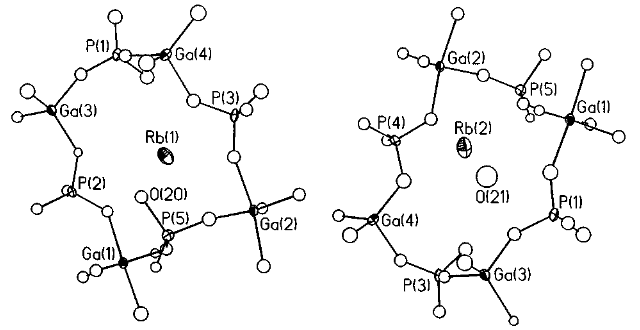

Figure 2. Windows of two types of channels in the $Rb_2[Ga_4(HPO_4)(PO_4)_4]\cdot 0.5H_2O$ structure viewed along [100]. Thermal ellipsoids are shown at 60% probability. O(20) is the hydroxo oxygen of HPO_4; O(21) is the water oxygen.

of gallium and phosphorus atoms (Figure 2). The hydroxo group of HPO_4 is directed into the channel which is occupied by Rb(1) (type 1). The second type of channel has more open space in which Rb(2) and occluded water molecule reside. The shortest O···O distances across the windows of type 1 and type 2 channels are 5.34 and 5.43 Å, respectively. Adjacent channels are interconnected through two types of lateral six-membered windows: one windiw is formed by the edges of three GaO_4 and three PO_4 tetrahedra, and the other by the edges of one GaO_6, two GaO_5, one PO_4 and two HPO_4 units. These lateral windows do not form straight channels. Cations Rb(1) and Rb(2) are nine- and ten-coordinate with repect to nearby ($d <$ 3.42 Å) oxygen atoms with $d(\mathrm{Rb{-}O})_{\mathrm{av}} = 3.089$ and 3.106 Å and bond-valence sums[17] of 1.03 and 1.08, respectively. The temperature factors of rubidium and water oxygen atoms are higher than those of the other atoms in the structure, consistent with them being extra-framework atoms.

The structure of $Rb_2[Ga_4(HPO_4)(PO_4)_4]\cdot 0.5H_2O$ is unique and is the second gallium phosphate reported to date with Ga:P ratio of 4:5. One of the most interesting structural features is the presence of GaO_6 octahedra, GaO_5 trigonal bipyramids and GaO_4 tetrahedra. In other microporous gallium phosphates most frameworks are composed of some combinations of four-, five-, or six-coordinated Ga atoms and PO_4 tetrahedra. $GaPO_4$-14 was the only known phosphate in which gallium atoms have mixed four-, five-, and six-co-ordination.[9] Although the organically templated gallium phosphate $[Me_2NH(CH_2)_2NHMe_2][Ga_4P_5O_{20}H]\cdot H_2O$ and the title compound have the same framework stoichiometry, they adopt considerably different structures. The former compound contains GaO_4 and PO_4 tetrahedra and GaO_6 octahedra, which are linked in an alternating manner to give a 3D framework structure, enclosing large cavities in which the diprotonated amine and occluded water molecules reside. Another interesting structural feature of the $[Me_2NH(CH_2)_2NHMe_2]$ salt is the large elliptical channels with puckered 16-membered windows.

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Supporting Information Available: Tables giving crystal data, anisotropic thermal parameters, and bond lengths and angles (3 pages). Ordering information is given on any current masthead pages.

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