$Ba_2GaH(P_2O_7)_2$

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Abstract

A new gallium phosphate, dibarium gallium hydrogen
bis(diphosphate), $Ba_2GaH(P_2O_7)_2$, has been synthesized
by high temperature–pressure hydrothermal reaction
and structurally characterized by single-crystal X-ray
diffraction. The structure consists of infinite chains of
corner-sharing GaO_6 octahedra and $H_{0.5}P_2O_7$ groups
linked by Ba^{2+} cations. The Ga atom lies on an inversion
center.

Comment

Gallium phosphates have shown a rich crystal chemistry
owing to the accessibility of more than one kind of coor-
dination polyhedron and the ability of Ga–O polyhedra
and phosphate tetrahedra to form a variety of complex
open-network structures. Despite the large number of
known microporous gallophosphates, the majority of
characterized AGaPO's (where A may be alkali metal or
protonated amine cations) are prepared *via* sol-gel meth-
ods or under mild hydrothermal conditions. We have
recently prepared the first microporous barium–gallium
phosphate, $Ba_2GaH(P_2O_7)_2$, under more rigorous con-
ditions, *i.e.* a temperature of 823 K and a pressure of
$\sim$2200 atm (1 atm = 101 325 Pa).

The title compound crystallizes in the triclinic system
and adopts a chain structure containing nine-coordinate
Ba, six-coordinate Ga and four-coordinate P atoms
(Fig. 1). The chains are topologically similar to that in
$Cs_2GaH_3(P_2O_7)_2$ (Gruntze *et al.*, 1988). All of the GaO_6
octahedra share the six vertices with four $H_{0.5}P_2O_7$
groups, in which the hydroxy H atom bridges two
interchain diphosphate groups. This results in polyhedral
sheets running parallel to the *ac* plane. Two types of
windows exist within the sheet: an eight-sided window,
surrounded by two GaO_6 octahedra, four $H_{0.5}PO_4$
tetrahedra and two PO_4 tetrahedra, is formed between
adjacent chains, and a four-sided window, surrounded by
two GaO_6 octahedra and two PO_4 tetrahedra, is formed
within the chains (Fig. 2). It is interesting to note that
the infinite $\{GaH(P_2O_7)_2\}_n$ chains in the Ba compound
have the same topology as the infinite $\{GaH_3(P_2O_7)_2\}_n$
chains in the Cs compound, except that the four-sided

window contains $H_{0.5}PO_4$ instead of PO_4 tetrahedra in
the latter compound. This also results in rather wide
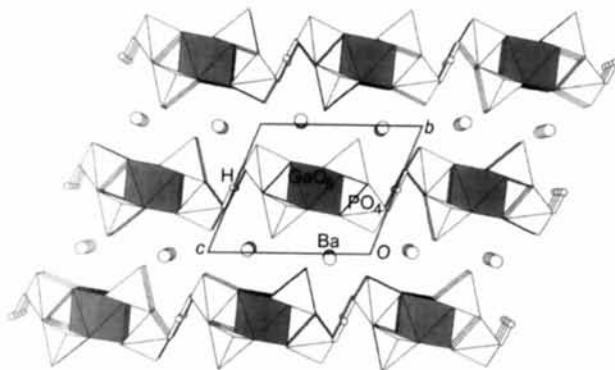six-sided windows in the Cs compound.

Fig. 1. Perspective view of the $Ba_2GaH(P_2O_7)_2$ structure down the *a*
axis; the *c* axis is horizontal. The octahedra and tetrahedra represent
GaO_6 and PO_4 groups, respectively. The large and small circles are
Ba and H atoms, respectively. The solid lines represent the O—H
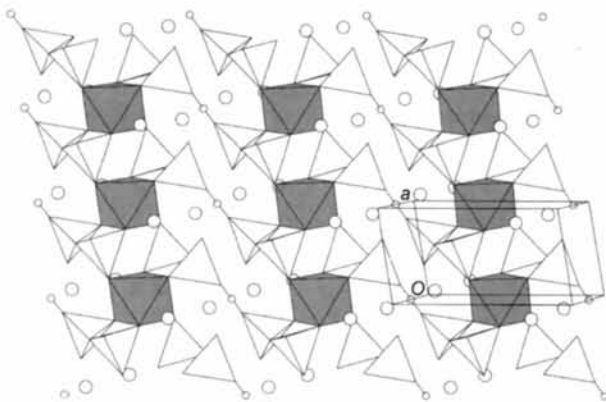bonds belonging to the $H_{0.5}PO_4$ groups.

Fig. 2. A section of a polyhedral sheet in the $Ba_2GaH(P_2O_7)_2$ structure
approximately parallel to the *ac* plane, with the *c* axis horizontal.

The H atom resides on an inversion center. The
two diphosphate groups which are linked by this H
atom belong to two chains. The two tetrahedra in the
diphosphate group are nearly in an eclipsed form, with
a P$\cdots$P distance of 2.964 Å and a P—O—P angle of
135.3°. As indicated by the thermogravimetric analysis,
one-half of a water molecule evaporated at $\sim$720 K from
two $H_{0.5}P_2O_7$ diphosphate groups.

Experimental

The hydrothermal reactions were performed in gold ampoules
contained in a Leco Tem–Pres autoclave where the pressure

was provided by water. Colorless crystals of $Ba_2GaH(P_2O_7)_2$ were obtained by reacting $Ba(OH)_2 \cdot 8H_2O$ (0.1830 g, 5.8 × 10^{-4} mol), Ga_2O_3 (0.0272 g, 1.45 × 10^{-4} mol), 3 M H_3PO_4 (0.386 ml, 1.16 × 10^{-3} mol) and water (0.054 ml, 3 × 10^{-3} mol) in a sealed gold ampoule (inner diameter: 0.485 cm) with 65% filling, and heated at 823 K and an estimated pressure of 2200 atm (1 atm = 101 325 Pa) for 8 h. The autoclave was cooled slowly (5 K h^{-1}) to 523 K and then cooled to room temperature by turning off the power to the furnace. The reaction product was obtained as a pure phase of $Ba_2GaH(P_2O_7)_2$. Thermogravimetric analysis was performed on a powder sample in flowing N_2 with a heating rate of 10 K min^{-1}.

Crystal data

$Ba_2GaH(P_2O_7)_2$	Mo $K\alpha$ radiation
$M_r = 693.29$	$\lambda = 0.71073$ Å
Triclinic	Cell parameters from 2755
$P\bar{1}$	reflections
$a = 4.7830\,(1)$ Å	$\theta = 2.57-25.00°$
$b = 7.5624\,(2)$ Å	$\mu = 10.128$ mm^{-1}
$c = 8.5690\,(2)$ Å	$T = 295$ K
$\alpha = 108.231\,(1)°$	Tabular
$\beta = 97.384\,(1)°$	$0.18 \times 0.12 \times 0.12$ mm
$\gamma = 105.236\,(1)°$	Colorless
$V = 276.43\,(2)$ Å^3	
$Z = 1$	
$D_x = 4.165$ Mg m^{-3}	
D_m not measured	

Data collection

Siemens SMART CCD diffractometer	1283 reflections with $F_o^2 > 3\sigma(F_o^2)$
ω scans	$R_{int} = 0.039$
Absorption correction: empirical (SADABS; Sheldrick, 1996)	$\theta_{max} = 28.71°$ $h = -6 \rightarrow 6$ $k = -10 \rightarrow 10$
$T_{min} = 0.163$, $T_{max} = 0.304$	$l = -11 \rightarrow 11$
2917 measured reflections	
1313 independent reflections	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.018$	$\Delta\rho_{max} = 0.77$ e Å^{-3}
$wR(F^2) = 0.047$	$\Delta\rho_{min} = -1.09$ e Å^{-3}
$S = 1.140$	Extinction correction:
1283 reflections	$F_o^* = kF_o[1 + 0.001\chi F_c^2$
98 parameters	$\times \lambda^3/\sin(2\theta)]^{-1/4}$
H-atom parameters not refined	Extinction coefficient: $\chi = 0.161$
$w = 1/[\sigma^2(F_o^2) + (0.0155P)^2 + 0.6777P]$, where $P = (F_o^2 + 2F_c^2)/3$	Scattering factors from SHELXS86 (Sheldrick, 1990)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ba1	0.14471 (4)	0.47386 (2)	0.74143 (2)	0.01141 (11)
Ga1	0	0	0	0.00717 (12)
P1	0.37741 (17)	0.17382 (11)	0.37407 (9)	0.0084 (2)
P2	0.45503 (17)	−0.18274 (12)	0.13899 (9)	0.0070 (2)
O1	0.1607 (5)	0.1548 (3)	0.4887 (3)	0.0124 (4)
O2	0.6694 (5)	0.3316 (4)	0.4667 (3)	0.0143 (4)
O3	0.2511 (5)	0.2062 (3)	0.2156 (3)	0.0108 (4)
O4	0.4215 (6)	−0.0387 (3)	0.3121 (3)	0.0129 (4)
O5	0.3449 (5)	−0.3872 (3)	0.1411 (3)	0.0123 (4)
O6	0.2599 (5)	−0.1613 (3)	−0.0051 (3)	0.0100 (4)
O7	0.2198 (5)	0.1317 (4)	−0.1320 (3)	0.0115 (4)

Table 2. *Selected distances (Å)*

Ba1—O5^i	2.672 (2)	Ga1—O3	1.983 (2)
Ba1—O1	2.718 (2)	P1—O2	1.500 (2)
Ba1—O2^{ii}	2.738 (2)	P1—O1	1.527 (2)
Ba1—O2^{iii}	2.761 (2)	P1—O3	1.531 (2)
Ba1—O6^{iv}	2.789 (2)	P1—O4	1.607 (2)
Ba1—O5^v	2.833 (2)	P2—O5	1.503 (2)
Ba1—O3^{ii}	3.136 (2)	P2—O7^{iii}	1.515 (2)
Ba1—O5^{iv}	3.182 (2)	P2—O6	1.526 (2)
Ba1—O7^{vi}	3.185 (2)	P2—O4	1.598 (2)
Ga1—O6	1.953 (2)	O1—H1	1.260 (2)
Ga1—O7	1.959 (2)		

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

The minimum in the difference map is 0.75 Å from Ba1.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXTL-Plus*.

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