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BRIEF COMMUNICATION

Synthesis and Characterization of a Three-Dimensional Gallium Phosphate, $[NH_3(CH_2)_4NH_3][Ga_4(HPO_4)(PO_4)_4]$

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A new three-dimensional gallium phosphate, $[NH_3(CH_2)_4NH_3][Ga_4(HPO_4)(PO_4)_4]$, has been synthesized under solvothermal conditions at 433 K in the presence of 1,4-diaminobutane and its structure determined using room-temperature single-crystal X-ray diffraction data ($M_r = 844.91$, monoclinic, space group $P2_1$, $a = 5.0404(2)$, $b = 22.738(3)$, $c = 9.2968(9)$ Å, $\beta = 103.800(6)°$; $V = 1034.72$ Å^3, $Z = 2$, $R = 2.77\%$, and $R_w = 3.13\%$ for 2053 observed data ($I > 3(\sigma(I))$). The structure consists of GaO_4 and PO_4 tetrahedra and GaO_5 trigonal bipyramids linked to generate an open three-dimensional framework containing 4-, 8-, and 12-membered rings of alternating gallium and phosphorus-based polyhedra. 1,4-Diaminobutane dications reside in the two-dimensional pore network and are hydrogen-bonded to the inorganic framework. © 1999 Academic Press

INTRODUCTION

Open-framework gallium phosphates (GaPOs), which have the potential to exhibit microporous behaviour, can be synthesized under mild solvothermal conditions in the presence of structure-directing agents such as organic amines and alkali-metal or complex metal cations. The resulting materials show great structural diversity, as gallium can readily adopt 4-, 5-, or 6-coordination in oxygen-based polyhedra. Although the majority of three-dimensional framework GaPOs have Ga:P ratios of 1:1, e.g., GaPO-14 (4-, 5-, and 6-coordinate gallium) (1), GaPO-21 (4- and 5-coordinate gallium) (2), and cloverite (4-coordinate gallium) (3), a few materials are known in which the Ga:P ratio differs from unity. To date these are $[Me_2NH(CH_2)_2NHMe_2][Ga_4(HPO_4)(PO_4)_4]\cdot H_2O$ (4- and 6-coordinate gallium) (4), $[NH_3(CH_2)_4NH_3]_2[Ga_4(HPO_4)_2(PO_4)_3(OH)_3]\cdot yH_2O$ (6-coordinate gallium) (5), $Na_3[Ga_5(PO_4)_4O_2(OH)_2]\cdot 2H_2O$ (5- and 6-coordinate gallium) (6), $Rb_2[Ga_4(HPO_4)(PO_4)_4]0.5H_2O$ (4-, 5-, and 6-coordinate gallium) (7), and d-$Co(en)_3[Ga_2(HPO_4)_3(PO_4)]$ (4-coordinate gallium) (8).

In the present work, we report the synthesis and characterization of $[NH_3(CH_2)_4NH_3][Ga_4(HPO_4)(PO_4)_4]$, a new three-dimensional gallium phosphate with Ga:P ratio 4:5. The framework structure, which contains GaO_4 and GaO_5 polyhedra, is very different from those of the three- and one-dimensional GaPOs $[NH_3(CH_2)_4NH_3]_2[Ga_4(HPO_4)_2(PO_4)_3(OH)_3]\cdot yH_2O$ ($y \sim 6$) (6) and $[NH_3(CH_2)_4NH_3][Ga(PO_4)(HPO_4)]$ (9), which also encapsulate 1,4-diaminobutane dications.

EXPERIMENTAL

Single crystals of the title compound, $[NH_3(CH_2)_4NH_3][Ga_4(HPO_4)(PO_4)_4]$, were prepared under solvothemal conditions. 1,4-Diaminobutane (1 cm^3) and a small amount of a mineralizer, $Si(OEt)_4$ (0.1 cm^3) (10), were added to a dispersion of Ga_2O_3 (ca. 1 g) in ethylene glycol (6 cm^3). The mixture was stirred for 10 min and orthophosphoric acid (2 cm^3, 85% by weight) was added to give a gel of overall composition Ga_2O_3: 5.4 H_3PO_4(aq): 20.2 ethylene glycol: 0.08 $Si(OEt)_4$: 1.9 1,4-diaminobutane. The gel was stirred until homogenous, sealed in a Teflon-lined stainless-steel autoclave, and heated at 433 K for 7 days. The solid product was collected by filtration, washed with water, and left to dry in air at 343 K. The product contained two components present as single crystals of quality suitable for diffraction studies; colorless rectangular blocks of $[NH_3(CH_2)_4NH_3][Ga(PO_4)(HPO_4)]$ (9) (orthorhombic, $a = 9.109(1)$, $b = 11.021(1)$, $c = 11.987(1)$ Å, space-group, $Pnaa$) and colorless rectangular plates of the title compound. The powder X-ray diffraction pattern of a bulk sample confirmed that the former phase was the major component in the product. Energy-dispersive X-ray emission analysis, performed using a JEOL 2000FX analytical electron microscope with α-$GaPO_4$ calibration standard, showed that the crystallites examined had Ga : P ratios of

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ca. 1 : 2 and 4 : 5 and contained no silicon. The synthesis was repeated several times using gels with Ga_2O_3 : 1,4-diaminobutane ratios in the range 1 : 1 to 1 : 4, but it was not possible to synthesize the title compound as a pure phase.

Room-temperature X-ray diffraction data were collected for a crystal of the title compound using an Enraf–Nonius CAD4 diffractometer (graphite-monochromated Cu$K\alpha$ radiation ($\lambda = 1.5418$Å)) (Table 1). The unit cell was determined to be monoclinic from 24 well-centered reflections over the angle range $(14 \leq \theta \leq 42)^\circ$ and the cell parameters were optimized by least-squares refinement. Intensity data were then measured using the ω–2θ scan technique. Three standard reflections were measured every hour during the data collection; no significant intensity variations were observed. Data were corrected for absorption using ψ-scans and further corrected for Lorentz and polarization effects within the program RC93 (11). The systematic absence in the data (0k0, $k = 2n$) was consistent with that required for $P2_1$ (No. 4 (12)) and $P2_1/m$ (No. 11), but successful structure solution was only possible in the former space group. The nonhydrogen framework atoms were located using the direct methods program SIR92 (13) and the carbon and nitrogen atoms of the template were subsequently found in difference Fourier maps. All Fourier calculations and least-squares refinements were carried out using the CRYSTALS suite of programs (14). It was not possible to locate the framework or template hydrogen atoms in the Fourier maps. Hydrogen atoms of the template were therefore placed geometrically. In the final cycle, 316 parameters, including anisotropic thermal parameters for all nonhydrogen framework and template atoms, were refined. A three-term Chebyshev polynomial was applied as a weighting scheme (15) and the refinement converged to give $R = 0.0277$ ($R_w = 0.0313$). Atomic coordinates and isotropic thermal parameters are given in Table 2 and selected interatomic distances and bond angles in Table 3.

TABLE 1
Crystallographic Data for $[NH_3(CH_2)_4NH_3]$ $[Ga_4(HPO_4)(PO_4)_4]$

Formula	$[NH_3(CH_2)_4NH_3][Ga_4P_5O_{20}H]$
M_r	844.91
Crystal size (mm)	0.03 × 0.06 × 0.33
Crystal habit	Fragment of colorless plate
Crystal system	Monoclinic
Space group	$P2_1$
a (Å)	5.0404(2)
b (Å)	22.738(3)
c (Å)	9.2968(9)
β (°)	103.800(6)
Cell volume (Å^3)	1034.72
Z	2
Temperature (K)	293
ρ_{calc} (gcm^{-3})	2.71
$\mu_{CuK\alpha}$ (cm^{-1})	106.67
θ_{max}	72
Scan type	ω–2θ
Unique data	2150
Observed data ($I > 3\sigma(I)$)	2053
R_{merge}	0.0209
Weighting scheme	Chebyshev 3 term
Residual electron density (min, max) (eÅ^{-3})	− 0.82, 1.21
Number of parameters refined	316
R	0.0277
R_w	0.0313

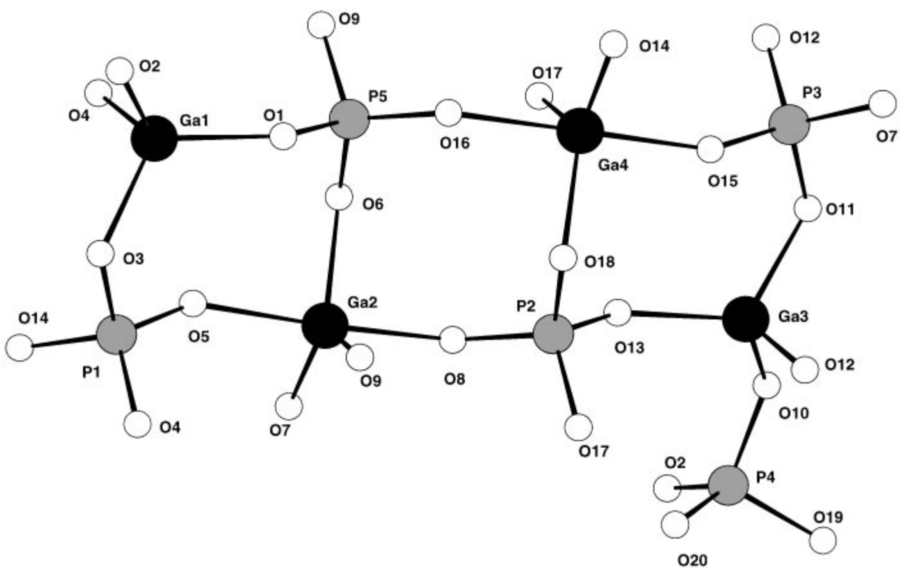

FIG. 1. The local coordination of the framework atoms in the title compound. The framework hydrogen atom is attached to O(19). Drawing package, CAMERON (16).

TABLE 2
Fractional Atomic Coordinates and Equivalent Isotropic Temperature Factors (Å^2) for $[NH_3(CH_2)_4NH_3][Ga_4(HPO_4)(PO_4)_4]$

Atom	x	y	z	U_{eq}[a]
Ga(1)	0.8195(1)	0.21119(3)	0.74583(7)	0.0109
Ga(2)	0.1796(1)	0.06307(3)	0.60166(6)	0.0090
Ga(3)	1.0681(1)	0.42714(3)	0.98302(7)	0.0111
Ga(4)	− 0.4287(1)	0.07737(3)	0.15127(7)	0.0093
P(1)	0.3500(3)	0.15500(6)	0.8777(1)	0.0091
P(2)	− 0.8839(3)	0.01690(6)	0.2691(1)	0.0087
P(3)	0.4052(3)	− 0.01722(6)	0.8770(1)	0.0100
P(4)	0.6830(3)	0.33047(6)	0.8638(1)	0.0129
P(5)	− 0.3686(3)	0.12765(6)	0.4841(1)	0.0086
O(1)	0.7649(9)	0.1866(2)	0.5561(4)	0.0140
O(2)	0.7179(9)	0.2890(2)	0.7401(4)	0.0174
O(3)	0.1796(8)	0.2140(2)	0.8515(4)	0.0143
O(4)	0.6346(8)	0.1674(2)	0.8537(5)	0.0157
O(5)	0.1892(8)	0.1105(2)	0.7780(4)	0.0129
O(6)	− 0.1983(8)	0.0751(2)	0.5481(4)	0.0138
O(7)	0.3519(8)	0.0009(2)	0.7134(4)	0.0142
O(8)	− 0.8618(9)	0.0098(2)	0.4346(4)	0.0143
O(9)	− 0.6540(8)	0.1231(2)	0.5147(4)	0.0152
O(10)	0.9654(9)	0.3506(2)	0.9561(5)	0.0179
O(11)	1.4114(8)	0.4282(2)	1.1028(4)	0.0140
O(12)	0.8708(9)	0.4679(2)	1.0927(5)	0.0193
O(13)	1.0270(8)	0.4617(2)	0.8019(4)	0.0127
O(14)	− 0.6139(8)	0.1415(2)	0.0428(4)	0.0117
O(15)	− 0.4472(8)	0.0321(2)	− 0.0238(4)	0.0144
O(16)	− 0.3905(9)	0.1367(2)	0.3198(4)	0.0129
O(17)	− 0.5967(8)	0.0230(2)	0.2435(4)	0.0123
O(18)	− 1.0473(8)	0.0727(2)	0.2046(4)	0.0132
O(19)	0.5749(9)	0.2928(2)	0.9808(5)	0.0214
O(20)	0.4957(9)	0.3802(2)	0.8028(5)	0.0217
N(1)	0.005(1)	0.2040(3)	0.1996(7)	0.0325
N(2)	0.331(1)	0.4375(2)	0.5356(6)	0.0230
C(1)	0.184(2)	0.2527(3)	0.270(1)	0.0477
C(2)	0.035(2)	0.2988(3)	0.3351(9)	0.0447
C(3)	0.259(2)	0.3419(3)	0.400(1)	0.0532
C(4)	0.132(2)	0.3948(3)	0.452(1)	0.0492

[a]Note that U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

DISCUSSION

The framework structure is assembled from a network of GaO_4, GaO_5, and PO_4 polyhedra (Fig. 1). There are four crystallographically distinct gallium atoms, of which two, Ga(1) and Ga(3), are tetrahedrally coordinated to oxygen ($Ga–O_{av} = 1.827$ Å, $(O–Ga–O)_{av} = 109.44°$) and two, Ga(2) and Ga(4), are trigonal bipyramidally coordinated (axial $Ga–O_{av} = 1.909(4)–2.042(4)$ Å, equatorial $Ga–O_{av} = 1.864$ Å). All the GaO_4 and GaO_5 polyhedra share their vertices with phosphorus-based tetrahedra. There are five crystallographically distinct PO_4 units, four of which share all vertices with either GaO_4 or GaO_5 units. The fifth, P(4), shares only two of its vertices with GaO_4 tetrahedra. Of the two terminal P(4)–O bonds, one has partial double-bond character (P(4)–O(20), 1.495(4) Å), whilst the other, rather longer bond (P(4)–O(19), 1.580(4) Å), constitutes a P–OH group. This assignment is confirmed by bond-valence calculations (17). The Ga- and P-based polyhedra are linked in an alternating manner to give an open three-dimensional framework of formula $[Ga_4(HPO_4)(PO_4)_4]^{2-}$ containing cavities in which the 1,4-diaminobutane dications reside (Fig. 2). Both nitrogen atoms of the diamino cation are within hydrogen-bonding distance of a number of framework oxygen atoms (N(1)...O distances 2.937(7), 2.999(7), and 3.028(7) Å to O(7), O(18), and O(14), respectively; N(2)...O distances 2.752(7), 2.912(6), 2.947(7), and 3.098(7) Å to O(20), O(17), O(8), and O(8′), respectively).

TABLE 3
Selected Interatomic Distances (Å) and Angles (°) for $[NH_3(CH_2)_4NH_3][Ga_4(HPO_4)(PO_4)_4]$

Ga(1)–O(1)	1.807(4)	P(1)–O(3)	1.580(4)
Ga(1)–O(2)	1.840(4)	P(1)–O(4)	1.530(4)
Ga(1)–O(3)^a	1.847(4)	P(1)–O(5)	1.477(4)
Ga(1)–O(4)	1.819(4)	P(1)–O(14)^b	1.533(4)
Ga(2)–O(5)	1.953(4)	P(2)–O(8)^c	1.525(4)
Ga(2)–O(6)	1.871(4)	P(2)–O(13)	1.517(4)
Ga(2)–O(7)	1.844(4)	P(2)–O(17)	1.528(4)
Ga(2)–O(8)^a	1.941(4)	P(2)–O(18)	1.553(4)
Ga(2)–O(9)^a	1.883(4)	P(3)–O(7)	1.536(4)
Ga(3)–O(10)	1.817(4)	P(3)–O(11)^d	1.532(4)
Ga(3)–O(11)	1.821(4)	P(3)–O(12)^e	1.522(4)
Ga(3)–O(12)	1.836(4)	P(3)–O(15)^b	1.528(4)
Ga(3)–O(13)	1.825(4)	P(4)–O(2)	1.529(4)
Ga(4)–O(14)	1.889(4)	P(4)–O(10)	1.546(4)
Ga(4)–O(15)	1.909(4)	P(4)–O(19)	1.580(4)
Ga(4)–O(16)	2.042(4)	P(4)–O(20)	1.495(4)
Ga(4)–O(17)	1.824(4)	P(5)–O(1)^f	1.576(4)
Ga(4)–O(18)^a	1.870(4)	P(5)–O(6)	1.508(4)
		P(5)–O(9)	1.535(4)
N(1)–C(1)	1.479(4)	P(5)–O(16)	1.518(4)
N(2)–C(4)	1.475(4)		
C(1)–C(2)	1.498(5)		
C(2)–C(3)	1.510(5)		
C(3)–C(4)	1.495(5)		

O(5)–Ga(2)–O(6)	87.9(2)	O(14)–Ga(4)–O(15)	92.5(2)
O(5)–Ga(2)–O(7)	92.1(2)	O(14)–Ga(4)–O(16)	81.0(2)
O(6)–Ga(2)–O(7)	125.1(2)	O(15)–Ga(4)–O(16)	170.7(2)
O(5)–Ga(2)–O(8)^a	172.9(2)	O(14)–Ga(4)–O(17)	123.3(2)
O(6)–Ga(2)–O(8)^a	88.3(2)	O(15)–Ga(4)–O(17)	95.8(2)
O(7)–Ga(2)–O(8)^a	85.4(2)	O(16)–Ga(4)–O(17)	93.3(2)
O(5)–Ga(2)–O(9)^a	92.1(2)	O(14)–Ga(4)–O(18)^a	122.1(2)
O(6)–Ga(2)–O(9)^a	108.0(2)	O(15)–Ga(4)–O(18)^a	91.9(2)
O(7)–Ga(2)–O(9)^a	126.8(2)	O(16)–Ga(4)–O(18)^a	86.1(2)
O(8)^a–Ga(2)–O(9)^a	94.7(2)	O(17)–Ga(4)–O(18)^a	113.6(2)

Note. $Ga(1)O_4$ and $Ga(3)O_4$ tetrahedra; O–Ga–O angles in the range 102.3(2)°–115.6(2)°

PO_4 tetrahedra; O–P–O angles in the range 101.6(2)°–115.4(2)°

Ga–O–P angles in the range 118.8(2)°–148.8(3)°

Symmetry transformations used to generate equivalent atoms: $^a1 + x, y, z$; $^b1 + x, y, 1 + z$; $^c - x, y - 1/2, 1 - z$; $^d2 - x, y - 1/2, 2 - z$; $^e1 - x, y - 1/2, 1 - z$; $^fx - 1, y, z$.

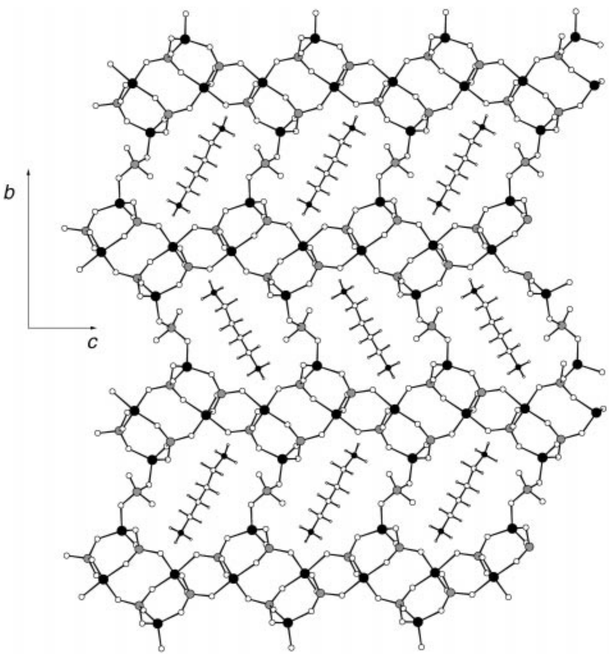

FIG. 2. View of the title compound $[NH_3(CH_2)_4NH_3][Ga(HPO_4)(PO_4)_4]$ along the *a* axis showing the 4- and 12-membered rings of gallium- and phosphorus-based polyhedra and the location of the diprotonated 1,4-diaminobutane cations.

The channels parallel to the *a* axis are elliptical and are bounded by 12-membered rings of alternating GaO_n ($n = 4,5$) and PO_4 polyhedra (cross-pore distances O(13)...O(14), 11.974(6) and O(2)...O(10), 7.809(6) Å) (Fig. 3). The hydroxo group of each $HP(4)O_4$ unit is directed into the channel and involved in hydrogen bonding to framework oxygen O(3) (O(19)...O(3), 2.735(6) Å). A second series of channels bounded by irregular 8-membered rings runs parallel to the *c*-axis. The two sets of channels intersect to generate a two-dimensional pore network.

Although $[NH_3(CH_2)_4NH_3][Ga_4(HPO_4)(PO_4)_4]$ has the same framework stoichiometry as $[Me_2NH(CH_2)_2NHMe_2][Ga_4(HPO_4)(PO_4)_4]\cdot H_2O$ (**I**) (4) and $Rb_2[Ga_4(HPO_4)(PO_4)_4]0.5H_2O$ (**II**) (7), the structure is, to date, unique. The title compound is constructed from GaO_4 and GaO_5 polyhedra and contains elliptical channels bounded by 12-membered rings. Compound (**I**), built from GaO_4 and GaO_6 polyhedra, also contains elliptical channels but these are bounded by 16-membered rings (cross-pore O...O distances $\sim 16.50 \times 6.65$ Å). Compound (**II**), built from GaO_4, GaO_5 and GaO_6 polyhedra, contains circular channels which have a ring size of 8 and diameter $\sim$5.4Å. A further GaPO with Ga:P 4:5, $[NH_3(CH_2)_4NH_3]_2[Ga_4(HPO_4)_2(PO_4)_3(OH)_3]\,.\,yH_2O$ (6), contains only octahedrally coordinated gallium and has 20-ring windows (cross pore O...O distances $\sim 13.37 \times 7.35$ Å). The latter material, which also uses 1, 4-diaminobutane as the structure directing agent, was prepared under aqueous conditions rather than the essentially nonaqueous conditions described in the present work. The one-dimensional material $[NH_3(CH_2)_4NH_3][Ga(PO_4)(HPO_4)]$ (9), which is built entirely from tetrahedral GaO_4 and PO_4 units, is a major product of both syntheses.

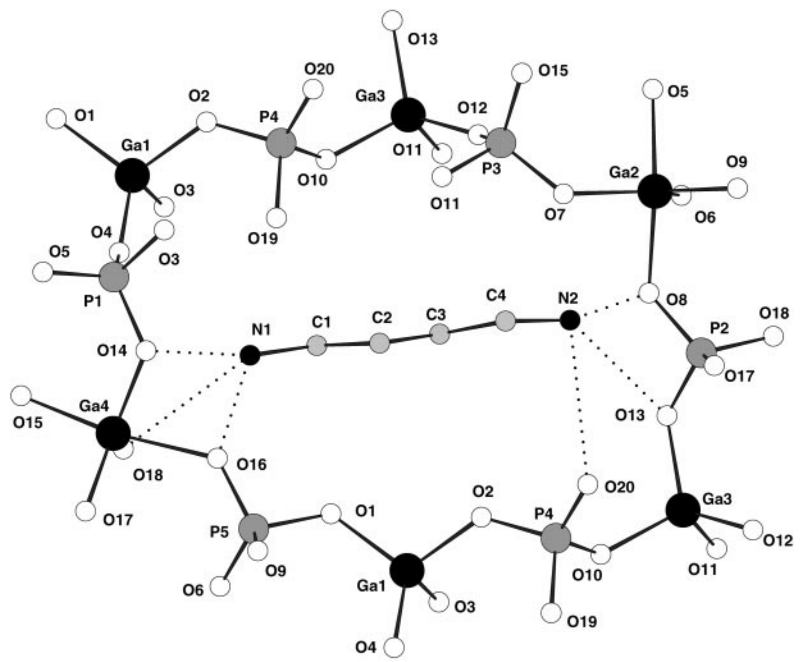

FIG. 3. View of the 12-membered ring of alternating GaO_n ($n = 4,5$) and PO_4 polyhedra. The intraframework and framework-diamine hydrogen bonds are shown as dotted lines (the framework hydrogen atom attached to O(19) is omitted).

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