

# Synthesis and Characterization of a Large-Pore, Open-Framework Gallium Phosphate, $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3]_2[\text{Ga}_4(\text{HPO}_4)_2(\text{PO}_4)_3(\text{OH})_3] \cdot y\text{H}_2\text{O}$ ( $y \sim 5.4$ ), and Its Vanadium–Gallium Phosphate Analogue, $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3]_2[\text{Ga}_{4-x}\text{V}_x(\text{HPO}_4)_2(\text{PO}_4)_3(\text{OH})_3] \cdot y\text{H}_2\text{O}$ ( $x \sim 0.4$ , $y \sim 6$ )

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IN HONOR OF PROFESSOR PETER DAY, F.R.S., ON THE OCCASION OF HIS SIXTIETH BIRTHDAY

A new three-dimensional gallium phosphate,  $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3]_2[\text{Ga}_4(\text{HPO}_4)_2(\text{PO}_4)_3(\text{OH})_3] \cdot y\text{H}_2\text{O}$  ( $y \sim 5.4$ ), has been synthesized under hydrothermal conditions at 433 K in the presence of 1,4-diaminobutane and its structure determined using room-temperature single-crystal X-ray diffraction data ( $M_r = 1084.03$ , tetragonal, space group  $I4_1/a$ ,  $a = 15.261(1)$ ,  $c = 28.898(2)$  Å;  $V = 6730.4$  Å<sup>3</sup>,  $Z = 8$ ,  $R = 4.09\%$  and  $R_w = 4.45\%$  for 3093 observed data ( $I > 3(\sigma(I))$ ). The structure consists of chains of  $\text{GaO}_6$  octahedra and  $\text{PO}_4$  tetrahedra cross-linked by additional  $\text{PO}_4$  tetrahedra to generate a three-dimensional framework containing large tunnels in which 1,4-diaminobutane dications and water molecules reside. The tunnels are bounded by 20-ring windows of alternating gallium- and phosphorus-based polyhedra. The framework is closely related to that of a 1,3-diaminopropane encapsulating iron (III) phosphate,  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]_2[\text{Fe}_4(\text{HPO}_4)_2(\text{PO}_4)_3(\text{OH})_3] \cdot y\text{H}_2\text{O}$  ( $y \sim 9$ ). Further syntheses in the presence of  $\text{V}_2\text{O}_5$  show that up to 12% of the Ga(III) can be replaced by V(III) with retention of the large-pore framework structure. © 1999 Academic Press

## INTRODUCTION

A number of open-framework gallium phosphates (GaPOs) have now been synthesized under mild solvothermal conditions using organic amines or diamines as structure-directing agents. Gallium can exhibit 4-, 5-, or 6-coordination in oxygen-based polyhedra within these materials, leading to a wide range of structure types. The majority of the three-dimensional framework GaPOs characterized to date have Ga:P ratios of 1:1 and some, e.g., GaPO-14 (4-, 5-, and 6-coordinate gallium) (1), GaPO-21 (4- and 5-coordinated gallium) (2), and GaPO-25 (4-coordinate gallium) (3), are structural analogues of aluminum phos-

phates (AlPOs). There are also some gallium phosphate frameworks such as cloverite (4) which remain, as yet, unique. The latter has a particularly interesting structure containing large apertures bounded by “20 ring windows” of alternating  $\text{GaO}_4$  and  $\text{PO}_4$  tetrahedra. A few three-dimensional GaPOs also exist in which the Ga:P ratio differs from unity. Only one of these,  $[\text{Me}_2\text{NH}(\text{CH}_2)_2\text{NHMe}_2][\text{Ga}_4\text{P}_5\text{O}_{20}\text{H}] \cdot \text{H}_2\text{O}$  (4- and 6-coordinate gallium) (5), encapsulates organic species within the pores. The remainder,  $\text{Na}_3\text{Ga}_5\text{P}_4\text{O}_{18}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$  (5- and 6-coordinate gallium) (6),  $\text{Rb}_2[\text{Ga}_4\text{P}_5\text{O}_{20}\text{H}]0.5\text{H}_2\text{O}$  (4-, 5-, and 6-coordinate gallium) (7), and  $d\text{-Co(en)}_3[\text{H}_3\text{Ga}_2\text{P}_4\text{O}_{16}]$  (4-coordinate gallium) (8), incorporate either alkali-metal or complex metal cations.

It is well known that the inclusion of heteroatoms in open-framework phosphates can lead to the modification of the physical and chemical properties of the parent compounds. A range of transition metals have recently been incorporated into gallium phosphate frameworks to give *Me*GaPOs (*Me* = Mn, Fe, Co, Zn) with both zeolitic and new structure types; e.g.,  $(\text{C}_5\text{NH}_6)[\text{MeGa}_2\text{P}_3\text{O}_{12}]$  (*Me* = Mn, Fe, Co, Zn) (9, 10) and  $[\text{C}_4\text{NH}_{10}][\text{MeGaP}_2\text{O}_8]$  (*Me* = Co, Zn) (11,12) are structural analogues of laumontite and gismondine, respectively, whereas  $[\text{C}_6\text{N}_2\text{H}_{14}]_2[\text{Me}_4\text{Ga}_5\text{P}_9\text{O}_{36}]$  (*Me* = Co, Zn) (13, 14),  $[\text{C}_7\text{NH}_{14}][\text{MeGa}_3\text{P}_4\text{O}_{16}]$  (*Me* = Co, Zn) (14, 15), and the series UCSB-6, -8 and -10 (16) have new structure types.

In the present work, we report the synthesis and characterization of  $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3]_2[\text{Ga}_4(\text{HPO}_4)_2(\text{PO}_4)_3(\text{OH})_3] \cdot y\text{H}_2\text{O}$  ( $y \sim 5.4$ ), a new three-dimensional gallium phosphate made in the presence of 1,4-diaminobutane. To our knowledge, this is the first GaPO with Ga:P ratio 4:5 containing  $\text{GaO}_6$  octahedra as the only gallium polyhedra. In addition, we show that it is possible to replace up to ~12% of the gallium with vanadium to produce a new

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VGaPO. The structures of both materials, which closely resemble that of an iron phosphate,  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]_2[\text{Fe}_4(\text{HPO}_4)_2(\text{PO}_4)_3(\text{OH})_3] \cdot y\text{H}_2\text{O}$  ( $y \sim 9$ ) prepared by Lii and Huang (17), contains large apertures bounded by 20-ring windows of alternating  $\text{FeO}_6$  and  $\text{PO}_4$  polyhedra in which the diaminocations and water molecules reside.

## EXPERIMENTAL

### Synthesis and Initial Characterization

Single crystals of the title compound,  $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3]_2[\text{Ga}_4(\text{HPO}_4)_2(\text{PO}_4)_3(\text{OH})_3] \cdot y\text{H}_2\text{O}$ , were prepared under hydrothermal conditions (Reaction (i), Table 1).  $\text{Ga}_2\text{O}_3$  (ca. 0.345 g) was dispersed in water by stirring and a small amount of  $\text{Si}(\text{OEt})_4$ , which acts as a mineralizer (18), was added. Aqueous  $\text{H}_3\text{PO}_4$  (85% by weight) and 1,4-diaminobutane were then added, and the gel was stirred until homogenous, sealed in a Teflon-lined stainless-steel autoclave, and heated at 433K for 7 days. A new Teflon liner was used for this reaction. The solid products were collected by filtration, washed with water, and left to dry in air at 343K.

The vanadium-substituted analogue,  $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3]_2[\text{Ga}_{4-x}\text{V}_x(\text{HPO}_4)_2(\text{PO}_4)_3(\text{OH})_3] \cdot y\text{H}_2\text{O}$ , can be synthesized either as single crystals (Reaction (ii)) or as polycrystalline powder (Reaction (iii)), by the addition of  $\text{V}_2\text{O}_5$  to the initial reaction mixture.  $\text{V}_2\text{O}_5$  (ca. 0.364 and 0.036 g for Reactions (ii) and (iii), respectively) was dispersed in water with 0.345 g  $\text{Ga}_2\text{O}_3$  and the above synthetic procedure repeated.

Powder X-ray diffraction patterns of the bulk products of Reactions (i)–(iii) were recorded on a Philips PW1710 diffractometer using graphite-monochromated  $\text{CuK}\alpha$  radiation ( $\lambda_1 = 1.5406\text{\AA}$ ). Energy-dispersive X-ray emission analyses were performed using a JEOL 2000FX analytical electron microscope with  $\alpha\text{-GaPO}_4$  and  $\alpha\text{-VOPO}_4 \cdot 2\text{H}_2\text{O}$  (19) as calibration standards.

The major component of the product of Reaction (i) consisted of colorless rectangular blocks of edge lengths ca. 0.3–0.5mm, together with a few colorless tetragonally elongated octahedra of the title compound. Both products were studied by single-crystal X-ray diffraction. The blocks had lattice parameters very similar to those obtained previously for  $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3][\text{Ga}(\text{PO}_4)(\text{HPO}_4)]$  (20) (orthorhombic,  $a = 9.109(1)$ ,  $b = 11.021(1)$  and  $c = 11.987(1)$  Å; space-group, *Pnaa*). The octahedra had lattice parameters previously unknown for a gallium phosphate (tetragonal,  $a = 15.261(1)$ ,  $c = 28.898(2)$  Å) but similar to those of the iron phosphate  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]_2[\text{Fe}_4(\text{HPO}_4)_2(\text{PO}_4)_3(\text{OH})_3] \cdot y\text{H}_2\text{O}$  (tetragonal,  $a = 15.401(3)$ ,  $c = 28.942(1)$  Å) (17). The single-crystal study of the GaPO is described below.

The product of Reaction (ii) consisted of very pale green tetragonally elongated octahedral crystals present as the major phase, together with some grey/green powder which could be removed by suspension in water. Several of the crystals were reserved for single-crystal X-ray diffraction studies. The lattice parameters were similar to those obtained for the new unsubstituted gallium phosphate prepared in Reaction (i) ( $a = 15.276(2)$ ,  $c = 28.929(2)$  Å). Energy-dispersive X-ray analysis of a finely ground sample of the crystals showed that each crystallite examined contained Ga, V, and P, but no Si. The P: (Ga + V) ratio was 1.22(6), in reasonable agreement with the value of 1.25 predicted from the single-crystal studies. The Ga:V ratio varied slightly from crystallite to crystallite with ~7–12% of the total metal content being vanadium (Mean composition  $\text{Ga}_{0.74(4)}\text{V}_{0.08(2)}\text{PO}_z$  (oxygen content cannot be determined by this technique)). The separated grey/green powder has yet to be identified, although it appears from the analytical electron microscopy results to contain a number of vanadium-rich gallium phosphates. The major component of the powder has P: (Ga + V) = 0.84(2) and a mean composition  $\text{V}_{1.11(5)}\text{Ga}_{0.06(3)}\text{PO}_z$ .

TABLE 1  
Summary of Gel Compositions and Reaction Products

Reaction	Gel Composition	Products
(i)	$\text{Ga}_2\text{O}_3$ : 13.5 $\text{H}_3\text{PO}_4$ : 176 $\text{H}_2\text{O}$ : 0.3 $\text{Si}(\text{OEt})_4$ : 8.7 $\text{NH}_2(\text{CH}_2)_4\text{NH}_2$	major product: $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3][\text{Ga}(\text{PO}_4)(\text{HPO}_4)]$ (single crystals) (19) minor product: $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3]_2[\text{Ga}_4(\text{HPO}_4)_2(\text{PO}_4)_3(\text{OH})_3] \cdot y\text{H}_2\text{O}$ (single crystals)
(ii)	$\text{V}_2\text{O}_5$ : $\text{Ga}_2\text{O}_3$ : 13.5 $\text{H}_3\text{PO}_4$ : 176 $\text{H}_2\text{O}$ : 0.3 $\text{Si}(\text{OEt})_4$ : 8.7 $\text{NH}_2(\text{CH}_2)_4\text{NH}_2$	major product: $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3]_2[\text{Ga}_{4-x}\text{V}_x(\text{HPO}_4)_2(\text{PO}_4)_3(\text{OH})_3] \cdot y\text{H}_2\text{O}$ (single crystals) minor product: unidentified green powder
(iii)	0.1 $\text{V}_2\text{O}_5$ : $\text{Ga}_2\text{O}_3$ : 13.5 $\text{H}_3\text{PO}_4$ : 176 $\text{H}_2\text{O}$ : 0.3 $\text{Si}(\text{OEt})_4$ : 8.7 $\text{NH}_2(\text{CH}_2)_4\text{NH}_2$	sole product: $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3]_2[\text{Ga}_{4-x}\text{V}_x(\text{HPO}_4)_2(\text{PO}_4)_3(\text{OH})_3] \cdot y\text{H}_2\text{O}$ (pure polycrystalline phase)

Reaction (iii) produced a pale-green polycrystalline sample. The powder X-ray diffraction pattern of this product (Table 2) could be indexed fully on the basis of a tetragonal unit cell with refined lattice parameters ( $a = 15.234(4)$ ,  $c = 28.908(9)$  Å) similar to those obtained from the single-crystal study of the VGaPO. Energy-dispersive X-ray analysis confirmed that the product was monophasic with an average P:(Ga + V) ratio of 1.23(6) with ~5–13% of the metal content being vanadium. Combustion analysis gave the following results: C: 7.71%; H: 3.88%; N: 4.45%. The C:N ratio is 2, confirming that the 1,4-diaminobutane is present intact in the material. Thermogravimetric analysis was performed using a Stanton Redcroft STA 1500 thermal analyser over the temperature range 293–1073 K at a heating rate of 10 K min<sup>-1</sup> under flowing nitrogen. The sample lost weight gradually in a series of poorly resolved small steps over this range with a total weight loss at 1073 K of ~24%. Assuming a mean composition of [NH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>NH<sub>3</sub>]<sub>2</sub>[Ga<sub>3.6</sub>V<sub>0.4</sub>(HPO<sub>4</sub>)<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>(OH)<sub>3</sub>]·yH<sub>2</sub>O, the weight loss corresponds to loss of the two amine and approximately six extraframework water molecules. The combustion analysis results suggest a rather different value for  $y$  (~15) and the possibility that the sample lost water on storage prior to heating cannot be ruled out. The latter behavior was observed by Lii and Huang for the iron-phosphate analogue (17).

#### Single-Crystal X-Ray Diffraction

A tetragonally elongated octahedral single crystal of the GaPO title compound from the product of Reaction (i) was mounted on a thin glass fiber using cyanoacrylate adhesive. X-ray data were collected at room temperature using an Enraf–Nonius CAD4 diffractometer (graphite-monochromated CuK $\alpha$  radiation ( $\lambda = 1.5418$  Å)). The crystallographic data are summarized in Table 3. The unit cell was determined to be tetragonal from 24 well-centered reflections over the angle range ( $22 \leq \theta \leq 27$ )° and the cell parameters were optimized by least-squares refinement ( $a = 15.261(1)$ ,  $c = 28.898(2)$  Å). Intensity data were then collected over the angle range ( $0 \leq \theta \leq 74.33$ )° using the  $\omega$ - $2\theta$  scan technique. Three standard reflections were measured every hour during the data collection and no significant intensity variations were observed. Data were corrected for absorption using  $\psi$ -scans and further corrected for Lorentz and polarization effects within the program RC93 (21).

The systematic absence conditions in the reduced data suggested that the space group was  $I4_1/a$  (No. 88 (22)), which was subsequently confirmed to be the correct choice by the successful refinement of the structure. The structure was solved by direct methods using the program SIR92 (23) and all nonhydrogen framework atoms were located. All subsequent Fourier calculations and least-squares refine-

**TABLE 2**  
Powder X-Ray Diffraction Data for [NH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>NH<sub>3</sub>]<sub>2</sub>[Ga<sub>4-x</sub>V<sub>x</sub>(HPO<sub>4</sub>)<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>(OH)<sub>3</sub>]·yH<sub>2</sub>O ( $x \sim 0.4$ ,  $y \sim 6$ )

Relative intensity	$2\theta_{\text{obs}}/\text{deg}$	$d_{\text{obs}}/\text{Å}$	$d_{\text{calc}}/\text{Å}$	$h$	$k$	$l$
100	6.405	13.789	13.877	1	0	1
2	10.065	8.781	8.799	1	1	2
5	10.685	8.273	8.287	1	0	3
1	11.435	7.732	7.743	2	0	0
4	12.075	7.324	7.340	0	0	4
8	12.940	6.836	6.837	2	0	2
4	13.200	6.702	6.726	1	2	1
1	14.570	6.075	6.079	1	1	4
3	15.745	5.624	5.629	1	2	3
2	16.220	5.460	5.468	1	0	5
6	17.370	5.101	5.102	2	2	2
6	19.205	4.618	4.615	1	3	2
1	19.915	4.455	4.450	1	2	5
5	20.370	4.356	4.358	2	2	4
4	21.040	4.219	4.218	3	2	1
2	21.590	4.113	4.107	2	0	6
19	21.975	4.042	4.043	1	3	4
7	22.770	3.902	3.901	3	2	3
8	23.145	3.840	3.839	4	0	0
3	24.050	3.697	3.693	4	1	1
3	25.025	3.555	3.558	2	1	7
14	25.600	3.477	3.475	4	1	3
18	25.940	3.432	3.431	3	1	6
9	27.115	3.286	3.287	2	0	8
5	27.620	3.227	3.225	3	0	7
4	28.190	3.163	3.164	1	0	9
5	28.770	3.101	3.101	2	4	4
1	29.260	3.050	3.049	5	0	1
1	29.685	3.007	3.006	4	0	6
11	30.570	2.922	2.923	2	1	9
3	31.565	2.832	2.832	5	2	1
4	32.315	2.768	2.769	1	4	7
4	32.995	2.713	2.710	3	4	5
4	33.645	2.662	2.662	4	4	2
3	34.415	2.604	2.604	1	0	11
3	36.365	2.469	2.469	3	5	4
3	36.855	2.437	2.436	4	1	9
4	37.645	2.388	2.387	2	6	2
1	39.030	2.306	2.307	5	3	6
2	39.570	2.276	2.274	3	6	1
5	40.815	2.209	2.210	5	4	5
3	41.705	2.164	2.164	6	2	6
1	43.080	2.098	2.099	4	6	2
1	45.515	1.991	1.989	3	7	2
2	48.005	1.894	1.895	8	0	2
1	49.080	1.855	1.855	5	6	5
2	50.595	1.803	1.803	1	8	5
1	51.535	1.772	1.772	2	4	14

Note. CuK $\alpha$ 1 Radiation. Refined tetragonal lattice parameters at 293 K:  $a = 15.234(4)$ ,  $c = 28.908(9)$  Å.

ments were carried out using the CRYSTALS suite of programs (24). The carbon and nitrogen atoms of the template and six extra-lattice water oxygen sites were located in

TABLE 3  
Crystallographic Data for  $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3]_2$   
 $[\text{Ga}_4(\text{HPO}_4)_2(\text{PO}_4)_3(\text{OH})_3] \cdot y\text{H}_2\text{O}$  ( $y \sim 5.4$ )

Formula	$[\text{NH}_3(\text{CH}_2)_4\text{NH}_3]_2[\text{Ga}_4(\text{HPO}_4)_2(\text{PO}_4)_3(\text{OH})_3] \cdot 5.38\text{H}_2\text{O}$
$M_r$	1084.03
Crystal size (mm)	$0.4 \times 0.3 \times 0.3$
Crystal habit	Colorless tetragonally-elongated octahedron
Crystal system	Tetragonal
Space group	$I4_1/a$
$a$ (Å)	15.261(1)
$c$ (Å)	28.898(2)
Cell volume (Å <sup>3</sup> )	6730.4
$Z$	8
Temperature (K)	293
$\rho_{\text{calc}}$ (gcm <sup>-3</sup> )	2.14
$\mu_{\text{CuK}\alpha}$ (cm <sup>-1</sup> )	69.3
Unique data	3437
Observed data ( $I > 3\sigma(I)$ )	3093
$R_{\text{merge}}$	0.0285
Residual electron density (min, max) (eÅ <sup>-3</sup> )	-0.67, 1.21
Number of parameters refined	226
$R$	0.0409
$R_w$	0.0445

difference Fourier maps. A common isotropic temperature was refined for the latter oxygen atoms together with their individual positions and occupancies. The total occupancy of the water sites corresponded to the composition  $y = 5.38(2)$ . It was not possible to locate any framework or template hydrogen atoms in the Fourier maps. Hydrogen atoms of the template were therefore placed geometrically.

In the final cycle, 226 parameters, including anisotropic thermal parameters for all nonhydrogen framework and template atoms, were refined. The data were corrected for extinction by the method of Larsen (25) and a three-term Chebyshev polynomial was applied as a weighting scheme (26). The refinement converged to give  $R = 0.0409$  ( $R_w = 0.0445$ ).

Fractional atomic coordinates and isotropic thermal parameters are given in Table 4 and selected bond distances and angles in Table 5. The local coordination of the framework atoms are shown in Fig. 1.

Intensity data were also collected at room temperature using the above procedure for an octahedral crystal of the VGaPO from Reaction (ii) (crystal dimensions  $0.08 \times 0.08 \times 0.11$  mm). The refined tetragonal lattice parameters were  $a = 15.267(2)$ ,  $c = 28.929(2)$  Å. The structural model shows no significant differences from that of the unsubstituted gallium phosphate (final  $R$  values,  $R = 0.0546$ ,  $R_w = 0.0587$ ).

TABLE 4  
Fractional Atomic Coordinates, Isotropic Thermal Parameters (Å<sup>2</sup>), and Site Occupancies for  $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3]_2$   
 $[\text{Ga}_4(\text{HPO}_4)_2(\text{PO}_4)_3(\text{OH})_3] \cdot y\text{H}_2\text{O}$  ( $y \sim 5.4$ )

Atom	$x$	$y$	$z$	$U(\text{iso})$	Occ <sup>a</sup>
Ga(1)	-0.00867(2)	-0.05058(2)	0.04642(1)	0.0140	
Ga(2)	0.09480(2)	-0.18008(2)	-0.05070(1)	0.0133	
P(1)	0.17514(4)	-0.02222(5)	0.00108(2)	0.0139	
P(2)	-0.07017(5)	0.04455(5)	0.13829(2)	0.0131	
P(3)	0	-0.25	0.03744(3)	0.0130	
O(1)	0.1173(1)	-0.0374(1)	0.04438(7)	0.0170	
O(2)	0.1068(1)	-0.1217(1)	-0.11098(7)	0.0192	
O(3)	-0.1305(1)	-0.0445(1)	0.03154(7)	0.0175	
O(4)	0.1785(1)	-0.2720(1)	-0.06803(7)	0.0181	
O(5)	-0.0123(1)	-0.0141(1)	0.10885(7)	0.0181	
O(6)	-0.1501(1)	-0.0141(1)	0.15368(8)	0.0213	
O(7)	0	-0.25	-0.0757(1)	0.0204	
O(8)	0.0823(1)	-0.2429(1)	0.00744(7)	0.0166	
O(9)	0.0068(1)	-0.0842(1)	-0.02483(7)	0.0161	
O(10)	-0.0094(1)	-0.1693(1)	0.06851(7)	0.0173	
O(11)	0.2619(1)	0.0166(1)	0.01672(7)	0.0191	
O(12)	0.1896(1)	-0.1092(1)	-0.02491(7)	0.0167	
O(100)	0.5594(6)	0.3257(7)	0.0906(3)	0.095(2)	0.65(1)
O(101)	0.5737(6)	0.0573(6)	-0.0194(3)	0.095(2)	0.65(1)
O(102)	0.6286(9)	0.2000(9)	0.0333(5)	0.095(2)	0.42(1)
O(103)	0.516(1)	0.2155(9)	-0.0792(5)	0.095(2)	0.38(1)
O(104)	0.587(1)	0.229(1)	-0.0013(8)	0.095(2)	0.26(1)
O(105)	0.576(1)	0.264(1)	0.0803(6)	0.095(2)	0.33(1)
N(1)	0.1560(2)	-0.0527(2)	0.1421(1)	0.0374	
N(2)	0.2516(2)	-0.3051(2)	0.0242(1)	0.0342	
C(1)	0.2429(3)	-0.0893(3)	0.1519(2)	0.0465	
C(2)	0.2538(4)	-0.1830(4)	0.1387(2)	0.0578	
C(3)	0.2446(4)	-0.1990(3)	0.0872(2)	0.0509	
C(4)	0.2612(4)	-0.2948(3)	0.0743(2)	0.0507	
H(10)	0.1543	0.0101	0.1520	0.0401	
H(11)	0.1106	-0.0865	0.1596	0.0401	
H(12)	0.1437	-0.0567	0.1082	0.0401	
H(20)	0.2540	-0.0839	0.1858	0.0631	
H(21)	0.2873	-0.0541	0.1345	0.0631	
H(30)	0.3134	-0.2027	0.1486	0.0537	
H(31)	0.2083	-0.2183	0.1551	0.0537	
H(40)	0.2879	-0.1613	0.0705	0.0541	
H(41)	0.1839	-0.1827	0.0775	0.0541	
H(50)	0.3220	-0.3118	0.0837	0.0361	
H(51)	0.2179	-0.3331	0.0906	0.0361	
H(60)	0.2624	-0.3677	0.0156	0.0361	
H(61)	0.2949	-0.2667	0.0080	0.0361	
H(62)	0.1909	-0.2881	0.0148	0.0361	

<sup>a</sup>Occupancy is 1.00 unless stated.

## RESULTS AND DISCUSSION

The gallium phosphate framework is very similar to that found in the iron phosphate,  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]_2$   $[\text{Fe}_4(\text{HPO}_4)_2(\text{PO}_4)_3(\text{OH})_3] \cdot y\text{H}_2\text{O}$  ( $y \sim 9$ ) (17) and is constructed from  $\text{GaO}_6$  octahedra and  $\text{PO}_4$  tetrahedra. The basic building unit is the  $\text{Ga}_4\text{O}_{20}$  tetramer (Fig. 1) consisting of a central pair of edge sharing  $\text{Ga}(1)\text{O}_6$  octahedra

**TABLE 5**  
**Selected Bond Distances (Å) and Angles (°) for**  
**[NH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>NH<sub>3</sub>]<sub>2</sub>[Ga<sub>4</sub>(HPO<sub>4</sub>)<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>(OH)<sub>3</sub>]·yH<sub>2</sub>O**

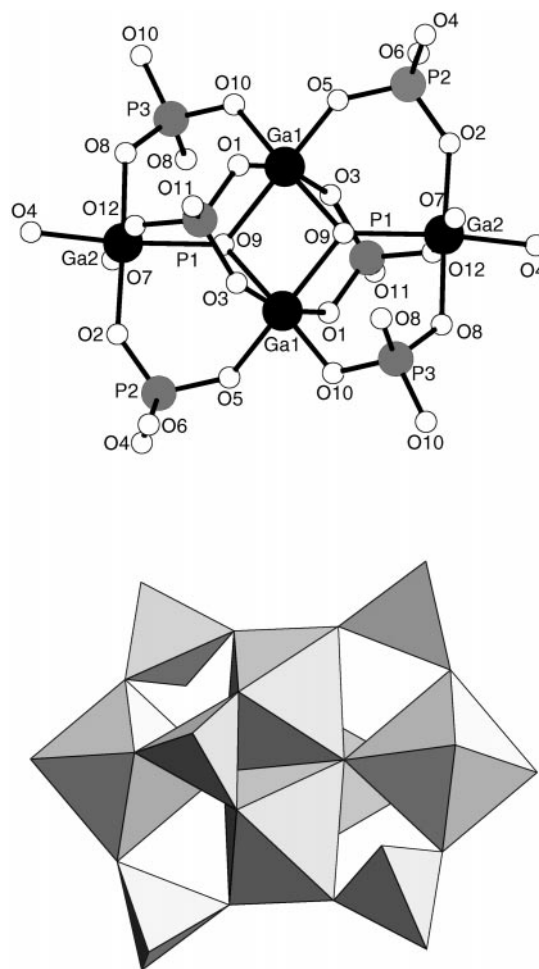
Ga(1)–O(1)	1.934(2)	Ga(2)–O(2)	1.965(2)
Ga(1)–O(3)	1.910(2)	Ga(2)–O(4)	1.963(2)
Ga(1)–O(5)	1.888(2)	Ga(2)–O(7)	1.938(2)
Ga(1)–O(9)	2.135(2)	Ga(2)–O(8)	1.944(2)
Ga(1)–O(9) <sup>a</sup>	2.150(2)	Ga(2)–O(9)	2.121(2)
Ga(1)–O(10)	1.922(2)	Ga(2)–O(12)	1.955(2)
P(1)–O(1)	1.549(2)	P(3)–O(8)	1.531(2)
P(1)–O(3) <sup>a</sup>	1.546(2)	P(3)–O(8) <sup>c</sup>	1.531(2)
P(1)–O(11)	1.519(2)	P(3)–O(10)	1.530(2)
P(1)–O(12)	1.541(2)	P(3)–O(10) <sup>c</sup>	1.530(2)
P(2)–O(2) <sup>a</sup>	1.523(2)	N(1)–C(1)	1.467(5)
P(2)–O(4) <sup>b</sup>	1.517(2)	N(2)–C(4)	1.464(6)
P(2)–O(5)	1.518(2)	C(1)–C(2)	1.489(7)
P(2)–O(6)	1.577(2)	C(2)–C(3)	1.512(8)
		C(3)–C(4)	1.530(7)
O(1)–Ga(1)–O(3)	162.83(9)	O(2)–Ga(2)–O(4)	92.14(9)
O(1)–Ga(1)–O(5)	91.59(9)	O(2)–Ga(2)–O(7)	89.3(1)
O(3)–Ga(1)–O(5)	99.92(9)	O(4)–Ga(2)–O(7)	89.84(7)
O(1)–Ga(1)–O(9)	83.41(8)	O(2)–Ga(2)–O(8)	177.38(9)
O(3)–Ga(1)–O(9)	84.41(8)	O(4)–Ga(2)–O(8)	86.07(8)
O(5)–Ga(1)–O(9)	174.37(9)	O(7)–Ga(2)–O(8)	88.7(1)
O(1)–Ga(1)–O(9) <sup>a</sup>	83.05(8)	O(2)–Ga(2)–O(9)	93.37(8)
O(3)–Ga(1)–O(9) <sup>a</sup>	84.29(8)	O(4)–Ga(2)–O(9)	174.14(8)
O(5)–Ga(1)–O(9) <sup>a</sup>	89.76(8)	O(7)–Ga(2)–O(9)	92.22(6)
O(9)–Ga(1)–O(9) <sup>a</sup>	87.07(8)	O(8)–Ga(2)–O(9)	88.49(9)
O(1)–Ga(1)–O(10)	96.51(9)	O(2)–Ga(2)–O(12)	91.02(9)
O(3)–Ga(1)–O(10)	96.64(9)	O(4)–Ga(2)–O(12)	90.63(9)
O(5)–Ga(1)–O(10)	87.72(9)	O(7)–Ga(2)–O(12)	179.39(9)
O(9)–Ga(1)–O(10)	95.39(8)	O(8)–Ga(2)–O(12)	90.92(9)
O(9) <sup>a</sup> –Ga(1)–O(10)	177.44(8)	O(14)–Ga(2)–O(12)	87.27(8)
O(1)–P(1)–O(3) <sup>a</sup>	109.9(1)	O(8)–P(3)–O(8) <sup>c</sup>	111.0(2)
O(1)–P(1)–O(11)	108.4(1)	O(8)–P(3)–O(10)	110.6(1)
O(3) <sup>a</sup> –P(1)–O(11)	108.0(1)	O(8) <sup>c</sup> –P(3)–O(10)	108.2(1)
O(1)–P(1)–O(12)	110.3(1)	O(8)–P(3)–O(10) <sup>c</sup>	108.2(1)
O(3) <sup>a</sup> –P(1)–O(12)	109.4(1)	O(8) <sup>c</sup> –P(3)–O(10) <sup>c</sup>	110.6(1)
O(11)–P(1)–O(12)	110.9(1)	O(10)–P(3)–O(10) <sup>c</sup>	108.1(2)
O(2) <sup>a</sup> –P(2)–O(4) <sup>b</sup>	113.5(1)	Ga(1)–O(1)–P(1)	127.4(1)
O(2) <sup>a</sup> –P(2)–O(5)	112.3(1)	Ga(2)–O(2)–P(2) <sup>a</sup>	140.8(1)
O(4) <sup>b</sup> –P(2)–O(5)	110.1(1)	Ga(1)–O(3)–P(1) <sup>a</sup>	126.8(1)
O(2) <sup>a</sup> –P(2)–O(6)	107.5(1)	Ga(2)–O(4)–P(2) <sup>d</sup>	137.3(1)
O(4) <sup>b</sup> –P(2)–O(6)	107.1(1)	Ga(1)–O(5)–P(2)	136.5(1)
O(5)–P(2)–O(6)	105.8(5)	Ga(2)–O(8)–P(3)	127.2(1)
Ga(2)–O(7)–Ga(2) <sup>f</sup>	136.2(2)	Ga(1)–O(10)–P(3)	124.3(1)
Ga(1)–O(9)–Ga(1) <sup>a</sup>	92.93(8)	Ga(2)–O(12)–P(1)	123.8(1)
Ga(1)–O(9)–Ga(2)	125.2(1)	Ga(2)–O(9)–Ga(2) <sup>a</sup>	123.32(9)
N(1)–C(1)–C(2)	114.7(4)	N(2)–C(4)–C(3)	109.1(4)
C(1)–C(2)–C(3)	113.3(5)	C(2)–C(3)–C(4)	112.2(4)

Note. Symmetry transformations used to generate equivalent atoms: <sup>a</sup> –x, –y, –z; <sup>b</sup> y + 1/4, 1/4 –x, z + 1/4; <sup>c</sup> –x, –y – 1/2, z; <sup>d</sup> 1/4 –y, x – 1/4, 1/4 –z.

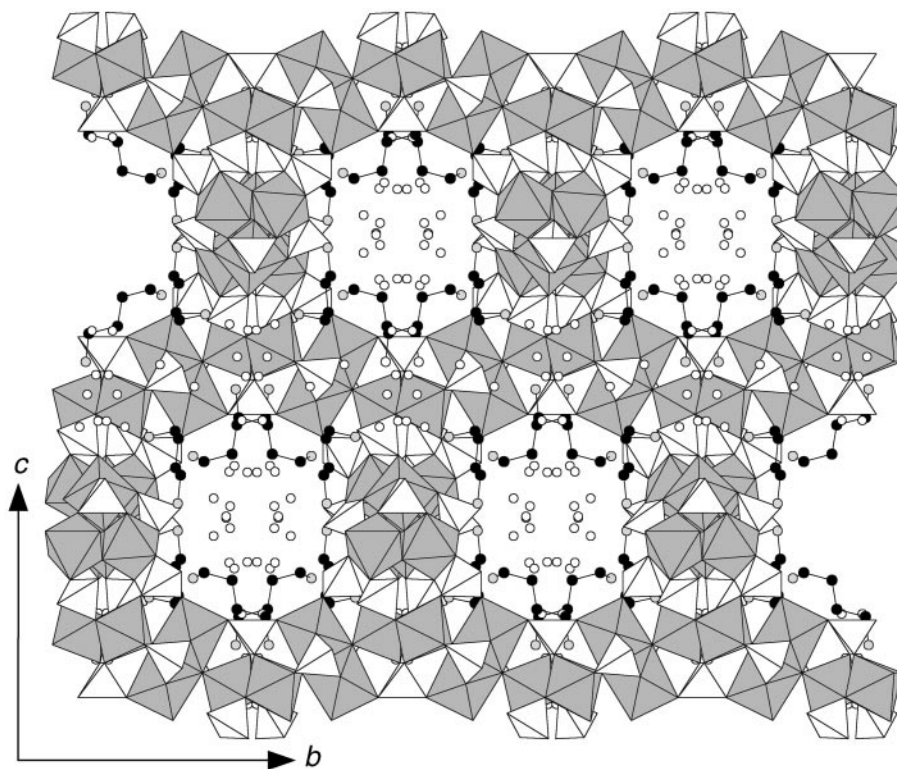
connected via O(9) atoms to which two additional Ga(2)O<sub>6</sub> octahedra are attached by corner sharing also via O(9). Both types of GaO<sub>6</sub> polyhedra have far from regular octahedral coordination, the distortion being greater in the Ga(1)O<sub>6</sub> edge-sharing units. The tetramers are in turn

linked together via Ga(2)–O(7)–Ga(2) bonds to form infinite gallium–oxygen chains running parallel to the *a* and *b* axes (<100> directions). Oxygen atoms O(7) and O(9) thus bridge two and three metal centers, respectively. The remaining oxygens in the tetramers each bond to a phosphorus atom in one of the three crystallographically distinct PO<sub>4</sub> groups. Two of the PO<sub>4</sub> groups, P(1)O<sub>4</sub> and P(2)O<sub>4</sub>, have bonds to only three adjacent metal atoms, whereas P(3)O<sub>4</sub> connects to four metal centers. For P(2)O<sub>4</sub>, the fourth P–O bond length is significantly longer than the other three (P(2)–O(6), 1.577(2) Å), implying the presence of a P(2)–O(6)H group. For P(1)O<sub>4</sub>, O(11) is bonded only to P(1), suggesting some multiple-bond character, although the P(1)–O(11) bond length is not particularly short (1.519(2) Å), partly because of a strong hydrogen bonding interaction to a neighboring P(2)–O(6)H group (O(6)···O(11), 2.629(3) Å).

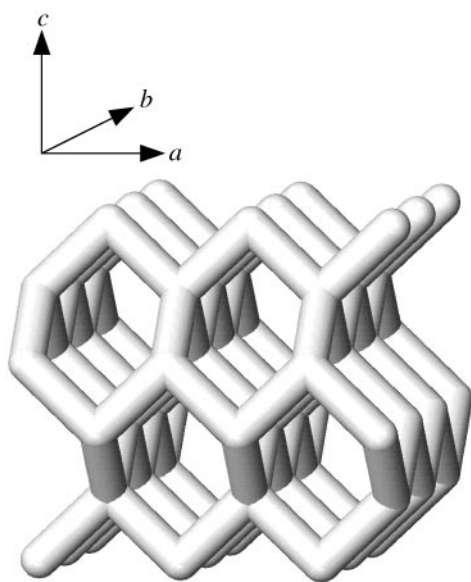
The P(2)O<sub>4</sub> units cross link the perpendicular gallium–oxygen chains to generate a three-dimensional framework structure containing large zig-zag tunnels running parallel



**FIG. 1.** “Ball and stick” and polyhedral representations of the tetrameric gallium cluster in the title GaPO. (Drawing package, ATOMS (27).)



**FIG. 2.** Polyhedral view of the title compound  $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3]_2[\text{Ga}_4(\text{HPO}_4)_2(\text{PO}_4)_3(\text{OH})_3] \cdot y\text{H}_2\text{O}$  along the  $a$  axis showing the location of the 1,4-diaminobutane dications and extra-framework water molecules (hydrogen atoms and hydrogen bonds not shown). Key:  $\text{GaO}_6$  octahedra shown shaded;  $\text{PO}_4$  tetrahedra shown unshaded; C, N, and water O atoms shown as black, gray, and white circles respectively. (Drawing package, ATOMS (27).)



**FIG. 3.** Schematic view of the pore system in the title compound showing channels as cylindrical rods. Zig-zag tunnels run parallel to the  $a$  and  $b$  axes and intersect to form a three-dimensional pore network. (Drawing package, ATOMS (27).)

to the  $a$  and  $b$  axes in which the diprotonated 1,4-diaminobutane cations and water molecules reside (Fig. 2). Each nitrogen of the diamino cation is within hydrogen bonding distance of four framework oxygens (N(1)...O distances in the range 2.895(4)–3.020(4) Å, N(2)...O distances in the range 2.794(4)–2.955(4) Å). The framework hydrogen atoms, required for charge balancing the diamino cations, could not be located in Fourier maps. However, bond-valence calculations (28) suggest that the metal bridging oxygen atoms, O(7) and O(9), are protonated, as well as O(6), to give the overall framework stoichiometry  $[\text{Ga}_4(\text{HPO}_4)_2(\text{PO}_4)_3(\text{OH})_3]^{4-}$ .

The zig-zag tunnels intersect to form an extended three-dimensional pore network (Fig. 3). Within the tunnels are 20-ring windows formed by alternating  $\text{GaO}_6$  and  $\text{PO}_4$  units (Fig. 4) with O(11)...O(11) and O(10)...O(10) cross-pore distances of 7.350(4) and 13.370(4) Å, respectively.

## CONCLUSIONS

The GaPO framework is similar to that of the iron phosphate,  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]_2[\text{Fe}_4(\text{HPO}_4)_2(\text{PO}_4)_3(\text{OH})_3] \cdot y\text{H}_2\text{O}$ , prepared previously using 1,3-diaminopropane rather than the 1,4-diaminobutane used in the

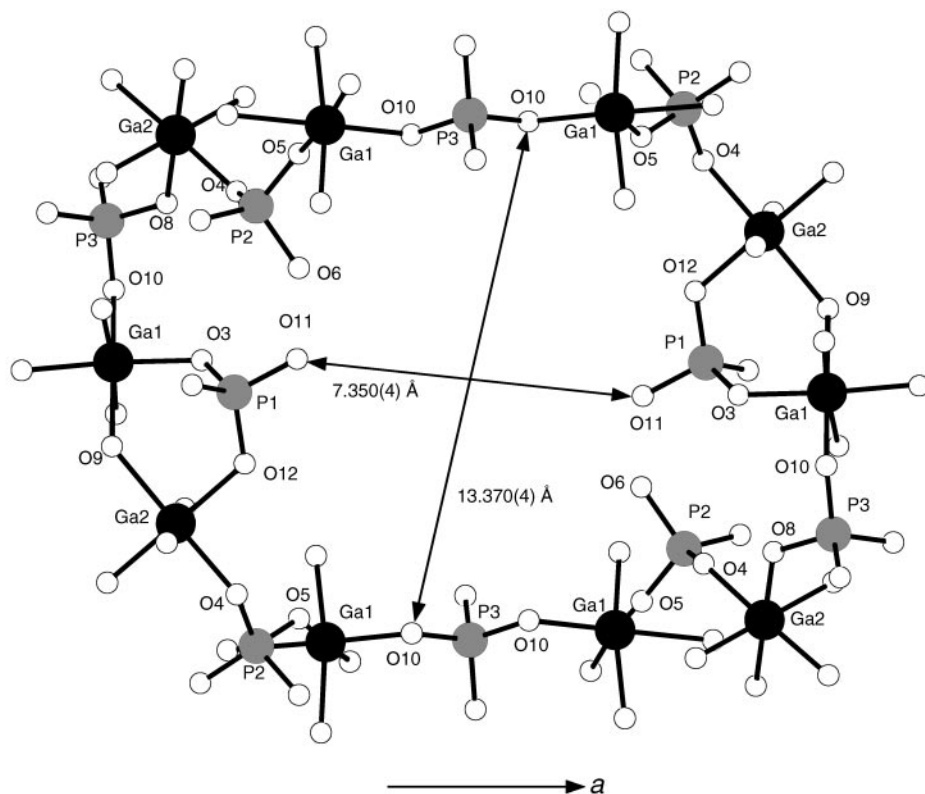


FIG. 4. View along the vector [011] of the 20-ring window constructed from alternating GaO<sub>6</sub> and PO<sub>4</sub> polyhedra. (Drawing package, ATOMS (27).)

present work. Both GaPO and FePO materials have very low framework densities of 10.7 and 10.5  $X$  atoms per 1000 Å<sup>3</sup> respectively (where  $X = (\text{Ga} + \text{P})$  or  $(\text{Fe} + \text{P})$ ), comparable with that of 11.1  $X$  atoms per 1000 Å<sup>3</sup> for the GaPO cloverite, which also contains 20-ring apertures.

The gallium–oxygen framework contains two interesting features; Ga–OH–Ga bridges, which, to our knowledge, have not been previously reported in unsubstituted GaPOs, but which have recently been identified in a fluorinated material [C<sub>10</sub>N<sub>2</sub>H<sub>10</sub>][Ga<sub>7</sub>(PO<sub>4</sub>)<sub>6</sub>F<sub>3</sub>(OH)<sub>2</sub>]·2H<sub>2</sub>O (29), and Ga<sub>4</sub>O<sub>20</sub> tetrameric units. The tetrameric units occur in other GaPO materials including NH<sub>4</sub>[Ga<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>(OH)(H<sub>2</sub>O)]·H<sub>2</sub>O (30) (isotypic with AlPO-15 (31)), GaPO<sub>4</sub>·2H<sub>2</sub>O (32), and GaPO<sub>4</sub>-C<sub>7</sub> (33), all of which have structures closely related to that of the mineral leucophospite (34,35). These materials have no Ga–OH–Ga bridges linking adjacent tetramers as in the title compound, but each corner-sharing GaO<sub>6</sub> unit has instead a terminal Ga–OH<sub>2</sub> group. The tetramers are linked solely by PO<sub>4</sub> groups to generate a three-dimensional framework structure which contains cavities bounded by 8-membered rings. The framework densities are correspondingly much higher than those of the title compound and are ~17.8  $X$  atoms per 1000 Å<sup>3</sup>.

Synthesis in the absence of vanadium in a new Teflon liner (Reaction (i)) produces the title compound in only very small amounts, the major product being [NH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>NH<sub>3</sub>][Ga(PO<sub>4</sub>)(HPO<sub>4</sub>)] (19), a one-dimensional gallium phosphate. The presence of vanadium in the synthesis mixture (even in trace amounts from a used liner once containing vanadium) appears to promote formation of the large-pore structure. It is possible to prepare either single crystals or pure polycrystalline material with the same structure as the title GaPO but incorporating ~5–12% vanadium onto the gallium sites. Given the pale-green color of the products it is likely that the vanadium is present as V<sup>3+</sup>. Reduction of V<sup>5+</sup> to V<sup>3+</sup> in the presence of an organic amine has been reported previously in the formation of VPO<sub>4</sub>·2H<sub>2</sub>O from V<sub>2</sub>O<sub>5</sub>, H<sub>3</sub>PO<sub>4</sub> and tripropylamine (36).

The incorporation of small amounts of redox-active transition metal into such a large pore material as the title compound could have important catalytic consequences and these are currently being investigated.

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