

# New Gallium Phosphate Frameworks Containing 1,4-Diaminobutane and 1,5-Diaminopentane: $[\text{NH}_3(\text{CH}_2)_x\text{NH}_3][\text{Ga}_4(\text{PO}_4)_4(\text{HPO}_4)]$ and $[\text{NH}_3(\text{CH}_2)_x\text{NH}_3][\text{Ga}(\text{PO}_4)(\text{HPO}_4)]$ ( $x = 4$ and $5$ )

Judith L. Kissick,\* Andrew R. Cowley,† and Ann M. Chippindale\*<sup>1</sup>

\*Department of Chemistry, University of Reading, Whiteknights, Reading, Berks RG6 6AD, UK; and †Chemical Crystallography Laboratory, 9 Parks Road, Oxford OX1 3PD, UK

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Two new gallium phosphates,  $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3][\text{Ga}_4(\text{PO}_4)_4(\text{HPO}_4)]$  (I) and  $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3][\text{Ga}(\text{PO}_4)(\text{HPO}_4)]$  (II), have been synthesized under solvothermal conditions in the presence of 1,4-diaminobutane and their structures determined using room-temperature single-crystal X-ray diffraction data. Compound (I) ( $M_r = 844.90$ , triclinic, space group  $P-1$ ,  $a = 9.3619(3)$ ,  $b = 10.1158(3)$  and  $c = 12.6456(5)$  Å,  $\alpha = 98.485(1)$ ,  $\beta = 107.018(2)$  and  $\gamma = 105.424(1)^\circ$ ;  $V = 1070.39$  Å<sup>3</sup>,  $Z = 2$ ,  $R = 3.68\%$  and  $R_w = 4.40\%$  for 2918 observed data [ $I > 3(\sigma(I))$ ]) consists of  $\text{GaO}_4$  and  $\text{PO}_4$  tetrahedra and  $\text{GaO}_5$  trigonal bipyramids linked to generate an open three-dimensional framework containing 4-, 6-, 8-, and 12-membered rings of alternating Ga- and P-based polyhedra. 1,4-Diaminobutane dications are located in channels bounded by the 12-membered rings in the two-dimensional pore network and are held to the framework by hydrogen bonding. Compound (II) ( $M_r = 350.84$ , monoclinic, space group  $P2_1/c$ ,  $a = 4.8922(1)$ ,  $b = 18.3638(6)$  and  $c = 13.7468(5)$  Å,  $\beta = 94.581(1)^\circ$ ;  $V = 1227.76$  Å<sup>3</sup>,  $Z = 4$ ,  $R = 2.95\%$  and  $R_w = 3.37\%$  for 2050 observed data [ $I > 3(\sigma(I))$ ]) contains chains of edge-sharing 4-membered rings of alternating  $\text{GaO}_4$  and  $\text{PO}_4$  tetrahedra constituting a backbone from which hang 'pendant'  $\text{PO}_3(\text{OH})$  groups. Hydrogen bonding between the GaPO framework and the diamine dications holds the structure together. A previously reported phase,  $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3][\text{Ga}_4(\text{PO}_4)_4(\text{HPO}_4)]$  (V), structurally related but distinct from its stoichiometric equivalent, (I), has been prepared as a pure phase by this method. Two further materials,  $[\text{NH}_3(\text{CH}_2)_5\text{NH}_3][\text{Ga}_4(\text{PO}_4)_4(\text{HPO}_4)]$  (III) (triclinic, lattice parameters from PXD:  $a = 9.3565(4)$ ,  $b = 5.0156(2)$  and  $c = 12.7065(4)$  Å,  $\alpha = 96.612(3)$ ,  $\beta = 102.747(4)$  and  $\gamma = 105.277(3)^\circ$ ) and  $[\text{NH}_3(\text{CH}_2)_5\text{NH}_3][\text{Ga}(\text{PO}_4)(\text{HPO}_4)]$  (IV) ( $M_r = 364.86$ , monoclinic, space group  $P2_1/n$ ,  $a = 4.9239(2)$ ,  $b = 13.2843(4)$  and  $c = 19.5339(7)$  Å,  $\beta = 96.858(1)^\circ$ ;  $V = 1268.58$  Å<sup>3</sup>,  $Z = 4$ ,  $R = 3.74\%$  and  $R_w = 4.44\%$  for 2224 observed room-temperature data [ $I > 3(\sigma(I))$ ]), were also prepared under similar conditions in the presence of 1,5-diamino-

pentane. (III) and (IV) are structurally related to, yet distinct from (I) and (II) respectively. © 2002 Elsevier Science (USA)

**Key Words:** solvothermal synthesis; crystal structure; single-crystal XRD; GaPO; gallium phosphate; organically templated; open-framework structure; chain structure.

## INTRODUCTION

The synthesis of new microporous materials is of continuing interest because of their potential applications as molecular sieves, ion-exchangers, solid heterogeneous catalysts and as hosts for encapsulated species used in non-linear optics and quantum electronics (1). A growing class of such materials are the metal phosphates (2) and particular interest has focused on those of aluminum and gallium since their discoveries in 1982 (3) and 1985 (4) respectively. Open-framework gallium phosphates (GaPOs) can be synthesized in solvothermal reactions using alkali metals, organic amines or diamines as structure-directing agents. As gallium can readily adopt 4-, 5-, or 6-coordination in oxygen-based polyhedra under these conditions, GaPO frameworks exhibit great structural diversity; many monomeric, chain (1-D), layered (2-D) and three-dimensional (3-D) examples are now known with a number of stoichiometries and Ga:P ratios of 1:3 (1-D (5)), 1:2 (monomeric (6), 1-D (7), 2-D (8), 3-D (9)), 4:7 (1-D (10)), 2:3 (2-D (11)), 3:4 (1-D (12)), 4:5 (3-D (13)), 1:1 (2-D (14), 3-D (1, 15)) and 5:4 (3-D (16)).

The present work is concerned with two classes of such materials; 3-D GaPOs with Ga:P ratio of 4:5 and chain GaPOs with Ga:P ratio of 1:2. Four 3-D phases with Ga:P ratio of 4:5 have previously been characterized:  $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3][\text{Ga}_4(\text{PO}_4)_4(\text{HPO}_4)]$  (4- and 5-coordinate gallium) (13) herein referred to as (V),  $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3][\text{Ga}_4(\text{PO}_4)_3(\text{HPO}_4)_2(\text{OH})_3] \cdot y\text{H}_2\text{O}$  (6-coordinate gallium) (17),  $[\text{Me}_2\text{NH}(\text{CH}_2)_2\text{NHMe}_2][\text{Ga}_4(\text{PO}_4)_4(\text{HPO}_4)] \cdot \text{H}_2\text{O}$

<sup>1</sup>To whom correspondence should be addressed. Fax: 0118-931-6331. E-mail: a.m.chippindale@rdg.ac.uk.



(4- and 6-coordinate gallium) (18) and  $\text{Rb}_2[\text{Ga}_4(\text{PO}_4)_4(\text{HPO}_4)] \cdot 0.5\text{H}_2\text{O}$  (4-, 5- and 6-coordinate gallium) (19). Four 1-D phases with Ga:P ratio of 1:2 are also known:  $[(1R, 2R)\text{-(NH}_3)_2\text{C}_6\text{H}_{10}][\text{Ga}(\text{OH})(\text{HPO}_4)_2] \cdot 2\text{H}_2\text{O}$  (20) and  $\text{Na}_3[\text{Ga}(\text{OH})(\text{PO}_4)(\text{HPO}_4)]$  (21), both of which contain chains of *trans*-edge-sharing  $\text{GaO}_5(\text{OH})$  octahedra, and  $[\text{NH}_3(\text{CH}_2)_x\text{NH}_3][\text{Ga}(\text{PO}_4)(\text{HPO}_4)]$  ( $x = 3$  (22), 4 (23)), which contain chains of alternating corner sharing  $\text{GaO}_4$  and  $\text{PO}_4$  tetrahedra.

Here we report the synthesis and structural characterization of four new GaPO materials prepared using pyrophosphoric acid as the phosphorus source in the presence of either 1,4-diaminobutane or 1,5-diaminopentane:  $[\text{NH}_3(\text{CH}_2)_x\text{NH}_3][\text{Ga}_4(\text{PO}_4)_4(\text{HPO}_4)]$  ( $x = 4$ , (I); 5, (III)), which have 3-D frameworks with Ga:P ratio 4:5, and  $[\text{NH}_3(\text{CH}_2)_x\text{NH}_3][\text{Ga}(\text{PO}_4)(\text{HPO}_4)]$  ( $x = 4$ , (II); 5, (IV)) with a chain structure and Ga:P ratio of 1:2. The GaPO framework found in (I) is related yet distinct from that of its stoichiometric equivalent  $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3][\text{Ga}_4(\text{PO}_4)_4(\text{HPO}_4)]$  (V) (13), which was also prepared as a pure phase in this work. The structure of (III) appears to be similar to that of another related phase, AlPO-HDA  $[\text{NH}_3(\text{CH}_2)_x\text{NH}_3][\text{Al}_4(\text{PO}_4)_4(\text{HPO}_4)]$  ( $x = 5$  (24), 6 (25)). To our knowledge, the GaPO chain architecture found in both (II) and (IV) has not been observed previously in a gallium phosphate.

## EXPERIMENTAL

Compounds (I) – (V) were prepared as single crystals and pure polycrystalline powders under solvothermal conditions using either 1,4-diaminobutane ((I), (II) and (V)) or 1,5-diaminopentane ((III) and (IV)) as the structure-directing agent (Table 1). The initial concentrations of all

reagents used, except pyrophosphoric acid, were the same in each reaction as were the heating temperature (433 K) and heating time (7 days). The reaction products were characterized by powder X-ray diffraction, using a Siemens D5000 diffractometer (graphite monochromated  $\text{CuK}\alpha$  radiation), Energy-Dispersive Analytical X-ray Analysis (EDAX), performed using a Philips CM20 transmission electron microscope with an Oxford Instruments INCA energy TEM 200 microanalysis system ( $\alpha$ - $\text{GaPO}_4$  calibration standard), combustion analysis and thermogravimetric analysis under flowing  $\text{N}_2$ , using a Stanton Redcroft STA1000 thermal analyser (Table 2).

In a typical reaction, single crystals of  $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3][\text{Ga}_4(\text{PO}_4)_4(\text{HPO}_4)]$  (I), were prepared by dispersing  $\text{Ga}_2\text{O}_3$  (0.8752 g) in ethylene glycol by stirring, followed by an addition of 1,4-diaminobutane and a small amount of  $\text{Si}(\text{OEt})_4$ , which acts as a mineralizer (Reaction (iii), Table 1). Pyrophosphoric acid,  $\text{H}_4\text{P}_2\text{O}_7$ , (5.5368 g, liquid at RT, Aldrich, 80%) was then added dropwise and the mixture stirred until a homogenous gel was formed. The sample was sealed in a Teflon lined stainless-steel autoclave, and heated at 433 K for 7 days. The solid products were collected by filtration, washed with water and dried in air at room temperature. The bulk of the product consisted of thin colorless plates of (I) suitable for single-crystal X-ray studies with some white polycrystalline material identified by powder X-ray diffraction as the previously reported stoichiometrically equivalent material  $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3][\text{Ga}_4(\text{PO}_4)_4(\text{HPO}_4)]$  (V) (Monoclinic, space group  $P2_1$ ,  $a = 5.0705(2)$ ,  $b = 22.650(1)$ ,  $c = 9.2801(6)$  Å,  $\beta = 103.42(1)^\circ$  (13)). A pure polycrystalline sample of (I) was subsequently prepared using the same method but under less acidic conditions (Reaction (ii), Table 1).

TABLE 1  
Summary of Synthetic Conditions

Reaction	Gel composition <sup>a</sup>		Product composition	Product formula	
	$\text{Ga}_2\text{O}_3$	$\text{H}_4\text{P}_2\text{O}_7$			
(i)	1.00	4.04	Single phase: clusters of needle-like crystals	$[\text{NH}_3(\text{CH}_2)_4\text{NH}_3][\text{Ga}(\text{PO}_4)(\text{HPO}_4)]$	(II)
(ii)	1.00	6.12	Single phase: polycrystalline powder	$[\text{NH}_3(\text{CH}_2)_4\text{NH}_3][\text{Ga}_4(\text{PO}_4)_4(\text{HPO}_4)]$	(I)
(iii)	1.00	6.66	Mixed phase (a) small plate-like crystals (b) polycrystalline powder	(a) $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3][\text{Ga}_4(\text{PO}_4)_4(\text{HPO}_4)]$ (major component) (b) $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3][\text{Ga}_4(\text{PO}_4)_4(\text{HPO}_4)]$ (minor component)	(I) (V) (13)
(iv)	1.00	7.51	Single phase: clusters of needle-like crystals	$[\text{NH}_3(\text{CH}_2)_4\text{NH}_3][\text{Ga}_4(\text{PO}_4)_4(\text{HPO}_4)]$	(V) (13)
(v)	1.00	3.21	Single phase: block-like crystals	$[\text{NH}_3(\text{CH}_2)_5\text{NH}_3][\text{Ga}(\text{PO}_4)(\text{HPO}_4)]$	(IV)
(vi)	1.00	6.27	Single phase: feather-like crystals	$[\text{NH}_3(\text{CH}_2)_4\text{NH}_3][\text{Ga}_4(\text{PO}_4)_4(\text{HPO}_4)]$	(III)

<sup>a</sup>All reactions were carried out using ethylene glycol ( $\text{HOCH}_2\text{CH}_2\text{OH}$ , EG) as solvent at 433 K and for 7 days. Reactions (i)–(iv) use 1,4-diaminobutane (1,4-dab) as the organic template and have a ratio  $\text{Ga}_2\text{O}_3\text{:EG:1,4-dab}$  of 1.00:21.47(4):3.62(2). Reactions (v) and (vi) use 1,5-diaminopentane (1,5-dap) as the organic template and have a ratio  $\text{Ga}_2\text{O}_3\text{:EG:1,5-dap}$  of 1.00:21.48(2):3.61(2).

**TABLE 2**  
**Results of CHN, TGA and EDAX Analyses**

Reaction	Sample	CHN analysis (%) <sup>a</sup>			TGA analysis <sup>b</sup>		EDAX
		C	H	N	Weight loss (%)	T(K)	Ga:P ratio
(ii)	(I)	5.73(5.69)	1.89(1.79)	3.10(3.32)	9.69(10.67)	633–813	0.82(6)
(i)	(II)	12.71(13.69)	4.22(4.31)	7.09(7.98)	25.31(25.85)	593–713	0.55(3)
(vi)	(III)	7.25(6.99)	2.37(2.00)	3.10(3.26)	11.79(11.90)	633–793	0.83(6)
(v)	(IV)	16.37(16.46)	4.20(4.70)	7.45(7.68)	27.94(28.01)	573–713	0.50(1)
(iv)	(V)	5.73(5.69)	1.84(1.79)	3.25(3.32)	12.22(10.67)	673–793	0.80(6)

<sup>a</sup>Calculated values are shown in parentheses.

<sup>b</sup>Calculated value for the loss of the unprotonated amine are shown in parentheses.

The synthetic procedure was repeated by adjusting the acid content to prepare compounds (II), (III), (IV) and (V) (Table 1) which were subsequently confirmed as pure phases (Table 2). It was found that the product of Reaction (v), consisting of single crystals of (IV), disintegrated on washing in water and so was washed with glacial acetic acid and methanol before drying in air. This method has been used previously to preserve single crystals of  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3][\text{Co}(\text{HPO}_4)]$  prepared by a similar solvothermal route (26).

The single crystals of (III) produced in Reaction (vi) were found to be of insufficient quality for a full structure solution (*vide infra*). A powder X-ray pattern of the finely ground crystals could, however, be indexed fully on the basis of a triclinic unit cell with refined lattice parameters:  $a = 9.3565(4)$ ,  $b = 5.0156(2)$  and  $c = 12.7065(4)$  Å,  $\alpha = 96.612(3)$ ,  $\beta = 102.747(4)$  and  $\gamma = 105.277(3)^\circ$ . These values

are similar to those obtained by Yu *et al.* for  $[\text{NH}_3(\text{CH}_2)_5\text{NH}_3][\text{Al}_4(\text{PO}_4)_4(\text{HPO}_4)]$  (AlPO-HDA,  $x = 5$ ) ( $a = 9.2450(9)$ ,  $b = 5.0657(5)$  and  $c = 12.688(2)$  Å,  $\alpha = 96.02(1)$ ,  $\beta = 102.88(1)$  and  $\gamma = 105.89(1)^\circ$  (24)), suggesting that these GaPO and AlPO structures are related.

### Single-Crystal Structure Determination

Crystals of (I), (II), (III) and (IV) from Reactions (iii), (i), (vi) and (v) (Table 1) were each mounted on a glass fiber with acrylonitrile (superglue) and intensity data collected at room temperature using an Enraf-Nonius Kappa CCD diffractometer (graphite monochromated  $\text{MoK}\alpha$  radiation, 0.71073 Å). The data were processed using DENZO and SCALEPACK (27). Full crystallographic details are given in Table 3.

**TABLE 3**  
**Crystallographic Data for (I), (II), and (IV)**

	(I)	(II)	(IV)
Formula	$[\text{NH}_3(\text{CH}_2)_4\text{NH}_3][\text{Ga}_4(\text{PO}_4)_4(\text{HPO}_4)]$	$[\text{NH}_3(\text{CH}_2)_4\text{NH}_3][\text{Ga}(\text{PO}_4)(\text{HPO}_4)]$	$[\text{NH}_3(\text{CH}_2)_5\text{NH}_3][\text{Ga}(\text{PO}_4)(\text{HPO}_4)]$
$M_r$	844.90	350.84	364.87
Crystal size (mm)	$0.2 \times 0.05 \times 0.02$	$0.2 \times 0.03 \times 0.03$	$0.2 \times 0.08 \times 0.08$
Crystal habit	Colorless plate	Colorless needle	Colorless block
Crystal system, Space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$
$a$ (Å)	9.3619(3)	4.8922(1)	4.9239(2)
$b$ (Å)	10.1158(3)	18.3638(6)	13.2843(4)
$c$ (Å)	12.6456(5)	13.7468(5)	19.5339(7)
$\alpha$ (°)	98.485(1)	90	90
$\beta$ (°)	107.018(2)	94.581(1)	96.858(1)
$\gamma$ (°)	105.424(1)	90	90
Cell volume (Å <sup>3</sup> )	1070.39	1231.06	1268.58
$Z$	2	4	4
Temperature (K)	293(2)	293(2)	293(2)
$\rho_{\text{calc}}$ (g cm <sup>-3</sup> ), $\mu_{\text{Mo}}$ (mm <sup>-1</sup> )	2.62, 5.43	1.89, 2.51	1.91, 2.44
Radiation, wavelength (Å)	$\text{MoK}\alpha$ , 0.71073	$\text{MoK}\alpha$ , 0.71073	$\text{MoK}\alpha$ , 0.71073
Unique, obs data ( $I > 3\sigma(I)$ )	4832, 2918	2764, 2050	2899, 2224
$R_{\text{merge}}$	0.0287	0.0502	0.0246
Residual electron density (min, max) (eÅ <sup>-3</sup> )	-0.92, 1.77	-0.45, 0.35	-0.691, 0.509
No. of parameters refined	320	158	204
$R(F)$ , $R_w(F)$	0.0368, 0.0440	0.0295, 0.0337	0.0374, 0.0444

The structures of (I), (II) and (IV) were solved by direct methods using the program SIR92 (28) and all non-hydrogen framework atoms located. Subsequent Fourier calculations and least-squares refinements on  $F$  were carried out in the CRYSTALS suite of programs (29). The C and N atoms of the templates and the framework and template H atoms were located in difference Fourier maps. (I) and (II) showed no evidence of disorder of the 1,4-diaminobutane template whereas the 1,5-diaminopentane in (IV) did show disorder which was modelled successfully as two molecules with occupancies of 0.64(2) and 0.36(2). The template H atoms were placed geometrically during the refinement procedure in each case.

In the final cycles, positional and anisotropic thermal parameters for all non-hydrogen framework and template

**TABLE 4**  
Fractional Atomic Coordinates, Isotropic Thermal Parameters ( $\text{\AA}^2$ ) and Site Occupancies for  $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3][\text{Ga}_4(\text{PO}_4)_4(\text{HPO}_4)]$  (I)

Atom	$x$	$y$	$z$	$U(\text{iso})$
Ga(1)	0.77725(6)	0.09779(6)	0.51184(5)	0.0100
Ga(2)	0.78445(6)	-0.39832(6)	0.51664(5)	0.0101
Ga(3)	0.49811(7)	0.20143(6)	0.22769(5)	0.0121
Ga(4)	0.51244(7)	-0.30883(6)	0.21973(5)	0.0126
P(1)	0.4170(2)	-0.0454(1)	0.3245(1)	0.0105
P(2)	0.4229(2)	-0.5353(1)	0.3350(1)	0.0110
P(3)	0.8408(2)	0.3394(1)	0.3923(1)	0.0095
P(4)	1.1550(1)	0.1613(1)	0.6044(1)	0.0093
P(5)	0.4957(2)	0.1896(2)	-0.0171(1)	0.0172
O(1)	0.5608(4)	0.0559(4)	0.4198(3)	0.0144
O(2)	0.7317(4)	0.0739(4)	0.6428(3)	0.0160
O(3)	0.8304(4)	0.2849(4)	0.4980(3)	0.0128
O(4)	0.9955(4)	0.1416(4)	0.6191(3)	0.0161
O(5)	0.8091(5)	-0.0222(4)	0.4016(3)	0.0172
O(6)	0.5678(4)	-0.4297(4)	0.4274(3)	0.0150
O(7)	0.7272(4)	-0.4566(4)	0.6359(3)	0.0130
O(8)	0.8217(5)	0.4864(4)	0.4057(3)	0.0142
O(9)	0.9966(4)	0.3478(4)	0.3733(3)	0.0139
O(10)	0.8377(4)	-0.2120(4)	0.5025(3)	0.0130
O(11)	0.3844(4)	0.0217(4)	0.2212(3)	0.0148
O(12)	0.4330(5)	0.3153(4)	0.3137(4)	0.0193
O(13)	0.7107(4)	0.2384(4)	0.2836(3)	0.0136
O(14)	0.4458(5)	0.2315(5)	0.0838(3)	0.0202
O(15)	0.4305(5)	-0.1913(4)	0.2861(4)	0.0229
O(16)	0.4003(4)	-0.4844(4)	0.2234(3)	0.0123
O(17)	0.7242(4)	-0.2699(4)	0.2866(3)	0.0134
O(18)	0.4698(5)	-0.3184(5)	0.0679(3)	0.0195
O(19)	0.6590(5)	0.1662(5)	0.0284(4)	0.0241
O(20)	0.3720(5)	0.0606(5)	-0.1029(4)	0.0255
N(1)	0.9560(8)	0.4037(6)	0.7422(5)	0.0310
N(2)	1.0454(6)	-0.0655(6)	0.7643(4)	0.0229
C(1)	1.052(1)	0.468(1)	0.8648(6)	0.0401
C(2)	0.9541(9)	0.4668(9)	0.9373(6)	0.0399
C(3)	0.9894(8)	-0.1063(7)	0.8580(5)	0.0244
C(4)	1.0174(8)	0.0211(7)	0.9482(5)	0.0249
H(19)	0.636(9)	0.076(8)	0.055(7)	0.03(2)

**TABLE 5**  
Selected Bond Distances ( $\text{\AA}$ ) and Angles ( $^\circ$ ) for  $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3][\text{Ga}_4(\text{PO}_4)_4(\text{HPO}_4)]$  (I)

Ga(1)–O(1)	1.913(4)	P(2)–O(6)	1.510(4)
Ga(1)–O(2)	1.861(4)	P(2)–O(7) <sup>d</sup>	1.538(4)
Ga(1)–O(3)	1.873(4)	P(2)–O(12) <sup>a</sup>	1.529(4)
Ga(1)–O(4)	1.983(4)	P(2)–O(16)	1.548(4)
Ga(1)–O(5)	1.855(4)		
		P(3)–O(3)	1.538(4)
Ga(2)–O(6)	1.923(4)	P(3)–O(8)	1.536(4)
Ga(2)–O(7)	1.865(4)	P(3)–O(9)	1.529(4)
Ga(2)–O(8) <sup>a</sup>	1.862(4)	P(3)–O(13)	1.536(4)
Ga(2)–O(9) <sup>b</sup>	1.991(4)		
Ga(2)–O(10)	1.867(4)	P(4)–O(4)	1.522(4)
		P(4)–O(5) <sup>b</sup>	1.528(4)
Ga(3)–O(11)	1.823(4)	P(4)–O(10) <sup>b</sup>	1.528(4)
Ga(3)–O(12)	1.809(4)	P(4)–O(17) <sup>b</sup>	1.538(4)
Ga(3)–O(13)	1.817(4)		
Ga(3)–O(14)	1.834(4)	P(5)–O(14)	1.523(4)
		P(5)–O(18) <sup>c</sup>	1.535(4)
Ga(4)–O(15)	1.810(4)	P(5)–O(19)	1.563(5)
Ga(4)–O(16)	1.822(4)	P(5)–O(20)	1.505(4)
Ga(4)–O(17)	1.819(4)		
Ga(4)–O(18)	1.826(4)	O(19)–H(19)	1.01(8)
P(1)–O(1)	1.505(4)	O(11)–Ga(3)–O(12)	105.4(2)
P(1)–O(2) <sup>c</sup>	1.533(4)	O(11)–Ga(3)–O(13)	113.6(2)
P(1)–O(11)	1.548(4)	O(12)–Ga(3)–O(13)	112.3(2)
P(1)–O(15)	1.534(4)	O(11)–Ga(3)–O(14)	109.2(2)
		O(12)–Ga(3)–O(14)	108.2(2)
O(1)–Ga(1)–O(2)	93.9(2)	O(13)–Ga(3)–O(14)	108.0(2)
O(1)–Ga(1)–O(3)	92.4(2)		
O(2)–Ga(1)–O(3)	114.5(2)	O(15)–Ga(4)–O(16)	104.4(2)
O(1)–Ga(1)–O(4)	174.9(2)	O(15)–Ga(4)–O(17)	114.9(2)
O(2)–Ga(1)–O(4)	81.1(2)	O(16)–Ga(4)–O(17)	112.0(2)
O(3)–Ga(1)–O(4)	88.9(2)	O(15)–Ga(4)–O(18)	113.2(2)
O(1)–Ga(1)–O(5)	91.7(2)	O(16)–Ga(4)–O(18)	104.0(2)
O(2)–Ga(1)–O(5)	132.5(2)	O(17)–Ga(4)–O(18)	108.0(2)
O(3)–Ga(1)–O(5)	112.3(2)		
O(4)–Ga(1)–O(5)	92.3(2)		
O(6)–Ga(2)–O(7)	91.6(2)		
O(6)–Ga(2)–O(8) <sup>a</sup>	95.3(2)		
O(7)–Ga(2)–O(8) <sup>a</sup>	124.4(2)		
O(6)–Ga(2)–O(9) <sup>b</sup>	171.6(2)		
O(7)–Ga(2)–O(9) <sup>b</sup>	83.6(2)		
O(8) <sup>a</sup> –Ga(2)–O(9) <sup>b</sup>	93.1(2)		
O(6)–Ga(2)–O(10)	89.8(2)		
O(7)–Ga(2)–O(10)	124.8(2)		
O(8) <sup>a</sup> –Ga(2)–O(10)	110.4(2)		
O(9) <sup>b</sup> –Ga(2)–O(10)	87.3(2)		

Note. O–P–O angles in  $\text{PO}_4$  tetrahedra lie in the range 104.3(3)–114.3(2) $^\circ$ . N(1)–C(1) and N(2)–C(3) bond lengths have values of 1.487(9) and 1.498(8)  $\text{\AA}$  and C–C bond lengths lie in the range 1.47(1)–1.53(1)  $\text{\AA}$ . Symmetry transformations used to generate equivalent atoms:

- <sup>a</sup>  $x, y-1, z$ .  
<sup>b</sup>  $2-x, -y, 1-z$ .  
<sup>c</sup>  $1-x, -y, 1-z$ .  
<sup>d</sup>  $1-x, -y, -z$ .  
<sup>e</sup>  $1-x, -1-y, 1-z$ .

**TABLE 6**  
Fractional Atomic Coordinates and Isotropic Thermal Parameters ( $\text{\AA}^2$ ) for  $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3][\text{Ga}(\text{PO}_4)(\text{HPO}_4)]$  (**II**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (iso)
Ga(1)	0.70579(6)	0.09146(2)	0.02142(2)	0.0131
P(1)	1.1831(1)	0.06278(4)	-0.10817(5)	0.0130
P(2)	0.7973(2)	0.25023(4)	0.04726(6)	0.0168
O(1)	0.8795(4)	0.0651(1)	-0.0852(2)	0.0182
O(2)	0.8106(5)	0.1717(1)	0.0907(2)	0.0225
O(3)	1.3475(4)	0.1039(1)	-0.0248(2)	0.0199
O(4)	1.2773(5)	-0.0172(1)	-0.1096(2)	0.0205
O(5)	1.2121(4)	0.0965(1)	-0.2063(2)	0.0202
O(6)	0.5463(4)	0.2895(1)	0.0766(2)	0.0252
O(7)	0.8192(5)	0.2467(1)	-0.0613(2)	0.0296
O(8)	1.0413(5)	0.2925(1)	0.1022(2)	0.0237
N(1)	1.2875(6)	0.2482(1)	0.3390(2)	0.0257
N(2)	1.3213(5)	-0.0914(1)	0.3090(2)	0.0208
C(1)	1.2793(8)	0.1779(2)	0.2849(3)	0.0289
C(2)	1.3116(8)	0.1145(2)	0.3546(3)	0.0301
C(3)	1.2902(8)	0.0426(2)	0.3007(3)	0.0309
C(4)	1.3310(8)	-0.0225(2)	0.3661(3)	0.0289
H(1)	1.19(1)	0.286(2)	0.090(3)	0.04(1)

**TABLE 7**  
Selected Bond Distances ( $\text{\AA}$ ) and Angles ( $^\circ$ ) for  $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3][\text{Ga}(\text{PO}_4)(\text{HPO}_4)]$  (**II**)

Ga(1)–O(1)	1.818(2)	P(2)–O(2)	1.560(2)
Ga(1)–O(2)	1.807(2)	P(2)–O(6)	1.507(2)
Ga(1)–O(3) <sup>a</sup>	1.831(2)	P(2)–O(7)	1.505(3)
Ga(1)–O(4) <sup>b</sup>	1.822(2)	P(2)–O(8)	1.567(2)
P(1)–O(1)	1.544(2)	O(8)–H(1)	0.78(5)
P(1)–O(3)	1.544(2)		
P(1)–O(4)	1.539(2)		
P(1)–O(5)	1.502(2)		
O(1)–Ga(1)–O(2)	120.7(1)	O(2)–P(2)–O(6)	110.5(1)
O(1)–Ga(1)–O(3) <sup>a</sup>	104.46(9)	O(2)–P(2)–O(7)	109.6(1)
O(1)–Ga(1)–O(4) <sup>b</sup>	109.7(1)	O(2)–P(2)–O(8)	105.5(1)
O(2)–Ga(1)–O(3) <sup>a</sup>	107.7(1)	O(6)–P(2)–O(7)	114.2(2)
O(2)–Ga(1)–O(4) <sup>b</sup>	105.3(1)	O(6)–P(2)–O(8)	103.9(1)
O(3) <sup>a</sup> –Ga(1)–O(4)	108.4(1)	O(7)–P(2)–O(8)	112.8(1)
O(1)–P(1)–O(3)	106.7(1)	Ga(1)–O(1)–P(1)	133.8(1)
O(1)–P(1)–O(5)	109.5(1)	Ga(1)–O(2)–P(2)	123.4(1)
O(3)–P(1)–O(5)	112.6(1)	<sup>c</sup> Ga(1)–O(3)–P(1)	128.6(1)
O(1)–P(1)–O(4)	109.9(1)	<sup>d</sup> Ga(1)–O(4)–P(1)	134.7(1)
O(3)–P(1)–O(4)	109.7(1)		
O(4)–P(1)–O(5)	109.4(1)		

Note. N(1)–C(1) and N(2)–C(4) bond lengths have values of 1.488(4) and 1.489(4)  $\text{\AA}$  and C–C bond lengths have values of 1.499(5), 1.507(5) and 1.514(5)  $\text{\AA}$ .

Symmetry transformations used to generate equivalent atoms:

<sup>a</sup>  $x-1, y, z$ .

<sup>b</sup>  $x-\frac{1}{2}, -y, -z$ .

<sup>c</sup>  $x+1, y, z$ .

<sup>d</sup>  $2-x, -y, -z$ .

**TABLE 8**  
Fractional Atomic Coordinates, Isotropic Thermal Parameters ( $\text{\AA}^2$ ) and Site Occupancies for  $[\text{NH}_3(\text{CH}_2)_5\text{NH}_3][\text{Ga}(\text{PO}_4)(\text{HPO}_4)]$  (**IV**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (iso)	Occ <sup>a</sup>
Ga(1)	0.34035(6)	0.47173(3)	0.58531(2)	0.0240	
P(1)	0.2814(2)	0.44154(9)	0.73308(5)	0.0338	
P(2)	-0.1766(1)	0.60575(6)	0.56296(4)	0.0245	
O(1)	0.1313(4)	0.5827(2)	0.5645(1)	0.0289	
O(2)	0.2807(5)	0.3972(2)	0.6595(1)	0.0376	
O(3)	-0.3048(4)	0.5153(2)	0.5967(1)	0.0323	
O(4)	-0.3036(5)	0.6152(2)	0.4875(1)	0.0335	
O(5)	-0.2129(5)	0.7025(2)	0.6001(1)	0.0356	
O(6)	0.0404(5)	0.4017(3)	0.7655(2)	0.0429	
O(7)	0.3069(7)	0.5534(3)	0.7310(2)	0.0546	
O(8)	0.5347(6)	0.3926(3)	0.7783(2)	0.0436	
N(1)	-0.192(1)	0.6582(3)	0.7536(2)	0.0600	
N(2)	-0.6990(6)	0.8021(2)	0.6119(2)	0.0371	
C(10)	-0.102(2)	0.6517(8)	0.8287(3)	0.0592	0.64(2)
C(11)	-0.191(4)	0.707(1)	0.8208(6)	0.0645	0.36(2)
C(20)	-0.312(2)	0.693(1)	0.8711(4)	0.0619	0.64(2)
C(21)	-0.261(7)	0.639(1)	0.8785(7)	0.0780	0.36(2)
C(30)	-0.680(2)	0.842(1)	0.4439(5)	0.0788	0.64(2)
C(31)	-0.752(5)	0.796(1)	0.4446(8)	0.0706	0.36(2)
C(40)	-0.873(3)	0.848(1)	0.4982(5)	0.0938	0.64(2)
C(41)	-0.821(4)	0.886(1)	0.4887(5)	0.0448	0.36(2)
C(5)	-0.734(2)	0.8889(4)	0.5660(3)	0.0815	
H(1)	0.69(1)	0.412(5)	0.770(3)	0.07(2)	

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

atoms, and positional and isotropic thermal parameters for the framework hydrogen atoms were refined. A three-term Chebyshev polynomial was applied as a weighting scheme in each case (30). Atomic parameters and selected bond distances and angles are given in Tables 4 and 5 for (**I**), in Tables 6 and 7 for (**II**) and in Tables 8 and 9 for (**IV**).

Crystals of (**III**) (Reaction (vi), Table 1) were found to be of poor quality. The unit cell is triclinic with lattice parameters of  $a = 9.364(4)$ ,  $b = 5.021(1)$  and  $c = 12.692(9) \text{\AA}$ ,  $\alpha = 96.50(4)$ ,  $\beta = 102.83(5)$  and  $\gamma = 105.44(2)^\circ$ , with no evidence of the cell doubling along the  $b$  axis observed for (**I**). A partial structure solution showed that the twin components are related by a  $180^\circ$  rotation about the  $b$  axis but the space group could not be assigned unambiguously.

## RESULTS

### $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3][\text{Ga}_4(\text{PO}_4)_4(\text{HPO}_4)]$ (**I**)

The framework structure of  $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3][\text{Ga}_4(\text{PO}_4)_4(\text{HPO}_4)]$  (**I**) is assembled from a network of  $\text{GaO}_4$ ,  $\text{GaO}_5$  and  $\text{PO}_4$  polyhedra (Fig. 1). There are four crystallographically distinct Ga atoms, of which two, Ga(1) and Ga(2), have trigonal bipyramidal coordination

**TABLE 9**  
**Selected Bond Distances (Å) and Angles (°)**  
**for [NH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>NH<sub>3</sub>][Ga(PO<sub>4</sub>)(HPO<sub>4</sub>)] (IV)**

Ga(1)–O(1)	1.815(2)	P(2)–O(2)	1.553(3)
Ga(1)–O(2)	1.808(2)	P(2)–O(6)	1.506(3)
Ga(1)–O(3)	1.829(2)	P(2)–O(7)	1.493(4)
Ga(1)–O(4) <sup>a</sup>	1.825(2)	P(2)–O(8)	1.581(3)
P(1)–O(1)	1.544(2)	O(8)–H(1)	0.83(6)
P(1)–O(3)	1.541(3)		
P(1)–O(4)	1.536(3)		
P(1)–O(5)	1.497(3)		
O(1)–Ga(1)–O(2)	118.8(1)	O(2)–P(2)–O(6)	109.9(2)
O(1)–Ga(1)–O(3)	106.1(1)	O(2)–P(2)–O(7)	110.1(2)
O(1)–Ga(1)–O(4) <sup>a</sup>	109.8(1)	O(2)–P(2)–O(8)	106.0(2)
O(2)–Ga(1)–O(3)	108.7(1)	O(6)–P(2)–O(7)	115.8(2)
O(2)–Ga(1)–O(4) <sup>a</sup>	105.5(1)	O(6)–P(2)–O(8)	103.2(2)
O(3)–Ga(1)–O(4) <sup>a</sup>	107.4(1)	O(7)–P(2)–O(8)	111.2(2)
O(1)–P(1)–O(3)	106.7(1)	Ga(1)–O(1)–P(1)	134.0(1)
O(1)–P(1)–O(5)	109.6(1)	Ga(1)–O(2)–P(2)	123.5(2)
O(1)–P(1)–O(4)	108.8(1)	Ga(1) <sup>b</sup> –O(3)–P(1)	129.0(1)
O(3)–P(1)–O(4)	109.5(1)	Ga(1) <sup>a</sup> –O(4)–P(1)	133.4(2)
O(3)–P(1)–O(5)	112.6(2)		
O(4)–P(1)–O(5)	109.6(1)		

Note. N–C and C–C bond lengths lie in the ranges 1.4596–1.485(7) and 1.504(8)–1.562(8) Å, respectively.

Symmetry transformations used to generate equivalent atoms:

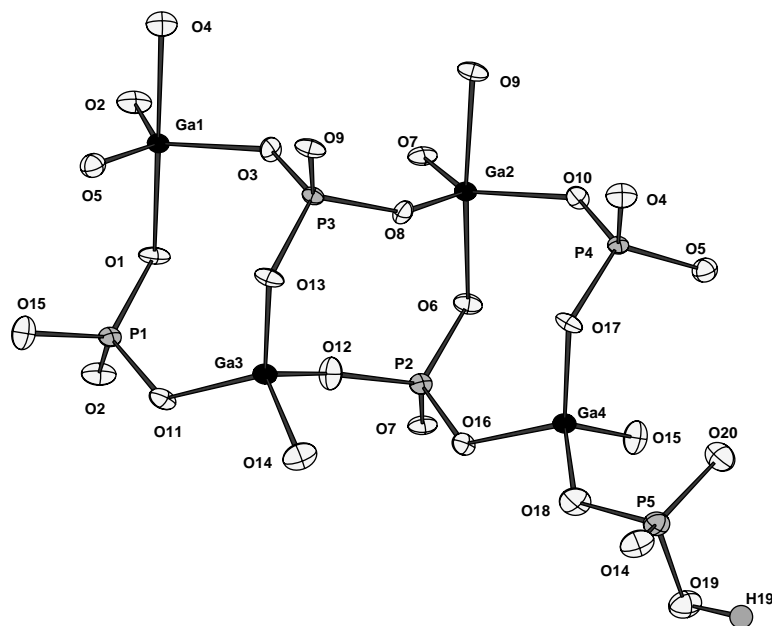
<sup>a</sup>  $-x, 1-y, 1-z$ .

<sup>b</sup>  $x-1, y, z$ .

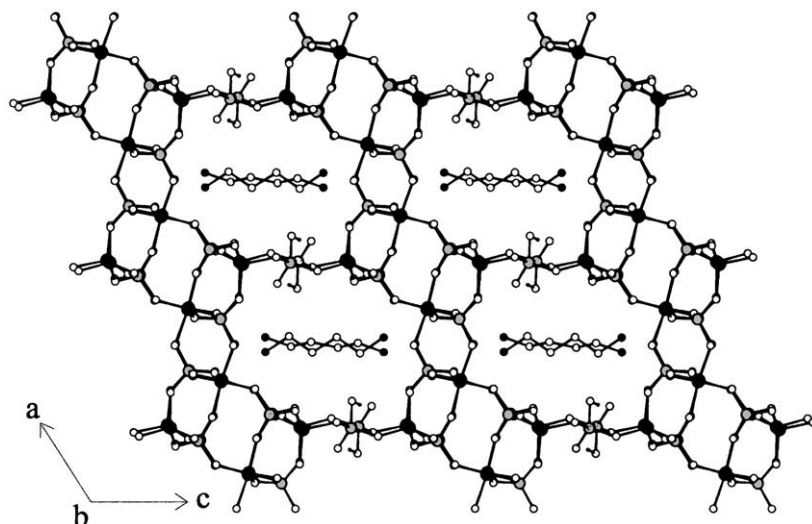
(axial Ga–O<sub>av</sub> = 1.953 Å, equatorial Ga–O<sub>av</sub> = 1.859 Å) and two, Ga(3) and Ga(4), are tetrahedrally coordinated to O (Ga–O<sub>av</sub> = 1.820 Å, O–Ga–O<sub>av</sub> = 109.4°). The

GaO<sub>4</sub> and GaO<sub>5</sub> polyhedra share all their vertices with phosphorus-based tetrahedra. There are five crystallographically distinct PO<sub>4</sub> units, four of which share all vertices with either GaO<sub>4</sub> or GaO<sub>5</sub> units (P–O<sub>av</sub> = 1.531 Å, O–P–O<sub>av</sub> = 109.5°). The fifth, P(5), shares only two of its vertices with GaO<sub>4</sub> tetrahedra. Of the two terminal P(5)–O bonds, one has partial double bond character (P(5)–O(20), 1.505(4) Å), whilst the other, rather longer bond (P(5)–O(19), 1.563(5) Å), constitutes a P–OH bond. This assignment is confirmed by difference Fourier and bond-valence calculations (31). The Ga- and P-based polyhedra are linked in an alternating manner to give an open 3-D framework of formula [Ga<sub>4</sub>(PO<sub>4</sub>)<sub>4</sub>(HPO<sub>4</sub>)]<sup>2-</sup> containing cavities in which the charge balancing 1,4-diaminobutane dications reside (Fig. 2). Both N atoms of the two crystallographically distinct diaminocations are within H-bonding distance of a number of framework O atoms (N(1)⋯O(3, 4, 7, and 9) distances between 2.896(7) and 3.086(7) Å and N(2)⋯O(4, 5, 9, and 20) distances between 2.843(7) and 3.021(7) Å).

The framework of (I) can also be described as being composed of a series of columns of face sharing double six-rings (D6R) stacked along the *b* axis (Fig. 3a). These columns are connected by four-membered rings (4MR), through five-coordinate Ga atoms, to form layers that lie parallel to the *a* axis (Fig. 3b). P(5)O<sub>3</sub>(OH) units link these layers together to form the 3-D framework enclosing an intersecting 2-D pore network. The two sets of elliptical channels formed lie parallel to the *a* and *b* axes and are bounded by 8- and 12-membered rings (8MR and 12MR) of alternating GaO<sub>*n*</sub> (*n* = 4, 5) and PO<sub>4</sub> polyhedra, respectively. The channels bounded by the 12MR have

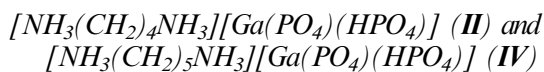


**FIG. 1.** The local coordination of the framework atoms in (I) (drawing package, CAMERON (36)).



**FIG. 2.** View of (I) along the *b* axis showing the 12MR of the open 3-D framework and the location of two crystallographically distinct diprotonated 1,4-diaminocations. Black spheres in framework = Ga atoms, light gray spheres in framework = P atoms, white spheres in framework = O atoms, dark gray spheres in template = N atoms, white spheres in template = C atoms and black spheres = H atoms (drawing package, CAMERON (36)).

cross-pore dimensions, O(14)⋯O(18) and O(4)⋯O(9), of 8.533(6) and 9.454(5) Å, respectively. There are two distinct types of 8MR alternating in chains running parallel to the *a* axis (Fig. 4). One type contains all four terminal P(5)–O(20) and P(5)–O(19)H groups from the two adjacent P(5) units and the O⋯O separation between O(19) and O(20) bonded to adjacent P(5) atoms is 2.587(7) Å, indicating the presence of strong intra-framework H-bonding. The second type of 8MR does not contain any of the terminal P(5)–O(H) groups and consequently has no cross-channel hydrogen bonding interactions. Along the chain of 8MR, there are alternating short (3.943(3) Å) and long (6.207(3) Å) P(5)⋯P(5) distances, across the first and second types of 8MR respectively.



The structure of  $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3][\text{Ga}(\text{PO}_4)(\text{HPO}_4)]$  (II) consists of infinite gallophosphate chains of formula  $[\text{Ga}(\text{PO}_4)(\text{HPO}_4)]^{2-}$  running parallel to the *a* axis and linked by hydrogen bonding interactions to 1,4-diaminobutane dications. Within the chains, both the Ga and P atoms are tetrahedrally coordinated to oxygen atoms and have bond lengths and angles similar to those observed in other gallophosphates ( $\text{Ga}-\text{O}_{\text{av}} = 1.820$  Å,  $\text{O}-\text{Ga}-\text{O}_{\text{av}} = 109.4^\circ$  and  $\text{P}-\text{O}_{\text{av}} = 1.538$  Å,  $\text{O}-\text{P}-\text{O}_{\text{av}} = 109.45^\circ$ ) (Fig. 5). The structure contains two crystallographically distinct  $\text{PO}_4$  units. P(1) has one terminal P(1)–O bond possessing some multiple-bond character (P(1)–O(5), 1.502(2) Å). The remaining P(1)–O bonds bridge to three adjacent  $\text{GaO}_4$  units to form 4-membered rings (4MR),

which in turn are joined along opposite edges to form a zigzag chain or ‘backbone’ (Fig. 6). The second phosphorus, P(2), shares only one of its vertices with  $\text{GaO}_4$  tetrahedra to form a long bond (P(2)–O(2), 1.560(2) Å) which extends away from the zigzag chain forming a ‘dangling’ or ‘pendant’ phosphate. Of the three terminal P(2)–O bonds, two correspond to partial multiple bonds (P(2)– $\text{O}_{\text{av}} = 1.506$  Å) and the last, rather longer bond (P(2)–O(8), 1.567(2) Å), constitutes a P–OH group as confirmed by location of the hydrogen atom in the difference Fourier map and bond-valence calculations (31). The separation of the oxygens between adjacent P(2) $\text{O}_3(\text{OH})$  groups (O(6)⋯O(8), 2.524(3) Å), is sufficiently short to suggest the presence of intra-chain H-bonding. The packing of the chains in (II) can be described by a 2-fold screw ( $2_1$ ) axis parallel to the *b* axis at  $1/4c$  (Fig. 7a). The charge-balancing 1,4-diaminobutane dications lie in between the chains and are stacked on top of each other along the *a* axis. Both N atoms of the diaminocation are within H-bonding distance of a number of chain O atoms (N(1)⋯O(5, 7 and 7') and N(2)⋯O(5, 5', 6 and 8) distances lie in the ranges 2.764(4)–2.936(3) Å and 2.740(3)–3.086(3) Å, respectively).

The gallium-phosphate chains in (IV) have the same connectivity as those observed in (II) and also show strong intra-chain H bonding (O(6)⋯O(8), 2.535(3) Å) (Fig. 6). The packing of the chains can also be described by a 2-fold screw axis ( $2_1$ ) parallel to the *b* axis at  $1/4c$  (Fig. 7b). However, due to the crystallization of (IV) in a different setting of the space group (No. 14) the OH groups of adjacent chains alternate along the *a* axis whereas in (II) adjacent chains are packed in such a way that the OH

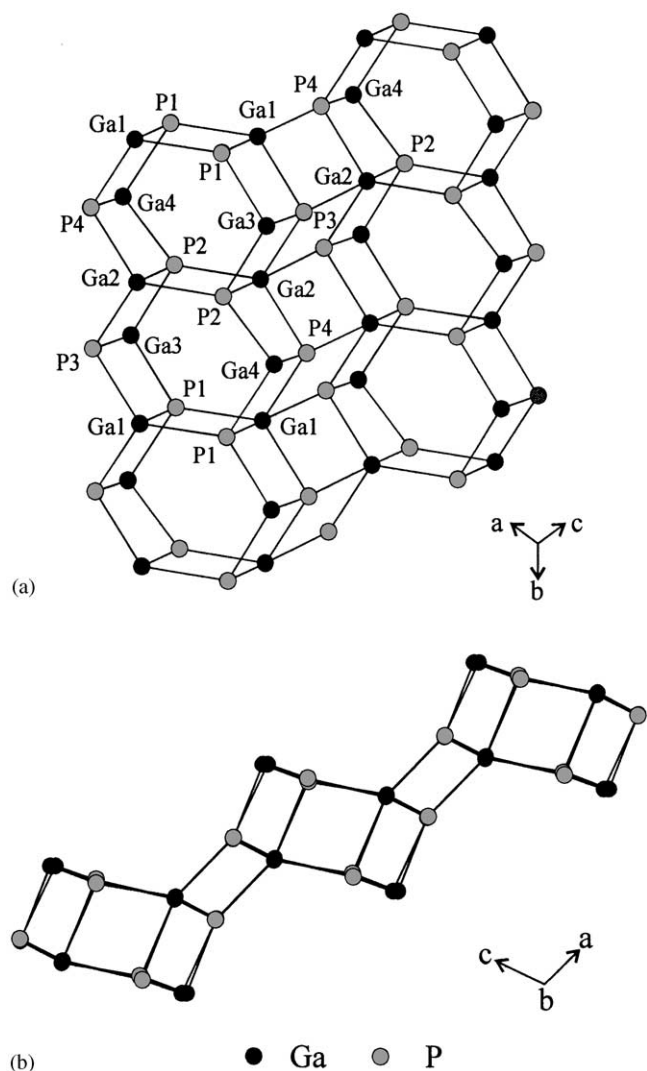


FIG. 3. View of (I) showing (a) two columns of D6R connected through 4MR to form (b) layers that lie parallel to the  $a$  axis. Oxygen atoms have been omitted for clarity, (drawing package, ATOMS (37)).

groups align in the same direction along the  $a$  axis. The 1,5-diaminopentane dications, which are modelled as disordered over two positions, lie between the chains stacked along the  $a$  axis and are hydrogen bonded to the same oxygens of the chain as in (II) ( $N(1)\cdots O(5, 7$  and  $7')$  and  $N(2)\cdots O(5, 5', 6$  and  $8)$  distances lie in the ranges 2.820(4)–3.046(4) Å and 2.766(3)–3.101(3) Å, respectively).

## DISCUSSION

Four new GaPO phases:  $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3][\text{Ga}_4(\text{PO}_4)_4(\text{HPO}_4)]$  (I),  $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3][\text{Ga}(\text{PO}_4)(\text{HPO}_4)]$  (II),  $[\text{NH}_3(\text{CH}_2)_5\text{NH}_3][\text{Ga}_4(\text{PO}_4)_4(\text{HPO}_4)]$  (III) and  $[\text{NH}_3(\text{CH}_2)_5\text{NH}_3][\text{Ga}(\text{PO}_4)(\text{HPO}_4)]$  (IV) are reported in this work together with a fifth, previously known compound

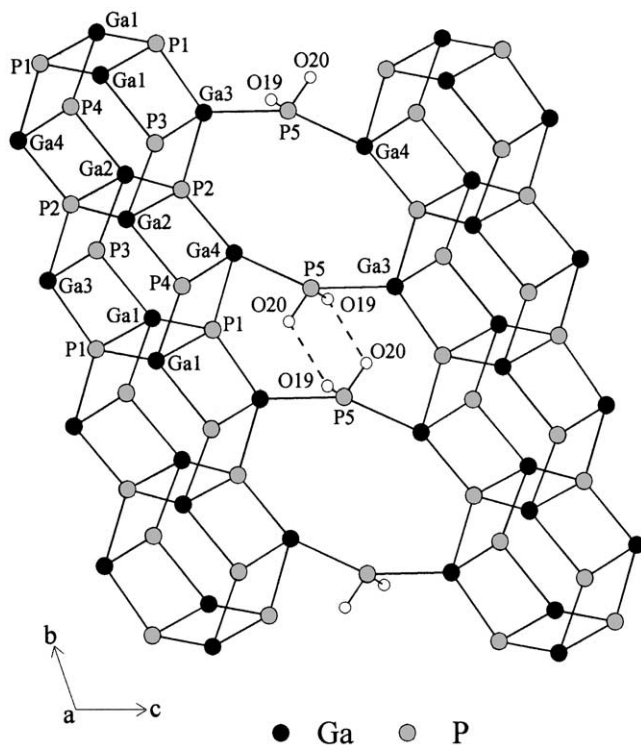


FIG. 4. View of (I) showing the 8MR channels (only O(19) and O(20) are shown, other O atoms and template atoms are omitted for clarity. Dashed lines correspond to H-bonds between O(19) and O(20) of adjacent P(5) atoms (drawing package, ATOMS (37)).

$[\text{NH}_3(\text{CH}_2)_4\text{NH}_3][\text{Ga}_4(\text{PO}_4)_4(\text{HPO}_4)]$  (V) (13), which has been prepared as a pure phase for the first time. The formation of these different framework structures results

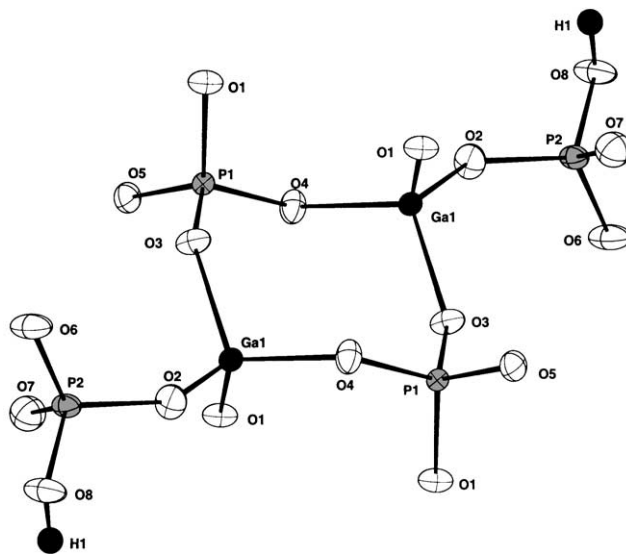
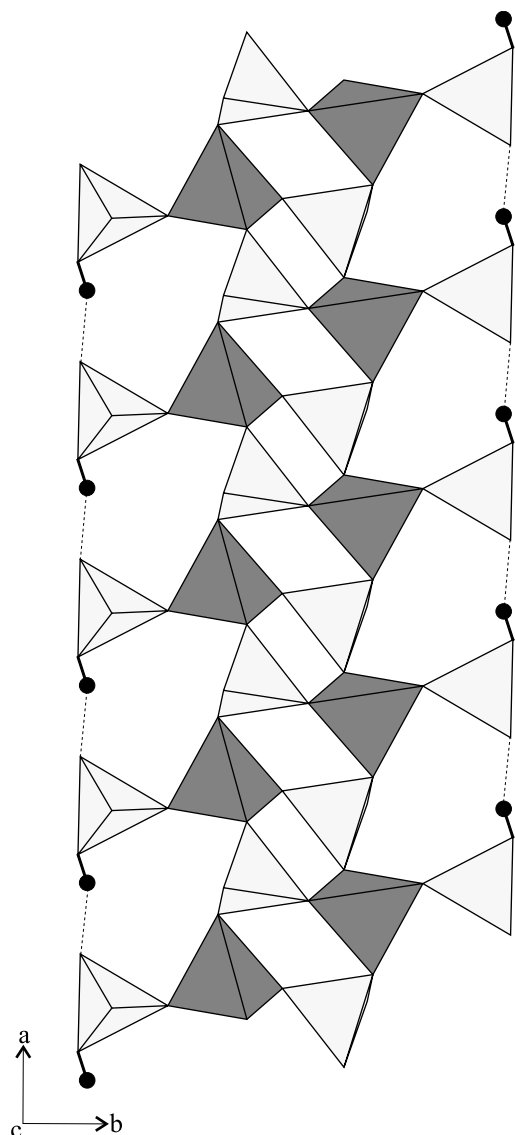


FIG. 5. The local coordination of the framework atoms in (II), the framework hydrogen atom is attached to O(8) (drawing package, CAMERON (36)).



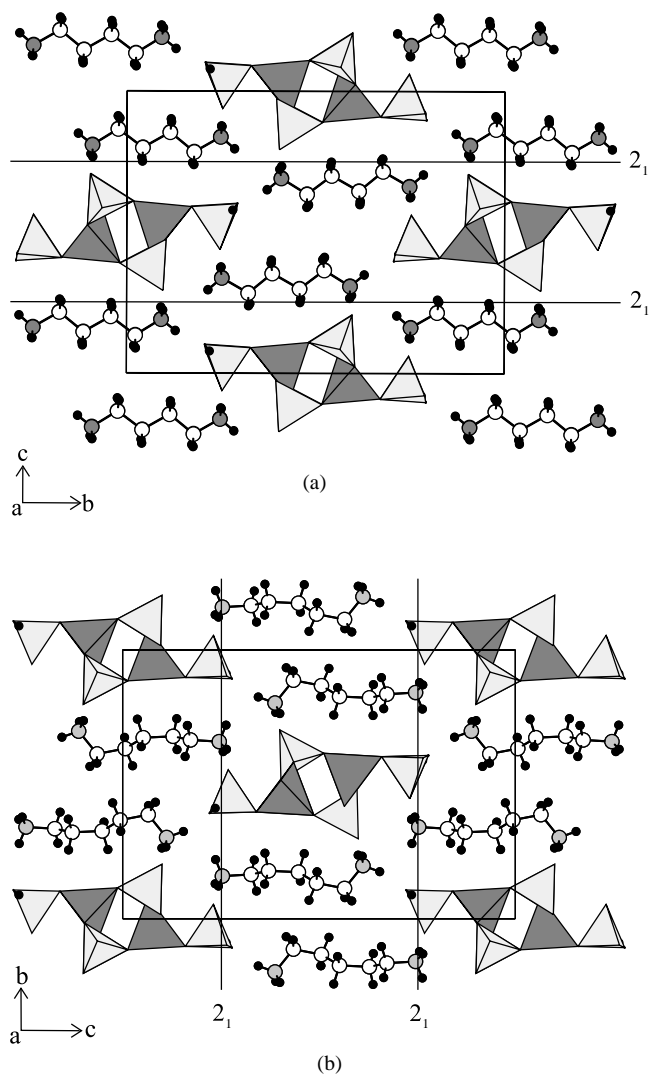


**FIG. 6.** View of zigzag chains of 4MR in (II). Dashed lines correspond to intra-chain H-bond between O(6) and O(8) of adjacent P(2) atoms. Dark gray tetrahedra = GaO<sub>4</sub>, light gray tetrahedra = PO<sub>4</sub> and black spheres = H atoms. The chains in (IV) are similar (drawing package, ATOMS (37)).

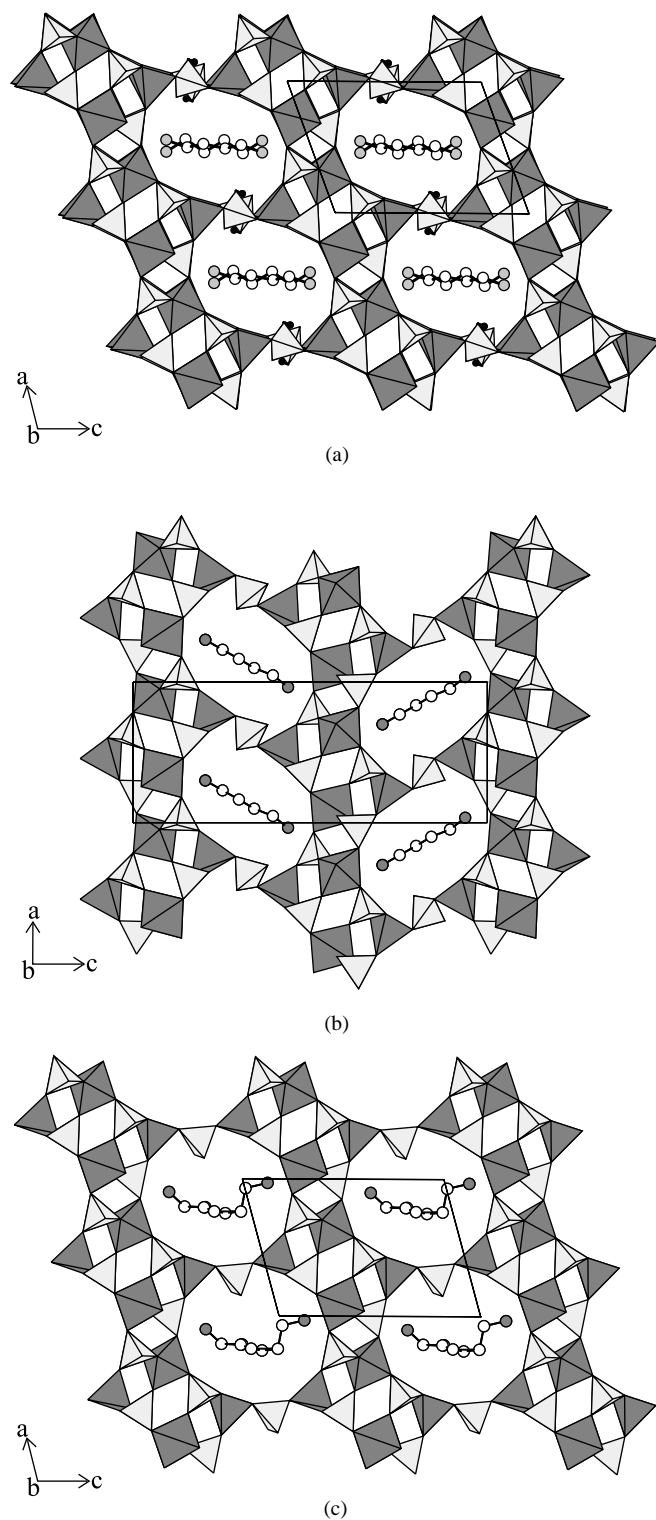
from variations in the composition of the initial gel. Pyrophosphoric acid was used as the source of phosphorus in each case and increasing the acid content leads to a change from a 1-D to 3-D GaPO framework containing either 1,4-diaminobutane or 1,5-diaminopentane as the structure-directing agent. No pyrophosphate (P<sub>2</sub>O<sub>7</sub>) groups are observed in these materials suggesting that the pyrophosphoric acid is hydrolyzed to orthophosphoric acid, H<sub>3</sub>PO<sub>4</sub>, under the reaction conditions used. This suggests that orthophosphoric acid may be used as the

source of P with similar results. It has subsequently proved possible to prepare both the 3-D framework (III) and 1-D chain (IV) materials templated with 1,5-diaminopentane using H<sub>3</sub>PO<sub>4</sub>. However, using 1,4-diaminobutane the only product formed over a range of orthophosphoric acid concentrations was found to be (V), the known 3-D structure, [NH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>NH<sub>3</sub>][Ga<sub>4</sub>(PO<sub>4</sub>)<sub>4</sub>(HPO<sub>4</sub>)], with no evidence for the formation of either (I) or (II).

(I) has an open framework similar to those found in related materials; the stoichiometric equivalent GaPO,



**FIG. 7.** Views of (a) (II) and (b) (IV) along the *a* axis showing the packing of the [Ga(PO<sub>4</sub>)(HPO<sub>4</sub>)]<sup>2-</sup> chains around the 2-fold screw axis (2<sub>1</sub>). In (b) only one of the disordered 1,5-diaminopentane cations is shown for clarity. Dark gray tetrahedra = GaO<sub>4</sub>, light gray tetrahedra = PO<sub>4</sub>, dark gray spheres = N atoms, white spheres = C atoms and black spheres = H atoms (drawing package, ATOMS (37)).



**FIG. 8.** Views of (a) (I), (b) (V) and (c) AlPO-HDA ( $x = 5$ ) along the  $b$  axis showing the packing of the D6R–4MR layers and the alignment of the linking  $\text{PO}_3(\text{OH})$  groups. Dark gray polyhedra =  $\text{GaO}_x$ , light gray tetrahedra =  $\text{PO}_4$ , dark gray spheres = N atoms, white spheres = C atoms and black spheres = H atoms (drawing package, ATOMS (37)).

$[\text{NH}_3(\text{CH}_2)_4\text{NH}_3][\text{Ga}_4(\text{PO}_4)_4(\text{HPO}_4)]$  (V) (13), and the AlPOs,  $[\text{NH}_3(\text{CH}_2)_x\text{NH}_3][\text{Al}_4(\text{PO}_4)_4(\text{HPO}_4)]$  ( $x = 5, 6$ ) (AlPO-HDA) (24, 25) (Fig. 8a, b and c ( $x = 5$ ), respectively). The AlPO framework (AlPO-HDA) is identical when either 1,5-diaminopentane (triclinic, space group  $P1$ ,  $a = 9.2450(9)$ ,  $b = 5.0657(5)$  and  $c = 12.688(2)$  Å,  $\alpha = 96.02(1)$ ,  $\beta = 102.88(1)$  and  $\gamma = 105.89(1)^\circ$  (24)) or 1,6-diaminohexane (monoclinic, space group  $Cc$ ,  $a = 17.682(1)$ ,  $b = 5.108(1)$  and  $c = 25.488(1)$  Å and  $\beta = 103.07(1)^\circ$  (25)) is used as template. Both (V) and AlPO-HDA are assembled from alternating  $(\text{Ga}/\text{Al})\text{O}_n$  ( $n = 4, 5$ ) and  $\text{PO}_4$  units to form D6R–4MR layers, which are connected by  $\text{PO}_3(\text{OH})$  units as described for (I). However, the assembly of the 3-D framework from these equivalent building blocks is different in the three materials. In (I) and AlPO-HDA the D6R–4MR layers lie parallel to the  $a$  axis so that each layer is exactly above an identical layer. The layers in (V), however, are stacked in such a way that adjacent layers are related by a 2-fold screw axis ( $2_1$ ). The alignment of the  $\text{PO}_3(\text{OH})$  groups which connect these layers also differs between the compounds (Fig. 8). In (I), as discussed, the  $\text{P}(5)\text{O}_3(\text{OH})$  groups are arranged so that there are pairs of strong intra-framework hydrogen bonds in alternate 8MR lying parallel to the  $b$  axis. In both AlPO-HDA and (V), however, there is only one type of 8MR. In the former, each 8MR contains one hydrogen bonding interaction of the type  $\text{O}_2(\text{OH})\text{P} = \text{O} \cdots (\text{HO})\text{PO}_3$  ( $\text{O} \cdots \text{O}$ ,  $\sim 2.74$  Å) [25], whilst the orientation of the  $\text{P} = \text{O}$  and  $\text{P} - \text{OH}$  groups of the  $\text{PO}_3(\text{OH})$  units in the latter preclude any such cross-channel interactions. As a consequence of these differences, the lattice parameter along the  $b$  axis is approximately doubled in (I) ( $\sim 10.1$  Å) compared to that observed for AlPO-HDA and (V). The structure of compound (III) could not be determined fully but the refined lattice parameters are very similar to those of AlPO-HDA prepared using 1,5-diaminopentane suggesting that the materials may be isostructural.

(II) and (IV) contain GaPO chains of the same connectivity which consist of a gallium-phosphate backbone with ‘pendant’  $\text{PO}_3(\text{OH})$  groups. Although another 1-D GaPO,  $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3][\text{Ga}(\text{PO}_4)(\text{HPO}_4)]$  (23), with the same stoichiometry exists, it has a different chain structure consisting of 4MR of alternating corner sharing  $\text{GaO}_4$  and  $\text{PO}_4$  tetrahedra with no ‘pendant’ groups. Pendant  $\text{PO}_3(\text{OH})$  groups have been observed in  $[\text{Ga}_4(\text{C}_{10}\text{H}_9\text{N}_2)_2(\text{PO}_4)(\text{H}_{0.5}\text{PO}_4)_2(\text{HPO}_4)_2(\text{H}_2\text{PO}_4)_2] \cdot \text{H}_2\text{O}$  (10) which consists of structurally unrelated chains containing  $\text{GaO}_4$  tetrahedra and  $\text{GaO}_5\text{N}$  octahedra that incorporate the structure-directing amine. The present chains have, however, been observed in a number of other phosphate systems including those of Al (32, 33), Co (26) and Zn (34, 35). These have the same connectivity as observed in (II) and (IV) but with different packing of the amine templates.

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