

Synthesis and Characterization of $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3][\text{Ga}(\text{PO}_4)(\text{PO}_3\text{OH})]$, a One-Dimensional Gallophosphate

Ann M. Chippindale,¹ Andrew D. Bond, Ashley D. Law, and Andrew R. Cowley

Chemical Crystallography Laboratory, University of Oxford, 9 Parks Rd., Oxford OX1 3PD, United Kingdom

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A new one-dimensional gallium phosphate, $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3][\text{Ga}(\text{PO}_4)(\text{PO}_3\text{OH})]$, has been synthesized under solvothermal conditions at 433 K in the presence of 1,4-diaminobutane and the structure determined using room-temperature single-crystal X-ray diffraction data ($M_r = 350.84$, orthorhombic, space group $Pnaa$, $a = 9.109(1)$, $b = 11.021(1)$, $c = 11.987(1)$ Å; $V = 1203.3$ Å³, $Z = 4$, $R = 2.84\%$ and $R_w = 3.54\%$ for 937 observed data ($I > 3(\sigma(I))$). The structure contains chains of alternating corner sharing GaO_4 and PO_4 tetrahedra between which lie diaminocations. The chains are held together by both strong interchain and chain-diamine hydrogen-bonding interactions giving rise to a new three-dimensional structure. This is compared with the structures of $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3][\text{Ga}(\text{PO}_4)(\text{PO}_3\text{OH})]$ and related aluminophosphates. © 1998 Academic Press

INTRODUCTION

Since 1982, a large number of microporous aluminophosphates (AIPOs) have been reported encompassing a wide range of structure types, both zeolitic and novel. Three-dimensional AIPO framework structures are common, e.g., AIPO₄-5 (1) and AIPO₄-34 (chabazite) (2), as are two-dimensional ones, e.g., $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3]_{1.5}[\text{Al}_3(\text{PO}_4)_4]$ (3) and $[\text{C}_5\text{NH}_6][\text{Al}_2(\text{PO}_4)(\text{PO}_3\text{OH})_2]$ (4). The one-dimensional AIPO frameworks prepared to date contain Al both in octahedral coordination, e.g., $\text{Na}_4\text{Al}(\text{PO}_4)_2(\text{OH})$ (5) and $\text{Na}_3\text{Al}(\text{PO}_4)(\text{PO}_3\text{OH})(\text{OH})$ (6), and tetrahedral coordination, e.g., $[\text{C}_{10}\text{N}_2\text{H}_9][\text{Al}(\text{PO}_4)(\text{PO}_2(\text{OH})_2)]$ (7), $[\text{C}_5\text{H}_9\text{NH}_3]_5[\text{Al}_3(\text{PO}_4)_4(\text{PO}_3\text{OH})]$ (8), and $[\text{C}_7\text{H}_{13}\text{NH}_3]_5[\text{Al}_3(\text{PO}_4)_4(\text{PO}_3\text{OH})]$ (9). In the last three examples, the chains consist of ‘backbones’ of edge-sharing ‘4-rings’ assembled from alternating PO_4 and AlO_4 units, the first having additional ‘pendant’ $\text{PO}_2(\text{OH})_2$ units and the second and third, which are isostructural, having ‘pendant’ $\text{PO}_3(\text{OH})$ units. A further series of tetrahedra-based one-dimensional AIPOs has also been prepared containing $[\text{AlP}_2\text{O}_8^{3-}]_n$ chains assembled from corner-sharing ‘4-rings’

and containing no pendant groups. Examples include $[\text{NH}_4][\text{NH}_3(\text{CH}_2)_2\text{NH}_3][\text{Al}(\text{PO}_4)_2]$ (10), $[\text{H}_3\text{O}][\text{NH}_3(\text{CH}_2)_2\text{NH}_3][\text{Al}(\text{PO}_4)_2]$ (11), and $[\text{Et}_3\text{NH}][\text{Al}_2(\text{PO}_3\text{OH})_2]$ (12), all of which have the same chain topology assembled from AlO_4 and PO_4 tetrahedra, but different interchain and chain-amine interactions leading in turn to different three-dimensional structures.

Gallophosphates (GaPOs) exhibit a structural diversity similar to that of AIPOs. Many three-dimensional, but fewer two-dimensional, GaPO framework structures have been reported and include $[\text{Me}_2\text{NH}(\text{CH}_2)_2\text{NHMe}_2][\text{Ga}_4(\text{PO}_4)_4(\text{PO}_3\text{OH})]$ (13) and $[\text{NH}_3(\text{CH}_2)_2\text{NH}_3]_{0.5}[\text{GaPO}_4(\text{OH})]$ (14) respectively. However, to date, there are only two examples known of GaPOs containing one-dimensional gallium-phosphate frameworks. $\text{Na}_3\text{Ga}(\text{PO}_3\text{OH})(\text{PO}_4)(\text{OH})$ (6) is isostructural with $\text{Na}_3\text{Al}(\text{PO}_3\text{OH})(\text{PO}_4)(\text{OH})$ (6) and contains anionic chains of formula $[\text{Ga}(\text{PO}_4)(\text{PO}_3\text{OH})(\text{OH})^{3-}]_n$ in which the Ga has octahedral coordination, while $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3][\text{Ga}(\text{PO}_4)(\text{PO}_3\text{OH})]$ contains tetrahedral Ga in $[\text{Ga}(\text{PO}_4)(\text{PO}_3\text{OH})^{2-}]_n$ chains (15).

In this work, we report the synthesis and structural characterization of a new one-dimensional GaPO, $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3][\text{Ga}(\text{PO}_4)(\text{PO}_3\text{OH})]$, and an alternative method for the synthesis of the previously reported phase $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3][\text{Ga}(\text{PO}_4)(\text{PO}_3\text{OH})]$. Although the two materials contain similar GaPO chains, the stacking of the chains in the two structures is very different and will be described.

EXPERIMENTAL

Synthesis and Initial Characterization

The title compound, $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3][\text{Ga}(\text{PO}_4)(\text{PO}_3\text{OH})]$, can be synthesized either as single crystals (Reaction (i), Table 1) or polycrystalline powder (Reaction (ii)) by a solvothermal method *via* predominantly nonaqueous gel precursors. In each reaction, Ga_2O_3 (approximately 1g) was dispersed in ethylene glycol by stirring and the 1,4-diaminobutane added with a small amount of $\text{Si}(\text{OEt})_4$. The latter reagent has been shown previously to act as a

¹To whom correspondence should be addressed.

TABLE 1
Summary of Gel Compositions and Reaction Products

Reaction	Gel composition	Products
(i)	Ga ₂ O ₃ : MnCl ₂ ·4H ₂ O : 8H ₃ PO ₄ : 20HOCH ₂ CH ₂ OH : 0.3Si(OEt) ₄ : 5NH ₂ (CH ₂) ₄ NH ₂	[NH ₃ (CH ₂) ₄ NH ₃][Ga(PO ₄)(PO ₃ OH)] (single crystals) and unidentified polycrystalline MnPO phase
(ii)	Ga ₂ O ₃ : 8H ₃ PO ₄ : 20HOCH ₂ CH ₂ OH : 0.3Si(OEt) ₄ : 5NH ₂ (CH ₂) ₄ NH ₂	[NH ₃ (CH ₂) ₄ NH ₃][Ga(PO ₄)(PO ₃ OH)] (pure polycrystalline powder)
(iii)	Ga ₂ O ₃ : 6.8H ₃ PO ₄ : 25.2HOCH ₂ CH ₂ OH : 0.1Si(OEt) ₄ : 4.2NH ₂ (CH ₂) ₃ NH ₂	[NH ₃ (CH ₂) ₃ NH ₃][Ga(PO ₄)(PO ₃ OH)] ^a (pure single crystals)

^aPreviously reported synthesis of this phase employed heating a gel of composition GaO(OH) : H₃PO₄ : 10Me₂SO : HF : 1.2NH₂(CH₂)₃NH₂ : 13H₂O at 423 K for 24 hours (15).

mineralizer under solvothermal conditions (16). For Reaction (i), MnCl₂·4H₂O was also added at this point. Finally, aqueous H₃PO₄ (85% by weight) was added and each gel stirred until homogenous, sealed in a Teflon-lined stainless-steel autoclave, and then heated at 433 K for 7 days. The solid products were collected by filtration, washed with water, and left to dry in air at 343 K.

Powder X-ray diffraction patterns of the bulk products of Reactions (i) and (ii) were recorded on a Philips PW1710 diffractometer using CuK α radiation ($\lambda = 1.5406 \text{ \AA}$) and energy-dispersive X-ray emission analysis was performed using a JEOL 2000FX analytical electron microscope with α -GaPO₄ as calibration standard. Silicon was not present in any of the crystallites examined.

The product of Reaction (i) consisted of colorless blocks of the title compound and white polycrystalline powder. The latter was shown by energy-dispersive X-ray emission analysis to be a manganese-phosphate phase, which remains, as yet, unidentified. Reaction (ii) produced a white polycrystalline sample of the title compound. The powder X-ray diffraction pattern of this product could be indexed fully on the basis of an orthorhombic unit cell with refined lattice parameters similar to those obtained from the single-crystal study ($a = 9.111(2)$, $b = 11.012(3)$, $c = 11.994(3) \text{ \AA}$). Energy-dispersive X-ray analysis showed the product to be monophasic with an average P:Ga ratio of 1.9(1). Combustion analysis gave the following results: C: 13.40%; H: 4.33%; N: 7.49%, with no chlorine present. These values compare reasonably well with those calculated from the proposed formula, [NH₃(CH₂)₄NH₃][Ga(PO₄)(PO₃OH)]: C: 13.69%; H: 4.31%; N: 7.98%.

[NH₃(CH₂)₃NH₃][Ga(PO₄)(PO₃OH)] was also prepared by a similar method in the presence of 1,3-diaminopropane (Reaction (iii), Table 1). The product, which was monophasic as confirmed by combustion analysis and powder X-ray diffraction, contained single crystals with lattice parameters similar to those obtained by Loiseau *et al.* for [NH₃(CH₂)₃NH₃][Ga(PO₄)(PO₃OH)] (15) (triclinic,

spacegroup $P - 1$, $a = 8.311(1)$, $b = 8.615(1)$, $c = 8.883(1) \text{ \AA}$, $\alpha = 111.66(1)$, $\beta = 107.57(1)$, $\gamma = 98.42(1)^\circ$).

Single-Crystal X-ray Diffraction

It was observed that crystals of the title compound became brittle on exposure to air and, as a result, a single crystal from the product of Reaction (i) was sealed into a thin-walled glass capillary prior to study. X-ray data were collected at room temperature using an Enraf-Nonius MACH3 (CAD4) diffractometer (graphite-monochromated CuK α radiation ($\lambda = 1.5418 \text{ \AA}$)). The crystallographic data are summarized in Table 2. The unit cell was determined as orthorhombic from 24 well-centered reflections over the

TABLE 2
Crystallographic Data for [NH₃(CH₂)₄NH₃][Ga(PO₄)(PO₃OH)]

Formula	[NH ₃ (CH ₂) ₄ NH ₃][GaP ₂ O ₈ H]
M_r	350.84
Crystal size (mm)	0.1 × 0.1 × 0.3
Crystal habit	Colorless block
Crystal system	Orthorhombic
Space group	<i>Pnaa</i>
a (Å)	9.109(1)
b (Å)	11.021(1)
c (Å)	11.987(1)
Cell volume (Å ³)	1203.3
Z	4
ρ_{calc} (gcm ⁻³)	1.97
μ (cm ⁻¹)	141.9
Unique data	1222
Observed data ($I > 3\sigma(I)$)	937
R_{merge}	0.021
Residual electron density (min, max) (eÅ ⁻³)	-0.79, 0.56
Number of parameters refined	100
R	0.0284
R_w	0.0354

angle range ($20.56 \leq \theta \leq 23.64$)° and the cell parameters were optimized by least-squares refinement ($a = 9.109(1)$, $b = 11.021(1)$, $c = 11.987(1)$ Å). Intensity data were then collected over the angle range ($0 \leq \theta \leq 74.33$)° using the ω -2 θ 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 ψ -scans and further corrected for Lorentz and polarization effects within the program RC93 (16).

The systematic absence conditions in the reduced data ($0kl$: $k + l$ odd; $h0l$, $hk0$: h odd) suggested that the space group was $Pnaa$ (nonstandard setting of No. 56 (18)), which was subsequently confirmed as correct by the successful refinement of the structure. The structure was solved by direct methods using the program SIR92 (19) and all non-hydrogen framework atoms were located. The template carbon, nitrogen, and hydrogen atoms and the framework hydrogen atom were then located in difference Fourier maps. All Fourier calculations and subsequent least-squares refinements were carried out using the CRYSTALS suite of programs (20). The positions of all the hydrogen atoms were refined without restraint, with the isotropic thermal parameters fixed at 0.05 \AA^2 . In the final cycle, 100 parameters, including anisotropic thermal parameters for all nonhydrogen atoms, were refined. The data were corrected for extinction by the method of Larsen (21) and a three-term Chebyshev polynomial was applied as weighting scheme (22). The refinement converged to give $R = 0.0284$ ($R_w = 0.0354$).

Fractional atomic coordinates and isotropic thermal parameters are given in Table 3 and selected bond distances and angles in Table 4. The local coordination of the framework atoms is shown in Fig. 1.

TABLE 3
Fractional Atomic Coordinates and Isotropic Thermal Parameters (\AA^2) for [NH₃(CH₂)₄NH₃][Ga(PO₄)(PO₃OH)]

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (iso)
Ga(1)	0.2965(1)	0.25	0.25	0.0190
P(1)	0.5416(1)	0.3135(1)	0.4062(1)	0.0184
O(1)	0.5432(2)	0.3961(1)	0.5095(1)	0.0238
O(2)	0.5353(2)	0.1816(2)	0.4368(2)	0.0277
O(3)	0.4079(2)	0.3527(2)	0.3341(1)	0.0251
O(4)	0.1832(2)	0.3444(2)	0.1599(1)	0.0263
N(1)	0.1644(3)	-0.0463(2)	0.0697(2)	0.0293
C(1)	0.1553(4)	-0.0916(3)	0.1857(2)	0.0361
C(2)	0.1737(4)	-0.2268(3)	0.1905(2)	0.0353
H(1)	0.264(5)	-0.056(4)	0.045(3)	0.05
H(2)	0.102(5)	-0.088(4)	0.023(3)	0.05
H(3)	0.147(4)	0.030(4)	0.058(3)	0.05
H(11)	0.222(5)	-0.052(4)	0.228(3)	0.05
H(12)	0.057(5)	-0.065(4)	0.216(3)	0.05
H(21)	0.109(5)	-0.269(4)	0.148(3)	0.05
H(22)	0.268(5)	-0.245(3)	0.148(3)	0.05
H(100)	0.5	0.5	0.5	0.05

TABLE 4
Selected Bond Distances (Å) and Angles (°) for [NH₃(CH₂)₄NH₃][Ga(PO₄)(PO₃OH)]

$2 \times \text{Ga}(1)\text{--O}(3)$	1.824(2)	$\text{N}(1)\text{--C}(1)$	1.480(4)
$2 \times \text{Ga}(1)\text{--O}(4)$	1.820(2)	$\text{C}(1)\text{--C}(2)$	1.500(4)
		$\text{C}(2)\text{--C}(2)$	1.515(6)
$\text{P}(1)\text{--O}(1)$	1.537(2)		
$\text{P}(1)\text{--O}(2)$	1.500(2)	$\text{O}(1)\text{--H}(100)$	1.217(2)
$\text{P}(1)\text{--O}(3)$	1.555(2)		
$\text{P}(1)\text{--O}(4)$	1.552(2)		
$\text{O}(3)\text{--Ga}(1)\text{--O}(3)$	112.4(1)	$\text{O}(1)\text{--P}(1)\text{--O}(2)$	112.2(1)
$\text{O}(3)\text{--Ga}(1)\text{--O}(4)$	106.78(7)	$\text{O}(1)\text{--P}(1)\text{--O}(3)$	106.9(1)
$\text{O}(3)\text{--Ga}(1)\text{--O}(4)$	110.01(8)	$\text{O}(1)\text{--P}(1)\text{--O}(4)$	105.9(1)
$\text{O}(4)\text{--Ga}(1)\text{--O}(4)$	110.9(1)	$\text{O}(2)\text{--P}(1)\text{--O}(3)$	112.0(1)
		$\text{O}(2)\text{--P}(1)\text{--O}(4)$	111.7(1)
$\text{Ga}(1)\text{--O}(3)\text{--P}(1)$	124.8(1)	$\text{O}(3)\text{--P}(1)\text{--O}(4)$	107.8(1)
$\text{Ga}(1)\text{--O}(4)\text{--P}(1)$	130.4(1)		
		$\text{P}(1)\text{--O}(1)\text{--H}(100)$	118.6(1)
$\text{N}(1)\text{--C}(1)\text{--C}(2)$	111.4(2)	$\text{O}(1)\text{--H}(100)\text{--O}(1)$	180
$\text{C}(1)\text{--C}(2)\text{--C}(2)$	111.8(3)		

RESULTS AND DISCUSSION

The structure consists of infinite gallophosphate chains of formula $[\text{GaP}_2\text{O}_8\text{H}^{2-}]_n$ containing '4-rings' assembled from vertex-sharing GaO_4 and PO_4 tetrahedra. Charge

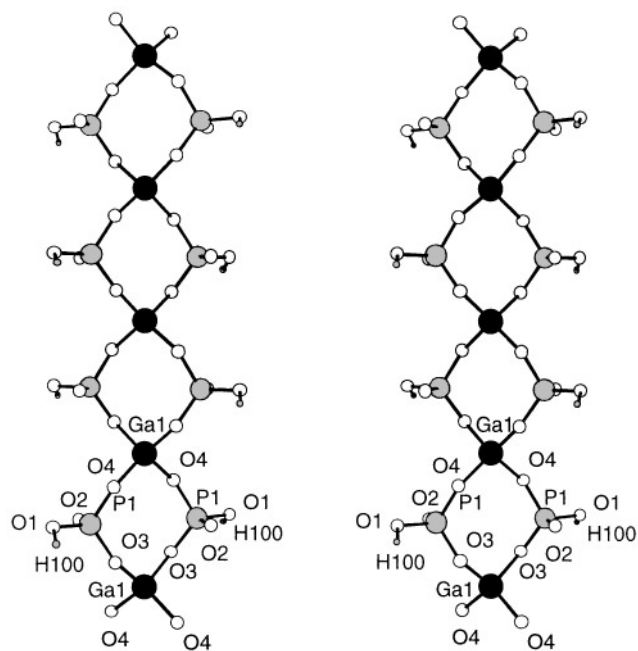


FIG. 1. Stereoview of the $[\text{Ga}(\text{PO}_4)(\text{PO}_3\text{OH})]^{2-}_n$ unit along the *b* axis showing the chains of corner sharing '4-rings' built from $\text{Ga}(1)\text{O}_4$ and $\text{P}(1)\text{O}_3(\text{OH})$ tetrahedra. Note: H(100) occupies a special position midway between two chains. (Drawing package, ATOMS (23)).

balance is achieved by the presence of diprotonated diamine cations located between the chains.

The structure contains one crystallographically distinct GaO_4 unit and one distinct PO_4 unit with bond-length values close to those observed in other GaPOs containing similar polyhedra ($\text{Ga}(1)-\text{O}_{\text{av}}$, 1.822(2) Å and $\text{P}(1)-\text{O}_{\text{av}}$, 1.537(2) Å). For example, in $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3][\text{Ga}(\text{PO}_4)(\text{PO}_3\text{OH})]$, $\text{Ga}-\text{O}_{\text{av}} = 1.815(9)$ Å and $\text{P}-\text{O}_{\text{av}} = 1.532(2)$ Å (15). Two oxygens of the PO_4 unit are involved in bridging to adjacent GaO_4 units while the other two form terminal phosphorus-oxygen groups. Of the latter groups, one has a significantly shorter bond length ($\text{P}(1)-\text{O}(2)$, 1.500(4) Å),

implying that it is a $\text{P}=\text{O}$ group and the other has a significantly longer bond length ($\text{P}(1)-\text{O}(1)$, 1.555(2) Å), suggesting that oxygen O(1) is protonated. A hydrogen atom H(100) was located in a difference Fourier map on a special position equidistant from the O(1) atoms in adjacent chains ($\text{O}(1)-\text{H}(100)$, 1.217(2) Å), resulting in a short, symmetric hydrogen bond ($\text{O}(1)-\text{H}(100)\cdots\text{O}(1')$, 2.433(3) Å).

The $[\text{GaP}_2\text{O}_8\text{H}^{2-}]_n$ chains run parallel to the a axis and are linked through the $\text{O}(1)-\text{H}(100)\cdots\text{O}(1')$ hydrogen-bonding interactions to form a three-dimensional gallium-phosphate structure (Fig. 2). The anionic framework is charge balanced by diprotonated 1,4-diaminobutane cations,

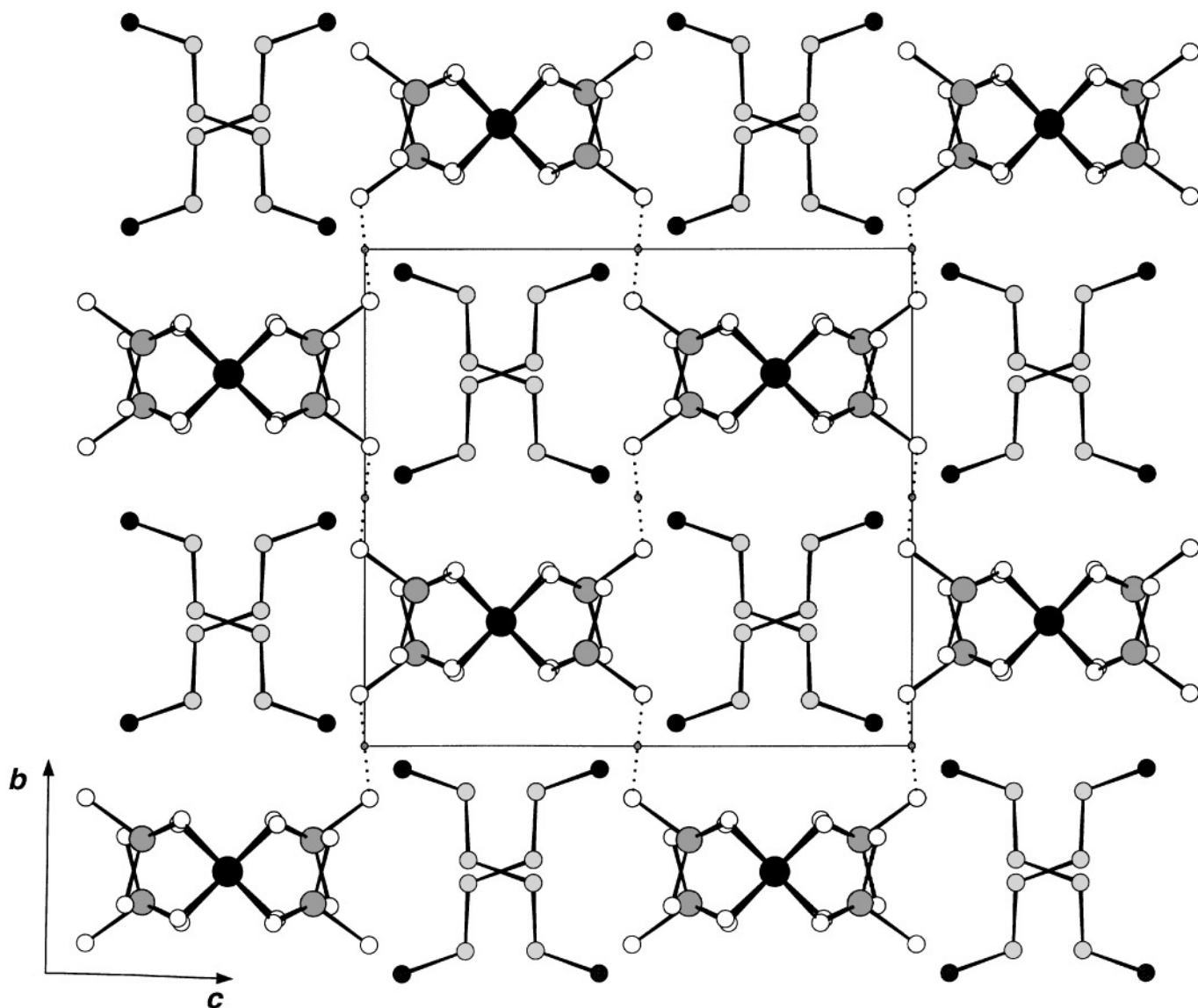


FIG. 2. View of the title compound $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3][\text{Ga}(\text{PO}_4)(\text{PO}_3\text{OH})]$ along the a axis showing the linking of the GaPO chains through symmetrical interchain hydrogen bonds (represented as dotted lines) to form a '3-dimensional' gallophosphate structure. Diprotonated 1,4-diaminobutane cations reside between the chains and are hydrogen bonded to the inorganic framework (hydrogen atoms and chain-diamine hydrogen bonds not shown). (Drawing package, CAMERON (24)).

which are also hydrogen bonded to the gallium-phosphate chains. The nitrogen N(1) of the organic cation interacts with two oxygens in the same GaPO chain (N(1)⋯O(2), 2.841(3), N(1)⋯O(1), 2.832(3) Å) and a third in an adjacent chain (N(1)⋯O(2)', 2.774(3) Å).

CONCLUSIONS

The chain GaPO [NH₃(CH₂)₄NH₃][Ga(PO₄)(PO₃OH)] containing organic cations and tetrahedrally coordinated gallium has been prepared under solvothermal conditions in

the presence of ethylene glycol. Single crystals of the material can be synthesized in the presence of manganese(II) chloride hydrate and the transition metal is not ultimately incorporated into the gallophosphate phase. Omission of the manganese chloride leads to the formation of a pure sample of [NH₃(CH₂)₄NH₃][Ga(PO₄)(PO₃OH)], but in the form of a polycrystalline powder. The role of the transition metal in the mechanism of crystallization is, as yet, unclear, but other GaPO phases have also been observed to require the presence of heterometals for their production as single crystals, *e.g.*, the formation of crystals

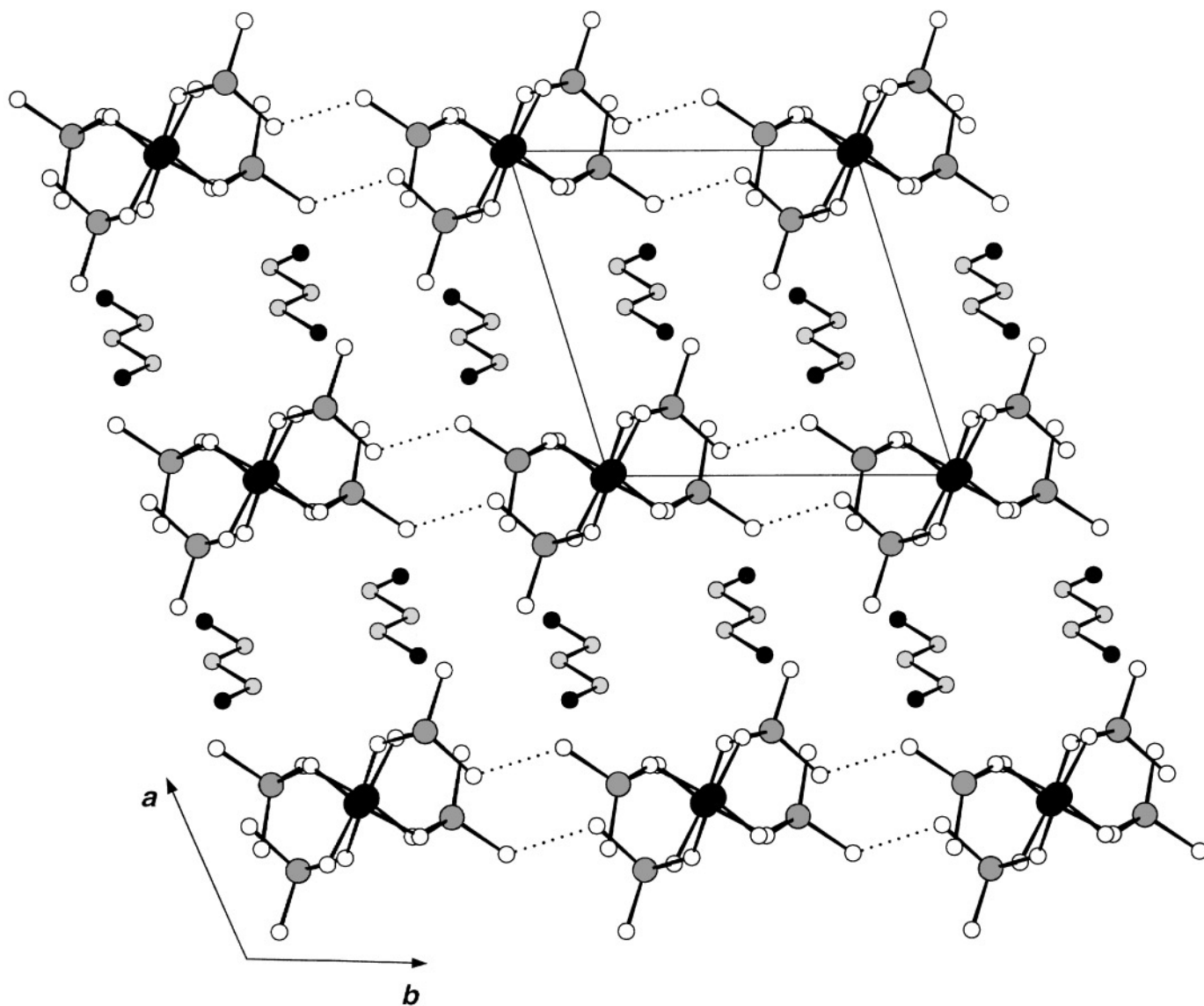


FIG. 3. View of [NH₃(CH₂)₃NH₃][Ga(PO₄)(PO₃OH)] along the *c* axis (15). Hydrogen bonding interactions (represented as dotted lines) between neighboring GaPO chains generate a 'layered' gallophosphate structure. Diprotonated 1,3-diaminopropane cations reside between the layers and are hydrogen bonded to the inorganic framework (hydrogen bonds not shown). All hydrogen atoms have been omitted (Drawing package, CAMERON (24)).

of $[\text{Me}_2\text{NH}(\text{CH}_2)_2\text{NHMe}_2][\text{Ga}_4\text{P}_5\text{O}_{20}\text{H}]\cdot\text{H}_2\text{O}$ requires a source of magnesium (13, 25). $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3][\text{Ga}(\text{PO}_4)(\text{PO}_3\text{OH})]$ can also be prepared as a pure phase using ethylene glycol; the previously reported synthesis employed dimethyl sulphoxide as solvent (15).

The gallium-phosphate chains in $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3][\text{Ga}(\text{PO}_4)(\text{PO}_3\text{OH})]$ are similar to those observed in $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3][\text{Ga}(\text{PO}_4)(\text{PO}_3\text{OH})]$ (15) and the $[\text{AlP}_2\text{O}_8^{3-}]_n$ chains in $[\text{NH}_4][\text{NH}_3(\text{CH}_2)_2\text{NH}_3][\text{Al}(\text{PO}_4)_2]$ (10), $[\text{H}_3\text{O}][\text{NH}_3(\text{CH}_2)_2\text{NH}_3][\text{Al}(\text{PO}_4)_2]$ (11), and $[\text{Et}_3\text{NH}][\text{Al}_2(\text{PO}_3\text{OH})_2]$ (12). All these compounds contain MO_4 and PO_4 tetrahedra alternately linked to form ribbons of corner sharing '4-rings'. The chain structure can accommodate some degree of flexibility; the angle between the planes containing the Ga and P atoms of adjacent rings has approximate values 40.9, 57.9, 67.9, and 82.2° in the compounds $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3][\text{Ga}(\text{PO}_4)(\text{PO}_3\text{OH})]$, $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3][\text{Ga}(\text{PO}_4)(\text{PO}_3\text{OH})]$ (15), $[\text{NH}_4][\text{NH}_3(\text{CH}_2)_2\text{NH}_3][\text{AlP}_2\text{O}_8]$ (10), and $[\text{Et}_3\text{NH}][\text{Al}_2(\text{PO}_3\text{OH})_2]$ (12) respectively.

The packing arrangements of the chains in the two GaPO compounds are different from each other and also from those observed in the AlPO phases, leading to two new distinct three-dimensional structures. The structure of $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3][\text{Ga}(\text{PO}_4)(\text{PO}_3\text{OH})]$ described above is similar to that of $[\text{Et}_3\text{NH}][\text{Al}_2(\text{PO}_3\text{OH})_2]$ (12), although the latter has an additional framework hydroxyl group and incorporates intrachain as well as interchain hydrogen bonding. In $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3][\text{Ga}(\text{PO}_4)(\text{PO}_3\text{OH})]$ (15), the $[\text{GaP}_2\text{O}_8\text{H}^{2-}]_n$ chains run parallel to the *c* axis and are linked *via* strong interchain hydrogen bonds ($\text{O}\cdots\text{O}'$, 2.443(2) Å) to two-dimensional gallium-phosphate 'layers' in the *bc* plane (Fig. 3). The anionic layers stack along the *a* axis in an AAAA arrangement and are charge-balanced by diprotonated 1,3-diaminopropane cations occupying interlayer sites. An extensive network of hydrogen bonds links the organic cation and the gallophosphate framework to generate a structure which, as yet, has no aluminophosphate analog.

As the templates present in the gallophosphate materials differ only in the lengths of their carbon skeletons, but not their ability to hydrogen bond, the difference in chain packing is solely a consequence of the differing template sizes. The layer structure of $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3][\text{Ga}(\text{PO}_4)(\text{PO}_3\text{OH})]$ might therefore be expected to accommodate templates of various sizes in the interlayer void, but the three-dimensional nature of the structure of $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3][\text{Ga}(\text{PO}_4)(\text{PO}_3\text{OH})]$ imposes limits on the size of charge-balancing species occluded.

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