

Judith L. Kissick and Ann M.
Chippindale*Department of Chemistry, University of Reading,
Whiteknights, Reading RG6 6AD, EnglandCorrespondence e-mail:
a.m.chippindale@reading.ac.uk

Key indicators

Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$
 R factor = 0.028
 wR factor = 0.074
Data-to-parameter ratio = 12.8For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.**[NH₃(CH₂)₃NH₃][Ga(P₂O₇)(H₂PO₄)]: a new organically templated gallium phosphate-diphosphate**

Propane-1,3-diammonium gallium phosphate diphosphate, [NH₃(CH₂)₃NH₃][Ga(P₂O₇)(H₂PO₄)], consists of anionic chains containing GaO₆ octahedra linked by tetrahedral P₂O₇ diphosphate and PO₂(OH)₂ units charge-balanced by 1,3-diaminopropane dications. The chains, which are held together by a network of hydrogen bonds involving both interchain and chain–diamine interactions, are isostructural with those previously observed in [NH₃(CH₂)₂NH₃][Ga(P₂O₇)(H₂PO₄)]. Different packing arrangements are, however, adopted in the two materials.

Received 14 January 2002
Accepted 22 January 2002
Online 8 February 2002

Comment

Reported here is the second example of an organically templated gallophosphate in which PO₄ and P₂O₇ groups coexist as independent units. The title compound, [NH₃(CH₂)₃NH₃][Ga(P₂O₇)(H₂PO₄)], consists of one-dimensional polymeric gallium phosphate-diphosphate anions of formula [Ga(P₂O₇)(H₂PO₄)]_x²⁻ running parallel to the *c* axis, which are charge-balanced by 1,3-diaminopropane dications lying in the interchain spaces (Fig. 1). The chains are isostructural with those found in [NH₃(CH₂)₂NH₃][Ga(P₂O₇)(H₂PO₄)] (Chippindale, 2000). However, the packing of the chains and amine dications is different in the two materials; the title compound crystallizes in *C2/c*, whereas [NH₃(CH₂)₂NH₃][Ga(P₂O₇)(H₂PO₄)] crystallizes in *Cc*.

One crystallographically distinct Ga atom and two distinct P atoms are present in octahedral GaO₆ and tetrahedral-based PO₄ and P₂O₇ units with site symmetries $\bar{1}$, 2 and 1, respec-

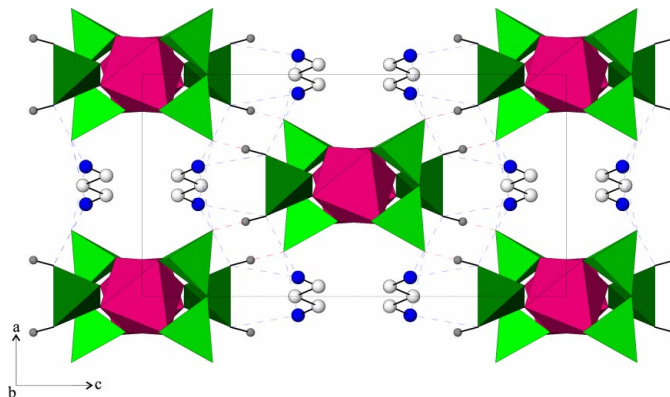


Figure 1

View of [NH₃(CH₂)₃NH₃][Ga(P₂O₇)(H₂PO₄)], showing the packing of the chains along the *c* axis and the interchain and chain–amine hydrogen bonding. Dark-green tetrahedra = PO₄, mid-green tetrahedra = P₂O₇, pink octahedra = GaO₆, blue spheres = N atoms, white spheres = C atoms and grey spheres = H atoms. Dashed red lines = interchain hydrogen bonds and dashed blue lines = chain–amine hydrogen bonds. Template H atoms have been omitted for clarity.

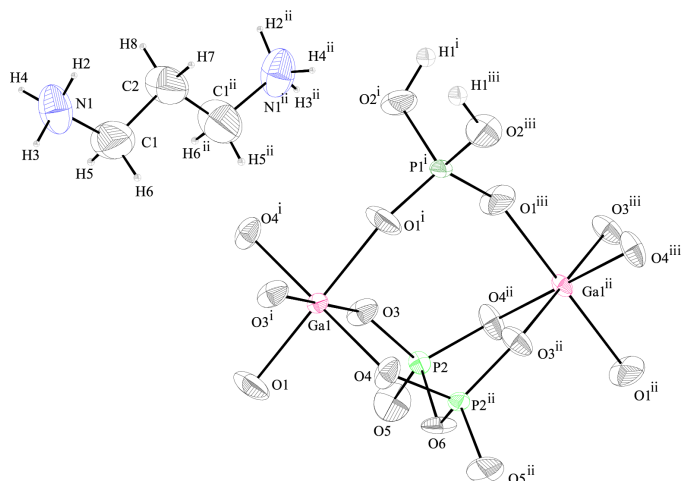


Figure 2

Local coordination of atoms in $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3][\text{Ga}(\text{P}_2\text{O}_7)(\text{H}_2\text{PO}_4)]$ (50% probability displacement ellipsoids). [Symmetry codes: (i) $-x, -y, -z$; (ii) $-x, y, -z + \frac{1}{2}$; (iii) $x, -y, z + \frac{1}{2}$]

tively (Fig. 2). The GaO_6 octahedra share all their vertices with phosphorus-based bridging units. The P1-based phosphate group bridges adjacent Ga atoms *via* O1. The remaining P1—O2 bonds are substantially longer, consistent with the observation in difference Fourier maps of H atoms associated with these atoms. This is confirmed by bond-valence calculations (Brown & Altermatt, 1985). The P2-based diphosphate group has an eclipsed conformation and bridges the Ga atoms through O3—P2—O4 linkages. The P2—O6 bond is significantly longer than the other P2—O bonds but is of comparable length to P—O bonds of P—O—P diphosphate linkages in other metal diphosphates (Chippindale, 2000; Mandel, 1975). The remaining P2—O5 bond corresponds to a P—O bond with some degree of multiple-bond character.

The structure is held together by both interchain and chain-amine hydrogen bonding. The P1—O2H groups of the $\text{P1O}_2(\text{OH})_2$ units and the terminal P2—O5 groups of the diphosphate units in neighbouring chains are sufficiently close for hydrogen bonding to occur between them to generate a three-dimensional assembly. Additional hydrogen bonding occurs between the NH_3 group of the diamination and the framework atoms O2, O4 and O5 (Table 2).

Experimental

Single crystals of $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3][\text{Ga}(\text{P}_2\text{O}_7)(\text{H}_2\text{PO}_4)]$ were prepared under solvothermal conditions. Ga_2O_3 (0.876 g) was dispersed in ethylene glycol (5.6 ml) by stirring, followed by addition of 1,3-diaminopropane (1.1 ml) and a small amount of $\text{Si}(\text{OEt})_4$ which acts as a mineralizer. Aqueous H_3PO_4 (3 ml, 85 wt%) was then added and the gel stirred until homogeneous, sealed in a Teflon-lined steel autoclave, and heated at 433 K for 7 d. The solid product was collected by filtration, washed copiously with water, and dried in air at 353 K. A clear colourless crystal was isolated from the bulk sample for analysis. Powder X-ray diffraction and CHN analysis (calculated for $\text{C}_3\text{H}_{14}\text{GaN}_2\text{O}_{11}\text{P}_3$: C 8.65, H 3.39, N 6.72%; experimental: C 8.61,

H 3.56, N 6.76%) showed that the sample was monophasic. This was confirmed by Energy Dispersive Analytical X-ray (EDAX) analysis performed using a Phillips CM20 Transmission Electron Microscope which showed that all crystallites contained Ga and P but no Si and had a Ga:P ratio of 0.33 (2). Thermogravimetric analysis using a Stanton Redcroft STA 1000 Thermal Analyser over the range 553–883 K, at a heating rate of 10 K min^{-1} under flowing N_2 , showed a smooth weight loss of 18.2%, over the range 553–883 K, to give a black X-ray amorphous product. Loss of 1,3-diaminopropane would correspond to a weight loss of 17.8%.

Crystal data

$(\text{C}_3\text{H}_{12}\text{N}_2)[\text{Ga}(\text{P}_2\text{O}_7)(\text{H}_2\text{PO}_4)]$
 $M_r = 416.79$
 Monoclinic, $C2/c$
 $a = 8.5390$ (7) Å
 $b = 15.9795$ (15) Å
 $c = 9.2826$ (6) Å
 $\beta = 102.007$ (5)°
 $V = 1238.89$ (17) Å³
 $Z = 4$

$D_x = 2.235 \text{ Mg m}^{-3}$
 Cu $K\alpha$ radiation
 Cell parameters from 23 reflections
 $\theta = 10\text{--}27^\circ$
 $\mu = 7.36 \text{ mm}^{-1}$
 $T = 293$ (2) K
 Needle, colourless
 $0.30 \times 0.05 \times 0.03 \text{ mm}$

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.675$, $T_{\max} = 0.809$
 2586 measured reflections
 1267 independent reflections
 1082 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.036$
 $\theta_{\text{max}} = 74.2^\circ$
 $h = -10 \rightarrow 10$
 $k = -19 \rightarrow 19$
 $l = -11 \rightarrow 0$
 3 standard reflections
 frequency: 60 min
 intensity decay: 2.8%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.074$
 $S = 1.11$
 1267 reflections
 99 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0406P)^2 + 1.2495P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.002$
 $\Delta\rho_{\text{max}} = 0.76 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.86 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Ga1—O3	1.949 (2)	P2—O3	1.518 (2)
Ga1—O1	1.976 (2)	P2—O4 ⁱ	1.530 (2)
Ga1—O4	1.977 (2)	P2—O6	1.615 (1)
P1—O1	1.497 (2)	N1—C1	1.485 (3)
P1—O2	1.580 (2)	C1—C2	1.502 (3)
P2—O5	1.505 (2)		
O1 ⁱⁱⁱ —Ga1—O1	180	O5—P2—O3	113.59 (10)
O3 ⁱⁱⁱ —Ga1—O3	180	O5—P2—O4 ⁱ	111.03 (10)
O4—Ga1—O4 ⁱⁱ	180	O3—P2—O4 ⁱ	111.65 (9)
O3—Ga1—O1 ⁱⁱ	91.64 (7)	O5—P2—O6	106.84 (10)
O3—Ga1—O1	88.36 (7)	O3—P2—O6	107.07 (8)
O3—Ga1—O4	93.58 (7)	O4 ⁱ —P2—O6	106.16 (7)
O1—Ga1—O4	90.21 (7)	P1—O1—Ga1	144.43 (11)
O3—Ga1—O4 ⁱⁱ	86.42 (7)	P2—O3—Ga1	135.12 (10)
O1—Ga1—O4 ⁱⁱ	89.79 (7)	P2 ⁱ —O4—Ga1	126.05 (10)
O1 ⁱⁱⁱ —P1—O1	117.08 (14)	P2—O6—P2 ⁱ	119.78 (14)
O1 ⁱⁱⁱ —P1—O2	110.44 (9)	N1—C1—C2	112.9 (2)
O1—P1—O2	107.11 (9)	C1 ⁱ —C2—C1	108.2 (3)
O2—P1—O2 ⁱⁱⁱ	103.88 (13)		

Symmetry codes: (i) $-x, y, \frac{1}{2} - z$; (ii) $-x, -y, -z$; (iii) $-x, y, -\frac{1}{2} - z$.

Table 2
Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O2-H1 \cdots O5^i$	0.97 (2)	1.56 (2)	2.526 (2)	179 (4)
$N1-H2 \cdots O2^{ii}$	0.89	2.10	2.810 (3)	136
$N1-H3 \cdots O4^{ii}$	0.89	2.00	2.862 (3)	163
$N1-H4 \cdots O5^{iii}$	0.89	1.87	2.755 (3)	175

Symmetry codes: (i) $\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$; (ii) $\frac{1}{2} - x, \frac{1}{2} - y, -z$; (iii) $-\frac{1}{2} - x, \frac{1}{2} - y, -z$.

The C, N and H template atoms and the framework H atoms were located in difference Fourier maps. The fractional coordinates and isotropic displacement parameters of the framework H atoms were refined. However, the template H atoms were placed geometrically during the final refinement procedure and constrained to ride on their parent atoms with $U_{iso}(H) = 1.2U_{eq}(C/N)$.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to

solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ATOMS* (Shape Software, 1998); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

AMC thanks the EPSRC for research grant GR/N37490.

References

- Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* **B41**, 244–247.
 Chippindale, A. M. (2000). *Chem. Mater.* **12**, 818–816.
 Enraf–Nonius (1994). *CAD-4 EXPRESS*. Enraf–Nonius, Delft, The Netherlands.
 Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
 Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
 Mandel, N. S. (1975). *Acta Cryst.* **B31**, 1730–1734.
 North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
 Shape Software (1998). *ATOMS*. Shape Software, 521 Hidden Valley Rd., Kingsport, TN 37663, USA.
 Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.