

$(C_4H_{12}N_2)_3[Ga_4(OH)_2(H_2PO_4)_2(HPO_4)_4(PO_4)_2]$:
a new organically templated gallium phosphate

Chia-Her Lin* and Sue-Lein Wang

Department of Chemistry, Chung-Yuan Christian University, Chung-Li 320, Taiwan

Correspondence e-mail: chiaher@cycu.edu.tw

Key indicators

Single-crystal X-ray study

T = 295 K

Mean $\sigma(C-C)$ = 0.006 Å

R factor = 0.029

wR factor = 0.078

Data-to-parameter ratio = 13.7

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

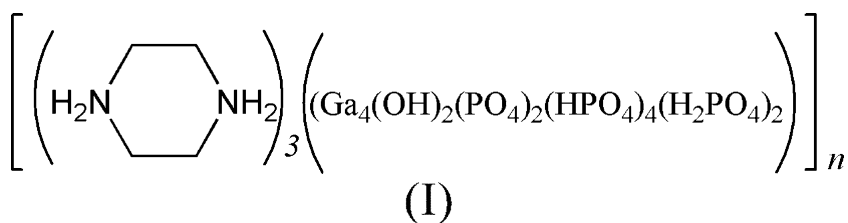
The solvothermal reaction of gallium oxide with phosphoric acid in water/ethylene glycol in the presence of piperazine gave the title compound, bis(piperazinium) bis(dihydrogenphosphato)tetra- μ_2 -hydrogenphosphato-di- μ_3 -hydroxo-di- μ_3 -phosphato-tetragallate(III), $(C_4H_{12}N_2)_3[Ga_4(OH)_2(H_2PO_4)_2(HPO_4)_4(PO_4)_2]$. The compound is isostructural with its Fe^{III} analogue, and contains one-dimensional anionic chains with piperazinium cations lying between them. The tetranuclear anionic building blocks and the piperazinium cations lie on inversion centres.

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Comment

The synthesis of open-framework transition-metal phosphates has been a subject of intense research owing to their interesting structural chemistry and potential applications in catalysis. A large number of these materials have been synthesized using organic amines as structure-directing agents (Cheetham *et al.*, 1999). They commonly adopt three-dimensional framework structures, with only a few having two-dimensional layer or one-dimensional chain structures. Similarly, for gallium phosphates, there have been only a few reported materials with one-dimensional chain structures (Chippindale *et al.*, 1998; Lin & Lii, 1998; Chen *et al.*, 2000).



The title compound, (I) (Fig. 1), is a one-dimensional gallium phosphate that is isostructural with its Fe^{III} analogue $(C_4H_{12}N_2)_3[Fe_4(OH)_2(H_2PO_4)_2(HPO_4)_4(PO_4)_2] \cdot H_2O$ (Zima & Lii, 1998). The one-dimensional anionic framework structure constructed along the *a* axis (Fig. 2) is essentially indistinguishable in the two compounds. However, there are small differences in the positions of the piperazinium cations between the chains, and the Fe^{III} structure contains one solvent water molecule per formula unit, which is not present in (I). The tetranuclear anionic building blocks and the piperazinium cations lie on inversion centres. The piperazinium cations in (I) form N—H \cdots O hydrogen bonds (Table 1) to the framework, and O—H \cdots O hydrogen bonds (Table 1) are also formed between one-dimensional chains.

Experimental

The solvothermal synthesis of (I) was carried out at 433 K for 3 d in a Teflon-lined acid digestion bomb with an internal volume of 23 ml, followed by slow cooling to room temperature at 6 K h⁻¹. A single-phase product consisting of transparent colourless crystals of (I) was obtained from a mixture of piperazine (0.345 g), Ga₂O₃ (0.140 g), 85% H₃PO₄ (0.60 ml), H₂O (6.0 ml) and ethylene glycol (6.0 ml). Powder X-ray diffraction measurements confirmed the phase purity. Elemental analysis found: C 10.71, H 2.45, N 6.25%; calculated: C 10.32, H 3.21, N 5.93%.

Crystal data

(C₄H₁₂N₂)₃[Ga₄(OH)₂(H₂PO₄)₂·(HPO₄)₄(PO₄)₂]
M_r = 1345.19
 Triclinic, *P* $\bar{1}$
a = 6.2754 (3) Å
b = 13.0604 (5) Å
c = 13.6268 (6) Å
 α = 117.208 (1)°
 β = 98.796 (1)°
 γ = 93.053 (1)°
V = 971.90 (7) Å³
Z = 1
D_x = 2.298 Mg m⁻³
 Mo *K*α radiation
 μ = 3.20 mm⁻¹
T = 295 (2) K
 Needle, colourless
 0.50 × 0.15 × 0.10 mm

Data collection

Bruker SMART 1K CCD diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.512, *T_{max}* = 0.726
 9405 measured reflections
 4155 independent reflections
 3742 reflections with *I* > 2σ(*I*)
R_{int} = 0.037
 θ_{max} = 28.1°

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.029
wR (*F*²) = 0.078
S = 1.03
 4155 reflections
 304 parameters
 H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0443P)^2 + 0.7591P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.76 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.73 \text{ e \AA}^{-3}$

Table 1 Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1 <i>D</i> ...O10 ⁱ	0.90	2.05	2.884 (3)	153
N1—H1 <i>C</i> ...O11	0.90	1.80	2.691 (3)	171
N3—H3 <i>C</i> ...O6 ⁱⁱ	0.90	1.82	2.717 (3)	174
N3—H3 <i>D</i> ...O16	0.90	1.84	2.726 (3)	170
O8—H8...O4 ⁱ	0.82 (1)	1.88 (1)	2.674 (3)	166 (4)
O12—H12...O16 ⁱⁱⁱ	0.82 (1)	1.73 (1)	2.540 (3)	171 (4)
O15—H15...O3 ^{iv}	0.81 (1)	2.03 (1)	2.829 (3)	166 (4)

Symmetry codes: (i) *x* - 1, *y*, *z*; (ii) *x*, *y* - 1, *z*; (iii) -*x*, -*y*, -*z*; (iv) -*x*, -*y* + 1, -*z* + 1.

All H atoms were visible in difference Fourier maps. Those bound to C and N were placed in idealized positions (C—H = 0.97 Å, N—H = 0.90 Å) and allowed to ride during subsequent refinement with *U_{iso}*(H) = 1.2*U_{eq}*(C,N). H atoms bound to O were refined with the O—H distance restrained to 0.82 (1) Å, and with *U_{iso}*(H) = 1.5*U_{eq}*(O).

Data collection: SMART (Bruker, 1997); cell refinement: SAINT (Bruker, 1997); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Bruker, 2001); program(s) used to refine

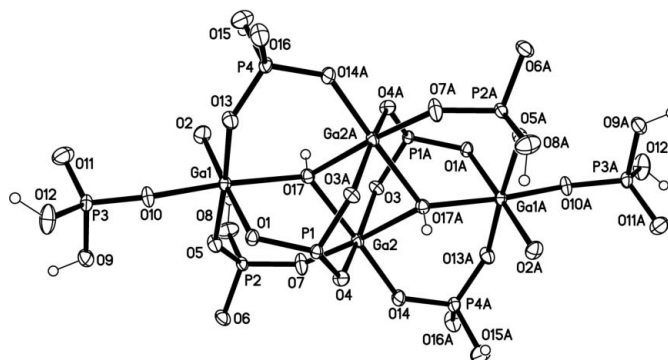


Figure 1 Tetranuclear building unit in the framework structure of (I) showing displacement ellipsoids at the 50% probability level for non-H atoms. H atoms are shown as arbitrary spheres. The suffix A denotes atoms generated by the symmetry operator (1 - *x*, 1 - *y*, 1 - *z*). The chains are formed by connection of O2 and O2A in this unit to symmetry equivalents of P1 and P1A in adjacent units.

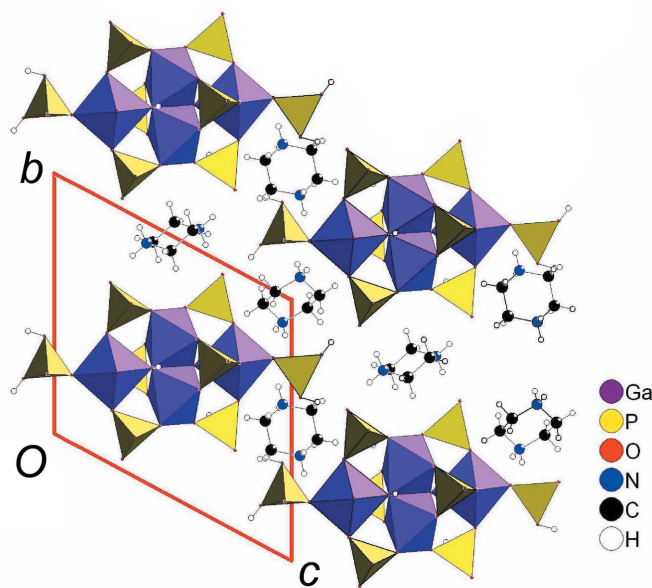


Figure 2 Structure of (I) viewed along the *a* direction.

structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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