Crystal Structure of the Gallophosphate Framework: *X*-Ray Characterization of $Ga_9P_9O_{36}OH{\cdot}HNEt_3$

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A gallophosphate, $Ga_9P_9O_{36}OH{\cdot}HNEt_3$, has been synthesised and its framework structure has been determined by single crystal *X*-ray diffraction.

Recently, the syntheses of open framework aluminophosphates with structures and properties similar to aluminosilicate zeolites have been reported.[1—3] This was followed by the report[4] of the gallophosphates, some of which are analogues of aluminophosphate molecular sieves ($AlPO_4$-n). Replacement of aluminium in a framework structure should result in materials with unique properties and structures, with a variety of cavity and pore geometries. Reported here is the synthesis and the single crystal *X*-ray structure of a gallophosphate, $Ga_9P_9O_{36}OH{\cdot}HNEt_3$.

The gallophosphate was synthesised by a hydrothermal procedure and associated with a specific 'template,' triethylamine. An aqueous mixture of hydrated GaOOH, phosphoric acid, and Et_3N (1.5 Et_3N : 1.0 Ga_2O_3 : 1.2 P_2O_5 : 50 H_2O) was heated at 180 °C for 4 days under autogeneous pressure. Comparison with the characteristic *X*-ray powder diffraction patterns of the $AlPO_4$ frameworks reported[1,4—7] so far indicated that the gallophosphate had a unique, novel structure.

The structure† was solved by direct methods and refined using block matrix-least-squares. On the basis of the elemental analysis, the asymmetric unit contents shown in Figure 1 appear to be $Ga_3P_3O_{12}{\cdot}\frac{1}{3}OH\frac{1}{3}HNEt_3$, $\frac{1}{3}H^+$ being added to the organic unit to balance the charge of the inorganic unit.

† *Crystal data:* $Ga_3P_3O_{12}{\cdot}\frac{1}{3}OH{\cdot}\frac{1}{3}HNEt_3$, M_r = 524.74; space group $P6_3$, a = 12.2665(32), c = 16.7462(50) Å, U = 2182.16 Å^3, Z = 6; D_c = 2.396 g cm^{-3}; number of reflections for cell refinement 25; crystal shape: hexagonal prism, 40 × 100 μm long; Mo-K_α 0.71069 Å, graphite monochromator, Nicolet XRD R_3 diffractometer; h, ± k, l; scan mode θ–2θ, variable speed; 1188 unique out of 3885 measured intensities [$I > 2.60\sigma(I)$]; μ = 61.81 cm^{-1}, SHELXTL; isotropic thermal parameters. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

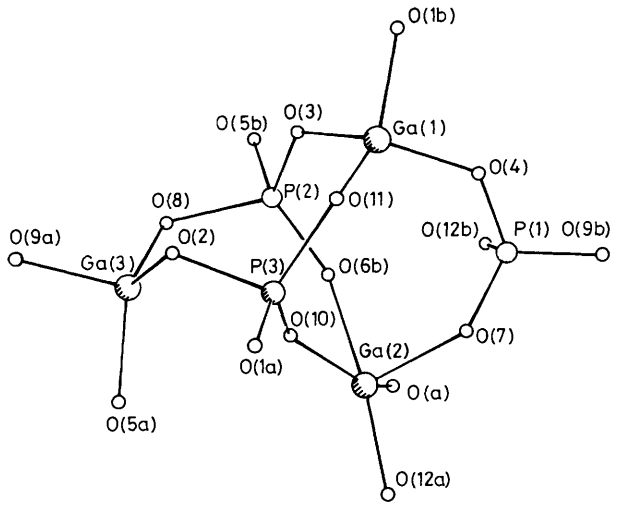

Figure 1. The asymmetric unit of the gallophosphate structure. Selected and average bond lengths: P–O 1.55, Ga(1)–O 1.791, Ga(2)–O 1.920, Ga(2)–O(a) 1.836, Ga(3)–O 1.820 Å. O(a) represents the position of a hydroxy group.

Each phosphorus atom is tetrahedrally co-ordinated and shares an oxygen atom with four adjacent gallium atoms. Of the three types of gallium atoms, two lie at tetrahedral centres, and the third is located in a distorted trigonal bipyramid. Twelve of the thirteen types of oxygen atom are bonded to one phosphorus and one gallium atom, whereas the thirteenth, the position of a hydroxy group, is symmetrically bonded to three gallium atoms (type 2). All the co-ordination polyhedra are vertex-shared. The co-ordination states of the gallium atoms are related to those in $GaPO_4$-14 reported by Parise[4] in which gallium atoms are 4-, 5-, and 6-co-ordinated with oxygen atoms or hydroxy groups.

In the three-dimensional net, there are two open channels running along the *c* axis as shown in Figure 2; the smaller passes through the origin and its axis coincides with the *c* axis, while the larger coincides with the three-fold axis and accommodates the charged triethylamine template. Both the channels are formed from gallium and phosphorus equilaterial triangles of different sizes, perpendicular to the *c* axis.

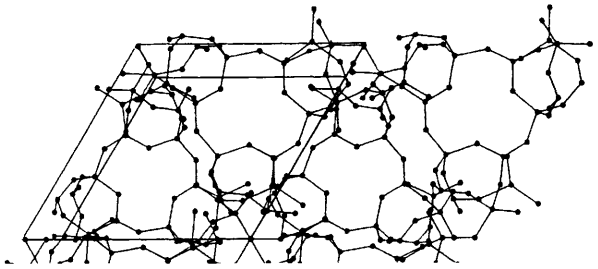

Figure 2. Packing plot projected along *c* showing the framework structure, with O, Ga, and P atoms all indicated by small filled circles.

Alternatively, they can be viewed as zigzag 6-rings packed in the direction of the *c* axis, in which gallium and phosphorus atoms are cross-linked *via* oxygen atoms. As a result, the gallium and phosphorus atoms in the channels are not aligned.

The two channels are connected in the 001 plane through 10- and 8-rings to form a hexagonal packing pattern with a rectangular cross-section.

In summary, a gallophosphate with an open framework structure has been synthesised and its crystal structure solved. It has channels in both the 001 and 010 planes which accommodate the triethylamine template.

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