A Novel Mixed Octahedral–Tetrahedral Framework: *X*-Ray Characterization of a Microporous Gallophosphate, $Ga_2P_2O_8(OH)H_2O{\cdot}NH_4{\cdot}H_2O{\cdot}0.16$ PrOH ($GaPO_4$-C_7)

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The structure of the microporous gallophosphate, $Ga_2P_2O_8(OH)H_2O{\cdot}NH_4{\cdot}H_2O{\cdot}0.16$ PrOH, consists of gallium-centred octahedra and phosphorus-centred tetrahedra as basic building units to form three-dimensional channels with the 8-ring running along the *a*, *b*, and *c* axes in which NH_4^+ cations are located in pairs.

Recently the syntheses of a series of microporous aluminophosphates ($AlPO_4$-n) have been reported,[1—3] some of which are analogues of the aluminosilicate zeolite molecular sieves. Subsequently a number of aluminophosphate derivatives containing silicon, boron, gallium, and various transition metal atoms were synthesized.[4—6] The syntheses and structures of some microporous gallophosphates have also been reported.[7—10] Compared to the aluminophosphates, the gallophosphates possess more complicated framework structures, which result from the variety in the co-ordination of the gallium atom. Reported here is the *X*-ray crystal structure of another member of the gallophosphate family ($GaPO_4$-C_n), $GaPO_4$-C_7 [$Ga_2P_2O_8(OH)H_2O{\cdot}NH_4{\cdot}H_2O{\cdot}0.16$ PrOH].

The title compound was synthesized by a hydrothermal method. An aqueous mixture of hydrated GaO_2H, phosphoric acid, and propylamine with the gel composition 2.2 $PrNH_2$: 1.0 Ga_2O_3 : 1.2 P_2O_5: 50 H_2O was heated at 200 °C for 3 days under autogenous pressure. Comparison with the characteristic *X*-ray powder diffraction patterns of the $AlPO_4$ and $GaPO_4$ frameworks reported so far indicated that the gallophosphate had a unique, novel structure.

The structure† consists of gallium-centred octahedra and phosphorus-centred tetrahedra. The composition analysis of the sample corresponds to the asymmetric unit content $Ga_2P_2O_8(OH)H_2O{\cdot}NH_4{\cdot}H_2O{\cdot}0.16$ PrOH. The co-ordination environment of gallium and phosphorus atoms in the asymmetric unit is shown in Figure 1. Each phosphorus atom is tetrahedrally co-ordinated and shares an oxygen atom with an adjacent gallium atom. Both gallium atoms are co-ordinated with six oxygen atoms and lie in the slightly distorted octahedra. Eight of the ten types of oxygen atoms are bonded to one phosphorus atom and one gallium atom, while the ninth, O(10), representing the position of a water molecule, is only bonded to one gallium atom [Ga(1)]. The tenth type of oxygen atom, [O(1)], representing a hydroxy group, is co-ordinated to three gallium atoms [Ga(1), Ga(2) and Ga(2a)].

The structure consists of an open gallophosphate framework with the inclusion of disordered PrOH molecules and

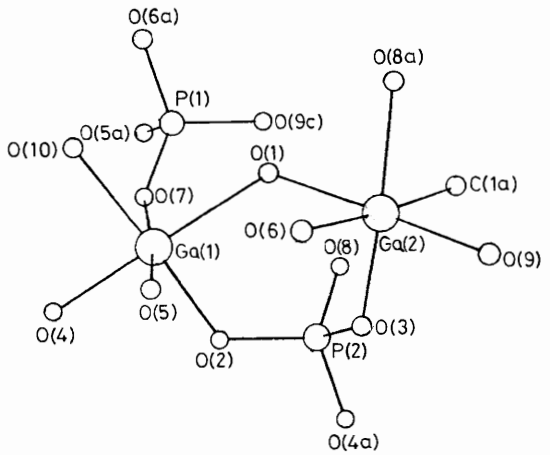

Figure 1. The structure of $GaPO_4$-C_7 showing the co-ordination of Ga and P atoms. Selected average bond lengths: P–O 1.535, Ga(1)–O 1.974, Ga(1)–O(10) 2.032, Ga(1)–O(1) 2.131, Ga(2)–O 1.989, Ga(2)–O(1) 2.136 Å. O(10) from a water molecule, O(1) from a hydroxy group.

† *Crystal data*: for $Ga_2P_2O_8(OH)H_2O{\cdot}NH_4{\cdot}H_2O{\cdot}0.16$ PrOH, monoclinic system, space group $P2_1/n$, a = 9.681(3), b = 9.657(3), c = 9.762(3) Å, β = 102.90(2)°, U = 889.59 Å^3, D_c = 2.86 g/cm^3, Z = 4, μ(Mo-K_α) = 67 cm^{-1}, λ = 0.7107 Å, crystal dimension 0.3 × 0.2 × 0.2 mm, R = 0.0361, R_w = 0.0342 for 2946 unique observed reflections with $|F| \geq 3\sigma(|F|)$ collected at 20 °C on a Nicolet R_3 four-circle diffractometer by using the ω-scan technique with variable scan speed from 4.0 to 29.3°/min in the range of $3° \leq 2\theta \leq 67°$. The structure was solved by direct methods and refined by block-matrix least-squares. All computations were carried out on an Eclipse S/250 computer using the SHELXTL program. All hydrogen atoms except those in PrOH were revealed from a difference Fourier map. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue 1.

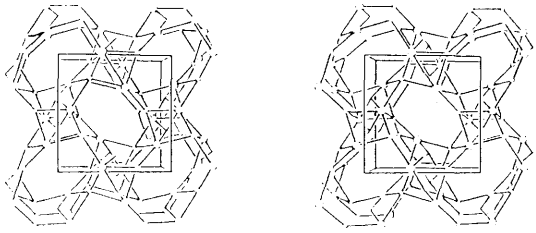

Figure 2. Stereoview plot of the $GaPO_4$-C_7 framework structure along the *c* axis showing the framework with Ga (big circles) and P (small circles) atoms.

NH_4^+ cations to balance the framework charge. The three-dimensional framework along the *c* axis is shown in Figure 2. In the structure there are 3-, 4-, and 8-membered rings composed of GaO_6 octahedra and PO_4 tetrahedra. Also the structure possesses three-dimensional channels running along [100], [010] and [001], respectively. All the channels are built by cross packing of boat-shaped 8-membered rings.

One of the unique structural features of $GaPO_4$-C_7 is that all Ga atoms are 6-co-ordinated with O atoms, while in other microporous gallophosphates[7—10] most Ga atoms are 5- and 6-co-ordinated, with some remaining 4-co-ordinated. The group of three gallium-centred octahedra linked by one oxygen atom (OH) is another feature of the $GaPO_4$-C_7 structure, although the co-ordination of the oxygen atom in this way is similar to that in $AlPO_4$-15, where one oxygen atom is co-ordinated to three aluminium atoms.[11]

In the synthesis of $GaPO_4$-C_7 the propylamine molecule was used as the templating agent, but the *X*-ray diffraction showed that NH_4^+ cations are located in pairs in the channels. The propyl alcohol molecules formed from the hydrolysis of propylamine molecules in the synthesis systems would be distributed in a disordered manner in the channels, thereby not contributing to crystal reflection. It seems that both inorganic NH_4^+ cations and organic alcohol molecules act as the templates to balance the charge of the framework and fill the channels.

In summary, the microporous gallophosphate, $GaPO_4$-C_7, consists of an open gallophosphate framework with GaO_6 octahedra and PO_4 tetrahedra, having 8-membered ring channels running along [100], [010], and [001]. These channels contain ordered NH_4^+ cations and disordered PrOH molecules as the structure-directing agents.

Received, 14th December 1988; Com. 8/04909B

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