Synthesis and Structure of a Novel Open-framework Gallium Phosphate $[Me_2NH(CH_2)_2NHMe_2]^{2+}[Ga_4P_5O_{20}H]^{2-}\cdot H_2O$

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The synthesis and structural characterisation of the title compound, the first gallium phosphate to be prepared with Ga : P ratio 4 : 5, are described; the 3D structure is unique and contains large pores in which the *N,N,N′,N′*-tetramethylethylenediamine cations and water molecules reside.

There has recently been much interest in the synthesis of new open-framework materials, especially metal phosphates, because of their potential sorption and catalytic properties. The literature now contains numerous examples of gallium phosphates (GaPOs) with 3D structures, some of which have frameworks analogous to those of AlPOs and aluminium silicates,[1–3] and others of which are unique.[4,5] Most of the GaPOs reported to date have Ga : P ratios of 1 : 1, although there is one example, $Na_3Ga_5(PO_4)_4O_2(OH)_2\cdot 2H_2O$, which has Ga : P > 1.[6] This behaviour is in contrast to the AlPO family, where a number of compounds with Al : P ratios less than unity have been identified. These show a range of structure types including isolated AlPO clusters (Al : P, 1 : 4),[7] chains (Al : P, 1 : 2),[8] layers (Al : P, 2 : 3 and 3 : 4)[9,10] and 3D frameworks (Al : P, 5 : 6).[11] Here we describe the synthesis, structural and thermal characterisation of the first GaPO with Ga : P ratio of 4 : 5. The 3D structure is unique and there is no known AlPO with this metal : phosphorus ratio.

The title compound was synthesised under hydrothermal conditions from a predominantly nonaqueous system. Ga_2O_3 (1 g) and MgO (0.1 g) were dispersed in butan-1-ol (7.8 cm^3) by stirring and *N,N,N′,N′*-tetramethylethylenediamine (2 cm^3) added. $Si(OEt)_4$ (0.12 cm^3) was then added to act as a mineraliser and the solution stirred for a further 10 min. Finally orthophosphoric acid (1 cm^3, 85% by mass) was added to give a gel of overall composition Ga_2O_3: 0.5 MgO: 3.25 H_3PO_4: 16

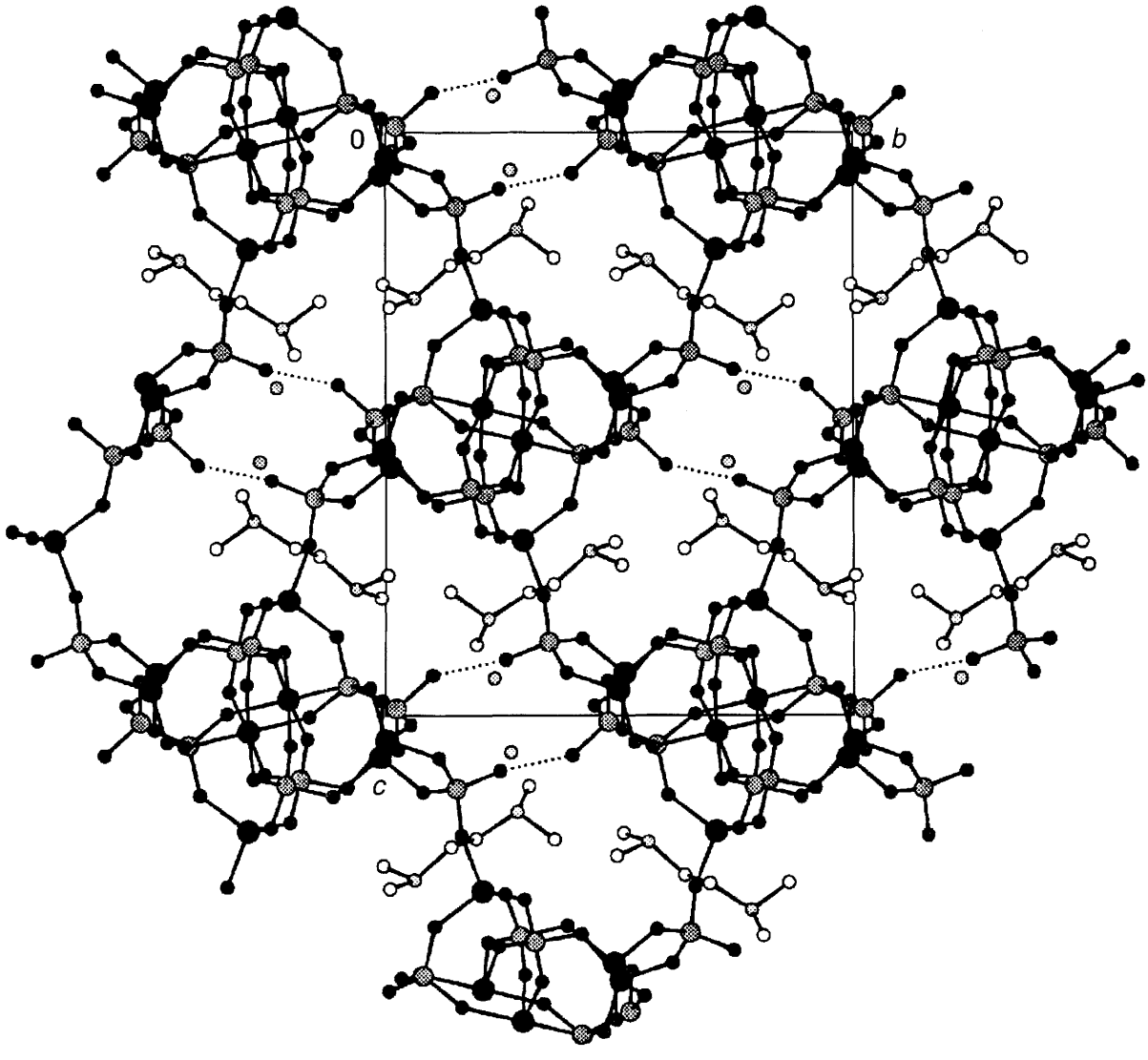

Fig 1 View of title compound along the *a*-axis showing large elliptical channels. Hydrogen bonding between P=O and P–OH groups is represented by broken lines. (N.B. The framework Ga atoms are represented as black spheres, P as larger shaded spheres and O as smaller shaded spheres. In the amine cations, N is shaded and C unshaded. Hydrogen atoms are omitted).

butan-1-ol: 0.1 $Si(OEt)_4$: 2.5 amine. The gel was sealed in a Teflon-lined stainless steel autoclave and heated at 180 °C for 7 d. The solid product was collected by filtration, washed with distilled water and dried at 80 °C. Examination under the optical microscope revealed white polycrystalline material and two distinct, colourless, crystalline components; large, faceted, block-shaped crystals of the title compound and small faceted crystals of the α-quartz analogue of $GaPO_4$. Analytical electron microscopy of a finely ground sample of the product mixture showed no magnesium or silicon present in any of the crystallites examined. Three components, with Ga : P ratios of 4 : 5, 1 : 1 and 1 : 2, were distinguished corresponding to the title compound, $GaPO_4$ and an unidentified phase, respectively. A polycrystalline sample of the title compound was subsequently prepared from a gel of the same composition but in the absence of MgO and with butan-2-ol replacing butan-1-ol. The powder X-ray diffraction pattern indicated that this product was single phase and this was further confirmed by C, H and N analysis. (Found: C, 8.31; N, 3.02; H, 2.33%. Calc. C, 8.09; N, 3.14; H, 2.36%.) Thermogravimetric analysis of the pure powdered sample over 15–800 °C shows two broad mass losses; one corresponding to water loss (*ca.* 2% by mass over 90–250 °C) and the other to partial amine loss (*ca.* 10% by mass 320–600 °C). A powder X-ray pattern of the final product indicates that the major decomposition product is the low-cristobalite form of $GaPO_4$.[12] A crystal was selected from the original sample for study by four-circle diffractometry.†

The structure consists of a network of GaO_4 and PO_4 tetrahedra and GaO_6 octahedra. Of the four crystallographically distinct Ga atoms, three are tetrahedrally coordinated to oxygen [$Ga–O_{av}$ = 1.83 Å, $(O–Ga–O)_{av}$ = 109.2°] and the fourth octahedrally coordinated [$Ga–O_{av}$ = 1.96 Å, $(O–Ga–O)_{av}$ = 176.4, 90.0°]. All the GaO_4 and GaO_6 vertices are shared with PO_4 units. Three of the five crystallographically distinct PO_4 groups are almost regular tetrahedra [$P–O_{av}$ = 1.53 Å, $(O–P–O)_{av}$ = 109.4°] and have fully shared vertices. The two remaining PO_4 groups each share three vertices with Ga polyhedra but also contain either a P=O or a P–OH group of lengths 1.496 and 1.539 Å, respectively. The Ga and P units are linked in an alternating manner to give an open 3D framework of formula $[Ga_4P_5O_{20}H]^{2-}$ containing cavities in which the diprotonated amine and occluded water molecules reside. The most interesting features are the large elliptical channels (major and minor axes dimensions of approximately 16.50 and 6.65 Å, respectively) running parallel to the *a*-axis which have puckered windows containing 16 Ga/P atoms (Fig. 1). Strong hydrogen bonds are formed between P=O and P–OH groups across the window (O···O 2.52 Å), effectively dividing it into three smaller channels, two of which are approximately circular. Each amine dication straddles two of the elliptical channels. One end of the dication is linked to a bridging oxygen in the framework through hydrogen bonds (N···O 2.91 Å) whilst the other end is hydrogen bonded to a water molecule (N···OH_2 2.66 Å), which in turn is bonded to the P=O group of the framework (H_2O···O=P 2.73 Å). Large elliptical channels have also been identified in JDF-20, $[Al_5P_6O_{24}H]^{2-}·2[N(Et)_3H]^+$,[11] the only 3D aluminium phosphate prepared to date with a Al : P ratio less than 1.

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† *Crystal data* for $Ga_4P_5O_{21}C_6N_2H_{21}$, M = 890.98, orthorhombic, space group $P2_12_12_1$, a = 9.574(4), b = 14.000(3), c = 17.435(5) Å, V = 2330.3 Å^3, Z = 4, μ(Cu-Kα) = 95.53 cm^{-1}, D_c = 2.54 g cm^{-3}. Data were collected on an Enraf-Nonius CAD4 diffractometer using the ω-2θ technique, for the range $0 < 2\theta < 144°$. Crystal size 0.85 × 0.45 × 0.2 mm. The total number of reflections measured was 3379, of which 2600 were unique and 2574 had $I > 3\sigma(I)$. The structure was solved by direct methods (SHELX-86).[13] All nonhydrogen atoms were located easily in Fourier maps and the hydrogen atoms on the template molecules were placed geometrically. Refinement of 343 variables was by full-matrix least squares analysis (CRYSTALS).[14] The final residuals R and R_w were both 0.028. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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