Preparation and crystal structure of a new gallium phosphate $[H_3N(CH_2)_3NH_3]^{2+}[GaH(PO_4)_2]^{2-}$ from water–Me_2SO

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A novel gallium phosphate is synthesized in the presence of 1,3-diaminopropane from water–dimethyl sulfoxide (Me_2SO); its structure consists of twisted chains of GaO_4 and PO_4 tetrahedra separated by diprotonated 1,3-diaminopropane.

Zeolite like materials are generally synthesized from an aqueous system under hydrothermal conditions. During the last decade, some reports[1–3] have mentioned the influence of the organic or mixed organic–water solvents on the preparation of the microporous compounds. A wide variety of alcohols (mainly glycols) has been tested for the synthesis of zeolites and also phosphate-based compounds.[4] The use of organic solvents has resulted in the discovery of new open-framework structures such as the aluminophosphates JDF-20[5] and DAF-1[6] for example, and therefore has opened the field for the investigation of new microporous compounds. Nevertheless, although some work has reported that the use of apolar organic solvents may induce the growth of large single crystals with dimensions in the size range 0.4–5.0 mm,[7] the influence of such solvents has been less studied.

We report here on the synthesis of a new gallium phosphate from organic–water mixtures in the presence of 1,3-diaminopropane as a structurant agent. With this organic template, in the purely aqueous system and depending on the pH of the reaction, the fluorinated gallium phosphates[8] ULM-3, ULM-4 and ULM-6 have been obtained. Some attempts have been performed by using mixed alcohol–water solvents (butan-1-ol, ethylene glycol) but no effect has been observed for the formation of these phases in these conditions. However, the utilization of less polar molecules like dimethyl sulfoxide (Me_2SO) shows significant changes for the crystallization of such compounds. This paper deals with the preparation and the crystal structure of $[H_3N(CH_2)_3NH_3]^{2+}[GaH(PO_4)_2]^{2-}$, a new gallium phosphate hydrothermally synthesized from a non-purely aqueous system in which Me_2SO was used as the co-solvent.

The reagents were gallium oxyhydroxide [GaO(OH)], phosphoric acid (H_3PO_4, Fluka 99%), hydrofluoric acid (HF, RP Normapur 40%), dimethyl sulfoxide (Me_2SO, Aldrich 99.9%) and 1,3-diaminopropane (DAP, Aldrich, 99%). The starting mixture, with molar ratio 1 GaO(OH) : 1 H_3PO_4 : 1 HF : 1.2 DAP : 10 Me_2SO : 13 H_2O, was placed in a Teflon-lined stainless-steel autoclave and heated at 150 °C for 24 h. The as-synthesised crystalline product was filtered off, washed with distilled water and dried at room temperature. Examination under an optical microscope indicated a powder corresponding to GaO(OH) and colourless large faceted prismatic-shaped crystals of the title compound. A suitable single crystal was easily isolated for the structure determination by X-ray diffraction.†

The structure consists of infinite macroanionic chains of empirical formula $[GaH(PO_4)_2]^{2-}$ separated by $[H_3N(CH_2)_3NH_3]^{2+}$ cations. The basic structural unit of the inorganic chain contains one Ga and two P centred tetrahedra. All of the vertices of the GaO_4 tetrahedron are shared with the PO_4 units, with Ga–O distances in the range 1.810–1.831 Å. The two inequivalent crystallographic PO_4 tetrahedra share two vertices with the GaO_4 unit (P–O 1.553–1.565 Å) and each PO_4 group has two terminal oxygen atoms (P–O 1.503–1.531 Å). The GaO_4 and PO_4 tetrahedra are linked in a strictly alternating manner giving rise to an infinite square-twisted chain running along [001]. This type of ribbon has previously been reported as

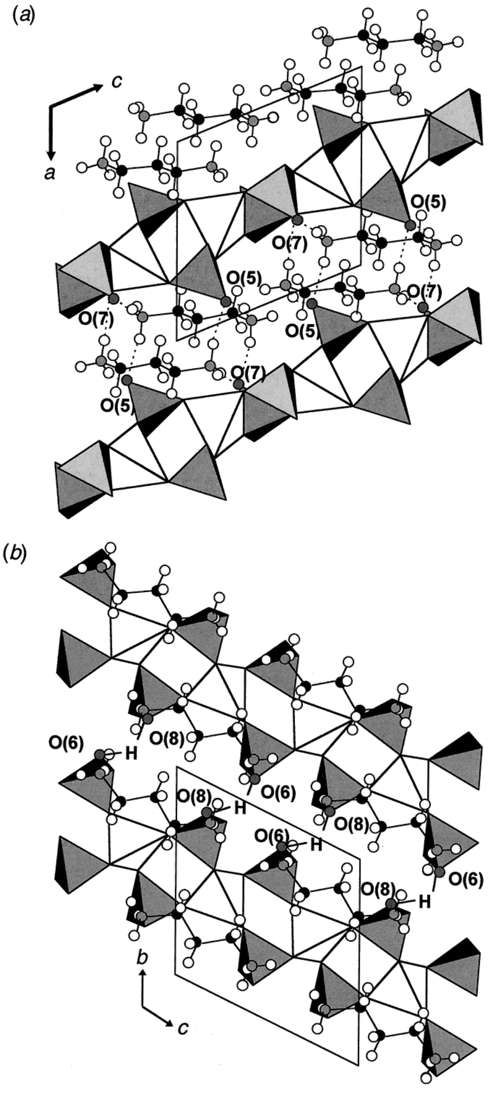

Fig. 1 (*a*) View of the structure of $[H_3N(CH_2)_3NH_3][GaH(PO_4)_2]$ along [010] showing the hydrogen bonds (dotted lines) between the inorganic chain and the diprotonated 1,3-diaminopropane. (*b*) View of the structure along [100] showing the connection of two adjacent chains *via* hydrogen atoms between the PO_4 groups. For both figures, GaO_4 and PO_4 tetrahedra are indicated by white and grey shaded polyhedra, respectively. Nitrogen atoms are represented by grey circles, carbon atoms by black circles and hydrogen atoms by open circles. The terminal oxygens (with corresponding labels) of the PO_4 tetrahedra are indicated by grey circles at the vertices of the polyhedra.

ts in Smith's nomenclature.[9] Along [100], the cohesion of the structure [Fig. 1(*a*)] is ensured by strong hydrogen bonds between the hydrogen atoms of the ammonium groups of the organic molecule and one terminal oxygen atom of each PO_4 tetrahedron [labelled O(5) and O(7) on the figure] with the distance range $d_{\mathrm{N-H\cdots O}}$1.868–1.923 Å. Indeed, the valence units for the corresponding oxygen atoms O(5) and O(7) are 1.45 and 1.47, respectively, instead of 2 expected for an oxygen atom. To satisfy the electroneutrality of the structure, one hydrogen atom must be added. The valence-bond analysis indicates that this hydrogen may be shared between O(6) (valence unit = 1.23) and O(8) (valence unit = 1.22) oxygen atoms from two distinct PO_4 tetrahedra [Fig 1(*b*)]. Moreover, the short O(6)···O(8) distance (2.444 Å) suggests the presence of positive charge between these two anions. Along [010], the cohesion of the structure is completed by hydrogen bonds between this hydrogen atom and the terminal oxygen atoms O(6) and O(8) of the PO_4 groups.

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Footnotes

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† *Crystal data* for $[H_3N(CH_2)_3NH_3][GaH(PO_4)_2]$: triclinic space group $P\bar{1}$ (no. 2); $a = 8.325(1)$, $b = 8.633(1)$, $c = 8.903(1)$ Å, $\alpha = 111.725(5)$, $\beta = 107.559(6)$, $\gamma = 98.394(6)°$, $U = 542.2(1)$ Å^3, $Z = 2$, $M_r = 336.82$, $D_c = 2.06$ g cm^{-3}, crystal dimensions: 0.152 × 0.0684 × 0.912 mm, μ(Mo-Kα) = 28.63 cm^{-1}, λ = 0.710 69 Å, X-rays monochromatised by graphite. The data were collected on a Siemens AED-2 four-circle diffractometer in the range $2\theta \leqslant 80°$. A total of 5255 reflections with $I \geqslant 2\sigma(I)$ was considered for the refinement. The data were corrected for Lorentz-polarisation and absorption effects. The structure was solved by direct methods analysis (SHELXS-86): one gallium and two phosphorus atoms were first located and all the remaining atoms except the isolated hydrogen atoms between the PO_4 groups were revealed from the difference Fourier map. The Fourier map analysis indicated three electron density residues around the two nitrogen atoms corresponding to the ammonium groups. Refinement (147 variables) was performed by full-matrix least-squares analysis (SHELXL-93): the reliability factors converged to $R = 0.032$, $wR_2 = 0.091$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/445.

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