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The room-temperature crystallisation of a one-dimensional gallium fluorophosphate, $Ga(HPO_4)_2F{\cdot}H_3N(CH_2)_3NH_3{\cdot}2H_2O$, a precursor to three-dimensional microporous gallium fluorophosphates

Richard I. Walton,[a] Franck Millange,[a] Armel Le Bail,[b] Thierry Loiseau,[c] Christian Serre,[c] Dermot O'Hare[a]* and Gérard Férey[c]

[a] *Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, UK OX1 3QR. E-mail: dermot.ohare@chem.ox.ac.uk*

[b] *Université du Maine, Laboratoire des Fluorures, CNRS ESA 6010, Avenue O. Messiaen, 72085 Le Mans Cedex 9, France*

[c] *Institut Lavoisier, UMR CNRS 8637, Université de Versailles Saint Quentin-en-Yvelines, 45, Avenue des Etats-Unis, 78035 Versailles Cedex, France*

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The one-dimensional gallium fluorophosphate $Ga(HPO_4)_2F{\cdot}H_3N(CH_2)_3NH_3{\cdot}2H_2O$ 1 crystallises at room temperature from an aqueous mixture of Ga_2O_3, H_3PO_4, 1,3-diaminopropane, and HF; compound 1 converts to the three-dimensional microporous fluorophosphate ULM-3 on heating to 160 °C under hydrothermal conditions.

The determination of the crystallisation mechanisms of microporous solids is currently a great challenge in solid-state chemistry, because of the huge importance of these materials in many industrial applications (for example the use of aluminosilicate zeolites in catalysis, ion-exchange and gas absorption).[1] It is hoped that a detailed understanding of how microporous solids are formed will enable the rational design of new materials with properties required for a particular use.[2,3] We have studied the hydrothermal crystallisation of fluorophosphates of aluminium and gallium *in situ*, using both time-resolved energy-dispersive X-ray diffraction (EDXRD)[4–6] and NMR spectroscopy.[7] In our EDXRD study of open-framework gallium fluorophosphates of the ULM-*n* family[8] we have observed novel crystalline intermediate phases when the source of phosphorus was changed from H_3PO_4 to P_2O_5.[4–6] The compounds are only stable under hydrothermal conditions, and so structural characterisation has proved extremely difficult. In order to gain a greater understanding of these new transient phases we have investigated the crystallisation of metastable frameworks structures from reaction gels at low temperature.

We now report the crystallisation of a one-dimensional fluorophosphate, $Ga(HPO_4)_2F{\cdot}H_3N(CH_2)_3NH_3{\cdot}2H_2O$ **1**, at room temperature. Compound **1** was prepared by standing at room temperature the reaction mixture usually heated in a hydrothermal bomb to prepare ULM-3 $[Ga_3(PO_4)_3F_2{\cdot}H_3N(CH_2)_3NH_3{\cdot}H_2O]$.[9] 1 g of Ga_2O_3 was used, the mixture placed in a Teflon tube covered with film and stood for 1 week. A laboratory powder X-ray diffraction pattern of the solid product after recovering and washing with water showed that a novel crystalline phase had been produced, although contaminated with unreacted GaOOH and poorly crystalline β-Ga_2O_3, present in the Ga_2O_3 starting material. Examination of the solid product using a JEOL 2000FX transmission electron microscope, equipped with a Link 'Pentafet' EDX detector, revealed it to consist of well-formed thin sheets of maximum dimension ≈ 3 μm, mixed with a small quantity of shapeless material. X-Ray microanalysis using a $GaPO_4$ calibrant showed the plate-like crystallites to contain Ga and P in the ratio 1 : 2, and emissions characteristic of O, F, C and N were observed. The contaminant material contained only Ga and O, presumably the unreacted gallium oxides. A sample of the phosphorus-rich gallium fluorophosphate was subsequently prepared in a virtually pure form, by changing the reagent ratios; the Ga : P ratio in the initial gel was changed to be 1 : 2, the amount of HF doubled, and the pH adjusted to the same value as in the first reaction mixture (≈ 5.5) by addition of the appropriate amount of 1,3-diaminopropane. This sample exhibits only the strongest Bragg reflection of GaOOH, and the impurity is present in a very small amount (less than 0.5% on the basis of the diffraction results, *vide infra*). It has not been possible to prepare crystals of suitable size for single-crystal diffraction studies; for example if the reaction mixture is stood for longer periods (up to four months) no change in the sample nature is observed and seeding the mixture with pre-made sample afforded no larger crystals. If HF is omitted from the reaction mixture, then the only crystalline material produced is 1,3-propanediammonium phosphate hydrate.[10]

Powder X-ray diffraction data were collected from the new gallium fluorophosphate at room temperature on Station 2.3 of the Daresbury SRS in a 0.5 mm diameter glass capillary. An X-ray wavelength of 1.30041 Å was used, selected using a Si(110) double-crystal monochromator. The data were successfully indexed by the autoindexing program TREOR[11] on a triclinic unit cell (a = 7.0736 Å, b = 8.5062 Å, c = 11.6205 Å, α = 107.48°, β = 102.10°, γ = 90.28°) with good figures of merit [$M(25)$ = 24, $F(25)$ = 90.6]. An *ab initio* approach was taken to the structure solution† and the final Rietveld plot is shown in Fig. 1.

The X-ray structure determination reveals that **1** is constructed from only $\{GaO_4F_2\}$ octahedra and $\{PO_3OH\}$ tetrahedra. All bond distances [$Ga{-}O_{av}$ = 1.99(2) Å, $Ga{-}F_{av}$ = 1.869(2) Å, $P{-}O_{av}$ = 1.54(1) Å, $P{=}O_{av}$ = 1.51(2) Å] agree very well with those previously reported for gallium fluorophos-

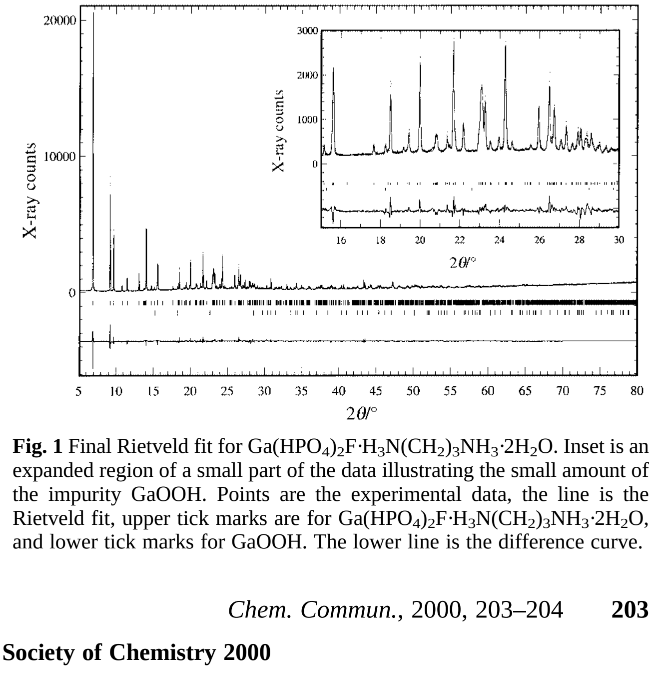

Fig. 1 Final Rietveld fit for $Ga(HPO_4)_2F{\cdot}H_3N(CH_2)_3NH_3{\cdot}2H_2O$. Inset is an expanded region of a small part of the data illustrating the small amount of the impurity GaOOH. Points are the experimental data, the line is the Rietveld fit, upper tick marks are for $Ga(HPO_4)_2F{\cdot}H_3N(CH_2)_3NH_3{\cdot}2H_2O$, and lower tick marks for GaOOH. The lower line is the difference curve.

phates.[8] The Ga polyhedra share the axial fluorines to produce an almost linear chain and all the (equatorial) oxygens are shared with the $\{PO_4\}$ tetrahedra. These phosphorus polyhedra bridge pairs of gallium octahedra along the chain on both sides (Fig. 2). Two of the phosphorus oxygens are terminal; these are assigned as one P–OH and one P=O per tetrahedron on the basis of charge-balancing considerations. Infra-red spectroscopy gave further evidence for the presence of this bonding; bands at 1380 cm^{-1} and 1005 cm^{-1} are assigned to the vibrations of phosphorus–oxygen bonds of P=O and P–OH respectively[12] and these are absent in ULM-3 in which all $\{PO_4\}$ oxygens are shared with Ga.[9] The chains of composition $Ga(HPO_4)_2F^{2-}$ are separated by charge-balancing $H_3N(CH_2)_3NH_3^{2+}$ cations and occluded water molecules. Thermogravimetric analysis is in agreement with the formulation of $Ga(HPO_4)_2F \cdot H_3N(CH_2)_3NH_3 \cdot 2H_2O$: a mass loss between 50 °C and 90 °C corresponds to the loss of the occluded water (observed 8.7%, expected 9.1%), and a mass loss between 300 °C and 700 °C corresponds to loss of the amine (observed 22.3%, expected 21.3%), presumably accompanied by collapse of the structure. The structure type has not previously been observed for an anionic gallium phosphate with organic counterions, although the arrangement of octahedra and tetrahedra is well known in the mineral chemistry of metal silicates, sulfates and phosphates,[13] Two one-dimensional anionic gallium phosphates, $Ga(PO_4)(HPO_4)^{2-}$, with charge-compensating alkylammonium cations are known and both of these were made using solvothermal methods.[14,15] In these compounds gallium is found only in tetrahedral sites. It is noteworthy that the previously reported one-dimensional gallophosphates have a Ga : P ratio of 1 : 2, and our new compound follows this pattern.

The use of ambient conditions to crystallise metal phosphates has previously received some attention, but the reagents used differ considerably from those usually used in solvothermal crystallisations.[16] It is interesting that the use of mild reaction conditions favours the formation of phosphates with low-dimensional structures, and thus it would appear that solvothermal conditions are necessary to synthesise three-dimensional (microporous) phosphates. The importance of the current work is that we have prepared a novel 1D phase at room temperature from *exactly* the same reaction mixture which yields a 3D phase if treated hydrothermally. The fact that the new chain phase contains only 6-coordinate gallium, whereas the hydrothermally-prepared ULM-3 contains both 5- and 6-coordinate gallium, is entirely consistent with recent *in situ* NMR spectroscopy results for related systems. For the aluminium fluorophosphate AlPO-CJ2 it was determined that there is a modification of Al coordination in solution from 6 to 5 on going from room temperature to hydrothermal conditions.[7] Such an observation will be of utmost importance in describing a reaction mechanism for the crystallisation and our structural data give some independent confirmation of this result. Heating **1** at 160 °C under hydrothermal conditions results in complete dissolution after ≈ 40 min followed by the almost immediate appearance of the 3D framework solid ULM-3.[17] Compound **1** may be thought of as a solid precursor to ULM-3 and we are investigating its possible transformation to other related gallium fluorophosphates, by the addition of other reagents. We have also recently shown that if H_3PO_4 is replaced by P_2O_5 in the room temperature reaction, a different gallium fluorophosphate is produced with a Ga : P ratio of 1 : 2. The structure of this second phase, which closely resembles material recovered by quenching from the hydrothermal synthesis of ULM-3 using P_2O_5,[6] we will report elsewhere.

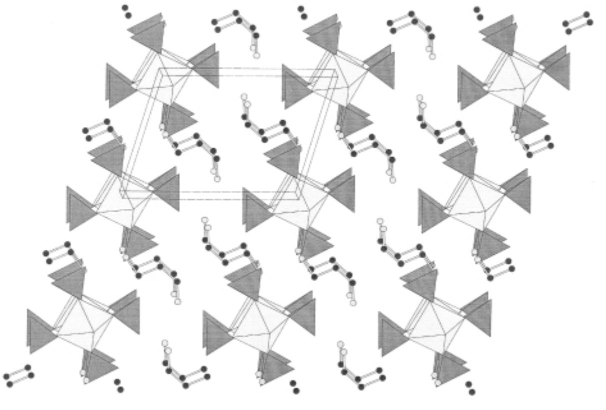

Fig. 2 A polyhedral view of the structure of $Ga(HPO_4)_2F \cdot H_3N(CH_2)_3NH_3 \cdot 2H_2O$ along *a*. Dark grey polyhedra are $\{PO_3OH\}$ tetrahedra and light grey polyhedra $\{GaO_4F_2\}$ octahedra. Black circles are carbon, and grey circles nitrogen. Occluded water molecules are not shown for clarity. The unit cell is shown by the faint line.

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Notes and references

† The data were first analysed with a 'whole pattern fitting' algorithm to determine accurately the profile shape function, background and cell parameters. This preliminary study provided good estimates of R_{wp} and χ^2 that could be reached during structure refinement (16.9% and 2.0 respectively). The structure was solved in the space-group $P\bar{1}$. The gallium positions were located using the program EXPO.[18] The Reverse Monte Carlo program ESPOIR[19] was used to locate phosphorus and oxygen atoms of the inorganic framework, with gallium atoms fixed at the positions found by direct methods. The positions of the nitrogen and carbon atoms of the 1,3-diaminopropane and oxygen atoms of occluded water were found using Fourier difference maps with the previously found atoms constrained. In the final refinement cycle, atomic constraints on the inorganic macroanion (Ga–O, P–O and O–O distance constraints) were removed. A two-phase refinement was performed to account for the presence of the crystalline impurity GaOOH and the refinement converged with agreement factors $R_p = 20.0\%$, $R_{wp} = 18.4\%$, $R_B = 9.6\%$ $\chi^2 = 2.8$.

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