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Ambient temperature crystallisation of a lamellar gallium fluorophosphate from the synthesis solution of microporous ULM-5

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The layered gallium fluorophosphate $Ga_3F_2(OH)_4(H_2PO_4)(HPO_4)_3$ $[H_3N(CH_2)_6NH_3]_2{\cdot}3.5H_2O$ (1) crystallises at room temperature from the supernatant liquid taken during the hydrothermal synthesis of the large-pore material ULM-5; the phase has a topology not previously seen among the Group 13 phosphates.

For almost 20 years a great deal of research has focussed on the synthesis of open-framework phosphates. The work was instigated by Wilson *et al.* who first described aluminium phosphates with zeolite-like structures for potential use in applications such as gas separation, ion-exchange and catalysis.[1] Phosphates of metals from almost every group of the Periodic Table have now been synthesised, usually using the hydrothermal technique ($T \approx 200$ °C).[2] In certain cases these new materials have found use as selective catalysts for organic transformations, further fuelling interest in their properties.[3,4] As well as 3D zeolite-like frameworks, the phosphates exhibit structures of lower dimensionalities, ranging from layered (2D) through chain (1D) to molecular (0D). Understandably, recent research in the area has focussed on determining the reaction mechanism of the formation of phosphates, with the goal of the rational synthesis of a new framework material of pre-designed architecture by application of appropriate synthetic conditions. For example, Taulelle *et al.* have shown by *in situ* NMR the existence of oligomers in the solution[5] whereas Rao *et al.* have, in the past few months, proposed an aufbau principle for the building up of 3D zinc phosphates from lower dimensional structures.[6]

The gallium fluorophosphates represent a large family of open-framework materials that we have been studying.[7] During *in situ* X-ray diffraction studies on their hydrothermal synthesis a number of crystalline transient phases have been observed which appear prior to the crystallisation of the expected product.[8,9] The structural characterisation of these intermediates has been hampered by the fact they are metastable and have never been stabilised under ambient conditions. We have recently begun a study of the isolation of metastable phases from the same reaction mixtures used to the prepare open-framework 3D phases, with the aim of a deeper understanding of the solution chemistry involved in the reactions and of producing possible structural models for the intermediate phases.[10–12]

The novel, layered gallium fluorophosphate **1** was isolated as single crystals from the supernatant liquid remaining after one hour under hydrothermal conditions of the reactant mixture that forms the large-pore gallium fluorophosphate ULM-5.† Structure solution was successfully performed by single-crystal X-ray diffraction and this reveals an unusual topology not previously seen in phosphate chemistry.‡ The phosphate layers have empirical formula $[Ga_3P_4O_{20}F_2H_9]^{4-}$ and are intercalated with charge balancing 1,6-hexanediammonium cations, as well as occluded water molecules [Fig. 1(a)]. Fig. 1(b) shows a view of the structure perpendicular to a single layer, and illustrates how the solid is constructed from corner-sharing $\{H_xPO_4\}$ tetrahedra, and $\{GaO_3(OH)_2F\}$ and $\{GaO_4F_2\}$ octahedra. The $\{GaO_4F_2\}$ units share axial fluorines with two $\{GaO_3(OH)_2F\}$ units to produce a trimer, which is bridged on both sides by four $\{H_xPO_4\}$ tetrahedra. There are three types of $\{H_xPO_4\}$ tetrahedra: the first is shared between three gallium atoms and has a unique terminal P–O bond of 1.575(5) Å corresponding to a P–OH moiety; the second is shared between two gallium atoms and presents two terminal P–O bonds [1.543(5) Å and 1.584(5) Å] while the third is also shared between two gallium atoms but has one longer (1.60 Å) and one shorter P–O bond type (1.49 Å), corresponding to P–OH and P=O moieties.

The secondary building unit (SBU) of the structure can be thought of as a $Ga_3F_2(OH)_2(H_xPO_4)_4$ heptamer, as shown in Fig. 2(a). These are bound by P–O–Ga linkages to produce the porous layer containing ten-ring windows. The lamellar structure of **1** is novel, but parts of the structure bear a striking resemblance to a chain gallium fluorophosphate we have recently isolated at room temperature.[10] The latter phase is constructed from infinite chains of $\{GaO_4F_2\}$ octahedra and

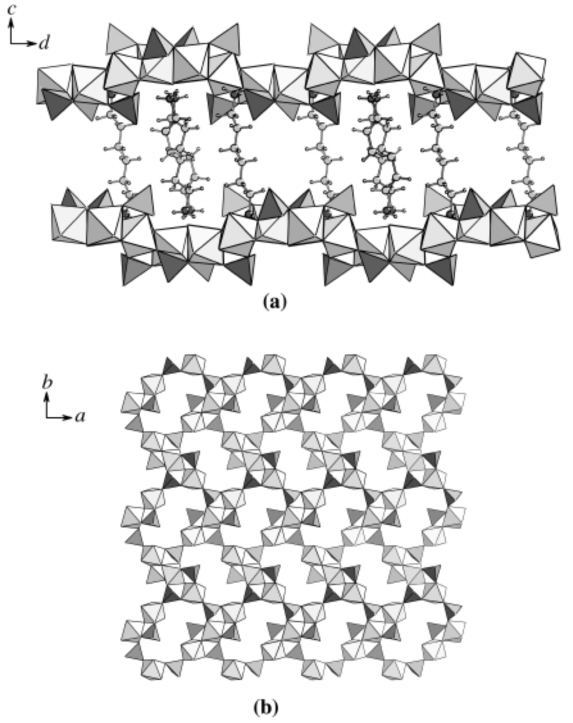

Fig. 1 Polyhedral view of the title compound (a) parallel to the layers, along *a*, showing intercalated 1,6-hexanediammonium cations, and (b) perpendicular to the layers, along *c* (occluded species not shown for clarity). Dark grey polyhedra are phosphorus-centred and pale grey gallium-centred, dark grey circles are N, pale grey circles C, and smaller pale grey circles H.

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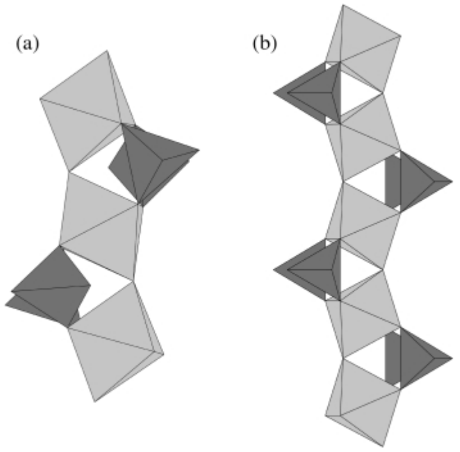

Fig. 2 (a) Polyhedral view of the secondary building unit of the title compound (b) part of the infinite chain of the 1D material Ga(HPO$_4$)$_2$F·H$_3$N(CH$_2$)$_3$NH$_3$·2H$_2$O with the tancoïte-type.[10]

{HPO$_4$} tetrahedra whose mode of linking is exactly the same as the SBU in the new phase, as illustrated in Fig. 2(b).

We have now isolated phosphates with 1D,[10] 2D (this work) and 3D[12] structures at room temperature, and thus for our system there is no evidence for a particular stability of low-dimensional structures at low temperature. All of these phases have structures not previously seen for the gallium fluorophosphates when hydrothermal synthesis is used and therefore room temperature crystallisation provides a route to novel, open-framework phases. What is particularly noteworthy about the new compound, and the other phases we have now isolated at room temperature, is the existence of gallium in solely octahedral sites, whereas the phases produced under hydrothermal conditions may contain gallium in four-, five- and six-coordinate sites. NMR studies on a related system also showed the transformation of six-coordinate metal centres to a lower coordination number site when hydrothermal conditions are reached.[5] In order to test the generality of this crystallisation model, we are currently surveying phases produced from other gallium fluorophosphate systems under mild conditions.

Notes and references

† The title compound crystallised from the supernatant liquid taken during the synthesis of the gallium fluorophosphate ULM-5.[13] The reaction mixture, 2 GaOOH : 1 P$_2$O$_5$: 1.3 NH$_2$(CH$_2$)$_6$NH$_2$: 1 HF : 80 H$_2$O (initial pH = 2.5), was sealed in a Teflon-lined, 23 mL autoclave and placed in a furnace preheated at 180 °C for 1 h. After cooling to room temperature, the solid product was recovered by suction filtration and identified by powder X-ray diffraction as a new crystalline phase GaP$_2$O$_7$(OH$_{1-x}$F$_x$)(C$_6$H$_{18}$N$_2$)·nH$_2$O.[14] The filtrate was retained and allow to stand at room temperature in a closed Teflon vessel. After several months, colourless, rod-shaped crystals of **1** were recovered.

‡ *Crystal data*: for Ga$_3$F$_2$(OH)$_4$(H$_2$PO$_4$)(HPO$_4$)$_3$[H$_3$N(CH$_2$)$_6$NH$_3$]$_2$·3.5H$_2$O: M = 999.6, colourless crystals, 0.36 × 0.14 × 0.04 mm, monoclinic, space group $P2_1/c$, a = 10.201(2), b = 14.417(4), c = 23.195(6) Å, β = 95.91(3)°, V = 3393.0(2) Å^3, Z = 4, D_c = 1.957 g cm^{-3}, μ = 2.659 mm^{-1}, index ranges $-12 \leqslant h \leqslant 12$, $-18 \leqslant k \leqslant 10$, $-28 \leqslant l \leqslant 27$, total data 20 065, independent data with $I_o > 2\sigma(I_o)$ 6931. Intensity data were collected at room temperature with a Siemens SMART three-circle diffractometer equipped with a CCD bidimensional detector [λ(Mo-Kα) = 0.71073 Å]. Data reduction was performed with the SAINT software and absorption corrections were applied using the SADABS program.[15] The structure was solved by direct methods and refined by full-matrix, least squares based on F^2 using the SHELXTL software package.[16] All non-hydrogen atoms were refined anisotropically except water molecules. All water molecules were unambiguously located although two of them (Ow3, Ow4) present a disorder with half occupancy of two sites. Hydrogens from the organic molecules were placed in calculated positions and treated as riding (N–H = 0.89 and C–H = 0.97 Å). Number of variables = 395; final $R(F)$ = 0.0562, wR (F^2) = 0.1319, GOF 1.026, minimum and maximum peak in difference electron density map −0.987 and 0.962 e Å^{-3}.

CCDC 161556. See http://www.rsc.org.suppdata/cc/b1/b102753k/ for crystallographic data in .cif or other electronic format.

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