Crystallization of a Large-Pore Three-Dimensional Gallium Fluorophosphate under Mild Conditions**

Richard I. Walton, Franck Millange, Thierry Loiseau, Dermot O'Hare,* and Gérard Férey

Microporous solids continue to be the focus of much attention as we enter the 21st century because of their catalytic and shape-selective absorptive properties which find widespread application in diverse areas such as cracking of crude oil, gas separation, water softening in detergents, radioactive waste remediation, and as drying agents.[1] Although aluminosilicate zeolites (both naturally occurring and synthetic) are perhaps the best known microporous materials,[2] in the last twenty years a huge number of new inorganic framework materials has been synthesized containing elements from virtually all groups in the Periodic Table, and almost all exhibiting structures not seen in zeolite chemistry.[3] One widely studied family is the open-framework phosphates which have been the subject of intense research since 1982 when Wilson et al. reported aluminum phosphates with zeolite-like structures.[4] Much discussion of the formation mechanism of microporous phosphates (usually prepared under hydrothermal conditions) has taken place recently,[5–7] but still there remains little experimental evidence on which to base a general formation mechanism. An understanding of the formation mechanism of microporous materials would allow the rational synthesis of new materials with properties tailored for a specific application.[8]

We have recently studied the synthesis of open-framework aluminum and gallium fluorophosphates, a large family of materials that exhibit chain and layered structures as well as three-dimensional zeolite-like structures,[5] with the aim of collecting data to formulate a reaction mechanism. We have performed a systematic study of the influence of experimental conditions on the outcome of a reaction (choice of reagents, temperature, pH, time etc.),[5, 9] and in situ studies of the hydrothermal reactions using X-ray diffraction[10–13] and NMR spectroscopy.[14] A third approach we have very recently adopted is the stabilization of materials which might have the role of precursors to microporous solids.[15] We have recently isolated a new chain gallium fluorophosphate at room temperature from a reaction mixture which if heated under hydrothermal conditions yields a three-dimensional (3D) phase.[15] We have also discussed its transformation into an open-framework material.[16] Herein we describe the crystallization under very moderate conditions of a three-dimensional open-framework gallium fluorophosphate, with large pores constructed from 20-ring windows.

The new material $Ga_4(HPO_4)_2(PO_4)_3(OH)_2F \cdot [NH_3(CH_2)_4NH_3]_2 \cdot 6H_2O$, designated ICL-1, was isolated from an aqueous reaction mixture (containing Ga_2O_3, H_3PO_4, HF, and 1,4-diaminobutane)[17] which if heated under hydrothermal conditions in a sealed autoclave at 180 °C yields the known small-pore 3D phase ULM-3.[18] The same mixture was held at 50 °C for 20 days and powder X-ray diffraction showed that a novel phase had been produced. After 20 days at room temperature the same phase is produced, albeit with lower crystallinity. The sample prepared at 50 °C was selected for detailed characterization. Transmission electron microscopy revealed the presence of well-formed square-tile-shaped crystallites of maximum dimension 4 μm. Microanalysis was performed on the crystallites by measuring the fluorescence spectrum and converting the observed ratio of the intensities of the gallium L and phosphorus K emissions into relative atomic concentrations using a calibration constant calculated by similar study of the crystalline material $GaPO_4$ (quartz structure type). This revealed that the new phase contains Ga and P in the ratio 1:1.3(1), and that O, F, C, H, and N are also present.

Although a phase-pure sample of ICL-1 could be readily obtained, we found no means of producing crystals suitable for single-crystal X-ray diffraction (for example by seeding the reaction mixture with previously made crystallites, or by performing the reaction for extended periods), and so we turned to powder X-ray diffraction for structural characterization. The CRYSFIRE software[19] was used to index the diffraction data and the unit cell with the highest figures of merit was found to be tetragonal with $a = 15.25$ and $c = 28.88$ Å. Evaluation of the systematic absences using the program CHECKCELL[20] restricted the space-group to $I4_1/a$. A search of the literature revealed that three phosphates have similar cell parameters, and the same space group; one iron phosphate ($[Fe_4(OH)_3(HPO_4)_2(PO_4)_3][H_3N(CH_2)_3NH_3]_2 \cdot xH_2O$),[21] and one gallium phosphate ($[Ga_4(OH)_3(HPO_4)_2(PO_4)_3][H_3N(CH_2)_3NH_3]_2 \cdot 5.4\,H_2O$) with a vanadium-substituted analogue ($[Ga_{3.6}V_{0.4}(OH)_3(HPO_4)_2(PO_4)_3][H_3N(CH_2)_3NH_3]_2 \cdot 6\,H_2O$).[22] None of these materials contains fluorine, but given the similarity in cell parameters the structures were used as a starting point to model the diffraction data from the new phase. Elemental microanalysis allowed the formula of the material to be deduced, and location of the fluorine in the material was aided by comparison to the large number of already known gallium fluorophosphates[23] Figure 1 shows the final Rietveld fit to the data.

The structure of ICL-1 is constructed from gallium in six-coordinate $\{GaO_4(OH)_2\}$ and $\{GaO_5(OH)F\}$ polyhedra and $\{PO_4\}$ and $\{HPO_4)$ tetrahedra. It is very similar to previously characterized iron and gallium phosphates, whose structures have already been discussed.[21, 22] The constituent polyhedra are linked (edge- and corner-sharing gallium units and corner-sharing phosphorus units) to produce a three-dimensional,

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[**] This work was supported by EPSRC and the Novartis Trust Fund. The EPSRC provided access to Daresbury Laboratory. We are grateful to L. M. D. Cranswick of Daresbury Laboratory for valuable discussions, Dr. S. O'Leary (Oxford) for performing the thermogravimetric analysis (TGA) measurements, and Professor K. Kuroda (Waseda University) for performing the gas adsorption measurements. The authors acknowledge the EPSRC-funded Collaborative Computational Project Number 14 (http://www.ccp14.ac.uk) for software resources applied in data analysis.

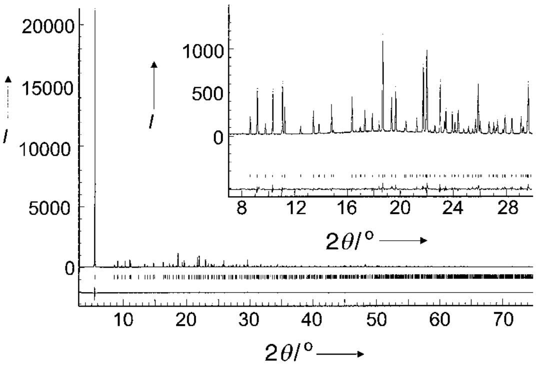

Figure 1. Observed (points) and calculated (line) powder X-ray data for the title compound ($\lambda = 1.3005$ Å). The lower line is the difference curve. The inset shows the detailed pattern between 2θ values of 8 and 30°. I is the X-ray intensity (arbitrary units).

open-framework structure. The most important feature of the structure is the presence of channels, running in a zigzag manner along the *a* and *b* axes (Figure 2). These channels are bounded by rings constructed from 20 $\{GaO_4(OH)_2\}$, $\{GaO_5(OH)F\}$, and $\{PO_4\}$ polyhedra. These rings are among the largest known for gallium and aluminum phosphates (only found elsewhere in the gallium fluorophosphate cloverite[24] and the aluminum phosphate JDF-20[25]). The overall negative charge of the gallium fluorophosphate framework is balanced by 1,4-butyldiammonium cations which reside in the voids, along with water molecules.

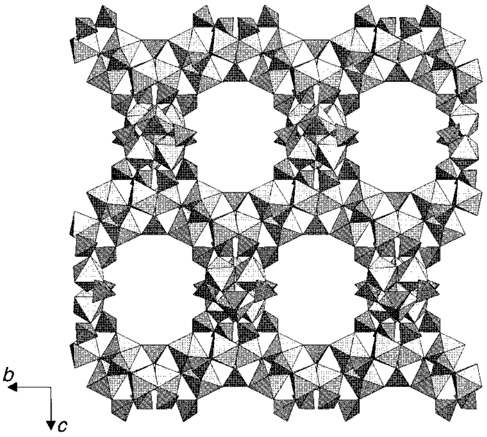

Figure 2. The structure of the title compound viewed along the *a* axis showing channels constructed from 20-ring windows. Dark gray tetrahedra are $\{PO_4\}$ units and pale gray polyhedra are $\{GaO_5F\}$ units. Occluded amine molecules and water molecules are not shown for clarity.

In order to exploit the potential for microporosity in ICL-1, the occluded species must be removed. Thermodiffractometry experiments were performed to test whether the open-framework was maintained on heating. On heating to 200 °C in a dry helium atmosphere the diffraction data showed that the largest *d* spacing (101) reflection, characteristic of the pore system, remains unchanged, although more subtle changes in the powder diffraction pattern at higher angle were apparent. Thermogravimetric analysis (TGA) shows that at 180 °C the occluded water is totally removed. Figure 3 shows a simulation of the X-ray powder pattern of the structure excluding all water molecules compared with the data measured at 180 °C. The excellent agreement between these two diffractograms (it should be noted that the relative intensities of the experimental data are subject to preferred orientation effects) shows that the open-framework is retained on dehydration; this is a defining characteristic of a zeolitic phase. Figure 4 shows the a view of a single channel of the dehydrated material, which illustrates that although the charge-balancing amine remains in the structure it lines the pore wall, leaving considerable free space in the center of the channels. The dimensions of the pores (maximum 10 Å (N−N contact) × 7.8 Å (C−C contact)) of the inorganic–organic hybrid are similar to many commercially important zeolites, for example faujasite (zeolites X and Y) and mordenite.[26] Nitrogen adsorption experiments on a sample degassed at 120 °C under vacuum showed a Type I isotherm typical of a microporous material, and a BET surface area of 146 m^{2}g^{-1} was determined. Further TGA experiments were performed to confirm the microporous character of the material; it was found that on heating to 180 °C, and subsequent cooling to room temperature in air, the mass of the sample returned to about 75% of its original value after only 2 h. This shows the reversibility of the dehydration. Dehydration to leave a truly microporous material is very unusual in phosphate chemistry, although such behavior has recently been reported for a Ni[27] and a Zn[28] phosphate, both having channels constructed from 24-ring windows and both prepared under hydrothermal conditions.

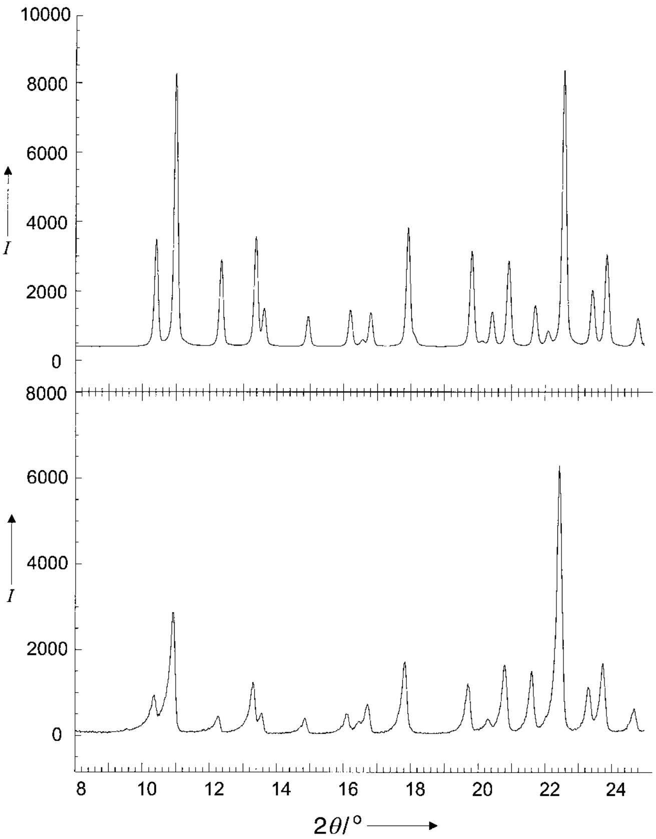

Figure 3. Simulated X-ray powder pattern ($Cu_{K\alpha}$) for the dehydrated form of the title compound (top) and diffraction data measured from the material at 180 °C (bottom).

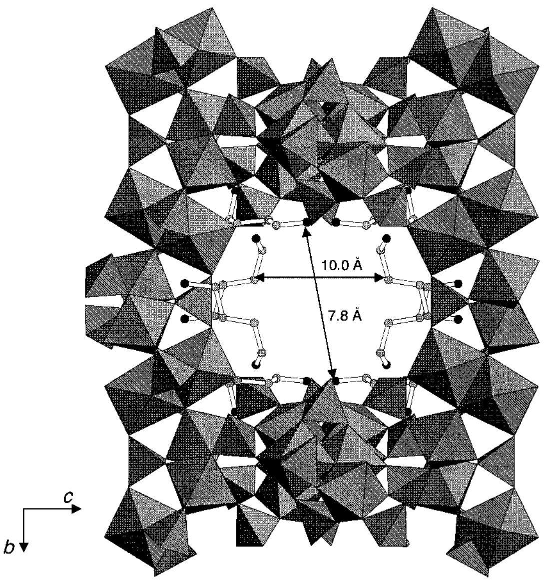

Figure 4. A view of one of the pores of the dehydrated phase, with selected interatomic distances between amine molecules marked to illustrate the void in the center of the channels. Black circles are nitrogen atoms and gray circles are carbon atoms.

All other aluminum or gallum phosphates with three-dimensional open-framework structures have been prepared by using hydrothermal conditions. The two previous studies of the low-temperature (<50 °C) crystallization of Group 13 phosphates have described the synthesis of materials with chain[15] or layered[29] structures. Interestingly, one silicate system described by Oberhagemann et al. exhibits similar behavior: at low temperature low-dimensional phases (1D and 2D) are produced, whereas under hydrothermal conditions the same reaction mixtures produce zeolitic (3D) phases.[30] At first glance, the formation of metastable low-dimensional structures followed by transformation into structures of higher dimensionality might appear to be the basis for a general reaction mechanism for the formation of open-framework structures. Indeed, Ozin and co-workers postulated that three-dimensional aluminum phosphates might be formed via metastable chain and layered phases,[6] and other groups since have assumed the same model.[31, 32] However, there is little direct experimental evidence for this crystallization model and our current work shows that metastable three-dimensional phosphates may crystallize at close to room temperature.

A further model for crystallization of phosphates was recently postulated by Rao and co-workers who suggested that certain open-framework materials may form via amine phosphate intermediates and by using this hypothesis they synthesized a huge number of new materials.[7] The same workers also showed that a monomeric zinc phosphate cluster would transform into an open-framework 3D material on heating at 50 °C.[33] We have found very different behavior for the system we have studied; we have never observed the formation of amine phosphates and we find that metal fluorophosphates encapsulating amines form equally as readily at very moderate temperatures. In terms of reaction mechanism for our particular system our work on the formation of gallium fluorophosphates under mild conditions has shown that at low temperature materials containing solely six-coordinate Ga are produced, whereas it is well known that under hydrothermal conditions materials containing four-, five-, or six-coordinate Ga can be formed.[5] This is consistent with recent in situ NMR studies on a closely related aluminum fluorophosphate system which showed a modification of metal coordination number in solution from six to five once hydrothermal conditions are reached.[14] Perhaps an equally important result from our work is that new potentially zeolitic materials can be formed at low temperature, phases which are unstable under hydrothermal conditions. This offers new possibilities in the synthesis of new microporous phases.

Experimental Section

Powder X-ray diffraction data were recorded on Station 2.3 of the Daresbury synchrotron radiation source, UK, from a sample contained in a 0.7 mm diameter quartz capillary. Station 2.3 receives X-rays from the synchrotron source (which operates with an average energy of 2 GeV and a beam current of typically 200 mA) from a dipole insertion device. The incident X-ray wavelength was 1.3005 Å using a Si (111) monochromator and data collection over the angular range 3 to 75° 2θ, with a step 0.01°. Whole pattern fitting using the program FULLPROF[34] led to $R_{wp} = 0.0868$, $\chi^2 = 5.54$ and $R_i = 0.0479$. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax:(+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-411407. Variable-temperature powder X-ray diffraction measurements were performed by using a Siemens D5000 diffractometer ($Cu_{K\alpha}$ radiation) equipped with an Anton Paar furnace (HTK1200) under a flow of dry He. The diffractometer was used in reflection mode and data measured over the angular range $2\theta = 5-25°$ in order to observe the most intense low-angle Bragg reflections. Temperature steps of 10 °C were typically used from room temperature to 600 °C, and the temperature was stabilized for 5 min before beginning data collection.

Received: July 18, 2000 [Z15472]

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A One-Dimensional Metallocyclophane with Columnar Aromatic Stacking: The Silver(I) η^2-Coordination Complex of 1,2-Benztriphenylene[**]

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Cation–π interactions between metal ions and polycyclic aromatic hydrocarbons (PAHs) provide a powerful tool for building novel molecular architectures and allow the introduction of a wide variety of useful electrical and electrochemical properties.[1–5] With the aim of designing new solids with structural diversity and desirable physical and chemical properties, we synthesized a number of organosilver(I) complexes of PAHs with remarkable features, such as W-type sandwiches,[2, 6] helical structures,[7] and double-decker,[5] triple-decker,[7] and multidecker frameworks.[5] In spite of these achievements, complexes with high conductivity are very rare. The dependence of the electrical conductivity of the complexes on the manner in which their aromatic rings are stacked has not been investigated. Here we present the unprecedented supramolecular architecture of the *para*-metallocyclophane polymer $[Ag_{0.5}(btp)_{0.5}(ClO_4)_{0.5}]$ (**1**; btp = 1,2-benztriphenylene), which shows an interesting cyclophane structure,[8] unusual aromatic interactions, and high electrical conductivity.

Cyclophanes form an important class of organic molecules. Since the first report on the synthesis of [2.2]paracyclophane (**2**), in which two benzene rings are held face to face by methylene bridges,[8a,b] the attractively simple naming of **2** led to the development of the cyclophane nomenclature for bridged aromatic compounds.[9] Complex **1** shows interesting structural similarities to cyclophanes such as **2**, [2.2](2.7)pyrenophane (**3**),[10] and the like,[8, 10–15], and hence can be regarded as a metallocyclophane, in which metal ions form the bridges. The silver(I) ions and the T-shaped planar btp ligand are assembled into a stacked structure with high electrical conductivity.

The reaction of btp with $AgClO_4$ in *p*-xylene leads to formation of **1**. The X-ray structural determination[16] revealed a one-dimensional framework held together by cation–π interactions between Ag^I and btp and perchlorate

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[**] This work was partly supported by a Grant-in-Aid for Science Research (Nos. 11874092 and 12440189) and that in Priority Areas (No. 10149104, "Metal-Assembled Complexes") from the Ministry of Education, Science, Culture and Sports in Japan.

1433-7851/00/3924-4555 $ 17.50+.50/0