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The synthesis of gallium phosphate frameworks with and without fluoride ions present: attempts to direct the synthesis of double four-ring containing materials

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During attempts to synthesise gallium phosphate materials containing the double four-ring building unit, three pyridine-templated gallium fluorophosphates and one pyridine-templated gallium phosphate were prepared and their structures solved using single crystal X-ray diffraction experiments. None of the three fluorophosphates contained the double four-ring unit, while the material prepared in the absence of fluoride did. This overturns some of the conventional wisdom that fluoride is necessary to specifically form the double four-ring unit. The synthetic conditions needed to prepare the materials and possible relationships between the building units found in the solids are discussed.

Introduction

Microporous solids, such as the aluminosilicate zeolites and aluminium/gallium phosphates are important materials, with applications in catalysis, ion exchange and gas separation and are increasingly being studied as host species for nanochemistry. Gallium phosphates are known with many different framework topologies, many of which are analogues of zeolites. The utility of microporous materials in many applications is intimately connected with their structural architecture and so the ability to control the structure of materials is an important goal in today's chemical research. Our research focuses on attempts to understand the synthesis of gallium phosphate materials more fully, with an ultimate goal of being able to target specific architectures. This paper reports our attempts to direct the structure of these solids towards those containing one particular type of structural unit, the double four-ring (D4R).

The mechanism of synthesis of aluminium and gallium phosphate materials has been the subject of much discussion recently, with excellent recent reviews coming from O'Hare,[1] Ozin[2] and Férey.[3,4] Férey has put forward the theory of microporous material formation based on molecular building units, termed pre-nucleation building units (PNBUs).[4,5] These PNBUs are thought to be present in solution and condense, either as they are or after undergoing small rearrangement/isomerisation reactions, to form the resultant solid. This theory finds support in some elegant experiments performed by Férey and Taulelle and co-workers where the PNBUs have been identified using *in situ* NMR.[5]

The solid microporous phases are described in terms of their secondary building units (SBUs). These SBUs could either have the same structure as the PNBUs, or be fragments that are closely related to the PNBUs depending on whether or not rearrangement/isomerisation has occurred prior to, or during, condensation. This theory leads directly to the synthetic strategy that control over the PNBU species present in solution should allow some measure of control over the architecture of the final product. A particularly attractive PNBU to target would be one with cuboidal structure known as the double four ring (D4R, Fig. 1). These D4R units are found in a number of different microporous material structures, and are particularly common in gallium phosphate materials such as cloverite,[6] ULM-5,[7] ULM-18,[8] MU-15[9] and cyclam-GaPO[10] amongst others.[11–13] The feature in common amongst all these gallium phosphate species is that the D4R unit has a fluoride unit occluded at its centre. No empty gallium phosphate D4R units have yet been reported. The large number of structures containing this unit has led to the postulation that the fluoride acts to 'template' (*i.e.* preferentially form) the D4R species.[9] This could either occur through preferential formation of a PNBU with the D4R topology, or by formation of a D4R precursor that subsequently undergoes rearrangement on crystallisation to form materials with the D4R SBU. There is no direct evidence of a templating effect by fluoride in gallium phosphates (by showing, for example, that the D4R PNBU is the predominant species in solution), but there is much evidence based on the structures of the final solids. For example, in the presence of fluoride, azamacrocycle-containing gallium phosphates contain the D4R unit, with fluoride occluded at its centre.[10,13] In the absence of fluoride, however, a similar structure is formed but without the D4R unit.[14] In other systems, such as the silica zeolites, fluoride ions are also located predominantly inside small SBU cages such as D4Rs.[15] The presence of fluoride in these materials has some interesting effects on the overall structure of the materials leading to, for example, unexpected nonlinear optical properties.[16]

As well as D4Rs, it is also known that SBUs of different topology are also found in fluoride-containing gallium phosphate materials. This range of SBU species can be accounted for either by reorganisation/isomerisation reactions of the type described by Férey, Taulelle and co-workers,[5] or by

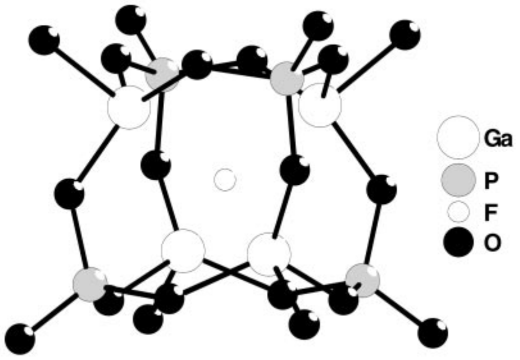

Fig. 1 The double four-ring (D4R) secondary building unit present in a number of gallium phosphate materials.

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the fact that the templating of D4R PNBUs only occurs under certain conditions, and outside these conditions other competing mechanisms may take over, such as those based on chains as described by Ozin and co-workers .[2] However, the evidence seems to suggest that it should be possible, given the right conditions, to prepare materials containing the D4R unit preferentially.

It is also interesting to note that if a material contains only D4R units, and is linked through all eight of the corners to other D4R units, the resulting structure is geometrically limited to the ACO[17] or the LTA topology, assuming each D4R is linked to eight other D4Rs. Other topologies would only be produced when the D4R is present in association with other SBUs, or the framework is interrupted (*i.e.* not fully condensed). Surprisingly, considering the wide range of gallium phosphates containing the D4R unit, none so far reported has the ACO structure.

The combination of fluoride-templated D4R units and the geometrical constraints on how these units are able to condense led us to believe that this system provided an excellent opportunity for the designed synthesis of a framework composition that had not previously been prepared. Our goal at the beginning of this work was then to prepare gallium phosphate materials that contained only the fluoride-templated D4R unit and identify the conditions under which this occurred. Assuming that the solid phase would be formed on full condensation, then this material would have either the ACO or LTA network topologies, assuming linking occurs to eight other D4R units (*i.e.* no four-ring linkages). We chose to start this study using pyridine as a solvent as the gallium phosphate–pyridine–fluoride–organic template system has been shown by a number of groups to be a rich source of new phases and has yielded a number of materials that contain the D4R unit. Pyridine can also act as a relatively small guest molecule that could fulfil any space filling stabilisation and charge compensation that might be required in the structure. A schematic diagram of the synthetic rationale behind this type of preparation is shown in Fig. 2. This synthetic strategy is different to the normal preparative techniques for these types of open framework material, which make use of organic templating molecules (usually cationic) to direct the channel structure of the resulting solid. In this case, the channel/pore structure is determined not by the size or shape of any guest species but by the geometric constraints of linking the cuboidal D4R units together. Of course, to stabilise the structure the materials will contain guest species, but they can be regarded simply as 'space fillers' rather than true templates.

In this paper we report the results of varying the reaction conditions on the resultant products. This method produced three different GaPO phases from fluoride-containing media, all of which were fully characterised using single crystal X-ray diffraction. None of these phases contained the D4R building unit, although one does contain an SBU that is closely related to the D4R unit, and may have been formed from a D4R PNBU. Surprisingly, control experiments, which we have reported in a recent communication,[18] done in the absence of fluoride ion did produce a material that contained the D4R unit, but containing oxygen and not fluoride occluded at the centre of the D4R unit. This unexpected result overturns some of the conventional wisdom that has grown up surrounding the supposed specific templating of D4R units by fluoride ions.

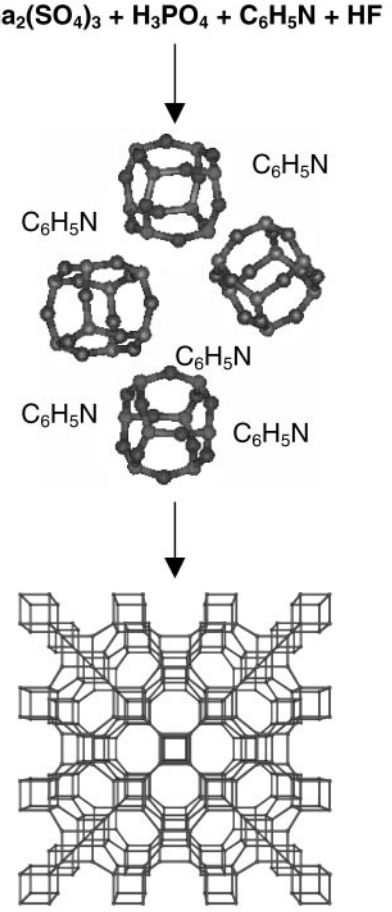

Fig. 2 Proposed synthesis of microporous materials based on preferential formation of D4R PNBUs in solution, followed by condensation to form the ACO network structure type.

Experimental

The solvothermal synthesis of pyridine GaPOs was carried out using a range of mixtures of pyridine and water as the solvents under various conditions (*e.g.* different pHs and heating temperatures). In general 0.2 g of phosphoric acid (85% aqueous solution, Aldrich) was diluted with water (unless no water was used) and pyridine (total volume 10 ml). Gallium sulfate (0.5 g, 99.9%, Aldrich) was added to this with vigorous stirring followed by 0.02 ml of hydrofluoric acid and any pH modifier used (either hydrochloric acid or trimethylamine). The completed synthesis mixture was aged with stirring for 30 minutes, transferred to a Teflon-lined stainless steel autoclave, and heated for a set time at a set temperature between 150 and 180 °C. Samples were recovered by vacuum filtration, washed with water and acetone and dried at room temperature.

Initial sample identification was by powder X-ray diffraction (PXRD) using a Phillips Xpert diffractometer with reflective geometry using CuK$_\alpha$ radiation. Single crystal X-ray diffraction (SCXRD) data were collected in St. Andrews using a Rigaku AFC7S four circle diffractometer (CuK$_\alpha$ radiation) and a Bruker AXS CCD diffractometer (MoK$_\alpha$ radiation), and at the high flux microcrystal diffraction facility (station 9.8) of the synchrotron radiation source (SRS), Daresbury. CCDC reference numbers 135560, 156915, 156916 and 155357. See http://www.rsc.org/suppdata/jm/b1/b100471i/ for crystallographic data in CIF or other electronic format.

Solid state magic angle spinning ^{31}P, ^{13}C, ^{1}H, ^{15}N and ^{19}F nuclear magnetic resonance (MAS NMR) data were collected by the EPSRC solid state NMR service, Durham, UK on a Varian Unity 300 300 MHz spectrometer.

Results and discussion

Synthesis from fluoride media

In total, three phases have been prepared from varying reaction mixtures and conditions. These have been designated [pyr,F]-GaPO-1, [pyr,F]-GaPO-2 and [pyr,F]-GaPO-3.

The products of the reactions can be controlled to some extent by varying the pH of the reaction mixture using tetramethylammonium hydroxide (TMA), hydrochloric acid or sodium hydroxide, although it has to be remembered that the concept of pH in predominantly non-aqueous solutions is not necessarily the same as that in aqueous ones. When sodium hydroxide is used as the pH modifier the product of the reaction is invariably gallophosphate berlinite. Using TMA, however, the three phases can be prepared. Fig. 3(a) shows the effect of changing the pH on the major products of several preparations. Each preparation was repeated a number of times, and the bars in the graph indicated the percentage of preparations at each pH where that particular phase was the major product. Interestingly, despite the fact that any of the phases can be prepared under the same conditions, the products were invariably single phase or contained only a small amount of the second or third phase. At low pHs (up to 5.5) the dominant product is [pyr,F]-GaPO-1, although the similar [pyr,F]-GaPO-2 phase is also produced in some cases. Between pH 5.5 and 8.5 [pyr,F]-GaPO-1 and -2 are produced from roughly an equal number of preparations. In addition to these [pyr,F]-GaPO-3 is produced in this range of pH, but it seems that the [pyr,F]-GaPO-1 and -2 structures are still favoured over this material. It is interesting to note the wide range of conditions over which [pyr,F]-GaPO-1 and -2 are formed, and the relatively narrow range of conditions over which [pyr,F]-GaPO-3 is formed. Above pH 8..5 there is no sign of the [pyr,F]-GaPO-1 phase and the [pyr,F]-GaPO-2 structure is strongly favoured, although between pH 8.5 and 9.5 [pyr,F]-GaPO-3 is also sometimes produced. It should also be noted that a TMA templated GaPO structure is a common product at high pH (9.5 and above), probably because of the high concentration of TMA in the reaction mixture.

Temperature also seems to have some effect on the product of these reactions. [pyr,F]-GaPO-3 synthesis is unaffected by variations in synthesis temperature between 150 and 180 °C, however, at the lower end of this temperature range (150–160 °C) [pyr,F]-GaPO-1 is favoured while above 160 °C [pyr,F]-GaPO-2 is more prevalent. [pyr,F]-GaPO-1 and -2 seem to be slightly favoured at longer heating times (more than 96 hours at various temperatures between 150 and 180 °C) but there is no obvious separation of the two structures.

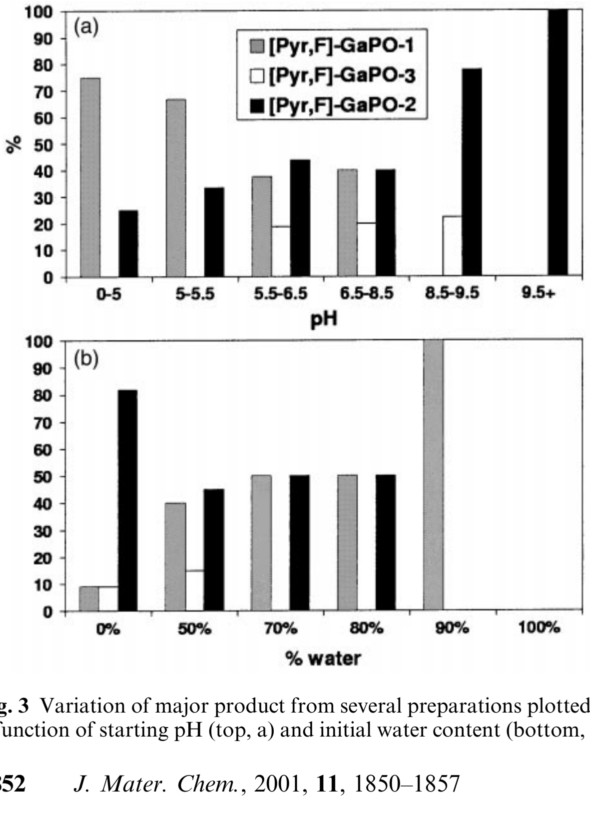

Fig. 3 Variation of major product from several preparations plotted as a function of starting pH (top, a) and initial water content (bottom, b).

The level of water present in the solvent mixture is of some importance (Fig. 3(b)). Again [pyr,F]-GaPO-1 and -2 are favoured through a range of water contents from zero *added* water (some water from the phosphoric acid is always present) to 100% water for which the product is always berlinite. [pyr,F]-GaPO-3 is only produced by reactions in which the solvent mixture is composed of 50% water or less. Above 50% water, it is exclusively [pyr,F]-GaPO-1 and -2 that are formed. This is not surprising given that the pyridinium cation 'template' in [pyr,F]-GaPO-1 and -2 is complexed to a water molecule (see below), and so more water present would naturally mean more of these pyridine–water complexes present.

Synthesis from non-fluoride media

Similar synthetic conditions to those described above but in the absence of any added HF produced a different phase entirely to those listed above, designated [pyr,O]-GaPO-4. It was prepared by a solvothermal synthesis using a mixture of pyridine and water as the solvent. 2 ml of phosphoric acid (85% weight solution in water, Aldrich) was diluted with 2 ml of distilled water and to this 0.5 g of gallium sulfate (99.9%, Aldrich) was added with stirring, followed by 8 ml of pyridine (99%, Fischer) giving an approximate gel composition of $Ga_2O_3:P_2O_5:8$ pyridine : 8 H_2O. This mixture (approximate pH 6) was stirred for 30 minutes to allow homogenisation of the gel and transferred to a Teflon lined stainless steel autoclave which was heated at 150 °C for 72 hours. The product, a crop of tiny colourless crystals, was recovered by suction filtration, washed with water and acetone and dried at 40 °C.

Structural characterisation

The structures of all four GaPO phases have been determined using X-ray crystallography during the course of this study.

[pyr,F]-GaPO-1. The crystal structure of [pyr,F]-GaPO-1 was solved from microcrystal XRD data collected at the SRS.[19] Details of the data collection are given in Table 1.

The main SBU present in [pyr,F]-GaPO-1 is the double six-ring (D6R) shown in Fig. 4. Each D6R unit consists of six phosphate groups, four tetrahedral GaO_4 units and two GaO_4F_2 octahedra. The two fluorine atoms form a bridge between gallium atoms in two neighbouring D6R units, giving rise to chains of D6Rs. Each of the D6R units is also linked into four other D6Rs *via* single four-rings to form the three dimensional structure. The pore structure of the resulting solid can be thought of as interconnecting eight-ring channels. Encapsulated in the channels are pyridine and water molecules, with minimum distances close enough to be thought of as hydrogen bonding (see below).

Alternatively, the structure can be thought of as consisting of two parts. The first is a zeolite type layer made up of four-rings which form chains in which units of three edge sharing rings are linked together by corner sharing rings. All of the gallium and phosphorus atoms in this part of the structure are tetrahedrally coordinated to four oxygen atoms. These zeolite-like layers are linked into a three dimensional structure by a second unit made up of two octahedral gallium atoms (linked by two fluorine atoms in equatorial positions) and two phosphorus atoms; giving rise to a three dimensional structure with eight-ring channels. This linking of zeolite-like layers by an octahedral gallium motif is similar to that observed in the previously reported CYCLAM-GaPO structure,[10] in which an octahedral gallium–CYCLAM complex joins the layers. When viewed parallel the (101) direction the structure closely resembles that of the zeolite ABW,[20] which is comprised of eight-rings linked by four-rings, this topology has been observed for a number of zeolite analogues.[21] The

Table 1 Details of the crystal structure determination experiments for [pyr,F]-GaPO-1, -2, -3 and [pyr,O]-GaPO-4

Identification code	[pyr,F]-GaPO-1	[pyr,F]-GaPO-2	[pyr,F]-GaPO-3	[pyr,O]-GaPO-4
Empirical formula	$(GaPO_4)_3F\cdot C_5H_6N\cdot 0.5H_2O$	$(GaPO_4)_3F\cdot C_5H_6N\cdot 0.5H_2O$	$(GaPO_4)_4(OH)\cdot 2F\cdot 2(C_5NH_6)$	$H_8Ga_4P_4O_{20}(O)\cdot 2(C_5H_6N)$
Formula weight	602.18	602.18	873.95	907.04
Temperature/K	150(2)	293(2)	293(2)	293(2)
Wavelength/Å	0.68490	0.71073	0.71073	1.54178
Crystal system	Triclinic	Triclinic	Monoclinic	Tetragonal
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$I\bar{4}2m$
Unit cell dimensions	$a=11.391(4)$ Å $\alpha=71.04(3)°$ $b=12.414(3)$ Å $\beta=68.39(2)°$ $c=12.846(4)$ Å $\gamma=66.88(2)°$	$a=9.265(5)$ Å $\alpha=94.36(6)°$ $b=9.397(8)$ Å $\beta=90.64(5)°$ $c=9.238(5)$ Å $\gamma=103.67(5)°$	$a=12.157(3)$ Å $\alpha=90°$ $b=14.202(3)$ Å $\beta=91.848(2)°$ $c=13.065(5)$ Å $\gamma=90°$	$a=13.016(3)$ Å $\alpha=90°$ $b=13.016(3)$ Å $\beta=90°$ $c=7.356(4)$ Å $\gamma=90°$
Volume/Å^3	1518.3(8)	778.9(9)	2254.6(11)	1246.2(8)
Z	4	2	4	2
Calculated density/Mg m^{-3}	2.630	2.650	2.578	2.417
Absorption coefficient/mm^{-1}	5.682	5.538	5.120	8.333
$F(000)$	1164	580	1700	892
Crystal size/mm	0.02 × 0.02 × 0.01	0.5 × 0.5 × 0.5	0.2 × 0.2 × 0.2	0.1 × 0.1 × 0.1
Theta range for data collection/°	1.95–29.25	2.78–25.02	2.67–25.01	4.8–60.14
Reflections collected/unique	14097/7704	2730/2730	3964/3964	562/302
Data/restraints/parameters	7704/0/469	2730/0/235	3964/0/347	302/0/59
Goodness-of-fit on F^2	1.207	1.020	1.123	1.089
Final indices [$I>2\sigma(I)$]	$R1=0.0454$, $wR^2=0.1272$	$R1=0.0276$, $wR^2=0.0788$	$R1=0.0485$, $wR^2=0.1437$	$R1=0.0704$, $wR^2=0.1838$
R indices (all data)	$R1=0.0481$, $wR^2=0.1288$	$R1=0.0313$, $wR^2=0.0809$	$R1=0.0776$, $wR^2=0.1593$	$R1=0.0790$, $wR^2=0.1953$
Largest diff. peak and hole/e Å^{-3}	1.766 and −1.364	0.548 and −0.75	1.350 and −1.21	0.589 and −1.267

$Ga_2P_2F_2O_8$ unit causes half of the eight-ring channels to be distorted to a pseudo-circular shape, while the others maintain the oval form normally observed in gallium phosphates. The pyridine template is protonated and hydrogen bonded to a solvent water molecule, which is disordered over two crystallographic sites. The strong binding of this water molecule is illustrated by thermogravimetric analysis, which shows a mass loss corresponding to the loss of water at around 250 °C (observed 1.2%; calculated 1.5%). A second mass loss corresponding to loss of pyridine occurs between 330 and 360 °C (observed 12.94%; calculated 13.3%).

The ^{31}P MAS NMR spectrum of [pyr,F]-GaPO-1 has three peaks at −1.2, −13.7 and −20.5 ppm. These are of roughly equal intensity, suggesting that the six crystallographic sites are separated into three pairs of indistinguishable phosphorus environments. Close inspection of the structure does show three pairs of phosphorus environments that are almost identical, members of each pair being in separate D6R units, which would account for this overlap of phosphorus resonances. The ^{19}F spectrum shows only one resolvable peak at −101.9 ppm; again, this means that the two crystallographic sites are almost 'equivalent' by NMR at this resolution. It also indicates that the fluorine is only found in the Ga–F–Ga bonds.

[pyr,F]-GaPO-2. The structure of [pyr,F]-GaPO-2 was solved from laboratory single crystal data, the details of the experiment are given in Table 1. It is a gallophosphate analogue of the ALPO UT-6, reported by Ozin and co-workers.[22] The structure is topologically almost identical to that of [pyr,F]-GaPO-1, containing the same D6R secondary building units (Fig. 4) linked in exactly the same fashion. The difference between the two structures is that [pyr,F]-GaPO-1 crystallises in a larger unit cell than -2, leading to two types of eight-ring channel (Fig. 5). In [pyr,F]-GaPO-2, however, there is only one type of chanel. All the D6R units in [pyr,F]-GaPO-2 are crystallographically equivalent, while in [pyr,F]-GaPO-1 there are two sets of D6R units, differing in orientation by only a few degrees. This change in orientation is not enough to change the connectivity of the structure as a whole, but only distorts the framework somewhat, and alters the positions of the encapsulated water molecules.

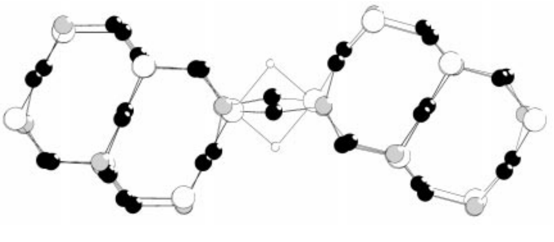

Fig. 4 Two D6R units, which are present in both [pyr,F]-GaPO-1 and -2, linked *via* fluoride bridges.

The similarity in structure between [pyr,F]-GaPO-1 and -2 is quite striking (Fig. 5), and the causes of the difference is difficult to understand. As mentioned above, the pyridinium cation in both -1 and -2 is coordinated to a water molecule, and one difference between the two structures is the distance between the two species. In [pyr,F]-GaPO-1 the N–O distances are 2.894 and 2.818 Å, while in [pyr,F]-GaPO-2 it is 3.031 Å. The subtle difference in symmetry may be a consequence of this very slight difference in the structure-directing complex. This would also go some way to explaining the trends with synthesis pH shown in Fig. 3(a) with the shortest distance occurring in the phase formed in the most acidic conditions.

The TGA trace for [pyr,F]-GaPO-2 contains two obvious, reasonably sharp mass losses. The first between about 300 and 400 °C is attributed to the loss of pyridine (observed 11.9%, calculated 13.3%). The second mass loss between 400 and 600 °C (~10%) is presumably associated with dehydration and dehydrofluorination that occurs as the structure collapses. The ^{31}P and ^{19}F MAS NMR spectra are almost identical to those for [pyr,F]-GaPO-1, as would be expected for such similar structures.

[pyr,F]-GaPO-3. The third pyridine-GaPO structure was determined from laboratory single crystal XRD data, details of the data collection are given in Table 1. This structure (Fig. 6) was previously reported by Weigel *et al.*[23] Full crystallographic data are presented here for the first time. The central

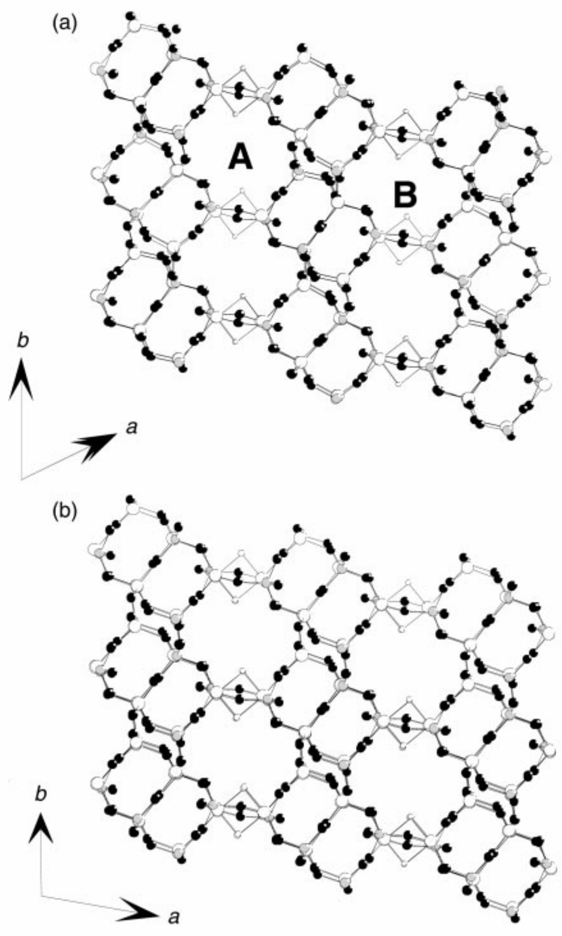

Fig. 5 Comparison of the structures of [pyr,F]-GaPO-1 (a) and [pyr,F]-GaPO-2 (b). Note the presence of two types of channel in [pyr,F]-GaPO-1, labelled A and B, while there is only one type of channel present in [pyr,F]-GaPO-2.

structural motif of [pyr,F]-GaPO-3 (Fig. 7) is, at first glance, completely different to either the expected D4R unit or the D6R present in [pyr,F]-GaPO-1 and [pyr,F]-GaPO-2. It looks comparable to the zeolite [$4^4$6] SBU seen in zeolites ZON[24] and AFR,[25] in that if the fluorine atoms are ignored the unit consists of four four-rings and a six-ring (Fig. 4). However, closer inspection reveals that it is closely related to the D4R unit, differing only in that one side of the cuboid is 'opened up', possibly the consequence of an isomerisation reaction (see below). The two fluorine atoms in the SBU are located in the centre of two of the four-ring faces, bound to two gallium atoms, this leads to a distortion of the four-rings. All of the gallium atoms are five coordinate (GaO_4F) with a slightly distorted trigonal bipyramidal geometry (the equatorial oxygen atoms are angled towards the axial fluorine) and typical Ga–O and Ga–F bond lengths (around 1.8 Å and 2 Å respectively). The pseudo [$4^4$6] units are bound together by four-rings to form eight-ring windows which each enclose two pyridine template molecules. Due to the unusual shape and linking of the SBUs there appear to be two types of eight-ring window, one with its longest dimension aligned with the (010) axis and the other along the (001). These are clearly visible when the structure is viewed along the (100) axis (Fig. 6). The structure is interrupted, containing two OH groups, bound to Ga(3) and P(4). When the structure is viewed along the (001) axis these appear to protrude into a channel containing the pyridine molecules. Interrupted structures are common in extra-large pore molecular sieves, however in this case the distance between the oxygen atoms across the pores, O(5) and O(17), is 2.515 Å, which would suggest that hydrogen bonding occurs between the free –OH groups to stabilise the structure. Thermal analysis shows a gradual mass loss between 200 and 400 °C, thought to correspond to the loss of pyridine from the structure (observed 14.8%, calculated 18.5%). A second mass loss at around 550 °C may be due to the condensation and loss of the free OH groups (observed 2.2%, calculated 1.8%). Powder XRD subsequent to TGA showed that the structure had completely broken down on removal of the pyridine from the channels of the structure.

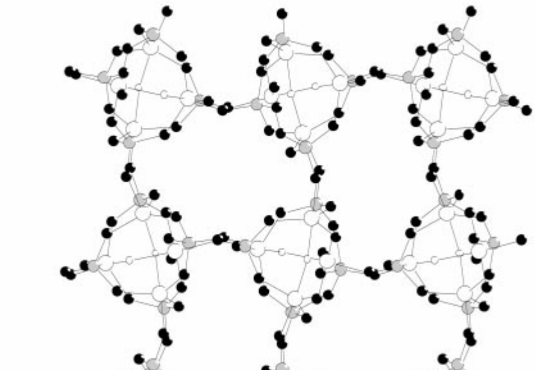

Fig. 6 The framework structure of [pyr,F]-GaPO-3.

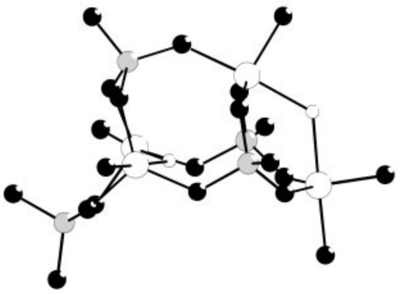

Fig. 7 The secondary building unit found in [pyr,F]-GaPO-3.

[pyr,O]-GaPO-4. In contrast to the other three structures described above, the [pyr,O]-GaPO-4 does contain the D4R unit (Figs. 8 and 9). However, in this case it is now oxygen, rather than fluorine, that is encapsulated at the centre of the

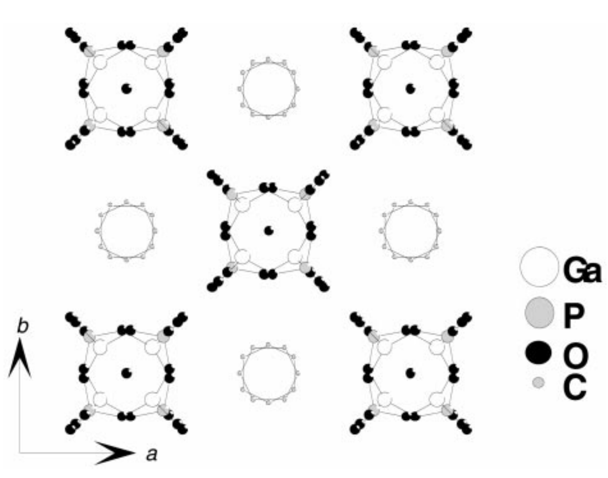

Fig. 8 The structure of [pyr,O]-GaPO-4, clearly showing the oxygen atom at the centre of the D4R unit. Carbon, nitrogen and hydrogen atoms of the pyridine molecules are shown as shaded spheres.

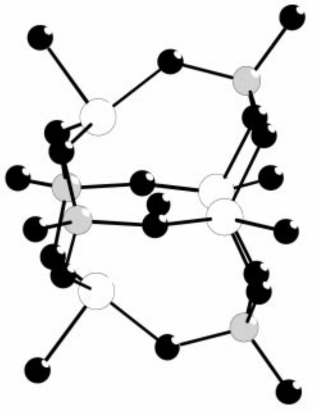

Fig. 9 The D4R unit present in [pyr,O]-GaPO-4.

D4R.[18] This is surprising, given the large amount of evidence that has accumulated over recent years indicating that D4R units are preferentially formed only in the presence of fluoride ions. This is the first case, as far as the authors are aware, of any atom other than fluorine being found at the centre of the D4R unit in gallium phosphate materials, although oxygen has been found at the centre of similar iron phosphate units. The structure itself is in fact a molecular D4R anion. Patarin and co-workers, using rather more complicated organic cations than pyridine, have prepared similar anionic species containing fluoride.[11] The structure was originally solved using laboratory single crystal X-ray diffraction. Close inspection of the structural model revealed quite large thermal displacement parameters on a number of the oxygen atoms, which indicated possible disorder present. Subsequent X-ray diffraction experiments carried out using the high-flux single crystal X-ray diffraction station 9.8 at the Synchrotron Radiation Source, Daresbury, UK, indicated that the structure was best described using a larger unit cell, indicated by the presence of weak super cell reflections. The tetragonal super cell has unit cell dimensions $a = 18.3247$ Å, and $c = 14.6191$ Å. The structure solution did indeed give a disordered model, with two D4R units of different orientations present, which is probably indicative of twinning in the structure. The correct description of [pyr,O]-GaPO-4 is probably a complicated twin of two domains, each having different orientation with respect to the other. However, no simple twin law could be resolved, and the final refinement was carried out using the disordered model. Despite the twinning of the structure, the presence of D4R units is clearly illustrated by the experiments.

The ^{31}P MAS NMR experiments show one resonance at 4.0 ppm (together with a small amount of impurity, which is probably due to the berlinite $GaPO_4$ phase). The resonance for the fluoride encapsulated D4R anions prepared by Patarin and co-workers is around -4.0 ppm; no such resonance is visible in this spectrum. To ensure that no fluoride was present from accidental contamination a ^{19}F spectrum was taken, which confirmed no fluorine was present.

An interesting feature of this type of anion is the location of the protons. For fluoride-encapsulated D4R units in the layered material ULM-18, it has been shown very elegantly by NMR and by recent quantum chemical modelling that there is a proton associated with the fluoride inside the D4R. In the case of [pyr,O]-GaPO-4, the ^{15}N MAS NMR spectrum shows only one resonance at -182 ppm, indicating that the pyridine molecules in the material are protonated, as would be expected given the synthesis conditions used in the synthesis. There are two pyridinium cations per D4R unit, and so this must have an overall charge of -2. This can be fulfilled by either eight protons on the external oxygen atoms of the D4R, or seven on the exterior and one inside, or six on the exterior and two inside. There is no evidence from our work as yet to support any of these models. However, fluoride and hydroxide have been shown to occupy the same crystallographic sites in the same structure, and so one might expect there to be an equivalence between the two inside the D4R units. This would mean that OH or OH_2 would be the most likely species to be encapsulated. Taulelle *et al.* have also postulated that the presence of protons inside the D4R units plays an important part in the nucleation and crystal growth of these types of materials.[26] Further experiments are however needed to differentiate between the three possible models described above for the [pyr,O]-GaPO-4 structure.

The structure itself shows a quite clear relationship to the ACO framework that is the target structure in this work. In this case however, the D4R units are connected to each other purely by hydrogen bonds, leading to a more open structure, but one that has essentially the same connectivity as the ACO framework. Because of the geometry of the hydrogen bonds, however, the spatial orientation of the D4R units with respect to each other is also slightly different, leading to essentially a one-dimensional channel structure rather than a three-dimensional one. Unsurprisingly, [pyr,O]-GaPO-4 is not thermally stable, the structure collapsing at temperatures as low as 200 °C.

Attempts to dissolve the [pyr,O]-GaPO-4 material in water were unsuccessful. However, the solid does dissolve in basic media (aqueous KOH). ^{31}P NMR of the resulting solution showed one peak, shifted only slightly downfield from that seen in the solid, indicating that the D4R units are probably still intact. Attempts to co-crystallise the anions with other cations are currently in progress.

Do fluoride ions template gallium phosphate D4Rs?

From the results of this synthetic and structural work, it seems likely that there are two regimes in the [pyr,F]-GaPO-*n* system. [pyr,F]-GaPO-1 and [pyr,F]-GaPO-2 can be synthesised over a wide range of composition and pH values and both contain the D6R SBU. It is difficult to see how this unit could be formed by isomerisation of a PNBU that has the D4R structure. It is perhaps more likely that these structures could be formed by condensation of chains of four-rings as described by Ozin and co-workers rather than from a relatively large D6R PNBU.[2] [pyr,F]-GaPO-3 on the other hand does have a SBU that is closely related to the D4R structure. In this case it is fairly easy to envisage a rearrangement that could take place simply by addition of fluoride as shown in Fig. 10. Changes in structure between PNBU and SBU in the synthesis of aluminium phosphates have been fully characterised in some elegant NMR experiments previously. This rearrangement could take place by opening up of one side of the cuboid structure, followed by an intramolecular attack by the fluoride. This possible opening up of one side of the D4R unit has interesting similarities with molecular analogues of D4R species such as the polyhedral oligomeric silsesquioxanes (POSS), where this kind of reaction has been identified as being high yield and highly specific.[27–30] In this case the stability of the 'open' POSS D4R unit has been rationalised as producing a slight release of strain that is present in the 'closed' D4R. In the case of the [pyr,F]-GaPO-3 structure, there is the further advantage of introducing a little more flexibility into the structure, perhaps allowing the optimal conformation for condensation to be formed. This may be the reason why we have so far failed to prepare a fully condensed analogue of the ACO framework structure. To form this framework from the relatively inflexible D4R PNBU may be energetically disfavoured with respect to a small rearrangement of the unit to form a more flexible PNBU, which might then condense to form a three-dimensional structure more easily.

The fact that an oxygen-occluded D4R has been prepared in this work does not mean that D4R units are not 'templated' by fluoride. It does however mean that the situation is not as

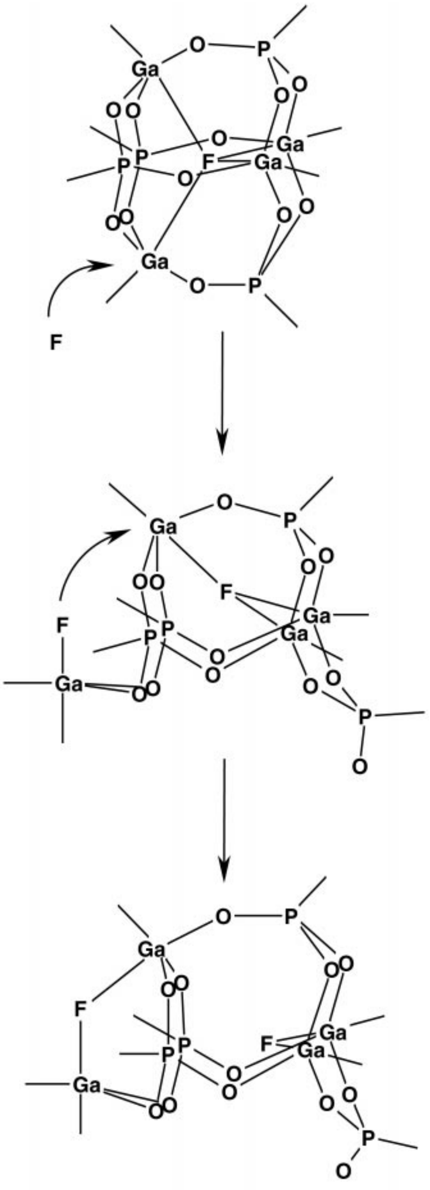

Fig. 10 A comparison between the D4R unit present in cyclam-GaPO and the SBU found in [pyr,F]-GaPO-3. [pyr,F]-GaPO-3 might be formed by a rearrangement between the two species by addition of a fluoride ion to a D4R PNBU, followed by condensation.

clearcut as was first thought. The evidence that fluoride does stabilise the D4R unit still exists, and as we have postulated above, the fluoride occluded D4R may be involved in the mechanism of [pyr,F]-GaPO-3 synthesis. However, it is equally clear that in this particular system, the F-occluded D4R is not the favoured product over a wide range of conditions.

In summary, the evidence from this study seems to suggest that materials containing the D4R, or units closely related to it, are formed in this type of system. However, in the fluoride synthesis, the two materials containing the D6R units were synthesised in more preparations and over a much wider range of conditions than those containing the D4R-like SBU. This would seem to suggest that the presence of fluoride ions does not specifically template the D4R species under most conditions in this system, merely that it is one of several units, possibly as low as two units, that might be stabilised by the presence of the fluoride ions in the mixture. The relative stability of the various possible building units may change depending on the synthesis conditions studied (*e.g.* different solvents), and so the D4R maybe more strongly stabilised in other systems.

Surprisingly, in the absence of fluoride the material prepared, [pyr,O]-GaPO-4, does contain the D4R unit as an molecular ionic species. This would seem to suggest that the D4R unit is present as a PNBU in solution under these conditions. This species opens up many interesting questions regarding the role of the encapsulated atom in directing the D4R structure. It also, as described above, raises some interesting questions regarding the location and role of the charge balancing protons, which need further experimental and theoretical modelling to answer.

Conclusions

We have shown that in the chosen system, a number of fluoride-containing gallium phosphate species can be prepared. However, none of these have the desired D4R unit, and only one of the three has a secondary building unit that can be described as being related to a D4R. We have therefore not yet achieved our goal of preparing an ACO type framework containing only D4R units. The results suggest that the fluoride ions do not act as a specific template for the D4R unit in this system under most conditions. We have also shown for the first time that oxygen-encapsulated D4R units can be prepared. This is in contrast to the perceived wisdom that has grown up surrounding the templating of D4R units only by fluoride. Further work is in required to identify the PNBUs present in these syntheses using *in situ* spectroscopy.

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