JOURNAL OF Materials CHEMISTRY

Further evidence of the efficiency of the fluoride route illustrated by the hydrothermal synthesis and crystal structure of the hydroxyfluorogallophosphate Mu-20†

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Received 9th March 2001, Accepted 20th June 2001
First published as an Advance Article on the web 3rd August 2001

In the present paper, the synthesis and structure determination of a new three-dimensional microporous hydroxyfluorogallophosphate, denoted Mu-20, is reported. This material was obtained by hydrothermal synthesis in the presence of ethylenediamine as organic template, using the fluoride route. Its structure was determined by single crystal X-ray diffraction. The symmetry is tetragonal, space group $P4_2/ncm$, with the following unit-cell parameters: $a=b=10.043(7)$ Å and $c=13.828(10)$ Å.

The three-dimensional framework of Mu-20 is completely built from chains obtained by connection of four-membered rings (4 MR) which consist of 2 Ga and 2 P atoms. In these 4 MR, the two gallium atoms are bridged by a fluorine atom. The resulting framework displays two channel systems delimited by non-planar 7 and 8 MR openings, in the *a* and *c* direction, respectively. The protonated amine is disordered inside the pores. This material was characterized by elemental and thermal analyses, XRD, SEM and ^{13}C, ^{19}F and ^{31}P solid state NMR spectroscopy.

1. Introduction

Crystallized microporous materials are divided in two main families: zeolites (framework Si, O, Al) and metallophosphates (aluminophosphates (Al, O, P), gallophosphates (Ga, O, P)…). Due to their relative low thermal stability, compared to zeolites, the number of industrial applications involving metallophosphates is not significant. Nevertheless, these phosphates are presently of great interest because of the wide diversity of structures and pore openings they present. This is specially true in the case of gallophosphates, where gallium can adopt 4-, 5- as well as 6-coordination. This characteristic gives rise to new materials without any analogues in aluminosilicate series, as for instance in the new large-pore gallophosphate reported by Lin *et al.*[1] Furthermore, the fluoride method, intensively developed in our laboratory[2] represents a major breakthrough in the course of synthesizing increasingly open materials. This is well illustrated by the synthesis of cloverite[3] the microporous solid possessing the largest ring-size opening for a three-dimensional channel system. In this material, F^- acts as a structure-directing agent, stabilizing small structural units, called double-four ring (D4R) units. Since this time, such an environment has been encountered in many other fluorogallophosphates. Most of them belong to the Mu-*n* family, the latest being Mu-15.[4] This very specific templating effect towards D4R units (cloverite cannot be prepared without fluoride) makes the gallophosphates very interesting for the understanding of the mechanism of formation of microporous materials.[5]

Gallophosphate materials usually crystallize under hydrothermal conditions ($T<200$ °C) in the presence of an organic molecule. The family of α,ω-diaminoalkanes displays a strong templating effect. Ethylenediamine, for instance, was used to prepare several gallophosphates using[6] or not using[7,8] the fluoride route. In the present paper, we report the synthesis of another ethylenediamine-containing fluorogallophosphate. This material, denoted Mu-20, was characterized by several techniques such as XRD, chemical analysis, SEM, TG/DTA and multi-nuclear solid-state NMR spectroscopy. Its structure, determined from single crystal X-ray data, is also described.

2. Experimental

A previous result obtained in our laboratory showed the strong structure-directing role of the cyclam molecule in the Ga_2O_3–P_2O_5 (GaPO) system. The introduction of the latter in the reacting gels led to the discovery of two gallophosphates, *i.e.*, Mu-5 and Mu-6, obtained in the presence and absence of fluoride anions, respectively.[9,10] Nowadays, the synthesis of increasingly "exotic" organic templates, able to direct the formation of more open structures, represents a great challenge for scientists. Based on these observations, we pursued the idea of using a bulky cyclam derivative, 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,7,11,14-tetraene, which was prepared according to a procedure recently published.[11] Unfortunately, all our attempts to synthesize this molecule *via* this route failed. The only product obtained was 4,9-dimethyl-5,8-diazadodeca-2,4,8,10-tetraene-2,11-diol, hereafter denoted 3DTD. This molecule was thus introduced in the synthesis mixtures. Experiments were also performed in the presence of ethylenediamine as a structure directing species. The different results obtained are summarized in Tables 1 and 2 and are discussed further.

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†Electronic supplementary information (ESI) available: anisotropic displacement parameters, selected bond lengths and angles, ^{13}C CP MAS NMR and ^{31}P MAS NMR spectra of Mu-20. See http://www.rsc.org/suppdata/jm/b1/b102263f/

DOI: 10.1039/b102263f

Table 1 Syntheses performed in the system Ga_2O–P_2O_5–HF–3DTD–H_2O (3DTD = 4,9-dimethyl-5,8-diazadodeca-2,4,8,10-tetraene-2,11-diol). Starting molar composition 1 Ga_2O_3 : 1 P_2O_5 : x HF : 1 3DTD : 80 H_2O

Sample	HF (x)	Crystallization time/days	Product(s) (XRD)
A1	0	4	$GaPO_4$-12
B1	0.5	4	Phase A[a]
C1	2	4	Phase A + Mu-20
D1	2	1	Mu-20[b] + quartz

[a]Non-identified phase. [b]The underlined phase corresponds to the major phase.

Table 2 Syntheses performed in the system Ga_2O_3–P_2O_5–HF–en–H_2O (en for ethylenediamine). Starting molar composition 1 Ga_2O_3 : 1 P_2O_5 : x HF : 1 en : 80 H_2O

Sample	HF (x)	Crystallization time/days	Product(s) (XRD)
A2	0.25	4	Phase A[ab] + $GaPO_4$-12
B2	0.5	4	Phase A[a] + ULM-4
C2	1	3	Mu-20 + ULM-4
D2	2	2	Mu-20

[a]Non-identified phase. [b]The underlined phase corresponds to the major phase.

2.1. Reactants

The reactants were ethylenediamine (en) (Aldrich, 98%), 3DTD, 85% aqueous phosphoric acid (H_3PO_4, Prolabo, Normapur) and 40% aqueous hydrofluoric acid (HF, Prolabo, Normapur). The gallium source was an amorphous gallium oxide hydroxide that was prepared by heating a gallium nitrate solution (Rhône-Poulenc) at 250 °C for 24 h.

2.2. Synthesis procedure

Mu-20 was obtained as a pure phase after a hydrothermal treatment of a mixture with the following molar composition: 1 Ga_2O_3 : 1 P_2O_5 : 2 HF : 1 en : 80 H_2O.

As an example, for sample D2 (Table 2), the gel was prepared by adding, under stirring, the gallium source (0.28 g) to H_3PO_4 (0.29 g) and water (1.7 g). After homogenization, HF (0.13 g) and en (0.076 g) were successively introduced. The pH value was adjusted to 4–4.5 with tripropylamine, the latter presenting no structure-directing effect in the fluorine-containing gallophosphate system.[12] The resulting gel was mixed at room temperature for 1 h and transferred into a 20 mL PTFE-lined stainless steel autoclave. The crystallization was carried out at 170 °C under static conditions. After two days of heating, the product was recovered, washed with distilled water and dried at 60 °C overnight.

2.3. Thermal analysis

Prior to analysis, the solids were kept in a humid atmosphere over a saturated aqueous solution of NH_4Cl ($P/P_0 = 0.85$) for 24 h to set the hydration state. Thermogravimetric (TGA) and differential thermal (DTA) analyses were performed under air on a Setaram Labsys thermoanalyser with a heating rate of 3 °C min^{-1}.

2.4. Powder X-ray diffraction

The XRD powder data were recorded, in Debye–Scherrer geometry, on a STOE STADI-P diffractometer, equipped with a curved germanium (111) primary monochromator and a linear position-sensitive detector (6° 2θ) using Cu-Kα_1 radiation ($\lambda = 1.5406$ Å). A Huber photographic chamber (model 631) was used for the high-temperature XRD analysis, the latter being also performed using Cu-Kα_1 radiation.

Table 3 Recording conditions of the MAS and CP MAS NMR spectra

	^{19}F	^{13}C CP	^{31}P	
	MAS	MAS	MAS	CP MAS
Chemical shift standard	$CFCl_3$	TMS	85% H_3PO_4	
Frequency/MHz	376.5	75.47	161.98	
Pulse width/μs	3	6.5	3	
Flip angle	π/2	π/2	π/2	
Contact time/ms	—	2	—	0.1
Recycle time/s	20	4	8	
Spinning rate/Hz	10000	5000	8000	
Number of scans	24	1450	56	

2.5. Chemical analysis

Ga and P analysis was performed by inductively coupled plasma emission spectroscopy. F^- content was determined using a fluoride ion-selective electrode after mineralization, and C and N analyses by coulometric and catharometric determinations, respectively, after calcination of the samples.

2.6. ^{13}C, ^{19}F and ^{31}P solid-state NMR spectroscopy

The ^{13}C CP MAS NMR spectrum was recorded on a Bruker MSL 300 spectrometer and ^{19}F and ^{31}P NMR spectra on a Bruker DSX 400 spectrometer. The recording conditions for the CP MAS and MAS spectra are given in Table 3.

2.7. Structure determination

For the structure determination, a single crystal fragment with dimensions 100 × 50 × 50 μm^3 was selected from the batch and mounted on a Picker STOE diffractometer. 396 Reflections were recorded up to θ 49.84° (using Cu-Kα radiation) in omega scan mode. A summary of the experimental and crystallographic data is reported in Table 4. The structure was solved by direct methods using SHELXS-86[13] and refined using SHELXL-93.[14] The refinement converged to $R_1 = 0.0322$

Table 4 Experimental and crystallographic parameters for the structure analysis of the hydroxyfluorogallophosphate Mu-20

Chemical formula	$Ga_3P_2O_{12}F_3C_2N_2H_{16}$
Crystal system	Tetragonal
Crystal space group	$P4_2/ncm$
a/Å	10.043(7)
b/Å	10.043(7)
c/Å	13.828(10)
M/g mol^{-1}	588.27
D_c/g cm^{-3}	2.802
V/Å^3	1395(2)
Z (formula units/cell)	4
Crystal size/μm^3	100 × 50 × 50
Diffractometer	Picker 4-circle Stoë
Radiation source and wavelength/Å	Cu-Kα, 1.54178
μ/mm^{-1}	10.040
Absorption correction	Not applied
T/K	293(2)
θ range/°	6.23–49.84
$hkl_{min,\ max}$	0 0 0, 9 9 13
Independent reflections	396
Observed reflections	364
Observation criterion	$I > 2\sigma(I)$
Data/restraints/parameters	396/30/75
Structure solution program	SHELXS-86 (Sheldrick, 1990)
Structure refinement program	SHELXL-93 (Sheldrick, 1993)
Residuals (observed data)	$R_1 = 0.0322$; $wR_2 = 0.0916$
Residuals (all data)	$R_1 = 0.0354$; $wR_2 = 0.0938$
Goodness-of-fit (all data)	$S(F^2) = 1.259$
Largest diff. peak and hole/e Å^{-3}	0.378 and −0.478

Table 5 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for the hydroxyfluorogallophosphate Mu-20: standard deviations in parentheses

Atom	*x*	*y*	*z*	*U*(eq)
Ga(1)	0	0	0	19(1)
Ga(2)	−1236(1)	−1236(1)	−1779(1)	14(1)
P	976(2)	976(2)	−2083(2)	14(1)
F(1)	−2500	−2500	−1128(5)	15(2)
O(1)	999(4)	999(4)	−957(4)	18(2)
O(2)	−33(4)	−33(4)	−2445(4)	16(2)
O(3)	−2634(5)	−601(4)	−2570(3)	20(1)
X_2[a]	1636(4)	−107(4)	761(3)	20(1)
N(1)	3817(7)	1183(7)	−535(7)	39(3)
C(1)	4305(13)	33(15)	−35(17)	54(6)
$O(1)_W$	2646(15)	−2079(12)	−1421(8)	76(5)

[a] The X_2 position is half occupied by F and OH groups (see text).

($R_1 = \Sigma||F_0|-|F_c||/\Sigma|F_0|$) and $wR_2 = 0.0916$ ($R_2 = \{\Sigma w(F_0{}^2 - F_c{}^2)^2/\Sigma w(F_0{}^2)^2\}^{1/2}$) for 364 reflections ($I > 2\sigma(I)$). The atomic coordinates and isotropic displacement parameters are given in Table 5.

CCDC reference number 162393.

See http://www.rsc.org/suppdata/jm/b1/b102263f/ for crystallographic data in CIF or other electronic format.

3. Results and discussion

3.1. Synthesis and crystal morphology

Table 1 summarizes the most characteristic synthesis results obtained using 3DTD as organic template.

A synthesis gel free of fluoride anions leads to the formation of the well known gallophosphate $GaPO_4$-12 (sample A1). The introduction of a small amount of fluoride allows the preparation of an unknown phase (phase A, sample B1). The structure determination of the latter is still in progress and will be published elsewhere. A typical XRD powder pattern of this phase is reported in Fig. 1. A mixture of phase A and the title compound Mu-20 is obtained from a fluoride rich-containing gel, after 4 days at 170 °C (sample C1). The decrease of the heating time prevents the formation of phase A (sample D1), but whereas the crystals of Mu-20 are quite large in the case of sample C1, their size is much smaller after only 1 day of crystallization. Surprisingly, after such a heating time, the XRD analysis revealed the presence of quartz-type gallophosphate.

The ^1H and ^{13}C liquid NMR spectra of both materials (phase A and Mu-20) show undoubtedly that a decomposition of the template into ethylenediamine occurs during the synthesis. This explains the formation, in the absence of F^-, of $GaPO_4$-12, which is known to crystallize in the presence of ethylenediamine as organic template.[7]

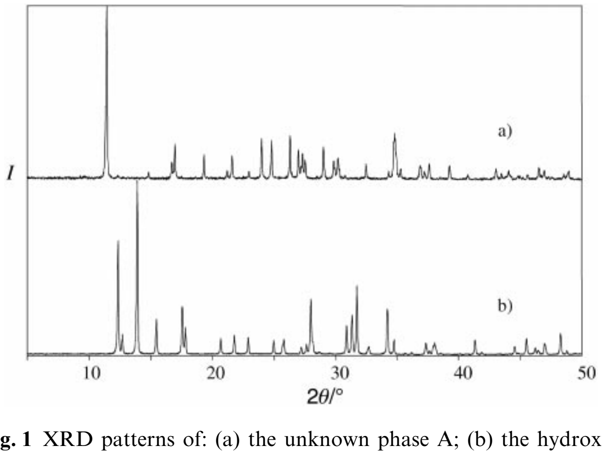

Fig. 1 XRD patterns of: (a) the unknown phase A; (b) the hydroxyfluorogallophosphate Mu-20 (radiation Cu-Kα_1).

To see if the *in-situ* decomposition of the organic molecule influences the nature of the product synthesized, as was the case in the aluminophosphate system,[15,16] the same type of experiment was performed, but directly with ethylenediamine as the structure-directing agent. The main results obtained are summarized in Table 2.

They resemble those obtained with 3DTD and therefore it appears that ethylenediamine is therefore the organic template involved in the preparation of phase A and Mu-20. Nevertheless, some differences exist. First, in this case, phase A and Mu-20 never crystallize simultaneously. Phase A is formed with $GaPO_4$-12 for a low concentration of F^- anions (sample A2). A slight increase of the latter leads to the co-crystallization of phase A and fluorogallophosphate ULM-4 (as minor phase, sample B2). The synthesis of this solid was previously reported by Loiseau, also in the presence of ethylenediamine.[6] ULM-4 is still obtained as a minor phase at a moderate fluoride concentration ($x = 1$) but appears now with Mu-20 (sample C2). Working with a large amount of F^- ($x = 2$) allows the preparation of Mu-20 as a pure phase (sample D2), the corresponding XRD powder pattern being shown in Fig. 1. The major difference with the results obtained with 3DTD is that no trace of quartz-type gallophosphate can be detected. Since the crystals of Mu-20 in sample D2 are very small, a single crystal of Mu-20 was selected from batch C1 for the structure determination. As mentioned above, the crystals are relatively large and it was possible to eliminate the non-desired phase (phase A) by a repeated sonication and decantation process. After such a treatment, the crystals of Mu-20 display a truncated bipyramidal morphology with a size close to $100 \times 50 \times 50\ \mu m^3$ (Fig. 2).

3.2. Chemical and thermal analyses

According to the elemental and thermal analyses, the chemical composition of the as-synthesized Mu-20 sample (sample D2) in wt% is Ga : 35.7; P : 10.5; F : 9.1; N : 4.8; C : 4.1.

The C/N molar ratio is close to 1 as in ethylenediamine and shows that the template (∼ 10.6 wt%) is occluded intact in the

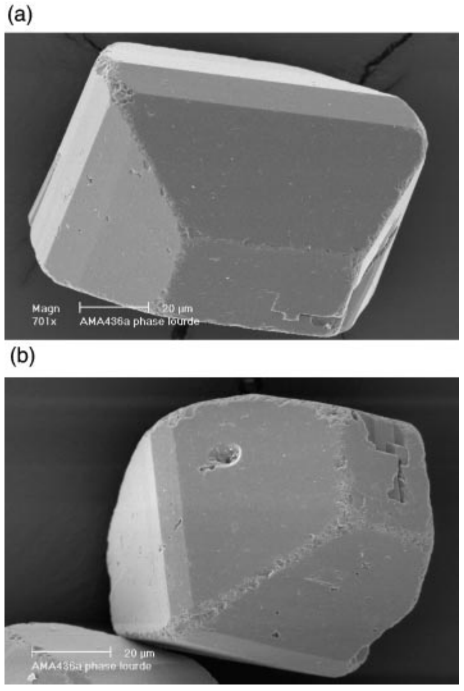

Fig. 2 Scanning electron micrographs of the hydroxyfluorogallophosphate Mu-20 showing the truncated bipyramidal morphology of the crystals.

structure. The Ga/P molar ratio (1.5) is quite different from that usually observed in the GaPO system, *i.e.*, 1.[17]

The elemental analysis is in good agreement with the unit cell formula found by the structure analysis: $Ga_{12}P_8O_{36}F_{12}[C_2N_2H_{10}]_4 \cdot 12H_2O$.

The thermal stability under air of Mu-20 was investigated using high-temperature XRD analysis and TG/DTA thermal analysis. The TG and DTA curves of the pure as-synthesized Mu-20 sample are shown in Fig. 3. The total weight loss, close to 25%, occurs mainly in two steps. The first one, before 300 °C and close to 10%, results from endothermic reactions and corresponds to the removal of the water molecules occluded in the structure combined with water arising from dehydroxylation reactions (due to the presence of Ga–X_2–Ga groups (X_2 = F/OH), see structure description) or the departure of fluorine. Between 300 and 800 °C, a second weight loss, of about 15% and corresponding on the DTA curve to a series of endo- and exo-thermic peaks, is observed. The first one corresponds to the departure of fluorine or water, also arising from the dehydroxylation process, and amorphization of the compound. This assumption is confirmed by the high-temperature XRD analysis, which shows a complete collapse of the structure after heating the sample above 350 °C, whereas a cristobalite-type gallophosphate material crystallizes above 600 °C. This thermal behavior is often observed for microporous gallophosphates.[4,18–20] The endothermic peaks are combined with a broad exothermic peak (located at *ca.* 470 °C) revealing the beginning of the decomposition of the organic template. The black color of the residue obtained at 800 °C confirmed that the decomposition is not complete. This is achieved by calcination of the sample above 1000 °C. Indeed, an additional third weight loss, close to 4%, is observed, corresponding to the total removal of the organic species. This is confirmed by the final white color of the compound. It is noted that such a behavior, *i.e.*, complete removal of the template only at high temperature, has previously been reported for many gallophosphates.[18,19,21]

3.3. Structure determination and description

On the basis of the Weissenberg photographs, the powder pattern (Fig. 1) was indexed in the tetragonal symmetry. This diffractogram fits well the unit-cell parameters determined from the single crystal structure analysis: $a = b = 10.043(7)$ Å and $c = 13.828(10)$ Å. Crystal structure solution was standard, SHELX direct methods revealed the framework atoms and the disordered template. The hydrogen atoms were placed with geometrical constraints assuming NH_3 end groups for the template. The structure shows clearly the presence of two types of X atoms (X_1 and X_2), bridging gallium atoms, on Wyckoff positions 4e and 16j, respectively. On the first position (4e), the Ga–X_1 distances are equal to 2.01 Å which corresponds well with a Ga–F–Ga group (X_1 = a fluorine atom = F(1)).[18] On the second position (16j), the Ga–X_2 distances are slightly shorter (1.954–1.991 Å) and more difficult to assign. As will be shown below by ^{19}F MAS NMR spectroscopy (see section 3.5), two types of bridging fluorine atoms are present with a population ratio equal to 2 : 1. According to the chemical and microprobe analyses, the number of F atoms per unit cell is close to 12. As the 4e position is clearly fully occupied, it corresponds to 4 F atoms, which means that 8 F atoms have to be localized on the 16j position. The remaining 8 atoms are therefore oxygens or OH groups. This probably explains the shorter corresponding bond length (1.954–1.991 Å *cf.* 2.01 Å). The 16j position is half occupied by oxygen or OH groups. To maintain the electroneutrality of the compound, the presence of OH groups is more likely (X_2 = F/OH). This is furthermore confirmed by a bond valence calculation using the relation proposed by Brown,[22] which gives a sum of bond valence of 1.85 for an OH group, compared to 1.05 for a bridging oxygen atom. The X-ray diffraction technique does not allow one to distinguish which positions correspond to fluorine or to OH groups.

The three-dimensional framework of Mu-20 is completely built up from four-membered rings (4 MR) which are the fundamental building blocks of the structure (Fig. 4a). In these units, consisting of 2 Ga, 4 O and 2 P atoms with Ga–O–P linkages, the two gallium atoms are bridged *via* the fluoride atom F(1), and the 4 MR are therefore not planar. The latter are connected into chains (Fig. 4b), two consecutive chains being linked together by six-coordinated gallium atoms (Fig. 4c) *via* Ga–O–P and Ga–X_2–Ga (X_2 = F/OH) bonds. These connections lead to a layer perpendicular to the [100] direction (Fig. 5) which displays a channel system delimited by a non-planar 7 MR (Ga–O–P or Ga–F–Ga or Ga–X_2–Ga bridges) occluding water molecules. Due to the symmetry (tetragonal), the same layer is observed perpendicular to the [010] direction. The resulting 3-D framework presents channels parallel to [001] direction (Fig. 6) also occupied by water and delimited by non-planar 8 MR openings (composed of Ga–O–P bridges, see insert to Fig. 6). Because of the presence of the X_2 bridging atoms, the ring size aperture is quite small and is close to 5 Å (see Fig. 6).

Concerning the organic template, as shown in Fig. 7, the latter lines the pore walls (along the three crystallographic directions) and therefore does not alter the pore opening. It appears from the single crystal data set that the protonated ethylenediamine molecule is disordered. Indeed, all the carbon atoms are disordered over two sites (see Fig. 7b). This disorder disappears when the structure is solved in a lower symmetry space group (orthorhombic) but, unfortunately the displacement parameters of the carbon atoms are very large and much larger than those of the nitrogen atoms. Furthermore, the final

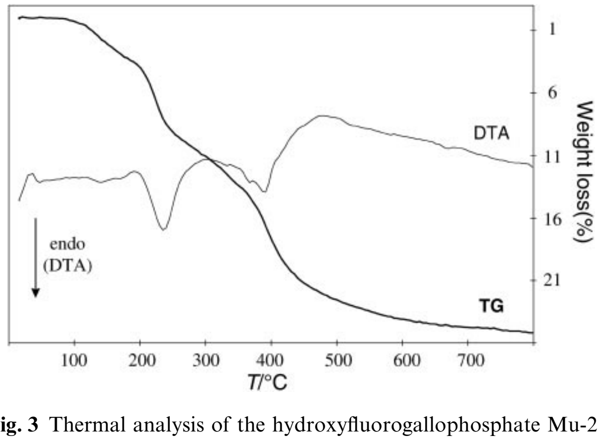

Fig. 3 Thermal analysis of the hydroxyfluorogallophosphate Mu-20.

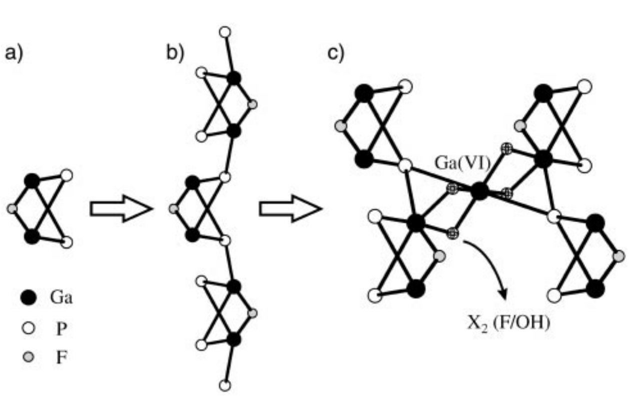

Fig. 4 (a) Fundamental building unit of the structure of Mu-20, (b) alternately connected into chains, (c) connection of two consecutive chains *via* a six-coordinate gallium atom (for clarity, framework oxygens, the organic template and the water molecules are omitted).

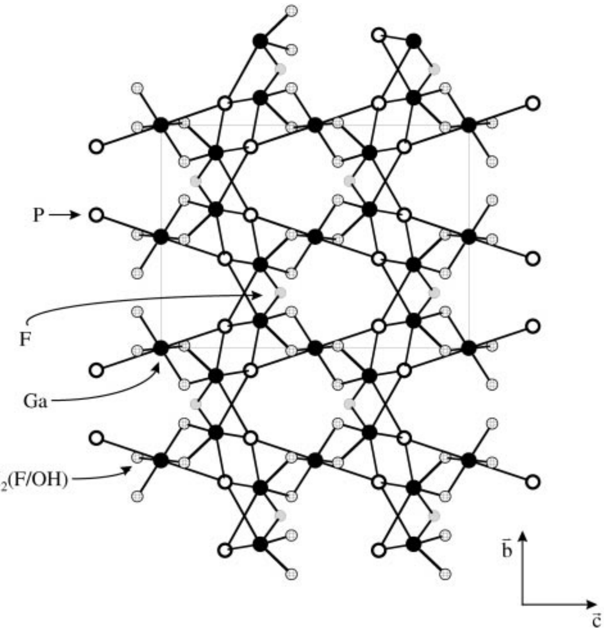

Fig. 5 Projection of the structure of Mu-20 along the [100] direction, showing the one-dimensional channel system delimited by 7 MR openings (for clarity, the framework oxygens, the organic template and the water molecules are omitted).

R value remains higher than that obtained with the tetragonal symmetry ($>4\%$). Based on this, a disorder of the organic molecule is more likely.

In Mu-20, all the gallium atoms are in 6-fold coordination with bridging oxygen atoms ($1.890(4) < d(\text{Ga–O}) < 1.940(6)$ Å), hydroxy or fluorine groups ($1.954(4) < d(\text{Ga–X}_2) < 1.991(4)$ Å) and fluorine atoms ($d(\text{Ga(2)–F(1)}) = 2.008(3)$ Å). They display a distorted square bipyramidal geometry with angle values close to 90° (78.6(2)–101.4(2)°) and 180° (168.6(2)–180.0(2)°). Concerning the phosphorus atoms, all are in 4-fold coordination with oxygen atoms. They adopt an almost perfect tetrahedral environment (average O–P–O angle 109.5°) with distances in the usual range for P–O bonds ($1.519(7) < d(\text{P–O}) < 1.558(6)$ Å).

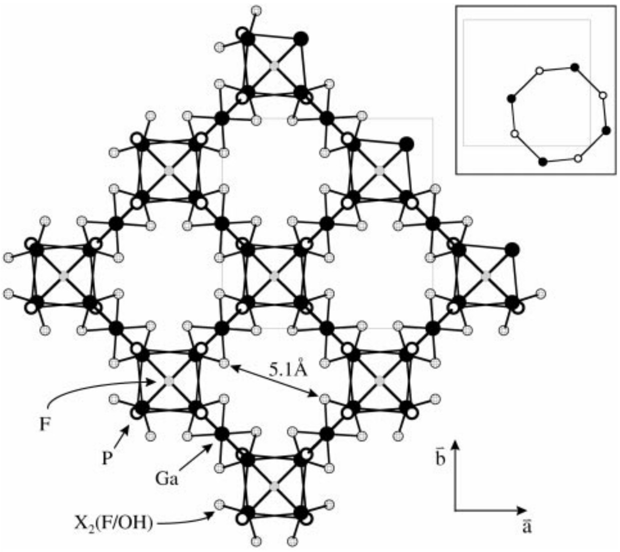

Fig. 6 Projection of the structure of Mu-20 along the [001] direction, showing the one-dimensional channel system delimited by 8 MR openings (see insert) (for clarity, the framework oxygens, the organic template and the water molecules are omitted).

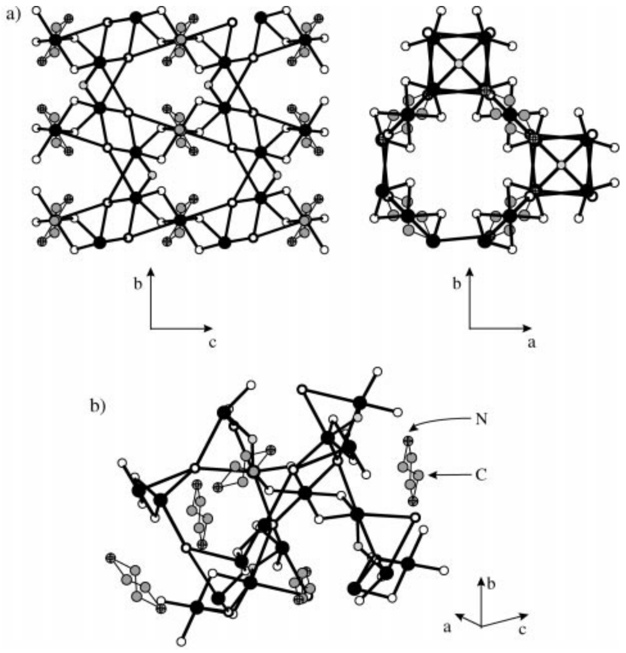

Fig. 7 (a) Projection of the structure of Mu-20 along the [100] and [001] directions showing the localization of the organic template, (b) view of the structure showing the disordered template which is duplicated due to symmetry factors (for clarity, the framework oxygens and the water molecules are omitted).

3.4. ^{13}C NMR spectroscopy

The ^{13}C CP MAS NMR spectrum of the pure Mu-20 sample (sample D2, Table 2) displays only one peak at +38.6 ppm (reference TMS), corresponding to the two carbons of the CH_2 groups. This single signal is in full agreement with the structure determination which proposes the existence of only one crystallographic site for the carbon atoms of the ethylenediamine molecule.

3.5. ^{19}F NMR spectroscopy

The ^{19}F MAS NMR spectrum of the title compound is given in Fig. 8. Two main resonances are observed close to −110 and −130 ppm (reference $CFCl_3$). Based on the structure, they

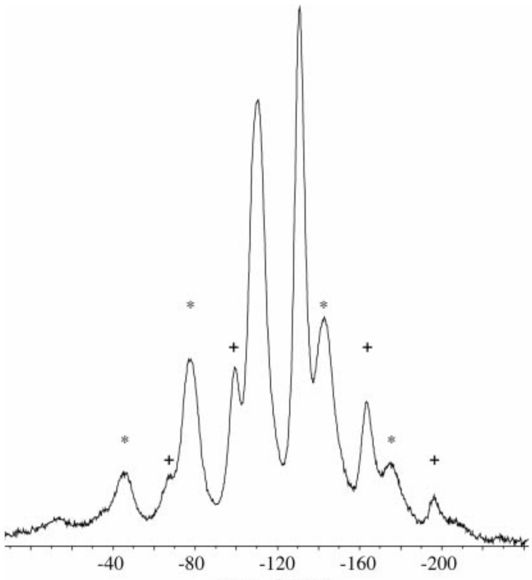

Fig. 8 ^{19}F MAS NMR spectrum of the hydroxyfluorogallophosphate Mu-20 (* and +: spinning side bands of the resonances located at −110.6 and −130.7 ppm, respectively).

correspond to the bridging fluorine atoms (Ga–F–Ga). Whereas the first chemical shift (−110 ppm) is encountered for many fluorogallophosphates presenting such an environment for the F atoms, as for example Mu-17[18] or $GaPO_4$-CHA,[23] the second one (−130 ppm) is more unusual. However, recently Loiseau *et al.* have synthesized a hydroxyfluorogallophosphate in which the bridging fluorine atoms lead to chemical shift values near −122 and −124 ppm.[24]

A tentative assignment of these two resonances has been performed on the basis of the structural data. It appears that the atom $F(X_2)$ interacts preferentially with water molecules *via* hydrogen bonds ($d(F(X_2)–O(1)_w) = 2.74(4)$ Å). This might lead to a down-field shift of the corresponding resonance, the peak observed at −110 ppm being therefore attributed to $F(X_2)$. The deconvolution of both peaks confirms this assignment since the intensity ratio $F(X_2)/F(1)$ is about 2 : 1, which is in agreement with the structure determination.

3.6. ^{31}P NMR spectroscopy

The ^{31}P MAS NMR spectrum of the fluorogallophosphate Mu-20 shows a single peak at −11.1 ppm (reference 85% H_3PO_4). The latter is in the range usually observed for Q^4 groups ($P(OGa)_4$) and corresponds to the one crystallographic phosphorus site of the structure. The intensity of this resonance is clearly increased after ^1H–^{31}P cross polarization. The enhancement of this signal reveals an interaction between the oxygen atom O(1) linked to this phosphorus and the organic template (short oxygen–proton distance, *i.e.*, $d(O(1)–N(1)) = 2.896(4)$ Å.

4. Conclusion

The hydrothermal synthesis of the three-dimensional hydroxyfluorogallophosphate Mu-20 and its crystal structure have been described in this work. This compound, prepared *via* the fluoride route and using ethylenediamine as the organic structure-directing species, shows gallium atoms in only six-fold coordination. The fluorine atoms occluded in the material exhibit also a single type of environment. They bridge two gallium atoms. The framework displays two channel systems delimited by non-planar 7 and 8 MR openings, in the *a* and *c* directions, respectively, in which water molecules are located. The protonated amine is disordered and lines the pore walls.

The use of 4,9-dimethyl-5,8-diazadodeca-2,4,8,10-tetraene-2,11-diol as organic template to direct the formation of new microporous solids failed the latter decomposing into ethylenediamine during the crystallization process. Nevertheless, it is interesting to note that crystals, large enough for a structure determination, were only obtained using this organic template. Indeed, the direct introduction of ethylenediamine into the reaction mixture led only to small crystallites. The *in-situ* decomposition of the organic molecule seems therefore to be the key factor for the formation of these large crystals.

Acknowledgements

We would like to thank "Institut Français du Pétrole" (IFP) which kindly provided the gallium nitrate source.

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