JOURNAL OF
Materials
CHEMISTRY

Hydrothermal synthesis (in water–dimethylformamide) and crystal structure of MIL-30, a new layered fluorinated gallium phosphate with 1,3-diaminopropane and dimethylamine as templates

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Received 25th November 1999, Accepted 14th February 2000
Published on the Web 22nd March 2000

A new fluorinated gallium phosphate has been synthesized under mild solvothermal condition using a mixed water–dimethylformamide solvent. It has been characterized by single-crystal X-ray diffraction. $Ga_3(PO_4)_3F_3{\cdot}N_2C_3H_{12}{\cdot}NC_2H_7$ (MIL-30), obtained at 180 °C (3 days), crystallizes in the orthorhombic space group $P2_12_12_1$ (no. 19), $a=8.8107(2)$, $b=10.2258(2)$, $c=20.9082(3)$ Å, $V=1883.75(6)$ Å^3. The structure is built up from layers of corner linked hexameric $Ga_3(PO_4)_3F_3$ units separated by protonated 1,3-diaminopropane and dimethylamine (coming from the decomposition of the co-solvent dimethylformamide). The hexamer consists of GaO_4F_2 octahedra, GaO_4F trigonal bipyramids and PO_4 tetrahedra which share corners. Within the layer, the connection mode of the hexameric building unit is similar to that found in the three-dimensional open-framework ULM-3.

Introduction

The synthesis of new open-framework structures is the subject of great interest because of their potential applications in the area of catalysis and gas separation.[1] These materials are usually hydrothermally prepared under mild conditions ($T<200$ °C, autogenous pressure) by means of amine molecules as structure directing agent. The studies were first devoted to the family of zeolite compounds[2] (aluminosilicates) and was extended to that of metal phosphates after the discovery of the new class of microporous aluminophosphates $AlPO_4$-*n*[3] by the researchers of Union Carbide in 1982. Since then, a large number of phosphate-based solids including the combination of a variety of metals (B, Al, Ga, In, Ge, Sn, Sb, transition metals, *etc.*) has been reported in the literature.[1] However, the formation mechanisms of these phases under hydrothermal conditions are poorly understood because of the complexity of the chemical systems. As well as the synthesis using aqueous media, the use of organic systems (alcohol, amine, amide, *etc.*) as the main solvent was previously successfully developed for the synthesis of microporous compounds.[4,5] This method has opened new opportunities for making novel open-frameworks, such as for example the aluminophosphate JDF-20[6] with 20-ring channels. The production of large crystals ranging from 0.4 to 5 mm has also been described.[7] The nature of the organic solvent may thus induce drastic effects on the formation of porous solids and some investigations have been undertaken into the synthesis of fluorinated phosphates of the ULM-*n* series[8] in non-aqueous media. For example, it was shown that if the dimethyl sulfoxide solvent is used in the presence of 1,3-diaminopropane, a chain-like $GaPO_4$ structure[9] is obtained instead of the 3D frameworks ULM-3[10] and ULM-4[11] formed in aqueous conditions. Our efforts were then focused on the replacement of water by organic systems with similar properties, *i.e.* high dielectric constant, high dipolar moment. The alkyl formamide family is a good candidate for this purpose and this paper reports on the synthesis of a fluorinated gallium phosphate in the presence of 1,3-diaminopropane and the influence of the amount of dimethylformamide ($\varepsilon=38$) used as co-solvent with water. This procedure results in the formation of a new layered gallium phosphate $Ga_3(PO_4)_3F_3{\cdot}N_2C_3H_{12}{\cdot}NC_2H_7$, called MIL-30, in which the presence of dimethylamine comes from the decomposition of dimethylformamide. Such behaviour has already been described for the preparation of a series of aluminophosphates with different alkyl formamide molecules. For these phases, the product of decomposition of the formamide molecule is the unique source of the structure directing agent for the formation of two-dimensional (Mu-4[12] and Mu-7[13]) or three-dimensional networks (GIS,[14] SOD[15]). The paper reports on the X-ray diffraction analysis of the gallium phosphate MIL-30 and its structural relationship with ULM-3.

Experimental

Synthesis

All the syntheses were carried out under mild hydro/solvothermal conditions using gallium oxyhydroxide [GaO(OH), hydrothermally prepared from gallium metal (Rhône Poulenc, 4 N) in water at 200 °C during 24 hours], phosphoric acid (H_3PO_4, 85% Prolabo), hydrofluoric acid (HF, 40%, Prolabo), 1,3-diaminopropane ($H_2N(CH_2)_2NH_2$, 99%, Aldrich, denoted DAP), dimethylformamide ($(CH_3)_2NCHO$, 99.8%, SDS, denoted DMF) and deionized water. The reactions were performed in 23 ml Teflon-lined stainless steel Parr bombs under autogeneous pressure for 3 days. The molar compositions of the starting gels were: 1 GaOOH (0.713 g) : 1 H_3PO_4 (0.5 ml) : 1 HF (0.25 ml) : 1 DAP (0.6 ml) : y DMF : x H_2O ($y=7.69-0.23x$, y DMF + x H_2O corresponds to 3.85 ml). The DMF/H_2O ratio was varied in the range from 0 to 3.22 in order to observe the influence of the solvent on the nature of the phases formed in this system (Fig. 1) at 180 °C. Even when 3.85 ml of DMF and 0 ml of deionized water were used, some water comes from the solution of phosphoric and hydrofluoric acids in water. After filtering off and washing with deionized water, the resulting white product was first characterized by powder X-ray diffraction (Brüker D5000, copper radiation). When a small amount of dimethylformamide was added to the

DOI: 10.1039/a909315j

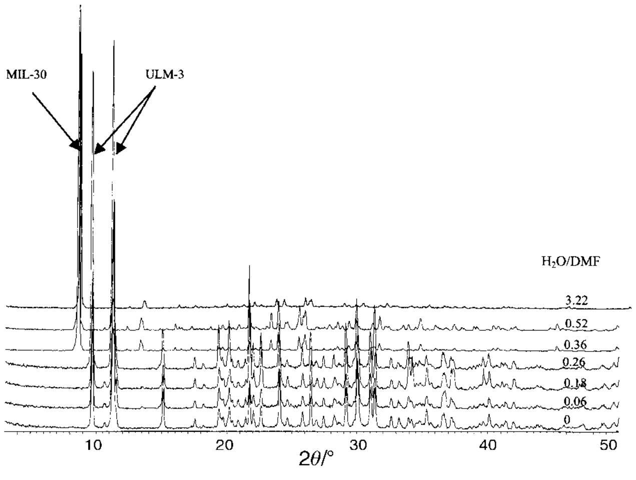

Fig. 1 Evolution of the XRD patterns as a function of the H_2O/DMF ratio at 180 °C (reaction time: 3 days).

reaction mixture, only ULM-3 was formed. From DMF/$H_2O = 0.36$, ULM-3 crystallized together with another phase which corresponded to the title compound MIL-30. Upon increasing the DMF/H_2O ratio, MIL-30 was formed at the expense of ULM-3 and for DMF/$H_2O = 0.52$, only MIL-30 was obtained. This phase was present for DMF/H_2O up to 3.22, and attempts made with higher DMF concentrations (DMF/$H_2O < 13$) always led to the formation of the title solid.

In order to avoid the decomposition reaction of the organic solvent, the synthesis temperature was lowered to 120 °C and a second phase appeared. It consisted of a chain-like structure with a ratio P/Ga = 2, identical to the fluorinated iron phosphate ULM-14.[16] Its structure description will be presented elsewhere.[17]

The chemical formula deduced from the crystal structure is $Ga_3(PO_4)_3F_3 \cdot N_2C_3H_{12} \cdot NC_2H_7$ and is in good agreement with the chemical analysis for fluorine (exp.: 7.9%; calc.: 8.4% wt), nitrogen (exp.: 6.4%; calc.: 6.2% wt) and carbon (exp.: 9.0%; calc.: 8.9% wt).

Structure determination

The structure of MIL-30 was determined by means of single crystal analysis. The intensity data were recorded on a Siemens SMART three-circle diffractometer equipped with a CCD bidimensional detector (molybdenum radiation). The crystal-to-detector distance was 45 mm allowing for the data collection up to 60° (2θ) and slightly more than one hemisphere of data was recorded. An empirical absorption correction was applied using the SADABS program.[18] The structure of MIL-30 was solved by direct methods in the non-centric space group $P2_12_12_1$ and refined by full-matrix least squares using the SHELXTL package.[19] The gallium and phosphorus atoms were located by direct methods and all the other non-hydrogen atoms (F, O, C, N) placed from subsequent Fourier-difference map calculations. The location of fluorine atoms was deduced from the analysis of the anisotropic thermal parameters and bond valence calculations. The hydrogen atoms of the two amine molecules were placed with geometrical restraints in the riding mode and refined anisotropically. The final refinement converged at $R1(F) = 0.0582$ and $wR2(F^2) = 0.1339$ for 2648 reflections [$I > 2\sigma(I)$]. Crystal data and details of the data collection are summarized in Table 1. The resulting atomic coordinates and the selected bond distances of MIL-30 are listed in Tables 2 and 3 respectively.

CCDC reference number 1145/209.

Table 1 Experimental and crystallographic parameters for the structure analysis of $Ga_3(PO_4)_3F_3 \cdot H_3N(CH_2)_3NH_3 \cdot H_3CNH_2CH_3$ (MIL-30)

Chemical formula	$Ga_3P_3O_{12}F_3N_3C_5H_{20}$
Formula weight/g mol^{-1}	673.31
Crystal system	orthorhombic
Space group	$P2_12_12_1$ (no. 19)
Absorption coefficient/mm^{-1}	4.609
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0582$, $wR2 = 0.1339$
R indices (all data)	$R1 = 0.0788$, $wR2 = 0.1436$
Unit cell dimensions:	
a/Å	8.8107(2)
b/Å	10.2258(2)
c/Å	20.9082(3)
Unit cell volume/Å^3	1883.75(6)
Temperature of data collection/K	293(2)
Z	4
Measured/independent reflections and R(int)	5733/3371 [R(int) = 0.0626]

Thermogravimetry

Thermogravimetric analysis was carried out on a TA Instrument type 2050 thermoanalyzer under nitrogen gas flow with a heating rate of 2 °C min^{-1}. The TG curve (Fig. 2) shows 3 events between 25 and 1050 °C. The first weight loss (1.22%) below 200 °C can be assigned to adsorbed DMF molecules at the surface of the materials. The second weight loss occurring between 300 and 450 °C is attributed to the departure of two amine molecules (exp.: 18.09%; calc.: 18.14%). Powder X-ray diffraction indicates that the structure is collapsed after the removal of the organic part. The third weight loss which is continuously observed from 500 to 1050 °C for MIL-30 may correspond to the fluorine present in the solid (exp.: 7.97%; calc.: 8.38%). The final decomposition product is dense $GaPO_4$ (high cristobalite form) at 1050 °C.

Structure description

The structure of MIL-30 consists of infinite layers of $[Ga_3(PO_4)_3F_3]^{3-}$ intercalated by diaminopropane and dimethylamine (Fig. 3 and 4). The layer is built up from the linkage of hexameric units containing three phosphorus atoms and three gallium atoms (Fig. 5). The phosphorus atoms are tetrahedrally coordinated with P–O distances ranging from 1.514 to 1.582 Å. The PO_4 groups share all their vertices with the gallium polyhedra except P(2) which exhibits one terminal bond (P(2)–O(7) = 1.534 Å). The gallium presents two types of coordination: two of three crystallographically distinct gallium atoms are fivefold coordinated (distorted trigonal bipyramid) by four oxygen and one fluorine atoms and three oxygen (Ga(1)) and two fluorine atoms (Ga(3)), respectively. The fluorine atoms are located in the apical vertices. The axial Ga–(O,F) distances are in the range 1.962–2.080 Å while the

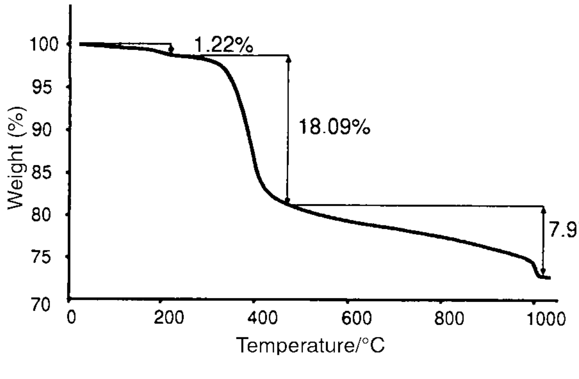

Fig. 2 TG curve of $Ga_3(PO_4)_3F_3 \cdot N_2C_3H_{12} \cdot NC_2H_7$ (MIL-30) under N_2, 2 °C min^{-1}.

Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Ga_3(PO_4)_3F_3{\cdot}H_3N(CH_2)_3NH_3{\cdot}CH_3NH_2CH_3$ (MIL-30). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	*y*	*z*	*U*(eq)
Ga(1)	4618(2)	7945(1)	7914(1)	12(1)
Ga(2)	8136(2)	6361(1)	7679(1)	14(1)
Ga(3)	3482(2)	8193(1)	6251(1)	16(1)
P(1)	1222(4)	8255(3)	7452(1)	15(1)
P(2)	6260(4)	6134(2)	8992(1)	14(1)
P(3)	5449(5)	5985(2)	6777(1)	14(1)
F(1)	6833(9)	8029(6)	7777(3)	23(2)
F(2)	4465(9)	8897(5)	7087(3)	19(2)
F(3)	2391(9)	7624(7)	5540(3)	31(2)
O(1)	4544(10)	6320(7)	7390(3)	14(2)
O(2)	4951(11)	6860(7)	6197(3)	22(2)
O(3)	1778(11)	7858(8)	6759(3)	21(2)
O(4)	7607(11)	5985(8)	8526(4)	21(2)
O(5)	7158(11)	6200(8)	6883(4)	18(2)
O(6)	2456(10)	7974(7)	7969(4)	14(2)
O(7)	6740(11)	6830(7)	9609(3)	22(2)
O(8)	4838(11)	9542(7)	8424(4)	20(2)
O(9)	4890(10)	6845(7)	8677(3)	16(2)
O(10)	9270(10)	4732(7)	7547(4)	20(2)
O(11)	9846(12)	7423(8)	7601(5)	29(2)
O(12)	4272(12)	9703(7)	5854(4)	28(3)
N(1)	394(15)	11114(9)	4797(4)	31(3)
N(2)	12437(14)	4931(10)	8229(5)	29(3)
C(1)	−319(17)	10012(11)	5169(6)	22(3)
C(2)	11764(16)	4411(11)	8833(5)	17(3)
C(3)	11173(18)	5516(12)	9241(6)	29(4)
N(3)	166(24)	5650(16)	6133(8)	85(6)
C(4)	8697(26)	9510(18)	8973(13)	102(9)
C(5)	−781(29)	5924(24)	5612(9)	91(9)

equatorial Ga–O distances, slightly shorter, range ng from 1.865 to 1.886 Å. For the Ga(3) polyhedron, one of the two fluorine atoms is in a terminal position corresponding to a shorter Ga–F distance (Ga(3)–F(3) = 1.863 Å). Such a situation was previously reported in the fluorinated gallium phosphates $GaPO_4$-CJ2[20] or ULM-9[21] in which one of the fluorine atoms points toward the ammonium groups. The terminal Ga–F distances were 1.903 Å for $GaPO_4$-CJ2 and 1.800 Å for ULM-9 and correspond to the shortest distances within the coordination polyhedron. The third gallium atom (Ga(1)) is octahedrally coordinated by four oxygen and two fluorine atoms. These two fluorine atoms are in *cis* positions within the octahedron and the two trigonal bipyramids are connected to the octahedron through the bridging fluorine atoms. Three phosphate groups share two or three of their vertices with the resulting gallium trimer. This hexameric entity is a common feature in the fluorinated gallium phosphates since it has been observed in many 2D and 3D structures (ULM-3,[10] ULM-4,[11] ULM-5,[22] ULM-8,[23] ULM-16,[24] TREN-GaPO,[25] DAO-GaPO[26]). The connection of the hexamers by the free remaining vertices (except O(7) and F(3) which are terminal) generates the infinite inorganic sheets in the plane (001) with respect of the strict Ga–O–P alternation (Fig. 3). The layers

Table 3 Bond lengths [Å] and angles [degrees] for $Ga_3(PO_4)_3F_3{\cdot}H_3N(CH_2)_3NH_3{\cdot}CH_3NH_2CH_3$ (MIL-30)

Ga(1)–O(6)	1.908(9)
Ga(1)–O(8)	1.960(7)
Ga(1)–O(9)	1.965(7)
Ga(1)–F(1)	1.975(9)
Ga(1)–F(2)	1.990(6)
Ga(1)–O(1)	1.991(7)
Ga(2)–O(11)	1.865(9)
Ga(2)–O(4)	1.871(8)
Ga(2)–O(5)	1.882(8)
Ga(2)–O(10)	1.962(8)
Ga(2)–F(1)	2.066(7)
Ga(3)–F(3)	1.863(7)
Ga(3)–O(3)	1.871(9)
Ga(3)–O(2)	1.883(8)
Ga(3)–O(12)	1.886(8)
Ga(3)–F(2)	2.080(6)
P(1)–O(11)#1	1.514(10)
P(1)–O(6)	1.560(9)
P(1)–O(10)#2	1.572(7)
P(1)–O(3)	1.582(8)
P(2)–O(7)	1.534(7)
P(2)–O(4)	1.542(9)
P(2)–O(9)	1.555(8)
P(2)–O(12)#3	1.570(8)
P(3)–O(5)	1.537(10)
P(3)–O(1)	1.547(8)
P(3)–O(8)#3	1.555(7)
P(3)–O(2)	1.571(7)
N(1)–C(1)	1.51(2)
N(2)–C(2)	1.494(14)
C(1)–C(3)#2	1.53(2)
C(2)–C(3)	1.51(2)
N(3)–C(5)	1.40(2)
N(3)–C(4)#3	1.55(3)

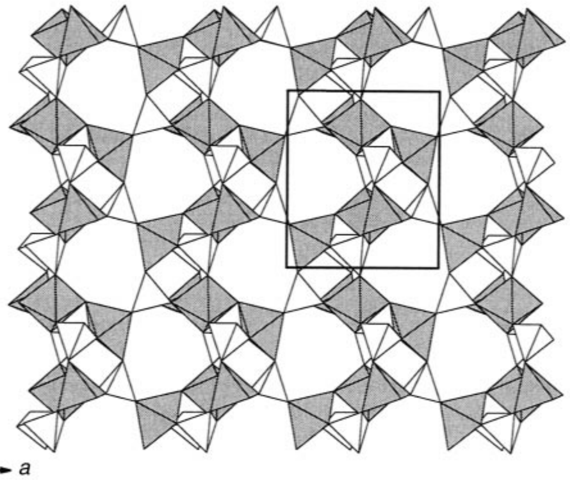

Fig. 3 Polyhedral representation of the inorganic layer in the plane (001).

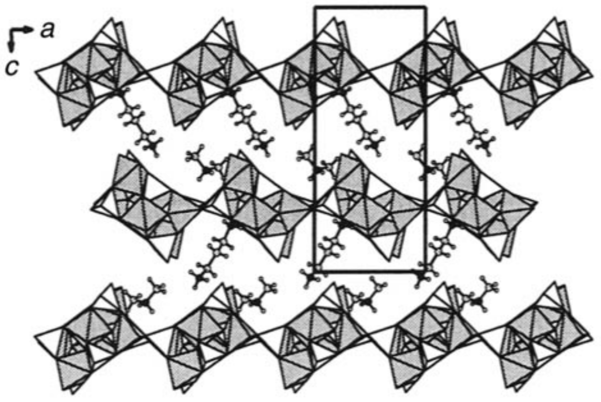

Fig. 4 View of the structure of $Ga_3(PO_4)_3F_3{\cdot}N_2C_3H_{12}{\cdot}NC_2H_7$ (MIL-30) along *b*.

stack along [001] *via* a 2_1 screw axis operation. However, the arrangement of the building units differs from that found in the other lamellar gallium phosphates ULM-8 (prepared with tris(aminoethyl)amine) and DAO-GaPO (prepared from a pyridine/1,8-diaminooctane mixture[26]). In MIL-30, the hexameric units have the same orientation within the inorganic sheet whereas two adjacent hexamers have opposite orientations in ULM-8 or DAO-GaPO. The connection mode is reminiscent of that occurring in the ULM-3 structural type. The ULM-3 topology is generated from the hexamer-based layers of MIL-30 which are joined through Ga–O–P bonds from the remaining free corners (O(7) and F(3)). The 1,3-diaminopropane and dimethylamine molecules are observed in the interlayer region. The dimethylamine comes from the decomposition of the dimethylformamide co-solvent used during the hydrothermal synthesis. Both are assumed to be protonated in order to balance the three negative charges of the inorganic sheet. The cohesion of the structure is mainly ensured through the interactions of the NH_3^+ groups of the 1,3-diaminopropane with the inorganic layer *via* strong hydrogen bonds (Fig. 6). The nitrogen atom N(2) interacts preferentially with the two bridging fluorine atoms from the central GaO_4F_2 octahedron (N(2)···F(1) = 2.93 Å; N(2)···F(2) = 3.00 Å) and some oxygen atoms (N(2)···O(1) = 2.92 Å). This situation is usually encountered in the case of the interactions between diamines and the hexameric block. The second nitrogen atom N(1) of the diaminopropane is directed toward the oxygen atoms of phosphate groups belonging to the same and opposite layers. The strongest interactions occur between the terminal oxygen atoms O(7) ($N(1){\cdots}O(7)_{opposite} = 2.85$ Å and $N(1){\cdots}O(7)_{same} = 2.91$ Å) and the oxygen atoms O(8) ($N(2){\cdots}O(8)_{opposite} = 2.95$ Å). Although the valence bond criterion is not satisfied for the oxygen atom O(7) (valence sum 1.2), an additional hydrogen (corresponding to a hydroxy group, P–OH) is not visible from the Fourier difference map analysis. The valence of the oxygen O(7) must be completed by the hydrogen bonding with the diaminopropane molecule.

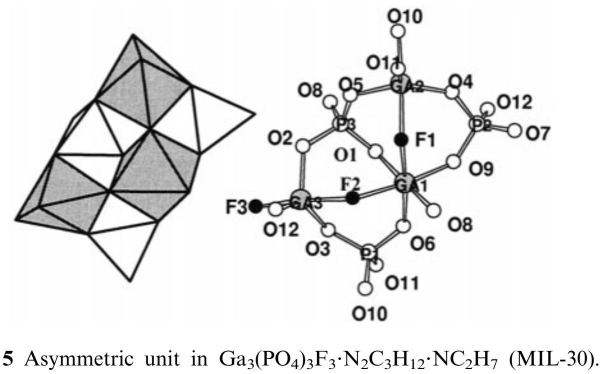

Fig. 5 Asymmetric unit in $Ga_3(PO_4)_3F_3{\cdot}N_2C_3H_{12}{\cdot}NC_2H_7$ (MIL-30). White tetrahedra: PO_4; grey polyhedra: $GaO_3(O,F)_2$ and GaO_4F_2 units; black circles: fluorine; white circles: oxygen.

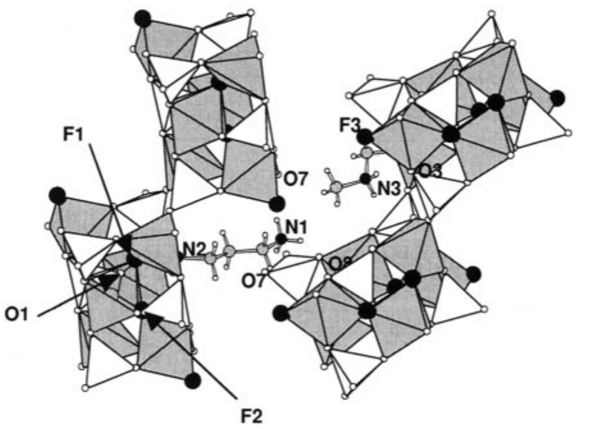

Fig. 6 Interaction scheme between amines and the inorganic sheet. Larger black circles represent the fluorine atoms. Small open circles represent oxygen atoms (hydrogen atoms for the amine molecule). Only the labels of the anions involved in the strongest hydrogen bond interactions are indicated.

The dimethylamine molecule also interacts with the inorganic network through the NH_2^+ group. Strong hydrogen bond type interactions are mainly observed with anions of the oxygen atom O(3) (N(3)···O(3) = 2.97 Å) and the fluorine in the terminal position (N(3)···F(3) = 3.07 Å) from the GaO_3F_2 entity.

Discussion

The presence of two different amine molecules as structure directing agent has already been reported by Cheetham *et al.*[25–28] in open-framework gallium phosphates. By using the combination of the HF/pyridine mixture and an amine, three-dimemsional frameworks have been made in which the pyridine and the amine were found in distinct pores of the structure. For example, in the case of the TREN-GaPO,[25] the tren molecule adopts the larger 12-ring channels whereas the pyridine resides in the 8-ring ones.

In the layered structure of MIL-30, beside the rôle of charge compensator, the two types of organic molecules exhibit different behaviours. The diaminopropane is responsible for the cohesion of the structure and acts as an organic pillar linking the layers together. The dimethylamine plays another role. It interacts with the terminal fluorine atom F(3) and therefore prevents further condensation of the layers for the formation of the three-dimensional framework. This specific interaction is at the origin of the condensation limitation giving rise to the lamellar structure. If only the diaminopropane is used as a structure directing agent, the condensation process is not stopped and the 3D framework with the ULM-3 topology is produced. This point confirms the specific role of the dimethylamine as a condensation inhibitor during the hydrothermal process. The occurrence of interactions between the diaminopropane and the terminal P–O bond would be due to the existence of the negative charge coming from the non-bonded PO_4 groups and would be a consequence of the crystal growth. The isolation of the layered structure derived from the 3D framework can give us new insights into the mechanism of the process occurring during the hydrothermal synthesis. A model of the mechanism[29] which involves the formation of 3-D frameworks from 1-D chains and 2-D layered phases was previously proposed for the synthesis of aluminophosphate with organic templates. In agreement with this hypothesis, the MIL-30 would be a precursor for the formation of the ULM-3 framework.

The other point is the rôle of the dimethylformamide solvent.

It has a significant influence because the attempts to synthesize the MIL-30 phase from a diaminopropane/dimethylamine mixture in water were unsuccessful. Only the ULM-3 compound is obtained in this case. A ^{13}C NMR experiment was performed on the liquid phase resulting from the synthesis of MIL-30. The ^{13}C spectrum is typical of that expected for DMF with additional much less intense peaks corresponding to dimethylamine. This observation indicates that a small part of the DMF is decomposed into dimethylamine during the hydrothermal reaction. Moreover, if MIL-30 is hydrothermally heated with water at 180 °C, the resulting product is ULM-3 too. So the presence of both dimethylamine and DMF seems to induce the formation of a 2-dimensional solid instead of a 3-dimensional open-framework.

This means that not only does the dimethylformamide acts as solvent, but its decomposition also plays a major rôle. Indeed, compared to the hexameric unit in other ULM compounds, the hexameric unit here possesses three fluorine ions instead of the usual two. It may be expected that the reactive protonated dimethylamine coming from dimethylformamide forms an ion pair with fluorine coming from the solution. Once this pair is inserted between the layers, an exchange between OH groups of the hexameric unit and F(3) could occur, a consequence of which would be to stop the condensation and prevent the formation of ULM-3.

The use of a polar organic solvent also indicates that the oligomeric condensation within the system is not drastically modified because the same hexameric building unit is observed in both final phases ULM-3 and MIL-30 which are obtained with water and dimethylformamide/water, respectively. The same experiments made with the apolar solvent dimethyl sulfoxide had previously shown that another one-dimensional solid[9] with tetrahedral gallium units and GaP_2 stoichiometry was formed without any structural relationship with the other fluorinated gallium phosphates.

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