JOURNAL OF SOLID STATE CHEMISTRY 120, 197–203 (1995)

Oxyfluorinated Compounds with Open Structures

XV. Synthesis and Crystal Structure of ULM-13, a New Layered Fluoroaluminophosphate Templated with 1,6-Diaminohexane: $Al_4(PO_4)_3(HPO_4)F_6$, $(N_2C_6H_{18})_{2.5}$, 3 H_2O

Jean Renaudin and Gérard Férey

Laboratoire des Fluorures, URA CNRS 449, Université du Maine, avenue Olivier Messiaen, 72017 Le Mans Cedex, France

Received May 18, 1995; in revised form August 7, 1995; accepted August 9, 1995

ULM-13, formulated $Al_4(PO_4)_3(HPO_4)F_6$, $(N_2C_6H_{18})_{2.5}$, 3 H_2O, is a new layered fluoroaluminophosphate obtained by hydrothermal synthesis using 1,6-diaminohexane as a template. It crystallizes in the orthorhombic space group *Pnma*, $a = 9.501(2)$ Å, $b = 14.140(2)$ Å, $c = 27.057(4)$ Å, $V = 3634.95$ Å^3, $Z = 4$, $\rho_m = 1.74$ g cm^{-3}. The refinement of data leads to $R = 0.056$ for 3562 independent reflections. The structure is built up from macroanionic sheets in which (PO_4) tetrahedra share all their vertices with three (AlO_4F_2) octahedra and one (AlO_3F) tetrahedron. Protonated 1,6-diaminohexane and water molecules are interleaved between the sheets. The organic molecules exhibit two orientations: either perpendicular to the inorganic sheets or in an oblique configuration, the latter exhibiting disorder in the alkyl chain. © 1995 Academic Press, Inc.

INTRODUCTION

Numerous phosphate-based molecular sieves have been studied during the last 10 years. After the discovery of new aluminophosphates labeled $AlPO_4$-*n* (1), Guth *et al.* introduced a new route of synthesis by adding fluorine to the starting mixture (2). Using this method, our research efforts for catalysis applications have focused on a new series of fluorometallophosphates, labeled ULM-*n* (for Université Le Mans), in the systems MO_x-P_2O_5-HF-amine-H_2O with M = Al, Ga, V, Fe (3–5, and references therein). The various structures of these microporous compounds demonstrate the influence of the templating agent as well as that of fluorine, allowing for the proposal of a mechanism of formation (6). The nature of the solvent is another influencing parameter. Recent studies using nonaqueous solvent systems (including monoalcohols or glycols) revealed the effect on the crystal growth (7) or on the dimensionality of the structures (8, 9).We have attempted to verify the role of the solvent by studying various (water/ethanol) mixtures and report here the crystal structure of a new layered fluoroaluminophosphate ULM-13, formulated $Al_4(PO_4)_3(HPO_4)F_6$, $(N_2C_6H_{18})_{2.5}$, 3 H_2O.

EXPERIMENTAL

ULM-13 was obtained by classical hydrothermal synthesis (453 K, 24 hr, autogenous pressure in a Teflon vessel) starting from a stirred mixture of Al_2O_3 (calcined alumina)–dilute H_3PO_4 (21 wt.%)–dilute HF (10 wt.%)–1,6 diaminohexane (Aldrich, 98%) and ethanol in the molar ratio 2 Al:2 P:2 F:1 amine:40 EtOH:60 H_2O. After reaction, the resulting material was filtered, washed with ethanol and dried in air. Numerous colorless platelets appeared, gathered in the form of sea urchins with a common point of crystallization.

The fluorine content of the compound was analyzed by ionometry using an Orion potentiometer equipped with a fluoride-specific electrode. Thermal gravimetric analysis was performed on a TGTDA92 Setaram apparatus under argon gas flow with a heating rate of 2°C/min between 300 and 800 K.

The X-ray powder diffractogram is typical of a layered material with a large intensity for the first peak while further reflections are rather weak (Fig. 1). Furthermore, the observed intensities are highly altered by strong orientation effects.

Some crystals were separated from the bulk and sorted under a polarizing microscope. Their quality was then checked by Laue photographs. The intensity data of a selected single crystal were collected on a Siemens-S.T.O.E. AED2 four-circle diffractometer with the conditions summarized in Table 1. Corrections for Lorentz and polarization effects were applied. The observed systematic extinctions are consistent with the space group *Pnma*.

STRUCTURAL DETERMINATION

The structure was solved by direct methods using option TREF of the program SHELXS-86 (10). The refinement

0022-4596/95 $12.00
Copyright © 1995 by Academic Press, Inc.
All rights of reproduction in any form reserved.

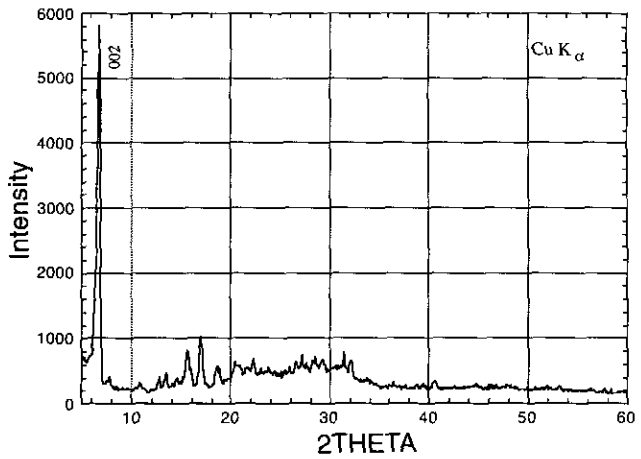

FIG. 1. X-ray powder diffractogram of ULM-13 (wavelength, Cu$K\alpha$).

calculations were performed using the program SHELXL-93 (11). After positioning the Al and P cations, the anions and a first amine backbone were located from successive Fourier maps. The fluorine and oxygen sites were assigned after analyzing the bond valences (see description below). One hydrogen atom, H(8), was clearly found from a peak of electronic density at ≈1 Å from the O(8) atom. The others were located by applying geometrical constraints on the 1,6-diaminohexane molecule (option HFIX in program SHELXL-93). At this stage, the refinement converges to $R_1 = 0.065/wR_2 = 0.224$ with anisotropic thermal parameters for all nonhydrogen atoms, but the corresponding difference Fourier map exhibits five unbalanced residues (between 2.1 and 3.5 e^- Å^{-3}). A careful examination of the location of these residues shows that they may be attributed to carbons which approximate a second disordered molecule of 1,6-diaminohexane.

Further refinements were carried out with these carbon atoms using a half-occupancy factor for atoms C(12) to C(15) together with the same isotropic thermal parameter. Furthermore, restraints were applied to the C–C bond lengths in order to maintain the geometry of the molecule (option DFIX in SHELXL-93). Finally, some trials were undertaken in the subgroups $Pna2_1$ and $P2_12_12_1$ but with

TABLE 1
Crystallographic Characteristics

Symmetry: orthorhombic Space group: *Pnma* (no. 62)
Cell parameters from 20 reflections in the range $14° < \theta < 15°$: a = 9.501(2) Å; b = 14.140(2) Å; c = 27.057(4) Å; V = 3634.9 Å^3; Z = 4; M = 952.41 g mole^{-1}
Density: 1.74 g cm^{-3} (calculated)
Crystal size: 0.54 × 0.18 × 0.075 mm^3
Radiation: Mo$K\alpha$ (λ = 0.71073 Å)
Linear absorption coefficient: 4.2 cm^{-1}
Transmission factors: $T_{max} = 0.97/T_{min} = 0.93$
Scan mode: $\omega - \theta/2$
Aperture: 4.5 × 4.5 mm^2
Intensity measurements up to $2\theta = 65°$
36 steps per reflection, 4 sec max. per step
Indices: $0 \le h \le 14$, $0 \le k \le 21$, $0 \le l \le 40$
265 refined parameters
7283 measured reflections
3562 independent reflections with $F/\sigma(F) > 4$
Weighting scheme: $w = 1/(\sigma(F_0)^2 + (0.1045\ P)^2 + 1.84\ P)$
Final residuals: R_1 (F_0) = 0.056/wR_2 (F_0^2) = 0.183
Electron density in final Fourier difference map: maximum = 1.9e-Å^{-3}, minimum = −1.1e- Å^{-3}

TABLE 2
Atomic Coordinates and Displacement Parameters for Non-H Atoms

Atom	Site	x	y	z	U_{eq} (Å^2)
P(1)	8d	0.1563(1)	0.5966(1)	0.98169(3)	0.0120(1)
P(2)	4c	0.0859(1)	1/4	0.91510(4)	0.0119(2)
P(3)	4c	0.4571(1)	1/4	0.99543(4)	0.0134(2)
Al(1)	8d	0.1822(1)	0.3751(1)	0.00629(3)	0.0121(2)
Al(2)	4c	0.7538(1)	1/4	0.93165(5)	0.0122(2)
Al(3)	4c	0.6887(1)	1/4	0.07625(5)	0.0142(3)
F(1)	8d	0.7023(2)	0.1611(2)	0.88643(8)	0.0299(5)
F(2)	8d	0.2409(2)	0.4028(2)	0.06940(7)	0.0207(4)
F(3)	4c	0.1510(3)	1/4	0.02775(10)	0.0151(5)
F(4)	4c	0.6490(4)	1/4	0.13669(11)	0.0346(8)
O(1)	8d	0.1259(2)	0.3398(2)	0.94250(8)	0.0175(4)
O(2)	8d	0.1946(3)	0.6527(2)	0.02757(10)	0.0293(6)
O(3)	8d	0.3692(2)	0.3399(2)	0.99158(9)	0.0192(5)
O(4)	8d	0.9981(2)	0.5921(2)	0.97372(9)	0.0197(5)
O(5)	8d	0.2219(2)	0.4982(1)	0.98384(9)	0.0174(4)
O(6)	8d	0.2193(3)	0.6468(2)	0.93541(9)	0.0222(5)
O(7)	4c	0.5662(3)	1/4	0.95448(14)	0.0241(8)
O(8)	4c	0.1644(4)	1/4	0.86356(14)	0.0251(8)
O(9)	4c	0.9334(3)	1/4	0.89913(12)	0.0171(6)
O(10)	4c	0.5279(4)	1/4	0.04685(15)	0.0301(8)
O(w1)	4c	0.4372(5)	1/4	0.8492(2)	0.064(2)
O(w2)	4c	0.0253(11)	1/4	0.7711(3)	0.116(3)
O(w3)	4c	0.7469(12)	1/4	0.7897(3)	0.157(5)
C(1)	8d	0.0200(4)	0.0177(3)	0.84528(14)	0.0299(8)
C(2)	8d	0.9266(5)	0.0080(4)	0.80099(15)	0.041(1)
C(3)	8d	0.5119(5)	0.0002(5)	0.74632(15)	0.048(1)
C(4)	8d	0.4217(5)	0.5003(4)	0.79276(15)	0.044(1)
C(5)	8d	0.5108(4)	0.9996(4)	0.83976(14)	0.037(1)
C(6)	8d	0.4257(4)	0.4823(3)	0.88551(13)	0.0298(8)
N(1)	8d	0.0608(3)	0.5369(2)	0.10884(11)	0.0237(6)
N(2)	8d	0.5138(3)	0.0282(2)	0.93017(11)	0.0269(6)
N(10)	4c	0.2807(15)	1/4	0.1287(3)	0.125(5)
Residues (refined with the same U_{iso} value)					
C(11)	4c	0.288(2)	1/4	0.1850(7)	0.150(5)
C(12)*	4c	0.427(4)	1/4	0.2121(12)	0.150(5)
C(13)*	4c	0.381(4)	1/4	0.2882(13)	0.150(5)
C(14)*	4c	0.504(4)	1/4	0.2834(14)	0.150(5)
C(15)*	4c	0.080(4)	1/4	0.1638(13)	0.150(5)

* These sites were refined with a half-occupancy factor.

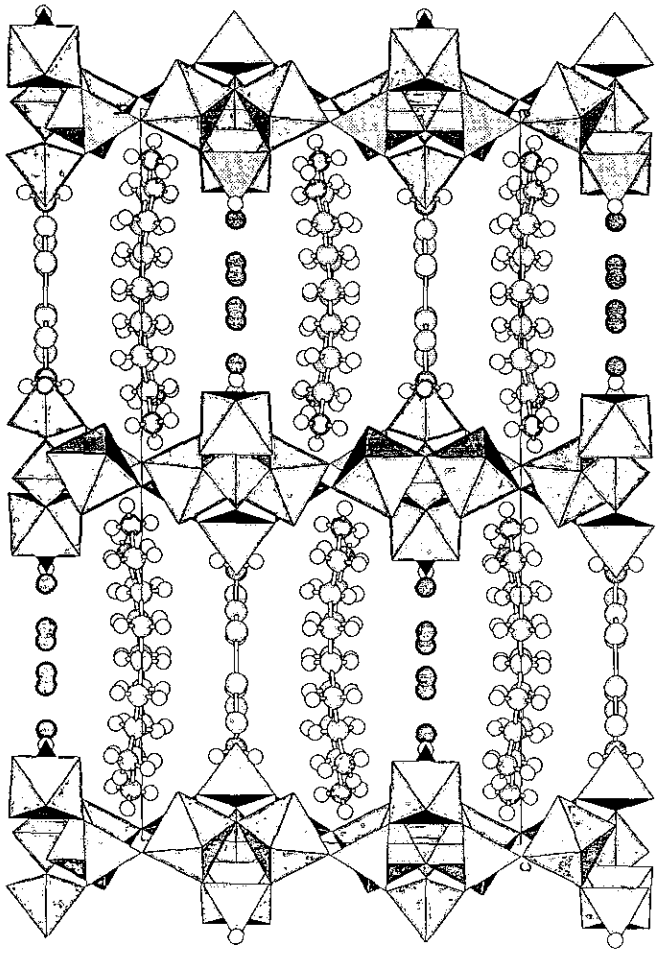

FIG. 2. [100] projection of ULM-13 structure showing the alternating layers, H_2O–inorganic sheet–diamine along the c axis.

no significant improvement. The final parameters are listed in Table 2 for nonhydrogen atoms. The anisotropic thermal parameters, the hydrogen positions, and the list of structure factors are available upon request.

DESCRIPTION OF THE STRUCTURE

The structure of ULM-13 is built up from the stacking along [001] of macroanionic sheets, formulated $[Al_4(PO_4)_3(HPO_4)F_6]^{5-}$, separated from each other by organic layers consisting of 1,6-hexanediammonium cations and water molecules (Fig. 2).

1. The $[Al_4(PO_4)_3(HPO_4)F_6]^{5-}$ Sheets

Owing to the different multiplicities of the six cationic sites, the asymmetric unit is composed of eight polyhedra in two groups of four (Fig. 3), three (PO_4) and one (HPO_4) tetrahedra alternating with three (AlO_4F_2) octahedra and one (AlO_3F) tetrahedron. Table 3 reports the corresponding environment of the P and Al atoms: the average P–O distance (1.53 Å) is similar to previously observed values (4, 12) with the longest distance, P(2)–O(8), corresponding to the P–OH bond. The Al(1) and Al(2) sites are octahedrally coordinated with four oxygen ($\langle Al-O\rangle$ = 1.870 Å) and two fluorine atoms ($\langle Al-F\rangle$ = 1.841 Å). The F(3) atom links two octahedra whereas other fluorine atoms are terminal. This explains the longer Al(1)–F(3) distance. The third Al(3) site is tetrahedrally coordinated, with one fluorine atom F(4) in a terminal position. This unusual feature was confirmed by a valence bond analysis (Table 4) based on the data from Brese and O'Keeffe (13). The calculated valence for Al(3) is in agreement with a fluorine atom in this site.

A simplified way to describe the inorganic sheet is to use secondary building units (hereafter called SBU) as introduced in the previous works about the ULM-*n* series (3–5). For this description, the asymmetric unit must be divided in two tetrameric SBU. The first, composed of two $Al(1)O_4F_2$ octahedra sharing corners with two tetrahedra around P(2) and P(3), is similar to those observed in morinite (14), minyulite (15), or $AlPO_4$-CJ2 (16), whereas the second is quite new because two $P(1)O_4$ tetrahedra are linking both an $Al(2)O_4F_2$ octahedron and an $Al(3)O_3F$ tetrahedron, but no connection is made between the two aluminum sites. These two types of SBU share three vertices, two O(4) and one O(9), alternating P and Al polyhedra in order to rebuild the asymmetric unit. In this manner, the O(5) atoms link two SBU along the **c** axis, giving rise to a four-membered cavity (Fig. 4). Finally, a last type of connection between the two SBU involves the O(7) and O(10) atoms along the **a** axis, thus forming an 8-ring.

2. The $[(NH_3\text{-}(CH_2)_6\text{-}NH_3)_{2.5}{}^{5+}, 3\ H_2O]$ Layers

Inserted between the inorganic sheets are three water molecules and two crystallographically distinct 1,6-diami-

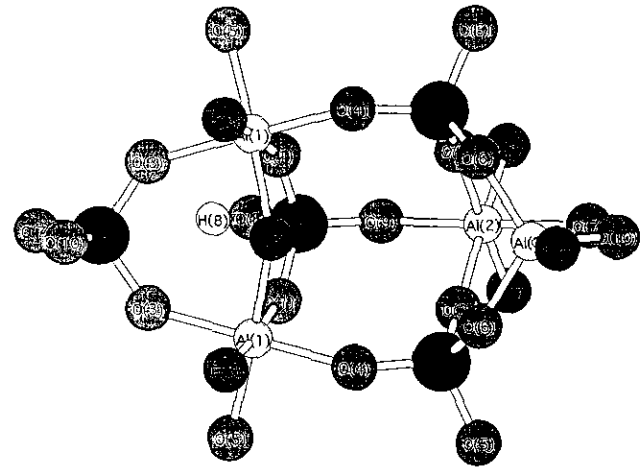

FIG. 3. Perspective view of the $[Al_4(PO_4)_3(HPO_4)F_6]^{5-}$ asymmetric unit.

TABLE 3
Interatomic Distances (Å) and Bond Angles (°) in Cationic Polyhedra

Al(1)	F(2)	O(4)	O(1)	O(5)	F(3)	O(3)
F(2)	**1.839(2)**	2.554(3)	3.714(3)	2.685(3)	2.583(3)	2.589(2)
O(4)	87.5(1)	**1.855(2)**	2.733(2)	2.706(3)	2.645(2)	3.740(3)
O(1)	176.7(1)	94.1(1)	**1.874(2)**	2.668(3)	2.645(2)	2.668(2)
O(5)	92.4(1)	92.8(1)	90.4(1)	**1.882(1)**	3.767(3)	2.649(3)
F(3)	87.8(1)	90.0(1)	89.4(1)	177.2(1)	**1.885(1)**	2.622(3)
O(3)	88.0(1)	175.2(1)	90.2(1)	89.2(1)	88.0(1)	**1.888(2)**
Al(2)	F(1)	F(1)	O(2)	O(2)	O(7)	O(9)
F(1)	**1.821(2)**	2.514(3)	3.644(3)	2.524(2)	2.575(3)	2.552(3)
F(1)	87.3(2)	**1.821(2)**	2.524(2)	3.644(3)	2.575(3)	2.552(3)
O(2)	174.7(1)	87.6(1)	**1.829(3)**	2.749(3)	2.698(2)	2.702(2)
O(2)	87.6(1)	174.7(1)	97.4(2)	**1.829(3)**	2.698(2)	2.702(2)
O(7)	88.1(1)	88.1(1)	93.2(1)	93.2(1)	**1.886(3)**	3.795(3)
O(9)	86.0(1)	86.0(1)	92.2(1)	92.2(1)	171.8(2)	**1.920(3)**
Al(3)	F(4)	O(10)	O(6)	O(6)		
F(4)	**1.678(3)**	2.693(4)	2.738(3)	2.738(3)		
O(10)	104.5(2)	**1.723(4)**	2.851(3)	2.851(3)		
O(6)	106.9(1)	111.3(1)	**1.729(3)**	2.919(2)		
O(6)	106.9(1)	111.3(1)	115.0(2)	**1.729(2)**		
P(1)	O(2)	O(4)	O(5)	O(6)		
O(2)	**1.518(3)**	2.519(3)	2.498(3)	2.507(3)		
O(4)	112.0(2)	**1.519(2)**	2.520(2)	2.466(3)		
O(5)	110.3(1)	111.8(1)	**1.526(2)**	2.477(3)		
O(6)	109.1(1)	106.5(1)	106.8(2)	**1.559(2)**		
P(2)	O(9)	O(1)	O(1)	O(8)		
O(9)	**1.511(3)**	2.515(3)	2.515(3)	2.396(4)		
O(1)	112.3(1)	**1.519(2)**	2.540(3)	2.508(4)		
O(1)	112.3(1)	113.5(1)	**1.519(2)**	2.508(4)		
O(8)	101.6(2)	108.2(1)	108.2(1)	**1.582(4)**		
P(3)	O(7)	O(3)	O(3)	O(10)		
O(7)	**1.518(4)**	2.475(3)	2.475(3)	2.521(5)		
O(3)	108.9(1)	**1.525(2)**	2.545(2)	2.472(4)		
O(3)	108.9(1)	113.1(2)	**1.525(2)**	2.472(4)		
O(10)	111.1(1)	107.4(1)	107.4(1)	**1.545(4)**		

nohexane molecules which must be protonated to balance the five negative charges of the inorganic asymmetric unit. The atomic positions of the first $[NH_3\text{-}(CH_2)_6\text{-}NH_3]^{2+}$ cation are well defined and it has a classic stretched conformation (Fig. 5). Its orientation, perpendicular to the inorganic sheet, is discussed below. On the other hand, as mentioned above, disorder is encountered for the second 1,6-hexanediammonium cation which has an oblique orientation toward the sheets. Both ends of the cation are well defined by N(10) and C(11) sites which are fully occupied, but the central part is not as well defined due to the four carbons in the half-occupied sites C(12) to C(15). The reason for this disorder might be due to the two possible orientations presented in Fig. 6. Starting from a common bond, N(10)–C(11), the molecule can be oriented either along the [-101] direction with the atom order C(12) to C(15) then C(11)–N(10) or along the [101] direction with the reverse order C(15) to C(12). Of course, the resulting interatomic distances and angles are highly altered in spite of restraints applied during the refinement with only the N(10)–C(11) and C(11)–C(12) distances being satisfactory. Another indicator of the disorder in the central car-

TABLE 4
Valence Bond Analysis of ULM-13

	P(1)	P(2)	P(3)	Al(1)	Al(2)	Al(3)	H	Σ =
F(1)					0.95/0.48		0.12	**0.60**
F(2)				0.45			0.19	**0.65**
F(3)				0.40/0.80			0.01	**0.81**
F(4)						0.70		**0.70**
O(1)		2.54/1.27		0.55				**1.82**
O(2)	1.28				1.23/0.62			**1.90**
O(3)			2.47/1.24	0.53				**1.77**
O(4)	1.26			0.57				**1.84**
O(5)	1.24			0.53				**1.77**
O(6)	1.13					1.62		**1.94**
O(7)			1.26		0.53			**1.79**
O(8)		1.04					0.95	**1.99**
O(9)		1.28			0.48			**1.76**
O(10)			1.17			0.82		**1.99**
Σ =	**4.91**	**4.86**	**4.91**	**3.05**	**3.19**	**3.14**	—	

bon chain is the total length of this molecule, which is 8.11 Å measured between terminal nitrogen atoms instead of 8.72 Å for the first diamine. It is worth noting that oblique diammonium cations and water molecules alternate along the **c** axis. Finally the multiplicity of the sites N(10) to C(15) implies one-half cation per formula unit, which is sufficient for the charge balance.

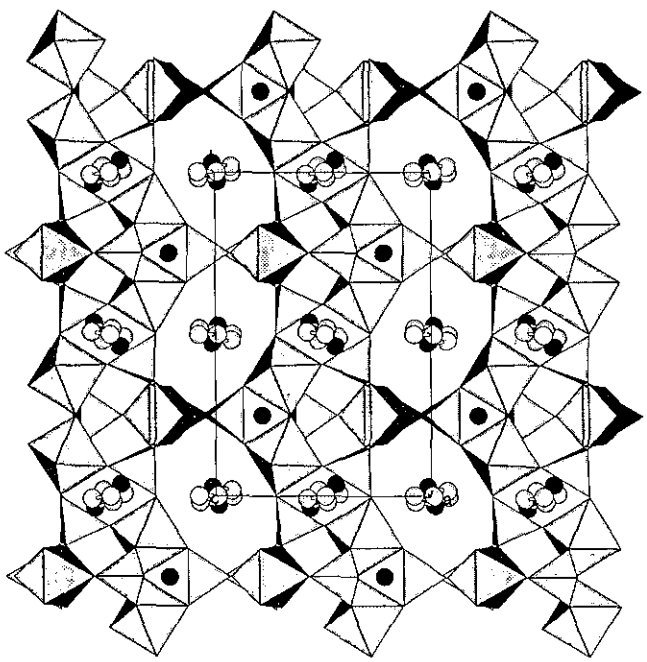

FIG. 4. [001] projection at level $z = 1/2$ of the inorganic sheet showing the two kinds of SBU and their linkages. The nitrogen atoms (black circles) are also projected in their respective cavities.

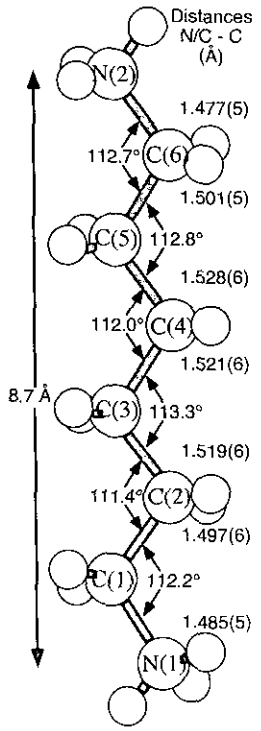

FIG. 5. [010] projection of the first hexanediammonium cation with interatomic N–C or C–C distances (Å) and angles.

3. *The Hydrogen Bonds*

A very complex network of hydrogen bonds (Table 5) interconnects the structure framework. As previously observed in our series of ULM-*n* compounds, the strongest hydrogen bonds involve the highly electronegative fluoride ions. This is indeed the case for the F(1) and F(2) terminal sites but less pertinent for the F(3), which bridges two Al(1) atoms, and the F(4), which has a short bond with the Al(3); this feature is confirmed by the valence bond analysis (Table 4).

The N(1), N(2), and N(10) atoms are linked to anions by strong hydrogen bonds in order to ensure the connection between the inorganic sheets and the organic layers. From Fig. 4, it is evident that the N(1) atom is projected through the four-membered cavity defined by two consecutive SBU whereas the N(2) atom is completely inserted in the 8-ring. Therefore, the straight diamines are truly anchored at both ends inside the inorganic sheets. In contrast, the hydrogen bonds around the water molecules are rather weak (except between O(*w*1) and O(8)-H groups) and this explains the large thermal displacement observed for the three sites.

DISCUSSION

The first striking feature in ULM-13 is the high fluorine content. The chemical analysis (experimental = 10,4 wt.%;

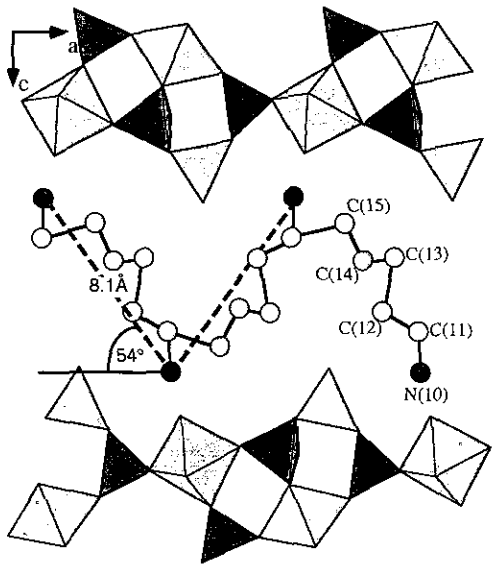

FIG. 6. [010] projection at level $y = 1/4$ of the disordered hexanediammonium cations with the two possible orientations and the neighboring polyhedra of the inorganic sheets.

TABLE 5
Hydrogen-Bond Scheme in ULM-13

Hydrogen bond	N—H	H ··· F(O)	N ·· F(O)
N(1)—H(1D) ··· F(2)	0.89	1.918	2.77
N(1)—H(1E) ··· F(1)	0.89	1.988	2.86
N(1)—H(1C) ··· O(1)	0.89	2.037	2.85
N(2)—H(2E) ··· F(1)	0.89	2.032	2.85
N(2)—H(2D) ··· O(3)	0.89	2.156	2.85
N(2)—H(2C) ··· F(2)	0.89	2.119	2.93
N(10)—H(10A) ··· F(2)	0.89	2.059	2.72
N(10)—H(10B) ··· F(2)	0.89	2.100	2.72
N(10)—H(10C) ··· F(3)	0.89	2.507	2.99
Hydrogen bond	**O—H**	**H ··· F(O)**	**O ·· F(O)**
O(8)—H(8) ··· O(*w*1)	0.87	2.047	2.62
O(8) ·· O(*w*2)	—	—	2.83
O(*w*2) ·· O(*w*3)	—	—	2 × 2.68
O(*w*3) ·· F(1)	—	—	2.93

expected value, 11,97%) corresponds to 5.2 F^- ions per formula unit, close to the value of six which arises from the structural determination. This means that a partial substitution by hydroxyl groups may occur in the aluminum polyhedra. However, such a substitution would noticeably increase the valence of the Al^{3+} ions, which is already greater than 3 (Table 4). Further investigations of this partial substitution via solid state NMR experiments are in progress. This high fluorine content, compared to previous experiments using only water as a solvent, might be the first consequence of syntheses in an alcohol medium. A second effect is related to the nature of the SBU in the final compound, which is very different from that occuring in pure water.

The thermogram of ULM-13 is very similar to those previously published for the analogous compounds ULM-4 (3) and ULM-8 (4) since it reveals two classical weight losses (Fig. 7). Three water molecules are lost below 150°C (experimental = 6.3%, theoretical = 5.67%) and the dehydrated compound remains stable up to 310°C. Above this temperature, the amines decompose (exp. = 32.2%, th. = 30.97%). The XRD pattern of the resulting compound at 500°C exhibits broad peaks, some of which correspond to the cristobalite form of $AlPO_4$ (JCPDS file no. 11-0500). The range of stability of the anhydrous compound is particularly interesting. Between 150 and 310°C, ULM-13 is very microporous with a hybrid organic-inorganic skeleton. Some exchange and/or absorption capacity experiments are now in progress.

Particular attention must be paid to the behavior of the templating molecules. Generally, in metallophosphates, monoamine templating molecules are more often lying between the sheets (12) and diamine molecules adopt an oblique configuration. This is the case for zirconium phosphates (17) and for a series of substituted AlPO compounds labelled SCS-22 (18), the diamines of which form a calculated angle of ca. 60° with the sheet. When replacing amines by esters in zirconium phosphate derivatives, the alkyl chains can be straightened and oriented perpendicular to the ZrPO4-type layers by swelling the products in alcohols (19). Surprisingly, in ULM-13, two kinds of behavior are intrinsically observed; most of 1,6-diaminohexane mole-

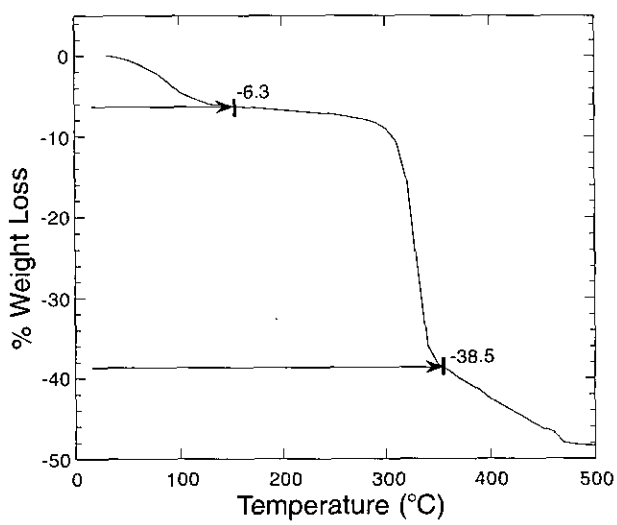

FIG. 7. Thermogravimetric analysis of ULM-13 between 300 and 800 K.

cules (80%) are perpendicular to the inorganic sheets and can be considered as pillars, whereas the other diamines are inclined at an angle of 54° (Fig. 5) and act as compressed springs. Since the strength of the hydrogen bonds is nearly equal for each diammonium group (Table 5), the roles of the two diamines can be seen as both antagonistic and complementary. If one diamine tends to repulse the inorganic sheets, the other one prevents the sheets from displacement and vice versa.

Finally, further syntheses are now in progress using diamines with longer alkyl chains ($C_nH_{2n+4}N_2$ with $n > 6$). A detailed paper concerning these compounds and related solid state NMR experiments will be published elsewhere.

ACKNOWLEDGMENTS

The authors are very indebted to Pr. M. Leblanc for his help in the X-ray data collection and Dr. T. Loiseau for valuable discussions.

REFERENCES

1. S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Cannon, and E. M. Flanigen, *J. Am. Chem. Soc.* **104,** 1146 (1982).
2. J. L. Guth, H. Kessler, and R. Wey, *Stud. Surf. Sci. Catal.* **60,** 63 (1991).
3. M. Cavellec, D. Riou and G. Ferey, *Eur. J. Solid State Inorg. Chem.* **31,** 583 (1994).
4. F. Serpaggi, T. Loiseau, D. Riou, G. Ferey, and W. Hosseini, *Eur. J. Solid State Inorg. Chem.* **31,** 595 (1994).
5. D. Riou and G. Ferey, *Eur. J. Solid State Inorg. Chem.* **31,** 605 (1994).
6. G. Ferey, *J. Fluorine Chem.* **72,** 187 (1995).
7. A. Kuperman, S. Nadimi, S. Oliver, G. A. Ozin, J. M. Garces, and M. M. Olken, *Nature* **365,** 239 (1993).
8. R. H. Jones, A. M. Chippindale, S. Natarajan, and J. M. Thomas, *J. Chem. Soc. Chem. Commun.,* 565 (1994).
9. S. Oliver, A. Kuperman, A. Lough, G. A. Ozin, J. M. Garces, M. M. Olken, and P. Rudolf, *Stud. Surf. Sci. Catal.* **84,** 219 (1994).
10. G. M. Sheldrick, *in* 'Crystallographic Computing 3" (Sheldrick, Krüger, and Goddard, Eds.), pp. 175–189. Oxford Univ. Press, Cambridge, UK (1985).
11. G. M. Sheldrick, "SHELXL-93: A Program for the Refinement of Crystal Structure Determination," University of Göttingen, 1993.
12. A. M. Chippindale, A. V. Powell, L. M. Bull, R. H. Jones, A. K. Cheetham, J. M. Thomas, and R. Xu, *J. Solid State Chem.* **96,** 199 (1992).
13. N. Brese and M. O'Keeffe, *Acta Crystallogr. B* **47,** 192 (1991).
14. F. C. Hawthorne, *Can. Mineral.* **17,** 93 (1979).
15. A. R. Kampf, *Am. Mineral.* **62,** 256 (1977).
16. G. Ferey, T. Loiseau, P. Lacorre, and F. Taulelle, *J. Solid State Chem.* **105,** 179 (1993).
17. U. Costantino, *in* "Inorganic Exchange Materials" (A. Clearfield, Ed.), p. 111. CRC Press, Boca Raton, FL (1982).
18. B. Kraushaar-Czarnetzki, W. H. J. Stork, and R. J. Dogterom, *Inorg. Chem.* **32,** 5029 (1993).
19. S. Yamanaka, *Mater. Sci. Forum* **152–153,** 69 (1994).