JOURNAL OF SOLID STATE CHEMISTRY 111, 403–415 (1994)

Oxyfluorinated Microporous Compounds

VII. Synthesis and Crystal Structure of ULM-5, a New Fluorinated Gallophosphate $Ga_{16}(PO_4)_{14}(HPO_4)_2(OH)_2F_7$, $[H_3N(CH_2)_6NH_3]_4$, 6 H_2O with 16-Membered Rings and Both Bonding and Encapsulated F^-

Thierry Loiseau and Gérard Férey[1]

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

Received July 9, 1993; accepted November 5, 1993

Hitherto unknown $Ga_{16}(PO_4)_{14}(HPO_4)_2(OH)_2F_7$, $[H_3N(CH_2)_6NH_3]_4$, 6 H_2O was obtained by hydrothermal synthesis (453 K, 24 hr, autogeneous pressure) from a mixture of Ga_2O_3, P_2O_5, HF, 1,6-diaminohexane, and H_2O in the ratio 1 : 1 : 2 : 1 : 80. It is orthorhombic (space group $P22_12_1$ (No. 18)) with a = 10.252(2) Å, b = 18.409(4) Å, c = 24.639(7) Å, V = 4649.8(9) Å^3, Z = 4. The three-dimensional network is built up from three types of basic building units; the first, close to that already encountered for ULM-3 and -4, consists of corner-linked $[Ga_3(PO_4)_2(HPO_4)F_2]$ hexameric units composed of two PO_4 tetrahdra, one HPO_4 tetrahedron, two GaO_4F trigonal bipyramids, and one GaO_4F_2 octahedron, with fluorine atoms shared between the gallium polyhedra; the second is very similar to the first except that one of the trigonal bipyramids is replaced by a tetrahedron $GaO_3(OH)$; the third is octameric $Ga_4(PO_4)_4$ and can be considered in a first approximation as formed by a cube of corner-linked GaO_4 and PO_4 tetrahedra, which encapsulate a fluorine atom. It is shown that this fluorine is bonded in fact to two of the four gallium of this cube. For the first time, both bonding and encapsulated F^- are present in the same structure. The framework delimits 16- and 6-membered ring channels along [100] and 8-membered ones along [010]. The diprotonated amines are inserted in the 16-membered ovoid channels, whose free aperture is 12.20 × 8.34 Å. The water molecules are in the 6-membered tunnels.

INTRODUCTION

Since the discovery of a new series of microporous aluminophosphates $AlPO_4$-n (1), synthesized by using organic amines or quaternary ammoniums cations as templates, numerous phosphate-based molecular sieves have been reported (2–4). Several years ago, Guth *et al.* (5) developed a new route of synthesis in the presence of fluorine. The addition of fluoride ions in the reaction medium seems to induce mineralization and allows the crystallization of zeolites at neutral or acidic pH and the partial substitution (6) of silicon by other tri- or tetravalent metals. Moreover, as encountered in many phases (7), fluorine is also incorporated to the open frameworks. The best example is cloverite (8), with three-dimensional 20-membered ring channels, in which the fluorine is located at the center of a double four-ring (D4R) cage.The same configuration for fluorine surrounding is observed in other compounds such as the pure-silica octadecasil (AST) (9) or the LTA-type $GaPO_4$ (7).

Recently (10–15), we focused our attention on the synthesis a new series, labeled *ULM-n* (12–15), of fluorinated alumino- and gallophosphates in the systems M_2O_3 (M = Al, Ga)–P_2O_5–HF–template–H_2O. In these phases, the situation of fluorine is different since it is directly involved in the coordination sphere of M, as also observed in $GaAsO_4$ −2 (16). In ULM-3 and ULM-4 (14, 15), linear diamines were used from ethylenediamine to 1,5-diaminopentane. In order to see the influence of the length of the diamine on the structure of the corresponding compounds, we carried out experiments with amines $H_2N(CH_2)_nNH_2$ ($n > 5$). We report here the preparation and characterization of the new phase synthesized with diaminohexane (hereafter noted DAH) as template: $Ga_{16}(PO_4)_{14}(HPO_4)_2(OH)_2F_7$, $[H_3N(CH_2)_6NH_3]_4$, 6 H_2O or *ULM-5*.

EXPERIMENTAL

Synthesis and Thermal Analysis

The title compound was prepared by hydrothermal synthesis under autogeneous pressure. The reactants were gallium oxide (Ga_2O_3, Merck 99%+), phosphoric acid (85% H_3PO_4, Prolabo RP Normapur), hydrofluoric acid (40% HF, Prolabo RP Normapur), and 1,6-diaminohexane

[1] To whom correspondence should be addressed.

0022-4596/94 $6.00

($H_2N(CH_2)_6NH_2$, Aldrich 99%+). The starting mixture corresponding to the molar composition 1 Ga_2O_3, 1 P_2O_5, 2 HF, 1 DAH, and 80 H_2O was placed without stirring in a Teflon-lined stainless-steel autoclave, heated at 453 K for 24 hr, and then cooled to room temperature for 24 hr. The pH of the synthesis rises from 2 before heating to 4 at the end of the reaction. The obtained crystalline product was filtered off, washed with distilled water, and dried at room temperature. Table 1 gives the calculated X-ray powder pattern of the title compound.

TGA measurements were performed on a Perkin–Elmer thermoanalyzer under argon flow with heating rate of 5°C/min between 300 and 973 K.

Structure Determination

A prismatic-shaped single crystal was selected from the sample for structural analysis by X-ray diffraction. Its quality was tested by optical observation and Laue photographs. Intensity data collection was performed with a Siemens AED-2 four-circle diffractometer with conditions of data collection summarized in Table 2 and lead to a description of the structure with the space group $P22_12_1$ (No. 18). The noncentric character was confirmed by SHG measurements. The data were corrected for Lorentz polarization and absorption effects. The scattering factors and anomalous dispersion corrections were taken from the "International Tables for X-ray Crystallography" (17). The structure was solved by using the direct method analysis of the SHELXS-86 program (18). Gallium and phosphorus atoms were first located. The anions of the matrix were then found by different Fourier maps. Refinement was performed by full-matrix least-squares analysis of SHELX-76 (19). The location of the fluorine atoms was deduced from valence bond calculations (20) and examination of the thermal parameters. At this stage of the refinement, some the nonhydrogen atoms of the amino group became visible. The refinement with anisotropic thermal parameters for Ga, P, O, and F and isotropic ones for C and N give $R_w = 0.050$ and $R = 0.044$ for the good enantiomer. The other gave worse R factors (0.065). Further Fourier difference syntheses did not provide realistic positions for the hydrogen atoms.

The atomic coordinates with isotropic thermal parameters and selected bond distances and angles are listed in Tables 3 and 4, respectively. Table 5 povides the valence bond analysis of the compound. The list of U_{ij} and of structure factors can be obtained upon request to the authors.

TABLE 1
Calculated Interplanar *d*-Spacings (Å)and Calculated Intensities for $Ga_{16}(PO_4)_{14}(HPO_4)_2(OH)_2F_7$, 4 H_3N–$(CH_2)_6NH_3$, 6H_2O (ULM-5)

h k l	d_{calc}	I_{calc}
0 1 1	14.74	100
0 0 2	12.32	82
0 2 0	9.20	4
0 2 2	7.37	12
1 1 2	7.24	21
1 2 1	6.598	6
1 0 3	6.4098	8
0 0 4	6.1597	5
0 3 3	4.9158	3
2 1 1	4.8416	3
0 1 5	4.7602	7
2 0 2	4.7327	4
0 4 0	4.6023	5
2 1 3	4.2321	2
1 4 1	4.1389	3
0 0 6	4.1065	2
1 3 4	4.0023	4
1 2 5	4.0001	4
2 1 5	3.4881	3
1 5 2	3.3357	8
1 0 7	3.3291	3
3 1 2	3.2415	8
3 2 1	3.1769	4
3 0 3	3.1551	5
0 3 7	3.0532	4
1 5 4	3.0201	3
1 1 8	2.9125	3
0 1 9	2.7079	4
3 5 2	2.4545	4

DESCRIPTION OF THE STRUCTURE

The main feature of the structure appears on the perspective view close to the [100] direction (Fig. 1): the existence of very large ovoid channels formed by the stacking of 16-membered rings and, between three of them, the appearance of a 6-membered one. The space filling representation in Fig. 2 gives a better view of the large dimensions of the channel: 14.9 × 11.14 Å between the nuclei determining the two diagonals of the oval, representing a free aperture of 12.20 × 8.34 Å for the inserted species. Orthogonally, 8-membered ring channels exist (Fig. 3) along [010] (free aperture, 3.11 × 3.19 Å).

The largest pores are built up from three different types of secondary building units (hereafter noted *sbu*) shared by corners. Their common feature is a strict Ga–P alternation within the unit, but also between them. Two of them, denoted A and B, are hexameric with 3Ga + 3P; the third is an octamer Ga4P4. If the coordination of phosphorus atoms is tetrahedral as usual, with P–O distances within 1.486–1.594 Å, the diversity of the coordination polyhedra around gallium (three types) and the nature of the ligands forming these polyhedra as well requires a detailed description for each of them.

TABLE 2
Conditions of the X-Ray Data Collection of $Ga_{16}(PO_4)_{14}(HPO_4)_2F_7(OH)_2$, 4 H_3N–$(CH_2)_6$–NH_3, 6H_2O (ULM-5)

Determination of cell parameters	30 reflections at $2\theta \approx 30°$
Space group	$P22_12_1$ (No. 18)
Cell dimensions	a = 10.252(2) Å
	b = 18.409(4) Å
	c = 24.639(7) Å
Volume/Z	4649.8(9) Å^3/Z = 2
Wavelength/monochromator	0.71073 Å (Mo $K\alpha$)/graphite
Temperature	293 K
Scan mode	ω-2θ
Step scan	$37 \leq N \leq 41$, every 0.035° and 4 sec
Aperture	3 × 3 mm^2
Crystal dimensions	0.2662 × 0.0532 × 0.076 mm^3
Natural faces	{100}, {−10−2} ± {010}, ±{001}
Absorption corrections	Gaussian method
Transmission factors	T_{min} = 0.770, T_{max} = 0.963
Absorption coefficient	μ = 49.2 cm^{-1}
Angular range of data collection	$2\theta \leq 50°$
Range of measured h, k, l	$0 \leq h \leq 12$, $0 \leq k \leq 21$, $0 \leq l \leq 29$
Standard reflections (3)	4 0 10, −4 0 10, 6 0 0
Measured every	60 mn
Measured reflections	4594
Independent reflections ($\|F\| > 6\sigma(\|F\|)$)	2876
Weight	$w = 0.599/(\sigma^2(F) + 0.01226F^2)$
Secondary extinction	$X = 1.1 \times 10^{-7}$
Number of refined parameters	344
Final Fourier residuals	−1.71 to 1.68 e · Å^{-3}
R_w/R	0.050/0.044

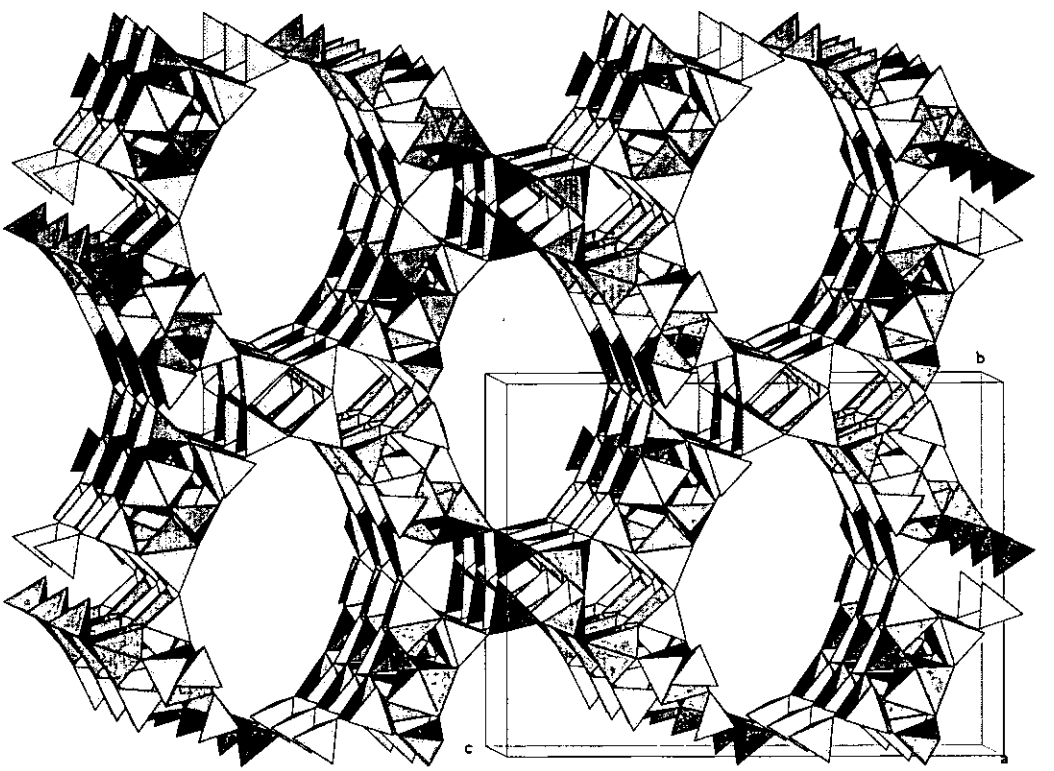

FIG. 1. Perspective view of ULM-5 close to [100]. The amino groups have been omitted for clarity.

TABLE 3

Atomic Coordinates and Equivalent Isotropic Factors in $Ga_{16}(PO_4)_{14}(HPO_4)_2(OH)_2F_7$, 4 H_3N–$(CH_2)_6NH_3$, $6H_2O$ (ULM-5)

	x	y	z	B_{eq} (Å^2)
Ga(1)	1142(2)	0860(1)	4328(1)	1.27(7)
Ga(2)	0772(5)	3507(1)	1602(1)	5.1(2)
Ga(3)	3807(2)	9331(1)	4417(1)	1.02(7)
Ga(4)	3978(2)	4205(1)	2653(1)	0.70(6)
Ga(5)	4071(2)	6745(1)	1541(1)	0.88(6)
Ga(6)	1035(2)	6095(1)	2601(1)	0.75(6)
Ga(7)	0823(2)	8000(1)	2241(1)	0.78(6)
Ga(8)	4224(2)	2307(1)	2311(1)	0.73(6)
P(1)	1023(4)	4376(2)	2678(2)	1.0(2)
P(2)	4158(4)	0980(2)	4383(2)	0.8(1)
P(3)	9164(5)	4159(2)	0623(2)	1.1(2)
P(4)	6056(4)	0928(2)	2326(2)	08(1)
P(5)	9008(4)	1703(2)	3601(1)	0.9(1)
P(6)	4182(5)	3590(2)	1451(2)	1.0(2)
P(7)	6224(4)	3229(2)	2987(2)	09(2)
P(8)	1248(4)	2078(2)	2085(2)	09(2)
F(1)	8323(9)	2140(5)	2460(4)	1.4(4)
F(2)	3321(10)	3153(5)	2630(4)	1.6(5)
F(3)	4227(9)	1912(5)	3067(4)	1.3(4)
F(4)	7301(13)	½	0	1.5(6)[a]
O(1)	1310(13)	4171(6)	2076(5)	1.8(3)
O(2)	2379(10)	4372(6)	2956(4)	1.0(2)
O(3)	0425(10)	5133(6)	2682(5)	1.4(2)
O(4)	0177(11)	3834(7)	2968(5)	1.5(2)
O(5)	5314(11)	4037(6)	9969(5)	1.4(2)
O(6)	5821(14)	4772(6)	9115(4)	1.7(2)
O(7)	7215(10)	3723(6)	9385(4)	0.9(2)
O(8)	4979(12)	3497(6)	9077(4)	1.3(2)
O(9)	0126(12)	3681(8)	0933(5)	1.9(2)
O(10)	7756(12)	3895(6)	0723(5)	1.7(2)
O(11)	9314(17)	4924(7)	0844(5)	2.8(4)
O(12)	9567(12)	4065(7)	0021(5)	2.1(3)
O(13)	5183(11)	1496(7)	2051(5)	1.4(2)
O(14)	6312(11)	1078(6)	2933(5)	1.3(2)
O(15)	5416(10)	0186(6)	2269(5)	1.2(2)
O(16)	2595(11)	5944(6)	2964(4)	1.0(2)
O(17)	9271(11)	2487(6)	3445(4)	1.1(2)
O(18)	9927(13)	1522(7)	4072(5)	1.7(2)
O(19)	7637(12)	1574(6)	3806(5)	1.5(2)
O(20)	0638(11)	3849(6)	8129(4)	1.1(2)
O(21)	4388(10)	4130(6)	1921(4)	1.1(2)
O(22)	4223(12)	2799(6)	1609(4)	1.4(2)
O(23)	2826(12)	3748(7)	1171(6)	2.6(4)
O(24)	5265(14)	3704(7)	1034(5)	2.1(3)
O(25)	6100(12)	2742(6)	3493(4)	1.2(2)
O(26)	5828(11)	2813(6)	2474(5)	1.4(2)
O(27)	5329(10)	3904(6)	3092(5)	1.0(2)
O(28)	7578(12)	3504(6)	2920(5)	1.4(2)
O(29)	2621(12)	1786(7)	2176(5)	2.0(3)
O(30)	1189(12)	2556(6)	1575(5)	1.6(2)
O(31)	0368(12)	1419(6)	1984(5)	1.6(2)
O(32)	0801(11)	2528(6)	2569(5)	1.6(2)
O(33)	9093(14)	3370(6)	1989(4)	1.9(5)
Ow(1)	7204(16)	4570(9)	1958(6)	3.6(3)
Ow(2)	1869(20)	0836(11)	3413(8)	4[b]
Ow(3)	2502(32)	5067(17)	0677(15)	4[b]
N(1)	2561(20)	0227(10)	1894(7)	3.4(4)
N(2)	2330(23)	3371(11)	0017(9)	4.3(4)
C(1)	2084(26)	0050(14)	1349(9)	4[b]
C(2)	2988(43)	0366(22)	0955(17)	4[b]
C(3)	2703(62)	1103(26)	0764(20)	4[b]
C(4)	2998(47)	1370(22)	0221(18)	4[b]
C(5)	3286(33)	2149(19)	0154(16)	4[b]
C(6)	2110(28)	2574(12)	0094(12)	4[b]
N(3)	7118(17)	2490(9)	1419(7)	2.3(3)
N(4)	7847(18)	2324(10)	8612(8)	2.9(3)
C(7)	6991(55)	1974(32)	0929(21)	4[b]
C(8)	8476(55)	1885(32)	0865(24)	4[b]
C(9)	7747(90)	1329(56)	0499(27)	4[b]
C(10)	7609(55)	1129(30)	9895(20)	4[b]
C(11)	8317(66)	1681(38)	9517(22)	4[b]
C(12)	7383(53)	1754(23)	9035(16)	4[b]

Note. The table U_{ij} can be obtained upon request.

[a] Special position 2b.

[b] Thermal parameters are fixed.

Hexameric Units

In each (100) plane, sbu are of the same kind at the same level: A species at $x \sim 0$ and B units at $x \sim 1/2$. Sbu A (Fig. 4a) provides a unique example of a trimer of gallium polyhedra which is composed of a central octahedron ($Ga(7)O_4(OH)F$, with ($Ga(7)$–O_{av} = 1.947 Å and Ga(7)–F = 1.953 Å), a trigonal bipyramid ($Ga(6)O_4F$ with ($Ga(6)$–O_{av} = 1.863 Å and Ga(6)–F = 2.039 Å), and a tetrahedron ($Ga(2)O_3(OH)$ with ($Ga(2)$–O_{av} = 1.843 Å). The octahedron shares its fluorine atom with the bipyramid and the (OH) group with the Ga(2) tetrahedron. The central PO_4 tetrahedron shares three of its corners with the three gallium polyhedra, while the external ones are linked to two of the three gallium polyhedra via corners.

Sbu B (Fig. 4b) is very close to the unit already encountered in ULM-3 and -4 (14, 15). The gallium atoms present two different coordinations: Ga(8) is octahedrally coordinated with four oxygens ($Ga(1)$–O_{av} = 1.929 Å) and two fluorine atoms ($Ga(1)$–F_{av} = 1.988 Å). The polyhedra around Ga(4) and Ga(5) are distorted trigonal bipyramids with a distance for Ga–F (2.051 and 2.018 Å) longer than that for Ga–O (1.827–1.919 Å for Ga(4) and 1.828–1.974 Å for Ga(5)). The two types of gallium polyhedra are linked together via the fluorine atoms and the resulting trimers $Ga_3O_{12}F_2$ of gallium polyhedra (two trigonal bipyramids and one octahedron) are isolated from each other by phosphorus tetrahedra. The only difference is that in ULM-3 and -4, all the phosphorus tetrahedra were PO_4, which shared all their vertices between the sbu, whereas in the title compound, P(6), corresponds to a HPO_4 entity,

TABLE 4
Selected Interatomic Distances (Å) and Angles (°) in $Ga_{16}(PO_4)_{14}(HPO_4)_2(OH)_2F_7$, 4 H_3N–$(CH_2)_6$–NH_3, 6H_2O (ULM-5)

		$P(1)O_4$ tetrahedron (sbu A)		
P(1)	O(4)	O(3)	O(2)	O(1)
O(4)	**1.503(13)**	2.506(17)	2.465(16)	2.562(17)
O(3)	111.9(7)	**1.523(12)**	2.536(15)	2.488(17)
O(2)	107.7(7)	111.3(6)	**1.550(11)**	2.458(16)
O(1)	113.6(7)	107.7(7)	104.5(7)	**1.559(13)**
		⟨P(1)–O⟩ = 1.534(12)		
		$P(2)O_4$ tetrahedron (sbu C)		
P(2)	O(8)	O(7)	O(6)	O(5)
O(8)	**1.509(13)**	2.450(16)	2.503(16)	2.437(17)
O(7)	108.5(7)	**1.510(11)**	2.493(16)	2.491(16)
O(6)	110.6(7)	110.0(7)	**1.534(12)**	2.555(16)
O(5)	106.0(7)	109.4(6)	112.3(6)	**1.542(13)**
		⟨P(2)–O⟩ = 1.524(12)		
		$P(3)O_4$ tetrahedron (sbu C)		
P(3)	O(11)	O(9)	O(10)	O(12)
O(11)	**1.518(13)**	2.445(20)	2.496(19)	2.585(18)
O(9)	106.9(8)	**1.527(14)**	2.515(17)	2.424(18)
O(10)	109.3(8)	110.1(7)	**1.543(13)**	2.557(17)
O(12)	114.8(7)	104.0(7)	111.5(7)	**1.549(13)**
		⟨P(3)–O⟩ = 1.534(13)		
		$P(4)O_4$ tetrahedron (sbu B)		
P(4)	O(15)	O(13)	O(14)	O(16)
O(15)	**1.522(12)**	2.482(17)	2.493(16)	2.537(15)
O(13)	108.6(7)	**1.534(13)**	2.580(17)	2.495(16)
O(14)	108.9(7)	113.9(7)	**1.543(13)**	2.490(16)
O(16)	111.0(6)	107.6(6)	106.9(6)	**1.557(12)**
		⟨P(4)–O⟩ = 1.539(12)		
		$P(5)O_4$ tetrahedron (sbu A)		
P(5)	O(19)	O(17)	O(18)	O(20)
O(19)	**1.512(13)**	2.534(16)	2.439(18)	2.553(16)
O(17)	113.5(5)	**1.518(12)**	2.448(17)	2.581(16)
O(18)	106.5(7)	106.8(7)	**1.532(13)**	2.490(16)
O(20)	110.9(6)	112.5(6)	106.0(7)	**1.586(11)**
		⟨P(5)–O⟩ = 1.537(12)		
		$HP(6)O_4$ tetrahedron (sbu B)		
P(6)	O(22)	O(24)	O(21)	O(23)
O(22)	**1.508(12)**	2.434(17)	2.574(16)	2.504(18)
O(24)	106.6(7)	**1.527(14)**	2.490(16)	2.524(20)
O(21)	115.2(6)	108.5(7)	**1.541(11)**	2.544(18)
O(23)	108.4(7)	108.7(8)	109.3(7)	**1.579(15)**
		⟨P(6)–O⟩ = 1.539(13)		
		$P(7)O_4$ tetrahedron (sbu B)		
P(7)	O(28)	O(26)	O(25)	O(27)
O(28)	**1.487(13)**	2.459(17)	2.501(16)	2.457(16)
O(26)	109.0(7)	**1.533(13)**	2.530(16)	2.572(16)
O(25)	111.4(7)	110.8(6)	**1.541(11)**	2.485(16)
O(27)	107.2(6)	112.2(7)	106.2(7)	**1.566(12)**
		⟨P(7)–O⟩ = 1.532(12)		

TABLE 4—*Continued*

$P(8)O_4$ tetrahedron (sbu A)

P(8)	O(32)	O(29)	O(31)	O(30)
O(32)	**1.523(13)**	2.507(17)	2.538(16)	2.482(17)
O(29)	110.8(7)	**1.523(13)**	2.453(17)	2.521(17)
O(31)	112.4(7)	106.8(7)	**1.532(12)**	2.471(16)
O(30)	108.5(7)	111.0(7)	107.3(7)	**1.535(13)**

⟨P(8)–O⟩ = 1.528(13)

$Ga(1)O_4$ tetrahedron (sbu A)

Ga(1)	O(11)	O(18)	O(7)	O(12)
O(11)	**1.835(13)**	3.050(19)	3.340(18)	2.841(18)
O(18)	111.6(6)	**1.853(13)**	3.063(17)	2.628(18)
O(7)	129.6(6)	111.3(5)	**1.856(11)**	2.944(16)
O(12)	100.5(6)	90.1(6)	104.7(5)	**1.861(13)**

⟨Ga(1)–O⟩ = 1.851(13)

$Ga(2)O_4$ tetrahedron (sbu A)

Ga(2)	O(1)	O(30)	O(9)	O(33)
O(1)	**1.778(12)**	3.22(16)	3.197(18)	2.718(19)
O(30)	128.2(6)	**1.803(11)**	2.825(18)	2.811(18)
O(9)	126.3(6)	103.0(6)	**1.805(13)**	2.867(16)
O(33)	92.3(5)	95.7(5)	98.2(6)	**1.984(14)**

Ga(2)–O(23), 2.400(15) and O(1)–O(23), 2.827(19); ⟨Ga(2)–O⟩ = 1.843(12)

$Ga(3)O_4$ tetrahedron (trigonal bipyramid with F(4)) (sbu C)

Ga(3)	O(10)	O(5)	O(6)	O(24)	F(4)
O(10)	**1.825(12)**	3.129(17)	3.181(17)	2.689(19)	2.744(12)
O(5)	117.1(5)	**1.842(12)**	2.555(16)	2.695(17)	2.702(15)
O(6)	119.8(6)	119.4(5)	**1.851(11)**	2.886(17)	2.690(14)
O(24)	93.6(6)	93.3(5)	102.0(5)	**1.863(13)**	4.067(15)
F(4)	85.2(2)	83.2(4)	82.5(4)	175.3(4)	**2.207(7)**

⟨Ga(3)–O⟩ = 1.845(12)

$Ga(4)O_4F$ trigonal bipyramid (sbu B)

Ga(4)	O(2)	O(27)	O(21)	O(15)	F(2)
O(2)	**1.827(10)**	2.572(10)	3.308(14)	2.768(15)	2.572(14)
O(27)	119.0(5)	**1.843(11)**	3.071(16)	2.635(16)	2.729(15)
O(21)	127.8(5)	112.2(5)	**1.857(10)**	2.793(16)	2.736(14)
O(15)	95.2(5)	88.9(5)	95.4(5)	**1.919(11)**	3.968(14)
F(2)	82.9(5)	88.8(4)	88.7(4)	175.8(5)	**2.051(9)**

⟨Ga(4)–(O, F)⟩ = 1.899(10)

$Ga(5)O_4F$ trigonal bipyramid (sbu B)

Ga(5)	O(14)	O(8)	O(25)	O(19)	F(3)
O(14)	**1.828(12)**	3.211(17)	3.367(16)	2.703(17)	2.652(15)
O(8)	122.2(5)	**1.840(13)**	2.915(16)	2.767(17)	2.724(16)
O(25)	132.8(5)	104.6(5)	**1.846(11)**	2.775(16)	2.669(15)
O(19)	90.5(5)	93.0(5)	93.1(5)	**1.974(13)**	3.991(15
F(3)	87.1(5)	89.7(5)	87.3(5)	177.1(5)	**2.018(9)**

⟨Ga(5)(–O, F)⟩ = 1.901(12)

$Ga(6)O_4F$ trigonal bipyramid (sbu A)

Ga(6)	O(20)	O(16)	O(31)	O(3)	F(1)
O(20)	**1.847(10)**	3.380(15)	3.044(16)	2.748(16)	2.677(14)
O(16)	131.9(5)	**1.853(11)**	3.164(17)	2.768(15)	2.612(14)
O(31)	110.3(5)	116.7(5)	**1.863(12)**	2.635(16)	2.745(15)
O(3)	94.7(5)	95.4(5)	89.2(5)	**1.889(11)**	3.927(14)
F(1)	86.9(5)	84.2(4)	89.3(4)	178.1(5)	**2.039(9)**

⟨Ga(6)–(O,F)⟩ = 1.898(11)

TABLE 4—*Continued*

Ga(7)O_5F octahedron (sbu A)

Ga(7)	O(4)	O(28)	O(32)	O(17)	F(1)	O(33)
O(4)	**1.917(13)**	2.735(17)	2.675(17)	2.897(17)	3.861(16)	2.790(16)
O(28)	90.8(5)	**1.925(12)**	3.859(17)	2.862(16)	2.859(15)	2.781(17)
O(32)	88.0(5)	117.2(5)	**1.936(12)**	2.669(16)	2.653(15)	2.741(17)
O(17)	97.4(5)	95.6(5)	87.1(5)	**1.939(10)**	2.691(14)	3.943(14)
F(1)	172.0(5)	95.0(4)	86.0(4)	87.5(4)	**1.953(9)**	2.664(15)
O(33)	90.3(5)	89.7(5)	87.8(5)	170.6(5)	84.3(4)	**2.018(10)**

⟨Ga(7)–(O,F)⟩ = 1.948(11)

Ga(8)O_4F_2 octahedron (sbu B)

Ga(8)	O(13)	O(29)	O(26)	O(22)	F(2)	F(3)
O(13)	**1.899(13)**	2.698(17)	2.721(17)	2.812(17)	3.871(16)	2.795(16)
O(29)	89.5(5)	**1.932(13)**	3.863(17)	2.851(17)	2.846(16)	2.754(16)
O(26)	90.5(5)	177.8(5)	**1.932(11)**	2.693(16)	2.673(15)	2.753(15)
O(22)	93.8(5)	94.4(5)	87.8(5)	**1.952(10)**	2.758(14)	3.946(14)
F(2)	175.5(5)	93.5(4)	86.3(5)	89.2(4)	**1.975(9)**	2.691(13)
F(3)	91.6(5)	88.9(5)	88.9(5)	173.7(4)	85.2(4)	**2.000(10)**

⟨Ga(8)–(O,F)⟩ = 1.948(11)

Template

1,6-diaminohexane (DAH) 1

N(1)–C(1)	1.47(3)	N(1)–C(1)–C(2)	108(3)
C(1)–C(2)	1.46(5)	C(1)–C(2)–C(3)	117(4)
C(2)–C(3)	1.47(6)	C(2)–C(3)–C(4)	124(4)
C(3)–C(4)	1.46(7)	C(3)–C(4)–C(5)	118(4)
C(4)–C(5)	1.47(5)	C(4)–C(5)–C(6)	112(3)
C(5)–C(6)	1.44(4)	C(5)–C(6)–N(2)	115(2)
C(6)–N(2)	1.50(3)		

1,6-diaminohexane (DAH) 2

N(3)–C(7)	1.54(6)	N(3)–C(7)–C(8)	94(4)
C(7)–C(8)	1.54(8)	C(7)–C(8)–C(9)	70(5)
C(8)–C(9)	1.55(10)	C(8)–C(9)–C(10)	140(7)
C(9)–C(10)	1.54(8)	C(9)–C(10)–C(11)	112(5)
C(10)–C(11)	1.56(8)	C(10)–C(11)–C(12)	103(5)
C(11)–C(12)	1.53(8)	C(11)–C(12)–N(4)	113(4)
C(12)–N(4)	1.55(5)		

Distances water molecules–framework

OW(1)–O(33)	2.94(2)	OW(2)–O(7)	2.70(2)
OW(1)–O(21)	3.00(2)	OW(2)–O(20)	2.73(2)
OW(1)–O(28)	3.10(2)	OW(2)–O(11)	2.76(2)
OW(1)–O(33)	3.24(2)	OW(2)–O(18)	2.86(2)
OW(3)–O(23)	2.74(4)	OW(3)–O(11)	3.30(4)
OW(3)–O(19)	3.06(3)	OW(3)–O(6)	3.45(4)

Distances template–framework[a]

N(1)–O(29)	2.95(2)	N(1)–O(28)	3.21(2)
N(1)–O(15)	3.05(2)	N(1)–O(3)	3.24(2)
N(1)–O(31)	3.15(2)	N(1)–O(27)	3.26(2)
N(2)–O(23)	3.97(3)	N(2)–O(9)	3.24(3)
N(2)–O(19)	2.99(3)	N(2)–O(18)	3.29(3)
N(2)–O(12)	3.11(3)	N(2)–O(5)	3.30(3)
N(3)–F(1)	2.92(2)	N(3)–O(22)	3.06(2)
N(3)–O(33)	2.95(2)	N(3)–O(26)	3.08(2)
N(3)–O(28)	2.98(2)	N(3)–O(22)	3.12(2)
N(4)–F(2)	2.84(2)	N(4)–O(17)	3.00(2)
N(4)–F(3)	2.88(2)	N(4)–O(7)	3.27(2)
N(4)–O(32)	2.93(2)	N(4)–O(18)	3.32(2)

Distance scheme of F(4) (trapped in the octameric unit sbu C)

F(4)–Ga(3)	**2.207(7)**	**F(4)–Ga(1)**	**2.792(9)**
F(4)–P(2)	**2.793(10)**	**F(4)–P(3)**	**2.899(10)**
F(4)–O(6)	2.690(14)	F(4)–O(7)	2.798(11)
F(4)–O(5)	2.702(15)	F(4)–O(12)	2.892(17)
F(4)–O(10)	2.744(12)	F(4)–O(11)	2.933(18)

[a] All distances carbon–framework are greater than 3.40 Å.

TABLE 5
Valence Bond Analysis of $Ga_{16}(PO_4)_{14}(HPO_4)_2(OH)_2F_7$, 4 H_3N–$(CH_2)_6NH_3$, 6H_2O (ULM-5)

	Ga(1)	Ga(2)	Ga(3)	Ga(4)	Ga(5)	Ga(6)	Ga(7)	Ga(8)	P(1)	P(2)	P(3)	P(4)	P(5)	P(6)	P(7)	P(8)	Σ	Charge
O(1)		0.878							1.170								2.048	2
O(2)				0.769					1.199								1.968	2
O(3)						0.651			1.255								1.906	2
O(4)							0.603		1.361								1.964	2
O(5)			0.739							1.225							1.964	2
O(6)			0.721							1.251							1.972	2
O(7)	0.711									1.335							2.046	2
O(8)					0.743					1.339							2.082	2
O(9)		0.817									1.275						2.092	2
O(10)			0.774								1.221						1.995	2
O(11)	0.753										1.307						2.060	2
O(12)	0.702										1.202						1.904	2
O(13)								0.633				1.251					1.884	2
O(14)					0.767							1.221					1.988	2
O(15)				0.600								1.293					1.893	2
O(16)						0.717						1.176					1.893	2
O(17)							0.568						1.307				1.875	2
O(18)	0.717												1.258				1.975	2
O(19)					0.517								1.328				1.845	2
O(20)						0.729							1.087				1.816	2
O(21)				0.709										1.228			1.937	2
O(22)								0.549						1.343			1.892	2
O(23)														1.108			1.108	2
O(24)			0.698											1.275			1.973	2
O(25)					0.731										1.228		1.959	2
O(26)								0.579							1.255		1.934	2
O(27)				0.737											1.148		1.885	2
O(28)							0.590								1.400		1.990	2
O(29)								0.579								1.289	1.868	2
O(30)		0.821														1.248	2.069	2
O(31)						0.698										1.258	1.956	2
O(32)							0.573									1.289	1.862	2
O(33)		0.503					0.459										0.962	2
F(1)						0.322	0.407										0.730	1
F(2)				0.313				0.383									0.696	1
F(3)					0.341			0.358									0.699	1
F(4)			0.205														0.410	1
Σ	2.883	3.019	3.137	3.128	3.099	3.117	3.200	3.081	4.985	5.150	5.005	4.945	4.980	4.954	5.031	5.084	—	—
Charge	3	3	3	3	3	3	3	3	5	5	5	5	5	5	5	5	—	—

Note. The results refer to the equations $s = \exp[R_0 - d)/0.37]$ (20) with R_0 = 1.703, 1.620, and 1.617 for Ga(O), Ga(F), and P, respectively.

the O(23)H hydroxy group being terminal. The association of the three types of phosphorus tetrahedra with the previously defined trimers leads to the basic asymmetric unit $[Ga_3(HPO_4)(PO_4)_2F_2]^-$.

Octameric Unit

Sbu C (Fig. 4c) is completely different from the two others and is closely related to the cage existing in Linde Å (7), cloverite (8), and in octadecasil (9). At a first approximation, it can be considered as a cube of corner shared tetrahedra, alternatively occupied by P and Ga, which encapsulate F^- ions. In such a hypothesis, fluorine is at the center of a cubooctahedron of oxygens (Fig. 5), distorted owing to the size of F^-. However, when the distances around fluorine are examined (Table 4) it clearly appears that F^- is off-center within the cube and approaches Ga(3) at 2.207 Å (i.e. 0.21 valence units in the bond valence analysis of Table 5), while the other distances to cations are larger than 2.80 Å (i.e., 0.02 v.u.). This means that F^- tends to participate to the coordination polyhedron of Ga(3), transforming it into a trigonal bipyramid. The comparison (Fig. 6 and Table 4) of the two polyhedra around Ga(1) and Ga(3) of the cage clearly show that, while $Ga(1)O_4$ remains a tetrahedron, with a distance of 0.556 Å between Ga and the basal plane of the tetrahe-

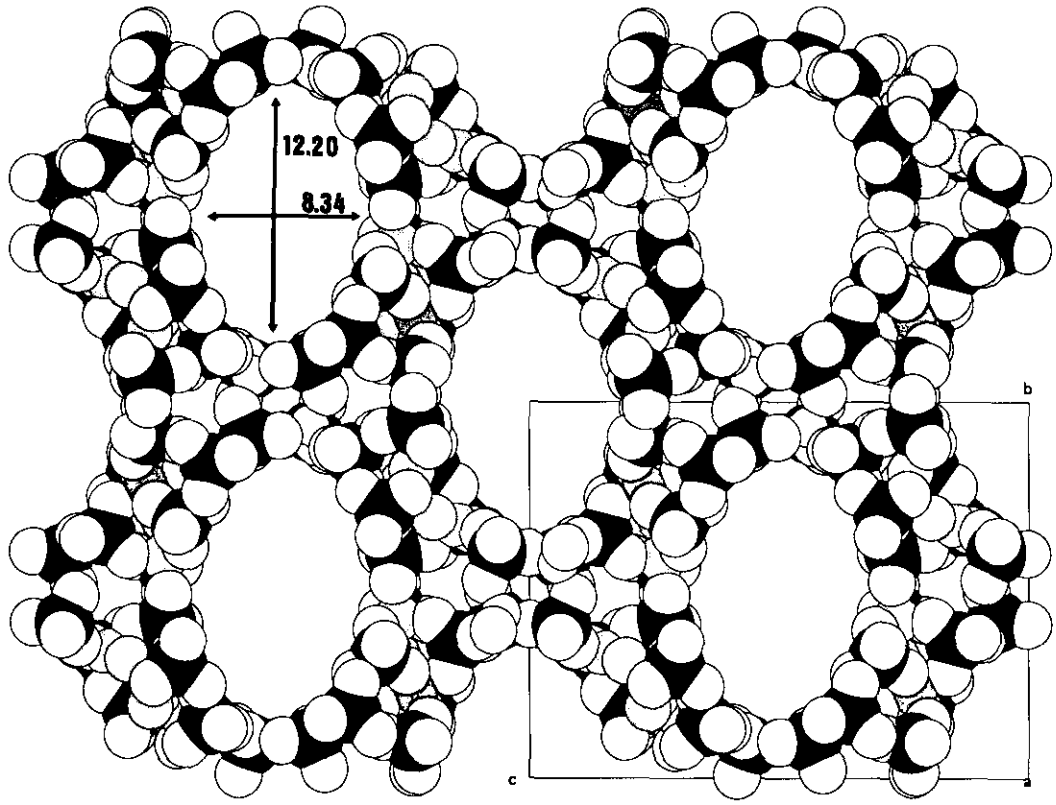

FIG. 2. Space filling representation of the (100) projection of the structure of ULM-5, with the dimensions of the free aperture of the tunnel.

dron, the existence of a Ga(3) O_4F bipyramid is obvious, the distance between Ga and the basal plane being reduced to 0.202 Å. Another fact corrborates this tendency of Ga(3): if one considers the *M*–O bonds (*M* = P, Ga) diametrally opposite to *M*–F ones, these M–O bonds are always the shortest of the considered polyhedron, except for Ga(3), where it is the longest. This allows us to consider the situation of the encapsulated fluorine as different from that existing in Linde A (7), cloverite (8), and octadecasil (9), where all the distances are equal. Here, F^- is not equally distributed between the polyhedra, but belongs to one of them. A further solid-state NMR study, currently in progress, will show the difference between the two situations.

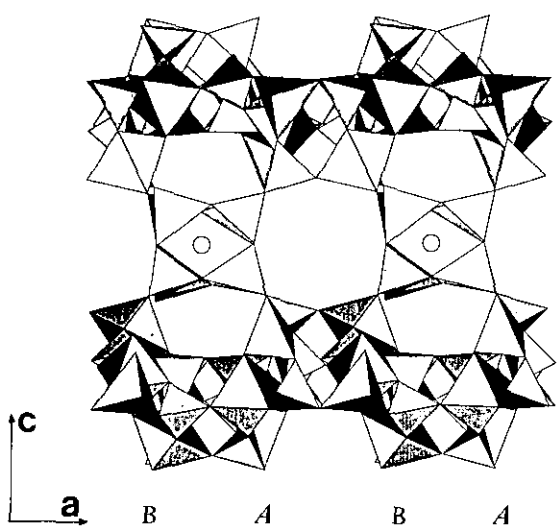

FIG. 3. [010] projection showing the eight-membered ring channels.

The three-dimensional network is built up of the linkage of these units and occurs via corners occupied by oxygens shared by both gallium and phosphorus atoms, except for P(6), which has a terminal OH. The connection of the three different asymmetric units is shown in Fig. 7. Cross-linked 16- and 8-membered channels are then formed along [100] and [010], respectively, with a strict Ga–P alternation for the polyhedra forming the channel. As mentioned at the beginning of this description, the association of the three different sbu leaves 8-membered ring channels along [010], but two types of channels along [100]: 6-membered ones within which the water molecules of the structure are located and very large tunnels, limited by 16 polyhedra. If the MCM-41 (21) family is excepted, this pecularity situates ULM-5 at the third rank for the largest pores evidenced up to now, behind 20-membered rings of cloverite (8) and JDF-20 (22), and the 18-membered rings of VPI-5 (23).

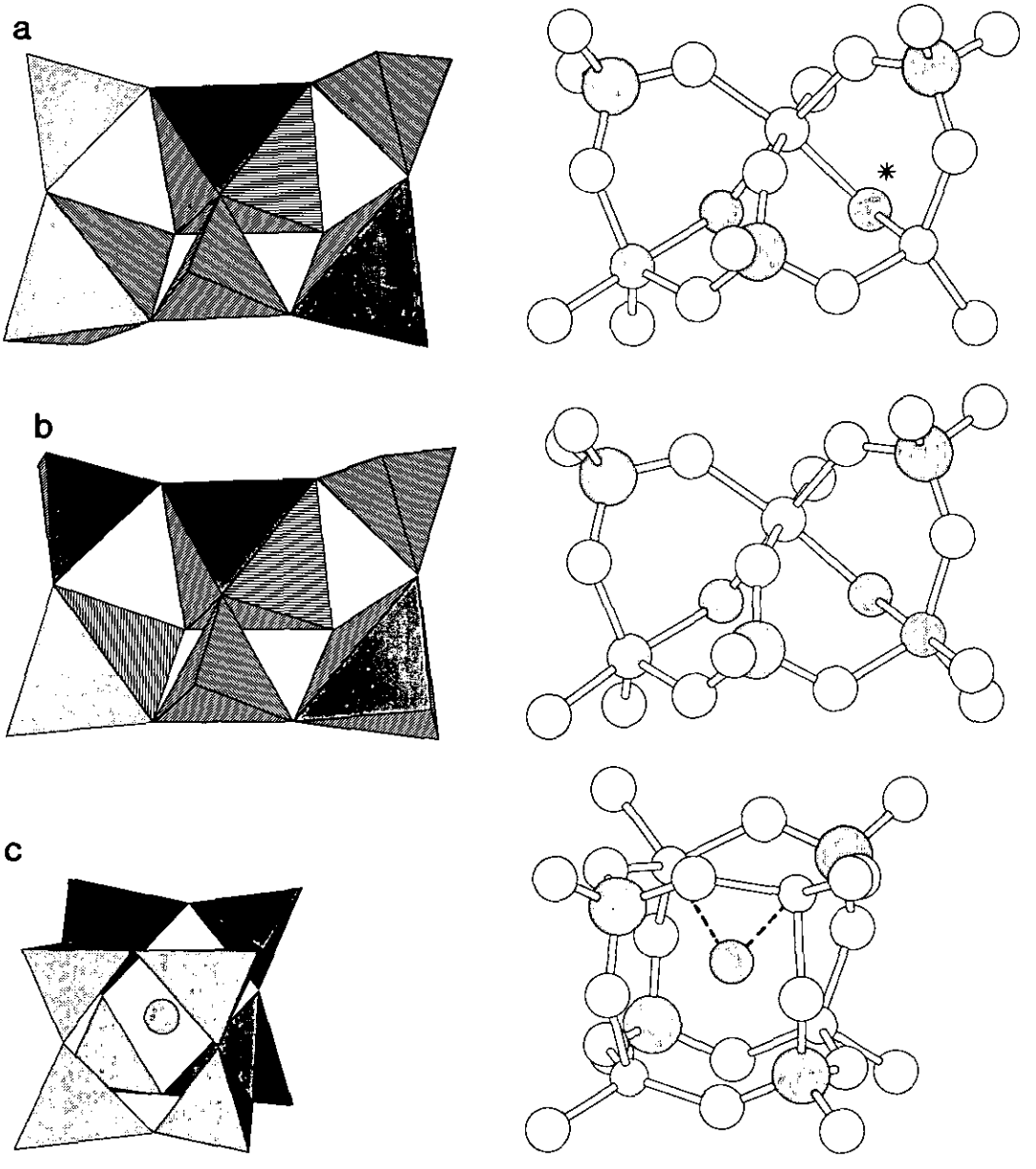

FIG. 4. Perspective view of (a) sbu A, (b) sbu B and (c) sbu C in both polyhedral and ball and stick representation. Gray spheres, P; large open circles, O; small open circles, Ga; small gray circles, F except in (a), where the asterisk on the gallium tetrahedron corresponds to OH.

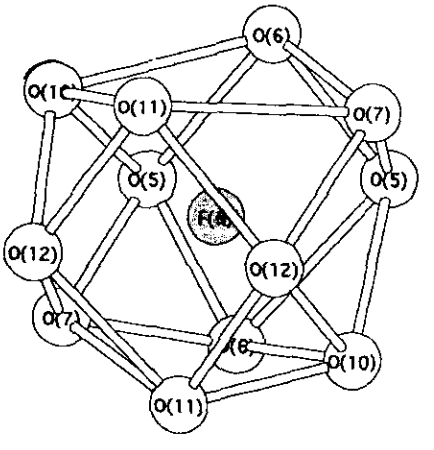

FIG. 5. Perspective view of the distorted cubooctahedron of oxygens around the encapsulated F in ULM-5.

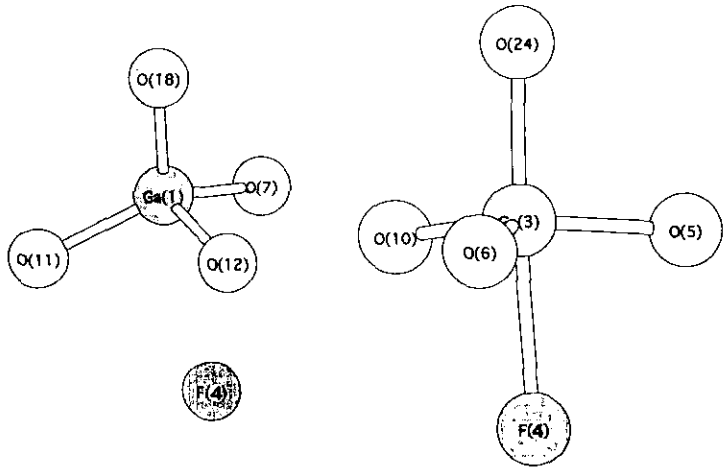

FIG. 6. Perspective view of the Ga(1) and Ga(3) polyhedra showing the influence of the proximity of fluroine on the change of coordination from tetrahedron to trigonal bipyramid for Ga(3).

The amines are located within the largest pores and clearly act, via strong hydrogen bonds (deduced from the very short distances between nitrogens and the oxygens of the framework), as bidentate templates in the tunnels. Their curved topology is represented on Figs. 8a and 8b. Unfortunately, we were not able to localize the hydrogen atoms of the organic molecule to describe quantitatively the hydrogen bond scheme in this new structure type. However, the negative charge of the framework obliges us to consider that the amines are diprotonated to satisfy the electroneutrality of the compound.

Finally, the TGA curve of ULM-5 (Fig. 9) shows that the water molecules first evolve the structure between 300 and 600 K (weight loss, calc, 4.3%; exp, 4.4%). The amine leaves the structure after, probably in a complicated way. The structure is maintained up to 780 K and destroyed above this temperature.

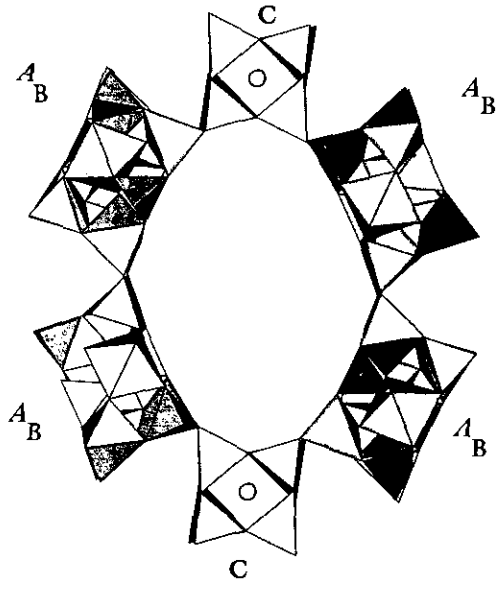

FIG. 7. The connection between sbu A, B, and C.

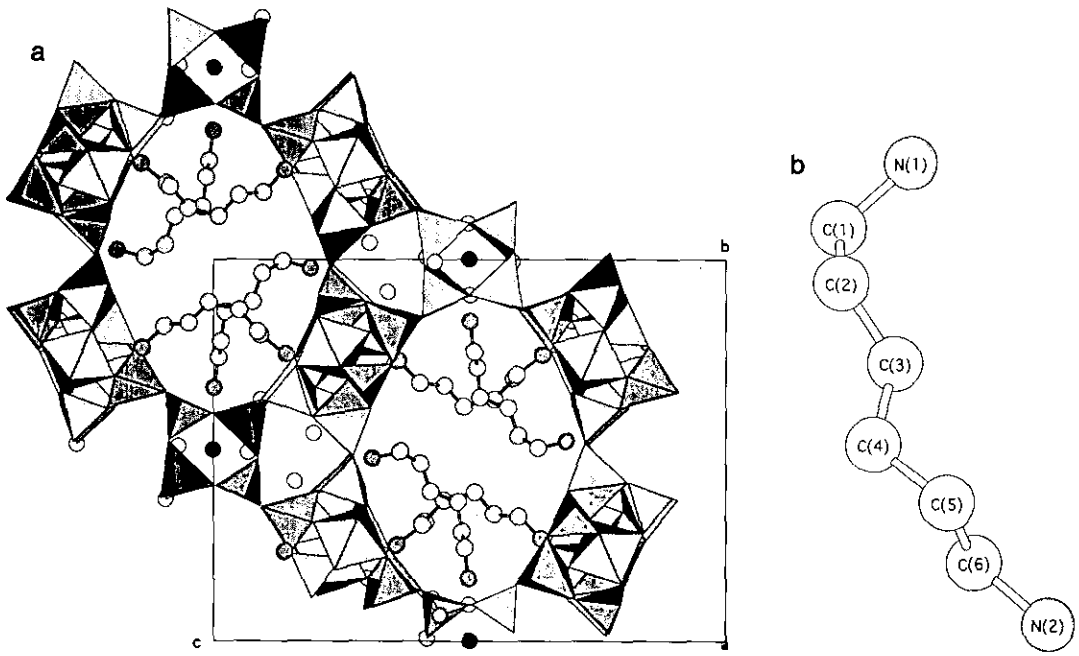

FIG. 8. Location of the amines within the tunnels (a) and conformation of one amine (b).

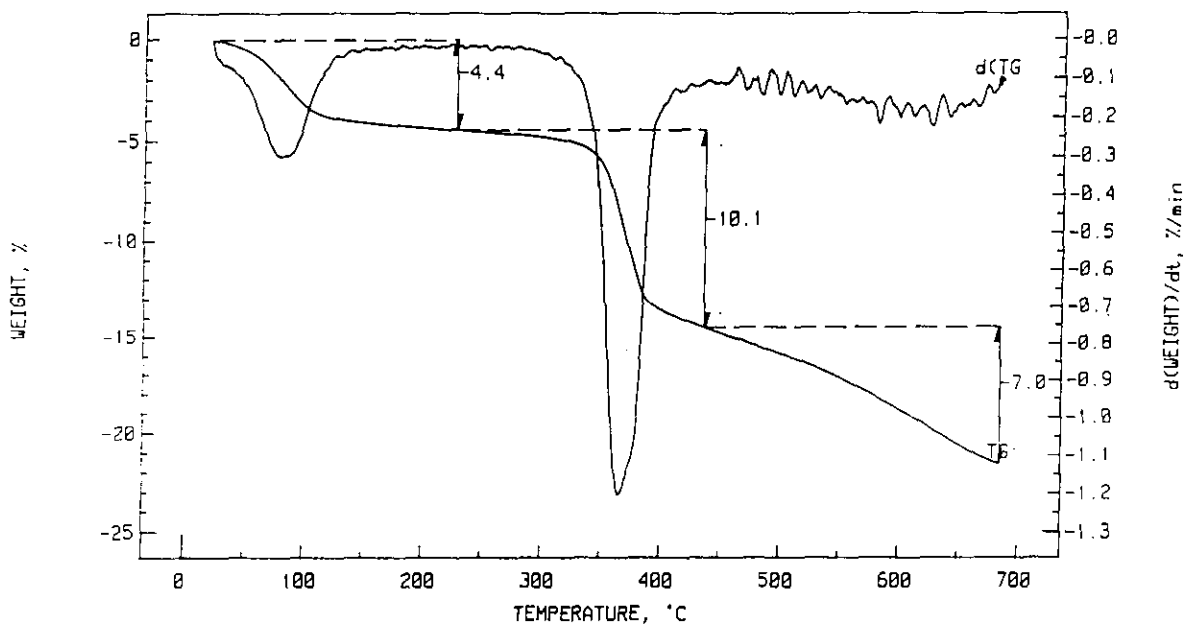

FIG. 9. TGA curve of ULM-5.

ACKNOWLEDGMENTS

The authors are very indebted to professors M. Leblanc and R. Retoux (Université du Maine) for their help during the X-ray data collection and to Dr. J. Durand (LPCM Montpellier), who realized the SHG measurements.

REFERENCES

1. S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Cannan and E. M. Flanigen, *J. Am. Chem. Soc.* **104,** 1146 (1982).
2. E. M. Flanigen, R. L. Patton, and S. T. Wilson, *Stud. Surf. Sci.Catal.* **37,** 13 (1988).
3. T. E. Gier and G. D. Stucky, *Nature* 349, 508 (1991).
4. R. Xu, J. Chen, and C. Feng, *Stud. Surf. Sci. Catal.* **60,** 63 (1991).
5. J. L. Guth, H. Kessler, and R. Wey, *Stud. Surf. Sci. Catal.* **28,** 121 (1986).
6. J. L. Guth, H. Kessler, J. M. Higel, J. M. Lamblin, J. Patarin, A. Seive, J. M. Chezeau, and R. Wey, *ACS Symp. Ser.* **398,** 176 (1989).
7. H. Kessler, *MRS Symp. Ser.* **233,** 47 (1991).
8. M. Estermann, L. B. McCusker, C. Baerlocher, A. Merrouche, and H. Kessler, *Nature* **352,** 320 (1991).

9. P. Caullet, J. L. Guth, J. Hazm, J. M. Lamblin, and H. Gies, *Eur. J. Solid State Inorg. Chem.* **28,** 345 (1991).
10. D. Riou, T. Loiseau, and G. Férey, *J. Solid State Chem.* **102,** 4 (1992).
11. G. Férey, T. Loiseau, P. Lacorre, and F. Taulelle, *J. Solid State Chem.* **105,** 179 (1993).
12. T. Loiseau and G. Férey, *J. Chem. Soc. Chem. Commun.* 1197 (1992).
13. T. Loiseau and G. Férey, *Eur. J. Solid State Inorg. Chem.* **30,** 369 (1993).
14. T. Loiseau, R. Retoux, P. Lacorre, and G. Férey, *J. Solid State Chem.* **111,** 427 (1994).
15. T. Loiseau, D. Riou, and G. Férey, *Eur. J. Solid State Inorg. Chem.*, in press.
16. J. Chen, L. Li, G. Yang, and R. Xu, *J. Chem. Soc. Chem. Commun.* 1217 (1989).
17. "International Tables for X-Ray Crystallography." Vol. IV Kynoch Press, Birmingham, 1974. [Present distributor: Kluwer Academic, Dortrecht]
18. G. M. Sheldrick, *in* "Crystallographic Computing," 3, (G. M. Sheldrick, C. Krüger, and R. Goddard, Eds.), p. 175. Oxford Univ. Press, London/New York, 1985.
19. G. M. Sheldrick, "SHELX-76, a Program for Crystal Structure Determination. University of Cambridge, 1976.
20. N. Brese and M. O'Keeffe, *Acta Crystallogr. Sect. B* **47,** 192 (1991).
21. C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, and J. S. Beck, *Nature* **359,** 710 (1992).
22. Q. Huo, R. Xu, S. Li, Z. Ma, J. M. Thomas, R. H. Jones, and A. M. Chippindale, *J. Chem. Soc. Chem. Comm.* 1197 (1992).
23. M. E. Davis, C. Saldarriaga, C. Montes, J. Garces, and C. Crowder, *Nature* **331,** 698 (1988).