

Synthesis and Characterization of the New Hydroxygallophosphate Mu-18 with a Framework Topology Closely Related to That of the Hydroxyaluminophosphate AlPO₄-EN3

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A new three-dimensional microporous gallophosphate, named Mu-18, was obtained by hydrothermal synthesis in the presence of 1-methylpiperazine as an organic template. Its structure was determined by single-crystal X-ray diffraction. The symmetry is orthorhombic, space group *Aba2* (No. 41), with $a = 18.035(18)$ Å, $b = 10.513(11)$ Å, and $c = 14.293(11)$ Å. The framework, closely related to that of the aluminophosphate AlPO₄-EN3, displays a one-dimensional channel system delimited by eight-membered ring openings. This new hydroxygallophosphate was characterized by XRD, SEM, elemental and thermal analyses, and ¹³C and ³¹P solid-state NMR spectroscopy.

1. Introduction

In 1982 Union Carbide Corp. developed a new generation of molecular sieves, AlPO₄-*n*, based on an aluminophosphate framework.¹ Synthesis of open framework phosphate is still, after nearly 20 years of effort, a main subject of research in microporous materials.² In this family of materials, aluminophosphates and gallophosphates have given a wide range of new structures. Recently, a new structure type (code AEN) has been proposed by the structure commission of the International Zeolite Association. The related material is the aluminophosphate AlPO₄-EN3.³ Its three-dimensional framework results in a stacking of 4 × 6 × 8 layers. As mentioned in Table 1, a large number of isotypic materials are reported in the literature. It was the case for the aluminophosphates: AlPO₄-53(A),⁴ JDF-2,⁵ MCS-1,⁶ UiO-12-as,⁷ and Mu-10⁸ but also for the gallophosphate GaPO₄-M2.^{9,10} With the exception of

Table 1. Unit Cell Parameters and Space Group for AlPO₄-EN3 and Its Related Materials

name	space group	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (deg)	ref
AlPO ₄ -EN3	<i>P2₁2₁2₁</i>	10.292	13.636	17.344	90	3
JDF-2	<i>Pcab</i>	10.281	13.844	17.064	90	5
MCS-1	N.A. ^a	17.45	10.31	13.63	90	6
GaPO ₄ -M2	<i>Pbca</i>	10.257	16.941	14.130	90	9, 10
Mu-10	<i>Pbca</i>	13.678	10.318	17.357	90	8
AlPO ₄ -53(A)	<i>P2₁2₁2₁</i>	10.321	13.631	17.454	90	4
UiO-12-as	<i>Pbca</i>	13.579	13.351	17.466	90	7
AlPO ₄ -21	<i>P2₁/a</i>	10.331	17.524	8.676	123.37	11, 12
Mu-18	<i>Aba2</i>	18.035	10.513	14.293	90	this work

^a N.A.: not available.

AlPO₄-21,^{11,12} the three-dimensional arrangement of the layers in all of these materials is very similar.

The present paper reports the synthesis, the characterization, and the structure determination of a novel three-dimensional hydroxygallophosphate [(C₅H₁₄N₂)₄Ga₂₄P₂₄O₉₆(OH)₈]·4H₂O named Mu-18 (Mu standing for Mulhouse). The structure of Mu-18 can also be described as a stacking of 4 × 6 × 8 layers but the connectivity scheme of these layers is different from that observed in AlPO₄-EN3. The structural relationship between these two materials is discussed.

2. Experimental Section

2.1. Synthesis. The reactants were 1-methylpiperazine (MPIP) (Aldrich, 99%) and phosphoric acid (Labosi, 85%). Two different gallium sources were used: the former was an amorphous gallium oxide hydroxide that was prepared by heating a gallium nitrate solution (Rhône-Poulenc) at 250 °C for 24 h and the latter a gallium oxide β-Ga₂O₃ (ICDD 41-1103) obtained after calcination of the former at 1000 °C for 6 h.

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Table 2. Conditions and XRD Results of the Synthesis of the Hydroxygallophosphate Mu-18 from a Gel Composition of 2.6:160:2:2(or 1) H₃PO₄:H₂O:MPIP:GaOOH(or β-Ga₂O₃)

sample	gallium source	crystallization time (days)	temp (°C)	XRD results ^a
A	β-Ga ₂ O ₃	6	180	Mu-18 + phase Z ^b
B	GaOOH	6	180	GaOOH
C	β-Ga ₂ O ₃	4	180	β-Ga₂O₃ + phase Z + ε Mu-18
D	β-Ga ₂ O ₃	2.5	180	β-Ga ₂ O ₃
E	β-Ga ₂ O ₃	6	150	β-Ga ₂ O ₃

^a Boldface type, major phase; ε, traces. ^b Nonidentified phase.

Mu-18 was never obtained as a pure phase. It crystallized with an unidentified phase (phase Z), which can be separated by a repeated rapid sedimentation process. The synthesis was performed by hydrothermal treatment at 180 °C of a mixture having the following molar composition: 1:1.3:2:160 β-Ga₂O₃:P₂O₅:MPIP:H₂O.

As an example, for sample A (Table 2), the gel was prepared by adding under stirring H₃PO₄ (0.39 g) to the mixture of the gallium source (0.28 g) and water (3.5 g). After a homogenization time of 10 min, the amine (0.25 g) was introduced. The pH value was close to 5.5. The resulting gel was mixed at room temperature for 1 h and transferred to a 20-mL PTFE-lined stainless steel autoclave. The crystallization was carried out at 180 °C under static conditions. After 6 days of heating, the product was recovered, washed with distilled water, and dried at 60 °C overnight.

2.2. Characterization. The powder XRD patterns were obtained with Cu Kα₁ radiation on a STOE STADI-P diffractometer equipped with a curved germanium (111) primary monochromator and a linear position-sensitive detector. High-temperature X-ray diffraction was performed using a variable temperature photographic chamber (Huber, model 631) attached to the same X-ray generator (Cu Kα₁ radiation) in which the sample was kept in a flow of dry air. To obtain the XRD pattern of phase Y (§ 3.2), an additional experiment was performed on Mu-18. The as-synthesized sample was loaded in a quartz capillary tube and heated at 350 °C for 3 h. The tube was then sealed at this temperature to avoid any rehydration and cooled to room temperature before XRD analysis.

The morphology and size of the crystals were determined by scanning electron microscopy using a Philips XL30 microscope.

Thermogravimetric (TGA) and differential thermal analyses (DTA) were performed under air on a Setaram Labsys therm analyzer with a heating rate of 5 °C/min until 850 °C. At this final temperature, a gray residue is obtained. Calcination at 1100 °C is necessary to obtain a white product and therefore the total amount of the organic template.

The amounts of Ga, P, and O in the hydroxygallophosphate Mu-18 were determined by scanning electron microprobe analysis on a Castaing type (CAMEBAX) electron microscope.

The ¹H liquid NMR spectrum was recorded on a Bruker AC 250 spectrometer. It allowed determination of the amount of template occluded in the structure.¹³ The sample was prepared by dissolution of a precise amount of Mu-18, 1,4-dioxane being used as an internal reference.

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

For the structure determination, a crystal with dimensions 90 × 80 × 50 μm³ was selected from the batch and mounted on a Picker 4-circle STOE diffractometer. Then, 1015 reflections were recorded from 4.9° up to 50° θ (using Cu Kα₁ radiation) in omega scan mode, of which 1007 fulfilled the condition $I > 2\sigma(I)$. A summary of the experimental and

Table 3. Recording Conditions of the MAS and CP MAS NMR Spectra

	¹³ C		³¹ P
	CP MAS	MAS	CP MAS
chemical shift standard	TMS	85% H ₃ PO ₄	85% H ₃ PO ₄
frequency (MHz)	75.47	161.98	161.98
pulse width (μs)	3.7	3.5	4.0
flip angle	π/2	π/2	π/2
contact time (ms)	1		0.1 and 1
recycle time (s)	8	30	5
spinning rate (Hz)	5000	8000	8000
number of scans	624	8	32

Table 4. Summary of the Experimental and Crystallographic Data of the Hydroxygallophosphate Mu-18

chemical formula	[(C ₅ H ₁₄ N ₂)Ga ₆ P ₆ O ₂₄ (OH) ₂]·H ₂ O
crystal system	orthorhombic
crystal space group	<i>Ab</i> a2
<i>a</i> (Å)	18.035(18)
<i>b</i> (Å)	10.513(11)
<i>c</i> (Å)	14.293(11)
<i>M</i> (g mol ⁻¹)	4569.5
density (calculated)	2.80
cell volume (Å ³)	2710(4)
<i>Z</i> (formula units/cell)	4
crystal size (μm)	90 × 80 × 50
diffractometer	PICKER 4-circle STOE
radiation source and wavelength (Å)	Cu Kα, 1.54178
absorption coefficient (mm ⁻¹)	11.134
absorption correction	not applied
<i>F</i> (000)	2208
data collection temperature (K)	293(2)
θ range (deg)	4.90 to 50.00
(<i>hkl</i>)min., (<i>hkl</i>)max.	0 0 -14, 17 10 7
independent reflections	1015
observed reflections	1007
data/restraints/parameters	1015/99/203
structure solution program	SHELXS-86 ¹⁴
structure refinement program	SHELXL-93 ¹⁵
residuals (observed data)	<i>R</i> ₁ = 0.0364; w <i>R</i> ₂ = 0.1041
[<i>I</i> > 2σ(<i>I</i>)]	
residuals (all data)	<i>R</i> ₁ = 0.0366; w <i>R</i> ₂ = 0.1045
goodness-of-fit (all data)	1.094
largest diff. peak and hole (e/Å ³)	1.627 and -0.859

Table 5. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å²) for the Hydroxygallophosphate Mu-18: Standard Deviations in Brackets

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Ga(1)	0.7028(1)	0.8079(1)	0.6485(1)	0.012 (1)
Ga(2)	0.6850(1)	0.6245(1)	0.3747(1)	0.015(1)
Ga(3)	0.6093(1)	0.8536(1)	0.0575(1)	0.012(1)
P(1)	0.5751(2)	0.6424(3)	0.5444(3)	0.016(1)
P(2)	0.7042(2)	0.8395(3)	0.8747(3)	0.014(1)
P(3)	0.6693(2)	0.6134(3)	0.1598(3)	0.013(1)
O(1)	0.7496(5)	0.6424(6)	0.1360(7)	0.013(2)
O(2)	0.6525(5)	0.6624(6)	0.2579(8)	0.020(2)
O(3)	0.7915(5)	0.8881(8)	0.6106(7)	0.016(2)
O(4)	0.6328(5)	0.8392(8)	0.9300(7)	0.020(2)
O(5)	0.6026(5)	0.6193(1)	0.4447(8)	0.023(2)
O(6)	0.6183(4)	0.7513(8)	0.5884(7)	0.019(2)
O(7)	0.6156(4)	0.6854(8)	0.0947(7)	0.015(2)
O(8)	0.7614(5)	0.7562(8)	0.9239(7)	0.023(2)
O(9)	0.6884(5)	0.7862(7)	0.7782(8)	0.023(2)
O(10)	0.7361(4)	0.9743(7)	0.8716(7)	0.018(2)
O(11)	0.5859(4)	1.0186(7)	0.0991(7)	0.015(2)
O(12)	0.5057(5)	0.8187(7)	0.0379(7)	0.018(2)
O(13)	0.6556(4)	0.9719(7)	0.6511(7)	0.018(2)
O(W)	0.4974(16)	0.2787(26)	0.7740(26)	0.057(8)
N(1)	0.5081(14)	0.6298(29)	0.8495(46)	0.173(13)
N(2)	0.4939(15)	0.3856(31)	0.9167(45)	0.176(13)
C(1)	0.4378(10)	0.5807(21)	0.8604(31)	0.173(13)
C(2)	0.4287(10)	0.4429(20)	0.8831(29)	0.173(13)
C(3)	0.5184(27)	0.7308(86)	0.7812(79)	0.173(13)

crystallographic data is reported in Table 4. The structure was solved by direct methods using SHELXS-86¹⁴ and refined using SHELXL-93.¹⁵ The refinement converged to *R*₁ = 0.0364 (*R*₁ = Σ||*F*_o - |*F*_c||/Σ|*F*_o|) and w*R*₂ = 0.1041 (*R*₂ = {Σw(*F*_o² - *F*_c²)²}/

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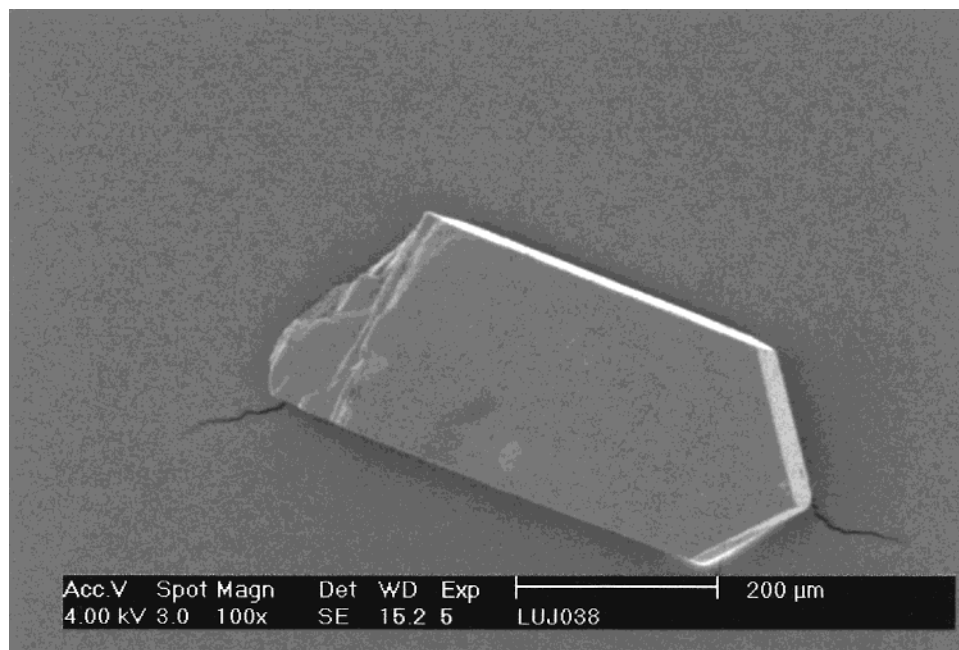


Figure 1. Scanning electron micrograph of a crystal of the hydroxygallophosphate Mu-18.

Table 6. Selected Bond Lengths for the Hydroxygallophosphate Mu-18^a

atoms	distances (Å)	atoms	distances (Å)
Ga(1)–O(6)	1.849(8)	Ga(3)–O(7)	1.849(8)
Ga(1)–O(9)	1.885(11)	Ga(3)–O(11)	1.882(8)
Ga(1)–O(3)	1.887(9)	Ga(3)–O(4)#1	1.877(11)
Ga(1)–O(13)	1.924(8)	Ga(3)–O(12)	1.924(9)
Ga(1)–O(1)#4	1.948(7)	Ga(3)–O(3)#2	1.978(9)
Ga(2)–O(5)	1.7925(10)	P(1)–O(12)#6	1.517(9)
Ga(2)–O(8)#2	1.829(9)	P(1)–O(11)#5	1.530(9)
Ga(2)–O(2)	1.813(11)	P(1)–O(6)	1.520(9)
Ga(2)–O(10)#3	1.829(8)	P(1)–O(5)	1.528(12)
P(2)–O(4)	1.511(11)	P(3)–O(13)#3	1.513(9)
P(2)–O(8)	1.524(10)	P(3)–O(2)	1.524(12)
P(2)–O(10)	1.531(8)	P(3)–O(1)	1.520(10)
P(2)–O(9)	1.517(12)	P(3)–O(7)	1.542(10)
N(1)–C(1)	1.38(2)	N(2)–C(1)#7	1.51(3)
N(1)–C(2)#7	1.45(2)	N(2)–C(2)	1.41(3)
N(1)–C(3)	1.45(3)		
C(1)–C(2)	1.494(11)		

^a Symmetry transformation used to generate equivalent atoms. #1: $x, y, z - 1$; #2: $-x + 3/2, y, z - 1/2$; #3: $x, y - 1/2, z - 1/2$; #4: $-x + 3/2, y, z + 1/2$; #5: $x, y - 1/2, z + 1/2$; #6: $-x + 1, -y + 3/2, z + 1/2$; #7: $-x + 1, -y + 1, z$.

$\sum w(F_o^2)^{1/2}$ for 1007 reflections ($I > 2\sigma(I)$). The atomic coordinates and isotropic displacement parameters are given in Table 5. Selected bond lengths and angles are reported in Tables 6 and 7, respectively.

3. Results and Discussion

3.1. Synthesis and Crystal Morphology. The most characteristic synthesis results are summarized in Table 2. Different gallium sources were tested. Mu-18 crystallizes only with β -Ga₂O₃. Under the same experimental conditions, when GaOOH is introduced in the starting mixture, no reaction occurs (compare samples A and B). From samples A, C, and D, it appears that the amount of β -Ga₂O₃ decreases when the crystallization time increases from 2.5 to 6 days. In the same period, the amount of Mu-18 increases and, after 6 days, this phase

Table 7. Selected Angles of the Hydroxygallophosphate Mu-18^a

atoms	angle (deg)	atoms	angle (deg)
O(6)–Ga(1)–O(9)	107.7(4)	O(7)–Ga(3)–O(11)	143.5(4)
O(6)–Ga(1)–O(3)	135.1(5)	O(7)–Ga(3)–O(4)#1	100.8(4)
O(6)–Ga(1)–O(13)	86.1(4)	O(7)–Ga(3)–O(12)	85.4(4)
O(6)–Ga(1)–O(1)#4	91.9(4)	O(7)–Ga(3)–O(3)#2	90.5(4)
O(9)–Ga(1)–O(3)	116.9(4)	O(11)–Ga(3)–O(4)#1	115.6(4)
O(9)–Ga(1)–O(13)	91.6(4)	O(11)–Ga(3)–O(12)	90.2(3)
O(9)–Ga(1)–O(1)#4	92.5(4)	O(11)–Ga(3)–O(3)#2	85.0(3)
O(3)–Ga(1)–O(13)	88.9(4)	O(4) #1–Ga(3)–O(12)	93.6(4)
O(3)–Ga(1)–O(1)#4	90.0(4)	O(4) #1–Ga(3)–O(3)#2	100.5(4)
O(13)–Ga(1)–O(1)#4	175.8(5)	O(12)–Ga(3)–O(3)#2	165.8(4)
O(5)–Ga(2)–O(8)#2	104.3(4)	O(12)#6–P(1)–O(11)#5	112.5(5)
O(5)–Ga(2)–O(2)	104.6(5)	O(12)#6–P(1)–O(6)	108.3(5)
O(5)–Ga(2)–O(10)#3	113.9(4)	O(12)#6–P(1)–O(5)	107.2(6)
O(8)#2–Ga(2)–O(2)	111.1(4)	O(11)#5–P(1)–O(6)	111.4(5)
O(8)#2–Ga(2)–O(10)#3	113.3(4)	O(11)#5–P(1)–O(5)	107.5(5)
O(2)–Ga(2)–O(10)#3	109.1(4)	O(6)–P(1)–O(5)	109.8(5)
O(4)–P(2)–O(8)	109.5(6)	O(13)#3–P(3)–O(2)	111.9(5)
O(4)–P(2)–O(10)	109.8(5)	O(13)#3–P(3)–O(1)	109.5(5)
O(4)–P(2)–O(9)	108.4(6)	O(13)#3–P(3)–O(7)	109.3(5)
O(8)–P(2)–O(10)	106.9(5)	O(2)–P(3)–O(1)	109.2(5)
O(8)–P(2)–O(9)	109.5(5)	O(2)–P(3)–O(7)	105.4(5)
O(10)–P(2)–O(9)	112.7(6)	O(1)–P(3)–O(7)	111.4(5)

^a Symmetry transformation used to generate equivalent atoms. #1: $x, y, z - 1$; #2: $-x + 3/2, y, z - 1/2$; #3: $x, y - 1/2, z - 1/2$; #4: $-x + 3/2, y, z + 1/2$; #5: $x, y - 1/2, z + 1/2$; #6: $-x + 1, -y + 3/2, z + 1/2$.

is obtained as a major phase and the unidentified phase Z cocrystallizes as a minor phase (sample A). For longer crystallization times (10 days) no evolution of the mixture can be noticed. For 2.5 days of synthesis (sample D) or at a lower temperature ($T = 150$ °C, sample E), the gallium source is still the only crystallized phase. Until now, attempts to synthesize Mu-18 or phase Z as pure phases were unsuccessful.

Mu-18 consists of large spheres of aggregated crystals. These spheres (diameter close to 5 mm) can be easily separated from the mixture (Mu-18 and phase Z) by a repeated rapid sedimentation process, leading thus to a pure Mu-18 sample. As shown in Figure 1, the crystals of Mu-18 display a rectangular prism morphology. Their size ranges from $40 \times 80 \times 80$ to $90 \times 250 \times 600$ μm .

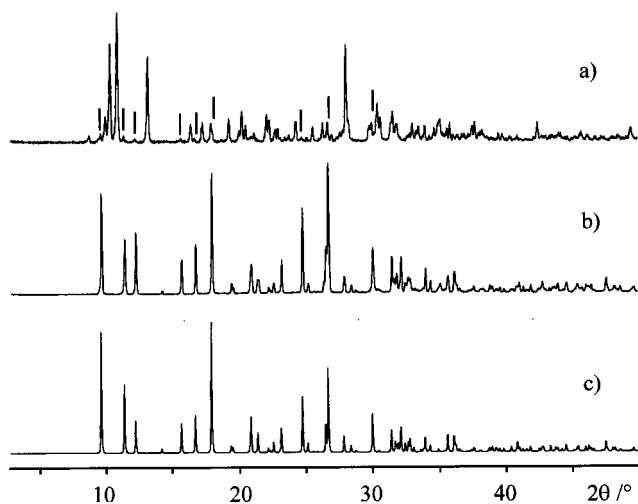


Figure 2. Powder XRD patterns (Cu $K\alpha_1$ radiation) of (a) phase Z containing traces of Mu-18 (peaks with thick lines belong to Mu-18) and (b) Mu-18 (after elimination of phase Z by a repeated rapid sedimentation process). (c) Simulated XRD pattern of Mu-18 calculated from the structure data.

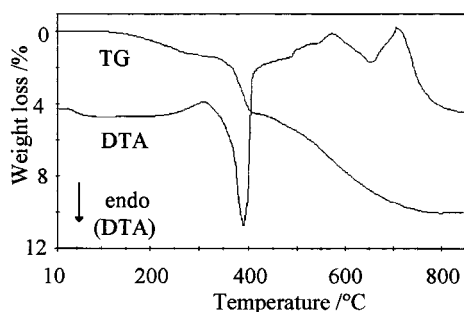


Figure 3. Thermal analyses under air of the hydroxygallophosphate Mu-18.

The XRD powder patterns of phase Z containing traces of Mu-18 and that of Mu-18 (after sedimentation) are reported in Figure 2a,b, respectively. For comparison the simulated XRD pattern of Mu-18 calculated from the structure data is given in Figure 2c.

Experiments are still in progress to characterize the unknown phase Z.

3.2. Chemical Formula Determination. According to the microprobe analyses and to the ^1H liquid NMR spectroscopy, the as-synthesized Mu-18 sample has the following composition (wt %): Ga, 36.9; P, 15.9; O, 34.9; amine, 9.2. It is in good agreement with the one obtained from the crystal structure determination: Ga, 36.6; P, 16.3; O, 37.8; amine, 8.9. The Ga/P molar ratio is close to 1, as observed for most of the microporous gallophosphates.

The thermal behavior of Mu-18 was investigated by high-temperature XRD analysis and TG/DTA thermal analysis. The TG and DTA curves of as-synthesized Mu-18 are given in Figure 3. The total weight loss occurs in four steps. The first one, before 350 °C (1.5 wt %), corresponds to the loss of water molecules located in the channels (see structure determination). It leads to a broad endothermic drift on the DTA curve. The second one, between 350 and 450 °C (3.7 wt %), corresponds to the removal of water arising from dehydroxylation reactions (presence of terminal Ga–OH groups) and to the partial decomposition of the organic template. According to the high-temperature XRD analysis, this

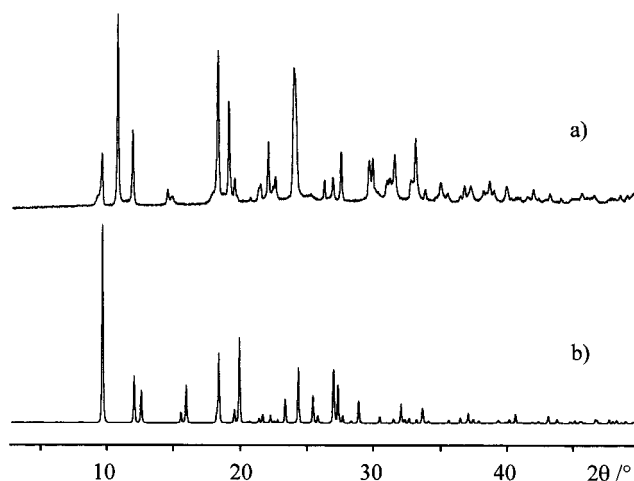


Figure 4. (a) Experimental XRD pattern (Cu $K\alpha_1$ radiation) of phase Y, and (b) simulated XRD pattern of $\text{AlPO}_4\text{-53(B)}$ calculated from the structure data of ref 3 ($\text{AlPO}_4\text{-53(B)}$ is the calcined form of $\text{AlPO}_4\text{-53(A)}$)

Table 8. Powder X-ray Diffraction Data of Phase Y

D (Å)	2θ (deg)	I (rel)	D (Å)	2θ (deg)	I (rel)
9.04	9.77	29	2.718	32.91	15
8.06	10.96	100	2.690	33.27	37
7.31	12.08	41	2.634	34.00	11
6.02	14.69	11	2.551	35.15	14
5.89	15.01	7	2.514	35.67	9
4.80	18.46	82	2.431	36.94	12
4.59	19.28	56	2.401	37.40	12
4.49	19.71	16	2.342	38.40	10
4.10	21.67	13	2.317	38.83	15
3.99	22.24	36	2.299	39.14	10
3.93	22.60	12	2.246	40.10	12
3.90	22.77	17	2.167	41.64	7
3.68	24.17	73	2.143	42.11	11
3.37	26.44	15	2.085	43.35	8
3.29	27.08	17	2.048	44.17	6
3.22	27.69	29	1.981	45.75	9
2.995	29.80	26	1.944	46.67	8
2.970	30.05	26	1.871	48.62	7
2.870	31.13	15	1.851	49.15	8
2.852	31.33	16	1.833	49.68	9
2.820	31.69	28			

second step corresponds to the transformation of Mu-18 in another unknown crystallized phase (phase Y). The XRD pattern and the main d spacings of phase Y are presented in Figure 4a and Table 8, respectively. It is worth noting that after calcination $\text{AlPO}_4\text{-53(A)}$ and UiO-12-as lead to crystalline dehydrated phases $\text{AlPO}_4\text{-53(B)}$ and UiO-12-500 , respectively, which are very similar. The XRD patterns of these two last phases represented in Figure 4b are different from the one of phase Y. At higher temperatures, between 450 and 800 °C, exothermic peaks are observed. They can be attributed to the oxidation and partial removal of the organic species (weight loss: 6.4 wt %). As previously observed for gallophosphates Mu-2¹⁶ and Mu-8,¹⁷ the complete removal of the amine occurs after heating the sample at 1100 °C (~1 wt %). The resulting material corresponds to dense phases, in particular, quartz-type gallophosphate. The total weight loss observed between 100 and 1100 °C is close to 12.5 wt %, which is in good agreement with the amounts of water and template

(16) Reinert, P.; Marler, B.; Patarin, J. *Mater. Sci.* **2000**, *35*, 1.

(17) Reinert, P.; Marler, B.; Patarin, J. *Microporous Mesoporous Mater.* **2000**, *39*, 509.

Table 9. Bond Valence Analysis of the Gallophosphate Mu-18, According to Brown¹⁸ (Results Refer to the Equation: $s = \exp[(R_0 - d)/B]$ with d = Experimental Distance, $R_0 = 1.62$, $B = 0.36$ for P–O and $R_0 = 1.73$, $B = 0.38$ for Ga–O)

atoms	H ^a	Ga(1)	Ga(2)	Ga(3)	P(1)	P(2)	P(3)	Σs	expected valence
O(1)		0.56					1.30	1.86	2
O(2)			0.79				1.35	2.14	2
O(3)	0.80	0.64		0.53				1.97	2
O(4)				0.68	1.35			2.03	2
O(5)			0.84		1.28			2.12	2
O(6)		0.75			1.25			2.00	2
O(7)				0.72		1.25		1.97	2
O(8)			0.77		1.34			2.11	2
O(9)		0.69			1.28			1.97	2
O(10)			0.76		1.24			2.00	2
O(11)				0.67	1.29			1.96	2
O(12)				0.57	1.36			1.93	2
O(13)		0.60				1.35		1.95	2
Σs	0.80	3.24	3.16	3.17	5.18	5.21	5.25		
expected valence	1	3	3	3	5	5	5		

^a On the basis of an O–H bond length of 0.96 Å.

determined by the crystal structure analysis (12.1 wt %). Taking into account all these analyses, the following unit cell formula can be proposed for the hydroxygallophosphate Mu-18: $[(C_5H_{14}N_2)_4Ga_{24}P_{24}O_{96}(OH)_8] \cdot 4H_2O$.

3.3. Structure Determination. On the basis of the Weissenberg photographs, the powder XRD pattern of Mu-18 presented in Figure 2b was indexed in the orthorhombic symmetry, space group *Aba2*, with the following refined unit cell parameters: $a = 18.035(18)$ Å, $b = 10.513(11)$ Å, and $c = 14.293(11)$ Å. The structure was then determined by single-crystal X-ray diffraction using direct methods. Because of the presence of some reflections with very weak intensity observable also on the Weissenberg film and in disagreement with the glide plane extinction rule, the structure was first solved in the lower symmetry monoclinic space group *Pn* but convergence problems for *Pn* and unreasonable stereochemistry feature for *Abm2* in the refinement showed that these space groups are unsuitable. Space group *Aba2* is confirmed as correct by the successful refinement.

From direct methods, the position of some gallium and phosphorus atoms were revealed and all the remaining atoms, except hydrogen atoms, were located from successive Fourier maps. The presence of an oxygen (O3) bridging two gallium atoms (Ga1 and Ga3) was clearly evidenced. A bond valence calculation using the relation proposed by Brown [$s = \exp[-(x - R_0)/B]$ with $R_0 = 1.73$ and 1.62; $B = 0.38$ and 0.36 for Ga–O and P–O distances, respectively]¹⁸ shows (Table 9) that this oxygen (O3) corresponds to an OH group. Despite disorder in the channels, the amine and a water molecule can also be located. To compensate the negative charge of the inorganic framework, the organic molecule has to be occluded in its diprotonated form. All the hydrogen atoms of the amine were placed with geometrical constraints.

3.4. Structure Description. The structure of Mu-18 displays three types of weakly distorted PO₄ tetrahedra (average P–O bond length = 1.525 Å). Three

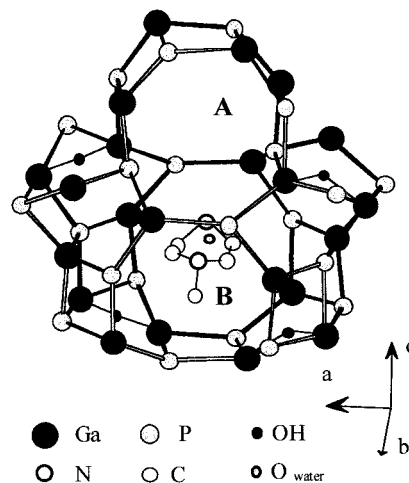


Figure 5. Perspective view of the structure along the *b* direction, showing the bridging OH groups the position of the amine and of the water molecules (for clarity, the framework oxygen atoms are omitted).

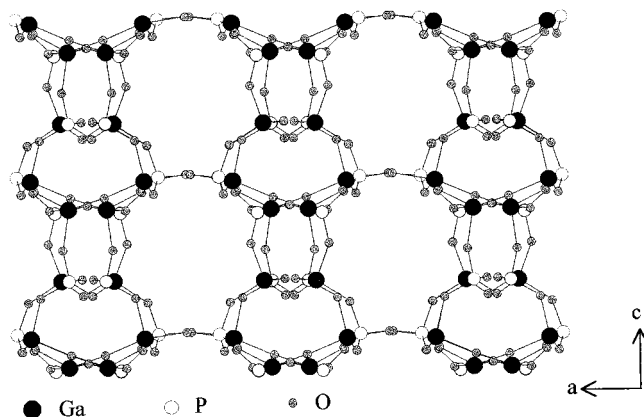


Figure 6. Projection of the structure of Mu-18 along the [010] direction, showing the one-dimensional channel system with eight-membered ring openings.

types of gallium atoms are also present: two in 5-fold coordination (Ga(1), Ga(3)) and one in 4-fold coordination (Ga(2)). For the GaO₄ tetrahedron, the average Ga(2)–O bond length is close to 1.819 Å, whereas for the two GaO₄(OH) trigonal bipyramids (Ga(1) and Ga(3)), the average Ga–O bond length is close to 1.899 Å. Each phosphorus shares its oxygen atoms with gallium neighbors. The gallium atoms in 5-fold coordination are connected to each other by their OH (O(3)) group (Figure 5). Such bridging OH groups have already been observed for the aluminophosphate AlPO₄-EN3³ and its related materials.^{4–12} For a more convenient description of the structure, the OH groups will not be taken into account in the following.

The structure of the hydroxygallophosphate Mu-18 can be described as a three-dimensional alternation of two types of cages: a small [4⁶8³] one (cage A) and a bigger [4⁹6⁸8³] one with large side pockets (cage B) (Figure 5). Each A cage is surrounded by six B cages. Such an arrangement delimits along the [010] direction a one-dimensional channel system with eight-membered ring openings occluding the disordered protonated amine and the water molecule (Figures 5 and 6). Large displacement parameters of these guest species confirm this disorder.

(18) Brown, I. D. In *Structure and Bonding in Crystals*; O'Keeffe, M., Navrotsky, A., Eds.; Academic Press: New York, 1981; Vol. 2, Chapter 14.

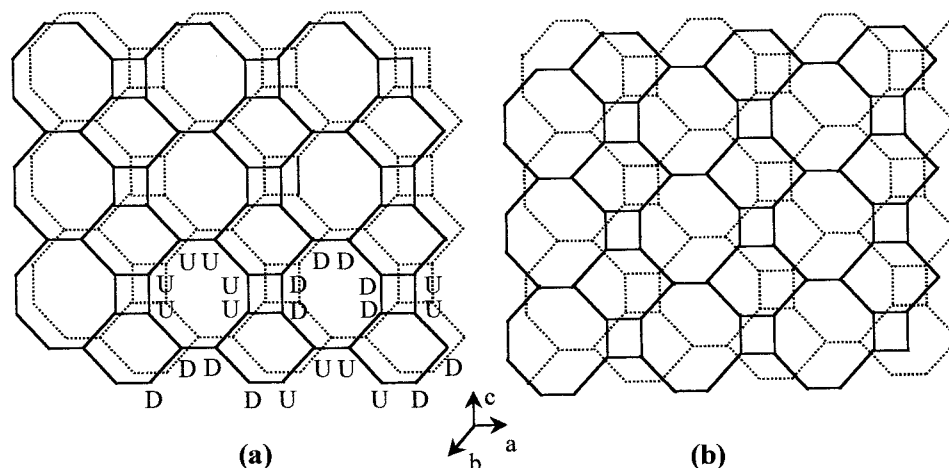


Figure 7. Idealized perspective views along the [010] direction of the structures of Mu-18 (a) and $\text{AlPO}_4\text{-EN3}$ (b) (for clarity the bondings between the layers along the b direction are omitted).

The framework topology can also be described with the notation upward (U) and downward (D) pointing branches as proposed by Smith et al.¹⁹ In this case, layers are considered. They are constituted by four- (sequence DUUD), six- (sequence DUUDDU), and eight-membered rings (sequence DDDDDUU). Actually, these $4 \times 6 \times 8$ layers are the same as those found in $\text{AlPO}_4\text{-EN3}$. The difference between the two structures comes from the stacking of the layers along the b direction. In Mu-18 two consecutive layers are connected via their four-membered rings units through a glide plane perpendicular to b whereas in $\text{AlPO}_4\text{-EN3}$ the four-membered rings of the upper layer are linked to the six-membered rings of the lower layer (Figure 7).

3.5. ^1H and ^{13}C NMR Spectroscopy. The liquid ^1H NMR spectrum of the dissolved Mu-18 in 6 M HCl shows that the 1-methylpiperazine molecule is partially decomposed (<20 wt %) in piperazine during the synthesis. Such a decomposition was recently observed for the synthesis of the microporous aluminophosphate published by Kerdarmath et al.²⁰ Our attempts to obtain the hydroxygallophosphate Mu-18 using piperazine as the organic template instead of 1-methylpiperazine were unsuccessful and led systematically to other unidentified phases. Unfortunately, in Mu-18 the disorder of the template is too pronounced to discuss the piperazine and 1-methylpiperazine distribution in the channels.

The ^{13}C CP MAS NMR spectrum reported in Figure 8 displays three resonances at δ 51.8 ($\text{CH}_2\text{-N-CH}_3$), 45.2 (CH_3), and 43.3 ppm ($\text{CH}_2\text{-NH}$). These values (reference TMS) are closer to those observed by ^{13}C liquid NMR spectroscopy, for pure the 1-methylpiperazine molecule at pH = 1 (δ 50.7, 44.2, and 41.6 ppm) than those obtained at pH = 11 (δ 55.1, 45.9, and 44.9 ppm). This confirms that the amine is occluded in the structure in its protonated form.

3.6. ^{31}P NMR Spectroscopy. The ^{31}P MAS NMR spectrum of Mu-18 displays two signals located at -8.9 and -18.5 ppm (Figure 9). Such chemical shift values are similar to those traditionally observed for PO_4 groups in microporous gallophosphates Mu-8¹⁷ and Mu-

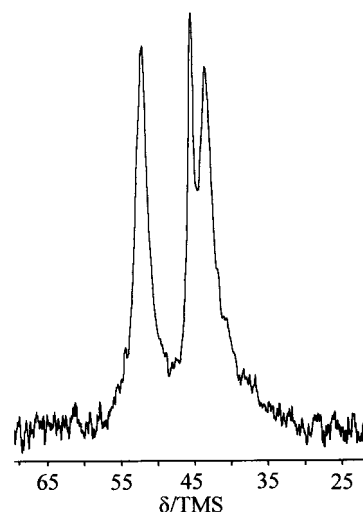


Figure 8. ^{13}C CP MAS NMR spectrum of the hydroxygallophosphate Mu-18.

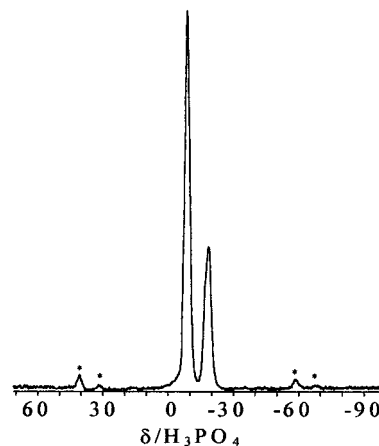


Figure 9. ^{31}P MAS NMR spectrum of the hydroxygallophosphate Mu-18 (* spinning sidebands).

15.²¹ The intensity ratio between the two peaks is close to 2:1, respectively, revealing the existence of three distinct crystallographic phosphorus sites as confirmed by the structure analysis. Moreover, whatever the contact time, no significant differences are observed

(19) Smith, J. V.; Rinaldi, F. *Mineral. Mag.* **1962**, *33*, 202.

(20) Kerdarmath, K.; Choudhury, A.; Natarajan, S. *Solid State Chem.* **2000**, *150*, 324.

(21) Matijasic, A.; Paillaud, J. L.; Patarin, J. *J. Mater. Chem.* **2000**, *10*, 1345.

between the MAS and CP MAS spectra, which indicates, in agreement with the structure determination, that no terminal P–OH groups are present. Unfortunately, a tentative assignment of these different signals to the different phosphorus sites using for instance the empirical relationship based on the sum of the valence of the oxygen atoms²² was not conclusive.

4. Conclusion

A new hydroxygallophosphate named Mu-18 was obtained in the presence of 1-methylpiperazine as the

(22) Cheetham, A. K.; Clayden, N. J.; Dobson, C. M.; Jakeman, R. J. B. *J. Chem. Soc., Chem. Commun.* **1986**, 195.

templating agent. Its three-dimensional framework results from the stacking of $4 \times 6 \times 8$ layers, which delimits a one-dimensional channel system with eight-membered ring openings occluding the organic template and water molecules. This framework topology is closely related to that of the hydroxyaluminophosphate $\text{AlPO}_4\text{-EN3}$. The two structures differ mainly by the connectivity scheme of the successive layers.

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