$Ga_4(PO_4)_4F\cdot N_2C_7H_{11}\cdot {}^1/_2H_2O$: A Three-Dimensional Open Framework with 12-Membered Pores and “Bowl-Shaped” Building Units

François Bonhomme,[†] Steven G. Thoma,[†] Mark A. Rodriguez,[‡] and Tina M. Nenoff*,[†]

Environmental Monitoring & Characterization Department, and Materials Characterization Department, Sandia National Laboratories, Albuquerque, New Mexico 87185-0755

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$Ga_4(PO_4)_4F\cdot N_2C_7H_{11}\cdot {}^1/_2H_2O$ was prepared solvothermally in pure form using 4-(dimethylamino)pyridine (4-DMAP) as a template in various solvents (pyridine, pyridine/water, and ethylene glycol) within a broad reaction temperature range (115−180 °C). Its structure was determined from X-ray single-crystal diffraction data at low temperature (−105 °C). $Ga_4(PO_4)_4F\cdot N_2C_7H_{11}\cdot {}^1/_2H_2O$ crystallizes in the monoclinic space group $C2/c$, with $a = 22.093(4)$ Å, $b = 13.904(2)$ Å, $c = 14.230(2)$ Å, $\beta = 98.431(3)°$, $V = 4324$ Å^3, and $Z = 8$. Its three-dimensional framework is composed of novel distorted “bowl-shaped” octameric double 4-ring units, which are built up by corner-sharing PO_4 and GaO_4 tetrahedra and GaO_4F trigonal bipyramids. The structure consists of a pseudohexagonal array of cylindrical 12-membered pores running parallel to the c axis hosting the protonated 4-DMAP molecules. These pores are interconnected along the b axis through double 8-ring windows. The framework remains stable up to 300 °C under oxygen.

Introduction

Open-framework crystalline materials are the subject of intense ongoing research owing to their industrial applications as catalysts and ion exchangers and in the area of gas separation. This class of materials was dominated by alumino-silicates until the discovery of porous alumino-phosphates by Flanigen et al.[1] in 1982. They were obtained by the same general hydrothermal methods used in classical zeolite synthesis.[2] Shortly after, Parise totally replaced aluminum by gallium and achieved the synthesis of a series of amine-templated gallophosphates.[3] The successful use of nonaqueous solvents such as alcohols, glycols, or amines in those systems was pioneered by Xu et al.[4,5] This new gallophosphate family was further expanded by Kessler et al.[6] who developed the “fluoride route”, which led to the synthesis of a vast number of fluoro-gallophosphates, many of which display new framework topologies. In these compounds, the gallium atoms can be tetra-, penta-, or hexacoordinated, and this flexibility leads to a great variety of structural building units.[7] The properties of the amine (i.e., basicity, size, and shape) play a central role in determining the nature of the final product by governing its dimensionality and pore size.[8]

In our search for novel fluoro-gallophosphates, we have been using the relatively bulky planar diamine, 4-(dimethylamino)pyridine (4-DMAP), as a structure-directing agent.

The 4-DMAP is also of interest because of its use as an alkylation catalyst.[9]

The use of this template has resulted in a novel three-dimensional microporous compound, $Ga_4(PO_4)_4F\cdot N_2C_7H_{11}\cdot {}^1/_2 H_2O$. In this work, we report on the synthesis, structural characterization, and properties of the title phase and contrast these features to those of previously reported fluoro-gallophosphates. In particular, we will focus on the description of a novel framework building unit, a distorted octameric double 4-ring.

Experimental Section

Synthesis. The title compound was prepared under mild solvothermal conditions using Teflon-lined 23-cm^3 Parr reactors. The chemicals used in the various reactions include hydrated gallium sulfate [Alfa Aesar], phosphoric acid [Fisher, 85 wt %], phosphorus pentoxide [Aldrich], hydrofluoric acid [Fisher, 49 wt %], 4-DMAP [Aldrich], pyridine [Fisher], ethylene glycol [Fisher], and deionized (D.I.) water.

Table 1 summarizes the synthesis conditions under which an X-ray pure phase was obtained. Typically, 0.5 mmol of gallium sulfate was dispersed or dissolved in the solvent, followed by addition of phosphoric acid or phosphorus pentoxide. After several minutes of homogenization, the 4-DMAP was added with stirring, followed by addition of hydrofluoric acid. The reactors were afterward heated without agitation

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* To whom correspondence should be addressed. E-mail: tmnenof@sandia.gov. Phone: (505) 844-0340.

[†] Environmental Monitoring & Characterization Department.

[‡] Materials Characterization Department.

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Table 1. Synthesis Conditions of Pure Samples

sample	starting composition; reactants and solvents (**molar ratios**)	temp.	time
13C	Ga **1**/P **2** (P_2O_5)/F **1**/4-DMAP **1**/pyridine **63**/H_2O **55**	178 °C	6 days
14C	Ga **1**/P **2** (H_3PO_4)/F **2**/4-DMAP **2**/ethylene glycol **88**	115 °C	14 days
15C	Ga **1**/P **2** (H_3PO_4)/F **1**/4-DMAP **2**/pyridine **63**	178 °C	6 days

for the specified time period and then cooled to room temperature overnight. The resulting white crystalline powder was filtered off, washed with D.I. water and ethanol and dried in air at 50 °C. In each case, the yield of the reaction, based on gallium is about 75%. Similar syntheses using only water as a solvent lead to dense $GaPO_4$ with α-quartz structure.

Characterization. An elemental analysis was performed on sample #15C by Galbraith Laboratories Inc. (Knoxville, TN). Methods included inductively coupled plasma-optical emission spectroscopy for gallium and phosphorus and an ion-selective electrode for fluorine. The measured atomic ratios are Ga/P = 0.98 and Ga/F = 4.12.

Thermal analysis were carried out on sample #15C on a TA Instruments SDT 2960 simultaneous thermogravimetric analyzer-differential thermal analyzer (TGA-DTA) under flowing oxygen (50 cm^3/min) and a heating rate of 5 °C/min. A representative TGA curve is given Figure 1.

The density of $Ga_4(PO_4)_4F{\cdot}N_2C_7H_{11}{\cdot}{}^1/_2H_2O$ was determined with 0.18 g of sample #13C using a Micromeritics AccuPyc 1330 helium displacement pycnometer.

Scanning electron micrographs were taken with a JEOL JSM-T300 SEM equipped with an energy-dispersive X-ray emission analyzer.

Structure Determination. The samples were first characterized by X-ray powder diffraction (diffractometer Siemens D500, Bragg–Brentano geometry, Ni-filtered Cu Kα radiation). The powder pattern of the sample #13C, shown in Figure 2, was initially indexed (program TREOR[10]) with a reasonable figure of merit[10] ($F(16) = 36$) by a *C*-centered monoclinic cell with approximate cell parameters $a = 22.06$ Å, $b = 13.89$ Å, $c = 7.11$ Å, and $\beta = 98.51°$. However, a subsequent structureless whole pattern fitting by the Le Bail method[11] (program FULLPROF98[12]) revealed several weak peaks unaccounted for that could be indexed by a doubling of the *c* axis. The extinction conditions[13] are consistent with the space group *C*2/*c* or *Cc* and the refined lattice constants at room temperature (internal standard silicon) are $a = 22.097(2)$ Å, $b = 13.896(1)$ Å, $c = 14.268(2)$, and $\beta = 98.57(1)°$; $V = 4332.2(8)$ Å^3. No significant variation of the cell parameters was observed for the different samples.

Although the samples #13C and #14C were pure, they did not provide untwinned single crystals of sufficient size and quality for X-ray diffraction measurements. Combining gallium sulfate, phosphoric acid, hydrofluoric acid, and 4-DMAP but using only pure pyridine as the solvent, we obtained a sample (Table 1, #15C) consisting of large, well-shaped, isolated transparent single crystals (see Figure 3 for typical morphology and crystal size). A platelike crystal suitable for X-ray data collection was selected from this sample and its quality checked by polarizing microscopy. It was mounted on a glass fiber with Fluorolube [Occidental Chemical Corp., Dallas, Texas] and transferred onto a Bruker AXS diffractometer. The intensities were measured at low temperature (−105 °C) to avoid a possible thermal disorder of the organic template. Slightly more than a hemisphere of data was collected with an acquisition time of 10 s per frame. The cell parameters and cell centering at −105 °C are similar to those obtained at room temperature, showing that no phase transition affecting the lattice occurred during cooling. Data collection and reduction were carried out with the SMART[14] and SAINT-PLUS[15] software. An empirical absorption correction was done with the program SADABS.[16] All subsequent calculations were performed within the WinGX system.[17] Crystal data and data collection parameters are given in Table 2.

The structure was solved by the direct methods in the space group *C*2/*c* and initially refined using the SIR-97[18] program. All 35 non-hydrogen atom sites were directly revealed. The assignment of the fluorine site was based on the value of its atomic displacement parameter and the absence of a P−F bond in such compounds. It is thus located on the only framework site bonded exclusively to gallium atoms. All the hydrogen atoms of the 4-DMAP molecule, including the proton bonded to N34, could be located from difference Fourier maps. Their positions were eventually refined with geometrical constraints with the riding atom model as implemented in SHELX97.[19] The non-hydrogen atoms were all refined anisotropically. Another guest molecule containing only one non-hydrogen atom was located within the structure and is likely a water molecule; we were however unable to locate any hydrogen atoms within bonding distance, probably because of orientational disorder. Although the sample was obtained from a nonaqueous reaction prep, water is always present in the starting mixture and comes from the hydrated gallium sulfate or the various acids. The full-matrix refinement based on F^2 converged to the following agreement indices: $R_1(F) = 0.0381$, $wR_2(F^2) = 0.0777$ for all 3115 data points and 315 parameters. Atomic coordinates and equivalent isotropic atomic displacement parameters for non-hydrogen atoms are given in Table 3. Selected interatomic distances and bond angles are given in Tables 4 and 5. Hydrogen atoms coordinates, anisotropic atomic displacement parameters, and observed and calculated structure factors are available as Supporting Information.

The formula unit obtained from the structure determination is $Ga_4P_4F_1O_{16.5}C_7N_2H_{12}$, in good agreement with the composi-

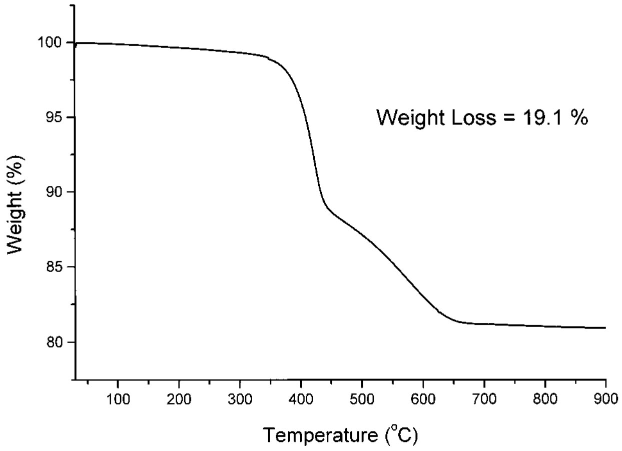

Figure 1. TGA curve of $Ga_4(PO_4)_4F{\cdot}N_2C_7H_{11}{\cdot}{}^1/_2H_2O$ under O_2 (5 °C/min) (sample #15C).

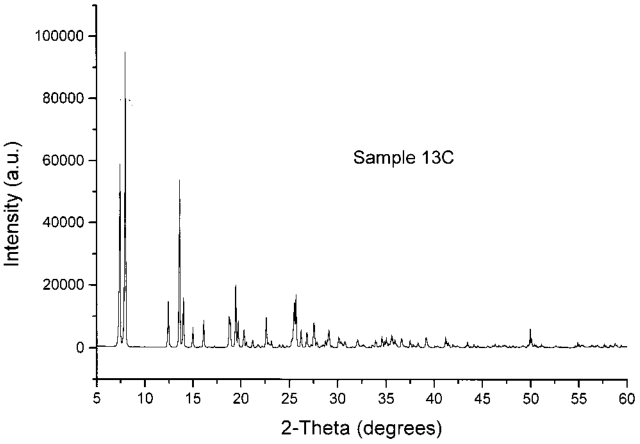

Figure 2. Powder X-ray diffraction pattern of $Ga_4(PO_4)_4F{\cdot}N_2C_7H_{11}{\cdot}{}^1/_2H_2O$ (Cu Kα radiation).

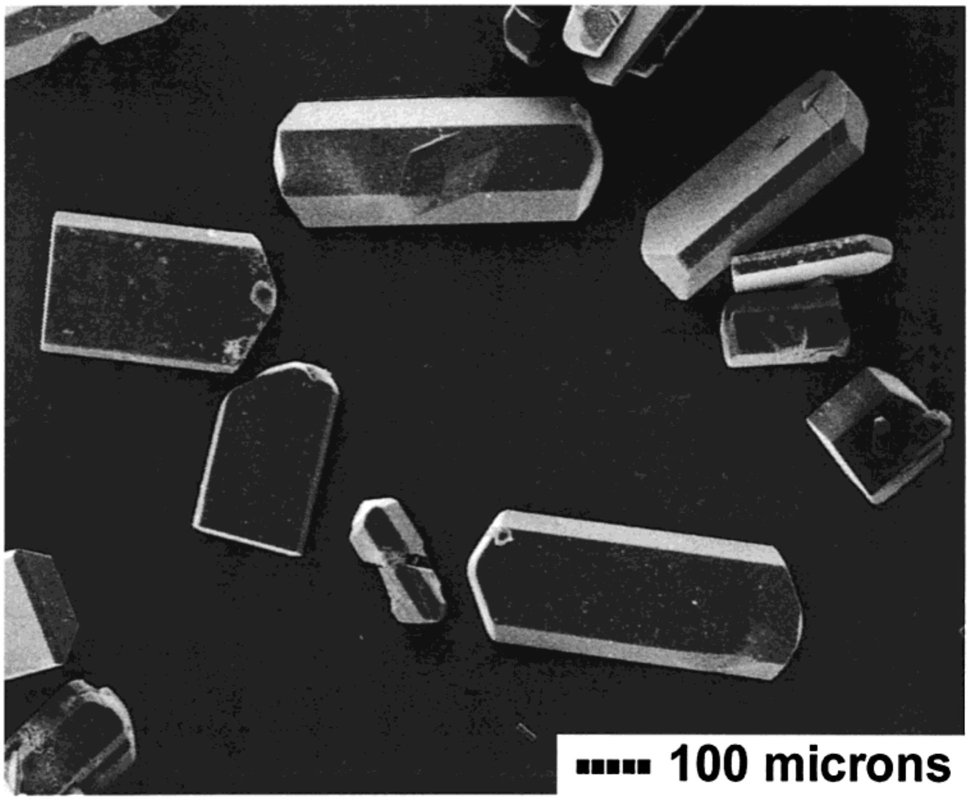

Figure 3. SEM micrograph of $Ga_4(PO_4)_4F{\cdot}N_2C_7H_{11}{\cdot}{}^1/_2H_2O$ (sample #15C).

Table 2. Crystal Data and Structure Refinement Parameters

compound	$Ga_4(PO_4)_4F[C_7N_2H_{11}]{\cdot}{}^1/_2H_2O$
empirical formula	$Ga_4P_4F_1O_{16.5}C_7N_2H_{12}$
formula weight	809.8 g/mol
temperature	168(2) K
wavelength	Mo Kα (0.71069 Å)
crystal system	monoclinic
space group	*C*2/*c*
unit cell dimensions	$a = 22.093(4)$ Å
	$b = 13.904(2)$ Å
	$c = 14.230(2)$ Å
	$\beta = 98.431(3)°$
cell volume	4323.9(12) $Å^3$
Z	8
density (calculated)	2.49 g/cm^3
density (measured)	2.47(2) g/cm^3
absorption coefficient	5.32 mm^{-1}
F(000)	3144
crystal size	0.27 × 0.17 × 0.04 mm
θ range for data collection	1.74°−23.26°.
index ranges	$-24 \le h \le 24$,
	$-13 \le k \le 15$,
	$-15 \le l \le 15$
reflections collected	9600
independent reflections	3115 [*R*(int) = 0.0403]
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	3115/0/314
goodness-of-fit on F^2	1.027
final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0302$, $wR_2 = 0.0748$
R indices (all data)	$R_1 = 0.0381$, $wR_2 = 0.0777$
largest diff. peak and hole	0.84 and −0.56 e $Å^{-3}$

tion derived from the elemental analysis: (in wt %, obs/calc), for Ga 34.81/34.44, P 15.76/15.30, and F 2.30/2.35. The measured density, 2.47(2) g/cm^3, agrees very well with the calculated one, 2.49 g/cm^3. Bond valence sums[20] (BVS) show that all the framework atoms have their expected valence (see Table 6). In particular, the BVS for the oxygen sites range from 1.85 to 2.14, indicating that none of them is likely to be bonded to a proton (in which case, by not taking into account the interaction with the proton, the BVS for the oxygen site is usually smaller than 1.25[21−23]). Furthermore, no residual electron density that could correspond to a hydroxyl group is observed. The BVS obtained for fluorine (0.78) is typical for fluoro-gallophosphates.[22,24] The framework composition is therefore $[(GaPO_4)_4F]^-$ and its formal charge is compensated by the monoprotonated 4-DMAP $[C_7N_2H_{11}]^+$, which indicates that the other guest molecule is a neutral species and thus is assigned as a water molecule.

Results

Structure Description. The structure of $Ga_4(PO_4)_4F{\cdot}N_2C_7H_{11}{\cdot}{}^1/_2H_2O$ contains four phosphorus sites and four

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Table 3. Fractional Atomic Coordinates for Non-hydrogen Atoms (with Standard Deviations in the Least Significant Digits in Parentheses) and Equivalent Isotropic Atomic Displacement Parameters (Å^2) (U_{eq} Is Defined as One-Third of the Trace of the Orthogonalized U_{ij} Tensor)

atom name	x/a	y/b	z/c	U_{eq}
Ga(1)	0.41649(2)	0.59588(3)	0.49217(3)	0.008
Ga(2)	0.66258(2)	0.70145(3)	0.41396(3)	0.009
Ga(3)	0.74448(2)	0.38940(3)	0.56007(3)	0.008
Ga(4)	0.66013(2)	0.60223(4)	0.69399(4)	0.010
P(5)	0.55780(6)	0.61956(8)	0.51652(9)	0.009
P(6)	0.76344(6)	0.60947(8)	0.55925(8)	0.009
P(7)	0.65629(6)	0.38147(8)	0.70640(8)	0.010
P(8)	0.67162(6)	0.71385(8)	0.89051(8)	0.008
F(9)	0.6678(1)	0.4652(2)	0.5304(2)	0.011
O(10)	0.7287(1)	0.6609(2)	0.9383(2)	0.010
O(11)	0.7857(1)	0.5058(2)	0.5690(2)	0.010
O(12)	0.6142(1)	0.6851(2)	0.9315(2)	0.014
O(13)	0.7242(1)	0.6384(2)	0.6344(2)	0.014
O(14)	0.4033(1)	0.6211(2)	0.3631(2)	0.011
O(15)	0.5576(1)	0.5240(2)	0.4636(2)	0.011
O(16)	0.6716(1)	0.4832(2)	0.7456(2)	0.015
O(17)	0.6458(1)	0.6841(2)	0.2886(2)	0.013
O(18)	0.7285(1)	0.6280(2)	0.4595(2)	0.012
O(19)	0.6783(1)	0.8298(2)	0.4275(2)	0.014
O(20)	0.5956(1)	0.6945(2)	0.4714(2)	0.015
O(21)	0.7104(1)	0.3417(2)	0.6622(2)	0.013
O(22)	0.5858(1)	0.6084(2)	0.6212(2)	0.015
O(23)	0.8203(1)	0.3229(2)	0.5950(2)	0.010
O(24)	0.4935(1)	0.6582(2)	0.5124(2)	0.011
O(25)	0.6620(1)	0.6945(2)	0.7839(2)	0.015
C(26)	0.6267(3)	0.1234(4)	0.6562(5)	0.044
C(27)	0.6623(3)	0.9531(5)	0.6647(4)	0.041
N(28)	0.6111(2)	0.0204(3)	0.6522(3)	0.026
C(29)	0.5535(2)	0.9915(3)	0.6375(3)	0.019
C(30)	0.5026(3)	0.0556(4)	0.6246(4)	0.026
C(31)	0.4450(3)	0.0214(4)	0.6102(4)	0.029
C(32)	0.4791(3)	0.8634(4)	0.6191(4)	0.030
C(33)	0.5381(3)	0.8916(4)	0.6349(4)	0.026
N(34)	0.4331(2)	0.9270(4)	0.6075(3)	0.030
Ow	$^1/_2$	0.2728(7)	$^3/_4$	0.105

Table 4. Selected Interatomic Distances (Å)

Ga(1)−O(12)	1.842(4)	Ga(1)−O(14)	1.851(3)
Ga(1)−O(15)	1.842(3)	Ga(1)−O(24)	1.894(3)
Ga(1)−F(9)	2.029(3)		
Ga(2)−O(17)	1.784(3)	Ga(2)−O(18)	1.818(4)
Ga(2)−O(19)	1.822(3)	Ga(2)−O(20)	1.795(4)
Ga(3)−O(10)	1.854(3)	Ga(3)−O(11)	1.852(3)
Ga(3)−O(21)	1.854(4)	Ga(3)−O(23)	1.914(4)
Ga(3)−F(9)	1.987(3)		
Ga(4)−O(13)	1.823(4)	Ga(4)−O(16)	1.814(4)
Ga(4)−O(22)	1.810(4)	Ga(4)−O(25)	1.808(4)
P(5)−O(15)	1.527(4)	P(5)−O(20)	1.534(4)
P(5)−O(22)	1.535(4)	P(5)−O(24)	1.511(4)
P(6)−O(11)	1.523(4)	P(6)−O(13)	1.527(4)
P(6)−O(18)	1.535(4)	P(6)−O(19)	1.529(4)
P(7)−O(14)	1.526(4)	P(7)−O(16)	1.540(4)
P(7)−O(17)	1.528(4)	P(7)−O(21)	1.534(4)
P(8)−O(10)	1.530(4)	P(8)−O(12)	1.525(4)
P(8)−O(23)	1.536(4)	P(8)−O(25)	1.524(4)

Table 5. Selected Bond Angles (deg)

F(9)−Ga(1)−O(14)	85.1(1)	F(9)−Ga(1)−O(15)	84.7(1)
F(9)−Ga(1)−O(24)	177.5(1)	F(9)−Ga(1)−O(12)	88.1(1)
O(14)−Ga(1)−O(15)	120.4(1)	O(14)−Ga(1)−O(24)	94.1(1)
O(14)−Ga(1)−O(12)	116.1(1)	O(15)−Ga(1)−O(24)	97.7(1)
O(15)−Ga(1)−O(12)	122.0(1)	O(24)−Ga(1)−O(12)	90.1(1)
O(18)−Ga(2)−O(20)	118.6(1)	O(18)−Ga(2)−O(17)	108.6(1)
O(18)−Ga(2)−O(19)	112.5(1)	O(20)−Ga(2)−O(17)	112.5(1)
O(20)−Ga(2)−O(19)	99.3(1)	O(17)−Ga(2)−O(19)	104.3(1)
F(9)−Ga(3)−O(11)	86.9(1)	F(9)−Ga(3)−O(21)	85.7(1)
F(9)−Ga(3)−O(10)	87.9(1)	F(9)−Ga(3)−O(23)	176.1(1)
O(11)−Ga(3)−O(21)	120.7(1)	O(11)−Ga(3)−O(10)	114.6(1)
O(11)−Ga(3)−O(23)	90.1(1)	O(21)−Ga(3)−O(10)	123.7(1)
O(21)−Ga(3)−O(23)	93.6(1)	O(10)−Ga(3)−O(23)	95.6(1)
Ga(1)−F(9)−Ga(3)	123.1(1)		
O(13)−Ga(4)−O(16)	111.6(1)	O(13)−Ga(4)−O(22)	114.9(1)
O(13)−Ga(4)−O(25)	101.2(1)	O(16)−Ga(4)−O(22)	109.7(1)
O(16)−Ga(4)−O(25)	111.9(1)	O(22)−Ga(4)−O(25)	107.2(1)
O(15)−P(5)−O(20)	110.3(2)	O(15)−P(5)−O(22)	111.2(2)
O(15)−P(5)−O(24)	110.8(2)	O(20)−P(5)−O(22)	107.9(2)
O(20)−P(5)−O(24)	107.9(2)	O(22)−P(5)−O(24)	108.4(2)
O(11)−P(6)−O(13)	113.3(2)	O(11)−P(6)−O(18)	110.8(2)
O(11)−P(6)−O(19)	104.9(2)	O(13)−P(6)−O(18)	110.1(2)
O(13)−P(6)−O(19)	108.9(2)	O(18)−P(6)−O(19)	108.8(2)
O(14)−P(7)−O(16)	112.3(2)	O(14)−P(7)−O(17)	105.6(2)
O(14)−P(7)−O(21)	112.1(2)	O(16)−P(7)−O(17)	108.7(2)
O(16)−P(7)−O(21)	109.6(2)	O(17)−P(7)−O(21)	108.3(2)
O(10)−P(8)−O(12)	112.4(2)	O(10)−P(8)−O(23)	110.0(2)
O(10)−P(8)−O(25)	110.0(2)	O(12)−P(8)−O(23)	107.1(2)
O(12)−P(8)−O(25)	109.4(2)	O(23)−P(8)−O(25)	107.7(2)

gallium sites. All phosphorus atoms are tetrahedrally coordinated with P−O distances ranging from 1.51 to 1.54 Å and O−P−O angles from 104.9° to 113.2°, which are typical values encountered in gallophosphates. The gallium atoms have two different types of environments: Ga2 and Ga4 are tetrahedrally coordinated with Ga−O distances between 1.784 and 1.823 Å and O−Ga−O angles from 99.3° to 118.6°, the Ga2 tetrahedron being the most distorted. Ga1 and Ga3 are 5-fold coordinated in a trigonal bipyramidal geometry by four O and one F. The bipyramids are fairly regular: within the trigonal plane Ga−O distances are between 1.842 and 1.854 Å and the O−Ga−O angles range between 114.7° and 123.7°. As expected, the axial Ga−O bond lengths are slightly longer (about 0.05 Å) than the equatorial ones. Ga1 and Ga3 are only about 0.13 and 0.10 Å, respectively, off the triangular basal plane. The fluorine is shared by both bipyramids and is bonded to Ga1 and Ga3 at distances of 2.029 and 1.987 Å, respectively. Those distances are typical for Ga−F bonds and shorter than those commonly observed for encapsulated F^- (Ga−F 2.3−2.6 Å). Every framework oxygen site is bonded to one phosphorus and one gallium and therefore no terminal oxygen is present in the structure.

The basic building block of this structure is a novel octameric unit (see Figure 4) reminiscent of the so-called “fluorine-centered double 4-ring (D4R)” unit frequently encountered in fluoro-gallophosphates (such as GaPO-LTA,[26] Cloverite,[27] Mu-15[28], or ULM-5,[21] for example). However, in this unique building block, two adjacent tetrahedral sites (Ga2 and P8) are not linked by a bridging oxygen atom, forming a “bowl-shaped” D4R unit. These octameric units are linked through P8−O−Ga4 and Ga2−O−P7 bonds and connect to form infinite columns running along the *c* axis. Adjacent columns are connected to each other by Ga−O−P bonds and form a 3D network. Six of those columns delimit a 12-membered cylindrical pore of approximately 6.8 Å in free diameter, parallel to the *c* axis (the free diameter values are based on an oxygen radius of 1.35 Å[29]). These

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Table 6. Bond Valence Sums (BVS) for the Framework Atoms

Ga(1): 3.20	Ga(2): 3.27	Ga(3): 3.17	Ga(4): 3.19	P(5): 5.11	P(6): 5.08	P(7): 5.03	P(8): 5.07	
F(9): 0.78	O(10): 1.98	O(11): 2.01	O(12): 2.02	O(13): 2.05	O(14): 2.00	O(15): 2.01	O(16): 2.03	O(17): 2.14
O(18): 2.04	O(19): 2.05	O(20): 2.09	O(21): 1.97	O(22): 2.05	O(23): 1.85	O(24): 1.97	O(25): 2.10	

pores are arranged in a pseudo-hexagonal array, as shown in Figure 5. The 4-DMAP molecules are lying perpendicular to the main axis of these channels (see Figure 6). Two adjacent pores are connected along the [010] direction through empty double 8-ring windows with a free diameter of 3.0 Å (see Figure 7). Along the [110] directions, two channels are separated by a zigzag ladder built up by alternating 4 and 6-membered rings. As the free diameter of these 6-rings is only 1.5 Å, the pores can be considered as isolated from each other in this direction. Every cylindrical channel is therefore only connected to two neighboring pores.

Thermal Stability. $Ga_4(PO_4)_4F\cdot N_2C_7H_{11}\cdot {}^1/_2H_2O$ has an initial weight loss below 300 °C attributed to the loss of the occluded water molecule. The TGA curve (see Figure 1) shows a main event between 350 and 650 °C due to the departure of the amine molecule and of the fluorine atoms. The framework collapses upon template removal and the end product is dense quartz-like $GaPO_4$. The observed total weight loss (19.1%) closely matches the expected value (18.6%) based on the composition derived from the structure determination. The compound is however stable under oxygen up to 300 °C as shown by X-ray powder diffraction. Prolonged heating at the midpoint of the weight loss (24 h at 430 °C under oxygen) leads to the removal of most of the volatile species (16.6% loss) and a partial destruction of the framework. The resulting amber-colored product is partly amorphized and shows only one strong X-ray diffraction peak, with an interplanar spacing $d \approx 11.4$ Å. This phase could not be further structurally characterized.

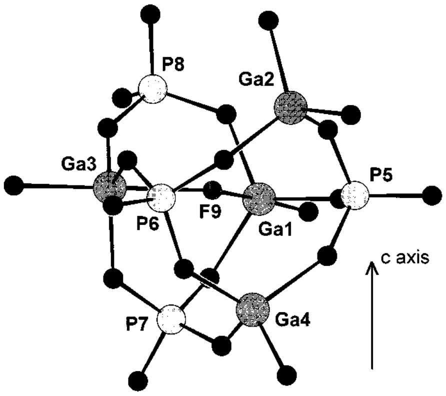

Figure 4. Distorted "bowl-shaped" D4R octameric unit in $Ga_4(PO_4)_4F\cdot N_2C_7H_{11}\cdot {}^1/_2H_2O$. Unlabeled black spheres: oxygen atoms. Drawing software: CAMERON.[25]

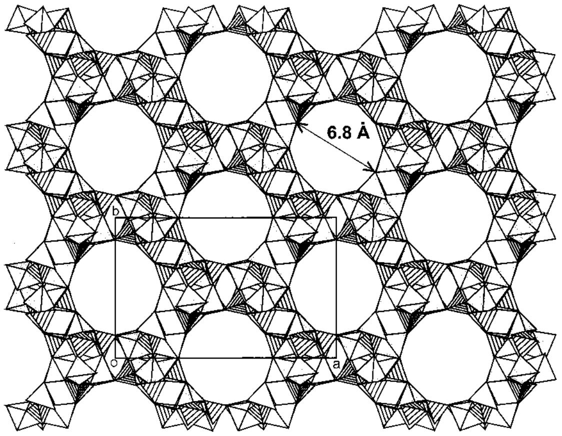

Figure 5. View of the structure of $Ga_4(PO_4)_4F\cdot N_2C_7H_{11}\cdot {}^1/_2H_2O$ along the *c* axis. Lined polyhedra: PO_4 tetrahedra. Guest molecules omitted for clarity. Drawing software: STRUPLO.[30]

Discussion and Conclusion

$Ga_4(PO_4)_4F\cdot N_2C_7H_{11}\cdot {}^1/_2H_2O$ is a fluorine poor three-dimensional open-framework fluoro-gallophosphate, with a framework oxygen-to-fluorine ratio of 16 to 1 and contains a novel "bowl-shaped" octameric building unit. In this class of compounds, only Mu-2,[32] whose structure consists of a cubic array of corner-linked fluorine-centered D4R, has a higher O/F ratio of 20/1. This ratio ranges usually between 6 (for ULM-3[33] or ULM-4,[34] for example) and 12 (for MIL-1[35] or MIL-20[24]). The cation density of $Ga_4(PO_4)_4F\cdot N_2C_7H_{11}\cdot {}^1/_2H_2O$ (14.8 atoms per 1000 Å^3) is an intermediate to the value of MIL-31[36] (12.7), which contains 18-membered channels, and to that of ULM-4[34] (16.2), containing cross-linked 10 and 8-membered channels. Cylindrical 12-membered pores arranged in a hexagonal array are common in zeolites (zeolite AFI, AFY, GME, LTL, MAZ, or OFF, for

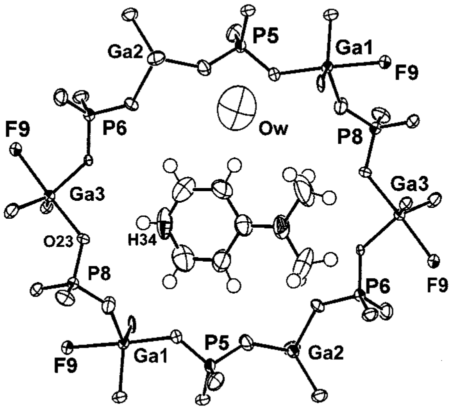

Figure 6. View of the guest molecules within the cylindrical 12-membered pore. Ellipsoid probability: 75%. Drawing software: ORTEP3 for Windows.[31]

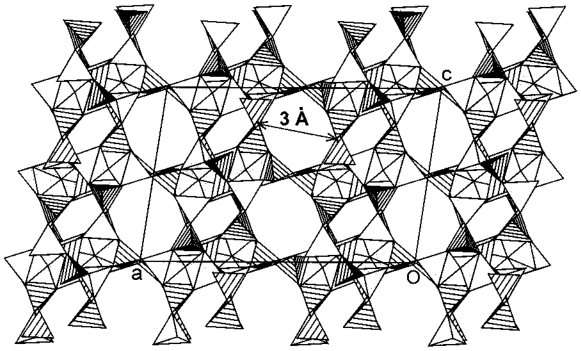

Figure 7. View of the double 8-ring windows along the *b* axis. Lined polyhedra: PO_4 tetrahedra. Guest molecules omitted for clarity. Drawing software: STRUPLO.[30]

example[29]). However, in those phases the channels are either isolated or fully connected to six other channels. In our present gallium fluorophosphate monoclinic compound, the pores are only effectively linked along one direction, the *b* axis. This topology therefore appears to be uncommon among microporous materials.

The strongest interaction of the organic 4-DMAP molecule with the framework occurs between the proton bonded to N34 and O23, with N34—O23 = 2.87 Å and H34—O23 = 2.04 Å (program PLATON[37]). It must be noted that O23 has the lowest BVS (1.85) of all the oxygen sites and is therefore the most likely to complete the necessary bond valence by hydrogen bonding with the organic template. All the other hydrogen to anion distances are above 2.45 Å, showing that the 4-DMAP does not interact very strongly with the pore walls. Interestingly, the fluorine atom, which is located within the octameric complex and away from the surface of the channels, is not involved in hydrogen bonding with the amine (shortest $d_{(F-N)} > 5.8$ Å), in contrast to the bonding pattern observed in most fluoro-gallophosphates. The recently characterized $Ga_4(PO_4)_4F_4$-$[N_4C_{24}H_{60}]$ (MIL-35[38]) does not contain hydrogen-bonded fluorine neither, as the shortest observed N—F distances exceed 3.9 Å. The absence of strong fluorine—amine interaction could ease the template removal, but so far our attempts to extract or exchange the template without collapsing the framework (i.e., by leaching in weakly acidic or basic solutions or by ion exchange in a sodium bicarbonate solution) have failed. The compound is stable at room temperature in common solvents (i.e., ethanol and DMF) but dissolves rapidly in basic (pH > 10) or acidic (pH < 3) aqueous solutions, therefore limiting the possibility of template extraction.

The planar diamine 4-DMAP has a relatively high pK_a of 9.8 and therefore has a low charge density. In the present compound, it is protonated once and associated with an octameric building unit of composition $[Ga_4P_4O_{16}F]^-$. Eight-membered units have a corresponding low negative charge density and are among the biggest building blocks commonly encountered in fluoro-gallophosphates; a bigger enneameric unit is however present in MIL-1[35] in conjunction with a very bulky aza-crown ether. The characteristics of the framework of $Ga_4(PO_4)_4F\cdot N_2C_7H_{11}\cdot {}^1/_2H_2O$ are therefore in accordance with the formation mechanism proposed by Férey.[8] Attempts to synthesize and fully characterize new gallophosphates with other amino-pyridine templates are in progress.

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