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New potential open-framework materials in gallophosphate systems. Preparation and crystal structure of $[NH_3(CH_2)_3NH_3]Ga_3(PO_4)_3(OH)_2 \cdot H_2O$ and $[NH_2(CH_2)_3NH_2]Ga_3(PO_4)_3(H_2O)$

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The synthesis and the structure of two new gallium phosphates $[NH_3(CH_2)_3NH_3]Ga_3(PO_4)_3(OH)_2 \cdot H_2O$ (GaP1) space group *Pcab*, $a = 10.043(3)$, $b = 15.989(4)$, $c = 18.308(6)$ Å and $[NH_2(CH_2)_3NH_2]Ga_3(PO_4)_3(H_2O)$ (GaP2) space group $Pbc2_1$, $a = 8.903(3)$, $b = 9.697(3)$, $c = 16.326(7)$ Å are presented. The syntheses were realised under hydrothermal conditions at 200 °C in the system Ga_2O_3–H_3PO_4–1,3-diaminopropane–H_2O. These two compounds crystallise with a 3D-framework, with localised channels. In the GaP2 structure, 1,3-diaminopropane (1,3-DAP) is, unusually, coordinated to a gallium atom.

Introduction

Since the discovery of the $AlPO_4$-*n* molecular sieves in 1982,[1] numerous phosphate-based microporous materials have been synthesised. One of the most important breakthroughs in this field was provided by Guth and Kessler who developed the fluoride method.[2] The introduction of fluoride ions in the medium appears to improve the crystallisation at acidic and neutral pH. These ions can either be inserted in the cages of the microporous structure or participate in the framework, leading to a large variety of new topologies as shown by Férey's group.[3]

However, the simultaneous presence of fluoride and hydroxy ions in numerous structures {*e.g.* $NH_4AlPO_4(OH)_{0.3}F_{0.7}$,[4] $[C_6N_2H_{14}]Ga_3(PO_4)(HPO_4)_2F_3(OH) \cdot 0.5H_2O$[5] and $[NH_3(CH_2)_6NH_3]_4Ga_{16}(PO_4)_{14}(HPO_4)_2F_7(OH)_2 \cdot 6H_2O$[6]} suggests that isostructural materials to the fluoride-containing microporous compounds can be prepared containing only hydroxy ions, since OH^- is isoelectronic with F^-. We report here, the preparation and the structural study of two new gallium phosphates obtained without fluorine: $[NH_3(CH_2)_3NH_3]Ga_3(PO_4)_3(OH)_2 \cdot H_2O$ (GaP1) and $[NH_2(CH_2)_3NH_2]Ga_3(PO_4)_3(H_2O)$ (GaP2). GaP1 is isostructural with $[NH_3(CH_2)_3NH_3]Ga_3(PO_4)_3F_2 \cdot H_2O$ prepared by Férey and coworkers.[7]

Experimental

The synthesis was performed under hydrothermal conditions. A mixture was prepared of Ga_2O_3 (0.188 g), H_3PO_4 (0.95 g), 1,3-diaminopropane (1,3-DAP) (0.30 g) and water (10 mL). After 4 days at 200 °C, under autogenous pressure in an autoclave, the mixture was filtered off, washed with water and air dried. The pH was equal to 5 at the end of the reaction. According to X-ray powder diffraction, two crystalline products, GaP1 and GaP2, were obtained with their formulae deduced from the structure determinations.

Suitable crystals were selected for both GaP1 and GaP2 and their structures determined by four-circle single-crystal X-ray diffractometry. Data were collected on an Enraf-Nonius CAD4 automatic diffractometer. Lattice parameters were refined with a least-squares method using 25 reflections. Space groups were determined from the examination of systematic reflection conditions. The structures were solved by interpretation of the Patterson map obtained with SHELXS,[8] and difference Fourier syntheses with anisotropic displacement factors for all the non-hydrogen atoms.[9] Refinements were against F^2. Refinement calculations were performed with the weighting schemes given in Tables 1 and 2 for GaP1 and GaP2, respectively. Empirical absorption corrections were applied.[10]

The X-ray powder patterns could be indexed on the basis of the two crystal structures.

Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, 2000, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/195. See http://www.rsc.org/suppdata/jm/a9/a905099j/ for crystallographic files in .cif format.

Results

Structure of $[NH_3(CH_2)_3NH_3]Ga_3(PO_4)_3(OH)_2 \cdot H_2O$ (GaP1)

Crystal data, conditions of data collection and refinement are reported in Table 1. Fractional atomic coordinates are listed in Table 3 while selected bond distances and angles are given in Table 4.

This compound is isostructural with the compound ULM-3, $[H_3N(CH_2)_3NH_3]Ga_3(PO_4)_3F_2 \cdot H_2O$, prepared and studied by Férey and coworkers. In this structure, polyhedra around Ga1 and Ga3 are trigonal bipyramids while the polyhedron around Ga2 is an octahedron. As expected, the longest Ga–O distances are observed for the highest coordination number being in the range 1.920–1.997 Å in the octahedron. For Ga1 and Ga3, the trigonal bipyramids are axially elongated and severely distorted in the equatorial plane with angles ranging from 111.1 to 135.9° for Ga1 and from 108.5 to 136.2° for Ga3. In all three environments, the variation of bond distances and the polyhedral deformations are much more marked in the present compound than in ULM-3.

Gallium atoms are linked together *via* phosphate groups and *via* the hydroxy groups O13 and O14 (*cf.* fluorine atoms in

Table 1 Crystal data, data collection and structure refinement for GaP1

Formula	$[NH_3(CH_2)_3NH_3]Ga_3(PO_4)_3(OH)_2 \cdot H_2O$
Colour/shape	Colourless/lozenge
Maximum crystal dimensions/mm	0.25 × 0.25 × 0.125
M	622.25
Space group	*Pcab*
T/K	293
Cell constants a, b, c/Å	10.043(3), 15.989(4), 18.308(6)
V/Å^3	2939.9(15)
Z	8
D_c/g cm^{-3}	2.812
μ(Mo-Kα)/mm^{-1}	5.878
Diffractometer/scan mode	Enraf-Nonius CAD4/ω–2θ
Wavelength, λ(Mo-Kα)/Å	0.71073
Monochromator	Graphite
Scan width/°	$0.80+0.35\tan\theta$
θ range for data collection/°	0–30
Range of h, k, l	0–14, 0–22, 0–25
Standard control reflections	(3 7 11) (−3 −1 5) (−2 4 −1)
Decay of standards (%)	<1
Reflections collected	4266
Reflections observed	2269 $[F_o > 4\sigma(F_o)]$
Structure refinement	SHELXL97
Structure solution	SHELXS97
No. of refined parameters	210
Secondary extinction factor	0.00050(11)
Weights	$1/[\sigma^2(F_o^2)+(0.0775P)^2+0P]$ where $P=(F_o^2+2F_c^2)/3$
Goodness-of-fit on F^2	1.197
R	0.0436 (0.1277 for all data)
wR	0.1164 (0.1352 for all data)
Largest peak and hole/e Å^{-3}	1.85/−1.85

ULM-3). The GaO_6, GaO_5 and PO_4 units are linked together giving rise to a building unit of composition $[Ga_3(PO_4)_3(OH)_2]^{2-}$ as shown in Fig. 1. The Ga1···Ga2 and Ga2···Ga3 distances are 3.490 and 3.379 Å, respectively.

The connection of these units generates a 3D-framework in which channels are observed in the [100] direction (Fig. 2). The dimensions of these channels are 9.155 Å (between O6 oxygen atoms) and 8.021 Å (between O9 oxygen atoms). We were not able to locate hydrogen atoms on the 1,3-DAP moieties but we assume the presence of diprotonated 1,3-DAP to ensure electroneutrality. Water molecules and 1,3-DAP dications are localised in the channels. The nitrogen atom N2 of the 1,3-DAP dication of GaP1 occupies two crystallographic sites (N21 and N22), with equal occupancies (0.50:0.50). It is common to observe disorder in terminal nitrogen atoms of structure directing organic amines used for hydrothermal synthesis of microporous compounds.[11]

Table 2 Crystal data, data collection and structure refinement for GaP2

Formula	$[NH_2(CH_2)_3NH_2]Ga_3(PO_4)_3(H_2O)$
Colour/shape	Colourless/platelet
Maximum crystal dimensions/mm	0.425 × 0.175 × 0.075
M	586.2
Space group	$Pbc2_1$
T/K	293
Cell constants a, b, c/Å	8.903(3), 9.697(3), 16.326(7)
V/Å^3	1409.5(9)
Z	4
D_c/g cm^{-3}	2.763
μ(Mo-Kα)/mm^{-1}	6.11
Diffractometer/scan mode	Enraf-Nonius CAD4/ω–2θ
Wavelength, λ(Mo-Kα)/Å	0.71073
Monochromator	Graphite
Scan width/°	$0.80+0.35\tan\theta$
θ range for data collection/°	2–30
Range of h, k, l	0–12, 0–13, 0–23
Standard control reflections	(4 0 −6) (0 4 −1) (−4 3 −3)
Decay of standards (%)	<1
Reflections collected	2119
Reflections observed	1876 $[F_o > \sigma(F_o)]$
Structure refinement	SHELXL97
Structure solution	SHELXS97
No. of refined parameters	217
Secondary extinction factor	0.0056(8)
Weights	$1/[\sigma^2(F_o^2)+(0.0803P)^2+0P]$ where $P=(F_o^2+2F_c^2)/3$
Flack x parameter	0.005(19)
Goodness-of-fit on F^2	0.776
R	0.0233 (0.0384 for all data)
wR	0.0659 (0.1149 for all data)
Largest peak and hole/e Å^{-3}	1.86/−1.74

Structure of $[NH_2(CH_2)_3NH_2]Ga_3(PO_4)_3(H_2O)$

Crystal data, conditions of data collection and refinement are reported in Table 2. Fractional atomic coordinates are listed in Table 5 while selected bond distances and angles are given in Table 6.

The gallium atoms show three different coordination spheres: GaO_5N, GaO_5 and GaO_4. The first surrounding corresponds to a slightly distorted octahedron with a mean Ga–O distance of 1.967 Å and a longer Ga–N distance

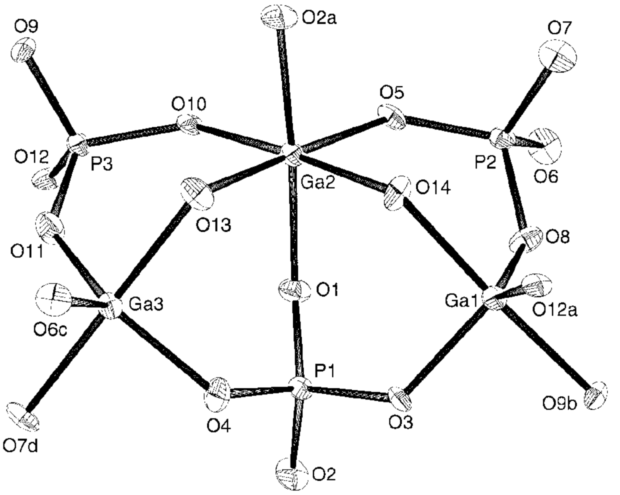

Fig. 1 ORTEP view of the building unit of GaP1, $[Ga_3(PO_4)_3(OH)_2]^{2-}$.

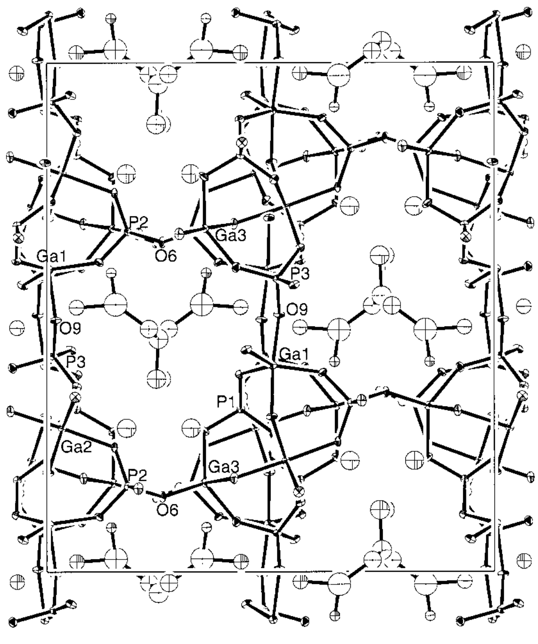

Fig. 2 View of the unit cell of GaP1 along the [100] direction.

Table 3 Fractional atomic coordinates and equivalent thermal parameters for GaP1

Atom	x	y	z	U_{eq}/Å^2
Ga1	0.34755(6)	0.99491(4)	0.40569(3)	0.00769(15)
Ga2	0.31552(7)	0.96521(4)	0.21765(4)	0.00779(16)
Ga3	0.16442(7)	1.14742(4)	0.17452(3)	0.00806(16)
P1	0.11577(15)	1.06658(10)	0.31906(8)	0.0071(3)
P2	0.33959(15)	0.81904(10)	0.33169(8)	0.0072(3)
P3	0.13779(15)	0.98475(10)	0.07580(8)	0.0076(3)
O1	0.1470(4)	0.9912(3)	0.2710(2)	0.0104(8)
O2	−0.0300(4)	1.0635(3)	0.3434(2)	0.0124(9)
O3	0.2032(4)	1.0681(3)	0.3885(2)	0.0115(9)
O4	0.1417(5)	1.1490(3)	0.2770(2)	0.0138(9)
O5	0.3025(4)	0.8490(3)	0.2552(2)	0.0099(9)
O6	0.2567(5)	0.7421(3)	0.3526(2)	0.0114(9)
O7	0.4884(4)	0.7958(3)	0.3361(2)	0.0126(9)
O8	0.3034(4)	0.8834(3)	0.3918(2)	0.0108(9)
O9	0.2190(4)	0.9802(3)	0.0052(2)	0.0093(9)
O10	0.2075(4)	0.9332(3)	0.1358(2)	0.0087(9)
O11	0.1168(5)	1.0768(3)	0.0984(2)	0.0131(9)
O12	−0.0015(4)	0.9462(3)	0.0634(2)	0.0098(9)
O13	0.3293(4)	1.0819(3)	0.1839(2)	0.0119(9)
O14	0.4115(4)	0.9972(3)	0.3047(2)	0.0108(9)
Ow	0.5101(7)	0.6780(4)	0.2177(4)	0.0470(17)
N1	0.3321(9)	0.7555(6)	0.1208(5)	0.049(2)
N21	0.4714(11)	0.8563(7)	−0.0872(6)	0.014(2)
N22	0.4965(15)	0.9333(9)	−0.0197(8)	0.031(3)
C2	0.4953(11)	0.7722(6)	0.0223(5)	0.042(2)
C1	0.3526(12)	0.7510(8)	0.0417(6)	0.052(3)
C3	0.5147(14)	0.8464(9)	−0.0253(8)	0.072(4)

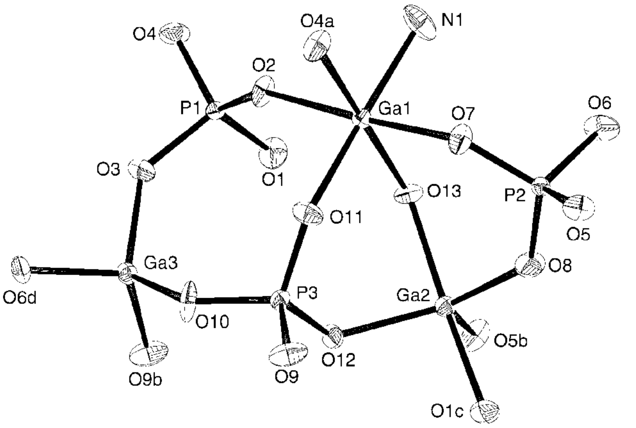

Fig. 3 ORTEP view of the building unit of GaP2, [$Ga_3(PO_4)_3(H_2O)(1,3\text{-}DAP)$].

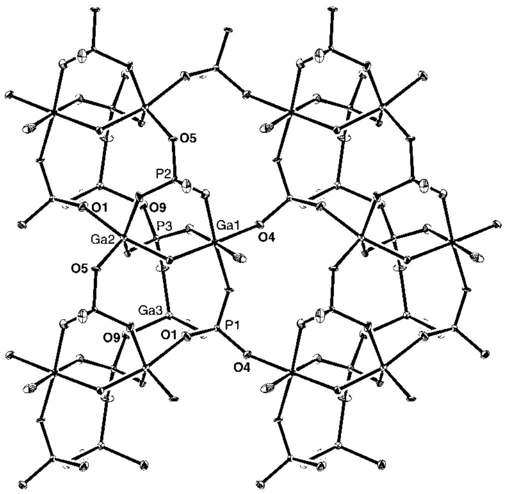

Fig. 4 View of the 'layers' parallel to the plane (001).

(2.056 Å). This latter bond is established with the diamine which acts as a monodentate ligand. The pentacoordination of Ga2 corresponds to a very distorted trigonal bipyramid. Axial elongation is always observed in this type of gallium environment but the substantial distortion in the equatorial plane, as also observed in GaP1, is unusual. The GaO_4 environment of Ga3, is of a fairly regular tetrahedron. The co-existence of these three coordination modes for gallium in one structure has already been observed, for example in $[C_{10}H_{16}N_2]Ga_7(PO_4)_6F_3(OH)_2\cdot(H_2O)_2$[12] and $[C_{12}H_{27}N_2]Ga_5(PO_4)_4(HPO_4)_2F_2$.[13]

The phosphorus atoms are tetrahedrally coordinated with P–O bond lengths in the range 1.517–1.542 Å and are comparable to those seen in other gallium phosphate compounds.

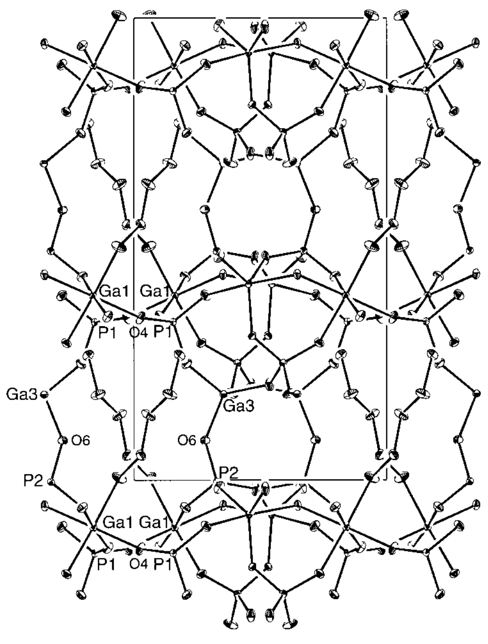

Fig. 5 Projection of the three-dimensional network of GaP2 along the [010] direction.

Table 4 Selected interatomic distances (Å) and angles(°) for GaP1^a

Around Ga1					
Ga1–O8	1.854(5)	Ga1–O9b	1.955(4)		
Ga1–O12a	1.872(4)	Ga1–O14	1.958(4)		
Ga1–O3	1.889(4)				
O8–Ga1–O12a	135.9(2)	O3–Ga1–O9b	88.15(18)		
O8–Ga1–O3	112.9(2)	O8–Ga1–O14	88.10(19)		
O12a–Ga1–O3	111.1(2)	O3–Ga1–O14	94.75(19)		
O8–Ga1–O9b	85.98(18)	O12a–Ga1–O14	90.63(18)		
O12a–Ga1–O9b	93.18(18)	O9b–Ga1–O14	174.05(19)		
Around Ga2					
Ga2–O10	1.920(4)	Ga2–O13	1.970(4)		
Ga2–O14	1.931(4)	Ga2–O5	1.986(4)		
Ga2–O2a	1.967(4)	Ga2–O1	1.997(4)		
O10–Ga2–O14	175.44(19)	O2a–Ga2–O13	89.26(19)	O10–Ga2–O1	87.60(18)
O10–Ga2–O2a	86.56(18)	O10–Ga2–O5	89.05(19)	O14–Ga2–O1	87.98(19)
O14–Ga2–O2a	97.86(19)	O14–Ga2–O5	89.70(19)	O2a–Ga2–O1	174.16(18)
O10–Ga2–O13	92.76(18)	O2a–Ga2–O5	91.76(19)	O13–Ga2–O1	90.92(19)
O14–Ga2–O13	88.43(19)	O13–Ga2–O5	177.98(18)	O5–Ga2–O1	88.24(18)
Around Ga3					
Ga3–O6c	1.843(4)	Ga3–O13	1.967(5)		
Ga3–O11	1.857(5)	Ga3–O7d	1.996(4)		
Ga3–O4	1.890(4)				
O6d–Ga3–O11	115.3(2)	O4–Ga3–O13	91.24(19)		
O6d–Ga3–O4	108.5(2)	O6d–Ga3–O7d	92.6(2)		
O11–Ga3–O4	136.2(2)	O11–Ga3–O7d	88.57(19)		
O6d–Ga3––O13	92.1(2)	O4–Ga3–O7d	89.1(2)		
O11–Ga3–O13	87.64(19)	O13–Ga3–O7d	174.85(19)		
Around P1					
P1–O1	1.526(5)	O1–P1–O2	109.8(3)	O1–P1–O4	110.5(3)
P1–O2	1.531(5)	O1–P1–O3	111.7(2)	O2–P1–O4	109.5(3)
P1–O3	1.545(4)	O2–P1–O3	107.7(2)	O3–P1–O4	107.5(3)
P1–O4	1.548(5)				
Around P2					
P2–O5	1.526(5)	O5–P2–O6	110.3(3)	O5–P2–O8	112.7(3)
P2–O6	1.534(5)	O5–P2–O7	111.1(3)	O6–P2–O8	103.2(2)
P2–O7	1.542(5)	O6–P2–O7	108.7(3)	O7–P2–O8	110.5(3)
P2–O8	1.551(4)				
Around P3					
P3–O9	1.530(4)	O9–P3–O10	109.5(2)	O9–P3–O12	109.8(2)
P3–O10	1.541(4)	O9–P3–O11	110.2(3)	O10–P3–O12	107.6(3)
P3–O11	1.543(5)	O10–P3–O11	112.4(2)	O11–P3–O12	107.2(3)
P3–O12	1.545(4)				
1,3-Diaminopropane					
N1–C1	1.465(14)	N1–C1–C2	110.7(9)		
N21–C3	1.225(16)	C3–C2–C1	116.1(10)		
N22–C3	1.405(19)	N21–C3–C2	126.9(13)		
C2–C3	1.485(17)	N22–C3–C2	137.0(13)		
C2–C1	1.515(15)	N21–C3–N22	83.9(12)		
Short contacts between Ow or 1,3-DAP and the framework					
Ow–N1	2.806(5)	N1–O5	2.895(7)	N21–O13h	2.846(5)
Ow–O7	2.882(6)	N21–O8f	2.824(8)	N22–O9i	2.922(8)
Ow–O13e	2.984(5)	N21–O7g	2.836(5)		

^{a}Symmetry transformations; a: $x+1/2$, $-y+2$, $-z+1/2$, b: $1/2-x$, y, $1/2+z$, c: x, $y+1/2$, $-z+1/2$, d: $x-1/2$, $-y+2$, $-z+1/2$, e: x, $y-1/2$, $1/2-z$, f: $1/2-x$, y, $z-1/2$, g: $1-x$, $3/2-y$, $z-1/2$, h: $1-x$, $2-y$, z, i: $x-1/2$, $2-y$, $1/2-z$.

The asymmetric building unit is [$Ga_3(PO_4)_3(H_2O)$(1,3-DAP)] (Fig. 3) in which Ga1 and Ga2 are connected by the oxygen atom O13 of the water molecule resulting in a shortest Ga···Ga distance of 3.465 Å. Such a situation, in which a water molecule bridges two metal atoms, has already been observed in iron phosphates, [DABCO]$Fe_4(PO_4)_4F_2(H_2O)_3$[14] and [$NH_3(CH_2)_3NH_3$]$Fe_4(PO_4)(HPO_4)_4F_3(H_2O)_4$.[15]

The three independent phosphate groups act as bridging ligands in this unit. Finally, all the oxygen atoms of the phosphate groups are coordinated to a gallium atom which results in a three-dimensional network. In these, asymmetric units are connected along [010] by oxygen atoms O1, O5 and O9 to create puckered chains, which in turn are connected by O4 to form 'layers' parallel to the (001) plane (Fig. 4). Linking of these 'layers', connected to each other by oxygen atoms O6, leads to the formation of a three-dimensional framework (Fig. 5). Channels are located along the *b* axis the largest and shortest dimensions of which are 8.490 Å (between O4 oxygen

Table 5 Fractional atomic coordinates and equivalent thermal parameters for GaP2

Atom	x	y	z	U_{eq}/Å^2
Ga1	0.83952(8)	0.80129(8)	0.3980	0.00725(19)
Ga2	0.45414(8)	0.82132(8)	0.42499(7)	0.00749(18)
Ga3	0.64590(8)	0.52076(8)	0.18569(7)	0.00795(19)
P1	0.84528(18)	0.47224(18)	0.34223(13)	0.0065(3)
P2	0.6727(2)	1.04363(18)	0.49615(13)	0.0068(3)
P3	0.5909(2)	0.81684(18)	0.25283(13)	0.0075(3)
O1	0.7161(6)	0.4413(6)	0.4000(4)	0.0141(10)
O2	0.8972(6)	0.6207(5)	0.3542(4)	0.0109(10)
O3	0.7912(7)	0.4538(6)	0.2516(4)	0.0139(10)
O4	0.9741(6)	0.3703(6)	0.3514(4)	0.0141(11)
O5	0.6628(6)	1.2001(5)	0.4840(4)	0.0125(11)
O6	0.7191(6)	1.0197(7)	0.5857(4)	0.0173(12)
O7	0.7966(6)	0.9889(6)	0.4409(4)	0.0135(10)
O8	0.5201(6)	0.9781(6)	0.4809(4)	0.0165(12)
O9	0.5373(6)	0.9466(6)	0.2067(4)	0.0158(11)
O10	0.6177(7)	0.7058(6)	0.1875(4)	0.0169(11)
O11	0.7337(6)	0.8535(6)	0.2971(4)	0.0126(10)
O12	0.4684(6)	0.7668(6)	0.3123(4)	0.0108(10)
O13	0.6475(5)	0.7342(6)	0.4450(4)	0.0103(10)
N1	0.9415(8)	0.7424(8)	0.5055(5)	0.0192(14)
N2	1.1801(7)	0.8687(7)	0.7707(4)	0.0127(12)
C1	1.0271(8)	0.8445(9)	0.5537(5)	0.0147(14)
C2	1.0570(10)	0.7945(9)	0.6409(6)	0.0203(16)
C3	1.1416(9)	0.9101(10)	0.6857(6)	0.0213(16)

Table 6 Selected interatomic distances (Å) and angles(°) for GaP2.

Around Ga1					
Ga1–O4a	1.944(5)	Ga1–O13	1.983(5)		
Ga1–O2	1.960(5)	Ga1–O7	1.986(6)		
Ga1–O11	1.964(6)	Ga1–N1	2.056(7)		
O4a–Ga1–O2	86.6(2)	O11–Ga1–O13	89.8(2)	O4a–Ga1–N1	93.0(3)
O4a–Ga1–O11	89.6(2)	O4a–Ga1–O7	89.2(2)	O2–Ga1–N1	87.0(3)
O2–Ga1–O11	92.9(2)	O2–Ga1–O7	175.8(2)	O11–Ga1–N1	177.4(3)
O4a–Ga1–O13	178.9(2)	O11–Ga1–O7	88.1(2)	O13–Ga1–N1	87.7(3)
O2–Ga1–O13	94.2(2)	O13–Ga1–O7	89.9(2)	O7–Ga1–N1	92.2(3)
Around Ga2					
Ga2–O5b	1.842(6)	Ga2–O13	1.946(5)		
Ga2–O8	1.868(6)	Ga2–O1c	1.954(5)		
Ga2–O12	1.919(6)				
O5b–Ga2–O8	116.2(3)	O12–Ga2–O13	89.0(2)		
O5b–Ga2–O12	111.3(3)	O5b–Ga2–O1c	92.9(2)		
O8–Ga2–O12	132.2(3)	O8–Ga2–O1c	82.1(3)		
O5b–Ga2–O13	97.8(2)	O12–Ga2–O1c	90.8(3)		
O8–Ga2–O13	89.6(2)	O13–Ga2–O1c	168.6(2)		
Around Ga3					
Ga3–O3	1.804(6)	Ga3–O10	1.812(6)		
Ga3–O6d	1.801(6)	Ga3–O9b	1.815(5)		
O3–Ga3–O6d	101.7(3)	O3–Ga3–O9b	112.9(3)		
O3–Ga3–O10	116.5(3)	O6d–Ga3–O9b	114.2(3)		
O6d–Ga3–O10	106.3(3)	O10–Ga3–O9b	105.4(3)		
Around P1					
P1–O1	1.517(6)	O1–P1–O2	109.7(3)	O2–P1–O3	108.8(3)
P1–O2	1.524(5)	O1–P1–O4	112.4(4)	O4–P1–O3	104.5(3)
P1–O4	1.521(5)	O2–P1–O4	111.9(3)	O1–P1–O3	109.3(3)
P1–O3	1.566(6)				
Around P2					
P2–O8	1.520(6)	O8–P2–O7	113.9(4)	O8–P2–O5	110.0(3)
P2–O7	1.521(6)	O8–P2–O6	109.4(4)	O7–P2–O5	108.1(3)
P2–O6	1.537(6)	O7–P2–O6	108.5(3)	O6–P2–O5	106.7(4)
P2–O5	1.533(6)				
Around P3					
P3–O11	1.505(6)	O11–P3–O10	111.6(4)	O11–P3–O9	107.6(3)
P3–O10	1.534(6)	O11–P3–O12	111.8(3)	O10–P3–O9	106.4(4)
P3–O12	1.539(5)	O10–P3–O12	109.1(3)	O12–P3–O9	110.2(3)
P3–O9	1.542(6)				
1,3-Diaminopropane					
N1–C1	1.477(10)	N1–C1–C2	112.0(7)		
N2–C3	1.485(11)	C1–C2–C3	107.3(7)		
C1–C2	1.526(12)	N2–C3–C2	111.2(7)		
C2–C3	1.536(13)				

[a]Symmetry transformations; a: $-x+2$, $y+1/2$, z, b: $-x+1$, $y-1/2$, z, c: $-x+1$, $y+1/2$, z, d: x, $-y+3/2$, $z-1/2$.

atoms) and 6.966 Å (between O6 oxygen atoms). The 1,3-DAP ligand, coordinated to Ga1 by the nitrogen atom N1, extends into the channels.

Discussion

Attempts are underway to obtain GaP1 and GaP2 separately and the time of reaction seems to be an important parameter. For a reaction time of one day, both GaP1 and GaP2 form with GaP1 as the major phase. This is consistent with the preparation of ULM-3, which is isostructural to GaP1, after one day. A four day reaction leads to the same products but GaP2 was now the main phase. Finally, if the reaction time is lengthened to one week, two products crystallise, GaP2 and $GaPO_4 \cdot 2H_2O$ (monoclinic, $a = 9.754$, $b = 9.639$, $c = 9.690$ Å, $\beta = 102.87°$, JCPDS file 22-1106). This series of synthesis has been repeated with a large variation in the Ga : P : amine ratios without altering the observed results. Thus, it seems that the so-obtained microporous materials are metastable phases which form prior to the stable phosphate.

The synthesis of these new gallium phosphates can be examined in the light of the general discussion, by Férey, on the design of new microporous compounds. Fluoride anions has been used in numerous syntheses and have been shown to act as a mineraliser in crystallizing microporous materials in acidic or neutral media. The present study shows that a given microporous structure obtained with fluorine can be reproduced without use of F^-. However, as previously suggested,[7] the fluoride ion seems to induce more homogeneous and better crystallised phases. The reaction with F^- leads to a unique compound ULM-3 while the synthesis without F^- gives two phases. Moreover, a thorough study of the structures shows a higher disorder in the compounds prepared without F^-.

pH is a very important parameter in these systems. In the series ULM-*n*, a variation of pH between 1 and 10 led to the following conclusions. Whatever the pH, the amine is diprotonated and non-coordinated. The linkages of the coordination polyhedra are influenced by the pH with trigonal bipyramids and octahedra being the only environments observed at medium pH. The present study shows that the situation may be less straightforward. Indeed, two rather different architectures are obtained at the same pH. GaP1, isostructural with ULM-3, is as expected, according to Férey *et al.* but GaP2 is not. Indeed, at pH 5, three types of polyhedra: tetrahedra, trigonal bipyramids and octahedra, are present in the same structure. However, this is not the first example of such a situation having already been observed for $[C_{10}H_{16}N_2]Ga_7(PO_4)_6F_3(OH)_2(H_2O)_2$[12] prepared at pH 5.5 and for $[C_{12}H_{27}N_2]Ga_5(PO_4)_4(HPO_4)_2F_2$[13] prepared at pH 6. The most remarkable feature in the GaP2 structure is, however, the coordination of the neutral amine. To our knowledge, it is the first example of such a situation in microporous structures. Generally in such compounds condensation giving rise to the solid is thought to occur between neutral units formed by the pairing of the building unit, with a formal charge of -2, and a diprotonated amine. In GaP2, the building unit is neutral and condensation occurs through the connection of oligomeric neutral phosphate complexes.

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