A New Organic-Inorganic Hybrid Gallophosphate Prepared in the Presence of Glycine

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A new layered gallophosphate, $Ga_4P_4O_{16}(C_2H_5NO_2)_4$, known as Mu-32 has been synthesised hydrothermally using the amino acid glycine ($H_2NCH_2CO_2H$) as an original template. Such a template has never been used before for the synthesis of microporous and phosphate-based materials such as gallophosphates. The structure was determined by a single-crystal X-ray diffraction study and further characterised by scanning electron microscopy, elemental and thermal analyses and by ^{13}C and ^{31}P solid-state NMR spectroscopy. The compound crystallises in the monoclinic space group $P2_1/c$ with a = 9.177(2), b = 5.1540(10), c = 12.513(3) Å and β = 90.67(3)°. The inorganic layer is built up from four-membered rings sharing T–O–T bonds. In addition to the nature of the template, the original properties of this new gallophosphate come from the coordination environment of the Ga which is only pentacoordinated with oxygen atoms and has strong bonds (Ga–O–C) between the organic template and the inorganic sheet.
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Introduction

During the last decade, extensive investigations by numerous researchers have given rise to many new open-framework materials.[1] Among these, the aluminophosphates,[2−6] gallophosphates[7−13] and zincophosphates[14−18] appear to be the most studied. These materials are typically synthesised under hydrothermal or solvothermal conditions in the presence of various organic amines as structure-directing agents. In several cases, the introduction of fluoride ions is crucial for the formation of the phosphate-based material.[19] F^- can act as a mineraliser, it can become trapped in the cages of the framework playing a templating role as shown in the fluorogallophosphate cloverite[20] or it may form a bridge between the atoms of the framework.[21] The amine molecules occupy the cavities or the channels of the framework and are usually removed by calcination of the synthesised sample. Most of the time, the organic molecules are hydrogen-bonded to the inorganic framework. They can also be directly linked to the inorganic structure via T−N or T−O−C bonds (T = Al, Zn,Ga, ...).[22,23] Such connections can be found, for instance, in the oxalate-phosphate[24,25] and -phosphonate systems where a P atom is directly linked to the carbon atom in PO_3R.[26−28] Aluminophosphates and gallophosphates showing such organic-inorganic bonds are rarely encountered. However, the use of the cyclam molecule (1,4,8,11-tetraazacyclotetradecane) as a structure-directing agent in these systems induces the crystallisation of such compounds (STA-6,[29] Cyclam-Co-$AlPO_4$,[30] Mu-5[31] and Mu-6[32]). It was shown, in the $AlPO_4$-SOD material synthesised in the presence of dimethylformamide, that the organic template is bonded to the inorganic framework via Al−O−C bonds.[33] More recently, bipyridine-gallophosphate hybrid materials have also been obtained.[34,35] In these compounds, Ga−N, F−N or Ga−O−Co−cyclam bonds have been revealed. The majority of the open-framework metal phosphates were synthesised in the presence of amines. To the best of our knowledge, there are no open-framework metal phosphates which have been prepared with bifunctional molecules such as amino acids (NH_2−R−COOH) as structure-directing agents.

In this paper, we describe the structure of a new layered gallophosphate, Mu-32, prepared with the amino acid glycine as an organic template. Its characterisation by thermal analysis, scanning electron microscopy and solid-state NMR spectroscopy is also reported.

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Results and Discussion

Synthesis and Crystal Morphology

The most characteristic synthetic results are summarised in Table 1. It has been shown that strongly acidic media are unfavourable for the formation of the gallophosphate Mu-32. Indeed a starting mixture with a pH of 1 induces the formation of a material called the "S phase" which is related to the mineral strengite (sample A, Table 1). Therefore TriPA was added in order to increase the initial pH to ca. 4−5.

With a TriPA/Ga_2O_3 molar ratio of 1.5 at 130 °C, the strengite phase crystallises (sample B, Table 1). It was necessary to increase the temperature to 170 °C in order to obtain large crystals of pure Mu-32 (sample C, Table 1). The influence of the gallium source was also studied. Instead of β-Ga_2O_3, the use of GaOOH (prepared by heating a gallium nitrate solution at 250 °C for 24 h) induces formation of larger crystals of Mu-32 but in this case, traces of an impurity can also be detected by XRD (sample D, Table 1). It should be noted that the presence of fluoride ions is of prime importance for the formation of Mu-32. They act as catalysts since their presence cannot be detected in the finally prepared material. On the other hand, β-Ga_2O_3 (sample E, Table 1) or a quartz-type gallophosphate is obtained (sample F, Table 1) in the absence of fluoride anions under similar reaction conditions and pH. Large crystals of Mu-32 display a hexagonal prismatic morphology as shown in Figure 1. Their average sizes are 150 × 830 × 980 μm.

The experimental XRD pattern of Mu-32 is reported in Figure 2 (a). For comparison, the simulated pattern calculated from the structural data is given in Figure 2 (b).

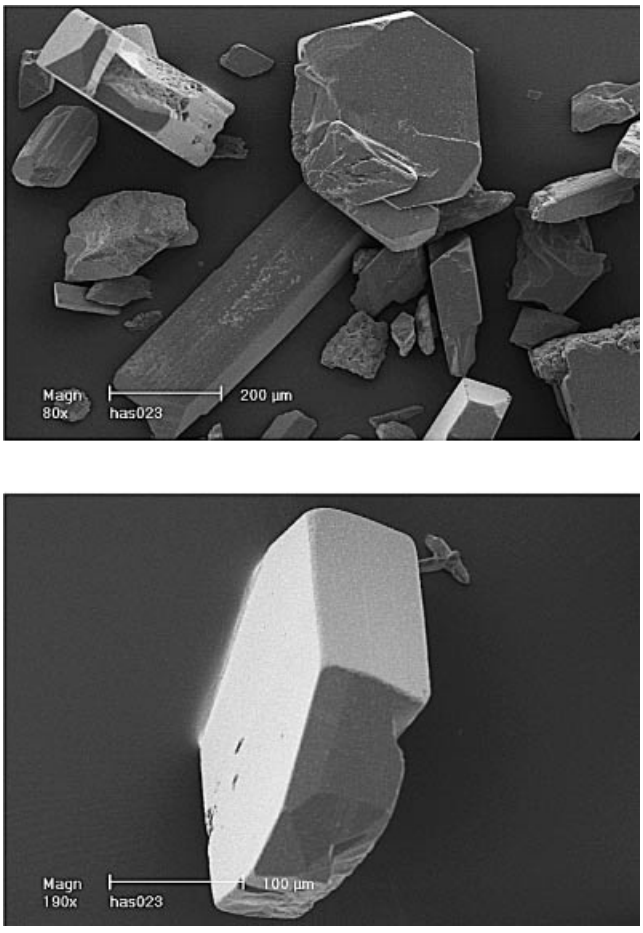

Figure 1. Scanning electron micrographs of some crystals of the gallophosphate Mu-32

Chemical Formula Determination

According to the microprobe and chemical analyses, the synthesised Mu-32 sample has Ga/P and C/N molar ratios close to 1 (Ga/P exp = 1.06) and 2 (C/N exp = 2.08), respectively. No fluoride was detected by scanning electron microprobe analysis.

The thermal behaviour of Mu-32 was investigated by TG/DTA thermal analyses. The TG and DTA curves of the material are given in Figure 3. The total weight loss occurs in two steps. The first occurs between 380 and 480 °C (23.8 wt%) and the second between ca. 480 °C and 1100 °C (3.8 wt%). The first weight loss is associated with the oxidation of the template (exothermic component on the DTA curve), consistent with the structure determination (weight loss expected: 27 wt%) and with a collapsing of the structure. The latter was confirmed by XRD analyses (not reported) recorded on an Mu-32 sample previously heated to 450 °C and by the presence in the DTA curve (reproducible) of an endotherm at about 450 °C. The second weight loss may correspond to dehydroxylation reactions including hydroxyl groups probably formed during the oxidation of the template by cleavage of the C(1)−O(3)−Ga(1) bonds (see struc-

Table 1. Synthesis performed using the system $Ga_2O_3/P_2O_5/x$HF/yTriPA/160H_2O

Sample	Composition of the starting gel		Crystallisation time [d]	Temp. [°C]	XRD results
	xHF	yTriPA [a]			
A	1	0	7	170	S phase[b]
B	1	1.5	7	130	S phase[b]
C	1	1.5	3	170	Mu-32
D[c]	1	1.5	7	170	Mu-32 + impurity[d]
E	0	0	7	170	β-Ga_2O_3
F	0	1.5	6	170	$GaPO_4$ quartz

[a] TriPA= tripropylamine (pH modifier). [b] Isostructural to the mineral strengite [(Fe,Al)PO_4·2H_2O, ICDD 15-0391]. [c] Gallium source: gallium oxyhydroxide, GaOOH. [d] Not identified, traces.

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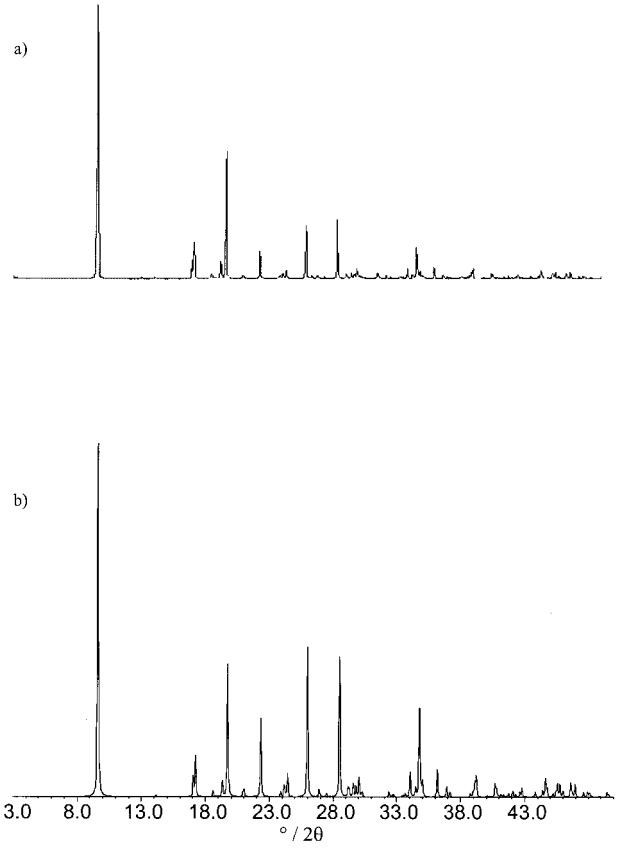

Figure 2. Experimental (a) and calculated (from crystal data) (b) XRD patterns of the gallophosphate Mu-32

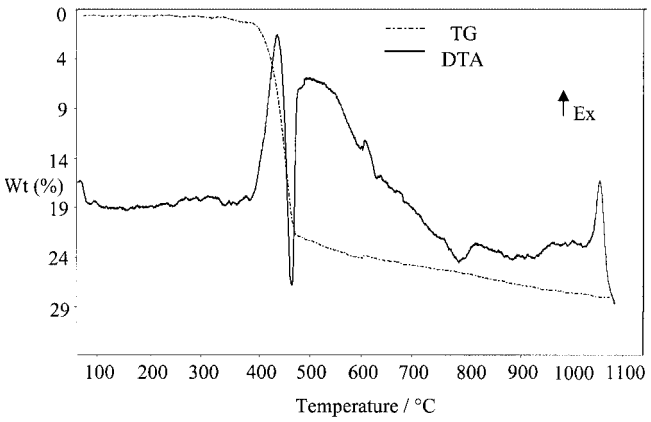

Figure 3. Thermal analyses (TG and DTA) of the gallophosphate Mu-32 under air

ture determination). After heating to 1000 °C, the XRD pattern of the sample showed that a cristobalite-type gallophosphate was formed (ICDD 89-3606). Its formation might also be the cause of the exothermic signal on the DTA curve at about 1050 °C. Taking into account the results of these analyses, the following unit cell formula can be proposed for the gallophosphate Mu-32: $Ga_4P_4O_{16}$-$(C_2H_5NO_2)_4$.

Structure Description

The framework of Mu-32 exhibits only four-membered rings formed by the alternation of Ga-centred trigonal pyramids (GaO_5) with P-centred tetrahedra (PO_4). This alternating pattern leads to the formation of an inorganic sheet parallel to the *bc* plane [Figure 4 (a)].

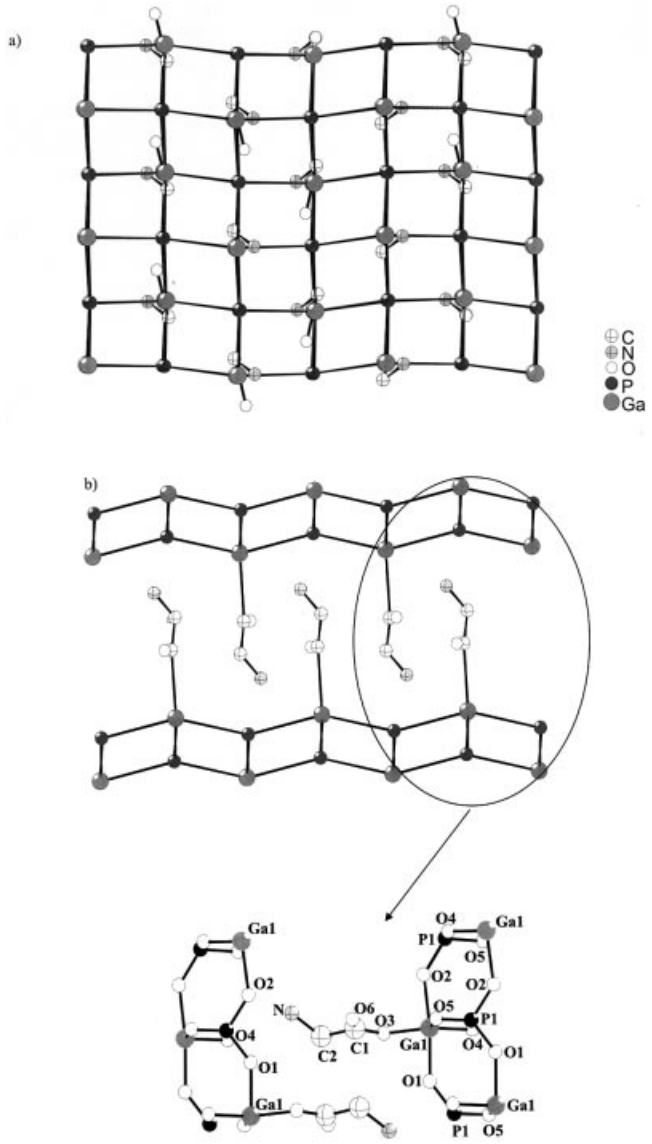

Figure 4. View along the [100] (a) and the [010] directions (b) of the framework of the gallophosphate Mu-32; oxygen atoms of the inorganic sheet are omitted for clarity

The most striking feature of this structure is the coordination sphere of each gallium atom. They are in pentacoordinate environments of oxygen atoms. Four oxygen atoms are shared with P-centred tetrahedra and the remaining one comes from the glycine template. The inorganic sheet interacts with the template via a hydrogen bond between its nitrogen atom and the O2 framework oxygen (bond length N···O2 = 2.821 Å) but also via a strong bond between its O3 oxygen (from OH group in the free glycine molecule) and the gallium atom of the inorganic layer (bond length

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O3···Ga1 = 1.913 Å) [Figure 4 (b)]. A bond valence calculation[36] performed on this O3 oxygen atom shows clearly that it corresponds to an oxygen atom and not to an OH group (Σs = 2.02, Table 2). The trigonal-pyramidal GaO_5 is quite regular since its angles, shown in Table 3, are close to the expected values of 90°, 120° and 180°. Nevertheless, it should be noted that the axial bonds of the pyramids, i.e. Ga1−O1 and Ga1−O2, are relatively longer than the equatorial ones, Ga1−O3, Ga1−O4 and Ga1−O5. In addition, the equatorial bond length Ga1−O3 is slightly longer than Ga−O4 and Ga−O5 since O3 bridges the gallium to the carbon atom C1. The phosphorus tetrahedra are quite regular with O−P−O angles in the range of 105.3(3)−111.9(3)°.

Table 2. Bond valence analysis of the gallophosphate Mu-32, according to Brown;[36] the 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; for C−O, $s = (d/R_0)^{-N}$ with R_0 = 1.37 and N = 4.4

Atoms	Ga1	P1	C1	Σs	Expected valence
O5	0.68	1.27		1.95	2
O4	0.67	1.22		1.89	2
O3	0.61		1.40	2.02	2
O2	0.55	1.29		1.84	2
O1	0.59	1.27		1.86	2
Σs	3.1	5.05			
Expected valence	3	5			

Table 3. Selected angles [°] in the gallophosphate Mu-32 (symmetry transformation used to generate equivalent atoms; #1: x, 0.5 − y, 0.5 + z; #2: $-x$, $-y$, 1 − z; #3: − x, 1 − y, 1 − z; #4: x, 0.5 − y, −0.5 + z

O5−Ga1−O4	114.46(9)	O1−P1−O4#3	110.81(12)
O5−Ga1−O3	123.88(10)	O2#1−P1−O4#3	108.51(12)
O4−Ga1−O3	121.63(10)	O5#2−P1−O4#3	108.49(13)
O5−Ga1−O1	93.09(10)	P1−O1−Ga1	134.87(16)
O4−Ga1−O1	91.81(11)	P1#4−O2−Ga1	137.77(16)
O3−Ga1−O1	87.18(11)	C1−O3−Ga1	121.73(25)
O5−Ga1−O2	91.06(10)	P1#3−O4−Ga1	134.98(13)
O4−Ga1−O2	91.86(11)	P1#2−O5−Ga1	128.31(14)
O3−Ga1−O2	85.59(11)	N−C2−C1	109.75(29)
O1−Ga1−O2	172.77(11)	O6−C1−O3	126.31(31)
O1−P1−O2#1	105.34(14)	O6−C1−C2	119.3(3)
O1−P1−O5#2	111.72(14)	O3−C1−C2	114.37(32)
O2#1−P1−O5#2	111.92(14)		

The structure of Mu-32 can be compared with that of the fluorogallophosphate ULM-9.[37] Although these 2D structures have different crystallographic data, they do have similar frameworks. Besides the conditions for their synthesis (structure-directing agent, ...), a difference can be observed in one of the equatorial bonds of the pentacoordinate gallium atom: the Ga−O−C bonds in Mu-32 are replaced by $Ga-F_{terminal}$ bonds in ULM-9.

NMR Spectroscopy

The ^{13}C CP MAS NMR spectra of the gallophosphate Mu-32 recorded at 4 kHz and 744 Hz display two isotropic chemical shifts at 45 (CH_2) and 160 ppm (C=O, oxygen O6) [Figure 5 (a and b)]. The resultant tensor associated with the carbonyl group cannot be decomposed into only one tensor. At least two tensors are necessary to reconstruct this part of the spectrum. Thus, the ^{13}C NMR spectrum enables the distinguishing of at least two kinds of carbonyl groups associated with the same isotropic chemical shift. It could reveal two different delocalisations of the electronic charge in the O6−C1−O3 bonds. Such a distinction cannot be observed by single-crystal XRD analysis.

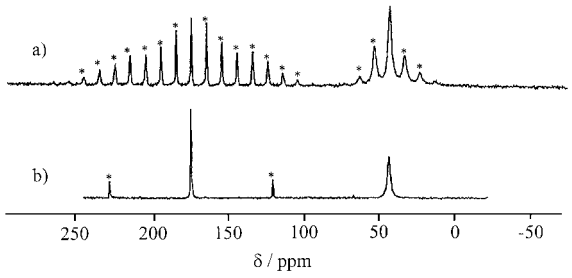

Figure 5. ^{13}C CP MAS NMR spectra of the gallophosphate Mu-32 recorded at 744 Hz (a), 4 kHz (b); * spinning side bands

The ^1H MAS NMR spectrum exhibits two signals at δ = 7.6 and 3.9 ppm (Figure 6). A decomposition allows the determination of the proportion of the different populations as 58 and 42%, respectively. These can be attributed to NH_3^+ and CH_2 groups, respectively, in agreement with the structure determination. The ^1H MAS NMR spectrum does not display a signal corresponding to an OH group (between δ = 9 and 12 ppm) which confirms that the glycine template is strongly bonded to the inorganic layer

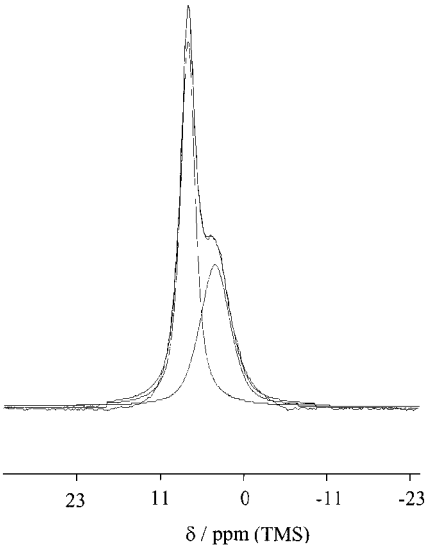

Figure 6. ^1H MAS NMR spectrum of the gallophosphate Mu-32; the two inner curves represent the decomposition of the spectrum

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through its oxygen atom O3 (OH group in the free glycine molecule).

The ^{31}P MAS NMR spectrum of Mu-32 displays only one signal located at $\delta = -9.2$ ppm (Figure 7) in agreement with the structural data in which only one crystallographic phosphorus site is present. Such a chemical shift value is similar to those traditionally observed for PO_4 groups in gallophosphates.[9,10]

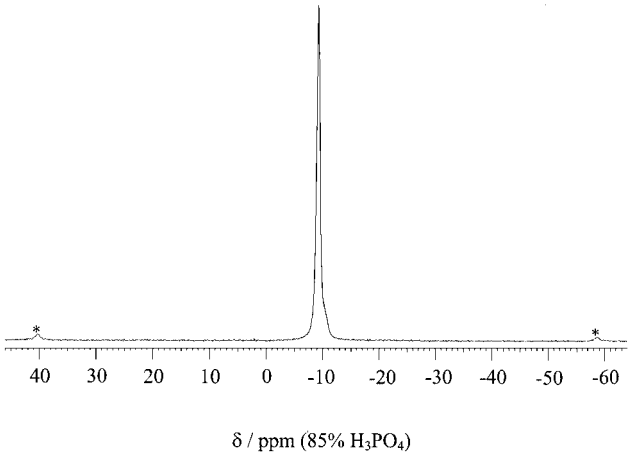

Figure 7. ^{31}P MAS NMR spectrum of the gallophosphate Mu-32; * spinning side bands

Conclusion

The gallophosphate Mu-32 shows several original features. The first is the nature of the template, i.e. the amino acid glycine, which has never been used before as a structure-directing agent in the synthesis of microporous and phosphate based materials such as gallophosphates. This work shows that under certain particular synthetic conditions, such an organic molecule can have a templating effect. The second feature comes from the coordination sphere of the gallium atoms. They are in pentacoordinate environments of oxygen atoms. Four oxygens are shared with P-centred tetrahedra and the last oxygen comes from the glycine template. The latter is, therefore, part of the framework.

Experimental Section

Synthesis: The reactants were glycine (Gly) (Fluka, 99%), phosphoric acid (Labosi, 85%) and hydrofluoric acid (Prolabo, 40%). The gallium source was the oxide β-Ga_2O_3 (ICDD 41-1103) obtained by heating a gallium nitrate solution to 250 °C for 24 h followed by calcination at 1000 °C for 6 h. Tripropylamine (TriPA) (Fluka, purum >98%) was used as a pH modifier. Previous experiments indicated that this amine does not play a templating role in the synthesis of gallophosphates in fluoride media.[31] Mu-32 was obtained by hydrothermal synthesis at 170 °C in a fluoride medium. The starting molar composition of the gel was: 1 Ga_2O_3/1 P_2O_5/1 HF/1 Gly/1.5 TriPA/160 H_2O. The gel was prepared by adding H_3PO_4 to the mixture of the gallium source and water with stirring. After a homogenisation time of 10 min, the amino acid glycine was introduced. Finally, the pH was adjusted to 4−5 with tripropylamine. The resultant gel was mixed at room temperature for 2 h and transferred to a 20-mL PTFE-lined stainless steel autoclave. The crystallisation was carried out at 170 °C under static conditions. After 3 d of heating, the product was recovered, washed with distilled water and dried at 60 °C overnight.

Structure Determination: On the basis of Weissenberg photographs, the powder XRD pattern of Mu-32 reported in Figure 2 (a) was indexed to the monoclinic crystal system, space group $P2_1/c$, with the following unit cell parameters: $a = 9.1766(3)$ Å, $b = 5.1520(16)$ Å, $c = 12.5093(4) =$ Å and $\beta = 90.6685(16)$. The structure was then determined by a single-crystal X-ray diffraction study using direct methods. A crystal with dimensions 200 × 90 × 50 μm was selected from the batch and mounted on a Picker 4-circle STOE diffractometer. 1036 reflections were recorded from 3.26° up to 24.95° in θ in the ω-scan mode, of which 1004 fulfilled the condition $I > 2\sigma(I)$. A summary of the experimental and crystallographic data is reported in Table 4. The structure was solved by direct methods using SHELXS-86[38] and refined using SHELXL-93.[39] The refinement converged to $R_1 = 0.0293$ $\{R_1 = \Sigma(F_o - F_c)/\Sigma F_o]$ and $wR_2 = 0.1041$ $\{R_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}\}$ for 1004 reflections $[I > 2\sigma(I)]$. Using direct methods, the positions of the Ga and P atoms were revealed and all the remaining atoms, except the hydrogen atoms, were located from successive Fourier maps. Hydrogen atoms were placed with geometrical constraints. None of the hydrogen atoms were refined with anisotropic displacement parameters. CCDC-236894 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail:

Table 4. Experimental and crystallographic data for the gallophosphate Mu-32

Chemical formula	$GaPO_4(C_2H_5NO_2)$
Crystal system	monoclinic
Crystal space group	$P2_1/c$
a [Å]	9.177(2)
b [Å]	5.1540(10)
c [Å]	12.513(3)
β [°]	90.67(3)
M [g.mol^{-1}]	894.8
Density (calcd.) [g ml^{-3}]	1.875
Cell volume [Å^3]	591.8(2)
Z (formula units/cell)	4
Crystal size [μm]	200 × 90 × 50
Diffractometer	PICKER 4-circle Stoe
Mo-K_α [Å]	0.71073
Absorption coefficient [mm^{-1}]	3.843
Absorption correction	not applied
$F(000)$	321
Data collection temperature [K]	293(2)
θ range [°]	3.26 to 24.95
(hkl)min., (hkl)max.	(−10,−6,−14), (10,0,0)
Independent reflections	1036
Observed reflections	1004
Data/restraints/parameters	1036/0/102
Residuals (observed data) $[I > 2\sigma(I)]$	$R1 = 0.0293$, $wR2 = 0.1041$
Residuals (all data)	$R1 = 0.0300$, $wR2 = 0.1062$
Goodness-of-fit (all data)	1.023
Largest diff. peak/hole [e·Å^{-3}]	1.395/−0.775

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deposit@ccdc.cam.ac.uk]. Selected bond angles and lengths are reported in Tables 3 and Table 5, respectively.

Table 5. Selected bond lengths [Å] in the gallophosphate Mu-32; symmetry transformation used to generate equivalent atoms: #1: x, 0.5 − y, 0.5 + z; #2: −x, −y, 1 − z; #3: − x, 1 − y, 1 − z; #4: x, 0.5 − y, −0.5 + z

Ga1−O5	1.873(3)	C2−N	1.476(18)
Ga1−O4	1.879(3)	C2−C1	1.519(7)
Ga1−O3	1.913(4)	C1−O6	1.223(4)
Ga1−O1	1.930(4)	O3−C1	1.270(6)
Ga1−O2	1.955(5)		
P1−O1	1.525(19)		
P1−O2#1	1.532(22)		
P1−O5#2	1.533(4)		
P1−O4#3	1.549(2)		

Characterisation: The powder XRD patterns were recorded with a STOE STADI-P diffractometer equipped with a curved germanium (111) primary monochromator and a linear position-sensitive detector using Cu-$K_{\alpha 1}$ radiation (λ = 1.5406Å). 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 with a Setaram Labsys thermoanalyser with a heating rate of 5 °C/min up to 1100 °C. At this final temperature, a white product was obtained indicating that the total amount of the organic template had been eliminated. The amounts of Ga, F and P in the gallophosphate Mu-32 were determined by scanning electron microprobe analysis with a Castaing type (CAMEBAX) electron microscope. Carbon and nitrogen quantities were determined by coulometric and catharometric methods, respectively. The ^{13}C CP MAS NMR spectrum was recorded with a Bruker MSL 300 spectrometer and the ^{1}H and ^{31}P MAS NMR spectra with a Bruker DSX 400 spectrometer. The recording conditions of the CP MAS and MAS spectra are given in Table 6.

Table 6. Recording conditions for the MAS and CP MAS NMR spectra

	^{13}C CP MAS	^{31}P MAS	^{1}H MAS
Chemical shift standard	TMS	85% H_3PO_4	TMS
Frequency [MHz]	75.47	161.98	400.14
Pulse width [μs]	3.7	3.5	5.8
Flip angle	π/2	π/2	π/2
Contact time [ms]	1	−	−
Recycle time [s]	8	30	8
Spinning rate [Hz]	5000	8000	20000
Number of scans	624	8	700

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