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Synthesis and X-Ray Structural Determination of a New Hydroxygallophosphate $Ga_3P_3O_{12}(OH)$, $H_3C{-}NH_2{-}CH_3$ Isotypic with $AlPO_4$-21

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$Ga_3P_3O_{12}(OH)$, $H_3C{-}NH_2{-}CH_3$ was obtained by hydrothermal synthesis (453 K, autogeneous pressure, 24 hr) from a mixture of Ga_2O_3, P_2O_5, HF, dimethylamine and H_2O in the ratio 1:1:2:2:80. It is monoclinic (space group $P2_1/n$ (No. 14)) with $a = 8.787(1)$ Å, $b = 17.783(3)$ Å, $c = 9.204(1)$ Å, $\beta = 109.56(1)°$, $V = 1355.2(5)$ Å^3, Z = 4. It belongs to the $AlPO_4$-21 (or $GaPO_4$–C4) structure type. The three-dimensional network is built up from corner-linked $[Ga_3(PO_4)_3(OH)]$ units composed of three PO_4 tetrahedra, two trigonal bipyramids, and one tetrahedron of gallium. As previously described, the framework delimits three-, four-, five-, and eight-membered rings. The protonated amine is inserted in the eight-membered tunnels which are along [100] and [001]. The hydrogen bonding scheme is discussed. © 1994 Academic Press, Inc.

INTRODUCTION

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

Recently, we synthesized new fluorinated alumino- and gallophosphates (10–13) in the systems M_2O_3 (M = Al, Ga)–P_2O_5–HF–template–H_2O. In these phases, which all contain primary amines, the case of fluorine is different since it is directly involved in the coordination sphere of M, as also observed in $GaAsO_4$-2 (14). In order to see if the nature of the amine has some influence on the insertion of F^- in the network, we studied the gallium system with the secondary amine dimethylamine (hereafter noted DMA). With it, fluorine does not incorporate the network. We report here the preparation and characterization of the fluorine-free phase $Ga_3P_3O_{12}(OH)$, $CH_3{-}NH_2{-}CH_3$,

TABLE 1

Details of the X-Ray Data Collection of $Ga_3(PO_4)_3(OH)$, $CH_3{-}NH_2{-}CH_3$

Determination of cell parameters	36 reflections ($24° \le 2\theta \le 30°$)
Space group	$P2_1/n$ (No. 14)
Cell dimensions	$a = 8.787(1)$ Å
	$b = 17.783(3)$ Å
	$c = 9.204(1)$ Å
	$\beta = 109.56(1)°$
Volume/Z	$V = 1355.2(5)$ Å^3 $Z = 4$
Wavelength	0.71069 Å (Mo$K\alpha$)
Scan mode	$\omega - 2\theta$
Step scan	$37 \le N \le 43$, every 0.035° and 4 sec
Aperture	3 × 3 mm^2
Crystal dimensions	0.031 × 0.247 × 0.236 mm^3
Natural faces	{010}, {1 −10}, {11 −1}
Absorption correction	Gaussian method
Transmission factors	$T_{max} = 0.800$, $T_{min} = 0.246$
Absorption coefficient	$\mu = 63.0$ cm^{-1}
Angular range of data collection	$2\theta \le 70°$
Range of measured h, k, l	$-14 \le h \le 13$, $0 \le k \le 28$, $0 \le l \le 14$
Standard reflections (3)	(5 5 2), (6 −5, −3), (−1 2 −6)
Measured every	60 mn
Maximum intensity variation	3%
Measured reflections	6123
Independent ref. ($\lvert F\rvert > 3\sigma\lvert F\rvert$)	4216
Number of refined parameters	217
Secondary extinction factor	0.0029
Weighting scheme:	$1.000/(\sigma^2(F) + 0.000257\,F^2)$
Final Fourier residuals	−0.82 to 0.87 $e^- \cdot$ Å^{-3}
R_w/R	0.026/0.030

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which is closely related to the so-called $AlPO_4$-21 structure type.

EXPERIMENTAL

Synthesis

The title compound was prepared by hydrothermal synthesis under autogeneous pressure. The reactants were gallium oxide (Ga_2O_3, Merck 99%+), phosphoric acid (85% H_3PO_4, Prolabo RP Normapur), hydrofluoric acid (40% HF, Prolabo RP Normapur), and dimethylamine (CH_3–NH–CH_3, Aldrich 99%+). The starting mixture corresponding to the molar composition 1 Ga_2O_3, 1 P_2O_5, 2 HF, 2 DMA, and 80 H_2O was placed without stirring in a Teflon-lined stainless-steel autoclave, heated at 453 K for 24 hr, and then cooled to room temperature for 24 hr. The pH of the synthesis rises from 2 before heating to 4 at the end of the reaction. The crystalline product, obtained in a pure form, was filtered off, washed with distilled water, and dried at room temperature.

Structure Determination

A rhombic-shaped single crystal was selected from the sample for structural analysis by X-ray diffraction. Its

TABLE 2

Atomic Coordinates ($\times 10^{-4}$) and Equivalent Isotropic Factors in $Ga_3P_3O_{12}(OH)$, CH_3–NH_2–CH_3

	x	*y*	*z*	B_{eq} (Å^2)
Ga(1)	0679(1)	2949(1)	3036(1)	0.60(1)
Ga(2)	1355(1)	1100(1)	1658(1)	0.63(1)
Ga(3)	5135(1)	3291(1)	1962(1)	0.82(1)
P(1)	3412(1)	4294(1)	3698(1)	0.68(2)
P(2)	3027(1)	2113(1)	9831(1)	0.80(2)
P(3)	2483(1)	1613(1)	5089(1)	0.71(2)
O(1H)	0349(2)	2095(1)	1783(2)	1.12(7)
O(2)	1949(2)	3782(1)	3146(2)	1.53(9)
O(3)	2420(2)	2442(1)	4620(2)	1.04(7)
O(4)	9502(2)	3032(1)	4391(2)	1.58(9)
O(5)	9033(2)	3532(1)	1425(2)	1.24(7)
O(6)	4584(2)	4125(1)	2802(2)	1.33(8)
O(7)	3292(2)	2793(1)	0926(2)	1.30(8)
O(8)	6012(2)	3616(1)	0555(2)	1.47(9)
O(9)	6540(2)	2696(1)	3428(2)	1.65(8)
O(10)	2447(2)	1088(1)	3762(2)	1.23(8)
O(11)	9290(2)	0810(1)	0426(2)	1.13(7)
O(12)	2782(2)	5092(1)	3356(2)	0.97(7)
O(13)	2732(2)	1407(1)	0627(2)	1.31(8)
N(1)	9294(3)	5116(2)	2169(3)	1.9(1)
C(1)	8707(6)	5649(3)	0847(6)	3.8(2)
C(2)	8336(8)	5137(4)	3229(7)	4.6(4)
H(1)	9210(70)	2110(30)	0950(70)	4.2(6)
H(2)	8890(60)	4660(30)	3980(60)	4.2(6)
H(3)	8640(70)	5670(20)	3860(60)	4.2(6)
H(4)	7080(50)	5100(30)	2460(60)	4.2(6)
H(5)	0260(70)	5200(30)	2660(70)	4.2(6)
H(6)	9270(70)	4610(30)	1850(70)	4.2(6)

TABLE 3

Selected Distances (Å) and Angles (°) in $Ga_3P_3O_{12}(OH)$, CH_3–NH_2–CH_3

P(1) tetrahedron: ⟨*P*(1)–*O*⟩ = *1.528 Å*

P(1)	O(2)	O(12)	O(11)	O(6)
O(2)	*1.517(2)*	2.430(4)	2.504(3)	2.515(2)
O(12)	106.4(1)	*1.518(3)*	2.503(3)	2.503(3)
O(11)	110.6(1)	110.5(1)	*1.529(2)*	2.516(2)
O(6)	110.2(1)	109.4(1)	109.7(1)	*1.546(2)*

P(2) tetrahedron: ⟨*P*(2)–*O*⟩ = *1.526 Å*

P(2)	O(4)	O(13)	O(9)	O(7)
O(4)	*1.510(2)*	2.432(4)	2.530(3)	2.510(2)
O(13)	106.9(1)	*1.519(3)*	2.514(3)	2.510(3)
O(9)	112.3(1)	110.7(1)	*1.536(2)*	2.458(2)
O(7)	110.8(1)	110.2(1)	106.0(1)	*1.541(2)*

P(3) tetrahedron: ⟨*P*(3)–*O*⟩ = *1.532 Å*

P(3)	O(5)	O(10)	O(3)	O(8)
O(5)	*1.521(2)*	2.473(4)	2.488(3)	2.507(2)
O(10)	108.4(1)	*1.529(3)*	2.537(3)	2.446(3)
O(3)	109.2(1)	111.9(1)	*1.532(2)*	2.554(2)
O(8)	109.7(1)	105.4(1)	112.1(1)	*1.547(2)*

Ga(3) tetrahedron: ⟨*Ga*(3)–*O*⟩ = *1.816 Å*

Ga(3)	O(8)	O(6)	O(7)	O(9)
O(8)	*1.809(2)*	2.897(3)	2.918(3)	3.010(2)
O(6)	106.4(1)	*1.812(3)*	2.927(3)	3.013(3)
O(7)	107.4(1)	107.8(1)	*1.812(2)*	3.013(2)
O(9)	111.6(1)	111.7(1)	111.7(1)	*1.830(2)*

Ga(1) trigonal bipyramid: ⟨*Ga*(1)–*O*⟩ = *1.894 Å*

Ga(1)	O(2)	O(4)	O[a](1H)	O(3)	O(5)
O(2)	*1.837(2)*	3.055(4)	3.371(5)	2.704(4)	2.560(3)
O(4)	111.1(1)	*1.837(2)*	3.204(4)	2.707(3)	2.766(4)
O(1H)	130.9(1)	118.0(1)	*1.870(2)*	2.707(3)	2.778(4)
O(3)	91.2(1)	90.4(1)	90.4(1)	*1.946(2)*	3.924(5)
O(5)	84.1(1)	91.8(1)	93.4(1)	175.3(1)	*1.982(2)*

Ga(2) trigonal bipyramid: ⟨*Ga*(2)–*O*⟩ = *1.902 Å*

Ga(1)	O(10)	O(13)	O(11)	O(12)	O(1H)
O(10)	*1.851(2)*	3.032(4)	3.415(5)	2.591(4)	2.770(3)
O(13)	109.9(1)	*1.852(2)*	3.152(4)	2.614(3)	2.916(4)
O(11)	133.8(1)	116.1(1)	*1.862(2)*	2.753(3)	2.621(4)
O(12)	86.0(1)	86.9(1)	92.5(1)	*1.948(3)*	3.942(5)
O(1H)	92.0(1)	98.4(1)	85.4(1)	174.7(1)	*1.998(3)*

Dimethylamine

N–C(1) 1.488(8) N–C(2): 1.491(6) C(1)–N–C(2): 113.7°(4)
C(2)–H(2) = C(2)–H(3) = C(2)–H(4) = 1.10 N–(H5): 0.83(1) N–(H6): 0.93(1)

[a] *O(1)–H(1) = 1.03(1)* Å.

TABLE 4
Valence Bond Analysis of $Ga_3P_3O_{12}(OH)$, CH_3–NH_2–CH_3

	P(1)	P(2)	P(3)	Ga(1)	Ga(2)	Ga(3)	H(1)	Σ
O(1H)	—	—	—	0.68	0.48	—	0.67	1.83
O(2)	1.31	—	—	0.75	—	—		2.06
O(3)	—	—	1.26	0.56	—	—		1.82
O(4)	—	1.33	—	0.75	—	—		2.08
O(5)	—	—	1.30	0.50	—	—		1.80
O(6)	1.20	—	—	—	—	0.80		2.00
O(7)	—	1.23	—	—	—	0.80		2.03
O(8)	—	—	1.21	—	—	0.81		2.02
O(9)	—	1.24	—	—	—	0.76		2.00
O(10)	—	—	1.27	—	0.72	—		1.99
O(11)	1.27	—	—	—	0.70	—		1.97
O(12)	1.31	—	—	—	0.55	—		1.86
O(13)	—	1.30	—	—	0.71	—		2.01
Σ	5.09	5.10	5.04	3.24	3.16	3.17	0.67	

Note. The results refer to the equation $s = \exp[(R_0 - d)/0.37]$ (18) with $R_0 = 1.730$ and 1.620 for Ga and P, respectively.

quality was tested by optical observation and Laue photographs. Intensity data collection was performed with a Siemens AED-2 four-circle diffractometer with conditions of data collection summarized in Table 1 and described the structure with the space group $P2_1/n$ (No. 14). The data were corrected for Lorentz polarization and absorption effects. The scattering factors and anomalous dispersion corrections were taken from the "International Tables for X-ray Crystallography" (15). The structure was solved by using the direct method analysis of the SHELXS-86 program (16). Gallium and phosphorus atoms were first located and all the remaining atoms except hydrogens of one methyl group were found by difference Fourier maps. Refinement was performed by full-matrix least-squares analysis of SHELX-76 (17) with anisotropic thermal parameters for all nonhydrogen atoms and with strains on C–H and N–H distances. The absence of fluorine was deduced from preliminary solid-state NMR measurements. The reliability factors converge to $R_w = 0.026$ and $R = 0.030$. The atomic coordinates with anisotropic thermal parameters and selected bond distances and angles are listed in Tables 2a, 2b, and 3, respectively. Table 4 provides the valence bond analysis of the compound and shows that O(1) corresponds to an OH group.

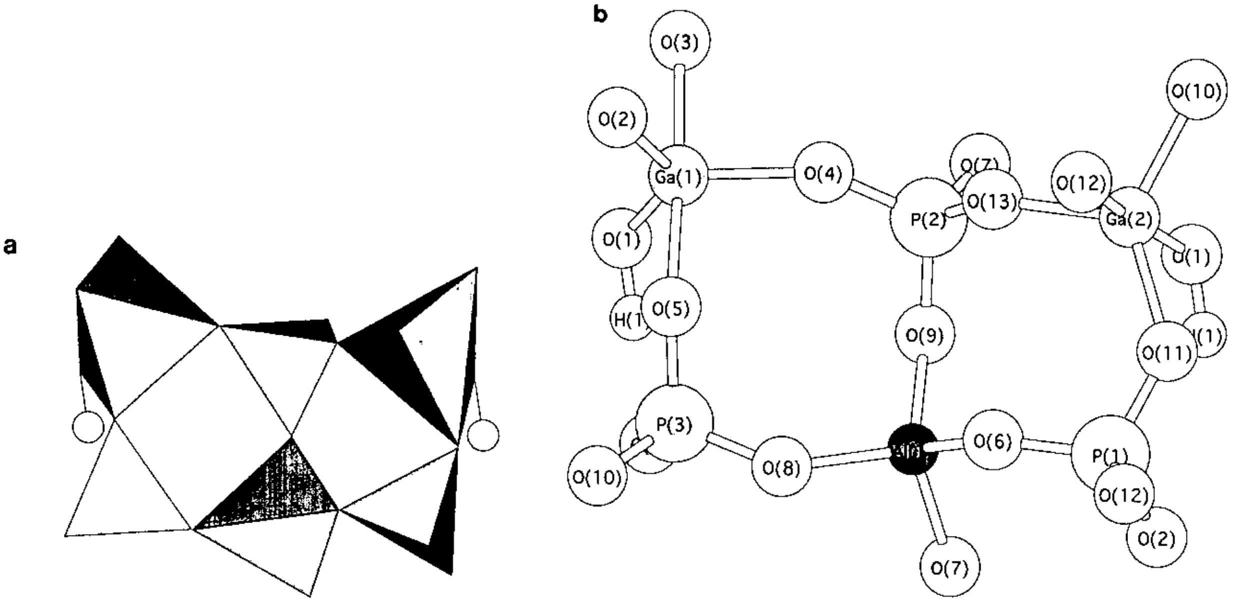

FIG. 1. (a) Polyhedral and (b) ball and stick model of the asymmetric unit. The labels of atoms correspond to Table 2. Ga(3) (not labeled) corresponds to the small black circle. The hydrogen atom of the hydroxy group is represented as small empty circles.

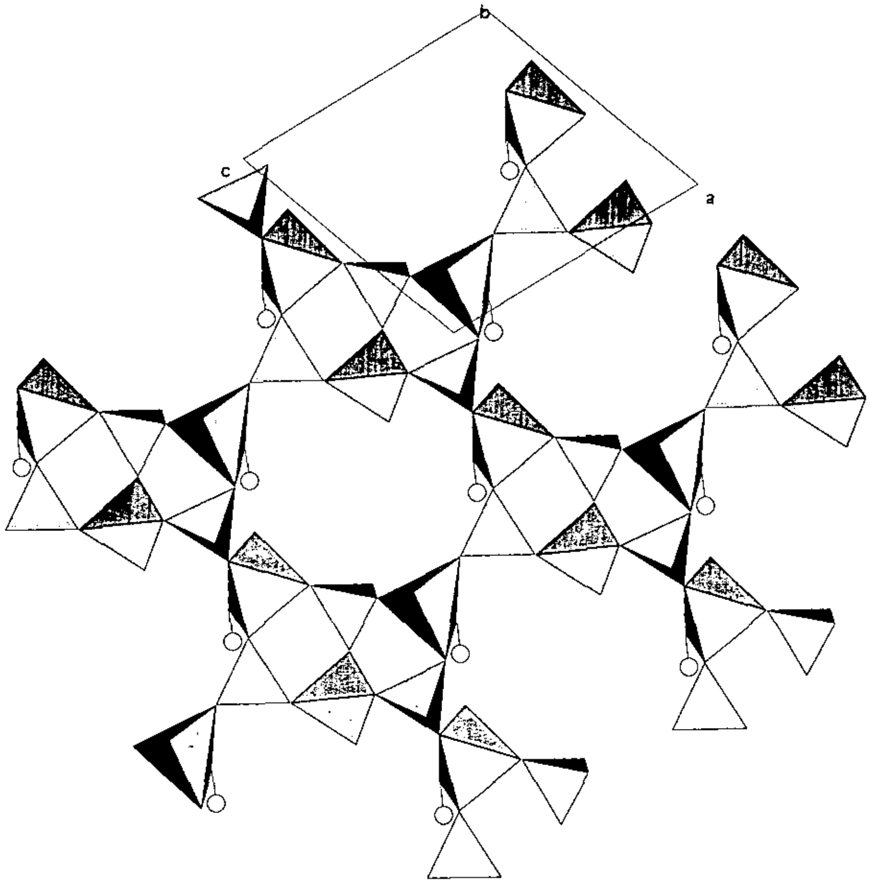

FIG. 2. Connection of the basic building units in the (010) plane, forming the single sheet (see text).

The list of structure factors can be obtained upon request to the authors.

DESCRIPTION OF THE STRUCTURE

This structure is closely related to the so-called $AlPO_4$-21 or $GaPO_4$–C4 structure type (19–24), already found when the medium did not contain fluoride ions. For aluminium compounds, the templates were *N*,*N*,*N*′,*N*′-tetramethyl-1,3-propanediamine (19), ethylenediamine, pyrrolidine, and pyridine (20); for gallium compounds, isopropylamine (21), ethylenediamine (22), and ethanolamine (23, 24) were used. The resulting compounds were formulated $M_3(PO_4)_3$, amine, and H_2O by the different authors. The previous structural descriptions, based on 3D-connected nets of cations (25), insisted on two facts: the existence of two coordinations for the metallic ion and the various kinds of rings (three-, four-, five-, and eight-membered) which exist in the structure. We propose here another description, based on the connection of basic building units, which allows one to see very simply how the framework is built up.

Indeed, the basic building unit (Fig. 1) consists of three types of PO_4 tetrahedra ($P–O_{av}$ = 1.529 Å), one $Ga(3)O_4$ tetrahedron ($Ga(3)–O_{av}$ = 1.816 Å), and two $GaO_4(OH)$ trigonal bipyramids ($Ga–O_{av}$ = 1.898 Å). By sharing corners and with a strict Ga–P alternation, they form planar double four-rings and the $[Ga_3(PO_4)_3(OH)_2]$ unit. These units share corners with the same Ga–P alternation (Fig. 2) to form sheets parallel to the (010) plane. The *n* glide plane does that when two consecutive sheets are shifted. They however share vertices (Fig. 3) in two ways, one between the PO_4 and the GaO_4 tetrahedra, the other between the gallium tetrahedron and the trigonal bipyramid, the shared vertex corresponding to the OH group. The resulting double layers are stacked one over each other (Figs. 4a and 4b) by sharing two corners between two basic building units and then creating the eight-membered channels along [100] and [001]. Protonated dimethylamine ions occupy these tunnels. The location of hydrogens of the C(1) methyl group was not possible, probably due to its free rotation within the tunnel, but the hydrogens fixed to C(2) and N were easily observed (Fig. 5). Examination of the hydrogen bonding between the amine and the framework shows that the organic ion is not strongly bound to the framework, except via one hydrogen (H(5)) of the amino group which points toward O(12) with a H· · ·O distance of 2.10(3) Å. All the other H· · ·O distances are larger than 2.70 Å.

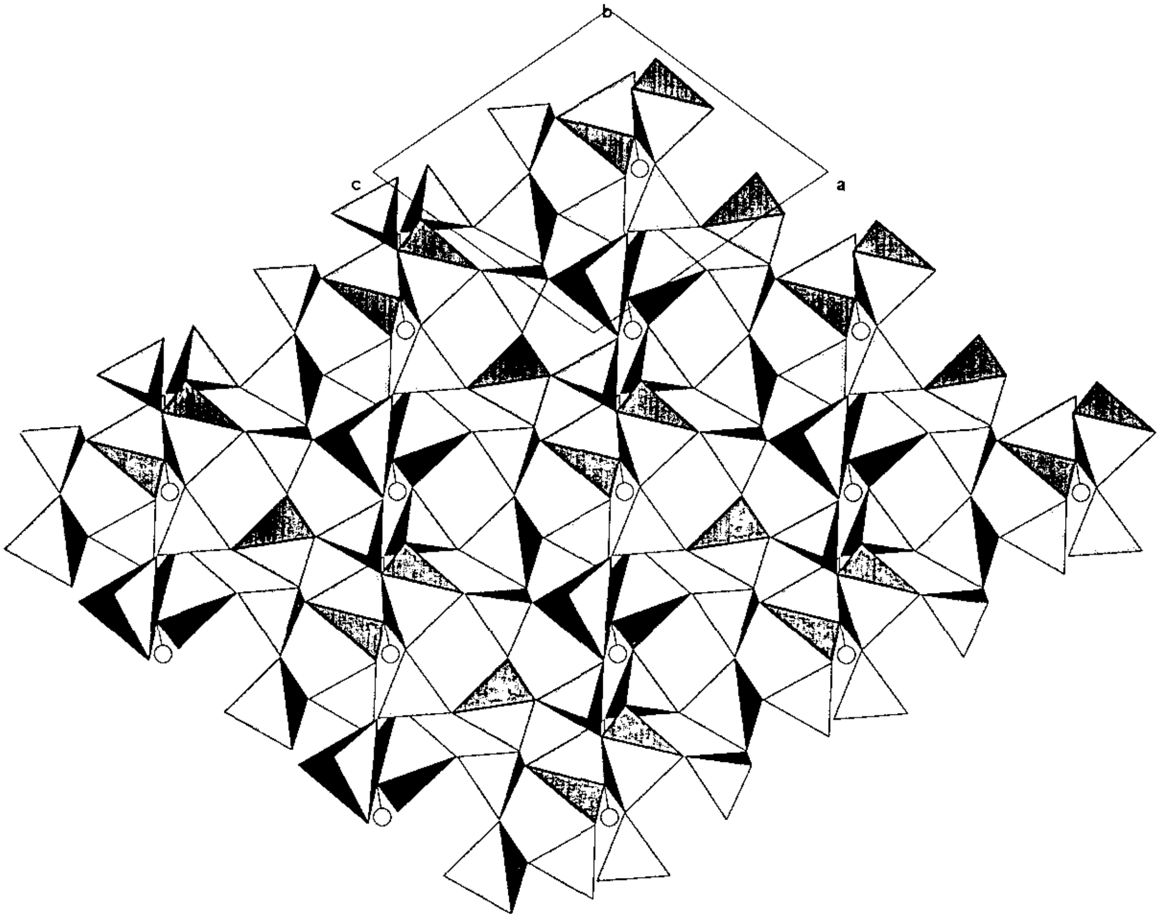

FIG. 3. Connection of two consecutive single sheets forming the double layer.

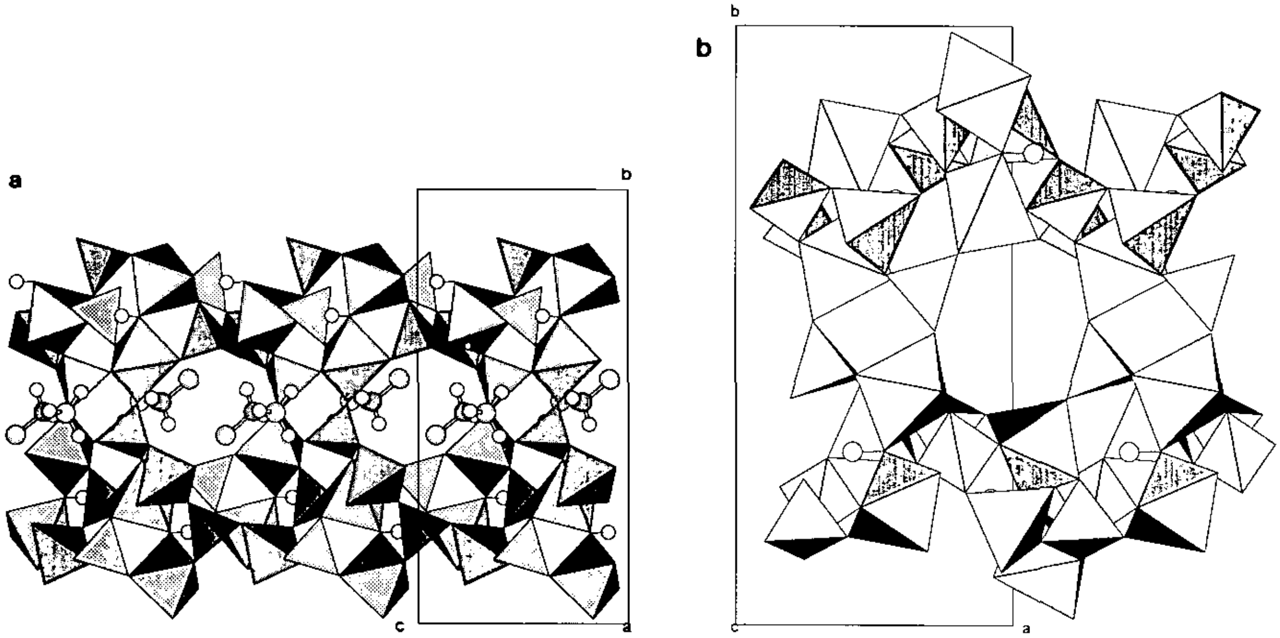

FIG. 4. [100] (a) and [001] (b) projections of the structure which shows the connection between the double layers and the existence of the eight-membered tunnels in which DMA ions are inserted, as shown in (a).

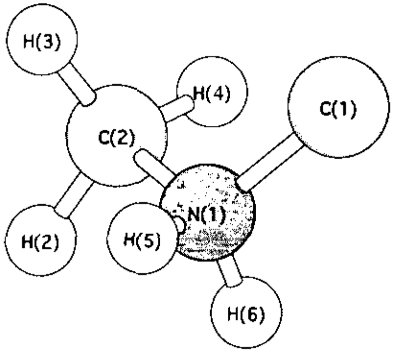

FIG. 5. Conformation of the visible part of the protonated DMA.

In conclusion, we have shown that the $AlPO_4$-21 structure type exists also when a secondary amine is used as template. Note that, in Ref. (19), *N,N,N′,N′*-tetramethyl-1,3-propanediamine was use as the starting "template," but it appeared plausible that each molecule broke into one propyl species and two dimethylammonium cations, and that the three fragments were encapsulated into the $AlPO_4$-21 crystal. We have proved also for the first time that the amine is protonated in this structure, and that, correlatively, one OH group exists in the network. Even when the synthesis is carried out in fluorinated medium, fluoride ions do not incorporate the framework, which is rather surprising. Supplementary experiments with both primary and secondary amines will be performed in order to see an eventual correlation between the primary or secondary character of the amine and whether F^- is incorporated in the lattice.

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