Structure Determination of $(N_2C_2H_{10})_4(NH_4)AlP_4O_{16}$: A New Aluminophosphate Templated by Ethylenediamine

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This paper deals with the synthesis and the X-ray determination of the structure of a new aluminophosphate with the formula $(N_2C_2H_{10})_4(NH_4)AlP_4O_{16}$. This acentric phase crystallizes in the tetragonal space group I-4 (no. 82) with parameters $a = 9.1545(5)$ Å, $c = 17.1810(8)$ Å, $V = 1439.9(2)$ Å^3, and $Z = 2$. The network of $(N_2C_2H_{10})_4(NH_4)AlP_4O_{16}$ consists of pentameric $[AlP_4O_{16}]$ clusters with a central AlO_4 tetrahedron sharing its four corners with four PO_4 tetrahedra. These isolated units are linked by strong hydrogen bonds between the oxygen atoms of the PO_4 groups and the hydrogen of the ammonium cations and the diprotonated ethylenediamine. © 1992 Academic Press, Inc.

Introduction

The solid compounds with microporous frameworks are particularly searched for their catalytic properties or to be used as molecular sieves. For these reasons, the $AlPO_4$-n family has been extensively studied since 1982 (*1*). Only a small number of phases characterized in this area present a P/Al ratio different from 1. Some examples known are $(Et_3NH)(H_2AlP_2O_8)$ (*2*), "$AlPO_4$-CJ" (P/Al = 2) (*3*), $Al_3P_4O_{20}(N_2C_6H_{23})$ (*4*), and $(2\text{-BuNH}_3)_2HAl_2P_3O_{12}$ (*5*).

This paper deals with the synthesis and the structure determination of $(N_2C_2H_{10})_4(NH_4)AlP_4O_{16}$, the first aluminophosphate which exhibits a P/Al ratio equal to 4.

Experimental

Sample preparation. The title compound was prepared hydrothermally from an aqueous mixture of Al_2O_3, P_2O_5, NH_4F, ethylenediamine, and H_2O in the ratio 1 : 1 : 2 : 20 : 30 and heated 3 days at 453 K in a teflon-walled autoclave under autogenous pressure. $(N_2C_2H_{10})_4(NH_4)AlP_4O_{16}$ was obtained as a minor product with the other crystalline phase $(N_2C_2H_8)AlF(HPO_4)$ previously described (*6*). The X-ray calculated powder pattern is given in Table I.

Structure determination. An almost-spherical crystal with a diameter approximately 200 μm was selected. Its quality was tested on Laue photographs and the X-ray diffraction data were collected on a Siemens AED2 four-circle diffractometer using Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å) monochromatized by graphite. The data were corrected for Lorentz and polarization effects

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TABLE I

CALCULATED X-RAY POWDER PATTERN
OF $(N_2C_2H_{10})_4(NH_4)AlP_4O_{16}$

$h\,k\,l$	d_{calc}	I_{calc}
0 0 2	8.59	13
1 0 1	8.08	69
1 1 0	6.473	9
1 1 2	5.170	38
1 0 3	4.855	10
2 0 0	4.577	74
0 0 4	4.295	38
1 2 1 + 2 1 1	3.983	40
1 1 4	3.579	7
2 1 3 + 1 2 3	3.331	100
2 2 0	3.237	6
2 0 4	3.132	28
2 2 2	3.029	7
3 1 2	2.7433	9
3 0 3	2.6931	10
2 2 4	2.5849	6
2 0 6	2.4276	13
3 2 5	2.0420	6

but no absorption correction was applied. The scattering factors and the anomalous dispersions corrections for Al^{3+}, P, O^{2-}, C, and H were from the "International Tables for X-ray Crystallography" (7). After examination of the intensities of the equivalent hkl reflections, the Laue group $4/m\ m\ m$ was eliminated. The crystal data and the conditions for intensity measurements are summarized in Table II.

The structure was solved in the noncentrosymmetric I-4 (no. 82) space group using the direct method option of SHELX (8). The heaviest atoms (P, Al, O) were first located, then the C, N, and H atoms were deduced from Fourier difference synthesis. The anisotropic refinement of all atoms except H converges to $R_w = 0.023$ and $R = 0.022$ for this enantiomer. The same calculation with $x\,y\,z$ changed into $-x\ -y\ -z$ gives $R_w = 0.025$ and $R = 0.023$. The atomic

TABLE II

CRYSTALLOGRAPHIC DATA AND CONDITIONS OF COLLECTION
OF $(N_2C_2H_{10})_4(NH_4)AlP_4O_{16}$

Determination of cell parameters	32 reflections at $2\theta \approx 30°$
Space group	I-4 (no. 82)
Cell dimensions	$a = b = 9.1545(5)$ Å
	$c = 17.1810(8)$ Å
Volume/Z	1439.9(2) Å^3 $Z = 2$
Wavelength/monochromator	0.71069 Å (Mo $K\alpha$)/graphite
Temperature	293 K
Scan mode	ω-2θ
Step scan	$36 \leq N \leq 42$, every 0.035° and 4 sec.
Aperture	3×3 mm^2
Absorption coefficient	$\mu = 3.49$ cm^{-1} $\mu R_{max} = 0.07$
Angular range of data collection	$2\theta \leq 70°$
Range of measured h, k, l	$-14 \leq h \leq 14$; $0 \leq k \leq 14$; $0 \leq l \leq 27$
Standard reflections (3)	3 3 0; 0 2 6; -3 3 0
Measured every	60 min
Maximum intensity variation	2.0%
Measured reflections	3634
Reflections $|F| > 6\sigma|F|$	2686
$R_{int.}$	0.013
Weight	$0.8643/(\sigma^2(F) + 0.000606\ F^2)$
Secondary extinction	0.0037(2)
Number of refined parameters	131
Final Fourier residuals	-0.33 to $+0.46$ e $\cdot$ Å^{-3}
R_w/R	0.023/0.022

TABLE IIIa

ATOMIC COORDINATES AND MEAN-SQUARE DISPLACEMENTS
FOR $(C_2N_2H_{10})_4(NH_4)AlP_4O_{16}$

Atom	X	Y	Z	B_{eq}
P	0.1648(0)	0.7869(0)	0.8875(0)	1.01(1)
Al	0	0	0	0.78(1)
N	0	0.5	0.75	1.80(5)
O(1)	0.5806(1)	0.6340(1)	0.5573(1)	1.59(3)
O(2)	0.6523(1)	0.7439(1)	0.6836(1)	2.21(3)
O(3)	0.8199(1)	0.7617(1)	0.5684(1)	2.13(3)
O(4)	0.7837(1)	0.5199(1)	0.6364(1)	2.00(3)
N(1)	0.8910(1)	0.2693(1)	0.5652(1)	1.92(3)
N(2)	0.3618(1)	0.7363(1)	0.6870(1)	1.80(3)
C(1)	0.8527(2)	0.6821(1)	0.3686(1)	2.11(4)
C(2)	0.8456(1)	0.1481(1)	0.6169(1)	2.20(4)
H(1)	0.645(2)	0.867(2)	0.418(1)	1.8(3)
H(2)	0.721(3)	0.981(3)	0.439(1)	3.2(5)
H(3)	0.747(3)	0.856(3)	0.482(1)	3.0(4)
H(4)	0.333(2)	0.655(2)	0.671(1)	1.7(3)
H(5)	0.448(2)	0.732(2)	0.690(1)	2.3(4)
H(6)	0.739(3)	0.831(2)	0.768(1)	2.5(4)
H(7)	0.370(3)	0.840(3)	0.585(1)	3.1(4)
H(8)	0.342(3)	0.939(3)	0.652(2)	3.5(5)
H(9)	0.657(2)	0.601(2)	0.834(1)	2.6(4)
H(10)	0.550(2)	0.626(2)	0.908(1)	3.0(4)
H(11)	0.920(2)	0.512(3)	0.723(1)	3.3(5)

Note. B_{eq} (Å^2) is defined as $B_{eq} = 8\pi^2(U_{11} + U_{22} + U_{33})/3$.

TABLE IIIb

ANISOTROPIC THERMAL PARAMETERS FOR $(N_2C_2H_{10})_4(NH_4)AlP_4O_{16}$ ($U_{ij} \times 10^4$)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P	147(1)	113(1)	123(1)	−13(1)	22(1)	−1(1)
Al	105(1)	105(1)	85(2)	0	0	0
N	237(5)	237(5)	213(8)	0	0	0
O(1)	168(3)	227(3)	209(3)	−104(3)	−72(3)	12(3)
O(2)	191(3)	444(5)	205(3)	−193(4)	−19(3)	27(3)
O(3)	163(3)	326(5)	321(4)	124(4)	−4(3)	−50(3)
O(4)	266(4)	189(3)	303(4)	36(3)	−80(3)	40(3)
N(1)	177(4)	295(5)	258(5)	−36(4)	−12(3)	14(3)
N(2)	183(4)	291(5)	211(4)	−88(4)	19(3)	14(3)
C(1)	279(5)	223(5)	299(6)	42(4)	33(4)	34(4)
C(2)	220(4)	280(5)	337(6)	33(5)	−27(5)	71(4)

Note. The vibrational coefficients relate to the expression $T = \exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$.
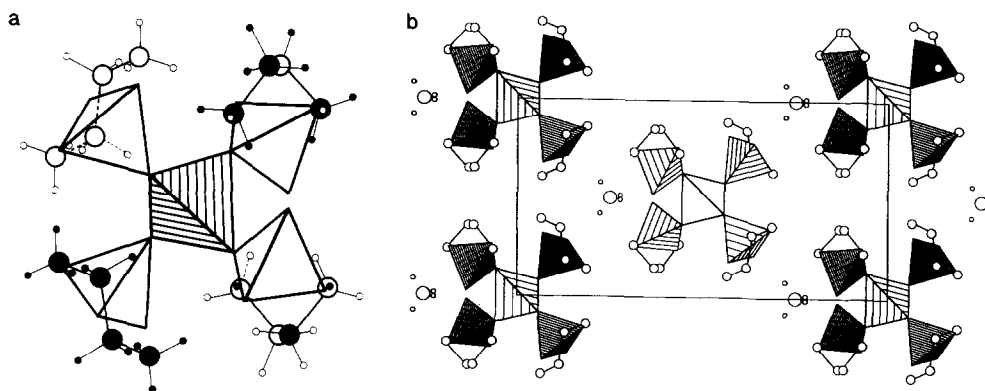
FIG. 1. (a) $AlP_4O_{16}(N_2C_2H_{10})_4$ pentameric unit (large circles for ethylenediamine N–C–C–N, small circles for H atoms). (b) Projection of $(N_2C_2H_{10})_4(NH_4)AlP_4O_{16}$ on the (100) plane (the ammonium cations and the skeleton of ethylenediamine are drawn).

coordinates and thermal parameters are listed in Tables IIIa and b, and the principal bond lengths and angles are listed in Table IV.

Description

$(N_2C_2H_{10})_4(NH_4)AlP_4O_{16}$ presents a tetrahedral edifice of corner-sharing AlO_4 and PO_4 tetrahedra. Each type of tetrahedron is almost regular with four distances Al–O of 1.737(1) Å for $AlO(1)_4$ and four distances P–O around 1.54 Å for PO_4 (Table IV). An $AlO(1)_4$ tetrahedron shares its four corners with four PO_4 tetrahedra to constitute a structural unit formulated $[AlP_4O_{16}]$ (Fig. 1a). The PO_4 tetrahedra present a particular feature with three terminal oxygens (O(2), O(3), and O(4)). The isolated pentamers of $(N_2C_2H_{10})_4(NH_4)AlP_4O_{16}$ (Fig. 1a) occupy the positions of an I lattice (Fig. 1b) and are held together by strong O–H linkages between the terminal oxygen of the PO_4 tetrahedra and the H atoms of the amino groups and of the ammonium cations. For clarity, the O–H linkages are not drawn on the figures, but the O–H bonds lengths are given in Table IV. This type of connection between the structural units gives rise to

TABLE IV

INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN $(N_2C_2H_{10})_4(NH_4)AlP_4O_{16}$

PO₄ tetrahedron			
P–O(1)	1.565(1)	O(1)–P–O(2)	106.74(6)
P–O(2)	1.525(2)	O(1)–P–O(3)	107.53(8)
P–O(3)	1.522(1)	O(1)–P–O(4)	109.48(6)
P–O(4)	1.532(1)	O(2)–P–O(3)	110.88(6)
		O(2)–P–O(4)	110.51(8)
		O(3)–P–O(4)	111.54(6)
AlO₍₁₎₄ tetrahedron			
Al–O(1)	1.737(1) (4×)	O(1)–Al–O(1)	111.0(1) (2×)
O(1)–O(1)	2.824(3) (4×)	O(1)–Al–O(1)	108.73(5) (4×)
O(1)–O(1)	2.863(2) (2×)		
Interatomic distances in the ethylenediamine			
C(1)–C(2)	1.517(1)		
N(1)–C(2)	1.481(2)		
N(2)–C(1)	1.486(2)		
N(1)–H(1)	0.87(2)		
N(1)–H(2)	0.83(2)		
N(1)–H(3)	0.89(2)		
N(2)–H(4)	0.83(2)		
N(2)–H(5)	0.79(2)		
N(2)–H(6)	0.85(2)		
C(1)–H(7)	0.93(2)		
C(1)–H(8)	0.90(3)		
C(2)–H(9)	0.97(2)		
C(2)–H(10)	1.03(2)		
Ammonium cation			
N–H(11)	0.88(2) (4×)		
H(11)–N–H(11)	116(3) (2×)		
H(11)–N–H(11)	106(1) (4×)		
Hydrogen bonds			
O(2)–H(5)	1.87(2)		
O(2)–H(6)	1.83(2)		
O(3)-H(2)	1.86(2)		
O(3)–H(3)	1.84(2)		
O(4)–H(1)	1.93(2)		
O(4)–H(4)	2.02(2)		
O(4)–H(11)	1.94(2)		

large cavities, and it may be thought that $(N_2C_2H_{10})_4(NH_4)AlP_4O_{16}$ can appear as a precursor which transforms at higher temperatures into two-dimensional $(N_2C_2H_8)$ $AlF(HPO_4)$ (6).

Acknowledgments

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