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Synthesis and Crystallographic X-Ray Determination of a New Layered Fluoroaluminophosphate: $AlF(HPO_4)$, Ethylenediamine

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This paper deals with the synthesis and the X-ray determination of the structure of hitherto unknown $AlF(HPO_4)$,ethylenediamine (*en*). This monoclinic phase crystallizes in space group $P2_1/c$ with unit cell parameters $a = 9.2855(6)$, $b = 7.0832(4)$, and $c = 9.6492(5)$ Å; $\beta = 101.544(6)°$; $V = 621.80(9)$ Å^3; and $Z = 4$. $AlF(HPO_4)$,*en* is a layered compound with sheets stacked along the *a* axis. These sheets are built up from isolated trans-chains of $Al(O_3F_2N)$ octahedra running along [010]. PO_4 tetrahedra ensure the linkage between the chains via three of their four vertices. The diamine plays two roles: it participates in the octahedral coordination of aluminium via the N(1) atom but also ensures the cohesion between the sheets by hydrogen bonds. This structure is closely related to α-$VO(HPO_4) \cdot 2H_2O$.

Introduction

Since 1982 (*1*) and the synthesis of a large number of new microporous molecular sieves based on aluminophosphate frameworks, the $AlPO_4$ family of materials has continuously increased (*2*) through the use of the known zeolite synthesis routes and the organic amines as templates. In such hydrothermal synthesis, which occurs in diluted aqueous solutions, the concentration of the amine is of the same magnitude as the other reactants and promotes the crystallization of $AlPO_4$-*n*.

It was interesting to know if the amine always plays the role of template when the synthesis is realized in a concentrated organic medium. This paper presents our first results and the new behavior of the amine (here ethylenediamine, denoted *en* in the following) in the compound $AlF(HPO_4)$,*en*.

Experimental

Sample preparation. The title compound was prepared hydrothermally. The synthesis was realized with a large excess of ethylenediamine. The aqueous mixture of Al_2O_3, P_2O_5, NH_4F, *en*, and H_2O (molar ratio 1 : 1 : 2 : 20 : 30) was heated for 3 days at 453 K in an autoclave under autogenous pressure. The resultant product was filtered and washed with water, and then dried in air. Two types of colorless crystals were selected: some plates corresponding to $AlF(HPO_4)$,*en*, whose structure is reported in this paper, and another crystalline phase, the data on which will be published elsewhere. The X-ray powder pattern is given in Table I.

Structure determination. The selected crystal was a plate with dimensions 330 × 270 × 210 μm limited by the {10-2}, {11-1}, and {010} forms. The crystal quality was

0022-4596/93 $5.00

TABLE I

X-RAY POWDER PATTERN OF $AlF(HPO_4)$,*en*

h	*k*	*l*	d_{obs}	d_{calc}	I_{calc}
1	0	0	9.08	9.09	100
0	1	1	5.662	5.663	11
1	1	0	5.585	5.583	8
1	1	−1	5.090	5.090	11
0	1	2	3.929	3.929	2
1	0	2	3.885	3.885	29
2	1	0	3.823	3.824	6
2	1	−1	3.774	3.774	1
2	0	−2	3.666	3.665	13
0	2	0	3.538	3.537	3
1	1	2	3.405	3.405	2
1	2	0	3.296	3.296	2
2	1	−2	3.255	3.254	26
1	2	−1	3.186	3.185	45
3	0	0	3.030	3.030	3
2	0	2	2.9886	2.9892	11
1	1	−3	2.9019	2.9014	6
2	2	−1	2.7720	2.7716	3
2	1	2	2.7548	2.7534	3
2	1	−3	2.6634	2.6627	3
1	1	3	2.6098	2.6092	4
0	0	4	2.3620	2.3628	3
3	0	2	2.3457	2.3454	6
4	1	0	2.1636	2.1637	5
1	3	−2	2.0968	2.0971	3
3	2	−3	2.0097	2.0102	2

tested on Laue photographs and the X-ray diffraction data were collected on a Siemens AED2 four-circle diffractometer using Mo$K\alpha$ monochromatized radiation (λ = 0.71069 Å). The crystal cell was obtained from long exposure rotation photographs and the space group $P2_1/c$ (No. 14) deduced from systematic extinction conditions ($0k0$, $k = 2n + 1$; $h0l$, $l = 2n + 1$). The scattering factors and the anomalous dispersion corrections for Al^{3+}, P, O^{2-}, F^-, C, N, and H were taken from the "International Tables for X-Ray Crystallography" (*4*). The data were corrected for Lorentz and polarization effects and an absorption correction based on the crystal morphology was applied. The crystal data and the conditions of intensity measurements are summarized in Table II.

The structure was solved by the direct methods option of SHELX (*5*) with all atoms in general positions. The Al, P, O, and F atoms were first located and the positions of the C, N, and H atoms subsequently deduced from difference Fourier synthesis maps. All atoms except visible H atoms were refined anisotropically; the final refinement converged to $R_w = R = 0.024$. The atomic coordinates and thermal parameters are listed in Tables IIIa and IIIb and the

TABLE II

CRYSTALLOGRAPHIC DATA AND CONDITIONS OF COLLECTION OF $AlF(HPO_4)$,*en*

Determination of cell parameters	34 reflections at $2\theta \approx 30°$
Space group	$P2_1/c$ (No. 14)
Cell dimensions	a = 9.2855(6) Å b = 7.0832(4) Å, c = 9.6492(5) Å β = 101.544(6)°
Volume/Z	621.80(9) Å^3, Z = 4
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	4 × 4 mm^2
Absorption corrections	Gaussian method
Absorption coefficient	μ = 5.83 cm^{-1}, μR_{max} = 0.19
Angular range of data collection	$2\theta \leq 70°$
Range of measured *h, k, l*	$-15 \leq h \leq 15$; $0 \leq k \leq 11$; $0 \leq l \leq 15$
Standard reflections (3)	−6 2 1; 5 2 3; 0 4 0
Interval between measurements	60 min
Maximum intensity variation	2.4%
Measured diffractions	3341
Independent reflections $\lvert F\rvert > 6\sigma\lvert F\rvert$	1768
Weight	$1/(\sigma^2(F) + 0.0002\,F^2)$
Number of refined parameters	136
Final Fourier residuals	−0.29 to +0.50 e · Å^{-3}
R_w/R	0.024/0.024

TABLE IIIa

ATOMIC COORDINATES AND MEAN-SQUARE DISPLACEMENTS FOR $AlF(HPO_4),en$

Atom	X	Y	Z	B_{eq}
P(1)	0.8043(0)	0.1296(1)	0.4151(0)	0.45(1)
Al(1)	0.0094(1)	0.8748(1)	0.2637(1)	0.48(2)
F(1)	0.0522(1)	0.1255(2)	0.2276(1)	0.75(3)
O(1)	0.8686(1)	0.9478(2)	0.3654(1)	0.77(5)
O(2)	0.6352(1)	0.1253(2)	0.3733(1)	0.88(4)
O(3)	0.8596(1)	0.3044(2)	0.3484(1)	0.82(5)
O(4)	0.8440(1)	0.1477(2)	0.5768(1)	0.85(4)
N(1)	0.1465(2)	0.3931(3)	0.4218(2)	1.07(6)
N(2)	0.5106(2)	0.2122(2)	0.6169(2)	1.07(6)
C(1)	0.3864(2)	0.3485(3)	0.5832(2)	1.04(6)
C(2)	0.2960(2)	0.3173(3)	0.4348(2)	1.02(6)
H(1)	0.291(3)	0.307(4)	0.914(3)	1.5(5)
H(2)	0.327(3)	0.322(4)	0.655(3)	1.5(5)
H(3)	0.107(3)	0.334(4)	0.490(3)	1.9(6)
H(4)	0.348(3)	0.127(5)	0.859(3)	2.0(6)
H(5)	0.479(3)	0.117(4)	0.626(3)	1.6(5)
H(6)	0.427(3)	0.023(4)	0.100(3)	1.3(5)
H(7)	0.149(3)	0.003(5)	0.951(3)	1.9(6)
H(8)	0.560(3)	0.261(4)	0.193(3)	1.6(5)

Note. B_{eq} (Å^2) is defined as $B_{eq} = 8\pi^2(U_{11} + U_{22} + U_{33} + U_{13}\cos\beta)/3$.

TABLE IIIb

ANISOTROPIC THERMAL PARAMETERS FOR $AlF(HPO_4),en$ ($U_{ij} \times 10^4$)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P	61(1)	58(1)	55(1)	0(1)	14(1)	1(2)
Al	80(2)	45(2)	57(2)	−3(2)	16(1)	1(2)
F	123(4)	50(3)	119(4)	−3(4)	43(3)	−2(4)
O(1)	127(5)	57(5)	128(5)	−10(4)	72(4)	2(4)
O(2)	62(4)	134(6)	130(5)	11(5)	−1(3)	−2(5)
O(3)	142(5)	67(5)	126(5)	18(4)	78(4)	−9(4)
O(4)	128(5)	135(6)	54(4)	−6(4)	3(4)	15(5)
N(1)	123(6)	162(7)	108(6)	−38(6)	−5(5)	23(6)
N(2)	116(6)	135(7)	141(6)	1(5)	−7(5)	−7(5)
C(1)	116(6)	156(8)	111(6)	−9(6)	−5(5)	−1(6)
C(2)	110(6)	171(7)	101(7)	−5(5)	5(5)	11(6)

Note. The vibrational coefficients relate to the expression $T = \exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$.

principal interatomic distances and angles in Table IV.

Description

$AlF(HPO_4),en$ presents a mixed framework of corner-sharing $Al(O_3F_2N)$ octahedra and PO_4 tetrahedra. The tetrahedron around phosphorus is almost regular with four usual P–O distances around 1.535 Å (Table IV). On the other hand, the coordination around the aluminium is very irregular. Indeed, each Al atom is linked to three oxygen and two fluorine ions with distances ranging from 1.847(1) to 1.868(1) Å but also to the N(1) atom of the ethylenediamine with a distance, Al–N(1), of 2.069(1) Å. Note that

TABLE IV

INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN $AlF(HPO_4),en$

	PO_4 tetrahedron		
P–O(3)	1.531(1)	O(4)–P–O(3)	109.1(1)
P–O(4)	1.534(1)	O(1)–P–O(3)	111.3(1)
P–O(1)	1.536(1)	O(2)–P–O(3)	108.4(1)
P–O(2)	1.541(0)	O(1)–P–O(4)	111.0(1)
		O(2)–P–O(4)	107.0(1)
		O(2)–P–O(1)	109.9(1)
	AlO_3F_2N octahedron		
Al–F	1.863(1)	O(3)–Al–F	90.8(1)
Al–F	1.868(1)	O(3)–Al–F	87.6(1)
Al–O(4)	1.847(1)	O(1)–Al–F	89.1(1)
Al–O(3)	1.851(1)	O(1)–Al–F	91.9(1)
Al–O(1)	1.858(1)	O(4)–Al–F	93.6(1)
Al–N(1)	2.069(1)	O(4)–Al–F	95.1(1)
		F–Al–F	171.2(1)
		N(1)–Al–F	86.0(2)
		N(1)–Al–F	85.3(1)
		O(4)–Al–O(3)	90.2(1)
		O(4)–Al–O(1)	93.6(1)
		O(1)–Al–O(3)	176.2(1)
		O(4)–Al–N(1)	176.7(2)
		O(3)–Al–N(1)	86.5(1)
		O(1)–Al–N(1)	89.7(1)
	Interatomic distances in the ethylenediamine		
	C(1)–C(2)	1.524(2)	
	N(1)–C(2)	1.470(2)	
	N(2)–C(1)	1.489(2)	
	N(1)–H(7)	0.79(3)	
	N(1)–H(3)	0.92(3)	
	N(2)–H(5)	0.75(3)	
	N(2)–H(8)	0.81(2)	
	C(1)–H(2)	0.99(3)	
	C(1)–H(6)	0.99(3)	
	C(2)–H(1)	0.90(3)	
	C(2)–H(4)	1.03(4)	

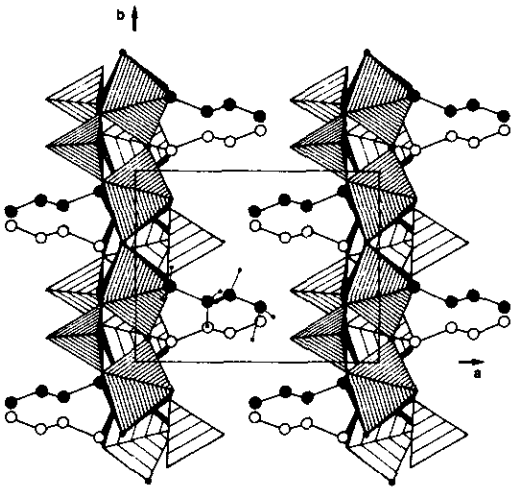

FIG. 1. Projection of $AlF(HPO_4)$,*en* along [001] (small circles for F, large circles for ethylenediamine N–C–C–N, H atoms drawn for one amine only).

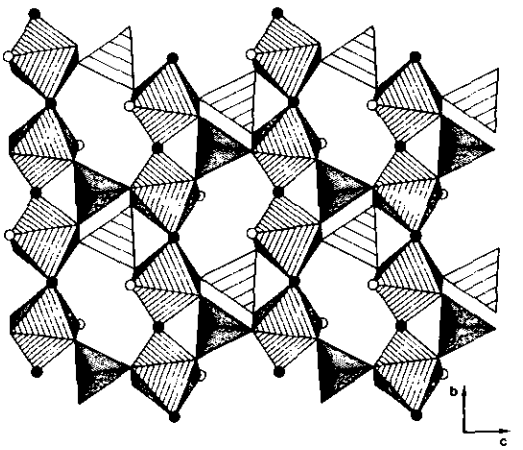

FIG. 2. Projection of $AlF(HPO_4)$,*en* along [100] (closed circles for F, open circles for N(1)).

no residual electron density appears in the vicinity of F^-. Such a residue was observed in $NH_4AlPO_4F_{0.7}(OH)_{0.3}$ (*6*) and suggests a statistical (OH, F) distribution for the anionic species linking two Al polyhedra. Here, it seems that F^- is the only bridging species. The resulting $Al(O_3F_2N)$ octahedron is slightly distorted (Table IV). The $Al(O_3F_2N)$ octahedra are linked by corners to form infinite trans-chains running along [010]. These isolated chains are cross-linked by the PO_4 tetrahedra (Fig. 1). Each tetrahedron shares two corners with two successive octahedra of the same chain and a third with an octahedron of an adjacent one, the linkage between two octahedra of the same chain being possible due to the tilting of the $Al(O_3F_2N)$ octahedra. These connections allow the build up of sheets parallel to (100) (Fig. 2). In these sheets, each PO_4 tetrahedron shows a free apex, corresponding to O(2), which seems exclusively linked to P. A valence bond analysis using the data of Brown (*7*) and O'Keeffe (*8*) (Table V) shows that O(2) needs to correspond to an OH group to satisfy bond valence requirements, despite the fact that no significant residue appears close to O(2) in the final Fourier difference synthesis. Under these conditions, each sheet is electrically neutral and is structurally closely related to those which exist in α-$VO(HPO_4) \cdot 2H_2O$ (*3*). In the last compound, one H_2O molecule was on the vanadium octahedron and the other was located between two sheets, partially ensuring

TABLE V

VALENCE BOND ANALYSIS[a] OF $AlF(HPO_4)$,*en*

	P	Al	C(1)	C(2)	H	Sum	Charge
O(1)	1.202	0.571	—	—	0.011	1.804	2
O(2)	1.185	—	—	—	0.117	1.302	2
O(3)	1.219	0.583	—	—	0.037	1.839	2
O(4)	1.208	0.589	—	—	0.015	1.812	2
F	—	0.423 + 0.418	—	—	0.043	0.884	1
N(1)	—	0.471	—	0.999	3.417	4.887	5
N(2)	—	—	0.949	—	4.105	5.054	5
H	—	0.128	—	—	—	—	—
Sum	4.814	3.183	—	—	*b*	*b*	*b*
Charge	5	3	—	—	—	*b*	*b*

[a] The bond valences were tested by means of the model proposed by Brown (*6*); it was worked out for a coordination sphere with a radius smaller than 2.8 Å for each atom belonging to the framework. The parameter values used in the determination of the bond valences are taken from Ref. (*7*).

[b] The bond valence sum around each hydrogen atom was not specified.

the cohesion of the structure. Here ethylenediamine plays two roles: (i) being a ligand of Al via N(1) and (ii) providing strong hydrogen bonds for stabilizing the layered structure. Indeed, the two hydrogens, H(8) and H(5), of the $N(2)H_2$ amino group give two strong O–H linkages with O(2) with distances of 1.99(3) and 2.02(3) Å, respectively.

To our knowledge, this is the first time that, in the crystal chemistry of the $AlPO_4$-*n* family, an amine plays via N the role of a ligand of aluminium besides its usual template part, probably due to the high concentration of amine in the solution. Another amine belonging to the $AlXO_4$ family of framework materials is $AlAsO_4$,ethanolamine (*9*) but, this time, the linkage of the amine to Al^{3+} occurs via the oxygen and not the nitrogen. Further work (in progress) will be devoted to the study of the nature of the occurring phases as a function of (i) the nature and (ii) the concentration of the amine.

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