Crystal structure of imidazolium trialuminium dodecaoxotriphosphate monohydroxide, $[\text{C}_3\text{H}_5\text{N}_2][\text{Al}_3\text{P}_3\text{O}_{12}(\text{OH})]$, $\text{AlPO}_4\text{-21}$

Kazumasa Sugiyama^{*I}, Junya Takashima^{II}, Michiyo Genba^{II} and Tokuhei Tagai^{III}

^I Tohoku University, Institute for Materials Science, Katahira 2-1-1, Aoba-ku, Sendai 980-8577, Japan

^{II} The University of Tokyo, Department of Earth and Planetary Science, Graduate School of Science, Hongo 7-3-1, Bunkyo-ku, Tokyo 113-0033, Japan

^{III} The University of Tokyo, University Museum, Hongo 7-3-1, Bunkyo-ku, Tokyo 113-0033, Japan

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Abstract

$\text{C}_3\text{H}_6\text{Al}_3\text{N}_2\text{O}_{13}\text{P}_3$, monoclinic, $P12_1/n1$ (no. 14), $a = 8.6191(4) \text{ \AA}$, $b = 17.803(1) \text{ \AA}$, $c = 9.0257(5) \text{ \AA}$, $\beta = 107.357(2)^\circ$, $V = 1321.9 \text{ \AA}^3$, $Z = 4$, $R_g(F) = 0.052$, $wR_{\text{ref}}(F^2) = 0.109$, $T = 293 \text{ K}$.

Source of material

Title compound was prepared by hydrothermal synthesis under autogeneous pressure. Typically, aluminium triisopropoxide (1.00 g) and imidazole (1.67 g) were first dispersed in H_2O (8 ml)

under stirring, and then 1.70 ml H_3PO_4 (85 wt%) was added dropwise to the above reaction mixture. The resulting gel was sealed in a Teflon-lined stainless steel autoclave and heated at 453 K for 4 days. The obtained crystals were washed with distilled water and dried at 323 K. The crystal of the title compound having the form of a transparent (010) platelet can be readily picked up from the washed sample and examined by the single crystal X-ray diffraction. The obtained sample includes another crystalline phase $\text{Al}_2[\text{HN}_4](\text{OH})(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ [1] together with very fine unknown compound. Further synthetic trials in this reaction system allowed no better results in obtaining pure $\text{AlPO}_4\text{-21}$ phase.

Experimental details

The structural refinement was carried out by using the framework positions reported [2]. Anisotropic analysis for the framework atoms was employed. Following the discussion of a variety of $\text{AlPO}_4\text{-21}$ structures, we assume that O1 represents a hydroxyl group which links two trigonal bipyramidal coordination polyhedra around Al1 and Al2. The possible hydrogen position of H1 was placed by the difference Fourier calculation and an isotropic temperature factor, $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{O1})$ was employed. During the refinement of the inorganic framework structure, non-hydrogen atoms of occluded imidazole molecules were also found in difference Fourier maps and could be located in the channel. The imidazole molecules were suggested to be protonated so as to maintain the charge balance of the title compound. Several least-squares calculations indicated that imidazole molecules were disordered on two overlapping positions and the present analysis fixed the occupation of 50 % for each position. Hydrogen atom attached to C and N were positioned geometrically and refined using a riding model ($d(\text{C}-\text{H}) = 0.93 \text{ \AA}$, $d(\text{N}-\text{H}) = 0.86 \text{ \AA}$ and $(U_{\text{iso}}(\text{H}) = 1.2 U_{\text{iso}}(\text{C}, \text{N}))$.

Discussion

A class of three dimensional (3D) aluminophosphate structures ($\text{AlPO}_4\text{-}n$) has been intensively synthesized under solvothermal or hydrothermal conditions by using a variety of amines acting as space fillers and charge compensators *i.e.* [3]. The reported $\text{AlPO}_4\text{-21}$ compounds were formulated as follows; $\text{Al}_3(\text{PO}_4)_3 \cdot \text{C}_2\text{H}_8\text{N}_2 \cdot \text{H}_2\text{O}$ (ethylenediamine) [2], $\text{Al}_3(\text{PO}_4)_3 \cdot \text{C}_4\text{H}_9\text{N} \cdot \text{H}_2\text{O}$ (pyrrolidine) [2], $\text{Al}_3\text{P}_3\text{O}_{12}\text{OH} \cdot 1.33\text{C}_7\text{H}_{21}\text{N}_2$ (*N,N,N',N'*-tetramethyl-1,3-propanediamine) [4], $\text{Co}_{0.12}\text{Al}_{5.88}\text{P}_6\text{O}_{24}(\text{OH})_2 \cdot \text{C}_2\text{H}_{10}\text{N}_2 \cdot 2\text{H}_2\text{O}$ (etylendiamine) [5], $\text{Al}_3\text{P}_3\text{O}_{12}\text{OH} \cdot \text{C}_2\text{H}_8\text{N}_2$ (dimethylenamine) [6] $\text{Al}_3\text{P}_3\text{O}_{12}\text{OH} \cdot \text{C}_4\text{H}_{14}\text{N}_2$ (*N*-methyl-1,3-diaminopropane) [7].

The title compound, $\text{C}_3\text{H}_5\text{N}_2 \cdot \text{Al}_3\text{P}_3\text{O}_{12}\text{OH}$, is new member of the $\text{AlPO}_4\text{-21}$ family. The PO_4 group has close to those for ideal

* Correspondence author (e-mail: kazumasa@imr.tohoku.ac.jp)

tetrahedral geometry with P—O distances ranging from 1.511(3) to 1.555(3) Å and P—O—P angles from 106.5(2)° to 111.9(2)°, which is typical for 3D aluminophosphate compounds. The interatomic distances with oxygens shared with tetrahedral Al (1.540(3)–1.555(3) Å; average 1.546 Å) are longer than any other distances with oxygens shared with trigonal-bipyramidal Al (1.511(3)–1.538(3) Å; average 1.521 Å), in particular.

Al1 and Al2 indicate five-fold coordination with approximately trigonal bipyramidal polyhedra. The Al1—O and Al2—O bond distances range between 1.794(3) and 1.921(3) Å and the O—Al1—O and O—Al2—O angles vary from 85.4(1)° to 169.5(1)°, by suggesting obvious deviation from those of regular Al₃O₄ tetrahedron. These two trigonal bipyramidal polyhedra are linked through a shared O1 and bond valence calculations suggested the undersaturated valence for the O1 site. This lead to find the possible H1 in the difference Fourier maps at about 0.8 Å from O1. This hydroxyl geometry allows hydrogen bonding to O3 across the five-membered ring. In AlO₄(OH) trigonal bipyramidal polyhedra, the apical oxygens and hydroxyls are more distant than the others; hydroxyls, $d(\text{Al1—O1}) = 1.845(3)$ Å, $d(\text{Al2—O1}) = 1.921(3)$ Å; apical oxygens $d(\text{Al1—O3}) = 1.854(3)$ Å, $d(\text{Al2—O12}) = 1.861(3)$ Å, $d(\text{Al1—O5}) = 1.874(3)$ Å. The Al₃O₄ tetrahedron is nearly regular with Al—O distances ranging from 1.724(3) to 1.757(3) Å and Al—O—Al angles from 105.6(2)° to 112.2(1)°.

Ribbon structures of edged-shared three- and five-membered rings run along [101] and are connected by a single tetrahedral chain so as to form the sheet structure (figure, top). The framework structure of AlPO₄-21 (figure, bottom) can be readily realized by the stacking of such sheet structures along [010], by sharing O12 corners between P1 and Al2 polyhedra and then creating the eight-membered channels along [101].

The protonated imidazolium cations [C₃H₅N₂]⁺ (IMH⁺) reside in eight-membered channels by producing hydrogen bonding between IMH⁺s and framework oxygens. Positional disorder of ImH⁺ molecules was suggested in the difference Fourier maps and this subsequently lead a statistical distribution model with two mutually exclusive positions, IMH1⁺ (N11, C21, N31, C41, C51) and IMH2⁺ (N12, C22, N32, C42, C52). Hydrogen bondings are found between N11 and N12 of the protonated imidazole and apical oxygens; $d(\text{N11} \cdots \text{O12}) = 2.82(1)$ Å and $d(\text{N12} \cdots \text{O5}) =$

2.87(1) Å. This structural feature well supports the positional disorder of IMH⁺ molecules. The previous reports suggested the octahedral coordination of Al in the AlPO₄-21 structure [3,6], nevertheless present analysis excludes such coordination. Octahedrally coordinated Al in AlPO₄-21 may reflect the residence of the doubly protonated templates in the channels.

Table 1. Data collection and handling.

Crystal:	colorless platelet, size 0.070 × 0.140 × 0.250 mm
Wavelength:	Mo K α radiation (0.71069 Å)
μ :	7.31 cm ⁻¹
Diffractometer, scan mode:	Rigaku R-Axis RAPID, ω
2 θ_{max} :	55°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	10515, 2987
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2386
$N(\text{param})_{\text{refined}}$:	212
Programs:	SHELXL-97 [8], ATOMS [9]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	x	y	z	U_{iso}
H(1)	4e		0.0000	0.2143	0.0872	0.016
N(11)	4e	0.50	0.961(1)	0.5313(5)	0.224(1)	0.032(2)
H(11)	4e	0.50	1.0646	0.5341	0.2424	0.038
C(21)	4e	0.50	0.888(1)	0.4908(6)	0.299(1)	0.027(2)
H(21)	4e	0.50	0.9373	0.4562	0.3763	0.032
N(31)	4e	0.50	0.727(1)	0.5065(5)	0.249(1)	0.031(2)
H(31)	4e	0.50	0.6531	0.4862	0.2820	0.037
C(41)	4e	0.50	0.703(1)	0.5578(6)	0.140(1)	0.040(3)
H(41)	4e	0.50	0.6039	0.5815	0.0941	0.048
C(51)	4e	0.50	0.841(2)	0.5717(8)	0.104(2)	0.048(3)
H(51)	4e	0.50	0.8557	0.6000	0.0221	0.058
N(12)	4e	0.50	0.911(2)	0.4933(8)	0.211(2)	0.067(3)
H(12)	4e	0.50	0.9522	0.4489	0.2169	0.080
C(22)	4e	0.50	0.939(2)	0.5416(8)	0.132(2)	0.052(3)
H(22)	4e	0.50	1.0033	0.5362	0.0661	0.062
N(32)	4e	0.50	0.870(1)	0.5996(7)	0.149(1)	0.047(3)
H(32)	4e	0.50	0.8801	0.6415	0.1055	0.056
C(42)	4e	0.50	0.782(3)	0.592(1)	0.238(2)	0.100(6)
H(42)	4e	0.50	0.7170	0.6282	0.2622	0.120
C(52)	4e	0.50	0.800(2)	0.5177(9)	0.296(2)	0.062(4)
H(52)	4e	0.50	0.7567	0.4928	0.3646	0.074

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P(1)	4e	0.3476(1)	0.42755(5)	0.3610(1)	0.0069(4)	0.0058(4)	0.0087(4)	-0.0008(3)	0.0002(3)	0.0001(3)
P(2)	4e	0.3069(1)	0.20783(5)	-0.0257(1)	0.0090(5)	0.0100(4)	0.0080(4)	-0.0026(4)	0.0020(4)	-0.0006(3)
P(3)	4e	0.2663(1)	0.16905(5)	0.4961(1)	0.0088(5)	0.0077(4)	0.0062(4)	0.0004(3)	-0.0002(3)	-0.0009(3)
Al(1)	4e	0.0772(1)	0.29557(6)	0.2874(1)	0.0068(5)	0.0066(5)	0.0088(5)	-0.0015(4)	0.0014(4)	-0.0009(4)
Al(2)	4e	0.1370(1)	0.10962(6)	0.1609(1)	0.0084(5)	0.0069(5)	0.0077(5)	0.0001(4)	0.0008(4)	-0.0012(4)
Al(3)	4e	0.5237(1)	0.32246(7)	0.1932(1)	0.0102(6)	0.0129(5)	0.0108(5)	0.0006(4)	0.0012(4)	-0.0024(4)
O(1)	4e	0.0448(3)	0.2061(2)	0.1795(3)	0.014(1)	0.011(1)	0.010(1)	0.005(1)	-0.004(1)	-0.003(1)
O(2)	4e	0.1931(3)	0.3810(2)	0.3084(3)	0.009(1)	0.010(1)	0.019(1)	-0.005(1)	-0.004(1)	0.002(1)
O(3)	4e	0.2466(3)	0.2508(1)	0.4384(3)	0.013(1)	0.007(1)	0.013(1)	0.001(1)	-0.003(1)	0.001(1)
O(4)	4e	-0.0543(3)	0.3065(2)	0.4075(3)	0.017(1)	0.021(2)	0.021(2)	0.005(1)	0.011(1)	0.003(1)
O(5)	4e	-0.0673(3)	0.3411(2)	0.1132(3)	0.014(1)	0.010(1)	0.012(1)	-0.002(1)	-0.004(1)	0.000(1)
O(6)	4e	0.4615(3)	0.4052(2)	0.2632(3)	0.016(1)	0.014(1)	0.017(1)	-0.000(1)	0.007(1)	-0.005(1)
O(7)	4e	0.3494(3)	0.2730(2)	0.0916(3)	0.015(1)	0.012(1)	0.015(1)	-0.001(1)	0.001(1)	-0.005(1)
O(8)	4e	0.6323(3)	0.3508(2)	0.0706(3)	0.018(2)	0.019(2)	0.023(2)	0.001(1)	0.011(1)	-0.002(1)
O(9)	4e	0.6509(3)	0.2693(2)	0.3453(3)	0.015(1)	0.015(1)	0.014(1)	0.001(1)	-0.005(1)	-0.001(1)
O(10)	4e	0.2489(3)	0.1135(2)	0.3632(3)	0.022(2)	0.012(1)	0.008(1)	0.005(1)	-0.004(1)	-0.003(1)
O(11)	4e	-0.0625(3)	0.0866(2)	0.0319(3)	0.011(1)	0.013(1)	0.012(1)	-0.002(1)	-0.001(1)	-0.003(1)
O(12)	4e	0.3008(3)	0.5093(1)	0.3324(3)	0.014(1)	0.005(1)	0.015(1)	-0.001(1)	0.003(1)	0.000(1)
O(13)	4e	0.2732(3)	0.1370(2)	0.0533(3)	0.013(1)	0.013(1)	0.017(1)	-0.000(1)	0.007(1)	0.003(1)

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