

Synthesis of a Chain Aluminophosphate Containing Racemic 1, 2-Diaminopropane

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Abstract: A one-dimensional chain aluminophosphate $C_{1.5}H_{7.5}N_{1.5}Al_{0.5}PO_4$ containing diprotonated racemic 1, 2-diaminopropane cations was synthesized from an alcoholic system. The compound consists of infinite inorganic $[AlP_2O_8]$ chains of alternately connected AlO_4 and $PO_2(=O)_2$ tetrahedral units and the racemic template molecules. The macroanionic chains contain corner-shared double four-membered rings.

Keywords: Chain aluminophosphate, crystal structure, solvothermal, racemic template.

Since the discovery of three-dimensional microporous aluminophosphates ($AlPO_4-n$)¹ in 1980s, a large number of novel chain, layered and open-framework aluminophosphates have been obtained from aqueous and non-aqueous systems. The synthesis of chiral microporous materials has been an important research subject since these materials may be used as enantioselective catalysts. The synthesis of zeolite β is one of the few successful examples in this respect. Recently, synthesis of layered aluminophosphates using chiral metal complexes² or organic amines^{3,4} as the structure-directing agents have been reported. Here we describe the synthesis and characterization of a new 1-D aluminophosphate, $C_{1.5}H_{7.5}N_{1.5}Al_{0.5}PO_4$, containing racemic 1, 2-diaminopropane molecules.

Experimental

The compound was synthesized with a solvothermal method by treating a gel with an empirical molar composition of $Al(i\text{-PrO})_3 : 10.2H_3PO_4 : 6.7(\pm)H_2NCH_2CH(CH_3)NH_2 : 72.5(\pm)HOCH_2CH(CH_3)OH$. The reaction mixture was sealed in a Teflon-lined stainless steel autoclave and heated at 180°C for 7 days under autogenous pressure. The resulting large single crystals were collected by filtration, washed with distilled water, and dried in air at ambient temperature.

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Results and Discussion

To date, there exist only three types of chain aluminophosphates synthesized by hydrothermal or solvothermal methods. The first type is $\text{Na}_4\text{Al}(\text{PO}_4)_2(\text{OH})^5$ containing $\text{AlO}_4(\text{OH})_2$ octahedra sharing *trans*-vertices to form an infinite chain, the second corresponds to the aluminophosphates with an Al:P ratio of 3:5 and their structures (such as $(\text{C}_7\text{H}_{13}\text{NH}_3)_5[\text{Al}_3\text{P}_5\text{O}_{20}(\text{OH})]^6$) are built up from rather complicated units. A third type of chain aluminophosphates is exemplified by $\text{AlP}_2\text{O}_8[\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3][\text{NH}_4]^7$, consisting of chains of corner-shared four-membered rings with an Al:P ratio of 1:2. The compound $\text{C}_{1.5}\text{H}_{7.5}\text{N}_{1.5}\text{Al}_{0.5}\text{PO}_4$ described in the current paper has an Al:P ratio of 1:2 as well, the structure of which is determined by single crystal X-ray diffraction. **Table 1** lists the crystallographic data for the compound and the selected bond distances and angles are summarized in **Table 2**. The as-synthesized compound consists of macroanionic chains separated by $[\text{NH}_4]^+$ and $(\pm)[\text{H}_3\text{NCH}_2\text{CH}(\text{CH}_3)\text{NH}_3]^{2+}$ cations (**Figure 1**). The one-dimensional macroanionic chain is constructed by tetrahedral AlO_4 and $\text{PO}_2(=\text{O})_2$ units. Each Al atom is tetrahedrally coordinated by four O atoms with the Al-O distances ranging between 0.1718(3) and 0.1728(3) nm and the O-Al-O angles ranging from 105.98(14) to 113.1(2)°. Two of the P atoms tetrahedrally coordinated by four O atoms are bonded to aluminum atoms through bridging O atoms with P-O bond lengths of 0.1531(3) and 0.1537(3) nm. The remaining P-O bond lengths characteristic of P=O bonds are 0.1498(3) nm for P-O(2) and 0.1507(3) nm for P-O(1). These values are in good agreement with those previously reported for other aluminophosphates⁷.

Table 1 Crystal data and structure refinement for $\text{C}_{1.5}\text{H}_{7.5}\text{N}_{1.5}\text{Al}_{0.5}\text{PO}_4$

Empirical formula	$\text{C}_{1.50}\text{H}_{7.50}\text{Al}_{0.50}\text{N}_{1.50}\text{O}_4\text{P}$
Formula weight	155.05
Crystal system	Orthorhombic
Space group	<i>Pccn</i>
Unit cell dimensions	$a = 1.68024(19)$ nm $b = 0.82662(9)$ nm $c = 0.86691(9)$ nm
Volume	$1.2041(2)$ nm ³
Z, Density (calculated)	$8, 1.711 \times 10^3$ Mg/m ³
Absorption coefficient	0.469 mm ⁻¹
F(000)	644
Absorption correction	Empirical
Max. and min. transmission	0.43152 and 0.31405
Goodness-of-fit on F^2	1.159
Final R indices [$I > 2\sigma(I)$] ^a	$R_1 = 0.0396, wR_2 = 0.0976$
R indices (all data)	$R_1 = 0.0476, wR_2 = 0.1013$
Largest diff. and hole	0.272×10^3 and -0.296×10^3 e·nm ⁻³

$$^a R_1 = \sum (\Delta F / \sum (F_0)); wR_2 = (\sum [w(F_0^2 - F_c^2)] / \sum [w(F_0^2)^2])^{1/2}, w = 1/\sigma^2(F_0^2).$$

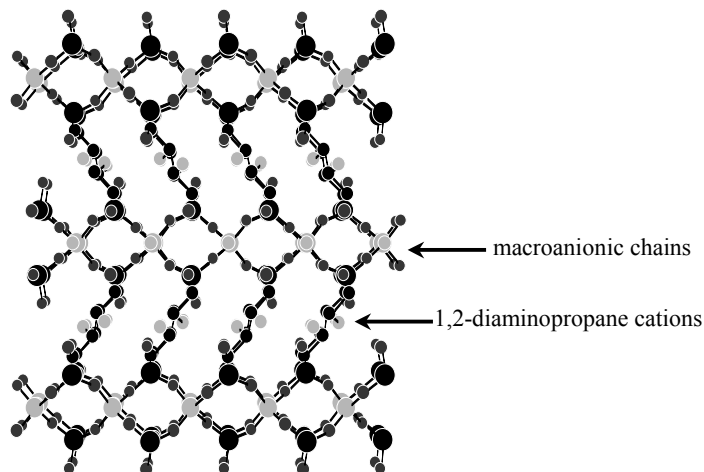
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Table 2 Selected bond distances [$\times 10^{-1}\text{nm}$] and angles [$^\circ$] for $\text{C}_{1.5}\text{H}_{7.5}\text{N}_{1.5}\text{Al}_0.5\text{PO}_4$

Al-O(3)#1	1.718(3)	P-O(3)	1.531(3)
Al-O(3)#2	1.718(3)	P-O(4)	1.537(3)
Al-O(4)	1.728(3)	O(3)-Al#4	1.718(3)
Al-O(4)#3	1.728(3)	C(1)-N(1)	1.494(5)
P-O(2)	1.498(3)	C(1)-C(1)#5	1.527(8)
P-O(1)	1.507(3)	C(1)-C(2)	1.555(9)
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O(3)#1-Al-O(3)#2	113.1(2)	O(2)-P-O(4)	110.51(17)
O(3)#1-Al-O(4)	105.98(14)	O(1)-P-O(4)	106.94(16)
O(3)#2-Al-O(4)	109.52(15)	O(3)-P-O(4)	107.61(17)
O(3)#1-Al-O(4)#3	109.52(14)	P-O(3)-Al#4	157.1(2)
O(3)#2-Al-O(4)#3	105.98(14)	P-O(4)-Al	150.4(2)
O(4)-Al-O(4)#3	112.9(2)	N(1)-C(1)-C(1)#5	109.5(4)
O(2)-P-O(1)	113.05(17)	N(1)-C(1)-C(2)	102.0(4)
O(2)-P-O(3)	108.57(16)	C(1)#5-C(1)-C(2)	118.6(5)
O(1)-P-O(3)	110.02(17)		

Symmetry transformations used to generate equivalent atoms: #1 $-x+3/2, y, z+1/2$
 #2 $x, -y+1/2, z+1/2$ #3 $-x+3/2, -y+1/2, z$ #4 $x, -y+1/2, z-1/2$ #5 $-x+1, -y, -z+2$

Figure 1 The racemic 1, 2-diaminopropane molecules lying between the aluminophosphate chains



Dark circle, P; gray, Al; small dark, C; small gray, N. Ammonium cations are omitted for clarity.

Chiral organic amine cations can be orderly arranged in aluminophosphate compounds^{3,4}. For instance, diprotonated racemic 1, 2-diaminopropane cations in a novel layered aluminophosphate $[\text{C}_3\text{H}_{12}\text{N}_2][\text{Al}_2\text{P}_2\text{O}_8(\text{OH})_2]\cdot\text{H}_2\text{O}^3$ are arrayed alternately in two rows with each row containing only one type of enantiomer. The protonated isopropanolamine cations of a new layered aluminophosphate $\text{Al}_3\text{P}_4\text{O}_{16}[\text{H}_3\text{NCH}_2\text{CH}(\text{OH})\text{CH}_3]_3^4$ exist in either a left-hand or a right-hand form and the two respective forms are arranged in a double layer fashion, each layer contains only one type of enantiomer.

The two enantiomers are separately arranged in these compounds. In the crystal structure of our compound, the two enantiomers of the chiral 1, 2-diaminopropane molecules are not distinguishable from each other, because the C(2) atom is statistically distributed.

Charge balance and hydrogen bonds are sufficed by the protonated amine cations (\pm)[H₃NCH₂CH(CH₃)NH₃]²⁺ and [NH₄]⁺. The diprotonated 1,2-diaminopropane ions with all six NH₃ protons, and the ammonium cations with all four protons, act as simple hydrogen-bond donors to the O(1) and O(2) terminal oxygens of the aluminophosphate chains. These hydrogen-bond distances are between 0.2725(4) and 0.2990(5) nm indicating that there is strong interaction of hydrogen bonds between macroanionic chains and protonated amines.

Acknowledgments

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