

Dual Function of Racemic Isopropanolamine as Solvent and as Template for the Synthesis of a New Layered Aluminophosphate: $[\text{NH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3]_3 \cdot \text{Al}_3\text{P}_4\text{O}_{16}$

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A new layered aluminophosphate $[\text{NH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3]_3 \cdot \text{Al}_3\text{P}_4\text{O}_{16}$ containing a racemic mixture of isopropanolamine has been synthesized using isopropanolamine as the predominant solvent and the template and its structure was determined by means of single-crystal X-ray diffraction. The title compound crystallizes in the trigonal space group $R\bar{3}$ with $M = 689.18$, $a = 13.1068(15)$ Å, $c = 26.935(4)$ Å, $Z = 6$, $V = 4007.2(9)$ Å³, $R = 0.0338$, and $R_w = 0.0982$. The structure consists of $[\text{Al}_3\text{P}_4\text{O}_{16}]^{3-}$ macroanionic sheets with a $4 \times 6 \times 12$ network stacked in an ABCABC sequence. The inorganic layers are constructed from alternating AlO_4 and $\text{PO}_3(=\text{O})$ tetrahedral units. The protonated isopropanolamine cations between inorganic layers are arranged in a double-layer fashion with each layer containing only one type of enantiomer. The as-synthesized product is characterized by powder X-ray diffraction, IR spectroscopy, inductive coupled plasma analysis, TGA and DTA.

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Key Words: layered aluminophosphate; synthesis; structure; isopropanolamine; solvent; template.

INTRODUCTION

It has been demonstrated that solvothermal synthesis results in the formation of a variety of 1-D chain, 2-D layer, and 3-D framework aluminophosphates (1, 2). These materials, which include the layered aluminophosphates with Al/P ratios of 4/5 (3), 3/4 (4, 5), 2/3 (6), and 1/2 (7) and the open-framework compounds JDF-20 (8) with Al/P = 5/6 and AlPO-HAD (9) with Al/P = 4/5, exhibit distinct stoichiometries. Without exception, all these aluminophosphates crystallize in the presence of a solvent and an organic template which are different species. Usually, the solvent is either water or alcohol whereas the template is an amine or a metal complex containing amine molecules as the ligands. In addition, the synthesis of chiral microporous materials continues to be an interesting research subject since these

materials may be used as enantioselective catalysts. One of the few successful examples in this respect is the synthesis of zeolite β with chirality (10). Recently, syntheses of layered aluminophosphates using chiral metal complexes as the structure-directing agents have also been reported (11–14). Here we describe the synthesis and characterization of a new 2-D aluminophosphate with 12-membered-ring macroanionic layers stacking in an ABCABC sequence. The crystals of the compound were grown through a novel route in which a racemic mixture of isopropanolamine functions as both the solvent and the template.

EXPERIMENTAL

The title compound was synthesized by solvothermally treating a gel formed from aluminum triisopropoxide ($\text{Al}(\text{i-PrO})_3$), phosphoric acid (85 wt%), and racemic isopropanolamine. The reaction mixture with an empirical molar composition of $\text{Al}(\text{i-PrO})_3:1.67 \text{H}_3\text{PO}_4:51 \text{NH}_2\text{CH}_2\text{CH}(\text{OH})\text{CH}_3:1.67 \text{H}_2\text{O}$ was stirred until it was homogeneous (the amount of water added to the reaction system with the phosphoric acid was minute as compared with that of isopropanolamine, and the presence of such a small amount of water should not affect the predominantly nonaqueous feature of the reaction medium) (1). Typically, 2.1 g of aluminum triisopropoxide was first dispersed into 40 ml of isopropanolamine with stirring, and 1.2 ml of phosphoric acid (85 wt%) was added slowly to the above mixture under continuous stirring. The final reaction mixture was sealed in a Teflon-lined stainless steel autoclave and heated at 180°C for 6 days under autogeneous pressure. The resulting large single crystals were collected by filtration, washed with distilled water, and dried in air at ambient temperature.

Powder X-ray diffraction (XRD) data were collected on a Siemens D5005 diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.5418$ Å). The elemental analyses were conducted on a Perkin-Elmer 240C element analyzer. Inductively coupled plasma (ICP) analysis was performed on a Perkin-Elmer

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Optima 3300DV spectrometer. A Perkin-Elmer DTA 1700 differential thermal analyzer was used to obtain the differential thermal analysis (DTA) curve and a Perkin-Elmer TGA 7 thermogravimetric analyzer to obtain the thermogravimetric analysis (TGA) curve in an atmospheric environment. The heating rate was $20^{\circ}\text{C min}^{-1}$ and the sample weight was 4.37 mg. The infrared spectrum was recorded within the $400\text{--}4000\text{ cm}^{-1}$ region on a Nicolet Impact 410 FTIR spectrometer using KBr pellets.

A colorless rhombohedral crystal of dimensions $0.15 \times 0.15 \times 0.05\text{ mm}$ was glued to a thin glass fiber with epoxy resin and mounted on a Bruker-AXS Smart CCD diffractometer equipped with a normal-focus, 2.4 kW sealed tube X-ray source (graphite-monochromated $\text{MoK}\alpha$ radiation, $\lambda = 0.71073\text{ \AA}$) operating at 50 kV and 40 mA. Intensity data were collected in 1271 frames with increasing ω (width of 0.3° and exposure time of 30 s per frame). The total numbers of measured reflections and observed unique reflections were 2753 and 1197, respectively. The agreement factor between equivalent reflections (R_{int}) was 0.033. Systematic absence and statistics of intensity distribution resulted in a space group of $R\bar{3}$ (No. 148) for $[\text{NH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3]_3 \cdot \text{Al}_3\text{P}_4\text{O}_{16}$. The structure was solved by direct methods. The aluminum and phosphorus atoms were first located, whereas the carbon, nitrogen, and oxygen atoms were found in the difference Fourier maps. The hydrogen atoms residing on the amine molecules were placed geometrically with their isotropic temperature factors being fixed at 0.08 during the structure refinements. The full-matrix least-squares refinements were against F^2 and included secondary extinction correction and anisotropic displacement parameters for nonhydrogen atoms. The structure solution and refinement were performed by using the SHELXTL program system (version 5.1) (15).

RESULTS AND DISCUSSION

Characterization

The ICP analysis for the title compound gives rise to an Al/P ratio of 3/4. The element analysis indicates that the contents of C, H, and N are 16.01, 4.25, and 5.86%, respectively, in good agreement with the values (15.67, 4.35, and 6.1%) based on the single-crystal structure formula (see Table 1).

The powder X-ray diffraction pattern for $[\text{NH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3]_3 \cdot \text{Al}_3\text{P}_4\text{O}_{16}$ is in good agreement with that simulated on the basis of the single-crystal structure (Fig. 1). The diffraction peaks on both patterns correspond well in position, suggesting that the as-synthesized sample is pure.

The IR spectrum of the compound exhibits a strong band at 3400 cm^{-1} due to stretching vibrations of the $-\text{OH}$ groups of the template. The band at 2921 cm^{-1} is also characteristic of a primary amine in its protonated form, whereas the bands at 1650 , 1538 , and 1384 cm^{-1} are related

TABLE 1
Crystal Data and Structure Refinement for
 $[\text{NH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3]_3 \cdot \text{Al}_3\text{P}_4\text{O}_{16}$

Empirical formula	$[\text{NH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3]_3 \cdot \text{Al}_3\text{P}_4\text{O}_{16}$
Formula weight	689.18
Temperature	293(2) K
Wavelength	0.71073 \AA
Crystal system	Trigonal
Space group	$R\bar{3}$
<i>a</i>	13.1068(15) \AA
<i>c</i>	26.935(4) \AA
<i>V</i>	4007.2(9) \AA^3
<i>Z</i>	6
Density (calc)	1.714 g/cm^3
μ	0.468 mm^{-1}
<i>F</i> (000)	2136
Crystal size	$0.15 \times 0.15 \times 0.05\text{ mm}$
2θ range	$7.34\text{--}46.40^{\circ}$
Index ranges	$14 \leq h \leq 10, -14 \leq k \leq 13, -26 \leq l \leq 26$
Total data collected	2753
Unique data	1197
<i>R</i>	0.0338
<i>R</i> _w	0.0982
$\Delta\rho$ max/min	0.634 and -0.338 e \AA^{-3}

to isopropanolamine (16). The main bands observed in the range of $478\text{--}1182\text{ cm}^{-1}$ are associated with the asymmetric stretching and bending vibrations of PO_4 units (17).

The thermogravimetric analysis shows a major weight loss occurring at about 200°C accompanied by a distinct endothermic effect. Following the major weight loss is a gradual one at higher temperatures. The total weight loss of the compound is about 33%, in accordance with that calculated on the basis of the empirical formula.

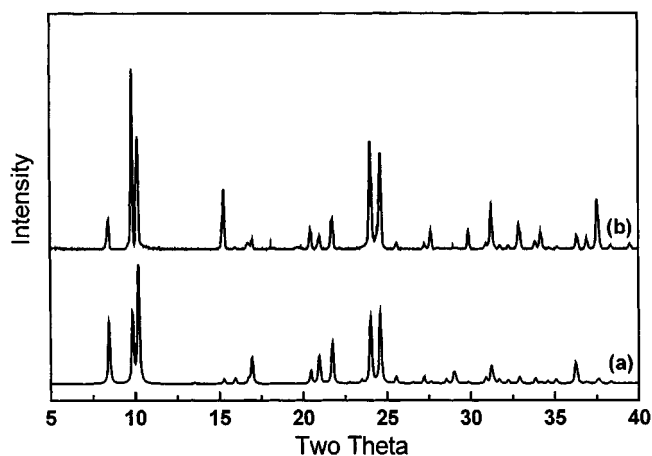


FIG. 1. Simulated (a) and experimental (b) powder X-ray diffraction patterns for $[\text{NH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3]_3 \cdot \text{Al}_3\text{P}_4\text{O}_{16}$

Powder X-ray diffraction shows that the title compound heated at 180°C retains its structure, whereas it transforms to AlPO_4 -trydimite after being heated at 270°C, suggesting that the structure is stable only in the presence of the template.

Description of the Structure

The crystallographic data are summarized in Table 1 and the atomic coordinates, bond distances, and selected bond angles are listed in Tables 2 and 3, respectively. There are one independent Al and two independent P atoms in the asymmetric unit (Fig. 2). Each of the two crystallographically independent P atoms shares three oxygen atoms with adjacent Al atoms and the P–O bond lengths range from 1.523(2) to 1.532(2) Å. The fourth P–O bond length characteristic of P=O groups is 1.485(3) Å for P(1)–O(2) and 1.486(4) Å for P(2)–O(5) (4, 18). The structure of the title compound consists of macroanionic layers of empirical formula $[\text{Al}_3\text{P}_4\text{O}_{16}]^{3-}$ and protonated isopropanolamine cations located in the interlayer region. The individual layer, which was also observed previously (4, 19, 20), is formed from a network of alternately connected AlO_4 and $\text{PO}_3(=\text{O})$ tetrahedral units through oxygen bridges. In the individual layer there exist 12-membered rings, each of which is surrounded by four-membered and phosphoryl-capped six-membered rings. The P=O groups capping the six-membered rings point to the interlayer region alternately above and below the sheet. The average Al–O bond distances (1.731 Å) and O–Al–O bond angles (109.5°) are in good agreement with those found for other aluminophosphates (see Table 3) (5, 21, 22).

TABLE 2
Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) of Nonhydrogen Atoms for $[\text{NH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3]_3 \cdot \text{Al}_3\text{P}_4\text{O}_{16}$

	x	y	z	U(eq)
P(1)	3314(1)	−1157(1)	455(1)	18(1)
P(2)	6667	3333	867(1)	18(1)
Al(1)	4770(1)	1481(1)	154(1)	19(1)
O(1)	2208(2)	−1940(2)	148(1)	31(1)
O(2)	3118(2)	−1427(2)	993(1)	35(1)
O(3)	3642(2)	115(2)	337(1)	28(1)
O(4)	5572(2)	2257(2)	665(1)	41(1)
O(5)	6667	3333	1419(1)	25(1)
O(6)	4322(2)	−1338(2)	276(1)	34(1)
O(7)	2262(3)	369(4)	8373(1)	75(1)
N(1)	4418(3)	901(4)	8694(1)	57(1)
C(3)	1208(4)	−934(5)	9056(2)	93(2)
C(2)	2317(4)	88(4)	8863(2)	55(1)
C(1)	3340(4)	−122(4)	8912(2)	52(1)

Note. U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3
Bond Lengths (Å) and Angles (°) for $[\text{NH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3]_3 \cdot \text{Al}_3\text{P}_4\text{O}_{16}$

P(1)–O(2)	1.485(3)	P(2)–O(5)	1.486(4)
P(1)–O(3)	1.532(2)	P(2)–O(4) #1	1.523(2)
P(1)–O(1)	1.532(2)	P(2)–O(4)	1.523(2)
P(1)–O(6)	1.532(2)	P(2)–O(4) #2	1.523(2)
Al(1)–O(4)	1.723(3)	Al(1)–O(6) #4	1.736(2)
Al(1)–O(3)	1.729(2)	O(1)–Al(1) #5	1.734(2)
Al(1)–O(1) #3	1.734(2)	O(6)–Al(1) #4	1.736(2)
O(7)–C(2)	1.381(5)	C(3)–C(2)	1.493(6)
N(1)–C(1)	1.498(6)	C(2)–C(1)	1.504(6)
O(2)–P(1)–O(3)	112.49(13)	O(5)–P(2)–O(4) #1	110.92(11)
O(2)–P(1)–O(1)	111.98(14)	O(5)–P(2)–O(4)	110.92(11)
O(3)–P(1)–O(1)	105.96(12)	O(4) #1–P(2)–O(4)	107.98(12)
O(2)–P(1)–O(6)	109.24(14)	O(5)–P(2)–O(4) #2	110.92(11)
O(3)–P(1)–O(6)	107.99(12)	O(4) #1–P(2)–O(4) #2	107.98(12)
O(1)–P(1)–O(6)	109.04(13)	O(4)–P(2)–O(4) #2	107.98(12)
O(4)–Al(1)–O(3)	109.61(12)	P(1)–O(1)–Al(1) #5	142.09(15)
O(4)–Al(1)–O(1) #3	111.45(13)	P(1)–O(3)–Al(1)	144.65(14)
O(3)–Al(1)–O(1) #3	108.06(11)	P(2)–O(4)–Al(1)	147.81(18)
O(4)–Al(1)–O(6) #4	110.32(13)	P(1)–O(6)–Al(1) #4	156.56(17)
O(3)–Al(1)–O(6) #4	110.84(11)	O(7)–C(2)–C(3)	114.5(4)
O(1) #3–Al(1)–O(6) #4	106.50(12)	O(7)–C(2)–C(1)	107.7(4)
C(3)–C(2)–C(1)	111.2(4)	N(1)–C(1)–C(2)	109.2(3)

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

The protonated amine cations $(\text{NH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3)^+$ reside in the interlayer space between the macroanionic layers. There are N–H⋯O and O–H⋯O hydrogen bonds between the protonated isopropanolamine and the terminal oxygen atoms of the phosphate groups. The observed

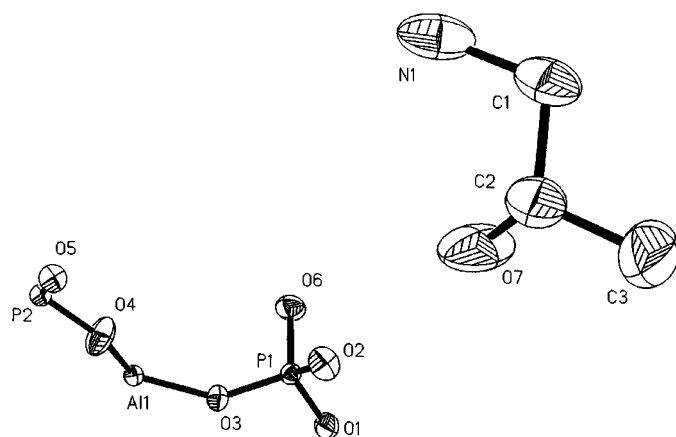


FIG. 2. ORTEP drawing of the asymmetric unit of $[\text{NH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3]_3 \cdot \text{Al}_3\text{P}_4\text{O}_{16}$. Thermal ellipsoids are shown at 50% probability.

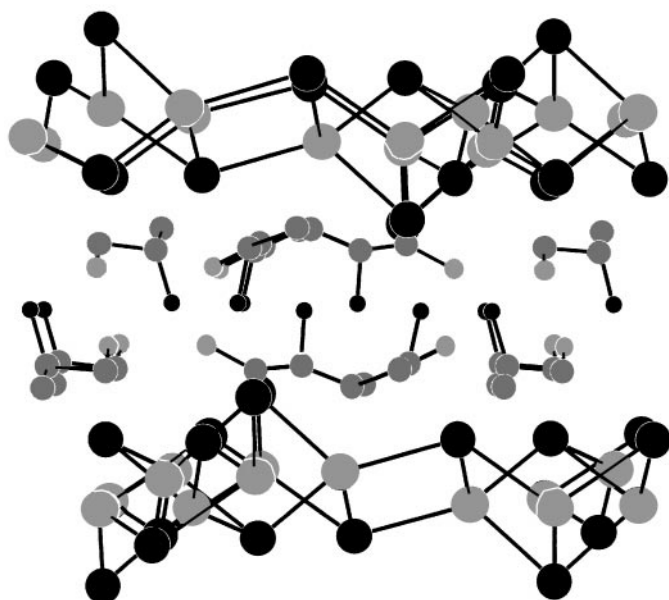


FIG. 3. Arrangement of template molecules for $[\text{NH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3]_3 \cdot [\text{Al}_3\text{P}_4\text{O}_{16}]$: double layers of DL-isopropanolamine between inorganic macroanionic sheets viewed along the plane of the layer with each layer containing a particular enantiomer. (O atoms in inorganic sheets are omitted for clarity.)

distances of the template N atom to the nearest terminal O atoms in the macroanionic layer are 2.819(4), 2.948(4), and 3.064(4) Å, respectively, whereas that of the template O atom to the nearest O atom of the phosphoryl group capping the six-membered ring is 2.861(3) Å. Hydrogen bonds are believed to play an important role in determining the structural features of layered aluminophosphates since the macroanionic sheets are held together through H bonds in different ways for differently layered aluminophosphates. In the title compound, the H bonds between the protonated isopropanolamine molecules and the inorganic sheets are arranged in such a manner that the 12-membered rings of different inorganic sheets do not superimpose one another. Figure 3 shows that the protonated isopropanolamine cations of the title compound exist in either a left-hand or a right-hand form and the two respective forms are arranged in a double-layer fashion with each layer containing only one type of enantiomer. This is in contrast with the situation of GTex-2 and $\text{D-Co}(\text{en})_3 \cdot \text{Al}_3\text{P}_4\text{O}_{16} \cdot 3\text{H}_2\text{O}$ reported previously in which only the metal complexes of a specific enantiomer are intercalated between inorganic layers (11,23). In another layered aluminophosphate the racemic DL-Co(en) $_3^+$ cations do exist but they are arranged as a single layer between two adjacent inorganic sheets (12).

Before the present work, only two typical stacking sequences for 2-D sheet aluminophosphates had been reported, i.e., AAAA and ABAB (6, 20). It is interesting that the stacking of the inorganic layers in the title compound is

in an unusual ABCABC sequence along the crystallographic c axis. In each stacking period there are three macroanionic layers, of which the layer B is generated from the layer A by the symmetry operation $t(\frac{2}{3}, \frac{1}{3}, \frac{1}{3})$ and the layer C from the layer A by $t(\frac{1}{3}, \frac{2}{3}, \frac{2}{3})$. Viewed along the [001] direction, the capped six-membered ring in the layer A positions just at the center of the 12-membered ring in layer B, and a similar stacking is observed for layers B and C but layers A and C do not overlap each other (Fig. 4). Unlike other 12-membered ring-containing sheet aluminophosphates (4, 19, 20), the title compound has no free 12-membered ring channels due to the blockage of the protonated organic molecules residing in the interlayer region.

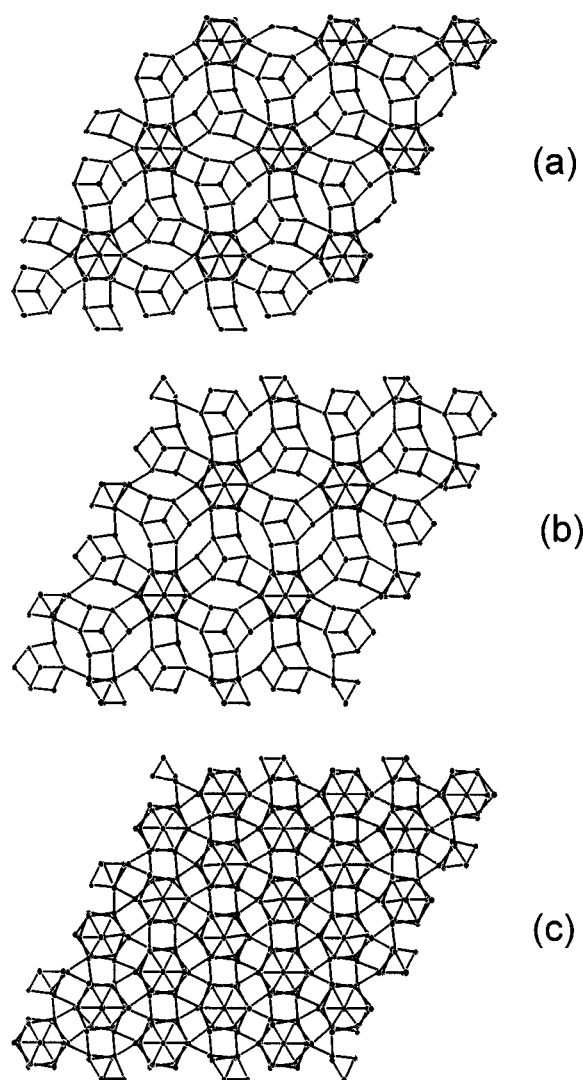


FIG. 4. Structure of $[\text{NH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3]_3 \cdot [\text{Al}_3\text{P}_4\text{O}_{16}]$ viewed along the c axis showing stacking of (a) macroanionic layers A and B, (b) layers A and C, and (c) three macroanionic layers in an ABC sequence. (O atoms are omitted for clarity.)

The choice of the solvent is important to the synthesis of 3-D open-framework and low-dimensional aluminophosphates (1, 24). The polarity, the chain length, the viscosity, and the boiling point of the solvent are all factors that may influence the crystallization of 1-D, 2-D, and 3-D aluminophosphates. The use of ethanalamine as a template has led to the formation of open-framework AlAsO_4 -1 and AlPO_4 -JDF which are isostructural with each other (25, 26). Both monoalcohols and diols have been used as the solvent for the formation of aluminophosphates containing a template that is normally an amine or amine-containing metal complex (6, 8). It is easily inferred that molecules that can function as both solvent and template for the crystallization of aluminophosphates should possess both hydroxyl and amino groups, and isopropanolamine is one of the ideal candidates. The hydroxyl group in isopropanolamine is indispensable to dissolving the reactant aluminum triisopropoxide and to forming hydrogen bonds, whereas the amino group acts as a moiety to direct the formation of the layered aluminophosphate.

CONCLUSION

Using racemic isopropanolamine as the predominant solvent and the template, a new layered aluminophosphate was synthesized under solvothermal reaction conditions. The compound contains macroanionic $[\text{Al}_3\text{P}_4\text{O}_{16}]^{3-}$ layers stacked in an unusual ABCABC sequence and the template molecules are protonated and intercalated between the inorganic macroanionic sheets. H bonds between the protons on the template molecules and the O atoms of the inorganic sheets prevail in the structure and they are believed to stabilize the layered structure. The synthesis of the title compound demonstrates that a molecule with $-\text{NH}_2$ and $-\text{OH}$ groups can function as both a solvent and a template for the formation of organic-inorganic hybrid materials and the synthetic route involving dual-functional molecules offers a valuable approach to preparing layered aluminophosphates with new structural features.

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