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Solid-State Synthesis and Characterization of Novel Aluminophosphates, $A_3Al_2P_3O_{12}$ (A = Na, K, Rb, Tl): Influence of A^+ Ions on the Coordination of Aluminum

R. Nandini Devi and K. Vidyasagar*

Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, India

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Four aluminophosphates, $A_3Al_2P_3O_{12}$ (A = Na, K (**1**), Rb (**2**), Tl (**3**)), have been synthesized by solid-state reactions and characterized by X-ray diffraction and NMR and IR spectroscopic techniques. Aluminum has trigonal bipyramidal coordination in the thallium compound and tetrahedral coordination in the others. Potassium, rubidium and thallium analogues have been structurally characterized by single-crystal X-ray diffraction and found to possess three-dimensional $(Al_2P_3O_{12})^{3-}$ anionic frameworks with channels occupied by A^+ countercations. These frameworks are built from corner connections of PO_4 tetrahedra with AlO_4 tetrahedra in **1** and **2** and with AlO_5 trigonal bipyramids in **3**. Pertinent crystal data are as follows: for **1**, orthorhombic space group $Pna2_1$, $a = 8.685(2)$ Å, $b = 16.947(2)$ Å, $c = 8.458(3)$ Å, $Z = 4$; for **2**, orthorhombic space group $Cmc2_1$, $a = 17.164(2)$ Å, $b = 8.6270(6)$ Å, $c = 8.8140(14)$ Å, $Z = 4$; for **3**, orthorhombic space group $Pna2_1$, $a = 6.1478(15)$ Å, $b = 10.396(3)$ Å, $c = 17.787(5)$ Å, $Z = 4$. Compound **3** is a rare example of an oxide possessing aluminum exclusively in trigonal bipyramidal coordination.

Introduction

A variety of oxides with the general formula $A_xM_2X_3O_{12}$ ($x \geq 0$), having different types of crystal structures such as $Fe_2(SO_4)_3$, NASICON, langbeinite, garnet, alluaudite etc., possess three-dimensional $M_2(XO_4)_3$ structural frameworks built from corner sharing of MO_6 octahedra with XO_4 tetrahedra.[1−5] These frameworks are neutral, as in $Fe_2(SO_4)_3$, or anionic, as in NASICON, with A^+ countercations in the interstitial free space of the framework. Phosphates in the A−M−P−O quaternary system form a large family of compounds possessing these types of $M_2X_3O_{12}$ frameworks. Research on the synthetic and structural chemistry of these materials continues to be pursued with the idea of obtaining them with accessible redox catalytic activity, anisotropic electrical conductivity, high ionic conductivity, and ion exchange properties. Among such phosphates, $Na_3Fe_2P_3O_{12}$ with the NASICON structure[6] is noteworthy from the structural point of view. It has octahedral coordination for Fe^{3+}, although Fe^{3+} is known to be stable in oxides in lower coordinations as well. For example, Fe^{3+} in $K_3Fe_2P_3O_{12}$ is present in both octahedral and square pyramidal coordinations.[7]

Aluminum is another trivalent ion that is similarly known to exist in four-, five-, and six-coordinations in oxides. It is surprising that no structurally characterized $A_3Al_2P_3O_{12}$ compound has been reported so far. $K_3Al_2P_3O_{12}$ and $Na_3Al_2P_3O_{12}$ are the only two compounds of this family realized in the phase studies of A−Al−P−O system by Berul et al.[8] and Ustyantsev et al.,[9] who reported the powder X-ray patterns without any further crystallographic information. In one of our crystal growth attempts, we isolated the single crystals of not the intended compound but an unexpected one, namely $K_3Al_2P_3O_{12}$, formed by the inadvertent reaction of a KPO_3 flux with an alumina crucible. Single-crystal X-ray diffraction study of these crystals revealed that $K_3Al_2P_3O_{12}$, in contrast to hitherto structurally characterized isomorphous $A_3M_2P_3O_{12}$ compounds, possesses a new type of structure with aluminum in tetrahedral coordination only. It is this lower coordination of aluminum in $K_3Al_2P_3O_{12}$ that prompted us to examine the influence of different monovalent A^+ ions and the method of preparation on the coordination of aluminum and structure type in $A_3Al_2P_3O_{12}$ compounds.

In this paper, we describe our solid-state synthetic attempts to prepare $A_3Al_2P_3O_{12}$ (A = alkali metal, Tl) compounds and successful crystal growth and characterization, by X-ray diffraction and spectroscopy, of the novel aluminophosphates $K_3Al_2P_3O_{12}$ (**1**), $Rb_3Al_2P_3O_{12}$ (**2**), and $Tl_3Al_2P_3O_{12}$ (**3**), with aluminum in exclusively tetrahedral or trigonal bipyramidal coordination.

Experimental Section

Synthesis. $Al(OH)_3$, NaH_2PO_4, KH_2PO_4, $NH_4H_2PO_4$, $RbNO_3$, and $TlNO_3$ of high purity were used for the solid-state synthesis of $A_3Al_2P_3O_{12}$ (A = Na, K (**1**), Rb (**2**), Tl (**3**)) compounds in polycrystalline form. These compounds were prepared by heating stoichiometric mixtures of appropriate chemicals, in open air, at initial low temperatures of 200−400 °C for 12 h to prompt the decomposition of the phosphates and then finally for 24 h at maximum temperatures of 900 °C for **1** and **2** and 700 °C for **3**. The temperatures were raised to the maximum values in steps of 100 °C, and the duration of heating in each step was 12 h. Three intermittent grindings were performed during the entire heating schedule.

Crystal Growth. Single crystals of $K_3Al_2P_3O_{12}$ (**1**) were formed in an inadvertent reaction of a KPO_3 flux with an alumina crucible in

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Table 1. Crystallographic Data for $A_3Al_2P_3O_{12}$ (A = K (**1**), Rb (**2**), Tl (**3**)) Compounds

empirical formula	$Al_2K_3O_{12}P_3$ (**1**)	$Al_2O_{12}P_3Rb_3$ (**2**)	$Al_2O_{12}P_3Tl_3$ (**3**)
a (Å)	8.685(2)	17.164(2)	6.148(2)
b (Å)	16.947(2)	8.6270(6)	10.396(3)
c (Å)	8.458 (3)	8.8140(14)	17.787(5)
V (Å^3)	1244.9(5)	1305.2(3)	1136.8(5)
Z	4	4	4
fw	456.09	595.20	951.91
space group	$Pna2_1$	$Cmc2_1$	$Pna2_1$
T (°C)	25 ± 2	25 ± 2	25 ±2
λ(Mo Kα) (Å)	0.710 73	0.710 73	0.710 73
ρ_{calcd} (g cm^{-3})	2.434	3.029	5.562
μ(Mo Kα) (mm^{-1})	1.598	11.540	43.025
R^a	0.0233	0.0290	0.0275
$R_w{}^b$	0.0575	0.0712	0.0609

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w|F_o|^2]^{1/2}$.

which a nominal composition of "$KCaNbTiP_2O_{11}$" and KPO_3 in a mass ratio of 1:5 were heated to a maximum temperature of 900 °C and then cooled to 750 °C at a rate of 3 °C/h, after which the furnace was turned off. Colorless block-shaped crystals of the rubidium compound (**2**) were grown using an $RbPO_3$ flux by heating a 3:6:1 mole ratio mixture of Rb_2CO_3, $NH_4H_2PO_4$, and $Al(OH)_3$ initially at 400 °C and then at a final temperature of 900 °C for 1 d followed by cooling to 750 °C at a rate of 3 °C/h. The crystals were isolated by washing away the flux with hot water. Similarly, needle-shaped crystals of the thallium compound (**3**) were obtained by heating a 3:6:1 mole ratio mixture of Tl_2CO_3, $NH_4H_2PO_4$, and $Al(OH)_3$ at a final temperature of 700 °C.

Characterization. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku desktop X-ray diffractometer using Ni-filtered Co Kα (λ = 1.7902 Å) radiation. Solid-state nuclear magnetic resonance (NMR) experiments were performed with magic-angle spinning (MAS) on a Bruker DSX 300 spectrometer operating at resonance frequencies of 78.2 and 121.5 MHz for ^{27}Al and ^{31}P, respectively. Chemical shifts were referenced to external standards of $Al(NO_3)_3$ for ^{27}Al and H_3PO_4 for ^{31}P. The spinning frequencies for ^{27}Al were 6.3, 4, 4.6, and 4.8 kHz for $Na_3Al_2P_3O_{12}$, **1**, **2**, and **3** and 7.5, 5.1, and 6.8 kHz in the case of ^{31}P for **1**−**3**. The recycle delay times were 15 μs for both, and pulse lengths were 5.0 μs for ^{27}Al and 4.0 μs for ^{31}P. Infrared spectra were recorded on a Bruker 17S 66V FT-IR spectrometer. The samples were ground with dry KBr and pressed into transparent disks.

Single-Crystal Structure Determination. Single crystals of compounds **1**−**3** suitable for X-ray diffraction were mounted on glass fibers with epoxy glue, and the data were collected on an Enraf Nonius CAD4 diffractometer by standard procedures. There was no detectable decay of the crystals during the data collection as judged from the invariance of intensities of three check reflections monitored at regular intervals. Absorption corrections based on azimuthal scans of reflections with χ = 90° were applied to the data sets. The observed systematic absences indicated that the possible space groups for compounds **1**−**3** are the noncentrosymmetric space groups $Pna2_1$, $Cmc2_1$, and $Pna2_1$ and the corresponding centrosymmetric ones, respectively. Both centrosymmetric and noncentrosymmetric space groups were tried for all three compounds. Only the noncentrosymmetric space groups were proved to be correct by successful structure solutions and refinements. The programs SHELXS-86 and SHELXL-93 were used for structure solution and refinement, respectively.[10] Pertinent crystallographic data for **1**−**3** are given in Table 1. The graphic programs[11] ATOMS and ORTEP were used to draw the structures. The alkali metal, aluminum, and phosphorus atoms were first located by direct methods. Refinement of their positions and subsequent difference Fourier maps led to the location of oxygen atoms. All the atoms were refined by full-matrix least-squares methods based on F^2.

For compounds **1** and **2**, the anisotropic refinements of all the atoms of the asymmetric units proceeded smoothly to give acceptable R values and the final difference Fourier maps had no chemically significant features. For **2**, the difference Fourier map contained only one peak with an electron density >1 e/Å^3, which was found to be a ghost of Rb(1). For compound **3**, on the other hand, only thallium atoms could be refined anisotropically and others were refined isotropically to give R = 0.0372 and R_w = 0.0876. The final difference Fourier map contained as many as 13 peaks with electron densities of ≥1 e/Å^3, the maximum being 1.72 e/Å^3. These peaks were found to be the ghosts of the existing atoms, indicating severe absorption problems. Therefore, an additional absorption correction using the DIFABS program[12] was applied to the isotropically refined data set. In the final refinement using the corrected data, seven atoms were refined anisotropically. This led to an improved R factor of 0.0275, an R_w value of 0.0609, and a better difference Fourier map with only four ghost peaks having electron densities of 1−1.20 e/Å^3. The chemical structure of **3** is not affected by the absorption problem and the correction applied to the data set. Several attempts to grow better crystals of **3** were not successful.

Results and Discussion

Four $A_3Al_2P_3O_{12}$ (A = Na, K (**1**), Rb (**2**), Tl (**3**)) compounds were synthesized in polycrystalline form by solid-state reactions. Lithium and cesium compounds could not be prepared. Crystal growth attempts using APO_3 fluxes yielded single crystals suitable for X-ray diffraction only in the case of rubidium (**2**) and thallium (**3**) compounds. Despite our several attempts using different fluxes, such as Na_3PO_4, NaCl, $NaPO_3$ etc., the sodium compound could not be grown as single crystals. The powder XRD patterns of compounds **1**−**3** compare well with those simulated by the program LAZY PULVERIX[13] using the crystallographic data, confirming the monophasic nature of the polycrystalline samples. The powder XRD pattern of the sodium compound does not resemble those of compounds **1**−**3**, indicating that its structure is different and could be indexed on an orthorhombic cell with the parameters a = 15.535(10) Å, b = 16.576(8) Å, and c = 8.188(9) Å.

Crystal Structures. Compounds **1**−**3** crystallize in different noncentrosymmetric space groups and possess three-dimensional $[Al_2P_3O_{12}]^{3-}$ anionic frameworks with one-dimensional channels occupied by countercations, K^+, Rb^+, and Tl^+. Aluminum has tetrahedral coordination in **1** and **2** and trigonal bipyramidal coordination in **3**. The final atomic positional and equivalent isotropic thermal parameters for compounds **1**−**3** are given in Table 2.

In **1** and **2**, the features of the anionic frameworks, built from corner-connected AlO_4 and PO_4 tetrahedra, are the same, and we discuss these features by taking **1** as an example. The crystallographically distinct atoms of the asymmetric unit of **1** are two aluminum, three phosphorus, twelve oxygen, and three potassium atoms. As shown in Figure 1, both $Al(1)O_4$ and $Al(2)O_4$ tetrahedra share all their corners with PO_4 tetrahedra. $Al(1)O_4$ shares two corners with $P(2)O_4$ and the other two corners with $P(3)O_4$ and $P(1)O_4$. Similarly, $Al(2)O_4$ shares two corners with $P(3)O_4$ and the other two corners with $P(2)O_4$ and $P(1)O_4$. Each $P(3)O_4$ is corner-connected to two $Al(2)O_4$ tetrahedra and one $Al(1)O_4$ whereas each $P(2)O_4$ is corner-connected to two $Al(1)O_4$ tetrahedra and one $Al(2)O_4$. $P(1)O_4$, on the other hand, shares only two corners, one with each AlO_4 type. This corner-connected tetrahedral network is three-dimensional and has intersecting channels, with windows of twelve-, six-, and eight-sided skewed rings parallel to the

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Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for $A_3Al_2P_3O_{12}$ (A = K (**1**), Rb (**2**), Tl (**3**)) Compounds

atom	*x*	*y*	*z*	U_{eq}[a]
		Compound **1**		
K(1)	1749(2)	4911(1)	8332(2)	34(1)
K(2)	4562(1)	3578(1)	6325(1)	23(1)
K(3)	133(1)	1014(1)	1089(1)	23(1)
P(1)	2608(1)	4973(1)	3630(2)	16(1)
P(2)	2966(1)	1887(1)	4348(2)	14(1)
P(3)	1599(1)	2867(1)	9420(2)	12(1)
Al(1)	1311(2)	3315(1)	2900(2)	14(1)
Al(2)	3513(1)	1607(1)	7996(2)	12(1)
O(1)	2625(4)	4767(2)	5347(5)	30(1)
O(2)	4110(4)	5272(2)	2989(5)	29(1)
O(3)	2074(4)	4249(2)	2616(5)	25(1)
O(4)	3691(3)	601(2)	8299(5)	25(1)
O(5)	1816(4)	1344(2)	3656(5)	31(1)
O(6)	2749(4)	2751(2)	3796(5)	26(1)
O(7)	4633(4)	1645(2)	3989(5)	35(1)
O(8)	2831(4)	1903(2)	6146(5)	25(1)
O(9)	2859(3)	3446(2)	9157(4)	20(1)
O(10)	823(4)	2932(2)	1053(4)	18(1)
O(11)	309(3)	2959(2)	8174(5)	20(1)
O(12)	2162(3)	1996(2)	9306(4)	16(1)
		Compound **2**		
Rb(1)	5000	1447(2)	3190(2)	43(1)
Rb(2)	3849(1)	4536(1)	264(1)	22(1)
P(1)	0	2349(3)	2473(3)	14(1)
P(2)	2947(1)	1707(2)	3405(2)	13(1)
Al	1673(1)	3473(2)	1809(3)	13(1)
O(1)	0	3035(10)	4025(10)	31(2)
O(2)	0	601(8)	2460(11)	21(2)
O(3)	706(3)	2969(6)	1502(7)	21(1)
O(4)	3478(3)	3038(6)	3123(7)	24(1)
O(5)	3281(3)	230(7)	2706(10)	35(2)
O(6)	2159(3)	3633(7)	105(8)	32(2)
O(7)	2111(3)	1949(6)	2796(7)	23(1)
		Compound **3**		
Tl(1)	2357(2)	3578(1)	1192(2)	34(1)
Tl(2)	2584(5)	1654(2)	7290(1)	36(1)
Tl(3)	2616(5)	1601(2)	5118(1)	34(1)
P(1)[b]	2609(8)	4915(4)	6215(10)	19(1)
P(2)	2483(27)	3725(11)	3302(7)	32(2)
P(3)[b]	2495(19)	3707(9)	9123(5)	7(2)
Al(1)[b]	2538(25)	837(10)	2917(7)	18(3)
Al(2)	2576(23)	805(10)	9582(7)	19(3)
O(1)[b]	547(21)	4134(13)	6180(23)	42(4)
O(2)[b]	4712(21)	4122(14)	6273(26)	41(4)
O(3)[b]	2330(42)	852(23)	1890(18)	17(6)
O(4)	2522(53)	765(30)	554(19)	35(8)
O(5)[b]	658(47)	4078(26)	2789(15)	25(6)
O(6)[b]	4494(42)	4269(23)	2948(13)	13(4)
O(7)[b]	2469(44)	2267(18)	3406(12)	20(5)
O(8)[b]	2026(36)	4326(20)	4064(13)	19(7)
O(9)[b]	2287(43)	4237(21)	8331(14)	23(6)
O(10)[b]	2711(37)	2266(18)	8976(13)	20(5)
O(11)[b]	593(46)	4104(26)	9630(15)	26(6)
O(12)	4592(53)	4185(33)	9523(18)	39(7)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] Isotropically refined atoms.

crystallographic axes *a*, *b*, and *c* respectively. It is evident from the unit cell diagram (Figure 2) that the phosphate tetrahedra point their unshared corner oxygen atoms toward these channels occupied by K^+ ions. This compound is isostructural with $K_3Al_2As_{1.92}P_{1.08}O_{12}$ reported earlier.[14]

The Al−O bond lengths (Table 3) are all similar and range from 1.726(4) to 1.746(4) Å. The phosphorus atoms in the phosphate tetrahedra form short P(3)−O(9), P(2)−O(5), P(1)−O(1), and P(1)−O(2) bonds of 1.480(4)−1.501(4) Å lengths with unshared oxygen atoms and long bonds of 1.526(4)−1.576(3) Å lengths with shared corner oxygen atoms. The maximum deviations in the O−Al−O and O−P−O bond angles from the ideal value of 109.4° are 7.1 and 6.7°, respectively. The O···O nonbonding edges are more uniform in PO_4 tetrahedra than in AlO_4 tetrahedra. K(2) and K(3) are respectively nine- and eight-coordinated with K−O bond lengths of 2.667(4)−3.522(3) Å whereas K(1) is only six-coordinated with one of the K−O bonds being 3.539 Å long.

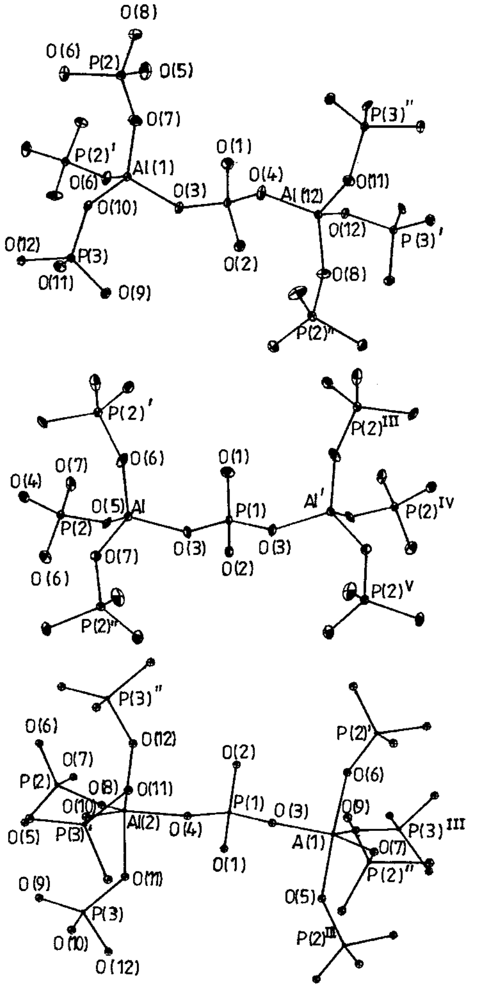

Figure 1. ORTEP plot of the Al/P/O framework showing the atom-labeling scheme in $A_3Al_2P_3O_{12}$ (A: K (**1**), top; Rb (**2**), middle; Tl(3), bottom) compounds. (50% thermal ellipsoids are shown for **1** and **2**, and atoms are of arbitrary radii for **3**.)

The number of crystallographically distinct atoms in the asymmetric unit of the *C*-centered cell of **2** (Table 2) is nearly half of those present in **1**. However, the structure of compound **2** is virtually the same as that of **1**. Al in **2** is equivalent to both Al(1) and Al(2) of **1** and P(2) in **2** is similarly equivalent to P(2) and P(3) of **1**. Both Rb(1) and Rb(2) are nine-coordinated, with some of Rb−O bonds as long as 3.562 Å. This higher nine-coordination of rubidium, when compared to the coordination of potassium in **1**, is probably responsible for the higher symmetry *C*-centered cell of **2**.

The asymmetric unit of compound **3** has the same number of crystallographically distinct atoms (Table 2) as that of compound **1**. The $[Al_2P_3O_{12}]^{3-}$ anionic framework is built from corner connections of PO_4 tetrahedra to all the corners of AlO_5 trigonal bipyramids. As shown in Figure 1, $P(1)O_4$ is the only tetrahedron that has unshared corner oxygen atoms, namely,

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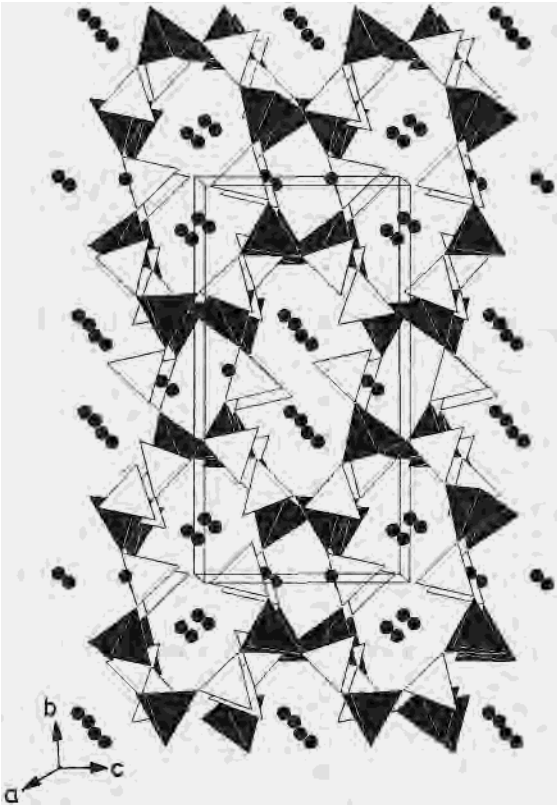

Figure 2. Polyhedral representation of the unit cell of $K_3Al_2P_3O_{12}$. Filled circles represent potassium atoms; white and black polyhedra represent PO_4 and AlO_4 tetrahedra, respectively.

Table 3. Selected Bond Lengths (Å) for $A_3Al_2P_3O_{12}$ (A = K (**1**), Rb (**2**), Tl (**3**)) Compounds

	compd **1**	compd **2**	compd **3**
P(1)−O(1)	1.493(4)	1.491(9)	1.507(14)
P(1)−O(2)	1.501(4)	1.507 (7)	1.537(14)
P(1)−O(3)	1.567(4)	1.577(5) × 2	1.55(3)
P(1)−O(4)	1.576(3)		1.47(4)
P(2)−O(4)		1.487(6)	
P(2)−O(5)	1.480(4)	1.527(6)	1.49(3)
P(2)−O(6)	1.548(3)	1.538(7)	1.50(3)
P(2)−O(7)	1.535(3)	1.546(6)	1.53(2)
P(2)−O(8)	1.526(4)		1.52(3)
P(3)−O(9)	1.487(3)		1.52(3)
P(3)−O(10)	1.542(4)		1.53(2)
P(3)−O(11)	1.546(4)		1.53(3)
P(3)−O(12)	1.557(3)		1.55(3)

compd **1**		compd **2**		comp **3**	
Al(1)−O(3)	1.733(3)	Al−O(3)	1.737(5)	Al(1)−O(3)	1.83(3)
Al(1)−O(6)	1.746(4)	Al−O(5)	1.711(7)	Al(1)−O(5)	1.93(3)
Al(1)−O(7)	1.726(4)	Al−O(6)	1.723(6)	Al(1)−O(6)	1.88(3)
Al(1)−O(10)	1.743(4)	Al−O(7)	1.745(6)	Al(1)−O(7)	1.72(2)
Al(2)−O(4)	1.732(3)			Al(1)−O(9)	1.82(2)
Al(2)−O(8)	1.746(4)			Al(2)−O(4)	1.73(3)
Al(2)−O(11)	1.731(3)			Al(2)−O(8)	1.81(2)
Al(2)−O(12)	1.744(3)			Al(2)−O(10)	1.86(2)
				Al(2)−O(11)	1.86(3)
				Al(2)−O(12)	1.84(4)

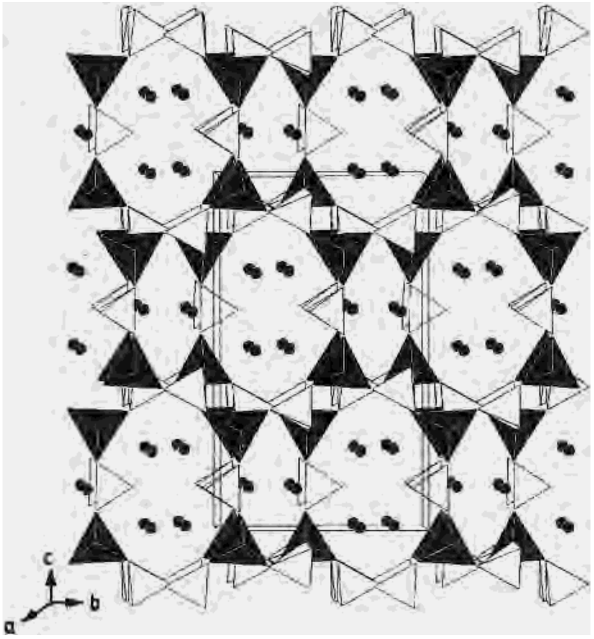

Figure 3. Polyhedral representation of the unit cell of $Tl_3Al_2P_3O_{12}$. Filled circles represent thallium atoms; white and black polyhedra represent PO_4 tetrahedra and AlO_5 trigonal bipyramids respectively.

O(1) and O(2), and shares two corners, one with each type of AlO_5 trigonal bipyramid. While $P(2)O_4$ is corner-connected to three $Al(1)O_5$ trigonal bipyramids and one $Al(2)O_5$, $P(3)O_4$ shares its corners with three $Al(2)O_5$ trigonal bipyramids and one $Al(1)O_5$. This anionic framework also contains channels, parallel to only the *a* axis, with windows of twelve- and eight-membered rings, and Tl^+ ions occupy these channels (Figure 3). To the best of our knowledge, this compound constitutes the first example of an oxide containing aluminum exclusively in trigonal bipyramidal coordination.

The P−O bond lengths (Table 3) of the phosphate tetrahedra in **3** vary more widely than those in the other two compounds. Unlike in **1** and **2**, the values of P(1)−O bond lengths in **3** do not indicate any distinction in bonding of P(1) with shared and unshared oxygen atoms. The $P(3)O_4$ tetrahedron, with a wider range (2.36(3)−2.63(4) Å) of nonbonding $O\cdots O$ edge lengths, is more distorted than the other two phosphate tetrahedra, and its tetrahedral bond angles deviate from the ideal value by as much as 11.6°. Al−O bond lengths in AlO_5 trigonal bipyramids vary from 1.72(2) to 1.93(3) Å. There is no distinction between apical and equatorial bond lengths in $Al(2)O_5$, whereas the apical bonds are longer than the equatorial ones in $Al(1)O_5$. The aluminum atoms, Al(1) and Al(2), are displaced from the best centers[15] of these trigonal bipyramids by 0.0107 and 0.0044 Å toward O(7) and O(4), respectively. Tl(1) is twelve-coordinated, whereas Tl(2) and Tl(3) are nine-coordinated, with Tl−O bond lengths ranging from 2.70(3) to 3.57(3) Å. Only the $Tl(1)O_{12}$ polyhedron is nonuniform with effectively no interacting atoms on one side of the coordination sphere, indicating the stereoactive nature[16] of the $6s^2$ lone pair of Tl(1). Thus, Tl(1) is distinctly different from the other two thallium atoms.

Contrary to the expected order of unit cell volumes, based on the ionic radii of A^+ ions, the unit cell volume (Table 1) of compound **3** is smaller than those of the other two compounds, indicating that the structures of compounds **1** and **2** are more porous. Our efforts to exchange A^+ ions of these compounds, by treatment with molten salts of ACl (A = Li, Na) and by stirring or refluxing these compounds with their aqueous solutions, resulted in the disintegration of the compounds.

The $[Al_2P_3O_{12}]^{3-}$ anionic frameworks of these three-dimensional compounds are thus distinctly different from those of the two-dimensional compounds with the empirical formula $(R)^{+}_{3-x}[Al_2P_3O_{12}H_x]^{x-3}$ ($x = 1, 2$; R = organic amine) reported

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Figure 4. ^{27}Al MAS NMR spectra of $A_3Al_2P_3O_{12}$ (A = Na, K (**1**), Rb (**2**), Tl (**3**)) compounds.

in the literature.[17−19] The two-dimensional compounds, synthesized under hydrothermal conditions, contain aluminum in both tetrahedral and trigonal bipyramidal coordinations. Our attempts to prepare $A_3Al_2P_3O_{12}$ compounds with different structural modifications, such as layered frameworks, by acid−base reactions of AH_2PO_4 (A = K, Rb) with $Al(OH)_3$ under hydrothermal conditions, have resulted in aluminophosphates, $A_{1.5}[Al_2P_2O_{8.5}(OH)_{0.5}(H_2O)]\cdot xH_2O$ ($x < 1$), with the $AlPO_4$-15 structure.[20]

Solid-State Nuclear Magnetic Resonance Spectroscopy. The ^{27}Al MAS NMR spectra of $Na_3Al_2P_3O_{12}$, **1**, and **2** (Figure 4) have single peaks at 38.2, 45.5, and 47.2 ppm, respectively, whereas that of **3** has an intense peak at 18.9 ppm. These values compare well with those reported[21] for tetrahedral and trigonal bipyramidal coordinations. The tetrahedral coordination of aluminum in $A_3Al_2P_3O_{12}$ compounds, with A^+ ions varying in size from Na^+ to Rb^+, changes to trigonal bipyramidal when the countercation is Tl^+, and the change seems to be required to accommodate the stereoactive lone pair of electrons on the $Tl(1)^+$ ions.

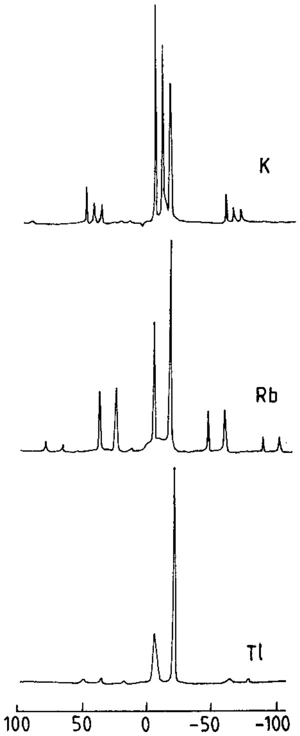

Figure 5. ^{31}P MAS NMR spectra of $A_3Al_2P_3O_{12}$ (A = K (**1**), Rb (**2**), Tl (**3**)) compounds.

The ^{31}P MAS NMR spectra of the three structurally characterized compounds, **1**−**3**, are shown in Figure 5. There are two signals observed at −20.19 and −5.97 ppm for **3**. The first one is attributed[21−23] to the phosphorus atom of the $P(1)O_4$ tetrahedron, which shares only two corners, and the second one is due to the phosphorus atoms of the other two tetrahedra, $P(2)O_4$ and $P(3)O_4$, which share all their corners. Similarly, the two signals at −16.38 and −3.43 ppm observed in the NMR spectrum of **2** are due to the P(1) and P(2) atoms, respectively. The NMR spectrum of **1** is sufficiently resolved, with three signals at −17.4, −11.1, and −4.5 ppm, to indicate the presence of the three crystallographically distinct phosphorus atoms P(1), P(2), and P(3). The NMR spectrum of $Na_3Al_2P_3O_{12}$ is more complicated, albeit with signals at δ ranging from −3 to −18 ppm, showing the presence of crystallographically distinct, tetrahedrally coordinated phosphorus atoms.

Infrared Spectroscopy. The infrared spectra of $A_3Al_2P_3O_{12}$ (A = Na, K (**1**), Rb (**2**), Tl (**3**)) compounds are all similar. Al/P−O bonds are reported[24] to have their asymmetric and symmetric stretching vibrational frequencies in the ranges 950−1200 and 600−400 cm^{-1} and bending frequencies in 400−550 cm^{-1} range, respectively. An unambiguous assignment of the peaks is not possible owing to an apparent overlap of the frequency ranges of the vibrational modes of Al/P−O bonds in this region. But the peaks in the range 1130−1000 cm^{-1} can be tentatively attributed to P/Al−O stretching, those in the 800−600 cm^{-1} range to P/Al−O asymmetric stretching. and those in the 600−400 cm^{-1} range to P/Al−O bending modes.

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However, the strong peak in the 1350 cm^{-1} region is attributed to a P−O stretching frequency.

Concluding Remarks. Four $A_3Al_2P_3O_{12}$ (A = Na, K (**1**), Rb (**2**), Tl (**3**)) aluminophosphates, synthesized by solid-state reactions, possess structures different from those of hitherto reported isomorphous $A_3M_2P_3O_{12}$ compounds and contain, as determined by solid-state NMR spectroscopy, aluminum exclusively in trigonal bipyramidal coordination in the thallium compound and tetrahedral coordination in the other three compounds. $Tl_3Al_2P_3O_{12}$ is a rare example of an oxide containing aluminum exclusively in trigonal bipyramidal coordination. It is the stereoactive lone pair of electrons on the Tl^+ ion and not the size of A^+ ions that seems to have brought about the change in the coordination of aluminum in these compounds.

It would be interesting to synthesize and study similar gallium and indium compounds, $A_3M_2P_3O_{12}$ (M = Ga, In). We have made some preliminary investigations in this direction and found, by X-ray powder diffraction, that the $K_3Ga_2P_3O_{12}$ compound is isostructural with the corresponding aluminum compound. We are making efforts to grow single crystals and structurally characterize other alkali metal analogues of gallium and indium compounds.

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Supporting Information Available: X-ray powder diffraction data and Tables of X-ray crystallographic files, in CIF format, for compounds **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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