

# The First Vanadium Aluminophosphates: Hydrothermal Synthesis and Structure of $\text{Cs}[(\text{VO})\text{Al}(\text{PO}_4)_2] \cdot \text{H}_2\text{O}$ , $\text{Rb}[(\text{VO})\text{Al}(\text{PO}_4)_2] \cdot \text{H}_2\text{O}$ , $(\text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_2)[(\text{VO})\text{Al}(\text{PO}_4)_2]$ , and $\text{CH}_3\text{NH}_3[(\text{VO})\text{Al}(\text{PO}_4)_2]$

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Received December 5, 1995; in revised form May 2, 1996; accepted May 9, 1996

The first vanadium aluminophosphates,  $\text{Cs}[(\text{VO})\text{Al}(\text{PO}_4)_2] \cdot \text{H}_2\text{O}$  (1),  $\text{Rb}[(\text{VO})\text{Al}(\text{PO}_4)_2] \cdot \text{H}_2\text{O}$  (2),  $(\text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_2)[(\text{VO})\text{Al}(\text{PO}_4)_2]$  (3), and  $\text{CH}_3\text{NH}_3[(\text{VO})\text{Al}(\text{PO}_4)_2]$  (4), have been hydrothermally prepared from a vanadium source,  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{O}$ , and a charge compensating organic species. The phosphates are built up from tetrahedrally coordinated aluminum and phosphorous atoms; phosphates (1), (2), and (3) contain octahedrally coordinated vanadium atoms, and phosphate (4) contains a square pyramidal vanadium atom. The frameworks in phosphates (1)–(4) are structurally related and incorporate cations of similar size and charge. In phosphate (3) the 1-aminoethane-2-ammonium cation is bonded through the nitrogen to the vanadium as a monodentate ligand, providing the sixth vertex of the vanadium octahedron, with the other five present as oxygen atoms. In phosphates (1), (2), and (4), the  $\text{Cs}^+$ ,  $\text{Rb}^+$ , and methylammonium cations, respectively, replace the charge compensating organic ligand present in phosphate (3). The four phosphates are conceptually constructed of one-dimensional aluminophosphate chains connected into three-dimensional frameworks via vanadium polyhedra that corner share to the phosphate tetrahedra. The Al is oxo bridged only to  $\text{P}^{5+}$  with no Al–O–V bonds present. Crystal data for (1): monoclinic, space group  $P2_1/n$  (#14) with  $a = 8.014(2)$ ,  $b = 8.088(2)$ ,  $c = 14.141(2)$  Å,  $\beta = 105.98(1)^\circ$ ,  $V = 881.2(4)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_{\text{calc}} = 3.262$  g · cm<sup>-3</sup>; for (2): monoclinic, space group  $P2_1/n$  (#14) with  $a = 7.880(2)$ ,  $b = 8.063(2)$ ,  $c = 14.062(2)$  Å,  $\beta = 105.83(1)^\circ$ ,  $V = 859.5(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_{\text{calc}} = 2.977$  g · cm<sup>-3</sup>; for (3): monoclinic, space group  $P2_1/n$  (#14) with  $a = 8.172(2)$ ,  $b = 14.232(2)$ ,  $c = 8.873(1)$  Å,  $\beta = 109.88(1)^\circ$ ,  $V = 970.5(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_{\text{calc}} = 2.299$  g · cm<sup>-3</sup>; for (4): triclinic, space group  $P\bar{1}$  (#2) with  $a = 8.151(1)$ ,  $b = 8.784(2)$ ,  $c = 7.842(2)$ ,  $\alpha = 116.22(2)^\circ$ ,  $\beta = 95.88(2)^\circ$ ,  $\gamma = 69.16(1)^\circ$ ,  $V = 469.7(2)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_{\text{calc}} = 2.191$  g · cm<sup>-3</sup>. © 1996 Academic Press, Inc.

## INTRODUCTION

Synthetic aluminophosphates have been extensively investigated since their discovery by Wilson and Flanigen and co-workers (1). Microporous aluminophosphates have

very diverse structures forming with four, five, and six coordinate aluminum atoms and a wide variety of organic templates. An example of both four and five coordinate aluminum atoms can be found in  $\text{AlPO}_4\text{-21}$ , which contains both tetrahedral and trigonal bipyramidal aluminum atoms (2). We have recently extended the hydrothermal synthesis of open framework phosphates to include transition element materials such as molybdenum phosphates (3). In addition, many new vanadium phosphates have been synthesized and include the microporous supercage material  $\text{Cs}_3[\text{V}_5\text{O}_6(\text{PO}_4)_2] \cdot x\text{H}_2\text{O}$  (4), the organically templated  $(\text{H}_3\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}_3)_4[\text{V}^{\text{III}}(\text{H}_2\text{O})_2(\text{V}^{\text{IV}}\text{O})_6(\text{OH})_2(\text{HPO}_4)_3(\text{PO}_4)_5] \cdot 3\text{H}_2\text{O}$  (5), and the mixed alkali metal/organic templated species  $[\text{HN}(\text{CH}_2\text{CH}_2)_3\text{NH}]\text{K}_{1.35}[\text{V}_5\text{O}_9(\text{PO}_4)_2] \cdot x\text{H}_2\text{O}$  (4) and  $(\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}_3)\text{K}[(\text{VO})_3(\text{PO}_4)_3]$  (6). Recent investigations into the formation of mixed transition metal phosphates have yielded encouraging results such as  $\text{Cu}_{0.5}(\text{OH})_{0.5}[\text{VOPO}_4] \cdot 2\text{H}_2\text{O}$  (7) and  $\text{Cu}_{0.5}[\text{VOPO}_4] \cdot 2\text{H}_2\text{O}$  (7),  $\text{Ni}(\text{H}_2\text{O})_4[\text{VO}(\text{PO}_4)_2]$  (8),  $[(\text{CH}_3)_4\text{N}]_2[\text{Fe}_2\text{Mo}_{12}\text{O}_{30}(\text{H}_2\text{PO}_4)_6(\text{HPO}_4)_2] \cdot n\text{H}_2\text{O}$  (9), and  $[(\text{CH}_3)_4\text{N}]_2\text{Na}_4[\text{Fe}_3\text{Mo}_{12}\text{O}_{30}(\text{H}_x\text{PO}_4)_8] \cdot n\text{H}_2\text{O}$  (9), as well as mixed metal aluminophosphates such as  $\text{K}[\text{Ni}(\text{H}_2\text{O})_2\text{Al}_2(\text{PO}_4)_3]$  (10) and  $\text{Cs}_9\text{Mo}_9\text{Al}_3\text{P}_{11}\text{O}_{59}$  (11). Most of the phosphates that have been synthesized contain either charge compensating alkali metal or organic cations, or combinations of alkali and organic cations, as templating species. Usually, the organic cation is hydrogen bonded to tunnel or cavity surfaces through N–H ··· O interactions; in phosphate (3), however, the charge compensating 1-aminoethane-2-ammonium cation is coordinated directly to the vanadium atom, forming one of the vertices of the octahedra. Other compounds in which this is observed are the recently prepared  $[\text{VO}(\text{PO}_4)(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_3)]$  (12) and the layered fluoroaluminophosphate  $[\text{AlF}(\text{HPO}_4)]$  (ethylenediamine) (13), which have 1-aminoethane-2-ammonium coordinated to the vanadium site and aluminum site, respectively, as a monodentate ligand. The diverse coordination environments and structural

TABLE 1  
Crystallographic Data for Cs[(VO)Al(PO<sub>4</sub>)<sub>2</sub>] · H<sub>2</sub>O (1), Rb[(VO)Al(PO<sub>4</sub>)<sub>2</sub>] · H<sub>2</sub>O (2),  
(NH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)[(VO)Al(PO<sub>4</sub>)<sub>2</sub>] (3), and (CH<sub>3</sub>NH<sub>3</sub>)[(VO)Al(PO<sub>4</sub>)<sub>2</sub>] (4)

	(1)	(2)	(3)	(4)
Empirical formula	VAIP <sub>2</sub> O <sub>10</sub> Cs	VAIP <sub>2</sub> O <sub>10</sub> Rb	VAIP <sub>2</sub> O <sub>9</sub> N <sub>2</sub> C <sub>2</sub>	VAIP <sub>2</sub> O <sub>9</sub> CN
<i>f</i> <sub>w</sub>	432.77	385.33	335.90	309.88
Color, habit	pale blue, prism	pale blue, prism	pale blue, plate	pale blue, prism
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i> (#14)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (#14)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (#14)	<i>P</i> $\bar{1}$ (#2)
<i>a</i> (Å)	8.014(2)	7.880(2)	8.172(2)	8.151(1)
<i>b</i> (Å)	8.088(2)	8.063(2)	14.232(2)	8.784(2)
<i>c</i> (Å)	14.141(2)	14.062(2)	8.873(1)	7.842(2)
$\alpha$ (deg)	90	90	90	116.22(2)
$\beta$ (deg)	105.98(1)	105.83(1)	109.88(1)	95.88(2)
$\gamma$ (deg)	90	90	90	69.16(1)
<i>V</i> (Å <sup>3</sup> )	881.2(4)	859.5(3)	970.5(2)	469.7(2)
<i>Z</i>	4	4	4	2
<i>D</i> <sub>c</sub> (g/cm <sup>3</sup> )	3.262	2.977	2.299	2.191
$\mu$ (cm <sup>-1</sup> )	56.98	70.98	14.85	15.20
Total reflections	2930	2865	3142	2931
Unique reflections	2754	2691	2963	2756
No. observed ( <i>I</i> > 3.00 $\sigma$ ( <i>I</i> ))	1967	1528	2153	1993
No. variables	136	136	154	136
<i>R</i>	0.027	0.027	0.039	0.045
<i>R</i> <sub>w</sub>	0.034	0.027	0.054	0.055
Trans. coeff.	0.89–1.00	0.78–1.00	0.97–1.03	0.85–1.00
Goodness of fit	1.62	1.39	2.52	2.34

connectivities of both the aluminophosphate and vanadium phosphate systems suggest that the addition of an aluminum source into the vanadium phosphate syntheses could likewise lead to very interesting new materials.

TABLE 2  
Positional Parameters and *B*(eq) for  
Cs[(VO)Al(PO<sub>4</sub>)<sub>2</sub>] · H<sub>2</sub>O (1)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (eq) <sup>a</sup>
Cs(1)	0.88102(4)	0.46499(4)	0.20895(2)	1.555(6)
V(1)	0.85670(10)	0.05434(9)	0.64246(6)	0.68(1)
P(1)	0.9625(1)	0.2234(1)	0.45809(8)	0.53(2)
P(2)	1.3580(1)	0.6085(1)	0.35406(8)	0.52(2)
Al(1)	1.2489(2)	0.4642(2)	0.53321(10)	0.56(2)
O(1)	1.0043(4)	0.1721(4)	0.7068(2)	1.18(6)
O(2)	0.8592(4)	0.1115(4)	0.5064(2)	0.92(6)
O(3)	1.0012(4)	0.1457(4)	0.3691(2)	0.92(6)
O(4)	1.1318(4)	0.2817(4)	0.5325(2)	0.90(6)
O(5)	1.1454(4)	0.6203(4)	0.5802(2)	1.05(6)
O(6)	0.9495(4)	0.0621(5)	0.1144(3)	1.39(7)
O(7)	1.2643(5)	0.5057(5)	0.4156(2)	1.38(7)
O(8)	1.3465(4)	0.7913(4)	0.3756(2)	0.93(6)
O(9)	1.2797(4)	0.5659(4)	0.2472(2)	0.95(6)
O(10)	1.1055(5)	0.6261(5)	0.0635(3)	1.83(8)

<sup>a</sup> *B*(eq) = 8/3  $\pi^2$ (*U*<sub>11</sub>(*aa*<sup>\*</sup>)<sup>2</sup> + *U*<sub>22</sub>(*bb*<sup>\*</sup>)<sup>2</sup> + *U*<sub>33</sub>(*cc*<sup>\*</sup>)<sup>2</sup> + 2*U*<sub>12</sub>(*aa*<sup>\*</sup>*bb*<sup>\*</sup>)  
cos  $\gamma$  + 2*U*<sub>13</sub>(*aa*<sup>\*</sup>*cc*<sup>\*</sup>)cos  $\beta$  + 2*U*<sub>23</sub>(*bb*<sup>\*</sup>*cc*<sup>\*</sup>)cos  $\alpha$ ).

While several of these organically templated molybdenum and vanadium phosphates have been demonstrated to be microporous, they are in general considerably less stable thermally than typical zeolites or aluminophosphates. Therefore, we attempted to incorporate AlO<sub>4</sub> tetrahedra into the framework in order to determine if it was possible to increase the thermal stability in the V–P–O system. The first results of our efforts in this area have produced the mixed vanadium aluminophosphates Cs[(VO)Al(PO<sub>4</sub>)<sub>2</sub>] · H<sub>2</sub>O (1), Rb[(VO)Al(PO<sub>4</sub>)<sub>2</sub>] · H<sub>2</sub>O (2), (NH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)[(VO)Al(PO<sub>4</sub>)<sub>2</sub>] (3), and CH<sub>3</sub>NH<sub>3</sub>[(VO)Al(PO<sub>4</sub>)<sub>2</sub>] (4).

## EXPERIMENTAL

### Syntheses

All of the syntheses were carried out in polytetrafluoroethylene-lined stainless steel containers under autogenous pressure. The following addition order of reactants was used for each reaction: H<sub>2</sub>O, H<sub>3</sub>PO<sub>4</sub>, organic species, AlCl<sub>3</sub> · 6H<sub>2</sub>O, and then addition of the vanadium source. The reactants were stirred briefly before heating. The 23 ml reaction vessels were filled to approximately 40% volume capacity. X-ray diffraction studies were performed using a Scintag XDS-2000 powder diffractometer with a high-

TABLE 3  
Selected Bond Distances (Å) and Angles (°) for  
Cs[(VO)Al(PO<sub>4</sub>)<sub>2</sub>] · H<sub>2</sub>O (1)

V(1)	O(1)	1.594(3)	V(1)	O(2)	1.985(3)
V(1)	O(3)	2.011(3)	V(1)	O(8)	2.012(3)
V(1)	O(9)	2.006(3)	P(1)	O(2)	1.510(3)
P(1)	O(3)	1.513(3)	P(1)	O(4)	1.544(3)
P(1)	O(5)	1.543(3)	P(2)	O(6)	1.530(3)
P(2)	O(7)	1.541(3)	P(2)	O(8)	1.517(4)
P(2)	O(9)	1.508(3)	Al(1)	O(4)	1.748(4)
Al(1)	O(5)	1.740(4)	Al(1)	O(6)	1.712(4)
Al(1)	O(7)	1.734(4)			
O(1)–V(1)–O(2)	102.2(2)	O(1)–V(1)–O(3)	100.3(2)		
O(1)–V(1)–O(8)	98.6(2)	O(1)–V(1)–O(9)	101.5(2)		
O(2)–V(1)–O(3)	87.2(1)	O(2)–V(1)–O(8)	87.5(1)		
O(2)–V(1)–O(9)	156.4(1)	O(3)–V(1)–O(8)	161.0(1)		
O(3)–V(1)–O(9)	88.1(1)	O(8)–V(1)–O(9)	89.5(1)		
O(2)–P(1)–O(3)	113.0(2)	O(2)–P(1)–O(4)	111.3(2)		
O(2)–P(1)–O(5)	109.0(2)	O(3)–P(1)–O(4)	110.5(2)		
O(3)–P(1)–O(5)	105.8(2)	O(4)–P(1)–O(5)	106.9(2)		
O(6)–P(2)–O(7)	108.2(2)	O(6)–P(2)–O(8)	107.0(2)		
O(6)–P(2)–O(9)	110.1(2)	O(7)–P(2)–O(8)	110.3(2)		
O(7)–P(2)–O(9)	108.0(2)	O(8)–P(2)–O(9)	113.1(2)		
O(4)–Al(1)–O(5)	107.6(2)	O(4)–Al(1)–O(6)	107.6(2)		
O(4)–Al(1)–O(7)	109.7(2)	O(5)–Al(1)–O(6)	107.0(2)		
O(5)–Al(1)–O(7)	113.1(2)	O(6)–Al(1)–O(7)	111.5(2)		
V(1)–O(2)–P(1)	137.0(2)	V(1)–O(3)–P(1)	130.7(2)		
P(1)–O(4)–Al(1)	129.2(2)	P(1)–O(5)–Al(1)	137.8(2)		
P(2)–O(6)–Al(1)	155.6(2)	P(2)–O(7)–Al(1)	145.1(2)		
V(1)–O(8)–P(2)	132.2(2)	V(1)–O(9)–P(2)	136.3(2)		

temperature diffraction chamber. The organic reagent used in each synthesis was required for the desired product to form.

*Cs[(VO)Al(PO<sub>4</sub>)<sub>2</sub>] · H<sub>2</sub>O (1)*. Hydrothermal reaction of CsVO<sub>3</sub>, AlCl<sub>3</sub> · 6H<sub>2</sub>O, piperidine, H<sub>3</sub>PO<sub>4</sub>, and H<sub>2</sub>O in a molar ratio of 2.2 : 1 : 6 : 16 : 600 at 200°C for 2 days produces pale blue prismatic crystals of (1) in 79% yield based on Al. The product is the only solid precipitating from solution and is a single phase based on comparison of its powder X-ray diffraction pattern to the pattern simulated from the atomic coordinates obtained from the single crystal X-ray structure. The excess vanadium remains in solution in the pale blue supernatant. A sample for X-ray diffraction was heated *in situ* from 30 to 600°C under vacuum at a rate of 1°C/min, after which an X-ray powder diffraction pattern was obtained to determine the crystallinity of the sample (see below).

*Rb[(VO)Al(PO<sub>4</sub>)<sub>2</sub>] · H<sub>2</sub>O (2)*. This phosphate is prepared hydrothermally from the reaction of RbVO<sub>3</sub>, AlCl<sub>3</sub>, diethylamine, H<sub>3</sub>PO<sub>4</sub>, and H<sub>2</sub>O in a molar ratio of 1 : 1 : 6 : 6 : 600 at 200°C for 3 days. Pale blue prismatic crystals of (2) are formed in 20% yield. Unidentified clear aluminophosphate crystals are also present. The optimum

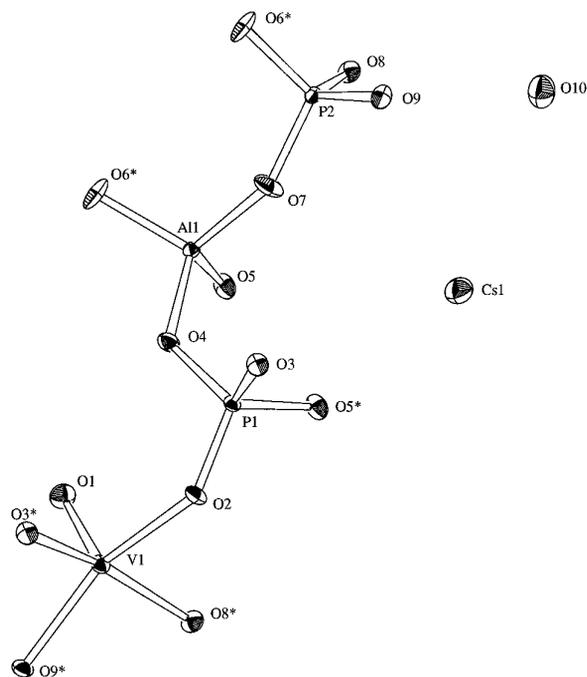


FIG. 1. An ORTEP drawing of the Cs[(VO)Al(PO<sub>4</sub>)<sub>2</sub>] · H<sub>2</sub>O structure showing the coordination of the metal atoms and the atomic numbering scheme.

conditions for the preparation of (2) have not yet been discovered, although many reaction variations have been attempted.

(NH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)[(VO)Al(PO<sub>4</sub>)<sub>2</sub>] (3). The hydrothermal reaction of V<sub>2</sub>O<sub>5</sub>, AlCl<sub>3</sub> · 6H<sub>2</sub>O, ethylenediamine, H<sub>3</sub>PO<sub>4</sub>, and H<sub>2</sub>O in a molar ratio of 1 : 1.3 : 6 : 7 : 600 at

TABLE 4  
Positional Parameters and *B*(eq) for  
Rb[(VO)Al(PO<sub>4</sub>)<sub>2</sub>] · H<sub>2</sub>O (2)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (eq)
Rb(1)	1.38265(7)	0.03902(7)	0.70729(4)	2.39(1)
V(1)	0.85549(9)	0.06055(9)	0.64311(5)	0.89(1)
P(1)	0.9641(1)	0.2219(1)	0.45648(7)	0.73(2)
P(2)	0.8580(1)	0.1042(1)	0.85336(7)	0.71(2)
Al(1)	1.2543(2)	0.0362(2)	0.96540(9)	0.79(2)
O(1)	1.0053(4)	0.1799(4)	0.7058(2)	1.55(6)
O(2)	0.8528(4)	0.1164(4)	0.5048(2)	1.04(6)
O(3)	0.8659(4)	0.3845(3)	0.4182(2)	1.14(6)
O(4)	0.9985(4)	0.1390(3)	0.3668(2)	1.07(6)
O(5)	1.1379(4)	0.2739(4)	0.5324(2)	1.03(6)
O(6)	1.5960(4)	−0.1226(4)	0.5664(2)	2.12(7)
O(7)	0.7747(4)	−0.0576(4)	0.7475(2)	1.14(6)
O(8)	0.7616(4)	−0.0086(4)	0.9172(2)	1.70(7)
O(9)	0.8538(4)	−0.2895(3)	0.8736(2)	1.09(6)
O(10)	1.0513(4)	−0.0525(4)	0.8828(2)	1.88(7)

TABLE 5  
Selected Bond Distances (Å) and Angles (°) for  
Rb[(VO)Al(PO<sub>4</sub>)<sub>2</sub>] · H<sub>2</sub>O (2)

V(1)	O(1)	1.590(3)	V(1)	O(2)	1.990(3)
V(1)	O(4)	2.005(3)	V(1)	O(7)	1.994(3)
V(1)	O(9)	2.006(3)	P(1)	O(2)	1.510(3)
P(1)	O(3)	1.543(3)	P(1)	O(4)	1.516(3)
P(1)	O(5)	1.547(3)	P(2)	O(7)	1.502(3)
P(2)	O(8)	1.532(3)	P(2)	O(9)	1.524(3)
P(2)	O(10)	1.523(3)	Al(1)	O(3)	1.740(3)
Al(1)	O(5)	1.747(3)	Al(1)	O(8)	1.728(3)
Al(1)	O(10)	1.707(3)			
O(1)–V(1)–O(2)	102.3(1)	O(1)–V(1)–O(4)	99.8(1)		
O(1)–V(1)–O(7)	102.6(1)	O(1)–V(1)–O(9)	99.4(1)		
O(2)–V(1)–O(4)	88.1(1)	O(2)–V(1)–O(7)	155.01(1)		
O(2)–V(1)–O(9)	87.7(1)	O(4)–V(1)–O(7)	88.4(1)		
O(4)–V(1)–O(9)	160.8(1)	O(7)–V(1)–O(9)	87.5(1)		
O(2)–P(1)–O(3)	109.8(2)	O(2)–P(1)–O(4)	112.6(2)		
O(2)–P(1)–O(5)	110.8(2)	O(3)–P(1)–O(4)	105.7(2)		
O(3)–P(1)–O(5)	106.0(2)	O(4)–P(1)–O(5)	111.6(2)		
O(7)–P(2)–O(8)	107.6(2)	O(7)–P(2)–O(9)	113.9(2)		
O(7)–P(2)–O(10)	109.6(2)	O(8)–P(2)–O(9)	110.1(2)		
O(8)–P(2)–O(10)	108.8(2)	O(9)–P(2)–O(10)	106.8(2)		
O(3)–Al(1)–O(5)	109.2(1)	O(3)–Al(1)–O(8)	113.2(2)		
O(3)–Al(1)–O(10)	105.8(2)	O(5)–Al(1)–O(8)	109.2(1)		
O(5)–Al(1)–O(10)	107.8(2)	O(8)–Al(1)–O(10)	111.6(2)		
V(1)–O(2)–P(1)	135.6(2)	P(1)–O(3)–Al(1)	136.2(2)		
V(1)–O(4)–P(1)	130.4(2)	P(1)–O(5)–Al(1)	125.8(2)		
V(1)–O(7)–P(2)	135.1(2)	P(2)–O(8)–Al(1)	147.3(2)		
V(1)–O(9)–P(2)	128.9(2)	P(2)–O(10)–Al(1)	152.6(2)		

200° C for 2 days produces pale blue crystals of **(3)** in 45% yield based on Al. Blue crystals of (H<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>NH<sub>3</sub>)<sub>2</sub>(H<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)[V<sup>III</sup>(H<sub>2</sub>O)<sub>2</sub>(V<sup>IV</sup>O)<sub>8</sub> / (OH)<sub>4</sub>(HPO<sub>4</sub>)<sub>4</sub>(PO<sub>4</sub>)<sub>4</sub>] · 2H<sub>2</sub>O (**14**), characterized by single crystal X-ray diffraction, are also present as approximately 50% of the solid precipitating from solution.

CH<sub>3</sub>NH<sub>3</sub>[(VO)Al(PO<sub>4</sub>)<sub>2</sub>] (**4**). The single crystals of this vanadium aluminophosphate were prepared hydrothermally from the reaction of NaVO<sub>3</sub>, AlCl<sub>3</sub> · 6H<sub>2</sub>O, methylamine, H<sub>3</sub>PO<sub>4</sub>, and H<sub>2</sub>O in a molar ratio of 2:1:15:10:1200 at 200°C for 3 days. Pale blue prismatic crystals were obtained in approximately 10% yield along with approximately 10% unidentified clear aluminophosphate crystals. This synthesis is not reproducible and attempts to alter the conditions to synthesize **(4)** have been unsuccessful.

#### X-Ray Crystallographic Studies

Structural measurements for phosphates **(1)**–**(4)** were made on a Rigaku AFC7R diffractometer with graphite monochromated MoK $\alpha$  radiation ( $\lambda(\text{MoK}\alpha) = 0.71069 \text{ \AA}$ ) and an 18 kW rotating anode generator. The data were

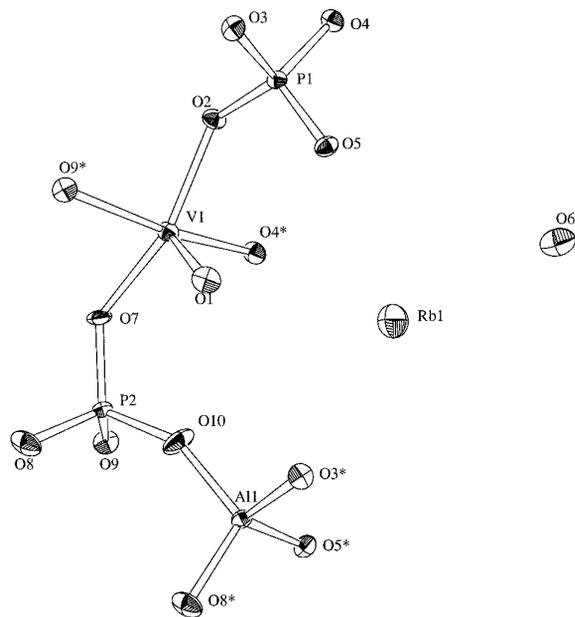


FIG. 2. An ORTEP drawing of the Rb[(VO)Al(PO<sub>4</sub>)<sub>2</sub>] · H<sub>2</sub>O structure showing the coordination of the metal atoms and the atomic numbering scheme.

collected at a temperature of  $20 \pm 1^\circ\text{C}$  using the  $\omega$ -2 $\theta$  scan technique to  $60.1^\circ$  in  $2\theta$  at a scan speed of  $16.0^\circ/\text{min}$  (in omega). Crystallographic data for these phosphates are listed in Table 1. The intensities of three standard reflections measured after every 150 reflections remained constant throughout the data collection for all except Rb[(VO)Al(PO<sub>4</sub>)<sub>2</sub>] · H<sub>2</sub>O (**2**), which had a decrease in intensity of 0.8% over the course of data collection. A linear correction factor was applied to the data to account for this. An empirical absorption correction using the program DIFABS was applied to all data (**15**) and the data were corrected for Lorentz and polarization effects. The structures were solved by direct methods (**16**). All nonhydrogen atoms were refined anisotropically. Neutral atom scattering factors were taken from Cromer and Waber (**17**) and anomalous dispersion correction was taken from those of Creagh and McAuley (**18**). All calculations were performed using the teXsan (**16**) crystallographic software package.

## RESULTS

Hydrothermal synthetic methods have been employed extensively in the preparation of microporous materials. The technique for the synthesis of aluminophosphates frequently employs a gel precursor and strict heating requirements making the procedure rather complex. The vana-

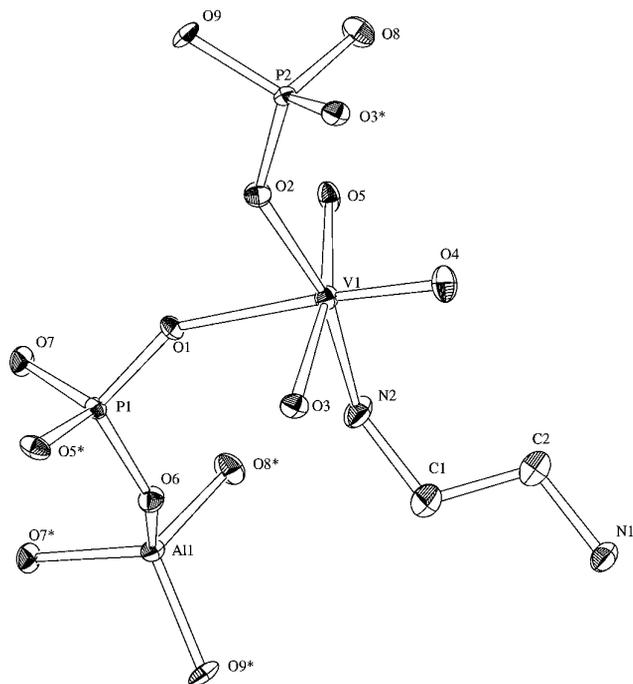


FIG. 3. An ORTEP drawing of the  $(\text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_2)[(\text{VO})\text{Al}(\text{PO}_4)_2]$  structure showing the coordination of the metal atoms and the atomic numbering scheme.

dium aluminophosphates, however, require very little effort for the formation of crystalline products. The title compounds were all synthesized using simple starting materials and relatively short heating periods.

TABLE 6  
Positional Parameters and  $B(\text{eq})$  for the Nonhydrogen Atoms of  $(\text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_2)[(\text{VO})\text{Al}(\text{PO}_4)_2]$  (3)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (eq)
V(1)	0.31316(9)	0.13144(5)	0.40467(8)	0.78(1)
P(1)	0.5477(1)	0.34205(7)	0.5368(1)	0.62(2)
P(2)	0.5347(1)	0.01827(7)	0.2659(1)	0.63(2)
Al(1)	0.2840(2)	0.48583(9)	0.5690(1)	0.76(2)
O(1)	0.4781(4)	0.2563(2)	0.4372(3)	0.86(5)
O(2)	0.5090(4)	0.0672(2)	0.3581(3)	0.99(6)
O(3)	0.4436(4)	0.1096(2)	0.6401(3)	0.95(5)
O(4)	0.1765(4)	0.0473(2)	0.3836(4)	1.34(6)
O(5)	0.2133(4)	0.1792(2)	0.1767(3)	0.99(5)
O(6)	0.4078(4)	0.3824(2)	0.6015(3)	0.95(6)
O(7)	0.5837(4)	0.4186(2)	0.4281(3)	1.04(6)
O(8)	0.3787(4)	0.0311(2)	0.1121(4)	1.31(6)
O(9)	0.6973(4)	0.0005(2)	0.2203(4)	1.19(6)
N(1)	0.1946(5)	0.1429(3)	0.6113(4)	1.21(7)
N(2)	0.1472(5)	0.2348(3)	0.4559(5)	1.40(7)
C(1)	0.0604(7)	0.2149(4)	0.5752(6)	2.1(1)
C(2)	0.1031(7)	0.1611(4)	0.4956(7)	2.5(1)

### Structure of $\text{Cs}[(\text{VO})\text{Al}(\text{PO}_4)_2] \cdot \text{H}_2\text{O}$ (1)

The positional and thermal parameters for the nonhydrogen atoms found in (1) are given in Table 2 and selected bond distances and angles are listed in Table 3. Figure 1 illustrates the coordination environment as well as the atom numbering scheme used in the tables. This structure is constructed of vanadium octahedra and aluminum and phosphorus tetrahedra. The vanadium octahedra consist of one short V–O bond ( $\text{V}(1)\text{--O}(1) = 1.594(3) \text{ \AA}$ ) *trans* to one very long V–OH<sub>2</sub> bond ( $\text{V}(1)\text{--O}(10) = 2.488(4) \text{ \AA}$ ), with the other four oxygen bonds having an average bond length of 2.003 Å. Valence sum calculations (19) indicate that the long bond formed with O(10) contributes only 3% to the +4 valence of the vanadium atom. The Cs<sup>+</sup> cations reside in tunnels that run along [010] and are coordinated to eight oxygen atoms with distances ranging from 3.100(3) to 3.347(4) Å. The average bond distance in the aluminum tetrahedra is 1.734 Å.

TABLE 7  
Selected Bond Distances (Å) and Angles (°) for  $(\text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_2)[(\text{VO})\text{Al}(\text{PO}_4)_2]$  (3)

V(1)	O(1)	2.189(3)	V(1)	O(2)	2.004(3)
V(1)	O(3)	2.020(3)	V(1)	O(4)	1.605(3)
V(1)	O(5)	2.024(3)	V(1)	N(2)	2.151(4)
P(1)	O(1)	1.501(3)	P(1)	O(5)	1.524(3)
P(1)	O(6)	1.554(3)	P(1)	O(7)	1.548(3)
P(2)	O(2)	1.520(3)	P(2)	O(3)	1.522(3)
P(2)	O(8)	1.529(3)	P(2)	O(9)	1.535(3)
Al(1)	O(6)	1.753(3)	Al(1)	O(7)	1.733(3)
Al(1)	O(8)	1.719(3)	Al(1)	O(9)	1.730(3)
N(1)	C(2)	1.484(6)	N(2)	C(1)	1.488(6)
C(1)	C(2)	1.493(7)			
O(1)–V(1)–O(2)	84.2(1)	O(1)–V(1)–O(3)	84.5(1)		
O(1)–V(1)–O(4)	173.8(1)	O(1)–V(1)–O(5)	83.1(1)		
O(1)–V(1)–N(2)	79.7(1)	O(2)–V(1)–O(3)	88.0(1)		
O(2)–V(1)–O(4)	102.0(1)	O(2)–V(1)–O(5)	91.5(1)		
O(2)–V(1)–N(2)	163.8(1)	O(3)–V(1)–O(4)	96.2(1)		
O(3)–V(1)–O(5)	167.5(1)	O(3)–V(1)–N(2)	92.0(1)		
O(4)–V(1)–O(5)	96.1(1)	O(4)–V(1)–N(2)	94.1(2)		
O(5)–V(1)–N(2)	85.0(1)	O(1)–P(1)–O(5)	111.8(2)		
O(1)–P(1)–O(6)	109.8(2)	O(1)–P(1)–O(7)	108.6(2)		
O(5)–P(1)–O(6)	109.5(2)	O(5)–P(1)–O(7)	110.1(2)		
O(6)–P(1)–O(7)	106.8(2)	O(2)–P(2)–O(3)	113.6(2)		
O(2)–P(2)–O(8)	110.5(2)	O(2)–P(2)–O(9)	107.5(2)		
O(3)–P(2)–O(8)	107.1(2)	O(3)–P(2)–O(9)	109.6(2)		
O(8)–P(2)–O(9)	108.6(2)	O(6)–Al(1)–O(7)	109.5(1)		
O(6)–Al(1)–O(8)	104.8(2)	O(6)–Al(1)–O(9)	109.8(2)		
O(7)–Al(1)–O(8)	113.8(2)	O(7)–Al(1)–O(9)	108.2(2)		
O(8)–Al(1)–O(9)	110.6(2)	V(1)–O(1)–P(1)	146.2(2)		
V(1)–O(2)–P(2)	137.9(2)	V(1)–O(3)–P(2)	128.3(2)		
V(1)–O(5)–P(1)	133.8(2)	P(1)–O(6)–Al(1)	134.9(2)		
P(1)–O(7)–Al(1)	142.5(2)	P(2)–O(8)–Al(1)	164.3(2)		
P(2)–O(9)–Al(1)	147.5(2)	V(1)–N(2)–C(1)	120.5(3)		
N(2)–C(1)–C(2)	109.1(4)	N(1)–C(2)–C(1)	110.0(4)		

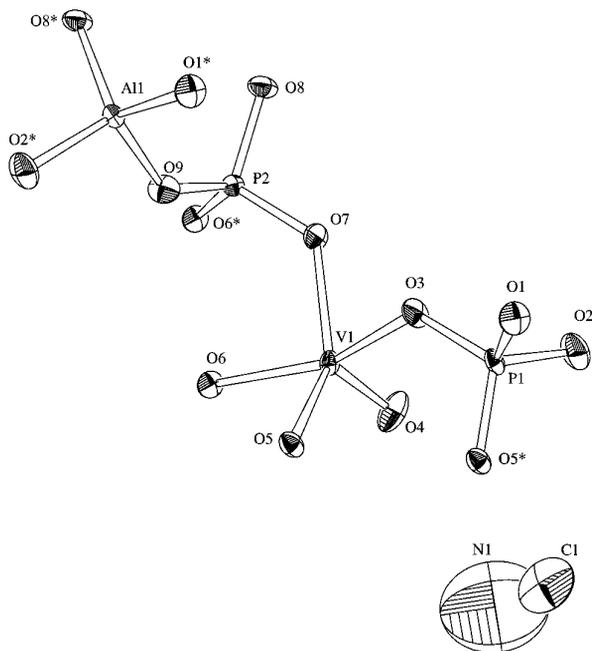


FIG. 4. An ORTEP drawing of the  $\text{CH}_3\text{NH}_3[(\text{VO})\text{Al}(\text{PO}_4)_2]$  structure showing the coordination of the metal atoms and the atomic numbering scheme.

### Structure of $\text{Rb}[(\text{VO})\text{Al}(\text{PO}_4)_2] \cdot \text{H}_2\text{O}$ (2)

The vanadium atoms in this structure also exhibit octahedral coordination. Table 4 lists positional and thermal parameters for the atoms in (2) while Table 5 gives selected bond distances and angles. The numbering scheme used in the tables as well as the coordination environments for the metal centers are shown in Fig.

TABLE 8  
Positional Parameters and  $B(\text{eq})$  for  
 $\text{CH}_3\text{NH}_3[(\text{VO})\text{Al}(\text{PO}_4)_2]$  (4)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (eq)
V(1)	0.22803(10)	0.68704(10)	0.4542(1)	0.94(1)
P(1)	0.4729(1)	0.2798(1)	0.2434(2)	0.96(2)
P(2)	0.0020(1)	0.9127(1)	0.2323(2)	0.90(2)
Al(1)	0.2393(2)	1.0309(2)	0.0778(2)	0.88(2)
O(1)	0.6180(4)	0.1751(4)	0.0812(5)	0.70(7)
O(2)	0.3538(5)	0.1705(5)	0.2108(5)	2.06(8)
O(3)	0.3681(4)	0.4591(4)	0.2370(5)	1.55(6)
O(4)	0.1293(5)	0.6165(5)	0.5502(6)	2.23(8)
O(5)	0.4512(4)	0.6941(4)	0.5660(4)	1.23(6)
O(6)	1.1416(4)	0.9519(4)	0.6133(4)	1.22(6)
O(7)	0.0871(4)	0.7362(4)	0.2513(5)	1.45(6)
O(8)	-0.0779(4)	0.8631(4)	0.0355(4)	1.46(6)
O(9)	0.1445(4)	0.9898(5)	0.2335(5)	1.63(7)
N(1)	0.215(2)	0.438(2)	0.833(1)	15.1(5)
C(1)	0.290(2)	0.293(2)	0.0687(3)	16.5(6)

TABLE 9  
Selected Bond Distances (Å) and Angles (°) for  
 $\text{CH}_3\text{NH}_3[(\text{VO})\text{Al}(\text{PO}_4)_2]$  (4)

V(1)	O(2)	1.993(3)	P(2)	O(6)	1.509(3)
V(1)	O(4)	1.578(3)	P(2)	O(7)	1.525(3)
V(1)	O(5)	1.946(3)	P(2)	O(8)	1.549(3)
V(1)	O(6)	1.978(3)	P(2)	O(9)	1.536(4)
V(1)	O(7)	1.979(3)	Al(1)	O(1)	1.728(3)
P(1)	O(1)	1.537(3)	Al(1)	O(2)	1.717(4)
P(1)	O(2)	1.525(4)	Al(1)	O(8)	1.734(3)
P(1)	O(3)	1.522(3)	Al(1)	O(9)	1.732(4)
P(1)	O(5)	1.510(3)	N(1)	C(1)	1.27(2)
O(3)–V(1)–O(4)	102.2(2)	O(6)–P(2)–O(9)	111.3(2)		
O(3)–V(1)–O(5)	86.7(1)	O(7)–P(2)–O(8)	106.3(2)		
O(3)–V(1)–O(6)	154.4(1)	O(7)–P(2)–O(9)	109.3(2)		
O(3)–V(1)–O(7)	83.7(1)	O(8)–P(2)–O(9)	108.5(2)		
O(4)–V(1)–O(5)	111.2(2)	O(1)–Al(1)–O(2)	110.2(2)		
O(4)–V(1)–O(6)	103.4(2)	O(1)–Al(1)–O(8)	112.2(2)		
O(4)–V(1)–O(7)	109.3(2)	O(1)–Al(1)–O(9)	107.2(2)		
O(5)–V(1)–O(6)	84.9(1)	O(2)–Al(1)–O(8)	109.6(2)		
O(5)–V(1)–O(7)	139.5(1)	O(2)–Al(1)–O(9)	107.2(2)		
O(6)–V(1)–O(7)	87.1(1)	O(8)–Al(1)–O(9)	110.3(2)		
O(1)–P(1)–O(2)	109.1(2)	P(1)–O(1)–Al(1)	148.4(2)		
O(1)–P(1)–O(3)	107.3(2)	P(1)–O(2)–Al(1)	155.6(3)		
O(1)–P(1)–O(5)	111.5(2)	V(1)–O(3)–P(1)	126.3(2)		
O(2)–P(1)–O(3)	110.0(2)	V(1)–O(5)–P(1)	137.0(2)		
O(2)–P(1)–O(5)	106.9(2)	V(1)–O(6)–P(2)	136.7(2)		
O(3)–P(1)–O(5)	112.2(2)	V(1)–O(7)–P(2)	130.3(2)		
O(6)–P(2)–O(7)	111.8(2)	P(2)–O(8)–Al(1)	138.4(2)		
O(6)–P(2)–O(8)	109.5(2)	P(2)–O(9)–Al(1)	137.9(2)		

2. The slightly distorted octahedron surrounding the vanadium atom contains a vanadyl oxygen with a short bond (V(1)–O(1) = 1.590(3) Å) *trans* to a long V–OH<sub>2</sub> bond (V(1)–O(6) = 2.514(3) Å). The other four V–O bonds have an average bond length of 1.999 Å. According to valence sum calculations (19), the long V–OH<sub>2</sub> bond contributes 2.5% to the + 4 valence of the vanadium. As in phosphate (1), the Rb<sup>+</sup> cation resides in tunnels that run along [010] and are coordinated to eight oxygen atoms with distances ranging from 2.968(3) to 3.282(3) Å. The aluminum atom exhibits normal tetrahedral coordination with an average Al–O bond distance of 1.730 Å.

### Structure of $(\text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_2)[(\text{VO})\text{Al}(\text{PO}_4)_2]$ (3)

The coordination environment of the octahedral vanadium and tetrahedral aluminum atoms present in this structure along with the atom numbering scheme are shown in Fig. 3. Positional and thermal parameters of the atoms in phosphate (3) are given in Table 6, and selected bond distances and angles for nonhydrogen atoms are listed in Table 7. The vanadium centers present in (3) are bonded to one nitrogen atom and five distinct oxygen atoms. The

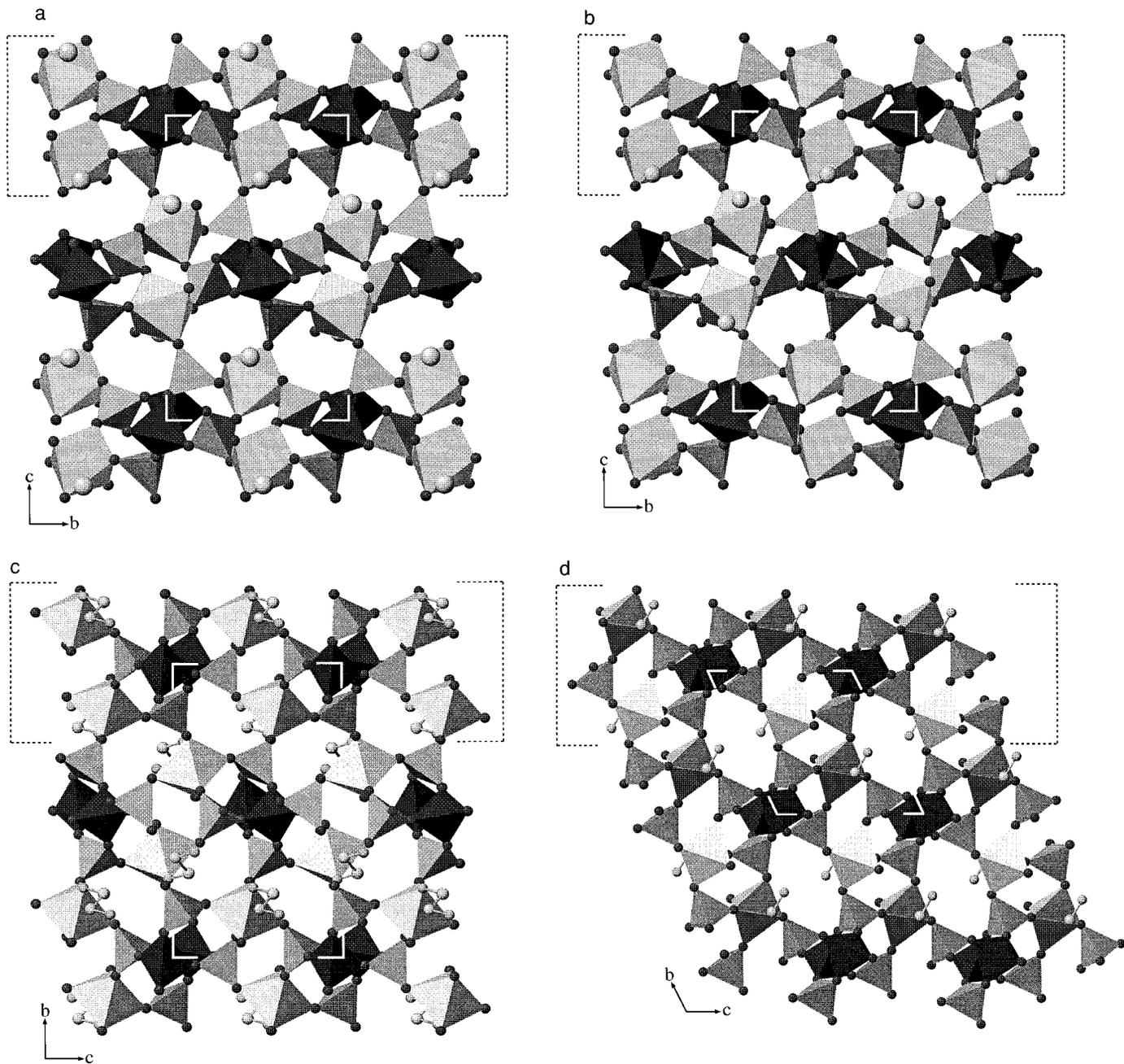


FIG. 5. Unit cell contents of (a)  $\text{Cs}[(\text{VO})\text{Al}(\text{PO}_4)_2] \cdot \text{H}_2\text{O}$  (1), (b)  $\text{Rb}[(\text{VO})\text{Al}(\text{PO}_4)_2] \cdot \text{H}_2\text{O}$  (2), (c)  $(\text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_2)[(\text{VO})\text{Al}(\text{PO}_4)_2]$  (3), and (d)  $\text{CH}_3\text{NH}_3[(\text{VO})\text{Al}(\text{PO}_4)_2]$  (4) projected down [100] with the conceptual layers in brackets. Dark tetrahedra represent the aluminum atoms, light tetrahedra represent the phosphorus atoms, and light gray small spheres represent the oxygen atoms. The carbon atoms present in (3) and (4) are shown as black spheres. The corners of the unit cell are drawn in white within the structure.

nitrogen atom from the 1-aminoethane-2-ammonium cation ( $\text{V}(1)\text{--}\text{N}(2) = 2.151(4) \text{ \AA}$ ) is *cis* to a short vanadyl oxygen ( $\text{V}(12) = \text{O}(4) = 1.605(3) \text{ \AA}$ ). This vanadyl oxygen is *trans* to one long V–O bond ( $\text{V}(1)\text{--}\text{O}(1) = 2.189(3) \text{ \AA}$ ). The other three oxygen atoms that complete the octahedron around the vanadium have an average bond length of  $2.106 \text{ \AA}$ . Tunnels that run parallel to [101] contain the

1-aminoethane-2-ammonium cations. The tetrahedral aluminum atoms have an average phosphate oxygen bond length of  $1.734 \text{ \AA}$ .

#### Structure of $\text{CH}_3\text{NH}_3[(\text{VO})\text{Al}(\text{PO}_4)_2]$ (4)

The coordination environment around the V and Al atoms and the atoms numbering scheme are shown in Fig.

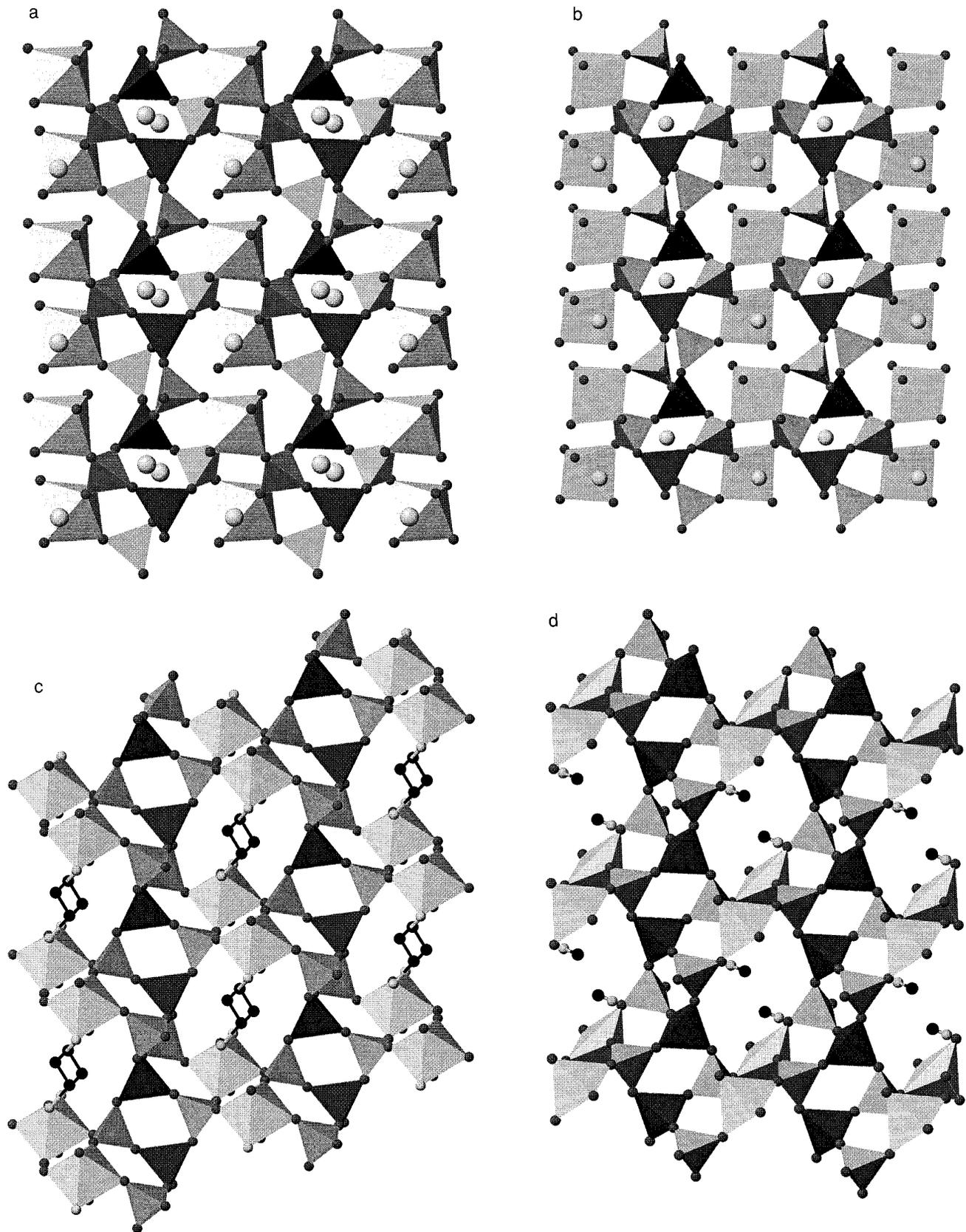


FIG. 6. View perpendicular to the layers in (a) (1), (b) (2), (c), (3), and (d) (4) showing the corner connectivity of the polyhedra and the location of the templating species with the structure.

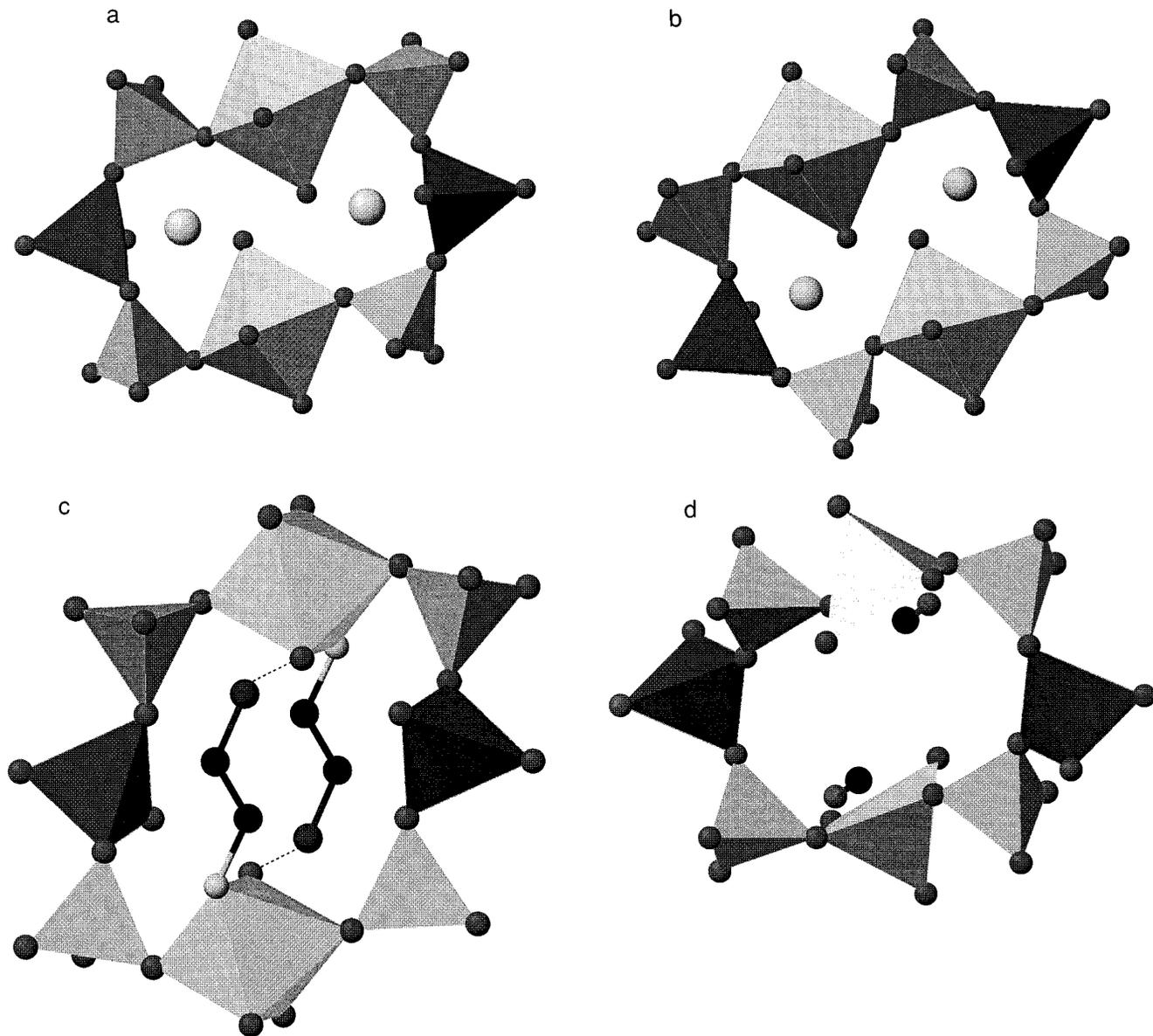


FIG. 7. The 8-rings found in (a) (1) with the  $\text{Cs}^+$  cations, (b) (2) with the  $\text{Rb}^+$  cations, (c) (3) with the 1-aminoethane-2-ammonium cations, and (d) (4) with the methylammonium cations.

4. Presented in Table 8 are the positional and thermal parameters of the atoms in phosphate (4) and selected bond distances and angles are listed in Table 9. The vanadium sites found in this phosphate are square pyramidal in geometry with five oxygen atoms forming the vertices. The vanadium atom is bonded to four oxygen atoms with an average bond length of 1.974 Å and one short vanadyl oxygen with bond length 1.578(3) Å (V(1)–O(4)). The methylammonium cations reside in tunnels that run along [011]. The average Al–O bond length is 1.728 Å.

## DISCUSSION

Phosphates (1), (2), and (3) have comparable structures assembled from vanadium octahedra, aluminum tetrahedra, and phosphorus tetrahedra. The structure of phosphate (4) varies in the square pyramidal coordination of the vanadium atoms as compared to the octahedral vanadium coordination found in phosphates (1), (2), and (3). The framework in each of the phosphates is quite similar, forming with cavities that accommodate the size differing  $\text{Cs}^+$ ,  $\text{Rb}^+$ ,  $\text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_2^+$ , and  $\text{CH}_3\text{NH}_3^+$  cations without

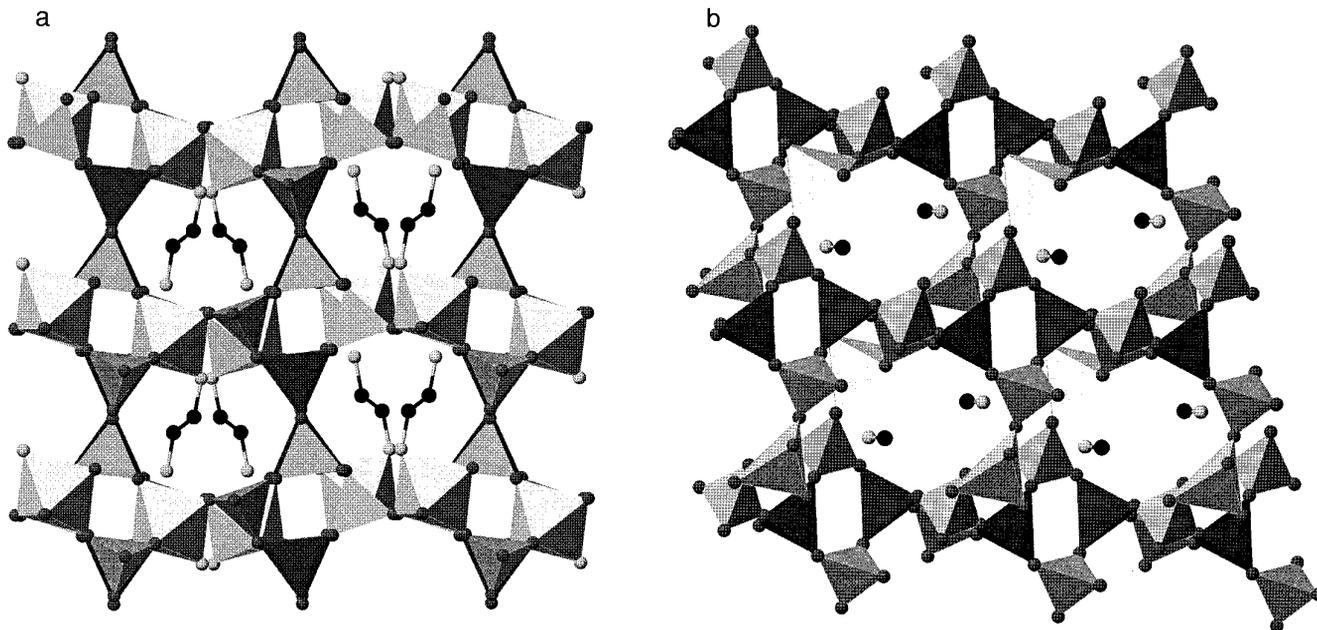


FIG. 8. Projection of (a) (3) down [101] showing the cavities where the ethylenediamine ligand resides and (b) (4) down [011] showing the placement of the methylammonium cations.

grossly perturbing the structure. The 1-aminoethane-2-ammonium ligand provides an integral connection to the framework as well as acting as a cavity occupant, allowing for the commonly diprotonated cation to be singly protonated and able to fit into the same sized cavity that the smaller cations occupy. The similar topology of the phosphates is evident in Fig. 5, which is a view projected down [100]. The structures can be envisioned as having conceptual “layers” that lie in planes parallel to (100). Views perpendicular to these layers show the corner sharing connection between the vanadium octahedra, aluminum tetrahedra, and phosphorus tetrahedra in phosphates (1), (2), and (3) and the corner sharing connection between the square pyramidal vanadium atoms, tetrahedral aluminum, and phosphorus atoms in phosphate (4) (Fig. 6). As shown in Fig. 6d, there is a *cis* and *trans* arrangement of the vanadium square pyramidal sites present in phosphate (4). The layers contain 8-rings (Fig. 7) assembled from two aluminum, two vanadium, and four phosphorus polyhedra joined in such a way that no  $M-O-M$  bonds ( $M = V, Al$ ) are formed. The cations reside inside the cages formed from this connectivity and the protonated end of the ligand found in (3) is hydrogen bonded to the vanadyl oxygen ( $N(1) \cdots O(4) = 2.710(5) \text{ \AA}$ ). The water molecules present on the vanadium centers in (1) and (2) are also located inside these cages and form a hydrogen bond with each other ( $O(10)-O(10)$  in (1) =  $2.929(8) \text{ \AA}$  and  $O(6)-O(6)$  in (2) =  $2.854(7) \text{ \AA}$ ). The connection of these 8-rings into three-dimensions forms

the conceptual one-dimensional aluminophosphate chains that propagate down **a**. In phosphates (1), (2), and (3), which contain three layers per repeat unit, each adjacent layer is shifted along [010] in phosphate (1) and (2) and along [001] in phosphate (3) by 1/2 and connected to

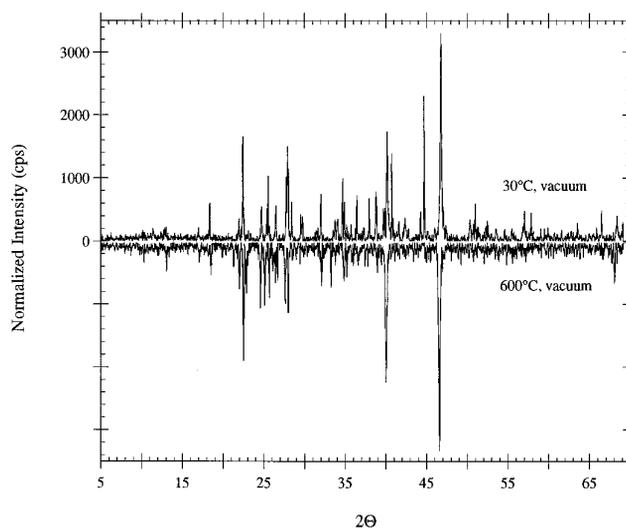


FIG. 9. Powder X-ray diffraction patterns of  $Cs[(VO)Al(PO_4)_2] \cdot H_2O$  (1). The top pattern shows the sample under vacuum at room temperature. The sample was then heated *in situ* under vacuum to  $600^\circ C$  at a rate of  $1^\circ C/min$ . The diffraction pattern obtained at  $600^\circ C$  (vacuum) is the bottom pattern.

each other via corner sharing vanadium octahedra and phosphorus tetrahedra. Phosphate (**4**) consists of only two layers per repeat unit which are not shifted relative to each other. The ethylenediamine ligand in (**3**) fills voids that run along [101] (Fig. 8a), with its protonated end (N(1)) forming additional hydrogen bonds with O(5) ( $N(1) \cdots O(5) = 2.758(4) \text{ \AA}$ ) and with O(2) ( $N(1) \cdots O(2) = 2.894(5) \text{ \AA}$ ). Figure 8b shows the voids in (**4**) that run along [011]. The protonated end of the methylammonium cation likely forms very weak hydrogen bonds with O(7) ( $N(1)-O(7) = 3.142(1) \text{ \AA}$ ).

Temperature controlled X-ray diffraction measurements on  $Cs[(VO)Al(PO_4)_2] \cdot H_2O$  (**1**) indicate considerable thermal stability (Fig. 9). The sample was heated from room temperature to 600°C at a rate of 1°C/min, with scans obtained after every 100°C to monitor crystallinity. As shown in Fig. 9, the sample retained its crystallinity throughout the heat treatment and at 600°C has shown no indication of degradation. Higher temperature X-ray diffraction measurements as well as ion exchange properties and sorption measurements are currently being studied.

Phosphates  $Cs[(VO)Al(PO_4)_2] \cdot H_2O$  (**1**),  $Rb[(VO)Al(PO_4)_2] \cdot H_2O$  (**2**),  $(NH_3CH_2CH_2NH_2)[(VO)Al(PO_4)_2]$  (**3**), and  $CH_3NH_3[(VO)Al(PO_4)_2]$  (**4**) represent the first known examples of three-dimensional vanadium aluminophosphates. The large number of structurally and chemically interesting vanadium phosphates and aluminophosphates has been expanded to include the existence of these mixed vanadium aluminum phosphate systems. These first examples show that there is significant potential for the preparation of thermally stable and topologically unique zeolitic materials in the V–Al–P–O system.

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