3700 *Inorg. Chem.* **1993,** *32,* 3700–3704

Octahedral–Tetrahedral Framework Solids of the Vanadium Phosphate System. Hydrothermal Syntheses and Crystal Structures of the Vanadium(III) Phosphate $Cs[V^{III}_2(PO_4)(HPO_4)_2(H_2O)_2]$ and of the Mixed-Valence Species $K[(V^{IV}O)V^{III}(HPO_4)_3(H_2O)_2]$

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Received June 1, 1992

The cesium vanadium phosphate $Cs[V^{III}_2(PO_4)(HPO_4)_2(H_2O)_2]$ (**1**) and the potassium vanadium phosphate $K[(V^{IV}O)V^{III}(HPO_4)_3(H_2O)_2]$ (**2**) have been hydrothermally synthesized and structurally characterized by single-crystal X-ray methods. Green phosphate **1** is monoclinic, space group $P2_1/a$, with $a = 10.004(1)$ Å, $b = 17.812(3)$ Å, $c = 6.370(2)$ Å, $\beta = 97.02(2)°$, and $Z = 4$, while green phosphate **2** is monoclinic, space group $P2_1/n$, with $a = 6.399(3)$ Å, $b = 10.275(2)$ Å, $c = 17.810(2)$ Å, $\beta = 96.12(2)$,° and $Z = 4$. These new reduced vanadium phosphates, built up from corner-sharing VO_6 octahedra and PO_4 tetrahedra, have anionic, three-dimensional framework structures that contain Cs^+- and K^+-filled voids.

While not as numerous as the silicates, the phosphates also constitute a large class of solid-state materials. Many inorganic phosphates with extremely complicated structures are known, and many possess notable ion-exchange or interlayer ionic mobility.[2] A variety of phosphate structural types, containing mixed octahedral–tetrahedral frameworks, have been described in the molybdenum phosphate system.[3] High-temperature solid-state reactions have yielded compounds such as $Cs_4Mo_8P_{12}O_{52}$,[4] $Cs_4Mo_{10}P_{18}O_{66}$,[5] $Cs_3Mo_4P_3O_{16}$,[6] and many others,[3] while hydrothermal reactions have also produced novel structures such as the inclusion aggregate $[Na_{14}Mo_{24}P_{17}O_{97}(OH)_{31}]^{6-}$,[7] covalently bonded, one-dimensional polymers such as $(Et_4N)_2[Mo_4O_8(PO_4)_{2/2}(H_{1.5}PO_4)_2]\cdot 2H_2O$,[8] the layered structures $(Pr_4N)(NH_4)[Mo_4O_8(PO_4)_2]$[9] and $Na_3[Mo_2P_2O_{11}(OH)]\cdot 2H_2O$,[10] and several microporous, three-dimensional framework materials.[3,11]

While the lamellar vanadyl phosphates $[VOPO_4]$[12] and α-$[VOPO_4]\cdot 2H_2O$[13] and the related solid pyrophosphate $[(VO)_2P_2O_7]$[14] have been extensively studied,[15] other vanadophosphate solids of the M^{n+}–V^{m+}–phosphate system have only recently received much attention. However, the structural diversity of the system is apparent from the numerous reports of vanadium phosphates containing V(V) and/or V(IV).[16–18] On the other hand, V(III)–containing species have remained elusive.[19] We have synthesized several additional members of this class of reduced vanadophosphates such as α- and β-$Rb[V^{III}(HPO_4)_2]$,[20] $Na[V^{III}(HPO_4)_2]$,[20] $NH_4[V^{III}(HPO_4)_2]$,[20] and a unique "stair-step" layered compound $K_2[V(VO)_2(PO_4)_2(HPO_4)(H_2PO_4)\cdot 2H_2O]$, containing interlayer K^+ cations.[20] Recently we reported the structure of the first 3-D vanadium phosphate with organic templates that were incorporated by direct synthesis, which contained chiral double helices[21] The dramatic influences of the alkali metal cation and reaction conditions upon composition and structure of the resultant vanadophosphate are illustrated by the isolation of $Cs[V^{III}_2(PO_4)(HPO_4)_2(H_2O)_2]$ (**1**) and of the unique

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Table I. Crystallographic Data

	1	**2**
empirical formula	$CsH_6V_2P_3O_{14}$	$KH_7V_2P_3O_{15}$
fw	551.70	473.89
cryst dimens (mm)	0.180 × 0.120 × 0.100	0.200 × 0.200 × 0.100
lattice params (Å, deg)	a = 10.004(1) b = 17.812(3) c = 6.370(2) β = 97.02(2)	a = 6.399(3) b = 10.275(2) c = 17.810(2) β = 96.12(2)
V (Å^3)	1126.5(4)	1164.4(5)
T (°C)	20	20
space group	$P2_1/a$ (No. 14)	$P2_1/n$ (No. 14)
Z value	4	4
D_{calc} (g/cm^3)	3.253	2.703
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
μ(Mo Kα) (cm^{-1})	52.68	24.02
residuals:[a] R; R_w	0.045; 0.048	0.033; 0.035

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

Table II. Positional Parameters and B(eq) Values (Å^2) for **1** and **2**

atom	x	y	z	B(eq)[a]
		Compound **1**		
Cs(1)	0.47759(6)	0.19905(3)	0.20100(9)	1.81(2)
V(1)	0.6788(1)	0.35868(7)	0.7097(2)	0.32(5)
V(2)	0.8162(1)	0.55157(7)	0.2284(2)	0.38(5)
P(1)	0.3643(2)	0.3007(1)	0.6716(3)	0.38(7)
P(2)	0.8724(2)	0.5122(1)	0.7427(3)	0.29(7)
P(3)	0.6326(2)	0.3950(1)	0.1990(3)	0.48(8)
O(1)	0.2931(5)	0.3132(3)	0.4397(8)	0.8(1)
O(2)	0.3088(5)	0.2292(3)	0.7514(7)	0.6(1)
O(3)	0.3372(5)	0.3700(3)	0.8017(7)	0.5(1)
O(4)	0.5170(5)	0.2906(3)	0.6659(7)	0.6(1)
O(5)	0.5558(5)	0.4526(3)	0.6782(8)	0.9(1)
O(6)	0.8338(5)	0.4286(3)	0.7579(8)	0.7(1)
O(7)	0.8235(5)	0.5582(3)	0.9225(8)	0.6(1)
O(8)	1.0248(5)	0.5183(3)	0.7447(7)	0.49(9)
O(9)	0.7988(5)	0.5468(3)	0.5383(8)	0.8(1)
O(10)	0.9541(5)	0.6396(3)	0.2854(8)	1.2(1)
O(11)	0.6704(5)	0.4775(3)	0.1843(8)	0.8(1)
O(12)	0.6719(5)	0.3502(3)	0.0160(7)	0.6(1)
O(13)	0.4729(5)	0.3921(3)	0.1917(8)	1.1(1)
O(14)	0.6912(5)	0.3584(3)	0.4056(7)	0.7(1)
		Compound **2**		
V(1)	0.2763(2)	0.1491(1)	0.66622(8)	0.79(5)
V(2)	0.6410(2)	0.2960(1)	0.47808(8)	0.99(6)
K(1)	0.5781(4)	0.0732(3)	0.8476(1)	4.9(1)
P(1)	0.1935(3)	0.3315(2)	0.8120(1)	0.88(8)
P(2)	0.7619(3)	0.1046(2)	0.6268(1)	0.86(8)
P(3)	0.4460(3)	0.4343(2)	0.6148(1)	0.93(8)
O(1)	0.2421(7)	0.4711(5)	0.7873(3)	0.9(2)
O(2)	−0.0539(8)	0.3091(5)	0.7897(3)	1.5(2)
O(3)	0.2368(8)	0.3189(5)	0.8975(3)	1.1(2)
O(4)	0.3073(7)	0.2318(5)	0.7702(3)	0.9(2)
O(5)	0.2366(8)	0.0740(5)	0.5572(3)	1.5(2)
O(6)	0.5877(7)	0.1312(5)	0.6753(3)	1.2(2)
O(7)	0.8043(8)	−0.0468(5)	0.6257(3)	1.5(2)
O(8)	0.9636(7)	0.1696(5)	0.6636(3)	1.2(2)
O(9)	0.7125(8)	0.1426(5)	0.5448(3)	1.5(2)
O(10)	0.9905(9)	0.3368(7)	0.4997(4)	3.3(3)
O(11)	0.3944(8)	0.2743(5)	0.4574(3)	1.7(3)
O(12)	0.6277(8)	0.4063(5)	0.5703(3)	1.3(2)
O(13)	0.3133(8)	0.5498(5)	0.5851(3)	1.4(2)
O(14)	0.5546(8)	0.4665(5)	0.6971(3)	1.4(2)
O(15)	0.2948(7)	0.3205(5)	0.6195(3)	1.1(2)

[a] $B_{eq} = (8\pi^2/3)[U_{11}(aa^*) + U_{22}(bb^*) + U_{33}(cc^*) + 2U_{12}a^*b^* \cos\alpha + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha]$.

Table III. Selected Interatomic Distances (Å)

1		**2**	
Cs(1)–O(1)	3.246(5)	V(1)–O(1)	2.016(5)
Cs(1)–O(1)	3.339(5)	V(1)–O(4)	2.027(5)
Cs(1)–O(2)	3.188(5)	V(1)–O(5)	2.080(6)
Cs(1)–O(4)	3.361(5)	V(1)–O(6)	1.991(5)
Cs(1)–O(7)	3.355(5)	V(1)–O(8)	2.008(5)
Cs(1)–O(8)	3.238(5)	V(1)–O(15)	1.957(5)
Cs(1)–O(10)	3.450(5)	V(2)–O(3)	2.004(5)
Cs(1)–O(10)	3.436(5)	V(2)–O(9)	1.998(5)
Cs(1)–O(12)	3.602(5)	V(2)–O(10)	2.268(6)
Cs(1)–O(12)	3.260(5)	V(2)–O(11)	1.597(5)
Cs(1)–O(13)	3.439(5)	V(2)–O(12)	2.004(5)
Cs(1)–O(14)	3.694(5)	V(2)–O(13)	1.983(5)
Cs(1)–O(14)	3.455(5)	K(1)–O(1)	3.166(6)
V(1)–O(2)	2.031(5)	K(1)–O(4)	2.655(5)
V(1)–O(4)	2.015(5)	K(1)–O(6)	3.133(6)
V(1)–O(5)	2.073(5)	K(1)–O(10)	2.971(7)
V(1)–O(6)	1.983(5)	K(1)–O(11)	3.088(6)
V(1)–O(12)	1.967(5)	K(1)–O(12)	2.835(5)
V(1)–O(14)	1.955(5)	K(1)–O(13)	2.900(6)
V(2)–O(3)	2.067(5)	K(1)–O(14)	2.786(6)
V(2)–O(7)	1.963(5)	P(1)–O(1)	1.542(5)
V(2)–O(8)	2.011(5)	P(1)–O(2)	1.607(5)
V(2)–O(9)	2.004(5)	P(1)–O(3)	1.524(5)
V(2)–O(10)	2.034(6)	P(1)–O(4)	1.501(5)
V(2)–O(11)	1.961(5)	P(2)–O(6)	1.506(6)
P(1)–O(1)	1.575(5)	P(2)–O(7)	1.579(5)
P(1)–O(2)	1.503(5)	P(2)–O(8)	1.536(5)
P(1)–O(3)	1.529(5)	P(2)–O(9)	1.512(5)
P(1)–O(4)	1.543(5)	P(3)–O(12)	1.503(6)
P(2)–O(6)	1.545(5)	P(3)–O(13)	1.521(5)
P(2)–O(7)	1.536(5)	P(3)–O(14)	1.589(5)
P(2)–O(8)	1.527(5)	P(3)–O(15)	1.525(5)
P(2)–O(9)	1.543(5)		
P(3)–O(11)	1.523(5)		
P(3)–O(12)	1.505(5)		
P(3)–O(13)	1.594(6)		
P(3)–O(14)	1.521(5)		

V^{III}/V^{IV} mixed-valence species $K[(V^{IV}O)V^{III}(HPO_4)_3(H_2O)_2]$ (**2**), which we describe in this paper.

Experimental Section

The reactions were carried out under autogeneous pressure in polytetrafluoroethylene lined stainless steel vessels.

$Cs[V_2(PO_4)(HOP_4)_2(H_2O)_2]$ (1). Reaction of $Cs_4V_2O_7$ (100 mesh, 99.9%), V (325 mesh, 99.5%), H_3PO_4 (85 wt %), H_2O, and $C_6H_5N(CH_3)_3Cl$ (98%) in a mole ratio of 1:2:46:800:1.1 for 48 h at 200 °C gives a 69% yield of green crystalline **1**, which was washed with water and dried in air.

$K[V(VO)(HPO_4)_3(H_2O)_2]$ (2). Reaction of KVO_3 (200 mesh, 99.9%), V (325 mesh, 99.5%), H_3PO_4 (85 wt %), and H_2O in a mole ratio of 2:1:10:104 for 48 h at 200 °C gives a 26% yield of light green crystalline **2**, which was washed with water and dried in air.

X-ray Crystallography. The experimental X-ray data are summarized in Table I, the atomic coordinates and isotropic thermal parameters are listed in Table II, and some selected bond distances are found in Table III.

Results and Discussion

The coordination chemistry of vanadium is dominated by the oxophilicity of the metal in the +4 and +5 oxidation states.[22] However, in aqueous solution the +2 and +3 oxidation states are also accessible, and variable oxidation states are a persistent theme of the cluster chemistry of vanadium.[23] The coordination geometries at vanadium centers are also highly variable, such that tetrahedral, square-pyramidal, and octahedral types are known for V(IV) while V(V) can assume square-pyramidal, trigonal-bipyramidal, and octahedral geometries. Vanadium(III) complexes characteristically exhibit octahedral geometry.

Oxidation states from 3+ to 5+ have been observed in the vanadium phosphate system, and the vanadium sites adopt square pyramidal as well as both regular and distorted octahedral geometries. The solids are thus constructed from VO_6 octahedra and PO_4 tetrahedra usually through corner-sharing interactions but also occasionally through edge sharing. This fundamental structural motif is deceptively simple, as the details of the octahedral–tetrahedral connectivity allow the construction of solid

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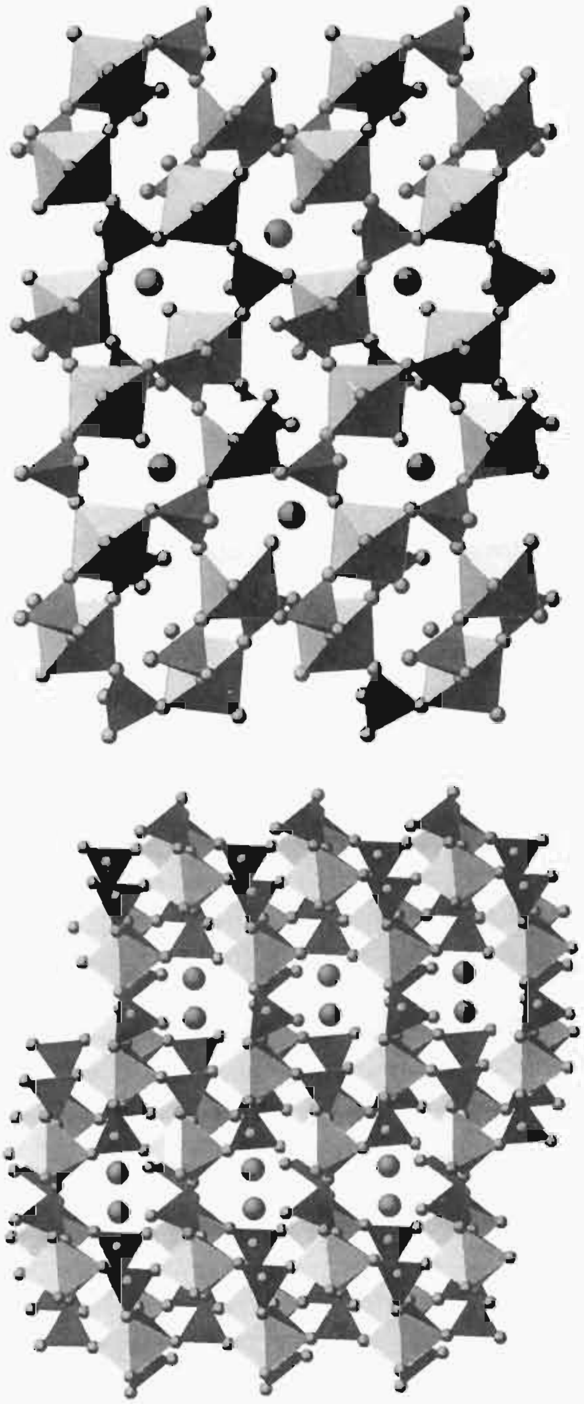

Figure 1. Polyhedral representations of the structure of $Cs[V^{III}_2(HPO_4)_2(PO_4)(H_2O)_2]$ (1) down (a, top) the *c* axis with *b* vertical and *a* horizontal and (b, bottom) down the *a* axis with *b* vertical and *c* horizontal. The V and P are represented by octahedra and tetrahedra, respectively, and the Cs^+ cations by the large spheres.

lattices displaying vastly different three-dimensional structures, varying tunnel volumes and cation occupancies. These features are illustrated by the structures of $Cs[V^{III}_2(PO_4)(HPO_4)_2(H_2O)_2]$ (1) and $K[(V^{IV}O)V^{III}(HPO_4)_3(H_2O)_2]$ (2).

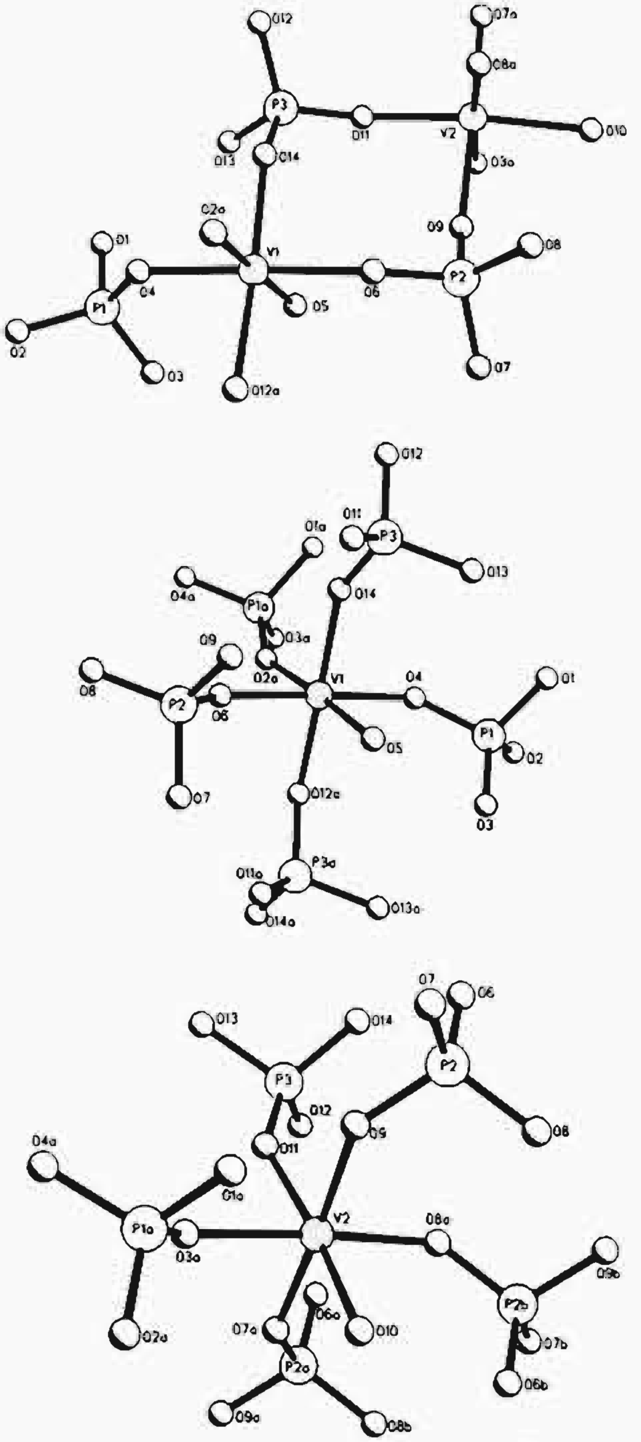

Figure 2. Primary building blocks of the structure of $Cs[V^{III}_2(HPO_4)_2(PO_4)(H_2O)_2]$ (1): (a, top) environments of the crystallographically unique vanadium and phosphorus centers; (b, middle) and (c, bottom) perspective views of the vanadium coordination spheres.

Figure 1a,b shows polyhedral projections of the unit cell contents of 1 down the *a* and *c* axes. The crystallographically unique vanadium and phosphorus sites produce an eight-membered cyclic structure V(1)–O(6)–P(2)–O(9)–V(2)–O(11)–P(3)–O(14), with an adjacent corner-sharing tetrahedron contributed by P(1) (Figure 2a). As shown in Figure 2b,c, the vanadium coordination spheres consist of distorted octahedra of five oxygen donors shared with five adjacent $\{PO_4\}$ tetrahedra and one oxygen atom from an aquo ligand. Valence sum calculations[24] confirm that the vanadium centers are both in the +3 oxidation state, an observation also consistent with the approximately regular octahedral geometry with bond distances in the relatively narrow 1.95–2.08-Å range (Table III). This vanadium coordination geometry is distinctly different from that reported for the other structurally characterized V(III) phosphates $Ca_2[V(PO_4)(HPO_4)_2]\cdot H_2O$ and $Ca_2[V(PO_4)(P_2O_7)]$,[19] which exhibit vanadium coordination to $\{PO_4\}$ and/or $\{P_2O_7\}$ units exclusively.

Two of the three unique phosphorus sites are present as $[HPO_4]^{2-}$ units, sharing three oxygen donors with each of three

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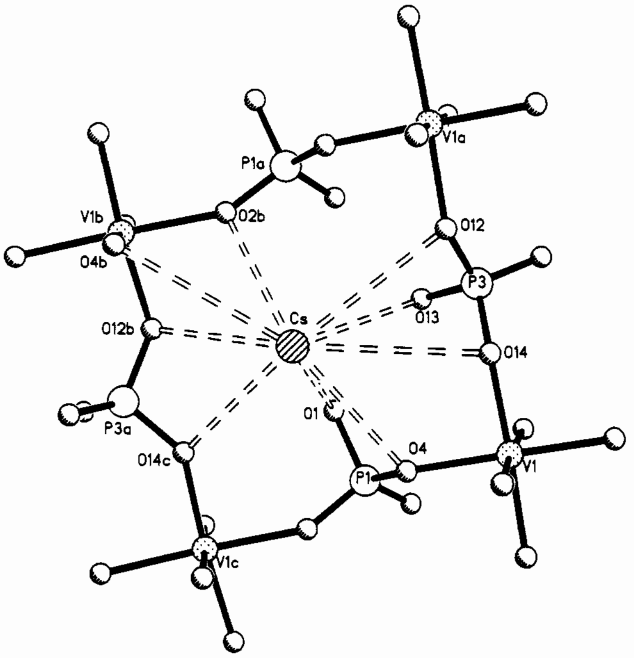

Figure 3. View of the Cs^+ cation environment in $Cs[V^{III}_2(HPO_4)_2(PO_4)(H_2O)_2]$ (**1**).

adjacent vanadium centers and exhibiting a terminal –OH group. The P–O bond distances, P(1)–O(1) (1.575(5) Å) and P(3)–O(13) (1.594(6) Å), clearly distinguish the protonated oxygen sites. The third phosphorus center is present as $(PO_4)^{3-}$ with oxygen bridging to each of four adjacent vanadium sites. Expansion in the *bc* plane of the asymmetric unit of Figure 2a reveals the fundamental structural motif of structure **1**, two fused 8-membered rings in turn fused to two adjacent 16-membered rings. The large V–O–P cycles are generated by corner-sharing alternation of four vanadium octahedra and four phosphorus tetrahedra. The larger 16-membered rings are seen to stack along the *a* axis so as to produce channels, which are occupied by the Cs^+ cations. The Cs^+ environment is illustrated in Figure 3 with a ball and stick representation. When viewed down the crystallographic *a* axis, the vanadophosphate framework consists of double "layers" of one vanadium octahedron plus one phosphorus tetrahedron in thickness, connected through the P(1) tetrahedra. The connectivity found within these layers is somewhat reminiscent of the well-known $MOPO_4$ structure types, but with the $(M^{3+}–OH_2)$ moiety substituting for $(M^{5+}–O)$ and phosphate groups inserted between the layers.

In addition to the more covalent V–O and P–O bonds, and the ionic Cs–O bonds, there are several strong hydrogen bonds within the structure of **1** which are likely an important factor in determining which structure can form under given synthetic conditions. Both of the terminal P–OH bonds form short H-bonded contacts (O(1)–O(9) = 2.667 Å and O(13–O(3) = 2.710 Å). Both of the water ligands bound to the vanadium centers also form hydrogen bonds to other atoms of the framework. One water (O(5)) contacts atoms O(6) and O(11) at 2.798 and 2.815 Å, respectively. The remaining water (O(10)) probably has the two H atoms disordered toward three framework atoms as it contacts O(3), O(4), and O(6) at 2.806, 2.730, and 2.576 Å, respectively.

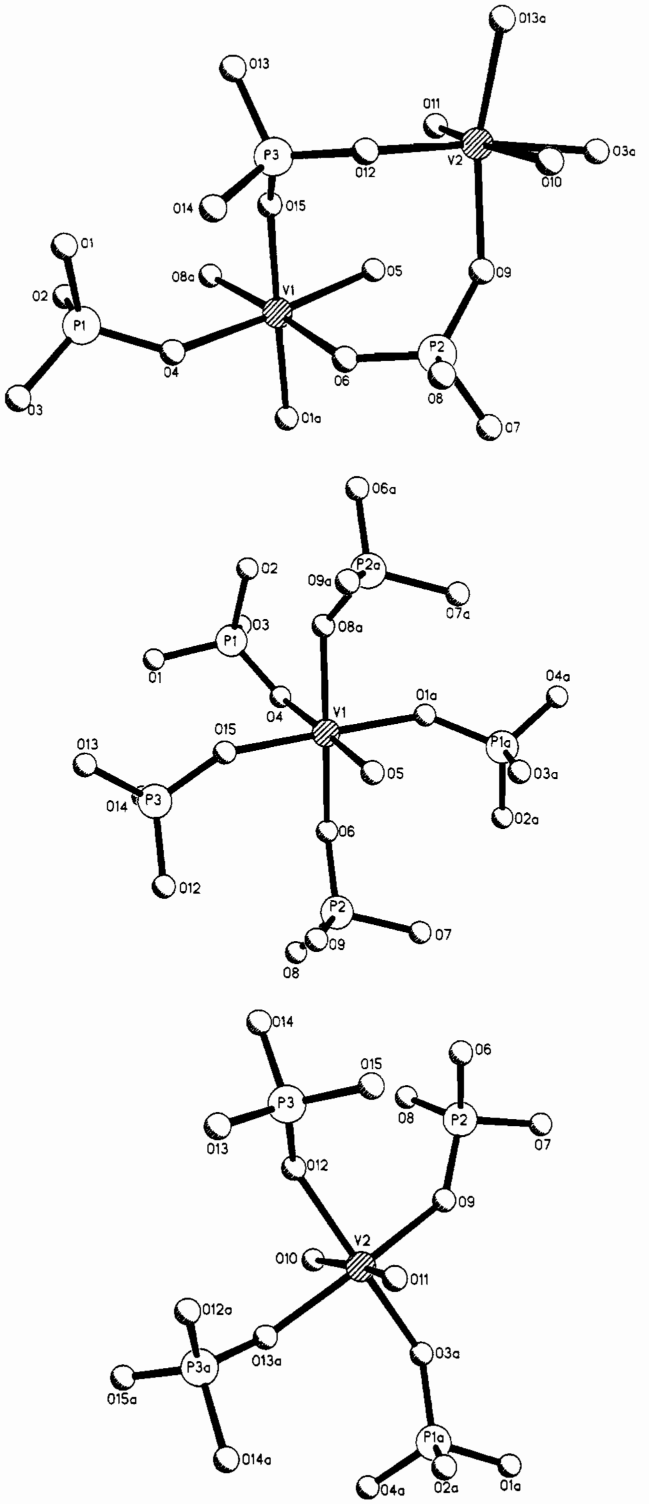

Figure 4. Primary building blocks of the structure of $K[(V^{IV}O)V^{III}(HPO_4)_3(H_2O)_2]$ (**2**): Views showing the environments of the crystallography unique vanadium and phosphorus centers.

The species $K[(V^{IV}O)V^{III}(HPO_4)_3(H_2O)_2]$ (**2**) is a unique example of a mixed-valence V(IV)/V(III) species in the vanadium phosphate system. The environments of the crystallographically unique vanadium and phosphorus centers are shown in Figure 4a–c. While the asymmetric unit at first glance may appear identical to that of **1**, there are noteworthy structural characteristics unique to **2**. The coordination geometry about the V(III) site V(1) is essentially identical to that of the vanadium centers of **1**, with V(1) coordinated to each of five oxygen donors from five adjacent $[HPO_4]^{2-}$ tetrahedra and to the oxygen of an aquo ligand. However, the V(2) site is structurally distinct, reflecting the constraints of the +4 oxidation state and the presence of a terminal oxo group. Thus, the V(2) center is bonded to four oxygen donors of each of four adjacent $[HPO_4]^{2-}$ units, the oxygen donor of an aquo ligand, and a terminal oxo-group O(11). The strong *trans* influence of the multiply-bonded oxo group is reflected in the long V(2)–O(10) distance of 2.30 Å. The bond lengths, given in Table III, and valence sum calculations for the vanadium centers of **2** confirm the oxidation-state assignments.

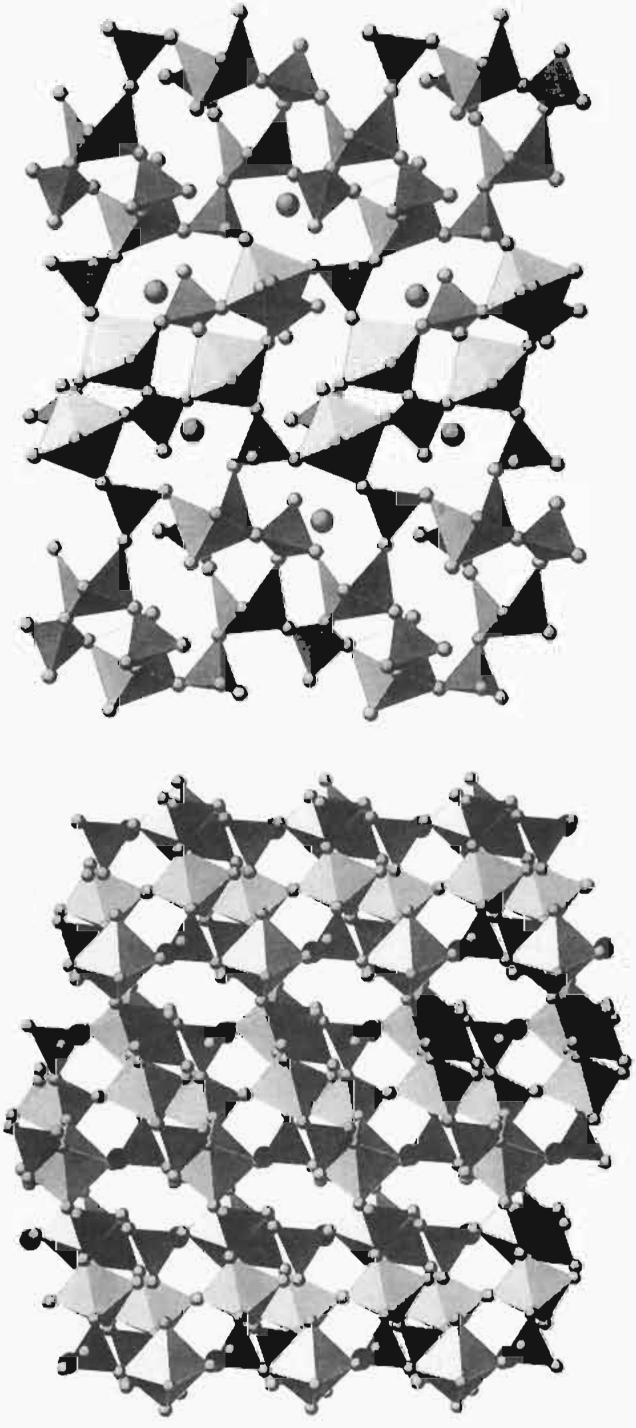

Figure 5. Polyhedral representation of the structure of K[$V^{IV}O$)-$V^{III}(HPO_4)_3(H_2O)_2$] (2) viewed down (a, top) the *a* axis with *c* vertical and *b* horizontal and (b, bottom) the *b* axis with *c* vertical and *a* horizontal. The K^+ cations are the large gray spheres in (a) but are represented by black spheres in (b).

One feature of the structure of **2**, which produces dramatic geometric variations from that of **1**, is the presence of exclusively $[HPO_4]^{2-}$ tetrahedra which can each bridge to only three adjacent vanadium centers. In contrast, the structure of **1** has been seen to contain both $[PO_4]^{3-}$ and $[HPO_4]^{2-}$ units. The presence of the $[PO_4]^{3-}$ tetrahedra, with four vertices available for bridging to V centers, affords greater flexibility for connectivity in **1**. Moreover, the presence of the terminal oxo group on V(2) of **2** removes an additional potential vertex interaction and further limits the structural flexibility of **2**. The structural constraints imposed by the coordination polyhedra may be appreciated by expansion of the asymmetric unit of Figure 4a in the *bc* plane.

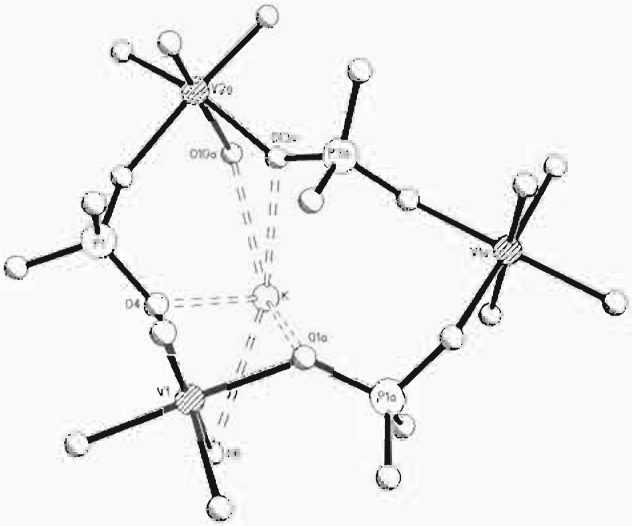

Figure 6. View of the spatial relationship of the K^+ cation to the 12-membered cycle in K[($V^{IV}O)V^{III}(HPO_4)_3(H_2O)_2$] (2).

While structure **2** shares with **1** the common motif of two fused eight-membered rings, these are in turn fused to a 12-membered cyclic unit, composed of alternating vertex-sharing octahedra and tetrahedra.

The repetition of this structural theme viewed along the crystallographic a and c axes produces the view of the structure shown in Figure 5a,b. The tunnel structure adopted by **2** is clearly revealed by the polyhedral representations. However, in contrast to **1**, the volume of the channels produced by the stacking of 12-membered rings is more restrictive, which results in the K^+ cation occupying a position distinctly removed from the center of the ring as shown in Figure 6. The "lamellar" nature of the structure is apparent, with the vanadophosphate "layers" formed parallel to the diagonal of the *ac* plane. This "interlamellar" region is occupied by the K^+ cations and the P(2) tetrahedra which crosslink the planes. The aquo ligand O(10) also projects into the interlamellar space.

As in the case of **1**, there are several hydrogen bonds influencing the structure of the framework of **2**. The three terminal P–OH oxygen atoms (O(2), O(7), O(14)) form contacts to other O atoms with O(2) H-bonded to O(7) and O(8) at 2.743 and 2.672 Å, respectively, while O(14) contacts O(1) at 2.691 Å. Both of the water molecules are near two other O atoms with O(5) bonding to O(15) and O(3) at 2.783 and 2.736 Å, respectively, and O(10) contacting O(3) and O(13) at 2.813 and 2.607 Å.

The structure of **2** is quite distinct from the observed for the only other mixed-valence vanadium phosphate structures described, $Na_{0.5}VOP_4·2H_2O$ and $K_{0.50}VOPO_4·1.5H_2O$.[17] Not only are the latter V(V)/V(IV) species, rather than the more unusual V(IV)/V(III) type adopted by **2**, but they are also examples of a class III mixed-valence system,[24] where the crystallographic sites are indistinguishable and the electrons are presumably delocalized. In contrast, compound **2** is of the class I type where the distinguishable geometries of V(1) and V(2) imply that the V(III) d^2 site is localized on V(1) while the V(IV) d^1 site is associated with V(2).

Acknowledgment. The work at Syracuse University was partially supported by NSF Grant CHE 9119910. We are grateful to Dr. Bev Vincent, Molecular Structure Corp., for the solution of the X-ray data.

Supplementary Material Available: Tables of experimental crystallographic details, thermal parameters, and selected interatomic distances and angles (24 pages). Ordering information is given on any current masthead page.