A Stair Step Layer Structure Encapsulating Interlayer K^+ Cations: Hydrothermal Synthesis, Crystal Structure, and Magnetic Properties of the Mixed-Valence Vanadium Phosphate $K_2[(V^{IV}O)_2V^{III}(PO_4)_2(HPO_4)(H_2PO_4)(H_2O)_2]$

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The V–P–O system is of considerable contemporary interest because of its relevance to catalysis[2,3] and by virtue of a rich and complex crystal chemistry which remains as yet incompletely realized. Variations in the vanadium oxidation state and in the vanadium to phosphorus ratio have yielded numerous well-characterized phases. The pseudobinary oxovanadium(V) α-$VOPO_4$ and related intercalatable phases have been widely studied for their catalytic properties,[4–6] while the oxovanadium(IV) phosphates $VO(HPO_4)\cdot nH_2O$ and $VO(H_2PO_4)_2$ exhibit a large variety of structure types displaying a range of low-dimensional magnetic interactions.[7–11] The mixed-valence V^{III}/V^{IV} phase $V_2VO(P_2O_7)_2$[12] has been characterized, while vanadium(III) phosphates remain relatively elusive but are represented by VPO_4.[13] Furthermore, the chemistry of the vanadium phosphate system may be dramatically extended by the introduction of other metal cations. Thus, both high-temperature[14] and hydrothermal techniques[15] may be exploited in the preparation of $M^{n+}/V^{m+}/$phosphates (M = alkali or alkaline earth metal cation) with lamellar or tunnel structures containing cation-filled voids. Since the steric and electronic requirements of the cations are reflected in the structures adopted by these solids, we have been systematically investigating the influences of alkali metal cations on the synthesis and structures of reduced vanadium phosphates. In particular, we have focused on the synthetic and structural consequences of introducing vanadium metal to produce vanadium phosphate networks with low-valent sites. Although V(III)-containing systems have been described only recently,[15d,16] they afford a variety of structural types exhibiting unusual octahedral–tetrahedral frameworks. We recently discovered the structurally distinct α- and β-forms of $Rb[V^{III}(HPO_4)_2]$,[17] the unusual aquo-coordinated cesium vanadium phosphate $Cs[V_2^{III}(PO_4)(HPO_4)_2(H_2O)_2]$,[17] and infinite 1-D ($-V^{IV}-O-V^{V}-O-$) chains in $Cs[(V_2O_3)(HPO_4)_2(H_2O)]$.[17] We have also reported the first examples of organically templated 3-D vanadium phosphates $[(CH_3)_2NH_2]K_4[V_{10}O_{10}(H_2O)_2(OH)_4(PO_4)_7]\cdot 4H_2O$[18] and $(H_3NCH_2CH_2NH_3)_2(H_3NCH_2CH_2NH_2)[V(H_2O)_2(VO)_8(OH)_4(HPO_4)_4(PO_4)_4]\cdot 2H_2O$.[19] The dramatic influences of reaction conditions upon composition and structure of the resultant vanadophosphates are again demonstrated in the isolation of $K_2[(V^{IV}O)_2V^{III}(PO_4)_2(H_2PO_4)(HPO_4)(H_2O)_2]$, a unique example of a mixed-valence V(III,IV,IV) phosphate with a stair step layered structure exhibiting both inter- and intralamellar K^+ cation encapsulation sites.

Table I. Crystallographic Data

formula: $V_3H_7O_{20}P_4K_2$	$Z = 2$
crystal system: triclinic	$d_{calc} = 2.800$ g cm^{-3}
space group: $P\bar{1}$	$T = 20$ °C
$a = 10.571(2)$ Å	λ(Mo Kα) = 0.710 69 Å
$b = 12.815(3)$ Å	$\mu = 26.83$ cm^{-1}
$c = 6.407(2)$ Å	no. of data obs $[I > 3\sigma(I)] = 952$
$\alpha = 102.73(2)°$	no. of variables = 162
$\beta = 97.43(2)°$	$R^a = 0.069$
$\gamma = 105.26(2)°$	$R_w{}^b = 0.073$
$V = 800(1)$ Å^3	

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

Experimental Section

Green crystals of $K_2[(V^{IV}O)_2V^{III}(PO_4)_2(HPO_4)(H_2PO_4)(H_2O)_2]$ (**1**) were prepared by the reaction of vanadium metal, KVO_3, Bu_4NBr, H_3PO_4, and H_2O in the molar ratio 1:9:0.5:41:417 in a 23-mL polytetrafluoroethylene-lined vessel heated at 240 °C for 48 h. After washing with water and air-drying, the yield is ca. 40% based on total vanadium introduced into the reaction. On several occasions, when vessels that had been used previously for other vanadium phosphate reactions were used, compound **1** was contaminated with other byproducts. However when new vessels were used, **1** was consistently obtained as a single-phase product.

Crystallographic details are provided in the tables and in the supplementary material.

Results and Discussion

X-ray structural analysis (Table I) of **1** revealed the presence of layers of distorted vanadium polyhedra and phosphorus tetrahedra with K^+ cations occupying the interlamellar region.

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Table II. Atomic Coordinates and B_{eq} Values for 1

atom	x	y	z	B_{eq},[a] Å^2
V1	0.6100(4)	0.6301(4)	0.3396(8)	0.7(2)
V2	0.8531(5)	1.1601(4)	0.6257(8)	1.0(2)
V3	0.6047(5)	0.9076(4)	0.9737(8)	1.3(2)
K1	0.7735(6)	0.4438(5)	0.582(1)	1.8(2)
K2	0.8948(6)	0.7801(6)	0.802(1)	2.4(2)
P1	0.5512(7)	0.6337(6)	0.822(1)	0.6(2)
P2	0.7689(7)	1.1660(6)	1.113(1)	1.2(3)
P3	0.6586(7)	0.9006(6)	0.474(1)	1.1(3)
P4	0.9169(7)	0.5956(6)	0.229(1)	1.3(3)
O1	0.639(1)	0.632(1)	0.657(3)	0.5(3)
O2	0.632(1)	0.632(1)	0.031(3)	0.1(3)
O3	0.459(2)	0.633(1)	0.301(3)	1.7(4)
O4	0.832(1)	0.628(1)	0.387(3)	0.6(3)
O5	0.709(2)	0.796(1)	0.442(3)	1.4(4)
O6	0.581(2)	0.463(1)	0.251(3)	0.7(3)
O7	0.850(1)	1.156(1)	0.927(3)	0.2(3)
O8	0.854(1)	1.166(1)	0.315(2)	0.2(3)
O9	0.667(2)	1.178(2)	0.586(3)	2.0(4)
O10	1.049(2)	1.140(1)	0.668(3)	1.8(4)
O11	0.939(1)	1.326(1)	0.725(3)	0.5(3)
O(12)	0.791(2)	1.001(1)	0.529(3)	1.5(4)
O(13)	0.633(2)	1.077(1)	1.063(3)	1.2(4)
O14	0.505(2)	0.738(1)	0.860(3)	0.6(3)
O15	0.568(1)	0.896(1)	1.266(3)	0.3(3)
O16	0.760(2)	0.910(2)	1.005(3)	2.7(5)
O17	0.578(1)	0.910(1)	0.656(2)	0.1(3)
O18	0.738(2)	1.282(1)	1.143(3)	1.7(4)
O(19)	0.936(2)	0.476(1)	0.230(3)	1.7(4)
O20	0.847(2)	0.590(1)	−0.009(3)	2.4(4)

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

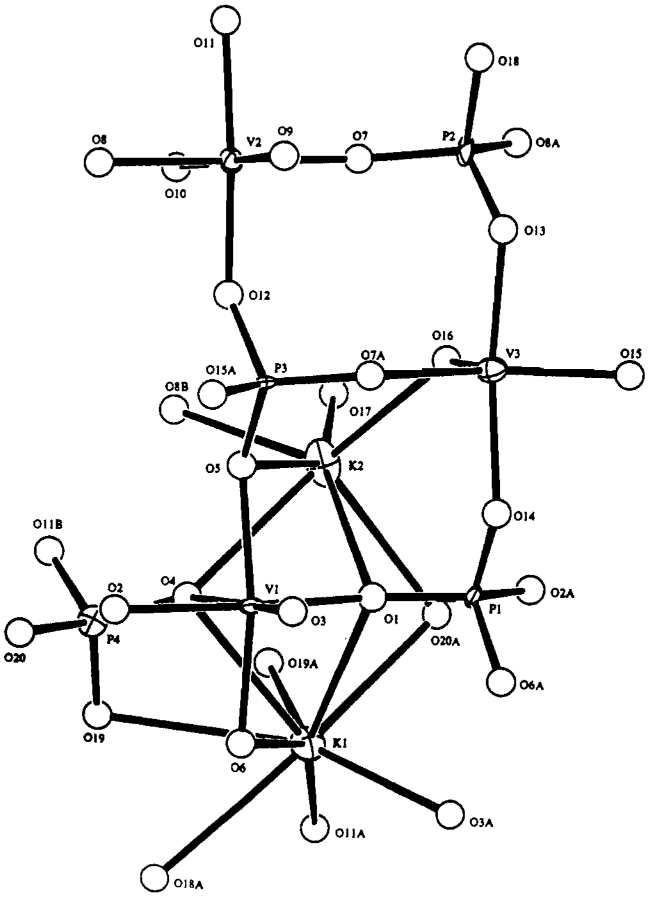

Figure 1. Numbering scheme for the atoms in 1.

Table III. Selected Intramolecular Bond Distances (Å) and Angles (deg) for 1

V1–O1	2.01(2)	P1–O1	1.50(2)
V1–O2	2.02(2)	P1–O2	1.50(2)
V1–O3	1.60(2)	P1–O6	1.54(2)
V1–O4	2.34(2)	P1–O14	1.52(2)
V1–O5	2.03(2)	P2–O7	1.56(2)
V1–O6	2.02(2)	P2–O8	1.48(2)
V2–O7	1.95(2)	P2–O13	1.53(2)
V2–O8	2.012(2)	P2–O18	1.58(2)
V2–O9	2.03(2)	P3–O5	1.55(2)
V2–O10	2.15(2)	P3–O12	1.56(2)
V2–O11	2.00(2)	P3–O15	1.51(2)
V2–O12	1.90(2)	P3–O17	1.53(2)
V3–O13	2.05(2)	P4–O4	1.50(2)
V3–O14	2.07(2)	P4–O11	1.54(2)
V3–O15	1.99(2)	P4–O19	1.60(2)
V3–O16	1.62(2)	P4–O20	1.58)2)
V3–O17	2.03(2)		
O1–V1–O2	165.1(6)	O1–P1–O14	112(1)
O1–V1–O3	100.3(8)	O2–P1–O6	111.7(9)
O1–V1–O4	81.2(6)	O2–P1–O14	109(1)
O1–V1–O5	86.2(7)	O6–P1–O14	103.4(9)
O1–V1–O6	90.8(6)	O7–P2–O8	107.7(9)
O2–V1–O3	94.5(8)	O7–P2–O13	115(1)
O2–V1–O4	83.9(6)	O7–P2–O18	107(1)
O2–V1–O5	89.7(7)	O8–P2–O13	112(1)
O2–V1–O6	87.9(6)	O8–P2–O18	110(1)
O3–V1–O4	178.3(8)	O13–P2–O18	106(1)
O3–V1–O5	100.6(8)	O5–P3–O12	103(1)
O3–V1–O6	100.4(8)	O5–P3–O15	110(1)
O4–V1–O5	78.9(6)	O5–P3–O17	112.8(9)
O4–V1–O6	80.1(6)	O12–P3–O15	111(1)
O5–V1–O6	159.0(7)	O12–P3–O17	112(1)
O7–V2–O8	179.3(7)	O15–P3–O17	107.2(9)
O7–V2–O9	91.1(8)	O4–P4–O11	115.8(9)
O7–V2–O10	88.6(7)	O4–P4–O19	111(1)
O7–V2–O11	90.2(7)	O4–P4–O20	109(1)
O7–V2–O12	91.0(7)	O11–P4–O19	103.6(9)
O8–V2–O9	88.2(7)	O11–P4–O20	108(1)
O8–V2–O10	92.1(7)	O19–P4–O20	109(1)
O8–V2–O11	89.6(6)	V1–O3–K1	142(1)
O8–V2–O12	89.2(7)	V1–O4–K1	92.2(5)
O9–V2–O10	179.4(8)	V1–O4–K2	91.4(6)
O9–V2–O11	91.9(7)	V1–O4–P4	133(1)
O9–V2–O12	94.2(8)	V1–O5–K2	95.4(7)
O10–V2–O11	88.6(7)	V1–O5–P3	132(1)
O10–V2–O12	85.2(7)	V1–O6–K1	100.3(6)
O11–V2–O12	173.7(7)	V1–O6–P1	129(1)
O13–V3–O14	159.0(7)	V2–O7–K2	114.5(7)
O13–V3–O15	90.8(7)	V2–O7–P2	145(1)
O13–V3–O16	98.8(8)	V2–O8–K2	116.6(6)
O13–V3–O17	89.5(7)	V2–O8–P2	143(1)
O14–V3–O15	87.3(7)	V2–O11–P4	135(1)
O14–V3–O16	102.1(9)	V2–O12–P3	141(1)
O14–V3–O17	85.9(6)	V3–O13–P2	124(1)
O15–V3–O16	100.4(9)	V3–O14–P1	134(1)
O15–V3–O17	161.9(6)	V3–O15–P3	132(1)
O16–V3–O17	97.4(9)	V3–O16–K2	135(1)
O1–P1–O2	107.1(9)	V3–O17–P3	136.6(9)
O1–P1–O6	113.1(9)		

Atomic coordinates are given in Table II, and selected bond distances and angles are given in Table III. The atoms in the asymmetric unit and the numbering scheme are shown in Figure 1. As shown in Figure 2a, which is an illustration of the unit cell contents viewed parallel to the layers, the structure consists of parallel ribbons in which corner-sharing vanadium octahedra and phosphorus tetrahedra alternate (Figure 2b). There are three chemically and crystallograhically unique vanadium centers in 1. The V1 site consists of a V(IV) center coordinated by corner-sharing to the oxygen donors of four adjacent phosphorus tetrahedra in the layer, to a terminal oxo group projecting out of the layer, and to oxygen of the P4 phosphate group which bridges adjacent layers. This latter bond (2.34(2) Å) is significantly lengthened as a consequence of the *trans* influence of the oxo group. In contrast, the V2 site has a less distorted octahedral environment characteristic of V(III) centers, including ligation to two aquo groups and a wide range of bond lengths from 1.90 to 2.15 Å.[16] The valence sum calculations for V1 and V2 confirm their oxidation-state assignments. The most unusual coordination

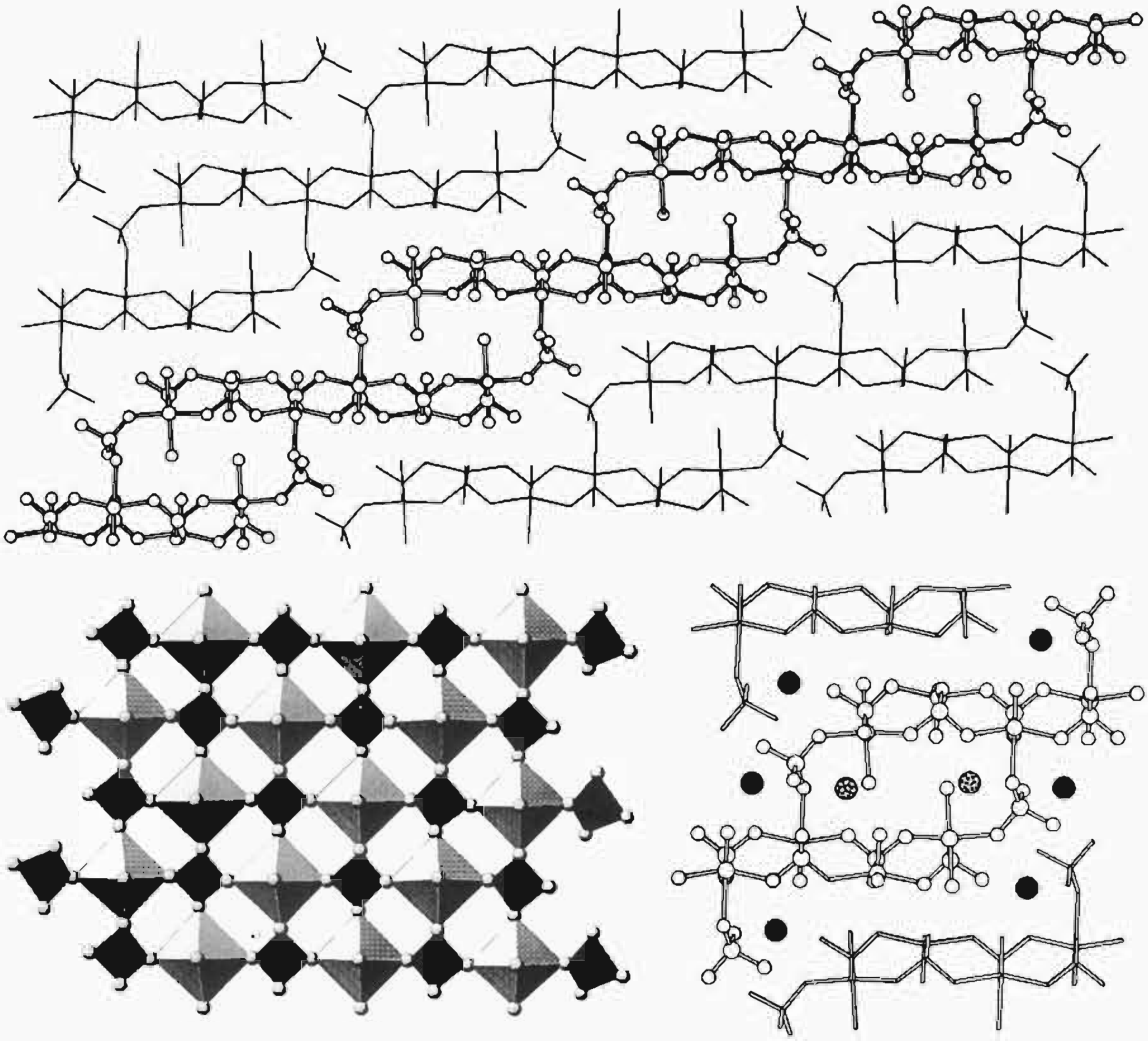

Figure 2. (a) Top: View of the structure of **1** along the *a* axis showing a "step" layer, which consists of infinite ribbons six polyhedra in width. The V2 and P2 chains define the edges of the "steps". (b) Lower left: Polyhedral representation viewed perpendicular to the plane of an individual ribbon. The ribbon is infinitely long parallel to *c* (vertical direction in figure) while the edges of the ribbon are terminated in HPO_4 and H_2PO_4 groups. The long, essentially nonbonding (2.55(2) Å) V3–O13a contact is included in the coordination sphere of V3 to contrast the structure of this ribbon to the $MOPO_4$ structure type. (c) Lower right: A section of the structure of **1** showing the location of the K2 cations (stippled) within the layers. The interlayer K1 cations are represented as gray spheres.

geometry occurs at V3, a V(IV) center bonded to a terminal oxo group and to four oxygen donors of adjacent phosphorus tetrahedra within the layer, in a fashion similar to that observed for V1. However, there is an additional very weak interaction with a phosphate oxygen of a neighboring layer. The V3–O13A bond distance of 2.55(2) Å is unusually long, even for a bond *trans* to a terminal oxo group. The valence-bond calculations[21] indicate that this interaction contributes about 4% to the total calculated valence of *ca.* 3.9 of the V center. In the figures, this interaction is therefore not represented as a drawn bond except in Figure 2b.

Another unusual feature of the structure is the presence of $(PO_4)^{3-}$, $(HPO_4)^{2-}$ and $(H_2PO_4)^-$ tetrahedra (Figure 2b), a feature previously reported for the structure of $K_2[(VO)_2(PO_4)(HPO_4)(H_2PO_4)]\cdot1.125H_2O$.[15d] The P1 phosphate tetrahedra, $(PO_4)^{3-}$, adopt tetradentate bridging modes to four adjacent vanadium polyhedra within the layer. The $(HPO_4)^{2-}$ unit of P2 bridges three vanadium centers within the layer and projects a pendant –OH group from the outer edges of the ribbon. The $(H_2PO_4)^-$ unit, containing P4, at the edges of the ribbons serves to interconnect the adjacent ribbons via strong H-bonds at 2.69(2) Å between O19 of the $\{H_2PO_4\}$ group and O18 of the $\{HPO_4\}$ group. These H-bonds connect each ribbon to its two neighbors in the "staircase" to produce the stair step layer motif shown in Figure 2a.

The stacking and interleaving of the stair step layers produce two distinct cation sites, one between and one within the layers. The K2 cations occupy the voids within the steps of a single "stair" (Figure 2c). This occupied site is defined by the channel formed by the step layers and the P4 tetrahedra which bridge adjacent steps of the same stair. In contrast, the K1 cations occupy positions between adjacent "stairs" in a region bounded by the P4 edge of one step and the weak V3–O13A interactions between steps of neighboring stairs (Figure 2a).

Comparison of the structure of **1** to that of the previously reported $K_2[(VO)_2(PO_4)_2(HPO_4)(H_2PO_4)]\cdot1.125H_2O$[16b] reveals the role of the V(III) in expansion of the step layers from the 4-connect geometry of the latter to the 6-connect motif adopted by **1**. Furthermore, the aquo ligands associated with the V(III) center project into the interlamellar region, providing strong K- - -O bonding. These structural observations suggest that introduction of reduced vanadium into the synthesis of vanadium

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phosphate materials enhances the flexibility of the connectivity patterns adopted between vanadium octahedra and phosphorus tetrahedra, thereby considerably enriching the structural chemistry which may be derived. In other words, the presence of the octahedral V(III) seems to disrupt the tendency to form the well-known planar layers, of the $MoOPO_4$ structure type, that have been found in so many vanadium phosphate materials.

The magnetic susceptibility of **1** was measured from room temperature to 4.2 K. Phosphate **1** displayed Curie–Weiss behavior at the higher temperatures measured. Curie–Weiss fitted parameters: Curie constant = 1.664 95 emu K/mol, Θ = –6.50 K, and TIP = 0.00026 emu/mol. The room-temperature effective magnetic moment of the material is 3.69 μ_B per formula unit (three V). For a system that contains one spin $S = 1$ [V(III)] and two spins $S = {}^1/_2$ [V(IV)], the expected spin-only magnetic moment is 3.74 μ_B and the expected Curie constant is 1.75, in excellent agreement with the observed parameters. From these data, we may calculate a g value that corresponds to $g = 1.951$, assuming that this is an average value for the three vanadium centers.

Conclusions

A new mixed-valence vanadium phosphate has been prepared by hydrothermal synthesis and has been characterized by single-crystal X-ray diffraction and magnetic susceptibility measurements. The structure can be thought of as a ribbon, excised from a $VOPO_4$-like layer, with the edges of the ribbons terminated in P–OH groups and V^{3+} octahedra. The stacking of the layers generates two different sites for the K^+ cations, one within and one between the layers.

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Supplementary Material Available: An additional listing of crystal data, text giving details of the structure determination, and a table of anisotropic thermal parameters (7 pages). Ordering information is given on any current masthead page.