

Hydrothermal Synthesis and Crystal Structure of the Vanadyl(IV) Hydrogen Phosphate Hydrate $K_2(VO)_2P_3O_9(OH)_3 \cdot 1.125H_2O$

Kwang-Hwa Lii* and Hung-Jen Tsai

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A new phosphate $K_2(VO)_2P_3O_9(OH)_3 \cdot 1.125H_2O$ has been synthesized hydrothermally in a sealed quartz glass tube under autogeneous pressure by slowly cooling from 450 °C a mixture of $K_4V_2O_7$, V_2O_5 , and 7.25 M H_3PO_4 and characterized by single-crystal X-ray diffraction and thermogravimetric analysis. The title compound crystallizes in the triclinic space group $P\bar{1}$ with $a = 6.404$ (2) Å, $b = 8.9512$ (9) Å, $c = 12.070$ (1) Å, $\alpha = 106.234$ (9)°, $\beta = 98.61$ (2)°, $\gamma = 103.33$ (2)°, $V = 629.2$ (2) Å³, $Z = 2$, $R = 0.025$, and $R_w = 0.028$ for 1896 unique reflections with $I > 2.5\sigma(I)$. The structure consists of slabs of corner-sharing vanadium oxide octahedra and hydrogen phosphate groups lying in the ab plane with atom K(1) between the slabs. Within a slab there are channels where atom K(2) and a water of hydration are located. Each channel results from the stacking of the edges of four octahedra and four tetrahedra.

Introduction

Until recently alkali-metal vanadium phosphates with the vanadium in the oxidation state 4+ were relatively rare. $LiVOPO_4$ ¹ and $K_2VOP_2O_7$ ² were essentially the only structurally well-characterized examples. Prompted by this state of underdevelopment and the fact that vanadyl(IV) pyrophosphate, $(VO)_2P_2O_7$, is an efficient catalyst for the oxidation of *n*-butane and *n*-butene to maleic anhydride,³ we initiated a synthetic program to explore new structures that might exist in the A-V(IV)-P-O system. Our synthetic approaches were 2-fold, namely solid-state reactions and hydrothermal methods. The products from high-temperature solid-state synthesis usually represent the thermodynamically most stable phases. The hydrothermal method, in contrast to solid-state synthesis, is particularly well suited to the synthesis of low-temperature phases and metastable compounds. Our initial survey of this system by solid-state synthesis indicates that many new compounds are present. We have prepared $A_2V_3P_4O_{17}$ ($A = Cs, Rb$),⁴ β - $K_2V_3P_4O_{17}$,⁵ $PbV_3P_4O_{17}$,⁶ and $A_2VOP_2O_7$ ($A = Cs, Rb$).⁷ In hydrothermal experiments, we have now found that crystals of vanadium phosphates can be grown in sealed quartz glass tubes. In this work, we present the hydrothermal synthesis and structural characterization of the vanadyl(IV) hydrogen phosphate hydrate $K_2(VO)_2P_3O_9(OH)_3 \cdot 1.125H_2O$.

Experimental Section

Synthesis. $K_4V_2O_7$ (99.9%) and V_2O_5 (99.9%), which were obtained from Cerac Inc., were used as received. H_3PO_4 (85%) was obtained from Merck. The i.d. of the quartz glass tube was 0.8 cm, and the o.d. was 1.0 cm. The experiment was based on the method of Rabenau for the hydrothermal synthesis of chalcogenides.⁸ Typical reactions consisted of sealing 0.494 g of $K_4V_2O_7$, 0.2 g of V_2O_5 , and 2.5 mL of 7.25 M H_3PO_4 (aq) solution in a quartz glass tube 9 cm in length. After the volume of the starting materials was subtracted from the total volume of the ampule, the degree of fill was found to be 56%. The ampule was inserted into a cold-seal pressure vessel (Tempres MRA 112R), and the free volume remaining in the bore hole was calibrated with water from a buret. The water was subsequently removed from the bore hole. To counterbalance the pressure inside the ampule, water was used. The amount of water that was added to the bore hole was 5% more than the degree of fill in the ampule in order to prevent an explosion. The closed end of the pressure vessel was inserted into a tube furnace, while the joint remained on the outside. The pressure vessel was maintained at 450 °C

and autogeneous pressure for 36 h and then slowly cooled to room temperature at 12 °C/h. The cooled glass ampule was rolled in several layers of paper and opened by tapping with a hammer. The resulting light green crystalline solid was removed, washed with water, and dried in air at ambient temperature. Visual microscopic inspection showed that the green product was contaminated with a small amount of colorless material.

Thermal Analysis. Thermogravimetric (TG) analysis was performed on a crushed sample of manually selected crystals of the title compound, using a Du Pont 951 thermogravimetric analyzer. The X-ray powder pattern of the sample agreed well with that calculated from single-crystal data. The TG experiment was performed in a N_2 atmosphere with the heating rate at 5 °C/min. In order to characterize the decomposition products, an experiment was performed in which the title compound was heated in flowing N_2 at 800 °C for 12 h. The products of this heat treatment gave an X-ray powder pattern corresponding to that of a mixture of α - $K_2V_3P_4O_{17}$ ⁹ and $K_2(VO)_2P_3O_7$.²

Single-Crystal X-ray Diffraction. A light green crystal having the dimensions 0.40 × 0.15 × 0.06 mm was selected for indexing and intensity data collection on an Enraf Nonius CAD4 diffractometer with graphite-monochromated $Mo K\alpha_1$ radiation. Of the 2441 reflections measured (max $2\theta = 50^\circ$, octants collected $\pm h, \pm k, \pm l$, scan mode $\theta/2\theta$), 2222 were unique and 1896 reflections were considered observed ($I > 2.5\sigma(I)$) after LP and empirical absorption corrections. Corrections for absorption effects were based on ψ scans of a few suitable reflections with χ values close to 90°. On the basis of statistical distribution and successful solution and refinement of the structure, the space group was determined to be $P\bar{1}$. Direct methods (NRCVAX)¹¹ were used to locate the metal atoms, with the remaining non-hydrogen atoms being found from two successive difference Fourier maps. Neutral-atom scattering factors and corrections for anomalous dispersion were taken from common sources.¹² The contents of the asymmetric unit at this stage consisted of 2 potassium, 2 vanadium, 3 phosphorus, and 15 oxygen atoms. A difference Fourier map revealed a peak (2.2 e/Å³) at the special position 1g, which was at a distance of 2.73 Å from K(2). Bond strength calculations were carried out at this stage to help locate any hydrogen atoms. Five of the oxygen atoms were found to be considerably undersaturated; valence sums of 1.66, 1.11, 1.46, 1.13, and 0.246 vu (vu = valence units) were calculated for O(3), O(8), O(9), O(12), and O(15). The value for O(15) is typically associated with the presence of two hydrogen atoms. The other values suggest that O(3) and O(9) share a common hydrogen atom, while O(8) and O(12) are each bonded to an unshared hydrogen atom. The necessary five hydrogen atoms were located by scrutiny of a difference Fourier map. If an oxidation state of 4+ is assigned to the V atoms, which is reasonable on the basis of the calculated oxygen state from bond strength-bond length equation (vide infra), then the peak mentioned previously must be assigned as the oxygen atom, O(16), of a partially occupied water molecule. Although it was not possible to crystallographically locate the hydrogen atoms bonded

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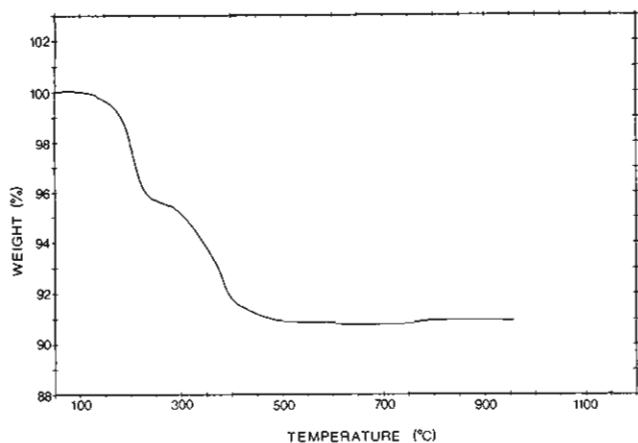


Figure 1. Thermogravimetric analysis of $K_2(VO)_2P_3O_9(OH)_3 \cdot 1.125H_2O$ in flowing N_2 at $5^\circ C/min$.

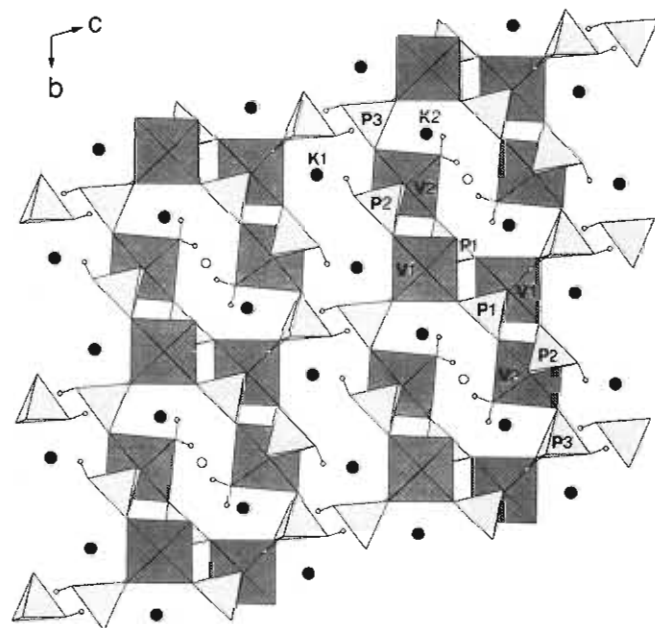


Figure 2. View of the $K_2(VO)_2P_3O_9(OH)_3 \cdot 1.125H_2O$ structure along [100]. In this representation, the corners of octahedra and tetrahedra are O^{2-} ions; the V and P ions are at the center of each octahedron and tetrahedron, respectively. Solid circles are K^+ ions; large open circles are O(16); small open circles are H atoms. The O(16) site is only one-eighth occupied on average.

to O(16), the evidence for the partially occupied O(16) site being H_2O as distinct from OH^- with compensating H reassignment was that the valence sums for all the other oxygen atoms were rather close to 2 vu. The O(16) position refined to an occupancy of 0.251 (7). Atom O(16) was regarded as disordered since the axial oscillation photographs did not reveal any superlattice reflections. The final cycles of full-matrix least-squares refinement including the secondary extinction coefficient, the occupancy factor for O(16), and anisotropic thermal parameters for all other non-hydrogen atoms converged at $R = 0.025$ and $R_w = 0.028$, giving the final stoichiometry $K_2(VO)_2P_3O_9(OH)_3 \cdot 1.125H_2O$. The final difference Fourier map was flat to less than $\pm 0.43 e/\text{\AA}^3$.

Results and Discussion

Thermal Analysis. The TG analysis (Figure 1) shows water loss in two steps near 200 and 380 °C. Since the horizontal mass plateau near 250 °C is not pronounced, the mass-loss value in each step cannot be accurately determined. The first weight loss ($\sim 4.08\%$) corresponds to the loss of water of hydration and can be compared with the calculated value of 3.895%. The second weight loss ($\sim 4.97\%$) occurs at higher temperature and is close to the 5.194% expected for the reaction $2K_2(VO)_2P_3O_9(OH)_3 \rightarrow \alpha-K_2V_3P_4O_{17} + K_2(VO)P_2O_7 + 3H_2O$. The observed total weight loss of 9.05% agrees well with that calculated from the formula (9.089%).

Table I. Crystallographic Data for $K_2(VO)_2P_3O_9(OH)_3 \cdot 1.125H_2O$

$K_2(VO)_2P_3O_9(OH)_3 \cdot 1.125H_2O$	space group = $P\bar{1}$
$a = 6.404(2) \text{ \AA}$	$fw = 520.277$
$b = 8.9512(9) \text{ \AA}$	$T = 23^\circ C$
$c = 12.070(1) \text{ \AA}$	$\lambda = 0.70930 \text{ \AA}$
$\alpha = 106.234(9)^\circ$	$\rho_{\text{calcd}} = 2.746 \text{ g/cm}^3$
$\beta = 98.61(2)^\circ$	$\mu = 25.6 \text{ cm}^{-1}$
$\gamma = 103.33(2)^\circ$	transm coeff = 0.833–1.0
$V = 629.2(2) \text{ \AA}^3$	$R(F_o) = 0.025$
$Z = 2$	$R_w(F_o) = 0.028$

Table II. Atomic Coordinates and Equivalent Isotropic Thermal Parameters for $K_2(VO)_2P_3O_9(OH)_3 \cdot 1.125H_2O$

atom	x	y	z	$B_{\text{iso}}, \text{\AA}^2$ ^a
K(1)	0.75406 (14)	0.76339 (11)	0.08056 (8)	1.85 (4)
K(2)	0.95859 (16)	0.20571 (11)	0.33792 (9)	2.11 (4)
V(1)	0.16793 (9)	0.86377 (7)	0.36035 (5)	0.75 (2)
V(2)	0.50384 (9)	0.55641 (7)	-0.23660 (5)	0.69 (3)
P(1)	0.67410 (14)	0.82473 (11)	0.39833 (8)	0.71 (3)
P(2)	0.00282 (14)	0.48636 (11)	0.20390 (8)	0.75 (4)
P(3)	0.32367 (16)	0.03549 (11)	0.14307 (8)	1.02 (4)
O(1)	0.2763 (4)	0.0968 (3)	0.46713 (21)	1.05 (10)
O(2)	0.8628 (4)	0.8861 (3)	0.34355 (22)	1.03 (11)
O(3)	0.4798 (4)	0.8749 (3)	0.33849 (3)	1.13 (11)
O(4)	0.3856 (4)	0.3569 (3)	-0.37449 (22)	1.21 (10)
O(5)	0.1915 (4)	0.4380 (3)	0.26193 (23)	1.15 (11)
O(6)	0.0524 (4)	0.6647 (3)	0.21588 (22)	1.13 (10)
O(7)	0.8013 (4)	0.4179 (3)	0.24532 (23)	1.16 (12)
O(8)	0.0476 (5)	0.6002 (3)	-0.06340 (22)	1.61 (12)
O(9)	0.5418 (5)	0.9945 (4)	0.1793 (3)	2.57 (16)
O(10)	0.6290 (4)	0.7944 (3)	-0.13861 (22)	1.27 (11)
O(11)	0.1706 (4)	0.9911 (3)	0.21806 (23)	1.41 (12)
O(12)	0.7815 (6)	0.0742 (4)	-0.0092 (3)	2.96 (16)
O(13)	0.8267 (4)	0.2230 (3)	0.54104 (23)	1.56 (12)
O(14)	0.4841 (4)	0.5140 (3)	0.12858 (23)	1.43 (11)
O(15)	0.5190 (5)	0.3401 (3)	0.39107 (24)	1.91 (12)
O(16) ^b	0	1/2	1/2	4.1 (4)
H(1) ^c	0.453	0.247	0.401	4.2
H(2)	0.600	0.398	0.457	4.2
H(3)	0.531	0.952	0.257	5.1
H(4)	0.113	0.698	-0.034	3.9
H(5)	0.705	0.071	0.049	3.9

^a B_{iso} is the mean of the principal axes of the thermal ellipsoid. ^b The occupancy factor for O(16) is 0.251 (7). ^c The atomic coordinates and thermal parameters for all the H atoms are fixed.

Table III. Bond Distances (\AA) for $K_2(VO)_2P_3O_9(OH)_3 \cdot 1.125H_2O$ ^a

K(1)–O(2)	2.967 (3)	K(1)–O(6)	2.784 (3)
K(1)–O(8)	3.084 (3)	K(1)–O(9)	2.820 (3)
K(1)–O(10)	2.756 (3)	K(1)–O(11)	2.881 (3)
K(1)–O(12)	3.234 (3)	K(1)–O(14)	2.748 (3)
K(1)–O(14)a	2.909 (3)	K(2)–O(1)	2.887 (3)
K(2)–O(2)	2.807 (3)	K(2)–O(5)	2.727 (3)
K(2)–O(7)	2.758 (3)	K(2)–O(9)	2.913 (4)
K(2)–O(11)	2.804 (3)	K(2)–O(13)	2.686 (3)
K(2)–O(16)	2.735 (1)	V(1)–O(1)	2.014 (2)
V(1)–O(2)	1.996 (2)	V(1)–O(3)	2.037 (2)
V(1)–O(6)	2.008 (2)	V(1)–O(11)	2.312 (3)
V(1)–O(13)	1.593 (3)	V(2)–O(4)	1.967 (2)
V(2)–O(5)b	2.011 (2)	V(2)–O(7)b	2.010 (2)
V(2)–O(10)	2.025 (3)	V(2)–O(14)a	1.597 (3)
V(2)–O(15)b	2.302 (3)	P(1)–O(1)f	1.528 (3)
P(1)–O(2)	1.528 (3)	P(1)–O(3)d	1.563 (3)
P(1)–O(4)a	1.513 (3)	P(2)–O(5)	1.515 (3)
P(2)–O(6)c	1.514 (3)	P(2)–O(7)	1.514 (3)
P(2)–O(8)g	1.602 (3)	P(3)–O(9)	1.556 (3)
P(3)–O(10)h	1.500 (3)	P(3)–O(11)d	1.492 (3)
P(3)–O(12)h	1.585 (3)	O(15)–H(1)e	0.89
O(15)–H(2)e	0.83	O(3)–H(3)b	1.38
O(8)–H(4)b	0.82	O(9)–H(3)	1.12
O(12)–H(5)c	0.92		

^a Symmetry codes: (a) $1 - x, 1 - y, -z$; (b) $1 + x, y, z$; (c) $x, 1 + y, z$; (d) $1 + x, 1 + y, z$; (e) $2 - x, 2 - y, 1 - z$; (f) $2 - x, 2 - y, -z$; (g) $1 - x, 2 - y, -z$; (h) $-1 + x, y, z$.

Structural Description. Table I lists the crystallographic data. Final atomic coordinates and B_{iso} values are listed in Table II.

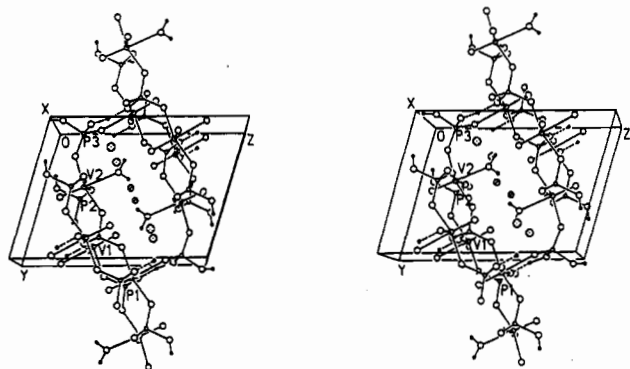


Figure 3. Stereoscopic view of a channel in the $K_2(VO)_2P_3O_9(OH)_3 \cdot 1.125H_2O$ structure: dotted circles, K^+ ions; shaded circles, O(16); large open circles, O atoms; medium open circles, P atoms; small open circles, H atoms. The O(3)–H(3)–O(9) hydrogen bonds are shown as dashed lines. The O(16) site is only one-eighth occupied on average.

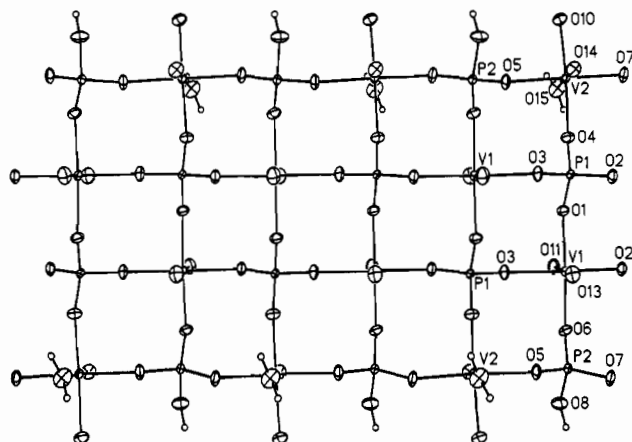


Figure 4. Section of a 4-connected net in the $K_2(VO)_2P_3O_9(OH)_3 \cdot 1.125H_2O$ structure. Thermal ellipsoids are shown at the 60% probability level.

Selected interatomic distances are given in Table III. A polyhedral representation of the structure along [100] is presented in Figure 2. The structure consists of slabs of corner-sharing vanadium oxide octahedra and hydrogen phosphate groups lying in the ab plane with atom K(1) between the slabs. Within a slab there are channels where atom K(2) and a water of hydration are located. Each channel results from the stacking of the edges of four octahedra and four tetrahedra. Figure 3, a stereoscopic view of a channel, shows clearly how the polyhedra are connected. The structure is alternately described as consisting of 4-connected plane nets in which vanadium octahedra and phosphate tetrahedra alternate (Figure 4). Adjacent nets are held together by bridging $H_2P(3)O_4$ groups and O(3)–H(3)–O(9) hydrogen bonding to form infinite slabs within the ab plane. Since atom H(3) shows a slight preference for protonation at the O(9) site than at the O(3) site (1.12 vs 1.38 Å), the structural formula may be written as $K_2(VO)_2(PO_4)(HPO_4)(H_2PO_4) \cdot 1.125H_2O$. It is noted that the $H_2P(3)O_4$ group of a net is weakly coordinated trans to the vanadyl

group V(1)=O of an adjacent net. Linkages between adjacent slabs are made merely by O–K–O bonding.

Vanadium ions at V(1) and V(2) sites have a common environment, which is a gross distortion of a regular octahedron; one short V=O bond length is 1.59 Å, which is about 0.4 Å shorter than the four equatorial V–O bonds, but the sixth bond is much longer, ~2.3 Å. This geometry often occurs with compounds containing the oxovanadium(IV) ion. The valence of V can be assessed by summing the bond valences of V–O bonds. Using the Brown–Altermatt form for the bond length–bond valence relation for V(IV)–O,¹³ we obtain 4.07 and 4.11 for V(1) and V(2), respectively. Each V(1)O₆ octahedron shares its five corners with five different phosphate groups with the sixth vertex, O(13), pointing into the channel within a slab. The V(2) coordination sphere consists of a vanadyl group directed toward the interlayer space, four oxygens in the equatorial positions belonging to four phosphate groups, and a water molecule weakly bonded trans to V(2)=O(14). Each P(1)O₄ group is coordinated to three V(1) atoms and one V(2) atom and contains O(3), which shares H(3) with the O(9) atom belonging to an adjacent $H_2P(3)O_4$. The O(3)–O(9) distance of 2.485 Å represents a strong hydrogen bond. The coordination geometry of P(2) contains an unshared OH group directed toward the interlayer space and three oxygens coordinated to one V(1) and two V(2) atoms. The P(3) coordination sphere consists of O(9) hydrogen-bonded to H(3), two oxygens coordinated to one V(1) atom and one V(2) atom, and an unshared OH group. The shortest P(3)–O bond (1.492 Å) involves the oxygen atom, O(11), which is weakly bonded to V(1) in a direction trans to the multiply bound terminal oxygen. The coordination number of K^+ can be determined by the maximum bond distance for K–O by using the procedure of Donnay and Allmann.¹⁴ Accordingly, K(1) and K(2) are bound to eight oxygen atoms (distance 2.748–3.234 Å) and nine oxygen atoms (distance 2.686–2.913 Å), respectively.

In conclusion, a new phosphate $K_2(VO)_2P_3O_9(OH)_3 \cdot 1.125H_2O$ has been synthesized hydrothermally by using a quartz glass ampule as a reaction container and characterized by single-crystal X-ray diffraction and TG analysis. In the experiment the quartz glass ampule must be placed in an autoclave along with pressure compensation. However, it is usable up to about 500 °C, since at higher temperatures the glass tubes always explode. Ductile metal tubings made of gold or platinum are suitable for reactions under more severe conditions. This research shows that inexpensive quartz glass tubes are useful as reaction containers in relatively low PT hydrothermal experiments in the synthesis of vanadium phosphates.

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Supplementary Material Available: Tables of anisotropic thermal parameters and bond angles (4 pages); a listing of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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