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Hydrothermal Synthesis and Characterization of Vanadyl(IV) Hydrogenphosphate, $K_2(VO)_3(HPO_4)_4$

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A new phosphate, $K_2(VO)_3(HPO_4)_4$, has been synthesized hydrothermally and characterized by single-crystal X-ray diffraction, thermogravimetric analysis, and magnetic susceptibility. The title compound crystallizes in the monoclinic space group $P2/c$ with $a = 10.756(1)$, $b = 9.147(3)$, $c = 8.662(1)$ Å, $\beta = 112.842(9)°$, $Z = 2$, and $R = 0.034$. The structure is built from infinite chains of vertex-sharing vanadium oxide octahedra and HPO_4 groups with the potassium cations located in sites within tunnels and cages in the structure. These infinite chains have alternating short and long V–O bonds. Each phosphate tetrahedron shares vertices with three octahedra, but two of these belong to the same infinite chain.

Introduction

We are currently undertaking a synthesis and structural study on the alkali metal vanadyl phosphates. These phosphates are of interest for their complex tetrahedral–octahedral network structures. Potentially the study of these compounds allows for the better understanding of the factors affecting their crystal structures. Our synthetic approach was solely a high-temperature solid state reaction. Another approach, which we have recently studied, is the hydrothermal method. In contrast to the solid state synthesis, the hydrothermal method is particularly suited for the synthesis of low-temperature phases and metastable compounds. We recently characterized the layer-like hydrate $K_2(VO)_2P_3O_9(OH)_3 \cdot 1.125H_2O$ by single crystal X-ray diffraction and thermogravimetric analysis (*1*). To our knowledge, no alkali metal vanadyl(IV) hydrogenphosphate hydrate had been reported. This paper expands on our earlier work and describes the synthesis and structural characterization of $K_2(VO)_3(HPO_4)_4$.

Experimental

Synthesis

$K_4V_2O_7$ (99.9%), VO_2 (99.5%), and V_2O_3 (99.9%), which were obtained from Cerac Inc., were used as received. H_3PO_4 (85%) was obtained from Merck. A mixture of 2.5 g $K_4V_2O_7$, 1.12 g VO_2, and 1.01 g V_2O_3 (molar ratio K : V = 2 : 3) was added to 13 ml of 7.25 *M* H_3PO_4 and sealed in a 23-ml Teflon-lined autoclave (Parr Instruments). The reaction vessel was maintained at 240°C and autogenous pressure for 4 days before slow cooling to room temperature. The product was filtered, washed several times with water, rinsed with acetone, and dried in air at ambient temperature. It was found that in

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addition to the well-formed blue-green crystals of the title compound, with dimensions up to 2.5 mm, a small amount of light green needle crystals of $K_2(VO)_2P_3O_9(OH)_3 \cdot 1.125H_2O$ also crystallized from the reaction. Separation from the title compound was performed easily because of the differences in color, crystal habit, and size. Previous preparation of $K_2(VO)_2P_3O_9(OH)_3 \cdot 1.125H_2O$ was under relatively severe conditions (450°C, ~1 kbar). The contents of K, V, and P of a single-phase product of the title compound were analyzed by using an ICP-AE spectrometer after dissolving the sample in 8 *N* HNO_3. Anal. Calcd for $K_2(VO)_3(HPO_4)_4$: K, 11.80%; V, 23.05%; P, 18.69%. Found: K, 11.1; V, 21.9%; P, 19.0%. The experimental results for K and V were about 5% lower than the theoretical values.

Single-Crystal X-Ray Diffraction

A blue-green crystal, having the dimensions 0.45 × 0.20 × 0.15 mm, was selected for indexing and intensity data collection on an Enraf Nonius CAD4 diffractometer with graphite-monchromated Mo$K\alpha$ radiation. Axial oscillation photographs along the three axes were taken to check the symmetry properties and unit cell parameters. Of the 1927 reflections measured (octants collected $h, k, +l$), 1808 were unique and 1691 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° ($T_{\max}, T_{\min} = 1.0, 0.903$). An examination of the intensity data showed the systematic absences $l = 2n + 1$ for $h0l$ reflections. Based on statistical distribution and successful solution and refinement of the structure, the space group was determined to be $P2/c$ (No. 13). Direct methods (NRCVAX) (*2*) were used to locate the metal atoms, with the remaining nonhydrogen atoms being found from successive difference Fourier maps. Neutral-atom scattering factors and corrections for anomalous dispersion were taken from common sources (*3*).

It was found that atom V(1) was disordered over the two sites. When the structure was refined with a single-site V(1) atomic position, the agreement factor $R = 0.073$ and atom V(1) showed very large U_{11} value (0.164 Å^2). A model of two disordered sites was used with their occupancy factors fixed at 0.5. Atom V(2), which was initially located at $2f$ special positions, exhibited a very large U_{33} value (0.125 Å^2), suggesting a positional disorder. A model of two disordered sites, which were related by twofold symmetry, was then used for atom V(2). The multiplicity for each metal atom was allowed to refine using the high-angle data ($2\theta > 20°$), and the multipliers were: K(1) 0.983(9); K(2) 0.99(1); V(1) 0.49(1); V(1)′ 0.50(1); V(2) 0.492(4). Therefore, the K sites were considered fully occupied, and the occupancy factors for the disordered V sites were 50% in subsequent refinement. A few cycles of refinement using the total data resulted in reasonable thermal parameters and a much lower *R* factor (0.036). Bond-strength calculations were carried out at this stage to help locate any hydrogen atoms. Two of the oxygen atoms were found to be considerably undersaturated; valence sums of 1.31 and 1.11 v.u. being calculated for O(1) and O(9), respectively. The necessary two hydrogen atoms were located by careful scrutiny of a difference Fourier map. Subsequent refinement including the atomic coordinates and anisotropic thermal parameters for all nonhydrogen atoms, and isotropic thermal parameters for hydrogen atoms converged at $R = 0.034$ and $R_w = 0.039$. In the final difference Fourier map the deepest hole was -0.63 e/Å^3, and the highest peak 0.72 e/Å^3. Table I lists the crystallographic data. Final atomic coordinates and thermal parameters are reported in Table II.

The data crystal was checked for super

TABLE I

SUMMARY OF CRYSTAL DATA, INTENSITY MEASUREMENTS, AND REFINEMENT PARAMETERS FOR $K_2(VO)_3(HPO_4)_4$

Crystal data	
Crystal system	Monoclinic
Space group	$P2/c$
Cell constants	$a = 10.756(1)$, $b = 9.147(3)$, $c = 8.662(1)$ Å, $\beta = 112.842(9)°$
Z	2
Density (calcd)	2.803 g/cm^3
Abs. coeff. (Mo$K\alpha$)	27.3 cm^{-1}
Intensity measurements	
λ (Mo$K\alpha$)	0.70930 Å
Scan mode	$\theta/2\theta$
Scan rate	5.5°/min
Scan width	$0.6° + 0.35° \tan \theta$
Maximum 2θ	55°
Standard reflections	$(1\bar{1}4)$, (423), $(\bar{3}37)$ (measured every 1 hr, no decay)
Unique reflections measured	1927
Structure solution and refinement	
Reflections included	1691 ($I > 2.5\ \sigma(I)$)
Parameters refined	144
Agreement factors^a	$R = 0.034$, $R_w = 0.039$
GOF	1.20
$(\Delta\rho)_{max}$; $(\Delta\rho)_{min}$	0.72 e/Å^3; -0.63 e/Å^3

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, where $w = 1.0/\sigma^2(F_o)$.

lattice by Weissenberg photographs. Neither the axial oscillation photograph along the b-axis nor the zero-layer Weissenberg ($h0l$) photograph with long exposure time revealed any superstructure spots.

Thermal Analysis

Thermogravimetric analysis (TG), using a Du Pont 951 thermogravimetric analyzer, was performed on a crushed sample of manually selected crystals of the title compound. The X-ray powder pattern of the sample agreed well with that calculated from single-crystal data. The TG experiment was performed in flowing N_2 with a heating rate of 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 700°C for 12 h. The product of this heat treatment gave an X-ray powder pattern corresponding to that of α-$K_2V_3P_4O_{17}$ (*4*).

Magnetic Measurements

A 155.41-mg polycrystalline sample was used to collect variable-temperature magnetic susceptibility $\chi(T)$ data from 4 to 300 K in a magnetic field of 3 kG using a Quantum Design SQUID magnetometer. As suggested by Selwood (*5*), diamagnetic contributions for K^+, V^{4+}, P^{5+}, and O^{2-} were estimated and were subtracted from the experimental susceptibility data to obtain the molar paramagnetic susceptibilities of the compound. The data was least-squares fitted from 20 to 300 K to the relation $\chi_M = C/(T - \theta)$, where C is the molar Curie constant and θ is the Weiss constant.

Results and Discussion

Structural Description

Selected bond distances are given in Table III. As shown in Fig. 1, the structure is built from vertex-sharing vanadium oxide octahedra and phosphate tetrahedra with potassium cations located in sites within tunnels and cages in the structure. Vanadium octahedra share *trans* vertices to form infinite chains running along the [101] direction, and are linked together in three dimensions by phosphate tetrahedra (see Fig. 2). These infinite chains have alternating short and long V–O bonds. Each phosphate tetrahedron bonds to two adjacent octahedra ($V(1)O_6$ and $V(2)O_6$) in one chain and a single octahedron ($V(1)O_6$) in a neighboring chain, introducing "kinks" into the · · · V=O · · · V=O · · · chains (see Fig. 3). The bond angle at the shared O atom, O(10), between V(1) and V(2) is 134.1°, whereas the V(1)–O(3)–V(1) bond angle is

TABLE II

ATOMIC COORDINATES AND THERMAL PARAMETERS FOR $K_2(VO)_3(HPO_4)_4$

Atom	x	y	z	B_{iso}(Å^2)[a]
K(1)	$\frac{1}{2}$	−0.82719(14)	$\frac{1}{4}$	2.64(7)
K(2)	0	−0.38976(15)	$\frac{1}{4}$	2.62(7)
V(1)	0.83952(16)	−0.75459(14)	0.14825(16)	0.43(5)[b]
V(1)′	0.77584(16)	−0.74853(14)	0.11101(16)	0.46(5)[b]
V(2)	−0.51305(18)	−0.25662(12)	0.21487(11)	0.56(7)[b]
P(1)	−0.26901(8)	−0.50223(9)	−0.14715(10)	0.61(3)
P(2)	0.23805(8)	−0.05136(9)	0.19832(10)	0.57(3)
O(1)	−0.3324(3)	−0.3914(3)	−0.0596(3)	1.50(11)
O(2)	−0.61623(24)	0.1031(3)	−0.2187(3)	1.14(9)
O(3)	0	−0.7643(4)	$\frac{1}{4}$	0.92(13)
O(4)	0.16739(23)	−0.3974(3)	0.0213(3)	0.93(19)
O(5)	−0.23062(24)	−0.1125(3)	−0.2221(3)	0.84(9)
O(6)	−0.61782(24)	0.4116(3)	−0.2187(3)	1.04(9)
O(7)	−0.17840(24)	−0.9139(3)	−0.0122(3)	0.90(9)
O(8)	−0.19621(24)	−0.4109(3)	−0.2301(3)	0.87(9)
O(9)	−0.1492(3)	−0.1313(3)	0.2194(3)	1.34(10)
O(10)	−0.39109(25)	0.2618(3)	−0.0088(3)	1.05(10)
H(1)	0.657	0.571	0.032	3.9(14)[c]
H(2)	0.842	0.913	0.128	3.6(23)[c]

Anisotropic thermal parameters (Å^2 × 100)[d]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
K(1)	1.91(6)	1.47(6)	7.09(11)	0	2.23(7)	0
K(2)	2.13(6)	1.82(6)	6.31(10)	0	1.97(6)	0
V(1)	0.60(7)	0.44(6)	0.63(6)	0.00(6)	0.28(5)	−0.01(4)
V(1)′	0.67(7)	0.53(6)	0.54(6)	0.03(6)	0.24(5)	0.05(4)
V(2)	0.51(8)	0.62(4)	0.77(9)	0.05(4)	0.02(8)	−0.01(3)
P(1)	0.97(4)	0.65(4)	0.78(4)	−0.09(3)	0.43(3)	0.08(3)
P(2)	0.86(4)	0.56(4)	0.77(4)	−0.02(3)	0.33(3)	−0.16(3)
O(1)	3.00(15)	1.60(13)	1.65(12)	0.57(11)	1.53(11)	0.12(11)
O(2)	0.99(11)	1.34(12)	1.56(12)	−0.34(9)	0.03(9)	0.35(10)
O(3)	0.88(16)	1.46(17)	0.90(15)	0	0.08(12)	0
O(4)	1.09(11)	1.32(12)	1.08(11)	−0.04(9)	0.40(9)	0.56(9)
O(5)	1.40(12)	0.60(11)	1.41(11)	0.11(9)	0.78(9)	−0.23(9)
O(6)	1.08(11)	1.66(12)	0.97(11)	0.44(10)	0.13(9)	0.00(9)
O(7)	1.40(11)	1.12(12)	0.71(11)	0.11(9)	0.21(9)	−0.20(9)
O(8)	1.21(11)	0.97(12)	1.04(11)	−0.16(9)	0.34(9)	0.36(9)
O(9)	2.57(14)	1.27(12)	1.96(13)	0.74(10)	1.66(11)	0.36(10)
O(10)	1.64(12)	1.30(12)	1.17(11)	−0.04(10)	0.66(10)	0.11(9)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

[b] The occupancy factor is 0.5.

[c] The atomic coordinates for the H atoms are fixed.

[d] Anisotropic temperature factors are of the form Temp = $\exp[-2\pi^2(h^2U_{11}a^{*2} + \ldots + 2hkU_{12}a^*b^* + \ldots)]$.

173.1°. Within an infinite chain the topological repeating unit consists of 1 $V(2)O_6$, 2 $V(1)O_6$ octahedra, and four HPO_4 groups. Each octahedron shares its vertices with two octahedra and four tetrahedra. The number of octahedra with which each tetra-

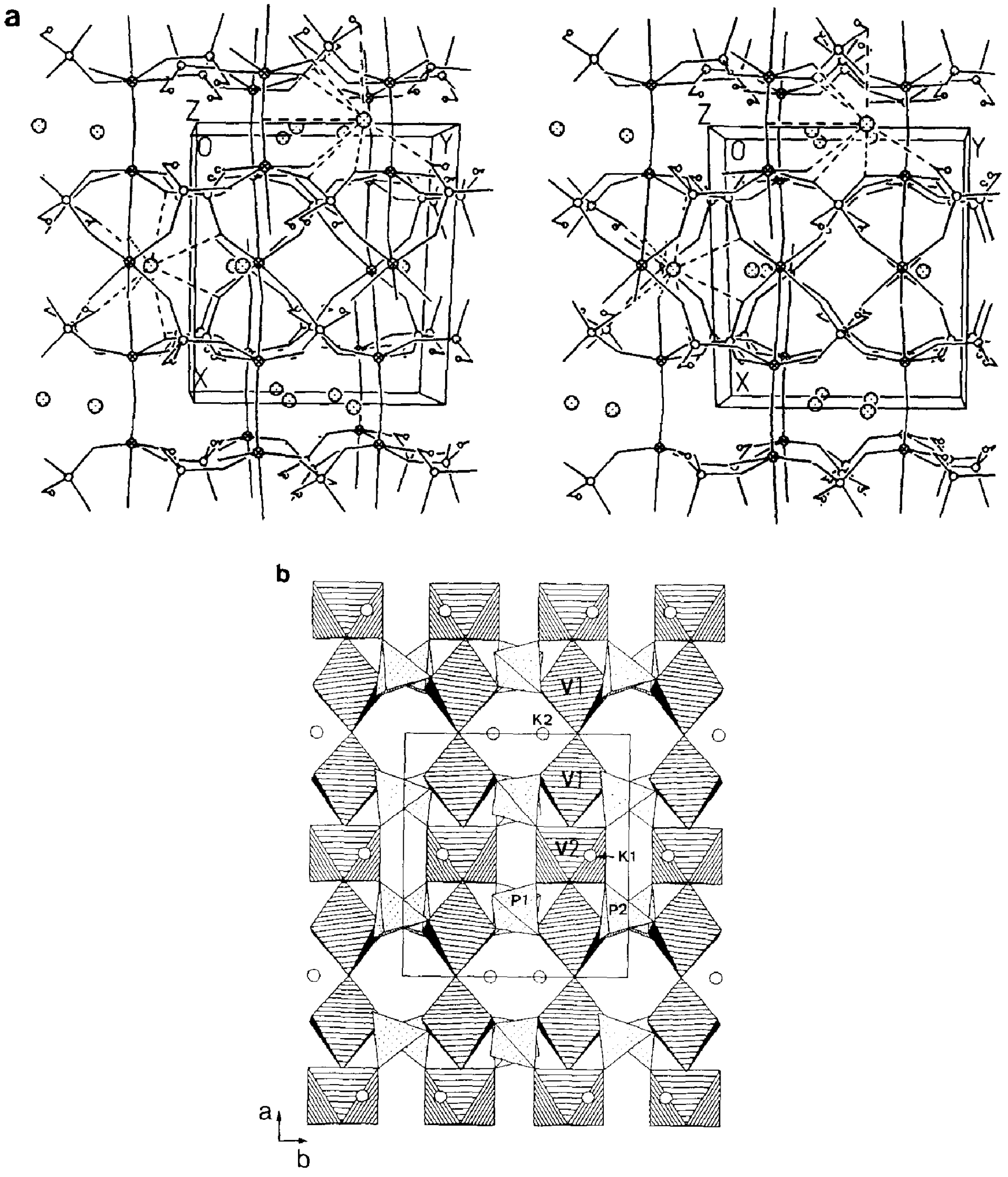

FIG. 1. (a) Stereoscopic view of the $K_2(VO)_3(HPO_4)_4$ structure along the *c*-axis. Dotted circles, K atoms; cross-hatched circles, V atoms; medium open circles, P atoms; small open circles, H atoms. For clarity, the radii for O atoms are set equal to zero, and only one site for both V atoms is shown in this plot. The K–O bonds are shown as dashed lines. (b) A polyhedral representation of the structure along the *c*-axis. For clarity, the H atoms are not shown.

hedron shares vertices is three. Therefore, the contribution to the chemical formula made by each unit is $(VO_3)_3(HOPO_{3/2})_4$ (a shared vertex counting as 1/2 O and unshared vertex as O).

It is interesting to compare the way in

TABLE III

BOND DISTANCES (Å) FOR $K_2(VO)_3(HPO_4)_4$

K(1)–O(1)d	2.767(3)	K(1)–O(1)e	2.767(3)
K(1)–O(2)d	2.876(3)	K(1)–O(2)e	2.876(3)
K(1)–O(5)d	2.866(2)	K(1)–O(5)e	2.866(2)
K(1)–O(10)f	3.017(2)	K(1)–O(10)g	3.017(2)
K(2)–O(4)	3.153(2)	K(2)–O(4)d	3.044(3)
K(2)–O(4)1	3.153(2)	K(2)–O(4)k	3.044(3)
K(2)–O(8)d	2.844(3)	K(2)–O(8)k	2.844(3)
K(2)–O(9)	2.811(3)	K(2)–O(9)l	2.811(3)
V(1)–O(3)n	1.607(2)	V(1)–O(4)o	2.003(3)
V(1)–O(5)e	1.991(3)	V(1)–O(7)n	1.971(3)
V(1)–O(8)e	1.966(3)	V(1)–O(10)f	2.325(3)
V(1)′–O(3)n	2.243(2)	V(1)′–O(4)o	2.003(3)
V(1)′–O(5)e	1.946(3)	V(1)′–O(7)n	2.019(3)
V(1)′–O(8)e	1.947(3)	V(1)′–O(10)f	1.692(3)
V(2)–O(2)q	1.967(3)	V(2)–O(2)i	2.007(3)
V(2)–O(6)q	1.989(3)	V(2)–O(6)i	2.028(3)
V(2)–O(10)q	1.680(3)	V(2)–O(10)i	2.239(3)
P(1)–O(1)	1.571(3)	P(1)–O(4)d	1.517(2)
P(1)–O(6)r	1.534(2)	P(1)–O(8)	1.505(2)
P(2)–O(2)t	1.524(2)	P(2)–O(5)u	1.519(3)
P(2)–O(7)d	1.520(2)	P(2)–O(9)l	1.577(3)
O(1)–H(1)m	0.914	O(9)–H(2)m	0.861
V(1)–V(1)′	0.636(2)	V(2)–V(2)p	0.563(2)

Note. Symmetry codes (d) $-x, -1-y, -z$; (e) $1+x, -1-y, 0.5+z$; (f) $1+x, -1+y, z$; (g) $-x, -1+y, 0.5-z$; (i) $x, -y, 0.5+z$; (k) $x, -1-y, 0.5+z$; (l) $-x, y, 0.5-z$; (m) $-1+x, -1+y, z$; (n) $1+x, y, z$; (o) $1-x, -1-y, -z$; (p) $-1-x, y, 0.5-z$; (q) $-1-x, -y, -z$; (r) $-1-x, -1+y, -0.5-z$; (s) $x, 1+y, z$; (t) $1+x, -y, 0.5+z$; (u) $-x, -y, -z$.

which the vertices are shared in the title compound with those in α-$VOPO_4$ (*6*) and β-$VOPO_4$ (*7*). In both polymorphs of $VOPO_4$, each tetrahedron shares all its vertices with octahedra. Each octahedron shares four vertices with tetrahedra and two with other octahedra. In α-$VOPO_4$, each PO_4 tetrahedron links four ReO_3-type chains forming a 3D structure. In β-$VOPO_4$, each PO_4 tetrahedron shares its vertices with four VO_6 octahedra but two of these belong to the same chain, so that kinks are introduced into the · · · V═O · · · V═O · · · chains. In $K_2(VO)_3(HPO_4)_4$, each HPO_4 group links two chains as compared to four in α-$VOPO_4$ and three in β-$VOPO_4$.

The VO_6 groups in the title compound are far from regular. Vanadium ions, at both the V(1) and the V(2) sites, have a common environment which is a gross distortion of an octahedron; one short V═O bond length is ~1.60–1.69 Å, which is ~0.3–0.4 Å shorter than the four equatorial V–O bonds, but the sixth bond is much longer, ~2.2–2.3 Å. This geometry often occurs with compounds containing vanadyl ion VO^{2+}, that has a strong bond with σ and π character. 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 relationship for V^{4+}–O (*8*), we obtain 4.18, 3.94,

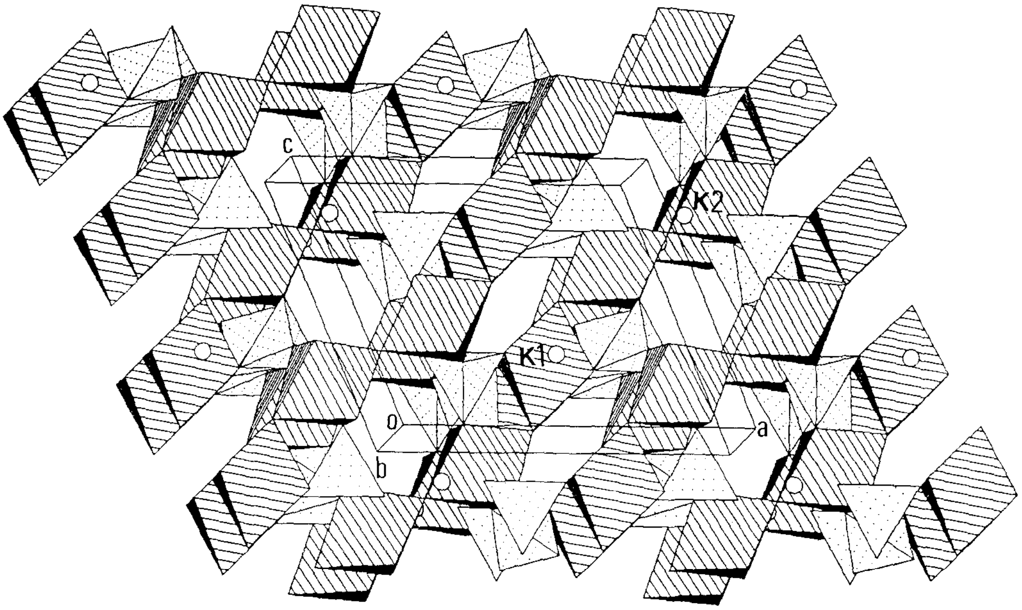

FIG. 2. A polyhedral representation of the $K_2(VO)_3(HPO_4)_4$ structure along the *b*-axis. For clarity, the H atoms are not shown.

and 3.87 for V(1), V(1)′, and V(2), respectively. These are in agreement with the formal oxidation state +4 based on the stoichiometry. Each HPO_4 group contains three oxygens shared with 2 V(1) and 1 V(2), and an OH group coordinated only to the K^+ cation. Bond-valence sums of the P–O bonds are 5.05 and 5.00 for P(1) and P(2), respectively.

Whereas atom K(1) is located in a cage surrounded by four chains, atom K(2) resides in a tunnel running along the *c*-axis. The window of the tunnel is formed by the edges of four $V(1)O_6$ octahedra and two $P(1)O_4$ tetrahedra. The coordination number of K^+ can be determined by the maximum bond distance for K–O using the procedure by Donnay and Allmann (*9*). Accordingly, both K(1) and K(2) are eight coordinate, with K–O distances in the range 2.77–3.15 Å. Bond valence sums of the K–O bonds are 1.09 and 0.91 for K(1) and K(2), respectively. It is noted that there are empty tunnels in the structure, suggesting the possibility of inserting extra ions into the structure.

Thermal Analysis

The TG analysis shows a one-step weight loss beginning approximately at 400°C and with a maximum slope at 418°C. The weight loss (5.48%) compared well with the 5.435% expected for the reaction $K_2(VO)_3(HPO_4)_4 \rightarrow \alpha\text{-}K_2V_3P_4O_{17} + 2H_2O$.

Magnetic Susceptibility

A plot of the reciprocal molar susceptibility for polycrystalline $K_2(VO)_3(HPO_4)_4$ vs temperature (Fig. 4) is linear above ~10 K. The solid line in the figure is the fit of the data from 20 to 300 K according to $\chi = C/(T - \theta)$ with the Curie constant $C = 1.027$ cm^3 · K/mol and the Weiss constant $\theta = -10.7$ K. From the relation $C/3 = N\mu_{\text{eff}}^2/3k_B$, one obtains the effective magnetic moment $\mu_{\text{eff}} = 1.66\ \mu_B$ per vanadium, which is close to

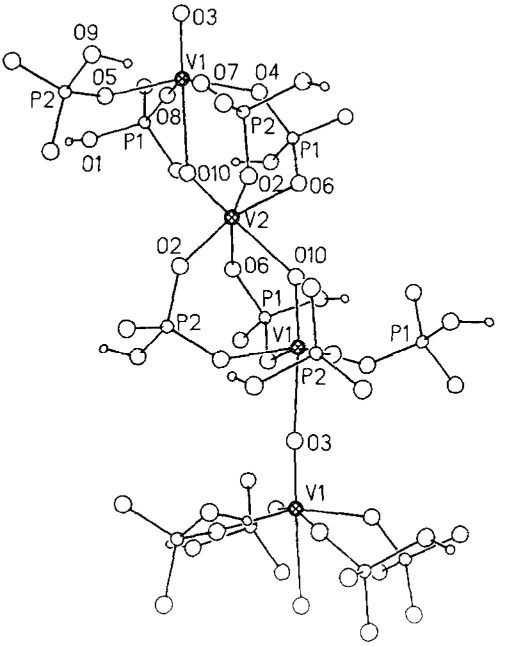

FIG. 3. A section of a chain of VO_6 octahedra in $K_2(VO)_3(HPO_4)_4$. Cross-hatched circles, V atoms; large open circles, O atoms; medium open circles, P atoms; small open circles, H atoms. For clarity, only one site for both V atoms is shown in this plot.

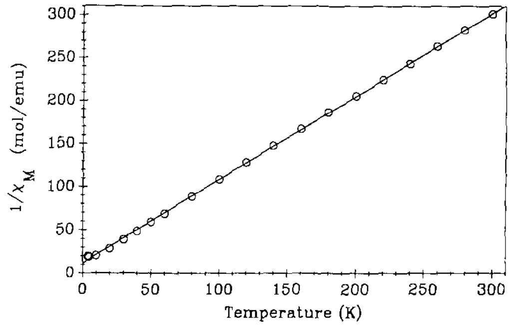

FIG. 4. Inverse molar magnetic susceptibility of $K_2(VO)_3(HPO_4)_4$ vs temperature.

the spin-only value for a d_1 ion of 1.73 μ_B and within the range observed for several vanadyl(IV) compounds (*10*). The magnetic interactions responsible for the deviation of the data below ~10 K from the Curie–Weiss fit are antiferromagnetic.

In conclusion, a new vanadyl(IV) hydrogenphosphate $K_2(VO)_3(HPO_4)_4$ was synthesized hydrothermally under mild conditions using a Telfon-lined autoclave, and structurally characterized by single-crystal X-ray diffraction. Both TG analysis and magnetic susceptibility data confirm the formula. The compound crystallizes in a new structure type. The hydrothermal synthesis from elements or organic cations in place of K^+ is under way and could generate novel frameworks.

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