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Synthesis and Characterization of $KV_3P_4O_{16}$: A New Mixed-Valence Vanadium(III,IV,IV) Disphosphate

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A new mixed-valence vanadium diphosphate, $KV_3P_4O_{16}$, was synthesized by solid-state reaction and its structure was determined from single-crystal X-ray diffraction data. Brown crystal of $KV_3P_4O_{16}$ crystallizes in the monoclinic space group $P2_1/m$ (No. 11) with $a = 5.201(1)$, $b = 12.661(2)$, $c = 9.476(2)$ Å, $\beta = 94.11(2)°$, $V = 622.4(2)$ Å^3, $Z = 2$, $R = 0.0293$, $R_w = 0.0333$ for 1108 unique reflections with $I > 2.5\,\sigma(I)$. Edge-sharing pairs of VO_6 octahedra are connected by sharing corners to form strings along the b axis. The strings formally contain $V^{3.5+}$ (one V^{3+} and one V^{4+}) and are connected through P_2O_7 groups such that layers in the ab plane are formed. Adjacent layers are linked in three dimensions by VO^{2+} vanadyl groups. The structure consists of tunnels where the K^+ cations are located. The structural formula is $K(V_2O)(VO)(P_2O_7)_2$. Variable-temperature powder magnetic susceptibility data confirm the presence of one V^{3+} and two V^{4+} ions per formula unit.

Introduction

Mixed-valence compounds have been the subject of innumerable studies owing to their interesting physical properties. However, only a limited number of mixed-valence vanadium phosphates have been reported (*1–4*). Prompted by this state of underdevelopment, we have been exploring mixed-valence compounds with new structures in the A–V–P–O system (A = alkali metal). Recently, we synthesized $RbV_3P_4O_{17+x}$ ($x = 0.14$) (*5*) in which the average valence of V is +4.43, indicating the simultaneous presence of V^{4+} and V^{5+}. Its structure may be regarded as built up from ReO_3-type infinite chains along the tetragonal c axis (in which each VO_6 octahedron shares two opposite vertices) and four-membered chains parallel to the ⟨110⟩ directions, which are linked by P_2O_7 groups to form a three-dimensional structure. Although the V atoms in $RbV_3P_4O_{17+x}$ could be described as octahedrally coordinated the distortion from a regular octahedron is so great that the coordination is better described as square pyramid. The square pyramid geometry often occurs with complexes containing VO^{2+} or VO^{3+}. Since $V^{3+}O_6$ octahedron exhibits rather regular V–O bond distances, it is also of interest from a basic research point of view to prepare and characterize a complex phosphate containing both V^{3+} and V^{4+}.

A few potassium vanadium phosphates are known at present. The K–V^{IV}–P–O phases include $K_2VOP_2O_7$ (*6*), $KVOPO_4$ (*7*), α- and β-$K_2V_3P_4O_{17}$ (*8, 9*). A diphosphate containing V^{III} has been observed in KVP_2O_7, which is isostructural with

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$CsVP_2O_7$ (*10*). In this report we describe the preparation, crystal structure, and magnetic susceptibility of $KV_3P_4O_{16}$ in which the average valence of V is 3.67.

Experimental

Synthesis

$K_4V_2O_7$ (99.9%), V_2O_3 (99.9%), V_2O_5 (99.9%), VO_2 (99.5%), and P_2O_5 (99.9%), obtained from Cerac Inc., were used as received. $K_4P_2O_7$, obtained from Johnson Matthey Inc., was dried under vacuum at 300°C overnight. Loading of the reactants was carried out in a glovebox which was flushed with nitrogen. Brown crystals of the title compound were first obtained as one of the major products by heating a pressed pellet of $K_4V_2O_7$, V_2O_3, V_2O_5, and P_2O_5 (mole ratio 1 : 3 : 2 : 8) in a sealed silica tube at 820°C for 24 hr followed by slow cooling to room temperature. A single-crystal X-ray diffraction study showed the brown crystal to be the new compound $KV_3P_4O_{16}$. The other major product was identified by powder X-ray diffraction as α-$K_2V_3P_4O_{17}$ (*8*). Powder X-ray diffraction patterns were obtained with a Rigaku powder diffractometer and Cu$K\alpha$ radiation. Subsequently, the title compound was obtained as a single-phase material by heating a reaction mixture of $K_4P_2O_7$, VO_2, V_2O_3, and P_2O_5 in a 1 : 8 : 2 : 7 molar ratio in a sealed silica tube at 750°C for 1 day with an intermediate grinding, and then at 820°C for 1 day. The powder X-ray pattern of the brown polycrystalline product compared well with that calculated from the single-crystal data. The indexed X-ray powder diffraction pattern of $KV_3P_4O_{16}$ recorded at room temperature is given in Table I. The compound appeared air-stable in the laboratory atmosphere for at least several hours, which was checked by powder X-ray diffraction and infrared spectroscopy. An IR spectrum in the 3000–4000 cm^{-1} range did not reveal the presence of OH groups. Attempts to dissolve the sample in either

TABLE I

X-RAY POWDER DIFFRACTION DATA FOR $KV_3P_4O_{16}$ (a = 5.213(4), b = 12.653(5), c = 9.472(7) Å, β = 94.14(6)°; λ = 1.5418 Å)

$h\ k\ l$	$2\theta_{obs}$ (degrees)	d_{obs} (Å)	d_{calc} (Å)	I_{obs}
0 0 1	9.3	9.5	9.447	95.1
0 1 1	11.7	7.56	7.570	9.4
0 2 0	13.9	6.37	6.326	0.5
0 2 1	16.9	5.25	5.257	18.4
1 0 0	17.1	5.18	5.199	24.2
1 1 0	18.5	4.80	4.809	24.7
0 0 2	18.8	4.72	4.724	1.8
1 0 1	20.1	4.42	4.422	70.9
1 1 1	21.3	4.17	4.175	1.3
1 2 0	22.1	4.02	4.017	83.4
0 3 1	23.1	3.85	3.851	62.8
1 2-1	23.6	3.77	3.773	21.1
1 2 1	24.6	3.62	3.624	11.2
1 1-2	25.6	3.48	3.488	48.0
1 0 2	26.4	3.38	3.377	100.0
1 3 0	27.2	3.28	3.276	1.8
0 4 0	28.2	3.16	3.163	80.7
0 1 3	29.2	3.06	3.056	35.9
0 4 1	29.8	3.00	3.000	62.3
0 2 3	31.7	2.82	2.819	4.5
1 0-3	32.2	2.78	2.784	26.5
1 3-2	32.5	2.75	2.751	51.1
1 1-3	32.9	2.72	2.719	55.2
1 3 2	34.0	2.64	2.636	21.5
1 4 1	34.9	2.57	2.573	13.5
1 1 3	35.1	2.56	2.557	12.6
2 1 0	35.3	2.54	2.546	48.0
2 1-1	35.9	2.50	2.504	1.5
2 0 1	36.5	2.46	2.462	1.0
1 2 3	37.3	2.41	2.414	1.0
1 4-2	37.7	2.39	2.385	1.5
1 4 2	39.0	2.31	2.309	7.2
1 5 0	39.6	2.28	2.275	3.5
0 5 2	40.4	2.23	2.231	13.0
1 0-4	40.8	2.21	2.211	28.7
2 1 2	41.5	2.18	2.178	1.7
0 6 0	42.9	2.11	2.109	16.6
1 5-2	43.6	2.08	2.076	28.3
0 6 1	43.9	2.06	2.058	11.7
1 5 2	44.7	2.03	2.025	2.0
2 2-3	46.0	1.97	1.976	11.2
2 3 2	46.4	1.96	1.958	4.5
2 0 3	46.9	1.94	1.937	4.0
1 6-1	47.3	1.92	1.924	4.0
1 6 1	47.7	1.91	1.904	4.5
0 0 5	48.1	1.89	1.890	9.5
0 1 5	48.7	1.87	1.869	2.0
1 6-2	50.0	1.82	1.823	1.5
2 5 0	50.3	1.81	1.813	18.4
2 5-1	50.8	1.80	1.798	2.6

aqua regia or $H_2SO_{4(aq)}$ always resulted in a very small amount of insoluble residue. The contents of K, V, P, and Si of the solution were analyzed by using an ICP-AE spectrometer. Analysis: Calcd: K, 6.837%; V, 26.726%; P, 21.667%. Found: K, 6.38%; V, 24.9%; P, 21.0%. The Si content was less than 50 ppm. The experimental results for K and V were a little lower than the theoretical values.

Magnetic Measurements

Variable-temperature magnetic susceptibility $\chi(T)$ data were obtained from 4 to 300 K in a magnetic field of 3 kG using a Quantum Design SQUID magnetometer on 154.75 mg of polycrystalline sample. Diamagnetic contributions for K^+, P^{5+}, and O^{2-} were estimated as suggested by Selwood (*11*), which were subtracted from the experimental susceptibility data to obtain the molar magnetic susceptibilities (χ_M) of the compound. The data were least-squares fitted from 4 to 300 K to the relation $\chi_M = C/(T - \theta)$, where C is the molar Curie constant and θ is the Weiss constant.

Single-Crystal X-Ray Diffraction

A brown crystal having the dimensions $0.05 \times 0.10 \times 0.23$ mm was selected for indexing and intensity data collection on an Enraf Nonius CAD4 diffractometer with graphite-monochromated Mo$K\alpha$ radiation. Axial oscillation photographs along the three axes were taken to check the symmetry properties and unit cell parameters. Of the 1596 reflections measured (max 2θ = 55°, octants collected $\pm h, +k, +l$, scan mode ω-2θ), 1494 were unique and 1108 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° (*12*). An examination of the intensity data showed the systematic absences $k = 2n + 1$ for $0k0$ reflections. Based on statistical distribution and successful solution and refinement of the structure, the space group was determined to be $P2_1/m$ (No. 11). Direct methods (NRCVAX) (*13*) were used to locate the metal atoms, and the phosphorus and oxygen atoms were located by using the Fourier synthesis section of the program. Neutral-atom scattering factors and corrections for anomalous dispersion were from common sources (*14*).

V(2) lies in the mirror plane and V(1) is at the general position. The coordination environment of V(2) is distorted square pyramidal which often occurs with complexes containing oxovanadium(IV) ion. The compound can be formulated as $KV^{4+}V_2^{7+}P_4O_{16}$. Atom V(1) has an average valence of +3.5, indicative of the simultaneous presence of V^{3+} and V^{4+}. Edge-sharing pairs of $V(1)O_6$ octahedra are connected by O(1) to form strings parallel to the b axis. It was noted that atom O(1) was located at 2e special position and had U_{22} about three times of U_{11} or U_{33}, suggesting positional disorder of O(1) along the b axis. Assuming the oxidation states of V(1) were statistically disordered, a displacement of O(1) from the special position was allowed with its occupancy factor fixed at 0.5. However, the atomic coordinates and thermal parameters for O(1) had to be alternatively fixed in the refinement. The model including disordered O(1) allowed one to distinguish V^{3+} and V^{4+} on the basis of V–O bond distances (vide infra). The multiplicity of the K and V atoms were allowed to refine, and the multipliers were K 0.998(6), V(1) 0.988(3), and V(2) 0.997(5). Therefore, the metal atom sites were considered fully occupied in subsequent refinement. The secondary extinction coefficient was also refined. The final cycle of full-matrix least-squares refinement gave R and R_w values of 0.029 and 0.033, respectively. The final difference map was flat to less than ± 0.6 e/Å^3. It was noted that the K atom had large thermal parameters and the refined ellipsoids for most of the other atoms appeared to have rather anisotropic shapes.

Peak profile analysis (ω-scan) on the data crystal using a Nicolet *R*3*m*/*V* diffractometer showed normal peak profiles (FWHM = 0.33°). Axial oscillation photographs with long exposure time did not reveal any superlattice reflections. An intensity data set was also collected and the structural analysis results were essentially the same as those from the previous data set.

Results and Discussion

Structural Description

Table II lists the crystallographic data. Final atomic coordinates and B_{iso} are listed in Table III. Selected interatomic distances are given in Table IV. The structure of $KV_3P_4O_{16}$ contains edge-sharing pairs of $V(1)O_6$ octahedra which are connected by atoms O(1) to form strings running along the *b* axis (Fig. 1). The V(1)–O(1)–V(1)b bond angle is 174.8°. Strings are connected through P_2O_7 groups such that layers in the *ab* plane are formed (Fig. 2). Adjacent layers are linked in three dimensions by vanadium atoms, V(2), via P–O–V–O–P connections (i.e., corner-sharing PO_4 tetrahedra with $V(2)O_5$ square pyramids). A view down the *a* axis is presented in Fig. 3. The apical vanadyl oxygen of one $V(2)O_5$ square pyramid points to the open square face of adjacent $V(2)O_5$. The structure consists of tunnels

TABLE II

SUMMARY OF CRYSTAL DATA, INTENSITY MEASUREMENTS, AND REFINEMENT PARAMETERS FOR $KV_3P_4O_{16}$

Crystal data	
Crystal system	Monoclinic
Space group	$P2_1/m$ (No. 11)
Cell constants	a = 5.201(1), b = 12.661(2), c = 9.476(2) Å, β = 94.11(2)°, V = 622.4(2) Å^3
Z	2
Density (calculated)	3.051 g/cm^3
Abs. coeff. (Mo$K\alpha$)	30.7 cm^{-1}
Intensity measurements	
λ (Mo$K\alpha$)	0.70930 Å
Scan mode	$\theta/2\theta$
Scan rate	5.5°/min
Scan width	0.70° + 0.35° tan θ
Maximum 2θ	55°
Standard reflections	$(26\bar{4})$, $(2\bar{9}0)$, $(13\bar{2})$ (measured every 1 hr, no decay)
Unique reflections measured	1576
Structure solution and refinement	
Reflections included	1108
Parameters refined	122
Agreement factors[a]	R = 0.0293, R_w = 0.0333
GOF	1.34
$(\Delta\rho)_{max}$; $(\Delta\rho)_{min}$	0.60 e/Å^3; −0.60 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 $w = 1.0/\sigma^2(F_o)$.

TABLE III

ATOMIC COORDINATES AND THERMAL PARAMETERS FOR $KV_3P_4O_{16}$

Atom	x	y	z	B_{iso} (Å^2)[a]
K	0.5	0.5	0.5	3.99(9)
V(1)	0.39253(13)	0.39707(6)	0.08903(7)	0.85(3)
V(2)	0.98973(19)	0.25	0.59508(10)	0.61(4)
P(1)	0.14919(19)	0.63536(8)	0.12274(10)	0.41(4)
P(2)	0.92348(19)	0.36609(8)	0.28983(10)	0.49(4)
O(1)[b]	0.4042(8)	0.2608(5)	0.0958(4)	0.75(19)
O(2)	0.9141(6)	0.35969(22)	0.4493(3)	1.06(11)
O(3)	0.6893(5)	0.42276(21)	0.2251(3)	0.83(10)
O(4)	0.1756(5)	0.41146(22)	0.2485(3)	0.84(10)
O(5)	0.9084(8)	0.25	0.2269(4)	0.77(15)
O(6)	0.3736(5)	0.56918(20)	0.0722(3)	0.58(9)
O(7)	0.2151(8)	0.75	0.0679(4)	0.73(15)
O(8)	0.1043(5)	0.39705(22)	0.9487(3)	0.94(11)
O(9)	0.2932(9)	0.25	0.6214(5)	1.97(20)
O(10)	0.1485(6)	0.64106(21)	0.2818(3)	0.90(11)

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

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
K	3.45(10)	6.74(14)	4.90(12)	2.15(10)	−0.14(9)	−3.58(11)
V(1)	0.60(3)	1.79(4)	0.82(3)	0.10(3)	0.02(2)	−0.28(3)
V(2)	1.02(5)	0.69(4)	0.60(4)	0	0.07(4)	0
P(1)	0.61(5)	0.39(5)	0.55(5)	0.03(4)	0.05(3)	0.00(4)
P(2)	0.80(5)	0.48(5)	0.61(5)	0.01(4)	0.14(4)	0.03(4)
O(1)	1.03(21)	0.83(25)	0.99(21)	−0.1(3)	0.02(17)	−0.2(3)
O(2)	2.69(17)	0.85(13)	0.52(13)	0.35(12)	0.40(12)	0.07(11)
O(3)	0.84(14)	0.78(13)	1.50(14)	0.04(10)	−0.24(11)	0.03(11)
O(4)	0.80(14)	1.14(14)	1.32(14)	−0.26(11)	0.56(11)	−0.26(12)
O(5)	1.78(22)	0.53(18)	0.63(19)	0	0.15(16)	0
O(6)	0.81(13)	0.50(12)	0.96(13)	0.05(10)	0.40(10)	−0.09(11)
O(7)	1.67(21)	0.46(18)	0.74(19)	0	0.69(16)	0
O(8)	0.83(13)	1.10(14)	1.60(15)	−0.03(11)	−0.24(11)	0.09(12)
O(9)	1.84(24)	3.1(3)	2.5(3)	0	−0.23(20)	0
O(10)	2.10(16)	0.77(13)	0.58(13)	0.00(12)	0.32(11)	0.01(11)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.
[b] The occupancy factor for O(1) is 0.5.
[c] Anisotropic temperature factors are of the form: Temp = $\exp[-2\pi^2(h^2U_{11}a^{*2} + \cdots + 2hkU_{12}a^*b^* + \cdots)]$.

TABLE IV

BOND DISTANCES (Å) FOR $KV_3P_4O_{16}$

K–O(2)	2.859(3)	K–O(2)*a*	2.859(3)
K–O(3)	3.013(3)	K–O(3)*a*	3.013(3)
K–O(4)	3.034(3)	K–O(4)*a*	3.034(3)
K–O(10)	3.204(3)	K–O(10)*a*	3.204(3)
V(1)–O(1)	1.728(7)	V(1)–O(1)*b*	2.000(7)
V(1)–O(3)	1.966(3)	V(1)–O(4)	1.958(3)
V(1)–O(6)	2.187(3)	V(1)–O(6)*c*	2.065(3)
V(1)–O(8)	1.931(3)	V(2)–O(2)	1.978(3)
V(2)–O(2)*b*	1.978(3)	V(2)–O(9)	1.580(5)
V(2)–O(10)	1.975(3)*a*	V(2)–O(10)*d*	1.975(3)
P(1)–O(6)	1.541(3)	P(1)–O(7)	1.588(2)
P(1)–O(8)*e*	1.496(3)	P(1)–O(10)	1.509(3)
P(2)–O(2)	1.518(3)	P(2)–O(3)	1.506(3)
P(2)–O(4)*f*	1.509(3)	P(2)–O(5)	1.586(2)

Note. Symmetry codes: (*a*) $1 - x, 1 - y, 1 - z$; (*b*) $x, 0.5 - y, z$; (*c*) $1 - x, 1 - y, -z$; (*d*) $1 - x, -0.5 + y, 1 - z$; (*e*) $-x, 1 - y, -z$; (*f*) $1 + x, y, z$.

where the K^+ cations are located. Each tunnel is formed by the edges of 2 $V(1)O_6$ octahedra, 2 $V(2)O_5$ square pyramids, and 4 PO_4 tetrahedra. The structural formula of the title compound is $K(V_2O)(VO)(P_2O_7)_2$. The large thermal parameters for the K atom suggest positional disorder and can be rationalized by the tunnels in the structure. The refinement of K off the 2*d* special position was unsuccessful. The large U_{11} values for atom V(2) and its equatorial oxygen atoms, O(2) and O(10), are attributed to the positional disorder along the *a* axis. A similar phenomenon occurs in α-VPO_5 (*15*) and $Zn_2VO(PO_4)_2$ (*16*). The reasons for other oxygen atoms having rather anisotropic ellipsoids can also be attributed to the disordering of the metal atoms.

In the $V(2)O_5$ square pyramid the V atom is displaced 0.559 Å from the plane through four equatorial oxygen atoms toward the apical oxygen atom O(9). The V(2)–O(9) bond length is 1.580 Å and is about 0.4 Å shorter than the four equatorial V–O bonds. The short bond is typical of a VO^{2+} vanadyl group which has a strong bond with both σ and π characters. The distance from O(9) to the V atom of an adjacent $V(2)O_5$ is 3.65 Å and the V(2)–O(9) $\cdots$ V(2) angle is 167.1°. 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 (*17*), bond valence = $\exp[(R - d_{V\text{-}O})/0.37\ \text{Å}]$, where $R = 1.784$ Å for V^{4+}–O, we obtain +4.11 for V(2).

The model with atom O(1) disordered in two sites results in two types of $V(1)O_6$ polyhedron. One type has a short V–O bond length of 1.73 Å and five V–O bond lengths

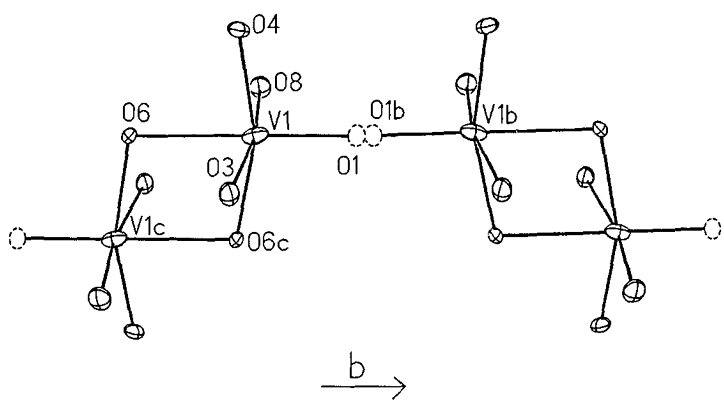

FIG. 1. A section of a string in $KV_3P_4O_{16}$ containing edge-sharing pairs of $V(1)O_6$ octahedra connected by O(1). Atom O(1), which is disordered in two sites, is represented by dotted circles. Thermal ellipsoids are shown at the 60% probability level.

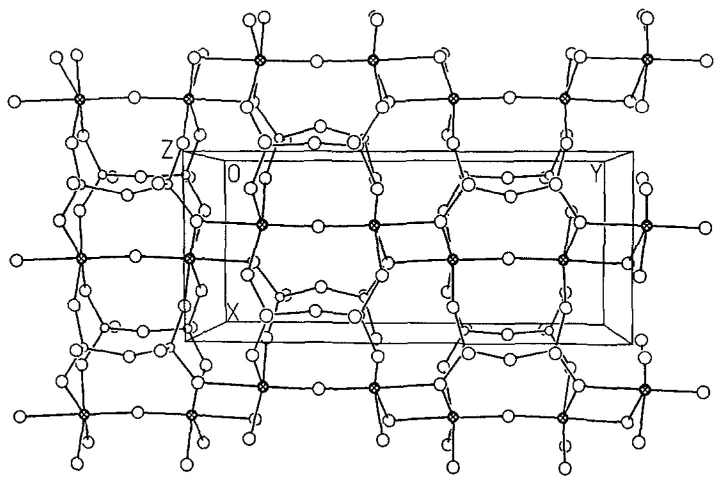

FIG. 2. A view of a layer in $KV_3P_4O_{17}$ along the c axis. The V, P, and O atoms are represented by cross-hatched, small, and large open circles, respectively. For clarity, the disorder of O(1) is not shown in the figure.

ranging from 1.93 to 2.19 Å. Using the bond-length–bond-valence relation for V^{4+}–O, we obtain the bond valence sum +3.90. The other type is more regular and has V–O bond lengths in the range 1.93 to 2.19 Å. Using the relation for V^{3+}–O gives a bond valence sum of +2.91. Based on the above discussion the oxidation state +4 can be assigned to V(2), and the strings formally contain $V^{3.5+}$ (one V^{3+} and one V^{4+}).

The V atoms within an edge-sharing pair of $V(1)O_6$ octahedra are 3.34 Å apart, being

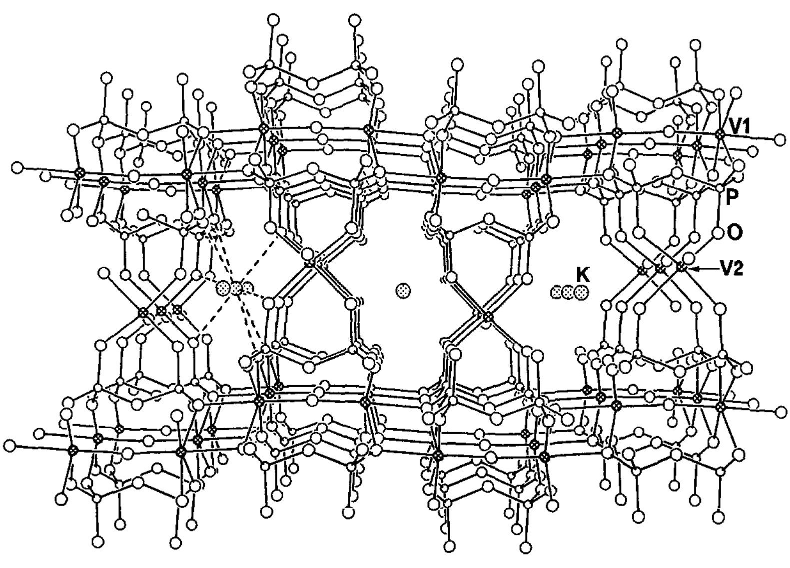

FIG. 3. A view of the structure of $KV_3P_4O_{16}$ along the a axis. The K, V, P, and O atoms are represented by dotted, cross-hatched, small, and large open circles, respectively. The K–O bonds are represented by dashed lines.

actually displaced in their octahedra away from each other and indicating the absence of V–V bonding. As indicated by the O–O distances (2.63–2.96 Å), the $V(1)O_6$ octahedron is markedly distorted because of edge sharing. The shared edge is shortened (2.63 Å) and the edges parallel to the V–V axis are elongated (2.80, 2.96 Å). The octahedron shows two longer V(1)–O bonds and four shorter ones. The longer distances correspond to those from V to the common oxygen atoms. For the same reason, the O(6)–V(1)–O(6)c bond angle is considerably smaller than the angle (O(1)–V(1)–O(4)) *trans* to it (76.5 vs 94.9°). The PO_4 tetrahedra forming each diphosphate group exhibit an eclipsed configuration since the bridging oxygen atom resides on a mirror plane. The P atoms shift away from the bridging oxygen atom giving rise to three shorter and one longer P–O bond in each P_2O_7 group. The P–O–P bond angles involving the bridging oxygen atoms are 132.2 and 135.9° for $P(1)_2O_7$ and $P(2)O_7$, respectively. The coordination number of K^+ can be determined by the maximum bond distance for K–O using the procedure by Donnay and Allmann (*18*) with the revised radii of Shannon (*19*) leading to 3.35 Å. Accordingly, the K^+ ion is eightfold coordinated by oxygen atoms at distances ranging from 2.859 to 3.204 Å. The K^+ ion has bond valence sum 0.75, which is considerably lower than the expected value 1.0. The tunnels appear a little too big for K^+ cations which is also indicated by the high thermal parameters of K.

Magnetic Susceptibility

A plot of the reciprocal molar susceptibility for $KV_3P_4O_{16}$ as a function of temperature is linear (Fig. 4), suggestive of independent paramagnetic spins of V ions in the structure. The solid line in the figure is the fit according to $\chi_M = C/(T - \theta)$ with the Curie constant $C = 1.75$ cm^3 − K/mol and the Weiss constant $\theta = -9.30$ K. From the

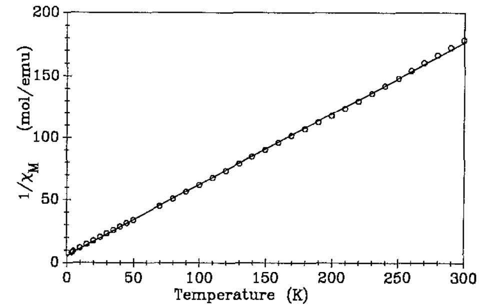

FIG. 4. Inverse molar magnetic susceptibility ($1/\chi_M$) vs temperature for $KV_3P_4O_{16}$. The solid line is a theoretical fit to the data from 4 to 300 K according to $\chi_M = C/(T - \theta)$.

relation $C = N\mu_{eff}^2/3k_B$ one obtains the effective magnetic moment $\mu_{eff} = 3.74\ \mu_B$ per formula unit, which is in excellent agreement with that (3.74 μ_B) expected for 2 moles of isolated V^{4+} ($S = 1/2$) and one mole of isolated V^{3+} ($S = 1$) with the Lande g factor $g = 2$. Thus the magnetic susceptibilities confirm the presence of one V^{3+} and two V^{4+} ions in $KV_3P_4O_{16}$.

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