

SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

Synthesis, Structure, and Physicochemical Properties of $K[VO_2(SeO_4)(H_2O)]$ and $K[VO_2(SeO_4)(H_2O)_2] \cdot H_2O$

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Received December 22, 2009

Abstract—The vanadium(V) complexes $K[VO_2(SeO_4)(H_2O)]$ and $K[VO_2(SeO_4)(H_2O)_2] \cdot H_2O$ were synthesized using original procedures; their physicochemical properties were studied, and the crystal structure was determined on the basis of X-ray diffraction and neutron diffraction data. The structure of $K[VO_2(SeO_4)(H_2O)_2] \cdot H_2O$ is composed of VO_6 octahedra connected to form infinite chains by bridging SeO_4 tetrahedra. Each VO_6 tetrahedron has short terminal V–O bonds forming the bent dioxovanadium group VO_2^+ .

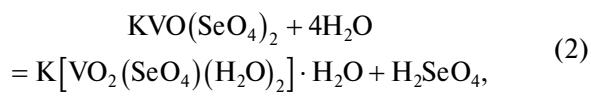
The unit cell parameters of $K[VO_2(SeO_4)(H_2O)_2] \cdot H_2O$ are $a = 6.4045(1)$ Å, $b = 9.9721(2)$ Å, $c = 6.6104(1)$ Å, $\beta = 107.183(1)^\circ$, $V = 403.34$ Å³, $Z = 2$, monoclinic system, space group $P2_1$. The complex $K[VO_2(SeO_4)(H_2O)]$ forms a two-dimensional layered structure composed of highly distorted VO_6 octahedra having two short terminal V–O bonds and SeO_4 groups coordinated simultaneously by three vanadium atoms. This compound crystallizes in the monoclinic system (space group $P2_1/c$): $a = 7.3783(1)$ Å, $b = 10.5550(2)$ Å, $c = 10.3460(2)$ Å, $\beta = 131.625(1)^\circ$, $V = 602.894(5)$ Å³, $Z = 4$. The vibrational spectra of the studied compounds are fully consistent with their structural features.

DOI: 10.1134/S0036023611080262

$M_2O-V_2O_5-SO_3-H_2O$ systems (where M is an alkali element except for lithium) model the active component of vanadium sulfuric acid catalysts at the hydrochemical stage of their synthesis [1]. A characteristic feature of these and similar systems, where M is an alkali metal, thallium(I), or ammonium, is the formation of complexes of the following composition: $M[VO_2(SO_4)(H_2O)_2] \cdot H_2O$ ($M = K, Rb, Tl, NH_4$) [1–3], $M[VO_2(SO_4)(H_2O)_2]$ ($M = Cs, NH_4$) [1, 3, 4], $M_{0.67}Na_{0.33}[VO_2(SO_4)(H_2O)_2]$ ($M = K, Rb, Cs, NH_4$) [1, 5, 6]. The compounds were synthesized by crystallization from sulfuric acid solutions and by hydrolysis of $MVO(SO_4)_2$ under saturated water vapor at room temperature. Keeping $KVO(SO_4)_2$ in a saturated water vapor atmosphere at 40°C for many hours gave the monohydrate $K[VO_2(SO_4)(H_2O)]$, which was studied by X-ray diffraction [7]. A similar selenate complex, $K[VO_2(SeO_4)(H_2O)]$, is known to be formed upon spontaneous dehydration of $K[VO_2(SeO_4)(H_2O)_2] \cdot H_2O$ at room temperature [1]. Since no published data on the structure and properties of $K[VO_2(SeO_4)(H_2O)]$ and $K[VO_2(SeO_4)(H_2O)_2] \cdot H_2O$ were available, the key goal of this work was to study the formation conditions, crystal structure, and the physicochemical properties of these compounds.

EXPERIMENTAL

The synthesis procedures of $K[VO_2(SeO_4)(H_2O)_2] \cdot H_2O$ and $K[VO_2(SeO_4)(H_2O)]$ were based on the following reactions



Reaction (2) was performed by keeping $KVO(SeO_4)_2$ in a closed desiccator above water for a week. The $K[VO_2(SeO_4)(H_2O)_2] \cdot H_2O$ crystals thus formed were separated from the mother liquor by vacuum filtration, washed with acetone, dried at room temperature and stored in bottles with little free volume. The synthesis of the monohydrate $K[VO_2(SeO_4)(H_2O)]$ included the following operations. Potassium metavanadate KVO_3 was dissolved in dilute selenic acid prepared from 85% reagent grade H_2SeO_4 , and the solution was heated to 70°C and concentrated at this temperature to precipitate the crystals of $K[VO_2(SeO_4)(H_2O)]$, which were collected on a vacuum filter, washed with acetone, and dried at 40°C. In addition, this compound was obtained by spontaneous dehydration of $K[VO_2(SeO_4)(H_2O)_2] \cdot H_2O$ taking

Table 1. Atom coordinates and thermal parameters ($U_{\text{iso}} \times 10^2, \text{\AA}^2$) in the structure $\text{K}[\text{VO}_2(\text{SeO}_4)(\text{H}_2\text{O})]$

Atom	Position	x/a	y/b	z/c	$U_{\text{iso}}/U_{\text{eq}} \times 10^2$
K	4e	0.3370(3)	0.0701(2)	0.2528(2)	5.7(2)
V	4e	0.0759(3)	0.0919(2)	0.7440(2)	4.5(1)
Se	4e	0.8999(2)	0.1955(1)	0.3615(1)	4.6(1)
O(1)	4e	0.1139(8)	0.1894(5)	0.5729(5)	3.5(3)
O(2)	4e	0.2269(8)	0.9468(4)	0.7186(5)	4.0(3)
O(3)	4e	0.7956(8)	0.0565(4)	0.5858(6)	4.7(3)
O(4)H2	4e	0.4527(8)	0.1617(4)	0.9096(5)	4.8(3)
O(5)	4e	0.6796(8)	0.2941(5)	0.2918(5)	5.2(3)
O(6)	4e	0.1311(7)	0.0353(4)	0.9136(5)	4.7(3)
O(7)	4e	0.0200(8)	0.2284(5)	0.2760(6)	6.0(3)
H(1)	4e	0.557(4)	0.146(3)	0.035(2)	5.00
H(2)	4e	0.551(4)	0.158(3)	0.876(3)	5.00
		$wR\rho$	$R\rho$	$R(F^2)$	CHI^2
X-rays		1.88	1.31	3.47	2.811
Neutrons		2.18	1.74	3.57	2.811

place on keeping the sample in a closed desiccator above a dehydrating agent (P_2O_5). Potassium metavanadate KVO_3 needed for reaction (3) was synthesized by solid-state annealing of a stoichiometric mixture of

special-purity grade K_2CO_3 and V_2O_5 . The completeness of conversion and the purity of products were checked using a POLAM S-112 transmission light polarization microscope and by X-ray diffraction. The

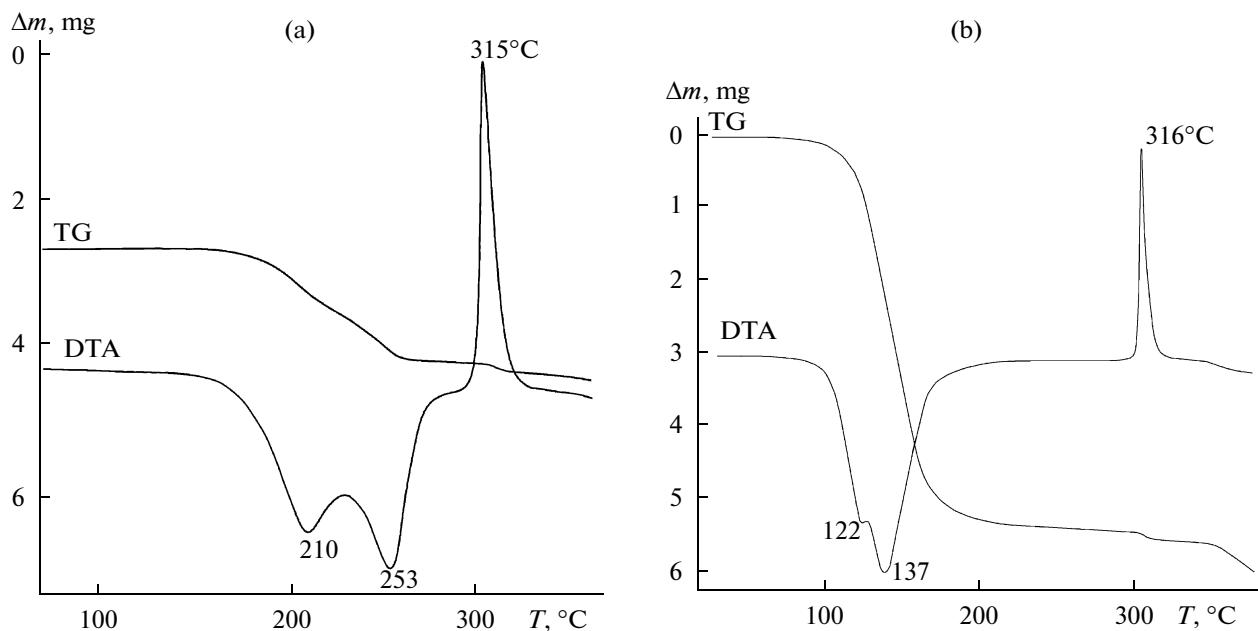
**Fig. 1.** TG and DTA curves for (a) $\text{K}[\text{VO}_2(\text{SeO}_4)(\text{H}_2\text{O})]$ and (b) $\text{K}[\text{VO}_2(\text{SeO}_4)(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ powders.

Table 2. Interatomic distances (d) and bond angles (ω) in $\text{K}[\text{VO}_2(\text{SeO}_4)(\text{H}_2\text{O})]$

Bond	$d, \text{\AA}$	Bond	$d, \text{\AA}$
V–O(1)	2.221(4)	K–O(1)	2.924(5)
V–O(2)	2.011(5)	K–O(2)	3.035(4)
V–O(3)	1.612(4)	K–O(3)	2.803(4)
V–O(4)	2.210(4)	K–O(3)	2.776(4)
V–O(6)	1.629(4)	K–O(4)	3.089(4)
V–O(7)	2.016(5)	K–O(5)	3.285(5)
Mean	1.95	K–O(5)	2.940(6)
$\text{V}^{+5}\text{VI}-\text{O}^{-2}\text{III}^*$	<i>1.90</i>	K–O(6)	2.771(4)
		K–O(6)	2.870(4)
Se–O(1)	1.642(4)	K–O(7)	3.012(5)
Se–O(2)	1.671(5)	Mean	2.95
Se–O(5)	1.640(5)	$\text{K}^+\text{X}-\text{O}^{-2}\text{III}^*$	2.95
Se–O(7)	1.653(4)		
Mean	1.65		
$\text{Se}^{+6}\text{IV}-\text{O}^{-2}\text{III}^*$	<i>1.64</i>		
Angle	ω, deg	Angle	ω, deg
O(1)VO(2)	82.8(2)	O(3)VO(7)	96.9(2)
O(1)VO(3)	93.1(2)	O(4)VO(6)	90.1(2)
O(1)VO(4)	72.7(2)	O(4)VO(7)	81.3(2)
O(1)VO(6)	162.8(2)	O(6)VO(7)	95.8(2)
O(1)VO(7)	80.9(2)		
O(2)VO(3)	98.0(2)	O(1)SeO(2)	110.6(2)
O(2)VO(4)	80.5(2)	O(1)VO(5)	114.0(2)
O(2)VO(6)	95.6(2)	O(1)VO(7)	109.8(2)
O(2)VO(7)	158.4(2)	O(2)VO(5)	106.8(2)
O(3)VO(4)	165.9(2)	O(2)VO(7)	104.2(2)
O(3)VO(6)	104.1(2)	O(5)VO(7)	11.1(2)
VO(1)Se	124.2(2)	VO(7)Se	121.8(3)
VO(2)Se	125.0(3)		

* The mean values are shown in bold and the sums of crystal radii according to [12] are given in italics.

IR absorption spectra were measured on a Vertex 80 Bruker FT IR spectrometer in the range of 200–4000 cm^{-1} for powdered samples (CsI pellets), the Raman spectra were recorded using a RAMII attachment module compatible with the Vertex 80 FT IR spectrometer ($\lambda = 1064 \text{ nm}$, $P = 500 \text{ mW}$). Thermogravimetric analysis was carried out on a Shimadzu DTG-60 thermal analyzer at a heating rate of 10 K/min in air.

The X-ray diffraction patterns were measured in $\text{Cu}K_{\alpha 1}$ radiation on a STADI-P automated diffractometer equipped with mini-PSD in the transmission geometry with a scanning step $\Delta 2\theta = 0.02^\circ$ in 2θ angle range from 2° to 120° . Polycrystalline silicon ($a = 5.43075(5) \text{ \AA}$) was used as the external standard. The possible impurity phases were identified using the Powder Diffraction Database ICDD PDF2 (ICDD, USA, Release 2007). The neutron diffraction patterns were measured on a D7A setup of the IVV 2M reactor (manufactured in the town of Zarechnyi) in 2θ angle range from 5° to 135° with a step of 0.05° at the neutron wavelength $\lambda = 1.532 \text{ \AA}$. The crystal structures were solved and refined using simultaneously neutron and X-ray diffraction data and EXPO and GSAS software [8, 9]. The line profile was approximated by the pseudo-Voigt function $I(2\theta) = \eta^*L(2\theta) + (1 - \eta)^*G(2\theta)$ (L and G are the Lorentz and Gauss functions, respectively), and the angular dependence of the line width was approximated by the relation $(\text{FWHM})^2 = Utan^2\theta + Vtan\theta + W$, where FWHM is the full width at half maximum. The background level was specified as a combination of fifteen Chebyshev polynomials. The structural parameters obtained upon the refinement and the shortest interatomic distances and bond angles are presented in Tables 1–4.

RESULTS AND DISCUSSION

Microscopic analysis showed that spontaneous dehydration of $\text{K}[\text{VO}_2(\text{SeO}_4)(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ whose powder is deeply yellow-colored affords slightly colored yellowish phase of $\text{K}[\text{VO}_2(\text{SeO}_4)(\text{H}_2\text{O})]$; the originally coarse prismatic crystals of the trihydrate are converted to agglomerates of very small particles of the new compound. By crystallization from a selenium acid solution, we isolated well-formed crystals of $\text{K}[\text{VO}_2(\text{SeO}_4)(\text{H}_2\text{O})]$ as skew-angle plates and up to 50 μm -long prisms colored intensely yellow, as opposed to $\text{K}[\text{VO}_2(\text{SO}_4)(\text{H}_2\text{O})]$, which is colored orange [7]. The cleavage of the crystals of $\text{K}[\text{VO}_2(\text{SeO}_4)(\text{H}_2\text{O})]$ is perfect on pinacoid (010) and moderate in other orientations; the refractive indices are $Ng = 1.757$ (light-yellow), $Nm = 1.692$ (colorless), and $Np = 1.656$ (colorless). The well-formed prismatic crystals of $\text{K}[\text{VO}_2(\text{SeO}_4)(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ are a combina-

Table 3. Atom coordinates and thermal parameters ($U_{\text{iso}} \times 10^2$, Å²) in the structure K[VO₂(SeO₄)(H₂O)₂] · H₂O

Atom	Position	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	$U_{\text{iso}}/U_{\text{eq}} \times 10^2$
K	<i>2a</i>	0.2971(8)	0.8465(7)	0.8081(8)	2.9(2)
V	<i>2a</i>	0.6110(5)	0	0.3823(5)	0.9(1)
Se	<i>2a</i>	0.0737(4)	-0.0022(7)	0.2721(4)	2.5(1)
O(1)	<i>2a</i>	0.464(2)	0.538(1)	0.860(2)	2.1(1)
O(2)	<i>2a</i>	0.320(2)	0.627(1)	0.470(2)	2.1(1)
O(3)	<i>2a</i>	0.448(2)	0.286(1)	0.735(2)	2.1(1)
O(4)	<i>2a</i>	0.306(2)	0.378(1)	0.313(2)	2.1(1)
O(5)	<i>2a</i>	0.917(2)	0.947(1)	0.417(2)	2.1(1)
O(6)	<i>2a</i>	0.308(2)	0.981(1)	0.428(2)	2.1(1)
O(7)	<i>2a</i>	0.015(2)	0.916(1)	0.060(2)	2.1(1)
O(8)	<i>2a</i>	0.959(2)	0.659(1)	0.782(2)	2.1(1)
O(9)	<i>2a</i>	0.137(2)	0.139(1)	0.788(2)	2.1(1)
H(1)	<i>2a</i>	0.770(4)	0.793(2)	0.675(4)	3.7(3)
H(2)	<i>2a</i>	0.115(4)	0.128(3)	0.927(2)	3.7(3)
H(3)	<i>2a</i>	-0.009(3)	0.133(3)	0.677(3)	3.7(3)
H(4)	<i>2a</i>	0.672(3)	0.724(2)	0.246(5)	3.7(3)
H(5)	<i>2a</i>	0.784(4)	0.920(2)	0.824(3)	3.7(3)
H(6)	<i>2a</i>	0.544(4)	0.226(3)	0.676(5)	3.7(3)
		<i>wRp</i>	<i>Rp</i>	<i>R(F²)</i>	<i>CHI²</i>
X-rays		2.77	2.04	4.81	2.187
Neutrons		1.05	0.83	4.61	2.187

tion of three pinacoids, (100), (010), and (001), and two rhombic prisms, (110), (011). The acute angle between the faces of the rhombic prism (011) at the bisecting line of *Np* is close to 64°. Pleochroism is weakly manifested with color change from light yellow (*Ng*) to colorless (*Np*). The refractive indices of the K[VO₂(SeO₄)(H₂O)₂] · H₂O crystals are much lower than those for the monohydrate: *Ng* = 1.656 (light yellow), *Nm* = 1.619 (colorless), and *Np* = 1.575 (colorless).

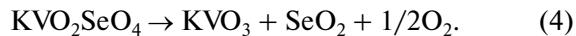
The dehydration of K[VO₂(SeO₄)(H₂O)] occurs in two stages, which are characterized by minima in the DTA curve at 210 and 253°C and an inflection in the TG curve (Fig. 1a). The exotherm in the DTA curve with a maximum at 315°C is caused by crystallization of the amorphous dehydration product of the nominal composition KVO₂SeO₄. The slight inflection in the TG curve is caused by partial decomposition of the compound with removal of selenium dioxide and oxy-

Table 4. Interatomic distances (d) and bond angles (ω) in $\text{K}[\text{VO}_2(\text{SeO}_4)(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$

Bond	$d, \text{\AA}$	Bond	$d, \text{\AA}$
V—O(1)	1.578(10)	K—O(1)	3.241(11)
V—O(2)	1.577(12)	K—O(1)	2.974(11)
V—O(3)	2.265(11)	K—O(2)	3.166(11)
V—O(4)	2.279(10)	K—O(3)	3.043(11)
V—O(5)	1.979(9)	K—O(4)	2.899(12)
V—O(6)	2.059(9)	K—O(5)	3.146(10)
Mean	1.956	K—O(6)	2.868(11)
$\text{V}^{+5}\text{VI}-\text{O}^{-2}\text{III}^*$	<i>1.90</i>	K—O(7)	2.885(12)
		K—O(8)	2.829(12)
Se—O(5)	1.658(9)	K—O(9)	3.083(11)
Se—O(6)	1.562(10)	Mean	3.013
Se—O(7)	1.570(10)	$\text{K}^+\text{X}-\text{O}^{-2}\text{III}^*$	2.95
Se—O(8)	1.650(10)	O(2)—O(3)	2.79(1)
Mean	1.610	O(2)—O(9)	2.92(1)
$\text{Se}^{+6}\text{IV}-\text{O}^{-2}\text{III}^*$	<i>1.64</i>	O(3)—O(9)	2.58(1)
		O(4)—O(7)	2.73(1)
		O(4)—O(8)	2.73(1)
Angle	ω, deg	Angle	ω, deg
O(1)VO(2)	112.3(7)	O(4)VO(5)	77.9(4)
O(1)VO(3)	84.9(6)	O(4)VO(6)	78.6(4)
O(1)VO(4)	161.7(6)	O(5)VO(6)	154.6(4)
O(1)VO(5)	100.2(4)	VO(5)Se	126.9(6)
O(1)VO(6)	98.9(4)	VO(6)Se	131.1(6)
O(2)VO(3)	162.7(4)	O(5)SeO(6)	102.3(4)
O(2)VO(4)	86.0(4)	O(5)SeO(7)	109.3(5)
O(2)VO(5)	93.1(5)	O(5)SeO(8)	111.3(5)
O(2)VO(6)	94.9(5)	O(6)SeO(7)	117.8(6)
O(3)VO(4)	76.8(4)	O(6)SeO(8)	106.5(6)
O(3)VO(5)	81.3(3)	O(7)SeO(8)	109.5(5)
O(3)VO(6)	84.0(3)		

* The mean values are shown in bold and the sums of crystal radii according to [12] are given in italics

gen, which becomes very intensive above 400°C and ends in the formation of potassium metavanadate



Note that the expected weight loss of the $\text{K}[\text{VO}_2(\text{SeO}_4)(\text{H}_2\text{O})]$ sample upon dehydration is 6.36 wt % and the experimental value is 6.42 wt %. The expected weight loss upon decomposition to give potassium metavanadate according to reaction (4) is 51.22 wt % and the experimental value is 51.31 wt %. The DTA curve of $\text{K}[\text{VO}_2(\text{SeO}_4)(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ (Fig. 1b) shows two minima at 122 and 137°C, and the exotherm caused by crystallization of the amorphous phase of KVO_2SeO_4 is shifted to lower temperature (298°C).

The crystal structure of anhydrous KVO_2SO_4 is composed of [10] VO_6 octahedra connected to form infinite zigzag-like chains by sharing the vertex oxygen atoms, and the sulfate groups connect these chains to form three-dimensional framework. The dioxovanadium group VO_2^+ has one short terminal bond, V—O (1.599 Å) and one 1.717 Å long bond between the vanadium atom and the oxygen atom incorporated in the V—O—V bridge. When water molecules are introduced in the structure to give $\text{K}[\text{VO}_2(\text{SO}_4)(\text{H}_2\text{O})]$, this gives rise to infinite isolated chains directed along the a axis and composed of VO_6 octahedra connected by sharing vertex oxygen atoms in *cis*-positions and bridging sulfate groups (Figs. 2b, 3b) [7]. The dioxovanadium VO_2^+ group contains two shortest vanadium—oxygen bonds one of which is terminal bond (1.599 Å) located at the vertex of the VO_6 octahedron, while the other V—O bond (1.682 Å) is incorporated in the oxygen bridge connecting the neighboring vanadium atoms. The oxygen atom of the vanadium-coordinated water molecule occupies a vertex of the VO_6 octahedron opposite to the short terminal V—O bond. The length of the V—O bond in the $(\text{V}—\text{OH}_2)$ structural fragment is 2.276 Å. On passing to the trihydrate $\text{K}[\text{VO}_2(\text{SO}_4)(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$, the structure becomes composed of chains [6, 11] formed by distorted VO_6 octahedra, which are linked by bridging sulfate groups. Two short terminal V—O bonds (with lengths of 1.592 and 1.587 Å) form the dioxovanadium group VO_2^+ , having an angular (*cis*) configuration.

On the basis of X-ray and neutron diffraction studies, we found that unlike $\text{K}[\text{VO}_2(\text{SeO}_4)(\text{H}_2\text{O})]$, $\text{K}[\text{VO}_2(\text{SO}_4)(\text{H}_2\text{O})]$ crystallizes in the monoclinic system (space group $P2_1/c$) with the parameters $a = 7.3783(1)$ Å, $b = 10.5550(2)$ Å, $c = 10.3460(2)$ Å, $\beta = 131.625(1)^\circ$, $V = 602.894(5)$ Å³, $Z = 4$) and has a two-dimensional layered structure composed of highly distorted VO_6 octahedra and SeO_4 groups each being

coordinated by three vanadium atoms (Figs. 2a, 3a). The layers are composed of pairs of VO_6 octahedra oppositely oriented in space and connected by bridging SeO_4 tetrahedra each forming one bond with other neighboring VO_6 octahedron through the bridging O(7) atom. The distortion of the VO_6 octahedron is caused by the fact that the V–O bond lengths are considerably different (Table 2), the two shorter terminal V–O bonds (1.612 and 1.629 Å) being located at an angle of 104.06° thus forming a dioxovanadium VO_2^+ group with angular (*cis*) configuration. The water molecule is coordinated to vanadium in the direction opposite to the shortest V–O bond located at a vertex of the VO_6 octahedron. The bond length between vanadium and oxygen of the coordinated water molecule (V–OH₂) is 2.210 Å. The Se–O interatomic distances within the SeO_4 tetrahedra are similar (Table 2), and the mean Se–O bond length is 1.65 Å, which is in good agreement with the sum of the crystal radii (1.65 Å) [12].

The anionic layers are parallel to the *bc* plane and the potassium atoms are located between the layers in the sites with C.N. = 10.

The trihydrate $\text{K}[\text{VO}_2(\text{SeO}_4)(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ is isostuctural to the corresponding sulfate $\text{K}[\text{VO}_2(\text{SO}_4)(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ and crystallizes in the monoclinic system (space group $P2_1$) with the unit cell parameters $a = 6.4045(1)$ Å, $b = 9.9721(2)$ Å, $c = 6.6104(1)$ Å, $\beta = 107.183(1)^\circ$, $V = 403.34$ Å³, $Z = 2$. The lattice is formed by infinite chains $n[(\text{VO}_2(\text{SeO}_4)(\text{H}_2\text{O})_2)]^-$ extended along the *a* axis (Fig. 4). The chains are composed of VO_6 octahedra connected by the bridging oxygen atoms, O(5) and O(6), of the SeO_4 tetrahedra. The vanadium atoms are surrounded by two bridging (*trans*) atoms O(5) and O(6), two terminal (*cis*) atoms, O(1) and O(2), which form the VO_2^+ group, and two (*cis*) atoms, O(3) and O(4) of the water molecules. The O(1) and O(2) atoms of the dioxovanadium groups are in *trans*-positions to the O(3) and O(4) atoms of water. In the VO_6 octahedron, the V–O distances differ considerably, the shortest distances being present in the dioxovanadium VO_2^+ group (1.577 and 1.578 Å) and the longest distances being those to the coordinated water oxygens (2.279 and 2.265 Å). The former is attributable to the formation of double vanadyl bonds and the latter is related to the structural manifestation of the *trans*-effect for the oppositely located oxygen atoms. The V–O(5) and V–O(6) distances are intermediate (1.979 and 2.059 Å). The SeO_4 tetrahedron is formed by two (*cis*) bridging (O(5) and O(6)) and two terminal (O(7) and O(8)) oxygen atoms. Despite the inequivalence of the Se–O interatomic distances (Table 4) in the tetrahedra, the

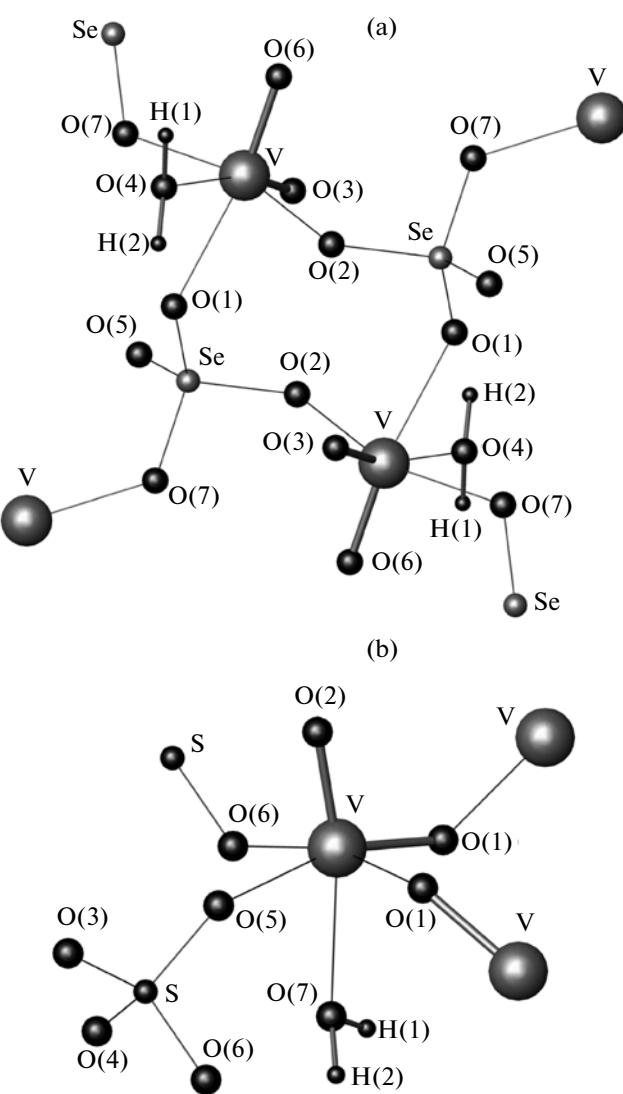


Fig. 2. Fragment of the structure of the $[\text{VO}_2(\text{XO}_4)(\text{H}_2\text{O})_2]^-$ anion in (a) $\text{K}[\text{VO}_2(\text{SeO}_4)(\text{H}_2\text{O})]$ and (b) $\text{K}[\text{VO}_2(\text{SO}_4)(\text{H}_2\text{O})]$.

mean values almost coincide with the theoretical value of 1.63 Å [12]. The water molecule of crystallization formed by H(2), H(3), and O(9) atoms is situated near the selenate O(8) atom. The K⁺ cations occur in a nine-vertex polyhedron formed by seven oxygen atoms of the polymeric anions (2 × O(1), O(2), O(5), O(6), O(7), O(8)), oxygen atoms of two coordinated water molecules (O(3) and O(4)) and the O(9) atom of the crystallization water molecule. The average K–O distance is close to the theoretical value of 2.95 Å (Table 4) for C.N. = 10 [12].

Since the vanadium–oxygen interatomic distances in the VO_6 octahedron are considerably different, the

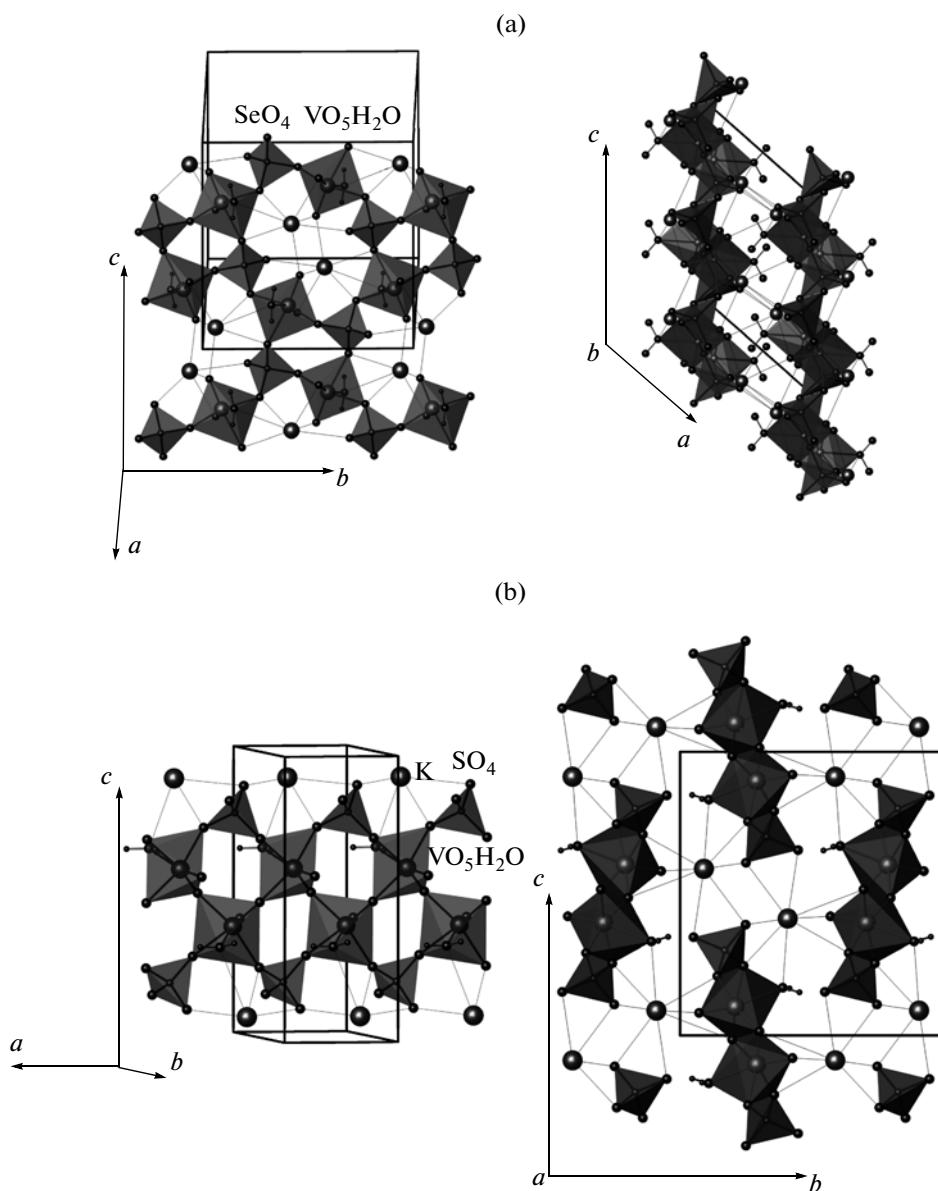


Fig. 3. Schematic view of the crystal structure of (a) $\text{K}[\text{VO}_2(\text{SeO}_4)(\text{H}_2\text{O})]$ and (b) $\text{K}[\text{VO}_2(\text{SO}_4)(\text{H}_2\text{O})]$. The selenium (sulfur) atoms are located in the tetrahedra and vanadium atoms are in the octahedra.

V–O bond vibrations occur in the vibrational spectra of sulfate and selenate derivatives over a broad frequency range. The vibrations of short terminal V–O bonds in KVO_2SO_4 and $\text{K}[\text{VO}_2(\text{SO}_4)(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ structures occur at ~ 895 – 950 and 876 – 936 cm^{-1} , respectively [10, 11]. The 590 – 635 cm^{-1} modes are caused by vibrations of longer V–O bonds in the (V–O)–S structural fragment with interatomic distances of about 2 \AA (for selenate anions, 525 – 535 cm^{-1}). Figure 5 shows the IR and Raman spectra of the synthesized selenate complexes $\text{K}[\text{VO}_2(\text{SeO}_4)(\text{H}_2\text{O})]$ and $\text{K}[\text{VO}_2(\text{SeO}_4)(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ and Table 5 presents the spectral frequencies. The key difference between the vibration spectra of complexes described as $\text{K}[\text{VO}_2(\text{XO}_4)(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ with the same type of structure is due [13] to the mass effect (a selenium atom is heavier than the sulfur atom) and is expressed as overlap of the regions of VO_2^+ internal vibrations and vibrations of tetrahedral SeO_4^{2-} (800 – 930 cm^{-1}), and this complicates interpretation of the spectra, whereas in

sized selenate complexes $\text{K}[\text{VO}_2(\text{SeO}_4)(\text{H}_2\text{O})]$ and $\text{K}[\text{VO}_2(\text{SeO}_4)(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ and Table 5 presents the spectral frequencies. The key difference between the vibration spectra of complexes described as $\text{K}[\text{VO}_2(\text{XO}_4)(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ with the same type of structure is due [13] to the mass effect (a selenium atom is heavier than the sulfur atom) and is expressed as overlap of the regions of VO_2^+ internal vibrations and vibrations of tetrahedral SeO_4^{2-} (800 – 930 cm^{-1}), and this complicates interpretation of the spectra, whereas in

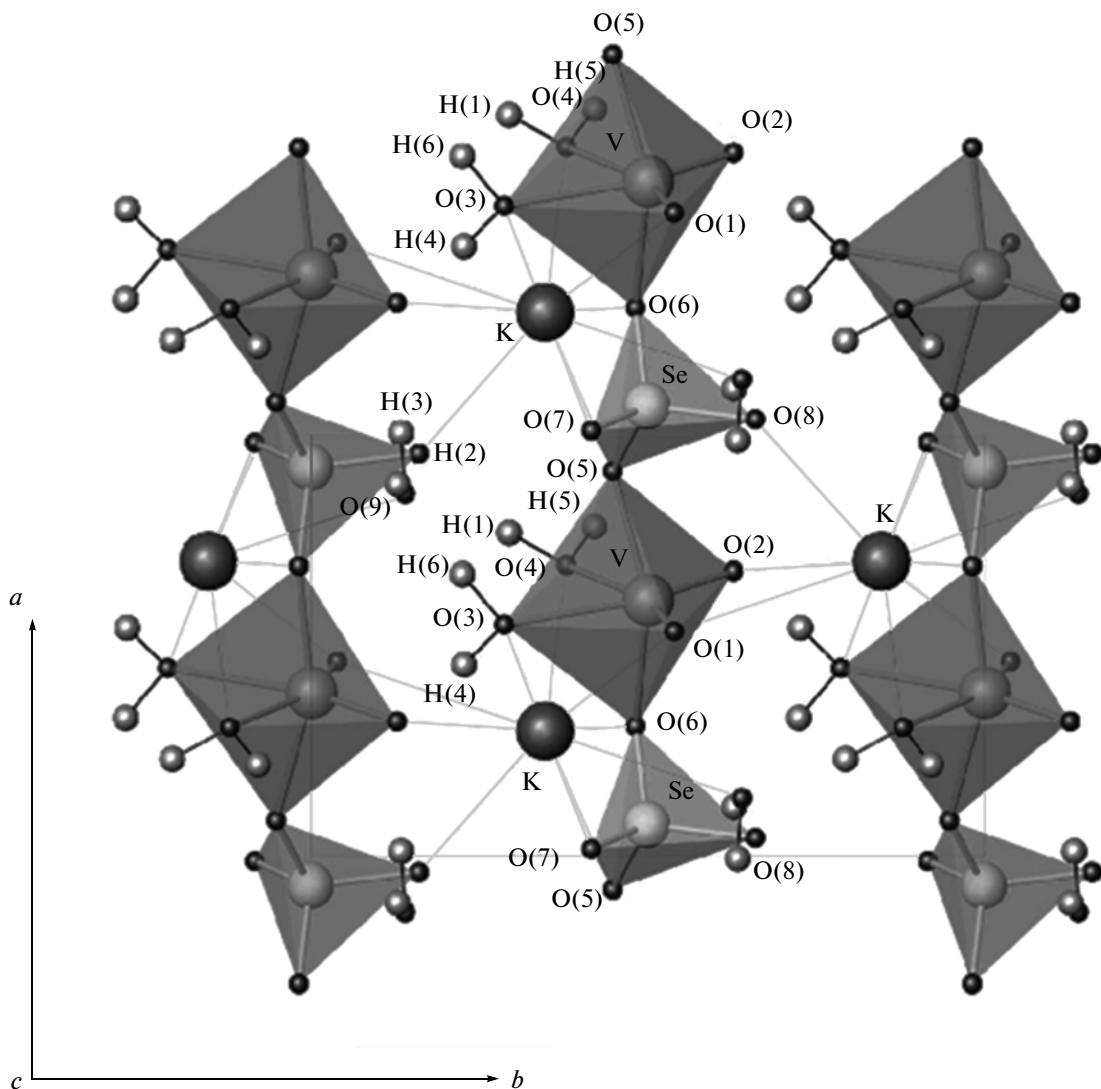


Fig. 4. Schematic view of the crystal structure of $\text{K}[\text{VO}_2(\text{SeO}_4)(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$. The selenium atoms are located in the tetrahedra and vanadium atoms are in the octahedra.

the case of sulfate tetrahedron and the dioxovanadium group, the vibration regions are located apart from each other [11]. In addition to this feature, the increase in the weight induces a considerable low-frequency shift of the bridging oxygen vibrations in $\text{V}-\text{O}-\text{Se}$ and $\text{V}\cdots\text{OH}_2$. The “free” SeO_4^{2-} of T_d symmetry is responsible for four internal vibrations: stretching modes $\nu_1(A) = 837$ and $\nu_3(F_3) = 873 \text{ cm}^{-1}$ and bending modes $\nu_2(E) = 345$ and $\nu_4(F_2) = 415 \text{ cm}^{-1}$. Of these, only symmetric ν_1 and ν_2 modes are Raman-active [14]. In the non-centrosymmetric lattice, the rule of mutual exclusion does not hold, and for the bridging

SeO_4 tetrahedron and for the distorted VO_6 octahedron, all of the internal vibrations are both IR- and Raman-active. The modes $\nu_3 = 860$, $\nu_1 = 813\text{--}817$, $\nu_4 = 420\text{--}426$, and $\nu_2 = 353 \text{ cm}^{-1}$ can be assigned to SeO_4^{2-} modes in the IR and Raman spectra of $\text{K}[\text{VO}_2(\text{SeO}_4)(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$. The presence of two bands in the bending region of water molecules $\delta(\text{H}_2\text{O}) = 1630\text{--}1684 \text{ cm}^{-1}$ in the IR spectrum of this compound indicates that the water molecules are non-equivalent. The torsion modes of vanadium-coordinated water molecules are only IR-active: $\rho(\text{H}_2\text{O}) = 743 \text{ cm}^{-1}$. The rather intense Raman line with a maximum at 260–

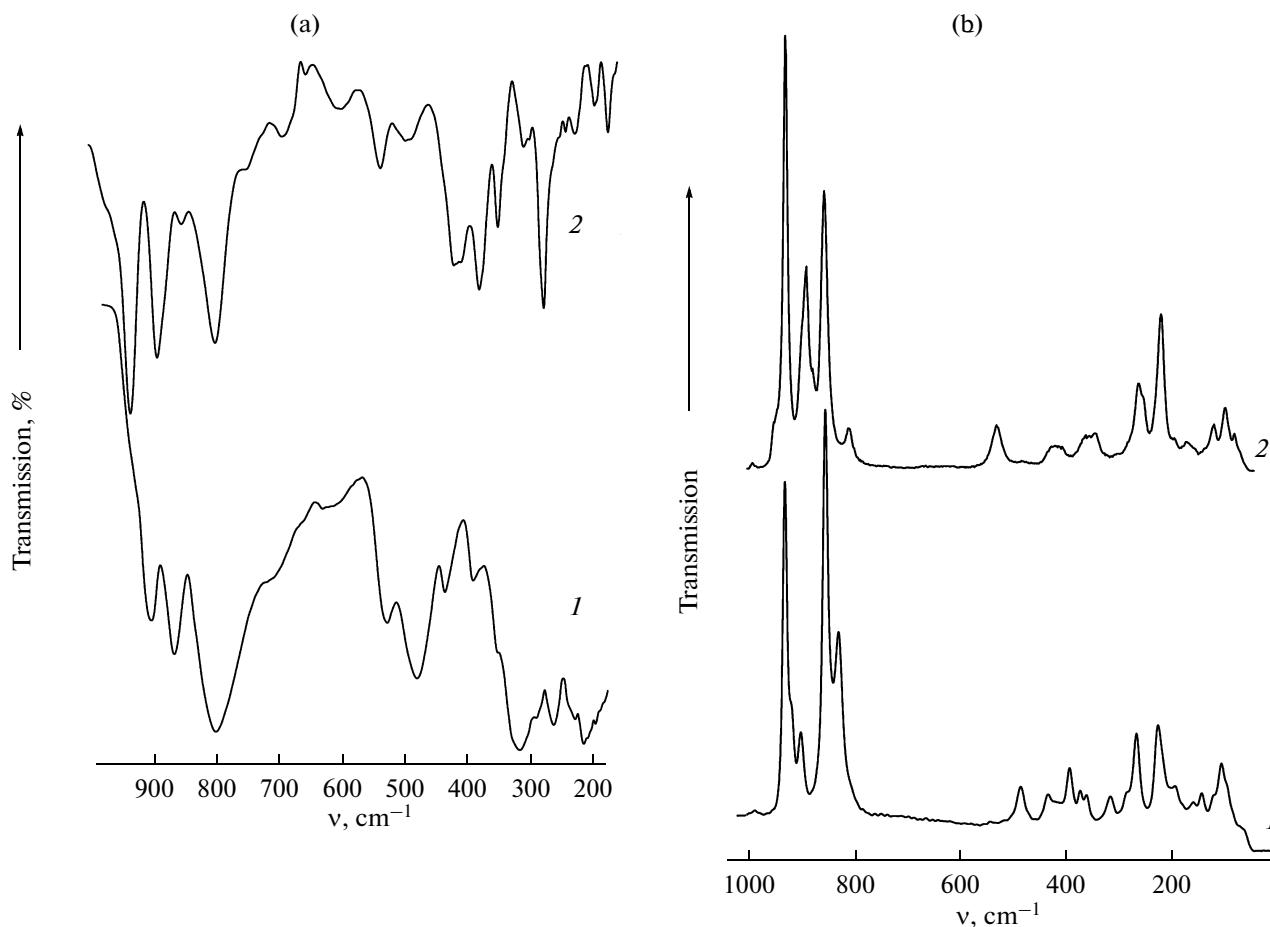


Fig. 5. Vibrational spectra of (1) $\text{K}[\text{VO}_2(\text{SeO}_4)(\text{H}_2\text{O})]$, (2) $\text{K}[\text{VO}_2(\text{SeO}_4)(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$: (a) IR spectra, (b) Raman spectra.

268 cm^{-1} can be initiated, according to published data [14], by displacement of oxygen atoms in the vanadium-coordinated water molecule. The external optical modes (below 225 cm^{-1}) are superpositions of translational (T) and rotational (R) motions of cations and anions in the lattice [15].

The vibrational spectra of $\text{K}[\text{VO}_2(\text{SeO}_4)(\text{H}_2\text{O})]$ are in line with the presence of bent dioxovanadium group VO_2^+ , where the vibrations of the short terminal V—O bonds occur at 933–903 cm^{-1} (Fig. 5, Table 5). The IR and Raman spectra of $\text{K}[\text{VO}_2(\text{SeO}_4)(\text{H}_2\text{O})]$, like the spectra of $\text{K}[\text{VO}_2(\text{SeO}_4)(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$, do not show splitting of the asymmetric stretching (ν_3) and bending (ν_4) frequencies of the SeO_4 group. In the $\nu(\text{H}_2\text{O})$ stretching region, the IR spectrum exhibits three weak bands: at 3512, 3254, and 3169 cm^{-1} ; the $\delta(\text{H}_2\text{O})$ bending vibrations are responsible for the narrow band with the absorption maximum at 1620 cm^{-1} ; the tor-

sion vibrations $\rho(\text{H}_2\text{O})$ of vanadium-coordinated water molecules account for the weak band at 716 cm^{-1} . In the Raman spectrum of $\text{K}[\text{VO}_2(\text{SeO}_4)(\text{H}_2\text{O})]$, the vibrations of water molecules are weak; nevertheless, the $\nu(\text{H}_2\text{O})$ stretching region shows two medium-intensity lines with maxima at 3491 and 3327 cm^{-1} .

Thus, sulfate and selenate complexes of the same type, $\text{K}[\text{VO}_2(\text{XO}_4)(\text{H}_2\text{O})]$ and $\text{K}[\text{VO}_2(\text{XO}_4)(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$, tend to have common structural motifs: dioxovanadium group VO_2^+ and the XO_4^{2-} group. However, whereas $\text{K}[\text{VO}_2(\text{XO}_4)(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ are isostructural compounds, the crystal structure of $\text{K}[\text{VO}_2(\text{SeO}_4)(\text{H}_2\text{O})]$ differs considerably from that of $\text{K}[\text{VO}_2(\text{SO}_4)(\text{H}_2\text{O})]$. The key difference is that the complex anion $[\text{VO}_2(\text{SeO}_4)(\text{H}_2\text{O})]^-$ in the structure of $\text{K}[\text{VO}_2(\text{SeO}_4)(\text{H}_2\text{O})]$ forms layers in which the VO_2^+ group with angular (*cis*) configuration includes two shorter terminal V—O bonds (1.612 and 1.629 Å) and

Table 5. IR and Raman wave numbers (cm^{-1}) for $\text{K}[\text{VO}_2(\text{SeO}_4)(\text{H}_2\text{O})]$ and $\text{K}[\text{VO}_2(\text{SeO}_4)(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$

K $[\text{VO}_2(\text{SeO}_4)(\text{H}_2\text{O})]$			K $[\text{VO}_2(\text{SeO}_4)(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$		
IR	Raman	Assignment	IR	Raman	Assignment
3512 w*	—	$\nu(\text{OH})-\text{H}_2\text{O}$	3519 w	—	$\nu(\text{OH})-\text{H}_2\text{O}$
3254 w			3482 w	3491 m	
3169 w			3306 s	3327 m	
1620 w	—	$\delta(\text{H}_2\text{O})$	1684 m	—	$\delta(\text{H}_2\text{O})$
			1630 m		
~930 sh	933 s	$\nu_{\text{as}}(\text{cisVO}_2)$	932 s	933 vs	$\nu_{\text{as}}(\text{cisVO}_2)$
904 s	903 m	$\nu_{\text{s}}(\text{cisVO}_2)$	895 s	894 s	$\nu_{\text{s}}(\text{cisVO}_2)$
868 s	857 vs	$\nu_3(\text{SeO}_4)$	860 w	860 s	$\nu_3(\text{SeO}_4)$
802 vs	832 m	$\nu_1(\text{SeO}_4)$	817 s	813 m	$\nu_1(\text{SeO}_4)$
716 sh	—	$\rho(\text{H}_2\text{O})$	743 m	—	$\rho(\text{H}_2\text{O})$
530 m		$\nu(\text{V}-\text{O}-\text{SeO}_3)$	527 m	535 m	$\nu(\text{V}-\text{O}-\text{SeO}_3)$
482 s	489 m	$\nu_4(\text{SeO}_4)$	420 m	426 w	$\nu_4(\text{SeO}_4)$
393 vs	397 m		379 w	370 w	
—	377 w		—	349 w	
355 sh	366 w	$\nu(\text{V}-\text{OH}_2)$	353 m		$\nu(\text{V}-\text{OH}_2)$
319 vs	320 m	$\nu_2(\text{SeO}_4)$	313 m		$\nu_2(\text{SeO}_4)$
293 sh	—	Bending and torsion modes	281 vs	268 w	Bending and torsion modes
265 s	271 m		246 w	260 m	
231 m	231 m		231 w	225 m	
217 s	—		201 m	201 w	
199 m	—		179 w	176 w	

* sh stands for shoulder; s stands for strong; vs stands for very strong; m stands for medium; w stands for weak; sh stands for shoulder.

the SeO_4 group is coordinated by three vanadium atoms in the layer.

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