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Hydrated Phases in the V_2O_5–K_2O–SO_3–H_2O System. Preparation and Structures of $K[VO_2(SO_4)(H_2O)]$ and $K[VO_2(SO_4)(H_2O)_2]\cdot H_2O$

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In the V_2O_5–K_2O–SO_3–H_2O phase system, the oxo–sulfato–vanadates(V) $K[VO_2(SO_4)(H_2O)]$ and $K[VO_2(SO_4)(H_2O)_2]\cdot H_2O$ have been prepared by controlled hydrolysis of $K[VO_2(SO_4)]$ as crystals suitable for X-ray structure determination. The structure of $K[VO_2(SO_4)(H_2O)]$ consists of ribbons formed by VO_6 octahedra, which share two adjacent corners, and by SO_4 tetrahedra, which bridge pairs of the octahedra. $K[VO_2(SO_4)(H_2O)_2]\cdot H_2O$ possesses a chain structure. A single strand is made of SO_4 tetrahedra and VO_6 octahedra with two terminal oxygen atoms. In both structures, sulfate acts as an unidentate ligand only toward a single vanadium atom. Crystal data: $K[VO_2(SO_4)(H_2O)]$, orthorhombic, space group $P2_12_12_1$, $a = 467.31$ (7) pm, $b = 1069.6$ (2) pm, $c = 1156.7$ (2) pm, $Z = 4$, 1214 unique data, R (R_w) = 0.027 (0.032); $K[VO_2(SO_4)(H_2O)_2]\cdot H_2O$, monoclinic, space group $P2_1$, $a = 625.5$ (2) pm, $b = 985.5$ (2) pm, $c = 653.3$ (2) pm, $\beta = 107.01$ (2)°, $Z = 2$, 1130 unique data, R (R_w) = 0.024 (0.025). The vibrational spectrum of $K[VO_2(SO_4)(H_2O)_2]\cdot H_2O$ is interpreted with respect to its structure.

The system V_2O_5–K_2O–SO_3 has been extensively studied due to its relation to the active component of vanadium sulfuric acid catalysts.[1] The compounds isolated are usually very hygroscopic. The formulas of some hydrolysis products have been established.[2] However, their crystal structures have not been determined so far. One important stage in the preparation of most vanadium catalysts is the steeping of silica in aqueous solutions of H_2SO_4, V_2O_5, and K_2SO_3. Formation of the trihydrate $KVO_2SO_4\cdot 3H_2O$, besides $KHSO_4$ and polyvanadates, occurs under such conditions.[3] We present in this paper the crystal structures of this trihydrate, which has to be formulated as $K[VO_2(SO_4)(H_2O)_2]\cdot H_2O$, and of $K[VO_2(SO_4)(H_2O)]$. The latter compound has not been mentioned in previous studies. Both structures may give further insight in the structure and performance of the active components of the sulfuric acid catalyst.

Experimental Section

Preparation of the Compounds. $K[VO(SO_4)_2]$ was prepared according to Krasil'nikov and co-workers.[2]

$K[VO_2(SO_4)(H_2O)]$. $K[VO(SO_4)_2]$ was kept at 40 °C in an atmosphere of approximately 60% humidity. First a dark red-brown solution was formed, from which large orange prismatic crystals of $K[VO_2(SO_4)(H_2O)]$ precipitated after some weeks. They were filtered off and washed with cold ethanol.

$K[VO_2(SO_4)(H_2O)_2]\cdot H_2O$. The fully hydrated compound could be prepared as X-ray quality crystals by the following procedure: $K[VO_2(SO_4)_2]$ was kept at 20 °C in air, saturated with water vapor. The substance turned soon into a dark red-brown solution. First crystals of $KHSO_4$ precipitated from the solution, followed by platelike, yellow crystals of $K[VO_2(SO_4)(H_2O)_2]\cdot H_2O$, whereupon the crystals of $KHSO_4$ began to disappear more and more. The best results were obtained by filtering off the solids, which had formed after 3–4 weeks. They were washed with cold water. White crystals of $KHSO_4$ and platelike, yellow crystals of $K[VO_2(SO_4)(H_2O)_2]\cdot H_2O$ could be separated mechanically.

Structural and Spectroscopic Work. Crystal data and details of data collection are summarized in Table I. Data were collected at room temperature by using Nonius CAD4 and a Syntex $P2_1$ automated diffractometers, both equipped with a Mo radiation source ($\lambda(K\alpha) = 71.069$ pm) and a graphite monochromator. The structures were solved by direct methods and refined by standard least-squares methods (SHELXTL-PLUS program systems). All hydrogen atoms were located in difference syntheses and refined isotropically. The weighting scheme $w^{-1} = \sigma(F_o) + gF_o^2$ was used; for g, see Table I. Tables II and III contain the final atomic parameters; Tables IV and V contain relevant bond distances and bond angles.

Table I. Crystallographic Data for $KVO_2SO_4\cdot H_2O$ and $KVO_2SO_4\cdot 3H_2O$

chem formula	H_2KO_7SV	H_6KO_9SV
fw	236.1	272.2
a, pm	467.31 (7)	625.5 (2)
b, pm	1069.6 (2)	985.5 (2)
c, pm	1156.7 (2)	653.3 (2)
β, deg	90	107.01 (2)
V, nm^3	0.5781	0.3851
Z	4	2
space group	$P2_12_12_1$ (No. 19)	$P2_1$ (No. 4)
T, °C	25	25
λ, Å	0.710 69	0.710 69
d_{calc}, g·cm^{-3}	2.71	2.35
μ, cm^{-1}	27.1	20.7
g (in weighting scheme)	0.000 25	0.000 34
R^a	0.027	0.024
$R_w{}^b$	0.042	0.029

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

Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (pm^2 × 10^{-1}) of $K[VO_2(SO_4)(H_2O)]$

	x	y	z	$U_{eq}{}^a$
V	1725 (1)	2907 (1)	8981 (1)	11 (1)
K	2069 (2)	905 (1)	5878 (1)	21 (1)
S	1356 (2)	1703 (1)	3001 (1)	12 (1)
O(1)	1323 (6)	−1981 (2)	4852 (2)	15 (1)
O(2)	7022 (5)	−724 (2)	5796 (2)	17 (1)
O(3)	343 (6)	510 (2)	3463 (2)	23 (1)
O(4)	−2499 (6)	2507 (3)	6092 (2)	21 (1)
O(5)	1510 (6)	−1419 (2)	7090 (2)	17 (1)
O(6)	−1076 (6)	2415 (2)	2456 (2)	17 (1)
O(7)	222 (6)	−3906 (3)	6685 (2)	19 (1)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (pm^2 × 10^{-1}) of $K[VO_2SO_4(H_2O)_2]\cdot H_2O$

	x	y	z	$U_{eq}{}^a$
V	6097.3 (7)	0	3721.8 (7)	11.6 (1)
K	2888 (1)	8483 (1)	8050 (1)	23.8 (2)
S	767.0 (9)	9989 (2)	2688.8 (9)	12.1 (2)
O(1)	4622 (4)	5568 (3)	8700 (4)	24.5 (7)
O(2)	3261 (4)	6378 (3)	4816 (4)	23.0 (7)
O(3)	4507 (4)	2922 (3)	7374 (4)	20.6 (7)
O(4)	3043 (4)	2783 (3)	3083 (4)	19.9 (7)
O(5)	9275 (3)	9489 (3)	3975 (3)	15.1 (6)
O(6)	3069 (3)	9710 (3)	4128 (3)	17.2 (7)
O(7)	349 (4)	9201 (4)	729 (4)	26.8 (8)
O(8)	9541 (4)	6437 (3)	7718 (5)	26.7 (8)
O(9)	1272 (5)	1352 (4)	7833 (5)	25.6 (8)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

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Table IV. Important Bond Distances (pm) and Angles (deg) of $K[VO_2(SO_4)(H_2O)]$

V-O(1)	168.2 (2)	O(1)-V-O(1a)	91.0 (1)
V-O(1a)	196.6 (3)	O(1)-V-O(2)	95.7 (1)
V-O(2)	159.9 (3)	O(1)-V-O(5)	82.0 (1)
V-O(5)	208.3 (3)	O(1)-V-O(6)	163.9 (1)
V-O(6)	198.4 (2)	O(1)-V-O(7)	89.7 (1)
V-O(7)	227.6 (3)	O(1a)-V-O(2)	104.1 (1)
S-O(3)	146.2 (3)	O(1a)-V-O(5)	162.5 (1)
S-O(4)	144.9 (3)	O(1a)-V-O(6)	96.8 (1)
S-O(5)	148.3 (3)	O(1a)-V-O(7)	85.3 (1)
S-O(6)	150.6 (3)	O(2)-V-O(5)	92.6 (1)
O(7)···O(3)	285.8 (4)	O(2)-V-O(6)	96.0 (1)
O(7)···O(3a)	295.0 (4)	O(2)-V-O(7)	169.0 (1)
		O(5)-V-O(6)	86.5 (1)
O(3)-S-O(4)	111.4 (2)	O(5)-V-O(7)	78.7 (1)
O(3)-S-O(5)	107.4 (1)	O(6)-V-O(7)	77.0 (1)
O(3)-S-O(6)	110.5 (2)	V-O(1)-V(a)	140.2 (1)
O(4)-S-O(5)	112.7 (2)	V-O(5)-S	147.1 (2)
O(4)-S-O(6)	106.6 (2)	V-O(6)-S	130.8 (2)
O(5)-S-O(6)	108.3 (1)	H(1)-O(7)-H(2)	105 (9)

Table V. Important Bond Distances (pm) and Angles (deg) of $K[VO_2(SO_4)(H_2O)_2]\cdot H_2O$

V-O(1)	161.3 (3)	O(1)-V-O(2)	103.5 (1)
V-O(2)	164.1 (3)	O(1)-V-O(3)	91.9 (1)
V-O(3)	216.6 (3)	O(1)-V-O(4)	169.2 (1)
V-O(4)	233.0 (3)	O(1)-V-O(5)	98.8 (1)
V-O(5)	201.0 (2)	O(1)-V-O(6)	100.1 (1)
V-O(6)	200.8 (2)	O(2)-V-O(3)	164.6 (1)
S-O(5)	150.5 (3)	O(2)-V-O(4)	87.2 (1)
S-O(6)	150.2 (2)	O(2)-V-O(5)	95.3 (1)
S-O(7)	145.5 (3)	O(2)-V-O(6)	96.9 (1)
S-O(8)	145.3 (3)	O(3)-V-O(4)	77.4 (1)
O(2)···O(3)	273.5 (4)	O(3)-V-O(5)	82.1 (1)
O(2)···O(9)	285.8 (3)	O(3)-V-O(6)	80.1 (1)
O(3)···O(9)	263.3 (4)	O(4)-V-O(5)	80.4 (1)
O(4)···O(7)	279.0 (3)	O(4)-V-O(6)	77.8 (1)
O(4)···O(8)	278.2 (4)	O(5)-V-O(6)	154.4 (1)
V-O(5)-S	128.9 (2)	O(5)-S-O(6)	103.2 (1)
V-O(6)-S	131.6 (2)	O(5)-S-O(7)	109.8 (2)
O(6)-S-O(8)	110.1 (2)	O(5)-S-O(8)	110.9 (2)
O(7)-S-O(8)	112.5 (2)	O(6)-S-O(7)	110.0 (2)

Vibrational spectra of $K[VO_2(SO_4)(H_2O)_2]\cdot H_2O$ were recorded using a Bruker IFS 113v FT-IR-spectrometer (prepared as Nujol mulls and PE pellets) and a Coderg T 800 Raman spectrometer equipped with a triple monochromator (excitation at 514.5 and 647.1 nm). No vibrational spectra could be recorded from $K[VO_2(SO_4)(H_2O)]$. The substance is extremely sensitive toward moisture, organic solvents, or laser light.

Results and Discussion

$K[VO_2(SO_4)(H_2O)_2]\cdot H_2O$ is a member of the isostructural series of "trihydrates" $MVO_2SO_4\cdot 3H_2O$ (M = K, Rb, Tl, NH_4)[2,4] and had already been described by Berzelius in the first half of the 19th century.[5] KVO_2SO_4 reacts reversibly with water to form $KVO_2SO_4\cdot 3H_2O$. $K[VO_2(SO_4)(H_2O)]$ is an intermediate stage in this reaction. It has been detected and characterized to our knowledge for the first time. The structures of all three compounds are related.[1] The hydration/dehydration reaction is probably a topochemical process.

Structure of $K[VO_2(SO_4)(H_2O)]$. A ribbon-type structure is formed by VO_6 octahedra, which share two corners in a cis position, and by SO_4 tetrahedra, which bridge pairs of VO_6 octahedra along the margin of the ribbon (see Figures 1 and 2). The ribbons, with a repeating period of only 467.3 pm, extend along the *a* axis. Vanadium is coordinated by a vanadyl oxygen O(2) at a distance of 159.9 (3) pm. Opposite to it a water molecule is situated at a very long distance (227.6 (3) pm). Two of the four equatorial oxygens, O(5) and O(6) at distances of 208.3 (3) and 198.4 (2) pm, belong to sulfate ions. The remaining two, O(1) and O(1a), are involved in the V–O–V bridge bonds. These bonds are alternating short (168.2 (2) pm) and long (196.6 (3) pm). The former one is intermediate between a V═O double and a V—O single bond and weakens therefore noticeably the V—O(—S) bond in the trans position. The bond angles involved in the VOVO chain are 91.0 (1) (OVO) and 140.1 (1)° (VOV).

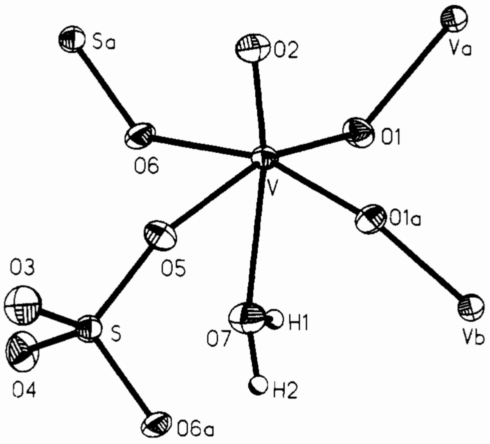

Figure 1. Structure and atom labeling of $K[VO_2(SO_4)(H_2O)]$.

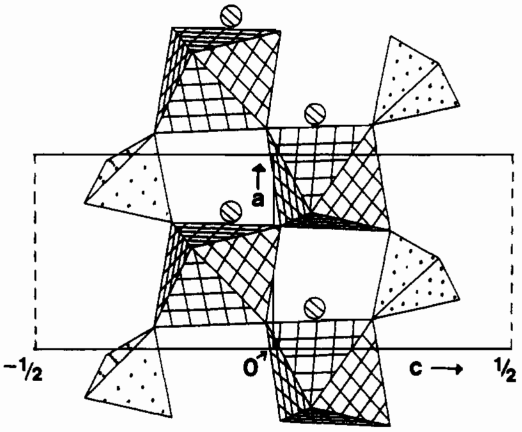

Figure 2. Polyhedral view of the ribbonlike structure of $K[VO_2(SO_4)(H_2O)]$. Dashed circles denote potassium ions; for the sake of clarity, only one of two ribbons within the unit cell is shown.

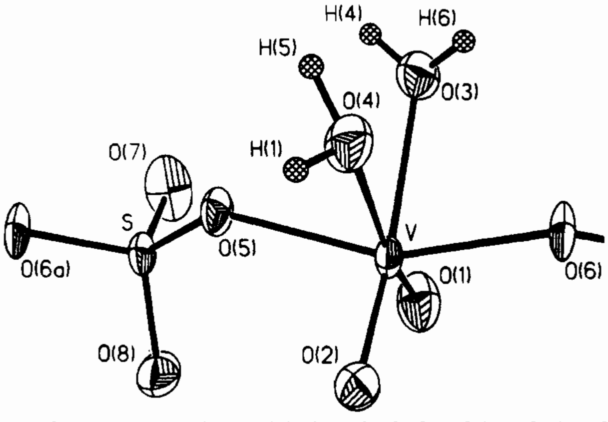

Figure 3. Structure and atom labeling of $K[VO_2(SO_4)(H_2O)_2]\cdot H_2O$.

The sulfate ion is distorted as usual. The bonds to the coordinating oxygen atoms O(5) and O(6) are significantly longer than the remaining two bonds to O(3) and O(4). The V–O–S angles are 128.9 (2) and 131.6 (2)°. O(3) is an acceptor of two hydrogen bonds from water molecules in neighboring ribbons; this causes a slight elongation of its bond compared to O(4). The potassium ion is situated in the space between three ribbons and is surrounded

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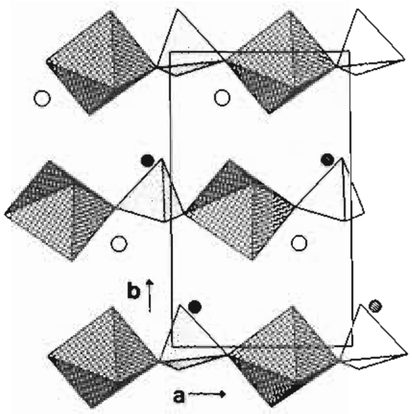

Figure 4. Strands of VO_6 octahedra and SO_4 tetrahedra in the structure of $K[VO_2(SO_4)(H_2O)_2]\cdot H_2O$. Open circles denote potassium ions; dashed circles denote water of crystallization.

within 310 pm by nine oxygen atoms.

Structure of $K[VO_2(SO_4)(H_2O)_2]\cdot H_2O$. The final stage of the hydration reaction possesses a chain structure. A single strand is made of alternating VO_6 octahedra and SO_4 tetrahedra, running along the *a* axis with a periodicity of 653.3 (2) pm. Between the strands the potassium ions and the uncoordinated water molecules are located (see Figures 3 and 4). Vanadium is again octahedrally coordinated. As a singularity within the structures of oxo–sulfato–vanadates(V) determined so far, vanadium bears here a terminal *cis*-dioxo group with two short bond distances, V–O(1) (161.3 (3) pm) and V–O(2) (164.1 (3) pm). The bonds differ slightly, because O(2) is involved in two hydrogen bonds, which originate from O(3), a coordinated water molecule, and from O(9), the water of crystallization. The O–V–O angle in the dioxo group is 103.5 (1)°. O(3) and O(4), from water molecules, are coordinated trans to O(1) and O(2). O(4) is very weakly bonded (233.0 (3) pm). The two sulfate oxygen atoms, O(5) and O(6), approximately in mutual trans positions at distances 201.0 (2) and 200.8 (2) pm, respectively, complete the coordination sphere. A similar bonding situation at vanadium has been found in $VO_2F_4^{3-}$[6] and in polymeric $VO_2F_2F_{2/2}^{2-}$.[7] The sulfate tetrahedron is distorted as usual. The bonds S–O(5) and S–O(6) are 5 pm larger than bonds to the noncoordinated oxygen atoms. These bonds span the widest angle, 112.5 (2)°, in the tetrahedron.

Vibrational Spectrum. The IR spectrum of $K[VO_2(SO_4)(H_2O)_2]\cdot H_2O$ has already been recorded and interpreted by Krasil'nikov.[4] The Raman spectrum is less obscured by the librational modes of the coordinated water molecules. The interpretation of the spectra is straightforward. The splitting of $\delta(H_2O)$ in two components at 1680 and 1630 cm^{-1} in the IR spectrum shows the presence of at least two different types of water molecules. $\nu_3(SO_4)$ is split widely into four components between 1227 and 1017 cm^{-1} (observed in the IR spectrum only), indicating a strong distortion. $\nu_1(SO_4)$ is observed at 1003 cm^{-1} in the IR spectrum and at 1006 cm^{-1} in the Raman spectrum. The *cis*-VO_2 group gives rise to three bands in both spectra: IR, 936 s, 902 s, 876 s cm^{-1}; Raman, 940 vs, 903 m, 880 vs cm^{-1}. They can be assigned to the symmetric and to two components of the antisymmetric V–O stretching vibrations.[6-8] In the lower frequency region, vibrational modes of H_2O (at 762, 720, and 617 cm^{-1} in the IR spectrum) can be distinguished. Further vibrations, e.g. $\nu_2(SO_4)$ and ν(V–O(–S)), cannot be assigned unambiguously.

Conclusions

In the hydrated oxo–sulfato–vanadates(V) $K[VO_2(SO_4)(H_2O)]$ and $K[VO_2(SO_4)(H_2O)_2]\cdot H_2O$, vanadium is six-coordinated. Whereas in anhydrous, strongly acidic solutions of V_2O_5 the VO^{3+} group prevails,[1] with increasing concentration of water, a transient state is reached between VO_3^+ and VO_2^+ moieties as expressed in the structure of $K[VO_2(SO_4)(H_2O)]$. Finally the VO_2^+ group dominates as shown by the structure of $K[VO_2(SO_4)(H_2O)_2]\cdot H_2O$. In all oxo–sulfato–vanadates(V) with known structures, sulfate acts as an unidentate ligand only toward a single vanadium atom. The structures of $K[VO_2(SO_4)(H_2O)]$ and $K[VO_2(SO_4)(H_2O)_2]\cdot H_2O$ are not directly related. In the former compound the sulfate ions are coordinated in cis positions at vanadium but in trans positions in the latter compound. A mechanism can be suggested by which the structures interconvert. It consists of breaking two bonds at vanadium, which are already strongly weakened by the trans effect, followed by a slight reorientation of the polyhedra, which allows the new polyhedral connectivity to be formed. The trihydrates $MVO_2SO_4\cdot 3H_2O$ (M = K, Rb, NH_4) are isostructural.[2] Cesium forms a dihydrate; its structure is unknown so far.

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Supplementary Material Available: Tables of crystallographic data, anisotropic thermal parameters, and hydrogen atom coordinates (3 pages); listings of calculated and observed structure factors (10 pages). Ordering information is given on any current masthead page.

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