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Crystal Structure and Spectroscopic Properties of $Na_2K_6(VO)_2(SO_4)_7$

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Red-brown crystals of a new mixed alkali oxo sulfato vanadium(V) compound $Na_2K_6(VO)_2(SO_4)_7$, suitable for X-ray determination, have been obtained from the catalytically important binary molten salt system $M_2S_2O_7$–V_2O_5 (M = 80% K and 20% Na). By slow cooling of a mixture with the mole fraction $X_{V_2O_5} = 0.24$ from 325 °C, i.e., just below the liquidus temperature, to the solidus temperature of around 300 °C, a dark reddish amorphous phase was obtained containing crystals of the earlier described V(V)–V(IV) mixed valence compound $K_6(VO)_4(SO_4)_8$ and $Na_2K_6(VO)_2(SO_4)_7$ described here. This compound crystallizes in the tetragonal space group $P4_32_12$ (No. 96) with $a = 9.540(3)$ Å, $c = 29.551(5)$ Å at 20 °C and $Z = 4$. It contains a distorted VO_6 octahedron with a short V–O bond of 1.552(6) Å, a long one of 2.276(5) Å trans to this, and four equatorial V–O bonds in the range 1.881(6)–1.960(6) Å. The deformation of the VO_6 octahedron is less pronounced compared to that of the known oxo sulfato V(V) compounds. Each VO^{3+} group is coordinated to five sulfate groups of which two are unidentately coordinated and three are bidentate bridging to neighboring VO^{3+} groups. The length of the S–O bonds in the S–O–V bridges of the two unidentately coordinated sulfato groups are 1.551(6) Å and 1.568(6) Å, respectively, which are unusually long compared to our earlier measurements of sulfate groups in other V(III), V(IV), and V(V) compounds.

Introduction

The industrial catalyst used for production of sulfuric acid, through oxidation of SO_2 by O_2 to SO_3 at 400−600 °C, is considered[1−3] to be a molten salt gas system, $M_2S_2O_7-V_2O_5/SO_2-O_2-SO_3-N_2$ (M = Na, K, Cs), supported on a porous kieselguhr carrier. During industrial operation, the catalytically active vanadium oxo sulfato complexes are formed by dissolution of V_2O_5 in the molten alkali pyrosulfates $M_2S_2O_7$. Thus, complexes of V(V) such as $(VO)_2O(SO_4)_4^{4-}$, $VO_2SO_4^-$, and polymeric $(VO_2SO_4)_n^{n-}$ seem to be formed[4−8] while reduction by SO_2 leads to V(IV) complexes as $VO(SO_4)_2^{2-}$, $VO(SO_4)_3^{4-}$, and polymeric forms of these.[8,9] At lower temperatures, that is, below around 440 °C, V(IV) and, in some cases, V(III) compounds start precipitating,[10] leading to deactivation of the industrial catalyst.[11−14] Previously, we have isolated and structurally characterized several of these compounds, for example, of V(IV),[15−17] $Na_2VO(SO_4)_2$,

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(1) Frazer, J. H.; Kirkpatrick, W. J. *J. Am. Chem. Soc.* **1940**, *62*, 1659.

(2) Topsoe, H. F. A.; Nielsen, A. *Trans Dan. Acad. Tech. Sci.* **1947**, *1*, 18.

(3) Villadsen, J.; Livbjerg, H. *Catal. Rev.—Sci. Eng.* **1978**, *17*, 203.

(4) Fehrmann, R.; Gaune-Escard, M.; Bjerrum, N. J. *Inorg. Chem.* **1986**, *25*, 1132.

(5) Folkmann, G. E.; Hatem, G.; Fehrmann, R.; Gaune-Escard, M.; Bjerrum, N. J. *Inorg. Chem.* **1993**, *32*, 1559.

(6) Boghosian, S.; Borup, F.; Chrissanthopoulos, A. *Catal. Lett.* **1997**, *48*, 145.

(7) Hansen, N. H.; Fehrmann, R.; Bjerrum, N. J. *Inorg. Chem.* **1982**, *21*, 744.

(8) Rasmussen, S. B.; Eriksen, K. M.; Fehrmann, R. *J. Phys. Chem. B* **1999**, *103*, 11282.

(9) Karydis, D. A.; Eriksen, K. M.; Fehrmann, R.; Boghosian, S. *J. Chem. Soc., Dalton Trans.* **1994**, 2151.

(10) Boghosian, S.; Fehrmann, R.; Bjerrum, N. J.; Papatheodorou, G. N. *J. Catal.* **1989**, *119*, 121.

(11) Eriksen, K. M.; Fehrmann, R.; Bjerrum, N. J. *J. Catal.* **1991**, *132*, 263.

(12) Eriksen, K. M.; Karydis, D. A.; Boghosian, S.; Fehrmann, R. *J. Catal.* **1995**, *155*, 32.

(13) Masters, S. G.; Chrissanthopoulos, A.; Eriksen, K. M.; Boghosian, S.; Fehrmann, R. *J. Catal.* **1997**, *166*, 16.

(14) Oehlers, C.; Fehrmann, R.; Masters, S. G.; Eriksen, K. M.; Sheinin, D. E.; Bal'zhinimaev, B. S.; Elokhin, V. I. *Appl. Catal.* **1996**, *147* (1), 127.

(15) Fehrmann, R.; Boghosian, S.; Papatheodorou, G. N.; Nielsen, K.; Berg, R. W.; Bjerrum, N. J. *Inorg. Chem.* **1990**, *29*, 3294.

(16) Fehrmann, R.; Boghosian, S.; Papatheodorou, G. N.; Nielsen, K.; Berg, R.; Bjerrum, N. J. *Inorg. Chem.* **1989**, *28*, 1847.

(17) Boghosian, S.; Eriksen, K. M.; Fehrmann, R.; Nielsen, K. *Acta Chem. Scand.* **1995**, *49*, 703.

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$K_4(VO)_3(SO_4)_5$, β-$VOSO_4$; of V(III),[18−21] $NaV(SO_4)_2$, $Na_3V(SO_4)_3$, $KV(SO_4)_2$, $CsV(SO_4)_2$; and of mixed valence V(IV)−V(V),[22] $K_6(VO)_4(SO_4)_8$. Concerning compounds of V(V), it has proven much more difficult to obtain suitable crystals for X-ray investigations, for example, because the molten $M_2S_2O_7$−V_2O_5 systems frequently form amorphous phases by cooling. However, during our previous studies[23−25] of the phase diagrams of the binary $M_2S_2O_7$−V_2O_5 systems (M = K, Rb, Cs), we have succeeded in isolating crystals of the dimeric V(V) compounds $M_4(VO)_2O(SO_4)_4$ and the Cs compound $CsVO_2SO_4$, which probably also have K and Rb analogues. So far, the crystal structure of $Cs_4(VO)_2O(SO_4)_4$ has been solved,[26] and ongoing[27] X-ray investigations of the K and Rb analogues exhibit a similar structure, that is, two distorted VO_6 octahedra form from short bonded V═O oxygens and bidentate coordinate sulfate and are joined by a common V−O−V bridging oxygen. Also, the structure of $CsVO_2SO_4$ has very recently[28] been solved, and here, the VO_6 octahedra are linked by bidentate bridging sulfate groups rather than through a common oxygen atom.

The present study is concerned with a new V(V) compound $Na_2K_6(VO)_2(SO_4)_7$, isolated previously[29] during our phase studies of the catalyst model system $M_2S_2O_7$−V_2O_5 (M = 80% K + 20% Na) together with the mixed valence V(IV)−V(V) compound $K_6(VO)_4(SO_4)_8$ as described in some detail in the X-ray investigation[22] of that compound.

Besides the interesting structural aspects of V(V) oxo sulfato compounds, these compounds may also play an important role in the reaction mechanism of SO_2 oxidation as reviewed recently.[30]

Experimental Section

Materials. The hygroscopic alkali pyrosulfates $Na_2S_2O_7$ and $K_2S_2O_7$ were prepared from their corresponding nonhygroscopic peroxodisulfates, $K_2S_2O_8$ (Merck, pro analysi) and $Na_2S_2O_8$ (Fluka, pro analysi), by thermal decomposition in dry nitrogen atmosphere at 300 °C, and the purity was checked by Raman spectroscopy as earlier described.[7,10] The alkali pyrosulfates were kept in sealed ampules, only opened and handled in a drybox with a controlled water content below around 5 ppm. The V_2O_5 used (CERAC, pure, 99.9%) was not hygroscopic and could be stored and handled also outside the drybox.

Table 1. Crystallographic Data for $Na_2K_6(VO)_2(SO_4)_7$

chemical formula $Na_2K_6(VO)_2(SO_4)_7$	fw 1086.9 g mol^{-1}
$a = 9.540(3)$ Å	space group $P4_32_12$ (No. 96)
$c = 29.551(5)$ Å	$T = 25$ °C
$V = 2689.5(13)$ Å^3	$\lambda = 0.710xx$ Å
$Z = 4$	$D_{calcd} = 2.684$ g cm^{-3}
	$R_1{}^a = 0.1472$ (0.0463)
	$R_2{}^b = 0.1068$ (0.0860)

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. R-values in parentheses refer to observed reflections only $[I > 2\sigma(I)]$. [b] $R_2 = [\sum w(|F_o|^2 - |F_o|^2)^2/\sum w(|F_o|^2)^2]^{1/2}$.

Synthesis of Crystalline $Na_2K_6VO_2(SO_4)_7$. During the study[29] of the phase diagram of the $M_2S_2O_7$−V_2O_5 (M = 80% K and 20% Na) pseudobinary catalyst model system, attempts were made to isolate possible compounds formed in the system. The phase diagram exhibits a maximum at the mole fraction $X_{V_2O_5} = 0.25$, probably corresponding to the mixed cation compound $M_3VO_2SO_4S_2O_7$ (M = 80% K and 20% Na) analogous to the earlier claimed[31] compound $K_3VO_2SO_4S_2O_7$ possibly formed in the $K_2S_2O_7$−V_2O_5 system.[23] Thus, the melt components $Na_2S_2O_7$, $K_2S_2O_7$, and V_2O_5 corresponding to the mole fraction $X_{V_2O_5} = 0.24$ were loaded into an ampule in the drybox, sealed, and heated to 325 °C, that is, just below the liquidus temperature of this composition.[29] The temperature was thereafter decreased stepwise during several hours to the solidus temperature of around 300 °C and finally cooled to room temperature. The ampule was inspected in an optical microscope. Several phases were observed: dark needle shaped pleochroistic crystals of the mixed valence V(IV)−V(V) compound $K_6(VO)_4(SO_4)_8$ as earlier described and characterized structurally,[22] a dark reddish brown amorphous phase containing most of the V(V) present, and, in this matrix, some red-brown crystals of which a suitable single crystal was picked for the X-ray investigation described here.

Spectroscopy. The powder IR spectrum was taken in KBr (∼1 mg in 100 mg of KBr) on a Perkin- Elmer 1000 infrared Fourier transform spectrometer. Raman spectra were obtained with the 647.1 nm line of a Spectra Physics argon ion laser on a sample of the crystalline compound.

X-ray Investigation. A single crystal with the dimensions 0.025 × 0.075 × 0.1 mm^3 was selected for the X-ray investigation and covered completely by epoxy glue.

Intensity data were measured at 20 °C on an Enraf-Nonius CAD-4F diffractometer using monochromated Mo Kα radiation and the ω-scan technique. The cell dimensions were determined by least-squares refinements based on the settings of 25 reflections. The intensities were corrected for Lorentz and polarization effects, but no correction for absorption was applied. The structure was solved by Patterson techniques, and positional and anisotropic thermal parameters were refined by full-matrix least-squares methods[32] based on $|F|^2$, with a weight function given as $w = (\sigma^2(|F_o|^2) + 0.2088P + (0.0427P)^2)^{-1}$, where $P = (2|F_o|^2 + |F_c|^2)/3$. Crystal data and R-values are given in Table 1. The final positional parameters are listed in Table 2. Lists of anisotropic temperature factors and lists of observed and calculated structure factors may be obtained from the authors.

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(18) Fehrmann, R.; Boghosian, S.; Papatheodorou, G. N.; Nielsen, K.; Berg, R. W.; Bjerrum, N. J. *Acta Chem. Scand.* **1991**, *45*, 961.

(19) Boghosian, S.; Fehrmann, R.; Nielsen, K. *Acta Chem. Scand.* **1994**, *48*, 724.

(20) Fehrmann, R.; Krebs, B.; Papatheodorou, G. N.; Berg, R. W.; Bjerrum, N. J. *Inorg. Chem.* **1986**, *25*, 1571.

(21) Berg, R. W.; Boghosian, S.; Bjerrum, N. J.; Fehrmann, R.; Krebs, B.; Sträter, N.; Mortensen, O. S.; Papatheodorou, G. N. *Inorg. Chem.* **1993**, *32*, 4714; **1994**, *33*, 402.

(22) Eriksen, K. M.; Nielsen, K.; Fehrmann, R. *Inorg. Chem.* **1996**, *35*, 480.

(23) Folkmann, G. E.; Eriksen, K. M.; Fehrmann, R.; Gaune-Escard, M.; Hatem, G.; Lapina, O. B.; Terskikh, V. *J. Phys. Chem. B* **1998**, *102*, 24.

(24) Abdoun, F.; Hatem, G.; Gaune-Escard, M.; Eriksen, K. M.; Fehrmann, R. *J. Phys. Chem. B* **1999**, *103*, 3559.

(25) Folkmann, G. E.; Hatem, G.; Fehrmann, R.; Gaune-Escard, M.; Bjerrum, N. J. *Inorg. Chem.* **1991**, *30*, 4057.

(26) Nielsen, K.; Fehrmann, R.; Eriksen, K. M. *Inorg. Chem.* **1993**, *32*, 4825.

(27) Nielsen, K.; Eriksen, K. M.; Fehrmann, R. In preparation.

(28) Eriksen, K. M.; Nielsen, K.; Fehrmann, R. In preparation.

(29) Karydis, D. A.; Boghosian, S.; Fehrmann, R. *J. Catal.* **1994**, *145*, 312.

(30) Lapina, O. B.; Bal'zhinimaev, B. S.; Boghosian, S.; Eriksen, K. M.; Fehrmann, R. *Catal. Today* **1999**, *51*, 469.

(31) Glazyrin, M. P.; Krasil'nikov, V. N.; Ivakin, A. A. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1980**, *25*, 1843.

(32) Sheldrick, G. M. *SHELXS-86 AND SHELXL-93*, *Programs for Crystal Structure Determination*; University of Göttingen: Göttingen, Germany, 1990, 1993.

Table 2. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for the Atoms in $Na_2K_6(VO)_2(SO_4)_7$ (in Å^2)

atom	x	y	z	U_{eq}[a]
V	0.3274(2)	0.4304(2)	−0.18522(5)	0.0127(3)
S1	0.3863(2)	0.1483(2)	−0.13135(7)	0.0140(5)
S2	0.0599(2)	0.2663(2)	−0.22342(8)	0.0183(5)
S3	0.6466(2)	0.4895(2)	−0.15426(8)	0.0183(5)
S4	0.2871(2)	0.7129(2)	−0.25000	0.0134(7)
Na	0.1598(4)	0.7276(4)	0.17773(12)	0.0261(9)
K1	0.1015(2)	0.4170(2)	0.26897(7)	0.0226(5)
K2	0.4404(3)	0.4360(3)	0.06224(8)	0.0478(7)
K3	0.8236(2)	0.4919(3)	0.15415(8)	0.0430(7)
O1	0.4082(6)	0.3527(6)	−0.2233(2)	0.0230(15)
O2	0.2160(6)	0.5354(6)	−0.1261(2)	0.0167(14)
O3	0.1421(6)	0.3961(6)	−0.2063(2)	0.0191(15)
O4	0.2996(6)	0.2767(6)	−0.1442(2)	0.019(2)
O5	0.3217(7)	0.6188(6)	−0.2116(2)	0.026(2)
O6	0.4825(6)	0.4921(6)	−0.1513(2)	0.0151(14)
O7	0.4785(6)	0.1129(6)	−0.1687(2)	0.023(2)
O8	0.4598(7)	0.1820(7)	−0.0906(2)	0.033(2)
O9	0.1569(6)	0.1598(6)	−0.2386(2)	0.0246(15)
O10	−0.0282(7)	0.3197(7)	−0.2594(2)	0.035(2)
O11	−0.0217(7)	0.2165(7)	−0.1847(2)	0.030(2)
O12	0.6876(6)	0.3935(6)	−0.1894(2)	0.028(2)
O13	0.6918(6)	0.4490(8)	−0.1096(2)	0.033(2)
O14	0.6856(6)	0.6333(6)	−0.1646(2)	0.035(2)
O15	0.3103(8)	0.8538(6)	−0.2344(2)	0.040(2)

[a] $U_{eq} = a\sum_i\sum_j U_{ij}\, a^*_i a^*_j \mathbf{a}_i\_\mathbf{a}_j$.

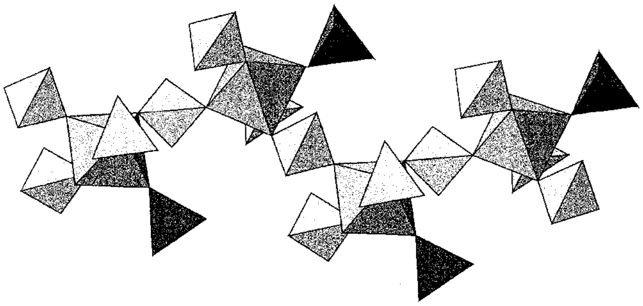

Figure 1. Zigzag chains of sulfur bridged vanadium octahedra. Dark tetrahedra have the central sulfur atom situated on the 2-fold axis and form bridges to the chains in the perpendicular direction.

Table 3. Bond Lengths in $Na_2K_6(VO)_2(SO_4)_7$ (in Å)

V−O1	1.552(6)	S2−O9	1.445(6)
V−O6	1.881(6)	S2−O10	1.447(6)
V−O3	1.903(6)	S2−O11	1.464(6)
V−O4	1.920(6)	S2−O3	1.551(6)
V−O5	1.960(6)		
V−O2	2.276(5)	S3−O12	1.438(6)
		S3−O13	1.442(6)
S1−O8	1.429(6)	S3−O14	1.454(6)
S1−O7	1.451(6)	S3−O6	1.568(6)
S1−O2	1.471(6)		
S1−O4	1.526(6)	S4−O15	1.438(7) (2×)
		S4−O5	1.485(6) (2×)

Table 4. Bond Angles in $Na_2K_6(VO)_2(SO_4)_7$ (deg)

O1−V−O6	98.3(3)	O9−S2−O10	113.1(4)
O1−V−O3	98.2(3)	O9−S2−O11	110.8(4)
O6−V−O3	163.5(3)	O10−S2−O11	112.3(4)
O1−V−O4	99.3(3)	O9−S2−O3	109.8(3)
O6−V−O4	90.7(3)	O10−S2−O3	104.6(4)
O3−V−O4	87.0(3)	O11−S2−O3	105.9(3)
O1−V−O5	99.4(3)		
O6−V−O5	86.9(3)	O12−S3−O13	114.1(4)
O3−V−O5	90.1(3)	O12−S3−O14	112.4(4)
O4−V−O5	161.3(3)	O13−S3−O14	111.6(4)
O1−V−O2	176.4(3)	O12−S3−O6	108.8(4)
O6−V−O2	79.7(2)	O13−S3−O6	104.6(4)
O3−V−O2	83.8(2)	O14−S3−O6	104.6(3)
O4−V−O2	77.7(2)		
O5−V−O2	83.6(2)	O15−S4−O15	113.0(6)
		O15−S4−O5	106.6(4) (2×)
O8−S1−O7	113.3(4)	O15−S4−O5	111.1(4) (2×)
O8−S1−O2	111.3(4)	O5−S4−O5	108.4(5)
O7−S1−O2	110.3(3)		
O8−S1−O4	107.2(4)		
O7−S1−O4	109.0(3)		
O2−S1−O4	105.4(3)		
O8−S1−O2	111.3(4)		
O7−S1−O2	110.3(3)		
O8−S1−O4	107.2(4)		
O7−S1−O4	109.0(3)		
O2−S1−O4	105.4(3)		

Discussion

Description of the Structure. Each asymmetric unit contains one vanadium(V) octahedron and $3^1/_2$ sulfate tetrahedra, one (S4) being situated on the 2-fold axis. Each vanadium is coordinated to 5 sulfate groups of which two are unidentately coordinated. The vanadium octahedra form sulfur (S1) bridged zigzag chains directed along *a* and *b* (Figure 1). A chain along *a* is linked to chains along *b* via the sulfur atom situated on the 2-fold axis, whereas there is no direct bridging between parallel chains.

The bond lengths and angles are given in Tables 3 and 4. The vanadium is hexacoordinated in a distorted octahedral arrangement with a short V−O bond of 1.552 Å, a long V−O bond of 2.276 Å trans to this, and four equatorial bonds in the range 1.881−1.960 Å. In Table 5, these values are compared to values of other V(V) oxosulfato vanadates found in the literature. It is obvious that the distortion from octahedral geometry is less pronounced in $Na_2K_6(VO)_2(SO_4)_7$ compared to the other compounds, where the distortion decreases from the left to the right in the table. Thus, the compounds containing the dioxovanadyl, VO_2^+, unit where both oxygens either are exclusively bonded to the vanadium atom or one of them is bridging between two V(V) centers exhibit large asymmetry. In these cases both of the V−O bond lengths of the VO_2^+ unit are short, indicating π character, leading to relatively large distortion of the horizontal plane of coordination compared to that of $Na_2K_6(VO)_2(SO_4)_7$. The absence of a cis oxygen in the VO^{3+} unit of the latter compound leads also to a more pronounced π character of the $V-O^{3+}$ bond as can be seen from the very short bond lengths for this compound (and the two similar VO^{3+} compounds) compared to the others.

Geometry of the SO_4^{2-} Groups. Regarding the coordination of the sulfate groups, the S2 and S3 sulfates are unidentately coordinated to the vanadium atom (by V−O3−S2 and V−O6−S3) with the S2−O3 and S3−O6 bonds of 1.551 and 1.568 Å being unusually long, longer than 118 out of 120 measured S−O distances in the sulfate groups of $K_4(VO)_3(SO_4)_5$, $KV(SO_4)_2$, $K_6(VO)_4(SO_4)_8$, $Na_2VO(SO_4)_2$, $Na_8(VO)_2(SO_4)_6$, $NaV(SO_4)_2$, $Na_3V(SO_4)_3$, $CsV(SO_4)_2$, $Cs_4(VO)_2O(SO_4)_4$, and β-$VOSO_4$.[15−22,26,35] The lengths of the remaining sulfur−oxygen bonds of S2 and S3 sulfates are

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(33) Richter V.-L.; Mattes, R. *Inorg. Chem.* **1991**, *30*, 4367.
(34) Richter, V.-L.; Mattes, R. Z. *Anorg. Allg. Chem.* **1992**, *611*, 158.
(35) Nielsen, K.; Boghosian, S.; Fehrmann, R.; Berg, R. W. *Acta Chem. Scand.* **1999**, *53*, 15.

Table 5. Selected Bond Lengths and Angles for Hexacoordinated V(V) Oxosulfato Vanadates[a] $K[VO_2(SO_4)(H_2O)_2]\cdot H_2O$ (**1**),[33] $KVO_2(SO_4)(H_2O)$ (**2**),[33] $Cs_4(VO)_2O(SO_4)_4$ (**3**),[26] $V_2O_3(SO_4)_2$ (**4**),[34] $KVO(SO_4)_2$ (**5**),[34] $NH_4VO(SO_4)_2$ (**6**),[34] $Na_2K_6(VO)_2(SO_4)_7$ (**7**)[b]

	1	**2**	**3**	**4**	**5**	**6**	**7**
V=O, Å	1.61−1.64	1.60	1.58	1.57	1.52	1.55	1.55
(O=V)-O_{tr}, Å	2.33	2.28	2.40	2.33	2.28	2.30	2.28
V−O_{eq}, Å	1.64−2.16	1.68−2.08	1.77−2.03	1.78−1.97	1.85−1.87	1.82−1.93	1.88−1.96
O=V−O_{eq}, deg	91.9−103.5	92.6−104.1	96.4−106.8	97.5−99.7	97−101	98−100	98.2−99.4
O_{eq}−V−O_{eq}, deg	80.1−96.9	82.0−96.8	69.5−103.0	81.7−98.7	79−101	88−90	86.9−90.7
O=V−O_{tr}, deg	169.2	169.0	163.8	178.7	174	177	176.4

[a] Key: tr, trans; eq, equatorial. [b] This work.

relatively short, in the range 1.438−1.464 Å. Sulfates S1 and S4 are bidentately coordinated to neighboring vanadium atoms (by V−O2−S1−O4−V and V−O5−S4−O5−V) and there are two S4 sulfates coordinated to each vanadium atom. This arrangement with two unidentate sulfates (S2 and S3) coordinated exclusively to one vanadium atom and three bidentate sulfates (S1 and two S4) bridging to two vanadium atoms satisfies the requirement for $3^1/_2$ sulfates per vanadium. Besides S2−O3 and S3−O6, also the S1−O4 bond is relatively long, probably because all three bonds involve oxygen strongly bonded in the equatorial plane of V(V), while the other S−O bonds of the three sulfur atoms either are uncoordinated or coordinated weakly (S1−O2) to the trans position of the other vanadium atom. It should be noted that the relatively large distortion of the sulfate groups found here, compared to those of the V(III), V(IV), and V(V) compounds listed previously, could be due to the expected lower electron density on the VO^{3+} unit in the present compound compared to the density on the central vanadium units of the other compounds. This leads to relatively shorter V−O and longer S−O bonds of the V−O−S units in the present compound.

Around the sulfur atoms, nearly tetrahedral angles have been found; however, they are deformed in such a way that O−S−O angles involving an oxygen atom bridging to vanadium are generally smaller than the ideal tetrahedral angle of 109.47°. This is believed to be due to repulsion from the short-bonded oxygens. The O−S−O angles *not* involving oxygen atoms bridging to vanadium increased to values above 109.47°. Generally, the S−O distances were found to depend on the angles in such a way that the larger the average of the three possible O−S−O angles involving a particular bond is, the smaller is the S−O distance of that bond. This is shown in Figure 2, where an approximately linear relationship (linear regression) is found which is similar to that observed for the 30 different sulfate groups in the $K_4(VO)_3(SO_4)_5$, $KV(SO_4)_2$, $K_6(VO)_4(SO_4)_8$, $Na_2VO(SO_4)_2$, $Na_8(VO)_2(SO_4)_6$, $NaV(SO_4)_2$, $Na_3V(SO_4)_3$, $CsV(SO_4)_2$, $Cs_4(VO)_2O(SO_4)_4$, and β-$VOSO_4$ structures.[15−22,26,35] This dependence indicates a general relationship between bond distances and hybridization of the central atom in tetrahedral groups as pointed out previously for the case of the sulfate group[16] as well as for the case of $AlBr_4^-$.[36,37]

Vibrational Spectra. If the $Na_2K_6(VO)_2(SO_4)_7$ crystal is considered to be composed of Na^+, K^+, VO^{3+}, and SO_4^{2-} ions, one should expect to observe the free group vibrations of the complex ions (here VO^{3+} and SO_4^{2-}), that is, a band due to the $\nu(V^V{=}O)$ stretching mode (above 1000 cm^{-1}) and bands near the positions of the four fundamentals (ν_1−ν_4) of the SO_4^{2-} ion that are known to span the following representation for a regular tetrahedral (T_d) configuration:

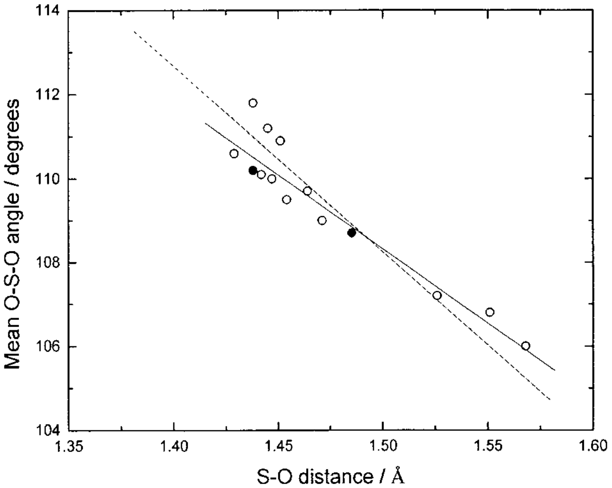

Figure 2. Plot of S−O distances for a particular bond versus the average of the three angles involving that bond and the other S−O bonds of the sulfate tetrahedron (○, ●). Points with 4-fold multiplicity are indicated by ●. The solid line is a regression for $Na_2K_6(VO)_2(SO_4)_7$. The dashed line is a regression for $K_4(VO)_3(SO_4)_5$, $KV(SO_4)_2$, $K_6(VO)_4(SO_4)_8$, $Na_2VO(SO_4)_2$, $Na_8(VO)_2(SO_4)_6$, $NaV(SO_4)_2$, $Na_3V(SO_4)_3$, $CsV(SO_4)_2$, $Cs_4(VO)_2O(SO_4)_4$, and β-$VOSO_4$.[15−22,26,35]

$$\Gamma_{vib} = A_1(\nu_1) + E(\nu_2) + 2F_2(\nu_3 + \nu_4)$$

All modes are Raman active, and only F_2 is IR allowed. In the usual approximation of weak couplings, modes labeled as ν_1 and ν_3 are bond stretchings and ν_2 and ν_4 are angle bendings. The wavenumbers of the fundamentals are well-known:[36] $\nu_1(A_1) \sim 983$ cm^{-1}, $\nu_2(E) \sim 450$ cm^{-1}, $\nu_3(F_2) \sim 1105$ cm^{-1}, and $\nu_4(F_2) \sim 611$ cm^{-1} according to Raman spectra of aqueous sulfate solutions. However, coordination of the sulfate ions and interactions with other ions in the crystal lattice are expected to reduce the symmetry, shift the fundamentals, and lift degeneracies of the sulfate modes. Furthermore, coordination of the vanadium atom and formation of VO_6 octahedra will give rise to (apart from the V=O stretch in the apical direction) bands due to V−O stretches in the equatorial plane and in the direction trans to V=O.

Infrared and Raman Spectra. The observed IR and Raman spectra are shown in Figures 3 and 4, and the band positions and tentative assignments are summarized in Table 6. As can be seen, many of the observed bands are common

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(36) Berg, R. W.; Poulsen, F. W.; Nielsen, K. *Acta Chem. Scand.* **1997**, *51*, 442.

(37) Berg, R. W. *Acta Chem. Scand.* **1997**, *51*, 455.

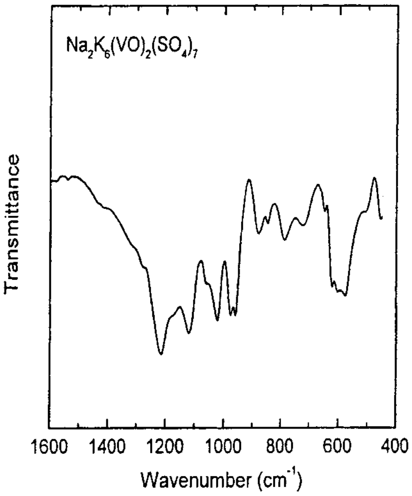

Figure 3. Infrared spectrum of $Na_2K_6(VO)_2(SO_4)_7$ powder in pressed KBr disk at room temperature. Resolution, ~5 cm^{-1}.

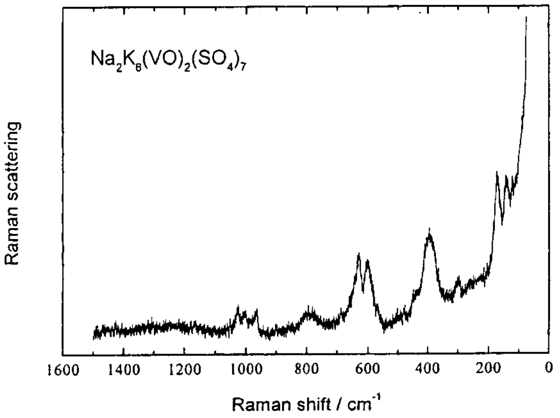

Figure 4. Raman spectrum of $Na_2K_6(VO)_2(SO_4)_7$ powder at room temperature. $\lambda_0 = 647.1$ nm; laser power, 180 mW; resolution, 6 cm^{-1}.

to both kinds of spectra. The characteristic V═O stretching is found at 1028 cm^{-1}, whereas a careful examination of the IR and Raman spectra leads to assignment of the S—O and V—O stretchings and of the split components of sulfate bendings. Extensive degeneracy of most of the normal modes must prevail.

Table 6. Infrared and Raman Bands (in cm^{-1}) for $Na_2K_6(VO)_2(SO_4)_7$ and Their Tentative Assignments[a]

IR powder in KBr disc	Raman powder ($\lambda_0 = 647.1$ nm)	tentative assignment
1320 w	1310 w	ν_3(str., SO_4^{2-})
1290 w		
1220 s	1230 w	
1185 w	1165 w	
1126 s		
1065 w		
1028 s	1028 m	ν(str., V=O^{3+})
	1005 m	ν_1(str., SO_4^{2-})[b]
980 s		
962 s	968 m	
880 m	895 w	ν[(V-O)-S][c]
875 w		
850 m	860 w	
792 m	790 m	
725 m		
700 w		
670 w	685 w	ν_4(bend., SO_4^{2-}) and ν(V-O_{eq})
655 m		
630 m	630 s	
610 w	605 s	
594 s		
580 w	570 w	
510 m	490 w	ν_2(bend., SO_4^{2-})
460 m	445 w	
	396 s	ν(V-O_{eq})
	302 m	ν[(O=V)-O_{tr}]
	260 w	ν_L[d]
	174 s	
	140 s	

[a] Intensity codes: s, strong; m, medium; w, weak. [b] S—$O_{terminal}$ modes corresponding to S—O bond lengths in the range 1.429—1.464 Å (see Table 3). [c] S—$O_{bridging}$ modes corresponding to S—O bond lengths up to 1.568 Å (see Table 3). [d] Lattice mode.

Relation to Catalysis. The compound $Na_2K_6(VO)_2(SO_4)_7$ has the alkali to vanadium molar ratio M/V = 4 where M = 75% K + 25% Na. This stoichiometry is very close to a typical industrial SO_2 oxidation catalyst (VK 38, Haldor Topsøe A/S, Denmark) where M/V = 3.8 and M = 80% K + 20% Na. However, in the molten state, our recent Raman, UV—vis, and NMR spectroscopic and electrochemical studies[6,8,9,39,40] give strong evidence for the presence of the dimeric V(V) complex $(VO)_2O(SO_4)_4^{4-}$ as the dominating V(V) species in the whole composition range up to M/V = 2, that is, $X_{V_2O_5} = 0.33$ in the $K_2S_2O_7$—V_2O_5 and the $Cs_2S_2O_7$—V_2O_5 binary systems. It is hard to believe that substituting 20% of $K_2S_2O_7$ with $Na_2S_2O_7$ should lead to a very different complex chemistry of the solution forming, for example, $(VO)_2(SO_4)_7^{8-}$ or possibly $VO(SO_4)_3^{3-}$ and $VO(SO_4)_4^{5-}$. This will be elucidated through planned spectroscopic studies of these melts.

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Supporting Information Available: Crystallographic data in CIF format. X-ray data (including experimental details, atomic coordinates, complete bond lengths and angles, and anisotropic thermal parameters). This material is available free of charge via the Internet at http://pubs.acs.org.

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(38) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Wiley: New York, 1986.

(39) Lapina, O. B.; Mastikhin, V. M.; Shubin, A. A.; Eriksen, K. M.; Fehrmann, R. *J. Mol. Catal.* **1995**, *99*, 123.

(40) Boghosian, S.; Chrissanthopoulos, A.; Fehrmann, R. *J. Phys. Chem. B* **2002**, *106*, 49.