Crystal Structure and Spectroscopic Characterization of $K_6(VO)_4(SO_4)_8$ Containing Mixed-Valent Vanadium(IV)−Vanadium(V)

Kim Michael Eriksen,[1a] Kurt Nielsen,[1b] and Rasmus Fehrmann*,[1a]

Chemistry Departments A and B, Technical University of Denmark, DK-2800 Lyngby, Denmark

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Pleochroistic crystals (dark green to colorless) of a mixed-valence V(IV)−V(V) compound, $K_6(VO)_4(SO_4)_8$, suitable for X-ray determination have been obtained from the catalytically important $K_2S_2O_7-V_2O_5/SO_2-O_2-SO_3-N_2$ molten salt−gas system, at ~400 °C. The compound crystallizes in the monoclinic space group $P2_1$ (No. 4) with $a = 8.931(2)$ Å, $b = 18.303\ (3)$ Å, $c = 9.971(2)$ Å, $\beta = 90.11(2)°$, and $Z = 2$. It contains two rather similar V(IV)−V(V) pairs of VO_6 octahedra distorted as usual having a short V−O bond of around 1.57 Å, a long bond of around 2.40 Å trans to this, and four equatorial bonds around 2.00 Å. The bond lengths of the V^VO_6 octahedra are significantly shorter than those found for the $V^{IV}O_6$ octahedra. The eight different SO_4^{2-} groups are all bridging bidentate between the V(IV) and V(V) atoms; a third oxygen is coordinated to a vanadium atom of a neighboring chain trans to the short V═O bond, and the fourth oxygen remains uncoordinated. The measured bond distances and angles show a considerable distortion of the SO_4 tetrahedra. This is confirmed by the IR spectra of the compound, where large shift and splitting of the sulfate ν_3 bands up to wave numbers of around 1300 cm^{-1} is observed. The ESR spectra of the compound exhibit weak anisotropy with $g_{iso} = 1.972 \pm 0.002$ and $\Delta B_{pp} = 65 \pm 2$ G. The compound may cause the deactivation for industrial sulfuric acid catalysts observed around 400 °C in highly converted $SO_2-O_2-N_2$ gas mixtures.

Introduction

This paper constitutes a part of our thorough study of the molten salt gas system $M_2S_2O_7-V_2O_5/SO_2-O_2-SO_3-N_2$ (M = Na, K, or Cs) at 300−600 °C. This system is a realistic model of the catalyst used for the production of sulfuric acid, *i.e.* catalyzing the reaction $SO_2 + {}^1/_2O_2 \rightleftharpoons SO_3$. Previous papers have dealt with properties of the pyrosulfate solvent melt, the complex formation of vanadium in the melts and the compounds that can be isolated from the model system.[2,3] Also industrial catalysts are under investigation, including *in situ* spectroscopic and activity measurements of working catalysts.[4,5,7] In this way the chemistry of model melts and real catalysts can be compared and linked together.

An important part of the work has been the study of compounds that precipitate from the model melts[4] and from the melts of real catalysts.[5,7] In the case of real catalysts the compounds are distributed in the fine pores of an inert solid support of kieselguhr (diatomaceous earth).[8] This precipitation has proven[4,5] to cause the deactivation of industrial catalysts and model melts below ~440 °C. The deactivation has so far been studied in unconverted synthesis gas, *i.e.* 10% SO_2, 11% O_2, and 79% N_2, and the V(IV) compounds $NaVO(SO_4)_2$, $K_4(VO)_3(SO_4)_5$, and $Cs_2(VO)_2(SO_4)_3$ and the V(III) compounds $NaV(SO_4)_2$, $KV(SO_4)_2$, and $CsV(SO_4)_2$ have been isolated and characterized[9−14] by X-ray diffraction and spectroscopic methods. However, the gas entering the last bed of an industrial four-bed converter (without interstage SO_3 absorption), has a composition around 1% SO_2, 9% SO_3, 7% O_2, and 83% N_2 which corresponds to 90% conversion of the unconverted synthesis gas obtained through the first three catalyst beds. The present investigation describes our first attempt to isolate and characterize compounds that are formed in model melts and catalysts during deactivation in preconverted synthesis gas. We have investigated the $K_2S_2O_7-V_2O_5$ system in preconverted synthesis gas and isolated a mixed-valence V(IV)−V(V) compound, $K_6(VO)_4(SO_4)_8$. The crystal structure and IR and ESR spectroscopic data for the compound are presented.

Experimental Section

The equipment used for the synthesis included a gas mixing unit where SO_2, O_2, and N_2 could be mixed in any desired proportion by means of Brooks mass flow controllers (Model 5810 or 5850). When a very small flow was desired, *e.g.* around 1 mL/min, the gas mixture was fed from a premixed bottle, as the mass flow controllers are unstable in the low flow range. The gas mixture was dried by P_2O_5 (Sicapent, Merck) and led to a quartz preconverter, which was heated to ~520 °C. The preconverter contained either an industrial catalyst (VK 38 from Haldor Topsøe A/S, Denmark) or platinated silica made in the laboratory as earlier descibed.[4] The composition of the gas after absorption of SO_3 in H_2SO_4 (95−99%) was checked by a Shimadzu GC-8APT gaschromatograph equipped with a Supelco Chromosorp 102

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(1) (a) Chemistry Department A, Technical University of Denmark. (b) Chemistry Department B, Technical University of Denmark.

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column. The gas mixture was led to the reactor cell made of Pyrex where it, from below, passed a porous sintered-glass filter disk, bubbled through the melt before finally being led to the SO_3 absorber, the gaschromatograph and/or the vent. The reactor cell was mounted in a tiltable transparent double-walled, water-cooled quartz furnace equipped with a heating coil and regulated to within ±3 °C at 200−500 °C by an EUROTHERM E818 controller. This controller also allowed a programmed linear temperature change of the furnace, *e.g.* during the night. Further details of the experimental setup and the reactor cell can be found elsewhere.[4,7,10] The flow in the reactor cell could be reversed whereby the melt was filtered and the crystals isolated on the filter disk.

Materials. Dry $K_2S_2O_7$ was made by thermal decomposition of $K_2S_2O_8$ (Merck, pro analysi) as described earlier[15] and was kept on sealed ampules until loaded into the reactor cell in the drybox. The nonhygroscopic V_2O_5 was from Cerac (pure, 99.9%). Commercial gasses in steel-bottles were used: SO_2 (>99.9%), O_2 (99.8%, 0.2% Ar + N_2), and N_2 (<40 ppm H_2O + O_2).

Synthesis of Crystalline $K_6(VO)_4(SO_4)_8$. The compound has been obtained in three ways.

A. The two components of the melt, $K_2S_2O_7$ and V_2O_5, were weighed in the molar ratio K/V = 4.5 and added to the reactor cell in the drybox. The melt volume (density obtained from ref 16) did not exceed 1.5 mL in order to prevent foaming of the melt and to avoid a possible blocking of the exit tube. For the same reason the gas flow was kept low, *i.e.* in the range 8−15 mL/min. The reactor cell was transferred from the drybox to the quartz furnace and the inlet and outlet tubes quickly connected to the gas supply and the vent, respectively. The cell was then heated in the gas stream to 450 °C, which is well above the melting point of the mixture. The inlet gas composition corresponded to 90% preconverted standard synthesis gas, *i.e.* 1% SO_2, 9% SO_3, 6.5% O_2, and 83.5% N_2. After the flow was adjusted, the temperature was decreased continuously to 400 °C overnight. Thereafter, it was further cooled to 360 °C in 3 h by steps of 5−10 °C. Finally, it was reheated stepwise in the same way to 390 °C, where the gas flow was reversed and the melt filtered, leaving some crystals of the compound in the partly solidified bulk on the filter disk. The reactor cell was cooled, the inlet and outlet tubes closed with o-ring tightened joints whereafter the cell was transferred to the drybox. Here crystals could be scraped out through the outlet tube by a stainless steel pin or by cutting the reactor open just above the sintered disk with a glass saw.

The hygroscopic needle-shaped crystals were kept in a sealed ampule. The crystals exhibit a pronounced pleochroism, being almost black in one orientation and transparent in another.

B. The compound could also be obtained by an analogous procedure, where the gas composition was 10% SO_2, 11% O_2, and 79% N_2, *i.e.* not preconverted, but the flow was kept very low (~1 mL/min) leading to a high conversion due to the catalytic activity of the melt. The temperature was lowered from 450 to 410 °C overnight. Thereafter, the cell was reheated to 420 °C in order to melt most of the solidified bulk, and the melt could then be filtered by reversing the flow, leaving a rather large crop of well separated crystals on the filter disk. In this case the initial melt had the composition K/V = 4.7 corresponding to the eutectic mixture of the binary $K_2S_2O_7-V_2O_5$ system.[17,18]

C. During the construction[6] of the phase diagram of the $M_2S_2O_7-V_2O_5$ (M = 80% K + 20% Na) system, attempts were made to isolate the compound that seems to be formed at $X_{V_2O_5} = 0.25$ (M/V = 3), *i.e.* at the local maximum in the phase diagram. Melt components, with the composition $X_{V_2O_5} = 0.24$, were mixed in an ampule and sealed under vacuum. The ampule was heated to around 325 °C *i.e.* just below the liquidus temperature. During several hours, the temperature was then decreased stepwise to the solidus temperature (around 300 °C), and finally the ampule was cooled to room temperature. The ampule was inspected under microscope, and a few dark pleochroistic needle shaped crystals of $K_6(VO)_4(SO_4)_8$ were identified together with a dark reddish brown amorphous phase that presumably contained most of the vanadium and in the form of V(V). A small quantity of red-brown crystals was also found, and ongoing X-ray investigations have revealed it to be the mixed cation V(V) salt $(Na,K)_8(VO)_2(SO_4)_7$. The alkali composition has not been settled yet. The small part of the vanadium reduced from V(V) to V(IV) has presumably appeared due to the autodissociation of V(V) to V(IV) and O_2 in the ampule that contained no oxidizing atmosphere. Furthermore, the melt also contained $Na_2S_2O_7$, where sodium is known[19] to destabilize the oxidizing $S_2O_7^{2-}$ ion.

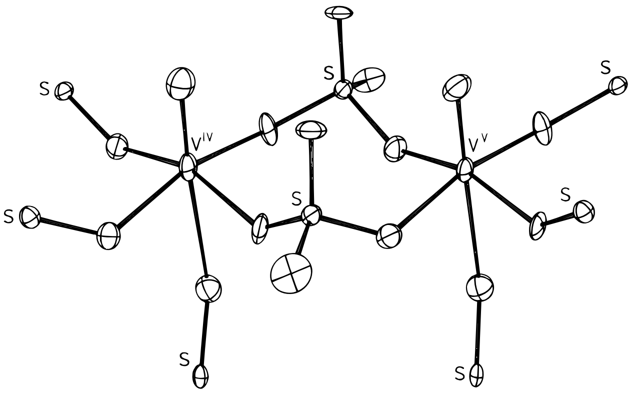

Figure 1. Plot of a V(IV)−V(V) pair, i.e. V1a−V1b, in the structure of $K_6(VO)_4(SO_4)_8$ (~ 1/4 of the unit cell).

Table 1. Crystallographic Data for $K_6(VO)_4(SO_4)_8$ Where *R* Values in Parentheses Are for Observed Reflections, $I > 2\sigma(I)$

fw	1270.84 g mol^{-1}	abs cor	empirical
crystal syst	monoclinic	t_{min}	0.680
space group	$P2_1$, No. 4	t_{max}	0.732
a, Å	8.931(2) Å	data collcn range	0° < θ < 35°; $h, k \geq 0$
b, Å	18.303(3) Å		
c, Å	9.971(2) Å	no. of reflcns measd	7340
β, deg	90.11(2)°	no. of obsd reflcns, $I > 2\sigma(I)$	4875
Z	2		
V, Å^3	1629.9(6) Å^3	extinction coeff	0.0024(2)
T, °C	20 °C	weight function, $P = \frac{1}{3}(F_o^2 + 2F_c^2)$	$1/[\sigma^2(F_o^2) + (0.0364P)^2 + 0.8774P]$
ρ_{calc}, g cm^{-3}	2.589		
λ, Å	0.710 73 Å (Mo Kα)		
		no. of parameters	489
cryst size, mm	0.08 × 0.12 × 0.27	no. of restraints	13
		R_1[a]	0.0814 (0.0330)
μ, cm^{-1}	25.19	R_2[b]	0.0837 (0.0703)
		residual charge density (max,min), e/Å^3	+1.161, −1.272

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_2 = [\Sigma w|F_o^2 - F_c^2|^2/\Sigma|F_o^2|^2]^{1/2}$.

Spectroscopy. The powder IR spectrum was taken in KBr (1.3 mg in 100 mg KBr) on a Bomem DA3.26 FTIR spectrometer. Resolution was ca. 1 cm^{-1}. The EPR spectrum was recorded on a modified JEOL JES-ME-1X X-band spectrometer.

X-ray Investigation

Determination of the Crystal Structure. A needle shaped single crystal with the dimensions 0.08 × 0.12 × 0.27 mm was examined. It was protected from the atmosphere by a cover of epoxy glue.

A total of 7340 independent reflections with $\theta \leq 25°$ and $h, k \geq 0$ were measured at 20 °C on an Enraf-Nonius CAD-4F four-circle diffractometer using monochromated Mo Kα-radiation and the ω-scan technique. The cell dimensions were determined by least-squares refinement based on the setting of 25 high-order reflections. The data were corrected for Lorentz and polarization effects. Absorption correction was carried out by an empirical method,[20] where the crystal

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shape is approximated by an ellipsoid and the size (in units of μ^{-1}) and orientation are treated as parameters. The refinement of the parameters is based on ψ-scans on 11 reflections and their symmetry equivalents, which amounts to 427 observations. The quantity minimized was $R = \sum w(I_{\mathrm{obs}} - I_{\mathrm{corr}}A)^2$, where A is the absorption coefficient. The minimization problem was accomplished by the SIMPLEX method.[21] The initial and final values of $R_{\mathrm{w}} = (R/\sum wI_{\mathrm{obs}}^2)^{1/2}$ are 0.037 and 0.022, respectively. An estimate of the linear absorption coefficient, μ, may be found as the cubic root of the ratio between the volume of the ellipsoid and the volume of the crystal. A value of 29.4 cm^{-1} was obtained, which is close to the actual value of 25.19 cm^{-1}. The minimum and maximum transmission coefficients are 0.680 and 0.732, respectively.

The crystal structure was solved by Patterson and Fourier techniques, and the structural parameters were refined by full-matrix least-squares methods based on F^2.[23] A total of seven reflections were omitted from the refinements either because of a very negative value or because of an outstanding discrepancy. During refinement, restraints were applied to O12a and O12b to prevent these anisotropic temperature factor parameters from becoming non-positive definite. The crystal possesses an approximate translation symmetry of ${}^1/_2\mathbf{c}$. This leads to two possible origins: (0,0,0) and $(0,0,{}^1/_4)$. Because almost all z-coordinates are approximate multiples of 1/8, both cases refine to the same structure. The crystal is twinned with coinciding (hkl) and $(\bar{h}kl)$ reflections, as shown by refinement of all possible twin combinations. The twin scale factor for the second component is 0.101(1), and inclusion of this parameter caused a significant decrease in $R_{\mathrm{w}}(F^2)$ from 0.1362 to 0.0837.

Crystal data are given in Table 1. The final positional parameters are listed in Table 2. Details of the data collection and the thermal parameters and further details on the structure are available as Supporting Information.

Table 2. Coordinates of the Atoms in $\mathrm{K_6(VO)_4(SO_4)_8}$[a–c]

atom	*x/a*	*y/b*	*z/c*	U_{eq},[d] Å^2
V1a	0.0400(1)	−0.3165(1)	0.1207(1)	0.0156(2)
V1b	0.0289(1)	−0.3145(1)	0.6218(1)	0.0136(2)
V2a	0.4700(1)	−0.6850(1)	0.1295(1)	0.0137(2)
V2b	0.4599(1)	−0.6798(1)	0.6277(1)	0.0147(2)
S1a	−0.3664(2)	−0.2884(1)	−0.3745(1)	0.0102(3)
S1b	−0.3636(2)	−0.2877(1)	−0.8758(1)	0.0107(3)
S2a	0.1332(2)	−0.2088(1)	0.8725(2)	0.0110(3)
S2b	0.1348(2)	−0.2080(1)	0.3771(2)	0.0112(3)
S3a	0.4976(2)	−0.0758(1)	0.1124(1)	0.0146(3)
S3b	0.4986(2)	−0.0752(1)	0.6244(1)	0.0151(3)
S4a	−0.0039(2)	−0.4204(1)	0.3728(2)	0.0146(3)
S4b	−0.0043(2)	−0.4228(1)	0.8639(2)	0.0132(3)
K1a	−0.0784(2)	−0.1180(1)	−0.8600(2)	0.0284(3)
K1b	−0.0761(2)	−0.1144(1)	−0.3795(2)	0.0319(4)
K2a	−0.2408(2)	−0.4969(1)	−0.8803(2)	0.0240(2)
K2b	−0.2564(3)	−0.5001(1)	−0.3703(2)	0.0241(2)
K3a	−0.4193(2)	0.1181(1)	0.1117(2)	0.0320(4)
K3b	−0.4250(2)	0.1197(1)	0.6298(2)	0.0333(4)
O1a	0.2078(6)	−0.3442(3)	−0.8817(5)	0.029(1)
O1b	0.1946(5)	−0.3430(3)	−0.3797(5)	0.027(1)
O2a	0.0513(5)	0.1273(3)	0.0241(4)	0.023(1)
O2b	0.0555(5)	0.1371(3)	0.5230(4)	0.0193(9)
O3a	0.0469(5)	−0.2447(3)	0.2725(5)	0.020(1)
O3b	0.0388(5)	−0.2470(3)	0.7699(5)	0.021(1)
O4a	−0.0540(5)	−0.3896(3)	−0.7566(5)	0.021(1)
O4b	−0.0616(5)	−0.3856(3)	−0.2614(5)	0.021(1)
O5a	0.0687(5)	−0.2272(2)	0.0046(4)	0.0179(9)
O5b	0.0657(5)	−0.2285(2)	0.5092(4)	0.0179(9)
O6a	−0.2119(5)	−0.2624(3)	−0.8878(5)	0.022(1)
O6b	−0.2146(5)	−0.2626(3)	−0.3780(5)	0.021(1)
O7a	−0.3061(5)	−0.1539(3)	0.8695(5)	0.021(1)
O7b	−0.2940(6)	−0.1501(3)	0.3733(5)	0.021(1)
O8a	−0.4606(5)	−0.2496(3)	−0.9805(4)	0.0174(9)
O8b	−0.4575(5)	−0.2484(3)	−0.4767(4)	0.018(1)
O9a	0.4460(6)	−0.1317(3)	0.7237(5)	0.021(1)
O9b	0.4469(6)	−0.1214(3)	0.2236(5)	0.024(1)
O10a	0.4380(5)	−0.1126(3)	0.9847(4)	0.018(1)
O10b	0.4472(5)	−0.1035(3)	0.4900(4)	0.0179(9)
O11a	0.4400(5)	0.2301(3)	0.2418(4)	0.020(1)
O11b	0.4324(5)	0.2339(3)	0.7455(4)	0.021(1)
O12a	0.2879(4)	−0.2351(3)	0.8656(5)	0.017(1)
O12b	0.2905(4)	−0.2319(3)	0.3765(5)	0.0165(9)
O13a	−0.3864(6)	−0.3677(2)	−0.3931(5)	0.020(1)
O13b	−0.3860(6)	−0.3667(2)	−0.8923(5)	0.021(1)
O14a	0.1163(5)	−0.1332(3)	0.8528(5)	0.023(1)
O14b	0.1154(5)	−0.1314(3)	0.3654(5)	0.020(1)
O15a	0.4181(5)	−0.0056(2)	0.1151(4)	0.0238(9)
O15b	0.4148(6)	−0.0075(3)	0.6444(5)	0.036(1)
O16a	0.6521(6)	−0.0710(3)	0.1092(5)	0.033(1)
O16b	0.6532(6)	−0.0679(3)	0.6342(5)	0.031(1)
O17a	−0.0844(6)	−0.4858(3)	0.4046(4)	0.031(1)
O17b	−0.0821(7)	−0.4900(3)	−0.1184(6)	0.037(1)
O18a	0.1595(5)	0.5716(3)	0.3771(6)	0.032(1)
O18b	0.1582(5)	0.5690(3)	0.8553(5)	0.024(1)

[a] The atoms labeled a and b are related by the approximate translational symmetry of ${}^1/_2\mathbf{c}$. [b] The temperature factor parameters are given in the Supporting Information. [c] Esd is given in parantheses.[d] $U_{\mathrm{eq}} = {}^1/_3\sum U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$.

Discussion

The Coordination Sphere of Vanadium. The crystal structure of $\mathrm{K_6(VO)_4(SO_4)_8}$ consists of two crystallographically independent $\ldots\mathrm{V^{V}O(SO_4)_2V^{IV}O(SO_4)_2}\ldots$ chains directed along *c*. The two crystallographically different V-ion in a chain are related by the approximate translational symmetry of ${}^1/_2\mathbf{c}$. Each sulfate group is bidentate and bridges a V(V) and a V(IV) ion by two equatorial oxygens. A third oxygen is coordinated to the trans position of the short $\mathrm{V{=}O}$ bond of a V ion in a neighboring chain, and the fourth oxygen remains uncoordinated. A part of the structure (∼${}^1/_4$ of the unit cell, or ${}^1/_2$ asymmetric unit) with thermal ellipsoids is shown in Figure 1. Important $\mathrm{V-O}$ distances and $\mathrm{O-V-O}$ angles of the $\mathrm{VO_6}$ octahedra are given in Table 3, including analogous distances and angles for the other half of the asymetric unit. For all vanadium atoms the usual[10,23] distortion of the surrounding oxygen octahedra is observed. The vanadium atom (in each $\mathrm{V(V)-V(IV)}$ pair) showing the shortest bond distances is attributed to V(V), i.e. V1b and V2a in Table 3. This is supported by a bond valence analysis[24] based on the measured $\mathrm{V-O}$ distances where valencies of 4.15−4.22 and 5.02−5.05 are found for the atoms atrributed to V(IV) and (V), respectively. The vanadium−oxygen distances for both the V(IV) and the V(V) atom of the mixed valence compound compares well to our previous investigations[9,10] on V(IV) compounds and of the dimer V(V) compound,[3] $\mathrm{Cs_4(VO)_2O(SO_4)_4}$, although the distance of ∼1.77 Å between vanadium and the bridging O atom of the latter compound is somewhat shorter than found for the other equatorially coordinated oxygens in the two structures. Two kinds of angles around 90° are found: those between the $\mathrm{V{=}O}$ bonds and the equatorial $\mathrm{V-O}$ bonds being in the range 97−103 and 96−103° for V(IV) and V(V), respectively, and those between the long trans $\mathrm{V-O}$ bonds and the equatorial $\mathrm{V-O}$ bonds being in the range 75−85 and 77−84°, respectively. In this way V(IV) and V(V) lie about 0.3 Å above the equatorial planes of the four oxygens. These values compare well to those found previously[3,9,10,12] for V(IV) and V(V) oxosulfato compounds. The torsion angle, defined by $\mathrm{O{=}V^{V}-V^{IV}{=}O}$, is 0.70° for the $\mathrm{V1a-V1b}$ pair and 1.06° for the $\mathrm{V2a-V2b}$ pair. The angle between $\mathrm{V1a-V1b{=}O}$ and $\mathrm{V1b-V1a{=}O}$ is 90.67° and 90.34°, respectively. For $\mathrm{V2a-V2b{=}O}$ and $\mathrm{V2b-V2a{=}O}$ these angles are 89.05° and 89.32°. Thus the joint $\mathrm{VO_6}$ octahedra are not twisted or tilted mutually. The $\mathrm{V(IV)-V(V)}$

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Table 3. O−V−O Bond Angles and V−O Distances[a]

angles (deg)				distances (Å)	
O1a−V1a−O2a	102.4(2)	O1b−V1b−O2b	102.5(2)	V1a−O1a	1.583(5)
O1a−V1a−O3a	101.2(2)	O1b−V1b−O3b	100.3(2)	V1a−O2a	1.950(5)
O1a−V1a−O4a	101.2(2)	O1b−V1b−O4b	100.3(2)	V1a−O3a	2.005(5)
O1a−V1a−O5a	97.5(2)	O1b−V1b−O5b	95.9(2)	V1a−O4a	2.000(5)
O1a−V1a−O6a	174.2(2)	O1b−V1b−O6b	175.8(2)	V1a−O5a	2.019(4)
O2a−V1a−O3a	156.4(2)	O2b−V1b−O3b	157.1(2)	V1a−O6a	2.461(5)
O2a−V1a−O4a	85.6(2)	O2b−V1b−O4b	88.7(2)		
O2a−V1a−O5a	93.2(2)	O2b−V1b−O5b	90.3(2)	V1b−O1b	1.569(5)
O2a−V1a−O6a	78.7(2)	O2b−V1b−O6b	79.6(2)	V1b−O2b	1.853(4)
O3a−V1a−O5a	84.2(2)	O3b−V1b−O5b	85.2(2)	V1b−O3b	1.927(5)
O3a−V1a−O6a	77.8(2)	O3b−V1b−O6b	77.5(2)	V1b−O4b	1.926(5)
O4a−V1a−O3a	89.4(2)	O4b−V1b−O3b	89.4(2)	V1b−O5b	1.961(4)
O4a−V1a−O5a	161.1(2)	O4b−V1b−O5b	163.7(2)	V1b−O6b	2.374(5)
O4a−V1a−O6a	84.5(2)	O4b−V1b−O6b	83.3(2)		
O5a−V1a−O6a	76.8(2)	O5b−V1b−O6b	80.4(2)	V2a−O7a	1.571(5)
O7a−V2a−O8a	100.9(2)	O7b−V2b−O8b	101.9(2)	V2a−O8a	1.902(5)
O7a−V2a−O9a	100.1(2)	O7b−V2b−O9b	102.1(2)	V2a−O8a	1.902(5)
O7a−V2a−O10a	98.7(2)	O7b−V2b−O10b	98.4(2)	V2a−O9a	1.910(5)
O7a−V2a−O11a	99.0(2)	O7b−V2b−O11b	99.3(2)	V2a−O10a	1.932(4)
O7a−V2a−O12a	177.7(2)	O7b−V2b−O12b	176.7(2)	V2a−O11a	1.933(5)
O8a−V2a−O9a	158.9(2)	O8b−V2b−O9b	155.8(2)	V2a−O12a	2.348(4)
O8a−V2a−O10a	89.1(2)	O8b−V2b−O10b	90.0(2)		
O8a−V2a−O11a	87.0(2)	O8b−V2b−O11b	86.8(2)	V2b−O7b	1.578(5)
O8a−V2a−O12a	79.2(2)	O8b−V2b−O12b	75.1(2)	V2b−O8b	1.961(5)
O9a−V2a−O10a	86.3(2)	O9b−V2b−O12b	81.0(2)	V2b−O8b	1.961(5)
O9a−V2a−O11a	91.2(2)	O10b−V2b−O9b	83.7(2)	V2b−O9b	2.007(5)
O9a−V2a−O12a	79.9(2)	O10b−V2b−O12b	83.3(2)	V2b−O10b	2.006(4)
O10a−V2a−O11a	162.2(2)	O11b−V2b−O9b	92.2(2)	V2b−O11b	1.982(5)
O10a−V2a−O12a	83.6(2)	O11b−V2b−O10b	162.4(2)	V2b−O12b	2.425(4)
O11a−V2a−O12a	78.7(2)	O11b−V2b−O12b	79.2(2)		

[a] Esd is given in parentheses.

distances in the chains of $K_6(VO)_4(SO_4)_8$ are found to be 4.976 Å for V1a−V1b and 4.967 Å for V2a−V2b. Owing to the long sulfate bridge between the vanadium atoms, these distances are much longer than the V−V distance of 3.51 Å found in $Cs_4(VO)_2O(SO_4)_4$.

The Geometry of the SO_4^{2-} Groups. All S−O distances and O−S−O angles of the eight different SO_4^{2-} groups in the structure are given in Table S3 of the Supporting Information. The S−O bond lengths and the O−S−O angles of the eight different SO_4^{2-} groups vary in the ranges 1.38−1.55 Å and 106−113°, respectively. This is a rather large scatter on the usual bond length of 1.47 Å found for sulfate groups,[25] whereas the angle interval is rather close to the 109° found for undistorted SO_4^{2-} octahedra. As previously,[12] the S−O distances have been plotted vs the average of the three angles involving this bond (Figure 2). As a result of the rather large deviation from the tetrahedral geometry of the SO_4^{2-} groups in $K_6(VO)_4(SO_4)_8$ the plot in Figure 2 shows a large spread of the points for this compound compared to the average of the previously investigated[12] V(III) and V(IV) compounds $NaV(SO_4)_2$, $Na_2VO(SO_4)_2$ and $K_4(VO)_3$ $(SO_4)_5$ (solid line) and the V(V) compound[3] $Cs_4(VO)_2O(SO_4)_4$ (dashed line). As in the latter compound, where two of the sulfate groups showed a marked deviation, many sulfate groups of $K_6(VO)_4(SO_4)_8$ exhibit a large discrepancy from the “normal” behavior. This is possibly due to the breakdown of the hypothesis[10] of sp^3 hybridization for many of the sulfate groups in the present structure. It seems unlikely that this is caused only by the packing forces of the crystal. It is rather due to a strong deformation of the sulfate groups resulting from the coordination to vanadium.

IR Spectra. The IR powder spectrum of the compound is shown in the supplemetary Figure S1. Inspection of the literature revealed[26] a very similar spectrum of a compound, which was formulated as $K_3V_2O_2(SO_4)_4$, but not confirmed by single crystal X-ray investigation. By comparison of the IR spectra (Table 4) of the compounds and the very analogous description of crystal habit and pleochroism, it is very likely that we are dealing with the same compound. The routes of synthesis described in ref 26 compare well with ours, also based on fusion of, *e.g.* $K_2S_2O_7$, V_2O_5 and $VOSO_4$. The analogous sodium compound is claimed to exist too.[26] The strong splitting of the ν_3 bands of the sulfate groups confirms the strong deformation of the sulfate ion from the ideal tetrahedral geometry.

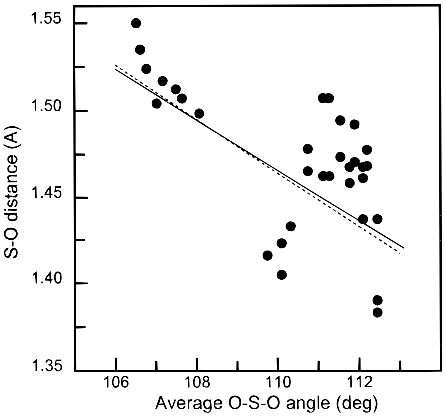

Figure 2. Plot of the S−O distances versus the average of the O−S−O angles involving this bond and the other three bonds of the sulfate tetrahedra. The line is an average regression line for the compounds $Na_2VO(SO_4)_2$, $K_4(VO)_3(SO_4)_5$, and $NaV(SO_4)_2$ taken from ref 12.

ESR Spectra. The powder ESR spectrum of $K_6(VO)_4(SO_4)_8$ is shown in the supplementary Figure S2. The weakly aniso-

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Table 4. Infrared Bands[a] (cm^{-1}) of $K_6(VO)_4(SO_4)_8$ and $K_3V_2O_2(SO_4)_4$[26] in KBr and Their Assignment

	$K_6(VO)_4(SO_4)_8$	$K_3V_2O_2(SO_4)_4$[26]
$\nu_3(SO_4^{2-})$ $\nu_1(SO_4^{2-})$	1287 m	1286
	1247 m	1247
	1199 m	1198
	1152 s	1148
	1140 w	
	1085 w	1083
	1050 m	1047
	1020 m	1017
$\nu(VO)$	1000 w	999
	992 w	992
	914 s	910
	853 s	853
$\nu_4(SO_4^{2-})$	669 w	667
	658 m	658
	650 w	650
	633 m	634
	604 w	604
	592 s	592
$\nu_2(SO_4^{2-})$	489 s	489
	448 s	447

[a] Key: w, weak; m, medium; s, strong.

tropic spectrum of the compound has $g_{iso} = 1.972 \pm 0.003$ and a line width $\Delta B_{pp} = 65 \pm 2$ G at room temperature, estimated from a simultaneous run of a Mn(II) standard. These values compare well with $g_{iso} = 1.967 \pm 0.001$ and $\Delta B_{pp} = 72 \pm 2$ G obtained previously[5] for the V(IV) compound $K_4(VO)_3(SO_4)_5$.

Comparison to Other V(IV)−V(V) Compounds. Very few mixed valence V(IV)−V(V) compounds (besides oxides) are known,[27−29] and so far only two crystal structures are reported,[30,31] both containing discrete $O{=}V^{IV}{-}O{-}V^{V}{=}O$ dimeric units with an almost linear V−O−V bridge. Characteristic distances and angles for the V(IV) and V(V) octahedral coordination spheres of these compounds and for $K_6(VO)_4(SO_4)_8$—which apparently is the only known with purely inorganic ligands—are summarized in Table 5. The compound with almost equivalent bond distances for the vanadium atoms has a solution ESR spectrum[30] that agrees with this crystallographic finding of indistinguishable atoms. In general the three known V(IV)−V(V) compounds exhibit common features of the first coordination sphere, where the bond lengths—and the volume of the coordination octahedra—are smaller around the assumed pentavalent vanadium atom. The values compare well with what has been found[3] for the V(V) dimer compound, $Cs_4(VO)_2O(SO_4)_4$.

Table 5. Selected Bond Lengths and Angles for Mixed Valence V(IV)−V(V) Compounds[a]

	$M_3[V_2O_3L_3]\cdot 3H_2O$[b]	$M[V_2O_3L_2]\cdot NaClO_4\cdot H_2O$[c]		$K_6(VO)_4(SO_4)_8$[d]	
		V(IV)	V(V)	V(IV)	V(V)
V═O (Å)	1.607	1.622	1.613	1.581	1.570
V−O_{br} (Å)	1.810	1.875	1.763		
(O═V)−L_{tr} (Å)	2.297	2.292	2.278	2.443	2.361
(O_{br}−V)−L_{tr} (Å)	2.041	2.019	2.013		
V−L_{eq}[e] (Å)	1.938	1.999	1.965	1.991	1.918
V−O_{br}−V (deg)	180	179.5			
O═V−L_{tr} (deg)	<180[f]	171.7	168.0	175.5	176.8
O═(V···V)═O[g] (deg)	180	164.3		0.9	

[a] Key: br, bridging; eq, equatorial; tr, trans. [b] M = NH_4^+, L = nitrotriacetate. All distances and angles are identical around the two vanadium atoms.[30] [c] M = Na, L = (*S*)-[[1-(2-pyridyl)ethyl]imino]diacetate.[31] [d] This work, average values for the two different V(IV)−V(V) pairs of the structure are given. [e] Average values for the four equatorial bonds. [f] No value is given in ref 30. [g] The angle between the V═O bonds seen along the imaginary V−V axis.

Relation to Catalysis. Investigations[32] of the possible compounds formed in the $K_2O{-}V_2O_5{-}V_2O_4{-}SO_3$ system have shown that several V(IV)−V(V) mixed valence compounds—besides $K_6(VO)_4(SO_4)_8$—may be formed in the catalyst model melts. Thus the V(IV)−V(V) compounds $K_3V_2O_3(SO_4)_3$, $K_5V_2O_3(SO_4)_4$, and $K_3V_2O_3(SO_4)_2S_2O_7$ are claimed to exist[32] but no single-crystal X-ray diffraction or ESR investigations have been reported. The possibility of mixed-valence compounds as catalyst deactivation products is supported by our recent spectroscopic work on model melts. This reveals that at low partial pressure ratios P_{SO_2}/P_{SO_3}, as in the present work, the V(IV) concentration drops drastically and the V(V) concentration rises making the precipitation of only V(IV) compounds (*e.g.* $K_4(VO)_3(SO_4)_5$) less likely. Ongoing *in situ* ESR spectroscopic investigations of industrial catalysts will hopefully clarify this matter.

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Supporting Information Available: Table S1, giving all crystallographic data, Table S2, giving the thermal parameters, Table S3, listing all distances and angles for the eight different sulfate groups of the structure, Figure S1, showing the IR spectrum, and Figure S2, showing the ESR spectrum of $K_6(VO)_4(SO_4)_8$ (8 pages). Ordering information is given on any current masthead page.

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